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Global database of surface ocean particulate organic carbon export fluxes diagnosed from the ^{234}Th technique

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Abstract

The oceanic biological carbon pump is an important factor in the global carbon cycle. Organic carbon is exported from the surface ocean mainly in the form of settling particles derived from plankton production in the upper layers of the ocean. The large variability in current estimates of the global strength of the biological carbon pump emphasises that our knowledge of a major planetary carbon flux remains poorly constrained. We present a database of 723 estimates of organic carbon export from the surface ocean derived from the ^{234}Th technique. The dataset is archived on the data repository PANGEA[®] (www.pangea.de) under doi:10.1594/PANGAEA.809717. Data were collected from tables in papers published between 1985 and early 2013 only. We also present sampling dates, publication dates and sampling areas. Most of the open ocean provinces are represented by several measurements. However, the Western Pacific, the Atlantic Arctic, South Pacific and the South Indian Ocean are not well represented. There is a variety of integration depths ranging from surface to 220 m. Globally the fluxes ranged from 0 to 1500 mg of C m⁻² d⁻¹.

1 Introduction

The concept of the biological carbon pump, dating from the late 1970's (Eppley and Peterson, 1979) quantifies the importance of oceanic primary production in the global carbon cycle. The biological carbon pump can be divided into three stages: the production of organic matter (and biominerals) in surface waters, the sinking of these particles into the deep ocean, and the subsequent decomposition of the settling (or settled) particles in the water column or the seabed. In this way the coupling of production and export processes allows the ocean to store CO₂ away from the atmosphere and contributes to the buffering of the global climate system. Without the oceanic biological carbon pump, atmospheric CO₂ concentrations would be almost twice their current levels (Sarmiento and Toggweiler, 1984). Recent studies have highlighted the challenge

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of quantifying the magnitude of the biological carbon pump with estimates ranging from 5–20 GtC yr⁻¹ (Henson et al., 2011).

There are several ways by which downward export fluxes can be estimated. We can divide the techniques into two groups: (1) indirect estimates based on nutrient uptake (Sanders et al., 2005; Henson et al., 2006; Pondaven et al., 2000), oxygen utilization (Jenkins, 1982), radioisotopes (Buesseler et al., 1998a; Cochran and Masque, 2003; Rutgers Van Der Loeff et al., 1997b; Le Moigne et al., 2012, 2013) or by synthesising numerous biological rate processes (Boyd and Newton, 1999), or (2) direct measurements from sediments traps (Lampitt et al., 2008).

Here we focus on the ²³⁴Th technique, that has the advantage that its fundamental operation allows a downward flux rate to be determined from a single water column profile of thorium coupled to an estimate of the POC/²³⁴Th ratio in sinking matter (Buesseler et al., 1992). This is highly advantageous in that it removes the complications associated with sediment trap deployments and provides an integrated estimate of export (over a timescale of weeks) rather than a snapshot of export rates (Lampitt et al., 2008).

Although several comprehensive world wide datasets of POC flux from sediment traps have been published (e.g. Honjo et al., 2008), to date no comprehensive thorium derived export dataset has been published. As part of the SeasFX project (Seasonal Variability in the Efficiency of Upper Carbon Export, <http://www.seasfx.info>, funded by the UK National Environment Research Council), we compiled a global database of ²³⁴Th derived POC export from the surface ocean (0–220 m). It comprises 723 data points from 1985 to 2013 covering most oceanic provinces. The dataset is archived on the data repository PANGEA[®] (www.pangea.de) under doi:10.1594/PANGAEA.809717.

