Marine Chemistry xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Mercury and methylmercury incidence and bioaccumulation in plankton from the central Pacific Ocean

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ARTICLE INFO

Article history:
Received 25 February 2015
Received in revised form 22 June 2015
Accepted 15 July 2015
Available online xxxx

Keywords:
Bioaccumulation
Plankton
Methylmercury
Inorganic mercury
Pacific Ocean

ABSTRACT

Open ocean samples of phytoplankton and zooplankton were collected from the central Pacific on board the R/V Kilo Moana in October of 2011. The cruise traveled from Hawaii to Samoa, progressing through a High Nutrient Low Chlorophyll (HNLC) zone, and an equatorial upwelling region. Phytoplankton samples were size fractioned into 0.2–5 μm, 5–20 μm, and >20 μm samples. Methylmercury concentrations were 2.91 ± 2.58 pmol g^{-1} (wet weight) for the overall <200 μm size fractions, and highest around the HNLC region. Phytoplankton bioconcentration factors (logBCFs) averaged to 5.69 ± 0.98 and were higher than the values found for coastal regions. Both %MeHg ([MeHg]/[Hg]) and logBCF values indicated that the lowest size fraction had the largest fraction of the HgT as MeHg, signifying enhanced accumulation of MeHg into smaller organisms. Zooplankton vertical net tows were completed from depths of 200 m up to ~10 m. Zooplankton samples were analyzed for carbon, nitrogen and sulfur in addition to Hg and MeHg at size fractionations of 0.2–0.5 mm, 0.5–1.0 mm, 1.0–2.0 mm and occasionally >2.0 mm. Zooplankton abundance and MeHg concentrations both peaked at Stations 3 and 5 (upwelling region). The %MeHg in the organisms was highest in the >2.0 mm size class, displaying MeHg bioaccumulation for increasing zooplankton sizes. Separate day and night net tows were collected at Stations 3 and 5 in order to investigate differences due to diurnal migration of zooplankton. There were higher concentrations of MeHg for all sizes in night collections of zooplankton at Station 5, but no discrepancy for Station 3. These results represent some of the few measurements of Hg and MeHg at the base of the open ocean food chain, and are significant as they represent the instigation of bioconcentration into the base of marine food webs.

1. Introduction

Mercury (Hg) is a substantiated global concern due to the high bioavailability of its organic form methylmercury (MeHg), which is a damaging neurotoxin (Clarkson and Magos, 2006), and highly bioaccumulative in aquatic food chains (Chen et al., 2008; Sunda, 2012). Mercury emissions have increased above natural environmental levels due to anthropogenic practices, such as high temperature combustion, artisanal gold mining and cement manufacturing (National Research Council, 2000). Due to its long atmospheric residence time, Hg has the ability to travel throughout the world, impacting remote regions such as the open ocean (Lamborg et al., 2014; Mason et al., 1994, 2012). Oceanic fish represent a critical source of MeHg into diets, as most humans consume seafood in higher quantities than freshwater fish (Chen et al., 2008; Sunderland, 2007). Nevertheless, little research has been undertaken at mercury's point of entry into open ocean marine food webs, primarily due to the fact that it is difficult to measure MeHg uptake and tropic transfer under natural conditions, as open ocean concentrations of inorganic Hg and MeHg are extremely low (<1 pM for MeHg) (Gill and Fitzgerald, 1985; Lamborg et al., 2014; Mason et al., 2012). As a result, uncertainty still exists related to the behavior of Hg and MeHg in lower trophic levels of the food chain in marine ecosystems. Likewise, the exact processes which drive and control natural bioaccumulation and trophic transfer are still unresolved for the open ocean.

