Supporting Information

to

Dissolved organic matter enhances microbial mercury methylation under sulfidic conditions

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Table S1. Thermodynamic data for equilibrium speciation modeling.

Reaction	log K	Reference
Hg-S Aqueous Speciation		
$Hg^{2+} + 2HS^- = Hg(SH)_2^0$	37.7	Benoit *et al.*[1]
$Hg^{2+} + 2HS^- = HgS_2H^- + H^+$	31.5	Benoit *et al.*[1]
$Hg^{2+} + 2HS^- = HgS_2^{2-} + 2H^+$	23.5	Benoit *et al.*[1]
$Hg^{2+} + HS^- = HgSH^+$	30.2	Benoit *et al.*[1]
Metacinnabar Precipitation		
$Hg^{2+} + HS^- = HgS(s) + H^+$	38±2	NIST Critical Database[2]
Hg-DOM Complexation		
$Hg^{2+} + 2RS^- = Hg(SR)_2$	42.0	Skyllberg[3]
$RS^- + H^+ = RSH$	10.0	Skyllberg[3]
Hg-CYS Complexation		
$Hg^{2+} + CYS^{2-} = HgCYS^0$	38.5	Basinger *et al.*[4]
$Hg^{2+} + 2H^+ + 2CYS^{2-} = Hg(HCYS)_2^0$	39.8	Basinger *et al.*[4]
$Hg^{2+} + 2CYS^{2-} = Hg(CYS)_2^{2-}$	45.3	Basinger *et al.*[4]

