IOWA STATE UNIVERSITY
Digital Repository

Ecology, Evolution and Organismal Biology Publications

Ecology, Evolution and Organismal Biology

2019

Resolving a paradox—high mercury deposition, but low bioaccumulation in northeastern Puerto Rico

James B. Shanley
U.S. Geological Survey

Mark Marvin-DiPasquale
U.S. Geological Survey

Oksana Lane
Biodiversity Research Institute

Wayne Arendt
U.S. Forest Service

Steven Hall
Iowa State University, stevenjh@iastate.edu

See next page for additional authors

Follow this and additional works at: https://lib.dr.iastate.edu/eeob_ag_pubs

 Part of the Biogeochemistry Commons, Ecology and Evolutionary Biology Commons, Oceanography and Atmospheric Sciences and Meteorology Commons, Poultry or Avian Science Commons, and the Sedimentology Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/eeob_ag_pubs/374. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Ecology, Evolution and Organismal Biology at Iowa State University Digital Repository. It has been accepted for inclusion in Ecology, Evolution and Organismal Biology Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

Resolving a paradox—high mercury deposition, but low bioaccumulation in northeastern Puerto Rico

Abstract

At a “clean air” trade winds site in northeastern Puerto Rico, we found an apparent paradox: atmospheric total mercury (THg) deposition was highest of any site in the USA Mercury Deposition Network, but assimilation into the local food web was quite low. Avian blood THg concentrations (n = 31, from eight species in five foraging guilds) ranged widely from 0.2 to 32 ng g−1 (median of 4.3 ng g−1). Within this population, THg was significantly greater at a low-elevation site near a wetland compared to an upland montane site, even when the comparison was limited to a single species. Overall, however, THg concentrations were approximately an order of magnitude lower than comparable populations in the continental U.S. In surface soil and sediment, potential rates of demethylation were 3 to 9-fold greater than those for Hg(II)-methylation (based on six radiotracer amendment incubations), but rates of change of ambient MeHg pools showed a slight net positive Hg(II)-methylation. Thus, the resolution of the paradox is that MeHg degradation approximately keeps pace with MeHg production in this landscape. Further, any net production of MeHg is subject to frequent flushing by high rainfall on chronically wet soils. The interplay of these microbial processes and hydrology appears to shield the local food web from adverse effects of high atmospheric mercury loading. This scenario may play out in other humid tropical ecosystems as well, but it is difficult to evaluate because coordinated studies of Hg deposition, methylation, and trophic uptake have not been conducted at other tropical sites.

Disciplines

Biogeochemistry | Ecology and Evolutionary Biology | Oceanography and Atmospheric Sciences and Meteorology | Poultry or Avian Science | Sedimentology

Comments

This article is published as Shanley, James B., Mark Marvin-DiPasquale, Oksana Lane, Wayne Arendt, Steven Hall, and William H. McDowell. "Resolving a paradox—high mercury deposition, but low bioaccumulation in northeastern Puerto Rico." *Ecotoxicology* (2019). doi: 10.1007/s10646-019-02108-z.

Authors

James B. Shanley, Mark Marvin-DiPasquale, Oksana Lane, Wayne Arendt, Steven Hall, and William H. McDowell

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/eeob_ag_pubs/374

Ecotoxicology
https://doi.org/10.1007/s10646-019-02108-z

Check for updates

Resolving a paradox—high mercury deposition, but low bioaccumulation in northeastern Puerto Rico

James B. Shanley[1] · Mark Marvin-DiPasquale[2] · Oksana Lane[3] · Wayne Arendt[4] · Steven Hall[5] · William H. McDowell[6]

Accepted: 5 September 2019
© This is a U.S. government work and not under copyright protection in the U.S.; foreign copyright protection may apply 2019

Abstract

At a "clean air" trade winds site in northeastern Puerto Rico, we found an apparent paradox: atmospheric total mercury (THg) deposition was highest of any site in the USA Mercury Deposition Network, but assimilation into the local food web was quite low. Avian blood THg concentrations (n = 31, from eight species in five foraging guilds) ranged widely from 0.2 to 32 ng g^{-1} (median of 4.3 ng g^{-1}). Within this population, THg was significantly greater at a low-elevation site near a wetland compared to an upland montane site, even when the comparison was limited to a single species. Overall, however, THg concentrations were approximately an order of magnitude lower than comparable populations in the continental U.S. In surface soil and sediment, potential rates of demethylation were 3 to 9-fold greater than those for Hg(II)-methylation (based on six radiotracer amendment incubations), but rates of change of ambient MeHg pools showed a slight net positive Hg(II)-methylation. Thus, the resolution of the paradox is that MeHg degradation approximately keeps pace with MeHg production in this landscape. Further, any net production of MeHg is subject to frequent flushing by high rainfall on chronically wet soils. The interplay of these microbial processes and hydrology appears to shield the local food web from adverse effects of high atmospheric mercury loading. This scenario may play out in other humid tropical ecosystems as well, but it is difficult to evaluate because coordinated studies of Hg deposition, methylation, and trophic uptake have not been conducted at other tropical sites.

Keywords Methylmercury · Trophic uptake · Demethylation · Puerto Rico · Sulfate reduction · Iron reduction

Introduction

Mercury (Hg) is a potent neurotoxin and a pervasive global pollutant that poses a risk to ecosystem and human health (Driscoll et al. 2013). Research on environmental cycling and trophic uptake of Hg has increased greatly over the last 25 years, but most research has focused on mid- and high-latitude ecosystems; Hg researchers have paid relatively scant attention to tropical landscapes (Sprovieri et al. 2017). The tropics merit greater attention because they are a reservoir for biodiversity and hold about half of the world's human population, including groups with diets high in fish, one of the main pathways of human exposure to Hg. The tropics may be a hotspot for Hg deposition from the global pool, even in the absence of point sources (Shanley et al. 2015).

Wet atmospheric Hg deposition in northeastern Puerto Rico, which receives trade winds from the northeast that cross mostly open ocean waters and is unimpacted by point sources, was higher than at any site in the continental USA

Supplementary information The online version of this article (https://doi.org/10.1007/s10646-019-02108-z) contains supplementary material, which is available to authorized users.

✉ James B. Shanley
jshanley@usgs.gov

[1] U.S. Geological Survey, P.O. Box 628, Montpelier, VT 05601, USA

[2] U.S. Geological Survey, Menlo Park, CA, USA

[3] Biodiversity Research Institute, Portland, ME, USA

[4] USFS, International Institute of Tropical Forestry, Luquillo, PR, USA

[5] Department of Ecology and Evolutionary Biology, Iowa State University, Ames, IA, USA

[6] Department of Natural Resources and the Environment, University of New Hampshire, Durham, NH, USA

Published online: 23 October 2019

(28 μg m^{-2} annually in 2005–2007) (Shanley et al. 2015; Shanley et al. 2008). These studies concluded that high convective cloud tops that form over the island landmass scavenge gaseous oxidized mercury (GOM) from the large pool of GOM known to exist in the upper free troposphere (Landing et al. 2010, Lyman and Jaffe 2012, Swartzendruber et al. 2006). Shanley et al. (2015) suggested that high Hg wet deposition could occur in other tropical settings where there is sufficient landmass to generate high convective cloud tops, but there are few data available.

The high Hg deposition was reflected in high streamwater Hg concentrations, mostly as particulate Hg, at Río Icacos, a high-elevation watershed (616–844 m) near the Hg deposition station. Stream particulate THg concentrations exceeded 100 ng L^{-1} and dissolved THg reached 5 ng L^{-1} during high flow periods. High Hg concentrations combined with high water flux in this rain forest landscape to yield an annual average stream THg flux at Río Icacos of 54 μg m^{-2} a^{-1} (Shanley et al. 2008), more than an order of magnitude greater than typical temperate sites (Shanley and Bishop 2012). The stream THg flux thus is the same order of magnitude as wet and dry THg inputs. Thus, despite above average soil organic matter for a tropical forest (Johnson et al. 2015), the landscape is relatively ineffective at retaining Hg.

Most Hg studies in the tropics have focused on Hg-contaminated sites, such as gold mining and ore processing sites in the Amazon basin (Fostier et al. 2000; Fadini and Jardim 2001; Silva-Filho et al. 2006) and Guyana (Howard et al. 2011). Outside of Puerto Rico, only two studies have reported on systematic atmospheric deposition measurements for at least a full year: Barbados (Guentzel et al. 2001) and Mexico (Hansen and Gay 2013). A few tropical studies have reported avian Hg burdens: Hispaniola (Townsend et al. 2013), Nicaragua (Lane et al. 2013), Belize (Evers 2008), and Puerto Rico (Burger and Gochfeld 1991; Burger et al. 1992b), but these studies had no associated atmospheric deposition monitoring. Limited work in tropical Africa has focused on Hg in fish in lakes and a large inland delta wetland (Black et al. 2011 and references therein). Several authors have investigated Hg methylation processes in the freshwater tropics, especially in the Amazon basin (Achá et al. 2011; Guimarães et al. 2000; Lázaro et al. 2016; Mauro et al. 2002; Roulet et al. 2001), but these studies did not assess trophic uptake.

Despite the high deposition and mobility of Hg at our Puerto Rican site, two lines of evidence hinted that the Hg may have a limited effect on the ecosystem. First, a pilot survey of various aquatic and terrestrial biota suggested that Hg concentrations were less than those in comparable mid-latitude species (M. Bank and the authors, unpublished data). Secondly, only ~0.3% of THg was present as methylmercury (MeHg) in unfiltered streamwater, a relatively low fraction (Shanley et al. 2008). The juxtaposition of high Hg deposition and low trophic uptake is not necessarily at odds, as inhibition of methylmercury formation will limit uptake (Wiener et al. 2006). However, landscape conditions at our site appeared to be conducive to methylation, including year-round warm temperatures (Murphy and Stallard 2012), above-average soil carbon (Johnson et al. 2015), ample sulfur availability (Peters et al. 2006), and occurrence of reducing microsites in surface soils (Hall et al. 2016). The apparent paradox prompted directed field campaigns to (i) confirm the preliminary finding of low trophic uptake by assessing Hg in avian blood, and (ii) investigate Hg(II)-methylation dynamics within soil and sediment. Our working hypothesis and rationale for this paper was that low net methylation was limiting trophic uptake despite high Hg deposition in this tropical wet forest. With the newly acquired information, we propose a reconciliation of the apparent paradox of biota that are exposed to high mercury loading but only sparingly bioaccumulate it.

