

**Interactive comment on “Insignificant enhancement of export flux in the highly productive Subtropical Front, east of New Zealand: a high resolution study of particle export fluxes based on  $^{234}\text{Th}$ : $^{238}\text{U}$  disequilibria” by K. Zhou et al.**

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Response to anonymous Referee #2

In this manuscript Zhou et al. present results on POC export based on  $^{234}\text{Th}$  measurements at high spatial resolution in the Subtropical Front area between New Zealand and the Chatham Rise during late-autumn early winter. Results show low to moderate export fluxes during this period over most of the study area, despite large variability in fluorescence and POC. The study presents several flaws (listed below) that should be addressed by the authors.

Response: We appreciate the constructive and critical comments from the reviewer, and have fully taken these comments into consideration during our revision of the manuscript.

1) The horizontal distribution of POC stocks and chlorophyll or fluorescence are not shown so it is difficult for the reader to see how they relate to the export estimates.

Response: In the original MS, we showed in Table 2 the POC stocks and chlorophyll data, with extensive discussion in the text. In the manuscript revision, as per the request from Reviewer #3, we have changed Figure 9 into histograms and grouped the stations into the three identified water types: low salinity ( $S < 34.5$ ), mid-salinity ( $34.5 < S < 34.8$ ) and high salinity waters ( $S > 34.8$ ). The histograms of POC stocks and chlorophyll are also included in the new Figure 9.

2) One that is typical for this kind of studies is that POC measurements in suspended matter and the resulting C/Th ratios are actually assumed to be representative for sinking matter. As a result, the variability in estimated POC export could as much reflect export as variability in POC concentrations in the samples. Further, as mentioned before, the horizontal distribution of POC stocks is not shown leaving the reader at odds to understand which of those two factors is actually determining.

Response: The reviewer raised an important issue regarding the C/Th ratio and its impact on estimates of POC flux. However, we disagree with the reviewer that the variability of our Th-derived POC flux should resemble that of POC concentrations. As mentioned in the text, POC flux was estimated empirically using the following equation:  $\text{POC flux} = \text{Th flux} \times (C/\text{Th})_{\text{sinking}}$ . The variability of POC fluxes is therefore a reflection of the variations in  $^{234}\text{Th}$  fluxes and C/Th ratios of sinking particles. Therefore, the variability in estimated POC export does not necessarily have to reflect that in POC concentrations, even though the bottle C/Th ratio was used in our study. This is clearly demonstrated by the data as presented. As listed in Table 2 and also shown in Figure 9a (see below), POC stocks were elevated in mid-salinity waters, compared to the low and high salinity waters. Conversely, POC export had a completely different distribution pattern that was similar between the three water types.

