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Effects of poisons and preservatives on the composition of organic matter in a sediment trap experiment

by Stuart G. Wakeham,[1] John I. Hedges,[2] Cindy Lee[3] and Tamara K. Pease[1]

ABSTRACT

Fluxes and molecular compositions of a group of major biochemical classes (lipids, lignin, pigments, amino acids, and carbohydrates) were compared among sediment traps treated with different poisons and preservatives and deployed for 1–2 months in a coastal marine environment. Fluxes and compositions of biochemicals were significantly more variable than bulk particle fluxes and elemental compositions. This observation was attributed to a greater influence of dead zooplankton "swimmers" in treated traps rather than differences in microbial decomposition due to the various treatments. Molecular compositions, especially of lipids, confirm the influence of zooplankton swimmers on the biochemical composition of the particulate material in treated traps compared to untreated controls even when large swimmers had been removed. An inventory of the major biochemicals we measured accounted for 25–45% of the organic carbon in our samples, with amino acids and sugars making up the bulk (80–90%) of the identified carbon.

1. Introduction

The major source of particulate organic matter in the ocean is the photosynthetic fixation of inorganic carbon by phytoplankton in surface seawater. Additional sources of particulate organic matter include compounds produced by secondary consumers and compounds transported to the ocean from continental regions. As particles sink and are attacked by heterotrophic consumers, labile organic material is preferentially lost relative to total organic carbon, and new organic compounds appear as a result of *in-situ* alterations (e.g. Lee and Cronin, 1984; Repeta and Gagosian, 1984; Wakeham and Lee, 1989). Sediment trap experiments are designed to evaluate the vertical flux and composition of this material as it sinks through the water column and thus provide a picture of production and alteration processes.

Trap deployments of up to a year or longer are now common. It is critical to studies of organic matter cycling that heterotrophic alterations do not continue in the trap itself and that the integrity of material collected in traps be maintained both

1. Skidaway Institute of Oceanography, P.O. Box 13687, Savannah, Georgia, 31416, U.S.A.
2. Department of Oceanography WB-10, School of Ocean and Fisheries Sciences, University of Washington, Seattle, Washington, 98195, U.S.A.
3. Marine Sciences Research Center, State University of New York, Stony Brook, New York, 11794, U.S.A.

qualitatively and quantitatively. Relatively few studies, however, have addressed the question of preservation of organic matter in traps. Gardner *et al.* (1983) reported a daily loss of 0.1–1% of organic matter in deep-ocean traps and recommended the use of poisons to prevent degradation of organic material. Knauer *et al.* (1984) tested the effectiveness of commonly used treatments (sodium azide, buffered formalin, and mercuric chloride) to preserve samples for the measurement of total organic carbon (OC) and total nitrogen (TN) and selected metals in the eastern North Pacific. The extent of loss of OC and TN varied with treatment used, although C:N ratios appeared to remain constant. Gunderson and Wassman (1990) tested the effects of chloroform in sediment trap collections and suggest several problems with its use.

We have conducted a series of experiments to provide a systematic evaluation of the effectiveness of commonly used poisons or inhibitors (treatments that retard bacterial activity but do not bind to the sample) and preservatives (fixatives that are chemically incorporated into tissue). A full description of the design of the field experiments is given in Hedges *et al.* (1993), along with results for bulk mass and elemental fluxes. Results from these field studies and from laboratory simulations on the effectiveness of various treatments tested in inhibiting bacterial activity are given in Lee *et al.* (1992), along with recommendations for effective concentrations of treatments to be maintained throughout long-term trap deployments. A major objective of our research was to determine the effectiveness of various treatments in inhibiting the decomposition or alteration of organic matter, and to meet this goal we have analyzed a wide spectrum of organic compound classes (amino acids, sugars, lipids, lignin, pigments) and individual compounds within each biochemical class. All of the compounds are widely distributed in various living organisms and many are valuable "biomarkers" for the sources and alteration of organic matter. Moreover, these compound classes span a range of biogeochemical labilities and physical properties. In this paper we present the results of our sediment trap experiments in terms of organic chemical fluxes and composition.

2. Experimental

a. Sediment trap experiments

Three sediment trap experiments were conducted in Dabob Bay, WA. Details of the rationale for conducting the experiments in Dabob Bay and descriptions of the sediment trap arrays, the treatments used, and initial sample processing are found in Hedges *et al.* (1993). The first experiment involved deployment of traps at 30 m and 60 m in January–February, 1988, during non-bloom conditions when terrigenous material dominated the sinking particle flux (hereafter referred to "30 m winter" and "60 m winter"). A second experiment at 60 m in March–April, 1989, collected material during a weak spring bloom ("60 m spring"). The third experiment sampled the fall bloom with traps at 60 m ("60 m fall"). In the following discussion, data for

duplicate arrays at 30 m and 60 m in the winter experiment (A3 and A4; Hedges *et al.,* 1993) were averaged for pigments and amino acids, whereas materials from only a single array were analysed for lipids, lignin, and carbohydrates due to the labor intensive nature of these measurements. In addition to arrays and treatments described above, particulate material was collected during short-term deployments of untreated traps during the winter and spring experiments. These traps were "harvested" every two days and samples were pooled to assess the nature of sinking particulate material present in the water column throughout each experiment.

b. Analytical methods

Sediment trap material was split for analysis of different compound classes (Hedges *et al.,* 1993). Samples for lignin, carbohydrate and elemental analyses were collected by centrifugation and a volume of the supernatant brine was saved for salt analyses (see Lee *et al.,* 1992 for results). Samples for lipid analyses were collected on ashed 90-mm glass fiber filters (GF/A) and rinsed with filtered seawater to remove poison brine. Samples for amino acids and pigments were filtered onto 47 mm Whatman GF/F filters and rinsed with filtered seawater. Before rinsing, part of the filtrate from the amino acid sample was saved for analyses of dissolved free amino acids. Filtration of the pigment sample was carried out under reduced light. A portion of the filtrate from the pigment sample was set aside for measurement of Hg.

Subsamples for lignin, carbohydrate and elemental analysis were freeze-dried, ground to pass a 42-mesh sieve and stored at room temperature. Wet and dry weights were determined for each of these unrinsed samples to allow the corresponding bulk flux and organic concentrations to be salt corrected. All of the other organic sample fractions were frozen for subsequent analysis.

i. Lipids. Lipids were extracted from the particles with chloroform-methanol (2:1, v/v) using ultrasonication (3 × 30 min). One aliquot of the lipid extract was analyzed by thin layer chromatography/flame ionization detection using an Iatroscan Mark III analyzer after triple developments (Parrish and Ackman, 1983; Volkman *et al.,* 1986). Hydrocarbons, wax esters + steryl esters, and fatty acid methyl esters were separated with hexane-diethyl ether-formic acid (95:5:0.5); triacylglycerols, free fatty acids, fatty alcohols, and sterols were separated with hexane-diethyl ether-acetic acid (60:17:0.15); and mono- and diacylglycerols, pigments and other polar lipids were separated with chloroform-methanol-water (80:15:2). Precisions for Iatroscan analyses are ±15–20%. A second aliquot of the total lipid extract was fractionated into constituent classes by adsorption chromatography on 5% deactivated silica gel using a series of solvents of increasing polarity (Wakeham *et al.,* 1980; Wakeham and Canuel, 1988). Sterols were analyzed as trimethylsilyl ethers by gas chromatography on a 30 m × 0.25 mm i.d. capillary column coated with DB-5 (5%-phenyl silicone).

Precision is typically ±15–20%. A third aliquot of the lipid extract was saponified with aqueous KOH/methanol (0.2 N and 5% distilled water) to free esterified carboxylic acids. The acids were extracted into hexane and methylated with 5% BCl_3-methanol. Fatty acid methyl esters (FAMEs) were isolated by silica gel column chromatography and were analysed by gas chromatography on a 30 m × 0.25 mm DB-225 (50%-cyanopropylphenylsilicone) capillary column. Precision for this procedure is ±10–15%.

ii. Lignin. Lignin-derived phenol monomers were produced by basic CuO oxidation and analyzed as their trimethylsilyl (TMS) derivatives by gas chromatography on a 30 m by 0.25 mm i.d. fused silica capillary column coated with SE-30 (100% dimethylpolysiloxane) liquid phase (Hedges and Ertel, 1982). The average precision of this method for individual single-ring phenols is ±5–10% of the measured yield.

iii. Pigments. The major chlorophyll pigments and their degradation products were analyzed by HPLC following 100% acetone extraction. Pigments were separated by gradient reverse-phase chromatography using the methanol/acetone/ion-pairing solution (tetrabutylammonium acetate-ammonium acetate) described by Mantoura and Llewellyn (1983), followed by fluorescence detection. Standards were prepared and quantified as described by Sun *et al.* (1991). Precision for this analysis was ±15–20%.

iv. Amino acids. Amino acids were measured by fluorescence-high pressure liquid chromatography after acid hydrolysis according to Lee and Cronin (1982). Filters were hydrolyzed under nitrogen at 110°C for 19 hrs with double-distilled 6 N HCl to free amino acids in peptide bonds (proteins and peptides) or adsorbed onto particles. Hydrolysates were dried *in vacuo,* taken up in water, and the free amino acids analyzed by HPLC using a modification of the Lindroth and Mopper (1979) *o*-phthaldialdehyde derivative HPLC technique. Precision for this procedure is ±10–15%.

v. Carbohydrates. Sediment trap materials were analyzed for individual aldose components by the method of Cowie and Hedges (1984a). The samples were pretreated with 72% H_2SO_4 for 2 hrs at room temperature, diluted to 1.2 M H_2SO_4, and hydrolyzed for 3 hrs at 100°C. After desalting and concentrating, individual aldoses were brought to anomeric equilibrium by heating for 48 hrs at 60°C in a 0.2 wt% solution of $LiClO_4$ in pyridine. Equilibrated aldose mixtures were converted to TMS derivatives and analyzed by gas chromatography on a 30 m by 0.25 mm i.d. capillary column coated with SE-30. Precision of this procedure for individual aldoses is ±5–10% of the measured yield.