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2 Data

2.1 The crux of the ^{234}Th technique

The radioactive short-lived Thorium-234 (^{234}Th , $t_{1/2} = 24.1$ d) has been used as a tracer of several transport processes and particle cycling in aquatic systems by different techniques (Van der Loeff et al., 2006). The most widespread application of the ^{234}Th approach is to estimate how much POC is exported into the deep ocean (Waples et al., 2006). ^{234}Th is the daughter isotope of naturally occurring 238-Uranium (^{238}U , $t_{1/2} = 4.47 \times 10^9$ yr) that is conservative in seawater and proportional to salinity in well oxygenated environments (Ku et al., 1977; Chen et al., 1986). Unlike ^{238}U , ^{234}Th is insoluble in seawater and is particle reactive in the water column (i.e. ^{234}Th adheres to particles as they form). As particles with ^{234}Th sink through the water column, a radioactive disequilibrium is formed between ^{238}U and ^{234}Th , that can be used to quantify the rate of particle export from the surface ocean.

Export rates of ^{234}Th from the surface ocean can be calculated using a one-box model (Coale and Bruland, 1987; Buesseler et al., 1992, 1998a; Cochran et al., 2000; Cochran and Masque, 2003; Savoye et al., 2006; Benitez-Nelson et al., 2001a; Verdeny et al., 2008). Assuming steady state (SS) conditions, $\frac{\partial A_2}{\partial t} = 0$ where the total ^{234}Th activity does not change with time, and no supply of ^{234}Th from physical processes (e.g. advection), the ^{234}Th flux ($\text{dpm m}^{-2} \text{d}^{-1}$), P , is calculated through the water column as,

$$P = \lambda \sum_{z=0}^{z=h} (A_2 - A_1) \cdot dz \quad (1)$$

A_1 is the total parent activity concentration (dpm m^{-3}) for ^{238}U ; A_2 is the total ^{234}Th activity concentration (dpm m^{-3}); λ is the decay constant of the daughter (d^{-1}), h is the sample depth and P is the loss of the daughter due to sinking particles ($\text{dpm m}^{-3} \text{d}^{-1}$).

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In ²³⁴Th studies generally advection effects are neglected as shown in Morris et al. (2007) with the exception of upwelling regions or areas of strong advection (Murray et al., 1992; Buesseler et al., 1998b). If several profiles of ²³⁴Th activities are measured at the same site over a certain period of time (weeks or months) a non steady state (NSS) model can be applied. The NSS model can be useful during high particle flux events such as the onset of a bloom (Buesseler et al., 1998b). The NSS model factors in the term, $\frac{\partial A_2}{\partial t}$ that was originally made to equal zero in the SS model (Eq. 2 below).

$$P = \lambda \sum_{z=0}^{z=h} \left[(A_2 - A_1) - \frac{\partial A_2}{\partial t} dz \right] \quad (2)$$

We report ²³⁴Th fluxes from both SS and NSS models in our database. Reported ²³⁴Th fluxes were integrated from depths ranging from the surface down to 220 m (Fig. 1). The vast majority of fluxes are integrated to between 100 and 150 m. A few studies report ²³⁴Th integrated over greater depths but not more than 220 m depth. In the final stage of the process, the estimated ²³⁴Th flux is converted to POC export by applying the ratio of POC to particulate ²³⁴Th activity.

2.2 Determination of POC : ²³⁴Th ratio of sinking particles

The accuracy of the Th method relies critically on estimating the POC/²³⁴Th ratio of material sinking from the upper ocean (Buesseler et al., 2006). This estimate is most frequently achieved by assuming that sinking carbon is contained within large particles, often greater than 50 µm in size (or 53 µm, depending on the mesh supplier), whereas organic carbon within small particles is suspended in the water column, and are therefore assumed to be insufficiently large and/or dense to sink (Bishop et al., 1977; Fowler and Knauer, 1986).

There is a considerable body of literature on how and why POC/²³⁴Th ratios vary with particle size and depth (see review in Buesseler et al., 2006), however there is little consensus on the most appropriate ratio to use. Numerous processes can

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5 impact POC/²³⁴Th ratios in the ocean including particle surface area to volume ratios (Santschi et al., 2006), solution chemistry issues (Guo et al., 2002; Hung et al., 2004), the chemical composition of particles and their affinity for ²³⁴Th (Szlosek et al., 2009), POC assimilation by foodwebs (Buesseler and Boyd, 2009), particle aggregation (Burd et al., 2000) and fragmentation (Maiti et al., 2010) and Th decay (Cai et al., 2006).

