



Article (refereed) – Published version

Le Moigne, Frederic A.C.; Pabortsava, Katsiaryna; Marcinko, Charlotte L.J.; Martin, Patrick; Sanders, Richard J.. 2014 Where is mineral ballast important for surface export of particulate organic carbon in the ocean? *Geophysical Research Letters*, 41 (23). 8460-8468. [10.1002/2014GL061678](https://doi.org/10.1002/2014GL061678)

This version available at <http://nora.nerc.ac.uk/508683/>

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at <http://nora.nerc.ac.uk/policies.html#access>

AGU Publisher statement: An edited version of this paper was published by AGU. Copyright (2014) American Geophysical Union. Further reproduction or electronic distribution is not permitted.

Le Moigne, Frederic A.C.; Pabortsava, Katsiaryna; Marcinko, Charlotte L.J.; Martin, Patrick; Sanders, Richard J.. 2014 Where is mineral ballast important for surface export of particulate organic carbon in the ocean? *Geophysical Research Letters*, 41 (23). 8460-8468. [10.1002/2014GL061678](https://doi.org/10.1002/2014GL061678)

To view the published open abstract, go to <http://dx.doi.org/10.1002/2014GL061678>

Contact NOC NORA team at
publications@noc.soton.ac.uk

RESEARCH LETTER

10.1002/2014GL061678

Key Points:

- Nonballast-associated POC often dominates the POC flux in the surface ocean
- Highest fraction of mineral-associated POC export in the North Atlantic
- High-latitude areas will not respond equally to changes in ballast availability

Supporting Information:

- Readme
- Figures S1 and S2 and Table S1

Correspondence to:

F. A. C. Le Moigne,
f.lemoine@noc.ac.uk

Citation:

Le Moigne, F. A. C., K. Pabortsava, C. L. J. Marcinko, P. Martin, and R. J. Sanders (2014), Where is mineral ballast important for surface export of particulate organic carbon in the ocean?, *Geophys. Res. Lett.*, *41*, 8460–8468, doi:10.1002/2014GL061678.

Received 26 AUG 2014

Accepted 22 OCT 2014

Accepted article online 25 OCT 2014

Published online 3 DEC 2014

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Where is mineral ballast important for surface export of particulate organic carbon in the ocean?

Frédéric A. C. Le Moigne¹, Katsiaryna Pabortsava², Charlotte L. J. Marcinko¹, Patrick Martin^{2,3}, and Richard J. Sanders¹

¹Ocean Biogeochemistry and Ecosystems, National Oceanography Centre, Southampton, UK, ²School of Ocean and Earth Science, University of Southampton, Southampton, UK, ³Earth Observatory of Singapore, Nanyang Technological University, Singapore

Abstract Correlations between particulate organic carbon (POC) and mineral fluxes in the deep ocean have inspired the inclusion of “ballast effect” parameterizations in carbon cycle models. A recent study demonstrated regional variability in the effect of ballast minerals on the flux of POC in the deep ocean. We have undertaken a similar analysis of shallow export data from the Arctic, Atlantic, and Southern Oceans. Mineral ballasting is of greatest importance in the high-latitude North Atlantic, where 60% of the POC flux is associated with ballast minerals. This fraction drops to around 40% in the Southern Ocean. The remainder of the export flux is not associated with minerals, and this unballasted fraction thus often dominates the export flux. The proportion of mineral-associated POC flux often scales with regional variation in export efficiency (the proportion of primary production that is exported). However, local discrepancies suggest that regional differences in ecology also impact the magnitude of surface export. We propose that POC export will not respond equally across all high-latitude regions to possible future changes in ballast availability.

1. Introduction

The biological carbon pump (BCP) is an important component of the global carbon cycle, exporting 5 to 10 Gt C yr⁻¹ from the surface ocean to the ocean's interior [Henson *et al.*, 2011]. In the deep ocean, strong correlations are observed between fluxes of particulate organic carbon and minerals [Klaas and Archer, 2002]. Therefore, it has been suggested that fluxes of minerals drive organic carbon flux, either by increasing particle density and thus sinking speed or possibly by physically protecting a proportion of the particulate organic carbon (POC) flux that leaves the surface from degradation [Armstrong *et al.*, 2002; François *et al.*, 2002; Klaas and Archer, 2002]. Several ocean models now use a mineral protection model to describe the flux of material to depth [Gehlen *et al.*, 2006; Yool *et al.*, 2013].

An obvious question to ask is whether similar patterns are seen in the surface ocean. Our previous analysis, based on limited data sets derived from ²³⁴Th disequilibria, revealed linear relationships between shallow export of organic carbon and biominerals and further showed that exported material appeared to be biomineral-rich relative to the average composition of surface particulate matter [Sanders *et al.*, 2010]. This suggests that a ballast effect is probably important in the surface export of POC. A much larger data set subsequently revealed considerable scatter in the relationship between mineral and POC export, suggesting that regional differences in ecology strongly impact particle flux [Le Moigne *et al.*, 2012]. In particular, we suggested that the unballasted pool can be large in diatom-dominated regions like the Southern Ocean (SO), which might explain the low transfer efficiencies (ratio of deep export over surface export, T_{eff}) reported by some studies in such regions [Le Moigne *et al.*, 2012].