Site description

The Luquillo Mountains are at 18°N in northeastern Puerto Rico, the easternmost island in the Greater Antilles, about 1600 km ESE of Miami, Florida (Fig. 1). Our research site was within the Luquillo Experimental Forest (LEF) in El Yunque National Forest. LEF is centered 35 km ESE of San Juan, and receives airflow off the Atlantic Ocean driven by northeasterly trade winds. The forest is mountainous, with peaks and ridges rising from sea level to 1075 m a.s.l. The Hg deposition station was in the northeastern part of the forest. Most of the soil, stream, and biota sampling took place in the Río Icacos basin, in the headwaters of Río Blanco, a few km to the SW of the deposition station on the south slope of the mountains (Fig. 1). Soils are sandy Inceptisols derived from the quartz diorite bedrock (Johnson et al. 2015). However, nearly all soils have aquic properties due to clay-rich B horizons that impede infiltration (Johnson et al. 2015).

Weather patterns that bring rainfall to Puerto Rico have marked seasonality (Scholl and Murphy 2014). Annual rainfall in the Luquillo forest averages 4200 mm (Murphy et al. 2017; Peters et al. 2006), with highest rainfall from April through December, and a distinctly drier January through March. The genesis of precipitation in winter and spring is trade wind-sea breeze showers from orographic uplift and frontal systems (Scholl and Murphy 2014). During summer and fall, the site receives rainfall from deep convection associated with tropical waves embedded in the prevailing easterly airflow. Tropical cyclones can produce heavy and intense rainfall. Mean annual temperature is 24 °C with only a 4 °C annual range in monthly averages.

Methods

Sediment and soil biogeochemistry

We conducted two discrete sampling and analysis campaigns—one for stream sediment and one for watershed soils (Fig. 2). In September 2008, as part of synoptic sampling of the five primary USGS Water, Energy, and Biogeochemical Budgets (WEBB) program locations (http://water.usgs.gov/webb/), we collected streambed surface sediment (top 0–2 cm) from three locations along a 2-km reach of Río Icacos (Fig. 2). In February 2012, we sampled surface soils (0–10 cm) at three positions along a hillslope transect—upland (midslope), transition (toeslope), and a low-lying wetland area within the Río Icacos floodplain (floodplain). The hillslope transect represented a typical catena for this watershed, but the floodplain sampling site was unusual, as most of the channel is flanked by steep hillslopes. Two sets of duplicate soil samples were collected at each transect point. We focused on 0–10 cm soils for this study based on findings at a nearby site, where anaerobic respiration and potential Fe(III) reduction (factors potentially linked to Hg(II) methylation), were greatest in near-surface soils and decreased with depth as a consequence of C limitation (Hall et al. 2016). The hydrology and geomorphology of this catena are described in detail by McDowell et al. (1992).

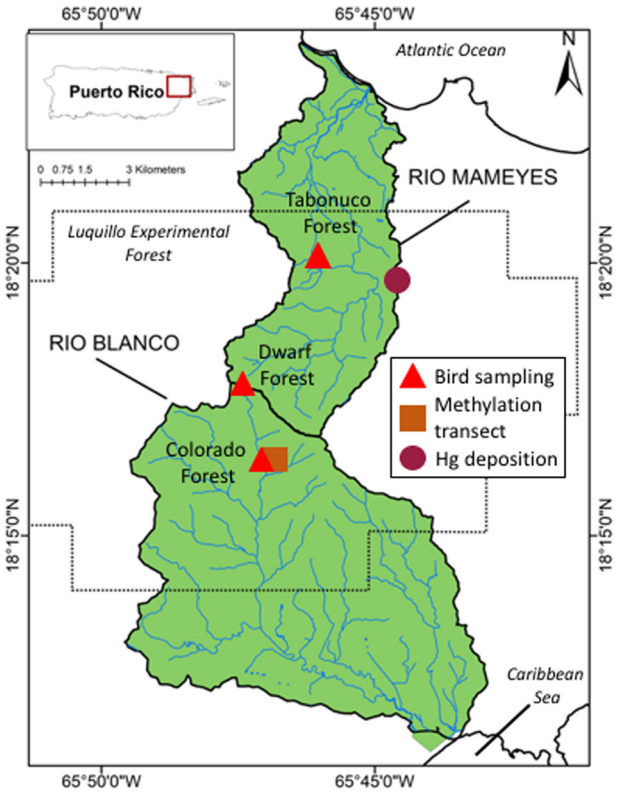

Fig. 1 Map of sampling sites and location within Puerto Rico

Streambed sediment and one set of soil duplicates were transferred into acid-cleaned glass mason jars. All jars were filled to the top to exclude oxygen, stored chilled, and shipped overnight to the USGS laboratory in Menlo Park, California, for further sub-sampling under anoxic conditions (Marvin-DiPasquale et al. 2008) for methylation/demethylation incubations, and for several Hg and biogeochemical parameters (Bradley et al. 2011; Hall et al. 2013; Hall and Silver 2015; Marvin-DiPasquale et al. 2008) (Table 1). Sediment/soil parameters determined in Menlo Park included THg, MeHg, reactive Hg ($Hg(II)_R$), total reduced sulfur (TRS), microbial sulfate reduction rate (SRR), percent mass loss-on-ignition (%LOI), and solutes in 0.45-µm-filtered porewater (collected by centrifugation) (Table 1).

The second set of replicate soil samples was collected primarily to determine Fe speciation. Extractions were initiated in the field and completed within two hours to minimize potential changes in soil Fe speciation associated with changes in redox conditions. Soil subsamples were extracted in solutions of 0.5 M HCl (1:10 ratio, soil:

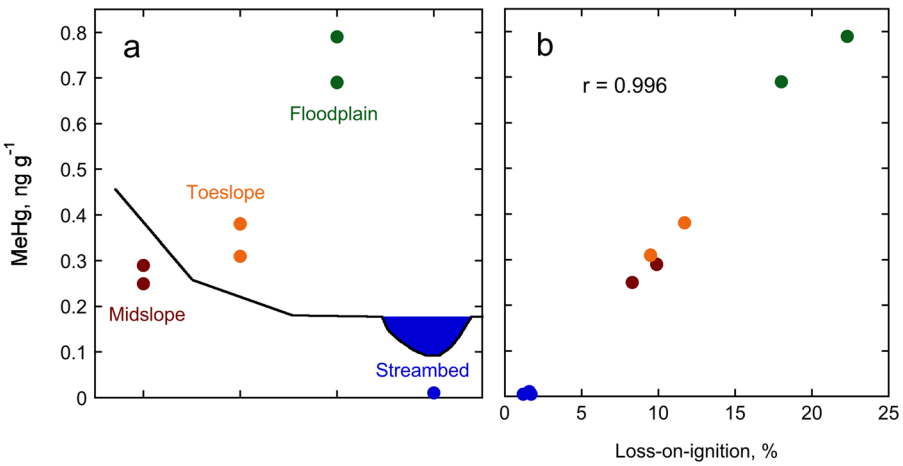

Fig. 2 **a** MeHg concentrations in soils (topmost 10 cm) and streambed sediment (topmost 2 cm) along a transect from hillslope to stream; **b** MeHg vs. loss-on-ignition (LOI) in soil and streambed sediments. LOI was used because %C was not measured on streambed sediment (but see Fig. A-1)

Table 1 Summary of soil and streambed sediment Hg metrics and relevant biogeochemistry for Río Icacos

Notation	Parameter	Units	Midslope soil		Toe of slope soil		Floodplain soil		Stream bed sediment		Reference
Mercury parameters			Mean	Dev.	Mean	Dev.	Mean	Dev.	Mean	Std. Dev.	
THg	Total mercury	(ng/g) dry wt.	48.52	2.26	51.34	7.36	127.60	15.65	2.93	1.34	Marvin-DiPasquale et al. 2011
MeHg	Methylmercury	(ng/g) dry wt.	0.27	0.02	0.34	0.03	0.74	0.05	<0.01		Marvin-DiPasquale et al. 2011
MeHg/THg (%MeHg)	percent methylmercury	%	0.34	0.01	0.41	0.05	0.28	0.03	<0.32		calculated
$Hg(II)_R$	inorganic reactive mercury	(ng/g) dry wt.	3.75	0.43	3.72	1.59	3.07	1.82	0.21	0.15	Marvin-DiPasquale et al. 2011
$Hg(II)_R$/THg ($\%Hg(II)_R$)	percent reactive mercury	%	7.80	1.26	6.95	2.10	2.26	1.15	6.71	1.97	calculated
K_{meth}	MeHg production potential rate constant	(1/d)	<0.001		<0.001		0.002	0.001	<0.001		Marvin-DiPasquale et al. 2011
K_{deg}	MeHg degradation potential rate constant	(1/d)	0.055	0.005	0.037	0.014	0.041	0.025			see text
MPP	MeHg production potential rate (calculated)	(pg/g dry sed/d)	<3.72		<3.62		4.49	0.91	<0.10		Marvin-DiPasquale et al. 2011
MDP	MeHg degradation potential rate (calculated)	(pg/g dry sed/d)	14.26	2.49	12.90	5.87	30.67	19.54			calculated from k_{deg} and native MeHg concentration, akin to Marvin-DiPasquale and Agee 2003
NMP	Net MeHg production, based on change in native $Me^{202}Hg$	(pg/g dry sed/d)	12.76	7.43	15.99	4.54	18.52	13.79			See text
Non-Mercury Parameters											
%dry wt.	Percent dry weight	%	62.6	0.6	55.8	4.2	47.1	1.9	76.0	1.6	Marvin-DiPasquale et al. 2008
BD	Wet bulk density	(g/cm^3)	1.51	0.02	1.47	0.06	1.30	0.02	1.81	0.09	Marvin-DiPasquale et al. 2008
POR	Porosity	(ml porewater /cm^3)	0.57	0.00	0.59	0.04	0.69	0.01	0.43	0.01	Marvin-DiPasquale et al. 2008
%LOI	Percent Weight Loss on ignition	(% of dry wt.)	9.15	0.80	10.59	1.12	20.14	2.12	1.47	0.25	Marvin-DiPasquale et al. 2008
%C	Percent Organic carbon	(% of dry wt.)	2.70	0.30	3.10	0.40	8.50	2.00			Hall and Silver 2015
%fines (silt and clay)	Percent Grain Size (% <63 micron)	(% <63 um)	40.87	2.60	36.30	1.15	77.28	7.00	1.43	0.57	Matthes et al. 1992
E_h (laboratory)	Oxidation-reduction potential	(mv)	+561	12	+527	43.00	+459	117	+497	27	Marvin-DiPasquale et al. 2008
pH (field)	pH	(pH units)	3.35	0.04	3.47	0.27	3.80	0.06	6.37	0.02	Marvin-DiPasquale et al. 2008
SRR	Microbial sulfate reduction rate	(nmol/g/d) dry wt.	0.02	0.01	0.04	0.04	0.60	0.10	0.05	0.01	Marvin-DiPasquale et al. 2008
TRS	Total reduced sulfur	(µmol/g) dry wt.	0.23	0.06	0.30	0.04	0.87	0.26	0.16	0.06	Marvin-DiPasquale et al. 2008
$Fe(II)_{HCl}$	Ferrous Iron, HCl extractable	(mg/g) dry wt.	0.15	0.01	0.18	0.10	0.22	0.00	0.13	0.02	Hall et al. 2016
$Fe(III)_{HCl}$	Ferric Iron, HCl extractable	(mg/g) dry wt.	1.55	0.02	1.15	0.69	0.44	0.24	11.84	6.75	Hall et al. 2016
$\%Fe(II)_{HCl}$	Ferrous iron, percent HCl extractable	%	9.01	0.75	14.09	0.80	38.65	14.42	1.48	0.97	Calculated
$Fe(III)_{SRO}$	Ferric Iron, short-range-ordered[a]	(mg/g) dry wt.	17.35	8.56	5.68	2.75	1.31	0.70			Hall et al. 2016
$Fe(III)_c$	Ferric Iron, crystalline[b]	(mg/g) dry wt.	19.94	10.30	5.81	5.71	0.06	0.03			Hall et al. 2016
$\%Fe(II)/Fe_T$	Ferrous iron, percent of total extractable Fe[c]	%	0.41	0.05	2.26	0.87	17.02	7.30			Calculated
CH_4	CH_4 flux	$\mu mol\ m^{-2}\ h^{-1}$	<5		<5		29.50	3.50			Hall et al. 2013
Porewater chemistry[d]											
$[SO_4^{2-}]$	Sulfate	(µmol/liter)	114.08	58.92	77.33	1.06	49.73	30.15	22.24	4.09	Marvin-DiPasquale et al. 2008
$[Cl^-]$	Chloride	(µmol/liter)	0.78	0.28	0.50	0.03	0.48	0.20	0.19	0.02	Marvin-DiPasquale et al. 2008
$[SO_4^{2-}]/[Cl^-]$	Sulfate to chloride molar ratio	Unitless	0.14	0.03	0.15	0.01	0.16	0.13	0.11	0.01	Calculated
[DOC]	Dissolved organic carbon	(mg/liter)	93.80	50.50	97.18	10.77	37.35	0.81	7.57	3.09	Marvin-DiPasquale et al. 2009a

