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Scavenging and retention of bismuth by marine plankton and biogenic particles

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Abstract

We did radiotracer experiments using ^{207}Bi to quantify the bioavailability, accumulation, and retention of bismuth in marine plankton and biogenic detritus. The accumulation of ^{207}Bi by two species of phytoplankton (*Dunaliella tertiolecta* and *Emiliana huxleyi*) was very rapid, approaching steady state after ~1 d. *Emiliana* cells without coccoliths reached a volume concentration factor (VCF) roughly twice that attained by cells with coccoliths. VCFs were 5×10^5 for *Dunaliella* and $(4–9) \times 10^6$ for *Emiliana* after exposure for approximately 5 d. The radioactivity associated with *Dunaliella* was released with a biological half-time of 3–5 d. Copepods (*Anomalocera patersoni* and *Acartia* species) grazing radiolabeled *Dunaliella* assimilated ~ 4% of the ingested ^{207}Bi. Unassimilated radioactivity, voided in fecal pellets, was lost from pellets relatively slowly (half-times of 26 d for *Anomalocera* and 58 d for *Acartia*). These release rates were similar to copepod fecal pellets that had scavenged ^{207}Bi directly from water. Scavenging of bismuth from water by fecal pellets was considerable and extremely rapid, and uptake rates were similar to those of various size fractions of marine snow collected in a sediment trap. Release of scavenged ^{207}Bi from the fresh fecal pellets was relatively slow, and very little release of radionuclide from the different size fractions of marine snow was observed. The biogeochemical behavior of bismuth in the marine environment closely resembles that of other particle-reactive uranium–thorium (U–Th) series and transuranic elements.

The element bismuth enters the oceans predominantly through atmospheric inputs, either from volcanic emissions or localized fossil fuel combustion (Lee et al. 1985/1986), or possibly enriched on the coatings of eolian dusts (Bertine et al. 1996). Bismuth (Bi), as the only group 15 element in oxidation state III, undergoes extensive hydrolysis with speciation appropriate for pH in seawater as $Bi(OH)_3$ (Byrne 2002). Such a neutral species suggests that the mechanisms for biotic scavenging could involve organic scavenging, as well as inorganic adsorption on oxy-hydroxide (e.g., manganese [Mn]) phases. Thus, owing to its extensive hydrolytic properties, bismuth displays strong particle reactivity and is therefore a potentially toxic metal to marine species. However, there is little information on the rate or extent of bismuth uptake and its accumulation by marine organisms such that Bi biogeochemical properties demand special attention in the marine environment.

Profiles of bismuth in seawater uniquely display surface enrichment in seawater from atmospheric deposition, extraction in the mixed layer, and regeneration at intermediate depths around 500 m (Lee et al. 1985/1986). This depth is roughly associated with the oxygen minimum and is suggested to correspond to the transport and dissolution of Mn phases, analogous to Bi enrichment in Mn nodules (Bertine et al. 1996). However, below the main thermocline, Bi concentrations decrease dramatically indicating marked scavenging from deep waters. Thus, the data suggest strong cyclic particle reactivity of bismuth in intermediate waters but efficient scavenging and removal at depth. This behavior appears unique to Bi (unlike transient lead [Pb] or plutonium [Pu]), such that its biogeochemical cycling in the marine environment is not well understood and therefore warrants further investigation.

In addition to stable bismuth, the gamma-emitting radionuclide ^{207}Bi ($t_{1/2}$ = 32.2 yr) has been produced by nuclear weapons testing, and its fallout into the marine environment has been documented by several studies (Aarkrog et al. 1984; Kim et al. 1997; Noshkin et al. 2001). In fact, at present it is still one of the fission products in highest concentration in Bikini atoll sediments (Schell et al. 1980; Noshkin et al. 2001). Ideally, the production of the natural radionuclide ^{210}Bi from ^{210}Pb in atmospheric radon-222 (^{222}Rn) provides the primary natural radiogenic source of bismuth to the marine environment for studying processes of atmospheric scavenging and biogenic uptake of bismuth from surface waters (Turekian et al. 1977; as reviewed in Church and Sarin 2008). The use of ^{210}Bi as an atmospheric tracer has been well documented, and the technique has been used to measure the short residence times of aerosols on timescales of days (Poet et al. 1972). Nevertheless, its use as a tracer of marine scavenging processes had not been explored earlier due to lack of a rapid and efficient technique to assay ^{210}Bi. However, a quantitative analytical technique now available should prove practical for use with freshly collected samples on board ship (Church et al. 1994). Considering its short radiometric half-life (5.01 d), the input of ^{210}Bi to oceanic surface waters could be applied to tracing and quantifying processes involved in its uptake by marine plankton and biogenic particles produced in the upper water column.

The sparse information available on concentrations of stable or radioactive bismuth in marine organisms mainly concerns benthic species. An early review of trace metal data reported levels of bismuth in mussels and oysters ranging from 4.0 to 6.0 μg (19–29 pmol) g^{-1} dry weight

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(Eisler 1981). However, more recently, much lower concentrations of bismuth have been measured in a variety of brown algae and noncalcareous red algae (5–140 ng [24–670 pmol] g^{-1} dry weight) as well as in muscle and liver of various marine fish (<1–100 ng [<5–480 pmol] g^{-1} dry weight; Lee 1982; Bertine et al. 1996; Agusa et al. 2007). Likewise, radioactive ^{207}Bi has also been detected in the brown macroalga, *Dictyota divaricata*, as well as in filtered particulate matter containing radiolarians, foraminifera, and sand grains, that was sampled from the bottom of Eniwetok atoll lagoon (Lowman and Palumbo 1962). Later studies at Eniwetok and Bikini atolls, in which ^{207}Bi in fish, mollusks, and crustaceans was measured, indicated that most of the ^{207}Bi taken up by various species of reef fish was associated with muscle tissue (Noshkin et al. 1984; Robison and Noshkin 1999). Furthermore, results from these radio-bismuth distribution studies in fish tissues also demonstrated an excess of ^{210}Bi in some species, suggesting that the excess is not environmentally derived but is translocated to muscle and liver following the decay of ^{210}Pb in bone (Noshkin et al. 1984). Aside from these few field measurements, which indicate that bismuth is taken up by marine organisms, virtually nothing is known about the rate of uptake and the degree to which it is retained in these species.

It is well known that marine plankton and the biogenic particles they produce play a major role in the biogeochemical cycling and vertical transport of many particle-reactive trace elements and radionuclides in the sea (*see* Fowler and Knauer 1986; Fowler and Fisher 2004; Stewart et al. 2008, for reviews). At the base of the food web, autotrophic phytoplankton accumulate such elements directly from water, and these elements can then be passed on to zooplankton grazers. The grazers either assimilate and retain these elements or excrete them in soluble and particulate form as part of the biogeochemical cycling process. Scavenging and release rates have been reported for a number of trace metals, fission products, natural-series radionuclides and transuranic elements in phytoplankton cells, zooplankton fecal pellets, molts, and carcasses (*see* Fowler and Knauer 1986; Fowler and Fisher 2004; Stewart et al. 2008, for reviews), as well as in bulk particulates collected in sediment traps (Jannasch et al. 1988; Fisher et al. 1991*a*; Reinfelder et al. 1993). Here we report similar quantitative information on bismuth behavior in lower trophic level organisms, which is critical for adequately understanding the biogeochemical cycle of stable bismuth as well as its natural-series radionuclide, ^{210}Bi, and fission product ^{207}Bi. Such information is important, particularly if either radionuclide can to be used to trace and quantify processes involving bismuth uptake by marine plankton and biogenic particles produced in the upper water column.

