Fukushima ^{137}Cs at the base of planktonic food webs off Japan

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Abstract

The potential bioaccumulation of ^{137}Cs in marine food webs off Japan became a concern following the release of radioactive contaminants from the damaged Fukushima nuclear power plant into the coastal ocean. Previous studies suggest that ^{137}Cs activities increase with trophic level in pelagic food webs, however, the bioaccumulation of ^{137}Cs from seawater to primary producers, to zooplankton has not been evaluated in the field. Since phytoplankton are frequently the largest component of SPM (suspended particulate matter) we used SPM concentrations and particle-associated ^{137}Cs to understand bioaccumulation of ^{137}Cs in through trophic pathways in the field. We determined particle-associated ^{137}Cs for samples collected at 20 m depth from six stations off Japan three months after the initial release from the Fukushima nuclear power plant. At 20 m SPM ranged from 0.65 to 1.60 mg L^{-1} and rapidly declined with depth. The ratios of particulate organic carbon to chlorophyll *a* suggested that phytoplankton comprised much of the SPM in these samples. ^{137}Cs activities on particles accounted for on average 0.04% of the total ^{137}Cs in seawater samples, and measured concentration factors of ^{137}Cs on small suspended particles were comparatively low (~10^2). However, when ^{137}Cs in crustacean zooplankton was derived based only on modeling dietary ^{137}Cs uptake, we found predicted and measured ^{137}Cs concentrations in good agreement. We therefore postulate the possibility that the dietary route of ^{137}Cs bioaccumulation (i.e., phytoplankton ingestion) could be largely responsible for the measured levels in the copepod-dominated (%) zooplankton assemblages in Japanese coastal waters. Finally, our data did not support the notion that zooplankton grazing on phytoplankton results in a biomagnification of ^{137}Cs.

Keywords

Fukushima, cesium, trophic transfer, phytoplankton, zooplankton

1. Introduction

Damage to the Fukushima Daiichi nuclear power plant (NPP) following the March 2011 earthquake in Japan resulted in one of the largest accidental releases of radioactivity into the ocean. According to the most recent estimates, the total amount of released ^{137}Cs into the North Pacific Ocean falls within a large range of 4-40 PBq (Buesseler, 2014). To understand the potential for public health impacts through the consumption of contaminated seafood, it is essential to also assess the bioaccumulation (= activity per unit mass) of Cs radionuclides at the basis of the marine foodweb. Phytoplankton, for example, can bioaccumulate diverse metals and radionuclides from the nuclear fuel cycle (Fisher, 1986), and these contaminants can then be taken up by multiple classes of zooplanktonic grazers in a process referred to as trophic transfer. Zooplankton can strongly influence the cycling, vertical flux, and retention times of metals in the oceans through scavenging, trophic transfer, and sinking debris (Fisher and Reinfelder, 1995). A number of laboratory culture studies have quantified the extent to which radionuclides concentrate in small planktonic assemblages including phytoplankton (Fisher, 1985, 1986; Giesy and Paine, 1977; Heldal *et al*., 2001; Sakaguchi *et al*., 1978). However, field studies have been sparse (Fisher and Fowler, 1987; Fowler and Fisher, 2005; Martin and Knauer, 1973) but are needed to validate experimentally derived parameters. Such validated parameters can then be used to predict the larger impacts of ocean radionuclide contamination for public health.

In this study, we measured Fukushima NPP radionuclides in suspended particles that contained marine phytoplankton, which were sampled from the surface layer of the ocean (20 m) off the Japanese coast in June 2011. We focused on the longer lived fission product ^{137}Cs (half-life = 30.1 years) over ^{134}Cs (half-life = 2 years), which was released in equal quantities (Buesseler *et al*., 2011) and showed similar patterns of bioaccumulation in zooplankton (Buesseler *et al*., 2012). We used ^{137}Cs activities on particles (mostly phytoplankton) together with previously published values for water and crustacean-dominated zooplankton sampled from six locations (Buesseler *et al*., 2012) to comparatively assess ^{137}Cs bioaccumulation in lower trophic level organisms in oceanic surface waters. This assessment could serve as a basis for further studies addressing radiocesium bioaccumulation in larger zooplankton and the potential for its biomagnification (i.e., mass-specific activities increase with trophic level) in the pelagic food web off the Japanese coast. While some previous compilations of Cs concentrations in marine food webs have indicated the potential for biomagnification in marine animals (Heldal *et al*., 2003), other studies have found little evidence of biomagnification (IAEA, 2004), suggesting that Cs behaves differently than other biomagnifying compounds such as for example methylmercury (MeHg). This study describes the partitioning of ^{137}Cs to particles suspended in Pacific waters off Japan following the Fukushima disaster of 2011 and the trophic transfer of ^{137}Cs in the pelagic food web in this region.

2. Materials and Methods

Samples were collected at several stations off the coast of Japan during the first international cruise aboard the RV Ka`imikai-O-Kanaloa (*RV KOK*) in June 2011 (Buesseler *et al*., 2012). From a total of 23 stations sampled during the cruise (Buesseler *et al*., 2012), we selected the six focus stations where sampling was most comprehensive (Fig. 1) and thus provide data on ^{137}Cs on particles ($^{137}Cs_{part.}$), concentration of suspended particulate matter (SPM) and chlorophyll *a* (Chl *a*).

2.1 Determination of ^{137}Cs levels on particles

To determine ^{137}Cs levels on particles ($^{137}Cs_{part.}$), particulate matter was collected onto Hytrex pre-filters (nominal pore size = 1.0 µm) by large volume *in situ* McLane pumps (http://www.mclanelabs.com). Note that nominally 1.0 µm-sized pore could have passed some of the slightly larger particles. Therefore, specific activities of ^{137}Cs (see section 2.3) converted based on $^{137}Cs_{part.}$ values could be underestimated. Problems in relation the inter-calibration of sampling method for POC have been discussed by Gardner *et al*. (2003) and Liu *et al*. (2005). Because the study of Liu *et al*. (2005) had used 70 µm mesh to study differences between *in situ* pumped particles and particles trapped on filters from Niskin bottle collected water, their conclusions cannot be used to properly assess uncertainty to the results presented in this study for approximately 1.0 µm-sized particles.