3 Results and discussion

3.1 Data sources

10 The dataset is archived on the data repository PANGEA[®] (www.pangea.de) under doi:10.1594/PANGAEA.809717. Latitude, longitude, date, POC flux, Primary production (when available), integration depth and references are given as metadata.

15 All fluxes were converted to mgC m⁻² d⁻¹ if not already reported in these units. Th derived POC export has been reported at 723 stations globally (Fig. 2). Some stations were part of transect cruises whereas others were part of small scale surveys or reoccupation at different seasons and years. Cruise name, sampling date, sampling area and reference investigator are given in Table 1 in addition to the literature reference.

20 Our database covers measurements published between 1985 and 2013. We did not include unpublished data in the manuscript and as the data compiled here derives from research already published, we assume that the originating authors and editors have undertaken steps necessary to control data quality. Figure 3 shows the cumulative number of thorium-derived export data published from 1985 to 2013. In years 1992, 1998 and 2002 the number of ²³⁴Th measurements increased. This is likely due to significant improvement in the ²³⁴Th methodology such as the introduction of the small volume technique (Benitez-Nelson et al., 2001b) and it also highlights carbon export programs such as the VERTIGO voyages in the Pacific ocean (Buesseler et al., 2008b,

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2009). It is important to mention that our database only references Th export related papers where data were presented in tables, rather than only graphically.

More POC fluxes are reported in the Northern Hemisphere (~ 60 % of the database) than in the Southern Hemisphere (Fig. 4). In the Northern Hemisphere, each month of the year has been sampled (Fig. 4). Spring time (May) and summer time have been most frequently sampled. In the Southern Hemisphere, although stations are more evenly distributed in time, no ^{234}Th derived POC export numbers are reported for winter months (July and August, Fig. 4).

3.2 Global POC export and ocean provinces

^{234}Th derived POC export estimates are reported in 32 out of 56 Longhurst provinces (Longhurst, 1991, that are based on the prevailing role of physical forcing as a regulator of phytoplankton distribution), with measurements in most of the large open ocean biomes (Fig. 2). Figure 5 shows the mean ^{234}Th derived POC export ($\text{mg m}^{-2} \text{d}^{-1}$) in each Longhurst province that has been sampled at least once. Only four provinces are only represented with one measurement (NASE, CCAL, CHIL and NECS, see Table 2 for details and provinces names).

Our dataset exhibits similar global patterns of POC export as those estimated with other methods e.g. (Laws et al., 2000; Schlitzer, 2004) with highest daily POC export rate occurring in the high latitude North Atlantic, the Arctic and the Southern Ocean. NASE and WTRA province located in subtropical and equatorial Atlantic (Fig. 5 and Table 2) are two exceptions to this trend with POC export of 450 ($n = 1$) and $250 \pm 200 \text{ mg m}^{-2} \text{d}^{-1}$ reported in Thomalla et al. (2008) and Charette and Moran (1999), respectively.

Thomalla et al. (2008) suggest that the occurrence of a short-lived bloom triggered by nutrient injection into the surface from a local upwelling event may explain the surprisingly high POC flux in the NASE region. Whereas Charette and Moran (1999) propose that scavenging of ^{234}Th by inorganic particles may have overestimated the POC flux in the WTRA region as also observed by Le Moigne et al. (2013) and Brew et al. (2009).

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3.3 Towards better understanding of the ocean's biological carbon pump

A portion of this database has already been used to extrapolate the local measurements to a global scale by correlation with satellite sea surface temperature fields (Henson et al., 2011). The resulting estimates of global integrated carbon export were significantly lower than those derived from new production measurement (Laws et al., 2000), at just $\sim 5 \text{ GtC yr}^{-1}$. However, the parameterisation of the export ratio presented in Henson et al. (2011) has relatively large uncertainty at cold sea surface temperature (SST) (see their Fig. 2). The export ratio is thought to be primarily driven by the type of phytoplankton present in the upper ocean, because large, dense phytoplankton cells sink rapidly and export more efficiently than smaller plankton. The variability in export ratio at low temperatures could therefore be due to strong seasonal shifts in phytoplankton community structure at high latitudes (i.e. low SST).

