

The decoupling of production and particulate export in the surface ocean

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Abstract. The relationship between primary production in the surface ocean and export of particulate organic carbon (POC) on sinking particles is examined in studies that have utilized ^{234}Th as a tracer of upper ocean export. Comparisons between production and export are made in a wide range of open ocean settings and seasons. The results indicate that much of the ocean is characterized by low POC export relative to primary production (export/production = $ThE < 5\text{-}10\%$). Exceptions to this pattern are found during blooms at high latitudes, accompanying spring blooms at midlatitudes, and perhaps in association with more episodic export pulses. These sites of high export are most often characterized by food webs dominated by large phytoplankton, in particular diatoms. These results can be used to better parameterize surface export in biogeochemical models in order to provide a more accurate prediction of the flow of C and associated nutrients in the oceans.

1. Introduction

Marine scientists have studied the processes which limit primary production in the upper ocean and the rates of uptake and fluxes of carbon, nutrients and associated elements that are involved in these biogeochemical cycles. One goal of such studies is to understand these processes sufficiently to predict the affects that modifications in ocean circulation, food web dynamics or nutrient inputs might have on the biological pump and its consequences for air-sea gas fluxes. A traditional view is that phytoplankton primary production, new production and export are well correlated, such that simple empirical relationships between these parameters can be made.

This paper examines the relationship between primary production and export of sinking particles from the upper ocean. To begin this analysis, an overview is made of the ^{234}Th method which has been recently developed for estimating sinking particulate organic carbon (POC) fluxes. Case by case comparisons are made where both POC export derived from ^{234}Th and primary production results are available. The term "decoupling" is used to refer to events or regions where shallow POC export is high relative to local production primary production rates. While most open ocean settings are characterized by relatively low and constant export ratios, the decoupling of production and export is characteristic of specific sites and events. At present, these high-export events are poorly represented in current biogeochemical models.

2. Background

In the late 1960s, "new production" was defined as phytoplankton production that was derived from nutrients supplied from outside the euphotic zone, such as upwelling, atmospheric deposition or nitrogen fixation [Dugdale and Goering, 1967]. In contrast, "regenerated production" was defined as production derived from nutrients recycled within the euphotic zone. The now well-known f ratio is the ratio of new to total production [Eppley and Peterson, 1979]. In earlier phytoplankton/nutrient models the input of external nutrients was balanced by the loss of nutrients from the euphotic zone on sinking particles. The sinking flux of particulate organic C was thought to be the only important biologically mediated process for the transport of atmospheric carbon dioxide to the deep ocean. Traditionally, phytoplankton primary production was estimated by measuring the incorporation of ^{14}C labeled substrate, and export of sinking particles was measured by upper ocean sediment traps. The export ratio, or e ratio, was defined as the ratio of export determined by shallow traps to primary production [Downs, 1989]. On appropriate time and space scales, new and export production were postulated to be in balance [Eppley and Peterson, 1979]. In general, oligotrophic regions were thought to have consistently low e or f ratios, while coastal settings or regions of high productivity were thought to have considerably higher e or f ratios, that is, regions of higher production also had disproportionately higher new and export production (e.g., see review by Eppley [1989]).

Some of these concepts regarding the relationship between primary, new and export production have been revised as biogeochemical studies have advanced in our field. For example, more recent ecosystem models now include a role for dissolved organic nutrients and carbon, both as a source and as a loss term in the biogeochemical budgets [e.g.,

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Fasham *et al.*, 1990]. In addition, the occurrence of high-nitrate, low-chlorophyll (HNLC) conditions in the upper ocean over large regions of the ocean has led to considerable attention on the role of micronutrients, such as Fe, as a limiting factor in phytoplankton production. Indeed, the iron hypothesis [Martin and Fitzwater, 1988] has recently been validated in the equatorial Pacific [Martin *et al.*, 1994; Coale *et al.*, 1996]. One conclusion of these studies is that the stimulation of biological production in the ocean due to increased iron availability during the last Glacial Maximum would lead to a decrease in atmospheric CO₂ due to increased export of carbon to marine sediments. While increasing production alone can lead to proportionally higher export, large variations in export can also be achieved by changing the ratio between production and export.

In this manuscript we compare ²³⁴Th-derived export fluxes and traditionally measured primary production rates. Considerable advances have been made in recent studies that use ²³⁴Th to derive upper ocean POC fluxes [Buesseler *et al.*, 1992a, 1995; Shimmiel and Ritchie, 1995; Bacon *et al.*, 1996; Murray *et al.*, 1996; Cochran *et al.*, 1995, 1997; Rutgers van der Loeff *et al.*, 1997]. The ratio between the export of POC derived from ²³⁴Th and primary production is defined here as "ThE" ratio (for Th Export; ThE = export/production). ThE ratios are thus distinct from but analogous to *f* or *e* ratios. ThE ratios are examined here from a wide range of open ocean settings and seasons in order to understand the controls on and magnitude of sinking particulate fluxes from the surface ocean.

2.1. Estimates of Upper Ocean Particulate Export

Oceanographers have relatively few methods for quantifying upper ocean particulate fluxes. These include the ²³⁴Th technique, sediment traps, and studies of particle abundances. While the most direct method of studying particle export is to deploy a "rain gauge" for sinking particles, that is, a sediment trap, the quantity and quality of material caught in upper ocean sediment traps has been recently called into question [Buesseler, 1991; Buesseler *et al.*, 1994]. At present, the extent of shallow trap biases is still being debated. It is unclear whether these biases might be due to hydrodynamics, preservation, or "swimmer"-related issues, and whether or not these can be effectively minimized [e.g., Knauer and Asper, 1989; W.D. Gardner, Sediment trap technology and sampling in surface waters, U.S. JGOFS report, <http://www-ocean.tamu.edu/JGOFS/contents.html>, 1996 and references therein]. Upper ocean traps are assumed to exhibit their best performance below the layers of high-shear and high-zooplankton abundances. To minimize shear, floating traps are preferred in the upper ocean; however, such free floating trap arrays are logistically limited to a few locations or deployments per cruise.

If particle abundances or stocks can be quantified, then one should be able to predict particulate fluxes if one has some a priori knowledge of sinking rates and particle composition. The stocks of large and small particles have become easier to measure using advances in transmissometer and camera techniques [Gardner and Walsh, 1990; Walsh and Gardner, 1992; Asper, 1996]. Unfortunately, the vertical flux is

inherently difficult to constrain from stocks. This is due to the widely varying composition and sinking rates of marine particles. Such particles can range in characteristics from rapidly sinking fecal pellets (hundreds to thousands of meters per day) to slowly settling marine snow (few to tens of meters per day; for overview see Fowler and Knauer [1986]).

The ²³⁴Th method, as developed by this author and elaborated upon below, works best in the euphotic zone and can resolve highly varying spatial and temporal changes in particle export. This is due to the relatively short half-life of ²³⁴Th (24.1 days), its nonselective particle reactivity, and recent improvements in ²³⁴Th sampling and at-sea analyses which allow for higher frequency data collection [Buesseler *et al.*, 1992b, 1995, Upper ocean export of particulate organic carbon in the Arabian Sea derived from Thorium-234, submitted to *Deep Sea Research, II*, 1997 (hereinafter referred to as Buesseler *et al.* (submitted manuscript, 1997)); Hartman and Buesseler, 1994]. The accuracy of this ²³⁴Th approach can best be demonstrated by comparing ²³⁴Th-derived POC and particulate organic nitrogen (PON) export rates and other biogeochemical rate estimates made during the Joint Global Ocean Flux Studies (JGOFS) experiments and other studies.

2.2. Particulate Organic Carbon Export Derived From ²³⁴Th

Thorium 234 was first measured in the oceans in the late 1960s [Bhat *et al.*, 1969]. It was shown that the ²³⁴Th activity was lower near the continental margins and reached secular equilibrium with its long-lived conservative parent, ²³⁸U, at relatively shallow depths (50-200 m). Thorium 234 was subsequently widely used as a particle "scavenging" tracer to examine particle residence times and transformation rates in the oceans [Santschi *et al.*, 1979; Kaufman *et al.*, 1981; Bacon and Anderson, 1982; Tsunogai *et al.*, 1986]. The link between biological processes and the extent of ²³⁴Th removal was first clearly demonstrated in a series of papers by Coale and Bruland [Coale and Bruland, 1985, 1987; Bruland and Coale, 1986]. They proposed that a relationship existed between ²³⁴Th removal rates and primary and new production in the open ocean. Based upon this evidence, Eppley [1989] suggested that ²³⁴Th could be used as a tracer of export production if the ²³⁴Th particle residence time could be applied to POC stocks. As pointed out by Murray *et al.* [1989], however, POC and particulate ²³⁴Th residence times may differ due to the preferential recycling of POC in the upper ocean.

A new approach was used starting with the U.S. JGOFS North Atlantic Bloom Experiment (NABE) to estimate POC fluxes from ²³⁴Th distributions. During this study, a clear relationship was found between the onset of the spring bloom, the subsequent drawdown of nutrients and CO₂, and the net removal of ²³⁴Th [Buesseler *et al.*, 1992a]. It was postulated that if the ²³⁴Th export rate could be quantified (from the ²³⁴Th activity balance), then POC or PON export fluxes via sinking particles could be determined simply by multiplying the ²³⁴Th export rate by the measured ratio of ²³⁴Th to POC or PON on sinking particles. Fundamentally, this ²³⁴Th method hinges on two issues. First, the export flux of ²³⁴Th must be accurately estimated from the ²³⁴Th:²³⁸U disequilibrium.

Second, the particles which are analyzed for ^{234}Th and POC must be characteristic of those carrying both elements below the euphotic zone.

2.3. Calculating ^{234}Th Export

The ^{234}Th activity balance in a given parcel of water can be described by the following equation:

$$\partial^{234}\text{Th} / \partial t = ({}^{238}\text{U} - {}^{234}\text{Th})\lambda - P + V \quad (1)$$

where $\partial\text{Th}/\partial t$ is the change in ^{234}Th activity with time, ${}^{238}\text{U}$ is the uranium activity determined from salinity (${}^{238}\text{U}$ (disintegrations per minute (dpm)) kg^{-1}) = 0.0686 salinity [Chen *et al.*, 1986]), ${}^{234}\text{Th}$ is the measured activity of total ${}^{234}\text{Th}$, λ is the decay constant for ${}^{234}\text{Th}$ (= 0.0288 d^{-1}), P is the net export flux of ${}^{234}\text{Th}$ on sinking particles, and V is the sum of advective and diffusive ${}^{234}\text{Th}$ fluxes. When the ${}^{234}\text{Th}$ activity balance is integrated from the surface to a given depth, net export P can be calculated on a $\text{dpm m}^{-2} \text{d}^{-1}$ basis.