Pumps were deployed at a depth of 20 m, and 1,000-2,000 L of seawater were pumped through pre-filters with pumping volumes determined by flow meters. In the laboratory, filters were ashed in glass beakers at 460°C for 10 h, and ash density was calculated prior to transferring ash to vials for gamma counting to assess any density-dependent efficiency losses. Activities of ^{137}Cs were determined by gamma counting for 2-3 days (the lower the sample activity, the longer the counting time) on a germanium well detector at 661 KeV with a detection limit of 0.1 Bq m^{-3} and overall uncertainty of 0.1-3.7% (see Pike *et al*., 2013 for more detail). Detector efficiencies were determined from a dilute uranium pitchblende ore standard (US EPA Environmental Monitoring Systems Lab) and river sediment standard (NBS 4350 B), as well as ^{137}Cs standard solution added to appropriate matrixes (Certified Cs standards are from Eckert and Ziegler Isotope Products; Valencia, California).

2.2 Characterization of particles

Seawater samples were taken in triplicate using a rosette sampler, with water collected at 3 depths (20, 50 and 100 m), with an exception of station 19 where water was sampled at 20, 50 and 200 m below surface. For the analysis of Chl *a* each replicate (volume ranges: 0.3 - 0.4 L and 1.5 - 2.5 L for the >0.2 and >2.0 µm size fractions, respectively) was passed through 0.2 and 2.0 µm polycarbonate filters. Filters were stored frozen (-20°C) until subsequent fluorometric analyses for Chl *a* using a Turner Design Trilogy fluorometer (Parsons *et al*., 1984). In addition, seawater was also filtered onto pre-combusted (2 h at 450ºC) glass fiber filters (GF/F) and analyzed for particulate organic carbon and nitrogen (POC, PON, respectively) on a CE Instruments Flash 1112 elemental analyzer (Cutter and Radford-Knoery, 1991). To determine levels of SPM (mg L^{-1}) 1.75–2.5 L samples of seawater were passed through pre-dried (24 h at 60ºC) and pre-weighed 1.0 µm polycarbonate filters. Particles that were collected onto the filters were washed with an isotonic ammonium formate solution (10 mL per filter), dried at 60ºC, and weighed using a microbalance (sensitivity ± 10 µg).

2.3 ^{137}Cs in bulk particles and in copepod food

We converted $^{137}Cs_{part.}$ into mass based on ^{137}Cs activities, which throughout this manuscript we will refer to as specific activities or $^{137}Cs_{part.}{}^{*}$ (Bq g^{-1} dry wt.). Note that this specific activity term is also used to indicate radioactivity per number of atoms, however, its use

in this study relates radioactivity per mass of particulate matter. Conversion to $^{137}Cs_{part.}^{*}$ was based on SPM concentrations from the depth of 20 m (see section 2.2, Table 1). To model ^{137}Cs bioaccumulation in crustacean zooplankton from ingested food, we further calculated ^{137}Cs in food (C_f) by using $^{137}Cs_{part.}^{*}$ values corrected by excluding the picoplankton (< 2 µm) fraction (Table 2), because copepods typically consume larger phytoplankton. $^{137}Cs_{part.}^{*}$ for each station was multiplied by the % of total Chl *a* associated with particles > 2 µm (shown in Table 2), yielding C_f values for each of six stations (Table 1).

2.4 Zooplankton abundance

Mesozooplankton and micronekton were collected by double-oblique tows using Bongo nets, which included 2 nets with an opening of 0.6 m in diameter each and a mesh size of 300 µm. Gear was equipped with flowmeters (General Oceanics Co., Ltd.) and temperature-depth loggers (JFE Advantech Co., Ltd.) to estimate the filtered water volume and the sampling depth. Nets were deployed during 2–5 hauls per station at a ship speed of ~2 knots to average maximum depths of 150–250 m. Biomass that was collected during the hauls was combined into one overall sample per station. Aliquots (1–10% of total volume) of the fresh samples were immediately preserved with 5% formalin onboard and later in the laboratory sorted into higher taxa, enumerated, and converted to abundance.

2.5 Dietary ^{137}Cs accumulation in zooplankton

Measured ^{137}Cs activities in zooplankton ($^{137}Cs_{zoo.}^{*}$) (Buesseler *et al*., 2012) and on particles (Table 1) were used to calculate the dietary ^{137}Cs accumulation in zooplankton. Modeling of the bioaccumulation of only aqueous (dissolved) Cs in zooplankton was not possible due to the lack of measured kinetic parameters for this process. Recently, an equilibrium-based bioaccumulation model was tested in which aqueous and dietary uptake pathways were not separated (Vives i Batlle, 2015). Others have applied an ecosystem model to evaluate the dynamics of ^{137}Cs in various planktonic organisms, including various size classes of phytoplankton and zooplankton in the North Pacific Ocean during a year following the events of Fukushima disaster (Belharet *et al*., 2015). Dynamic modeling can be used to incorporate a variety of factors that influence ^{137}Cs activities in various compartments of the system by relying on approximate parameters, but this was not intended in the present study. Here we took a snapshot of ^{137}Cs associated with large phytoplankton cells (> 2 µm) and their consumers (i.e. mainly copepods) in June of 2011 to determine the basic relationship between them. We argue that the dietary part of the steady-state bioaccumulation model (Eq. 1) can be used to approximate ^{137}Cs accumulation by zooplankton from ingested particles (Wang and Fisher, 1998). The assumption about the steady-state concentration of ^{137}Cs in biota is supported by experimental results in which both the phytoplankton and zooplankton come to equilibrium within a day (Heldal *et al*., 2001; Mathews and Fisher, 2008b). Moreover, steady-state is achieved on time scales that are comparable to growth and loss rates, both of which are on the order of per day. Finally, ^{137}Cs exposure to copepods was not expected to change significantly during several days, hence ^{137}Cs concentrations were assumed to remain relatively constant over the course of the sampling period. This is supported by the age of the water at the study sites, which was estimated at 32 days (Charette *et al*., 2013).