Soil samples are 0–10 cm depth and streambed sediments are 0–2 cm depth. Soil values based on duplicate samples along a hillslope to flood plain transect; sediment values based on three samples along a 2-km stream reach adjacent to the soil sampling transect. For soils (Midslope, Toe of slope and Floodplain), the error term reflects the deviation of n = 2 samples (DEV = (X1 −X2)/2). For the stream samples, the error term reflects the standard deviation (STDEV) of n = 3 samples

[a]$Fe(III)_{SRO}$ = [citrate-ascorbate extractable Fe] − $Fe(II)_{HCl}$

[b]$Fe(III)_c$ = [citrate-dithionite extractable Fe] − [citrate-ascorbate extractable Fe]

[c]$\%Fe(II)_T = Fe(II)_{HCl}/[\text{citrate-dithionite extracable Fe}] \times 100$

[d]Pore water was collected from elutriated samples, to generate sufficient aqueous volume for all analyses

extractant) and 0.2 M sodium citrate/0.05 M ascorbic acid (1:30 ratio, soil:extractant). HCl extractable Fe fractions included both ferrous iron ($Fe(II)_{HCl}$) and ferric iron $Fe(III)_{HCl}$. The citrate-ascorbate Fe fraction was used to calculate short-range-ordered Fe (Fe_{SRO}, Table 1), as modified from Hall and Silver 2015). Dried and ground subsamples were extracted in a citrate-dithionite solution (1:60 ratio, soil:extractant) to determine total extractable Fe (Fe_T), from which crystalline Fe ($Fe(III)_C$) was calculated by subtracting Fe_{SRO} (Table 1). We determined percent carbon (%C: assumed equal to % organic carbon based on soil acidity) on these samples by combustion on an elemental analyzer, and we also measured soil-atmosphere methane (CH_4) fluxes via static chambers (following Hall et al. 2013) at each soil-sampling site as an additional proxy for anaerobiosis. See supplementary OR material for detail on the trace gas sampling.

Hg methylation and demethylation incubations

Incubations were initiated within 24–48 h of sampling. For both streambed sediments and soils, methylmercury production rate constants (k_{meth}) and calculated potential (MPP) rates were assessed via stable isotope ($^{200}Hg^{2+}$) amendment with 22-hr bottle incubations (streambed sediment) or 5-hr bottle incubations (soils). The shorter incubation time for soils was in anticipation of higher MPP rates. Each site-specific sample set consisted of duplicate incubated samples plus one killed control (flash frozen immediately after isotope amendment). The final $^{200}Hg(II)$ amendment concentration was approximately 50 ng g^{-1} sediment wet weight, which for the three Río Icacos stream sites was equivalent to 66–69 ng g^{-1} dry wt., or more than an order of magnitude higher than the native THg concentration for these sandy stream samples (1.6–4.2 ng g^{-1} dry wt). For the soils, the final $^{200}Hg(II)$ amendment concentration was 74–105 ng g^{-1} dry wt., which was quite similar to the native THg concentration (44–144 ng g^{-1} dry wt.). Because $^{200}Hg(II)$ amendments were not at trace levels relative to native THg pools, the MPP incubation should be regarded as a 'potential rate' determination. The resulting end-product ($Me^{200}Hg$) was quantified by isotope dilution ICP-MS (Marvin-DiPasquale et al. 2011). Final concentrations were determined for each sample by subtracting the (nearly negligible) killed-control value for each site from the two incubation values.

In like manner, we assessed MeHg degradation rate constants (k_{deg}) and calculated mercury degradation potential (MDP) rates on soils only by incubating for six days after amendment with $Me^{201}Hg$ (1.6–2.2 ng g^{-1} dry wt., compared to native MeHg concentrations of 0.2–0.8 ng g^{-1} dry wt.), and determining rates from the loss of $Me^{201}Hg$ over time. The longer incubation time improves the chance of detecting loss, which is determined by difference. In addition, we tracked the concentration change in the native $Me^{202}Hg$ pool in the MDP samples as a measure of net MeHg production (NMP) (net degradation if negative), as this isotope was not added as an enriched amendment.

Avian blood sampling

During four days in May 2010 we captured 31 birds for blood Hg analysis by opportunistic mist netting in three forest types: elfin woodland near the summit of Mt. Britton (n = 2); high-elevation palo colorado forest near Río Icacos gage (n = 17); and low-elevation tabonuco forest near El Portal (n = 12) (Fig. 1). See McDowell et al. (2012) for a detailed description of these habitats. We did not target particular species, but were fortunate to capture birds representing all five feeding guilds, and all but one individual, a black-whiskered vireo *(Vireo altiloquus)*, were permanent residents. Of the 31 birds, 19 were bananaquits (*Coereba flaveola*), a small non-migratory nectarivore that also consumes flies, beetles, caterpillars, ants, bees, and spiders (Allen 1961; Stiles and Skutch 1989), mostly from the undersides of leaves (Cruz 1980). The remaining 12 birds represented seven species, with no more than 3 individuals of any species. Blood was collected non-lethally from the brachial vein using 27-gauge disposable needles and heparin-coated capillary tubes, stored in labeled vacutainers, and frozen within four hr of collection. Birds were handled under appropriate permits and released unharmed at the capture site.

We used the nonparametric Proportions (z-test) and Mann–Whitney Rank Sum Test (*U* statistic) to test for differences in Hg among bird populations. We compared blood THg concentrations of bird populations in the low-elevation tabonuco forest (n = 17) and the high-elevation palo colorado forest (n = 12) (for this comparison we excluded the two birds captured in elfin woodland). To avoid interspecies differences, we also compared blood THg in populations of bananaquit in the low-elevation (n = 8) and high-elevation (n = 10) groups.

Because Hg in bird blood is nearly 100% MeHg (Edmonds et al. 2010; Rimmer et al. 2005), blood was analyzed for THg only. THg was determined from the entire sample volume using USEPA method 7473 (EPA 1998) by gold-amalgamation atomic absorption spectroscopy following thermal desorption. The analytical instrument used was a Milestone DMA-80 at Biodiversity Research Institute (BRI), Wildlife Mercury Research Laboratory (WMRL) in Portland, Maine. Internal lab quality control included initial calibration and continuing verification, blanks, sample replication, and analysis of the commonly used certified reference materials DORM-3 and DOLT-4.

Blood samples were also analyzed for stable isotopes of C and N at the Boston University Stable Isotope Laboratory using automated continuous-flow isotope ratio mass spectrometry (Michener and Lajtha 2007). The samples were combusted in a EuroVector Euro EA elemental analyzer. The combustion gases (N_2 and CO_2) were separated on a GC column, passed through a reference gas box and introduced into a GV Instruments IsoPrime isotope ratio mass spectrometer; water was removed using a magnesium perchlorate water trap. Ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ are reported as standard delta (δ) notation and are expressed as the relative permil (‰) difference between the samples and international standards (Vienna Peedee Belemnite (V-PDB) carbonate and N_2 in air):

$$\delta X = \left(R_{sample}/R_{standard} - 1\right) \times 1000(‰)$$

where $X = {}^{13}C$ or ^{15}N and $R = {}^{13}C/{}^{12}C$ or $^{15}N/^{14}N$. The sample isotope ratio was compared to a secondary gas standard, the isotope ratio of which was calibrated to international standards. For $^{13}C_{V\text{-}PDB}$ the gas was calibrated against NBS 20 (Solenhofen Limestone). The $^{15}N_{air}$ gas was calibrated against atmospheric N_2 and International Atomic Energy Agency (IAEA) standards N-1, N-2, and N-3 (all were ammonium sulfate standards).

