Electronic Supplementary Material

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Mercury flux to sediments of Lake Tahoe, California-Nevada

Pages 1-9

Contents

Table ESM1 – total Hg in certified reference materials – p. 2

Figure ESM1 – Ti in sediment cores from Lake Tahoe – p. 3

Figure ESM2 – organic content in sediment cores from Lake Tahoe – p. 4

Figure ESM3 – ^{137}Cs in sediment cores from Lake Tahoe – p. 5

Evasion modeling – p. 6

Analysis of washout curves from seven sites in California and Nevada – p. 9

Table ESM1 Total mercury (Hg_T) measured via thermal combustion in reference materials NIST 1515, NIST 1645, and NRC BCSS-1. Certified values are shown in parentheses.

	Hg_T concentration (µg/g dry wt)		
Date	NIST 1515 (0.044 ± 0.004)	NIST 1645 (1.100 ± 0.500)	NRC BCSS-1 (0.130)
02 Oct 2007	0.041	1.003	0.134
02 Oct 2007	0.042	1.013	0.129
02 Oct 2007	0.041	1.064	0.127
03 Oct 2007	0.042	1.062	0.131
03 Oct 2007	0.040	0.973	0.131
03 Oct 2007	0.041	0.967	0.128
05 Oct 2007	0.042	1.008	0.135
05 Oct 2007	0.041	1.119	0.133
05 Oct 2007	0.042	1.021	0.135
09 Oct 2007	0.041	1.012	0.130
09 Oct 2007	0.041	0.998	0.132
11 Oct 2007	0.042	1.109	0.132

Fig. ESM1 Titanium (Ti) in Lake Tahoe sediment cores TAH-1 (black circles, black line) and TAH-2 (grey circles, grey line). Analyses were performed by ICP-MS and included two procedural replicates of NRC MESS-3 certified reference material (certified value for Ti of 0.44 ± 0.06 % dry wt). Results of the procedural replicates were 0.44 and 0.51 % dry wt.