We calculated ^{137}Cs in zooplankton ($C_{ss,f}$) according to:

$$C_{ss,f} = (AE \times IR \times C_f)/(k_{ef} + g) \quad (1)$$

with AE referring to the assimilation efficiency of ingested ^{137}Cs, C_f referring to ^{137}Cs concentration in food (as described in section 2.3), IR referring to the weight specific ingestion rate (g g^{-1} d^{-1}), k_{ef} referring to the ^{137}Cs efflux rate constant, and g (d^{-1}) referring to the growth rate constant of copepods.

Typically, steady-state concentrations of metals in marine copepods have been calculated by summing aqueous and dietary uptake (all details pertaining to the model are discussed by Fisher *et al*., 2000; Wang and Fisher, 1998). In contrast, this study calculated $C_{ss,f}$ in zooplankton that bioaccumulated only from ingested food particles that were dominantly composed of large phytoplankton cells. To calculate $C_{ss,f}$ we used mean values of experimentally determined, published bioaccumulation parameters for representative crustacean species. Due to limited availability of parameters for various zooplankton taxa our prediction is limited to copepods, even though the zooplankton community off Japan encompasses other zooplankton taxa (Nishikawa *et al*., in prep.). At the six stations sampled copepods contributed up to 84% of the zooplankton biomass (Buesseler *et al*., 2012), and the most abundant families were: Acartidae, Calanidae, Clausocalanidae, Eucalanidae and Metrinidae within order Calanoida and Oncaeidae within order Cyclopoida (Nishikawa *unpublished*). We therefore assumed copepods as the most representative of the sampled zooplankton communities. The dietary contribution of ^{137}Cs in bulk zooplankton was modeled using an AE of 63 ± 3% and a k_{ef} of 0.52 d^{-1} (error was not reported; we have used 10% as an error in sensitivity analysis – see below), which was determined for a branchiopod crustacean *Artemia salina* fed a diet of ^{137}Cs-labeled marine phytoplankton, *Isochrysis galbana* (Mathews and Fisher, 2008b). AE values for Cs for other crustaceans have not been published. IR in copepods depends on food particle density. For example, Berggreen *et al*. (1988) demonstrated experimentally an exponential rise of IR from ~0.1 d^{-1} (chosen as min IR value in the sensitivity analysis) at ~100 µg C L^{-1} of *Rhodomonas balthica* to a maximum value of ~1.3 d^{-1} (chosen as max IR value in the sensitivity analysis) at ~1500 µg C L^{-1} of *R. balthica*. The average POC level at 20 m at our study sites was 56 µg L^{-1} with a range of 20 – 173 µg L^{-1}, but POC levels were higher at 50 m (mean: 146 µg L^{-1}; range: 101 – 214 µg L^{-1}). Therefore, the highest POC level at any depth at any of the study sites was 214 µg L^{-1} which corresponds to an IR of 0.3 d^{-1} (used for our calculations) determined for the copepod *Acartia tonsa* (Berggreen *et al*., 1988). Literature values of maximum grazing rates for planktonic copepods, including species inhabiting waters of the North Pacific Ocean, range from 0.10 to 2.50 d^{-1} as summarized by Kishi *et al*. (2007). We have used an average growth rate constant (*g)* value of 0.05 d^{-1} as determined for *A. tonsa* from min and max values (0.01 and 0.45, respectively) taken from Berggreen *et al*., 1988). As growth depends on food ingestion, the g that was compatible with IR of 0.3 d^{-1} equaled 0.05 d^{-1} (see Fig. 9 in Berggreen *et al*. 1988). We conducted a sensitivity analysis to test how the predicted $C_{ss,f}$ was affected by errors associated with individual model parameters. To do that we have used min and max values for each individual parameter in Eq. 1 and predicted a range of potential $C_{ss,f}$ present at each station. S_p describes the % deviation of each $C_{ss,f}^{s}$ from the mean $C_{ss,f}$ and was calculated as

$$S_p = 100\% \times (C_{ss,f}^{s} - C_{ss,f})/C_{ss,f}^{s} \quad (2)$$

Values of S_p can be both negative and positive. Parameters that have the greatest influence model outcome are those for which absolute values of S_p are the highest.

3. Results and Discussion

In the waters off Japan in June 2011, approximately two months following the major discharge of radioactive Cs from the Fukushima NPP, we found low concentrations of ^{137}Cs on particles, ranging from 0.040 ± 0.004 to 1.100 ± 0.013 Bq m^{-3} (Table 3). Therefore only a small fraction (range of 0.02−0.08 % with an average of 0.04%) of the total ^{137}Cs water column inventory was associated with pump-collected particles (calculated as 100% × $^{137}Cs_{part.}$/ $^{137}Cs_{diss.}$; dissolved ^{137}Cs activity concentrations - $^{137}Cs_{diss.}$ from Buesseler *et al*., 2012). Fig. 2 depicts the magnitude of differences in values for dissolved and particulate ^{137}Cs activities in surface waters for each station.

The ratio of ^{134}Cs:^{137}Cs (~1.0; data not shown) on suspended particles indicates the radiocesium on particles was of Fukushima origin (Buesseler *et al*. 2012). Results of linear regression for dissolved and particulate ^{137}Cs at 20 m of depth at the six stations showed a strong positive relationship ($r^2 = 0.96$; Fig. 2). While $^{137}Cs_{diss.}$ declined exponentially down to 200 m, SPM showed a minimum at 100 m (Fig. 3). Assuming constant concentration factors (CF; activity per unit mass of particles divided by activity per unit mass of seawater, which for small suspended particles is equivalent with partition coefficient K_d; Table 3) throughout the water column, $^{137}Cs_{part.}$ below 20 m would be $<5\times10^{-3}$ Bq m^{-3} (i.e. below detection). Traps retrieved on June 5th of 2011 from station K2 that is located at 47°N, 160°E contained particles with ^{137}Cs activities of 0.19 ± 0.01 Bq g^{-1} at 500 m and 0.22 ± 0.02 Bq g^{-1} at 4810 m (Honda *et al*., 2013). Station K2 is positioned 4° east of the station 19, i.e., the eastern-most location of this study for which we report levels of $^{137}Cs_{part.}$. At 20 m at station 19 on June 12, 2011 the specific activity of ^{137}Cs was 0.13 Bq g^{-1}, which was similar to specific activities of particles that were collected by sediment traps at station K2 (Honda *et al*., 2013). Kusakabe *et al*. (2013) have reported ^{137}Cs specific activities for nearshore sediments (i.e. as close as 30 km to the shoreline) in the first six months following the release, but sediments further offshore were collected only afterwards. According to Kusakabe *et al*. (2013), specific activities of ^{137}Cs in sediments from stations F1, E1 and D1 (~30 km off Fukushima NPP) ranged from 70 to 150 Bq kg^{-1} dry wt., which is nearly two orders of magnitude higher than specific activities of 137Cs on small suspended particles at 20 m (stations 25 and 27 in this study; Table 3). This suggests that much of the radioactive cesium introduced to coastal waters was quickly removed from the water column and deposited in nearshore sediments.