3. Results and discussion

a. Bulk fluxes

This paper discusses the organic compound composition of the sediment trap materials as a function of treatment. The reader is referred to Lee *et al.* (1992) for a discussion of the effectiveness of the treatments in retarding bacterial activity and collection of swimmers and to Hedges *et al.* (1993) for a discussion of the effect of the various treatments on bulk mass and elemental fluxes. To summarize, however, the Lorenzen-type traps used in this study reproducibly collected similar fluxes of bulk particulate materials, although they were susceptible to washout during severe weather. Even under moderate current conditions, effective brine concentrations at the trap bottoms upon retrieval were about half of the initial levels due to mixing of the brine with ambient seawater (see Fig. 3 of Lee *et al.,* 1992). Only traps recovered with $>50\%$ of the poison added will be discussed here.

Trap samples were sieved through a 850-μm sieve before analysis and the material on the sieve removed and weighed (Table 1 of Hedges *et al.,* 1993). Low fluxes of these very large (>850 μm) particles were consistently observed in sediment traps that were untreated or treated with liquid chloroform, NaCl only (50 or 100 g/L), or antibiotics in NaCl (see also Fig. 5 of Lee *et al.,* 1992). In contrast, traps treated with $HgCl_2$, NaN_3, CH_2O or dissolved $CHCl_3$ (all prepared in 50 or 100 g/L of NaCl in seawater) often collected high fluxes of dead, large zooplankton on the 850-μm sieve. These comparisons indicate that the bulk of the dead zooplankton recovered in the treated traps swam in and were killed by the treatment used. Small dead "swimmers" in the <850 μm fraction that were not removed by sieving apparently did not contribute appreciably toward the flux of bulk particulate material collected in the treated trap (Hedges *et al.,* 1993).

Fluxes of particulate organic carbon (POC) and carbon-equivalents for the five major biochemical classes are shown in Figure 1 for each of the three trap deployment periods (and for 30 and 60 m depths during the winter experiment). For lignin and pigments there was relatively little variation in flux as a function of treatment among traps simultaneously deployed at one depth, although seasonal variations in flux were observed as discussed below. For the other biochemical classes, significant variations in flux with different treatments were observed. We can rely on detailed compositional analyses of some of these classes to assess whether this variability was due to the effectiveness of the treatment or to the collection of small swimmers.

b. Lipids

Lipids serve a variety of functions in all living organisms, including membrane structure, energy storage and mobilization, and regulation of metabolic processes (Sargent, 1976). Certain lipids have a source-specificity which makes them useful indicators of inputs from phytoplankton, zooplankton, bacteria and terrestrial plants. In our experiments, fluxes of lipids ranged between 3–10 mg C m^{-2} d^{-1} (Fig. 1;

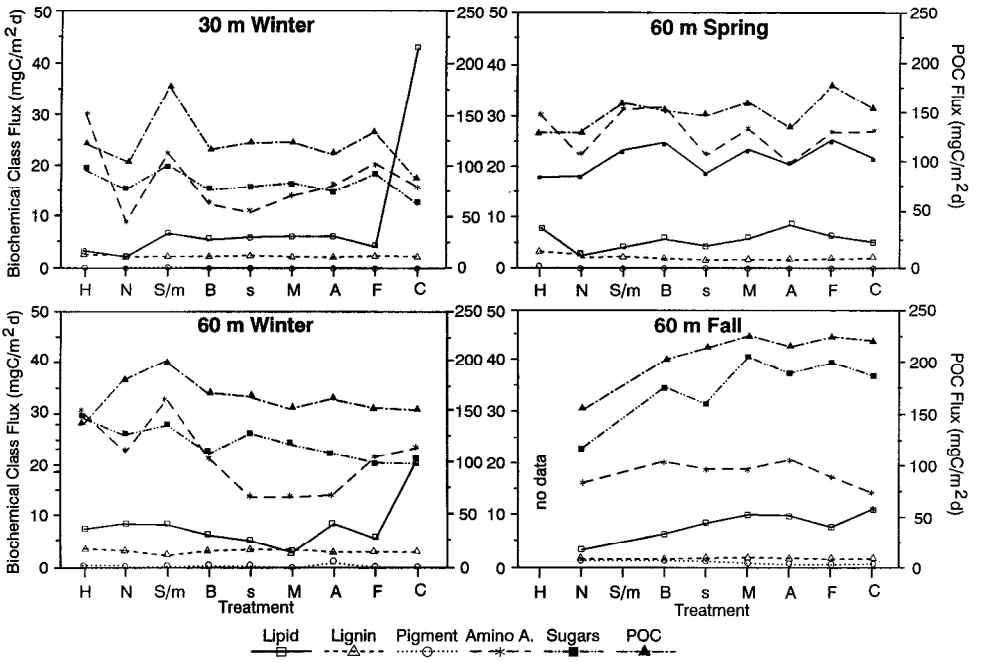

Figure 1. Fluxes of particulate organic carbon (POC; mg C m^{-2} d^{-1}), lipid, lignin, pigment, amino acids and sugars (mg C m^{-2} d^{-1}) vs. treatment in the three experiments. H = harvested control; N = untreated control; S/m = high salt, low mercury; B = antibiotics, low salt; s = low salt; M = high mercury, low salt; A = sodium azide, low salt; F = formaldehyde, low salt; C = chloroform, no salt. There were no samples for treatments H and S/m in fall. Note the different scales for POC vs. the biochemicals. Compound class-carbon was estimated assuming lipid to be 85% carbon, lignin to be 60% carbon, amino acids to be 40% carbon, and sugars to be 45% carbon.

excluding the chloroform treatments in winter as discussed below) for four trap sets (three experiments and two depths in the winter experiment). Mean fluxes for the three sets of 60 m traps were not significantly different between seasons (60 m winter mean = 5.7 ± 2.0 mg C m^{-2} d^{-1}; 60 m spring = 6.7 ± 1.9 mg C m^{-2} d^{-1}; 60 m fall = 8.0 ± 2.5 mg C m^{-2} d^{-1}), nor between the 30 and 60 m traps in winter (30 m winter = 5.3 ± 1.4 mg C m^{-2} d^{-1}). Lipid concentrations normalized to organic carbon (mg lipid/100 mg organic carbon; Table 1) allow comparisons between samples while minimizing the effect of dilution by widely varying amounts of inorganic material in field samples. The resulting concentrations were less variable with treatment than were lipid fluxes. This suggests that the lipid content of particles settling into the traps was relatively constant even though particle flux, and hence lipid flux, varied. Overall, lipids represented about 3–5% of POC.

In three of the four deployments (excluding the 60 m winter series), the flux of lipids in the unpoisoned control was the lowest of the eight treatments, generally

Table 1. Carbon-normalized compound class concentrations (yields) for the trap experiments.

Treatment	Lipid	Lignin	Pigments (yield mg/100 mg OC)	AA s	Sugars
30 m Winter					
H	2.8	3.0	0.08	68.1	25.5
N	2.5	2.3	0.09	25.2	26.1
S/m	4.5	1.4	0.15	36.1	19.9
B	5.5	2.1	0.07	32.5	22.8
s	5.7	2.1	0.11	26.1	23.6
M	5.9	1.9	0.02	36.2	23.6
A	6.5	2.1	0.02	41.8	23.4
F	3.6	1.9	0.02	45.3	24.2
C	57.2	2.7	0.05	55.1	24.3
60 m Winter					
H	5.0	2.4	0.10	53.5	28.4
N	4.6	1.7	0.11	25.3	22.4
S/m	4.2	1.1	0.13	37.5	22.1
B	3.6	1.8	0.19	34.1	20.3
s	3.0	1.9	0.21	26.2	24.3
M	1.8	2.1	0.01	37.0	23.6
A	5.0	1.7	0.51	41.1	20.9
F	3.4	1.8	0.09	45.3	20.0
C	13.4	1.8	0.06	55.2	20.0
60 m Spring					
H	6.9	2.3	0.13	62.3	23.5
N	2.0	1.6	0.03	45.7	22.1
S/m	2.7	1.5	0.01	53.8	23.3
B	4.0	1.4	0.04	55.2	26.1
s	3.2	1.2	0.05	48.5	20.4
M	3.8	1.1	0.02	36.2	23.4
A	6.6	1.3	0.02	54.9	24.3
F	3.8	1.1	0.02	26.2	21.8
C	3.5	1.3	0.02	45.3	22.5
60 m Fall					
H	n.d.	n.d.	n.d.	n.d.	n.d.
N	2.1	0.96	0.69	27.7	22.6
S/m	n.d.	n.d.	n.d.	n.d.	n.d.
B	3.1	0.68	0.53	26.1	26.1
s	4.0	0.74	0.46	23.9	22.5
M	4.5	0.71	0.26	20.5	27.6
A	4.5	0.66	0.23	24.4	26.5
F	3.4	0.67	0.16	20.0	26.9
C	5.0	0.67	0.18	16.2	25.6