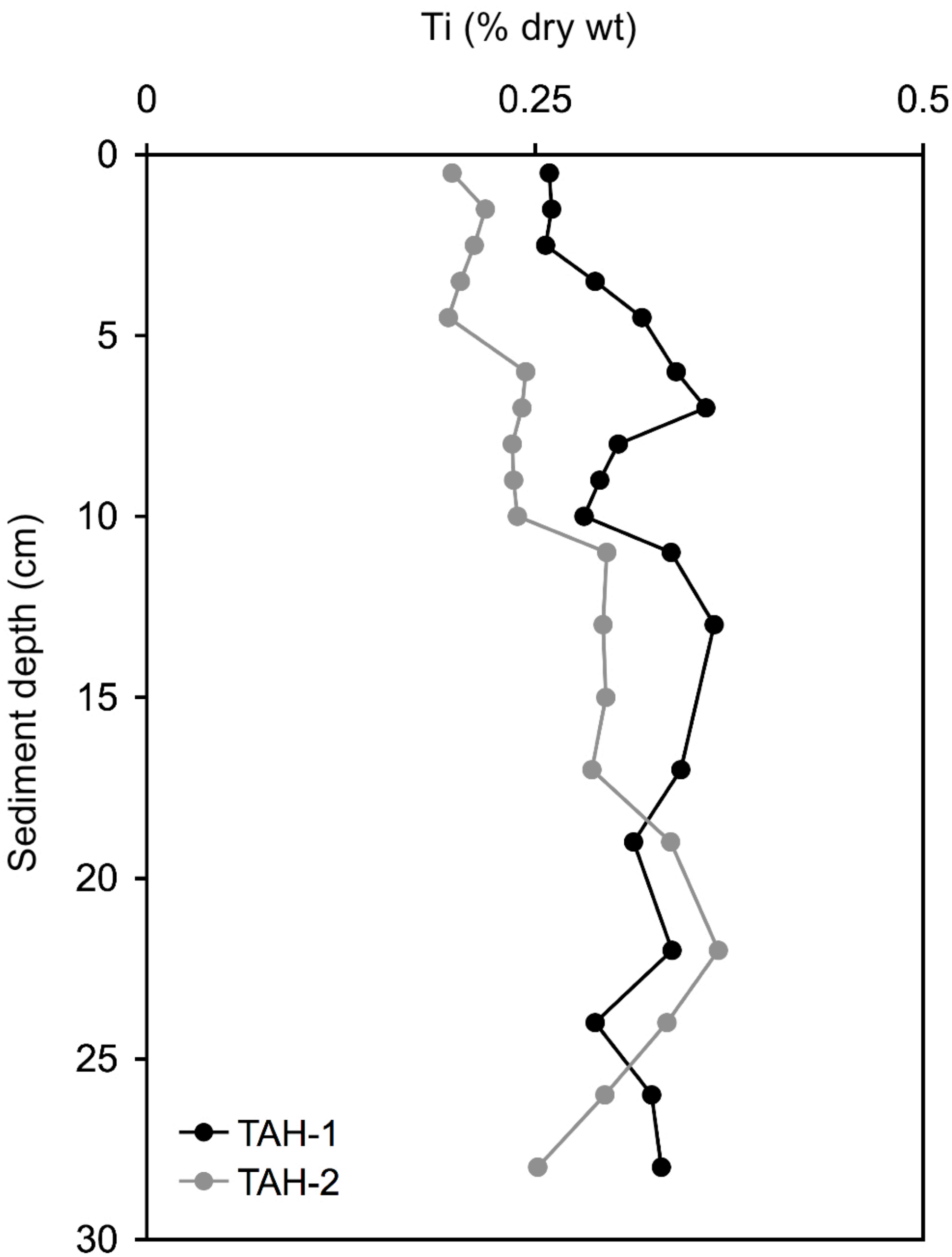


Fig. ESM2 Organic content (as loss on ignition) in Lake Tahoe sediment cores TAH-1 (black circles, black line) and TAH-2 (grey circles, grey line).