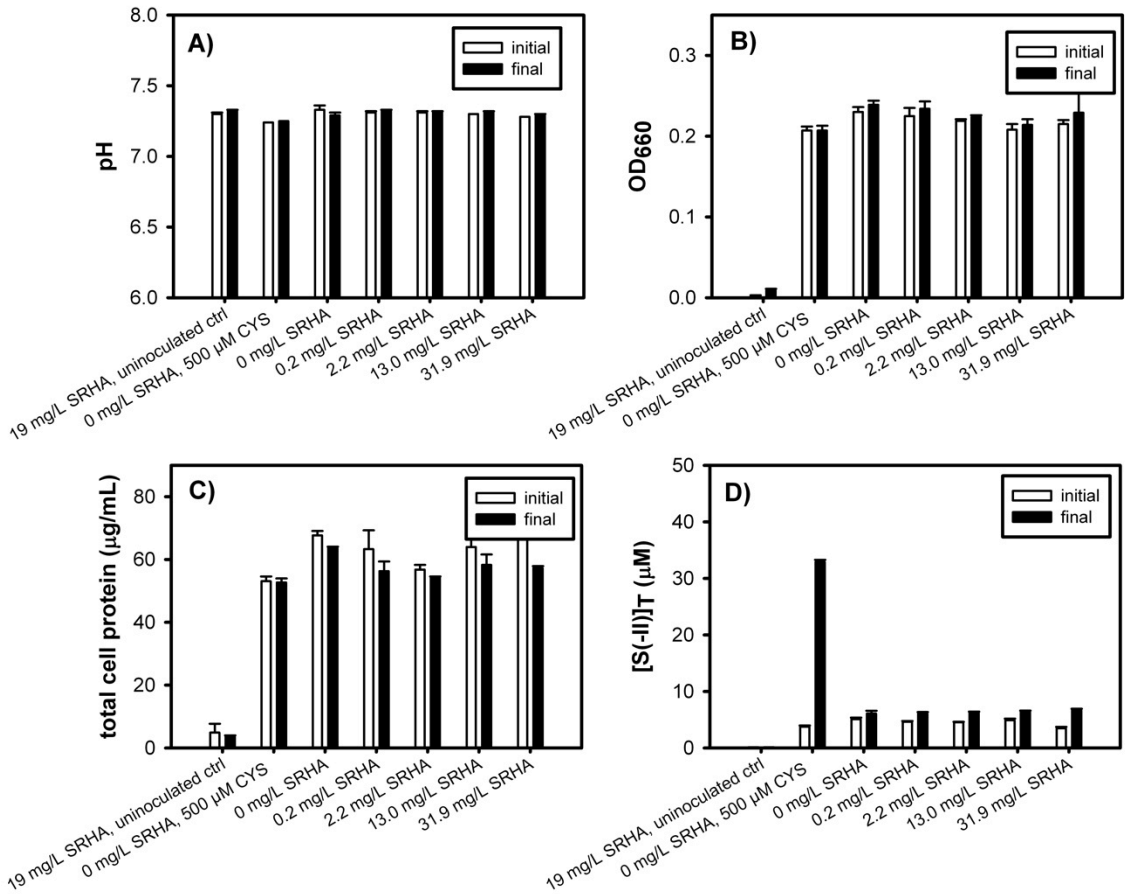

Figure S1. Initial and final **a)** pH, **b)** optical density, **c)** total cell protein, and **d)** sulfide in washed cell Hg-methylation assays of *D. desulfuricans* ND132 in the presence of Suwannee River humic acid (SRHA) or L-cysteine (CYS). Washed cells were incubated with 5.0 nM $^{201}HgCl_2$ for 3 hours at 31 °C. Initial measurements were taken at the beginning of the incubation, and final measurements after the 3 h incubation period. Error bars are standard deviations of triplicate methylation assays. These data correspond to the THg and MeHg data shown in Figure 1 in the main text.