The ${}^{234}\text{Th}$ export flux P is driven in most settings by the difference between the ${}^{238}\text{U}$ and ${}^{234}\text{Th}$ activities since the other terms contribute only slightly (<10%) to the overall activity balance. Most often, ${}^{234}\text{Th}$ activities are lowest in surface waters and increase with depth. In this case particulate ${}^{234}\text{Th}$ fluxes would increase with depth until secular equilibrium is reached. Alternative scenarios include the finding of subsurface flux maximum, that is, ${}^{234}\text{Th}$ activity minimum. Cases are also found where subsurface ${}^{234}\text{Th}$ activities are above equilibrium, indicating that remineralization of sinking particles is focused at these depths. Given that the ${}^{234}\text{Th}$ flux is driven by the difference between the ${}^{234}\text{Th}$ and ${}^{238}\text{U}$ activities, the propagated flux errors tend to increase with increasing water depth [Coale and Bruland, 1987]. If one goes below the depth of secular equilibrium, particulate fluxes can rarely be well constrained using this tracer (typically at depths >100-200 m).

Studies continue to expand upon earlier work where a steady state model and single vertical ${}^{234}\text{Th}$ profiles were used to calculate export fluxes (one-dimensional vertical models [e.g., Coale and Bruland, 1985, 1987]). Nonsteady state ${}^{234}\text{Th}$ models appear to be important during periods of significant ${}^{234}\text{Th}$ drawdown, such as during blooms [Buesseler *et al.*, 1992a; Cochran *et al.*, 1997], but not during most other periods [Tanaka *et al.*, 1983; Wei and Murray, 1992; Moran and Buesseler, 1993]. The significance of vertical upwelling in the ${}^{234}\text{Th}$ balance ("V" term in (1)) is found to be significant only in regions of high upwelling velocity. Examples include equatorial sites along 140°W in the Pacific [Buesseler *et al.*, 1995; Bacon *et al.*, 1996] and coastal sites during the SW Monsoon in the Arabian Sea (Buesseler *et al.*, submitted manuscript, 1997). Horizontal advection can be significant in nearshore sites, such as harbors, where horizontal scavenging of particle-reactive species within shallow waters is intensified (Portland Harbor (Ö. Gustafsson *et al.*, On the relative importance of horizontal and vertical transport of particle-reactive chemicals in the coastal ocean: Two-dimensional Th-234 modeling, submitted to *Continental Shelf Research*, 1997)). Details of these models can be found in the original references. Only the results of these studies are discussed below.

2.4. Calculating Particulate Organic Carbon Fluxes From ${}^{234}\text{Th}$ Fluxes

The determination of the vertical flux of POC from ${}^{234}\text{Th}$ uses the empirical relationship between POC and particulate ${}^{234}\text{Th}$ to convert from ${}^{234}\text{Th}$ flux (P in units of $\text{dpm m}^{-2} \text{d}^{-1}$; equation (1)) to POC export ($P \text{ POC}/{}^{234}\text{Th}$; units of $\text{mmol m}^{-2} \text{d}^{-1}$). Note that while the discussion here focuses on POC fluxes, measurement of C/N ratios allows for the application of this technique to determine PON export. The reliability of this approach can be demonstrated by comparing ${}^{234}\text{Th}$ derived export fluxes to other indicators of production and export determined in a variety of settings (see case by case discussion below). A similar ${}^{234}\text{Th}$ method has been recently applied to studies of hydrophobic organic compounds (PAHs [Gustafsson *et al.*, 1997]).

In order to determine particulate $\text{POC}/{}^{234}\text{Th}$ ratios, scientists have relied upon filtration or sediment traps for the collection of particulate material. Filtration has been conducted using either large-volume in situ pumps or bottle collection of total water samples. Analysis of filtered samples demonstrates that the $\text{POC}/{}^{234}\text{Th}$ ratio decreases significantly with increasing water depth. This indicates that organic carbon (OC) is preferentially remineralized off of sinking particles [see, for example, Bacon *et al.*, 1996, Figure 12]. Variations in the $\text{POC}/{}^{234}\text{Th}$ ratio might also be expected based upon particle size and characteristics. If the activity of the particle-reactive tracer ${}^{234}\text{Th}$ is simply proportional to surface area and POC is proportional to volume, then one would expect higher $\text{POC}/{}^{234}\text{Th}$ ratios on larger particles. Equal ratios would be expected if small particles simply aggregated into larger ones. Lower ratios on larger particles would occur if organic C is biologically or chemically remineralized during the aggregation process. Both lower (Arabian Sea (Buesseler *et al.*, submitted manuscript, 1997) and higher (Equatorial Pacific Process Study (EqPac) [Buesseler *et al.*, 1995; Bacon *et al.*, 1996]) $\text{POC}/{}^{234}\text{Th}$ ratios have been observed in particles collected on 53 μm relative to 1 μm pore sized filters. Therefore a single physical or biological process does not appear to account for the observed variations in $\text{POC}/{}^{234}\text{Th}$ with size. Fortunately, these particle size related differences are smaller than those found between different sites, seasons and depths (Table 1).

Sediment traps are an alternative to filtration for the collection of sinking particles for the analysis of $\text{POC}/{}^{234}\text{Th}$ ratios. However, if there are hydrodynamic problems with shallow traps, particle sorting can be expected [Butman *et al.*, 1986; Baker *et al.*, 1988]. Thus some particle types might be collected with higher or lower efficiencies than others based upon their settling velocities. In addition, swimmers have up to 3 orders of magnitude higher $\text{POC}/{}^{234}\text{Th}$ ratios [Coale, 1990; Buesseler *et al.*, 1994] since large zooplankton have high POC and low surface to volume ratios. As such, the contribution of swimmer POC to a trap might increase apparent $\text{POC}/{}^{234}\text{Th}$ ratios. Trap $\text{POC}/{}^{234}\text{Th}$ ratios were lower than filtered particles from the same depth in NABE [Buesseler *et al.*, 1992a] and larger in EqPac (see EqPac discussion below).

Ultimately, the goal of any POC and particulate ${}^{234}\text{Th}$ sampling scheme is to obtain a sample representative of those particles carrying both elements below the euphotic zone.

Table 1. Summary of Export and Production Studies Based Upon ²³⁴Th Approach

Site	Th Flux dpm m ⁻² d ⁻¹	POC/Th, μmol/dpm	POC Flux, mmol C m ⁻² d ⁻¹	Primary Productivity mmol C m ⁻² d ⁻¹	ThE Ratio, %	References and Comments	
<i>NABE 47°N 20°W; 0-75 m¹</i>							
April 25 - May 5, 1989: mean	1720	12	21	91	23	mean = average of minimum/maximum range minimum = lower limit from POC/Th from trap maximum = upper limit from POC/Th from filters	
minimum/maximum		4/20	7/35		8/38		
May 5 - May 19: mean	3350	15	49	98	50		
minimum/maximum		6/23	20/77		20/79		
May 19 - May 30: mean	3600	11	39	87	44	30/60	
minimum/maximum		7/14	26/52				
<i>BATS; 0-150 m; 1993-1995²</i>							
March - Oct. mean	650	4.6	2.6	36	11	POC/Th ratios from 150 m traps	
March - Oct. range	0-2500	2-9	<1-6	6-67	<1-56		
<i>EqPac; 0-100 m; 12°N to 12°S; 1992³</i>							
Spring 170°W	1500-2800	1.8 - 3.5	2-3.5	30-50	5-8	Data from 140°W used in Figure 2	
Spring 140°W	1300-2800	1.0-1.4	1-4	30-100	4-6		
Spring 125°W	1000-2000	1.0-2.0	1-4.5	20-80	5		
Spring 110°W	1000-1500	1.3-2.3	1-3.5	25-100	1-3		
Fall 140°W	1200-3500	1.0-1.4	1-4	60-120	3		
Fall 125°W	1500-3000	0.8-1.5	1-3.5	40-100	3-5		
Fall 110°W	1200-2500	1.5-2.0	2.5-3.5	50-110	3-6		
Fall 95°W	1000-2200	1.5-4	2-8	75	5-10		
<i>EqPac; 0-100 m; 140°W equator</i>							
Feb. 23, 1992	2340	2.5	6	60	10		<i>Murray et al. [1996]; Barber et al. [1996]</i> <i>Bacon et al. [1996]; Barber et al. [1996]</i> <i>Buesseler et al. [1995]; Chavez et al. [1996]</i> <i>Murray et al. [1996]; Barber et al. [1996]</i> <i>Bacon et al. [1996]; Barber et al. [1996]</i>
May 24-April 9, 1992 mean	2450	0.8	2.0	90	2.2		
April 30, 1992	2300	1.2	2.7	100	2.7		
Aug. 29, 1992	3150	3.0	9.5	100	10		
Oct. 3-21, 1992 mean	3800	0.7	2.8	120	2.3		
<i>NE Polynya, Greenland 0-50 m⁴</i>							
1992	300	47	13	20	65	1992 and 1993 SS uses steady state ²³⁴ Th model	
1993 (SS) ⁵	700	47	33	80	41	Average from north and west troughs	
1993 (NSS) ⁶	1500	47	70	80	88	1993 NSS uses nonsteady state ²³⁴ Th model	
<i>Weddell Sea/Polar Front 0-100 m⁷</i>							
Polar Front- Nov. bloom 1992	3200	9 ± 3	29	110	26	Used NSS model and production from <i>Jochem et al. [1995]</i>	
Marginal Ice Zone- Nov. bloom 1992	200-1300	20 ± 5	4-26	25	16-100		
<i>Bellingshausen Sea 0-100 m⁸</i>							
Station K 67° 36'S, 84° 56'W	1600	14	22	60 ± 5	37		
<i>Arabian Sea 0-100 m; 1995⁹</i>							
NE Monsoon (TN043)	<200-2000	3.5	1-7	50-120	1-6	Data from JOGFS southern transect	
Spring Intermonsoon (TN045)	500-2500	3	1-6	65-100	1-9	Export tends to increase near shore during all cruises	
Mid SW Monsoon (TN049)	1000-5500	3	2-17	115-130	1-10	C/Th taken from 100 m on Nitex	
Late SW Monsoon (TN050)	3000-5500	5	11-26	50-145	17-27		

1 Buesseler et al. [1992a]; nonsteady state ²³⁴Th model.2 Buesseler et al. [1997], this report; *Michaels et al. [1994]*.3 Buesseler et al. [1995]; *Chavez et al. [1996]*.4 *Cochran et al. [1995, 1997]*.

