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Organic particles in a shallow sediment trap: Substantial loss to the dissolved phase

Abstract—We used multivariate statistics to divide the solubilized organic matter in a shallow time-series trap into fractions derived from swimmers and from the passive flux. Most of the dissolved organic matter in the traps originated from swimmers, but the contribution from passively trapped material was also substantial. Accounting for this fraction attributable to the passively trapped material yields a vertical organic carbon flux 2.7 times larger than the conventional estimate, which is based on recovered particles only. For organic nitrogen, this correction is even greater (six times). Solubilization is a fast process that is significant within a few days.

Organic carbon (OC) export from the upper to the deep ocean is dominated by sinking particulate OC, the export of dissolved organic carbon (DOC) being comparatively unimportant (Kähler and Koeve 2001). The particle flux can be determined using sediment traps, but there are various problems with this approach. Three principal biases in sediment trap studies were addressed by Gardner (1999): (1) nonproportional sampling of the flux (Buesseler 1991), (2) animals entering the traps actively (''swimmers''; Lee et al. 1988), and (3) the solubilization of collected particles. Because the swimmers also solubilize, the latter two biases are connected. While the particulate remains of swimmers can be picked from the samples, their solubilization products cannot. Combined trap biases can be large, which is evident from major inconsistencies often observed between the particulate material recovered from traps deployed just below the euphotic zone and the vertical export flux of organic matter estimated from new production (Knauer et al. 1990; Buesseler et al. 1992). Thorium transfer from the upper water column into traps (Buesseler 1991; Buesseler et al. 1992) has often revealed substantial undersampling by sediment traps. Underestimation of the vertical flux due to the loss of collected particulate organic matter to the aqueous supernatants of the traps' collecting cups has recently been recognized to be significant in traps deployed in the Greenland Sea (Noji et al. 1999).

Before this, the portion of dissolved organic material attributable to the passive flux had been estimated in only a handful of samples (Knauer et al. 1990; Hansell and Newton 1994). Honjo et al. (1995) reported the solubilization of organic particles to be of minor importance in traps deployed deeper than 1,000 m, where swimmers are also less abundant (Lee et al. 1988; Gardner 1999). However, in shallow traps, the question of the swimmers' contribution to dissolved matter has always been crucial. The scarcity of measurements makes it difficult to generalize on the importance of the solubilization bias. Some potentially important factors that would affect results are the depth and duration of deployment, the quality of the collected organic matter, the impact of swimmers, and the poisons or preservatives used. The recent review of trap biases compiled by Gardner (1999) states: ''Several measurements indicate that the carbon loss by solubilization is at most a few percent a day in unpoisoned traps. Unless swimmers are prevented from entering the trap, most of any excess DOC signal in trap supernatant water is derived from herniating swimmers . . . . The apparent magnitude of the solubilization problem appears to be smaller than previously assumed.'' However, a few percent per day may be a substantial loss if traps are deployed yearround, and poisons, which are intended to suppress microbial decomposition of the collected material, do not keep particles from solubilizing (Lee et al. 1992).

Our data (Table 1) are from an annual deployment in 135-m depth, 200 m above bottom, in the Northeast Water (NEW) Polynia, Greenland (80°27′N, 11°01′W; Bauerfeind et al. 1997), using Kiel sediment traps, which are equipped with liquid-tight collecting cups (Kremling et al. 1996). The collecting cups contained seawater poisoned with $HgCl_2$ (0.07% final concentration). Swimmers were removed (''picked'') from the samples under ×20 and ×50 magnification in October and November 1993, at which time the supernatants were also decanted from the particulates and filtered through GF/F filters. The swimmers were mostly crustaceans, dominated by copepods. Chaetognaths and pteropods were occasionally present in significant quantities. Nonvolatile DOC and dissolved organic nitrogen (DON) were determined by high-temperature catalytic oxidation to CO_2 and NO, after the samples were acidified and sparged with CO_2-free gas (Kähler et al. 1997). DON values include some ammonia (~5–15%). For consistency, all measured concentrations and the number of swimmers are expressed as flux per square meter and collecting interval (t).

