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Total and Monomethyl Mercury in Terrestrial Arthropods from the Central California Coast

Cruz Ortiz Jr. · Peter S. Weiss-Penzias · Susanne Fork · A. Russell Flegal

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Abstract The aim of this project was to obtain a baseline understanding and investigate the concentration of mercury (Hg) in the tissue of terrestrial arthropods. The 4-month sampling campaign took place around Monterey Bay, California. Total mercury (HgT) concentrations (x ± SD, dry weight) for the captured specimens ranged from 22 to 188 ng g^{-1} in the Jerusalem crickets (Orthoptera: Stenopelmatidae); 65–233 ng g^{-1} in the camel crickets (Orthoptera: Rhaphidophoridae); 25–227 ng g^{-1} in the pill bugs (Isopoda: Armadillidiidae); 19–563 ng g^{-1} in the ground beetles (Coleoptera: Carabidae); 140–441 ng g^{-1} in the variegated meadowhawk dragonflies (Odonata: Libellulidae); 607–657 ng g^{-1} in the pacific spiketail dragonflies (Odonata: Cordulegastridae); and 81–1,249 ng g^{-1} in the wolf spiders (Araneae: Lycosidae). A subset of samples analyzed for monomethyl mercury (MMHg) suggest detrital pill bugs have a higher MMHg/HgT ratio than predatory ground beetles.

C. Ortiz Jr. · P. S. Weiss-Penzias · A. R. Flegal
Institute of Marine Science, University of California - Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, USA
e-mail: pweiss@ucsc.edu

A. R. Flegal
e-mail: flegal@ucsc.edu

C. Ortiz Jr. (✉)
Department of Environmental Engineering Sciences, Engineering School of Sustainable Infrastructure and Environment, University of Florida, 412 Black Hall, PO Box 116450, Gainesville, FL 32611-6450, USA
e-mail: cortiz@ufl.edu

S. Fork
Elkhorn Slough National Estuarine Research Reserve, PO Box 267, Moss Landing, CA 95039, USA
e-mail: skfork@gmail.com

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The novelty, scientific significance, and importance of the Article

The novelty and the importance of this study is that it's creating a baseline understanding of mercury cycling in terrestrial ecosystems. Unfortunately, there are very few other studies of mercury in terrestrial arthropod food chains for comparison. Hopefully this initial report will catalyze new studies on the role of atmospheric deposition in the biogeochemical cycling of mercury in terrestrial ecosystems. Moreover, the role of arthropods on the bioaccumulation and biomagnification of mercury in terrestrial food chains. Lastly, this investigation falls within BECT's aims and scope because it characterizes variations of mercury contamination. The motivation for this study came from an investigation which received significant press-coverage in 2012–2013 <http://green.blogs.nytimes.com/2012/03/28/coastal-california-fog-carries-toxic-mercury-study-finds/>.

Historic and on-going mercury contamination is of increasing concern for environmental and human health, as its toxic threshold continues to be lowered (Agency 2013; Organization 2010). That concern is based on the extensive bioaccumulation (factor of 10^7) of organic mercury to potentially toxic levels, especially in aquatic food chains (Fitzgerald et al. 2007; Scheulhammer et al. 2007). As a result, most research on the biomagnification of mercury has focused on aquatic environments. Arthropods are an important source of protein for many organisms (Zhang et al. 2009); furthermore, a few recent studies have determined that terrestrial food chains may be contaminated by

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the cross-habitat transfer of mercury by insects and spiders (Brasso and Cristol 2008; Cristol et al. 2008; Henderson et al. 2012).

Limited published data exist on Hg concentrations in terrestrial arthropods, and their potential as Hg pollution bioindicators needs further investigation. Terrestrial arthropods whose tissue is resistant to metallic pollutants are often used as biological indicators for metal contamination in soil (Dallinger et al. 1992; Udovic et al. 2009). It is also recognized that flying arthropods such as mosquitoes may also be a useful indicator of atmospheric Hg contamination (Hammerschmidt and Fitzgerald 2005). Thus, the current study aimed to evaluate the efficacy of using arthropods as indicators of Hg accumulation by measuring the concentration of Hg in the tissue of terrestrial arthropods from the central California coast, an environment well known for its persistent summer-time fog (Weiss-Penzias et al. 2012).

Methods and Materials

Samples were collected, using trace metal clean techniques at 3 sites around Monterey Bay, California: (1) Elkhorn Slough Estuarine Reserve (2) the University of California, Santa Cruz (UCSC), and (3) Chalk Mountain in Año Nuevo State Park (Fig. 1). The 4-month arthropod sampling campaign took place between March and October of 2012.