Results

Mercury and relevant biogeochemistry of streambed and soil

The downslope soil transect, from midslope to toeslope to floodplain, exhibited a progressive decrease in soil % dry weight (63–47%), and wet bulk density (1.51–1.30 g/cm^3), and a progressive increase in soil porosity (0.57–0.69), organic content (as %LOI, 9.1–20.1%), %fines (silt + clay; 40 to 77%), and pH (3.35–3.80) (mean values; Table 1). By comparison, the sandy (quartz diorite bedrock dominated) Río Icacos streambed sediment was the most elevated in % dry weight (76%), wet bulk density (1.81 g/cm^3), and pH (6.37), while having the lowest porosity (0.43), %LOI (1.5%), and %fines (1%). Across all sites, oxidation-reduction potentials (as E_h) at the time of sampling were notably oxic (+400 to +500 mv).

Mean THg concentrations were lowest in the streambed (2.9 ± 1.3 ng g^{-1}) and much higher in soils, from 50 ± 6 ng g^{-1} in hillslope soils (n = 4 sites, mid- and toeslope) to 128 ± 16 ng g^{-1} in the floodplain (n = 2 sites). MeHg concentrations were at or below detection (≤0.01 ng g^{-1} dry wt.) in the streambed, 0.31 ± 0.05 ng g^{-1} (n = 4) in the hillslope, and 0.74 ± 0.05 ng g^{-1} (n = 2) in the floodplain (Fig. 2, Table 1). These values equated to <0.4% MeHg in the streambed and ranged from 0.55 to 0.68% MeHg in soils. As a percentage of THg, $Hg(II)_R$ was lowest in the floodplain (2.3 ± 1.1%) (n = 2) compared to all other soil and sediment sites (7.1 ± 1.9%, n = 7) (Table 1). THg, MeHg, %fines, and %LOI were all strongly and positively intercorrelated, with Pearson r values ranging from 0.987 to 0.998 for the pairwise combinations (Fig. 2; Figure OR1).

Considering the well-oxygenated status of the soils and sediments sampled, it is not surprising that the biogeochemical metrics associated with microbial sulfate reduction all suggested minimal to no activity for this terminal heterotrophic anaerobic pathway. Specifically, SRRs associated with anoxic bottle incubations were very low in steam bed sediment (0.05 ± 0.01 nmol g^{-1} d^{-1}, n = 3) and hillslope soils (0.03 ± 0.03 nmol g^{-1} d^{-1}, n = 4) and higher but still low in the floodplain (0.60 ± 0.10 nmol g^{-1} d^{-1}, n = 2). Bulk substrate TRS was also lowest for the streambed (0.16 ± 0.01 μmol g^{-1}, n = 3) and hillslope soils (0.27 ± 0.07 μmol g^{-1}, n = 4) and low for floodplain sites (0.87 ± 0.26 μmol g^{-1}, n = 2). Further, porewater SO_4^{2-}/Cl^- molar ratios showed little difference among all sites (means ranged from 0.11 ± 0.01 for streambed sediment to 0.16 ± 0.13 for the floodplain), suggesting minimal differences in SO_4^{2-} depletion, relative to the conservative anion Cl^-, among the various soil/sediment environments. Finally, free sulfide was not measured in the soil samples but was below detection (<0.2 μmol L^{-1}) in the streambed samples.

In contrast to sulfur cycling, metrics associated with microbial iron redox cycling suggest a more active terminal heterotrophic pathway across the study sites. While concentrations do not represent rates, the relative pools of Fe(II) and Fe(III) give us some sense of a system poised for Fe cycling, with spatially consistent variation along the study transect. Specifically, the proportion of 0.5 M HCl-extractable Fe in the reduced Fe(II) form ($\%Fe(II)_{HCl}$) was lowest in the streambed (1.5 ± 1.0 mg g^{-1}, n = 3) and increased from the hillslope (11.6 ± 3.1 mg g^{-1}, n = 4) to the floodplain (38.6 ± 14.4 mg g^{-1}, n = 4), suggesting increasing microbial Fe(III) reduction from the streambed to the hillslope to the floodplain. Similarly, the proportion of Fe(II) relative to the total extractable Fe pool (via citrate-dithionite extraction) showed a similar progressive increase in $\%Fe(II)/Fe_T$ from midslope (0.4 ± 0.0 mg g^{-1}, n = 2), to toeslope (2.3 ± 0.9 mg g^{-1}, n = 2), to floodplain (17.0 ± 7.3 mg g^{-1}, n = 2) (streambed not sampled). Supporting the Fe(II) distribution, patterns in CH_4 fluxes from soils to the atmosphere provided complementary evidence for an increase of anaerobic microsites (i.e., conditions suitable for Hg methylation) from upslope to the floodplain. CH_4 fluxes were not different from zero (<5 μmol m^{-2} h^{-1}) at the midslope and toeslope sites, but floodplain soils had net positive CH_4 emissions of 26–33 μmol m^{-2} h^{-1}.

Methylation and demethylation incubations

Average MeHg production rate constants (k_{meth}), measured via incubation with the ^{200}Hg amendment, were below detection (<0.001) at all sites except the floodplain (0.002 ± 0.001 d^{-1}), as were subsequently calculated MPP rates at all sites (<4.0 pg g^{-1} d^{-1}) except the floodplain (4.5 ± 0.9 pg g^{-1} d^{-1}) (Fig. 3, Table 1). MPP rates should be considered as an upper limit, as the initially oxic samples were incubated under anoxic conditions. In contrast, MDP rates, measured in soils only, ranged from 7–50 pg g^{-1} d^{-1}, approximately 2 to 10 times higher than the corresponding MPP rates.

NMP rates, based on 6-day anoxic incubations and the change in the native $Me^{202}Hg$ pool, were low and generally increased downslope, but were not significantly different among sites (Table 1: midslope, 12.8 ± 7.4 pg g^{-1} d^{-1}; toeslope, 16.0 ± 4.5 pg g^{-1} d^{-1}; floodplain, 18.5 ± 13.8 pg g^{-1} d^{-1}).

Bird blood Hg concentrations

Total blood Hg concentrations were quite low, ranging from 0.2 to 32 ng g^{-1} wet weight, with a median of 4.3 ng g^{-1} (Fig. 4; Table OR1). Within the total sample population (n = 29, excluding the two elfin forest birds), Hg concentration was significantly greater (Proportions test, $p = 0.013$) in the low-elevation tabonuco forest (83% of birds greater than overall population median Hg concentration) relative to the high-elevation palo colorado forest (29% of birds greater than overall population median Hg concentration) Bird blood Hg in the 19 Bananaquits nearly spanned the range for the entire 31-bird sample population and was not different from the overall population (Proportions test, $p = 0.663$). Three species, with just one individual each, were either omnivorous (pearly-eyed thrasher *(Margarops fuscutatus)* and red-legged thrush *(Turdus plumbeus)*, both of which consume insects, land crabs, lizards, frogs, birds, and baby rats) or insectivorous (black-whiskered vireo). Despite these three individuals occupying higher trophic level feeding guilds, only the thrush was considerably above the population median (13.0 vs. 4.3 ng g^{-1}).

To minimize the interspecies effect, we compared bananaquit populations in the two forest types. As with the overall population, bananaquits had significantly higher blood Hg (Mann–Whitney Rank Sum Test, p = 0.009) in the low-elevation tabonuco forest (median 8.1 ng g^{-1}) than in the high-elevation palo colorado forest (median 3.1 ng g^{-1}). The two birds from the high-elevation elfin woodland site (a bananaquit and a Puerto Rican bullfinch (*Melopyrrha portoricensis*)) had blood THg concentrations well below the overall sample population median of 4.3 ng g^{-1}. Overall, Hg concentration in bird blood had a weak but significant positive correlation with $\delta^{15}N$ (Fig. 4; Table OR1).

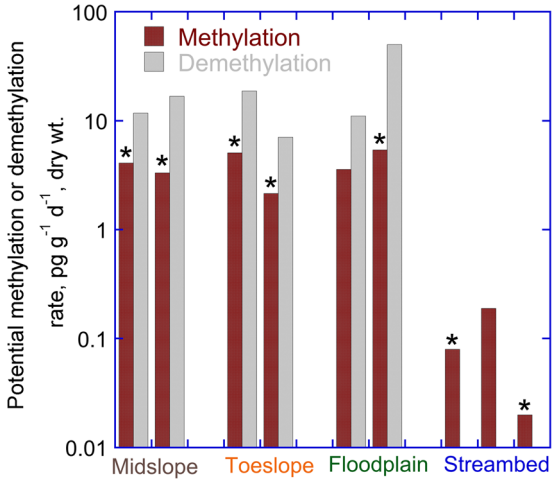

Fig. 3 Potential methylation and demethylation rates in soils and potential methylation rates in streambed sediment. Most of the methylation rates shown are the detection limits (marked by star) and should be considered as an upper bound to the potential rates

Discussion

Hg stocks, fluxes, and speciation at LEF

Given the high Hg wet deposition in this tropical wet forest that receives 2–5 m of rain per year, the relative importance of dry Hg deposition was an open question. Dry deposition of Hg in forested landscapes typically is 2–3 times wet deposition (St. Louis et al. 2001). Measurements from three years of litterfall in the Luquillo forest indicate that dry deposition was 1.5 times wet deposition (Risch 2017). Thus, the combined wet plus dry Hg deposition was quite elevated. The percentage of THg as MeHg (%MeHg) averaged only 0.06% in wet deposition (R. Brunette, Eurofins Scientific, unpubl. data, 2012) and 0.31% in litterfall (Risch 2017). These %MeHg values are well below global medians of 1.14% for wet deposition and 1.08% for litterfall (calculated from Shanley and Bishop (2012)).