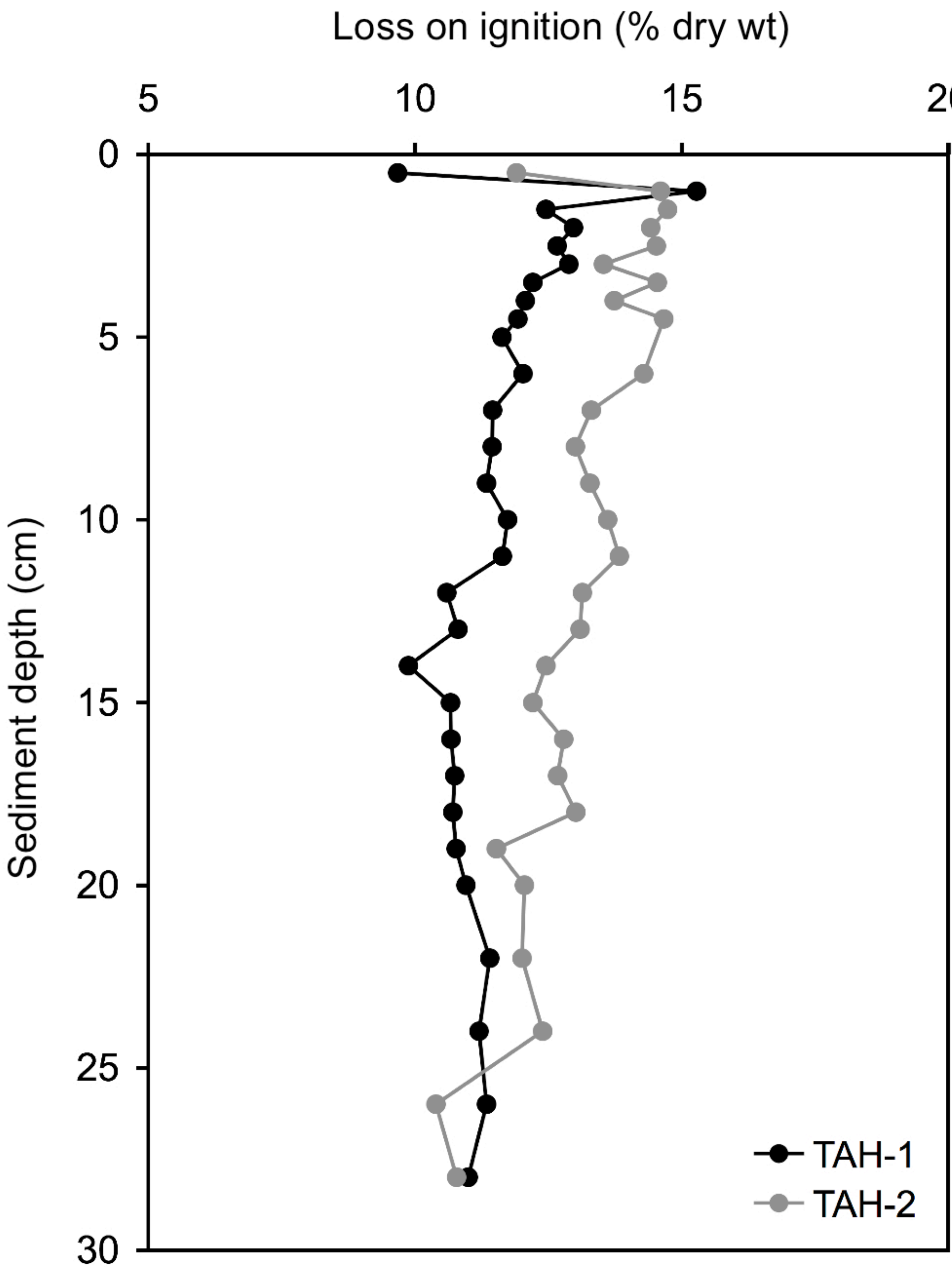
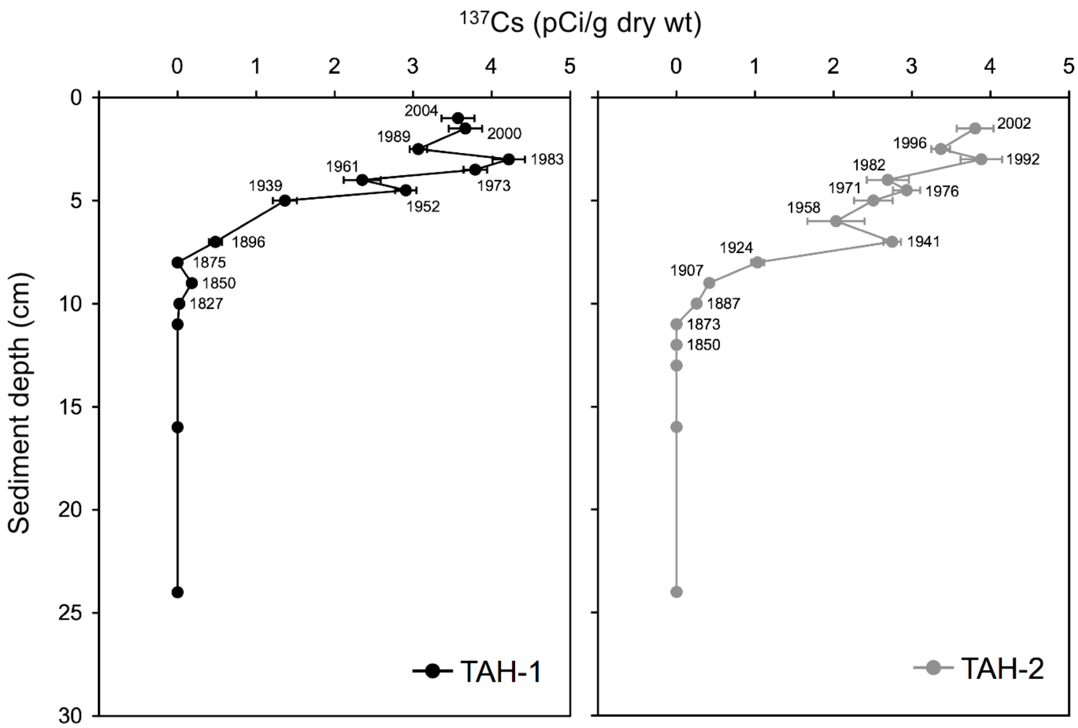


Fig. ESM3 ^{137}Cs in Lake Tahoe sediment cores TAH-1 (black circles, black line) and TAH-2 (grey circles, grey line); error bars represent 1 SD. The profiles show significant upward and downward movement from initial (1952) and maximum (1963) fallout of ^{137}Cs from nuclear weapons testing; numbers next to data points are age (yr) estimates from ^{210}Pb modeling.



