1	Fluxes of carbon and nutrients to the Iceland Sea surface layer and			
2	inferred primary productivity and stoichiometry			
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16	Abstract			
17	This study evaluates long-term mean fluxes of carbon and nutrients to the upper 100			
18	m of the Iceland Sea. The study utilises hydro-chemical data from the Iceland Sea			
19	time-series station (68.00 °N, 12.67 °W), for the years between 1993 and 2006. By			
20	comparing data of dissolved inorganic carbon (DIC) and nutrients in the surface layer			
21	(upper 100 m), and a sub-surface layer (100-200 m), we calculate monthly deficits in			
22	the surface, and use these to deduce the long-term mean surface layer fluxes that			
23	affect the deficits: vertical mixing, horizontal advection, air-sea exchange, and			
24	biological activity. The deficits show a clear seasonality with a minimum in winter,			
25	when the mixed layer is at the deepest, and a maximum in early autumn, when			
26	biological uptake has removed much of the nutrients. The annual vertical fluxes of			

DIC and nitrate amounts to 2.9 ± 0.5 and 0.45 ± 0.09 mol m⁻² yr⁻¹, respectively, and the annual air-sea uptake of atmospheric CO₂ is 4.4 ± 1.1 mol C m⁻² 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 7.3 ± 1.0 mol C m⁻² yr⁻¹. The typical, median C:N ratio during the period of net community uptake is 9.0, and clearly higher than Redfield, but is varying during the season.

34

35 1 Introduction

36 Increasing our knowledge of the oceanic cycles of carbon and nutrients, and how 37 they are linked, is crucial for improving ocean biogeochemical models and, thus, 38 producing better projections of oceanic response and feedback to a changing climate. 39 The biological carbon pump, i.e., the biologically driven transport of carbon from 40 the surface waters to the deep ocean, is a pathway that can sequester atmospheric CO_2 on long time scales (Falkowski et al., 1998; Sabine et al., 2004). With the present 41 42 increase in atmospheric CO₂ (http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html) 43 the strength of the future biological carbon pump is very uncertain, and warrants 44 further investigation (see, e.g., Passow and Carlson, 2012). To be able to reveal 45 changes in the oceans, we need repeated measurements and long-term time-series 46 stations, such as the Hawaii Ocean Time-series (HOT) and the Bermuda Atlantic 47 Time-series Study (BATS) (e.g., Church et al. 2013). In the Nordic Seas, the time-48 series stations in the Norwegian Sea (Ocean Weather Station Mike) and the Iceland 49 Sea, have greatly increased our knowledge of the carbon cycle in this region (e.g., 50 Skielvan 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 51

(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). The hydrographic properties of the Iceland Sea can generally be described as Arctic Intermediate Water overlying Arctic Deep Water (e.g., Swift and Aagaard, 1981). See Assthorsson et al. (2007) for a more detailed description.

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 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 estimates in this Arctic domain are in the range 75–179 g C m⁻² yr⁻¹, based on data and remote sensing (Thordardottir, 1984; Zhai et al., 2012).

65 There are several production terms used in the literature, illustrating somewhat 66 different fluxes. New production, as defined by Dugdale and Goering (1967), is the 67 production that results from allochthonous (new) nitrate added to the surface layer by 68 vertical or horizontal advection, or via air-sea exchange. This is different from total 69 production, which also includes nitrogen regenerated within the surface layer (see 70 Dugdale and Goering, 1967). Net community production (NCP) is defined as net 71 primary production minus community respiration (e.g., Platt et al., 1989). Estimates 72 of NCP have traditionally been based on bottle oxygen incubations (Gaarder and 73 Gran, 1927), but are often based on oxygen budgets (e.g., Falck and Gade, 1999) or 74 seasonal mixed-layer changes in oxygen or inorganic carbon, corrected for the air-sea 75 fluxes (e.g., Körtzinger et al., 2008; Frigstad et al., in prep), or oxygen-to-argon 76 (O₂/Ar) ratios (e.g., Reuer et al., 2007; Quay et al., 2012.). Export production is the