In high latitude regions, simultaneous measurements of upper ocean particulate organic carbon flux and phytoplankton community structure could help assessing how seasonal variability of the phytoplankton bloom alters the export ratio. The knowledge earned from this approach could then be applied to our global dataset, combining satellite-derived data on sea surface temperature, bloom stage and phytoplankton community structure. Ultimately, a revised parameterisation of the export ratio, including relevant seasonal information could be used to calculate a new global estimate of the magnitude of the biological carbon pump.

3.4 Significant gaps in the global dataset

Globally the fluxes ranged from 0 to $1500 \text{ mg of C m}^{-2} \text{ d}^{-1}$ (Fig. 6). In this database, some areas such as the Equatorial Pacific, Arabian Sea, South China Sea and the High Latitude North Atlantic are fairly well represented (Fig. 6). However, there are significant gaps that could potentially bias estimates of the global carbon export. Most notably, ^{234}Th derived POC fluxes are not reported for the Benguela system (BENG),

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the Mauritanian upwelling (CNRV; ETRA), the entire western pacific (consisting of numerous Longhurst's provinces), and the South Indian Ocean (ISSG).

Some of these areas are deemed to be high production and export regions due to the occurrence of upwelling. For example, deep (~ 2000 m) sediment trap measurements of POC export for the Mauritanian upwelling suggest that POC export can peak at 5 to 25 $\text{mg m}^{-2} \text{d}^{-1}$ (Fischer et al., 2009) and presumably higher in the upper water column. Also, in the Benguela system POC export has been estimated to be 550 $\text{mg m}^{-2} \text{d}^{-1}$ on the basis of nutrient uptake (Waldron et al., 1992). Provinces such as KURO and PSAW in the North West Pacific may also export a significant amount of POC ($\sim 120 \text{ mg m}^{-2} \text{d}^{-1}$ averaged over one year, Schlitzer, 2004). Although these regions represent a small percentage of the global surface area of the ocean, the lack of data in these high export areas could potentially result in lower estimates of global POC export.

We suggest that future studies should investigate ^{234}Th derived POC export flux in regions that are currently unsampled or undersampled. However, in upwelling regions where advective current velocities are high, the influence of advection and diffusion on the ^{234}Th model should be carefully assessed and estimated as done for example in Morris et al. (2007) or Buesseler et al. (1998a), and Charette et al. (1999).

4 Conclusions

Here we provide a global database of 723 published estimates of POC export derived from the ^{234}Th technique. Some notable gaps in the dataset are the Benguela system, the Mauritanian upwelling, the western pacific, and the South Indian ocean. This database could be used to provide revised and more robust estimates of the ocean's biological carbon pump.

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Table 1. Sampling year, area and reference of studies used on the database.