Further analysis of the global data set of deep particle flux by Wilson *et al.* [2012] has shown that the use of geographically weighted regression analysis (GWR), which allows model parameters to vary spatially, is more appropriate than the single multiple linear regression used by Klaas and Archer [2002] and Le Moigne *et al.* [2012] and others. GWR reveals spatial patterns in mineral carrying coefficients (Ccs, the statistical coefficients of a multiple regression model of POC flux versus biomineral flux; see section 2), which are likely driven by spatial variability in pelagic ecology [Wilson *et al.*, 2012]. Wilson *et al.* [2012] hypothesized that the variations observed in deep Ccs match the global pattern in T_{eff} ; namely, that T_{eff} is high in calcite-dominated regions and

low in opal-dominated regions. While this is the global T_{eff} pattern reported by some studies [François *et al.*, 2002; Henson *et al.*, 2012; Lam *et al.*, 2011], shipboard process studies have revealed that diatom blooms can lead to large export events characterized by high T_{eff} [Buesseler and Boyd, 2009; Martin *et al.*, 2011; Rynearson *et al.*, 2013; Smetacek *et al.*, 2012]. This basic disagreement about the effect of opal ballast underscores how limited our understanding of mineral ballast in the oceans is.

However, it is still unclear how the impact of ballasting on shallow POC export varies regionally and how it is linked to export efficiency (defined as shallow export over primary productivity, PE_{eff}). Here we examine the variability in surface mineral ballast Ccs using ^{234}Th -derived estimates of POC and mineral flux in the Arctic, Atlantic, and Southern Oceans (95 data points). We discuss the implications of our results for the role of minerals in the export of POC from the surface ocean.

2. Material and Methods

2.1. Flux Data

We updated our POC and mineral export database derived from ^{234}Th measurements published in Le Moigne *et al.* [2012] with data from six additional cruises (JC068, D357, D361, D369, JR271, and JR274). This extended data set includes observations from the Arctic ocean, the high-latitude North Atlantic (HLNA), the equatorial Atlantic, and the SO (Figure S1 in the supporting information). Locations, sampling dates, and references are given in Table S1 (supporting information). We used the ^{234}Th “small-volume” technique with inductively coupled plasma–mass spectrometry measurement of ^{234}Th extraction efficiency [Pike *et al.*, 2005]. Vertical profiles of ^{234}Th activity were integrated to 100 m and converted to estimates of downward ^{234}Th flux using a one-dimensional steady state model [Buesseler *et al.*, 1992].

These fluxes were then converted to estimates of downward particle flux using the POC: ^{234}Th or mineral: ^{234}Th ratio of large ($>53\ \mu\text{m}$) particles collected on Nitex screen using an in situ stand-alone pumping system deployed at a single depth beneath the mixed layer (from 20 to 70 m). Particles were then rinsed off the screen using thorium-free seawater, and the particle suspension split into equal subsamples. Each split was then analyzed for one of the following: ^{234}Th , POC, BSi, and particulate inorganic carbon (PIC) as in Le Moigne *et al.* [2013b].

Using the ^{234}Th approach has the great advantage of providing a large data set of surface export fluxes, albeit with the caveat that some of the seasonal variability of export flux may be missed. While this is unlikely to be a major issue in low-latitude areas where the seasonal cycle in export is weak [Waniek *et al.*, 2005], at high latitudes, where seasonal variability is stronger, our Th-derived export fluxes may have missed the episodes of large export often observed in such environments [Waniek *et al.*, 2005].

The aluminum concentration in large particles (PAI) was not measured; therefore, literature values were taken from Lambert *et al.* [1984] and Kuss and Kremling [1999] to estimate downward fluxes of Al following Le Moigne *et al.* [2012] and Honda and Watanabe [2010]. For the JR274 cruise in the Scotia Sea, we used the average PAI ($>53\ \mu\text{m}$) found in the plume of the Crozet Islands [Planquette *et al.*, 2009] ($\text{PAI} = 1.27\ \text{nmol l}^{-1}$) for stations in the plumes of chlorophyll *a* associated with South Georgia and the South Sandwich Islands and the average value from nonplume stations around Crozet [Planquette *et al.*, 2009] ($\text{PAI} = 0.23\ \text{nmol l}^{-1}$) for our nonplume stations. Table S1 summarizes the values of PAI used for each station. Lithogenic fluxes were estimated as $(100/8 \cdot \text{Al})$ [Honda and Watanabe, 2010] assuming that most PAI is of lithogenic origin, although it can be present in diatom frustules [Gehlen *et al.*, 2002]. All the flux data are listed in Table S1. Using literature values for PAI concentration to estimate the flux of lithogenics may introduce inaccuracies and represents a limitation of our method. However, lithogenic flux is a minor component of the flux and is generally much lower than the biomineral fluxes [Salter *et al.*, 2010]. The errors associated with our estimates of lithogenic flux therefore have only a limited impact on our conclusions.

2.2. Regression Model and Geographically Weighted Regression

We examined the relationship between mineral and POC fluxes using two different techniques. Initially, we used multiple linear regression analysis (MLRA) as in Honda and Watanabe [2010] and Le Moigne *et al.* [2012]. MLRA divides total POC flux ($\text{POC}_{\text{total}}$ flux) into four portions, three of which are considered to be associated

with the mineral phases BSi (POC_{BSi}), calcite (POC_{pic}), and lithogenic material (POC_{lith}). The fourth portion is the residual POC flux, which is considered the non-associated fraction (POC_{res}). MLRA takes the following form:

$$\text{POC}_{\text{total}} = \text{POC}_{\text{PIC}} + \text{POC}_{\text{BSi}} + \text{POC}_{\text{lith}} + \text{POC}_{\text{residual}} = a \cdot \text{PIC}_{\text{flux}} + b \cdot \text{BSi}_{\text{flux}} + c \cdot \text{Lith}_{\text{flux}} + d$$

where a , b , and c are defined as Ccs [Klaas and Archer, 2002], while d is the nonassociated portion of POC [Armstrong et al., 2002; Honda and Watanabe, 2010; Le Moigne et al., 2012].

We then used the geographically weighted regression (GWR) technique. The application of GWR to ocean particle flux data was carefully described and tested by Wilson et al. [2012]. We followed a similar approach to estimate geographically weighted carrying coefficients for each of the ballast components and the fraction of POC not associated with any mineral. In essence, the GWR analysis calculates “local carrying coefficients” at each sampling location for the ballast minerals and the residual, nonassociated POC [Wilson et al., 2012].