5 SS, Steady State Model.

6 NSS, Non-steady State Model.

7 *Rutgers van der Loeff et al. [1997]*.8 *Shimmield et al. [1995]*.9 Buesseler et al. (submitted manuscript, 1997); *Barber et al. (submitted manuscript, 1997)*.

The studies to date suggest that POC/²³⁴Th ratios are highest in surface waters under bloom conditions and at high latitudes, and lower in oligotrophic and HNLC regions in the open ocean (Table 1). Overall variations between sites and depths in POC/²³⁴Th are larger than observed differences based upon sampling technique, though continued studies in this area are warranted. The ²³⁴Th approach should be accurate as long we have properly quantified the POC/²³⁴Th ratio of particulate matter at a given site and depth. This only assumes that we are not missing a dominant class of sinking particles that also has a widely differing particle composition than those sampled.

2.5. *ThE* Ratios

The ²³⁴Th method provides for the opportunity to examine under what conditions (food web, season, latitude, etc.) export from the surface ocean is dominated by sinking particles. To begin this examination, I define *ThE* ratio as the ratio of POC export derived from ²³⁴Th to primary production. *ThE* ratios would be identical to *e* ratios (determined from the POC flux in traps and primary production) if the POC fluxes in shallow traps were in agreement with those derived from ²³⁴Th. However as mentioned above, disagreement is common, and examples of this will be pointed out on a case by case basis below.

Over appropriate time and space scales, new production should equal export production, that is, in steady state nutrient sources and sinks must be in balance. Sources of new production include the upwelling of nutrients, nitrogen fixation, deposition from the atmosphere, and coastal run-off. Losses out of the euphotic zone of nutrients and carbon occur as both a particulate flux (quantified here) and via the advection and diffusion of dissolved organic matter. The relative magnitude of each of these loss terms is just now being assessed, and the analysis taken here is one step in this direction.

One reason for studying variations in *ThE* is to quantify the role of upper ocean biogeochemical cycling in the removal of atmospheric CO₂ via its incorporation during photosynthesis into organic C and its removal from the surface ocean via sinking particles. In studying this export efficiency one must be careful about the timescales that are represented by any given measurement, that is, the integration timescales of the numerator and denominator in *e* or *ThE* ratios. For example, *ThE* ratios may be elevated in one region due to a particularly efficient biological pump characteristic of steady state conditions at a given site. Another reason might be a temporal offset in the timing of the end of a phytoplankton bloom and the onset of more efficient zooplankton grazing.

New and primary production rates are typically derived from 12 or 24 hour bottle incubations and hence represent a single day's average rate of C fixation or nutrient uptake at a single sample depth. Fluxes based upon ²³⁴Th reflect the flux conditions over the mean life of this tracer, that is, 31 days, hence this is a longer temporal integration of net export if steady state is assumed. Also, since both production and particulate export are strongly depth dependent, the relative ratio of these will depend upon the depth of integration. To date, complete time, depth and space resolved estimates of

production, export and other physical and biogeochemical parameters are simply not available to examine the finer details of these processes. Uncertainties and potential biases in ¹⁴C-based estimates of primary production (bottle-based artifacts; trace metal effects; in situ versus deck incubations, etc.) are also not considered in our analysis of these data.

In this paper an attempt is made to standardize the data to a comparison of total production integrated to the base of the euphotic zone (≈1% light level) and net export near the base of this zone. In practice, this depth includes ≥95% of integrated primary production and is typically within the range of 50-150 m (Table 1). When possible, an averaged integrated primary production rate for a given time period is used (see discussion of specific study sites).

When all of the POC export and primary production data are combined, one sees a wide range of POC fluxes throughout the oceans at both high and low production rates (Figure 1). Most of the POC fluxes are <10 mmol C m⁻² d⁻¹ (solid symbols in Figure 1). Therefore most *ThE* ratios are low and fall between 2 and 10%. Less commonly, *ThE* ratios >10-50% are found associated with high-latitude sites and blooms in the North Atlantic and the Arabian Sea (open symbols in Figure 1). Some unique high *ThE* ratios are also seen at the Bermuda Atlantic Time Series (BATS) site during very low productivity periods (< 30 mmol C m⁻² d⁻¹; Figure 1). We examine below in more detail each of the studies represented in Figure 1, in order to better understand the factors which initiate and regulate export in the oceans.

3. Results: Case Studies

3.1. North Atlantic Bloom Experiment

During the NABE four vertical profiles and time series surface water samples of ²³⁴Th were collected over a 2 month period during the onset of the spring bloom in the North Atlantic [Buesseler *et al.*, 1992a]. Higher frequency sampling suggested that the onset of stratification in late April was quickly followed by a drawdown in nutrients and later by a drawdown in total ²³⁴Th in early May. From the ²³⁴Th profiles and a nonsteady state model, ²³⁴Th fluxes were calculated to increase with depth throughout the euphotic zone (approximately upper 75 m). Fluxes of ²³⁴Th at 35 m first increased and reached a maximum in mid-May and then decreased later in the month.

Without a dedicated particulate POC/²³⁴Th sampling program, POC/²³⁴Th ratios were estimated from material collected on separate ≈1 μm diameter pore sized filters or from a 150 m sediment trap. Using the mean ratios, POC export at 75 m was calculated to increase from 20 to 50 mmol m⁻² d⁻¹ during early May and then decrease somewhat to 40 mmol m⁻² d⁻¹ in late May (Table 1). These POC fluxes were consistent with the observed drawdown of total CO₂ (C. Goyet and P.G. Brewer, unpublished data, 1992) and total N [Buesseler *et al.*, 1992a] estimated for this time period. Unfortunately, it is difficult to fully resolve the carbon or nutrient budget during NABE. This is due to the lack of reliable dissolved organic C or N data, the range in particulate POC/²³⁴Th ratios, and the need to consider mesoscale spatial variability in this area [McGillicuddy *et al.*, 1995a;b]. Despite

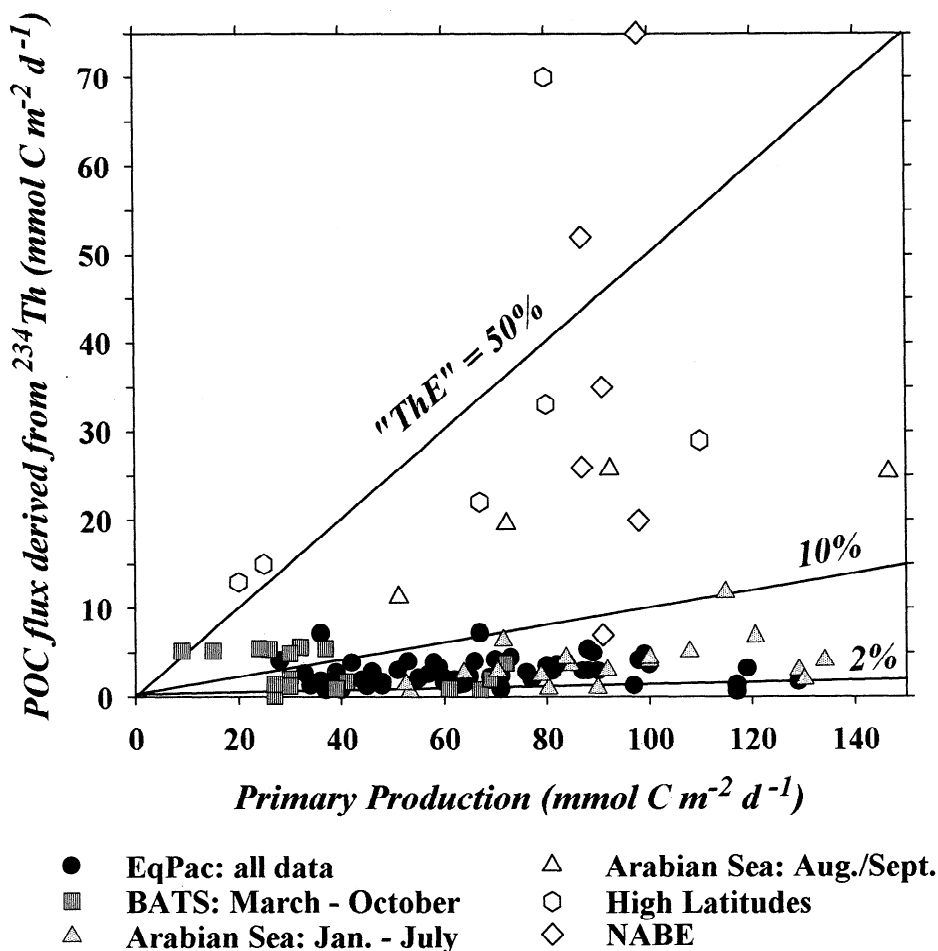


Figure 1. Summary plot of primary production versus POC flux derived from the ^{234}Th approach (both in units of $\text{mmol C m}^{-2} \text{d}^{-1}$). Points identified in legend correspond to case studies described in text, and data sources are outlined in detail in Table 1. Lines of $\text{TheE} = 50\%$, 10% and 2% are drawn for comparison to data.

these uncertainties, the ^{234}Th method supports the general conclusion of relatively high export of sinking particles during this bloom period.

Primary production rates during NABE were relatively constant, around $90\text{--}100 \text{ mmol C m}^{-2} \text{d}^{-1}$ (Table 1). Given the POC fluxes at 75 m, TheE ratios range from 8 to 79% with a peak in export during the middle and later part of this bloom (Table 1 and Figure 1). The ^{234}Th -derived POC fluxes were estimated using a nonsteady state model for three time intervals (early, mid and late bloom; Table 1). Multiple productivity measurements were averaged during these intervals. In this study, both measurements therefore represent mean rates calculated over comparable timescales.