Date	Area	<i>N</i>	Reference/Investigator
1987	Equatorial Pacific	4	Murray et al. (1989)
1992	Equatorial Pacific	65	Buesseler et al. (1995)
1992	Equatorial Pacific	24	Murray et al. (1996)
1992	Southern Ocean	1	Shimmiel and Ritchie (1995)
1992	Equatorial Pacific	2	Bacon et al. (1996)
1992	Southern Ocean	10	Rutgers van der Loeff et al. (1997a)
1992	Equatorial Pacific	16	Buesseler (1998)
1993–1994	Middle Atlantic Bight	7	Santschi et al. (1999)
1995	Arabian Sea	56	Buesseler et al. (1998b)
1996	Equatorial Atlantic	12	Charette and Moran (1999)
1996	Subarctic Pacific	3	Charette et al. (1999)
1996	Southern Ocean	6	Friedrich and van der Loeff (2002)
1997	Gulf of Maine	7	Charette et al. (2001)
1997	Southern Ocean	25	Cochran et al. (2000)
1997	China Sea	1	Cai et al. (2001)
1997–1998	Southern Ocean	41	Buesseler et al. (2001)
1997–1998	Southern Ocean	28	Buesseler et al. (2003)
1998–1999	Arctic	15	Amiel et al. (2002)
1999	North Pacific	4	Chen et al. (2003)
1999	Southern Ocean	8	Coppola et al. (2005)
1999	Labrador Sea	3	Moran et al. (2003)
2003	North Pacific	22	Kawakami et al. (2007)
2003–2005	Arctic	8	Lalande et al. (2008)
2003	Arctic	6	Rodriguez y Baena et al. (2008)
2004	Arctic	8	Lalande et al. (2007)
2004	Atlantic gyres	10	Thomalla et al. (2008)
2004	China Sea	36	Cai et al. (2008)
2004	Mediterranean Sea	4	Stewart et al. (2007)
2004–2005	Southern Ocean	20	Morris et al. (2007)
2004–2005	Atlantic	64	Buesseler et al. (2008a)
2004–2005	Pacific	45	Buesseler et al. (2009)
2005	Southern Ocean	5	Savoye et al. (2004)
2007	Arctic	36	Cai et al. (2010)
2007	North Atlantic	10	Sanders et al. (2010)
2007	Southern Ocean	14	Jacquet et al. (2011)
2008	Southern Ocean	27	Rutgers van der Loeff et al. (2011)
2008	South West Pacific	25	Zhou et al. (2012)
2008	Southern Ocean	11	Planchon et al. (2013)
2009	PAP site	10	Le Moigne et al. (2013)
2010	North Atlantic	20	Le Moigne et al. (2012)

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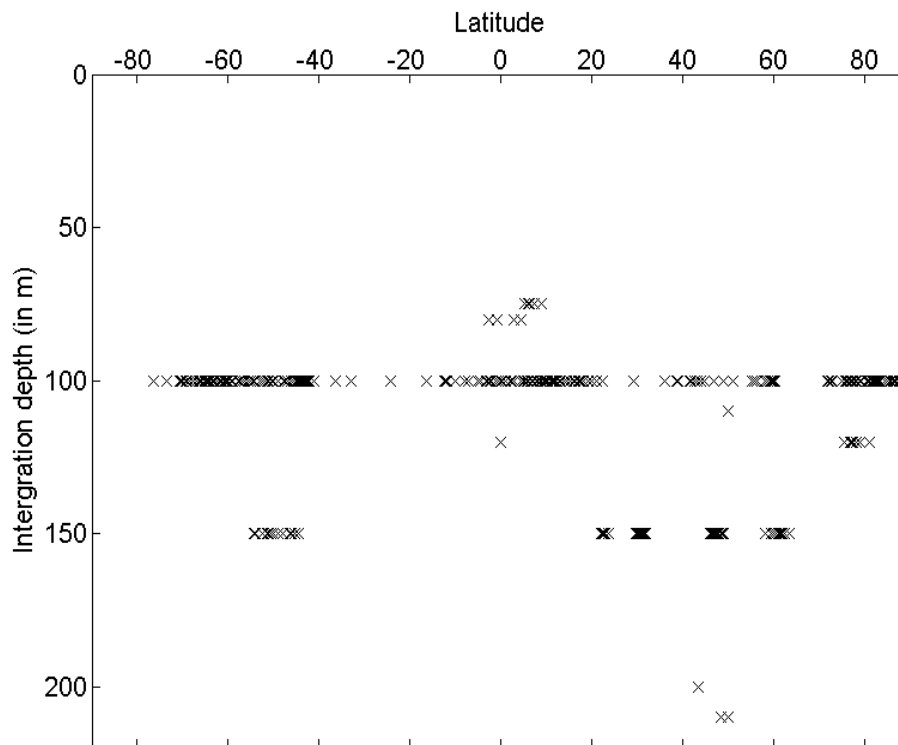
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Table 2. Mean POC flux ($\text{mgC m}^{-2} \text{d}^{-1}$) per Longhurst's provinces (Longhurst, 1991).

