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Global database of ratios of particulate organic carbon to thorium-234 in the ocean: improving estimates of the biological carbon pump

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Abstract. The ocean's biological carbon pump (BCP) plays a major role in the global carbon cycle. A fraction of the photosynthetically fixed organic carbon produced in surface waters is exported below the sunlit layer as settling particles (e.g., marine snow). Since the seminal works on the BCP, global estimates of the global strength of the BCP have improved but large uncertainties remain (from 5 to 20 $\mathrm{Gt\,C\,yr^{-1}}$ exported below the euphotic zone or mixed-layer depth). The ^{234}Th technique is widely used to measure the downward export of particulate organic carbon (POC). This technique has the advantage of allowing a downward flux to be determined by integrating the deficit of ^{234}Th in the upper water column and coupling it to the POC/^{234}Th ratio in sinking particles. However, the factors controlling the regional, temporal, and depth variations of POC/^{234}Th ratios are poorly understood. We present a database of 9318 measurements of the POC/^{234}Th ratio in the ocean, from the surface down to > 5500 m, sampled on three size fractions ($\sim> 0.7$ µm, $\sim$ 1–50 µm, $\sim> 50$ µm), collected with in situ pumps and bottles, and also from bulk particles collected with sediment traps. The dataset is archived in the data repository PANGAEA® under https://doi.org/10.1594/PANGAEA.911424 (Puigcorbé, 2019). The samples presented in this dataset were collected between 1989 and 2018, and the data have been obtained from published papers and open datasets available online. Unpublished data have also been included. Multiple measurements can be found in most of the open ocean provinces. However, there is an uneven distribution of the data, with some areas highly sampled (e.g., China Sea, Bermuda Atlantic Time Series station) compared to some others that are not well represented, such as the southeastern Atlantic, the south Pacific, and the south Indian oceans. Some coastal areas, although in a much smaller number, are also included in this global compilation. Globally, based on different depth horizons and climate zones, the median POC/^{234}Th ratios have a wide range, from 0.6 to 18 $\mathrm{\mu mol\,dpm^{-1}}$.

1 Introduction

The vertical export of photosynthetically produced particulate organic carbon, from the surface waters to the deep ocean (i.e., biological carbon pump; Eppley and Peterson, 1979), has a strong impact in the global carbon cycle. Through this process, the ocean stores carbon dioxide (CO_2) away from the atmosphere and buffers the global climate system (Kwon et al., 2009). Indeed, estimates suggest that atmospheric CO_2 levels would be 200 ppm higher than current concentrations without the biological carbon pump (Parekh et al., 2006). However, quantifying the magnitude of the biological carbon pump at both the regional and global scales is challenging and current assessments vary widely, with estimates ranging from 5 to 20 $\mathrm{Gt\,C\,yr^{-1}}$ being exported below the euphotic zone or the mixed-layer depth (Guidi et al., 2015; Henson et al., 2011; Laws et al., 2011).

Downward export fluxes of organic carbon can be estimated using (i) indirect approaches derived from nutrient uptake (Le Moigne et al., 2013a; Pondaven et al., 2000; Sanders et al., 2005), radioisotopes (Cochran and Masqué, 2003), satellite empirical algorithms (Dunne et al., 2007; Henson et al., 2011; Laws et al., 2011), underwater video systems (Guidi et al., 2008), or (ii) direct measurements using various designs of sediment traps (Buesseler et al., 2007; Engel et al., 2017; Lampitt et al., 2008; Owens et al., 2013) or marine snow catchers (Cavan et al., 2015; Riley et al., 2012).

Here we focus on the use of radioisotopes, specifically, ^{234}Th. The ^{234}Th approach allows us to quantify an export flux from (i) a water profile of ^{234}Th to obtain its deficit relative to ^{238}U combined with (ii) an estimate of the ratio of POC concentration to ^{234}Th activity (POC/Th ratio) in sinking matter (Buesseler et al., 1992). In reviewing POC/Th ratio variability using the data available at the time, Buesseler et al. (2006) found that the POC/Th ratios (i) increase or remain constant with increasing particle size and (ii) decrease with depth. Regionally, the POC/Th ratios vary largely between oceanic provinces and regimes (Puigcorbé et al., 2017a). The study of the biogeochemical behavior of ^{234}Th with regards to marine particles has received significant attention (Maiti et al., 2010; Le Moigne et al., 2013c; Puigcorbé et al., 2015; Rosengard et al., 2015; Santschi et al., 2006), and the availability of ^{234}Th-related data has been enhanced thanks to international and national programs such as GEOTRACES (Mawji et al., 2015; Schlitzer et al., 2018), JGOFS (Joint Global Ocean Flux Study) (Buesseler et al., 1998, 1995, 2001), or VERTIGO (Buesseler et al., 2008b), yet the factors controlling the variations in the POC/Th ratio as a function of region, time, particle size and type, and water column depth remain poorly understood. Assessing the influence of such factors on the POC/Th ratios will contribute to improve our modeling efforts and our capacity to predict the export and fate of the organic carbon produced in the surface layers. Indeed, the necessity to constrain the variability of the POC/Th was discussed and considered a priority at the technical meeting “The Application of Radionuclides in Studies of the Carbon Cycle and the Impact of Ocean Acidification” held at the International Atomic Energy Agency (IAEA) Environment Laboratories in Monaco in October 2016 (Morris et al., 2017).

Therefore, we compiled a database that comprises 9318 POC/Th ratios collected between 1989 and 2018 covering most oceanic provinces at depths ranging from 0 to > 5500 m. The particles were collected using collection bottles (i.e., Niskin), in situ pumps, or sediment traps, and they include bulk and size fractionated samples. This database significantly increases the pool of POC/Th ratio data available at the time of Buesseler et al. (2006) and enables us to test the influence of various factors on the variability of POC/Th ratios. Among other information, the influence of biogeochemical characteristics of the area (e.g., nutrient concentrations) together with the surface productivity levels, phytoplankton compositions, and zooplankton abundance could be examined through satellites products and/or global databases (e.g., Buitenhuis et al., 2013; Moriarty et al., 2013; Moriarty and O’Brien, 2013).

