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Release rates of trace elements and protein from decomposing planktonic debris. 2. Copepod carcasses and sediment trap particulate matter

by John R. Reinfelder[1,2], Nicholas S. Fisher[1,3], Scott W. Fowler[4] and Jean-Louis Teyssié[4]

ABSTRACT

In experiments designed to relate the release kinetics of various elements with that of protein from biogenic particles, ^{110m}Ag, ^{241}Am, ^{109}Cd, ^{60}Co, ^{75}Se and protein were measured over time in radiolabeled copepod carcasses and particles caught in unpoisoned sediment traps (mostly zooplankton fecal pellets and amorphous marine snow). Log-linear release rate constants (k) of ^{110m}Ag, ^{241}Am, ^{109}Cd, and ^{60}Co from carcasses ranged from 0.079 d^{-1} for ^{60}Co at 2°C to 0.130 d^{-1} for ^{109}Cd at 15°C, and did not vary significantly with temperature. ^{75}Se was lost most rapidly from copepod carcasses at 2°C, with k = 0.168 d^{-1}; however, at 15°C, ^{75}Se was in two compartments, with 56% in a rapidly exchanging pool (k = 0.391 d^{-1}) and 44% in a slowly exchanging pool (k = 0.107 d^{-1}). Protein displayed loss from two compartments at both temperatures. At 2°C, protein was lost slowly (k = 0.065 d^{-1}) for 1 wk, after which it was released from the carcasses very rapidly (k = 0.245 d^{-1}). At 15°C, however, the loss of protein from carcasses was more rapid over the first 2 d (k = 0.627 d^{-1}) than thereafter (k = 0.127 d^{-1}).

The k values of ^{110m}Ag, ^{241}Am, and ^{60}Co from sediment trap particles (15°C) ranged from 0.008 to 0.011 d^{-1}. Protein was lost twice as fast as ^{110m}Ag, ^{241}Am, and ^{60}Co, more slowly than half of the particulate ^{109}Cd and ^{75}Se in rapidly exchanging pools (k = 0.168 and 0.237 d^{-1}, respectively), and at rates comparable to ^{109}Cd and ^{75}Se in slowly exchanging pools. Overall, copepod carcasses and fecal pellets could act as vectors of these five elements and protein to the deep ocean, the vertical flux being dependent on settling velocity and water column temperature structure. Of the elements considered here, Se follows the cycling of protein most closely.

1. Introduction

Sinking particulate matter, notably sinking biogenic debris, mediates the vertical transport and geochemical cycling of a variety of particle-reactive metals and

1. Marine Sciences Research Center, State University of New York, Stony Brook, New York, 11794-5000, U.S.A.
2. Present address: Ralph Parsons Laboratory, Department of Civil Engineering, MIT, Cambridge, Massachusetts, 02139, U.S.A.
3. To whom reprint requests should be sent.
4. IAEA Marine Environment Laboratory, B. P. 800, MC 98012 Monaco.

metalloids in marine systems (Fowler and Knauer, 1986). Models describing the impact of sinking debris on the vertical flux of metals require estimates of the retention times of the metals in the debris as it undergoes decomposition during its descent in the water column (Fisher and Fowler, 1987). Moreover, the processes governing the release of metals from decomposing particles have not been well characterized in marine systems. Therefore, studies have recently been conducted to determine the release rates of a variety of metals from diverse forms of decomposing planktonic debris (Fisher *et al.,* 1991b; Fisher and Wente, 1993; Lee and Fisher, 1992a,b).

Many essential and non-essential metals are known to associate with protein in organisms. Class B metals associate with protein due to their strong affinity for sulfur, while class A metals bind mainly to oxides (Nieboer and Richardson, 1980). Additionally, many metals associate with protein as essential cofactors of specific enzymes or enzyme systems (Sunda, 1989). In surface waters, particulate protein is produced by phytoplankton, consumed by grazing zooplankton and removed through microbial and chemical remineralization processes and the sinking of biogenic particles. The turnover rates of dissolved amino acids in seawater are well studied (protein less so), but release rates of protein from particles have received comparatively little attention (Smith *et al.,* 1992). Some metals may be released from planktonic debris in direct proportion to the release of protein, while other metals may display no significant relationship with protein release, although such data are generally unavailable for marine systems.

To address this issue, we have conducted a series of radiotracer experiments in which the release of metals from zooplankton carcasses and from marine snow collected with unpoisoned sediment traps was determined simultaneously with measurements of protein release from these debris. We contrasted the behaviors of the metalloid Se, the transition metals Ag, Cd and Co, and the transuranic actinide Am.

Only two of these elements (Se and Co) have been shown to be essential to living organisms. Se may be expected to associate with protein, behaving somewhat similarly to S in organisms (Bowen, 1966); in surface waters organic selenides can be the dominant form of Se (Cutter and Bruland, 1984). Ag and to a lesser extent Cd have very strong affinities for S (Sillén and Martell, 1964) and may be expected to associate with protein in organisms. Cd can be assimilated from food with a high efficiency in planktonic invertebrates (Sick and Baptist, 1979; Reinfelder and Fisher, in prep.). Moreover, Ag, inorganic Se, and Cd display oceanic profiles similar to major nutrients (Whitfield and Turner, 1987; Cutter and Bruland, 1984) and may be recycled along with particulate organic carbon in surface waters. By contrast, Co and Am are scavenged metals (Whitfield and Turner, 1987; Clegg and Sarmiento, 1989) which do not display comparable recycling in surface waters. Am has no known biological function and is bound principally to organism surfaces, probably to

hydroxyl groups or oxide surfaces (Fisher *et al.,* 1983b). Am and Co display consistently low assimilation efficiencies in copepods (Reinfelder and Fisher, 1991; Fisher *et al.,* 1991a), and it may be expected that these metals would not directly follow protein in their release from decomposing debris.

2. Materials and methods

a. Radioactive copepods. The pontellid copepod *Anomalocera patersoni* was collected from surface waters off the coast of Monaco in the Ligurian Sea by several horizontal tows using a 333 μm nylon mesh. Copepods were carefully removed from the collection cup and maintained in the laboratory in glass fiber-filtered (1.6 μm effective retention) Mediterranean surface seawater (GFSW) and fed the diatom *Thalassiosira pseudonana* (clone 3H), which was grown in sterile filtered (0.2 μm Nuclepore) Mediterranean surface seawater (SFSW) enriched with f/2 nutrients (Guillard and Ryther, 1962). Copepods were acclimatized to laboratory conditions for 2 d before being fed radiolabeled diatoms, following established procedures (Fisher and Reinfelder, 1991; Reinfelder and Fisher, 1991).

