A reduced estimate of the strength of the ocean’s biological carbon pump

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[1] A major term in the global carbon cycle is the ocean’s biological carbon pump which is dominated by sinking of small organic particles from the surface ocean to its interior. Several different approaches to estimating the magnitude of the pump have been used, yielding a large range of estimates. Here, we use an alternative methodology, a thorium isotope tracer, that provides direct estimates of particulate organic carbon export. A large database of thorium-derived export measurements was compiled and extrapolated to the global scale by correlation with satellite sea surface temperature fields. Our estimates of export efficiency are significantly lower than those derived from the f-ratio, and we estimate global integrated carbon export as \( \sim 5 \) Gt C yr\(^{-1}\), lower than most current estimates. The lack of consensus amongst different methodologies on the strength of the biological carbon pump emphasises that our knowledge of a major planetary carbon flux remains incomplete. Citation: Henson, S. A., R. Sanders, E. Madsen, P. J. Morris, F. Le Moigne, and G. D. Quartly (2011), A reduced estimate of the strength of the ocean’s biological carbon pump, Geophys. Res. Lett., 38, L04606, doi:10.1029/2011GL046735.

1. Introduction

[2] The oceans are a major repository for inorganic carbon [Siegenthaler and Sarmiento, 1993]. An important component of this sink is the biological carbon pump (BCP), driven by the sinking of small organic particles from the surface ocean to its interior [Falkowski et al., 1998; Sabine et al., 2004]. Of the organic material generated via primary production (PP) by phytoplankton in surface waters, most is recycled in the upper ocean. A small fraction is exported to depth and sequestered away from the atmosphere for hundreds to thousands of years. The magnitude of the BCP is predicted to decline in response to global climate change, resulting in reduced ocean carbon storage and hence increased atmospheric CO\(_2\) levels [e.g., Matsumoto et al., 2010; Steinacher et al., 2010; Manizza et al., 2010]. Therefore, accurately quantifying the strength of the global BCP is essential to understanding the Earth’s carbon cycle and, by extension, the impact of continued anthropogenic perturbation of atmospheric CO\(_2\) levels.

[3] However, measuring the export flux of organic matter directly is challenging, so a common approach is to estimate the fraction of the total PP that is eventually exported (i.e., the export efficiency). Total PP includes production fuelled by both ‘new’ and ‘regenerated’ nitrogen [Dugdale and Goering, 1967]. New production (NP) is assumed to be principally fuelled by nitrate supplied from depth by vertical mixing, whilst regenerated production (RP) is supported by the uptake of nitrogen derived from the recycling of organic matter in the euphotic zone. Over sufficiently large time and space scales, export production is equivalent to new production [Eppley and Peterson, 1979], so that the fraction of PP that is exported can be expressed as NP/(NP+RP), known as the f-ratio [Dugdale and Goering, 1967].

[4] The most widely used estimate of global carbon export is derived from a linear relationship between observed f-ratio and sea surface temperature (SST) [Laws et al., 2000]. Applying this to satellite-derived PP and SST fields yields an estimate of global carbon export of \( \sim 12 \) Gt C yr\(^{-1}\). This is comparable to the 11 Gt C yr\(^{-1}\) obtained from a food-web model [Laws et al., 2000], but substantially lower than global application of the earliest export algorithm (21 Gt C yr\(^{-1}\)) [Eppley and Peterson, 1979].

[5] The empirical relationship derived in the Laws et al. (2000) study was based on f-ratio estimates from just 11 sites where comprehensive surveys of marine biogeochemistry had been conducted. At 7 of the 11 sites, f-ratio estimates were made using nitrogen isotope (\(^{15}\)N) experiments, which introduces an additional source of uncertainty [e.g., Fernandez and Raimbault, 2007]. This arises from the inherent assumption that all nitrate is supplied through wintertime mixing or upwelling of sub-surface waters, and that none is generated within the euphotic zone via the biologically mediated oxidation of ammonium (i.e., nitrification). At the time of Laws et al.’s (2000) study, nitrification was believed to occur almost entirely below the euphotic zone and thus contribute to the new nitrate pool. However, recent studies have demonstrated that nitrification rates are similar in surface and deep waters [Yool et al., 2007; Dore and Karl, 1996; Clark et al., 2008; Fernandez et al., 2009], suggesting that nitrification is an additional source of regenerated nitrate in the upper ocean. Indeed globally, nitrification in surface waters could supply up to half of the nitrate consumed by phytoplankton [Yool et al., 2007]. As a consequence, using the f-ratio to calculate export may result in an over-estimate of the magnitude of the BCP.