We used the GWR 4.0 software [Nakaya et al., 2009] (freely available at <http://www.st-andrews.ac.uk/geoinformatics/gwr/gwr-software/>). We used an adaptive Gaussian Kernel, which groups the data by the nearest neighbor approach. The Akaike Information Criterion, corrected for small sample bias (AICc) [Akaike, 1974], was used to define the optimal bandwidth following Wilson et al. [2012]. We also carried out a test of geographical variability (TGV) to test the spatial variability of the local Ccs provided by the GWR.

3. Results and Discussion

3.1. POC and Mineral Export Fluxes

In the following section, we briefly describe the magnitude of surface POC and mineral export fluxes (Figure 1). The highest levels of POC export are found in subpolar regions, with values in the Arctic being lower (Figure 1a). Rates of POC export are higher in the North Atlantic oligotrophic gyre (between 25°N and 0°N) than in the South Atlantic oligotrophic gyre (between 25°S and 0°S) (Figure 1a).

PIC export (Figure 1b) shows similar trends, with the Southern Hemisphere subpolar fluxes being lower than the Northern Hemisphere ones. The large PIC export fluxes in the SO are all located around the Crozet islands. The export of BSi (Figure 1c) shows similar patterns with subpolar fluxes in the Northern Hemisphere being larger than those in the Southern Hemisphere. The export flux of BSi in the Atlantic is mostly restricted to subpolar latitudes, as our data set does not include any diatom-dominated upwelling environments. Lithogenic export fluxes (Figure 1d) are very high at some of the northern subtropical gyre stations, moderate in parts of the subpolar North Atlantic, and low elsewhere. At midlatitudes, POC export still occurs while biomineral export is low. Mineral and organic carbon export fluxes are relatively low in the Arctic Ocean, reflecting the oligotrophic to mesotrophic character of the cold northern seas.

3.2. Results From MLRA and GWR

The MLRA yielded an R^2 of 0.22 and an AICc of 1139 (Table 1). The GWR increased the R^2 to 0.52 and reduced the AICc to 1098 (Table 1), indicating that the GWR described significantly more variability than the MLRA. Moreover, a comparison of correlograms (used to indicate the presence of autocorrelation at different spatial extents) for the MLRA and GWR model residuals indicated that the GWR model removed all significant spatial autocorrelation. The GWR model therefore provides a more unbiased estimate of the error associated with the Ccs when compared to the MLRA model estimates, which are significantly affected by spatial autocorrelation at multiple spatial scales (see Figure S2 in the supporting information). An analysis of variance analysis showed that the GWR model is a significant improvement on the global MLRA ($F(91,84) = 9.4$, $p < 0.001$). Formally, we reject the null hypothesis that there is no difference between the GWR and MLRA models. Finally, the test of geographical variability (TGV, Table 1) revealed significant spatial variation in the local Ccs for PIC and BSi (Diff of Criterion < -2 , indicating that variation in Ccs was significant), while there was only weak evidence of spatial variation in the Cc for lithogenic material. The GWR analysis yielded an optimal bandwidth [Nakaya et al., 2009] equal to 30 (this number indicates the sample size over which the GWR fits the regression locally) and thus includes interbasin influences [Wilson et al., 2012]. This effect was limited, however, as most of our data are concentrated in the Atlantic (Figure S1). We note that some calculated Ccs include the influence of data from quite distant locations. This is particularly true for Ccs obtained in the eastern equatorial south Atlantic, which were influenced by export fluxes measured in the Southern Ocean. This highlights the need for more export measurements from this specific area (Figure 1).

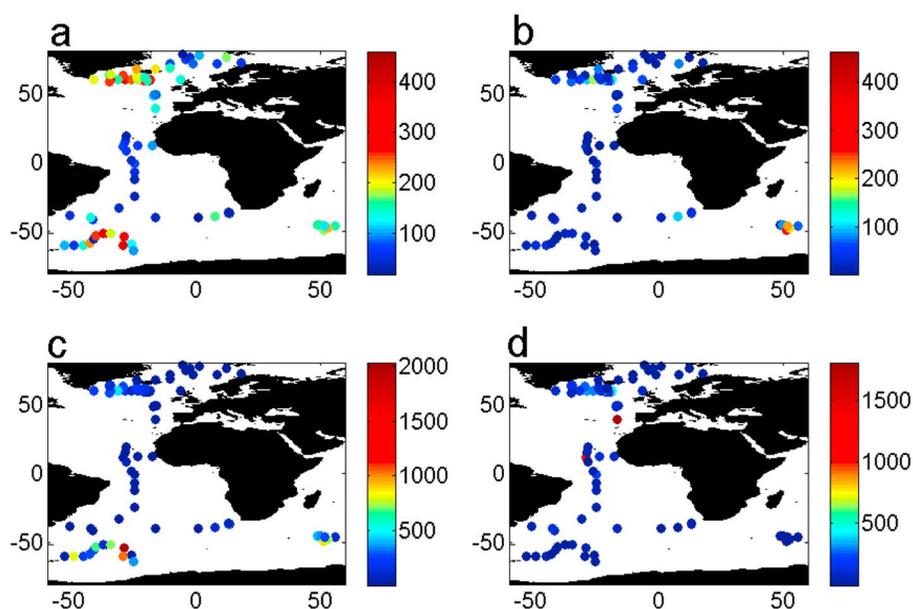


Figure 1. (a) POC, (b) PIC, (c) BSi, and (d) lithogenic material export (in $\text{mg m}^{-2} \text{d}^{-1}$) as a function of latitude and longitude ($^{\circ}$).

Henceforth, we discuss only the results of the GWR analysis. These results significantly increase the spatial coverage of our previous work [Le Moigne *et al.*, 2012] and demonstrate that GWR is an appropriate tool to analyze surface flux data.