Forested landscapes typically retain about 90% of atmospheric THg inputs, leaving 10% or less to run off in streamflow (Shanley and Bishop 2012). The portion of Hg that does not run off is retained in watershed soils and vegetation, and some Hg may also volatilize to the atmosphere (Krabbenhoft et al. 2005). At LEF, Río Icacos had an unusually low watershed retention (high stream THg export) (see tabulation in Shanley and Bishop (2012)), but stream Hg export may have been augmented by legacy Hg from gold ore processing in the watershed more than a century ago (Wardsworth 1949). Stream Hg export was dominated by particulate Hg. As in rainfall and throughfall, a low percentage of THg was in the MeHg form; %MeHg in whole water samples, generally dominated by particulate Hg, was 0.68% (Shanley et al. 2008), similar to %MeHg in

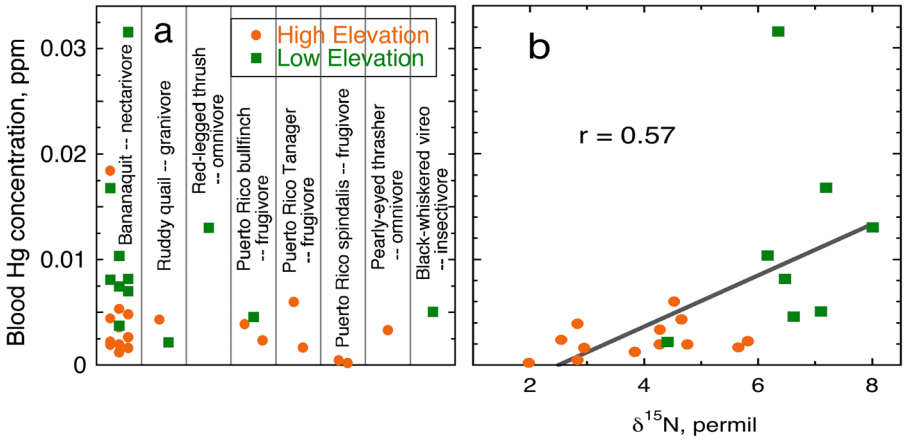

Fig. 4 **a** Bird blood Hg concentration in 31 birds sampled in Luquillo Experimental Forest; **b** relation of bird blood Hg concentration to $\delta^{15}N$ in these samples

soils. The corresponding global median percentage was 2.8% (calculated from Shanley and Bishop (2012)).

In soils and sediment, the distribution of THg across the sites was highly correlated with grain size (as %fines, $r = 0.98$) and organic content (as %LOI, $r = 0.99$), and MeHg concentration was also positively correlated with THg ($r = 0.99$) (Figure OR1), with all of these metrics most elevated at the floodplain site and lowest in the streambed sediment. Given the low number of observations ($n = 9$, including replicates), a high degree of co-correlation is not surprising. Anecdotally, we previously measured high MeHg concentrations of 7.7 ng L^{-1} (MeHg/THg = 3.3%) in organic-rich water in the epiphytic tank bromeliad at LEF (Shanley et al. 2008), suggesting that Hg, S, and organic C for Hg(II)-methylation were amply supplied from the atmosphere and forest canopy and were not limiting Hg(II)-methylation.

A less commonly measured Hg metric is the $Hg(II)_R$ fraction, which has been assessed in a number of studies as a proxy for chemically labile and microbially available Hg (II), and is used here and elsewhere (Marvin-DiPasquale et al. 2009a; Marvin-DiPasquale et al. 2009b; Marvin-DiPasquale et al. 2014) to calculate MPP rates (in combination with independently measured values of k_{meth}). Concentrations of $Hg(II)_R$ increased with substrate redox potential (E_h, $r = 0.85$) and $\%Hg(II)_R$ decreased with increasing TRS concentration ($r = -0.76$), microbial SR rate ($r = -0.72$) and k_{meth} ($r = -0.71$), similar to patterns reported in earlier research (Marvin-DiPasquale et al. 2009a, Marvin-DiPasquale et al. 2009b, Marvin-DiPasquale et al. 2014).

Trophic Hg uptake

Avian Hg blood concentration in Puerto Rican birds was strikingly low (Fig. 5). The Puerto Rican birds that we were able to capture by mist netting included mostly frugivores and nectarivores, which would be expected to have low body burden Hg, but their blood Hg levels were still at least a factor of five lower and generally an order of magnitude lower than birds in comparable feeding guilds at other tropical and temperate sites (Fig. 5) (Cristol et al. 2008; Evers and Duron 2006; Jackson et al. 2015; Lane et al. 2013). The extent of Hg bioaccumulation in the Puerto Rican birds followed the typical pattern of increase with increasing $\delta^{15}N$ (Fig. 4), a proxy for relative position in the feeding guilds (Cabana and Rasmussen 1994).

Avian blood Hg concentrations in Puerto Rico were anomalously low not only compared to mainland U.S. birds, but also compared to other tropical sites, including Belize, Nicaragua, and Hispaniola (Fig. 5). In Belize, more than half of 31 species of songbirds sampled had more than an order of magnitude higher Hg than the Puerto Rican birds (Evers 2008). Birds in Nicaragua had on average five times the blood Hg as in our Puerto Rican study, with 71 of 73 individuals having greater blood Hg than the median value of the 31 birds in Puerto Rico (Lane et al. 2013). In Hispaniola, Townsend et al. (2013) found a strong elevational gradient of blood Hg concentrations, with generally much lower values in birds in the lowland (near sea level) rain forest relative to the high-elevation cloud forest. Among the 13 sites sampled, birds from high-elevation cloud forest sites (up to 1800 m) had generally an order of magnitude higher Hg in their blood than at lowland sites, though the latter still had several-fold higher Hg than the Puerto Rican birds. Newer 2017 results (unpublished data available from co-authors Oksana Lane, Biodiversity Research Institute, Portland, ME, and Wayne Arendt, U.S. Forest Service, Luquillo, PR), however, show comparable or even lower bird blood Hg for bananaquits in city parks of coastal Santo Domingo than in the Puerto Rican mountains.

Though our most-sampled bird was the generally nectarivorous bananaquit, two lines of evidence suggest that bananaquits in LEF rely considerably on animal food sources and thus their low blood Hg is not solely a reflection of low trophic position. LEF is frequently impacted by tropical cyclones, which limit energetically expensive

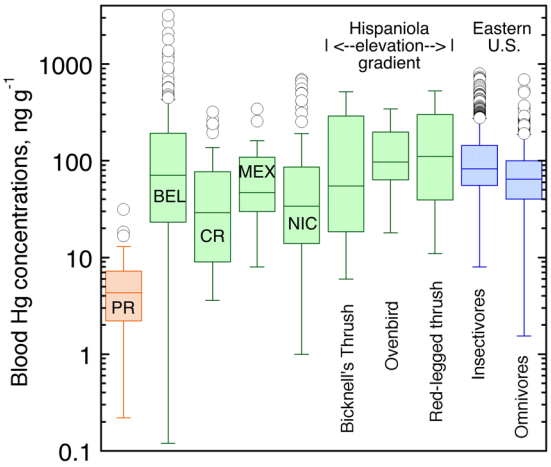

Fig. 5 Hg concentrations in the Puerto Rico birds sampled in this study compared to Hg concentrations in birds at other tropical sites and the northeastern USA. Orange: this study (PR = Puerto Rico). Green: other Caribbean and Central American sites (BEL = Belize, Evers 2008; CR Costa Rica, Biodiversity Research Institute (BRI), Portland Maine, unpublished data; MEX = Mexico, BRI, unpublished data; NIC Nicaragua, Lane et al. 2013; Hispaniola data for 3 species populating the majority of sites along an elevational transect (Townsend et al. 2013). Blue: northeast USA temperate sites (Jackson et al. 2015)

nectar production, as was found at similar elevations in other Puerto Rican forests (Ackerman et al. 1994; Melén-dez-Ackerman et al. 2000; Pérez et al. 2011). In Jamaica's Blue Mountains at a similar elevation to our study, Cruz (1980) found that invertebrates constituted 24% of the bananaquit diet. Secondly, the three LEF species of hummingbirds, which rely more strongly on nectar, collectively have only 3.2% the relative abundance of bananaquits at LEF (unpublished data available from co-author Wayne Arendt, U.S. Forest Service, Luquillo, PR). In contrast, the two hummingbird species in Santo Domingo, where nectar is plentiful from the urban ornamental plants and introduced tree and shrub species which constitute 71% of the city's arboreal species (Melendez-Ackerman et al., University of Puerto Rico at Río Piedras, unpubl. manuscript), have nearly 30% the relative abundance of bananaquit. More detail on the bananaquit diet is available in the supplemental OR material.

Aside from bananaquits, the only species common to sampling efforts in Puerto Rico and Hispaniola was the red-legged thrush. Only one individual was captured in Puerto Rico, but its blood Hg matched the very lowest Hg concentration of the 41 red-legged thrushes captured by Townsend et al. (2013) in Hispaniola (Fig. 5). The elevational gradient in Hispaniola was reversed in Puerto Rico, where birds had significantly higher Hg at a lower elevation site, possibly due to a more complex food web and presence of a nearby wetland. These differences within and across regions underscore the important role of habitat in trophic Hg uptake. But it is difficult to evaluate habitat effects without information on Hg deposition. As Townsend et al. (2013) noted for the Hispaniola study, atmospheric Hg deposition monitoring is a critical missing link that makes it difficult to distinguish the effects of Hg deposition from diet and other factors.

The literature on biotic uptake of Hg in Puerto Rico is limited, but some studies from the early 1990s assessed Hg in fauna in nearby coastal areas of Puerto Rico. Burger et al. (1992a) reported Hg lower than global averages in a variety of biota in and adjacent to freshwater-dominated coastal salt marshes in eastern Puerto Rico, although they had a high detection limit of 80 ng g^{-1}. Similarly, Burger et al. (1992b) found that cattle egrets *(Bubulcus ibis)* in eastern Puerto Rico had lower Hg than their urban counterparts. In contrast, Burger and Gochfeld (1991) found that Hg in tern feathers on the island of Culebra, Puerto Rico, was comparable or higher than in more urbanized areas. The relatively lower Hg in the terrestrial egret is consistent with our results, whereas Hg in terns is controlled by marine processes.

Some studies of Hg in fish in Puerto Rico run counter to our finding of low trophic uptake at LEF, with Hg concentrations near consumption advisory levels (Mansilla-Rivera and Rodríguez-Sierra 2011, Ortiz-Roque and López-Rivera 2004; Sastre et al. 1999), but these results are either from marine or contaminated sites. On the other hand, fish Hg in tropical Africa is well below global averages in lakes and the large inland Okavango delta wetland, leading Black et al. (2011) to refer to the "tropical African mercury anomaly". Black et al. (2011) did not resolve the anomaly, but discounted the lack of Hg in atmospheric deposition, pointing out that modeled Hg deposition on the African continent was higher than the global average (Selin et al. 2008). While the African anomaly mirrors our Puerto Rican paradox, a lake in Papua New Guinea (Bowles et al. 2001) and the Rio Negro in Brazil (Belger and Forsberg 2006) had much higher fish Hg.

