

# The POC/<sup>234</sup>Th ratio of settling particles isolated using split flow-thin cell fractionation (SPLITT)

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## Abstract

The common assumption that the ratio between particulate organic carbon (POC) and particulate  $^{234}\text{Th}$  obtained from shallow sediment traps and filterable particles are representative of the ratio in the total particle settling flux should be treated with caution in view of well-known biases associated with tethered shallow sediment traps and the decoupling between size and settling velocity of many natural particle regimes. To make progress toward reliably constraining the POC/ $^{234}\text{Th}$  ratio on truly settling particles, we have tested here a settling collection technique designed to remove any hydrodynamic bias; split flow-thin cell fractionation (SPLITT). These first results from a North Sea fjord and an open Baltic Sea time-series station indicates that the POC/ $^{234}\text{Th}$  ratio on the more complete particle-settling spectrum, isolated with SPLITT, was higher than the POC/ $^{234}\text{Th}$  ratio obtained simultaneously from tethered shallow sediment traps in seven out of seven parallel deployments with an average factor of 210%. The POC/ $^{234}\text{Th}$  ratio from the SPLITT was either in the same range or higher than that obtained on filtered “bulk” particles. To explain this novel data we hypothesize that the slowest settling fraction is organic-matter rich and does not strongly complex  $^{234}\text{Th}$  (i.e., high POC/ $^{234}\text{Th}$ ). We suggest that this ultra-slow sinking fraction is better collected by SPLITT than with tethered sediment traps because of minimized hydrodynamic bias.

This was tested using the ratio of POC/Al as a tracer of detrital mineral-ballast influenced settling velocity. The higher POC/Al ratios in SPLITT samples relative to in traps is consistent with the hypothesis that SPLITT is better suited for collecting also the slow-settling component of sinking particles. This important slow-settling component appears to here consist primarily of non-APS/TEP components of plankton exudates or other less-strongly  $^{234}\text{Th}$ -complexing organic matter. Further

applications of the SPLITT technique are likely to return increasingly new insights on the composition (including “truly settling” POC/<sup>234</sup>Th) of the total spectrum of particles settling out of the upper ocean.

## Introduction

The export flux of particulate organic carbon (POC) from the surface ocean is one of the largest sinks of atmospheric carbon dioxide on decadal-centennial time scales. Yet, it remains a challenge to accurately estimate this important component of the global carbon cycle. With the recognition that flux estimates from shallow sediment traps may be compromised by both hydrodynamic and biological factors (e.g., Buesseler, 1991, 1994, 2000; Gust et al., 1992; Gust and Kozerski, 2000; Steinberg et al., 1998; Gardner, 2000; Gustafsson et al., 2004), alternative flux indicators have been sought. In this regard, the past decade has witnessed a broad-scale application of the <sup>234</sup>Th proxy to provide regional estimates of POC export fluxes in the world ocean as part of the Joint Global Ocean Flux Study (JGOFS) and many other programs (e.g., this special volume).

The steady-state one-dimensional model for the <sup>234</sup>Th-derived POC flux is:

$$F_{POC} = \lambda \cdot (\{^{238}U_{tot}\} - \{^{234}Th_{tot}\}) \cdot z \cdot \frac{[POC]}{\{^{234}Th_{part}\}} \quad (1)$$

where  $F_{POC}$  is the sinking flux of organic carbon ( $\text{g m}^{-2} \text{d}^{-1}$ ),  $\lambda$  is the radioactive decay constant for <sup>234</sup>Th (0.0288  $\text{d}^{-1}$ ),  $\{^{238}U_{tot}\}$  and  $\{^{234}Th_{tot}\}$  is the total radioactivity concentration of <sup>238</sup>U and <sup>234</sup>Th in the mixed surface waters ( $\text{dpm m}^{-3}$ ),  $z$  (m) is the

surface ocean depth out of which settling export is considered, and  $[POC]$  and  $\{^{234}\text{Th}_{\text{part}}\}$  is the particulate organic carbon concentration ( $\text{g m}^{-3}$ ) and particulate  $^{234}\text{Th}$  activity concentration ( $\text{dpm m}^{-3}$ ) of truly settling matter from the base of the zone of interest.