Province number	Province name	Mean POC flux $\text{mgC m}^{-2} \text{d}^{-1}$	Standard deviation in POC flux	Number of samples
2	CHIL – Chile-Peru Current Coastal	176.00	0	1
5	SATL – South Atlantic Gyre	37.44	54.38	7
14	PEQD – Pacific Equatorial Divergence	46.20	40.43	71
15	MONS – Indian Monsoon Gyre	62.16	54.26	10
19	ARAB – NW Arabian Upwelling	85.18	82.45	48
20	WTRA – Western Tropical Atlantic	251.39	178.19	10
22	NECS – NE Atlantic Shelves	53.52	0	1
23	NASE – North Atlantic Subtropical Gyre (East)	488.40	0	1
24	PSAE – Pacific Subarctic Gyre (East)	49.00	32.39	6
26	INDE – East India Coastal	31.60	15.66	3
28	PNEC – North Pacific Equatorial Countercurrent	48.65	50.29	24
30	INDW – West India Coastal	33.60	52.43	18
32	NPTG – North Pacific Tropical Gyre	26.27	23.57	21
33	NATR – North Atlantic Tropical Gyre	91.20	128.98	2
34	MEDI – Mediterranean Sea, Black Sea	115.80	78.70	4
35	CCAL – California Upwelling Coastal	14.76	0	1
36	NWCS – NW Atlantic Shelves	127.08	97.75	14
37	NASW – North Atlantic Subtropical Gyre (West)	25.90	19.41	65
39	NADR – North Atlantic Drift	87.56	51.22	11
41	ARCT – Atlantic Arctic	242.34	122.65	16
42	SARC – Atlantic Subarctic	214.67	127.06	14
44	SSTC – South Subtropical Convergence	114.34	136.16	7
45	SPSG – South Pacific Subtropical Gyre	28.79	13.73	10
47	BERS – North Pacific Epicontinental	146.00	24.04	3
50	ANTA – Antarctic	156.95	100.90	67
51	SANT – Subantarctic	126.54	116.71	107
53	APLR – Austral Polar	195.07	233.32	41
54	BPLR – Boreal Polar	171.05	298.48	72

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**Fig. 1.** Integration depth of the ^{234}Th fluxes versus latitude.

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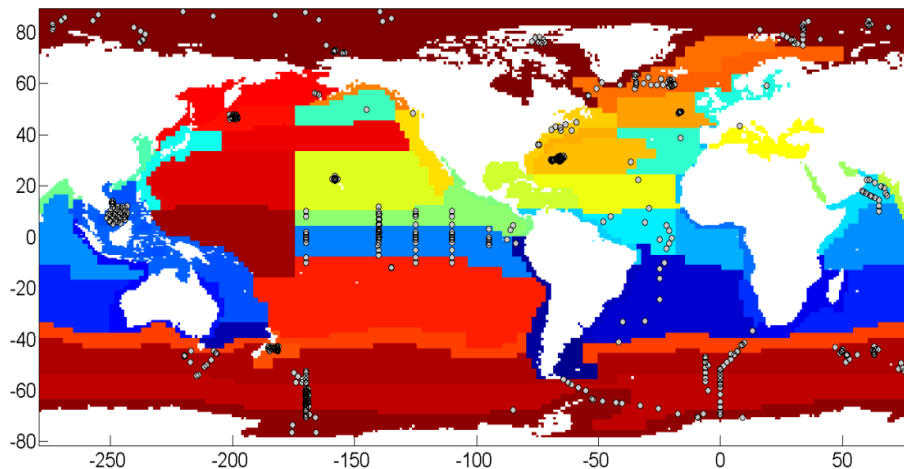


Fig. 2. Map showing the distribution of sampling stations. Longhurst oceanic (Longhurst, 1991) provinces are represented in different colours.