77 excess organic matter produced in the euphotic zone, on top of the production needed 78 to sustain the productive system (Dugdale and Goering, 1967; Eppley and Peterson, 79 1979). Thus, the export production cannot exceed the rate of added nutrients (i.e. new 80 production), and these fluxes have been assumed to be equivalent on an annual 81 average (Eppley and Peterson, 1979). 82 An issue under debate over the last few decades, is the universal validity of the so-83 called Redfield ratio, describing the stoichiometry between carbon and inorganic 84 nutrients in marine plankton, where the average C:N:P ratios are 106:16:1 (Redfield et 85 al., 1963). Observations of deviations from this relationship are numerous (e.g., 86 Takahashi et al., 1993; Anderson and Sarmiento, 1994; Daly et al., 1999; Körtzinger 87 et al., 2001; Koeve, 2006, Tamelander et al., 2013; Frigstad et al., 2014). It is 88 common practise to use the traditional Redfield ratio to convert changes of nutrients 89 into production of organic matter, both in observational and model studies (e.g., 90 Skjelvan et al., 2001; Falck and Anderson, 2005; Skogen et al., 2007), so any 91 significant variability or deviations of these ratios could have a marked impact on 92 estimated primary production. 93 In this study we use observational data of inorganic nutrients (nitrate, phosphate, 94 and silicate) and inorganic carbon (total dissolved inorganic carbon (DIC) and pCO_2) 95 from the upper layers of the Iceland Sea to evaluate annual fluxes of carbon and 96 nutrients into the surface layer, which we here define as the upper 100 m of the water 97 column. From these fluxes we estimate the long-term mean in primary production in 98 the Iceland Sea, and the related stoichiometric relationships. 99

100 2 Data

101 The study utilises data from the Iceland Sea time series station, located at 68.00

- 102 °N, 12.67 °W (Fig. 1). Surface sampling of DIC and *p*CO₂ started in 1983, and water
- 103 column sampling for DIC and *p*CO₂ started in 1991 and 1993, respectively (Ólafsson
- 104 et al., 2010). Here we include data of inorganic carbon, nutrient and hydrography
- between 1993 and 2006. For details of analytical methods and data quality, see Olsen
- 106 (2009), Olafsson and Olsen (2010) and Olafsson et al. (2010). The data are available
- 107 via the CARINA database (http://cdiac.ornl.gov/oceans/CARINA/Carina inv.html).
- 108 Monthly long-term surface wind speed data are from the NCEP/NCAR reanalysis
- 109 project (Kalnay et al., 1996), provided by the NOAA/OAR/ESRL PSD, Boulder,
- 110 Colorado, USA, from their web site at <u>http://www.esrl.noaa.gov/psd/</u>.
- 111 For the atmospheric CO₂ near Iceland we use Globalview data from
- 112 Vestmannaeyjar, south of Iceland, ICE_01DO (GLOBALVIEW-CO2, 2012), and the
- barometric pressure are monthly means of sea level pressure (SLP) obtained from
- 114 NOWW Fisheries Service, Environmental Research Division
- 115 (http://www.pfeg.noaa.gov/products/las.html).
- 116

117 **3** Methods

118 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

- 120 monthly mean profiles by averaging all data for every month, for the chosen depths (
- 121 every 10 m in the upper 300 m, every 50 m between 300 and 500 m, and then every

122 100 m from 500 down to the bottom (1900 m)) and further interpolated to the chosen

- 123 depth intervals, using piecewise cubic Hermite interpolation in Matlab® (see e.g.,
- 124 Fritsch and Carlson, 1980).

125 The sampling frequency for the different months during the course of the time 126 series sampling is shown in Table 1. The sampling program of the time-series station 127 is largely quarterly (February, May, August, and November), which is clearly seen in 128 Table 1. Four months (January, April, July, and December) have been sampled less 129 than three times, and for these months we use interpolated values. 130 The wintertime mixed layer in the Iceland Sea typically reaches down to 200 m at 131 the end of the winter mixing (Ólafsson, 2003), which is supported by our calculated 132 mean mixed layer depth (MLD) (Fig. 2). We tested several criteria for the MLD, 133 based on either a difference in temperature ($\Delta T = 0.2^{\circ}C$), or density ($\Delta \sigma_{e} = 0.01, 0.03$, 0.05, and 0.125 kg m⁻³), all referenced to a near-surface value at 10 m (see, e.g., de 134 135 Boyer Montégut et al., 2004). The temperature criteria gave unreasonably deep winter 136 convection, with median values of 600-800 m. All density criteria were shallower, however, the 0.125 kg m⁻³ criterion gave a median winter MLD of nearly 400 m, 137 138 which is not supported by depth profiles of hydrography or biogeochemical 139 parameters (Fig. 3), or by previous estimates (e.g., Ólafsson, 2003). The density difference criteria $\Delta \sigma_{e} = 0.05$ kg m⁻³ showed the highest agreement with Ólafsson 140 141 (2003) and was also used by Zhai et al. (2012), which is why we adopted this criteria 142 in the present study. However, the seasonal drawdown in nutrients and DIC (see Fig. 143 3) is largely confined to the upper 100 m. Based on this we define the upper 100 m as 144 the surface layer, and calculate the climatological fluxes in and out of this layer. The 145 approach is described in detail below.