Bulk DOC measured in the supernatants correlates positively with the particulate remains of the passive flux (residual POC; rPOC) but only weakly with the number of swimmers (Fig. 1A,B). The number of swimmers and rPOC vary independently of each other (Fig. 1C). Partial correlation analysis (Sokal and Rohlf 1995) resulted in a better correlation between DOC and swimmer number and rPOC as its independent determinants (Eq. 1). The numerical value of DOC (μmol m^{-2} per collecting interval) is expressed as the sum of linear functions of swimmer number and rPOC. An analogous relationship (Eq. 2) was obtained for DON versus residual PON (rPON) and swimmers.

$$\text{DOC} = 6.3[\pm 1.5] \times \text{swimmer No.} + 1.7[\pm 0.3] \times \text{rPOC}; \quad r^2 = 0.89 \qquad (1)$$

$$\text{DON} = 1.4[\pm 0.5] \times \text{swimmer No.} + 5.6[\pm 1.1] \times \text{rPON} \quad r^2 = 0.86 \qquad (2)$$

Dividing the swimmer and rPOC factors of Eq. 1 by those of Eq. 2 yields a swimmer-derived DOC:DON ratio of 4.5 and, with residual particulate C:N = 9.8 (regression coefficient of rPOC vs. rPON), a passive-flux–derived DOC:DON ratio of 3.0. Values of bulk DOC calculated from Eq. 1 com-

Table 1. Amounts of rPOC, DOC, and DON in sample supernatants, and number of swimmers, per collecting interval (*t*) of a trap deployed from August 1992 to June 1993 in the NEW Polynia, eastern Greenland. For timing of the collecting intervals (*t*), *see Fig. 2B.*

Cup No.	POC	PON	DOC	DON	Swimmers	Copepod	Crustacea	Others
	mmol m^{-2} t^{-1}				(No. m^{-2} t^{-1})	(%)		
1	5.76	0.60	19.92	5.53	1,170	58	98	2
2	16.96	1.53	39.83	12.09	999	72	94	6
3	11.07	1.07	20.05	5.36	794	66	93	7
4	11.95	1.30	22.06	5.92	1,285	56	87	13
5	4.25	0.56	12.34	3.43	764	32	82	18
6	1.64	0.23	6.33	1.57	2,214	9	19	81
7	4.98	0.43	9.51	2.83	1,946	13	20	80
8	1.48	0.18	6.40	2.07	569	44	47	53
9	3.76	0.55	26.95	10.63	1,351	77	78	22
10	3.94	0.49	31.03	5.75	1,916	99	100	0
11	3.21	0.36	17.47	4.71	1,351	97	100	0
12	1.88	0.26	14.28	4.51	1,462	79	82	18
13	1.69	0.23	13.86	4.24	1,637	81	89	11
14	1.09	0.12	4.59	1.33	758	49	70	30
15	2.82	0.36	16.26	5.18	1,430	79	85	15
16	1.02	0.14	5.61	1.83	674	54	59	41
17	1.88	0.17	9.74	3.36	1,017	70	87	13
18	1.90	0.25	7.41	2.61	690	75	95	5

pare satisfactorily with measured values (Fig. 1D). Attempts to refine this analysis by including swimmer type (Table 1) or fractions of passive flux (fecal pellet C, phytoplankton C, and residual carbon; from Bauerfeind et al. 1997) did not change the slope of the rPOC versus DOC partial correlation nor did they improve its fit. Including time as an independent variable did not improve the relationship either. Variation of residual DOC (calculated − measured) is not related to the time elapsed between sampling and the separation of the supernatants from the particulates (Fig. 1E). This figure includes the results of a 2-month deployment (Bauerfeind et al. 1997) in which the youngest sample was only 10 d old. It does not show less solubilization than the oldest sample. This suggests that the bulk of solubilization occurred shortly after the particles were deposited in the traps.