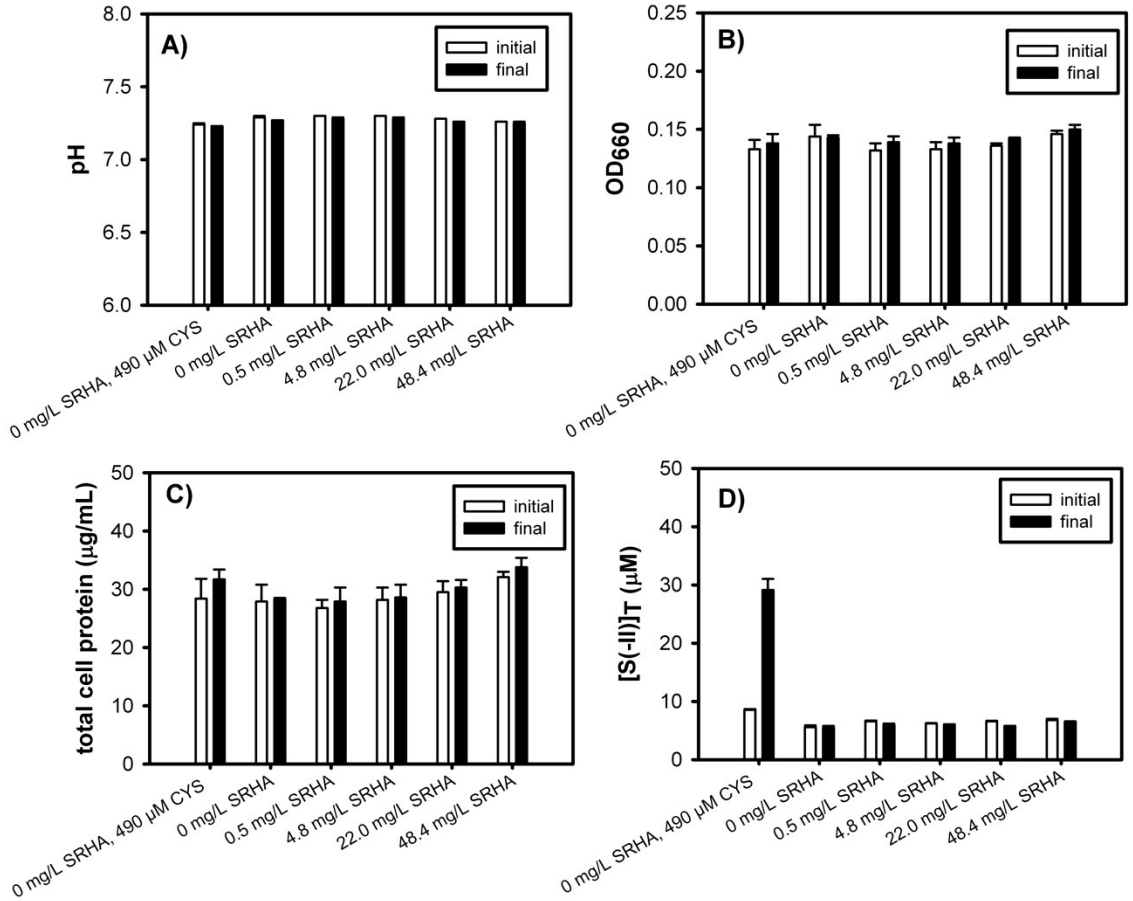

Figure S2. Initial and final **a)** pH, **b)** optical density, **c)** total cell protein, and **d)** sulfide in washed cell Hg-methylation assays of *D. desulfuricans* ND132 in the presence of Suwannee River humic acid (SRHA) or L-cysteine (CYS). Washed cells were incubated with 0.5 nM $^{201}HgCl_2$ for 3 hours at 31 °C. Initial measurements were taken at the beginning of the incubation, and final measurements after the 3 h incubation period. Error bars are standard deviations of triplicate methylation assays. These data correspond to the MeHg and THg data shown in Figure 1 in the main text.

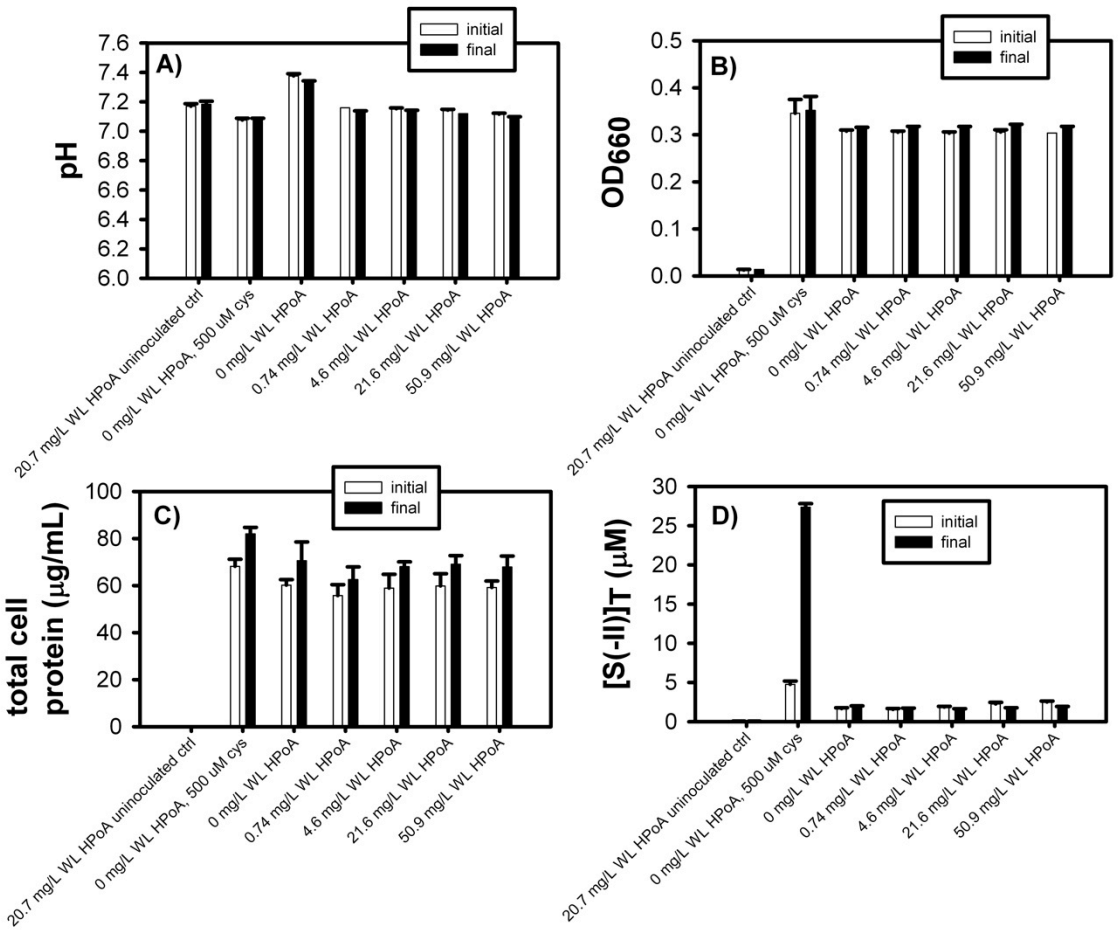

Figure S3. Initial and final **a)** pH, **b)** optical density, **c)** total cell protein, and **d)** sulfide in washed cell Hg-methylation assays of *D. desulfuricans* ND132 in the presence of Williams Lake hydrophobic acid (WLHPoA) or L-cysteine (CYS). Washed cells were incubated with 0.5 nM $^{201}HgCl_2$ for 3 hours at 31 °C. Initial measurements were taken at the beginning of the incubation, and final measurements after the 3 h incubation period. Error bars are standard deviations of triplicate methylation assays. These data correspond to the MeHg and THg data shown in Figure 2.