[6] An alternative approach to estimating particulate organic carbon (POC) export uses the particle tracer thorium-234 (\(^{234}\)Th). \(^{234}\)Th is the radiogenic daughter product of the naturally occurring soluble isotope uranium-238 (\(^{238}\)U), which is proportionally conserved in seawater [Chen et al., 1986]. Unlike \(^{238}\)U, \(^{234}\)Th is insoluble in seawater and readily adheres to particulate matter. As particles sink, a...
radioactive disequilibrium between $^{238}$U and $^{234}$Th arises, and when combined with data on the particulate ratio of POC,$^{234}$Th activity [Buesseler et al., 2006], an estimate of POC export is obtained. An equivalent to the f-ratio for the efficiency of particle export is the ThE-ratio, defined as: $^{234}$Th-derived export/PP [Buesseler, 1998].

[7] In order to estimate the total magnitude of the BCP, local measurements of export efficiency derived from the f- or ThE-ratio must be extrapolated to a global scale. Previous studies have demonstrated that SST is a good predictor of the f-ratio [Laws et al., 2000; Wohlers et al., 2009; Savoye et al., 2004], as the balance between production and respiration is strongly affected by temperature. As one moves from cold, sub-polar regions into warm, sub-tropical waters, respiration declines more slowly than production [Duarte and Agusti, 1998], resulting in a decreasing f-ratio. Using SST as a predictor is also an appealing option, as satellite-derived SST data are widely available permitting the calculation of global export production estimates.

2. Methods

[8] For this study a database of $^{234}$Th-derived export measurements was compiled from the literature (all details can be found in the auxiliary material).¹ All measurements are reported as the export at 100 m depth. Data from the Arctic and from shallow waters (<200 m depth) are excluded from the analysis. It should be noted that due to the predominance of open ocean thorium-export measurements in our dataset, our estimate of global carbon export does not explicitly parameterise the contribution from continental margins and shelves, potentially resulting in an underestimate of integrated export. However, the same is true of the f-ratio approach, and indeed almost all methodologies (an exception is that of Schlitzer [2000]), so our results remain directly comparable with previous estimates.

[9] ThE-ratio estimates are typically made using in situ PP measured during 12 or 24 hour incubations. However, the residence time of $^{234}$Th is considered to be ~2–20 days [Coale and Bruland, 1985] (shorter than its mean life of 24 days, due to scavenging), and therefore the export estimates using this method represents an integrated value over days to a couple of weeks. This introduces a mismatch in time scales with the instantaneous PP measured in situ. Here we account for the integration time scale of the $^{234}$Th-derived export by using the integrated satellite-derived PP over the 16 days prior to the in situ measurement. We term this the integrated thorium export ratio, ThE-ratio, to distinguish it from the original definition of the ThE-ratio based on instantaneous PP [Buesseler, 1998].

[10] Climatological 8-day composites of Level-3 SeaWiFS chlorophyll-a concentration, photosynthetically available radiation and AVHRR SST data were downloaded from http://oceancolor.gsfc.nasa.gov and http://pathfinder.nodc.noaa.gov/, respectively. All data were spatially averaged to a 1° grid. PP was derived from satellite data using the 3 principal algorithms (a detailed intercomparison of several PP algorithms is given by Carr et al. [2006]): the Vertically Generalized Production Model [Behrenfeld and Falkowski, 1997], Marra et al. [2003] and Carr’s [2001] algorithms and multiplied by the ThE-ratio to estimate particle export. Although PP is used to estimate both ThE-ratio and export, both the time (16-day vs. annual integral PP) and space (point observations of thorium-derived export vs. globally-resolved PP) scales are different. The in situ thorium export measurements listed in Table S1 (see auxiliary material) were compared with the corresponding satellite-derived export, calculated using each of the three PP algorithms. Carr’s [2001] algorithm was chosen for its ability to replicate the in situ export measurements with the lowest root mean square error and highest $r^2$. The error on the estimate of globally integrated carbon export is reported as the median relative error of measured versus predicted POC flux (=55%). This incorporates all the errors associated with the satellite-derived

Figure 1. Relationship between sea surface temperature, ThE-ratio (solid circles) and f-ratio (open circles). ThE-ratio regression line is an exponential fit, $\text{ThE}_{\text{r}} = 0.23(\pm0.04)\exp^{-0.08(\pm0.01)\times\text{SST}}$, $r^2 = 0.50$, $p < 0.01$, $n = 306$; values in brackets are the 95% confidence limits on the regression coefficients. $f$-ratio regression line is a linear fit, $f$-ratio = 0.63 – (0.02*SSST) (data taken from Laws et al. [2000]).