The GWR-derived PIC and BSi Ccs display some clear spatial trends, while lithogenic Ccs were less variable (Figure 2), as also indicated by the TGV (Table 1). However, all the Ccs differ substantially from the mean global values (Table 1), showing that a single global parameterization of a ballast mineral model is not an accurate description of shallow POC export.

GWR Ccs for PIC are high in the North Atlantic subtropical gyre, the HLNA, and the Nordic Seas (Figure 2a), with lower values seen in the South Atlantic subtropical gyre and the SO. The largest variability in Ccs is observed near the equator (Figure 2a). Ccs for BSi follow a similar latitudinal pattern to those for PIC but are less variable (Figure 2b). Finally, Ccs for lithogenic material vary very little (Figure 2c) but also tend to increase northward. The intercept (*d*) is high in the SO as previously observed [Le Moigne *et al.*, 2012] but is otherwise relatively constant across the data set, between 80 and 90 $\text{mg m}^{-2} \text{d}^{-1}$, with the lowest values seen in the Arctic and the North Atlantic subtropical gyre (Figure 2d and Table 1).

Table 1. Carrying Coefficients and Statistical Significance

	Carrying Coefficients ^a				Statistical Significance			
	PIC <i>a</i>	Bsi <i>b</i>	Lithogenic <i>c</i>	Intercept ^b <i>d</i>	AICc ^c	R^2	<i>n</i>	<i>p</i> Value
MLRA	0.25	0.15	0.08	105.33	1139	0.224	95	<0.001
GWR ^{d,e}	0.57 (−6.3)	0.26 (−2.2)	0.10 (−0.6)	89.00 (3.6)	1098	0.52	95	<0.001
Associated range for local Ccs ^f	1.22	0.27	0.27	14.17	-	-	-	-

^aAs described in section 2.

^bIn $\text{mg m}^{-2} \text{d}^{-1}$.

^cFollowing Akaike [1974].

^dCalculated using the “optimal bandwidth” [Nakaya *et al.*, 2009].

^eValues in brackets are the “Diff of Criterion” resulting from the test of geographical variability (TGV; see section 2). This allows an assessment of whether each regression coefficient is varying over space. If the Diff of Criterion is a positive value, this suggests no spatial variability in the local term. If the difference of AICc is less than two, there is no essential difference. If the Diff of Criterion is between −2 and +2, this suggests only “weak support” of the model comparison.

^fRange between the highest and lowest values observed from the local Ccs.