Thus, the main objective of this study was to carry out a series of controlled laboratory radiotracer experiments using ^{207}Bi to measure the bioavailability, bioaccumulation, assimilation, and retention of bismuth in marine plankton. In addition, the degree to which bismuth is scavenged and retained by various types of biogenic detrital particles was also investigated.

Methods

Plankton and particulates—The phytoplankton species used in the experiments, a chlorophyte *Dunaliella tertiolecta* and the coccolithophore *Emiliana huxleyi* (clones BTS06 without coccoliths and MCH No. 1 with coccoliths), were taken from stocks maintained at the International Atomic Energy Agency Marine Environment Laboratories (IAEA-MEL) in Monaco. The copepods were collected from surface waters off Monaco using oblique net tows and maintained in aquaria for at least 24 h before use.

Two types of copepods, a single neustonic calanoid species *Anomalocera patersoni* and a mixed batch of primarily *Acartia* spp., were collected during summer from surface waters approximately 3.5 km off Monaco using 500-μm and 200-μm mesh nets. The two groups were sorted by sequential sieving, and the mean dry weight (dry wt) of an individual *Anomalocera* was 150 μg and that of the mixed *Acartia* species was 42 μg. Natural fecal pellets produced by these copepods were collected using previously described methods (Small et al. 1979; Rodriguez y Baena et al. 2007). The copepods were immediately transferred to specially designed aquaria containing aerated, filtered seawater at 22°C and held for 6 h, during which time they voided their gastrointestinal tracts. The fecal pellets produced were then removed from the seawater by siphoning, and two size fractions of pellets separated by sequential sieving, one in the 10–43-μm range and a second between 43 and 150 μm. The two pellet collections were then stored in filtered seawater at 1°C for 2 d prior to being exposed to ^{207}Bi radiotracer in labeled seawater at 22°C.

During the 4 d preceding the collection of the copepods, a sediment trap was deployed in the same area at a depth of 80 m in a 200-m-deep water column following the protocols described in Fowler et al. (1991). The collection cup of the sediment trap was not poisoned, so the natural particulates collected were expected to be rich in bacterial and protozoan activity. The trap particulates were sorted and various fractions (pure fecal pellets of unknown origin, and the remaining nonpellet material in the 1–10-μm, 10–43-μm, 43–150-μm, and 150–1500-μm size ranges) were prepared. The temperatures used were 20°C for the phytoplankton experiments and 22°C for the copepod food chain transfer and biogenic particle experiments.

Radiotracer and radioanalysis—The radiotracer, carrier-free ^{207}Bi in 10 mol L^{-1} HCl, was titrated against NaOH to pH 2. The ^{207}Bi tracer was obtained from the laboratory of E. Goldberg, formerly at Scripps Institution of Oceanography, as supplied from Amersham (Bertine et al. 1996). It is currently available from Oak Ridge National Laboratories in nitric acid form. Preliminary experiments showed that the addition of small quantities of this stock solution to seawater did not significantly affect the pH of the seawater and did not affect the viability of the two phytoplankton species used in these experiments.

Gamma counting was performed with a Packard Autogamma counter and with a 7.6 × 7.6 cm well-type NaI crystal connected to a multichannel analyzer. Photon emissions of ^{207}Bi ($t_{1/2}$ = 32.2 yr) from 65 to 110 keV were

counted. Calibration of the instruments against known radionuclide standards permitted corrections to be made for sample geometry and detector type. Counting times varied depending on sample size and activity levels, and therefore counting times were selected to obtain count rates with propagated errors less than 5%.

The conditions and design of each of the different radiotracer experiments are outlined in the following paragraphs.

Bioaccumulation of Bi *by phytoplankton (experiment 1)*—The basic experimental protocols and methodologies employed closely followed those developed by Fisher et al. (1983*a*). Two strains of the coccolithophore were used, one with and one without coccoliths. Log-phase cells were cultured in 0.22-μm sterile-filtered Mediterranean surface seawater enriched in F/2 nutrients (Guillard and Ryther 1962) but without copper (Cu), zinc (Zn), and ethylenediaminetetraacetic acid (EDTA). These were subsequently harvested by centrifugation and resuspension in borosilicate glass flasks containing either 200 mL (*Emiliana*) or 400 mL (*Dunaliella*) of fresh, sterile-filtered seawater medium diluted to F/20. Cell densities in the flasks during the experiment were determined using a Fuchs-Rosenthal hemocytometer. The initial cell densities in the inoculated media were 5×10^4 cells mL^{-1} for *Dunaliella* and 5×10^3 cells mL^{-1} for *Emiliana*.

The conditions of the two uptake experiments were complete darkness and a 12 h light : dark cycle. During the exposure period, cell densities, pH, and filterable and nonfilterable ^{207}Bi radioactivity were monitored. Exposures were performed in triplicate, and control flasks with no added phytoplankton were also used to assess any formation of filterable radioactive particulates. Exposure commenced with the addition of an aliquot of ^{207}Bi radiotracer to each sterile flask, such that the radionuclide concentration was 15 Bq mL^{-1}. All flasks remained sealed to eliminate the entry of any atmospheric particulates into the radioactive medium. After swirling to resuspend the cells, samples were regularly withdrawn aseptically from each flask to measure the cell density (1 mL), radioactivity in the water (10 mL), and radioactivity associated with the cells (3 aliquots of 10 mL each). The latter value was calculated after filtration on a 0.2-μm Nuclepore filter. The exposure phase was terminated at 130 h.

Possible loss of radioactivity to the walls of each flask with time was examined using controls, as was the concentration of radioactivity available to the phytoplankton in the seawater medium. Accumulation of radiotracer by the cells was expressed using volume concentration factors (VCF), defined as the radioactivity per unit cell volume divided by the radioactivity per unit volume of water. For the calculation of the VCF, a mean cell volume of 91 μm^3 was used for *Dunaliella* (Fisher et al. 1983*a*) and of 50 μm^3 for *Emiliana*. This latter value was calculated assuming a spherical cell shape and a measured cell diameter of 4.6 μm.

Release of Bi *from phytoplankton (experiment 2)*—To examine the degree of retention of bismuth in phytoplankton, the *Dunaliella* cells, previously radiolabeled in constant darkness and on a 12 h light : dark cycle for 130 h, were subsequently placed in preconditioned dialysis sacs in aquaria that received 10-μm-filtered uncontaminated seawater at 22°C, flowing at approximately 1 liter per minute. This experiment was performed under 12 h of a dim light : dark cycle. The ^{207}Bi radioactivity associated with the cells was monitored at the beginning of the loss period and regularly thereafter for 6 d. The cell densities in the dialysis sacs were also monitored, as was loss of radioactivity from a control dialysis sac containing only a fresh aliquot of ^{207}Bi. The rate of release of ^{207}Bi from the cells over time was determined, and biological half-times ($T_{b1/2}$) of bismuth loss were computed for both uptake conditions generally following the procedures described by Fisher et al. (1983*a*).

Assimilation of ingested Bi *in copepods (experiment 3)*—Eighty adult *A. patersoni* were held overnight (22 h, 22°C) in a flask containing 400 mL 0.22-μm sterile-filtered seawater. These individuals were allowed to feed on phytoplankton (*Dunaliella*) that had previously been radiolabeled with ^{207}Bi and then dialyzed against noncontaminated seawater for 50 h in order to remove the labile, loosely bound fraction. The initial concentration of *Dunaliella* in the flask was 11.6×10^3 cells mL^{-1}.