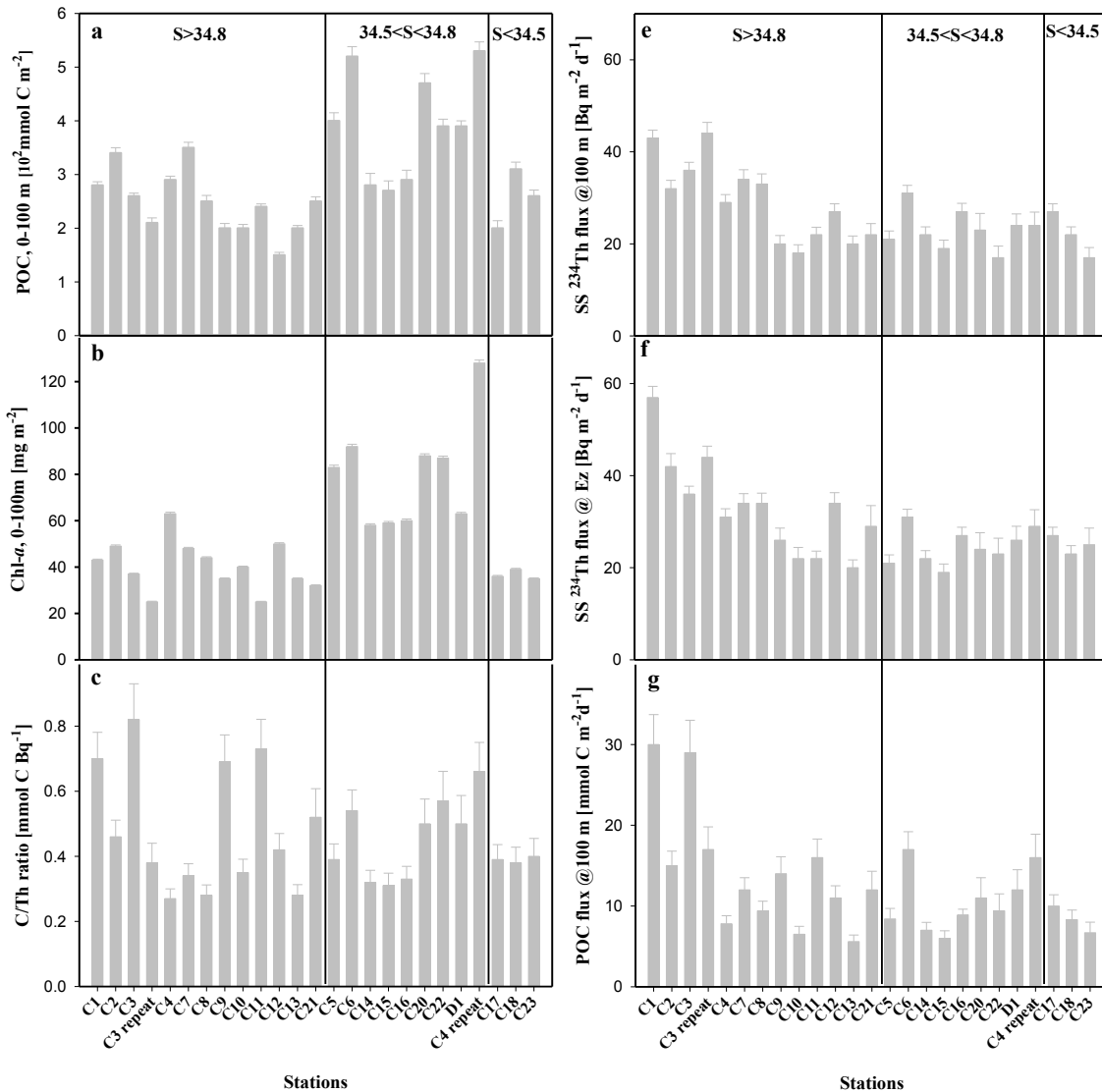


Fig. 1 Spatial distributions of: (a) POC inventory from 0-100 m, (b) Chl-*a* inventory from 0-100 m, (c) POC/Th ratio at 100 m, (d)  $^{234}\text{Th}$  fluxes at 100 m, (e)  $^{234}\text{Th}$  fluxes at the base of the Ez, and (f) POC fluxes at 100 m. All stations are separated into three water types: low salinity ( $S < 34.5$ ), mid-salinity ( $34.5 < S < 34.8$ ), and high salinity ( $S > 34.8$ ) waters.

3) The authors have studied the system presumably at the end of the growth season, possibly when silicic acid concentrations were low. No information about the latter is given in the manuscript, even though the authors mention the importance of community composition, in particular diatoms, in determining export. In addition, although phosphate concentrations are mentioned, they do not seem to refer to the study period. Could PP be low during this study because of limitation by macro-nutrients?