2 Data

2.1 The ^{234}Th approach

The short-lived radionuclide thorium-234 (^{234}Th, $t_{1/2} = 24.1$ d) is widely used to estimate the magnitude of POC that escapes the upper ocean layers (e.g., the euphotic zone) (Waples et al., 2006). ^{234}Th is the decay product of uranium-238 (^{238}U, $t_{1/2} = 4.47 \times 10^9$ yr). While uranium is conservative and proportional to salinity in well-oxygenated seawater (Chen et al., 1986; Ku et al., 1977; Owens et al., 2011), thorium is not soluble in seawater and it is scavenged by particles as they form and/or sink along the water column. As a consequence, a radioactive disequilibrium between ^{238}U and ^{234}Th can be observed, mainly in the upper layers of the water column, which at first approximation, is proportional to the numbers of particles exported and hence can be used to estimate particle and elemental export fluxes.

A one-box scavenging model (see review by Savoye et al., 2006, and references therein) is commonly applied to calculate ^{234}Th export rates. Steady-state (SS) or non-steady-state (NSS) conditions are assumed depending on the conditions at the sampling time and the possibility to reoccupy locations within an adequate timescale. Le Moigne et al. (2013b) reported ^{234}Th fluxes from both types of models in their database with flux integration depths spanning from the surface down to 300 m, although the most common integration depths were between 100 and 150 m. The choice of export depth when using the ^{234}Th technique is not trivial. Rosengard et al. (2015) provide recommendations to the various manners of choosing the export depth in order to integrate the ^{234}Th fluxes. Once the ^{234}Th export flux is estimated, it is multiplied by the ratio of POC to particulate ^{234}Th activity in sinking particles to obtain the POC flux. The sinking particles from which the ratio is measured should, ideally, be collected at the depth where the export has been estimated and represent the pool of particles that are driving the export of organic carbon.

2.2 The crux of the ^{234}Th approach: POC/Th ratios of sinking particles

The determination of the POC/Th ratio has been historically attained by assuming that sinking carbon is driven by large particles, generally >50 µm in size (researchers also use 51, 53, or 70 µm, depending on the mesh supplier) whereas organic carbon within small particles is assumed to remain suspended and therefore not contribute to the export flux (Bishop et al., 1977; Fowler and Knauer, 1986). However, recent studies have shown that small particles can be significant players in the particle export and should not be disregarded (Alonso-González et al., 2010; Durkin et al., 2015; Le Gland et al., 2019; Puigcorbé et al., 2015; Richardson, 2019), particularly in oligotrophic regions. The most common methods to obtain the particulate fraction to measure the POC/Th ratio are (i) in situ pumps (ISPs), which can allow for sampling different particle sizes; (ii) collection bottles (CBs) such as Niskin bottles, providing bulk particles, i.e., > 0.7 or 1 µm particles; (iii) sediment traps (STs); and although less common (iv) marine snow catchers. In some instances various methods have been used in combination (Cai et al., 2010; Maiti et al., 2016; Puigcorbé et al., 2015).

Different sampling devices have been shown to provide differences in POC/Th ratios, usually within a factor of 2 to 4 (Buesseler et al., 2006). The differences can be related to the collection of different particle pools and/or the enhanced presence of swimmers. STs collect sinking particles and may suffer from hydrodynamic discrimination and undersample slow-sinking particles (Gustafsson et al., 2004). CBs sample both sinking and suspended particles similar to ISPs. ISPs filter large volumes of water and have been suggested to potentially undersample some of the fast-sinking particles (Lepore et al., 2009) and sample neutrally buoyant C-rich aggregates (i.e., non-sinking but with high POC/Th ratios) (Lalande et al., 2008). Biases due to washout of large particles when using ISPs (Bishop et al., 2012) or aggregate collapse induced by their high cross-filter pressure (Gardner et al., 2003) may further enhance these differences. The presence of swimmers can also be an important bias of POC/Th ratios when not thoroughly removed, since they skew measurements towards higher values because of their high POC proportion compared to ^{234}Th (Buesseler et al., 1994; Coale, 1990).

2.3 POC/^{234}Th ratio variability

Despite the significant body of literature available on POC/Th ratios, more than 10 years after the review by Buesseler et al. (2006) we still cannot explain the variability of the POC/Th ratios with depth, time, particle type and size, or sinking velocity easily or at a global level. Changes with size and depth have been the most extensively examined. The relation between POC/Th ratio and particle size has been assessed before, with results suggesting that there is not a direct relationship. Previous studies have reported increasing ratios with increasing particle size (Benitez-Nelson et al., 2001; Buesseler et al., 1998; Cochran et al., 2000), which has been interpreted as an effect of the volume-to-surface area ratio of the particles, due to ^{234}Th being surface bound whereas C would be contained within the particles (Buesseler et al., 2006). Yet, a number of studies have reported the opposite trend (i.e., decreasing ratio with increasing particle size; Bacon et al., 1996; Hung et al., 2010; Planchon et al., 2013; Puigcorbé et al., 2015) or no clear change with size (Hung and Gong, 2010; Lepore et al., 2009; Speicher et al., 2006). Depth is another factor that has been considered when assessing the variability of POC/Th, since particles are produced in the surface layer and are remineralized on their transit along the water column (Martin et al., 1987). POC/Th ratios have been found to be attenuated with depth (Jacquet et al., 2011; Planchon et al., 2015; Puigcorbé et al., 2015). This is due to (in no order or importance) decreasing autotrophic production with increasing water depth, preferential C loss compared to ^{234}Th through remineralization processes, changes in superficial binding ligands along the water column, and/or scavenging of ^{234}Th during particle sinking resulting in enhanced particulate ^{234}Th activities (Buesseler et al., 2006; Rutgers van der Loeff et al., 2002), leading to significant variability in the attenuation rates. Theoretically, high sinking velocities may limit the variations in POC/Th ratios with depth, owing to shorter residence times limiting the impacts of biotic and abiotic processes. However, using specifically designed STs that segregate particles according to their in situ sinking velocities, Szlosek et al. (2009) observed no consistent trend between POC/Th ratios and sinking velocities.

The truth is that numerous processes can impact the POC/Th ratios apart from particle size or depth, such as particle composition or aggregation–disaggregation processes mediated by physical or biological activity (Buesseler and Boyd, 2009; Burd et al., 2010; Maiti et al., 2010; Szlosek et al., 2009), which adds a level of complexity to the prediction of their variability in the ocean. Yet, due to the significance of the POC/Th ratios for the accuracy of the ^{234}Th flux method, the effort should be made to constrain the factors that will impact its variability, and a number of environmental and biogeochemical parameters can be assessed with that goal at a global scale. Among others, surface productivity, phytoplankton composition, zooplankton abundance, mixed-layer depth, dust inputs to the surface ocean, and ice cover (Buitenhuis et al., 2013; Mahowald et al., 2009; Moriarty et al., 2013; Moriarty and O'Brien, 2013) are all potential candidates to test their global patterns against POC/Th ratio variability.