The mixed *Acartia* spp. were divided into four batches of 220 individuals each and placed in 400 mL of seawater. The flasks contained radiolabeled *Dunaliella* at a cell concentration of 14.4×10^3 cells mL^{-1}. As with *Anomalocera*, the *Acartia* spp. were allowed to feed overnight on the radiolabeled phytoplankton. At these cell densities the rate of cell filtration by copepods should not be affected (Fisher et al. 1991*b*).

After 22 h feeding on radiolabeled phytoplankton, the copepods that had ingested radioactive food were removed and gamma counted, and the cell densities and radiotracer concentrations in the water were determined. The copepods were then placed in uncontaminated seawater for 12 h and allowed to ingest uncontaminated *Dunaliella* to depurate their guts and to facilitate excretion of any unassimilated ^{207}Bi. After depuration they were gamma counted again assuming that none of the dissolved radioactivity was recycled from the phytoplankton surface or zooplankton exoskeleton. From knowledge of the quantity of cells ingested by each copepod and the mean ^{207}Bi radioactivity per cell (from experiment 2, above), the fraction of ingested bismuth that was assimilated into the tissues of these two species of copepod was computed.

Bi *scavenging by fresh copepod fecal pellets (experiment 4)*—In order to estimate the degree to which released fecal pellets can scavenge dissolved bismuth from the surrounding seawater as they sink, the uptake of ^{207}Bi by the two size fractions of freshly produced, natural copepod fecal pellets (i.e., small, 10–43 μm, and large, 43–150 μm) was compared. In this experiment the fecal pellets originally produced by the copepods and stored for 2 d at 1°C were used. Pellets were exposed to ^{207}Bi (5.5 Bq mL^{-1}) in 60 mL of 0.22-μm sterile-filtered seawater for 72 h, during which

time aliquots of the pellets were removed, filtered, and analyzed for radioactivity.

Note that 486 of the smaller, more compact fecal pellets (mean dry pellet weight = 5.31 μg) and 4170 of the larger, less compact pellets (mean dry pellet weight = 2.25 μg) were used to test the effect of pellet size and compactness on scavenging rate. The accumulation of radiotracer by the pellets was expressed using weight concentration factors (WCF values), defined as the radioactivity per unit dry weight of pellet normalized to concentration of radioactivity per unit weight of water. Note that WCF values are analogous to partition coefficients (K_d values) used for sediments and inorganic particulate matter. One might expect that uptake in terms of WCF values by the smaller pellets with larger relative surface area would be greater than by the larger ones, since surface adsorption plays a significant role and the WCF is based on unit weight of pellets.

Bi *scavenging by field-collected pellets and marine snow (experiment 5)*—In addition to the fresh, natural copepod pellets described in experiment 4, zooplankton fecal pellets were carefully separated from the bulk sediment trap samples by standard methods (Miquel et al. 1994). Most of these pellets appeared to be of copepod origin. The total fecal pellet fraction from the trap (4.79 mg dry wt) was then used to assess the scavenging of ^{207}Bi from water under the same conditions as the freshly produced copepod fecal pellets. The pellets (79.8 μg dry pellet mL^{-1}) were exposed in 60 mL of sterile-filtered seawater to 5.5 Bq mL^{-1} ^{207}Bi for 72 h, during which time aliquots were removed, filtered, and analyzed for radioactivity.

After the pellets were removed, the remaining particulate material was typical "marine snow" particles composed predominantly of biogenic debris (e.g., fragments of phytoplankton, zooplankton exoskeletons, appendages, mucus from appendicularian houses, uncharacterized flocs, etc.). This debris was sorted by sequential sieving, and the following size fractions and associated total weights were prepared: 1–10 μm (8.13 mg dry wt), 10–43 μm (18.28 mg), 43–150 μm (1.48 mg), and 150–1500 μm (3.44 mg). These four size fractions were then used to examine the particle scavenging of ^{207}Bi from water under the same conditions as the natural fecal pellets. As with the fecal pellets, the accumulation of radiotracer by marine snow particles was expressed as a concentration factor based on dry weight (WCF).

Release of Bi *from egested labeled fecal pellets (experiment 6)*—The grazing activities of copepods result in the "packaging" into fecal pellets of undigested phytoplankton debris containing any bismuth that was not assimilated. Once ejected, these pellets will sink and may release bismuth from the pellet and its content as they slowly decompose. To examine quantitatively this process, the radiolabeled fecal pellets produced by the copepods in the Bi assimilation experiment (experiment 3 above) were isolated by sieving onto a 20-μm mesh net. They were immediately transferred to dialysis sacs containing 0.22-μm sterile-filtered seawater and then placed in uncontaminated flowing seawater to measure the rate of ^{207}Bi release. Because of a gamma detector problem, the pellets could not be gamma counted for 4 d, during which time the pellets were thoroughly rinsed of any labile ^{207}Bi. Therefore, following that rinsing period, an initial gamma count of the pellets was made (T = 0), and thereafter they were periodically gamma counted for 14 d. The percentage of the remaining ^{207}Bi based on the initial activity at time T = 0 was plotted, and the half-time for bismuth release ($Tr_{1/2}$) from these pellets was computed following procedures described previously (Fisher et al. 1991*a*; Reinfelder et al. 1993; Wang et al. 1996).

Release of Bi *from fresh fecal pellets labeled from water (experiment 7)*—Fecal pellets that have scavenged dissolved bismuth from seawater (*see* experiments 4, 5 above) can also lose or exchange the element adsorbed to pellet surfaces as they sink and decompose. To see how this process compares with the release of bismuth from internally packaged phytoplankton debris within a pellet, the remaining natural fecal pellets containing scavenged ^{207}Bi were placed in preconditioned dialysis sacs and dialyzed against flowing uncontaminated seawater for 11 d. During this time the sacs were regularly gamma counted, and the rate of release of ^{207}Bi was determined for each fecal pellet fraction as described above.

Release of Bi *from field-collected marine snow (experiment 8)*—To follow release of scavenged ^{207}Bi from the trap-collected marine snow particles, the four size fractions of particles prepared in experiment 5 and exposed to radiotracer for 72 h were subsequently placed in separate dialysis sacs, and the amounts of radioactivity released over time were monitored in tandem with the fecal pellet samples described in experiment 7.

Results

Bioaccumulation of Bi *by phytoplankton*—The uptake of ^{207}Bi by the three phytoplankton cultures plotted as volume concentration factors (VCF) over time is depicted in Fig. 1. Uptake by all three cultures was rapid with steady state evident after only 1 to 2 d. Checks on radiotracer concentrations in the seawater in the experimental flasks, as well as in control flasks containing only labeled medium indicated that ^{207}Bi sorption to flask walls was minimal (<3%) during the experiment. In terms of the fraction of ^{207}Bi removed from the water through uptake by cells, there was little difference between cells maintained in constant darkness and those maintained on a light : dark cycle. It is apparent that the coccolithophore *Emiliana* took up approximately one order of magnitude more ^{207}Bi than the chlorophyte *Dunaliella*. Furthermore, under dark conditions *Emiliana* without coccoliths accumulated roughly twice as much ^{207}Bi as the cells with coccoliths. Cell densities under dark conditions remained constant throughout the experiment (i.e., 5×10^4 cells mL^{-1} for *Dunaliella* and 5×10^3 cells mL^{-1} for *Emiliana*), and these cultures showed a slight but continual increase in ^{207}Bi VCF over time. In the case of the cells exposed to light,

