

1 EVALUATING THE POTENTIAL EFFICACY OF MERCURY TOTAL MAXIMUM DAILY
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3 LOADS ON AQUEOUS METHYLMERCURY LEVELS IN FOUR COASTAL
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5 WATERSHEDS
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12 Supporting information includes text for laboratory methods and an interpretation of the
13 regression coefficients, regression results (Tables S1-S2), detailed data from the Mercury
14 Deposition Network (Table S3), and graphs of the residuals from the regression models for San
15 Francisco Bay estuary and Long Island Sound (Figure S1).

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17 1. Supporting information for laboratory methods

18 Laboratory methods for aqueous Hg_T and MeHg are briefly described, only to highlight
19 slight differences between labs. For all four sites, EPA Methods 1630 and 1631 (32-33) were
20 employed for the determination of aqueous MeHg and Hg_T , respectively.

21 *Aqueous Hg_T .* In all cases, samples were oxidized with 0.2N BrCl to release Hg(II)
22 followed by pre-reduction with hydroxylamine hydrochloride to reduce free Cl or Br. The
23 samples were further reduced with stannous chloride ($SnCl_2$), converting Hg(II) to the more
24 volatile Hg(0), which was purged from solution by argon gas. Quantification was by dual-stage
25 gold amalgamation/cold vapor atomic fluorescence spectrometry (CVAFS). The oxidation-
26 reduction steps follow established methods (34-37), although concentrations of BrCl,
27 hydroxylamine hydrochloride and $SnCl_2$ varied between labs. Vandal et al. (20) also reported
28 samples with high dissolved organic carbon were further oxidized with 1 mL of 4:1
29 H_2SO_4/HNO_3 solution and heated at 80 °C for 12 hours to alleviate Au-trap efficiency problems
30 associated with the formation of an uncharacterized volatile material (21, 57).

31 *Aqueous MeHg.* Acidified samples were distilled into receiving vials under N_2 flow,
32 according to methods described by Horvat et al. (38). The pH of the distillates was then adjusted
33 to 4.9 with 2M acetate buffer and ethylated using 1% sodium tetraethylborate, converting
34 nonvolatile MeHg to gaseous methylethylmercury, which was purged onto Tenax columns, then
35 thermally desorbed from the column and quantified by CVAFS. Rothenberg et al. (18) reported
36 for Mugu samples, 200 μ L of 1% ammonium pyrrolidine dithiocarbamate were added prior to
37 distillation to reduce interferants (58), while Vandal et al. (20) employed aqueous distillation (6-
38 8 ml min^{-1}) as a pre-extraction step to eliminate interferences (38, 59).

39 2. Supporting information for interpretation of regression estimates of the slope, holding other
40 variables constant (the equations are numbered as in the manuscript text). The interpretation for
41 the % change in Hg_T levels is valid only for small changes in x; i.e. 1-20%.

42 (8) *Mugu*: $Log_{10} MeHg = 1.7 + 0.38 Log_{10} Hg_T - 0.48 pH + 0.072 Temperature$

43 For a 1% increase in the concentration of Hg_T , the concentration of MeHg is expected to
44 increase by 0.38%

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46 For a 1 log unit increase in pH, the concentration of MeHg is expected to decrease by a
47 factor of 0.48 pM.

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49 For a 1-degree C increase in surface water temperature, the the concentration of MeHg is
50 expected to increase by a factor of 0.072 pM

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52 (9) *SF*: $Log_{10} MeHg = 1.3 + 0.28 Log_{10} Hg_T + 0.026 Temperature - 0.019 Salinity$
53 $- 0.32 Northern\ reach\ (coded\ 0,\ 1) - 0.29 pH$

54 Using the indicator variable for the northern reach, the regression equation may be re-
55 written:

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57 (9a) *Southern and central reach*: $Log_{10} MeHg = 1.3 + 0.28 Log_{10} Hg_T +$

58 $0.026 Temperature - 0.019 Salinity - 0.29 pH$

59 (9b) *Northern reach*: $Log_{10} MeHg = (1.3-0.32) + 0.28 Log_{10} Hg_T +$

60 $0.026 Temperature - 0.019 Salinity - 0.29 pH$

61 For a 1% increase in the concentration of Hg_T , the concentration of MeHg is expected to
62 increase 0.28%

63
64 For a 1-degree C increase in temperature, the concentration of MeHg is expected to
65 increase by a factor of 0.026 pM.