From Eq. 1, the passive-flux–derived DOC can be obtained by multiplying rPOC by 1.7, or, numerically, by subtracting 6.3 times the swimmer number from bulk DOC. Both calculations yield similar results (Fig. 2A). In some collecting intervals, almost all DOC is from the passive flux, but in most intervals, and for the annual average, the greater share of DOC is from the swimmers (Fig. 2B). The contribution of the passive flux is substantial, however: considering swimmer-corrected DOC, the total annual passive OC flux into the trap (rPOC plus passive-flux–derived DOC) is 2.7 times larger than the flux determined from the residual POC recovered from the traps alone, as has been the practice in almost all trap studies up to now. A similar factor of 2.5 was estimated by Noji et al. (1999) for a shallow trap in the Greenland Sea.

The molar C : N ratio of the bulk solubilized organic material varies between 2.9 and 3.9 (mean = 3.3; Fig. 1F), which is very low compared with the Redfield C : N ratio of 6.6. The C : N ratio of the particulate remains of the passive flux in the traps is between 8.0 and 11.6 (mean = 9.8). This is consistent with the assumption of structural polysaccharides (cellulose and chitin) being enriched in the particulate remains and with proteins (C : N = 3.8) and nucleic acids (C : N = 2.6) dominating the dissolved phase (Anderson 1995). However, both fractions added (rPOC, N + passive-flux–derived DOC, N) have C : N ratios between 3.8 and 4.2 only, which is not typical of marine particulate organic matter.

The only trap sample for which both dissolved C and N were reported (Hansell and Newton 1994) had a dissolved molar C : N ratio of 2.7. This was from an unpoisoned trap where OC removal by respiration may have contributed to the low value. In our trap, poisoned with $HgCl_2$, an explanation of the low C : N ratio may be the loss of fats, which contain no N. There is only circumstantial evidence for this. In a study from a 2,200-m trap (Körzinger et al. 1994), 0.02–0.2% of the particulate and dissolved organic matter collected was fat. The lipid content of marine plankton is, however, ~16% (Anderson 1995); hence, fat had been almost completely lost from the material. Fat is regularly found floating on stored plankton samples and sometimes on the supernatants of trap samples. To our knowledge, such material has never been quantified, and it is unknown how much of it may have been lost from the traps that have sample vials open to the top during collection. This is yet another potentially important bias in trap studies, and traps would have to be fitted with devices to collect ascending fat droplets to check it.

Our results have important consequences for a number of issues in marine biogeochemistry. The inadequacy of, or difficulty with, shallow traps in determining particle export quantitatively has been recognized, but traps have been assumed to provide a true record of the quality of the exported material. Our data show that one important quality, its C : N ratio, cannot be adequately assessed when considering the particulate remains of the passive flux only. Changes of the particle C : N ratio after deposition in the trap may be why different thorium-based flux corrections are necessary for carbon and nitrogen (Buesseler et al. 1992). Thus, it would