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¹Auxiliary materials are available in the HMTL. doi:10.1029/2011GL046735.
have ThE$_i$-ratios in the range of ~0.01 to 0.2, and temperate and sub-polar northern hemisphere waters have ThE$_i$-ratios between ~0.1 and 0.3. In the Southern Ocean (SST < 7°C), the ThE$_i$-ratio varies widely from ~0.1 to 0.7. Also plotted in Figure 1 is the f-ratio and SST data of Laws et al. [2000, Table 3]. Despite the considerable scatter in the ThE$_i$-SST plot, the two relationships are clearly different, with the ThE$_i$-ratio consistently lower than the f-ratio, particularly at mid-latitudes (SST ~7–20°C).

[13] Fitting an exponential function to the ThE$_i$-SST data produces the relationship ($\tau^2 = 0.5$, $p < 0.01$):

$$ThE_i - ratio = 0.23 \exp(-0.08* SST)$$

(2)

From a metabolic standpoint, an exponential relationship is more apposite than a linear fit, as the balance between respiration and production, which effectively drives the fraction of PP that is exported, is an exponential function of temperature [Lopez-Urrutia et al., 2006].

[14] Much of the scattered Southern Ocean data comes from a transect from the Polar Front to the retreating ice edge in the Ross Sea [Buesseler et al., 2003]. The large range of ThE$_i$-ratio values found there was attributed by the authors to the very different phytoplankton community structures encountered during the transect, indicating an important secondary control over ThE$_i$-ratios. An additional contributor to the scatter may be the spatial variability in thorium export, that varies on scales of ‘tens to hundreds of kilometres’ [Buesseler et al., 2009], i.e., potentially smaller than the 1° satellite data used here. Seasonal variability may also play a role, through phytoplankton succession and changes in ecosystem structure, nutrient availability and PP itself [Boyd and Trull, 2007]. Despite the scatter introduced by these factors, and the simplicity of the relationship, SST alone is still able to explain 50% of the variance in the ThE$_i$-ratio.

[15] A global map of the annual mean ThE$_i$-ratio (Figure 2a) shows the expected pattern of low ThE$_i$-ratios at low latitudes (between 40°N and 40°S), moderate values in northern hemisphere high latitudes and high ThE$_i$-ratios in the Southern Ocean. The export of POC calculated from multiplying the ThE$_i$-ratio by PP is shown in Figure 2b. POC export in the Northern Hemisphere high latitudes is ~25–30 gC m$^{-2}$ yr$^{-1}$, contrasting with similar latitudes in the Southern Ocean, where export is estimated at ~5–10 gC m$^{-2}$ yr$^{-1}$. The low latitudes have an export of ~1–5 gC m$^{-2}$ yr$^{-1}$, with higher values (~10–15 gC m$^{-2}$ yr$^{-1}$) in upwelling regions. The annually integrated global POC export derived from the ThE$_i$-ratio is 4 (±2.2) GtC yr$^{-1}$. This is two-thirds less than the export estimated using the f-ratio to SST relationship of Laws et al. [2000] (≈12 GtC yr$^{-1}$). Why is there such a large difference between export estimated from thorium measurements and that estimated from the f-ratio?

4. Discussion

[16] Part of the discrepancy between ThE$_i$ and f-ratio based estimates of export arises because the thorium approach only accounts for the export of particulate organic carbon. Contributions to export flux also come from the production, seasonal accumulation, subduction and respiration of dissolved organic carbon (DOC). As a global average, the contribution of DOC to global export in the open ocean is ~20% [Hansell and Carlson, 1998]. Adding...
in this contribution brings our estimate of globally integrated export to 5 Gt C yr\(^{-1}\), still ~60% lower than the f-ratio based estimate.