3 Results and discussion

3.1 Data classification

Our dataset is archived in the data repository PANGAEA® (http://www.pangaea.de), https://doi.org/10.1594/PANGAEA.911424 (Puigcorbé, 2019). Latitude, longitude, and sampling dates are reported. When dates of the individual stations were not reported in the original publications, we allocated the midpoint of the sampling period as the sampling date. The same was done when the specific sampling coordinates were not available (see details in the comments related to the dataset; https://doi.org/10.1594/PANGAEA.902103; Puigcorbé, 2019). The database consists of 9318 measurements of POC/Th ratios in the ocean. Particles were collected using in situ pumps (ISPs), water collection bottles (CBs), and sediment traps (STs). We refer to "bulk" (BU) for particles sampled using CBs and ISPs with a pore size filter of 0.2–1 µm. For this group of samples, particles > 0.7 µm were collected using GFF filters and > 1 µm using QMA filters. In some particular cases other types of filters, with a different pore size (e.g., 0.2, 0.45, or 0.6 µm) might have been used (see database for details). Hereafter, we use > 1 µm for the bulk particles. We refer to "small particles" (SPs) for particles usually collected using ISPs on a 1–50 µm mesh size and "large particles" (LPs) for particles usually collected using ISPs on mesh size > 50 µm (see details on other size ranges also used in the database). Finally, some POC/Th ratios were measured in sinking particles sampled using sediment traps (STs). Figure 1 shows the global distribution of POC/Th ratios grouped by these four categories: BU, LP, SP, and ST. The POC/Th ratios were obtained from particles collected at various depths from the surface to > 5500 m (Fig. 2). All the information on locations, dates, depth, size fractions/device (BU, SP, LP, and ST), and references is included as metadata in the online database and presented in Table 1.

Our database covers POC/Th measurements sampled between 1989 and 2018, including unpublished data from our laboratories or graciously made available to us by colleagues and data available in online databases. Figure 3 shows the number of POC/Th measurements available per year. In the years 1997, 2004, 2005, 2008, 2010, 2011, and 2013, the number of POC/Th measurements was > 500. This highlights dedicated carbon export programs such as the Joint Global Ocean Flux Study (JGOFS) (Buesseler et al., 1998, 1992, 1995, 2001; Murray et al., 1996, 2005), the VERTIGO (Vertical Transport in the Global Ocean) voyages in the Pacific Ocean (Buesseler et al., 2008b), and the GEOTRACES program (Mawji et al., 2015; Schlitzer et al., 2018), as well as the maintained effort of the time series stations (Kawakami et al., 2004, 2010, 2015; Kawakami and Honda, 2007). Sampling effort also varied depending on the month of the year (Fig. 3b), with late spring–summer months being the most highly sampled in both hemispheres. The Northern Hemisphere has been largely sampled in September, May, and June (49, 10, and 5 times more data than in the Southern Hemisphere, respectively), whereas the Southern Hemisphere has been more sampled in December and February (5 and 4 times more data than in the Northern Hemisphere, respectively), with no data available for the months of July and August and only five data points in September (austral winter). For the rest of the months, the Northern Hemisphere presents 1.4–1.8 times more data than the Southern Hemisphere. In the equatorial region (taken as the latitudes between −10 and 10° N) major sampling efforts took place in May, with no data collected in January and just eight data points available from December. The monthly distribution is, therefore, globally biased towards the warmer and more productive seasons, leaving the winter months largely undersampled, particularly in the Southern Hemisphere.

3.2 Global variability: climate zones and depth horizons

The global variability of POC/Th ratios looking at six different depths horizons (50, 100, 200, 500, 1000, and > 1000 m) and grouped by climatic zones (polar $> 66.5°$, subpolar 66.5–50°, temperate 50–35°, subtropical 35–23.5°, and tropical 23.5° N–23.5° S) is presented in Fig. 4. A PERMANOVA analysis was conducted to examine the data, and the results indicate that all the depth horizons defined here were significantly different ($p < 0.05$). Significant differences were also found between climatic zones, except between the temperate and subtropical zones and between the subtropical and the tropical zones, when considering all the data together. Statistical differences between zones within a certain depth range are shown in Fig. 4.

In general, we observe a reduction in POC/Th ratios with depth, previously reported by others (Buesseler et al., 2006), and likely mainly due to the remineralization of carbon along the water column. The decrease is particularly marked in the upper 200 m, where biological processes affecting the ratios are more intense, and then it smoothes below that depth horizon as the strength of these processes is more limited below the euphotic zone. It is worth noticing that some studies, particularly in coastal areas, presented extremely large POC/Th ratios (> 100 µmol dpm^{-1}, not included in Fig. 4). These high ratios are not always discussed in the publications, but the presence of live zooplankton (Buesseler et al., 2009; Savoye et al., 2008; Trull et al., 2008), especially in BU, ST, and LP fractions, when not picked out can be the cause for those high values and should be considered with caution.

Regarding the climate zones, there is significant variability, but, in general, large POC/Th ratios occur more often in productive and high-latitude regions relative to low-latitude

Table 1. Sampling year; area; number of samples for large particles (LPs), small particles (SPs), bulk (BU) particles, and particles collected with sediment traps (STs); and reference of studies used in the database. Note the following references refer to data published in several papers: Stukel et al. CCE refers to data published in Stukel et al. (2011, 2015, 2017, 2019); Stukel et al. CRD refers to data from Stukel et al. (2015, 2016). Buesseler JGOFS dataset Arabian Sea refers to data published in Buesseler et al. (1998) and also available at https://www.bco-dmo.org/project/2043 (last access: 3 June 2020). Buesseler JGOFS dataset Southern Ocean refers to data published in Buesseler et al. (2001) and also available at https://www.bco-dmo.org/project/2044 (last access: 3 June 2020). Kawakami North Pacific time series data are available at http://www.jamstec.go.jp/res/ress/kawakami/234Th.html (last access: 3 June 2020) and have also been published in Kawakami (2009), Kawakami et al. (2004, 2010, 2015), Kawakami and Honda (2007), and Yang et al. (2004). Further details regarding particle size specifications or sampling device can be found in the database file https://doi.org/10.1594/PANGAEA.902103.