It is imperative to fully comprehend the transport of Hg and MeHg into the lower oceanic trophic levels, as these reflect the inception of exposure. Algae accrue nutrients, including essential metals (e.g. iron, zinc) and unessential elements (e.g. Hg, lead, arsenic) from the surrounding media, and also release compounds that influence metal speciation. Phytoplankton population and composition therefore has a significant impact on the levels and availability of trace metals in marine waters. The remineralization of algae during sinking and bloom degradation also impact metal speciation and availability. The resultant formation of natural complexes influences uptake of many metals by biota. Prior research suggests that phytoplankton MeHg uptake occurs primarily via passive diffusion of neutral complexes across a cell membrane (Fisher and Reinfelder, 1995; Gorski et al., 2006; Lawson and Mason, 1998; Mason et al., 1996; Pickhardt and Fisher, 2007). Passive uptake of both species could also result after sorption of Hg and MeHg to cell surfaces (Fisher, 1985).

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http://dx.doi.org/10.1016/j.marchem.2015.07.005
0304-4203/

However, the possibility also exists that phytoplankton assimilate Hg and MeHg via active or facilitated transport. Active uptake of MeHg remains unspecified. It is probable that MeHg is likewise accumulated when cells acquire organic compounds which are strongly bound to MeHg, such as cysteine or other thiols (Lawson and Mason, 1998; Moye et al., 2002), as has been found to occur in bacteria (Ndu et al., 2012; Schaefer et al., 2011). Pickhardt and Fisher (2007) demonstrated that live cells accumulated more MeHg than dead cells in freshwater phytoplankton, suggesting possible uptake via active processes. This was not the case for inorganic Hg. Because MeHg permeates into cellular cytoplasm rather than being bound with the cellular membrane (Mason et al., 1996; Pickhardt and Fisher, 2007), transfer and accumulation into the marine food web is greater for MeHg than for inorganic Hg (Mason et al., 1996; Reinfelder and Fisher, 1991). Subsequently, MeHg is bioconcentrated in phytoplankton and transferred via consumption through the food chain to herbivorous zooplankton, planktivorous fish, and eventually larger predators, with the fraction of MeHg amplifying at each trophic level (Berntssen et al., 2003; Foster et al., 2012; Kim et al., 2004). Therefore, it is crucial to quantify Hg and MeHg movement from ocean waters into primary and secondary consumers, as this is where the principal biomagnification occurs (Le Faucher et al., 2014; Mason, 2002; Pickardt and Fisher, 2007).

Relatively little data have been published on natural concentrations of Hg in coastal ocean plankton (Foster et al., 2012; Hammerschnidt et al., 2013; Mason et al., 2012), and there is even less information concerning the open ocean. In addition, there has been little study of the concentrations of MeHg in different size fractions of plankton, except for those published recently by Hammerschnidt et al. (2013). Furthermore, quantified amounts of MeHg transfer have not been established for primary (phytoplankton) and secondary producers (zooplankton) for open ocean populations. Even though coastal ecosystems represent a large fraction of overall productivity for marine systems, the global expanse of the open ocean, and in particular the more productive regions such as the equatorial Pacific, warrant consideration in terms of importance towards Hg and MeHg bioaccumulation. This study presents measurements of size fractionated Hg and MeHg concentrations for open ocean phytoplankton and zooplankton. The results of this study indicate that concentrations in zooplankton increase with organism size and that the bioaccumulation factor for phytoplankton decrease as suspended particle concentration increase. Determining these values have helped to establish levels of Hg and MeHg at the base of the open ocean food chain, at the onset of marine bioaccumulation. Additionally, these data provide information to managers and modelers concerned with the bioaccumulation of MeHg into open ocean fish consumed by humans.

2. Methods

2.1. Sample collection

Phytoplankton and zooplankton samples were collected along a transect from Oahu, Hawaii to Apia, Western Samoa, with a brief stopover at the Island Republic of Kiribati (Fig. 1). The cruise occurred on the R/V Kilo Moana on October 3–23, 2011. The cruise transect traveled through a High Nutrient Low Chlorophyll (HNLC) zone (~Station 3) and the highly productive equatorial upwelling region (Station 5). Eight (out of twelve) stations were sampled for plankton, and Table 1 details the coordinates for each station sampled. Two stations, Stations 3 and 5, were occupied for a 3-day period, which yielded the opportunity to collect multiple temporal zooplankton samples, and compare concentrations in night and day zooplankton collections. Separate day and night net tows were collected in order to investigate any differences due to the possible occurrence of diurnal migrating zooplankton. Water and plankton were sampled using trace-metal clean techniques.