[17] Part of the difference between the ThEq and f-ratio estimates is likely due to nitrification in the upper ocean, which results in some production previously considered to be new, now being considered recycled [Yool et al., 2007; Dore and Karl, 1996; Diaz and Raimbault, 2000]. The fractional difference between the ThEq-ratio and the f-ratio is highest in the oligotrophic Atlantic and lower in the Southern Ocean and equatorial regions (Figure 2c). The relatively small difference between f- and ThEq-ratio at high latitudes and in equatorial regions suggests that the majority of production here is fuelled by new nutrients supplied by vertical transport, and that the contribution of nitrification is minor. At low latitudes, however, the large difference between f- and ThEq-ratio estimates suggests that nitrate regeneration by nitrification may comprise a substantial fraction of the euphotic zone nitrate pool in these regions. These spatial differences are consistent with in situ measurements of nitrification rates, which were estimated as supplying 2–16% of the total nitrate pool in the Peruvian upwelling [Fernandez et al., 2009], 20–40% of it in the temperate North Atlantic [Fernandez and Raimbault, 2007], and a “substantial majority” of it in the oligotrophic Atlantic [Clark et al., 2008].

[18] Whilst upper ocean nitrification potentially results in the f-ratio approach over-estimating export efficiency, additional uncertainty arises from nitrogen fixation, the process by which atmospheric N\(_2\) is converted into ammonium. The magnitude of this source of new nitrate was unknown at the time the f-ratio was originally defined, but current estimates suggest that global marine N\(_2\) fixation is ~120 TgN yr\(^{-1}\) [Codispoti et al., 2001; Gruber, 2004], equivalent to ~0.8 GtC yr\(^{-1}\), assuming Redfield stoichiometry. As a consequence of N\(_2\) fixation, using the f-ratio to calculate carbon export may result in an underestimate of ~7%. The overestimate of carbon export due to nitrification (by up to 50% [Yool et al., 2007]) is, on a global scale, larger than the underestimate arising from N\(_2\) fixation. This implies that the overall effect of using the f-ratio to calculate global export results in an overestimate of the magnitude of the BCP.

[19] Other approaches to estimating global carbon export suggest values ranging from ~5.7 GtC yr\(^{-1}\) [Lutz et al., 2007] to ~20 GtC yr\(^{-1}\) [Eppley and Peterson, 1979], with several estimates clustering around 10–12 GtC yr\(^{-1}\) [Dunne et al., 2007; Schlitzer, 2004; Laws et al., 2000]. It has been suggested that even the higher values are too low to balance the respiration by heterotrophic activity occurring in meso- and bathypelagic waters [Burd et al., 2010; del Giorgio and Duarte, 2002]. Estimates of export made at HOTS and BATS on the basis of oxygen or carbon isotope mass balance are ~5 times greater than those made here [Emerson et al., 2001]. Our global export estimate overlaps with that of Lutz et al. [2007], but is significantly lower than other previous estimates. Why do different methodologies arrive at such a wide range of estimates?

[20] The various approaches to estimating global carbon export each have their own sources of uncertainty, in addition to an issue common to all of the methods, that of sparse in situ data that, generally speaking, are unable to sample temporal or spatial variability. Episodic export events, seasonal and interannual variability, and spatial patchiness in particle export are not usually resolved. Scaling up these point measurements to create a global budget assumes that the data are truly representative of normal conditions, i.e., a degree of spatial and temporal homogeneity has to be assumed.

[21] In addition, there are sources of uncertainty specific to each approach for estimating export. The thorium method relies on determination of the POC:Th ratio, which can vary by sampling method, regionally and with depth [Buesseler et al., 2006]. Applying the f-ratio approach requires careful accounting of new and regenerated sources of nitrate, including nitrification, N\(_2\) fixation and atmospheric deposition. Estimating global-scale export from meso- and bathypelagic respiration entails large uncertainties in the measurements, particularly bacterial growth efficiency and cell carbon content [Burd et al., 2010]. Additional poorly characterised terms in the estimation of carbon export arise from horizontal advection of material [Benitez-Nelson et al., 2000] and active transport of carbon by zooplankton [Steinberg et al., 2000].

[22] The discrepancies between our thorium-based approach, the f-ratio method and mesopelagic metabolic activity suggest that we may be overlooking significant sources or sinks of carbon, or that there are problems with one or more of the measurement methodologies. What is clear is that our knowledge of a major planetary carbon flux is incomplete, and that continued research will be essential to our understanding of the role of upper ocean export in the global carbon cycle and regulation of atmospheric CO\(_2\).

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References


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