146

147 3.1 Calculation of deficits

We apply a box-model approach, which was developed for idealised annualplankton cycles (Evans and Parslow, 1985), and has been applied in, e.g., the

150 Greenland and the Norwegian Seas (Anderson et al., 2000; Skjelvan et al., 2001;

151 Falck and Anderson, 2005). Here we compute deficits (*DEF*) of nutrients and DIC in

152 the surface layer relative to a defined sub-surface layer:

153

154
$$DEF_X = \int_{100}^{0} \left([X_{SSL}] - [X_{SL}] \right)$$
 (1)

155

156 where X is the concentration of the constituent of interest (here nutrients and DIC), 157 SSL is the sub-surface layer, and SL is the surface layer. Thus the deficit increases 158 when there is a decrease in carbon or nutrients in the surface layer. While the surface 159 layer is chosen to be the upper 100 m, the sub-surface layer is defined as the layer 160 between 100 and 200 m, for which monthly mean concentrations are calculated and 161 applied in Eq. 1. Applying this on the monthly mean profiles, the deficits are 162 calculated for every 10 m interval in the upper 100 m, relative to the monthly mean concentration in the sub-surface layer, multiplied with 10, and summed up for each 163 164 month (Anderson et al., 2000).

165

166 3.2 Flux calculations

167 The change in the deficit (ΔDEF^X) of constituent *X* are explained by the sum of the 168 fluxes into and out of the surface layer; the vertical exchange with the deeper layers 169 (F_{vert}), the horizontal fluxes (F_{hor}), the biological production (F_{bio}), and the air-sea 170 exchange (F_{atm}):

171

172
$$\Delta DEF^{X} = F_{vert}^{X} + F_{hor}^{X} + F_{bio}^{X} + F_{atm}^{X}$$
(2)

174 Positive fluxes indicate a transport out of the surface layer. Regarding the time-series 175 station as a very thin section the horizontal fluxes will balance, and F_{hor} could then be 176 set to zero. We also assume no atmospheric input of nutrients, and thus F_{atm} is only of 177 importance for the calculations of the DIC fluxes. The uncertainty in the different 178 fluxes is estimated from error propagation of the standard deviations of the different 179 terms in the flux calculations. The uncertainties are discussed in Section 6. 180 The vertical flux to the surface layer can be calculated from Eq. (3) (Anderson et 181 al., 2000; Skjelvan et al., 2001; Falck and Anderson, 2005): 182

183
$$F_{vert}^{X} = \frac{v_{mix}}{H} DEF^{X}$$
(3)

184

185 where v_{mix} is the vertical entrainment velocity, and H is the thickness of the surface 186 layer. We estimate v_{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 187 188 of the mixed layer, which is the period from September to March seen from the 189 development of the MLD (Fig. 2). During the period from April to August there is a 190 decrease in the MLD, and for this period we apply a background mixing through the base of the mixed layer of 0.1 m d⁻¹ (Anderson et al., 2000; Skielvan et al., 2001), 191 which corresponds to a shallowing of 3.0 m month⁻¹. The applied entrainment 192 193 velocities are shown in Table 1. We here define v_{mix} as negative to get a negative flux 194 when directed into the surface layer. 195 The flux due to biological activity is given by Eq. 4: 196

197
$$F_{bio}^{X} = \Delta DEF^{X} - F_{vert}^{X} - F_{atm}^{X}$$
(4)