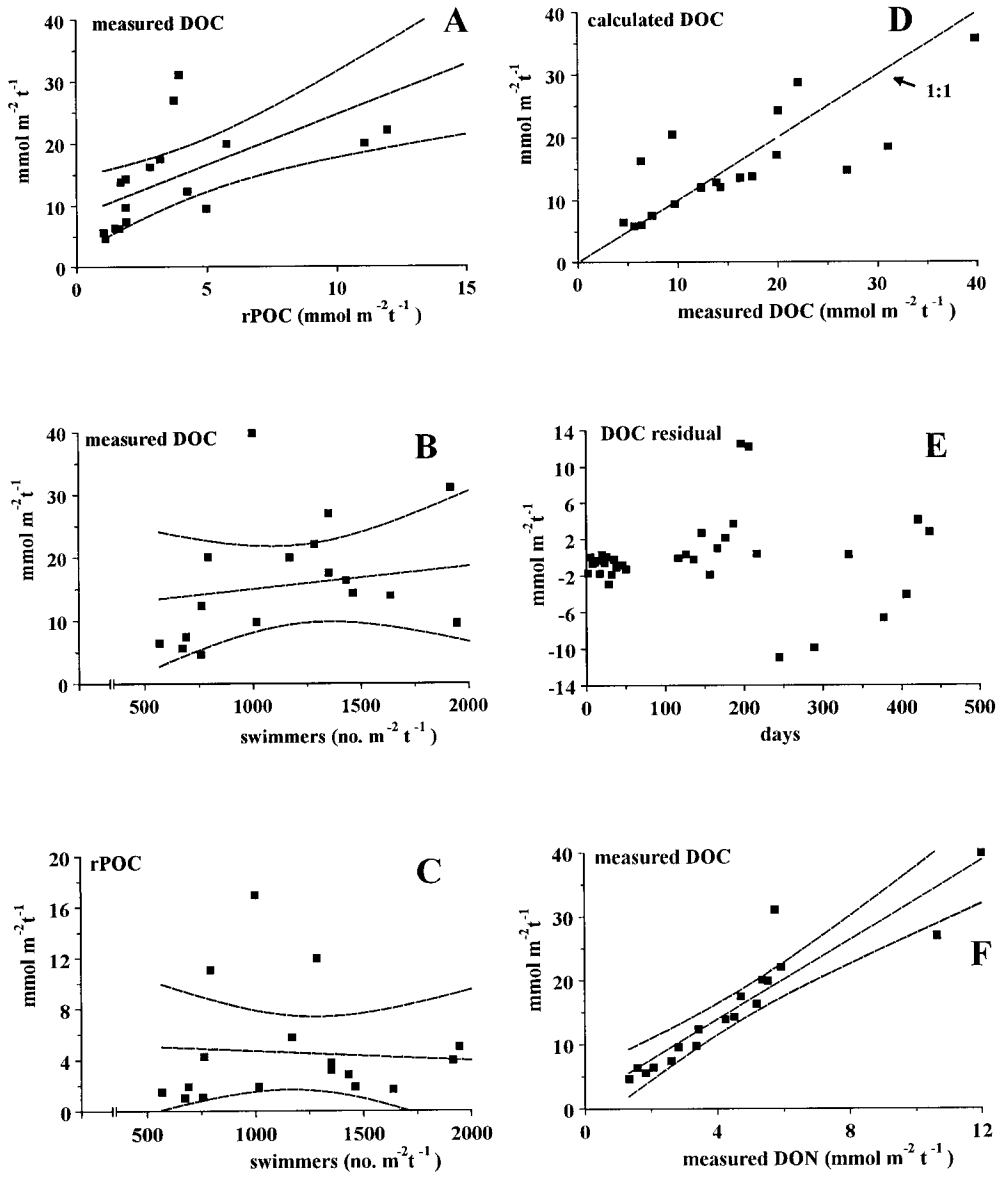

Fig. 1. Relationships between sediment trap flux components. (A) DOC in supernatants versus rPOC (slope = 1.6; $r^2 = 0.54$); (B) DOC in supernatants versus swimmer number ($r^2 = 0.03$); (C) rPOC versus swimmer number ($r^2 < 0.01$); (D) measured DOC versus DOC calculated by Eq. 1; (E) residual DOC, measured minus calculated by Eq. 1, in relation to time between sampling and separation of particles and supernatants. This includes additional 16 samples of a 2-month trap deployment; and (F) DOC versus DON (slope = 3.3; $r^2 = 0.96$). Correlation analyses were made using the statistical program package Statgraphics®; dotted lines represent 95% confidence intervals.

not be possible to correct for the solubilization of carbon by applying a factor determined with nitrogen, as Knauer et al. (1990) suggested. The measurement of both dissolved carbon and nitrogen is possible only in traps in which neither of these elements is contained in the fixatives (e.g., formalin and azide).