Sampling year	Area	LP *n*	SP *n*	ST *n*	BU *n*	Reference/investigator
1989	North Atlantic	–	–	6	12	Buesseler et al. (1992)
1991–1992	Buzzards Bay	–	–	–	7	Moran and Buesseler (1993)
1992	Equatorial Pacific	80	–	–	–	Bacon et al. (1996)
1992	Sargasso Sea	–	–	2	–	Buesseler et al. (1994)
1992	Equatorial Pacific	71	78	–	–	Buesseler et al. (1995)
1992	Atlantic sector of the Southern Ocean	–	–	–	31	Friedrich and Rutgers van der Loeff (2002)
1992	Central equatorial Pacific	–	–	124	–	Murray US JGOFS EqPac (Murray et al., 1996, 2005)
1992	Atlantic sector Southern Ocean	–	–	–	32	Rutgers van der Loeff et al. (1997)
1992	Bellingshausen Sea, Antarctica	–	–	–	3	Shimmield et al. (1995)
1992–1993	Northeast Water polynya, Greenland	–	–	–	11	Cochran et al. (1995)
1993	Middle Atlantic Bight	–	–	–	30	Santschi et al. (1999)
1993–1994	Station BATS, North Atlantic, and Gulf of Maine	–	–	–	4	Gustafsson et al. (1997)
1993–1996	Guaymas Basin	–	–	58	–	Smoak et al. (1999)
1994	Central Arctic Ocean	28	–	–	–	Moran et al. (1997)
1995	Arabian Sea	123	148	–	–	Buesseler JGOFS dataset Arabian Sea
1995	Wilkinson Basin and Jordan Basin	20	20	–	–	Charette et al. (2001)
1995	Beaufort Sea	–	–	–	22	Moran and Smith (2000)
1995	Atlantic sector Southern Ocean	–	–	–	80	Rutgers van der Loeff et al. (2002)
1995	NW Mediterranean Sea	–	–	3	15	Schmidt et al. (2002b)
1996	Subtropical and tropical Atlantic Ocean	25	22	–	–	Charette and Moran (1999)
1996–1997	Northeast Pacific Ocean	–	–	4	144	Charette et al. (1999)
1996–1997	Ross Sea	82	79	–	–	Cochran et al. (2000)
1996–1997	Gulf of Maine	–	–	–	7	Dai and Benitez-Nelson (2001)
1996–1997	Sargasso Sea	–	–	–	6	Kim and Church (2001)
1996–1998	Ross Sea	291	271	–	–	Buesseler JGOFS dataset Southern Ocean
1997	Southwestern Gulf of Maine	–	–	–	64	Benitez-Nelson et al. (2000)
1997	Sargasso Sea	–	–	3	–	Buesseler et al. (2000)
1997	Gulf of Lion	–	–	–	33	Giuliani et al. (2007)
1997	Northern Iberian Margin	–	–	–	22	Hall et al. (2000)
1997	Northern Adriatic Sea	–	–	–	23	Radakovitch et al. (2003)
1997–2000, 2002–2008	NW North Pacific	92	–	48	664	Kawakami North Pacific Time Series
1998	Arctic Ocean	–	–	–	19	Baskaran et al. (2003)
1998	Western Iberian Margin	–	–	–	12	Schmidt et al. (2002a)
1998–1999	North Water Polynya	15	–	45	–	Amiel et al. (2002)
1999	South China Sea	–	–	–	20	Cai et al. (2001)
1999	Canada Basin, Bering Sea	–	–	–	27	Chen et al. (2003)
1999	Barents Sea	–	–	5	25	Coppola et al. (2002)
1999	Crozet Basin	–	–	–	8	Coppola et al. (2005)
1999	Northern North Sea	–	–	–	24	Foster and Shimmield (2002)
1999	Labrador Sea	8	3	–	–	Moran et al. (2003)
1999–2000	North Pacific Subtropical Gyre	5	5	9	–	Benitez-Nelson et al. (2001)
2000	Gulf of Mexico	15	15	–	–	Guo et al. (2002)
2000	Canada Basin Arctic Ocean	–	–	–	25	Trimble and Baskaran (2005)
2000–2001	Gulf of Mexico	21	21	4	–	Hung et al. (2004)
2000–2002	Northern South China Sea	–	–	–	44	Chen et al. (2008)
2001	Subarctic Pacific	–	–	6	19	Aono et al. (2005)
2001	Gullmar fjord, Sweden	–	–	7	8	Gustafsson et al. (2006)

Table 1. Continued.