199	For the nutrients we assume a negligible atmospheric source, but when calculating the		
200	biological production from DIC, F_{bio} needs to be corrected for the air-sea flux (see		
201	below). The resulting fluxes are positive as long as the production is greater than the		
202	decay of organic matter, as is the case when there is a net biological uptake, removing		
203	DIC and nutrients from the surface layer.		
204	The air-sea flux of carbon can be calculated from the difference in partial pressure		
205	of CO_2 between seawater and air, the gas transfer velocity k , and the solubility of CO_2		
206	in seawater, K_o :		
207			
208	$F_{atm} = kK_0 \Delta pCO_2$	(5)	
209			
210	where		
211			
212	$\Delta pCO_2 = pCO_2^{sea} - pCO_2^{air}$	(6)	
213			
214	The solubility of CO ₂ in the Iceland Sea surface water was calculated afte	r Weiss	
215	(1974), using long-term monthly mean values of salinity and temperature in the uppe		
216	30 m. For the dependence of wind speed on the transfer velocity k we used the		
217	parameterisation of Sweeney et al. (2007) after Wanninkhof (1992):		
218			
219	$k = 0.27u^2 \sqrt{\frac{660}{Sc}}$	(7)	

where u is the long-term surface wind speed (m s⁻¹), and Sc is the Schmidt number. 221 The transfer coefficient was then converted to m month⁻¹ by multiplying with 222 223 (365.25/12)*(24/100). 224 To calculate the partial pressure in the atmosphere from the molar fractions 225 obtained from GLOBALVIEW we used the formulation: 226 $pCO_{2,atm} = XCO_2 \left(P_b - P_w \right)$ 227 (8)228 229 where P_b is the barometric pressure (in atmospheres), and P_w is the saturation water 230 vapour pressure calculated from temperature and salinity in the sea surface layer, 231 according to Cooper et al. (1998). Monthly mean seawater pCO_2 values were 232 calculated from observational data over the 13-year time period in the upper 30 m. 233

234 4 Results

235 The deficits of nutrients and DIC in the upper 100 m decrease from January to 236 March (Fig. 4), as a result of the deepened mixed layer depth (Fig. 2). The increase in 237 the deficits after March, related to biological production, continues until a maximum 238 in September, after which the deficits decrease again. There is a small decrease in 239 deficit in phosphate from May to June, which coincides with an almost unchanged 240 deficit in silicate and a slower rate of change of DIC. At the same time the change in 241 the nitrate deficit continues largely as before (Fig. 4). There is a significant uptake of 242 nutrients from winter to late summer (Fig. 3), but on average the system, never gets 243 fully depleted. The calculated fluxes deduced from a change in the deficits, related to 244 vertical mixing, air-sea exchange, and biological production, are presented in the 245 following section and are summarised in Table 2 and Figure 5.

247 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 shallow MLD are small. The annual vertical fluxes of DIC and nutrients to the mixed layer was estimated to be 2.9 $\pm 0.5 \text{ mol C m}^{-2} \text{ yr}^{-1}$, $0.45 \pm 0.09 \text{ mol N m}^{-2} \text{ yr}^{-1}$, $0.026 \pm 0.005 \text{ mol P m}^{-2} \text{ yr}^{-1}$, and $0.26 \pm 0.06 \text{ mol Si m}^{-2} \text{ yr}^{-1}$, for DIC, nitrate, phosphate, and silicate, respectively. The flux of DIC equals 35 g C m $^{-2} \text{ yr}^{-1}$. The presented uncertainties are calculated from error propagation of the terms in equation 3. (See details in Section 6.2).

255

256 4.2 Air-sea flux of CO_2

The air-sea flux is directed into the surface layer all year around, as the region is permanently undersaturated with respect to atmospheric CO₂ (Fig. 5). The calculated annual flux was 4.4 ± 1.1 mol C m⁻² yr⁻¹, which is consistent with the estimate of Ólafsson et al. (2009) of 4.5 mol C m⁻² yr⁻¹. When converted, the calculated flux into the Iceland Sea is 53 g C m⁻² yr⁻¹.

262

263 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. Phosphate shows a slightly different evolution, with no flux in June, and a broader peak in late summer, with a small maximum in August. The nutrients also show a negative flux in October, when there is still a net uptake of carbon.

269 The change in the deficit (ΔDEF) equals zero over the course of the year, and

270 hence there is a balance between the calculated fluxes (Eq. 2). For the nutrients, with

the assumption of negligible horizontal and air-sea fluxes, there is a balance between

272 the net vertical fluxes and the net biological fluxes, and the latter amounts to $0.45 \pm$

273 0.14 mol N m⁻² yr⁻¹, 0.026 ± 0.010 mol P m⁻² yr⁻¹, and 0.26 ± 0.16 mol Si m⁻² 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

276 nitrate, the addition of nitrate from vertical mixing must equal new production. In the

Iceland Sea this amounts to $0.45 \pm 0.09 \text{ mol N m}^{-2} \text{ yr}^{-1}$.