To produce radioactive diatoms, *T. pseudonana* cells were resuspended off a sterile 1 μm Nuclepore filter into 1 l of SFSW enriched with f/2 nutrients, but with no added Cu, Zn or EDTA. The initial cell density was adjusted to 4×10^4 cells ml^{-1} (=900 μg dry wt. l^{-1}). To these resuspended cells, 37 kBq ^{241}Am, 740 kBq ^{109}Cd, 37 kBq ^{110m}Ag, 222 kBq ^{60}Co, and 74 kBq ^{75}Se were added, resulting in concentrations of 1.21 nM, 39 nM, 286 nM, 3.11 nM, and 10.1 nM for each radionuclide, respectively. The ^{241}Am was added to the diatom culture flask in 5 μl of 3N HNO_3, the ^{109}Cd in 306 μl of 0.1 N HCl, the ^{110m}Ag in 25.4 μl of 0.1 N HNO_3, the ^{60}Co in 19 μl of 0.1 N HCl, and the ^{75}Se in 75 μl of 0.5 N NaOH. The pH of the uptake culture was maintained at 8 with the addition of 8 μl of 1 N NaOH immediately prior to radioisotope addition. After 5 d, the cell density of the culture had increased to 1.7×10^5 cells ml^{-1}. All of the radiolabeled cells were collected on sterile 1 μm Nuclepore filters and resuspended into 800 ml of radioisotope-free SFSW to which ~600 copepods were added.

The copepods were fed labeled diatoms in the dark at 15°C for 18 h, after which they were collected on a 333 μm Nitex mesh, rinsed with 10 ml SFSW and allowed to expire by asphyxiation over 1 h. The copepod carcasses were divided into two batches of 140 and 400 individuals for metal and protein release at 2 and 15°C, respectively. At both temperatures, carcasses were held in the narrow ends of plastic funnels (2 cm diam.) which were covered with 333 μm Nitex mesh. Each funnel rested in a beaker containing 600 ml of GFSW. Over the course of 14 d for the carcasses held at 2°C, and 9 d for those maintained at 15°C, the radioactivity of all carcasses in each of the funnels was measured and three whole animals were removed for individual protein analysis. After each sampling time, the remaining carcasses were returned in their funnels to a new 600 ml of radioisotope-free GFSW.

Table 1. Percent (by number) of total biogenic sediment trap particles identifiable by light microscopy, and the volume of individual zooplankton fecal pellets of each type. Values based on examination of an aliquot of the sediment trap sample.

	%	Vol. (μm^3)
Foraminifera	0.8	
Fish fecal pellets	0.8	
Zooplankton fecal pellets	98.4	
Cylindrical	27.7	6.5×10^7
Ellipsoid I (dark)	48.0	3.2×10^7
Ellipsoid II (light)	3.3	4.9×10^6
Spherical	19.3	8.7×10^6
Tabular	1.7	7.4×10^7

b. Radioactive sediment trap particles. Sinking particulate matter was collected in the Ligurian Sea in the area of copepod collection with an unpoisoned, moored sediment trap (Fowler *et al.,* 1991) deployed at 80 m (water temperature approx. 14°C) for 4 d. Methodologies for preparing and processing sediment trap samples have been described in detail elsewhere (Monaco *et al.,* 1987; Heussner *et al.,* 1988). Zooplankton "swimmers" were removed by first sieving the particles through 1500 and 600 μm mesh netting and subsequently hand-picking the remaining organisms under a dissecting microscope (Michaels *et al.,* 1990). The remaining particulate material was rich in biogenic debris with numerous plankton remains, zooplankton fecal pellets and flocculent mucous aggregates. The identifiable contents are described in Table 1. There were numerous foraminifera as well as fish fecal pellets (Heussner *et al.,* 1987). Most of the zooplankton fecal pellets were either ellipsoid (51%) or cylindrical (28%) in shape (Table 1) and were typical of those produced by copepods in these coastal waters (Teyssié *et al.,* 1990). Overall, the varied composition of the material was similar to what has been termed "marine snow" (Alldredge and Silver, 1988).

After removing the overlying seawater, 14 ml of the total 20 ml of sediment in one of the trap's two collection cups was transferred to a 60 ml capped plastic beaker and incubated with 37 kBq ^{241}Am, 740 kBq ^{109}Cd, 37 kBq ^{110m}Ag, 222 kBq ^{60}Co, and 74 kBq ^{75}Se for 18 h. As with the phytoplankton uptake culture, 8 μl of 1 N NaOH was added to the particulate material to maintain a pH of 8.

Following uptake of the five radioisotopes by the particles, 50 ml of SFSW was added to the incubation beaker. The slurry was swirled and the particles allowed to settle. After all visible particulate matter had settled ($\sim$4 h), 60.4 ml of overlying seawater were removed, leaving 4.04 ml of sediment on the bottom. Gamma radioactivity of the entire volume of settled particles was measured without removing it from the beaker. Triplicate 50 μl subsamples of the particles were then taken for protein analysis, after which 50 ml of radioisotope-free GFSW was added to the beaker. For subsequent samples, taken over a period of 5 months, the same protocol was followed except that GFSW was added to the particulate matter in volumes

equal to what was removed. Aliquots of overlying water were also measured for radioactivity and contained virtually all the radioactivity released from the particles; this radioactivity was in dissolved form (passing through 0.2 μm Nuclepore membranes). Throughout the 5-month incubation, the particles were held in the dark at 15°C.