Response: As we have pointed out in the text, the average inventories of Chl-*a*, POC and particulate  $^{234}\text{Th}$  of  $80 \pm 0.30 \text{ mg m}^{-2}$ ,  $(3.9 \pm 0.056) \times 10^2 \text{ mmol C m}^{-2}$ , and  $(7.5 \pm 0.060) \times 10^2 \text{ Bq m}^{-2}$ , respectively, in the mid-salinity waters, were clearly higher, compared to  $40 \pm 0.30 \text{ mg m}^{-2}$ ,

$(2.5 \pm 0.022) \times 10^2$  mmol C m<sup>-2</sup>, and  $(3.4 \pm 0.030) \times 10^2$  Bq m<sup>-2</sup> in the high salinity waters and  $37 \pm 0.23$  mg m<sup>-2</sup>,  $(2.6 \pm 0.073) \times 10^2$  mmol C m<sup>-2</sup>, and  $(5.7 \pm 0.084) \times 10^2$  Bq m<sup>-2</sup> in the low salinity waters. All three parameters indicated that primary productivity (PP) was elevated in the mid-salinity waters.

Our dissolved inorganic nitrogen (DIN, nitrite plus nitrate) and PO<sub>4</sub> measurements covered all stations, and have now been included in the MS. In the mid-salinity waters, DIN concentrations ranged from 3.6 to 13.9 μmol l<sup>-1</sup>, compared with ranges of 1.1-12.3 in high salinity waters, and 7.8-14.9 μmol l<sup>-1</sup> in the low salinity waters. These values are greater than the half-saturation constant for nitrate uptake by diatoms of 0.1-3 μmol l<sup>-1</sup> (Eppley et al. 1969), which implies that the diatom growth was unlikely to be limited by nitrate concentration. The PO<sub>4</sub> concentrations during the cruise ranged from 0.42-1.23 μmol l<sup>-1</sup> for the mid-salinity waters, compared to 0.19-1.0 μmol l<sup>-1</sup> in high salinity and 0.68-1.03 μmol l<sup>-1</sup> in low salinity waters. Thus, there were no indications of P limitation.

Concentrations of Si(OH)<sub>4</sub> were only measured at Stations C1 through C7 during the cruise. Based on this limited Si(OH)<sub>4</sub> data set, at mid-salinity stations (C5 & C6), Si(OH)<sub>4</sub> concentrations in the upper 100 m ranged from 0.39 to 3.43 μmol l<sup>-1</sup>, which was comparable to the range in high salinity waters (C1, C2, C3, C4 & C7, 0.91-3.11 μmol l<sup>-1</sup>). Chang and Gall (1998) indicated that the half-saturation constant (K<sub>s</sub>) for Si(OH)<sub>4</sub> uptake by diatoms is 0.8-3.4 μmol l<sup>-1</sup>, so it does seem that at the time of sampling diatoms were likely to be under Si(OH)<sub>4</sub> stress. Nevertheless, we tended to believe that Si is not yet limiting the PP because PP was significantly high at mid-salinity as compared to high salinity water regime despite Si(OH)<sub>4</sub> were at a similar level at both sites. In this context and based on the prior researches in the region, we believed that the study area at mid-salinity and at the sampling season, iron was still the limiting factor and the enhanced PP was at least partially resulting from the natural iron fertilization. Having said so, we still cannot rule out the Si limitation in particular at the late stage of the growth season, a statement has been thus added in the revised MS.

4) In the same line as the previous comment and despite the authors' statement that this was not the case, based on visual inspection of salinity and temperature profiles, the mixed layers, during this study seemed quite variable but mostly quite deep. One might argue that under these circumstances, PP must again have been quite low and export proportionally high. In short, I am not sure that the results are discussed in the proper context.

Response: Again, as mentioned above, the PP level indicated by the inventories of Chl-*a*, POC and particulate <sup>234</sup>Th was higher in the mid-salinity waters, compared to low and high salinity waters. However, Th-derived POC flux in the upper 100 m was not higher in the mid-salinity waters, being  $11 \pm 0.45$  mmol C m<sup>-2</sup> d<sup>-1</sup>, compared to  $14 \pm 0.39$  mmol C m<sup>-2</sup> d<sup>-1</sup> in high salinity and  $8.5 \pm 0.66$  mmol C m<sup>-2</sup> d<sup>-1</sup> in low salinity waters. We agree that the depths of the mixed layer were variable (e.g. 54-178 m) and sometimes deeper than 100 m, but as shown in Figure 5a, the lowest activities of total <sup>234</sup>Th occurred in the upper 100 m, which implied that most of the export was from the upper 100 m. In the original MS, we also discussed POC export from the euphotic zone (Ez) where the Ez depth was greater than that of the mixed layer. In any case, POC export from mid-salinity waters was not enhanced, compared to low and high salinity waters. Therefore, the effect of a variable and deeply mixed surface layer would not change our observation of high PP, but moderate POC export from mid-salinity waters within the Subtropical Front at the time of sampling.