The difficulty in reliably constraining the  $POC/^{234}\text{Th}$  ratio on truly settling particles (Eqn. 1) is perhaps the largest challenge with the  $^{234}\text{Th}$  proxy method. So far, the  $POC/^{234}\text{Th}$  ratio has been obtained either in shallow sediment traps or in filterable particles and has been assumed representative of total particle settling flux (e.g., Buesseler, 1998; Moran et al., 2003). The biases associated with tethered shallow sediment traps espoused above and the decoupling between size and settling velocity in natural particle regimes (e.g., Alldredge and Silver, 1988; Gustafsson and Gschwend 1997; Gustafsson et al. 2000a), suggest that this assumption should be treated with caution.

The  $POC/^{234}\text{Th}$  ratio from tethered sediment traps may be compromised by the minute presence of “swimmer” material as the ratio may be a factor of 1000 greater in zooplankton than on other collected particles (Coale, 1990; Buesseler et al., 1994). In contrast, POC solubilization inside the trap (Hansell and Newton, 1994) would yield an underestimate of the  $POC/^{234}\text{Th}$  ratio. Finally, hydrodynamic effects on tethered sediment traps are suspected of causing particle sorting (Butman et al., 1986; Gust and Kozerski, 2000; Gardner, 2000), including a suggested discrimination against a slowly-settling organic-rich pool (e.g., Gust and Kozerski, 2000; Gustafsson et al., 2004). Taken together, the  $POC/^{234}\text{Th}$  ratio obtainable in material from tethered shallow sediment traps is likely to be an imperfect estimate of the truly settling ratio.

Similarly unsatisfying, the  $POC/^{234}\text{Th}$  ratio on various filters reflects both suspended and sinking particles in unknown proportions. The filter-based approaches

are further weakened by the fact that different filtration procedures (e.g., bottle, *in situ* high-volume and low-volume approaches) may yield quite different estimates of [POC] (e.g., Moran et al., 1999) and presumably therefore also of the  $\text{POC}/^{234}\text{Th}$  ratio.

Returning to Eqn. 1, the application of the  $^{234}\text{Th}$  proxy to empirically estimate the POC export flux requires no mechanistic understanding of why the  $\text{POC}/^{234}\text{Th}$  ratio varies. Rather, it depends upon accurate, occasion-specific, measures of the  $\text{POC}/^{234}\text{Th}$  ratio on the complete flux-weighted spectrum of settling particles. To this end, we have tested a settling collection technique designed to remove any hydrodynamic bias; split flow-thin cell fractionation (SPLITT; Giddings, 1985; Gustafsson et al., 2000a). The objective was to evaluate how the  $\text{POC}/^{234}\text{Th}$  ratio of a complete particle settling spectrum, obtained with SPLITT, compares with  $\text{POC}/^{234}\text{Th}$  ratios obtained simultaneously by traditional filtration and shallow tethered sediment trap methods. Our initial findings on the differences between  $\text{POC}/^{234}\text{Th}$  ratio on SPLITT-isolated settling particles versus other techniques are interpreted with additional geochemical indices of the composition of the isolated particles and other system and technique-specific considerations.

## Materials and Methods

### *Principle and operation of the SPLITT technique*

Split flow thin cell fractionation (SPLITT) is a method where particles are separated during laminar fluid flow in a thin channel based on a combination of their hydrodynamic radius, wet density, and diffusion coefficient (Giddings, 1985; Fuh *et al.*, 1992). Hence, applied to surface water, SPLITT has an easily adjusted “cut-off” that instead of being based on particle size is based on particle settling velocity. It is a gentle separation method where the resulting fractions are obtained using a “virtual membrane” that is a continuously renewed liquid boundary layer. The cut-off is practically adjustable to obtain particles settling from  $> 0.5 \text{ m d}^{-1}$  to  $> 10 \text{ m d}^{-1}$  (e.g., Gustafsson *et al.*, 2000a).

While the technique has so far found its widest use in biomedical applications (e.g., Levin and Tawil, 1993), the application of SPLITT to the study of natural water particles is increasing (e.g., Keil *et al.*, 1994; 1997; Contado *et al.*, 1997; Gustafsson *et al.*, 2000a; Lee *et al.* 2001; Rings *et al.* 2004; Coppola *et al.*, 2005). However, the processing capacity of the SPLITT HC (for “high capacity”) cell, so far employed in all published natural water studies, is such that all studies but one have focused on riverine or suspended bottom sediment particles. Gustafsson and co-workers (2000a) demonstrated the applicability of the SPLITT HC cell for the settling fractionation of coastal surface water particles after a  $0.2 \text{ }\mu\text{m}$  cross-flow filtration (CFF) pre-concentration step. That study showed negligible effects of the CFF step on the composition of the isolated settling pool, good agreement between theoretical settling predictions and SPLITT-obtained calibrations with spherical monodisperse particle standards, and geochemically consistent settling fractionation patterns. Coppola *et al.* (2005) recently demonstrated the obtained settling velocity cut-off for standard

particles agreed with those theoretically predicted, and efficient applicability to natural water particles of a SPLITT EHC (for “extra-high capacity”) cell.