The physical character of the particles changed suddenly on the 10th day of the loss experiment, from a heterogeneous mass of stringy strands to a homogeneous, fine-grained sediment. Representative samples (50 μl) for protein analysis were difficult to obtain during the initial 10 d of release. Total protein weights measured in the particles while they were still in a heterogeneous form varied randomly among sampling times and were significantly lower than protein weights measured at time zero and after the particles became homogeneous. These observations suggest that unequal amounts of the particulate matter were sampled during the first 10 d and that protein was incompletely extracted from the stringy material. A reliable time zero protein measurement was obtained because 2 ml of the original 20 ml of freshly collected sediment trap material had been pre-homogenized in 8 ml TRIS-HCl (pH = 8) before protein analysis. Results for the particle protein weights are therefore given for samples from time zero and from 10 d through 161 d.

c. Analytical methods. Protein was determined with the BCA protein assay (Smith *et al.,* 1985) which is specific for quantification of peptide bonds. The variability in protein content among individual copepod carcasses was fairly large, with a mean coefficient of variation of 21%. The mean coefficient of variation for protein content among sediment trap particulate matter subsamples was 6.2%.

The radioactivity of all samples was measured with a high-purity GeLi detector interfaced to a multichannel analyzer and a computer equipped with spectra-analysis software, as described elsewhere (Fisher *et al.,* 1991b). The gamma emissions of ^{241}Am were measured at 60 keV, ^{109}Cd at 88 keV, ^{110m}Ag at 658 keV, ^{60}Co at 1333 keV, and ^{75}Se at 136 keV. Counting times ranged from 5 to 10 min and propagated counting errors were generally $<5\%$. All measurements were corrected for radioactive decay and loss of mass during sampling.

C and N were analyzed by high temperature oxidation using a Heraeus CHN-O-RAPID elemental analyzer. The organic C fraction was measured in samples pre-treated with 1 M H_3PO_4 to remove carbonates. Samples were run in duplicate and analytical errors for each replicate were 9.5% for N, 0.7% for total C, and 5.5% for organic C.

3. Results

After being placed into unlabeled seawater, the copepod carcasses lost radioisotopes into the dissolved phase at different rates (all losses reported reflect net losses

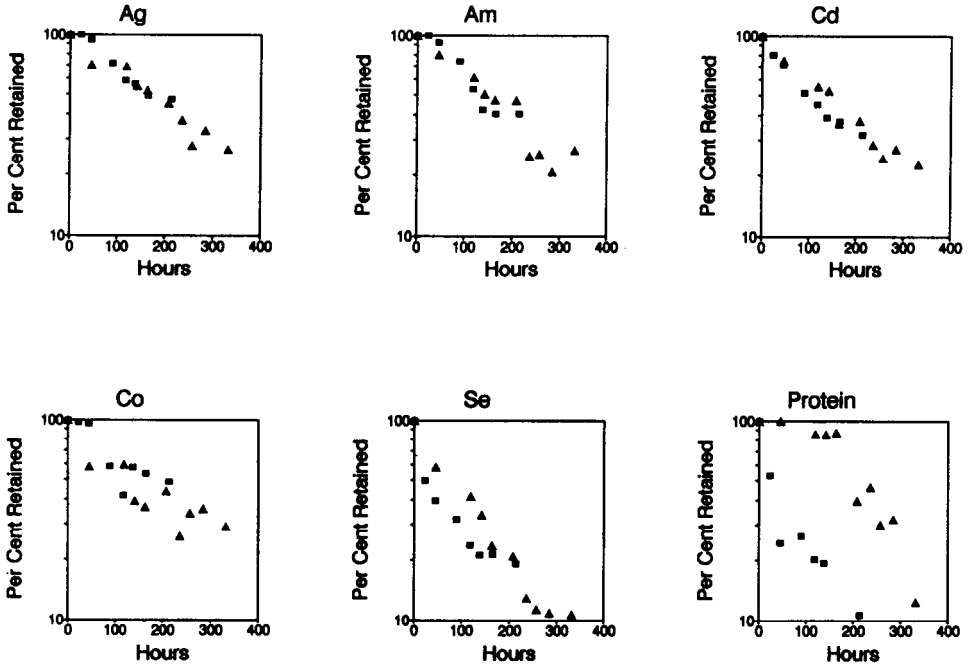

Figure 1. Retention (%) over time of ^{110m}Ag, ^{241}Am, ^{109}Cd, ^{60}Co, ^{75}Se, and protein in *A. patersoni* carcasses incubated at 2°C (▲) and 15°C (■).

from particles) (Fig. 1). Loss of ^{110m}Ag, ^{241}Am, ^{109}Cd and ^{60}Co conformed to a single compartment model, whereas loss of ^{75}Se conformed with a two-compartment model at 15°C but one compartment at 2°C and loss of protein conformed with a two-compartment model at both temperatures; compartmental analysis was conducted according to Comar (1955). Release rate constants (k) describing loss from the carcasses and retention half-times ($tr_{1/2}$s) in the particulate phase, both calculated from least squares fits of the log-linear data, are given in Table 2. Of the radioisotopes examined, ^{75}Se was lost at the greatest rate into the dissolved phase, while the rates of loss of ^{241}Am, ^{109}Cd, ^{60}Co, and ^{110m}Ag did not differ significantly from one another (Fig. 1, Table 2). The $t_{r1/2}$s of ^{75}Se at 15°C ranged from 1.8 d in the rapidly exchanging pool to 6.5 d in the slowly exchanging pool. The other radioisotopes had $t_{r1/2}$s of about 6–9 d at 2°C and of about 5–7 d at 15°C (Table 2). The $t_{r1/2}$s for protein were 10.6 d in the slowly exchanging pool (approx. 30% in pool) and 2.8 d in the rapidly exchanging pool at 2°C (approx. 70% in pool). At 15°C, the $t_{r1/2}$s of protein ranged from 1.1 d in the rapidly exchanging pool (about 64% in pool) to 5.5 d in the slowly exchanging pool (about 36% in pool). The overall $t_{r1/2}$ of protein at 2°C was 8.0 d (calculated by using 50% of the total protein lost); overall $t_{r1/2}$s for ^{75}Se and protein at 15°C are described by the release kinetics of the first, rapidly exchanging compartments.

Table 2. Log-linear release rate constants (k) and retention half-times ($t_{r1/2}$) of five radioisotopes and protein from copepod carcasses. (1) = first compartment; (2) = second compartment.