Phytoplankton (seston) samples were amassed from known volumes of water collected out of Go-Flo bottles at the depth of the chlorophyll maximum of each station (Table 1). Phytoplankton was concentrated on acid-cleaned polycarbonate filters for various size fractionations by filtering seawater through 0.2 μm, 5 μm, and occasionally 20 μm filters. Potential occurrence of zooplankton in these fractions was impeded using a 200 μm mesh shield prior to filtering. Volumes filtered ranged from 0.5–2 L for the smallest fraction to 2–5.5 L for the larger fractions. Given this fractionation, phytoplankton size classes will be referenced as <5 μm (for 0.2–5 μm fractions), 5–20 μm and >20 μm. The 20 μm fraction represents plankton of >20 μm but <200 μm. Samples were collected at each size fraction for fluorescence, which was measured on board using a handheld Turner aquafluor fluorometer. In order to assess phytoplankton concentrations on a mass basis, biomass was calculated using both the chlorophyll and phaeopigment measurements, assuming a constant carbon:chlorophyll ratio of 100 for the region (Claustre et al., 1999; Taylor et al., 2011; Wang et al., 2013). These values were further converted into biomass by assuming 40% carbon in biomass. The calculated phytoplankton biomass values were scaled by a factor of 3 to account for biomass from sources other than phytoplankton, such as bacteria, inorganic particles, fecal pellets and other detritus (Church, 2008; Libes, 1992). Thus, the reported concentrations reflect those of the different seston sizes. These concentration values are comparable to those collected by others using size fractionation approaches (e.g. Hammerschnidt et al., 2013).

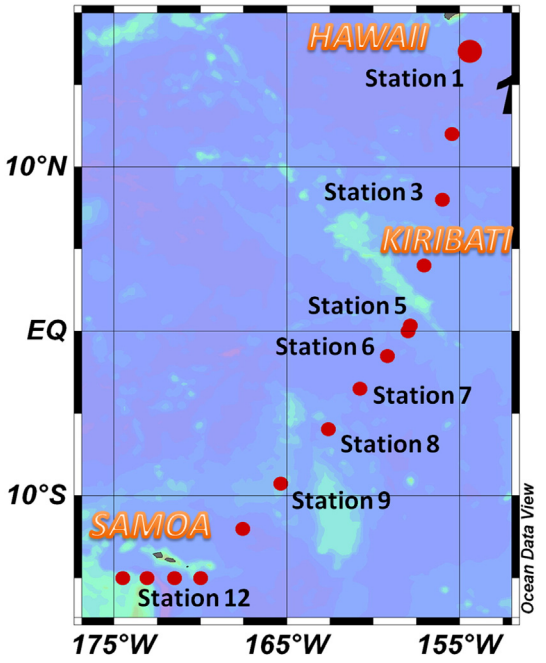

Fig. 1. Cruise track starting from Honolulu, Hawaii to Apia, Samoa, with a brief stopover in the Island Republic of Kiribati. Stations which were sampled for plankton are noted on the map, and locations are detailed in Table 1.

Table 1
Coordinates for plankton stations, and chlorophyll maximum depth sampled for phytoplankton, during the central Pacific research cruise.

Station #	Longitude (°W)	Latitude (°S)	Chl max. depth (m)
1	154.40	−17.00	115
3	156.00	−8.00	80
5	157.87	−0.36	40
6	160.77	3.50	75
7	162.61	5.96	75
8	165.36	9.25	79
9	167.56	12.00	60
12	173.10	15.00	125

Please cite this article as: Gosnell, K.J., Mason, R.P., Mercury and methylmercury incidence and bioaccumulation in plankton from the central Pacific Ocean, Mar. Chem. (2015), http://dx.doi.org/10.1016/j.marchem.2015.07.005