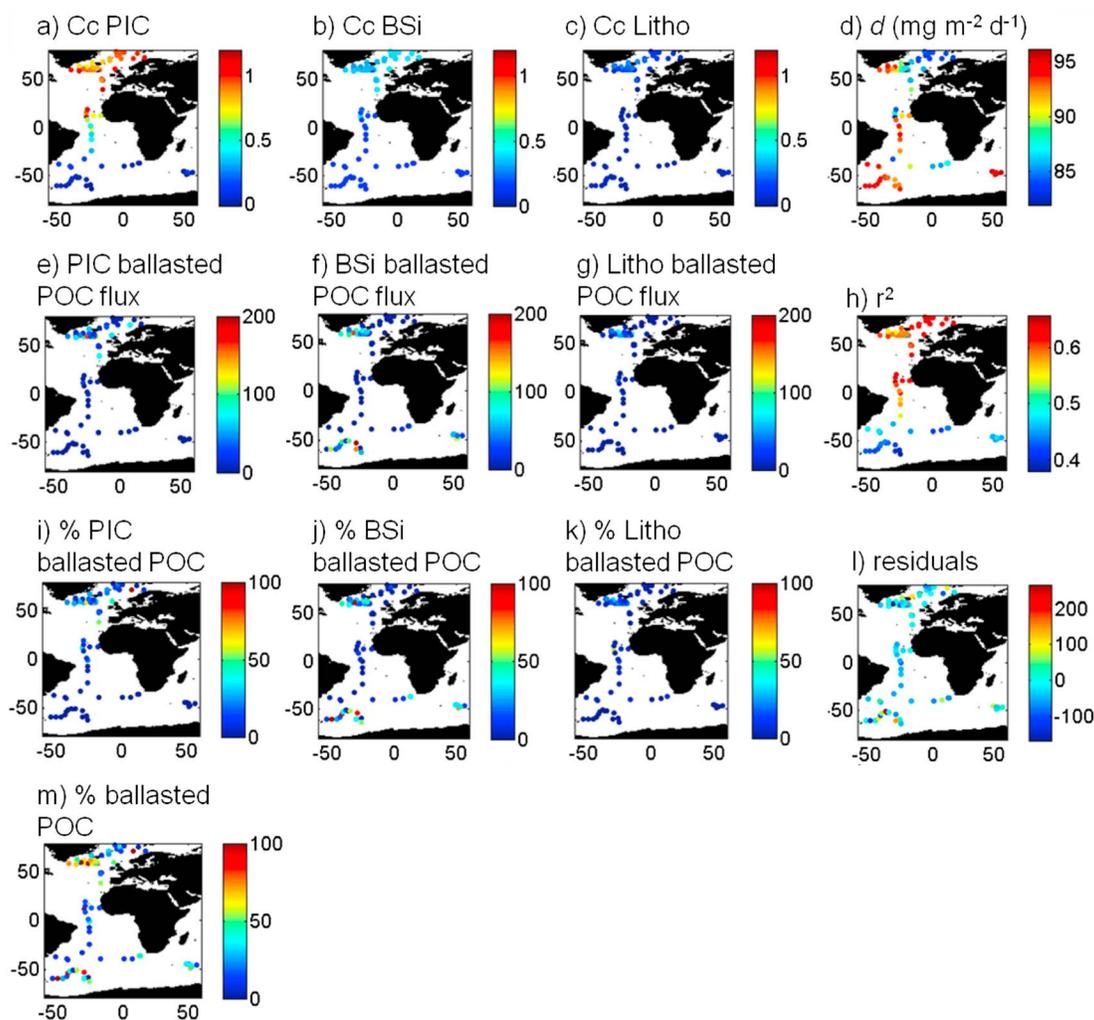


Figure 2. Geographically weighted carrying coefficients for (a) PIC, (b) BSi, and (c) lithogenic material. (d) Intercept (d or nonmineral-associated fraction; see section 2), (e) PIC-associated POC export ($\text{mg m}^{-2} \text{d}^{-1}$), (f) BSi-associated POC export ($\text{mg m}^{-2} \text{d}^{-1}$), (g) lithogenic-associated POC export ($\text{mg m}^{-2} \text{d}^{-1}$), (h) R^2 , (i), percentage of POC export ballasted by PIC, (j) percentage of POC export ballasted by BSi, (k) percentage of POC export ballasted by lithogenic material, (l) model residuals, and (m) percentage of ballasted POC export.

The GWR model fit the data better in the HLNA than in the SO and the Southern Atlantic (Figure 2h). This could be an artefact of having more data in the HLNA and Arctic than in the SO and Southern Atlantic (24 data points south of 45°S and 49 data points north of 45°N), as a higher density of data allows for a better model fit [Nakaya *et al.*, 2009]. Wilson *et al.* [2012, Figure 6] also observed a high correlation coefficient in regions with high sample density, such as the Arabian Sea, equatorial Pacific, and the sub-Arctic Pacific.

To ease the interpretation of the different ballast Ccs we obtained (Figures 2a–2d), we calculated the flux of POC associated with each mineral and the proportion of total POC flux associated with each mineral. The PIC-associated POC flux and the proportion of total POC flux associated with PIC are both highest in the HLNA (Figures 2e and 2i). The POC flux associated with BSi is the largest in the SO, although stations in the HLNA also have elevated BSi-associated POC fluxes (Figure 2f). The lithogenic-associated POC flux is low relative to the flux associated with the biominerals (Figure 2g). On average and globally, the proportions of total POC flux associated with PIC and lithogenics (14 and 6%, respectively) are smaller than the proportion of total POC flux associated with BSi (21%).

The proportion of POC flux associated with mineral ballast is highest in the HLNA and the SO (Figure 2m). With the exception of one station in the Barents Sea, the proportion of POC flux carried by biominerals is generally low in the Arctic Ocean. The high fraction of mineral-associated POC export at the Barents Sea station is likely due

to a coccolithophore bloom often observed in this region [Smyth *et al.*, 2004]. The proportion of total POC flux carried by each mineral (Figures 2i–2k) shows similar trend as described above. The fraction of export not associated with biominerals shows a wide range, often comprising the majority total POC export (62% on average), for example, in the transition regions between subpolar and subtropical environments (Figure 2m).

Overall, our analysis suggests that the ballasted fraction varies spatially and is highest in the HLNA (60% on average, mostly PIC and BSi) and SO (38% on average, mostly BSi) (Figures 2i, 2j, and 2m). Most of the export at low latitudes and in the Arctic is not associated with minerals.

3.3. Does Mineral Ballasting Help to Explain Global Patterns in POC Export Efficiency?

To fully understand the interaction between mineral and POC fluxes, one needs to assess the variation of mineral-associated POC fluxes not only at depth [Wilson *et al.*, 2012] but also in surface waters. This is because (1) the mineral content of particles exported from the surface does not necessarily reflect the average mineral content of suspended particles in surface waters [Le Moigne *et al.*, 2012] and (2) the dissolution/remineralization rates of the various POC and mineral phases do not necessarily covary in the water column [Milliman *et al.*, 1999; Ragueneau *et al.*, 2006], implying that the mineral Ccs in the surface ocean may differ from those in the deep ocean [Wilson *et al.*, 2012].

It has been suggested that minerals influence the transfer efficiency, T_{eff} , of flux through the mesopelagic [François *et al.*, 2002]. To investigate whether there might also be an association between the proportion of POC export that is mineral-associated and the export efficiency, PE_{eff} , we now compare our mineral-associated POC export data to the global pattern of PE_{eff} reported by Siegel *et al.* [2014].

Siegel *et al.* [2014] report the highest PE_{eff} in their data set from the HLNA (0.1–0.25), where our analysis shows the highest proportion PIC- and BSi-associated POC export (Figures 2i–2k). This suggests that in the HLNA, BSi and PIC do play a role in promoting POC export, as previously suggested by Sanders *et al.* [2010] and Buesseler and Boyd [2009].

Conversely, PE_{eff} is generally lower in the SO (0.01–0.15), where a lower proportion of the total POC export is mineral associated than in the HLNA (Figure 2m). Hotspots of high PE_{eff} in the SO occur mainly in the intense blooms stimulated by iron release from islands such as Kerguelen, Crozet, and South Georgia [Siegel *et al.*, 2014]. Export rates in these regions are enhanced relative to iron-limited areas of the SO (Figure 1a); however, the proportion of ballast-associated POC (mainly BSi-associated) does not vary significantly between the fertilized and the iron-limited regions (39 and 42%, respectively, Figure 2m).

In the subtropical gyres, where the spatial variability of mineral-associated POC export is reduced and the proportion of the POC flux associated with minerals is low (Figures 2e–2g and 2m), PE_{eff} is moderate (0.05–0.15) [Siegel *et al.*, 2014].