Sampling year	Area	LP *n*	SP *n*	ST *n*	BU *n*	Reference/investigator
2001	Arctic Ocean (marginal ice zone)	–	–	17	46	Gustafsson and Andersson (2012)
2001	Southern Ocean	38	36	–	–	Thomas Trull and Ken Buesseler (unpublished)
2002	Southern Ocean/south of the ACCF	39	40	–	–	Buesseler et al. (2005)
2002	Chukchi Sea	171	–	–	–	Moran et al. (2005)
2002	Bay of Biscay to Celtic Sea	–	–	–	24	Schmidt et al. (2013)
2003	Western Arctic Ocean	–	–	–	18	Ma et al. (2005)
2003	Southern Ocean	6	–	–	–	Rodriguez-Baena et al. (2008)
2003	NW Mediterranean Sea	4	–	20	–	Stewart et al. (2007)
2003	Western Arctic Ocean	–	–	–	32	Yu et al. (2010)
2003, 2005	Northern Barents Sea	24	–	24	–	Lalande et al. (2008)
2003–2006	Porcupine Abyssal Plain	7	–	5	–	Lampitt et al. (2008)
2004	Canadian Arctic Shelf	24	–	–	–	Amiel and Cochran (2008)
2004	South China Sea	–	–	–	169	Cai et al. (2008)
2004	Western Arctic Shelf Basin	38	–	45	–	Lalande et al. (2007)
2004	Western Arctic Ocean	206	–	–	–	Lepore et al. (2007)
2004	Sargasso Sea	–	–	2	–	Maiti et al. (2009)
2004	NW Mediterranean Sea	–	–	3	–	Schmidt et al. (2009)
2004	Southern Ocean	–	–	–	1	Smetacek et al. (2012)
2004	Eastern Mediterranean Sea	26	26	–	–	Speicher et al. (2006)
2004–2005	Tropical North Pacific (Hawaii)	103	115	8	–	Buesseler et al. (2008a)
2004–2005	North Pacific (ALOHA and K2)	35	97	–	–	Buesseler et al. (2009)
2004–2005	North Pacific Ocean	–	–	36	–	Lamborg et al. (2008)
2004–2005	Southern Ocean	20	–	–	–	Morris et al. (2007)
2005	South China Sea	16	15	–	–	Cai et al. (2006)
2005	Mediterranean Sea and NW Atlantic	37	32	15	–	Lepore et al. (2009)
2005	Tropical North Pacific (Hawaii)	13	13	2	–	Maiti et al. (2008)
2005	Kerguelen Plateau, Southern Ocean	26	–	–	–	Savoye et al. (2008)
2005	Ligurian Sea, NW Mediterranean Sea	–	–	22	–	Szlosek et al. (2009)
2005	Falkland Islands and Great Britain	10	10	–	82	Thomalla et al. (2006)
2005–2006, 2009	NW Gulf of Mexico and NW Pacific	35	34	25	–	Hung et al. (2010)
2006	Kuroshio Current	6	6	4	–	Hung and Gong (2007)
2006	Hung-Tsai Trough, southwestern Taiwan	–	–	–	30	Wei et al. (2009)
2006–2007	Sargasso Sea	20	20	12	–	Brew et al. (2009)
2006–2007	Sargasso Sea	9	9	9	–	Stewart et al. (2011)
2006–2008	Tsushima Basin, Sea of Japan	–	–	–	12	Kim et al. (2011)
2006–2008	South China Sea	–	–	17	–	Wei et al. (2011)
2006–2009, 2011–2012, 2014, 2016	California Current	47	–	60	–	Stukel et al. CCE
2007	Arctic Ocean	14	14	–	36	Cai et al. (2010)
2007	Southern Ocean	77	75	–	2	Jacquet et al. (2011)
2007	North Atlantic Ocean	20	–	–	–	Sanders et al. (2010)
2007	South China Sea	–	–	–	85	Zhou et al. (2013)
2008	Northwest Pacific	–	–	13	–	Hung et al. (2012)
2008	South China Sea	–	–	9	–	Hung and Gong (2010)
2008	Iceland Basin	–	–	9	–	Martin et al. (2011)
2008	Eastern Bering Sea	–	–	35	–	Moran et al. (2012)
2008	Southern Ocean	46	49	–	45	Planchon et al. (2013)
2008	Gulf of California and eastern tropical Pacific	83	83	8	–	Puigcorbé et al. (2015)
2008	Atlantic sector Southern Ocean	12	12	–	27	Rutgers van der Loeff et al. (2011)
2008	Chukchi Sea	–	–	–	79	Yu et al. (2012)
2008	Southern Ocean	–	–	–	146	Zhou et al. (2012)
2008–2009	West Antarctic Peninsula	1	1	4	–	Buesseler et al. (2010)
2008–2009	Southern Ocean and Sargasso Sea	–	26	–	–	Zhou et al. (2016)
2009	Porcupine Abyssal Plain	20	13	–	–	Le Moigne et al. (2013c)
2009	Southern Ocean	–	–	6	–	Martin et al. (2013)
2009	NW Mediterranean Sea	–	–	42	–	Viena Puigcorbé (unpublished) – FAMOSO
2009	Powell Basin of the Weddell Sea	–	–	5	6	Shaw et al. (2011)
2009	Cabo Verde archipelago	14	–	–	–	Turnewitsch et al. (2016)
2009–2010	Eastern Bering Sea	–	–	89	–	Baumann et al. (2013)

Table 1. Continued.

Sampling year	Area	LP *n*	SP *n*	ST *n*	BU *n*	Reference/investigator
2009–2011	South China Sea	–	–	–	777	Cai et al. (2015)
2009–2011	Saanich Inlet	–	–	–	76	Luo et al. (2014)
2010	Irminger Basin and Iceland Basin	–	–	8	–	Ceballos-Romero et al. (2016)
2010	Saronic Gulf	10	10	–	–	Evangeliou et al. (2013)
2010	North Atlantic Ocean	39	39	–	–	Le Moigne et al. (2012)
2010	NW Atlantic	11	–	–	–	Puigcorbé et al. (2017a)
2010	Costa Rica upwelling dome	13	–	10	–	Stukel et al. CRD
2010–2011	Southeastern Pacific	–	–	16	–	Haskell et al. (2013)
2010–2011	Atlantic Ocean	189	–	–	–	Owens et al. (2015)
2011	Tropical Atlantic	15	–	–	–	Pabortsava (2014)
2011	Kerguelen Plateau, Southern Ocean	48	52	–	–	Planchon et al. (2015)
2011–2012	Southern Ocean (Atlantic and Indian sectors)	27	–	–	–	Rosengard et al. (2015)
2012	Arctic Ocean	13	10	–	–	Le Moigne et al. (2015)
2012	Southeast of the Mississippi delta	39	38	11	–	Maiti et al. (2016)
2012	Atlantic sector Southern Ocean	8	–	2	–	Puigcorbé et al. (2017b)
2012	Eurasian Basin of the central Arctic	25	–	–	–	Roca-Martí et al. (2016)
2012	Atlantic sector Southern Ocean	19	–	22	–	Roca-Martí et al. (2017)
2013	Southeastern tropical Pacific	339	339	–	–	Black et al. (2018)
2013	Southern Ocean (South Georgia)	10	9	–	–	Elena Ceballos-Romero (unpublished)
2013	Southern Ocean	12	8	–	–	Le Moigne et al. (2016)
2013–2014	Arabian Sea and Bay of Bengal	–	–	–	4	Anand et al. (2018b)
2014	Bay of Bengal	–	–	–	13	Anand et al. (2017)
2014	Southern Indian Ocean to Arabian Sea	–	–	–	11	Anand et al. (2018a)
2014	North Atlantic Ocean	56	58	–	–	Lemaitre et al. (2018)
2014–2015	Tropical and subtropical North Pacific	53	49	5	–	Umhau et al. (2019)
2015	Arctic Ocean	17	17	–	28	Viena Puigcorbé (unpublished) – PS94
2016	Southern Ocean	21	22	–	36	Viena Puigcorbé (unpublished) – GP-Pr11
2017–2018	Levantine Basin (Mediterranean Sea)	–	–	3	19	Alkalay et al. (2020)
	Totals	3087	2039	947	3245	9318