Particle associated ^{137}Cs activities as well as specific activities of zooplankton were highest at station 29 (Table 3), likely reflecting the highest ^{137}Cs activity in seawater at this location (Buesseler *et al*., 2012). The high activities in seawater at station 29 were attributed to the formation of a large eddy at the time of sampling (Buesseler *et al*., 2012). The variability in CFs for suspended particles ($^{137}Cs_{part.}{}^{*}$ divided by $^{137}Cs_{diss.}$) and zooplankton ($^{137}Cs_{zoo.}{}^{*}$ divided by $^{137}Cs_{diss.}$) among the six stations was surprisingly low (2-fold and 8-fold for small suspended particles and zooplankton, respectively; Table 1), despite up to an order of magnitude variation in dissolved ^{137}Cs activities in the surface layer.

Since densities of zooplankton are typically highest in the upper 50 m of the water column (Kaeriyama *et al*., 2008), CFs for suspended particles and zooplankton were also calculated from ^{137}Cs activities for water collected from 20 m and these values were more

variable. Such high variability was especially evident at stations 25 and 29 where a sharp gradient in $^{137}Cs_{diss.}$ between surface and 20 m was apparent and CFs varied ~3 and 9-fold, respectively. These CFs for the small particles were within range of those reported for five species of marine phytoplankton assayed in culture (~10^2–10^3) (Heldal *et al*., 2001). The determined CFs (i.e. 10–78; Table 3) for zooplankton using surface water $^{137}Cs_{diss.}$ at the six stations were comparable to the value (CF = 40) suggested by the IAEA (2004) as well as to the range of 55–245 for copepod-dominated zooplankton collected off Japan prior to Fukushima disaster (Kaeriyama *et al*., 2008). Kaeriyama *et al*., (2015) have shown variability in ^{137}Cs activity concentrations (0.21 – 23 Bq kg^{-1} wet wt.) in zooplankton in Sendai Bay that was collected periodically following the Fukushima events. The order of magnitude variability in zooplankton ^{137}Cs activity concentrations was used to justify the order of magnitude difference in apparent concentration ratios (aCR - as proposed by Kaeriyama *et al*., 2015 instead of CF) of ^{137}Cs between the zooplankton and seawater (Kaeriyama *et al*., 2015). The authors of that study also suggested that the taxonomic make up of the sampled zooplankton could influence the aCR similarly to the results of the present study (Kaeriyama *et al*., 2015). While Kaeriyama *et al*., (2015) propose that there are four phases during which the aCR changes, and the dynamic equilibrium is reached only in phase IV, this theory should be more thoroughly tested and other factors influencing aCR or CF values should be included into the overall equation.

In the present study, the zooplankton CFs were 4–45 times lower than CFs for small particles at these stations (Table 3), thus providing no evidence for biomagnification of ^{137}Cs between the primary producers and primary consumers (zooplankton) in these waters. Estimated CFs of ^{137}Cs in marine phytoplankton (this study and Heldal *et al*., 2001) were lower than those of other metals (e.g. Zn, Th, Pb; IAEA 2004), where values commonly exceed 10^4 and do not vary significantly among phytoplankton species (Fisher, 1986; Fisher and Reinfelder, 1995). Because Cs behaves similarly to the essential alkali cation K^+ and may thus be taken up via K uptake channels (Avery, 1996), the relatively low CFs observed for ^{137}Cs in marine phytoplankton may be attributable to the much higher concentration of K in seawater (6–7 orders of magnitude higher than Cs in seawater). This is consistent with the order of magnitude higher CFs measured for ^{137}Cs in freshwater phytoplankton (2×10^3 to 43×10^3) (Cushing and Rancitelli, 1972), likely because of higher levels of competing K and stable Cs (~2 nM) in seawater. This is consistent with research conducted by Mearns *et al*. (1981), that demonstrated that bioaccumulation of Cs in aquatic animals may generally reflect the Cs : K ratios in their environment.

SPM (0.65 to 1.60 g L^{-1}) and Chl *a* (0.48 to 3.05 µg L^{-1}) were highest at 20 m (surface water was not collected for these analyses) (Table 1 and 2), and they both sharply declined with depth (Fig. 4). While $^{137}Cs_{part.}{}^{*}$ was not correlated to either Chl *a* or SPM at the six stations (not shown), the POC:Chl *a* ratio at 20 m (e.g. for the two stations closest to shore; station 25: POC:Chl *a* = 12; station 27: POC:Chl *a* = 25) suggests that small particles were principally comprised of phytoplankton cells (Fig. 4). The POC:Chl *a* ratios in this study were comparable to values for diatoms (15-55) and dinoflagellates (22-62) from Tokyo Bay (Sathyendranath *et al*., 2009). Phytoplanktonic origin of the small particles is frequently related to known ratio of Chl *a* to dry weight of algae of about 1:200 and the ratio of phytoplankton dry weight to POC of ~4 (Graf, 1989; Parsons *et al*., 1984), and thus a Chl *a*:POC ratio of 0.02. Molar ratio of C and N is also used as a proxy for the particle make up such that the Redfield C:N ratio of ~6.6 would indicate presence of living phytoplankton cells in sampled particles. The ratios of POC:PON observed for the suspended particles in this study suggest that the SPM at 50 m carried