66
67 For a 1 unit increase in the practical salinity scale for surface water, the concentration of
68 MeHg is expected to decrease by a factor of 0.019 pM.

69
70 For a 1 log unit increase in pH, the concentration of MeHg is expected to decrease by a
71 factor of 0.29 pM.

72
73 Compared to the sites in the northern reach, MeHg levels in the southern and central

74 reaches are on average higher by a factor of $2.1 = 10^{(1.3)}/10^{(1.3-0.32)}$
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76 (10) LIS: $\text{Log}_{10} \text{MeHg} = -0.27 - 0.21 \text{ CT River (coded 0, 1)} - 0.91 \text{ East LIS (coded 0, 1)}$

77 Using the indicator variables for the CT River and east LIS, the regression equation may
78 be re-written:

79
80 West LIS: $\text{Log}_{10} \text{MeHg} = -0.27$

81 CT River: $\text{Log}_{10} \text{MeHg} = -0.27 - 0.21$

82 East LIS: $\text{Log}_{10} \text{MeHg} = -0.27 - 0.91$

83 Compared to sites in the CT. River, the concentration of MeHg in western LIS is on
84 average 1.6 times higher ($1.6 = 10^{(-0.27)}/10^{(-0.27-0.21)}$).

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86 Compared to sites in eastern LIS, the concentration of MeHg in western LIS is on
87 average 8.1 times higher ($8.1 = 10^{(-0.27)}/10^{(-0.27-0.91)}$).

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90 (11) South Florida: $\text{Log}_{10} \text{MeH} = -1.0 + 0.84 \text{ Log}_{10} \text{Hg}_T$

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92 For a 1% increase in the concentration of Hg_T , the concentration of MeHg is expected to
93 increase 0.84%.

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95 Table S1. Bayesian information criterion (BIC) values and coefficients of determination (r^2) for
 96 multiple regression models for unfiltered surface water relating the concentration of Log_{10} MeHg
 97 to the concentration of Log_{10} Hg_T and other site specific variables. For all four sites, the best-fit
 98 model (lowest BIC) is listed first.

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100 (a) Mugu Lagoon regression results. Independent variables included log_{10} Hg_T , pH, temperature,
 101 tides (neap vs. spring), season (winter vs. spring), habitat (mudflats, creeks, salt marshes), and
 102 sites (coded 0=eastern and western arms, 1=central basin).

Mugu Lagoon: variables in the model	n	BIC	r^2
Log_{10} Hg_T , pH, Temp	26	29	0.58
Log_{10} Hg_T , pH, Temp, Season	26	31	0.61
Log_{10} Hg_T , pH, Temp, Season, Tides	26	32	0.64
Log_{10} Hg_T , pH, Temp, Season, Tides, Habitat	26	37	0.65
Log_{10} Hg_T , pH, Temp, Season, Tides, Habitat, Sites	26	40	0.66
Log_{10} Hg_T , pH, Temp, Season, Tides, Habitat, Sites, Salinity	25	43	0.65
pH, Temp	27	35	0.42
Log_{10} Hg_T	28	39	0.30
Temp	29	43	0.20
pH	27	44	0.09
Salinity	28	48	0.00
Intercept (null model)	29	46	0.00

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110 (b) San Francisco Bay estuary regression results. Independent variables included \log_{10} Hg_T,
 111 temperature, pH, season and sites (coded 0 for southern and central reaches (sites 1-16) and 1 for
 112 northern reaches (sites 17-26)).