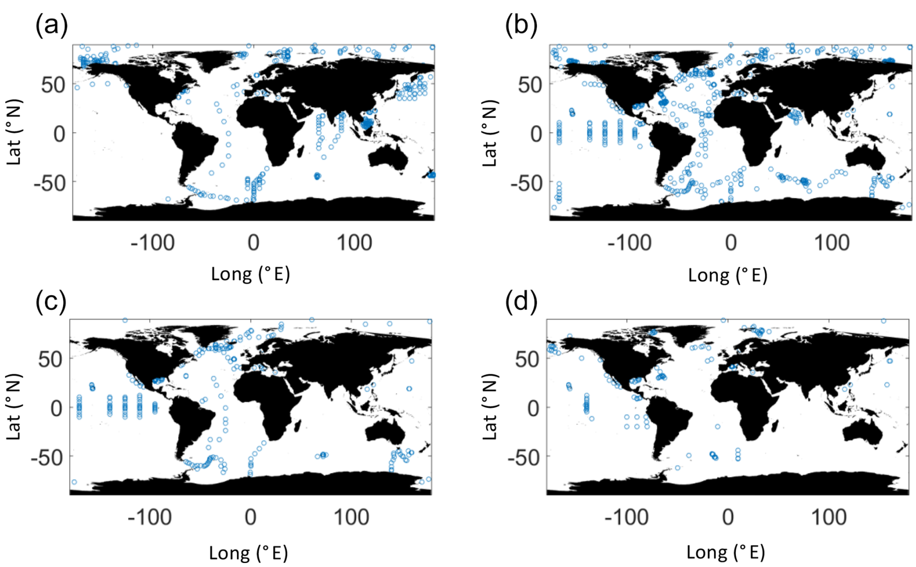

Figure 1. Maps showing the distribution of POC/Th ratios measured on **(a)** bulk particles, **(b)** large particles, **(c)** small particles, and **(d)** particles from sediment traps. See main text for details, Sect. 3.1 Data classification.

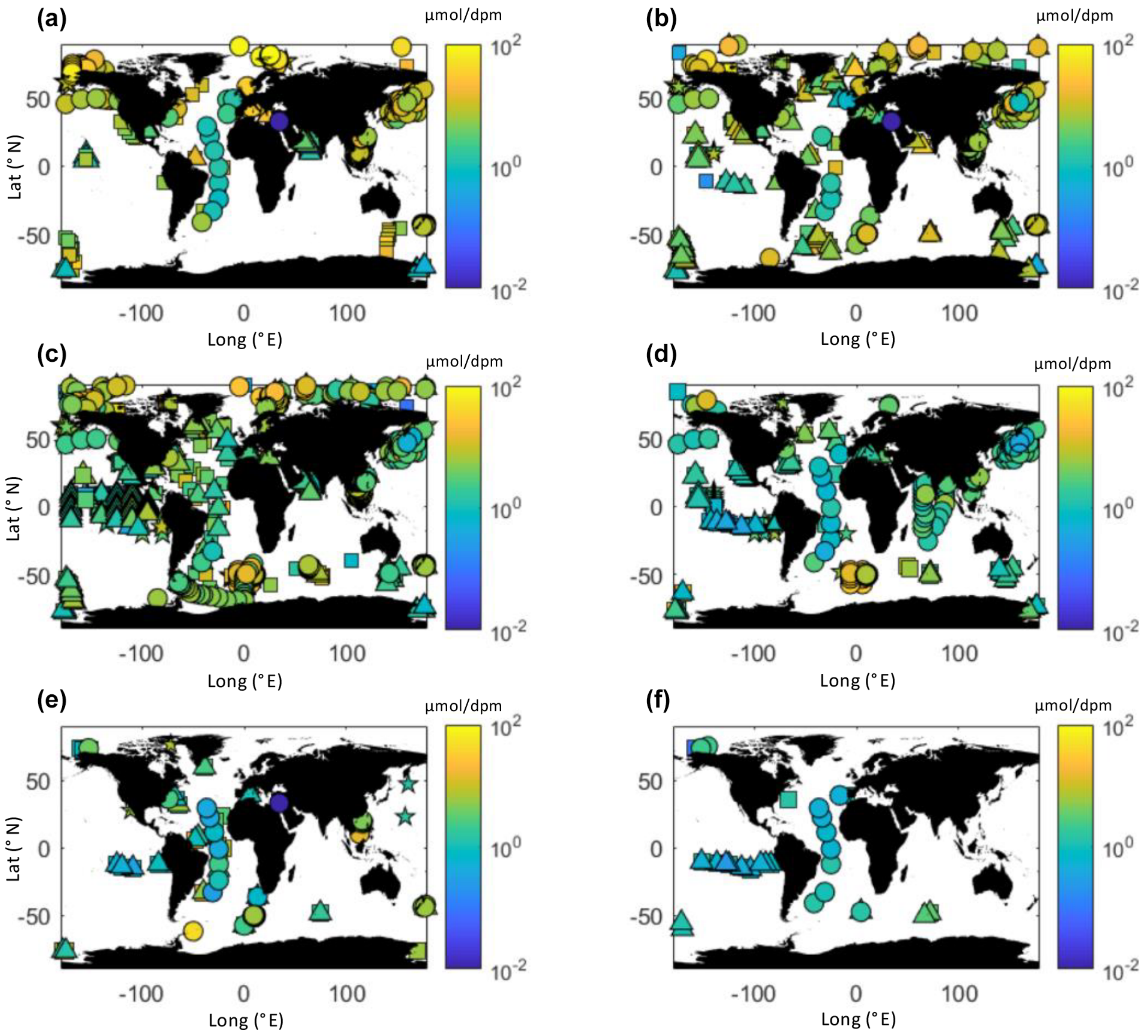

Figure 2. Global distribution of the POC/Th ratios ($< 100\,\mu$mol dpm^{-1}) **(a)** in surface, **(b)** at 50 m, **(c)** at 100 m, **(d)** at 200 m, **(e)** at 500 m, and **(f)** at 1000 m. Circles represent BU, squares represent LP, triangles represent SP, and stars represent ST (see main text for details, Sect. 3.1 Data classification.). Data correspond to samples collected at depths at ±5 m the nominal depth for all cases, except for panel **(f)** (±50 m).

tropical areas, particularly in the upper 200 m (Fig. 4). When looking at the different types of sampling methods, the link between latitude and magnitude of the ratio seems to be clear for ST and BU but quite variable for LP and SP (Fig. 5). High POC/Th ratios are usually associated with the presence of large phytoplankton groups, such as diatoms, which are dominant in high-latitude areas with no nutrient limitations, or where zooplankton populations are large and there is a significant input of fecal pellets, which should also have high POC/Th ratios. Low ratios, on the other hand, are commonly observed in warm oligotrophic areas where productivity is limited and the main phytoplanktonic groups are picoplankton (Buesseler et al., 2006). Exceptions do exist, but they are usually found in coastal areas where other factors could be influencing the planktonic community (e.g., seasonal upwelling, continental influence, river inputs).