phytoplantkonic signature in a range of 7.3-8.6 (Fig. 4). At station 23 the POC:PON ratio was lowest (=8.1) at 20 m and increased with depth. At the nearshore station 27, at 20 m this ratio was 124 (Table 2), with the high value largely driven by the very low PON (i.e. 0.32 μg L^{-1}) (Table 2). The high POC:PON ratio at station 27 (data not available for station 25 as PON was below the limits of detection) could be indicative of terrestrial input of organic matter, which has typically higher C:N ratios in comparison to marine phytoplankton (Mayer *et al*., 2007). Based on POC:Chl *a* and POC:PON ratios we conclude that at most stations, the small particle fraction in the upper 50 m of the water column was primarily composed of phytoplankton (Table 2). Differences in both the POC:Chl *a* and C:N ratios might also reflect some variability due to taxonomic differences (Sathyendranath *et al*., 2009). Furthermore, the ratio of POC and Chl *a* increased with depth, and this increase was most prominent at stations 21, 27 and 29 (Fig. 4). An increase in the POC:Chl *a* ratio with depth is to be expected as pigments of sinking phytoplankton decay more rapidly than many of the other organic compounds (Lee *et al*., 2000; Wakeham *et al*., 1997). Moreover, digestive enzymes of phytoplankton-grazing zooplankton degrade Chl *a* to pheopigments as they graze, further contributing to an increase in POC:Chl *a* ratio (Welschmeyer and Lorenzen, 1985). Hence, the steepest increase in POC:Chl *a* ratio might be expected where zooplankton grazers are most abundant. The POC:Chl *a* supports the assumption of SPM as a suitable approximation for the abundance of food particles that copepods could feed on in this study. Based on densities of SPM and zooplankton, only 0.6–7.3% of total (zooplankton + SPM) particulate matter could be attributed to zooplankton at the six stations (Table 1).

Ratios of predicted vs. measured ^{137}Cs activities in zooplankton ranged from 1.28 to 1.59 for 4 stations but the predicted ^{137}Cs activity in zooplankton for station 21 was ~3 times lower than the measured value, and ~10 times higher for station 29 (Table 1). Further, the sensitivity analysis revealed that the prediction of the ^{137}Cs in copepods is largely influenced by the ingestion rate value (S_p up to 333%), and less so by the growth rate value (S_p up to 41%). The influences of the other factors on ^{137}Cs bioaccumulation prediction were < 10% (not shown). Phytoplankton dynamics result in spatial and temporal variation in both species composition and cell abundances. Therefore given that copepod ingestion rate is dependent on food particle abundance (Berggreen *et al*., 1988), ^{137}Cs activities in zooplankton could further display spatial and temporal variation. Differences between the predicted and measured ^{137}Cs activities in the overall sampled zooplankton assemblages could also be explained by unknown ^{137}Cs bioaccumulation levels in zooplankton groups other than the predicted copepods (e.g. pteropods, chaetognaths etc.; Nishikawa et al., in prep.; Kaeriyama *et al*., 2008). Some of these differences might have influenced our predictions at stations 21 and 29, but this could not be assessed due to the lack of data.

The potential for trophic transfer of metals depends on the degree of metal partitioning into the cytoplasm of food particles, which strongly influences assimilation (Fisher and Reinfelder, 1995; Mathews and Fisher, 2008b; Reinfelder and Fisher, 1991). The subsequent transfer up to higher trophic levels in the food web is inversely related to the efflux rate of the metal from the organism. For example, transuranic elements and metals like lead (Pb) and thorium (Th) that display high particle reactivity (k_d values $\geq 10^5$) but low AEs (<5%) have little potential for bioaccumulation in aquatic animals and for their transfer to higher trophic levels (Fisher and Reinfelder, 1995). Similarly, metals with low particle reactivity for phytoplankton typically have little chance to build up in marine food chains (Fisher and Reinfelder, 1995). Conversely, metals with high particle reactivity and high AEs (e.g., MeHg) are known to

biomagnify in aquatic food chains (Cabana and Rasmussen, 1994; Chen *et al*., 2008; Reinfelder *et al*., 1998). In addition, MeHg has high concentration factors in phytoplankton ($\geq 10^5$), high AE (>75%) and low efflux rate constants from 0.010 to 0.019 d^{-1} in marine fish (Mathews and Fisher, 2008a), contributing to its biomagnification.

Cesium appears to be unusual among the metals, given its moderate bioaccumulation in animals from marine food webs (Heldal *et al*., 2003; IAEA, 2004) despite its weak association with phytoplankton (concentration factors in marine algae $<10^3$ (Heldal *et al*., 2001). However, few studies have specifically quantified the uptake of Cs from diet and water in marine animals. Despite the relatively high efflux rates from marine animals (Mathews and Fisher, 2008b), there is modest biomagnification of this element (Harmelin-Vivien *et al*., 2012; Heldal *et al*., 2003). We thus argue that the bioaccumulation of Cs in food webs could be a consequence of the uptake from the diet in zooplankton with teleosts acquiring substantial amounts of it from both the aqueous phase and their diet (Mathews and Fisher, 2009). In addition, Cs can further build up in piscivorous fish due to high assimilation efficiency (AEs ~80%) (Mathews and Fisher, 2008b; Mathews and Fisher, 2009). Following the nuclear accident in Chernobyl in 1986, ^{137}Cs was shown to biomagnify in pelagic food webs in the Norwegian and Barents Seas, where ^{137}Cs concentrations were an order of magnitude lower in amphipods, copepods, and krill than in piscivores such as cod and harbor porpoises (Heldal *et al*., 2003).

In summary, particulate ^{137}Cs constituted only a small fraction of the total ^{137}Cs in the water column, yet our calculations suggested that the phytoplankton portion of particulate matter could have been a substantial source of ^{137}Cs for zooplankton. Absence of ^{137}Cs biomagnification between phytoplankton and zooplankton off Japan following Fukushima events is indicated by lower zooplankton CFs in comparison to CFs of zooplankton diet (i.e. phytoplankton-rich particles). To complete the picture of Cs dynamics in copepods, studies that involve aqueous Cs uptake and retention are required. Moreover, in order to better predict the ^{137}Cs activities in diverse marine zooplankton, uptake and retention studies need to be undertaken for other taxonomic groups that are significant components of the overall biomass in coastal and open ocean waters.