Additional comments:

p. 9538, line 5: "free floating cylindrical moorings". Are the traps moored or free floating?

Response: Changed text to “free-floating cylindrical sediment traps”.

p. 9538, lines 22-27: It is not clear what the purpose of the description of fluxes in other areas (South China Sea, ALOHA etc ...) is. Can the authors be more specific what is particular to these areas that also applies to the region where this study was carried out? Otherwise this part of the text could be removed.

Response: The purpose of the description was to emphasize that Th has substantial spatial variations in marginal sea settings, such as the South China Sea, as well as the open ocean at Station ALOHA in the North Pacific Subtropical Gyre. Based on these previous studies, it was obvious that for the present study there was a need to sample  $^{234}\text{Th}$  at the highest possible spatial resolution. Furthermore, the use of the small volume Th technique in our study has significant advantages in the measurement of particle export within such dynamic regions as the Subtropical Front.

Section 2.3: For the sake of consistency why not use PON instead of PN?

Response: PN is more scientifically rigorous than PON due to the method used for determining this variable, i.e., via combustion in a CHN analyzer, which does not distinguish the organic N fraction.

p. 9542, lines 2-3: from visual inspection of salinity and temperature in Fig. 4, I do not understand how the authors can claim that the upper water column was well stratified. On the contrary, I see quite deep mixed layer at station C17 (~ 70 m) and C11 (~ 130 m). This is also reflected in the fluorescence, although this parameter is more "noisy" (also not surprising).

Response: In most instances, the term “stratification” generally refers to a warming or freshening of the near-surface layers, leading to a distinct density surface that limits isopycnal and diapycnal mixing. In our case, we should have been more specific about the depth of the essentially isothermal part of the upper water column, which may be as much as 150 m. We have modified the text to reflect this.

p. 9543, lines 14-16: I am not a specialist in the use of  $^{234}\text{Th}$  to estimate export and am quite surprised that only 10% of  $^{234}\text{Th}$  activity is found associated to particles. How can  $^{234}\text{Th}$  be a proxy for particle export when such a small fraction actually adheres to particles?

Response: The principal of  $^{234}\text{Th}$  method is related to the disequilibrium between total  $^{234}\text{Th}$  and its progenitor  $^{238}\text{U}$ . Since the half life of  $^{234}\text{Th}$  (24.1d) is much shorter than  $^{238}\text{U}$  ( $4.47 \times 10^9$  y),  $^{234}\text{Th}$  should be in secular equilibrium with  $^{238}\text{U}$  if there was no downward particle export. Therefore, the extent of the disequilibrium between total  $^{234}\text{Th}$  and  $^{238}\text{U}$  reflects the magnitude of particle export in the upper ocean (Buesseler et al., 1992; Waple et al., 2006; Cai et al., 2008). As such, one can conclude that it is the deficit between  $^{234}\text{Th}$  and  $^{238}\text{U}$  that actually determines the particle export rather than particulate  $^{234}\text{Th}$ . However, we agree that particulate  $^{234}\text{Th}$  is related to particle export. According to the two box model as shown below (Coale and Bruland, 1985), the mass balance equation for particulate  $^{234}\text{Th}$  can be shown:

$$\frac{\delta A_{\text{Th}_p}}{\delta t} = K_d A_{\text{Th}_d} - \lambda A_{\text{Th}_p} - P_{\text{Th}}$$