3.3 Contributing to global POC export estimates

The ^{234}Th approach has been used to derive an export model at the global scale that uses sea surface temperatures and net primary productivity from satellite products (Henson et al., 2011). The parametrization for this model has large uncertainties in the cold regions (low sea surface temperature), which lead to a reduced estimate of the global biological carbon pump (~ 5 Gt C yr^{-1}) compared to other satellite-derived export models (9–13 Gt C yr^{-1}; Dunne et al., 2007; Laws et al., 2011). A recent study by Puigcorbé et al. (2017a) estimated POC export fluxes in the North Atlantic using in situ data for the ^{234}Th method and compared it to three different satellite-derived export models: Dunne et al. (2007), Henson et al. (2011), and Laws et al. (2011). The conclusion was that, overall, the geographical trends were captured by all the approaches, but the absolute values between them

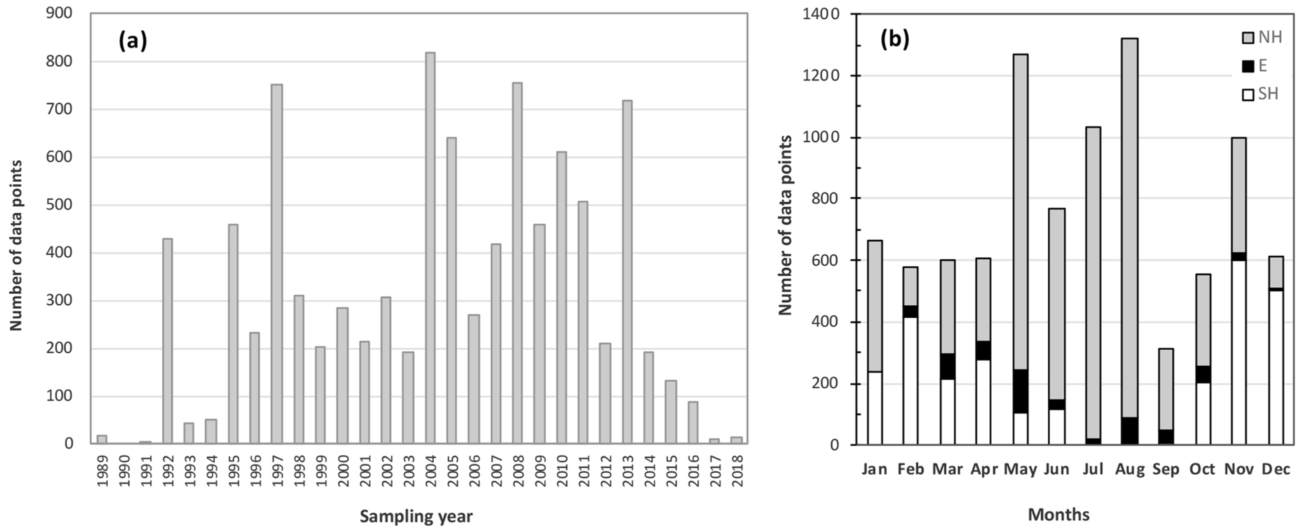

Figure 3. **(a)** Histogram of data sampled between 1989 and 2018. See Table 1 for details. **(b)** Number of samples per month of the year grouped as per sample collected in the Northern Hemisphere (NH; grey), in the Southern Hemisphere (SH; white), or at the Equator (E; −10 to 10° N; black).

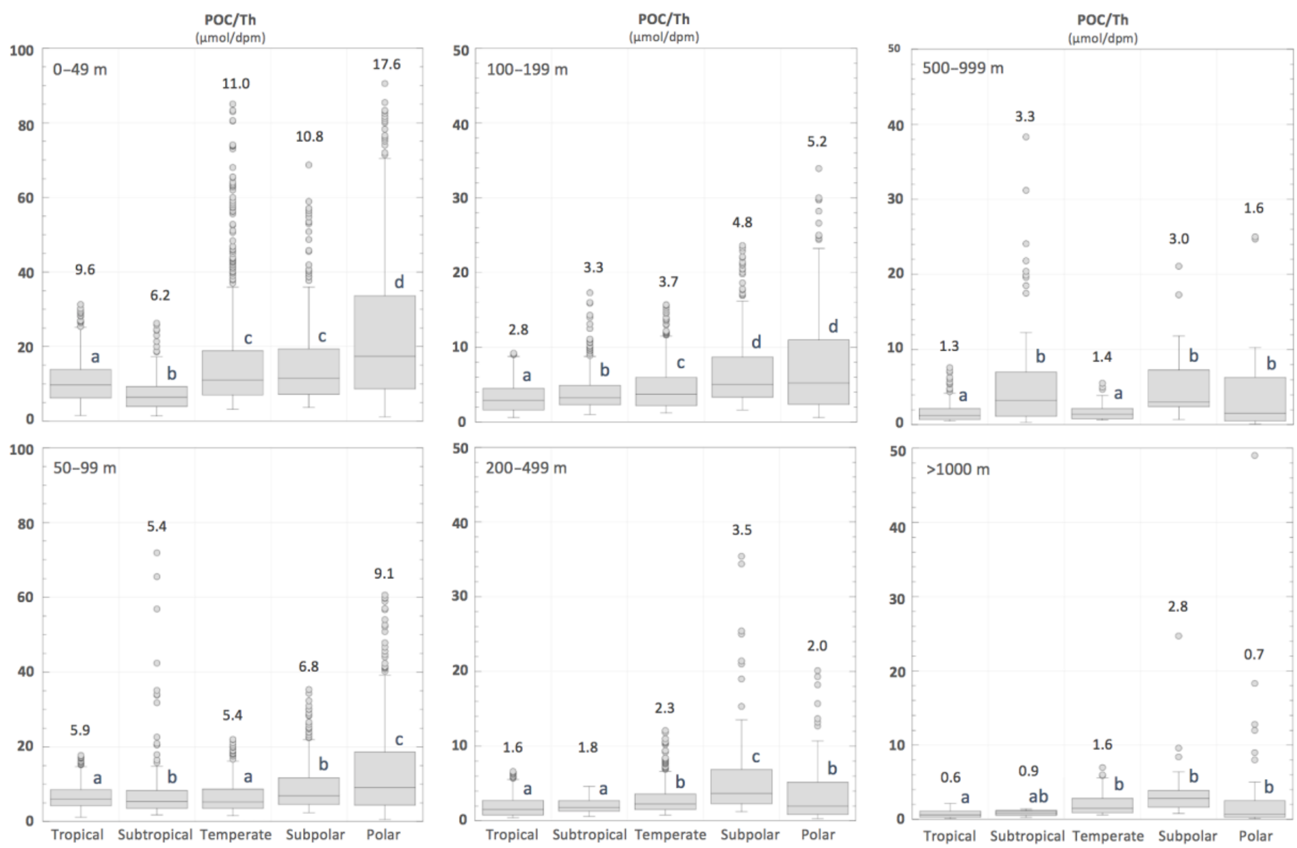

Figure 4. POC/Th ratio variability (box–whisker plots) of 90 % of the data sorted by climate zones and depth. The values shown on top of each box represent their median. Box plots within the same depth range (e.g., 0–49 m) sharing a letter are not significantly different. Note the different scale used between the 0 to 99 m and the 100 to > 1000 m plots.