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 the values have been interpolated because there is less data available in December and January. 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 $7.3 \pm 1.0 \text{ mol C m}^{-2} \text{ yr}^{-1}$, or $88 \pm 12 \text{ g C m}^{-2}$ 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 0.72 ± 0.10 mol N m⁻² yr⁻¹. The difference between the new and total production (0.27 ± 0.15 mol N m⁻² yr⁻¹) gives the regenerated production, which represents 37% of the total production. Then we get an *f*-ratio (i.e. the ratio between new and total production) of 0.63 in the Arctic domain of the Iceland Sea. Performing the same calculations for phosphate and silicate gives a total production of $0.036 \pm$ 0.006 mol P m⁻² yr⁻¹ and 0.40 ± 0.07 mol Si m⁻² yr⁻¹.

- 297
- 298

4.4 Stoichiometry of the calculated fluxes

299 An evaluation of the stoichiometric relationships between carbon and nutrients 300 show varying values during the year, as well as for the different fluxes (Table 3). 301 Evaluating the stoichiometry for the biological production is not straightforward 302 since the flux of carbon and nitrate do not show the same direction for all months. The 303 change in deficits of DIC and nitrate (Fig. 4), however, both show a net uptake from 304 April to September, so we will use this period to evaluate the biologically related 305 stoichiometry. The C:N ratios of the monthly biological production (Fig. 7), during 306 the period of seasonal drawdown of DIC and nitrate, differ between the early and the 307 late part of the season, with C:N ratios of 8.8-8.9 in April and May, and 9.1-9.8 308 between July and September, while the value in June is 7.4. 309

310 5 Discussion

311 5.1 Primary production in the central Iceland Sea

312 The main aim of this study is to investigate primary production and related

- 313 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). However, it could be representative of the whole Arctic
- 316 domain in the Nordic Seas, with similar hydro-chemical properties.

How realistic is our estimated annual net production (NCP) of 88 ± 12 g C m⁻² yr⁻¹ 317 318 in the Iceland Sea? Gudfinnsson (2012) found, from his data of daily productivity, an average annual phytoplankton productivity of 65 g C m⁻² yr⁻¹, and Thordardottir 319 (1984) presented an average annual primary production (1958–1982) in the Arctic 320 domain, in the vicinity of the time series station, of 75 g C m⁻² yr⁻¹, based on 321 measured ¹⁴C uptake at light saturation. A modelling study (Skogen et al., 2007), 322 suggests a mean annual production in the Iceland Sea at 70 g C m⁻² yr⁻¹, with an *f*-323 324 ratio of ~ 0.7 . These estimates show a large agreement with the estimates in our study, 325 giving more trust in our results, and the approach. The uncertainty in our presented 326 fluxes, and the approach in general, are discussed in Section 6. 327 From remote sensing data, Zhai et al. (2012) gave a production estimate in the Arctic domain of 179 ± 36 g C m⁻² yr⁻¹. This is more than twice as high as the 328 329 estimates based on in situ data. This has also been seen in other comparisons between 330 production estimates based on in situ and remote sensing data (see, e.g., Richardson et 331 al., 2005; Körtzinger et al., 2008; Frigstad et al., in prep). 332 The negative nutrient flux in October, when there is still a net uptake of carbon 333 (Fig. 5), is similar to what have been observed in the Norwegian Sea (Falck and 334 Anderson, 2005), which were explained largely by a build-up of dissolved organic 335 matter (DOM), which is relatively low in nutrients. We will discuss this further 336 below, in relation to the stoichiometry of the production. 337

338 5.2 Variable stoichiometry

The evaluation of the C:N ratios during seasonal drawdown (April to September)

of DIC and nitrate (Fig. 6) showed a clear deviation from the Redfield C:N ratio of

341 6.6, except in June, when the production was lower. The consumption of carbon