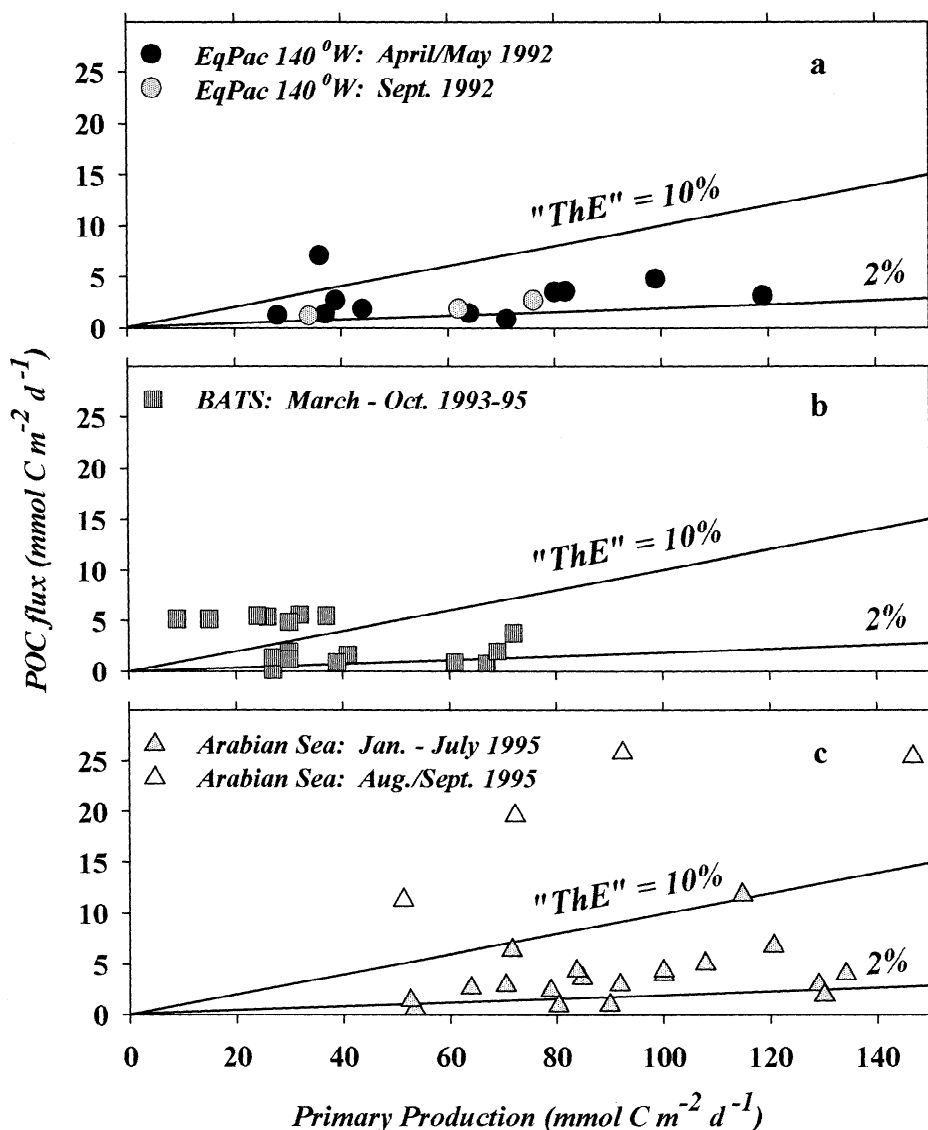
The time series trend in TheE ratio apparently tracked the progression of the food web and bloom dynamics as seen by other NABE investigators. After the onset of stratification, primary production rates increased rapidly and the buildup of a large diatom bloom was accompanied by a decrease in silicate [Lochte *et al.*, 1993]. It was during this diatom-dominated period that surface export fluxes peaked. It was not clear whether export was due to the aggregation and sinking of intact diatoms as Si (or some other micronutrient)

became depleted, or due to increased grazing pressure on the larger diatoms. As the bloom progressed, POC fluxes decreased by a factor of 2 from the upper 35 m [Buesseler *et al.*, 1992a]. This transition occurred as the phytoplankton community became dominated by smaller nanoplankton and microflagellates became the dominant grazers in the surface layer [Verity *et al.*, 1993].

Floating traps deployed at 150 m showed consistently lower ^{234}Th fluxes than those derived from the ^{234}Th activity balance at the same depth. This is one indication of a low trap collection efficiency [Buesseler *et al.*, 1992a]. Throughout the bloom the trap POC fluxes remained low. Therefore an export ratio derived directly from these traps would be significantly lower compared to POC export suggested by the ^{234}Th approach (e ratios from traps of only 8–13% [Martin *et al.*, 1993]).

3.2. Equatorial Pacific Process Study

Thorium 234 was utilized as a POC export tracer as part of three studies during the JGOFS EqPac (1) as a time series flux tracer at the equator at 140°W [Bacon *et al.*, 1996], (2) from



Figures 2. Plots of primary production versus POC flux derived from the ^{234}Th approach (both in units of $\text{mmol C m}^{-2} \text{d}^{-1}$; note change in vertical scale from Figure 1). Lines of $\text{ThE} = 10\%$ and 2% are drawn for comparison to data. (a) EqPac data from 140°W , (b) BATS data, and (c) Arabian Sea data. Data sources and details provided in Table 1 and text.

12°N to 12°S along a transect at 140°W using both floating traps and the ^{234}Th approach [Murray *et al.*, 1996], and (3) in a broader regional study of large-scale ^{234}Th distribution patterns and POC fluxes between 95°W to 170°W and 12°N to 12°S [Buesseler *et al.*, 1995]. In all three cases, measurements were conducted in both the boreal spring and fall of 1992. The spring cruises coincided with elevated surface ocean temperatures associated with El Niño (for overview, see Murray *et al.* [1994]).

In all of these studies, ^{234}Th -derived estimates of POC export were low throughout this HNLC region ($<10 \text{ mmol m}^{-2} \text{d}^{-1}$; Table 1). Along 140°W , POC fluxes generally increased near the equator [Buesseler *et al.*, 1995; Murray *et al.*, 1996]. East of 140°W , a POC export maximum was found near $4^\circ\text{--}6^\circ\text{N}$ along the 125°W and 110°W transects in the spring [Buesseler *et al.*, 1995]. A regional maximum in POC export

was found by Buesseler *et al.* [1995] in the fall south of the equator near 95°W which might be related to local upwelling as evidenced by cooler surface water temperatures in this area. Productivities ranged from a low of $20\text{--}30 \text{ mmol m}^{-2} \text{d}^{-1}$ at latitudes approaching 12°N and 12°S to a peak of $100\text{--}120 \text{ mmol m}^{-2} \text{d}^{-1}$ near the equator [Barber *et al.*, 1996; Chavez *et al.*, 1996]. Production and POC export were generally well correlated (Figure 2a; example of 140°W data taken from Buesseler *et al.* [1995] and Chavez *et al.* [1996]). ThE ratios were below 10% and frequently between 2 and 5% over this entire range of productivities (Figures 1 and 2a). There were some increases in both equatorial productivities and POC fluxes during the non-El Niño period, but ThE ratios still remained low ($<10\%$; Table 1).

The results from all three studies are in general agreement that this HNLC region is characterized by low ThE ratios.

There are, however, some smaller differences between studies in the exact magnitude of the POC flux estimates. All three research groups sampled at the same equatorial station along 140°W in 1992, and a comparison can be made between these three flux estimates. There is little difference in the ^{234}Th flux calculated by each group at this site (Table 1). This suggests that the ^{234}Th activity measurements and steady state models used by each group were in good agreement. In EqPac, the inclusion of an upwelling term (V in (1)) in the ^{234}Th model by all three groups led to roughly a doubling of ^{234}Th export at 100 m at the equatorial station near 140°W. At this site, upwelling is near its maximum for this region and the calculated fluxes are somewhat sensitive to the chosen upwelling rates. However, ThE ratios would remain <10% even if upwelling rates were doubled [Buesseler *et al.*, 1995; Bacon *et al.*, 1996]. Away from the equator and along other transects, upwelling is reduced and hence its affect on the ^{234}Th balance is minimal [Buesseler *et al.*, 1995].

The primary difference between these three EqPac studies is in the choice of material analyzed for $\text{POC}/^{234}\text{Th}$ ratios. These ratios tended to be higher in the floating traps (used by Murray *et al.* [1996]) than in filtered particles (used by Buesseler *et al.* [1995] and Bacon *et al.* [1996]). On average these differed by a factor of 2-3, though depth and regional variations in this ratio using any one sampling technique were much larger. Whether this difference is due to the inclusion of small amounts of "swimmer" material in the trap with extremely high $\text{POC}/^{234}\text{Th}$ ratios or artifacts related to large volume filtration techniques is not clear. This difference in $\text{POC}/^{234}\text{Th}$ between studies does lead directly to a similar difference in POC fluxes. Hence when compared to new production, the POC fluxes from Buesseler *et al.* [1995] and Bacon *et al.* [1996] were lower than new production rates (new production = 6 and 10 $\text{mmol C m}^{-2} \text{d}^{-1}$ at the equator 140°W in the spring and fall, respectively [McCarthy *et al.*, 1996]). Within errors the Murray *et al.* [1996] POC export fluxes are roughly equal to new production rates. Thus from these studies there is no consensus as to the extent to which advection of dissolved organic carbon (DOC) may be a significant loss term for organic C in this region.

It is difficult to estimate DOC loss rates in any study from the difference between POC export rates derived from ^{234}Th and new production rates derived from ^{15}N incubations. This is due to the uncertainties in both of these measurement techniques and the inherent difference in the timescales of ^{15}N uptake, POC loss measured by single ^{234}Th profiles and advective losses of DOC. Using a local C budget, Feely *et al.* [1995] calculated that slightly more C may be lost on average from the upper 40 m via DOC advection relative to POC export. However, the magnitude of this loss term is still being debated [Hansell *et al.*, 1998]. Despite these uncertainties in the balance of nutrient sources and losses, it is clear that the EqPac study area represents a region where a high proportion of primary production is fueled by recycled nutrients during both El Niño and non-El Niño conditions. The dominance of small nanoplankton and flagellate grazers in these HNLC regions is consistent with a tightly coupled food web scenario and low POC export derived from the ^{234}Th studies [Bidigare and Ondrusek, 1996; Binder *et al.*, 1996; Verity *et al.*, 1996; Landry *et al.*, 1997].

Compared to the ^{234}Th -derived fluxes, floating traps at 100 m in EqPac suggested significantly higher POC fluxes of up to 33-36 $\text{mmol m}^{-2} \text{d}^{-1}$ in the spring and fall [Murray *et al.*, 1996]. These standard trap data would suggest e ratios of up to 25-30%. The calibration of these trap fluxes using predicted and measured ^{234}Th fluxes suggested, however, that the traps had overcollected by an average factor of 3.5 (range 1.6 to 26) in the spring, and by a factor of 1.8 (1.0 to 3.0) in the fall at 100 m [Murray *et al.*, 1996]. These overcollection efficiencies were reduced to a factor of 1.6 and 1.3 on average in the 150 m trap, during the spring and fall, respectively. Reducing the overall trap fluxes by this correction factor brings the 100 m sediment trap data in line with the POC fluxes derived from the other ^{234}Th studies. However, there was little evidence of an equatorial maximum in POC export using these corrected trap fluxes.