If the solubilization of particles should prove to be generally as fast as our results imply (in experiments with zooplankton, solubilization was complete already after 10 d [Noji et al. 1999]), and if it should proceed at comparable rates in situ, then in the sea, solubilization should be most pronounced during the early phases of sinking, i.e., in the upper water column. Assuming a sinking speed of 100 m d^{-1}, a trap deployed at 1,000-m depth would collect almost completely leached material. Solubilization can hence be assumed to be important in shallow traps but less so in deep ones.

Several empirical relationships (Suess 1980; Betzer et al. 1984; Martin et al. 1987) relating the vertical organic matter flux to water depth have been established using sediment trap measurements but without taking solubilization in traps into account. Including this effect would most likely change

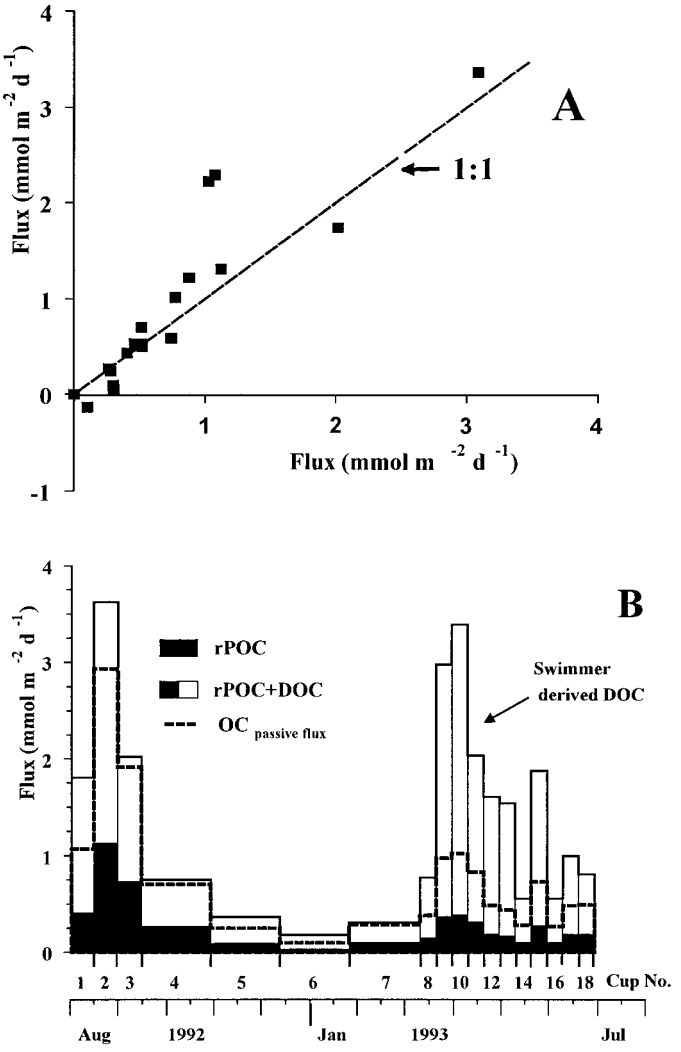

Fig. 2. OC flux and its components in swimmer-picked trap samples. (A) Passive C-flux calculated from Eq. 1 by adding 1.7 times rPOC to rPOC (x-axis) versus subtracting swimmer number times 6.3 from total OC (y-axis). (B) Annual flux pattern of OC. Solid bars, rPOC; dotted line, passive OC flux calculated from Eq. 1 by adding 1.7 times rPOC to rPOC; solid line, sum of passive-flux plus swimmer-contributed DOC (=rPOC + measured DOC). This figure also shows the timing of the collection intervals.

these relationships, especially in the upper water column, where the decrease of the flux with depth is likely to be more pronounced. The apparent discrepancy between this decrease, and the scarceness of microbes attached to sinking particles, described by Karl et al. (1988) as a ''particle decomposition paradox,'' may be due to the solubilization of the sinking particles and microbial utilization of the resulting dissolved matter. Our results imply this to be important, even more than hypothesized in the original context, which was based on the decrease with depth of trap fluxes determined without accounting for solubilization in the traps.