The proportion of POC flux carried by mineral does not so clearly correlate with the PE_{eff} . While we can only compare our export data to the climatology of PE_{eff} reported by Siegel *et al.* [2014] (and not directly with PE_{eff} at the time of sampling), the comparison suggests the following:

1. There are fundamental differences in the ways minerals promote POC export in different oceanic provinces. We know that mineral ballast can have different ballasting properties (particle nucleation and/or added density) depending on mineral type. For example, calcite-ballasted particles generally sink faster than opal-ballasted ones [Iversen and Ploug, 2010]. However, calcite originating from coccolithophores is more likely to ballast POC efficiently than calcite originating from foraminifera [Schmidt *et al.*, 2014]. This implies that there is no globally uniform relationship between export of one type of mineral and POC, contrary to earlier suggestions by Klaas and Archer [2002] and Sanders *et al.* [2010].
2. Factors other than the magnitude of mineral-associated POC flux are also likely to influence PE_{eff} . For instance, ecosystem functions such as the packaging of slowly sinking phytoplankton cells into large, fast-sinking fecal pellets may increase PE_{eff} regardless of the proportion of POC associated with minerals in the material grazed.

We suggest that these processes are potentially more important in the SO and the subtropical gyres than in the HLNA. This is consistent with observations of an inverse relationship between primary production and PE_{eff} in the SO, potentially due to grazing intensity [Maiti *et al.*, 2013], and the presence of large amounts of fecal pellets found in deep sediment traps located in the centers of the subtropical gyres [Pabortsava, 2014].

3.4. Implications

Our analysis reveals two important messages:

1. Globally, POC not associated with minerals often dominates total POC export out of the surface ocean (Figure 2k). While it is quite clear that this flux gets remineralized with increasing depth in the mesopelagic zone [Armstrong *et al.*, 2002; Honda and Watanabe, 2010], what drives the size of this unassociated flux in surface waters is unclear. As it is often a large proportion of the POC flux, it is important to understand the formation mechanism of this pool and how it may vary with future changes in the ocean. This pool may indeed play a role in setting POC remineralization depth, which has the potential to exert strong control over atmospheric CO₂ levels [Kwon *et al.*, 2009].
2. Surface mineral-associated POC fluxes are highly variable (Figures 2i–2k), but some of the variability correlates to a certain extent with the patterns of PE_{eff} presented by Siegel *et al.* [2014], suggesting that PIC and BSi can promote efficient export of POC. Our results suggest that this is most pronounced in the HLNA. Conversely, our results suggest that mineral ballast association may be of limited importance in explaining the variation of PE_{eff} in the SO and the subtropical gyres. Ecosystem processes like grazing intensity may be more important in these regions.

Comparing mineral-associated POC export with the global pattern of PE_{eff}, Siegel *et al.* [2014] has provided valuable information to specifically diagnose the local role of minerals. The comparison can also yield insights into regional patterns in T_{eff}.

In the HLNA, estimates of T_{eff} derived from sea surface temperature are low [Henson *et al.*, 2012]. However, the large mineral-associated surface flux of POC we observe in the HLNA is likely to sink fast and to be protected from remineralization in the mesopelagic [Engel *et al.*, 2009a; Engel *et al.*, 2009b; Le Moigne *et al.*, 2013a]. Hence, it is possible that T_{eff} in the HLNA is higher than proposed by Henson *et al.* [2012], as was indeed shown during process studies upon collapse of spring diatom blooms in the HLNA [Buesseler and Boyd, 2009; Martin *et al.*, 2011; Rynearson *et al.*, 2013]. In the SO, T_{eff} is also estimated to be low [Henson *et al.*, 2012], and since the proportion of mineral-associated POC flux is lower than in the HLNA, we propose that the POC is less protected and thus potentially more easily degraded by consumers. In this case, our results are in keeping with recent literature arguing that ecosystem structure is more important than ballast mineral in driving the T_{eff} in high-latitude diatom-dominated regions [Assmy *et al.*, 2013; Henson *et al.*, 2012; Lam *et al.*, 2011; Wilson *et al.*, 2012], although in the SO, too, it has been shown that the collapse of a diatom bloom can lead to a large export event characterized by high T_{eff} [Smetacek *et al.*, 2012].

Our results suggest that viewing the BCP as a two end-member system with high PE_{eff}/low T_{eff} occurring at high latitudes and low PE_{eff}/high T_{eff} occurring at low latitudes [Henson *et al.*, 2012] may miss some of the complexity inherent within the system. Rather, the processes driving PE_{eff} and T_{eff} are likely to be driven in turn by factors beyond just sea surface temperature. Thus, not all high-latitude regions are identical, and they cannot be described by the same “ballast” parameterization in ocean carbon models. For instance, POC export in the HLNA and the SO are unlikely to respond in the same way to any reduction in ballast mineral availability, as might be caused by ocean acidification, increased sea temperature, or deepening of the wind mixed layer [Sarmiento *et al.*, 2004; Zondervan, 2007]. We propose that the BCP in the HLNA may be more susceptible to reductions in ballast mineral availability than the BCP in other high-latitude regions in the world ocean. As the HLNA is a major contributor to global POC export [Falkowski *et al.*, 1998], any reduction in the export of POC there could have a significant impact on the level of atmospheric CO₂.

Acknowledgments

We would like to thank the captains and crews of the *R.R.S. Discovery*, *R.R.S. James Cook*, and *R.R.S. James Clark Ross*. We also gratefully thank Andy Milton, Mark Stinchcombe, Adrian Martin, Gary Watmough, Elena Ceballos-Romero, Mathew Cooper, Jeffrey Benson, and the National Marine Facilities technicians. We would like to give thanks to anonymous reviewers for their comments. This work was supported by the UK's Ocean acidification (NERC, NE/H017097/1), NERC (NE/G015732/1); UK GEOTRACES (NE/H006095/1) and the EU CalMarO (215157) programs. Data are held at the British Oceanographic Data Centre (<http://www.bodc.ac.uk/>).

Peter Strutton thanks two anonymous reviewers for their assistance in evaluating this paper.