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Tables and Figures

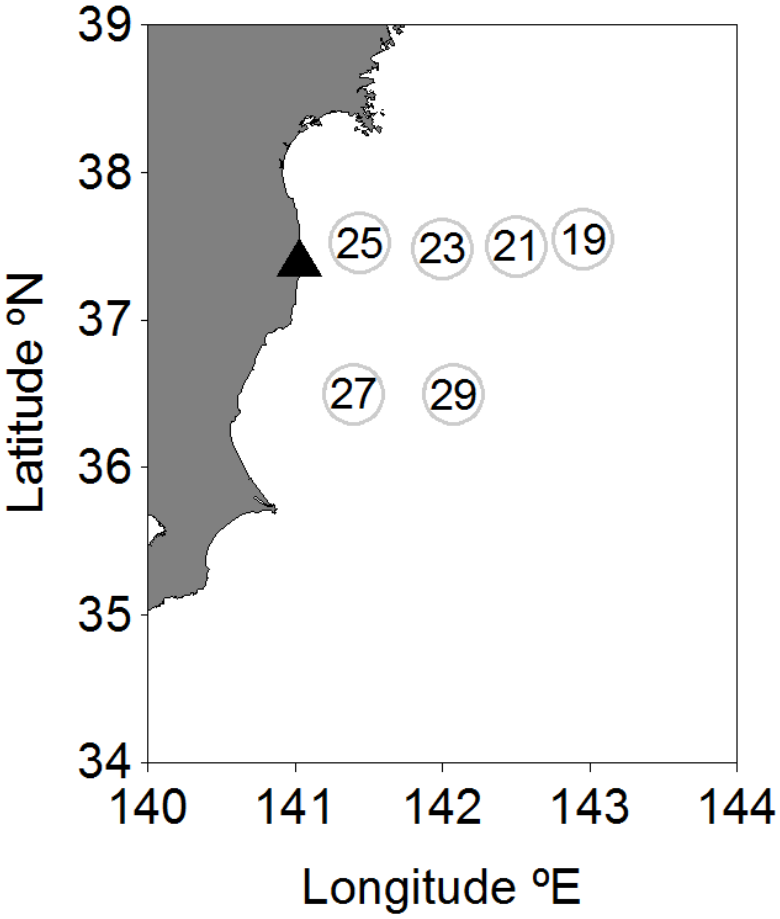

Figure 1. Sampling stations (gray circles) in Pacific off Japan; Fukushima NPP is depicted as a black triangle.

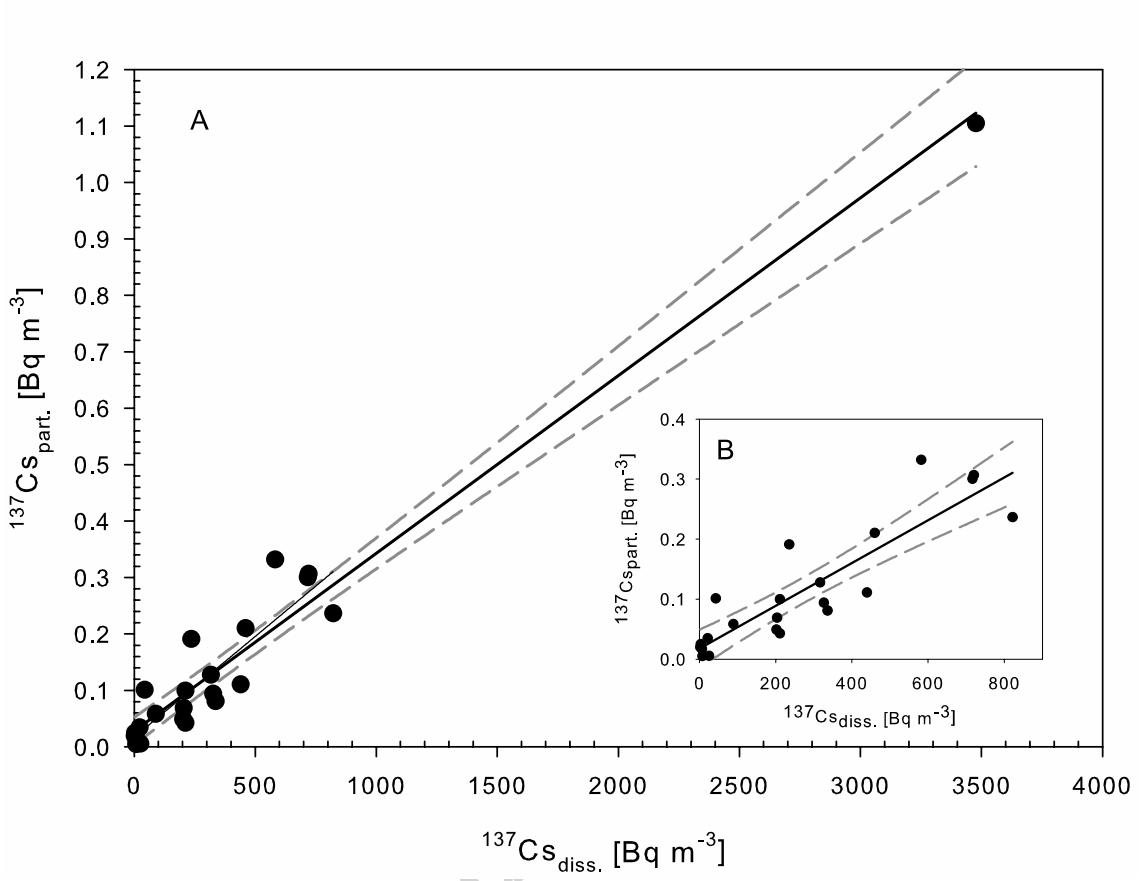

Figure 2. Linear regression (broken lines represent 95% confidence interval) of $^{137}Cs_{part.}$ (at 20m) and $^{137}Cs_{diss.}$ (surface) (A: $^{137}Cs_{part.} = 0.0003 \times ^{137}Cs_{diss.} + 0.0279$; $r^2=0.96$; B: $^{137}Cs_{part.} = 0.0004 \times ^{137}Cs_{diss.} + 0.0173$; $r^2=0.79$). A larger set of previously published (Buesseler et al. 2012) data was available for this regression (stations 0, 1, 4, 5, 7, 8, 12, 14, 18 - 32 in panel A and excluding station 29 in panel B).