In the present work, we used a SPLITT EHC cell (FFFractionation LLC, Salt Lake City, UT, USA), which enables 20 times higher processing capacity compared with the HC model used earlier. The theory, construction, composition, and operation of SPLITT is detailed in earlier methods papers (e.g., Giddings, 1985; Fuh et al., 1982; Springston et al., 1987; Keil et al., 1994; Gustafsson et al., 2000a; Coppola et al., 2005). The EHC-SPLITT cell dimensions were breadth of 14 cm, length of 100 cm and channel height of 500  $\mu\text{m}$ . Largely following the procedure described in Gustafsson et al. (2000a), seawater from the lower part of the seasonal pycnocline was pumped onboard with an *in situ* pump and pre-concentrated using a 0.2  $\mu\text{m}$  CFF (Millipore Pellicon 2 system with 0.5  $\text{m}^2$  polyvinyl difluoride [PVDF] membranes) to volumes of 0.5-1 liter (concentration factors in the range 40-150). This sample solution was immediately passed via a peristaltic pump and silicon tubing (Cole-Parmer Masterflex L/S model 7519-25 cartridge pump) into the SPLITT cell, first passing through a pulse dampener (and bubble trap). As carrier solution, < 3 kD CFF-processed (Millipore Pellicon 2 system with 0.5  $\text{m}^2$  regenerated cellulose membranes) seawater from the same location was used. The SPLITT fractionated solutions (called gravitoid “SPLITTate” and large-colloid “SPLITTate”, respectively) were collected in pre-weighed glass bottles and the mass of both fractions was determined by weighing after the complete fractionation of the sample. The SPLITT processing time was on the order of 30 minutes, with the total CFF pre-concentration period lasting for a few hours.

### ***SPLITT field applications: Study systems***

The SPLITT technique was applied in parallel with several other techniques to study the sinking fractionation of organic carbon during a 3-week long field campaign in March-April 2001 of the Gullmar fjord, on the west coast of Sweden (station Alsäck: 58°19.0'N, 11°32.0'E; 60 m depth). The surface water of this fjord is typical of a coastal temperate ecosystem and its plankton ecology and biogeochemistry has been continuously documented over the past twenty years (e.g., Lindahl, 1983; Lindahl, 1995; Tiselius and Kuylenstierna, 1996; Waite et al., 2005). The fjord surface layer, with salinities as low as 22 ‰, is a mixture of Baltic outflows, Kattegat waters and limited freshwater runoff, which overlies the Jutland Current positioned around the base of the pycnocline (about 20 m depth). The deepwater stems from Skagerrak/North Sea and has a salinity of 31-33 ‰. Heterotrophic and autotrophic flagellates dominated the surface waters during the spring bloom of 2001 both in terms of cell number and carbon stock (Waite et al., 2005). However, detailed time-series water column profiles of the stable carbon isotope composition of POC, along with time-series sediment trap data including gel analysis of particle size and type, suggested that a modest background population of diatoms, and particularly their exudates, was responsible for most of the carbon flux to depth (Waite et al., 2005).

Parallel applications of SPLITT, membrane filtration and bottom-tethered cylindrical traps were also performed during an expedition to the long-term time series station BY31 (Landsort Deep, 58°35'N 18°14'E; 40 km off Swedish coast; 459 m depth) in mid-August 2000. This station has been intensively monitored for hydrographic, biological, and chemical parameters since the 1890s (see references in the reviews Voipio, 1981; Fonselius and Valderrama, 2003). A high-intensity time-

series monitoring program with 22-25 observations per year has been operating at this site since 1990 (e.g., HELCOM, 1988; Larsson et al., 2001). In the brackish waters of the Baltic Sea, there is a permanent and strong halocline centered around 60-80 m (e.g., Kullenberg et al., 1981) with a strong seasonal pycnocline developing at around 10-15 m depth (e.g., Stigebrandt, 1985), below which density increases steadily with depth. The surface mixed layer exhibits well-documented seasonal variations in biogeochemical parameters typical of temperate shelf areas (Elmgren, 1984; Larsson et al., 2001; Gustafsson et al., 2004). The collection efficiency of common cylindrical sediment traps was recently reported for this station for a 24-month period and found to range from 35-118% in the winter-spring period, but exhibit worse under trapping in the summer and early fall with only 5-41%  $^{234}\text{Th}$  trapping efficiency (Gustafsson et al., 2004).