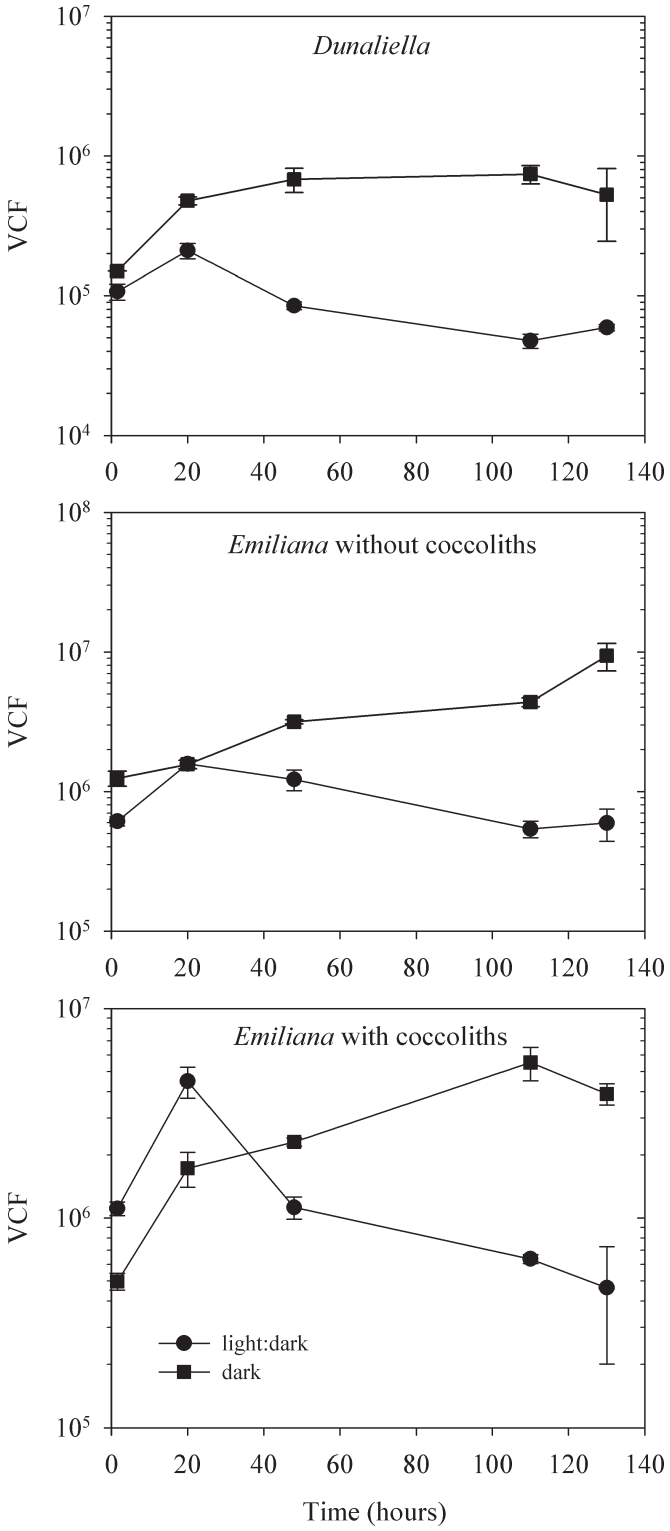

Fig. 1. Accumulation of ^{207}Bi by phytoplankton cells over time expressed as volume concentration factors (VCF), defined as radioactivity per unit cell volume divided by the radioactivity per unit volume of water. *See* text for cell volume calculation. The ^{207}Bi accumulation was measured under 12 h light : dark cycle and constant darkness conditions. Each data point represents the mean ± 1 σ of three separate samples.

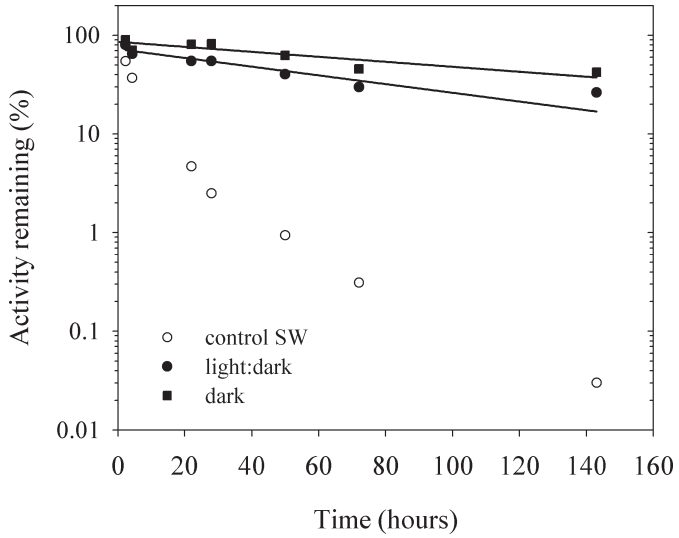

Fig. 2. Loss of accumulated ^{207}Bi from *Dunaliella* cells during dialysis in flowing seawater. Cells were previously radiolabeled under 12 h light : dark cycle and constant darkness conditions. Also shown is ^{207}Bi loss from a filtered control seawater medium spiked with radiotracer immediately preceding dialysis. Data points represent counts of single samples.

VCFs decreased steadily after 24 h, most likely due to an increase in biomass from cell division. For example, cell densities in these cultures increased from 5 to 25 × 10^4 cells mL^{-1} for *Dunaliella*, 5 to 40 × 10^3 cells mL^{-1} for *Emiliana* without coccoliths, and from 5 to 70 × 10^3 cells mL^{-1} for *Emiliana* with coccoliths. Owing to this artifact of biological dilution, we consider the best estimates of VCFs are those from nondividing cells held in darkness during the experiment, i.e., approximately 5 × 10^5, 4 × 10^6, and 9 × 10^6 for *Dunaliella*, *Emiliana* with coccoliths, and *Emiliana* without coccoliths, respectively.

Release of Bi *from phytoplankton*—Loss of accumulated ^{207}Bi from *Dunaliella* cells over a period of 6 d is shown in Fig. 2. It is evident that dissolved radioactivity in the control seawater, which did not contain any particles, was lost via dialysis very rapidly with approximately 98% of the spike removed after 1 d. This indicates that any ^{207}Bi released from the cells would be rapidly dialyzed into the external flowing seawater and therefore not likely to be recycled between water and cells within the sacs. The ^{207}Bi associated with the phytoplankton was released relatively slowly. Cell densities in both treatments remained essentially unchanged during the radiotracer loss phase. The log of percentage radionuclide retained was plotted against time, and release rate constants were determined by a nonlinear least squares fit of the retention data. Based on the rate constants determined between 2 and 143 h, the computed $T_{b1/2}$ values were 2.8 and 5.1 d for the cells that had accumulated ^{207}Bi on a 12 h light : dark cycle and those exposed in constant darkness, respectively.

Assimilation of ingested Bi *in copepods*—The results of the bismuth assimilation experiment are summarized in

Table 1. Assimilation of ^{207}Bi by copepods ingesting radiolabeled phytoplankton during 22 h (*see* text for exposure conditions and computation of assimilation efficiency).