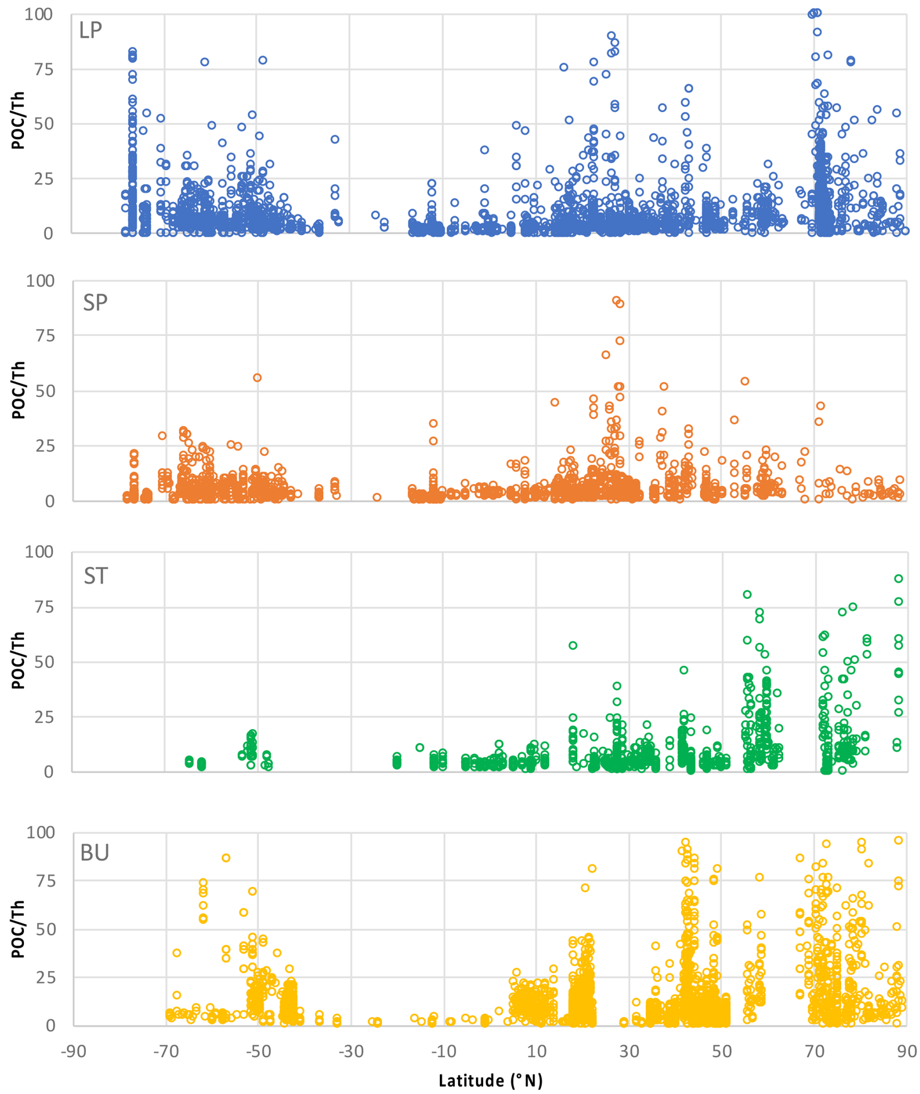

Figure 5. Latitudinal variability of the POC/Th ratios ($< 100\,\mu\mathrm{mol\,dpm}^{-1}$) grouped by large particles (LPs), small particles (SPs), sediment trap (ST) particles, and bulk (BU) particles.

could reach important discrepancies. In that study, the authors advised a revision of the parametrization of the models going beyond sea surface temperatures in order to adjust to specific ocean bioregions. This database sets a strong background to develop that parametrization and contribute to similar modeling efforts to constrain the global carbon export fluxes as done by Henson et al. (2011).

3.4 Significant gaps and recommendations

This database provides the global POC/Th ratios sampled from all the oceans up until 2018. The sampling coverage is significant but it is not evenly distributed. Areas such as the China Sea, Arabian Sea, northwestern Mediterranean Sea, central Pacific, and high latitudes of the Atlantic Ocean are well represented, whereas other areas, such as the oligotrophic gyres, west Pacific, or the Southern Ocean, present important gaps. The data are not evenly distributed between seasons either, with most of the sampling taking place during spring and summer in both hemispheres, which is also when the export fluxes are expected to be larger. High seasonality in undersampled areas could potentially bias our global view of the POC/Th ratios and have an impact on the Th-derived carbon export flux estimates.

It would be beneficial for future efforts to obtain data for those undersampled areas with high seasonality to better characterize the expected variability in the ratios within those areas and to cover a larger span of seasons in order to better understand the seasonality of POC/Th and thus be able to translate it more accurately to the global POC export estimates.

4 Data availability

Our dataset is archived in the data repository PANGAEA® (http://www.pangaea.de), under the following DOI: https://doi.org/10.1594/PANGAEA.911424 (Puigcorbé, 2019).

5 Conclusion

Here we provide a global database of 9318 estimates of POC/Th ratios collected between 1989 and 2018 at various depths from below the surface to > 5500 m using in situ pumps, collection bottles, and sediment traps. The observed pattern of POC/Th ratios reflects a decrease with depth and a link with the latitude, with higher ratios usually observed in high-latitude areas. Some noteworthy gaps in the dataset are the Benguela system, the Mauritanian upwelling, the western and south Pacific, and the southern Indian Ocean. The fall–winter months in both hemispheres are also underrepresented. The temporal and spatial undersampling of some areas could bias the global view of the POC/Th ratios. Despite the gaps, this database is the largest compilation POC/Th ratios to date and could be used to better understand the factors controlling the variation in ratios on a global scale. This will help revise and provide improved estimates of the ocean's biological carbon pump.

Author contributions. VP and FACLM compiled the dataset and prepared and reviewed the manuscript. All the authors contributed to the review of the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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