The composition of particles settling  $> 1 \text{ m d}^{-1}$  (Gullmar fjord time series) and at three different settling cut-offs ( $> 0.6$ ,  $> 1.0$ , and  $> 1.3 \text{ m d}^{-1}$ ; Landsort Deep, Baltic Sea), as isolated by the EHC-SPLITT system described above, was compared with the composition of “bulk” particles obtained by about  $1 \mu\text{m}$  filtration of 5-20 l seawater samples (GF/F for POC and polycarbonate for  $^{234}\text{Th}$  and Al) on five expeditions in the Gullmar fjord and three occasions in the Baltic Sea. The SPLITT results were also compared with short-term deployments of sediment traps positioned immediately below the seasonal pycnocline, at 30 m in the Gullmar fjord and at 40 m in the Baltic Sea. The employed cylindrical sediment traps system is commonly used for upper ocean and continental shelf studies and their design (Larsson et al., 1986; Broman et al., 1990) and detailed trapping protocol are previously reported (Gustafsson et al., 2004).

### *Analysis of samples from SPLITT and compared techniques*

The “SPLITTate” fractions were subsequently vacuum-filtered through 47 mm glass-fiber filters (about 0.7  $\mu\text{m}$ ; GF/F Whatman) for determination of particulate organic carbon (POC) or through 142 mm polycarbonate track-etch membrane filters (1.0  $\mu\text{m}$ ; Nuclepore Inc.) for particulate  $^{234}\text{Th}$ , following the method of Rutgers van der Loeff and Moore (1999). The GF/F filters were subsampled, transferred to pre-combusted Ag capsules and subjected to *in situ* 1M HCl microacidification (e.g., Gustafsson et al., 1997) prior to determination of POC with a Europa isotope ratio monitoring mass spectrometer. The  $^{234}\text{Th}$  filters were folded and assembled on plastic stubs for direct counting on low-background beta counters (Risö GM 25-5) following the procedures outlined by Rutgers van der Loeff and Moore (1999). After beta analysis, the polycarbonate filters, which were wrapped in polyethylene film throughout the procedure, was analyzed for major element composition using inductively-coupled plasma mass spectrometry (ICP-MS).

The POC,  $^{234}\text{Th}$ , and major element analysis of the other filter and tethered sediment trap samples were processed and analyzed in a similar fashion to that for the SPLITT samples. Additionally, the water column and sediment trap analysis of transparent exopolymer particles (TEP) was performed using Alcian Blue staining followed by spectrophotometric determination (Passow and Alldredge, 1995; Gustafsson et al., 2001).

The uncertainties in the POC and TEP data were based on analysis of triplicate samples, whereas that for  $^{234}\text{Th}$  had to be based on propagated counting errors, and the error for Al on repetitive analysis of standards. Results were quality assured and corrected for results from multiple blanks.

## Results and Discussion

### *The POC/<sup>234</sup>Th ratio from SPLITT compared with other approaches to collect settling particles*

Observations from both regimes suggest that higher POC/<sup>234</sup>Th ratios were found using SPLITT than the POC/<sup>234</sup>Th ratios obtained with tethered sediment traps or filters, operated simultaneously. In the Gullmar fjord spring bloom campaign, the POC/<sup>234</sup>Th ratio of the SPLITT-isolated particles settling > 1 m/d varied between 1.7 and 4.6 mg dpm<sup>-1</sup> (mean 3.2; n = 5) throughout the bloom (Fig. 1a). The SPLITT-isolated settling particles exhibited on average 214% higher POC/<sup>234</sup>Th ratio than particles from the tethered cylindrical trap (n = 4 parallel observations), and 50% higher than “bulk” particles (i.e., > 1 μm filters, n = 5 parallel observations). A single sample of the sub-micron colloidal particle phase (3 kD – 0.2 μm) isolated on 28 March 2001 exhibited a much higher ratio of 19 mg dpm<sup>-1</sup> (data not shown in Figure).