Species	*Anomalocera patersoni*	*Acartia* spp.
Number of copepods	80	880
Mean copepod dry weight (μg)	150	42
Total cells consumed	704,000	13,067,200
Mean phytoplankton activity (μBq cell^{-1})	56.03	56.03
Activity consumed (Bq copepod^{-1})	0.493	0.832
Activity retained (Bq copepod^{-1})	0.021	0.032
Assimilation efficiency (%)	4.3	3.9

Table 1. Despite differences in copepod weight and number of phytoplankton cells consumed, both copepod species assimilated approximately 4% of the ^{207}Bi ingested during 22 h.

Bi *scavenging by fecal pellets and marine snow*—The scavenging of ^{207}Bi by natural zooplankton fecal pellets is shown in Fig. 3. The upper panel, A, represents the uptake of ^{207}Bi in fecal pellets over time expressed as a percentage of the total radioactivity in the water, and the lower panel, B, indicates the increase in WCF during the 3-d exposure period. It is evident that the adsorption of bismuth on these biogenic particles is very rapid with a steady state in uptake reached after only approximately 24 h. The average WCF values between 24 and 72 h for the small and large freshly produced pellets and pellets from the sediment trap were 1.7×10^4, 4.9×10^3, and 7.6×10^3, respectively. As predicted, the small copepod pellet fraction with a larger total surface area took up roughly 3.5 times more bismuth than the larger copepod pellets and 2.3 times more than the mixed zooplankton pellets isolated from the sediment trap.

In a similar manner, four different size fractions of the remaining biogenic material (i.e., marine snow) isolated from the sediment trap rapidly adsorbed ^{207}Bi when exposed to the radiotracer for 3 d (Fig. 4). The two panels in Fig. 4 represent bismuth uptake as described above for the fecal pellet fractions. For most of the particulate size fractions adsorption was complete by 4 h of exposure. As expected, generally the largest percentage of ^{207}Bi removed from the water and bound to the particles was directly related to the total weight of particles exposed, except in the case of the 43–150-μm fraction where only 1.48 mg were available for the experiment. These particles removed a disproportionate amount of radiotracer; consequently, WCF values approaching 10^6 were calculated for this size fraction. Based on visual observation of particle composition of the various size fractions, there is no obvious reason why the intermediate size fraction (43–150 μm) should behave so differently from the other groups of particles. However, owing to the very low concentration of these particles (1.48 mg in 60 mL) exposed to the tracer, it is possible that a "particle concentration effect" occurred whereby the WCF (or K_d, the defined partition coefficient) actually increases with decreasing particle concentration. This effect is often seen in experiments measuring the K_d of sediments. Alternatively, this very high value may simply be due in part to the very low dry weights of material used to compute the WCF at each sampling time. Owing to our experimental design, it is not possible to accurately assess either of these aspects; therefore, this value is not considered to be reliable. Nevertheless, the WCF values for all the other size fractions varied little and were on the order of approximately 10^4, a value which appears to be more realistic for fine marine snow particles.

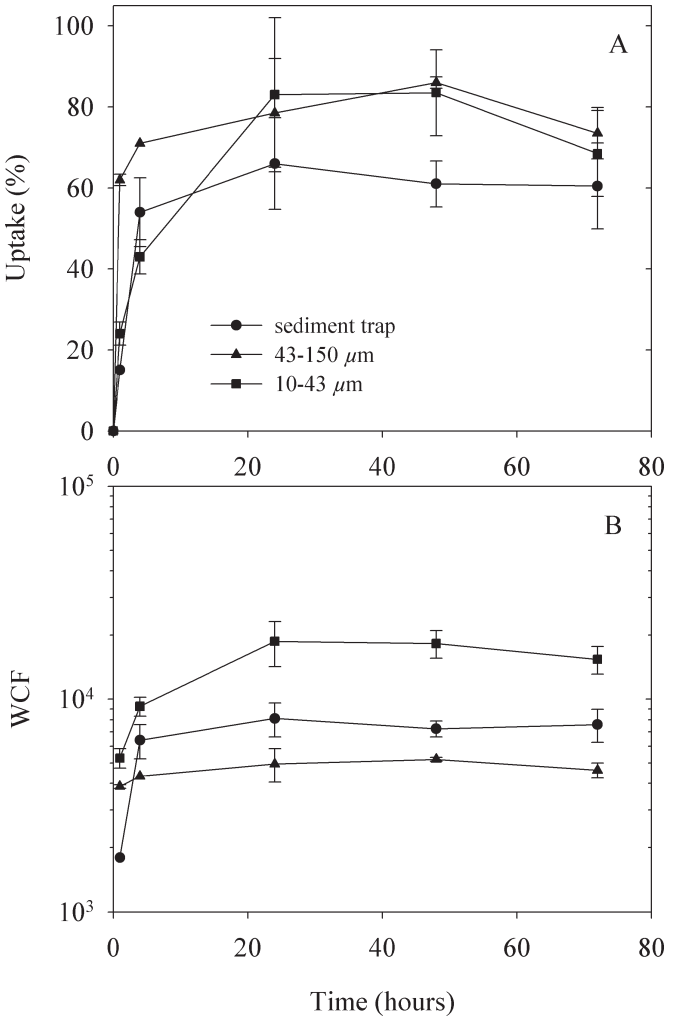

Fig. 3. Accumulation of ^{207}Bi from water by intact fecal pellets isolated from a sediment trap, and two size fractions of natural fecal pellets (10–43 μm and 43–150 μm) that were produced by copepods a few hours after collection from Monaco surface waters. The data points (mean $\pm$ 1 σ of three separate aliquots) indicate the radioactivity in the fecal pellets expressed as a percentage of (A) the total radioactivity in the water, and (B) as the WCF. *See* text for definition.

Release of Bi *from pellets labeled under different conditions*—The release of ^{207}Bi from fecal pellets produced

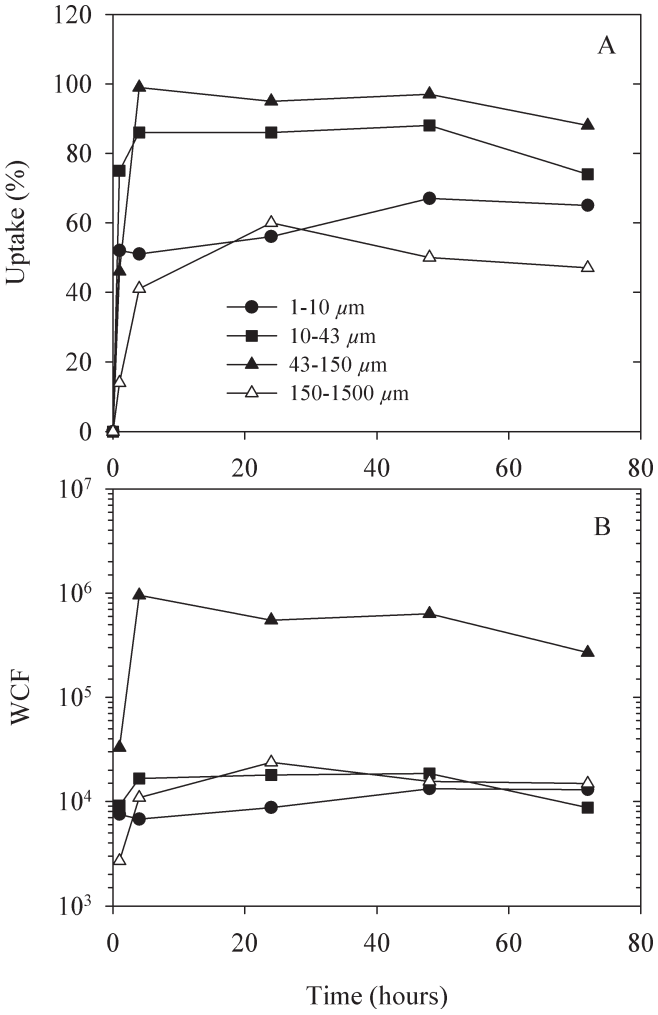

Fig. 4. Accumulation of ^{207}Bi from water by various size fractions of biogenic detrital material (with fecal pellets removed) isolated from a sediment trap: 1–10, 10–43, 43–150, and 150–1500 μm. The data points (counts of a single aliquot) indicate the radioactivity in the material expressed as a percentage of (A) the total radioactivity in the water, and (B) as the WCF. *See* text for definition.