The samples included detrital arthropods: Jerusalem crickets (Orthoptera: Stenopelmatidae) (n = 7), camel crickets (Orthoptera: Rhaphidophoridae) (n = 11), and pill bugs (Isopoda: Armadillidiidae) (n = 41); and predatory arthropods: ground beetles (Coleoptera: Carabidae) (n = 14), wolf spiders (Araneae: Lycosidae) (n = 58); pacific spiketail dragonflies (Odonata: Cordulegastridae) (n = 2); and variegated meadowhawk dragonflies (Odonata: Libellulidae) (n = 4). The adult dragonflies were captured with sweep nets, all the other arthropods were captured using pit fall traps; these methods of collection are described elsewhere (Chanthy et al. 2013; Greenslade 1964). Unbaited pitfall traps were deployed 2–4 consecutive nights and checked within 24 h of deployment.

The samples were placed in trace metal clean plastic containers, within a cooler, and then promptly transported to UCSC. There they were rinsed with high purity (18.2 MΩ cm) water (Milli-Q®) to remove surface contaminants. Then they were dried, placed in trace metal clean plastic containers, frozen, and lyophilized prior to analysis.

Mercury analyses were made using established trace metal clean techniques. The organisms (29–249 mg) were weighed (±0.1 mg), pulverized, transferred to 100 mL acid-cleaned volumetric flasks, and digested with 10–20 mL of H_2SO_4–HNO_3, using the methodology described elsewhere (Liang et al. 1994). HgT concentrations in digestates were then determined by cold vapor atomic fluorescence spectrometry (CVAFS) with established methods that quantitatively measure Hg in aqueous samples (Bloom and Fitzgerald 1988; Fitzgerald and Gill 1979). MMHg concentrations of six samples were then measured by CVAFS after distillation, aqueous ethylation, purge and trap (Liang et al. 1994). The accuracy of the HgT measurements was determined from concurrent analyses of (1) procedural blanks, (2) Hg^0 calibration standards, (3)

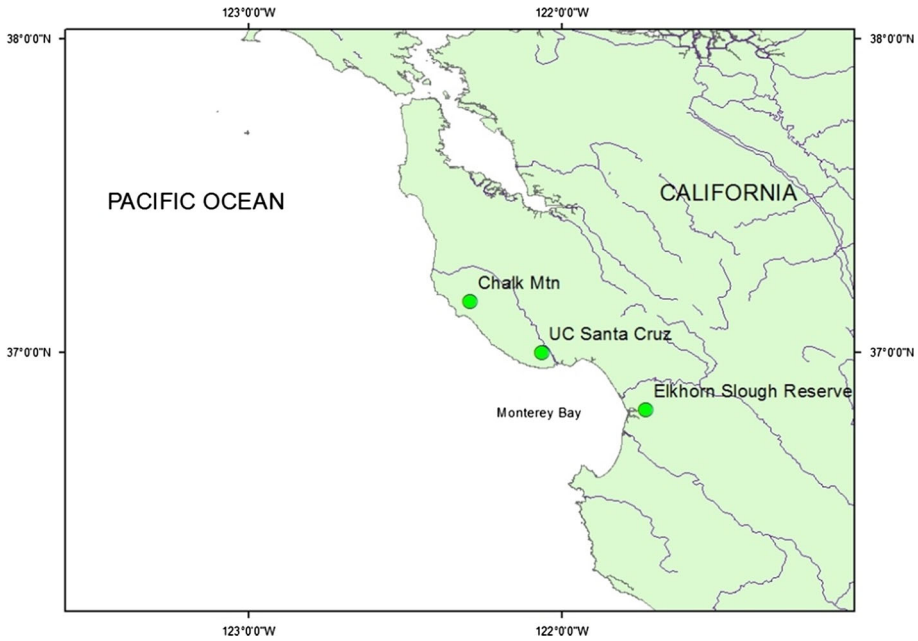

Fig. 1 Map of study location, Monterey Bay, California with sample sites at Elkhorn Slough Reserve (36°49′12.7″N, 121°44′10.7″W), the University of California, Santa Cruz (36°59′28.5″N, 122°03′40.7″W), and Chalk Mountain in Año Nuevo State Park (37°09′37.9″N, 122°17′24.8″W)

National Research Council of Canada Certified Reference Material (CRM) DORM-2 (dogfish muscle), (4) replicate aliquots from sample digests, and (5) replicate subsamples of arthropod digests from the parent samples. Three or more standard solutions were made for each analysis. All analyses had standard regressions with simple linear correlation coefficients (R^2) greater than 0.998. The HgT procedural blank ranged between 11 and 25 parts per trillion (ppt), and the HgT concentration of the CRM (DORM-2) ranged between 98 and 102 % of its certified value (4.64 ± 0.26 μg g^{-1}).