Evasion modeling

Assuming that the only significant input (*In*) of Hg to the lake is atmospheric and the sinks are evasion, sedimentation and the Truckee River, we can establish a mass balance equation (Eq. 1):

$$In = v[Hg] + s[Hg] + r[Hg]$$

where the fluxes are assumed to be first-order, and the rate constants for evasion, sedimentation, and river flux are represented by v, s, and r, respectively. Assuming that the net production of Hg^0 is equal to the evasion rate (steady-state), the term $v[Hg]$ can be replaced by the integrated net production rate over the water column. As this production appears to be largely light-driven, the integrated value can be taken to follow the light extinction equation as follows (Eq. 2):

$$P_t = \int_0^\infty P_o e^{-K_a z} dz = \frac{P_o}{K_a} = \frac{p[Hg]}{K_a}$$

where P_t is the total integrated production, P_o is the production rate at the surface, K_a is the extinction coefficient for the wavelengths of light (UVB) that are responsible for the reduction reaction, and z is the depth in the lake. Such a treatment is possible because the vertical mixed layer in the lake extends below the depth of light penetration, which implies that all the Hg^0 generated within the sunlit region of the lake will be available for evasion. Recasting this equation in first-order terms allows a connection between a specific production rate constant (p) that has likely not changed over time, the light attenuation coefficient (K_a) which has changed, and the overall evasion of Hg from the lake. Substituting this result for $v[Hg]$, and solving for $[Hg]$ yields (Eq. 3):

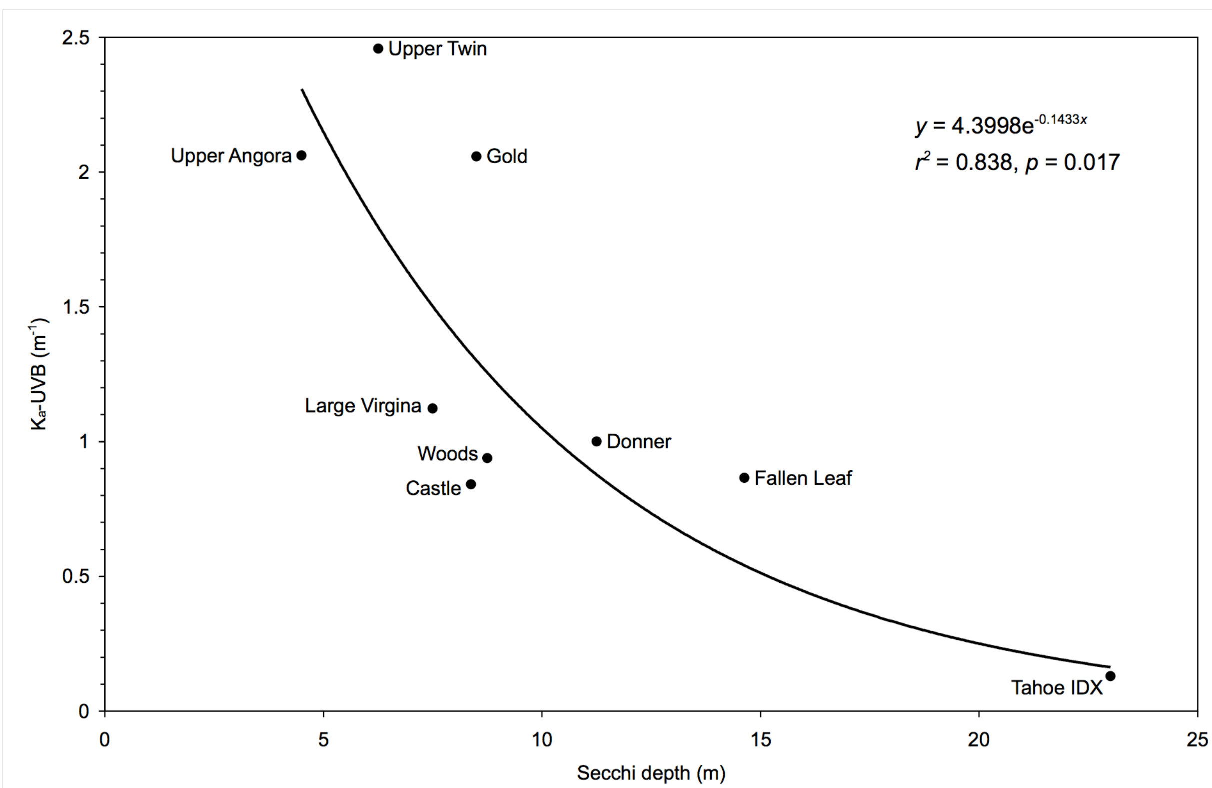
$$[Hg] = \frac{In}{\frac{p}{K_a} + s + r}$$

We may further simplify the equation above by assuming the loss through the Truckee River is not a large term in the mass balance (i.e., $r = 0$), due to the very long residence time of water in the lake. The ratio of the current to past Hg concentrations in the lake can therefore be estimated by the following (Eq. 4):

$$\frac{[Hg]_{now}}{[Hg]_{past}} = \frac{In_{now}}{In_{past}} \frac{\left(\frac{p}{K_a} + s\right)_{past}}{\left(\frac{p}{K_a} + s\right)_{now}}$$