by two species of copepods that had ingested radiolabeled phytoplankton was relatively slow (Fig. 5). Release rate constants were determined from a least squares fit of the retention data over the 14-d loss period. Although both species ingested the same radioactive food source, pellets produced by the larger neustonic species *Anomalocera* lost bismuth at a rate roughly twice as fast ($Tr_{1/2}$ = 26 ± 5 d) as those excreted by the smaller *Acartia* spp. ($Tr_{1/2}$ = 58 ± 7 d).

The release of ^{207}Bi from the natural, trap-collected fecal pellets that had previously scavenged ^{207}Bi from seawater for 72 h is shown in Fig. 6. In general the release rates of bismuth from the pellets harvested in the laboratory from freshly collected copepods were roughly similar for both size fractions. Half-times for bismuth release computed between 4.5 h and 11 d for the small and large size fractions were 33 ± 9 and 26 ± 7 d, respectively. On the other hand, over the same time interval, pellets isolated from a sediment

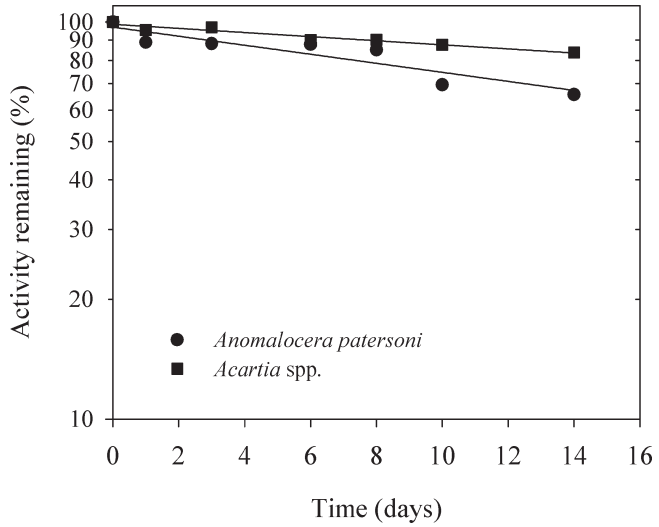

Fig. 5. Release of ^{207}Bi from copepod fecal pellets produced in the lab by *Anomalocera patersoni* and *Acartia* spp. that had ingested radiolabeled phytoplankton (*Dunaliella*). The pellets were dialyzed against flowing seawater for 14 d, and loss values are expressed as the percentage radioactivity remaining relative to that measured immediately after a 4-d prerinsing period. Each data point represents counts of the same pellets over time.

trap tended to release bismuth slightly more rapidly ($Tr_{1/2}$ = 17 ± 5 d).

Release of scavenged Bi *from sediment trap particles*—The release of sorbed radiotracer from four size fractions of

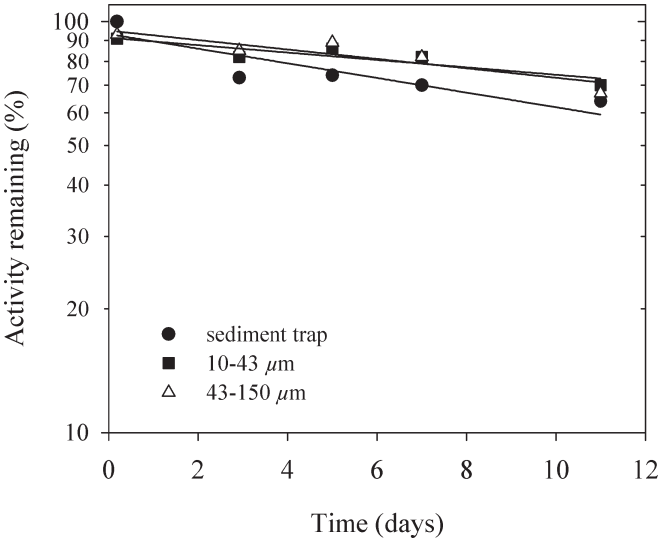

Fig. 6. Release of ^{207}Bi from natural fecal pellets during 11 d of dialysis against flowing seawater. The pellets had been previously radiolabeled with ^{207}Bi in seawater for 72 h. The data shown are for fecal pellets isolated from a sediment trap, and for two size fractions of natural fecal pellets (10–43 and 43–150 μm) from copepods that had been collected several hours previously in Monaco surface waters. The data points, based on counts of single samples, indicate the radioactivity in the fecal pellets expressed as a percentage of the total radioactivity measured in the pellets at the commencement of dialysis.

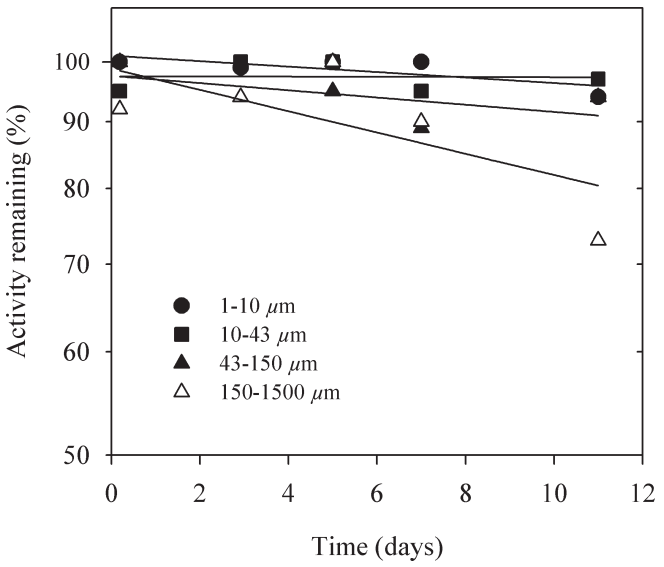

Fig. 7. Release of ^{207}Bi from various size fractions of bulk sediment trap material (with fecal pellets removed) during 11 d of dialysis against flowing seawater. The material had been radiolabeled by exposure to ^{207}Bi in seawater for 72 h. Size fractions were in the following ranges: 1–10, 10–43, 43–150, and 150–1500 μm. The data points, based on counts of single samples, indicate the radioactivity in the material expressed as a percentage of the total radioactivity measured in the bulk material at the commencement of dialysis.

bulk sediment trap material (with fecal pellets removed) during 11 d of dialysis against flowing seawater was extremely slow in almost all cases (Fig. 7). Release rate constants and resultant retention half-times were computed between 4.5 h and 11 d. Only the largest particle size fraction (150–1500 μm) displayed a $Tr_{1/2}$ (37 $\pm$ 22 d) that was similar to those measured in fecal pellets. The smaller size fractions displayed a strong retention of scavenged bismuth with computed $Tr_{1/2}$ values of 144 $\pm$ 75 d, 3470 $\pm$ 6940 d, and 108 $\pm$ 78 d for the 1–10-μm, 10–43-μm, and 43–150-μm fractions, respectively. As is evident in Fig. 7, the slopes of the regression lines are small but the scatter of data about the least squares regression is large, which leads to very large standard deviations for the computed slope values, particularly for the 10–43-μm size fraction. Therefore, these $Tr_{1/2}$ values for the release of scavenged bismuth from marine snow are best viewed only as order of magnitude estimates.