Similarly, at the Baltic Sea long-term time series station BY-31, the more complete particle settling spectrum isolated by the SPLITT system exhibited higher POC/<sup>234</sup>Th ratios than the standard tethered cylindrical sediment traps (Fig. 2a). During that mid-August 2000 campaign, three SPLITT samples were isolated over the course of three subsequent days with settling cut-offs of 0.6, 1.0, and 1.3 m d<sup>-1</sup>, respectively. This range in employed settling cut-offs was selected as the average settling velocity out of the mixed layer of <sup>234</sup>Th-carrying particles (> 1 μm in size) throughout a previously reported 2-year study (Gustafsson et al., 2004) was on average 1.6 ± 1.0 m d<sup>-1</sup> (1 s.d., n = 29). The POC/<sup>234</sup>Th ratio in all of the three SPLITT samples was significantly larger (by 207%) than that obtained in the sediment trap for the period. The trap-obtained POC/<sup>234</sup>Th ratio was typical for this site and period of year, as revealed from

a documented cyclic year-round variation in the  $\text{POC}/^{234}\text{Th}$  ratio from this Baltic Sea time-series station (Fig. 6 in Buesseler et al., this special volume). In this regime, the SPLITT ratio was in the same vicinity as that on bulk suspended particles (Fig. 2a).

Taken together, these first applications of the SPLITT technique to isolate the complete settling particle spectrum provide a coherent picture where in seven out of seven parallel deployments, SPLITT, the technique with minimal hydrodynamic bias, return results of higher  $\text{POC}/^{234}\text{Th}$  compared to that obtainable from the particles collected in moored sediment traps. The average elevation for all seven occasions, composed from two different temperate shelf regimes, is 210%. The  $\text{POC}/^{234}\text{Th}$  ratio from the SPLITT technique was also generally elevated relative to the corresponding filter-obtained ratio at the Gullmar fjord and about equal to “bulk” particles in the Baltic Sea. As elaborated below, there is no obvious mechanistic expectation of a SPLITT versus filter trend in this ratio.

***Mechanistic hypotheses of trends in  $\text{POC}/^{234}\text{Th}$  ratios among different approaches to collect settling particles***

To explain this novel data set with higher  $\text{POC}/^{234}\text{Th}$  ratio in SPLITT than in traps, we hypothesize that the slowest settling fraction is organic-matter rich and does not strongly complex  $^{234}\text{Th}$  (i.e., high  $\text{POC}/^{234}\text{Th}$ ). We suggest that this ultra-slow sinking fraction is better collected by SPLITT than with tethered sediment traps because of the minimized hydrodynamic bias in SPLITT compared to traditional traps. Hydrodynamic theory supports the notion that tethered traps may selectively under collect slowly settling amorphous and organic-matter rich aggregates due to inherent horizontal flow across the sediment trap mouth (e.g., Gust et al., 1996; Gust and Kozerski, 2000).

Net particle aggregate density is a determinant factor for settling and it has been suggested that minerals act as ballast (i.e., “rocks-in-the-flocs”) (e.g., Gustafsson and Gschwend, 1997; Gustafsson et al., 2000a, 2000b, Armstrong et al., 2002). As such, rapidly sinking particles should have a relatively lower POC/Al ratio compared with slowly sinking material. Hence, for our hypothesis to hold, the POC/Al ratio in the SPLITT isolated particles should be higher than in tethered sediment traps. This is tested below.

Independently from above, and not contingent thereof, a second suggestion is that the SPLITT-isolated particles may generally exhibit higher POC/<sup>234</sup>Th ratio than the bulk of surface ocean particles because these include not just settling material. We base this suggestion on suspended polyelectrolyte organic matter, such as humic matter, transparent exopolymer particles (TEP) and acidic polysaccharides (APS), which may effectively complex <sup>234</sup>Th (Niven et al., 1995; Quigley et al., 2002; Guo et al., 2002; Santschi et al., 2003; Hung et al., 2004), thus lowering the POC/<sup>234</sup>Th ratio on suspended particles. In essence, this organic matter has a higher density of ionized surface groups and thus a higher density of surface ligands per C atom. This property also renders the organic matter more hydrophilic, which lowers its tendency to aggregate (electrostatic repulsion) and makes it less likely to settle out. As a result, if this hypothesis is correct, POC/<sup>234</sup>Th ratios will generally tend to be lower on suspended particles. In contrast, organic matter with less (negatively) charged functional groups per C atom are both poorer at sorbing Th and more hydrophobic, thus rendering it more likely to aggregate and settle out, carrying a higher POC/<sup>234</sup>Th signal to depth on organic-rich slowly-settling aggregates. The above suggestion implies that the TEP/POC (alternatively, APS/POC) should be lower in hydrophobic and thus settling organic matter, and one should find lower TEP/POC in accurately-

collected isolates of settling particles than in suspended particles. This is also tested below.