n.d. = no data

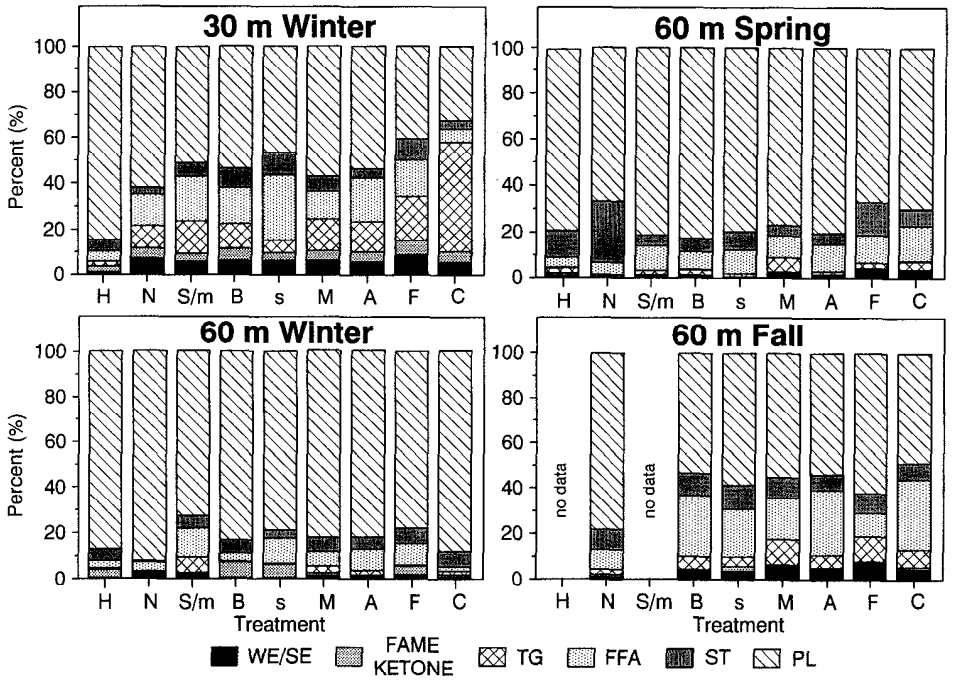

Figure 2. Cumulative abundances (percent, normalized to total lipid content) for major lipid classes as determined by Iatroscan vs. treatment. Treatment key as in Figure 1. WE/SE = wax esters + steryl esters; FAME = fatty acid methyl esters; TG = triacylglycerols; FFA = free fatty acids; ST = sterols; PL = polar lipids.

being 2–3x lower than in the high mercury (treatment "M" in Fig. 2) and azide (treatment "A") treatments (excluding the $CHCl_3$, treatment "C"). We attribute this trend to the inclusion of small (<850 μm) swimmers in the treated traps rather than to preferential loss of lipid material from the untreated control traps. If true, then lipid fluxes indicate that the high mercury and azide treatments kill the most swimmers (or selectively kill lipid-rich swimmers). The unusually high lipid fluxes and concentrations recorded in the chloroform-treated traps during the winter experiment were due to the fact that large dead swimmers were "pre-extracted" into the liquid chloroform treatment prior to processing in the laboratory. Even though the bodies of the swimmers were removed, their lipids were already in the chloroform. To counteract this problem, chloroform treatments in the spring and fall experiments consisted of chloroform-saturated seawater instead of liquid chloroform.

The class-composition of lipids (Fig. 2) showed that the composition of the lipids varied much more between samples than did the fluxes. For the purposes of this discussion, polar lipids dominated the lipid classes in nearly all samples, typically being 50–90% (mean for all traps was 67 ± 14%) of total lipid. Among the neutral

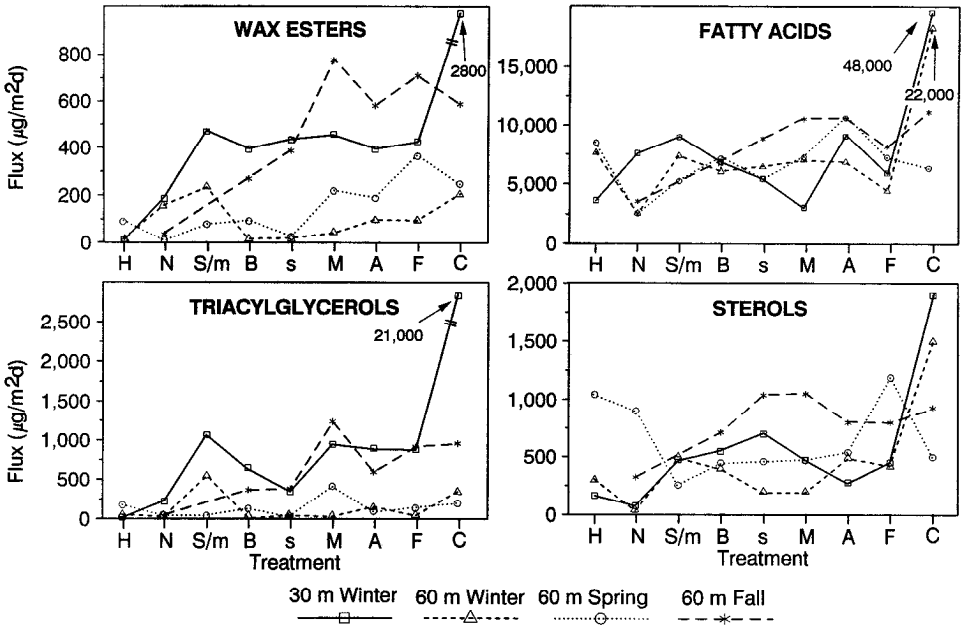

Figure 3. Fluxes (μg m^{-2} d^{-1}) for wax and steryl esters, triacylglycerols, total fatty acids, and sterols vs. treatment. Treatment key as in Figure 1.

lipids, free fatty acids, triacylglycerols, and sterols were most abundant (10–30% [mean = 7 ± 5%], 2–20% [mean = 13 ± 8%], and 3–12% [mean = 6 ± 5%], respectively). The abundances of free fatty acids was surprising, as they are generally not abundant in living organisms. However, those samples with the highest amounts of free fatty acids also contained lower amounts of polar lipids. For example the 30 m winter and 60 m fall sets contained the least polar lipids (47 ± 14% and 59 ± 9%, respectively) and most free fatty acids (16 ± 6% and 21 ± 8%) while the 60 m winter and 60 m spring traps contained the most polar lipid (83 ± 6% and 75 ± 6%, respectively) and the least free fatty acid (7 ± 4% and 11 ± 6%). Following death of organisms, polar lipids rapidly autolyze, yielding free fatty acids. This enzymatic decomposition may well not be slowed by the treatments we investigated. It might also be that the physical form of the polar lipids in material delivered to the 60 m winter and 60 m spring trap sets minimized autolysis, although this is highly speculative.

Fluxes of the major lipid classes are shown in Figure 3. For wax and steryl esters, which can be exclusively attributed to zooplankton (in fact probably only to calanoid copepods in Dabob Bay), fluxes into treated traps were almost always much greater than into the untreated controls, and still lower in the harvested traps compared to the untreated controls. For example, the flux of wax esters into the 30 m winter untreated trap was 180 μg m^{-2} d^{-1} vs. a mean of 400 ± 90 μg m^{-2} d^{-1} for all treated

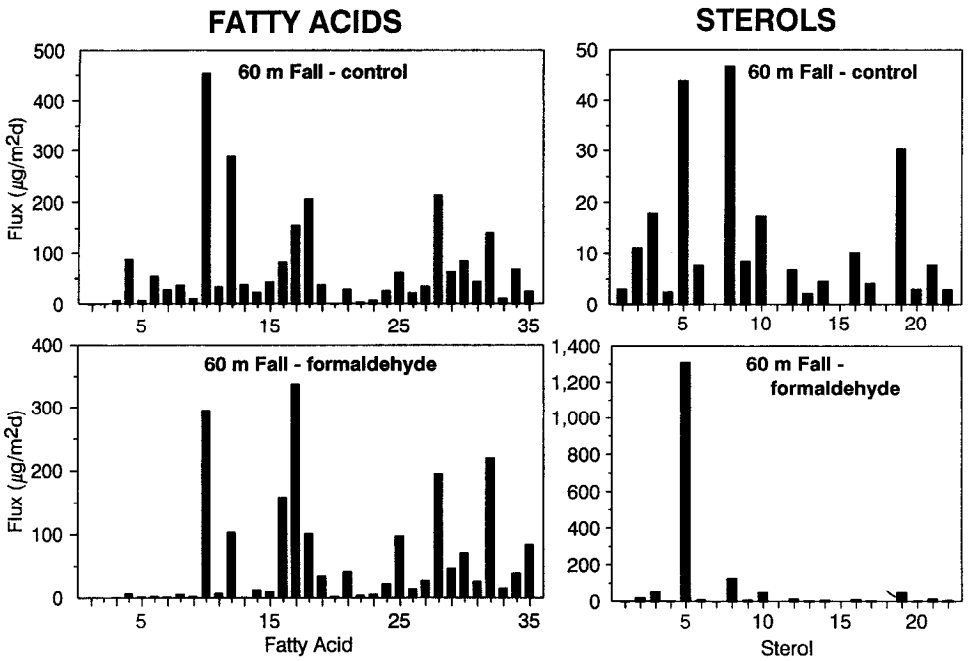

Figure 4. Fluxes (μg m^{-2} d^{-1}) of individual fatty acids and sterols in selected sediment traps for several experiments. Compound number key given in Table 2.

traps (excluding chloroform); similarly the wax ester flux into the 60 m spring control was 39 μg m^{-2} d^{-1} vs. 550 ± 170 μg m^{-2} d^{-1} for all treatments. Wax ester fluxes into the pooled harvested samples for these two experiments were about 10 μg m^{-2} d^{-1}. Variations in lipid composition did not always parallel variations in flux. The lipids in the untreated controls were not consistently depleted in wax ester relative to other lipids. For example, wax esters in the 30 m winter control accounted for 7.1% of total lipid vs. 6.3 ± 1.0% in the treatments. However, in the 60 m spring control, wax esters were quite depleted relative to those in the treated traps (1.0% for control vs. 5.5 ± 1.5% for treatments). This trend was less clear for triacylglycerols and sterols which have a mixed phytoplankton-zooplankton origin.