	2°C			
	% in pool	k (d^{-1})	std error	$t_{r1/2}$ (d)
^{110m}Ag	100	0.0933	0.0085	7.4
^{241}Am	100	0.1159	0.0141	6.0
^{109}Cd	100	0.1103	0.0087	6.3
^{60}Co	100	0.0789	0.0157	8.8
^{75}Se	100	0.1678	0.0131	4.1
protein-slow (1)	30	0.0652	0.0143	10.6
protein-rapid (2)	70	0.2450	0.0430	2.8
	15°C			
	% in pool	k (d^{-1})	std error	$t_{r1/2}$ (d)
^{110m}Ag	100	0.0999	0.0091	6.9
^{241}Am	100	0.1275	0.0159	5.4
^{109}Cd	100	0.1304	0.0107	5.3
^{60}Co	100	0.0955	0.0244	7.3
^{75}Se-rapid (1)	55.6	0.3906	0.1373	1.8
^{75}Se-slow (2)	44.4	0.1066	0.0209	6.5
protein-rapid (1)	63.6	0.6269	0.0626	1.1
protein-slow (2)	36.4	0.1269	0.0290	5.5

Temperature had a major effect on protein loss from the decomposing animals (Fig. 1), as would be expected due to microbial decomposition. After 1 wk incubation, only 20% of the protein remained in particulate form at 15°C, compared with almost 70% at 2°C, and after 9 d incubation only about 10% of the protein was particulate at 15°C while 30–40% was particulate at 2°C. The $t_{r1/2}$ of ^{75}Se in the slowly exchanging pool at 15°C was about 50% greater than its $t_{r1/2}$ at 2°C, but 56% of the ^{75}Se was in the rapidly exchanging pool at 15°C ($t_{r1/2}$ = 1.8 d) (Table 2). In contrast, the kinetics of release of ^{241}Am, ^{109}Cd, ^{60}Co and ^{110m}Ag were much less affected by temperature (Fig. 1, Table 2). Generally, there was slightly greater variability in the slope (release rate) data from the 15°C samples than from the 2°C samples, with the mean coefficient of variation being 17.8% in the former and 13.8% in the latter.

To compare radioisotope release rates with those of protein, Figure 2 displays the ratios of radioisotope:protein in the particulate phase over the course of the incubations at both temperatures. The initial radioactivity:mass of protein was normalized to 1 Bq μg^{-1} for each radioisotope. Ratio values holding at 1 over time indicate that radioisotope release rates equaled protein release rates. At 15°C, only ^{75}Se values stayed near 1, while the ratios for the other radioisotopes quickly rose to 2–4, reflecting the greater retention of the radioisotope than of protein in the

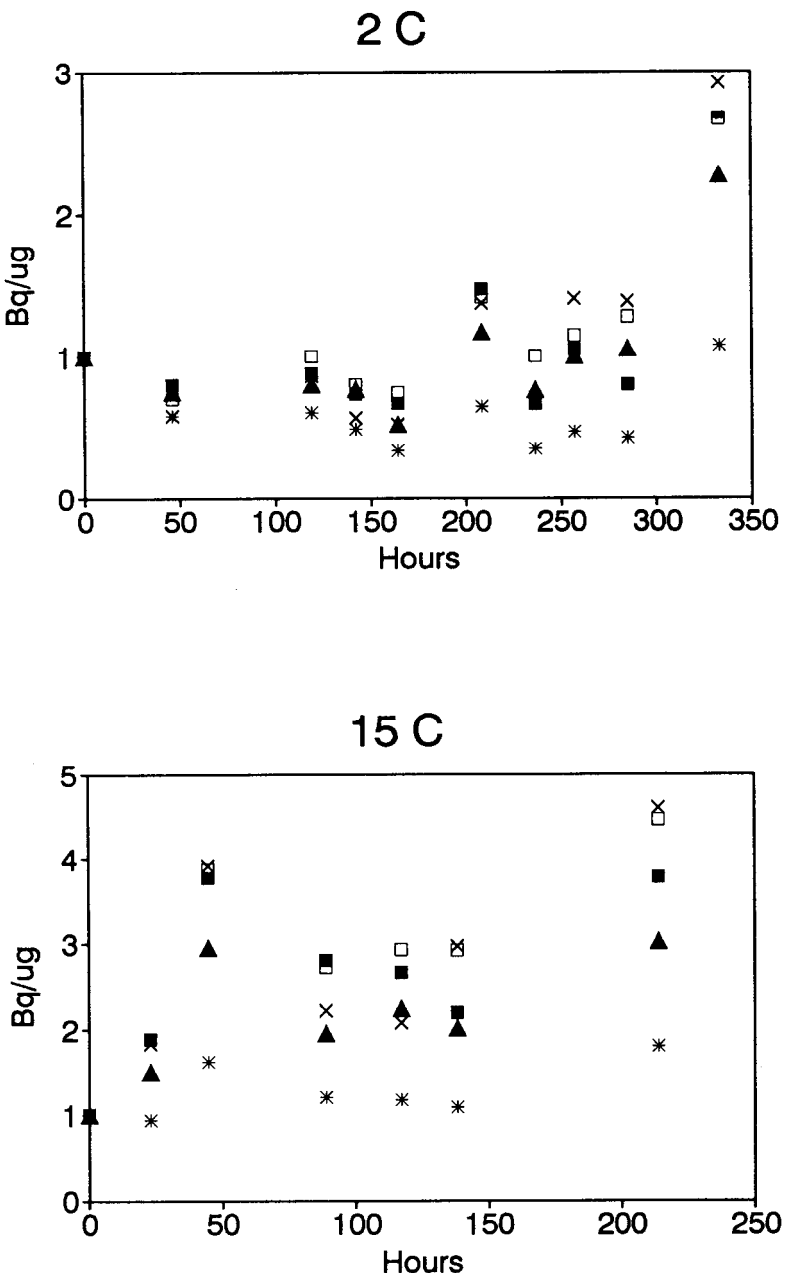

Figure 2. Ratios of isotope radioactivity:protein content (Bq μg^{-1} protein) of *A. patersoni* carcasses over time for ^{110m}Ag (□), ^{241}Am (■), ^{109}Cd (▲), ^{60}Co (X), and ^{75}Se (*) at 2°C and 15°C. Values normalized to initial sample at time zero.