Discussion

Among all the marine organisms for which such measurements have been made, phytoplankton most often display the highest concentration factors for many elements and radionuclides, primarily due to their small size and corresponding large relative surface area for sorption (Fisher and Reinfelder 1995; Fowler and Fisher 2004; IAEA 2004). Data compiled by Fisher and Reinfelder (1995) for a number of marine phytoplankton species indicate VCF values for the chlorophyte *Dunaliella* on the order of (1–6) $\times$ 10^4 for many of the heavy trace elements (e.g., Zn, silver [Ag], mercury [Hg], Pb) and as high as (1–6) $\times$ 10^5 for particle-reactive thorium (Th) and the transuranic elements americium (Am) and Pu. Likewise, their VCF compilation for the coccolith *Emiliana* shows a similar range of values for those elements. Our measured VCF for bismuth of 5 $\times$ 10^5 for *Dunaliella* agrees well with those reported for the more particle-reactive elements. However, the bismuth VCF measured in *Emiliana* with and without coccoliths, (4–9) $\times$ 10^6, is an order of magnitude higher than any value reported in the literature for *Emiliana*, or any other phytoplankton species including *Dunaliella*. It is clear from these comparisons that bismuth has a strong affinity for phytoplankton surfaces and is bioconcentrated to some of the highest levels that have been reported for trace elements, anthropogenic radionuclides, or natural-series radionuclides in marine phytoplankton (Fowler and Fisher 2004; IAEA 2004).

Bismuth taken up by phytoplankton over a 5-d period was subsequently released with a biological half-time ranging from approximately 3 to 5 d, depending upon the initial conditions under which the cells accumulated the radiotracer (Fig. 2). Although the difference in the degree of retention is small, it appears that ^{207}Bi was released slightly faster from *Dunaliella* that had accumulated the radiotracer under light : dark conditions than nonphotosynthesizing cells that were exposed to ^{207}Bi in constant darkness. In general, bismuth appears to behave similarly to the particle-reactive transuranic elements in phytoplankton in terms of both its degree of uptake and release rate. For example, Fisher et al. (1983*a*) report VCFs ranging from approximately 2 $\times$ 10^5 to 4 $\times$ 10^5 for plutonium, americium, and californium in *Dunaliella*. Furthermore, in similarly designed release rate experiments, they measured biological half-times of 10–12 d for ^{241}Am in diatom cells and reported that *Dunaliella* lost ^{241}Am at a faster rate than did the diatoms. Therefore our measured ^{207}Bi $T_{b1/2}$ values of 3 and 5 d are likely very similar to that measured for americium in the same species.

The high degree of uptake and strong retention observed for bismuth in phytoplankton cells suggests that stable bismuth and its radioactive isotopes are readily available for uptake into and passage through the marine food chain. This aspect was examined at the second trophic level by measuring ^{207}Bi assimilation into copepods, which had ingested radiolabeled phytoplankton followed by purging their gut of unassimilated radioactive food. The calculations in Table 1 indicate that the two copepod species retained approximately 4% of the radiotracer ingested during 22 h. Compared to recently compiled trace element assimilation data for copepods (Fisher and Reinfelder 1995; Fowler and Fisher 2004), the 4% assimilation efficiency measured for bismuth is very low and falls within the range of values (1–10%) reported for ingested plutonium and americium in copepods and other herbivorous crustacean zooplankton. Such low assimilation into the tissues of copepods indicates that most of the ingested bismuth is packaged and released in the form of fecal pellets. Unfortunately, to date there is no published information on bismuth concentrations in zooplankton fecal pellets or other

biogenic detrital particles. Nevertheless some insight can be gained from our ^{207}Bi tracer experiments with fecal pellets and marine snow.

Two size fractions of freshly produced copepod fecal pellets and mixed zooplankton fecal pellets collected in sediment traps rapidly scavenged ^{207}Bi from seawater and reached WCF values (or K_d values) ranging from $\sim 4.5 \times 10^3$ for large copepod pellets to $\sim 1.6 \times 10^4$ for the small copepod pellets after only 1 d exposure (Fig. 3). It is assumed that the primary mechanism for dissolved element scavenging by these fecal pellets is adsorption to the outer surface of the pellet, i.e., the peritrophic membrane that encases the pellet. This is most likely the reason why the small fecal pellets with a greater relative surface area attained a WCF nearly four times higher than that of the larger pellets.

As shown in Fig. 4, trapped marine snow particles from which fecal pellets were removed also scavenged ^{207}Bi to approximately the same extent ($K_d \sim 10^4$) and in one size fraction to a much greater degree ($K_d \sim 5 \times 10^5$). Since the latter very high K_d value is likely unreliable for the reasons outlined in the Results section, a K_d value of 1×10^4 is considered to be a reasonable approximation for scavenged bismuth in marine snow particles. In view of these results, when performing experimental simulations of element scavenging by fine particulates, it is preferable that the weights of particles and particle concentrations in the radiolabeled seawater be maintained as similarly as possible in order to avoid potential artifacts. Nevertheless, in general, our experimental data strongly suggest that zooplankton fecal pellets and other forms of biogenic debris, which sink at speeds of tens to hundreds of meters per day (Fowler and Knauer 1986), will readily scavenge dissolved bismuth via adsorption onto particle surfaces and transport it downward in the water column. This mechanism of dissolved bismuth scavenging and removal from the upper water column by sinking biogenic particles occurs in tandem with the zooplankton packaging of bismuth-containing phytoplankton cells and other particles into their fecal pellets that are subsequently released into the water column. With both mechanisms operating, it is very likely that in situ K_d values for stable bismuth (or radio-bismuth) in natural fecal pellets would be somewhat higher than those we report here from the soluble radiotracer scavenging experiment. This aspect could be examined by analyzing stable bismuth concentrations in freshly collected fecal pellets and relating those concentrations to the bismuth concentration in the surrounding seawater.

While direct scavenging of dissolved bismuth from the water by sinking fecal pellets will occur, as the pellets age they will also begin to decompose and release bismuth from the internally packaged phytoplankton cells as well as from the pellet surfaces. The results in Fig. 5 demonstrate that bismuth packaged into fecal pellets is slowly released to the water column at rates that are dependent on the zooplankton species or, more likely, the size and compactness of the pellets they produce. For the copepods we studied, the smaller more compact pellets produced by the mixed *Acartia* species retained approximately twice as much of their packaged bismuth as did the larger pellets egested by *Anomalocera* that had grazed the same radiolabeled phytoplankton. Presumably radiolabeled phytoplankton debris in the more compact pellets will have less contact with the surrounding seawater, thereby slowing the bismuth release process. Such a reduction in contact time of the egested phytoplankton debris with the surrounding seawater may be one reason why the ^{207}Bi release rate in these pellets ($Tr_{1/2}$ = 58 and 26 d) was longer than that for the living phytoplankton cells ($Tr_{1/2}$ = 3–5 d). In addition, following digestion the chemical and physical composition of the residual cell material may differ substantially from living cells, and consequently bismuth may be more strongly retained by this debris.