Major components of fatty acid and sterol compound distributions are illustrated in Figure 4. The 60 m fall control is typical of traps with mixed phytoplankton-derived components (e.g. 14:0 [bar *4* in Fig. 5] and 16:1 [*12*] fatty acids and 24-methylcholesta-5,22-dien-3β-ol [*8*], 24-methylcholesta-5,24(28)-dien-3β-ol [*10*] and 24-ethylcholest-5-en-3β-ol [*19*] among the sterols) and zooplankton-derived components (18:1ω9 [*17*] and cholest-5-en-3β-ol [*5*] (Sargent, 1976; Volkman, 1986). Palmitic acid (16:0 [*10*]) is ubiquitous in all organisms and hence provides little source information. Evidence for bacterial degradation is found in the relative abundances of branched C_{15} fatty acids (*iso*-C_{15} [*6*] and *anteiso*-C_{15} [*7*]) and 18:1ω11

(*18*) fatty acids. In contrast, the fatty acid and sterol distributions in the formaldehyde-treated 60 m trap from fall are typical of material enriched in zooplankton lipids, presumably from killed swimmers.

The variation in lipid flux and composition we observed is not surprising since lipid distributions can be remarkably sensitive to small fluctuations in planktonic—primarily zooplankton—contributions to the trap material. While a few swimmers may make relatively little impact on the mass flux of material into a trap and hence to POC flux, the inclusion of a few lipid-rich swimmers could make a substantial increase in the observed lipid flux, and have a major impact on the flux of compound classes (e.g. wax esters) or individual compounds (e.g. 18:1ω9 fatty acid and cholest-5-en-3β-ol) specific to zooplankton. Calanoid copepods, which dominate the zooplankton community in Dabob Bay (Shuman, 1978), often contain large lipid deposits, up to 70% dry weight (Sargent *et al.,* 1981). It is likely that the wax esters present in many of the treated traps result from the inclusion of copepods, or their remains, which were not removed by the 850 μm sieving. Microscopic analyses of subsamples of the <850 μm trap material did show the presence of a few small copepods in some of the traps. Whether the zooplankton were swimmers or detrital cannot be readily ascertained, but it is presumed that most were swimmers.

c. Lignin

Lignin polymers occur in conductive tissues of vascular land plants but are essentially absent from all other living organisms. CuO-derived lignin-phenols are used as indicators of specific vascular plant sources and as tracers of different types of land-derived organic matter in sediments (Hedges *et al.,* 1988a,b and references cited therein). In a year-long (1981–1982) sediment trap time-series in Dabob Bay, for example, Hedges *et al.* (1988a) estimated that terrigenous organic matter accounted for 10 to 90% of the total organic carbon in sinking particles, with maximal values in winter and lows during spring and fall plankton blooms. Vascular plant debris accounted for roughly half of the land-derived organic matter and was of predominately gymnosperm origin. Measured fluxes of bulk particulate material and terrigenous organic materials consistently increased with increasing depth in the water column.

Fluxes of lignin-phenols measured in our sediment trap experiments also varied seasonally (Fig. 1) and with depth, as did organic-carbon-normalized lignin concentrations (Table 1). High fluxes and concentrations of lignin-phenols were observed in winter (mean flux = 2.4 ± 0.5 mg C m^{-2} d^{-1}) when inputs of terrestrial material are high and inputs from planktonic material are low compared to fall (flux = 1.4 ± 0.1 mg C m^{-2} d^{-1}). There was relatively little variation in lignin-phenol flux and concentration among simultaneously collected materials in sediment traps with different experimental treatments (excepting the 60 m winter series), the variability being, for the most part, within analytical precision. Particulate lignin-phenols

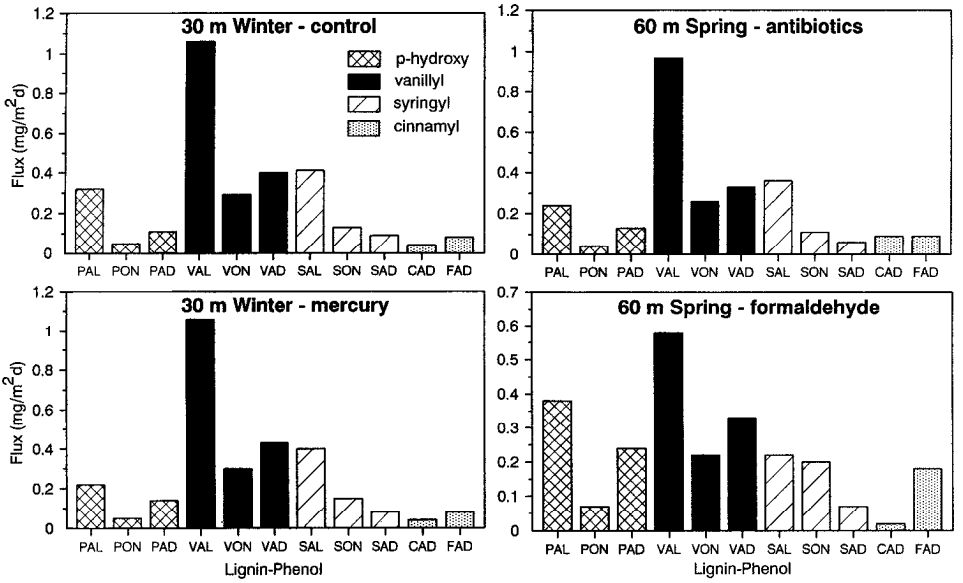

Figure 5. Fluxes (mg m^{-2} d^{-1}) for individual lignin-phenols in selected traps. PAL, *p*-hydroxybenzaldehyde; PON, *p*-hydroxyacetophenone; PAD, *p*-hydroxybenzoic acid; VAL, vanillin; VON, acetovanillone; VAD, vanillic acid; SAL, syringaldehyde; SON, acetosyringone; SAD, syringic acid; CAD, *p*-coumaric acid; FAD, ferulic acid.

accounted for about 1% of POC in fall, 2% of POC in the spring, and 4% of POC in the winter experiments (Fig. 1).

Lignin-phenol compositions of the sediment trap samples did not vary markedly with season or trap treatment (e.g. Fig. 5). Based on lignin-phenol composition determined in a variety of vascular plants, Hedges and Mann (1979) have described a series of lignin parameters which are useful for evaluating more subtle changes in vascular plant source inputs. For example, the ratio of syringyl phenols to vanillyl phenols (S/V) provides information on relative inputs from gymnosperms vs. angiosperms as gymnosperms yield only vanillyl phenols upon CuO oxidation whereas angiosperms produce both vanillyl and syringyl phenols. In our experiments, high S/V values during fall (Fig. 6) suggest greater relative inputs of angiosperm tissues relative to the other seasons. Cinnamyl phenols are relatively abundant in oxidation products only of nonwoody tissues so the ratio of cinnamyl phenols to vanillyl phenols (C/V) is useful for discrimination between woody and non-woody vascular plant tissues. C/V ratios during fall and spring (Fig. 6) indicate greater inputs of non-woody vascular plant tissues compared to winter. Nonetheless, there is again relative constancy between treatments, with generally only small compositional differences between treated and untreated traps.

The absence of direct evidence for better preservation of lignin in treated sediment traps is not too surprising because lignins are among the most stable

Table 2. Fatty Acid and sterol bar designations for Figure 5.

Bar #	Fatty Acid	Sterol
1	12:0	24-norcholesta-5,22E-dien-3β-ol
2	13:0	27-nor-5α(H)-cholesta-5,22E-dien-3β-ol
3	*i*-14:0	cholesta-5,2E-dien-3β-ol
4	14:0	5α(H)-cholest-22E-en-3β-ol
5	14:1	cholest-5-en-3β-ol
6	*i*-15:0	5α(H)-cholestan-3β-ol
7	*a*-15:0	cholesta-5,24-dien-3β-ol
8	15:0	24-methylcholesta-5,22E-dien-3β-ol
9	*i*-16:0	24-methyl-5α(H)-cholest-22E-en-3β-ol
10	16:0	24-methylcholesta-5,24(28)-dien-3β-ol
11	16:1ω7	24-methyl-5α(H)-cholest-24(28)-en-3β-ol
12	16:1ω9	24-methylcholest-5-en-3β-ol
13	16:2	24-methyl-5α(H)-cholestan-3β-ol
14	17:0	23,24-dimethylcholest-5,22E-dien-3β-ol
15	17:1	23,23-dimethyl-5α(H)-cholest-22E-en-3β-ol
16	18:0	24-ethylcholesta-5,22E-dien-3β-ol
17	18:1ω9	24-ethyl-5α(H)-cholest-22E-en-3β-ol
18	18:1ω11	23,24-dimethylcholest-5-en-3β-ol
19	18:2	24-ethylcholest-5-en-3β-ol
20	18:3	24-ethyl-5α(H)-cholestan-3β-ol
21	18:4	24-ethylcholesta-5,24(28)-dien-3β-ol
22	18:5	4α,23,24-trimethyl-5α(H)-cholest-22E-en-3β-ol
23	18:6	
24	20:0	
25	20.1	
26	20:2	
27	20:4ω3	
28	20:5ω3	
29	22:0	
30	22:1	
31	22:5ω3	
32	22:6ω3	
33	23:0	
34	24:0	
35	24:1	

organic components of sediment trap material from Dabob Bay (Hedges *et al.*, 1988b). In addition, the lignin-bearing components of particulate materials collected in the water column of Dabob Bay appear already to have been highly degraded (Hedges *et al.*, 1988a) and should be particularly refractory. The consistently lower carbon-normalized lignin concentrations in all treated 60 m fall samples likely resulted from dilution by swimmers in the <850 μm size fraction, as opposed to any direct effect on lignin preservation. This inference is supported by the elevated weight percentages of organic carbon, lower C/N ratios and higher fluxes of trapped,