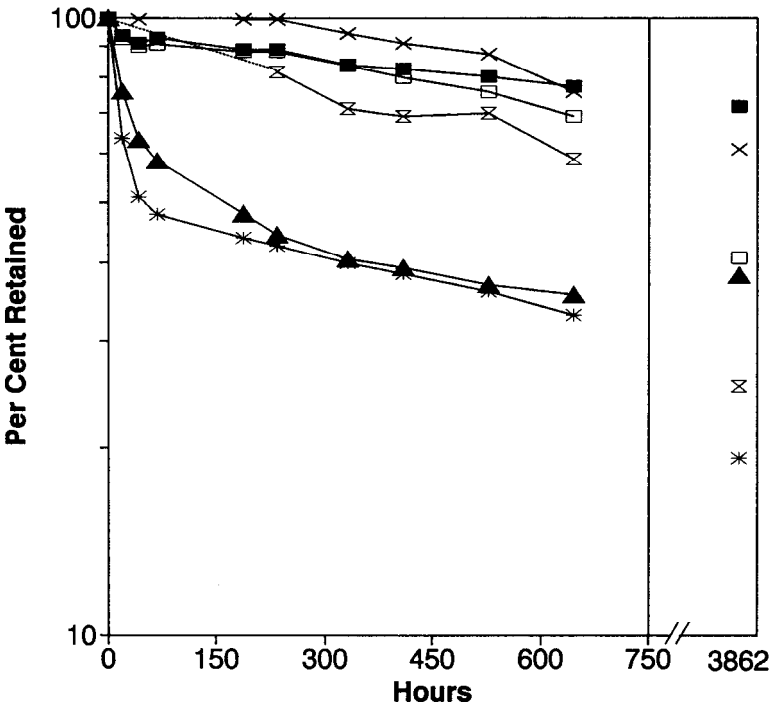

Figure 3. Retention (%) over time of ^{110m}Ag (□), ^{241}Am (■), ^{109}Cd (▲), ^{60}Co (X), ^{75}Se (*), and protein (⧖) in sediment trap particles. Dotted line indicates that no reliable protein samples were obtained before 10 d sample time (see Materials and methods).

decaying carcasses (Fig. 2). At 2°C, however, radioisotopes were lost more slowly than protein and ratios of radioactivity:protein therefore increased from ≤ 1 for all radioisotopes after 1 wk to values of 2–3 after 2 wks, with ^{75}Se staying ≈ 1 (Fig. 2).

The retention of all radioisotopes and of protein were significantly longer in the sediment trap particles than in the copepod carcasses. Over the first 4 wks incubation the ^{109}Cd and ^{75}Se loss rates from the sediment trap particles were nearly identical and were significantly greater than that of protein, while the loss rates of ^{60}Co, ^{110m}Ag, and ^{241}Am were less than that of protein (Fig. 3). The loss of both ^{109}Cd and ^{75}Se from the particulate phase conformed with a two-compartment model, whereas the loss of the other radioisotopes and the protein conformed with a single compartment model. The regression equations of the log-linear data describing loss from the sediment trap particles and the calculated $t_{r1/2}$s for the first 27 d incubation are presented in Table 3. The calculated k values ranged from 0.0080 d^{-1} for ^{241}Am to 0.2369 d^{-1} for ^{75}Se in the rapidly exchanging pool. The k of protein was 0.0184 d^{-1}, with a $tr_{1/2}$ of 37.7 d. ^{60}Co showed virtually no loss over the first 2 wks incubation and had a $t_{r1/2}$ of 77.9 d. ^{241}Am and ^{110m}Ag were lost very slowly as well, with $t_{r1/2}$s of 86.8 and 63.0 d, respectively.

Table 3. Log-linear release rate constants (k) and retention half-times ($t_{r1/2}$) of five radioisotopes and protein from sediment trap particles calculated with data from 0 to 646 hours. Cd and Se retention conformed with a two-compartment model; slopes and $t_{r1/2}$ given for each of the rapidly and slowly exchanging pools.

	% in pool	k (d^{-1})	std. error	$t_{r1/2}$ (d)
^{110m}Ag	100	0.0110	0.0010	63.0
^{241}Am	100	0.0080	0.0008	86.8
^{109}Cd-rapid	43.5	0.1679	0.0398	4.1
^{109}Cd-slow	56.5	0.0193	0.0029	35.8
^{60}Co	100	0.0089	0.0014	77.9
^{75}Se-rapid	50.4	0.2369	0.0743	2.9
^{75}Se-slow	49.6	0.0150	0.0003	46.3
protein	100	0.0184	0.0024	37.7

After 5 months incubation, loss rates of ^{109}Cd and ^{241}Am slowed to essentially zero, while the other radioisotopes and protein continued to be lost slowly from the particulate phase (Fig. 3). The ratios of radioactivity:protein in the particles for each radioisotope are plotted over time in Figure 4. As with Fig. 2, the values are normalized to an initial value of 1 Bq μg^{-1} protein. These ratios for ^{241}Am, ^{60}Co, and ^{110m}Ag increased to about 1.3 over the first 27 d of incubation, reflecting slower loss rates of these radioisotopes than of protein from the particles. Because ^{109}Cd and ^{75}Se were initially lost much more rapidly than protein but were subsequently lost

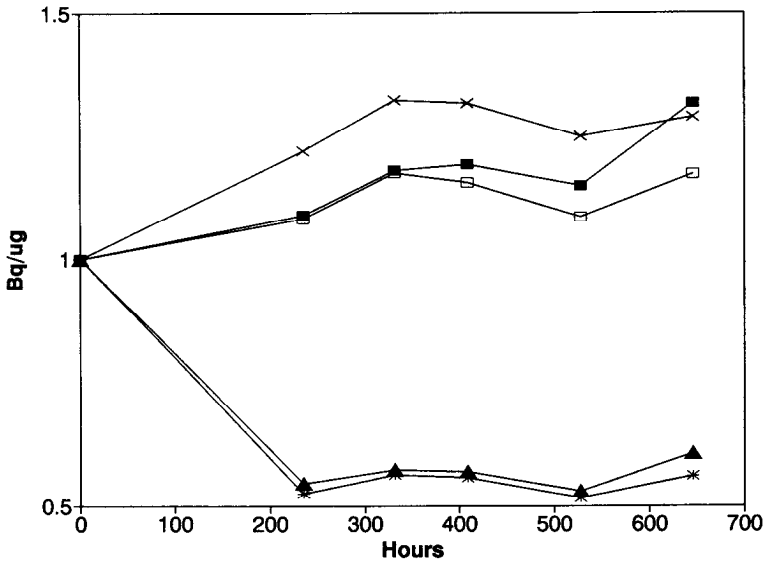

Figure 4. Ratios of isotope radioactivity:protein content of sediment trap particles (Bq μg^{-1} protein) over time for ^{110m}Ag (□), ^{241}Am (■), ^{109}Cd (▲), ^{60}Co (X), and ^{75}Se (*). Values normalized to initial sample at time zero.