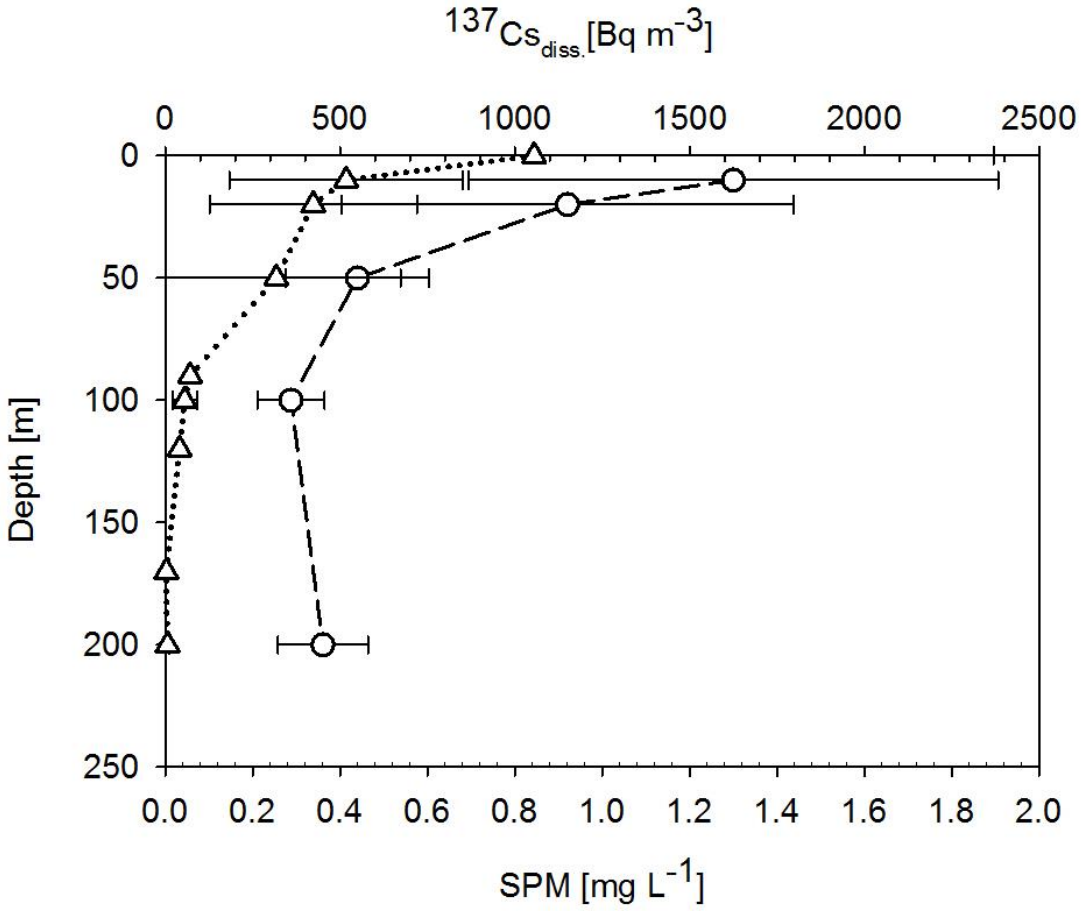

Figure 3. Depth profile of SPM (circles; 5 depths) and $^{137}Cs_{diss.}$ (triangles; 9 depths). Data points represent mean values for 6 stations ± SD. Values of $^{137}Cs_{diss.}$ have been previously published by Buesseler *et al*., (2012).

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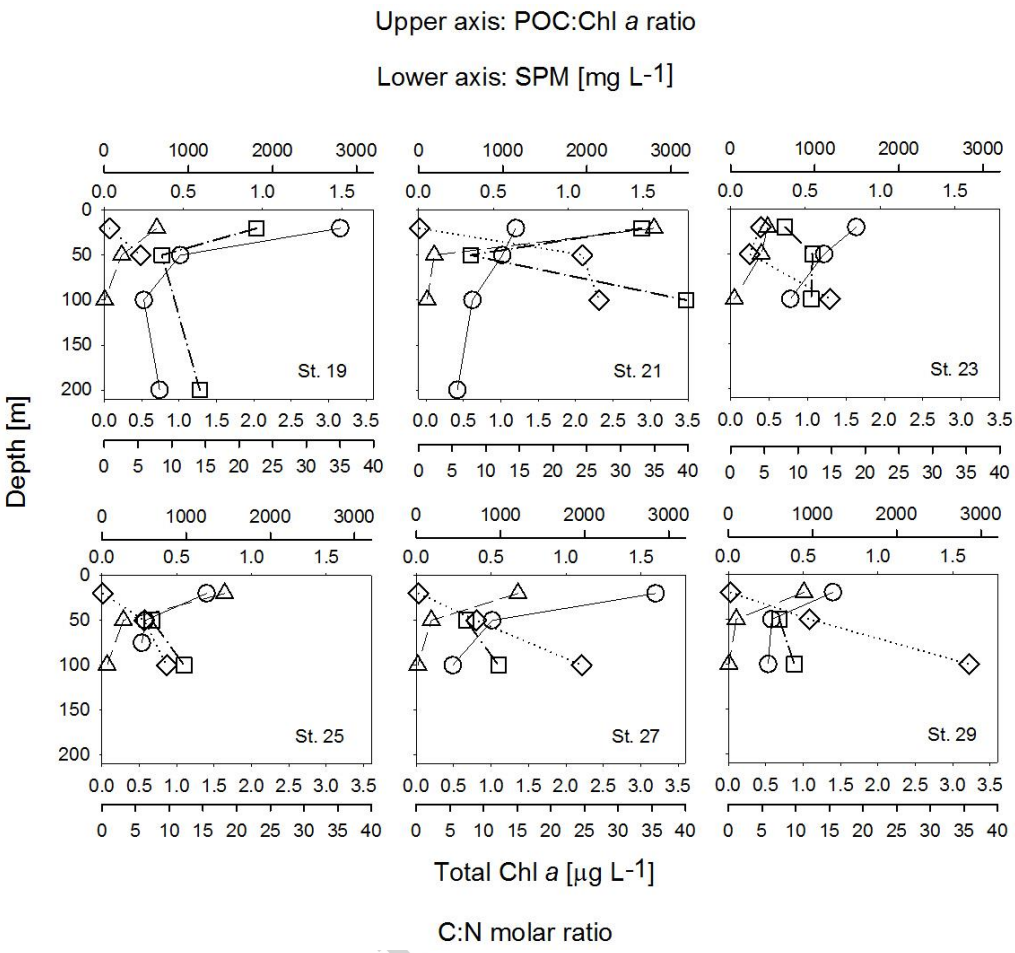