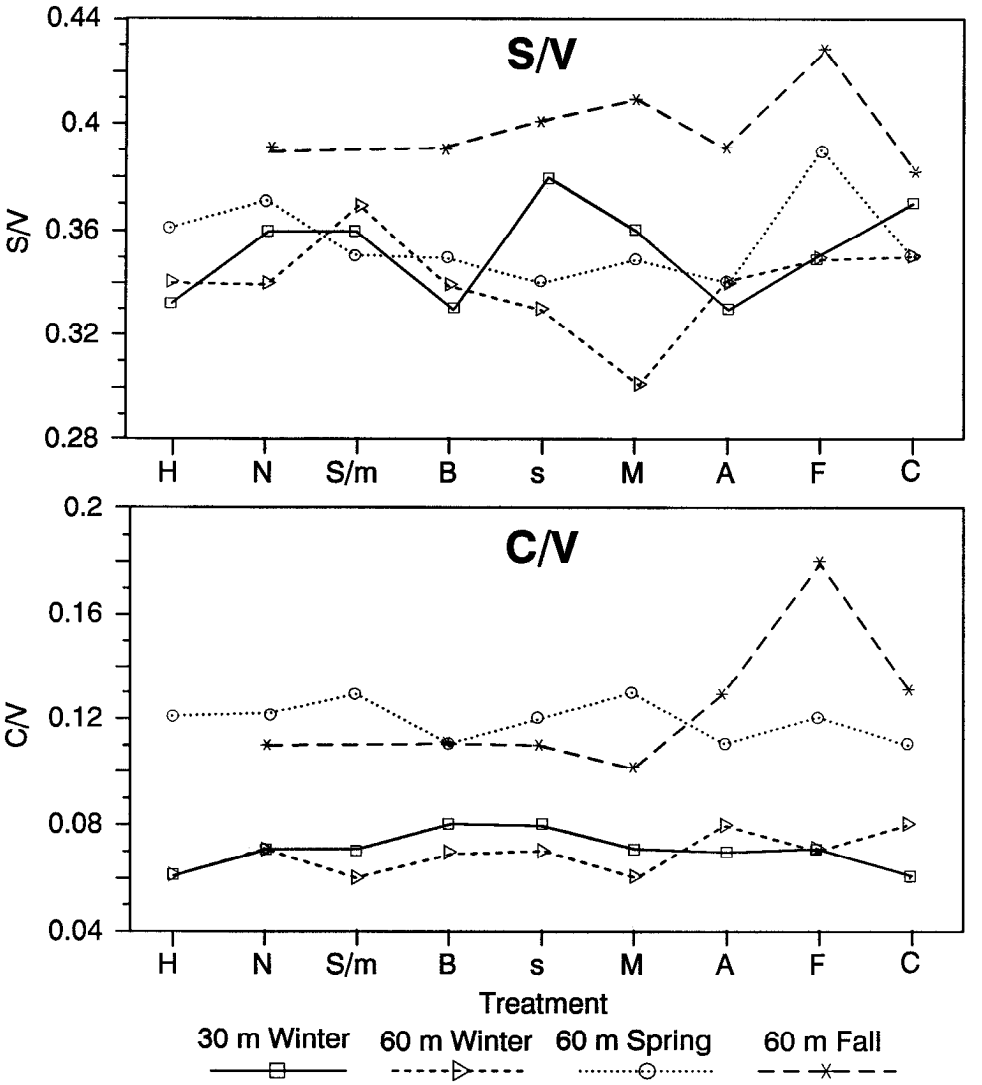

Figure 6. Ratios of syringyl phenols to vanillyl phenols (S/V) and ratios of cinammyl phenols to vanillyl phenols (C/V) vs. treatment. Treatment key as in Figure 1.

large, dead animals (Lee *et al.,* 1992; Hedges *et al.,* 1993) typical of preservative-treated samples collected during this more productive fall period.

d. Pigments

Fluxes of pigments (chlorophyll + pyrophaeophorbide + pheophorbide) were highest in the fall experiment, intermediate in the 60 m winter samples and lowest in spring (Figs. 1 and 7). Although precision of the pigment analyses was ±15–20%,

replication of fluxes between traps on the duplicate winter arrays was poorer, ~ ±35%. The difference between fluxes for the same treatment on duplicate arrays (i.e. arrays A3 and A4 at 30 m and A3 and A4 at 60 m for the winter experiment) was sometimes greater than the difference in fluxes using different treatments. Pigments made up only 0.02 to 0.08% of the total flux of organic carbon. The seasonal trends we observed are consistent with the fact that the fall experiment sampled a strong phytoplankton bloom in Dabob Bay, but there was only a weak bloom during the spring deployment. Fluxes into the 60 m winter traps were greater than into the shallower 30 m winter traps, as was true of the average fluxes of POC and most of the biochemical classes, most likely due to collection in the deeper traps of resuspended bottom sediments (Hedges *et al.,* 1988a,b) and to increased zooplankton grazing as discussed in the next section.

The composition of pigments in the traps (Fig. 7) was similar to previous analyses in Dabob Bay (Downs and Lorenzen, 1985; Welschmeyer and Lorenzen, 1985a,b; Furlong and Carpenter, 1988). Phaeopigments were generally more abundant than chlorophyll-*a*, leading to high phaeopigment to chlorophyll ratios (see Fig. 7). In the fall samples, essentially all of the pigment present was pyro-phaeophorbide. Chlorophyll-*a* was a relatively small fraction of the total pigment composition compared to fresh phytoplankton and upper-water column particulate matter in which Chl-*a* strongly dominates over its degradation products. Elevated fluxes of phaeopigments reflect the intense activity of crustacean grazers in this coastal bay. Grazing between the 30 and 60 m traps may account for part of the increased phaeopigment flux at 60 m in winter compared to 30 m. Fecal pellets or fragments were abundant in the trap material during all of the experiment periods.

It was also interesting to observe that in the 30 m winter traps the demetallated pyro-phaeophorbides were generally more abundant than the hydrolyzed phaeophorbides. This observation is consistent with the greater lability of the magnesium atom of Chl-*a* compared to the phytol-side chain and might reflect variable residence times for the plant-material in the zooplankton digestive system (Bidigare *et al.,* 1985). In this scenario, the pigment distribution in the shallower traps could be "fresher" than that of the deeper traps. The spring and particularly the fall samples were dominated by pyro-phaeophorbide. The absence of Chl-*a* in the fall samples was consistent with intense grazing by zooplankton on the phytoplankton bloom (Downs and Lorenzen, 1985). Intense grazing was also indicated by the great number of large swimmers collected during our study. For example, visual observations on shipboard revealed the presence of large numbers of amphipods clinging to the nylon trap-mooring lines during recovery of the traps.

Although pigments are generally thought to be a relatively labile part of particulate organic matter, there was surprisingly little variation in flux between the different treatments and sampling periods. On the other hand, the major fluctuations in phaeopigment:chlorophyll ratios indicate that significant compositional changes

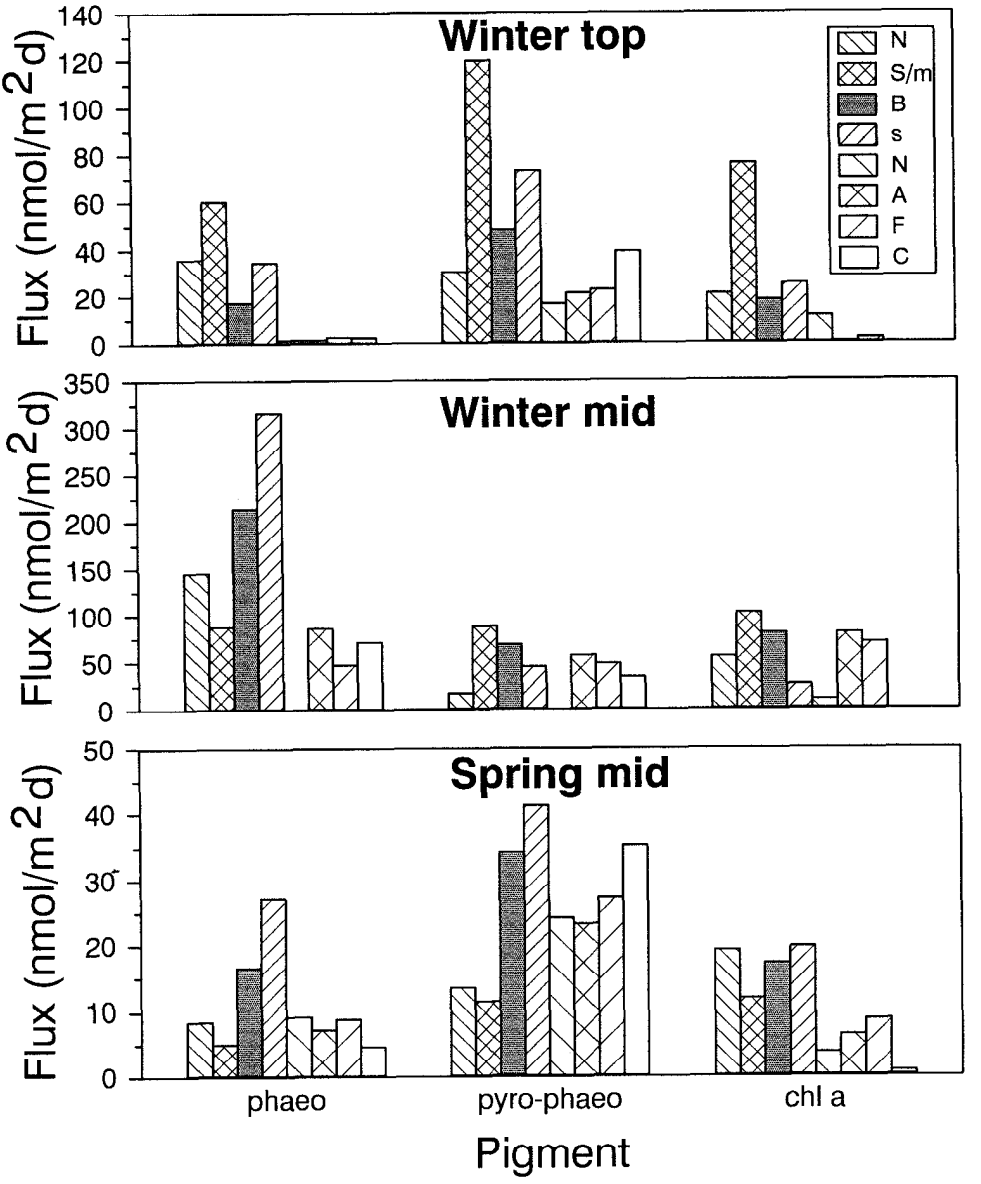

Figure 7. Fluxes (nmol m^{-2} d^{-1}) of individual pigment classes vs. treatment for three experiments. Corresponding data for the Fall experiment are not available. Phaeo = pheophorbides; pyro-phaeo = pyrophaeophorbides. Treatments key as in Figure 1.