References

- Akaike, H. (1974), A new look at the statistical model identification, *IEEE Trans. Autom. Control*, 19(6), 716–723, doi:10.1109/TAC.1974.1100705.
- Armstrong, R. A., C. Lee, J. I. Hedges, S. Honjo, and S. G. Wakeham (2002), A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals, *Deep Sea Res., Part II*, 49(1–3), 219–236.
- Assmy, P., et al. (2013), Thick-shelled, grazer-protected diatoms decouple ocean carbon and silicon cycles in the iron-limited Antarctic Circumpolar Current, *Proc. Natl. Acad. Sci. U.S.A.*, 110(51), 20,633–20,638.
- Buesseler, K. O., and P. W. Boyd (2009), Shedding light on processes that control particle export and flux attenuation in the twilight zone of the open ocean, *Limnol. Oceanogr.*, 54(4), 1210–1232.
- Buesseler, K. O., M. P. Bacon, J. K. Cochran, and H. D. Livingston (1992), Carbon and nitrogen export during the JGOFS North Atlantic bloom experiment estimated from ²³⁴Th-²³⁸U disequilibria, *Deep Sea Res., Part I*, 39(7–8), 1115–1137.

- Engel, A., J. Szlosek, L. Abramson, Z. F. Liu, and C. Lee (2009a), Investigating the effect of ballasting by CaCO₃ in *Emiliania huxleyi*: I. Formation, settling velocities and physical properties of aggregates, *Deep Sea Res., Part II*, 56(18), 1396–1407, doi:10.1016/j.dsr2.2008.11.027.
- Engel, A., L. Abramson, J. Szlosek, L. Zanfei, G. Stewart, D. Hirschberg, and C. Lee (2009b), Investigating the effect of ballasting by CaCO₃ in *Emiliania huxleyi*: II. Decomposition of particulate organic matter, *Deep Sea Res., Part II*, 56(18), 1408–1419.
- Falkowski, P. G., R. T. Barber, and V. Smetacek (1998), Biogeochemical controls and feedbacks on ocean primary production, *Science*, 281(5374), 200–206.
- François, R., S. Honjo, R. Krishfield, and S. Manganini (2002), Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochem. Cycles*, 16(4), 1087, doi:10.1029/2001GB001722.
- Gehlen, M., L. Beck, G. Calas, A. M. Flank, A. J. Van Bennekom, and J. E. E. Van Beusekom (2002), Unraveling the atomic structure of biogenic silica: Evidence of the structural association of Al and Si in diatom frustules, *Geochim. Cosmochim. Acta*, 66(9), 1601–1609, doi:10.1016/S0016-7037(01)00877-8.
- Gehlen, M., L. Bopp, N. Ernprin, O. Aumont, C. Heinze, and O. Ragueneau (2006), Reconciling ocean productivity, export fluxes and sediment composition in a biogeochemical ocean model, *Biogeosciences*, 3(4), 521–537.
- Henson, S. A., R. J. Sanders, and E. Madsen (2012), Global patterns in efficiency of particulate organic carbon export and transfer to the deep ocean, *Global Biogeochem. Cycles*, 26, GB1028, doi:10.1029/2011GB004099.
- Henson, S., R. Sanders, E. Madsen, P. Morris, F. A. C. Le Moigne, and G. Quartly (2011), A reduced estimate of the strength of the ocean's biological carbon pump, *Geophys. Res. Lett.*, 38, L046006, doi:10.1029/2011GL046735.
- Honda, M., and S. Watanabe (2010), Importance of biogenic opal as ballast of particulate organic carbon (POC) transport and existence of mineral ballast-associated and residual POC in the Western Pacific Subarctic Gyre, *Geophys. Res. Lett.*, 37, L02605, doi:10.1029/2009GL041521.
- Iversen, M. H., and H. Ploug (2010), Ballast minerals and the sinking carbon flux in the ocean: Carbon-specific respiration rates and sinking velocity of marine snow aggregates, *Biogeosciences*, 7, 2613–2624.
- Klaas, C., and D. E. Archer (2002), Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochem. Cycles*, 16(4), 1116, doi:10.1029/2001GB001765.
- Kuss, J., and K. Kremling (1999), Spatial variability of particle associated trace elements in near-surface waters of the North Atlantic (30°N/60°W to 60°N/2°W), derived by large volume sampling, *Mar. Chem.*, 68, 71–86.
- Kwon, E. Y., F. Primeau, and J. L. Sarmiento (2009), The impact of remineralization depth on the air-sea carbon balance, *Nat. Geosci.*, 2, 630–635.
- Lam, P. J., S. C. Doney, and J. K. B. Bishop (2011), The dynamic ocean biological pump: Insights from a global compilation of particulate organic carbon, CaCO₃ and opal concentrations profiles from the mesopelagic, *Global Biogeochem. Cycles*, 25, GB3009, doi:10.1029/2010GB003868.
- Lambert, C. E., J. K. B. Bishop, P. E. Biscaye, and R. Chesselet (1984), Particulate aluminium, iron and manganese chemistry at the deep Atlantic boundary layer, *Earth Planet. Sci. Lett.*, 70, 237–248.
- Le Moigne, F. A. C., R. J. Sanders, M. Villa-Alfageme, A. P. Martin, K. Pabortsava, H. Planquette, P. J. Morris, and S. J. Thomalla (2012), On the proportion of ballast versus non-ballast associated carbon export in the surface ocean, *Geophys. Res. Lett.*, 39, L15610, doi:10.1029/2012GL052980.
- Le Moigne, F. A. C., M. Gallinari, E. Laurenceau, and C. L. De La Rocha (2013a), Enhanced rates of particulate organic matter degradation by microzooplankton are diminished by added ballast minerals, *Biogeosciences*, 10, 5755–5765, doi:10.5194/bg-10-5755-2013.