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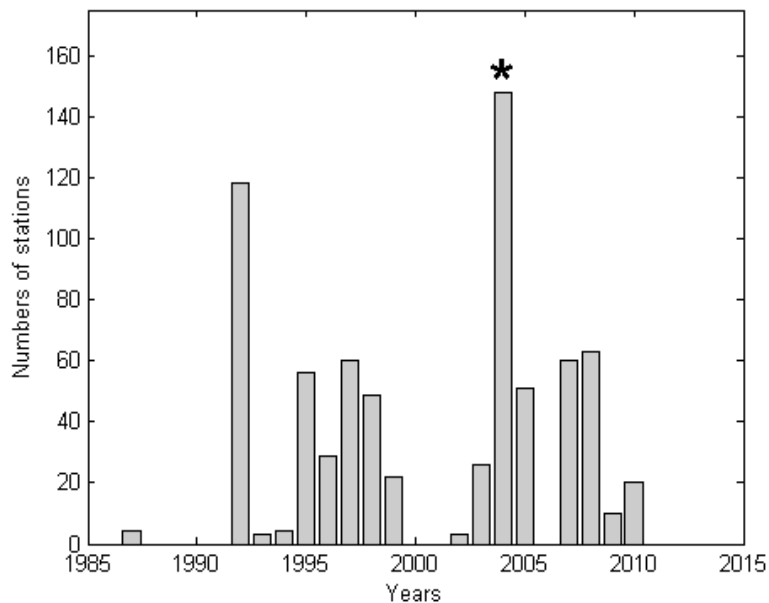
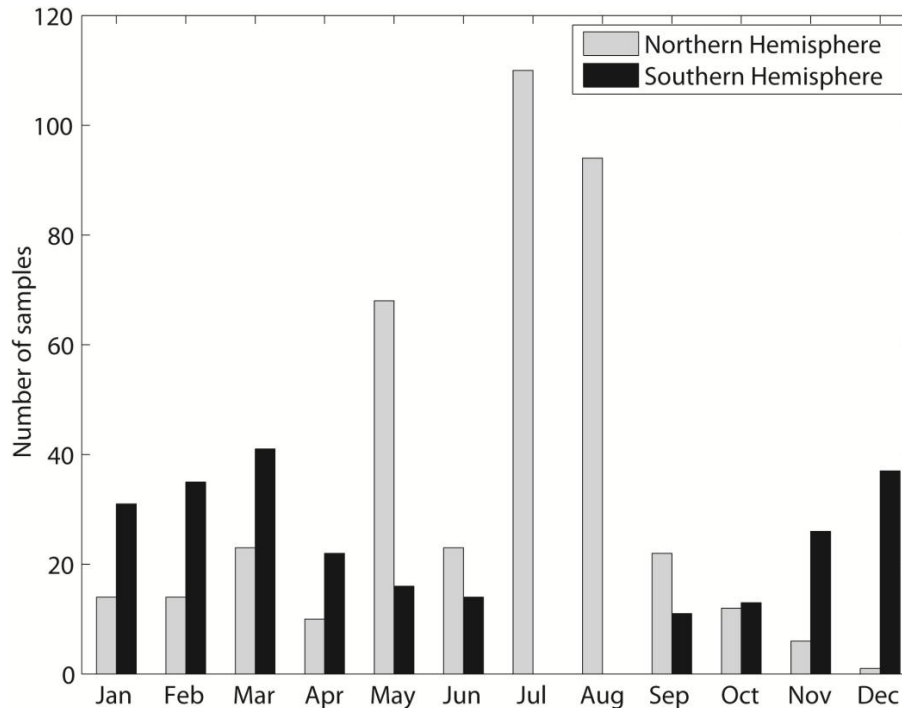


Fig. 3. Histogram of datapoints presented in table and published since 1987. The star indicates the year 2004 when VERTIGO study was undertaken.

