Supporting Information Table 1. Data set used for FITEQL mercury-polysulfide model.

	Data set	pH	Sulfide (M)	Soluble Hg (M)
1	P & H	7.83	1.017e-2	1.63e-7
2	P & H	7.83	1.017e-2	1.77e-7
3	P & H	9.04	1.089e-2	1.58e-5
4	P & H	8.25	1.81e-3	4.77e-8
5	P & H	8.53	1.92e-3	8.24e-7
6	P & H	9.40	6.06e-3	9.70e-7
7	P & H	9.40	6.06e-3	1.32e-6
8	P & H	7.03	7.24e-3	5.71e-7
9	P & H	9.20	5.92e-3	6.23e-6
10	P & H	8.19	4.07e-3	1.29e-6
11	P & H	6.66	3.78e-3	4.01e-8
12	P & H	6.75	4.89e-3	6.63e-7
13	P & H	6.64	7.29e-3	6.60e-7
14	P & H	7.43	3.12e-3	5.34e-8
15	P & H	6.58	6.41e-3	1.94e-7
16	P & H	6.33	1.35e-2	6.56e-8
17	P & H	7.20	2.30e-2	1.69e-6
18	Jay et al.	8.0	4.89e-5	1.71e-8
19	Jay et al.	8.0	5.26e-5	1.09e-8
20	Jay et al.	8.0	6.70e-5	1.39e-8
21	Jay et al.	7.0	2.25e-6	5.40e-9
22	Jay et al.	8.0	3.59e-4	7.21e-8
23	Jay et al.	8.0	4.81e-3	1.56e-6
24	Jay et al.	9.0	3.22e-3	4.37e-6
25	Jay et al.	8.0	6.25e-5	1.52e-8
26	Jay et al.	8.0	4.81e-3	2.59e-6
27	Jay et al.	9.0	8.36e-5	1.80e-7
28	Jay et al.	9.0	8.36e-5	1.81e-7
29	Jay et al.	9.0	3.47e-4	4.19e-7
30	Jay et al.	9.0	3.22e-3	6.24e-6
31	Jay et al.	10.0	7.53e-5	4.65e-7
32	Jay et al.	10.0	1.30e-4	7.56e-7
33	Jay et al.	10.0	1.96e-4	1.66e-6
34	Jay et al.	10.0	1.63e-3	9.04e-6
35	Jay et al.	7.0	2.52e-3	4.34e-8
36	Jay et al.	7.0	3.80e-3	4.96e-8

Supporting Information Table 2. Tableau for FITEQL model of mercury speciation in the presence of polysulfides.

Species	Log Equil. Const.	HS^-	HgS	S(0)	H^+
H^+	0	0	0	0	1
OH^-	-13.8	0	0	0	-1
H_2S	6.88	1	0	0	1
HS^-	0	1	0	0	0
S^{2-}	-17.0	1	0	0	-1
S_3^{2-}	-12.2	1	0	2	-1
S_4^{2-}	-9.22	1	0	3	-1
S_5^{2-}	-9.11	1	0	4	-1
S_6^{2-}	-9.32	1	0	5	-1
HS_4^-	-2.52	1	0	3	0
HS_5^-	-3.31	1	0	4	1
$HgS^0_{(aq)}$	-9.3	0	1	0	0
Hg^{2+}	-36.8	-1	1	0	1
$Hg(SH)_2$	1.0	1	1	0	1
$HgHS_2^-$	-4.5	1	1	0	0
HgS_2^{2-}	-13.0	1	1	0	-1
$HgSH^+$	-16.8	0	1	0	1
$Hg(S_5)S^{2-}$	optimized	1	1	4	-1
$Hg(S_5)_2^{2-}$	optimized	1	1	8	-1
HgS_5OH^-	optimized	0	1	4	-1
HgS_5	optimized	0	1	4	0
HgS_5HS^-	optimized	1	1	4	0

Supporting Information. Discussion of K_{ow} for HgS_5

We used the fragment method to estimate K_{ow} for uncharged species from various starting points, using the measured values of 25 for the Kow's of both $HgS^0_{(aq)}$ and $Hg(SH)_2$. It is unclear if the structure of $HgS^0_{(aq)}$ is HgS or HgSHOH; therefore, we have performed this exercise with both structures as starting points. Using the structure HgS as the true structure results in $HgS^0_{(aq)}$ and $Hg(SH)_2$ each predicting the other within a factor of approximately ten, while using HgSHOH results in an estimation of the K_{ow} for $Hg(SH)_2$ that is 400 times higher than the measured value. Further, the estimated formation constant for HgSHOH from Dyssen is much lower than that used in the model by Benoit et al. Therefore to obtain a range in the K_{ow} for HgS_5 we will use both of the measured starting points, assuming a structure of HgS for $HgS^0_{(aq)}$. This results in an order of magnitude range in our estimate of the concentration of HgS_5.

Supporting Information Table 3. Effect of structure of starting point on K_{ow}.

Starting pt. for fragment calc	Calculated K_{ow} for $HgS^0_{(aq)}$	Calculated K_{ow} for HgSHOH	Calculated K_{ow} for $Hg(SH)_2$	Calculated K_{ow} for HgS_5	Estimated conc. of HgS_5 (pM)
K_{ow} for $HgS^0_{(aq)}$ = 25	25	0.6	257	11,000	10
K_{ow} for HgSHOH =25	1,000	25	9,800	400,000	0.3
K_{ow} for $Hg(SH)_2$ =25	2.5	0.06	25	900	113

Sample calculation for calculating K_{ow} for HgS_5:

Starting point of HgS structure of $HgS^0_{(aq)}$.

Log K_{ow} for $HgS^0_{(aq)}$	1.4
Add 4 -S- fragments	+ 3.16
Factor for 2 single bonds	+(2-1)(-0.12)
Factor for 2 double bonds	+(2-1)(-0.38)
Log K_{ow} for HgS_5	4.06
K_{ow} for HgS_5	11,482

Supporting Information Table 4. Calculations for Estimating [HgS_5] from Dow.

$S(-II)_T$ (M)	D_{ow} (observed)	Contrib. to D_{ow} from $HgS^0_{(aq)}$ & $Hg(SH)_2$	$K_{ow}\chi_i$ for HgS_5	[HgS_5] when K_{ow} = 900 (pM)	[HgS_5] when K_{ow} = 11,000 (pM)
6.7×10^{-5}	4.5	0.39	4.1	146	12
3.6×10^{-4}	1.4 1.1	0.21 0.21	1.3 0.95	128 97	11 8
4.8×10^{-3}	0.12	0.02	0.10	113	9

(pH = 8 in all cases)

Supporting Information. Sensitivity analysis of model to HgS_xH^-