Results and Discussion

There is a lack of published values in the literature for comparison; furthermore, the values published have a very high variance, as is the case with this study. HgT concentrations (x ± SD, dry weight) of the 134 insects and spiders measured in this study, along with HgT values previously reported for some of those organisms (Cristol et al. 2008; Rimmer et al. 2010; Zhang et al. 2009) are listed in Table 1. There is no statistically difference ($p \leq 0.05$, *t* test) in HgT concentrations among any of the species measured at the different sites, those comparisons are limited by the high variance of mercury values. For example, the relative standard deviation (%) of HgT in spiders in our study was 73.6 ng g^{-1} (n = 58) and that in the study by Cristol et al. (2008) was 118.5 ng g^{-1} (n = 101). Due to this high variance, significant differences in Hg concentration between sites could not be established for any of the arthropods analyzed.

Predatory wolf spiders had the highest concentrations of HgT in this study, as is the case with two of the three compared studies, no other pattern was observed with the other groups of arthropods delineated in this study. There was notable temporal differences, although not statistically different ($p \leq 0.05$), in HgT concentrations of some of the arthropods in our study (Table 2). Although these comparisons might be an artifact of a small sample size, they warrant further investigation. Total mercury concentrations in wolf spider had relatively comparable HgT concentrations in March (255 ± 97 ng g^{-1}, n = 28), July (278 ± 127 ng g^{-1}, n = 5, and October (327 ± 173 ng g^{-1}, n = 20), but those average concentrations were all less than half of the average HgT concentration of wolf spiders in August (846 ± 312 ng g^{-1}, n = 5). The temporal difference coincided with the seasonal peak of fog that substantially increases the flux of MMHg in the study site. A similar, albeit much smaller, seasonal increase was also observed in camel crickets, but not pill bugs (Fig. 2). Fog data reported for 2012 was obtained from Monterey Regional Airport (MRY); mean daily visibility below 15.5 km is the threshold for reported fog occurrences at MRY and is indicative of a foggy day.

The positive covariance of high HgT concentrations in wolf spiders, and to a much lesser extent in camel crickets, does not seem to correspond with any known variables. Since the life span of male wolf spiders is about a year, with most adolescents in February through March (Punzo and Farmer 2006), HgT concentrations in the spiders should have been highest in October if that uptake was simply due to temporal bioaccumulation. And since the camel cricket population is relatively constant over time, with no seasonal period of intense reproduction (Lavoie et al. 2007), there does not appear to be a physiological explanation for the corresponding maximum in the HgT concentrations during August in that coastal zone. Although fog may be at question, at this time it cannot be determined because we know very little on how MMHg in fog impacts terrestrial ecosystems.

Table 1 Mean HgT concentrations for this and other studies, all concentrations expressed in (x ± SD, ng g^{-1} dry weight)

ID	This study		Zhang et al. (2009) Huludao, China	Rimmer et al. (2010) Vermont, USA	Cristol et al. (2008) Virginia, USA	
	(n)	Mean	Range	Mean	(n)	Mean
Spiders	58	401 ± 295	15–1,099	173 ± 81	101	1 240 ± 1 470
Camel Crickets	11	125 ± 62	12–866	10 ± 5	50	310 ± 1 220
Ground Beetles	14	134 ± 157		48 ± 67		
Pill Bugs	41	124 ± 47				
Jerusalem Crickets	7	109 ± 73				
Spiketail	2	632 ± 25				
Meadowhawk	4	220 ± 112				
Dragonflies	6	338 ± 209	233–1,2 432			
Moths–Butterflies				5 ± 7	137	380 ± 2,080

Table 2 Total mercury (HgT) results, (n) represents number of samples analyzed, all concentrations expressed in (x ± SD, ng g^{-1} dry weight)

ID	March		July		August		October	
	(n)	Mean	(n)	Mean	(n)	Mean	(n)	Mean
Wolf Spiders	28	255 ± 97	5	278 ± 127	5	846 ± 312	20	327 ± 173
Camel Crickets	3	62 ± 33	2	139 ± 29	2	217 ± 17	4	120 ± 29
Ground beetles	11	67 ± 47	2	470 ± 93	1	193	0	N/A
Pill Bugs	13	155 ± 29	13	107 ± 66	5	124 ± 13	10	151 ± 29
Jerusalem Cricket	2	20 ± 14	0	N/A	0	N/A	5	142 ± 53
Pacific Spiketail	0	N/A	0	N/A	2	634 ± 25	0	N/A
Meadowhawk	0	N/A	0	N/A	0	N/A	4	220 ± 112