The measured release half-times for bismuth in these pellets (58 and 26 d) are relatively long and are of the same order of magnitude as $Tr_{1/2}$ values for americium in fecal pellets produced by copepods (11–12 d, Wang et al. 1996) and euphausiids (41 and 51 d, Fisher et al. 1983*b*) that had ingested labeled diatoms. They also approximate those for americium (32 d), cerium (Ce; 23 d), europium (Eu; 14 d), and ruthenium (Ru; 34 d) in similar pellets that previously scavenged these particle-reactive elements directly from seawater (Fisher et al. 1991*a*). Furthermore, given the 4-d prerinse period before the ^{207}Bi-labeled pellets were first counted, the release half-times we measured are most likely related only to loss from the slowly exchanging, more tightly bound pool of bismuth within the pellets. For the natural fecal pellets that had scavenged ^{207}Bi directly from water for 72 h, the half-times for bismuth release ranged from 17 to 33 d with little difference in release rate noted between the two different copepod pellet size fractions (i.e., 33 and 26 d, Fig. 6). Likewise, the strong retention of scavenged bismuth by copepod fecal pellets mirrors that of other particle-reactive elements (e.g., Am, Ce, Eu, and Ru) that have been similarly measured in zooplankton fecal pellets (Fisher et al. 1991*a*).

It is noteworthy that the rates of bismuth release from zooplankton fecal pellets were generally similar (ranging from 17 to 58 d), whether the bismuth was primarily packaged in detritus within the pellet or was scavenged directly from seawater onto the external pellet surface. One might expect a more rapid desorption of the externally scavenged bismuth compared to release of the element from debris within the pellet. In fact, in both cases, some loss of bismuth could also occur by fragmentation of small particles as the pellets slowly decompose. There are reports in the literature that the peritrophic membrane encasing copepod fecal pellets can decompose in a matter of a few days; however, many copepod fecal pellet studies similar to ours have shown that such pellets maintain their integrity for up to 1 to 2 months with or without their pellicle intact (Small et al. 1979; Fisher et al. 1991*a*; Wang et al. 1996). Visual observation of the pellets used in our release experiments indicated that they maintained their integrity for the entire duration of both the uptake and release experiments (1–2 weeks) but that the pellicle was often broken or partially fragmented. This suggests that some of the labeled phytoplankton debris inside the pellet was in direct contact with seawater, and that some ^{207}Bi was

Table 2. Comparison of bismuth VCF and release half-time ($Tr_{1/2}$) in phytoplankton, assimilation efficiency (AE) in copepods ingesting phytoplankton, and $Tr_{1/2}$ in copepod fecal pellets (FP) with other particle-reactive radionuclides and elements. Comparable information for two biologically active elements (Zn and selenium [Se]) is included for comparison. Data are taken from Fisher and Reinfelder (1995), Wang et al. (1996), and Fowler and Fisher (2004), and phytoplankton VCF values refer to *Dunaliella tertiolecta* and *Emiliana huxleyi* whenever specified.

Element	Phyto VCF (10^5)	Phyto $Tr_{1/2}$ (d)	Copepod AE (%)	Copepod FP $Tr_{1/2}$ (d)
Bismuth	5–90	3–5	~4	30–60
Plutonium	1.6–2.2	—	1	7–19
Americium	1.1–1.8	11–29	1–10	10–215
Thorium	5–6	30–44	—	—
Polonium	0.4–0.7	—	29–55	—
Lead	0.5–0.8	10–280	—	—
Zinc	0.05–0.1	2–6	27–80	1–14
Selenium	0.005	3–173	97	9

desorbed without having to diffuse through an external membrane. Whatever the case, it appears that bismuth is lost from fecal pellets at roughly similar rates, whether it was initially adsorbed or bound to the chitinous membrane or ingested with the copepod's phytoplankton food.

The data we have obtained for bismuth VCF values and $Tr_{1/2}$ values in phytoplankton as well as assimilation efficiencies in copepods and $Tr_{1/2}$ values in their fecal pellets are summarized in Table 2 and compared with similar values for other particle-reactive radionuclides and trace elements. It is evident from the comparison that bismuth is highly reactive with biological surfaces and, in this respect, behaves very similarly to the long-lived transuranic radionuclides, plutonium and americium.

Compared to bismuth release rates in intact zooplankton fecal pellets ($Tr_{1/2}$ = 17–33 d), a mixture of fine marine snow particulate matter (without fecal pellets) collected in sediment traps generally released scavenged bismuth at much slower rates (Fig. 7). The most reliable $Tr_{1/2}$ values for the smallest size fractions ranged from approximately 3 to 5 months. This difference is most likely a function of the different particle compositions. For example, a relatively large fecal pellet will initially have much of the bismuth adsorbed or bound to ligands on the chitinous peritrophic membrane, whereas the finer marine snow particles are comprised of a wide variety of materials and compounds, including transparent exopolymers that presumably bind bismuth more tightly than a pellet. Only the largest size fraction of these sinking particulates (150–1500 μm) displayed a $Tr_{1/2}$ value (37 d) on the order of those measured in intact fecal pellets. In any case, all the scavenging data suggest that the very fine, slowly settling particles will retain and transport vertically a large fraction of the bismuth that has initially been accumulated until they dissolve or are aggregated and repackaged into larger, rapidly sinking particles such as fecal pellets.

The measurements that have been made of bismuth concentrations in seawater and its distribution with depth indicate that it is highly reactive with particles, most likely because of its proposed speciation as being mainly cationic hydroxyl complexes (Lee et al. 1985/1986). It is argued that the source of Bi is atmospheric, probably from volcanic emissions. However, since the highest concentrations of sedimentary Bi underlay those of eolian clay deposits in the North Pacific, Bi appears also to be transported on arid dust, perhaps by Mn oxide phases of desert varnish, in analogy to enrichment in Mn nodules and cycling at suboxic depths (Bertine et al. 1996).

High particle reactivity of Bi results in the type of depth profiles that show low bismuth concentrations in the upper mixed layer, presumably due to scavenging by biogenic particles, and increasing concentrations with depth until reaching a subsurface maximum around 500 m. By comparison to other particle-reactive metals (Th, Zn, Pb, and Am) Bi partitioning onto polysaccharide-enriched colloidal organic material is suggested (Quigley et al. 2002). Since polysaccharides are not strong chelators themselves, they apparently act as proxies for other extracelluar biopolymeric substances that can strongly bind particle-reactive elements (e.g., actinides), scavenging them from the ocean (Roberts et al. 2009).

Below these depths there is a definite decrease in bismuth concentration toward the bottom, suggesting a marked benthic scavenging from deep waters resulting in oceanic residence times of only decades (Lee et al. 1985/1986), as is the case for other natural nuclides like protactinium-231 (Pa^{231}), Pb^{210}, and polonium-210 (Po^{210}; as reviewed in Rutgers van der Loeff and Geibert 2008). These water column profiles of bismuth are also very similar to those that have been measured for plutonium, a particle-reactive element for which scavenging, vertical distribution, and downward flux have been shown to be largely controlled by biogenic particles (Fowler et al. 1983; Fowler and Knauer 1986). The results of our experiments on the association of ^{207}Bi with plankton and biogenic particles further support the view that bismuth behaves similarly to plutonium, as well as other particle-reactive, stable, and radioactive elements in the marine environment. In this respect, we conclude that bismuth and its radioisotopes, in particular natural ^{210}Bi, could serve as useful tracers to quantify shorter term marine scavenging processes in the upper water column.

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