Hg methylation and demethylation on the landscape

All indicators of methylation in soils and sediment tested in the LEF ecosystem hovered near our limits of detection. These include MeHg concentration itself, MPP, and the k_{meth} values on which MPP is partly based. MeHg concentrations averaged more than an order of magnitude lower than those in California wetlands (Marvin-DiPasquale et al. 2014) and a diversity of eight stream sites across the contiguous U.S. (Marvin-DiPasquale et al. 2009b). MPP rates were likewise an order of magnitude lower than those in the California wetlands but similar to those in the eight U.S. streams. Our finding of higher MeHg concentrations and

MPP rates in floodplain soils compared to stream sediments supported findings from freshwater stream catchments in New York and South Carolina, i.e. that both MeHg concentrations and MPP rates can be much higher in out-of-channel sub-habitats compared to in-channel streambed sediment (Bradley et al. 2011). That study suggested that the stream channel acts more as a conduit for dissolved and particulate THg and MeHg traveling via surface and subsurface flow from the out-of-channel habitats.

Anoxic microsites

All bed sediments and soils were well-oxygenated when sampled (Table 1). This condition is typical at LEF despite high soil water content. In a nearby catchment, Hall et al. (2013) demonstrated a poor relation between redox status and soil water content; copious water addition failed to induce anoxia. However, soil O_2 concentration at LEF has been shown to fluctuate over both short (day to day) and seasonal time scales, frequently dropping to less than 4%, i.e. less than 20% of atmospheric O_2 (Hall and Silver 2013; Silver et al. 1999). This variability generates spatial (microsites) and temporal reducing conditions where both SRB and FeRB, of which many species are obligate anaerobes, can thrive (Dubinsky et al. 2010; Hall et al. 2016). The occurrence of reducing microsites is supported by previous measurements of pervasive iron and sulfate reduction in these soils irrespective of short-term moisture variability (Hall et al. 2016, 2013), as well as appreciable TRS concentrations, elevated ratios of $\%Fe(II)/Fe_T$, and CH_4 efflux (Table 1). The presence of highly reduced groundwater at a nearby floodplain site (McDowell et al. 1992; McDowell et al. 1996) suggests the possibility of Hg methylation along deeper hydrologic flow paths. However, activity of Fe-reducing microbes (and presumably other anaerobes) appeared to be much greater in microsites at the soil surface, due to increased C limitation with depth (Hall et al. 2016).

Sulfate reducing bacteria

The methylation process has long been thought to be carried out by SRB. However, measured SR rates were low across all study sites (Table 1). If anything, in-situ SR rates in our oxygenated soils were likely lower than those measured in the lab under anoxic conditions, since SRB are strict anaerobes. SR rates at our LEF sites were two orders of magnitude less than similarly assayed freshwater in managed and agricultural wetlands in California (Marvin-DiPasquale et al. 2014) and a diversity of eight stream sites throughout the continental U.S. (Marvin-DiPasquale et al. 2009b). Solid phase TRS was also one to two orders of magnitude less than in both the California wetland and eight-stream studies. Relative to the other four USGS WEBB watersheds which were concurrently sampled, Río Icacos bed sediment had a median microbial SR rate that was an order of magnitude lower and TRS concentration that was more than 4-fold lower (Table OR2). Further, streambed porewater sulfate concentrations were low (Table 1) and in the range ($<30\ \mu mol\ L^{-1}$) that could limit the activity of SRB (Lovley and Klug 1986). Finally, the hillslope transect lacked the systematic downslope decrease in the porewater SO_4^{2-}/Cl^- molar ratio one might expect if microbial SR were active and increasing with soil organic and moisture content.

Iron reducing bacteria

Recent advances in molecular biology have demonstrated Hg(II)-methylation capacity in a much more taxonomically diverse array of microbes than previously recognized (Gilmour et al. 2013), including iron-reducing bacteria (FeRB) (Fleming et al. 2006; Kerin et al. 2006). In contrast to SRB, Fe(III)-reducing bacteria are abundant in terrestrial surface soils of the LEF (Dubinsky et al. 2010), and Fe reduction and oxidation occur at significant rates even under non-saturated conditions in this system (Hall et al. 2013). LOI, $\%Fe(II)_{HCl}$, and $\%Fe(II)/Fe_T$ each increased downslope from midslope to the floodplain (Table 1), indicating an increase in Fe(III)-reduction with increasing soil organic matter. A corresponding decrease in $Fe(III)_{HCl}$ and $Fe(III)_{SRO}$, both Fe (III) fractions that are readily available electron acceptors for microbial Fe reduction (Hyacinthe et al. 2006; Lovley and Phillips 1987), imply Fe(III) losses via reductive dissolution in surface horizons over pedogenic timescales.

The evidence that microbial Fe(III)-reduction is a more important terminal carbon flow pathway than microbial sulfate reduction in the sites studied does not necessarily imply that MeHg production was primarily controlled by FeRB. However, an FeRB control is supported by strong correlations of a number of key Hg cycling metrics with Fe cycling metrics. Specifically, MeHg concentration was positively correlated with both $\%Fe(II)_{HCl}$ ($r = 0.85$) and $\%Fe(II)/Fe_T$ ($r = 0.77$), although %MeHg was not correlated ($p < 0.05$) with these same two (or any) Fe metrics. Thus, while Fe(III)-reduction may be an important microbial process in these Puerto Rican soils/sediments, and metrics for Fe(III)-reduction are correlated with those for MeHg production, the low MeHg concentrations and k_{meth} (and MPP) rates suggest that conditions are sub-optimal for MeHg production.

Demethylation

Considering only MeHg concentrations and k_{meth} (and MPP) rates in assessing Hg cycling within a suite of sites can be

misleading if MeHg degradation plays a significant role in net MeHg production (Marvin-DiPasquale and Agee 2003; Marvin-DiPasquale et al. 2003). In the current study, values of k_{deg} and MDP exceeded corresponding values of k_{meth} and MPP by an order of magnitude (Table 1). Our values of k_{deg} were similar to those measured in Everglades (wetland) flocculent surface sediment (Marvin-DiPasquale and Oremland 1998) and somewhat lower than San Francisco Bay 0–4 cm surface sediment (Marvin-DiPasquale and Agee 2003), and much lower than those from a Hg-contaminated mining site (Marvin-DiPasquale et al. 2000). While the current results suggest that MeHg degradation exceeded MeHg production in these PR sites, it is difficult to directly compare these 'potential' rates due to differences in non-tracer level amendment concentrations and incubation times (6 days for MDP vs 1 day for MPP). However, NMP rates, measured over 6 days of anoxic incubation, suggest limited net positive MeHg production overall (Table 1). Note that as with measurements of microbial SR rates, MeHg production was optimized in the laboratory by the anoxic incubation conditions, in comparison to the more oxic field conditions. Thus, measured NMP rates should be considered upper limits for these substrates. More detail on the methylation experiments is available in the supplemental OR material.

Resolving the paradox

Our resolution of the paradox of high Hg deposition but low biotic uptake in this tropical wet forest rests on two main findings: (1) conditions for MeHg production are sub-optimal, i.e. oxic soil and sediment, thus inhibiting to strict anaerobic bacteria; and (2), potential rates for MeHg degradation are comparatively high. These two factors combine to limit net MeHg production, which results in low biotic Hg uptake. To the extent that there is low but measurable MeHg in the substrate, and low but measurable NMP rates observed under anoxic incubation conditions, there is some potential for MeHg production, likely associated with reduced microsites. However, it is unclear if this limited MeHg production is carried out by SRB that exhibit very low rates, or by FeRB that seem to dominate carbon flow in this setting.

In addition to the low net MeHg production in this system, its high rainfall and associated frequent flushing of watershed soils may limit the residence time of MeHg in the soil for biotic uptake to occur. In the adjacent Mameyes watershed, Scholl et al. (2015) determined from deuterium excess analysis that streamflow was a mix of 75% groundwater and 25% recent (<1 week old) rainfall. The latter component represents shallow flow and the short residence time implies that soils are frequently flushed. Despite the low MeHg/THg ratio in the stream, the high THg and water fluxes resulted in MeHg export that is an order of magnitude greater than the global average (calculated from Shanley and Bishop (2012)). Thus, the rate of hydrologic flushing of MeHg may keep pace with its net production rate in the soil. Moreover, MeHg in streamwater occurs primarily in the particulate phase (Shanley et al. 2008), which has limited biological availability.

A final factor that may contribute to the low biotic uptake is biomass dilution. Because of the increasing biodiversity toward the tropics (Eldridge 1998), MeHg uptake in the Luquillo forest food web may be distributed across a high faunal biomass so that the concentration at a given trophic level (feeding guild) is lowered. Birds at LEF have high areal biomass density, and energy flows through the avifaunal community at a rate that is at least double that in temperate forests (Wunderle and Arendt 2011). This doubled activity implies a relative dilution of available MeHg by one-half, so biomass dilution may also be a factor contributing to low bird blood Hg in this ecosystem.

Comparison to other tropical studies

Considering that the primary source of Hg in precipitation at this Puerto Rican site is GOM from the global pool present at high altitude, high Hg(II) wet deposition could occur in other tropical settings where there is sufficient landmass to generate high rain-forming convective clouds. However, there are few published studies of Hg in atmospheric deposition or streams in the tropics. Studies on methylation dynamics in the tropics have been more numerous, but most field research has been conducted in lakes and adjacent wetlands in the seasonally flooded floodplains of the Amazon and Paraguay River basins (Achá et al. 2011; Guimarães et al. 2000; Lázaro et al. 2016; Mauro et al. 2002; Roulet et al. 2001). A common thread of these studies is the importance of periphyton in open waters, wetlands, and adjacent wet forests as a methylation hotspot. Indeed, Molina et al. (2010) found that invertebrate food chains based on periphyton were the longest, with the greatest Hg bioaccumulation. As in our study, Correia et al. (2012) hinted that microbes other than SRB may be responsible for methylation in tropical systems. We found no analog in the literature to our methylation study in a forested tropical upland.