3.3. Bermuda Atlantic Time Series Site

Ongoing studies of upper ocean biogeochemistry have been conducted at the Bermuda Atlantic Time Series (BATS) site since October 1988 (overview provided by Michaels and Knap, [1996]). At least once per month, a wide range of biogeochemical parameters are measured, including primary production and particle export using floating traps. During 1993-1995, a 3 year study of ^{234}Th cycling was conducted in conjunction with the regular BATS cruises to examine trapping efficiencies at 150 m by comparing the measured trap ^{234}Th fluxes to those predicted from the water column ^{234}Th activities. While export fluxes were low and $^{234}\text{Th} : ^{238}\text{U}$ deficits small, a seasonal pattern of ^{234}Th drawdown and hence higher predicted particulate flux was seen in the late spring and summer months in each of the 3 years (first year reported by Michaels *et al.* [1994]; K.O. Buesseler, unpublished data, 1997).

From the monthly $\text{POC}/^{234}\text{Th}$ ratios in the traps and the calculated ^{234}Th fluxes, POC fluxes can be estimated (Table 1; fluxes estimated for periods when mixed layer depth <150 m, i.e., focus on March - October). When these fluxes are compared to total production rates during this time period, the data fall into two groups. First, many of the points lie within a region where production rates are below 70 $\text{mmol m}^{-2} \text{d}^{-1}$ and export is below 5 $\text{mmol m}^{-2} \text{d}^{-1}$, that is, ThE <2-5% (Figure 2b). These low export rates are consistent with the small ^{234}Th deficiencies and a tightly coupled food web thought to be characteristic of oligotrophic settings.

Second, there is evidence that during some periods of low productivity (< 40 $\text{mmol m}^{-2} \text{d}^{-1}$) POC export can at times remain near 5 $\text{mmol m}^{-2} \text{d}^{-1}$, hence ThE ratios exceeded 25% and even approached 50% at least once during this 3 year record (Figure 2b). The reason for such relatively high export is unclear and somewhat unexpected. Such features may be due to episodic new production events as first suggested by Goldman [1988, 1993]. Associated export events may have been missed with prior measurement strategies. At BATS, localized short-term productivity measurements are being compared with ^{234}Th -derived fluxes which average over longer timescales. Therefore, ^{234}Th -derived average export rates would include any episodic flux events. Alternatively, these anomalous export ratios may be due to errors related to

the low overall ^{234}Th fluxes (and hence high uncertainties in P) or mesoscale effects not included in our one-dimensional (1-D) model. The fact that ^{234}Th fluxes are higher over a 3 year period during the spring/summer months leads us to believe that these are real events. These samples with elevated POC flux do not have elevated $\text{POC}/^{234}\text{Th}$ ratios. Therefore the higher POC fluxes cannot be related to any artifacts due to swimmer contamination in the samples used to determine $\text{POC}/^{234}\text{Th}$ ratios. Where available for comparison, $\text{POC}/^{234}\text{Th}$ ratios on $\approx 1 \mu\text{m}$ pore sized filters are equal to or somewhat lower on average than those found in the trap (K.O. Buesseler, unpublished data, 1997). Even if the $\text{POC}/^{234}\text{Th}$ ratio is lowered, these events characterized by relatively high export during low productivity periods would remain.

Most of the instances of high ThE ratio occur during the summer months when there is a notable imbalance in the total C budget at BATS. At this time, the total C budget is decreasing and the measured C losses cannot account for this missing C [Michaels *et al.*, 1994]. The most likely reasons for the C imbalance at BATS is either a measurement problem with the traps missing a fraction of POC export, and/or due to advective features that are not considered in the 1-D balance of C at this site. The enhanced POC flux we estimate here cannot alone account for the C imbalance at BATS. At both the BATS and Hawaii Ocean Time Series Site, POC fluxes from shallow traps and primary production rates are poorly correlated [Karl *et al.*, 1996; Michaels and Knap, 1996]. Episodic processes such as nutrient injection, N_2 fixation and export events are poorly resolved with the standard sampling protocols. Ultimately, a better understanding of the importance of these short-term events is needed to close the C and N balances at these sites.

3.4. Arabian Sea Process Study

In the Arabian Sea, one might expect large seasonal variations in production and export to be driven by the strong monsoonal cycles. Indeed, prior records of sediment flux to deep moored sediment traps indicated that particulate export was highly episodic. In the central part of this basin, >40% of the annual flux arrived within a 25 day span during the summer Southwest Monsoon [Haake *et al.*, 1993]. In addition, onshore/offshore transects might be expected to show significant gradients in production and export. Recent results from the U.S. JGOFS Arabian Sea Process Study can be used to examine production and export relationships in this dynamic environment.

Thorium 234 was used as a POC export tracer on four cruises in the Arabian Sea between January and September 1995. Large seasonal and spatial variations in the ^{234}Th activity distributions were seen (Buesseler *et al.*, submitted manuscript, 1997). Increased upwelling during the SW Monsoon necessitated the inclusion of both nonsteady state and upwelling terms in our ^{234}Th flux model. Using the ^{234}Th export rates and $\text{POC}/^{234}\text{Th}$ measured on 53 μm pore sized filters, POC fluxes of <1 to >25 $\text{mmol m}^{-2} \text{d}^{-1}$ were found. The single largest feature in the POC flux results was the finding of a basin-wide export maximum during the late SW Monsoon (mid August to mid September cruise TN050).

During all seasons, the nearshore sites also exhibited elevated POC fluxes. Primary production rates in the Arabian Sea Study were high throughout the basin and during all seasons, with an enhancement during the SW Monsoon (R.T. Barber *et al.*, Primary productivity responses to the Arabian Sea monsoons, submitted to *Deep Sea Research, II*, 1997 (Table 1) (hereinafter referred to as Barber *et al.*, submitted manuscript, 1997).

The results indicated that the majority of Arabian Sea ThE ratios were low (<2-10%), similar to those found at BATS and EqPac (Figure 2c, solid symbols). Exceptions to this occurred during the late SW Monsoon, when ThE ratios >15-25% were seen (Figure 2c, open symbols). There was a clear lag between the onset of high production in the early SW Monsoon and higher export as the monsoon developed and diatoms became more abundant (R. Bidigare and R. Goericke, personal communications, 1997). Modeling has suggested that nearshore upwelling and advective transport offshore of silicate enriched waters may be responsible for enhanced diatom blooms in the NW Arabian Sea [Young and Kindle, 1994]. One hypothesis is that zooplankton grazers were abundant early in the bloom and thus able to keep down diatom abundances (M. Landry, personal communication, 1997).

The timing of this shallow export peak agreed with the flux maximum found in deep moored traps in 1995 (S. Honjo *et al.*, Monsoon controlled export fluxes to the interior of the Arabian Sea: U.S. JGOFS 1994-1995 experiment, submitted to *Deep Sea Research, II*, 1997). It also corresponded to the observed decrease in the upper 100 m in the stocks of total OC (D.A. Hansell and E.T. Peltzer, Spatial and temporal variations of total organic carbon in the Arabian Sea, submitted to *Deep Sea Research, II*, 1997) and Al and Fe (C.I. Measures and S. Vink, Seasonal variations in the distribution of Fe and Al in the surface waters of the Arabian Sea, submitted to *Deep Sea Research, II*, 1997). Profiles of POC export also suggested that POC export was strongly depth dependent, hence there was considerable remineralization between the surface and the onset of low oxygen waters below 100 m (Buesseler *et al.*, submitted manuscript, 1997). POC fluxes showed the most rapid attenuation with depth in the upper water column and near the bottom boundary layer (C. Lee *et al.*, Particulate organic carbon fluxes: Results from the U.S. JGOFS Arabian Sea Process Study, submitted to *Deep Sea Research, II*, 1997). Further analysis of the links between physical forcing, plankton dynamics and particulate export can be expected from the complete analysis of the JGOFS Arabian Sea data sets.

3.5. High Latitudes

Three quite interesting applications of the ^{234}Th approach have recently been made at high-latitude sites. Cochran *et al.* [1995, 1997] followed the progression of ^{234}Th during the opening of the NE Polynya off Greenland in the springs of 1992 and 1993. This region was characterized by relatively shallow ^{234}Th deficiencies (upper 50 m) and unusually high $\text{POC}/^{234}\text{Th}$ ratios (mean = 47 $\mu\text{mol dpm}^{-1}$; Table 1). POC fluxes as well as productivity increased in 1993 compared to 1992 and in both years ThE ratios of 50% and greater were

found (Table 1, and Figure 1). The good agreement between the ^{234}Th -derived POC fluxes in 1992 and the depletion of dissolved nutrients and dissolved inorganic carbon led Cochran *et al.* [1995, 1997] to conclude that the flux of biogenic particles out of the surface water dominated the removal of C and associated nutrients within the NE Polynya.

Another example of high relative POC export at high latitudes is found in data from the Polarstern ANT X/6 cruise in 1992. This cruise repeated a transect along the 6°W meridian during 6 weeks in the austral spring. A series of diatom blooms were sampled at the Antarctic Polar Front as evidenced by a biomass increase from 0.7 to greater than $4.0 \mu\text{mol chlorophyll } a \text{ L}^{-1}$ [Bathmann *et al.*, 1997]. Somewhat unexpectedly, biomass remained low at the sea ice edge further south (Figure 3). Accompanying this increase in production was an increase in particle export. This was documented by Rutgers van der Loeff *et al.* [1997] by a decrease in total ^{234}Th activities (Figure 3). Their estimated POC fluxes were quite high, with *ThE* ratios of 25% or more at the Polar Front during this bloom period (Table 1 and Figure 1). This was consistent with the hypothesis that accumulation rates below the Antarctic Polar Front were elevated due to efficient local export rather than lateral transport processes. These researchers concluded that export production in this dynamic setting was better predicted via the ^{234}Th approach than in parallel studies of nutrient inventories and carbon budgets.