did occur for different treatments. Perhaps swimmers sensed the treatments in the traps and, although not killed outright, evacuated their guts into the traps, thus contributing variable amounts of phaeopigments (Peterson and Dam, 1990). Alternatively, small swimmers were likely killed in some of the traps and their gut contents became part of the organic matter pool we analyzed as trap material.

e. Amino acids

Total fluxes of amino acids varied between 8–32 mg C m^{-2} d^{-1} (Fig. 1), with the highest fluxes recorded in spring. Amino acids together make up about 15–34% of the total organic carbon and 41–94% of the total organic nitrogen flux in all the samples. Amino acid concentrations were less variable than were fluxes, and in general, the concentrations were highest in spring (Table 1). Temporal trends in amino acid fluxes and concentrations were similar to the long-term observations of Cowie and Hedges (1992), where elevated amino acid concentrations can be taken as indicating a predominately autochthonous source for these compounds. Seasonal variations in the importance of marine (autochthonous) and terrigenous (allochthonous) organic matter sources to Dabob Bay have been described previously (Cowie and Hedges, 1992, and references therein). Fluxes measured in duplicate arrays (A3 and A4 in winter) varied ±20%, less than for the pigment fluxes. In the winter experiment, the mercury-brine treatment (S/m) gave the highest amino acid flux, most likely due to inclusion of the large number of zooplankton swimmers collected in these traps, but the amino acid concentration was not correspondingly elevated since the swimmers added both amino acids and organic carbon. In the spring and fall experiments, there was no correlation between amino acid flux and large (>850 μm) swimmers collected. No other clear-cut generalizations about differences between the treatments were apparent. Amino acid compositions of particles (e.g. Fig. 8) were typical of marine planktonic material and variations were not obviously related to treatments or seasons. This undoubtedly reflects the lack of specificity of the amino acids from different sources. Trophic transfers of amino acids do not result in significant compositional changes, so that, as opposed to lipids, there is little difference in amino acid composition between phytoplankton and zooplankton and, unlike pigments, between phytoplankton and fecal matter.

There are, however, a few amino acid compositional parameters that provide indications of input vs. decomposition. Muramic acid and the nonprotein amino acids, β-alanine and ornithine, have been used as evidence for bacterial transformation of particulate matter (Lee and Cronin, 1982, 1984; Lee *et al.,* 1983). These components were not detected in the trap samples from our experiments, suggesting that little decomposition occurred. Increased abundances of serine, threonine, and glycine in deep-sea particles have been used as indicators of preferential preservation of a protein-silica complex derived from diatom cell walls (Hecky *et al.,* 1973;

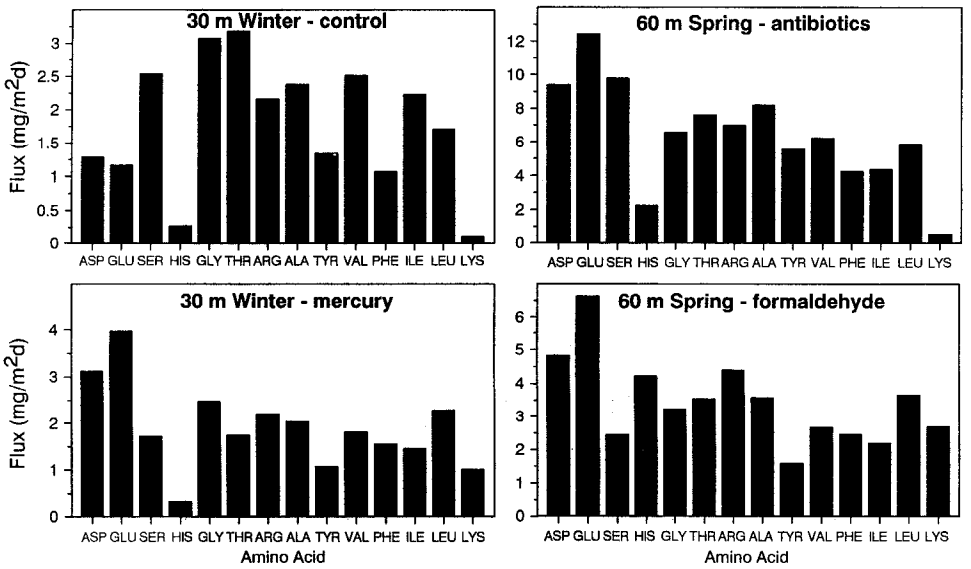

Figure 8. Fluxes (mg m^{-2} d^{-1}) for individual amino acids in selected traps. ASP, aspartic acid; GLU, glutamic acid; SER, serine; HIS, histidine; GLY, glycine; THR threonine; ARG, arginine; ALA, alanine; TYR, tyrosine; VAL, valine; PHE, phenylalanine; ILE, isoleucine; LEU, leucine; LYS, lysine.

Lee and Cronin, 1984; Cowie and Hedges, 1992). In the Dabob Bay traps, the percentage which glycine, for example, contributed to the total amino acid content (Fig. 9) varied between 6.5 and 13% with treatment and season but systematic trends are difficult to discern. The untreated spring and fall traps were enriched in glycine relative to treated traps from the same experiment, perhaps suggesting decomposition in these traps. Amino acids derived from calcareous organisms are characterized by high amounts of aspartic acid while siliceous organisms favor production of glycine. Thus, the aspartic acid:glycine ratio has been used as an indicator of relative inputs from calcareous vs. siliceous sources (Ittekkot *et al.,* 1984). Again, there were variations in the aspartic acid/glycine ratio within our trap data, although all ratios fall within the range reported earlier for the Panama Basin (Ittekkot *et al.,* 1984). Ratios of aspartic acid:glycine greater than unity can indicate a predominance of calcareous over siliceous organisms.

In the winter experiments, the flux of amino acids increased between 30 and 60 m for some treatments (e.g. N, S/m, B, s, F and C) but not for others (M and A). On the other hand, the proportion of C and N made up by amino acids decreased with depth in the same treatments (Fig. 1). The downward increasing fluxes were also observed for sugars (see below). Such trends are not surprising since the flux of bulk particulate material and most organic components typically increases with depth in Dabob Bay, most likely due to local resuspension of sediments poor in labile organic

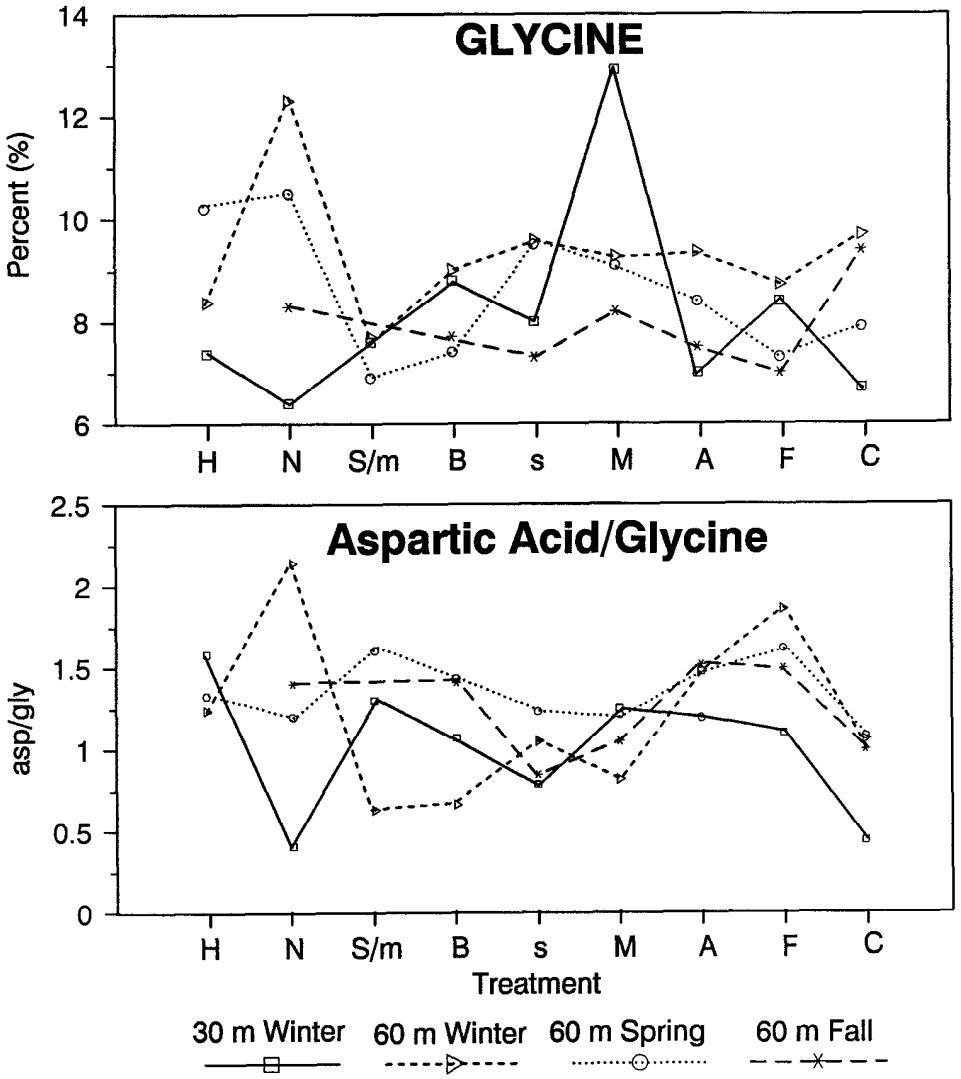

Figure 9. Percent glycine and aspartic acid/glycine ratios vs. treatment. Treatment key as in Figure 1.