The existing literature on Hg in the food web in the American tropics is scant, but shows that unlike this site in Puerto Rico, bioaccumulation of Hg at other tropical sites is comparable or even higher than in temperate latitudes. None of these tropical studies recorded Hg deposition nor investigated methylation processes. Therefore, it is challenging to interpret the sources and processes involved in the trophic transfers of Hg. The Townsend et al. (2013) avian study in Hispaniola was the most comprehensive in terms of number of species, individuals, and habitats sampled, and demonstrated a clear biomagnification of Hg when moving from coastal rain forest to mountain cloud forest. It is unknown

whether this shift is due to increased Hg deposition, increased net methylation, changes in the food web structure, or some combination of these factors. In our study, high Hg deposition poses a potential threat to the biota, but processes acting within LEF work to limit Hg bioaccumulation. Large information gaps remain as to whether elevated atmospheric Hg deposition (as observed in LEF) is widespread in Puerto Rico and the greater tropics, how diverse tropical landscapes cycle atmospherically deposited Hg, and ultimately how much Hg enters tropical food webs and the extent to which Hg poses a risk to human populations. Research should be augmented at existing tropical research sites to link currently uncoordinated investigations of atmospheric deposition, fluvial transport, methylation dynamics, and trophic uptake.

Acknowledgements We thank Angel Torres and Manuel Rosario for help with sampling, and USGS staff in Menlo Park (CA) for laboratory analyses (Jennifer Agee, Le Kieu, Evangelos Kakouros, and Michelle Beyer). We acknowledge Michael Bank for facilitating analysis of biota and vegetation samples, which motivated this study. This research was supported by the USGS Water, Energy, and Biogeochemical Budgets (WEBB) program, which was funded by USGS Climate Research and Development (now Land Resources Science Program). Supplemental support for MM-D was provided by the USGS Toxic Substances Hydrology Program. Support was also provided by NSF grant DEB-1457805 and the Luquillo Critical Zone Observatory NSF grant EAR-1331841. Part of this research was carried out in cooperation with the University of Puerto Rico. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval All applicable international, national, and/or institutional guidelines for the care and use of animals were followed.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

References

Achá D, Hintelmann H, Yee J (2011) Importance of sulfate reducing bacteria in mercury methylation and demethylation in periphyton from Bolivian Amazon region. Chemosphere 82:911–916

Ackerman JD, Rodríguez-Robles JA, Meléndez-Ackerman EJ (1994). A meager nectar offering by an epiphytic orchid is better than nothing. Biotropica 26:44–49

Allen R (1961) Birds of the Caribbean. The Viking Press, New York

Belger L, Forsberg BR (2006) Factors controlling Hg levels in two predatory fish species in the Negro river basin, Brazilian Amazon. Sci Total Environ 367:451–459

Black FJ, Bokhutlo T, Somoxa A, Maethamako M, Modisaemang O, Kemosedile T, Cobb-Adams C, Mosepele K, Chimbari M (2011) The tropical African mercury anomaly: lower than expected mercury concentrations in fish and human hair. Sci Total Environ 409:1967–1975

Bowles KC, Apte SC, Maher WA, Kawei M, Smith R (2001) Bioaccumulation and biomagnification of mercury in Lake Murray, Papua New Guinea. Can. J Fish Aquat Sci 58:888–897

Bradley PM, Burns DA, Murray KR, Brigham ME, Button DT, Chasar LC, Marvin-DiPasquale MC, Lowery MA, Journey CA (2011) Spatial and seasonal variability of dissolved methylmercury in two stream basins in the eastern United States. Environ Sci Technol 45:2048–2055

Burger J, Cooper K, Saliva J, Gochfeld D, Lipsky D, Gochfeld M (1992a) Mercury bioaccumulation in organisms from three Puerto Rican estuaries. Environ Mon Assess 22:181–197

Burger J, Gochfeld M (1991) Lead, mercury, and cadmium in feathers of tropical terns in Puerto Rico and Australia. Arch Environ Contam Toxicol 21:311–315

Burger J, Parsons K, Benson T, Shukla T, Rothstein D, Gochfeld M (1992b) Heavy metal and selenium levels in young cattle egrets from nesting colonies in the northeastern United States, Puerto Rico, and Egypt. Arch Environ Contam Toxicol 23:435–439

Cabana G, Rasmussen JB (1994) Modelling food chain structure and contaminant bioaccumulation using stable nitrogen isotopes. Nature 372:255

Correia RRS, Miranda MR, Guimarães JRD (2012) Mercury methylation and the microbial consortium in periphyton of tropical macrophytes: effect of different inhibitors. Environ Res 112:86–91

Cristol DA, Brasso RL, Condon AM, Fovargue RE, Friedman SL, Hallinger KK, Monroe AP, White AE (2008) The movement of aquatic mercury through terrestrial food webs. Science 320:335

Cruz A (1980) Feeding ecology of the Black-Whiskered Vireo and associated gleaning birds in Jamaica. Wilson Bull 92:40–52

Driscoll CT, Mason RP, Chan HM, Jacob DJ, Pirrone N (2013) Mercury as a global pollutant: Sources, pathways, and effects. Environ Sci Technol 47:4967–4983

Dubinsky EA, Silver WL, Firestone MK (2010) Tropical forest soil microbial communities couple iron and carbon biogeochemistry. Ecology 91:2604–2612

Edmonds ST et al. (2010) Geographic and seasonal variation in mercury exposure of the declining Rusty Blackbird. Condor 112:789–799

Eldridge N (1998) Life in the balance: humanity and the biodiversity crisis. Princeton Univ. Press., Princeton NJ, p. 240

EPA US (1998) Method 7473 (SW-846): mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry, Revision 0. Washington, D.C., p. 17

Evers DC (2008) Mercury in terrestrial birds of Belize. BioDiversity Research Institute, Gorham, Maine. Report BRI 2008-05, p. 14.

Evers DC, Duron M (2006) Developing an exposure profile for mercury in breeding birds of New York and Pennsylvania, 2005. BioDiversity Research Institute, Gorham, Maine. Report BRI 2006-11, p. 32

Fadini PS, Jardim WF (2001) Is the Negro River Basin (Amazon) impacted by naturally occurring mercury? Sci Total Environ 275:71–82

Fleming EJ, Mack EE, Green PG, Nelson DC (2006) Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium. Appl Environ Microbiol 72:457–464

Fostier AH, Forti MC, Guimaraes JRD, Melfi AJ, Boulet R, Espirito Santo CM, Krug FJ (2000) Mercury fluxes in a natural forested Amazonian catchment (Serra do Navio, Amapa State, Brazil). Sci Total Environ 260:201–211

Gilmour CC, Podar M, Bullock AL, Graham AM, Brown SD, Somenahally AC, Johs A, Hurt RA, Bailey KL, Elias DA (2013) Mercury methylation by novel microorganisms from new environments. Environ Sci Technol 47:11810–11820

Guentzel JL, Landing WM, Gill GA, Pollman CD (2001) Processes influencing rainfall deposition of mercury in Florida. Environ Sci Technol 35:863–873

Guimarães JRD, Meili M, Hylander LD, Silva EdCe, Roulet M, Mauro JBN, de Lemos RA (2000) Mercury net methylation in five tropical flood plain regions of Brazil: high in the root zone of floating macrophyte mats but low in surface sediments and flooded soils. Sci Total Environ 261:99–107

Hall SJ, Liptzin D, Buss HL, DeAngelis K, Silver WL (2016) Drivers and patterns of iron redox cycling from surface to bedrock in a deep tropical forest soil: a new conceptual model. Biogeochemistry 130:177–190

Hall SJ, McDowell WH, Silver WL (2013) When wet gets wetter: decoupling of moisture, redox biogeochemistry, and greenhouse gas fluxes in a humid tropical forest soil. Ecosystems 16: 576–589

Hall SJ, Silver WL (2013) Iron oxidation stimulates organic matter decomposition in humid tropical forest soils. Glob Change Biol 19:2804–2813

Hall SJ, Silver WL (2015) Reducing conditions, reactive metals, and their interactions can explain spatial patterns of surface soil carbon in a humid tropical forest. Biogeochemistry 125:149–165

Hansen AM, Gay DA (2013) Observations of mercury wet deposition in Mexico. Environ Sci Pollut Res 20:8316–8325

Howard J, Trotz MA, Thomas K, Omisca E, Chiu HT, Halfhide T, Akiwumi F, Michael R, Stuart AL (2011) Total mercury loadings in sediment from gold mining and conservation areas in Guyana. Environ Mon Assess 179:555–573

Hyacinthe C, Bonneville S, Van Cappellen P (2006) Reactive iron(III) in sediments: chemical versus microbial extractions. Geochim Cosmochim Acta 70:4166–4180

Jackson AK et al. (2015) Songbirds as sentinels of mercury in terrestrial habitats of eastern North America. Ecotoxicology 24:453–467

Johnson AH, Xing HX, Scatena FN (2015) Controls on soil carbon stocks in El Yunque National Forest. Puerto Rico Soil Sci Soc Am J 79:294–304

Kerin EJ, Gilmour CC, Roden E, Suzuki M, Coates J, Mason R (2006) Mercury methylation by dissimilatory iron-reducing bacteria. Appl Envirob Microbio 72:7919–7921

Krabbenhoft DP, Branfireun BA, Heyes A (2005) Biogeochemical cycles affecting the speciation, fate and transport of mercury in the environment. In: Parsons MB, Percival JB (eds). Mercury: sources, measurements, cycles, and effects, vol. 34. Mineralogical Association of Canada, Halifax, pp. 139–156

Landing WM, Caffrey JM, Nolek SD, Gosnell KJ, Parker WC (2010) Atmospheric wet deposition of mercury and other trace elements in Pensacola, Florida. Atmos Chem Phys 10:4867–4877

Lane OP, Arendt WJ, Tórrez MA, Castellón JCG (2013) Pilot assessment of mercury exposure in selected biota from the lowlands of Nicaragua. Mesoamericana 17:19–28

Lázaro WL, Díez S, da Silva CJ, Ignácio ÁRA, Guimarães JRD (2016) Waterscape determinants of net mercury methylation in a tropical wetland. Environ Res 150:438–445

Lovley DR, Klug MJ (1986) Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments. Geochim Cosmochim Acta 50:11–18

Lovley DR, Phillips EJ (1987) Rapid assay for microbially reducible ferric iron in aquatic sediments. Appl Environ Microbio 53:1536–1540

Lyman SN, Jaffe DA (2012) Formation and fate of oxidized mercury in the upper troposphere and lower stratosphere. Nat Geosci 5:114–117