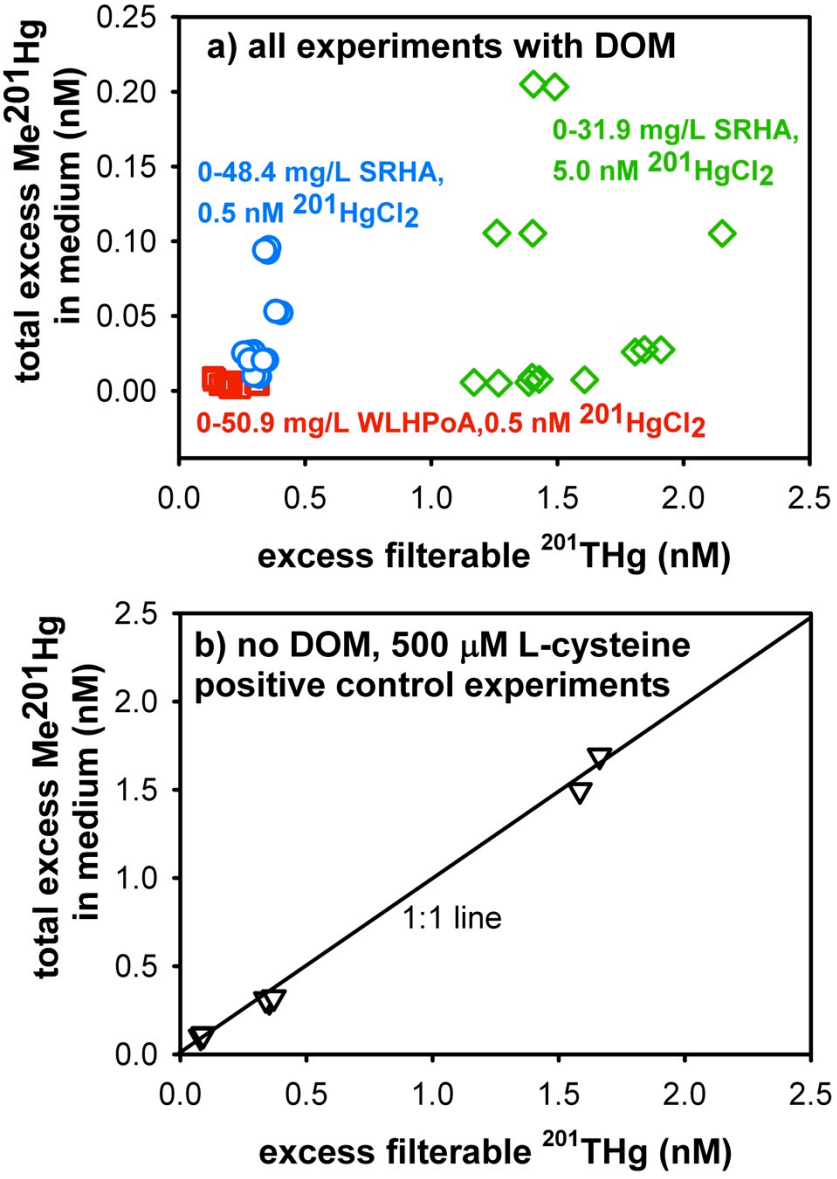

Figure S4. Relationship between filterable total Hg (THg) and total methylmercury (MeHg) production in washed cell assays with (**a**) dissolved organic matter or (**b**) or L-cysteine. SRHA = Suwannee River humic acid. WLHPoA = Williams Lake hydrophobic acid. Filterable ^{201}THg and total MeHg production were not strongly correlated in experiments with DOM isolates (r^2 = 0.15, p = 0.011). For experiments with L-cysteine addition, total MeHg production was strongly correlated with filterable THg (r^2>0.99, p < 10^{-7}).