matter (Hedges *et al.*, 1988b). The absence of a drop in amino acid flux between the 30 m and 60 m winter traps thus is likely due to a slightly larger number of protein(sugar)-rich swimmers collected in the upper traps that were treated with more potent poisons. Lipid compositions discussed above also indicate a preferential collection of swimmers in the shallower traps.

Another factor which could explain a loss of material in the treated samples is dissolution. Amino acids and proteins are some of the more soluble compounds we

analyzed. Our analyses of the trap brine solutions show extremely high DFAA concentrations (Lee *et al.,* 1992) indicating that dissolution is occurring. However, we do not yet know whether this might be a significant loss mechanism for the particulate pool. If so, it is surprising that the sugars did not show a similar loss. However, they may be present in a less soluble form.

f. Sugars

Polysaccharides are common structural and storage compounds in both marine and terrestrial organisms. Earlier studies suggested that individual neutral sugars (aldoses) released by hydrolysis together comprise roughly 5–15% of the total organic matter in sediment trap materials from Dabob Bay (Hedges *et al.,* 1988a) and appear to have mixed marine and terrestrial sources (Cowie and Hedges, 1984b). Fluxes of aldoses measured in our experiments ranged between 13–40 mg C m^{-2} d^{-1} (Fig. 1) with highest values in fall and lowest in winter. Carbon-normalized total aldose concentrations fell in the relatively narrow range of 20–28 mg/100 mg OC (Table 1), with no consistent patterns apparent with depth or season. These sugar concentrations are somewhat higher than those obtained for plankton but distinctly lower than concentrations characteristic of fresh vascular plant material (Cowie and Hedges, 1984b).

Typical aldose compositions for selected samples are shown in Figure 10. Relatively little compositional variation was observed. Three different aldose composition parameters (Hedges and Mann, 1979) were investigated as possible indicators of carbohydrate sources and treatment effects. These parameters included the combined weight percentage (on a glucose-free basis) of ribose plus fucose, %(RIB + FUC)b, which can be used to distinguish microbial (high ratio) versus vascular plant (low ratio) carbohydrate sources. The second parameter was the combined weight percentage (on a glucose-free basis) of lyxose plus arabinose, %(LYX + ARA)b, which distinguishes nonwoody vascular plant tissues from other aldose sources depleted in these compounds. The third indicator was the weight percent of glucose. This relatively reactive aldose was chosen because it might reflect the diagenetic state of the sample material (Hedges *et al.,* 1988b; Hamilton and Hedges, 1988).

The observed range of %(LYX + ARA)b in all of the sediment trap samples (Fig. 11) was narrow (8–12%) and apparently unrelated to any characteristic of the collection conditions. The parameter, %(RIB + FUC)b, exhibited more variability (11–17%) and generally was higher in the 60 m spring traps, likely due to slightly stronger bloom conditions than in winter. Weight percentages of glucose varied from about 28–40% and were typically lower in spring. This might be due to a greater input of glucose-poor plankton material during this time (Hedges *et al.,* 1988a).

None of the previously discussed aldose yield or composition parameters varied consistently with treatment. The absence of a signal due to small swimmers may

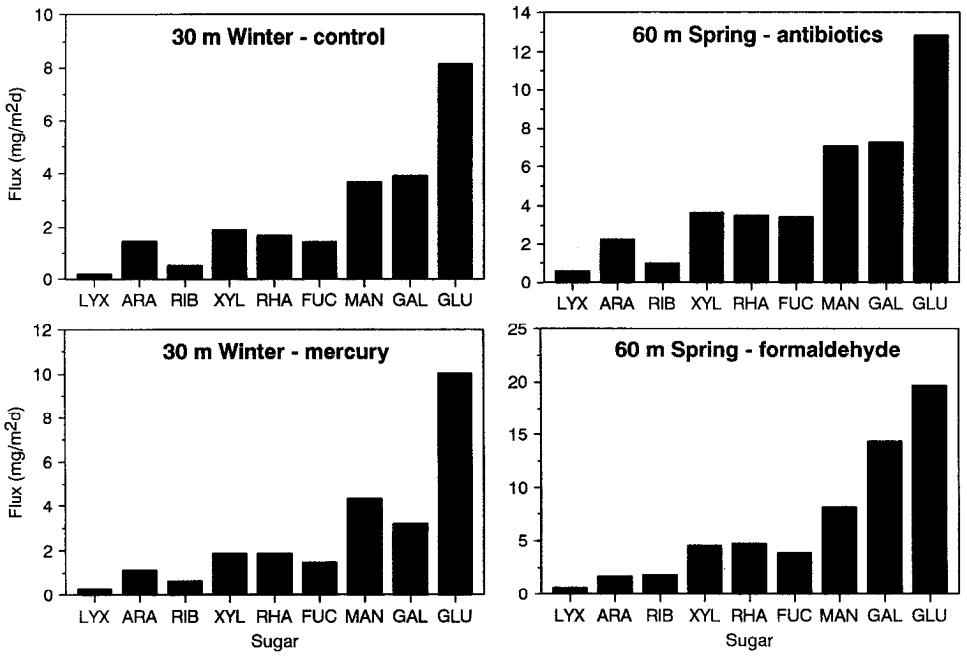

Figure 10. Fluxes (mg m^{-2} d^{-1}) for individual sugars in selected sediment traps for several experiments. LYX, lyxose; ARA, arabinose, RIB, ribose; XYL, xylose; RHA, rhamnose; FUC, fucose; MAN, mannose; GAL, galactose; GLU, glucose.

result from the fact that the aldose content and composition of zooplankton is generally similar to that of the trap material (Cowie and Hedges, 1984b), minimizing the dilution effect. In general carbohydrate compositions seemed to be insensitive to treatments. This result is somewhat surprising because aldoses, and especially glucose, are among the most reactive measured components of sediment trap materials in Dabob Bay and suffer extensive (50–70%) degradation at the water/sediment interface (Hedges *et al.,* 1988b). Degradation rates, however, may be too slow to produce measurable compositional trends in the course of approximately month-long tests, where the average residence time of material in the traps is only half that time.

g. Major biochemical inventory

One goal of the comprehensive analytical scheme employed in this study was to make possible an estimate of the fraction of total organic carbon which could be accounted for by lipids, lignin, pigments, sugars and amino acids, the major biochemical classes for which detailed structural analyses are currently possible. Previous studies have provided the contribution of single or several compound classes to total POC. For example, lipids typically comprise some 1–5% of upper ocean particulate