### ***Testing of hypotheses using ancillary Al and TEP data***

The POC/Al ratio may provide useful information on the relative importance of mineral ballasts in otherwise organic-dominated particle aggregates, as the POC reflects bulk organic matter and Al can be used as tracer for detrital mineral occurrence. For both the Gullmar fjord spring bloom time series and the open Baltic Sea samples, the POC/Al ratio is clearly higher in the SPLITT-isolated settling particles compared to the particles collected in the cylindrical trap. The average enhancement is a factor of 3-4 (n = 8 parallel deployments; Fig. 1b and 2b). This is consistent with the hypothesis that the elevated POC/<sup>234</sup>Th ratio in the SPLITT-settling particles, compared with particles in the traps, reflects the ability of SPLITT to better collect more slowly settling particles.

The relative importance of extracellular acidic polysaccharides on the settling flux of POC may be evaluated by comparing the TEP/POC in suspended and settling particles. Unfortunately, TEP was only quantified in the Gullmar fjord study in the bulk suspended matter and in the tethered sediment traps. TEP or APS may represent significant ligands for the chemical speciation of <sup>234</sup>Th in surface waters. However, given that TEP or APS frequently only accounts for a few per cent of the POC inventory (e.g., Guo et al., 2002) and is expected to have a very low net density, this speciation role may not necessarily translate into a correspondingly significant role for POC settling. In the Gullmar fjord, the TEP/POC ratio was indeed observed to be much higher in the bulk suspended particles than in the trapped material at 30 m (Fig. 1c). In fact, a geochemical mass balance model of TEP throughout the fjord spring

bloom campaign suggests that settling out of the mixed surface layer only accounted for 4% of the TEP removal (Gustafsson et al., in prep). Taken together, the ancillary geochemical data is in agreement with the proposed hypothesis, that the slowest sinking particles are organic-matter rich and not excessively  $^{234}\text{Th}$  complexing. APS/TEP-like material does not seem to dominate this important slow-settling component. Instead, it must consist of some other components of plankton exudates (Waite et al., 2005) or other poorly  $^{234}\text{Th}$ -complexing organic matter.

***Putative implications of the existence of a slow-settling particle pool with higher POC/ $^{234}\text{Th}$  ratio that is under collected with tethered traps***

The SPLITT observed more slowly settling particle pool with high POC/ $^{234}\text{Th}$  relative to sediment trapped POC/ $^{234}\text{Th}$  ratios is consistent with several other observations and apparent inconsistencies of our current empirical view of the upper ocean carbon cycle. This first study of POC/ $^{234}\text{Th}$  with SPLITT was performed in two temperate continental shelf regimes and is thus strictly only applicable to the studied systems. Nevertheless, given the well documented classical progression in phytoplankton speciation, primary and export production for these two time series stations, it is reasonable to anticipate that the general facets of settling, and the method aspects that have been documented here, may be relevant to consider also in other upper ocean regimes, including the open ocean. First, another novel technique also designed to collect the full spectrum of settling particles with minimized hydrodynamic bias, neutrally-buoyant sediment traps (NBST; Buesseler et al., 2000), also appears to obtain higher POC/ $^{234}\text{Th}$  ratios than what is observed in parallel deployments of traditional PIT traps and that in an open ocean setting (Buesseler et al., this special volume). The combined SPLITT and NBST data are consistent with