In conclusion, particulate organic matter recovered from traps does not mirror the C : N ratio of exported particles. Without knowing the C : N ratio of the particles' solubilization products, trap studies cannot adequately address questions concerning the relationship between the consumption ratio of C and N in the surface ocean and their export ratios. This is pertinent to questions such as whether carbon overconsumption, the uptake of carbon relative to nitrogen in excess of the Redfield ratio (Sambrotto et al. 1993; Kähler and Koeve 2001), is matched by the export of C-rich particulate matter, or even more generally, whether Redfield stoichiometry is valid in the surface ocean.

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Stable isotope values of lotic invertebrates: Sources of variation, experimental design, and statistical interpretation

Abstract—In a subset of a stream food web, whole-body isotope values of $\delta^{13}C$ and $\delta^{15}N$ were measured for eight populations of lotic invertebrates. Observed isotopic differences among species corresponded broadly to their trophic status, as also revealed by gut content analysis, but with some exceptions. Species within a guild of grazer/scraper mayflies differed significantly in $\delta^{13}C$; a predatory caddisfly (*Rhyacophila dorsalis*) and a collector/gatherer stonefly (*Leuctra inermis*) had statistically indistinguishable values of $\delta^{13}C$ and $\delta^{15}N$. The variation associated with the mean isotope value of each population was partitioned into the variation among individuals and the variation that arises from analysis by isotope ratio mass spectrometry. For some taxa, within-population variance was lower than or equal to the variance attributable to the measurement error of the mass spectrometer. The highest but conservative estimate of within-population variation was a mean coefficient of variation of 11% for $\delta^{15}N$ in a predator, *R. dorsalis.* The minimum detectable difference between two populations was negatively associated with the number of replicate samples and the number of individual animals combined in each replicate. The optimum number of replicate samples, therefore, varies depending on the hypotheses of interest.

Stable isotope analysis (SIA) has become an important technique for examining trophic interactions and elucidating energy flow pathways through food webs and ecosystems. In freshwater systems, the $^{13}C:^{12}C$ ratio ($\delta^{13}C$) can indicate the relative importance of autochthonous versus allochthonous sources of carbon (e.g., Jones et al. 1998). The dissolved inorganic carbon pool exploited by freshwater photosynthetic organisms is typically more depleted in ^{13}C than in atmospheric CO_2, which is the carbon source of terrestrial plants. Thus, the isotope value of allochthonous material in freshwater systems is usually more similar to that of terrestrial plants than to that of aquatic algae. Fractionation of isotopes along biochemical pathways can result in isotopic enrichment in animal tissues relative to their food source and thus indicate trophic status (e.g., Doucett et al. 1996). Nitrogen isotopes, $^{15}N:^{14}N$ ($\delta^{15}N$), are especially useful indicators of trophic status, because the loss of isotopically lighter ^{14}N via excretion results in a 3–5‰ enrichment in $\delta^{15}N$ of consumers relative to their food (Peterson and Fry 1987). In studies of freshwater food webs, SIA has often been used to characterize the mean stable isotope enrichment of different populations or taxa in a particular system at a particular time. Hitherto, the interpretation of stable isotope values in multispecies food webs has been based predominantly on verbal descriptions of isotope biplots; statistical analyses for hypothesis testing are less common. Further, the focus has been largely on the mean isotopic value of different populations, and less attention has been given to the ecological significance of within-population variation in isotope value. In part, this may relate to the large number of samples (many species and many replicates) required for food web studies and to the financial cost of SIA. Nevertheless, numerical analyses are required in order to exploit this valuable tool to its full potential. The success of such analyses will be restricted, in part by error and variation in the data, so the sources and magnitude of variation need to be identified and careful consideration given to the number of replicates required to test hypotheses.

There are two main sources of variation associated with estimates of the mean isotope value of a population: (1) variation among individuals within the population, and (2) variation that arises from analysis by isotope ratio mass spec-