Table 4. Dry weight, C, N, and protein content (mg) and molar carbon to nitrogen ratios of sediment trap particles. Values are for initial sample time at time zero (Ti) and final sample time (Tf).

	Ti	Tf
dry weight	687.4	198.6
C-total	51.1	12.7
C-org.	22.7	4.7
N	2.8	0.7
protein	13.6	3.4
C-total:N	21.2	21.2
C-org.:N	9.4	7.9

from particles at rates comparable to protein, their activity ratios to protein decreased from 1 to around 0.5 at 9 d, after which they remained constant (Fig. 4).

The dry weight of the sediment trap particles decreased by 71% over the entire 5 month incubation (Table 4). The organic C fraction decreased by 28%, from 3.30% of the dry weight at the beginning of the decomposition to 2.37% at the end; total C decreased at a slower rate (by 14%) than organic C (Table 4). Although protein and N decreased proportionately to total C, with ratios of protein:N remaining constant over time (Table 5), molar $C_{org.}$:N ratios decreased from 9.4 to 7.9 at the end of the experiment (Table 4). Over the incubation period, the ratios of metal radioactivity to dry weight, C, N, and protein content of the sinking particulate matter increased 2–3 fold for ^{241}Am and ^{60}Co, and by about 50% for ^{109}Cd and ^{110m}Ag; these ratios decreased by up to one third for ^{75}Se (Table 5). Ratios > 1 reflected more rapid loss of dry weight, C, N, and protein than of metal.

4. Discussion

The results suggest that the turnover of protein may influence the release of Se, but not Am, Cd, Co or Ag from decaying copepod carcasses. Similar release rates of Se and protein from animal carcasses would be expected, given the comparable behavior of Se and S in biological systems (Shrift, 1954; Wrench, 1978; Brown and Shrift, 1982) and specifically the association of Se with protein in marine invertebrates (Wrench and Campbell, 1981). The significantly faster loss of protein and ^{75}Se from carcasses at 15°C than at 2°C suggests that microbial activity controlled the release of protein and ^{75}Se, but not ^{241}Am, ^{109}Cd, ^{60}Co or ^{110m}Ag, as shown elsewhere (Lee and Fisher, 1992b). The initial loss of protein from carcasses at 2°C was slow, but after 1 wk this rate increased 4-fold. This may be a result of the presence of two pools of protein, the more rapidly exchanging of which could not be released until the slower pool (perhaps enveloping the more labile protein) was degraded. Alternatively, the bacteria which decomposed the carcasses at 2°C may have taken 1 wk to grow to sufficiently high levels to greatly enhance the protein decomposition (and

Table 5. Ratios of elements to dry weight, C, N, and protein in sediment trap particles. Ratios are kBq mg^{-1} for Ag, Am, Cd, Co, and Se. The ratios of C, N, and protein to dry weight, total and organic C, N, and protein are g g^{-1}. Values given for initial sample time at time zero (Ti) and final sample time (Tf).

		dry wt. (×1000)	C (total)	C (org.)	N	Protein
^{110m}Ag	Ti	35.84	0.48	1.09	8.74	1.81
	Tf	50.71	0.80	2.14	14.49	2.93
	Tf/Ti	1.41	1.65	1.97	1.66	1.62
^{241}Am	Ti	35.11	0.47	1.06	8.56	1.77
	Tf	87.24	1.37	3.68	24.93	5.04
	Tf/Ti	2.48	2.90	3.46	2.91	2.84
^{109}Cd	Ti	144.11	1.94	4.37	35.15	7.27
	Tf	191.29	3.00	8.07	54.66	11.05
	Tf/Ti	1.33	1.55	1.85	1.55	1.52
^{60}Co	Ti	173.27	2.33	5.25	42.26	8.74
	Tf	365.54	5.74	15.42	104.40	21.12
	Tf/Ti	2.11	2.46	2.94	2.47	2.42
^{75}Se	Ti	30.20	0.41	0.92	7.37	1.52
	Tf	20.15	0.32	0.85	5.76	1.16
	Tf/Ti	0.67	0.78	0.93	0.78	0.76
C (total)	Ti	0.074	—	2.25	18.15	3.75
	Tf	0.064	—	2.69	18.20	3.68
	Tf/Ti	0.86	—	1.19	1.00	0.98
C (org.)	Ti	0.033	0.444	—	8.05	1.66
	Tf	0.024	0.372	—	6.77	1.37
	Tf/Ti	0.72	0.839	—	0.84	0.82
N	Ti	0.0041	0.055	0.12	—	0.21
	Tf	0.0035	0.055	0.15	—	0.20
	Tf/Ti	0.85	1.00	1.19	—	0.98
Protein	Ti	0.020	0.266	0.6	4.83	—
	Tf	0.017	0.272	0.73	4.95	—
	Tf/Ti	0.87	1.02	1.22	1.02	—

hence the protein release rate). Although comparable release rates of ^{75}Se and protein were observed in the carcasses at 15°C, the release of ^{75}Se from copepod carcasses at 2°C was significantly faster than that of protein, suggesting that much of the ^{75}Se in the carcasses was in a highly labile, non-protein form.

The release rate constants (k) of radioisotopes and protein from sediment trap material over the first 27 d of incubation suggest that the slowly exchanging pools of ^{109}Cd and perhaps ^{75}Se closely followed the release of protein from these particles (Table 3). The k values of ^{241}Am, ^{60}Co, and to a lesser extent ^{110m}Ag, however, appeared to be independent of protein over the first month of the experiment. The strong particle-reactivity shown by ^{241}Am is consistent with its general behavior in marine systems (IAEA, 1985). Although Co is only moderately concentrated in

marine organisms, it is very highly concentrated in pelagic sediments ($K_d = 10^7$) and manganese nodules ($K_d = 6 \times 10^8$) (IAEA, 1985). Thus, in the sediment trap particles, which were incubated in the dark, the ^{60}Co may have been tightly bound to manganese oxides (or possibly as cobalt oxides) formed by bacteria present in the samples (Lee and Fisher, 1993).