Finally, a recent study by Shimmiel and Ritchie [1995] in the Bellingshausen Sea similarly showed relatively high export using the ^{234}Th approach at one site in open waters away from the marginal ice zone along the 85°W meridian. This site had both reasonably high ^{234}Th fluxes and $\text{POC}/^{234}\text{Th}$ ratios, hence POC fluxes derived from ^{234}Th were also elevated (*ThE* = 40%, Table 1 and Figure 1). All of these high-latitude sites are characterized by long periods of low productivity and ice cover followed by the rapid onset of spring blooms and high particulate export. The relatively high $\text{POC}/^{234}\text{Th}$ ratios found in the particulate samples from these high-latitude sites is consistent with the presence of large diatoms that are characteristic of these regions and high POC and Si fluxes in general [DeMaster, 1981; Codispoti *et al.*, 1991].

4. Discussion

Results from this limited set of case studies indicate that most of the surface open ocean is characterized by *ThE* ratios <5-10%. This suggests that there is generally a tight coupling between primary production and the flux of POC and associated nutrients out of the euphotic zone (Figure 1). While the concept of efficient recycling within the surface ocean is not new, it is the magnitude and exceptions to this rule that prove most interesting, that is, where production and export are decoupled and *ThE* ratios approach 50% or higher. These sites of relatively high organic C flux are found to be associated with either high-latitude blooms or seasonal and episodic export pulses at lower latitudes. All of these high-export events appear to be related to the occurrence of diatom blooms and large cells that are quickly removed from the surface ocean via aggregation and settling or via grazing.

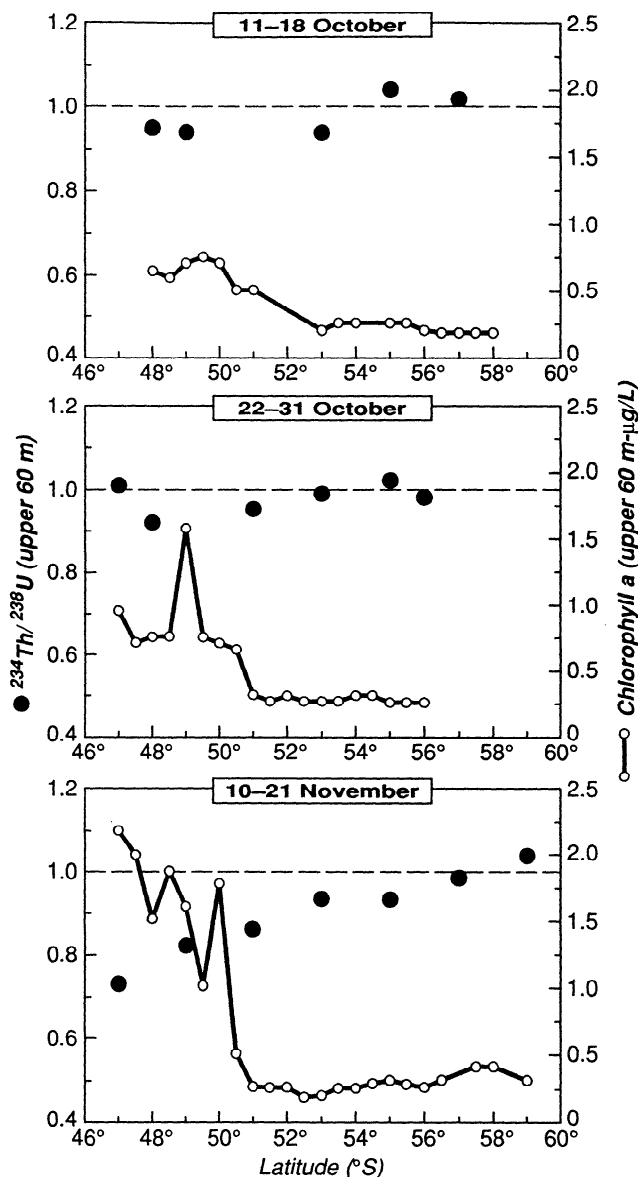


Figure 3. Summary of 0-60 m average ^{234}Th activities (solid circles, left axis) and chlorophyll *a* (line, right axis) for samples collected along 6°W in October/November 1992. The Polar Front was found at $46^\circ\text{--}50^\circ\text{S}$, and the northern edge of Marginal Sea Ice Zone shifted from 57° to 60°S (figure adapted from data of Bathmann *et al.* [1997] and Rutgers van der Loeff *et al.* [1997]).

These results based upon the ^{234}Th method are consistent with earlier studies that implicated the aggregation and sinking of large diatoms as an important vector in short-term export events [Smetacek, 1985; Goldman, 1988; Sancetta *et al.*, 1991].

The quantification of POC export using ^{234}Th allows us to study export processes on spatial and temporal scales relevant to food web dynamics. This opens up the possibility of distinguishing regions or events that play a disproportionately important role in surface export and therefore are critical to models of upper ocean biogeochemistry. The data support the

hypothesis that food web structure has a prominent role in determining the extent to which organic C and associated nutrients are recycled in or exported from the surface ocean [Michaels and Silver, 1988; Peinert et al., 1989]. If the structure of the food web plays an important role in determining export fluxes, then export events can either be initiated by the more predictable regional or seasonal progression of algal species, or by sporadic production associated with the short-term mixing of nutrients into the euphotic zone, as postulated by Goldman [1988, 1993].

In a simple flow analysis showing how the structure of the pelagic food web influences the resulting particle flux from the surface ocean, Michaels and Silver [1988] concluded that the large algae species play an important role in export production. Boyd and Newton [1995] used the Michaels and Silver model to explain a doubling in the 3100 m POC flux in 1989 relative to 1990 at the NABE site. In both years the surface productivity signal was similar and the dominant difference which could account for the enhanced POC export in 1989 was the size of the dominant phytoplankton species. In 1989, large chain-forming diatoms dominated the spring bloom as compared to a smaller diatom species in 1990 [Boyd and Newton, 1995].

Given that *ThE* ratios are generally low, export models are extremely sensitive to the parameterization of POC flux, since for similar surface water productivities, small changes in the export efficiency will lead to relatively large changes in the export of POC and associated elements. For example, a doubling of the POC flux as measured in a deep trap or recorded in deep-sea sediments need not be tied to a doubling in surface water production. It may, however, be related to smaller changes in the recycling efficiency due to environmentally driven changes in food web dynamics. Also, if diatoms are the main vector of POC export, then it must also be noted that many diatoms such as rhizosolenids have delicate shells that are rarely well preserved in marine sediments. Thus variations in surface flux driven by these organisms need not be reliably preserved in the marine sedimentary record [Sancetta et al., 1991].

Related to the strength of surface export is the decrease in POC flux with depth in the water column, that is, the remineralization rates of sinking particles. If local POC fluxes are driven by more delicate species of diatoms or more slowly settling material, then sinking POC may be remineralized at shallower depths. Therefore the relationship between POC flux versus depth will vary with season and site and a single parameterization of POC flux versus depth [e.g., Martin et al., 1987] will not be adequate in biogeochemical models. Thorium 234 is not often used to examine the extent of shallow remineralization since the flux of ^{234}Th out of the surface is rarely large enough to be measured as a subsurface excess of ^{234}Th above the activity already supported by its parent ^{238}U . When subsurface ^{234}Th excesses are seen, they are often single point maxima. POC flux curves derived from these profiles generally show a large increase in net POC flux from the surface to the base of the mixed layer followed by a decrease within the upper 100-200 m [see Bacon et al., 1996, Figure 13]. The decrease in POC flux is driven both by the decreasing $\text{POC}/^{234}\text{Th}$ ratio with depth on particles and the decreasing net ^{234}Th flux. Tracers with longer half-lives, such

as ^{228}Th [Cochran et al., 1993; Murnane et al., 1996] and the $^{210}\text{Pb}/^{210}\text{Po}$ pair [Bacon et al., 1976; Shimmiel and Ritchie, 1995], are needed to continue this analysis to examine midwater flux gradients.

If POC export in midlatitudes is patchy in both space and time, it will be generally undersampled using traditional methods in biological oceanography [Goldman, 1988]. The advantage of the ^{234}Th approach is that this tracer integrates over timescales of days to weeks, and episodic export events are less likely to be missed. Curious features in the BATS data include events characterized by high *ThE* ratios during low-productivity periods (Figure 2b). These might be caused by episodic pulses of material related to the mass sinking of rhizosolenid diatoms [Sancetta et al., 1991]. More frequent measurements in space and time would be needed for a detailed understanding of the relationship between nutrient limitations, food web characteristics, episodic new production events and particulate export.

While deep traps have recorded pulses of POC and diatom export related to blooms, they average over larger spatial and temporal scales and thus are less useful for tracking patchy surface export events or accurately predicting shallow ocean export fluxes. It should be noted that the trends in POC export presented here would look very different if shallow trap data were our only source of POC fluxes. In NABE, shallow trap POC fluxes were low and in EqPac high, thus leading to the opposite conclusion of a relatively low export efficiency during blooms and high particle export from HNLC regions. A recent study using shallow 50 m traps only to measure POC fluxes concluded that neither food web structure nor new production measurements could be used to predict the magnitude of POC export in the Gulf of St. Lawrence [Rivkin et al., 1996]. Whether this complete lack of any relationship between production and export is related to accuracy problems with the shallow traps that were used or due to the unique estuarine environment of this study site is still being debated [Boyd and Newton, 1997; Rivkin et al., 1997]. Logistically, the ^{234}Th approach is much simpler than shallow trapping programs, and increased spatial, depth and temporal coverage is possible. Studies to date suggest that relative changes in particle export are well constrained using ^{234}Th flux models. However, additional study of the characteristics of sinking particles and $\text{POC}/^{234}\text{Th}$ ratios will provide for a more accurate and precise estimate of POC export.

Changes in export via the biological pump, and circulation via the solubility pump, have the potential to influence air-sea exchange of CO_2 [Sarmiento, 1991]. Recently, it was shown that HNLC regions of the world's ocean are limited by the micronutrient Fe [Coale et al., 1996]. These results are used to support the hypothesis that increased dust input as seen in paleorecords, or the anthropogenic seeding of the Southern Ocean with iron, would result in a drawdown of atmospheric CO_2 via the biological pump [Martin, 1990]. Interestingly, it may not be the enhancement of total production in these experiments that would lead to increased POC fluxes. It was also noted that diatoms showed the greatest increase in biomass during repeated iron additions to HNLC waters [Coale et al., 1996]. Thus the preferential growth of the larger diatoms that are particularly favored by Fe inputs could

lead to an enhancement of export that is much higher than would be predicted from the observed productivity enhancement alone. As such, modulations in paleoceanographic proxies of sedimentation and records of the CO₂ content of trapped air in ice may be more correctly interpreted within the context of changes in food web dynamics and species assemblages and do not necessarily reflect an increase in total biological production in the surface ocean.