We do not know the current rate of evasion from Lake Tahoe with certainty, but it can be estimated by setting the production rate constant (p) = 0.01 (Rolfhus et al. 2003, *Journal of Geophysical Research,* Vol. 108, No. C11, 3353, doi:10.1029/2001JC001297), $[Hg]$ = 1 ng/L (Gustin et al. 2005, *Science of the Total Environment,* Vol. 347, 282-294), and $K_a = 4.3998e^{-0.1433secchi}$, with the mean secchi depth in 2007 of 21.4 m (<http://terc.ucdavis.edu/research/clarity.html>; accessed 14 August 2008). The negative exponential relationship between secchi depth and K_a for UVB (units of m^{-1}) was derived empirically from nine lakes, including Lake Tahoe in the Sierra Nevada and Cascade Mountains (see Fig. ESM3 below). Plugging p, $[Hg]$, and K_a into Eq. 2, we estimate a current evasion rate of 18 μg/m^2/yr. This flux is approximately the same as the contemporary sedimentation rate of 15-20 μg/m^2/yr. Therefore, currently $p/K_a = s$ and $(p/K_a + s)_{\mathrm{now}} = 2s$. Furthermore, as the value of K_a has increased since the preindustrial past by approximately a factor of 7 (clarity and light penetration have dropped), we find from our arguments presented above that $(p/K_a + s)_{\mathrm{past}} = 8s$. This suggests that concentrations in the lake are currently 4x higher today than they would have been had no change in lake clarity occurred. Using this information to solve Eq. 4 for In_{past} results in an estimate of 16 μg/m^2/yr, and since the preindustrial sedimentation rate is 2 μg/m^2/yr, we can also estimate a preindustrial evasional flux of 14 μg/m^2/yr. Thus, in comparison to the current situation where an estimated 50% of Hg inputs are lost to evasion, the evasional flux in the past may have been as much as 87.5% of inputs. While this model (1) is clearly a simplification of the system, (2) ignores changes in *s* as a result of eutrophication, and (3) is predicated on evasion rate estimates from other lakes, it demonstrates how changes in light penetration may have had a dramatic effect on the biogeochemical balance of Hg within the system, resulting in enhanced accumulation of Hg within the lake, and potentially within the lake's foodweb above that of the regional/global signal.

Fig. ESM4 Data from eight lakes in the Sierra Nevada Mountains and one lake in the Cascade Mountains (Castle) used to derive K_a-UVB from secchi depth for evasion modeling.



Analysis of washout curves from seven sites in California and Nevada

Washout is defined here as the removal of gases or particles from the atmosphere by scavenging onto precipitation. The washout coefficient (*a*) is derived from an inverse power regression of Hg wet deposition data, where precipitation amount (*P*) is the independent variable and its measured Hg concentration (*C*) is the dependent variable; $C = a \bullet P^{-1}$. The data used are from sites in California and Nevada monitored for Hg wet deposition by the Mercury Deposition Network (<http://nadp.sws.uiuc.edu/mdn/>; accessed 04 August 2008) and Steding and Flegal (2002, *Journal of Geophysical Research,* Vol. 107, No. D24, 4764, doi:10.1029/2002JD002081). Extreme values were identified via Grubbs' test and removed from datasets before analysis, which was performed with Sigma Plot (Systat Software, San Jose, CA). A summary of site information and analysis results is given below.

Site[a]	Latitude, longitude	Elevation (m asl)	*n*	Washout coefficent (*a*)	Asymptote (*Y0*)
Moffet Field/CA72[b]	37.4276, -122.0624	1	171	5.38	1.08
Long Marine Lab	36.9478, -122.0639	5	16	0.0554	6.62
CA20	41.5588, -124.0916	110	30	0.838	4.71
CA97	39.8237, -123.2382	418	58	29.1	4.61
NV98	39.5111, -119.7186	1340	14	7.65	15.4
CA94	34.1938, -116.9131	1724	22	7.86	13.7
CA75	36.5661, -118.7776	1902	94	12.7	8.88

[a]For reference, Lake Tahoe has an elevation of 1900 m asl and latitude and longitude of 39.10 and -120.05, respectively.
[b]This site is an outlier because of close proximity to point sources of atmospheric Hg pollution and was removed from the linear regression analysis (see text).