frequent observations of under collection of the settling flux with upper ocean tethered sediment traps as assessed through  $^{234}\text{Th}$  *in situ* calibrations (e.g., Buesseler, 1991). Four such  $^{234}\text{Th}$  *in situ* calibrations of trapping efficiencies, spanning over at least a full year each, have now been published with two in open ocean regimes (Buesseler et al., 2000; Benitez-Nelson et al. 2001) and two in coastal/shelf regimes (Wei and Murray, 1992; Gustafsson et al., 2004). Assessed collectively, all four of these studies exhibit a general sediment trap under collection of about a factor of 2 (SCOR Working Group 116, ms submitted). The SPLITT technique may thus contribute to explain this pattern of persistent under collection in tethered upper ocean traps by confirming such previous suggestions of hydrodynamic bias against slowly settling particles (Gust et al., 1996; Gust and Kozerski, 2000; Gustafsson et al., 2004). Given improved mechanistic understanding of the previously suggested under trapping (e.g., Michaels et al. 1994; Buesseler et al., 2000; Gustafsson et al., 2004), a better closure of the empirical measures of the upper ocean carbon balance in both open ocean sites (e.g., BATS; Michaels et al., 1994) and continental shelf regimes (e.g., station BY-31 open Baltic Sea; e.g., Gustafsson et al., 2004) may be achieved.

Application of the SPLITT technique, which collects also these slow-settling particles as part of its sampling of the total settling spectrum, is likely to return increasingly new insights on the composition and characteristics of the upper ocean settling particle flux. Further studies are encouraged to confirm the evolving picture of a more slowly settling particle compartment, with an elevated  $\text{POC}/^{234}\text{Th}$  ratio, which is frequently under collected with traditional upper ocean sediment traps.

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### **Figure captions**

Fig. 1. Comparison of the composition of particles isolated with different techniques during the spring 2001 Gullmar fjord campaign: A. the  $\text{POC}/^{234}\text{Th}$  ratio of particles isolated with sediment traps (grey), SPLITT (dark), and filters (light); B. the  $\text{POC}/\text{Al}$  ratio of particles isolated with sediment traps (grey) and SPLITT (dark); and C. the ratio of transparent exopolymer particles (TEP) to POC in particles isolated with sediment traps (grey) and filters (light). The error bars represent the propagated analytical uncertainty (1 s.d.) of the entire methods.

Fig. 2. Comparison of the composition of particles isolated with different techniques during the August 2000 open Baltic Sea BY-31 time series expedition: A. the POC/<sup>234</sup>Th ratio of particles isolated with SPLITT operated with three different settling-velocity cut-offs, with sediment traps, and with filters (light); B. the POC/Al ratio of particles isolated with SPLITT operated with three different settling-velocity cut-offs and with sediment traps. The error bars represent the propagated analytical uncertainty (1 s.d.) of the entire methods.