5. Conclusions

To increase our understanding of nutrient and carbon cycling in the surface ocean, we will need a better understanding of the fluxes of POC and associated elements out of the surface layers of the ocean. Regions or conditions of enhanced export will need to be identified and quantified. The ²³⁴Th method suggests that in the sites studied to date, the efficiency of the biological pump is low, that is, *ThE* <5-10%. Exceptions to this pattern are found during blooms at high latitudes, accompanying some spring blooms at midlatitudes, and perhaps in more episodic pulses throughout the year during relatively low productivity periods. More work is needed to quantify episodic and seasonal patterns of upper ocean export in the midlatitudes, since at these latitudes single events can be responsible for up to half of the local annual export [Sancetta *et al.*, 1991; Haake *et al.*, 1993]. Cases where relatively high POC export is found appear to be associated with food webs that are dominated by larger plankton, in particular diatom species. The importance of Fe and the impact of dust events in the paleorecord for the fertilization of the oceans need to be interpreted within the context of community structure. Variations in species assemblages can lead to larger changes in the rates of particulate export than one would predict from changes in total primary production rates alone, and these changes in export efficiency would be recorded in the sedimentary record.

At present, coupled physical/biogeochemical models will need to reexamine the current parameterization of POC export, which is often derived from single relationships between production (based on surface color) and export (based upon single trap flux versus depth relationships). The sensitivities of the models to the inclusion of episodic flux peaks or to the inclusion of seasonally varying *ThE* ratios need to be considered. If large diatoms are responsible for the bulk of surface-derived export, then inclusion of the dissolved Si cycle, and perhaps Fe limitation, will need to be included in these biogeochemical models as well. It would appear that events or regions of high surface export are characterized by a decoupling of production and export and that these events are undersampled and poorly represented in current global biogeochemical models. It therefore behooves us to learn more about the processes that initiate and regulate export so that we can better predict the cycling of major elements in the upper ocean.

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References

- Asper, V. L., Particle flux in the ocean: Oceanographic tools, in *Particle Flux in the Ocean*, edited by V. Ittekkot *et al.*, pp. 71-84, John Wiley, New York, 1996.
- Bacon, M. P., and R. F. Anderson, Distributions of thorium isotopes between dissolved and particulate forms in the deep sea, *J. Geophys. Res.*, **87**, 2045-2056, 1982.
- Bacon, M. P., D. W. Spencer, and P. G. Brewer, ²¹⁰Pb/²²⁶Ra and ²¹⁰Pb/²¹⁰Po disequilibria in seawater and suspended particulate matter, *Earth Planet. Sci. Lett.*, **32**, 277-296, 1976.
- Bacon, M. P., J. K. Cochran, D. Hirschberg, T. R. Hammar, and A. P. Flerer, Export flux of carbon at the equator during the EqPac time-series cruises estimated from ²³⁴Th measurements, *Deep Sea Res. II*, **43**, 1133-1154, 1996.
- Baker, E. T., H. B. Milburn, and D. A. Tennant, Field assessment of sediment trap efficiency under varying flow conditions, *J. Mar. Res.*, **46**, 573-592, 1988.
- Barber, R. T., M. P. Sanderson, S. T. Lindley, F. Chai, J. Newton, C. C. Trees, D. G. Foley, and F. P. Chavez, Primary productivity and its regulation in the equatorial Pacific during and following the 1991-1992 El Niño, *Deep Sea Res. II*, **43**, 933-969, 1996.
- Bathmann, U. V., R. Scharek, and C. D. Dubischar, Chlorophyll and phytoplankton species distribution in the Atlantic sector of the Southern Ocean in spring, *Deep Sea Res. II*, **44**, 51-68, 1997.
- Bhat, S. G., S. K. Krishnaswamy, D. Lal, D. Rama, and W. S. Moore, ²³⁴Th/²³⁸U ratios in the ocean, *Earth Planet. Sci. Lett.*, **5**, 483-491, 1969.
- Bidigare, R. R., and M. E. Ondrusek, Spatial and temporal variability of phytoplankton pigment distributions in the central equatorial Pacific Ocean, *Deep Sea Res. II*, **(43)**, 809-833, 1996.
- Binder, B. J., S. W. Chisholm, R. J. Olson, S. L. Frankel, and A. Z. Worden, Dynamics of picophytoplankton, ultraphytoplankton and bacteria in the central equatorial Pacific, *Top. Stud. Oceanogr. Equat. Pac.*, **2**, 43(4-6), 907-922, 1996.
- Boyd, P., and P. Newton, Evidence of the potential influence of planktonic community structure on the interannual variability of particulate organic carbon flux, *Deep Sea Res. I*, **42**, 619-639, 1995.
- Boyd, P., and P. Newton, Measuring biogenic carbon flux in the ocean, *Science*, **275**, 554, 1997.
- Brunland, K. W., and K. H. Coale, Surface water ²³⁴Th/²³⁸U disequilibria: Spatial and temporal variations of scavenging rates within the Pacific Ocean, in *Dynamic Processes in the Chemistry of the Upper Ocean*, edited by J. D. Burton, *et al.*, pp. 159-172, Plenum, New York, 1986.
- Buesseler, K. O., Do upper-ocean sediment traps provide an accurate record of particle flux?, *Nature*, **353**, 420-423, 1991.
- Buesseler, K. O., M. P. Bacon, J. K. Cochran, and H. D. Livingston, Carbon and nitrogen export during the JGOFS North Atlantic Bloom Experiment estimated from ²³⁴Th/²³⁸U disequilibria, *Deep Sea Res. I*, **39**, 1115-1137, 1992a.
- Buesseler, K. O., J. K. Cochran, M. P. Bacon, H. D. Livingston, S. A. Casso, D. Hirschberg, M. C. Hartman, and A. P. Flerer, Determination of thorium isotopes in seawater by non-destructive and radiochemical procedures, *Deep Sea Res. I*, **39**, 1103-1114, 1992b.
- Buesseler, K. O., A. F. Michaels, D. A. Siegel, and A. H. Knap, A three-dimensional time-dependent approach to calibrating sediment trap fluxes, *Global Biogeochem. Cycles*, **8**(2), 179-193, 1994.
- Buesseler, K. O., J. A. Andrews, M. C. Hartman, R. Belastock, and F. Chai, Regional estimates of the export flux of particulate organic carbon derived from thorium-234 during the JGOFS EqPac program, *Deep Sea Res. II*, **42**, 777-804, 1995.