342 relative to nitrate in excess of Redfield, a phenomena termed "carbon 343 overconsumption" (Toggweiler, 1993), was higher during the late summer production 344 (C:N ratio >9) compared to the early production peak (C:N ratio <9). Similar 345 increases in carbon overconsumption during the later part of the productive season 346 have been described in several studies from different ocean regions, and have been 347 explained by the build up of low-nitrogen DOM (e.g., Toggweiler, 1993; Williams, 348 1995; Kähler and Koeve, 2001; Körtzinger et al., 2001). Without any data of DOM in 349 the central Iceland Sea we cannot find direct evidence supporting this mechanism in 350 our study, but the similarity to the Atlantic-dominated Norwegian Sea (Falck and 351 Anderson, 2005) suggest that this may be a general feature also in the Nordic Seas. 352 This should be evaluated further in the future. Nonetheless, different mechanisms 353 seem to affect the flux of carbon and nitrogen during the season, as shown for 354 different regions (e.g., Banse, 1994; Kähler and Koeve, 2001; Frigstad et al., 2011). 355 If we compare the total new production and NCP during the year, from the values 356 in Table 2, we get a net C:N ratio of 16.2. This means that, if we would convert the 357 computed new production into export production, using the ratios of Redfield (6.6), or 358 Takahashi et al. (7.3), we would underestimate the export production by 55–60%, 359 assuming our estimated export production is reasonable. This confirms the findings 360 of, Sambrotto et al. (1993), who found that the actual carbon production exceeds any 361 estimate based on nitrogen consumption, converted by the Redfield C:N ratio, by 36-362 81%. 363 This illustrates the problem in converting new production into NCP, or export 364 production, using constant stoichiometric ratios. As discussed by Laws (1991) these 365 terms may not be related, and would assume that nitrate and carbon are assimilated by

366 autotrophs during new production, in the same ratio as carbon and nitrate are recycled

by heterotrophs. Furthermore, C:N ratios 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., 2014), with values as high as
~15.

371 An evaluation of the relationship between DIC and nitrate in the surface water 372 using the time-series data (not shown) gives a high agreement with the estimated stoichiometry in the region by Takahashi et al. (1993). However, this value represents 373 374 the relationship between measured properties in the surface waters over the year, 375 which includes the net effect of air-sea exchange, biological activities, and mixing. 376 Due to this, Banse (1994) cautioned against using observed in-situ DIC:nitrate 377 relationships to make statements about elemental ratios during biological production, 378 and respiration, and recommended smaller closed, controllable systems to find 379 mechanistic explanations of uptake ratios in the surface layer. 380

381 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 g C m⁻² 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 g C m⁻² yr⁻¹, or 70 g C m⁻² 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 g C m⁻² 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 g C m⁻² yr⁻¹ (Richardson et al., 2005). The likely range of annual primary production in the Greenland Sea is in the range 60–100 m⁻² 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 g C m⁻² 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 g C m⁻² yr⁻¹, with an *f*-ratio of ~0.75.

402 Falck and Anderson (2005) used a box model approach similar to the present

403 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

405 $0.23 \text{ Nm}^{-2} \text{ yr}^{-1}$, or 18 g C m⁻² yr⁻¹; when using the traditional Redfield C:N ratio (6.6).

406 Their new production estimate amounted to 0.51 mol N m⁻² yr⁻¹, or 41 g C m⁻² yr⁻¹,

407 using the same ratio. If equating their vertical flux of nitrate with new production, and

408 their total production with the sum of all positive biological fluxes during the year, we

409 get an *f*-ratio of 0.43. This is clearly lower than the earlier estimates mentioned above

410 (Rey, 2004; Skogen et al., 2007).

Earlier estimates of new production in the Norwegian Sea (70°N, 0°E) are in the range 21-29 g C m⁻² yr⁻¹ (Bodungen et al., 1995). These values agree with estimates of NCP, based on oxygen fluxes in the Norwegian Sea, of ~24-32 g C m⁻² 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

417 could partly be due to the oxygen-to-carbon conversion applied, mostly based on the 418 traditional Redfield ratio, but the only way to unravel real or artificial differences is to 419 analyse the whole region with the same method. This should be pursued in the near 420 future to investigate regional differences, but also to evaluate trends and changes in 421 the system. Nevertheless, the range of methods and approaches, both based on 422 observations and models, and different assumptions, including ours, still seems to 423 reach some consensus of annual primary production in the Nordic Seas of ~60-100 g $C m^{-2} vr^{-1}$. More work is needed to evaluate regional similarities and differences in 424 425 stoichiometry and any temporal trends in primary production. This will aid 426 understanding of the variability drivers in biological production, both natural and 427 anthropogenic, and how the increasing levels of atmospheric CO₂ will affect the 428 biological carbon pump.