San Francisco Bay: variables in the model	n	BIC	r²
Log ₁₀ Hg _T , Temp, Salinity, Sites, pH	92	21	0.65
Log ₁₀ Hg _T , Temp, Salinity, Sites, pH, Season	92	25	0.65
Log ₁₀ Hg _T , Temp, Salinity	92	43	0.50
Log ₁₀ Hg _T , Temp	95	70	0.32
Log ₁₀ Hg _T , Sites	95	74	0.29
Salinity	92	64	0.31
Log ₁₀ Hg _T	95	70	0.28
pH	95	95	0.072
Temp	98	98	0.042
Sites	95	102	<0.001
Intercept (null model)	95	97	0.00

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 114 (c) Long Island Sound and Connecticut River regression results. Independent variables included
 115 \log_{10} Hg_T and sites (coded 0=West Long Island Sound, 1=CT River, 3=East Long Island Sound).

Variables in the model	n	BIC	r²
Sites	33	43	0.41
Log ₁₀ Hg _T , Sites	33	44	0.45
Log ₁₀ Hg _T	33	53	0.14
Intercept (null model)	33	53	0.00

116
 117 (d) South Florida regression results. Independent variables included \log_{10} Hg_T and sites (0=other
 118 sites, 1=sites in the Everglades Nutrient Removal project).

Variables in the model	n	BIC	r²
Log ₁₀ Hg _T	216	152	0.32
Log ₁₀ Hg _T , Sites	216	153	0.34
Sites	216	211	0.11
Intercept (null model)	216	232	0.00

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120 Table S2. Regression results including the estimate of the slope (β), the standard error of the
 121 slope (se), the t-value, and the 95% probability the slope is significantly different from 0.

122 (a) Mugu Lagoon

Mugu Lagoon Aqueous Model				
	Estimate	SE	t-value	p-value
Intercept	1.7	1.2	1.4	0.18
Log₁₀ Hg_T	0.38	0.14	2.8	0.011
pH	-0.48	0.16	-3.0	0.0069
Temp	0.072	0.026	2.8	0.010

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125 b) San Francisco Bay estuary

	Estimate	SE	t-value	p-value
Intercept	1.3	0.72	1.8	0.083
Log₁₀ Hg_T	0.28	0.052	5.3	0.00
Temperature	0.026	0.0059	4.1	0.00
Salinity	-0.019	0.0028	-6.8	0.00
Sites¹	-0.32	0.059	-5.4	0.00
pH	-0.29	0.092	-3.1	0.00

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¹ Sites is coded 0 for southern and central reaches (sites 1-16) and 1 for northern reaches (sites 17-26).

129 (c) Long Island Sound and CT. River

	Estimate	SE	t-value	p-value
Intercept	-2.7	0.095	-2.8.	0.01
Site=CT River	-2.1	0.15	-1.4	0.19
Site=East LIS	-0.91	0.20	-4.6	0.00

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131 (d) South Florida

	Estimate	SE	t-value	p-value
Intercept	-1.0	0.069	-15	0.00
Log₁₀ Hg_T	0.84	0.083	10.	0.00

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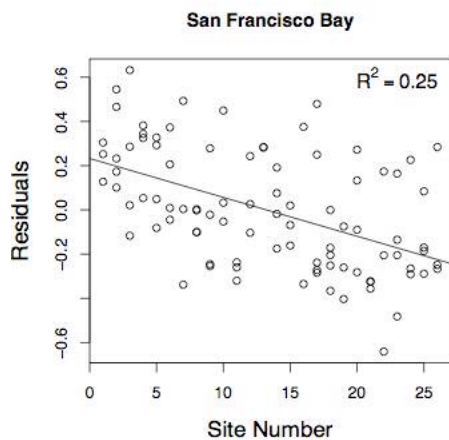
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137 Table S3. Hg_T concentration (pM) in precipitation from the Mercury Deposition Network (51).
 138 Precipitation data for CA94 were collected between May 2006 and April 2007, data for CA72
 139 were collected between December 2005 and December 2006, and data for FL34 and NY68 were
 140 collected between April 2005 and April 2006.