Mansilla-Rivera I, Rodríguez-Sierra CJ (2011) Metal levels in fish captured in puerto rico and estimation of risk from fish consumption. Arch Environ Contam Toxicol 60:132–144

Marvin-DiPasquale MC, Agee J (2003) Microbial mercury cycling in sediments of the San Francisco Bay-Delta. Estuaries 26:1517–1528

Marvin-DiPasquale MC, Agee J, Bouse R, Jaffe B (2003) Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. Environ Geol 43:260–267

Marvin-DiPasquale MC, Agee J, McGowan C, Oremland RS, Thomas M, Krabbenhoft D, Gilmour CC (2000) Methyl-mercury degradation pathways: a comparison among three mercury-impacted ecosystems. Environ Sci Technol 34:4908–4916

Marvin-DiPasquale MC, Agee JL, Kakouros E, Kieu LH, Fleck JA, Alpers CN (2011) The effects of sediment and mercury mobilization in the South Yuba River and Humbug Creek confluence area, Nevada County, California: Concentrations, speciation and environmental fate-Part 2: Laboratory Experiments. U.S. Geological Survey. Open-File Report no. 2010–1325B. Reston VA

Marvin-DiPasquale MC, Alpers CN, Fleck JA (2009a) Mercury, methylmercury, and other constituents in sediment and water from seasonal and permanent wetlands in the Cache Creek Settling Basin and Yolo Bypass, Yolo County, California, 2005−06. U.S. Geological Survey. Open-File Report no. 2009–1182

Marvin-DiPasquale MC, Lutz MA, Brigham ME, Krabbenhoft DP, Aiken GR, Orem WH, Hall BD (2009b) Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment-pore water partitioning. Environ Sci Technol 43:2726–2732

Marvin-DiPasquale MC, Lutz MA, Krabbenhoft DP, Aiken GR, Orem WH, Hall BD, DeWild JF, Brigham ME (2008) Total mercury, methylmercury, methylmercury production potential, and ancillary streambed-sediment and pore-water data for selected streams in Oregon, Wisconsin, and Florida, 2003–04. U.S. Geological Survey. Data Series 375. Report no. 2327-638X, https://doi.org/10.3133/ds375

Marvin-DiPasquale MC, Oremland RS (1998) Bacterial methylmercury degradation in Florida Everglades peat sediment. Environ Sci Technol 32:2556–2563

Marvin-DiPasquale MC, Windham-Myers L, Agee JL, Kakouros E, Kieu LH, Fleck JA, Alpers CN, Stricker CA (2014) Methylmercury production in sediment from agricultural and non-agricultural wetlands in the Yolo Bypass, California, USA. Sci Total Environ 484:288–299

Matthes WJJ, Sholar CJ, George JR (1992) Quality-Assurance Plan for the Analysis of Fluvial Sediment by Laboratories of the U.S. Geological Survey. U.S. Geological Survey, Open-File Report 91–467, Reston VA, p. 37

Mauro J, Guimarães J, Hintelmann H, Watras C, Haack E, Coelho-Souza S (2002) Mercury methylation in macrophytes, periphyton, and water—comparative studies with stable and radio-mercury additions. Anal Bioanal Chem 374:983–989

McDowell WH, Bowden WB, Asbury CE (1992) Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns. Biogeochem 18:53–75

McDowell WH, McSwiney CP, Bowden WB (1996) Effects of hurricane disturbance on groundwater chemistry and riparian function in a tropical rain forest. Biotropica 28:577–584

McDowell WH, Scatena FN, Waide RB, Brokaw N, Camilo GR, Covich AP, Crowl TA, Gonzalez G, Greathouse EA, Klawinski P, Lodge DJ, Lugo AE, Pringle CM, Richardson BA, Richardson MJ, Schaefer DA, Silver WL, Thompson J, Vogt DJ, Vogt KA, Willig MR, Woolbright LL, Zou X, Zimmerman JK (2012) Geographic and ecological setting of the Luquillo Mountains. In: Brokaw N, Crowl TA, Lugo AE, McDowell WH, Scatena FN, Waide RB, Willig MR (eds) A Caribbean forest tapestry: the multidimensional nature of disturbance and response. Oxford University Press, New York, pp. 72–163

Meléndez-Ackerman EJ, Ackerman JD, Rodríguez-Robles JA (2000) Reproduction in an orchid can be resource-limited over its lifetime. Biotropica 32(2):282–290

Michener R, Lajtha K (2007) Stable isotopes in ecology and environmental science. 2nd edn. Blackwell Publishing, Ltd. Oxford

Molina CI, Gibon F-M, Duprey J-L, Dominguez E, Guimarães J-RD, Roulet M (2010) Transfer of mercury and methylmercury along macroinvertebrate food chains in a floodplain lake of the Beni River, Bolivian Amazonia. Sci Total Environ 408:3382–3391

Murphy SF, Stallard RF (2012) Hydrology and Climate of Four Watersheds in Eastern Puerto Rico. In: Murphy SF, Stallard RF (eds). Water quality and landscape processes of four watersheds in eastern Puerto Rico. Professional Paper 1789. U.S. Geological Survey. Reston VA, pp. 43–83

Murphy SF, Stallard RF, Scholl MA, González G, Torres-Sánchez AJ (2017) Reassessing rainfall in the Luquillo Mountains, Puerto Rico: Local and global ecohydrological implications. PLOS ONE 12:e0180987

Ortiz-Roque C, López-Rivera Y (2004) Mercury contamination in reproductive age women in a Caribbean island: Vieques. J Epidemiol Community Health 58:756–757

Pérez ME, Meléndez-Ackermana EJ, Monsegur-Rivera OA (2011) Breeding system and pollination of Gesneria pauciflora (Gesneriaceae), a threatened Caribbean species. Flora 242:8–15

Peters NE, Shanley JB, Aulenbach BT, Webb RMT, Campbell DH, Hunt RJ, Larsen MC, Stallard RF, Troester J, Walker JF (2006) Water and solute mass balance of five small, relatively undisturbed watersheds in the US. Sci Total Environ 358:221–242

Rimmer CC, McFarland KP, Evers DC, Miller EK, Aubry Y, Busby D, Taylor RJ (2005) Mercury concentrations in Bicknell's Thrush and other insectivorous passerines in montane forests of northeastern North America. Ecotoxicology 14:223–240

Risch MR (2017) Mercury and methylmercury concentrations and litterfall mass in monthly litterfall samples collected at National Atmospheric Deposition Program site at El Verde, Puerto Rico in 2014-2016: U.S. Geological Survey data release, https://doi.org/10.5066/F7JW8CSF

Roulet M, Guimarães J-RD, Lucotte M (2001) Methylmercury production and accumulation in sediments and soils of an amazonian floodplain—effect of seasonal inundation. Water Air Soil Pollut 128:41–60

Sastre M, Reyes P, Ramos H, Romero R, Rivera J(1999) Heavy Metal Bioaccumulation in Puerto Rican Blue Crabs (Callinectes spp.) Bull Mar Sci B 4:209–217

Scholl MA, Murphy SF (2014) Precipitation isotopes link regional climate patterns to water supply in a tropical mountain forest, eastern Puerto Rico. Water Resour Res 50:4305–4322

Scholl MA, Shanley JB, Murphy SF, Willenbring JK, Occhi M, González G (2015) Stable-isotope and solute-chemistry approaches to flow characterization in a forested tropical watershed, Luquillo Mountains, Puerto Rico. Appl Geochem 63:484–497

Selin NE, Jacob DJ, Yantosca RM, Strode S, Jaeglé L, Sunderland EM (2008) Global 3-D land-ocean-atmosphere model for mercury: present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition. Glob Biogeochem Cycle 22:1–13

Shanley JB, Bishop K (2012) Mercury cycling in forested watersheds. In: Bank MS (ed). Mercury in the environment: pattern and process. University of California Press, Berkeley, CA

Shanley JB, Engle MA, Scholl M, Krabbenhoft DP, Brunette R, Olson ML, Conroy ME (2015) High mercury wet deposition at a "clean air" site in Puerto Rico. Environ Sci Technol 49: 12474–12482

Shanley JB, Mast MA, Campbell DH, Aiken GR, Krabbenhoft DP, Hunt RJ, Walker JF, Schuster PF, Chalmers A, Aulenbach BT, Peters NE, Marvin-DiPasquale M, Clow DW, Shafer MM (2008) Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. Environ Pollut 154:143–154

Silva-Filho EV, Machado W, Oliveira RR, Sella SM, Lacerda LD (2006) Mercury deposition through litterfall in an Atlantic Forest at Ilha Grande, Southeast Brazil. Chemosphere 65:2477–2484

Silver WL, Lugo A, Keller M (1999) Soil oxygen availability and biogeochemistry along rainfall and topographic gradients in upland wet tropical forest soils. Biogeochemistry 44:301–328

Sprovieri F et al. (2017) Five-year records of mercury wet deposition flux at GMOS sites in the Northern and Southern hemispheres. Atmos Chem Phys 17:2689–2708

St. Louis VL, Rudd JWM, Kelly CA, Hall BD, Rolfhus KR, Scott KJ, Lindberg SE, Dong W (2001) Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. Environ Sci Technol 35:3089–3098

Stiles FG, Skutch AF (1989) A guide to the birds of Costa Rica. Cornell University Press, Ithica, New York

Swartzendruber PC, Jaffe DA, Prestbo EM, Weiss-Penzias P, Selin NE, Park R, Jacob D, S Strode S, Jaegle L (2006) Observations of reactive gaseous mercury in the free-troposphere at the Mount Bachelor Observatory. J Geophys Res 111:D24301

Townsend JM, Rimmer CC, Driscoll CT, McFarland KP, Iñigo-Elias E (2013) Mercury concentrations in tropical resident and migrant songbirds on Hispaniola. Ecotoxicology 22:86–93

Wardsworth FH (1949) The development of the forest land resources of the Luquillo Mountains of Puerto Rico. Ph.D thesis, Univ. Michigan, AnnArbor, p. 481

Wiener JG, Knights BC, Sandheinrich MB, Jeremiason JD, Brigham ME, Engstrom DR, Woodruff LG, Cannon WF, Balogh SJ (2006) Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. Environ Sci Technol 40:6261–6268

Wunderle JM, Arendt WJ (2011) Avian studies and research opportunities in the Luquillo Experimental Forest: a tropical rain forest in Puerto Rico. For Ecol Mgmt 262:33–48