- Butman, C. A., W. D. Grant, and K. D. Stolzenbach, Predictions of sediment trap biases in turbulent flows: A theoretical analysis based on observations from the literature, *J. Mar. Res.*, *44*, 601-644, 1986.
- Chavez, F. P., K. R. Buck, S. K. Service, J. Newton, and R. T. Barber, Phytoplankton variability in the central and eastern tropical Pacific, *Deep Sea Res. II*, *43*, 835-870, 1996.
- Chen, J. H., R. L. Edwards, and G. J. Wasserburg, ^{238}U , ^{234}U and ^{232}Th in seawater, *Earth Planet. Sci. Lett.*, *80*, 241-251, 1986.
- Coale, K. H., Labyrinth of doom: A device to minimize the "swimmer" component in sediment trap collections, *Limnol. Oceanogr.*, *35*(6), 1376-1381, 1990.
- Coale, K. H., and K. W. Bruland, ^{234}Th : ^{238}U disequilibria within the California Current, *Limnol. Oceanogr.*, *30*(1), 22-33, 1985.
- Coale, K. H., and K. W. Bruland, Oceanic stratified euphotic zone as elucidated by ^{234}Th : ^{238}U disequilibria, *Limnol. Oceanogr.*, *32*(1), 189-200, 1987.
- Coale, K. H., et al., A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, *Nature*, *383*, 495-501, 1996.
- Cochran, J. K., K. O. Buesseler, M. P. Bacon, H. D. Livingston, Thorium isotopes as indicators of particle dynamics in the upper ocean: Results from the JGOFS North Atlantic Bloom Experiment, *Deep Sea Res.*, *40*, 1569-1595, 1993.
- Cochran, J. K., C. Barnes, D. Achman, and D. J. Hirschberg, Thorium-234/Uranium-238 disequilibrium as an indicator of scavenging rates and particulate organic carbon fluxes in the northeast water polynya, Greenland, *J. Geophys. Res.*, *100*, 4399-4410, 1995.
- Cochran, J. K., K. A. Roberts, C. Barnes, and D. Achman, Radionuclides as indicators of particle and carbon dynamics on the East Greenland Shelf, in *Radioprotection-colloques*, *32* (C2), *Proceedings of RADOX 96-97 "Radionuclides in the Oceans,"* edited by P. Germain, et al., pp. 129-136, Institut de Protection et de Surete Nucleaire, Cherbourg, France, 1997.
- Codispoti, L. A., G. E. Friederich, C. M. Sakamoto, and L. I. Gordon, Nutrient cycling and primary production in the marine systems of the Arctic and Antarctic, *J. Mar. Sys.*, *2*, 359-384, 1991.
- DeMaster, D., The supply and accumulation of silica in the marine environment, *Geochim. Cosmochim. Acta*, *45*, 1715-1732, 1981.
- Downs, J. N., Export of production in oceanic systems: Information from phaeopigment, carbon and nitrogen analyses, Ph.D. thesis, Univ. of Wash., Seattle, 1989.
- Dugdale, R. C., and J. J. Goering, Uptake of new and regenerated forms of nitrogen in primary productivity, *Limnol. Oceanogr.*, *12*, 196-206, 1967.
- Eppley, R. W., New production: History, methods, problems, in *Productivity of the Ocean: Present and Past*, edited by W. H. Berger, et al., pp. 85-97, John Wiley, New York, 1989.
- Eppley, R. W., and B. J. Peterson, Particulate organic matter flux and planktonic new production in the deep ocean, *Nature*, *282*, 670-680, 1979.
- Fasham, M. J. R., H. W. Ducklow, and S. M. McKelvie, A nitrogen-based model of plankton dynamics in the oceanic mixed layer, *J. Mar. Res.*, *48*, 591-639, 1990.
- Feely, R. A., R. Wanninkhof, C. E. Cosca, P. P. Murphy, M. F. Lamb, and M. D. Steckley, CO_2 distributions in the equatorial Pacific during the 1991-1992 ENSO event, *Deep Sea Res. II*, *42*, 365-386, 1995.
- Fowler, S. W., and G. A. Knauer, Role of large particles in the transport of elements and organic compounds through the oceanic water column, *Prog. Oceanogr.*, *16*, 147-194, 1986.
- Gardner, W. D., and I. D. Walsh, Distribution of macroaggregates and fine-grained particles across a continental margin and their potential role in fluxes, *Deep Sea Res. I*, *37*, 401-411, 1990.
- Goldman, J. C., Spatial and temporal discontinuities of biological processes in pelagic surface waters, in *Toward a Theory on Biological-Physical Interactions in the World Ocean*, edited by B. Rothschild, pp. 273-296, Kluwer Acad., Norwell, Mass., 1988.
- Goldman, J. C., Potential role of large oceanic diatoms in new primary production, *Deep Sea Res. I*, *40*, 159-168, 1993.
- Gustafsson, Ö., P. M. Gschwend, and K. O. Buesseler, Using ^{234}Th disequilibria to estimate the vertical removal rates of polycyclic aromatic hydrocarbons from the surface ocean, *Mar. Chem.*, *57*, 11-23, 1997.
- Haake, B., V. Ittekkot, T. Rixen, V. Ramaswamy, R. R. Nair, and W. B. Curry, Seasonality and interannual variability of particle fluxes to the deep Arabian Sea, *Deep Sea Res. I*, *40*, 1323-1344, 1993.
- Hansell, D. A., C. A. Carlson, N. R. Bates, and A. Poisson, Horizontal and vertical removal of organic carbon in the equatorial Pacific Ocean: A mass balance assessment, *Deep Sea Res. II*, in press, 1998.
- Hartman, M. C., and K. O. Buesseler, Adsorbers for in-situ collection and at-sea gamma analyses of dissolved thorium-234 in seawater, *WHOI Tech. Rep. 94-15*, 19 pp., Woods Hole Oceanogr. Inst., Woods Hole, Mass., 1994.
- Jochem, F. J., S. Mathot, and B. Quegner, Size-fractionated primary production in the open Southern Ocean in austral spring, *Polar Biol.* (15), 381-392, 1995.
- Karl, D. M., J. R. Christian, J. E. Dore, D. V. Hebel, R. M. Letelier, L. M. Tupas, and C. D. Winn, Seasonal and interannual variability in primary production and particle flux at station ALOHA, *Deep Sea Res. II*, *43*, 539-568, 1996.
- Kaufman, A., Y.-H. Li, and K. K. Turekian, The removal rates of ^{234}Th and ^{228}Th from waters of the New York Bight, *Earth Planet. Sci. Lett.*, *54*, 385-392, 1981.
- Knauer, G., and V. Asper, Sediment trap technology and sampling: Report of the U.S. GOFS working group on sediment trap technology and sampling, *U.S. GOFS Plann. Rep. 10*, 94 pp., U.S. GOFS Planning and Coordination Office, Woods Hole oceanographic Institution, woods Hole, MA, 1989.
- Landry, M. R., et al., Iron and grazing constraints on primary production in the central equatorial Pacific: An EqPac synthesis, *Limnol. Oceanogr.*, *42*(3), 405-418, 1997.
- Lochte, K., H. W. Ducklow, M. J. R. Fasham, and C. Stienen, Plankton succession and carbon cycling at 47°N 20°W during the JGOFS North Atlantic Bloom Experiment, *Deep Sea Res. II*, *40*, 91-114, 1993.
- Martin, J. H., Glacial-interglacial CO_2 change: The iron hypothesis, *Paleoceanography*, *5*(1), 1-13, 1990.
- Martin, J. H., and S. E. Fitzwater, Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic, *Nature*, *331*, 341-343, 1988.
- Martin, J. H., G. A. Knauer, D. M. Karl, and W. W. Broenkow, VERTEX: Carbon cycling in the northeast Pacific, *Deep Sea Res.*, *34*, 267-285, 1987.
- Martin, J. H., S. E. Fitzwater, R. M. Gordon, S. N. Hunter, and S. J. Tanner, Iron, primary production and carbon-nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment, *Deep Sea Res. II*, *40*, 115-134, 1993.
- Martin, J. H., et al., The iron hypothesis: Ecosystem tests in equatorial Pacific waters, *Nature*, *371*, 123-129, 1994.
- McCarthy, J. J., C. Garside, J. L. Nevins, and R. T. Barber, New production along 140°W in the equatorial Pacific during and following the 1992 El Niño event, *Top. Stud. Oceanogr. Equat. Pac.*, *2*, 43(4-6), 1065-1092, 1996.
- McGillicuddy, D. J., J. J. McCarthy, and A. R. Robinson, Coupled physical and biological modeling of the spring bloom in the North Atlantic, I, Model formulation and one dimensional bloom processes, *Deep Sea Res.*, *42*, 1313-1357, 1995a.
- McGillicuddy, D. J., A. R. Robinson, and J. J. McCarthy, Coupled physical and biological modeling of the spring bloom in the North Atlantic, II, Three dimensional bloom and post-bloom processes, *Deep Sea Res.*, *42*, 1359-1398, 1995b.
- Michaels, A. F., and A. H. Knap, Overview of the U.S. JGOFS Bermuda Atlantic time-series study and the Hydrostation S program, in *Top. Stud. Oceanogr. HOT/BATS*, *43*(2-3), 157-198, 1996.
- Michaels, A. F., and M. W. Silver, Primary production, sinking fluxes and the microbial food web, *Deep Sea Res.*, *35*, 473-490, 1988.
- Michaels, A. F., N. R. Bates, K. O. Buesseler, C. A. Carlson, and A. H. Knap, Carbon-cycle imbalances in the Sargasso Sea, *Nature*, *372*, 537-540, 1994.
- Moran, S. B., and K. O. Buesseler, Size-fractionated ^{234}Th in continental shelf waters off New England: Implications for the

- role of colloids in oceanic trace metal scavenging, *J. Mar. Res.*, *51*, 893-922, 1993.
- Murnane, R. J., J. K. Cochran, K. O. Buesseler, and M. P. Bacon, Least-squares estimates of thorium, particle, and nutrient cycling rate constants from the JGOFS North Atlantic Bloom Experiment, *Deep Sea Res.*, *43*, 239-258, 1996.
- Murray, J. W., J. N. Downs, S. Strom, C.-L. Wei, and H. W. Jannasch, Nutrient assimilation, export production and ^{234}Th scavenging in the eastern equatorial Pacific, *Deep Sea Res.*, *36*, 1471-1489, 1989.
- Murray, J. W., R. T. Barber, M. R. Roman, M. P. Bacon, and R. A. Feely, Physical and biological controls on carbon cycling in the equatorial Pacific, *Science*, *266*, 58-65, 1994.
- Murray, J. W., J. Young, J. Newton, J. Dunne, T. Chapin, and B. Paul, Export flux of particulate organic carbon from the central equatorial Pacific determined using a combined drifting trap- ^{234}Th approach, *Deep Sea Res. II*, *43*, 1095-1132, 1996.
- Peinert, R., B. von Bodungen, and V. S. Smetacek, Food web structure and loss rate, in *Productivity of the Ocean: Present and Past*, edited by W. H. Berger, et al., pp. 35-48, John Wiley, New York, 1989.
- Rivkin, R. B., et al., Vertical flux of biogenic carbon in the ocean: Is there food web control?, *Science*, *272*, 1163-1166, 1996.
- Rivkin, R. B., et al., Response to "Measuring biogenic carbon flux in the ocean" by P. Boyd and P. Newton, *Science*, *275*, 554-555, 1997.
- Rutgers van der Loeff, M. M., J. Friedrich, and U. V. Bathmann, Carbon export during the spring bloom at the southern polar front, determined with the natural tracer ^{234}Th , *Deep Sea Res. II*, *44*, 457-478, 1997.
- Sancetta, C., T. Villareal, and P. Falkowski, Massive fluxes of rhizosolenid diatoms: A common occurrence, *Limnol. Oceanogr.*, *36*, 1452-1457, 1991.
- Santschi, P. H., Y. Li, and J. Bell, Natural radionuclides in the water of Narragansett Bay, *Earth Planet. Sci. Lett.*, *45*, 201-213, 1979.
- Sarmiento, J. L., Oceanic uptake of anthropogenic CO_2 : The major uncertainties, *Global Biogeochem. Cycles*, *5(4)*, 309-313, 1991.
- Shimmield, G. B., and G. R. Ritchie, The impact of marginal ice zone processes on the distribution of ^{210}Pb , ^{210}Po and ^{254}Th and implications for new production in the Bellingshausen Sea, Antarctica, *Deep Sea Res. II*, *42*, 1313-1335, 1995.
- Smetacek, V. S., The role of sinking diatom life-history cycles: Ecological, evolutionary and geological significance, *Mar. Biol.*, *84*, 239-251, 1985.
- Tanaka, N., Y. Takeda, and S. Tsunogai, Biological effect on removal of Th-234, Po-210 and Pb-210 from surface water in Funka Bay, Japan, *Geochim. Cosmochim. Acta*, *47*, 1783-1790, 1983.
- Tsunogai, S., K. Taguchi, and K. Harada, Seasonal variation in the difference between observed and calculated particulate fluxes of Th-234 in Funka Bay, Japan, *J. Oceanogr. Soc. Jpn.*, *42*, 91-98, 1986.
- Verity, P. G., D. K. Stoecker, M. E. Sieracki, and J. R. Nelson, Grazing, growth and mortality of microzooplankton during the 1989 North Atlantic spring bloom at 47°N, 18°W, *Deep Sea Res. I*, *40*, 1793-1814, 1993.
- Verity, P. G., D. K. Stoecker, M. E. Sieracki, and J. R. Nelson, Microzooplankton grazing of primary production at 140°W in the equatorial Pacific, *Top. Stud. Oceanogr. Equat. Pac.*, *2*, 43(4-6), 1227-1256, 1996.
- Walsh, I. D., and W. D. Gardner, A comparison of aggregate profiles with sediment trap fluxes, *Deep Sea Res. I*, *39*, 1817-1834, 1992.
- Wei, C.-L., and J. W. Murray, Temporal variations of ^{234}Th activity in the water column of Dabob Bay: Particle scavenging, *Limnol. Oceanogr.*, *37*, 296-314, 1992.
- Young, D. K., and J. C. Kindle, Physical processes affecting availability of dissolved silicate for diatom production in the Arabian Sea, *J. Geophys. Res.*, *99*, 22,619-22,632, 1994.

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