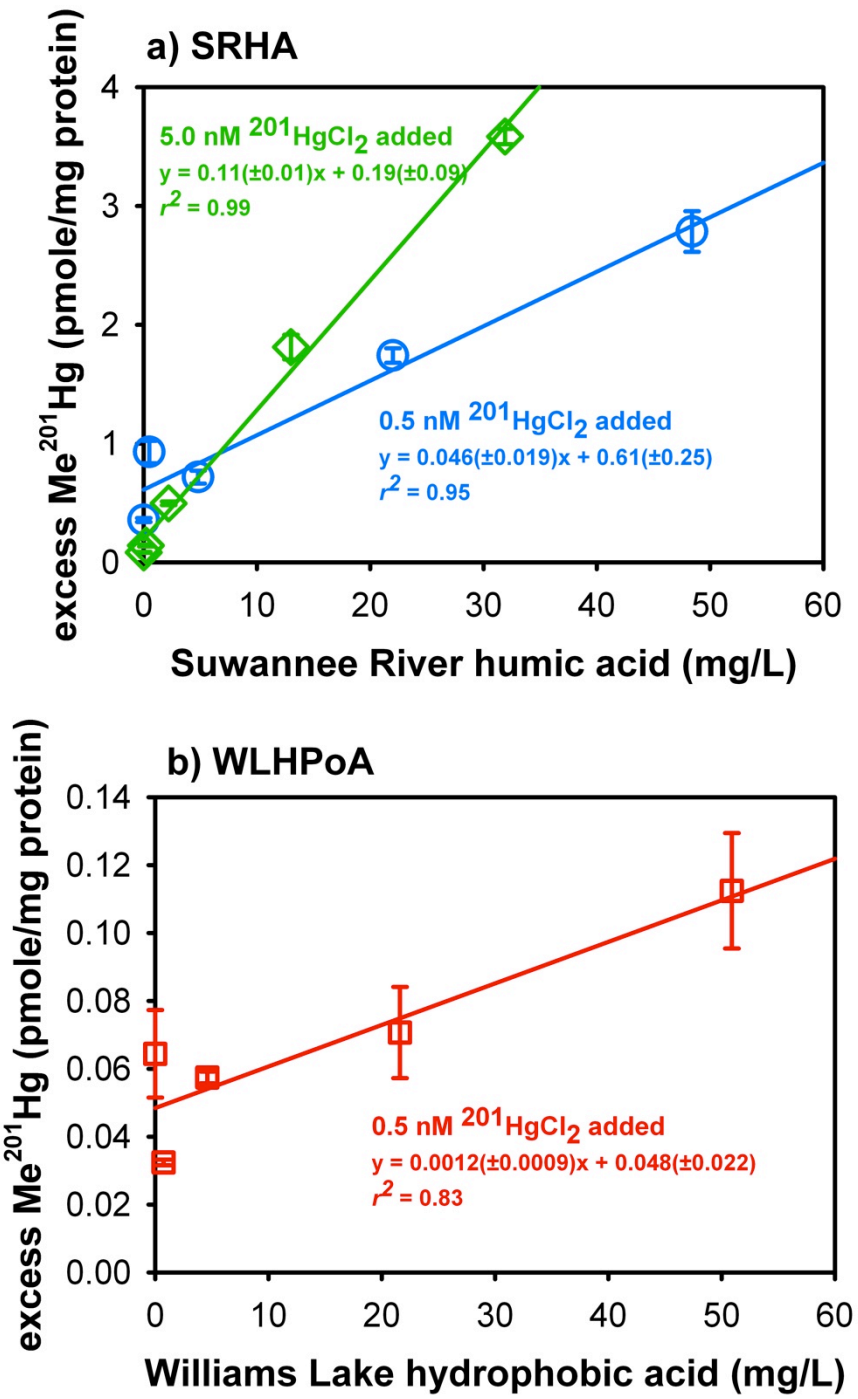

Figure S5. Methylmercury production is linearly dependent upon dissolved organic matter concentration in experiments with either (**a**) Suwannee River humic acid (SRHA) or (**b**) Williams Lake hydrophobic acid (WLHPoA).

References

(1) Benoit, J.; Gilmour, C.; Mason, R.; Heyes, A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* **1999**, *33*, 951-957.

(2) National Institute of Standards and Technology. NIST Critically Selected Stability Constants of Metal Complexes.

(3) Skyllberg, U. Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. *J. Geophys. Res.-Biogeo.* **2008**, *113*, G00C03.

(4) Basinger, M. A.; Casas, J.; Jones, M. M.; Weaver, A. D. Structural Requirements for Hg(II) Antidotes. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1419-1425.