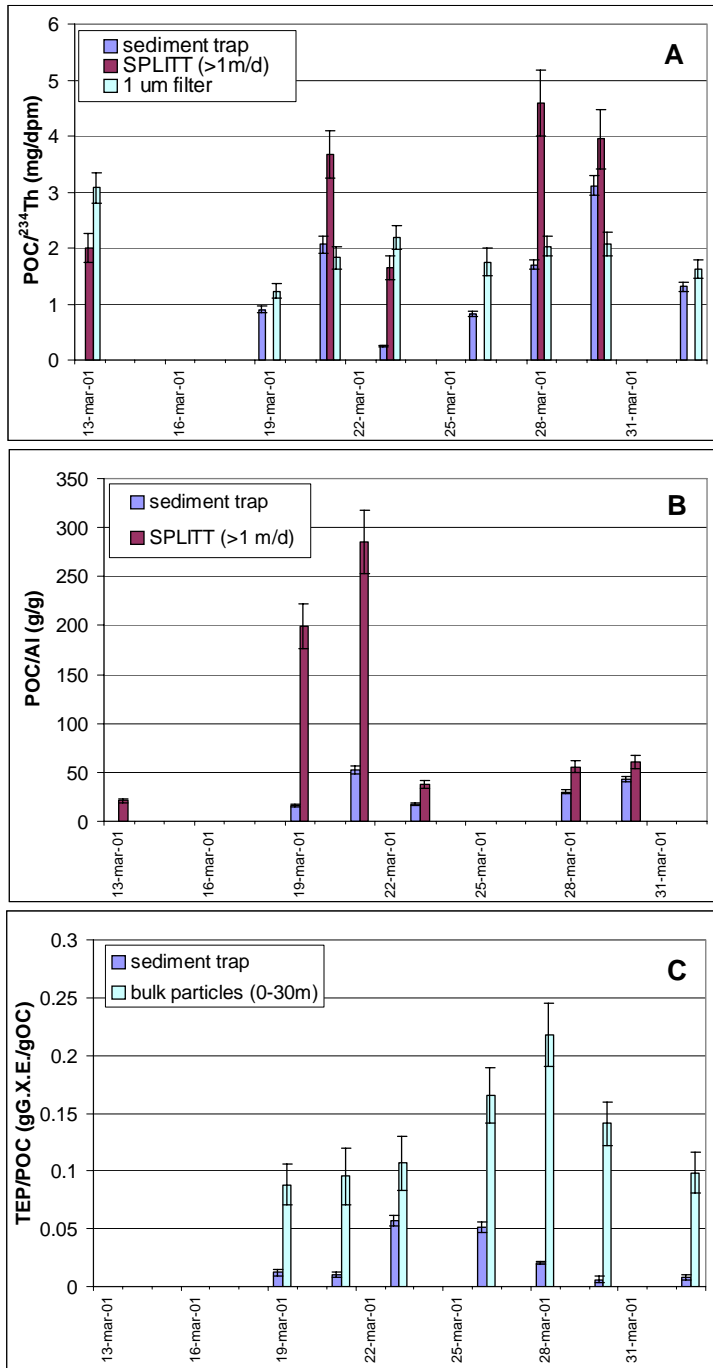


Fig. 1

Gustafsson et al.

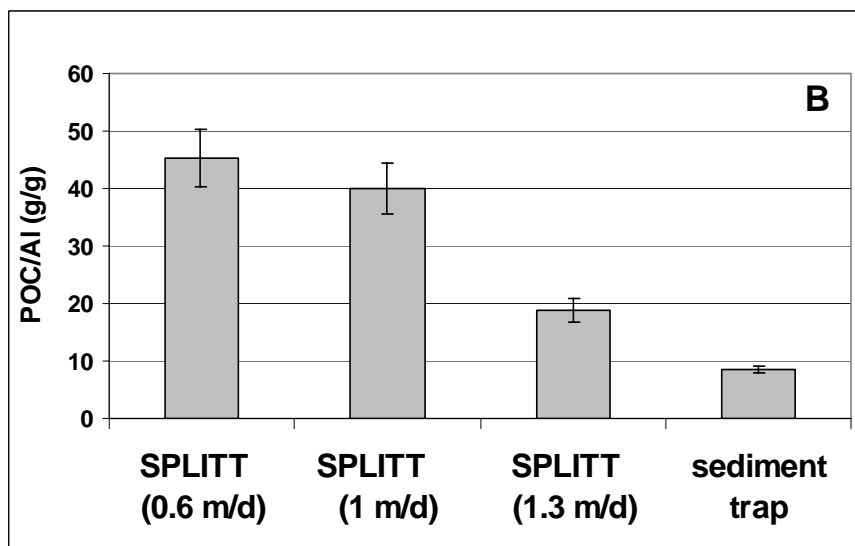
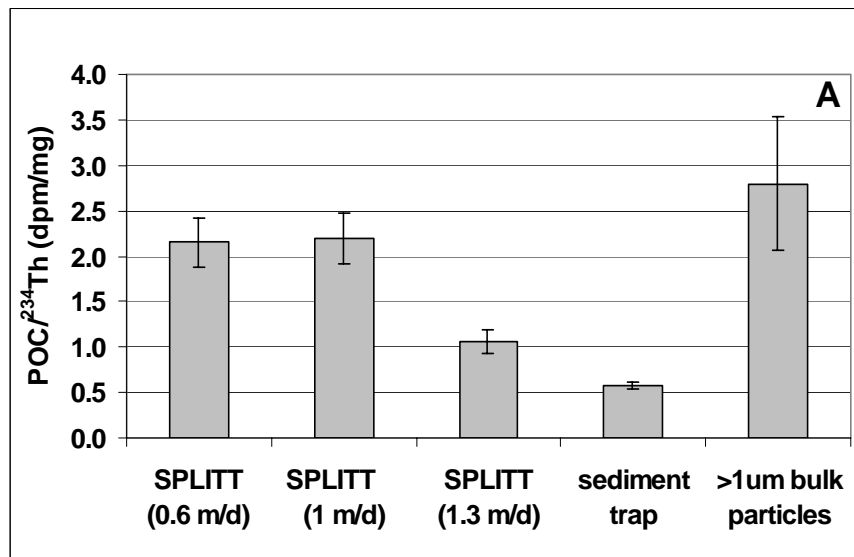


Fig. 2

Gustafsson et al