About half of the ^{109}Cd and ^{75}Se bound to sediment trap particles was in rapidly exchanging pools which were almost completely emptied in 4 to 8 d (i.e. after 5 $t_{r1/2}$s), whereas the ^{109}Cd and ^{75}Se in the slowly exchanging pools were released at rates comparable to that of protein. The large fraction of total ^{109}Cd and ^{75}Se in these particles found in the rapidly exchanging fractions may be due to the extensive association (typically 50–90%) of these elements with soluble constituents in the cytoplasm of marine phytoplankton (Reinfelder and Fisher, 1991). The phytoplankton can contribute to POM collected in sediment traps as algal aggregates, components of marine snow, or components of zooplankton fecal pellets (Alldredge and Gotschalk, 1989). Typically $<20\%$ of the other metals enter into the cytoplasm of algal cells (Reinfelder and Fisher, 1991). Cd can substitute for Zn in a mid-molecular weight (66 kD) organic molecule in a marine diatom's soluble cell extract (Price and Morel, 1990) and Se in phytoplankton is overwhelmingly found in a non-protein fraction of the cytosol (Bottino *et al.,* 1984; Fisher and Reinfelder, 1991), possibly as seleno-amino acids. The rapid loss of ^{109}Cd from the sediment trap particles may have been due to Cd's propensity to concentrate in the organic fraction of marine snow (Noriki *et al.,* 1985; Hebel *et al.,* 1986); Cd and organic compounds leach out of biogenic particles at similar rates (Lee and Fisher, 1992a,b) and might be expected to remineralize faster than inorganic fractions. The rapid loss of both ^{109}Cd and ^{75}Se from the sediment trap material also reflects their relatively low affinity for particles in seawater, in contrast to Co, Ag, and especially Am (IAEA, 1985).

Zooplankton fecal pellets, which can be important components of the sinking biogenic debris in the ocean (Angel, 1984; Fowler and Knauer, 1986; Small *et al.,* 1987), are rich in organic matter (Johannes and Satomi, 1966; Small *et al.,* 1983; Bathmann *et al.,* 1987) and may be proportionately rich in protein (Madin, 1982) considering that C:N ratios of sedimenting material increase with the proportion of total sinking C contributed by fecal pellets (Bathmann *et al.,* 1987). Copepod assimilation studies indicate that 40–70% of ingested protein is not assimilated and may therefore be packaged into fecal pellets (Reinfelder and Fisher, 1991). The sediment trap particulate matter collected here contained 2% protein by weight, much lower than the protein content of living zooplankton (53–64%, Parsons *et al.,* 1984) and phytoplankton (35–68%, Parsons *et al.,* 1961). The protein content of freshly produced *A. patersoni* fecal pellets (0.60 μg fecal pellet^{-1}) was slightly greater than that in the sediment trap pellets (0.54 μg fecal pellet^{-1}), suggesting little loss of protein from fecal pellets in the upper 80 m.

The protein:N ratios measured in the sediment trap particles were 4.83 and 4.95,

at the beginning and end of the incubation, respectively (Table 5). These values are in general agreement with those calculated from particulate hydrolyzed amino acid (protein) and organic nitrogen flux data (mean protein:N = 5.15) reported by Lee and Cronin (1982). Indirect measurements of protein in natural biogenic debris using the protein:N ratio of 6.25 (for pure protein) may yield erroneously high values due to the presence of non-protein "heteropolycondensates" such as chitin, N-containing humic acids, complexes of inorganic clays and amino groups, and bacterial mucopolysaccharides (Roman, 1983).

The C_{org}:N ratio of the sediment trap particles was comparable to C_{org}:N ratios measured in other sediment trap collected material (Martin *et al.,* 1987; Biscaye *et al.,* 1988; Laws *et al.,* 1989), marine snow in surface water (Alldredge and Silver, 1988) and pure zooplankton fecal pellets (Small *et al.,* 1983; Roy and Poulet, 1990). However, the concentrations of C and N in the trap particles examined here were lower than those generally found in oceanic particles, probably due to loss of organic matter during the 4-day deployment of our unpoisoned traps. Zooplankton fecal pellets, which made up most of the identifiable particulate material, can have C and N concentrations as high as 36% and 7.9%, respectively (Small *et al.,* 1983). The C_{org} content of the sediment trap particles was only 3.3% indicating that a significant fraction of the material weight was contributed by inorganic particles. This is consistent with low C_{org} concentrations in sediment trap particles from the Mediterranean (4.9%, Fowler *et al.,* 1991) and Santa Barbara Basin (3.3%, Dunbar and Berger, 1981), both being areas of high terrigenous particle input. The C_{org} content of sediment trap particles collected from surface waters from other regions, most of which were dominated by biogenic matter, range from 10% to 23% (Wakeham *et al.,* 1984; Noriki *et al.,* 1985; Biscaye *et al.,* 1988).

Although sediment trap particles collected from different areas of the ocean can have different organic C contents, the degradation rates of C_{org} in sinking particles may be comparable. Degradation rates of sediment trap material in laboratory incubations, such as those reported here, can be compared with estimates from field observations, assuming an appropriate particle settling velocity. Using biogenic debris collected in sediment traps placed at different depths in the water column, Walsh et al. (1988) calculated first-order C_{org} degradation rate constants according to:

$$k_z = (\ln F_o - \ln F)/z \tag{1}$$

where k_z is the rate constant (m^{-1}), F_o and F = measured fluxes (g m^{-2} d^{-1}) in upper and lower sediment traps, respectively, and z = depth interval between traps (m). Multiplying k_z by sinking rates (m d^{-1}) of the particles yields rate constants per unit time (k_t) (Walsh *et al.,* 1988).