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**Fig. 4.** Month when data were collected, separated into Northern and Southern Hemisphere.[Title Page](#)[Abstract](#)[Instruments](#)[Data Provenance & Structure](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[⏴](#)[⏵](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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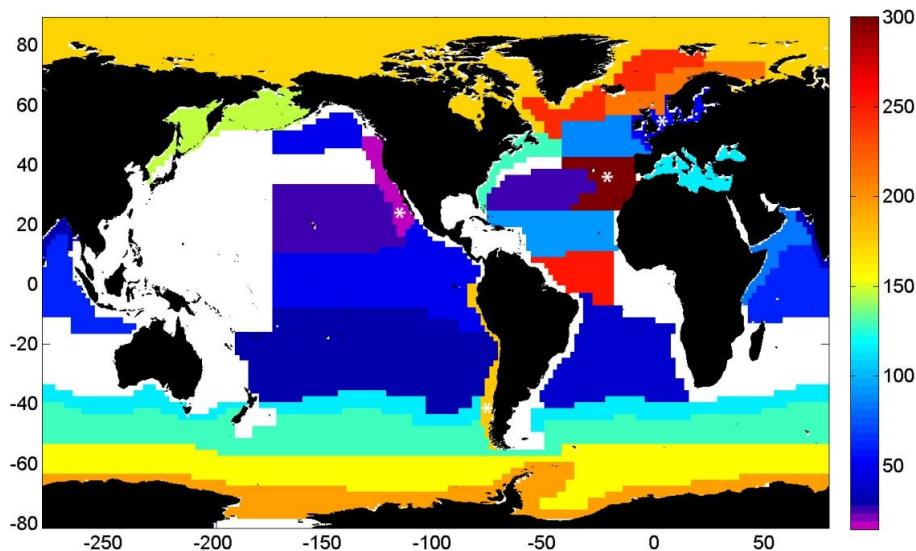


Fig. 5. Mean POC export ($\text{mg m}^{-2} \text{d}^{-1}$) in Longhurst provinces (provinces with only one measurement are marked with a star). Areas in white represent areas where no data have been presented.

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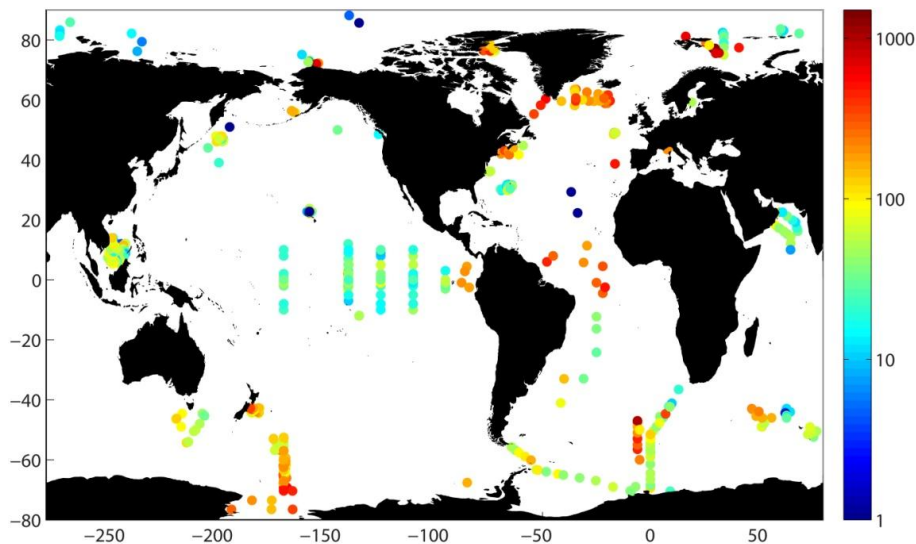


Fig. 6. Global distribution of POC export fluxes derived from the ^{234}Th technique (in $\text{mg m}^{-2} \text{d}^{-1}$).

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