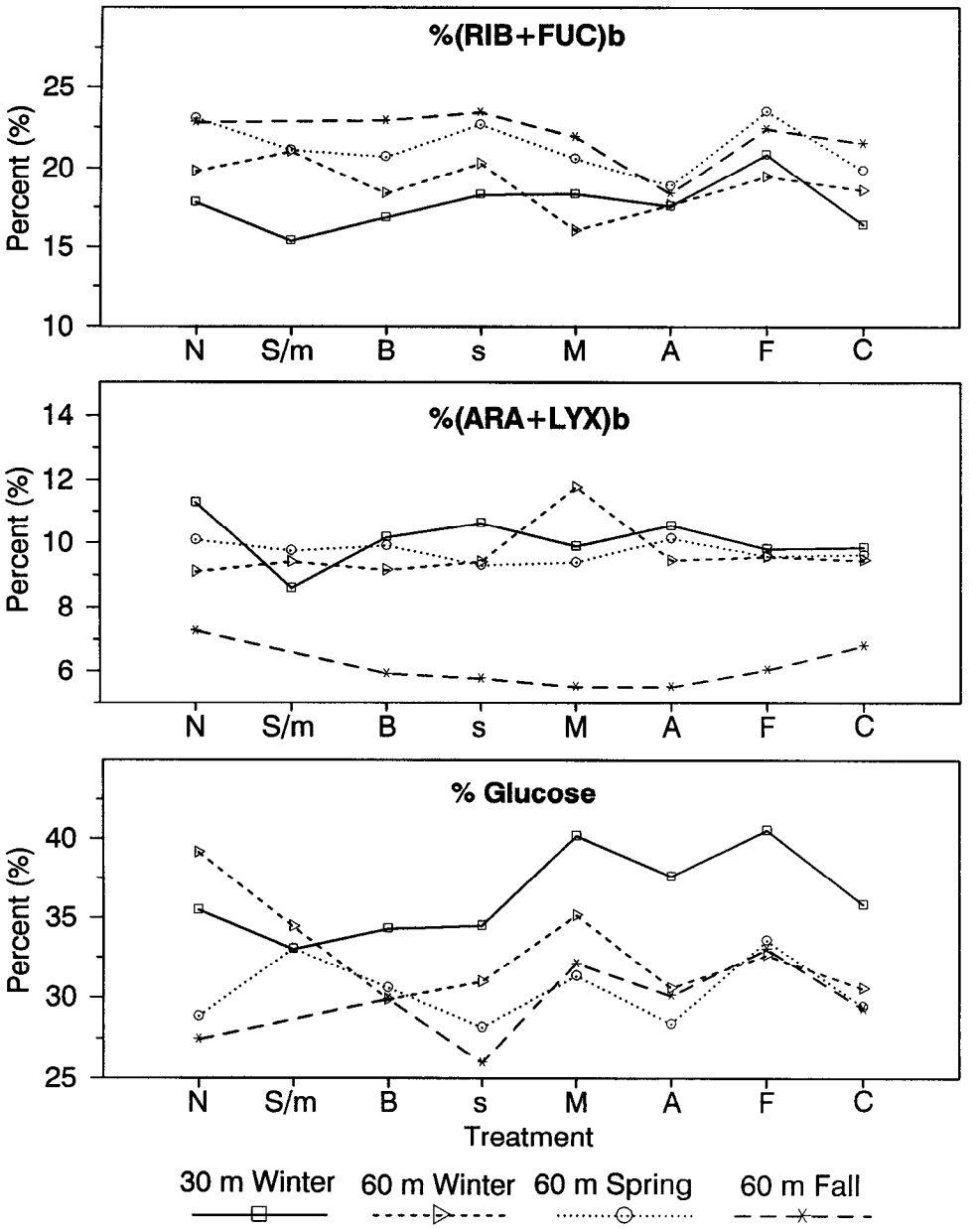

Figure 11. Weight percentages (on a glucose free basis) of ribose + fucose [%(RIB + FUC)b] and arabinose plus lyxose [%ARA + LYX)b] and weight percent of glucose (%GLUCOSE) vs. treatment. Treatment key as in Figure 1.

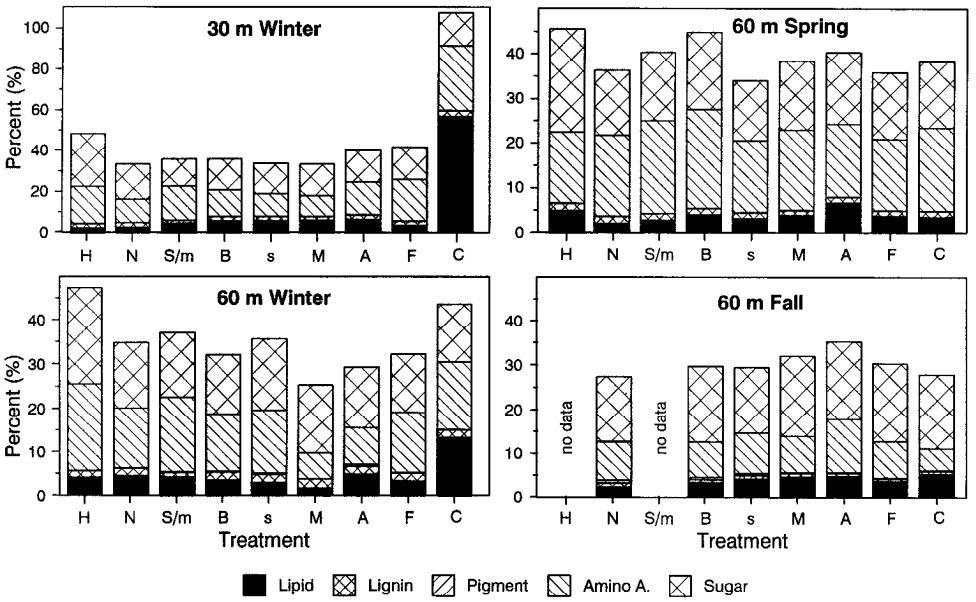

Figure 12. Cumulative compound class composition (compound class-C as percent of POC) vs. treatment. Compound class-carbon was estimated assuming lipid to be 85% carbon, lignin to be 60% carbon, amino acids to be 40% carbon, and sugars to be 45% carbon. Treatment key as in Figure 1.

organic matter (Wakeham *et al.,* 1980; Wakeham and Lee, 1989). About 10–50% of the organic carbon in oceanic particles is present in amino acids (Lee and Cronin, 1984). In previous Dabob Bay investigations (Hedges *et al.,* 1988a; Cowie and Hedges, 1992), lignin, polysaccharides, and amino acids were calculated to account for 0.5–7%, 6–14%, and 13–37%, respectively, of organic carbon in sediment trap material. In those studies, combined lignin/polysaccharide/amino acid-carbon averaged 37% of the total OC at 30 m depth, with a winter low of ~30% and a maximum of 53% in June. The contributions made by polysaccaharides were highest in summer, while the organic carbon contributed by lignin was highest in winter. This observation is consistent with the seasonal nature of marine vs. non-marine inputs of material to the water column of Dabob Bay.

We estimate that the five classes we measured account for 25–47% of organic carbon in our samples (Fig. 12). Discounting the chloroform treated traps in the winter experiment, which contain unrealistically high amounts of lipid, there are no significant differences between treatments or season (30 m winter mean = 36 ± 3%; 60 m winter = 33 ± 4%; 60 m spring = 39 ± 3%; 60 m fall 30 ± 3%). This consistency may be somewhat surprising considering the variability noted for some of the individual classes. It should be noted, however, that the major variations in flux of the organic compound classes were for relatively minor constituents, for example lipids,

whereas the major classes, amino acids and sugars, were more constant. One trend in the compound concentration data that we observed was the tendency for the untreated samples that were harvested daily to have a slightly higher flux of the major biochemicals relative to organic carbon than in the untreated controls that were allowed to remain in the traps during the deployment. This was particularly true for the amino acids and sugars. The daily harvest samples are the closest we could come to representing unaltered sinking material. This depletion in major biochemicals relative to total carbon could occur due either to preferential zooplankton grazing on the most labile material in the control trap or to microbial decomposition. Zooplankton grazing of particles in untreated traps has been observed indirectly in Lake Greifen (Lee *et al.,* 1987) and directly, via videocamera recorder, in traps from Port Susan, WA (unpublished).

The inability to account for roughly two-thirds of total organic carbon in our analyses is not out-of-line with expectations. While there have not been comparable inventories of particulate organic matter composition in the ocean, a survey of the literature dealing with individual classes of biochemicals leads to the conclusion that achieving a balance is not presently possible and that roughly half of the particulate organic matter in the marine water column consists of material that is not readily characterized at the molecular level, the abiotic "geomacromolecules" such as described by Tegelaar *et al.* (1989).

4. Overview

No outstanding aldose or lignin compositional differences were observed among synoptic samples receiving different treatments, but lipid compositions varied depending on the observed contribution of swimmers to trap material. We conclude that inclusion of only a few lipid-rich swimmers may have a major deleterious impact on the accuracy of measured lipid fluxes and on the lipid composition of the collected particulate matter, even though mass and POC flux may appear relatively unaffected. Amino acid and pigment fluxes showed high variability between treatments, but were not correlated with either the treatment used or the number of swimmers collected. These two compound classes are probably the most labile and thus subject to both preservation and swimmer effects.

Every one of the treatments that effectively limited microbial activity also resulted at some time in a swimmer artifact. Based on our chemical analyses, the major effect of the different treatments was the addition of relatively low masses of small (<850 μm) swimmers to treated samples collected during the spring. No compositional or flux differences were observed for any of the components discussed here that could be confidently sorted out and ascribed to improved preservation alone. On the other hand, certain aspects of lipid composition, such as wax ester content, clearly could be attributed to inclusion of swimmers.

These results do not conclusively indicate that poison/preservative/inhibitor

treatments should be avoided in sediment trap collections. The compositional effects of *in situ* degradation might be much greater for biochemicals such as lipids and amino acids that are more labile than lignins and aldoses. In addition, more extensive degradation no doubt would transpire over longer deployment periods and/or during stronger plankton blooms than occurred in our study periods. Although logistically more difficult, chemical differences in treatment effects might be more easily measured in the open ocean, away from the constant background of relatively refractory land-derived organic matter typical of coastal zones such as Dabob Bay.

Zooplankton pose a serious problem for sediment trap applications whether treatments are used or not. Even within untreated traps, living zooplankton can lead to elevated fluxes by defecating or natural death. In addition, zooplankton can feed on the accumulated particulate material and change its composition or mass, especially if they leave before defecating. As demonstrated here, any treatment that is lethal to zooplankton can lead to unnaturally large collections of these organisms.

In the case at hand, it is particularly difficult to discriminate whether elevated levels of labile biochemicals (such as amino acids and many lipids) in treated traps result from enhanced preservation or from an induced input of zooplankton swimmers rich in these compounds. In some cases, the impact of swimmers is particularly evident based on the lipid results. Inserted screens fine enough to exclude small zooplankton from trap bottoms are not effective barriers for poison loss and tend to clog, exposing the collected material to washout or reingestion (Hedges *et al.,* 1993). Most barriers that would physically exclude swimmers from a poisoned holding chamber also would bar naturally dead zooplankton "sinkers" that may at some times constitute a significant flux of organic matter.

Our work to date indicates that a variety of treatments are effective (at least under moderate bloom conditions) in essentially stopping microbial activity in sediment traps under field conditions (Lee *et al.,* 1992). The real challenge is to design a dependable sediment trap that can retain these treatments for long time periods (months to years) under conditions where the swimmer effect is minimized—without excluding passively sinking large particles or exposing the collecting material to washout or reingestion. Several designs have been proposed and are currently undergoing field evaluations (Coale, 1990; Peterson *et al.,* 1993).

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