C_{org} degradation rate constants ($k_t s$) calculated for oceanic sediment trap particles range from 0.01–0.08 d^{-1} (Honjo *et al.,* 1982; Walsh *et al.,* 1988) assuming a sinking

speed of 100 m d^{-1}. Using the calculated particle sinking speed (21 m d^{-1}) and organic matter flux data for Sargasso Sea particles reported by Brewer *et al.* (1980), C_{org} degradation rate constants of 0.004–0.02 d^{-1} can be calculated. For the laboratory sediment trap particle data, the first order degradation rate constant of C_{org} was calculated over the 161 d incubation period according to Eq. 2:

$$k_t = (\ln C_{org-0} - \ln C_{org-t})/t \quad (2)$$

where C_{org-0} and C_{org-t} are the mass of organic C at time zero and at 161 d, respectively, these being the only time points for which C_{org} was measured. (By directly measuring the degradation rates of the material, there is no need to use an assumed sinking speed to convert depth into time.) The calculated k_t was 0.01 d^{-1}, in good agreement with the field values from deeper waters and with the average degradation rate constant (0.025 d^{-1}) of C_{org} measured in salp fecal pellets incubated in the laboratory (Caron *et al.*, 1989).

The first order degradation rate constant for protein was calculated by fitting the data for the entire 161 d incubation period (which, for the sediment trap particles, was in a single pool only) to Eq. 3:

$$k_t = (\ln \text{protein}_0 - \ln \text{protein}_t)/t. \quad (3)$$

The protein k (0.0086 d^{-1}) was 48% of that calculated over the first 27 d (0.018 d^{-1}). The latter is about one third of the rate calculated for amino acid flux data below 400 m in various oceanic regions (0.058 d^{-1}) (Wakeham and Lee, 1993), and below the range of k values for surface waters (0.03–0.9) (Lee and Cronin, 1984), assuming settling velocities of 50 m d^{-1}. The protein loss rates observed in the sediment trap particles may have been slower than those in the field due to microbial growth in the experimental particles which would reduce the net loss of protein from the particulate phase. Attached bacteria, however, can enhance the release of protein from marine snow aggregates through the hydrolysis of protein followed by the release of amino acids into the dissolved phase (Smith *et al.*, 1992).

Protein was mobilized from sediment trap particles at a somewhat slower rate ($t_{r1/2}$ = 37.7 d) than that measured for decomposing phytoplankton ($t_{r1/2}$ = 25.1 d; Lee and Fisher, 1993), and at much slower rates than for copepod carcasses ($t_{r1/2}$ = 1.1 d), confirming that phytoplankton-derived particulate matter was the dominant source of organic matter in the sediment trap particles. While the metal to protein ratios of Ag, Am, Cd, and Co increased with time in the sediment trap particles by factors of 1.5 to 2.8 (Table 5), only the Ag and Am to protein ratios increased with time in decomposing phytoplankton (by factors of 1.2 and 1.3, respectively; Lee and Fisher, 1993). This indicates that Ag, Am, Cd, and Co were released from the sediment trap particles more slowly than protein, but only Ag and Am were released more slowly than protein in pure phytoplankton; Cd and Co were released from phytoplankton at faster rates than protein. The release of trace metals

from sinking particles which are relatively low in C_{org}, such as those we collected, is largely independent of associated protein, probably due to a high content of more refractory phases. The release of trace metals from phytoplankton, which represents the purely biogenic endpoint of oceanic particles, more closely follows the release of protein. Since the ratios of Se to protein decreased with time in both the sediment trap particles and the decaying phytoplankton, there is probably little association of this element with more refractory material in the sediment trap.

The release rates of the trace elements and protein from decomposing copepod carcasses were generally 10 times faster than those observed from sediment trap particles (Tables 2 and 3). The calculated $t_{r1/2}$ for rapidly exchanging ^{75}Se in carcasses held at 15°C (1.8 d) was somewhat greater than values (0.7–1.1 d) determined for ^{75}Se in *Acartia tonsa* and *Temora longicornis* carcasses at 18°C, whereas the $t_{r1/2}$ at 2°C (4.1 d) was 3–4 times greater than $t_{r1/2}$s (1.1–1.3 d) in *A. tonsa* and *T. longicornis* also at 2°C (Lee and Fisher, 1992b). For ^{241}Am, the $t_{r1/2}$ in sediment trap particles (87 d) was within the range of $t_{r1/2}$s (50–215 d) for *A. tonsa* and *T. longicornis* fecal pellets produced on a *T. pseudonana* diet and held at 18°C (Lee and Fisher, 1992b) and greater than that determined for euphausiid fecal pellets held at 13°C (41 d) (Fisher *et al.,* 1983a). Such rate data are unavailable for the other metals in zooplankton debris and comparisons are not possible.

Assuming that these $t_{r1/2}$s are representative of those occurring in the ocean, and given the sinking rates of these two types of particles (1800 m d^{-1} for an *A. patersoni* carcass, vol. = 0.5 mm^3 [Small *et al.,* 1979]; 50–100 m d^{-1} for sediment trap particles [Alldredge and Silver, 1988]), both copepod carcasses and sediment trap particles could contribute significantly to the vertical transport of elements and protein to the deep ocean. With $t_{r1/2}$ values of the 5 elements and protein in copepod carcasses ranging from 4.1 to 8.8 d at 2°C, $>75\%$ of a carcass' content of these elements and protein should be advected to deep waters (deeper than 3000 m), if not eaten during the descent. In warmer waters, much of the protein, Se and Cd should be lost in shallower depths; the exact extent of their loss would depend on the temperature structure of the water column and the fraction of each in rapidly exchanging pools for each batch of particles. Similarly, about half of the Am, Ag and Co and about 33% of the protein associated with sediment trap particulate material sinking at 50 m d^{-1} would be transported below 3000 m.

The rapid release of Se and Cd from these debris are consistent with oceanographic observations that these elements display nutrient-type vertical profiles and are part of the organic cycle in the ocean (Whitfield and Turner, 1987). Turnover rates for these elements in the water column are relatively fast, comparable with those of POC and other important constituents of biogenic particles such as P (Bruland, 1983; Cutter and Bruland, 1984; Noriki *et al.,* 1985). Ag also displays nutrient-type profiles (Martin *et al.,* 1983), although its release rates from the debris in this study suggest that its turnover rates should be much slower than Se and Cd. By

contrast, Co and Am are scavenged by sinking particles and recycle much slower than POC (Knauer *et al.,* 1982; Fowler *et al.,* 1983; Masuzawa *et al.,* 1989), similar to their behavior in the experiments reported here.

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