- Le Moigne, F. A. C., M. Villa-Alfageme, R. J. Sanders, C. M. Marsay, S. Henson, and R. Garcia-Tenorio (2013b), Export of organic carbon and biominerals derived from ²³⁴Th and ²¹⁰Po at the Porcupine Abyssal Plain, *Deep Sea Res., Part I*, 72, 88–101, doi:10.1016/j.dsr.2012.10.010.
- Maiti, K., M. Charette, K. Buesseler, and M. Kahru (2013), An inverse relationship between production and export efficiency in the Southern Ocean, *Geophys. Res. Lett.*, 40, 1557–1561, doi:10.1002/grl.50219.
- Martin, P., R. Lampitt, M. J. Perry, R. Sanders, C. Lee, and E. D'asaro (2011), Export and mesopelagic particle flux during a North Atlantic spring diatom bloom, *Deep Sea Res., Part I*, 58(4), 338–349.
- Milliman, J. D., P. J. Troy, W. M. Balch, A. K. Adams, Y. H. Li, and F. T. MacKenzie (1999), Biologically mediated dissolution of calcium carbonate above the isocline, *Deep Sea Res.*, 46, 1653–1670.
- Nakaya, T., M. Charlton, P. Lewis, C. Brunndon, J. Yao, and S. Fotheringham (2009), GW4 used guide. [Available at <http://www.st-andrews.ac.uk/geoinformatics/gwr/gwr-software/>, 1.39.]
- Pabortsava, K. (2014), Downward particle export and sequestration fluxes in the oligotrophic Atlantic Ocean, PhD thesis, Univ. of Southampton, Southampton, England.
- Pike, S. M., K. O. Buesseler, J. Andrews, and N. Savoye (2005), Quantification of Th-234 recovery in small volume sea water samples by inductively coupled plasma-mass spectrometry, *J. Radioanal. Nucl. Chem.*, 263(2), 355–360, doi:10.1007/s10967-005-0062-9.
- Planquette, H., G. R. Fones, P. J. Statham, and P. J. Morris (2009), Origin of iron and aluminium in large particles (>53 μm) in the Crozet region Southern Ocean, *Mar. Chem.*, 115, 31–42.
- Ragueneau, O., S. Schultes, K. Bidle, P. Claquin, and B. Moriceau (2006), Si and C interactions in the world ocean: Importance of ecological processes and implications for the role of diatoms in the biological carbon pump, *Global Biogeochem. Cycles*, 20, GB4S02, doi:10.1029/2006GB002688.
- Ryneerson, T. A., K. Richardson, R. S. Lampitt, M. E. Sieracki, A. J. Poulton, M. M. Lyngsgaard, and M. J. Perry (2013), Major contribution of diatom resting spores to vertical flux in the sub-polar North Atlantic, *Deep Sea Res., Part I*, 82, 60–71.
- Salter, I., A. E. S. Kemp, R. S. Lampitt, and M. Gledhill (2010), The association between biogenic and inorganic minerals and the amino acid composition of settling particles, *Limnol. Oceanogr.*, 55, 2207–2218, doi:10.4319/lo.2010.55.5.2207.
- Sanders, R., P. J. Morris, A. J. Poulton, M. C. Stinchcombe, A. Charalampopoulou, M. I. Lucas, and S. J. Thomalla (2010), Does a ballast effect occur in the surface ocean?, *Geophys. Res. Lett.*, 37, L08602, doi:10.1029/2010GL042574.
- Sarmiento, J. L., et al. (2004), Response of ocean ecosystems to climate warming, *Global Biogeochem. Cycles*, 18, GB3003, doi:10.1029/2003GB002134.
- Schmidt, K., C. L. De La Rocha, M. Gallinari, and G. Cortese (2014), Not all calcite ballast is created equal: Differing effects of foraminiferan and coccolith calcite on the formation and sinking of aggregates, *Biogeosciences*, 11, 135–145, doi:10.5194/bg-11-135-2014.
- Siegel, D. A., K. O. Buesseler, S. C. Doney, S. F. Sailley, M. J. Behrenfeld, and P. W. Boyd (2014), Global assessment of ocean carbon export by combining satellite observations and food-web models, *Global Biogeochem. Cycles*, 28, 181–196, doi:10.1002/2013GB004743.
- Smetacek, V., et al. (2012), Deep carbon export from the Southern Ocean iron-fertilized diatom bloom, *Nature*, 487, 313–319, doi:10.1038/nature11229.
- Smyth, T. J., T. Tyrrell, and B. Tarrant (2004), Time series of coccolithophore activity in the Barents Sea, from twenty years of satellite imagery, *Geophys. Res. Lett.*, 31, L11302, doi:10.1029/2004GL019735.

- Waniek, J. J., D. E. Schulz-Bull, J. Kuss, and T. Blanz (2005), Long time series of deep water particle flux in three biogeochemical provinces of the northeast Atlantic, *J. Mar. Syst.*, *56*(3–4), 391–415, doi:10.1016/j.jmarsys.2005.03.001.
- Wilson, J. D., S. Barker, and A. Ridgwell (2012), Assessment of the spatial variability in particulate organic matter and mineral sinking fluxes in the ocean interior: Implications for the ballast hypothesis, *Global Biogeochem. Cycles*, *29*, doi:10.1029/2012GB004398.
- Yool, A., E. E. Popova, and T. R. Anderson (2013), MEDUSA-2.0: An intermediate complexity biogeochemical model of the marine carbon cycle for climate change and ocean acidification studies, *Geosci. Model Dev.*, *6*, 1767–1811, doi:10.5194/gmd-6-1767-2013.
- Zondervan, I. (2007), The effects of light, macronutrients, trace metals and CO₂ on the production of calcium carbonate and organic carbon in coccolithophores—A review, *Deep Sea Res., Part II*, *54*(5–7), 521–537.