397

398 Figure 4. Vertical profiles of suspended particulate matter (SPM - circles), total Chl *a* (triangles),
399 POC : Chl *a* (diamonds) and C:N molar ratio (squares) at 6 stations: 19, 21, 23, 25, 27 and 29.

Sampling date	Station	Lat ºN	Long ºE	SPM mg L^{-1}	SPM + zooplankton mg L^{-1}	% zooplankton[a]	% copepods	C_f	$C_{ss,f}$ Bq kg^{-1} dry
6/12/11	19	37.5	143.0	1.49	1.56	4.7	65	61	20.4
6/13/11	21	37.5	142.5	0.65	0.70	7.3	52	18	5.9
6/14/11	23	37.5	142.0	0.84	0.89	5.6	58	117	38.9
6/15/11	25	37.5	141.4	1.07	1.09	2.3	51	122	40.5
6/16/11	27	36.5	141.4	1.60	1.61	0.6	84	117	38.9
6/16/11	29	36.5	142.1	0.70	0.75	6.0	76	990	328.

Table 1. Sampling dates and coordinates of the six sampling stations; densities of the small (i.e. SPM ≥1.0 μm; depth of 20 m) alone and when combined with the zooplankton. Dry mass of zooplankton was converted based on dry to wet weight ratio of 0.25. Zooplankton was collected by nets with mesh size of ≥300 μm; collection depth of zooplankton represents the integral of the water column with various maximum depths that ranged between 150 and 250 m; Buesseler *et al*., 2012; [a] % zooplankton = 100% × zooplankton ÷ (SPM + zooplankton). Zooplankton biomass was largely comprised of copepods – percentages for each station are listed. Comparison of model-predicted ($C_{ss,f}$) and measured ($^{137}Cs_{zoo.}{}^{*}$) ^{137}Cs bioaccumulated in zooplankton at six stations ([b] – values published in Buesseler *et al*., 2012) also summarized as $C_{ss,f}$: $^{137}Cs_{zoo.}{}^{*}$ ratios.

414

Station	Chlorophyl *a*				POC	PON	Molar POC:PON	POC:(
	Total	≥2 µm	≤2 µm	≥2 µm				
	µg L^{-1}			% Total	µg L^{-1}			
19	0.70 ± 0.10	0.34 ± 0.01	0.37 ± 0.10	47.9	46	2.36	22.3	6(
21	3.05 ± 0.06	0.83 ± 0.08	2.22 ± 0.02	27.2	38	1.34	33.2	1:
23	0.48 ± 0.01	0.20 ± 0.01	0.28 ± 0.004	41.7	173	25.0	8.1	36
25	1.64 ± 0.06	0.65 ± 0.01	1.00 ± 0.05	39.4	20	bd	-	1:
27	1.36 ± 0.07	0.85 ± 0.04	0.51 ± 0.03	62.5	34	0.32	124.1	2:
29	1.01 ± 0.05	0.64 ± 0.04	0.38 ± 0.02	62.7	27	bd	-	2'

415

416 Table 2. Mean ± 1 SD values for the total and size fractionated (≤2µm and ≥2µm) concentrations
417 of Chl *a* (µg L^{-1}), particulate organic carbon (POC), particulate organic nitrogen (PON), molar
418 ratio of C:N in particulate organic fraction, and the concentration ratio POC:Chl *a* at 20 m. bd:
419 below detection.

420

Station	$^{137}Cs_{part.}$	$^{137}Cs_{zoo.}$	$^{137}Cs_{part.}$*	$^{137}Cs_{zoo.}$* [a]	CF small particles	CF zooplankton
	Bq m^{-3}	mBq m^{-3}	Bq kg^{-1} dry wt.		near surface (at 20m)[a]	
19	0.190 ± 0.006	0.9	128	12.8	528 (434)	53 (43)
21	0.040 ± 0.004	0.9	62	17.3	294 (254)	78 (67)
23	0.240 ± 0.006	1.5	286	29.1	359 (278)	37 (29)
25	0.330 ± 0.001	0.5	308	26.2	525 (1441)	44 (121)
27	0.300 ± 0.007	0.2	188	19.9	257 (439)	27 (46)
29	1.100 ± 0.013	1.7	1571	34.2	446 (4026)	10 (87)

421

422 Table 3. ^{137}Cs activities on pump-collected particles from 20 m and in zooplankton from a range
423 of depths down to 150-250 m. ([a] – previously published by Buesseler et al. 2012); Both the
424 volume-based and specific activities of pump-collected particles and zooplankton are presented
425 here. Specific ^{137}Cs zooplankton activities together with zooplankton densities (converted from

426 wet wt. by a dry to wet weight factor of 0.25) have been used to back-calculate the volume-based
427 zooplankton activities. CFs for small particles as well as for zooplankton were calculated by
428 using dry weight-based activities.

429 Highlights

430 • We measured ^{137}Cs on the phytoplankton-rich suspended particles off Japan
431 • $\leq$ 0.08% of ^{137}Cs was associated with small suspended particles
432 • ^{137}Cs bioaccumulation in copepods is diet-driven despite low phytoplankton CFs
433 • ^{137}Cs biomagnification does not occur at the base of pelagic food web
434
435
436