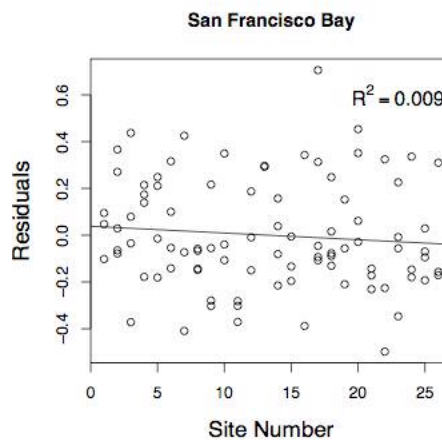
Site	MDN Site	MDN Location	n	Median Hg _T (pM)	Hg _T Range (pM)
Mugu Lagoon ¹	CA94	San Bernardino, CA.	18	50.43	14.50-240.0
San Francisco ¹	CA72	San Jose, CA.	23	47.45	17.50-109.9
South Florida	FL34	Everglades Nutrient Removal area	44	59.48	13.15-168.5
Long Island Sound ¹	NY68	Biscuit Brook, NY	46	29.18	6.400-112.6

141 ¹ Mercury deposition site CA94 is ~200 km east from Mugu Lagoon, while CA72 is ~80 km south from San
 142 Francisco Bay. NY99 in Orange County, NY, is closest to LIS (~ 100 km), but data are not yet available for this
 143 recently added site. NY68 in Biscuit Brook, NY is ~ 150 km west from Long Island Sound.
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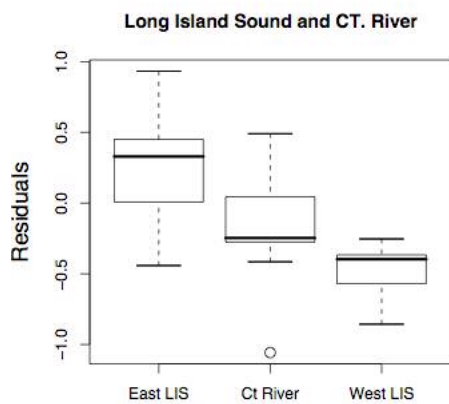
169 a.



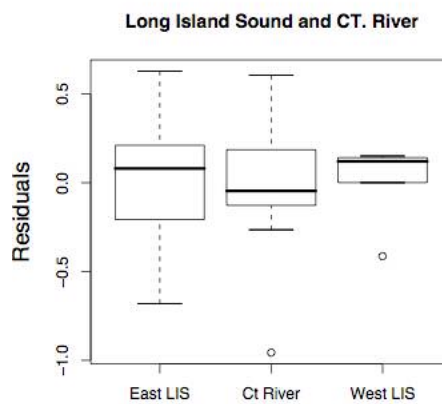
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171 c.



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173 Figure S1. Residuals for San Francisco Bay and Long Island Sound. Intra-site spatial variability
174 explained a significant portion of MeHg variability in both San Francisco Bay and Long Island
175 Sound. Residuals for the regression model should appear uncorrelated, i.e. $r^2=0.00$. In San
176 Francisco (Figure S1a) higher residuals were observed in the southern reach (site numbers 1-16),
177 where the regression model under-predicted, compared to the northern reach (site numbers 17-
178 26). For Long Island Sound, the regression model over-predicted for sites in east Long Island
179 Site, where dilution was highest (Figure S1c). For both sites, an indicator variable was added as
180 a predictor to the regression model to capture spatial variability. Residuals from the new
181 regression models (Figures S1b, S1d) appear less correlated.