429

430 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 in mind we proceed to evaluate the
uncertainty of the approach and the individual fluxes.

435

436 6.1 Deficit calculations

437 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

439 concentrations, and the uncertainties arising from the averaging procedures of the

440 monthly profiles. The uncertainty in the monthly surface layer concentrations (seen

441 from the average monthly standard deviation) is largest for silicate (values up to 40– 442 50%), but for nitrate and phosphate there is a maximum in late summer/early autumn, 443 when the concentrations are lowest by 20-30%. Due to the high concentrations of 444 DIC the uncertainty in these numbers is insignificant. If we propagate the 445 uncertainties in the surface concentrations and the reference concentrations and use 446 this as the overall uncertainty in the monthly deficits we get the values depicted in 447 Figure 4, which are quite substantial for some of the months, with a relative error of 448 up to 60-75% at or just after the early peak in production, but lower (10-40%) during 449 the later part of the year. The uncertainty in the values from the first part of the year, 450 during the period of deepened mixed layer, is rather low in an absolute sense, 451 compared to later in the year, but due to the low deficits in this period the relative 452 errors get very large (see Fig. 4).

453 There is a potential error in assessing the production, and related terms, in the 454 upper 100 m, when the MLD apparently reaches deeper in winter. However, the 455 vertical distribution of nutrients and DIC do show a homogeneous upper 100 m in 456 winter, followed by a gradient down to stable concentration at depths below ~300 m. 457 Profiles of salinity show the same feature (Fig. 3). Deficits were also calculated for 458 the upper 200 m (referenced to the monthly means between 100 and 200 m), and the 459 upper 300 m (referenced to the monthly means between 300 and 400 m). The 460 resulting deficits of carbon and nutrients showed an increasing degree of decoupling 461 with increasing depth of the surface layer, as shown in Figure 7. The C:N ratio during 462 the period of net biological uptake also varies considerably more with thicker surface 463 layer (not shown) compared to the upper 100 m. With a surface layer down to 200 m 464 the C:N uptake ratio is 20 during the spring peak, below 4 in June, and show values 465 between 13 and 19 from July to September. A surface layer of 300 m gives C:N

466 uptake ratios of 10 during the spring peak, followed by negative values during 467 summer, and a value of 4 in September. This suggests that processes other than 468 biological assimilation contributed much more to the distribution of nutrients and 469 carbon at these depths Since we mainly want to evaluate the fluxes of importance for 470 the production, and these seem to be confined to the upper 100 m, we argue that the 471 applied method best captures the biological production with the relatively shallow 472 surface layer we use. This may also be connected to the different water masses 473 present in the Iceland Sea, so it is important to evaluate different surface layer 474 thickness in different regions.

475

476 6.2 Vertical flux

477 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 478 479 increase in nutrient concentration during periods of deepened mixed layer depths 480 should equal the vertical fluxes. Since we estimate the vertical entrainment velocity 481 from the observed changes in MLD, there is both an uncertainty related to the chosen 482 method to calculate MLD, and the variability in the monthly MLD during the time 483 series. The variability-driven uncertainty in the mean monthly MLD is on average 484 \sim 30% (Fig. 2). The calculated uncertainty in the vertical fluxes of DIC, and nutrients 485 are all in the range 17–22% (see Table 2).

486

487 *6.3 Air-sea exchange*

488 From the propagation of the errors due to spread in mean pCO_2 values for atmosphere 489 and sea surface, and putting this error estimate in the flux calculation for each month,

490 we get an annual uncertainty of 1.1 mol C m^{-2} , which is 25% of the estimated annual 491 flux. This agrees with previous findings from the North Atlantic and the Nordic Seas 492 (Körtzinger et al., 2001; Olsen et al., 2003). Körtzinger et al. (2008) have estimated a 493 maximum error in calculated CO₂ fluxes of 40%.

494

495 *6.4 Biological production*

496 Since the biological production is calculated as the residual of all other terms (Eq. 4) 497 it also carries the uncertainty of each of these terms. Some of the uncertainty could be 498 connected to interannual variability in the timing of the peak in the productive events, 499 something that should be evaluated further in later studies. To estimate the uncertainty 500 in the ΔDEF term we use the relative error in the calculated deficits, and multiply 501 these with the ΔDEF values for each month, for each constituent. The relative error in 502 the deficit for the months with very low values (February–March) is unrealistically 503 large. For these months we instead use the uncertainty in MLD as the minimum error. 504 For February this is \sim 50%, and for March \sim 30%. The total estimated errors in the 505 biologically related fluxes are in the range 31-61% for the nutrients (highest for 506 silicate), but only 14% for carbon (Table 2).