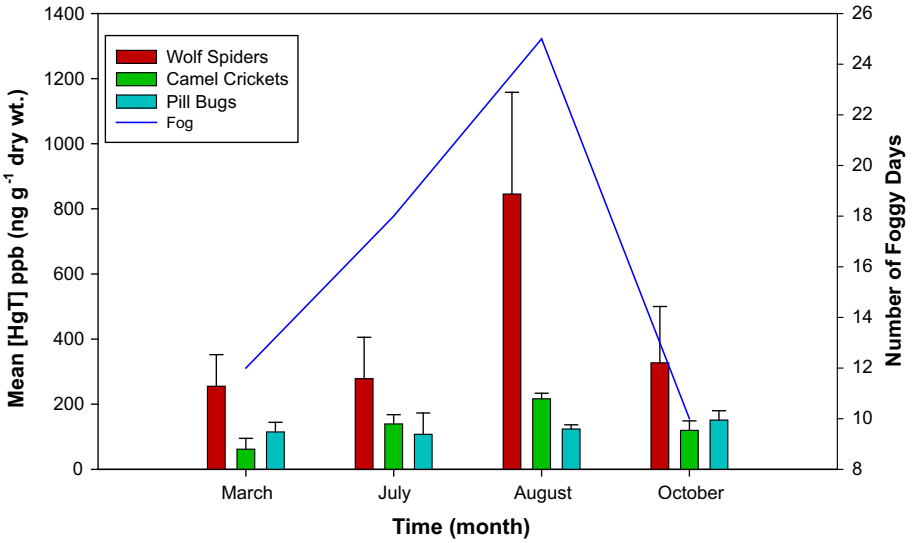

Fig. 2 2012 temporal variation of total mercury (HgT) concentrations and number of foggy days

The absence of a similar temporal peak in HgT concentrations of pill bugs may be due to many factors. One possibility is that pill bugs may be resistant to trace-metal contaminants in soil, as reported for some other arthropods (Dallinger et al. 1992; Udovic et al. 2009). Unfortunately, the sample size during the four sampling periods was quite small (n = 5–13) and there is no information on their mercury toxicokinetics to address their relatively consistent HgT concentrations. As primary consumers, Hg concentrations in pill bug tissue may reflect those in the ambient environment as opposed to Hg resulting from food chain transfer; this may render them potential bioindicators of Hg pollution.

Table 3 Monomethyl mercury (MMHg) Results for individual samples, all concentrations expressed in ng g^{-1} in dry weight

Location	Common name	[HgT]	[MMHg]	% MMHg
Elkhorn Slough	Wolf Spider	389	294	76
Santa Cruz	Wolf Spider	332	252	76
Elkhorn Slough	Pill bug	92	46	50
Santa Cruz	Pill bug	150	88	59
Elkhorn Slough	Ground Beetle	28	4	16
Santa Cruz	Ground Beetle	189	28	15

MMHg concentrations and ratios of MMHg/HgT (% MMHg) measured in the 6 arthropod subsamples (2 pill bugs, 2 ground beetles, and 2 wolf spiders) are listed in Table 3. While the MMHg analyses of the 3 types of arthropods was very small (n = 2), the variation in the % MMHg was surprisingly limited. As expected, the highest % MMHg was in predatory wolf spiders (76 %). The lower ratios in pill bugs (50–59 %) and predatory ground beetles (15–16 %), especially the latter, were surprising because inorganic mercury is not readily bioaccumulated and biomagnified. Therefore, those lower ratios may be an artifact of inorganic mercury sorbed on the insects exoskeletons and/or ingested sediments with relatively high amounts of inorganic mercury compared to organic mercury. Pill bugs, detrital arthropods, feed on decaying matter and live most of their life below soil (Capinera 2010). One explanation for the higher ratio found in pill bugs could be the uptake of MMHg provided by higher trophic level carrion; another

explanation could be their uptake of soil MMHg which has been synthesized by bacteria (Caffrey et al. 2010; Compeau and Bartha 1985; Kerin et al. 2006). Again, these and other factors cannot be assessed at this time because there is so little information on mercury in terrestrial arthropod food chains.

Marine fog along the central California coastline has been shown to contain higher Hg concentrations and higher ratios of MMHg/HgT than those seen in coastal rainwater (Weiss-Penzias et al. 2012); and fog is a major contributor to the hydrologic cycle in California's coastal redwood forests in the summer months (Azevedo and Morgan 1974; Dawson 1998; Ingraham and Matthews 1995). This data may partially substantiate a hypothesis that atmospheric deposition of mercury in coastal fog increases HgT in the tissue of terrestrial arthropods, but there is still too little information on the biological mechanism for the movement of Hg in coastal fog to terrestrial habitats.

In conclusion, the ratio of MMHg/HgT in pill bugs compared to that in ground beetles, and the covariance of HgT concentration in wolf spiders with the peak period of marine fog deposition are both intriguing. Unfortunately, there are very few other studies of mercury in terrestrial arthropod food chains for comparison. Hopefully this initial report will catalyze new studies on the role of atmospheric deposition in the biogeochemical cycling of mercury in terrestrial ecosystems. Moreover, the role of arthropods on the bioaccumulation and biomagnification of mercury in terrestrial food chains.

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