where  $\frac{\delta A_{Th_p}}{\delta t}$  is the temporal change of particulate  $^{234}\text{Th}$  activity,  $K_d$  is the scavenging rate of the dissolved  $^{234}\text{Th}$ ,  $\lambda$  is the decay constant of  $^{234}\text{Th}$  ( $0.02876 \text{ d}^{-1}$ ),  $A_{Th_d}$  and  $A_{Th_p}$  are the activities of dissolved and particulate  $^{234}\text{Th}$ , and  $P_{Th}$  is the downward  $^{234}\text{Th}$  export. Under steady state conditions, the above equation can be transformed into:  $P_{Th} = K_d A_{Th_d} - \lambda A_{Th_p}$ . Clearly,  $^{234}\text{Th}$  export is not only related to particulate  $^{234}\text{Th}$ , but also with the scavenging rate from dissolved  $^{234}\text{Th}$ .

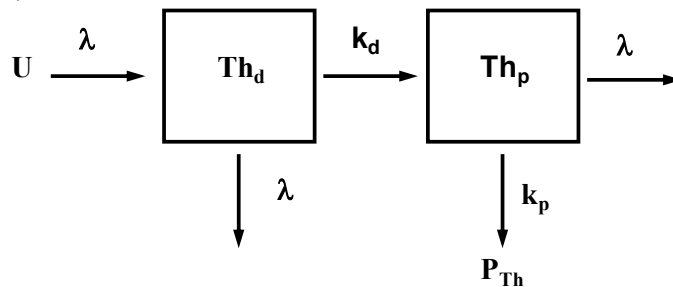


Fig. 2 A two box irreversible Th scavenging model (from Coale and Bruland, 1985)

p. 9546, lines 4-5: Even though temperature and salinity differences at the C3 site are not as large as for the C4 site, the differences still indicate that also at C3 a shift in water mass occurred. Unless the authors present evidence that this is not the case, their assumption and the use of a NSS model is not valid, even though the NSS and SS models give similar results.

Response: We fully agree that there was a slight shift in temperature and salinity between the two visits to Station C3. We have made a statement that the SS model needs to be tested in such dynamic regions like Subtropical Front. As pointed out by the reviewer, the difference between the two visits at the C3 site was much smaller than for the C4 site (i.e., only  $0.5^\circ\text{C}$  and  $0.02$  differences for temperature and salinity, respectively), which allowed us to undertake a first-order estimation of temporal variation on  $^{234}\text{Th}$  flux. NSS  $^{234}\text{Th}$  flux from the upper 10 m was calculated as  $4.1 \text{ Bq m}^{-2} \text{ d}^{-1}$ , compared to SS  $^{234}\text{Th}$  flux of  $4.0$  and  $4.1 \text{ Bq m}^{-2} \text{ d}^{-1}$  calculated between the two visits at C3. It is thus justified to suggest that our SS model was reasonably in order in our study region at the time of sampling.

p. 9551, lines 4-5: The probabilities indicated in the text for fluorescence do not correspond to values in Table 3.

Response: Revised.

Fig. 1: the numbers on the color scale are too small to be read. The same applies to the station numbers and the transect line is difficult to see.

Response: We have improved Figure 1 as requested by the reviewer.

Fig. 2: It would help the reader to understand processes such as mixing if the authors put the acronym of the different water masses (both surface and deep) in the figure.

Response: We have added labels of STW (Subtropical water) and SAW (Subantarctic water) onto the figure. Note that due to the location of the sampling stations in the Subtropical Front and the relatively shallow sampling depths effectively on the crest of the Chatham Rise, all of the samples

can be regarded as in the mixing zone between these two water masses, with no distinction of deeper underlying water masses, such as Antarctic Intermediate Water.

Fig. 5 & 6: As in Fig. 1, the numbers on the color scale and in the plots are much too small to be read.

Response: The numbers on the color scale of both Figure 5 and 6 has been enlarged.

Fig.9: It would be helpful if lines showing the limits for the different areas considered (low, mid and high salinity water) were reported in the figure.

Response: As requested by reviewer #3, we have changed Figure 9 into histograms, and divided all stations into three groups according to salinity (low, mid and high salinity water).

#### References

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