507

508 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 0.45 ± 0.09 mol N m⁻² yr⁻¹, based on nitrate added to the surface layer

via vertical mixing, and an annual net community production (NCP) of 7.3 ± 1.0 mol C m⁻² yr⁻¹ (or 88 ± 12 g C m⁻² 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 7.4-9.8, and 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.

521

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526

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- 716
- 717

719 Tables

720

Table 1. Monthly computed median mixed layer depths (MLD) and entrainment

722 velocities (v_{mix}). These are used when calculating the vertical fluxes. The values in

723	italic are interpolated	from surrounding month	ly data	. See text for detai	ls.
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Month	MLD	v _{mix} ^a	Number of
	Median (m)	$(m month^{-1})$	sampled months ^b
1	118	-29	2
2	147	-29	16
3	168	-21	3
4	116	-3	1
5	65	-3	14
6	30	-3	8
7	25	-3	1
8	21	-3	16
9	32	-11	4
10	37	-5	4
11	59	-22	14
12	89	-30	2

724 v_{mix} is defined as negative to get a negative flux into the surface layer.

⁷²⁵^bThis is the number of sampled months in the data set. For months sampled less than

three times, interpolated numbers have been used.

728**Table 2.** Summary of annual fluxes (mol m⁻² yr⁻¹) of carbon, nitrate, phosphate, and729silicate to the surface layer (upper 100 m) of the Iceland Sea; vertical flux (F_{vert}), air-730sea flux (F_{atm}), and biological production (F_{bio}). Negative values indicate a flux into731the surface layer. The horizontal fluxes are assumed to balance over the year and were732set to zero.

	Fvert	F _{atm}	F _{bio}
	$(mol m^{-2} yr^{-1})$	$(\text{mol } \text{m}^{-2} \text{ yr}^{-1})$	$(\text{mol } \text{m}^{-2} \text{ yr}^{-1})$
Carbon	-2.9 ± 0.5	-4.4 ± 1.1	7.3 ± 1.0^{a}
Nitrate	-0.45 ± 0.09	-	0.45 ± 0.14^{b}
Phosphate	-0.026 ± 0.005	_	0.026 ± 0.010
Silicate	-0.26 ± 0.06	-	0.26 ± 0.16

- ^aCorresponds to NCP
- ^bCorresponds to new production

736 **Table 3.** Stoichiometric (median) ratios of computed monthly vertical fluxes and of

biological production during the period of seasonal drawdown (net community

view of the second seco

	Vertical flux ^a	Net uptake ^a
	(Annual)	(Apr-Sep)
N:P	18.4	18.2 ^b
C:N	6.20	9.00
C:P	112	159 ^b
C:Si	11.1	25.9
N:Si	1.67	2.72
Si:P	10.5	13.3 ^b

^aWe use the median of the monthly values since some months show large deviations.

^bSince the biologically related flux of phosphate is zero in June these numbers are

741 only based on Apr–May, and July–Sept.

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743

745 Figure captions

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

748

Figure 2. Calculated mixed layer depth (MLD) at the Iceland Sea time-series station, using the density difference criteria of $\Delta \sigma_{0} 0.05$ 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 standard deviation (SD). The values for the months without shown data are interpolated.

749

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

750

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 standard deviation of the respective reference concentrations and the average monthly standard deviation in the surface layer. As for the MLD calculations, for the months sampled less than three times in the time series we have used interpolated values. See text for details.

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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 mol m⁻² month⁻¹. The figures show the vertical flux (F_{vert} ; solid black line), the biological production (F_{bio} ; green solid line), and the air-sea flux of CO₂ (F_{atm} ; red dashed line for carbon). The error bars show the propagated errors (see Section 6). Note that the scale on the y-axis is different for all constituents.

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Figure 6. 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

755 Sea. Then red line show the Redfield C:N ratio of 6.6.

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Figure 7. Comparison of calculated monthly-mean deficits of DIC and nitrate in the

758 Iceland Sea, for different thickness of the surface layer (SL). The nitrate deficits are

multiplied with the Redfield C:N ratio of 6.6.













