Add Hg Reactions from PHREEQC Database to PFLOTRAN Database

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Abstract

The Hg related reactions from PHREEQC database (phreeqc-scb.dat) are added into PFLOTRAN database (hanford.dat). We conduct speciation calculations with the cases in Dong et al. (2010) with PFLOTRAN and PHREEQC. The calculated results are in general agreement, indicating the consistency of the two databases and codes. Minor differences can be introduced when various activity calculation options are used in PFLOTRAN. For competition for ligands among metals such as Fe^{3+}, Cu^{2+}, as shown in Fig. 4 in Dong et al. (2010), differences in the complexation reactions for these metals between the two databases may introduce substantial differences in the calculation results.

1 Reactions

1.1 Aqueous Complexation Reactions

1.1.1 Hg^{2+} with Inorganic Species

$Hg^{2+} + H_2O \longleftrightarrow HgOH^+ + H^+$	$\log\_k = -3.397$	(1)
$Hg^{2+} + 2H_2O \longleftrightarrow Hg(OH)_2 + 2\,H^+$	$\log\_k = -5.98$	(2)
$Hg^{2+} + 3H_2O \longleftrightarrow Hg(OH)_3{}^- + 3\,H^+$	$\log\_k = -21.091$	(3)
$2\,Hg^{2+} + H_2O \longleftrightarrow Hg_2OH^{3+} + H^+$	$\log\_k = -3.297$	(4)
$3\,Hg^{2+} + 3\,H_2O \longleftrightarrow Hg_3(OH)_3{}^{3+} + 3\,H^+$	$\log\_k = -6.391$	(5)
$Hg^{2+} + Br^- \longleftrightarrow HgBr^+$	$\log\_k = 9.61$	(6)
$Hg^{2+} + 2\,Br^- \longleftrightarrow HgBr_2$	$\log\_k = 18.08$	(7)
$Hg^{2+} + 3\,Br^- \longleftrightarrow HgBr_3{}^-$	$\log\_k = 20.51$	(8)
$Hg^{2+} + 4\,Br^- \longleftrightarrow HgBr_4{}^{2-}$	$\log\_k = 21.74$	(9)
$Hg^{2+} + Br^- + H_2O \longleftrightarrow HgOHBr + H^+$	$\log\_k = 6.24$	(10)
$Hg^{2+} + Br^- + I^- \longleftrightarrow HgBrI$	$\log\_k = 21.12$	(11)
$Hg^{2+} + Br^- + 3\,I^- \longleftrightarrow HgBrI_3{}^{2-}$	$\log\_k = 28.02$	(12)
$Hg^{2+} + 2\,Br^- + 2\,I^- \longleftrightarrow HgBr_2I_2{}^{2-}$	$\log\_k = 26.80$	(13)
$Hg^{2+} + Citrate^{3-} \longleftrightarrow HgCitrate^-$	$\log\_k = 12.19$	(14)
$Hg^{2+} + Cl^- \longleftrightarrow HgCl^+$	$\log\_k = 7.31$	(15)
$Hg^{2+} + 2\,Cl^- \longleftrightarrow HgCl_2$	$\log\_k = 14.00$	(16)
$Hg^{2+} + 3\,Cl^- \longleftrightarrow HgCl_3{}^-$	$\log\_k = 14.925$	(17)
$Hg^{2+} + 4\,Cl^- \longleftrightarrow HgCl_4{}^{2-}$	$\log\_k = 15.535$	(18)
$Hg^{2+} + Cl^- + I^- \longleftrightarrow HgClI$	$\log\_k = 19.158$	(19)
$Hg^{2+} + Cl^- + H_2O \longleftrightarrow HgOHCl + H^+$	$\log\_k = 4.25$	(20)
$Hg^{2+} + CO_3{}^{2-} \longleftrightarrow HgCO_3$	$\log\_k = 11.47$	(21)
$Hg^{2+} + 2CO_3{}^{2-} \longleftrightarrow Hg(CO_3)_2{}^{2-}$	$\log\_k = 15.042$	(22)
$Hg^{2+} + HCO_3{}^- \longleftrightarrow HgHCO_3{}^+$	$\log\_k = 15.805$	(23)
$Hg^{2+} + CO_3{}^{2-} + H_2O \longleftrightarrow HgOHCO_3{}^- + H^+$	$\log\_k = 5.33$	(24)
$Hg^{2+} + EDTA^{4-} \longleftrightarrow HgEDTA^{2-}$	$\log\_k = 23.22$	(25)
$Hg^{2+} + EDTA^{4-} + H^+ \longleftrightarrow HgHEDTA^-$	$\log\_k = 26.85$	(26)
$Hg^{2+} + EDTA^{4-} + 2\,H^+ \longleftrightarrow HgH_2EDTA$	$\log\_k = 29.15$	(27)
$Hg^{2+} + EDTA^{4-} + H_2O \longleftrightarrow HgOHEDTA^{3-} + H^+$	$\log\_k = 13.68$	(28)
$Hg^{2+} + F^- \longleftrightarrow HgF^+$	$\log\_k = 1.57$	(29)

$$Hg^{2+} + I^- \longleftrightarrow HgI^+ \qquad \log\_k = 13.41 \tag{30}$$
$$Hg^{2+} + 2\,I^- \longleftrightarrow HgI_2 \qquad \log\_k = 24.63 \tag{31}$$
$$Hg^{2+} + 3\,I^- \longleftrightarrow {HgI_3}^- \qquad \log\_k = 28.41 \tag{32}$$
$$Hg^{2+} + 4\,I^- \longleftrightarrow {HgI_4}^{2-} \qquad \log\_k = 30.34 \tag{33}$$
$$Hg^{2+} + I^- + H_2O \longleftrightarrow HgOHI + H^+ \qquad \log\_k = 9.41 \tag{34}$$
$$Hg^{2+} + {NH_4}^+ \longleftrightarrow {HgNH_3}^{2+} + H^+ \qquad \log\_k = -0.444 \tag{35}$$
$$Hg^{2+} + 2{NH_4}^+ \longleftrightarrow {Hg(NH_3)_2}^{2+} + 2\,H^+ \qquad \log\_k = -0.688 \tag{36}$$
$$Hg^{2+} + 3{NH_4}^+ \longleftrightarrow {Hg(NH_3)_3}^{2+} + 3\,H^+ \qquad \log\_k = -9.432 \tag{37}$$
$$Hg^{2+} + 4{NH_4}^+ \longleftrightarrow {Hg(NH_3)_4}^{2+} + 4\,H^+ \qquad \log\_k = -17.676 \tag{38}$$
$$Hg^{2+} + {NO_3}^- \longleftrightarrow {HgNO_3}^+ \qquad \log\_k = -0.43 \tag{39}$$
$$Hg^{2+} + 2{NO_3}^- \longleftrightarrow Hg(NO_3)_2 \qquad \log\_k = -0.81 \tag{40}$$
$$Hg^{2+} + {PO_4}^{3-} \longleftrightarrow {HgPO_4}^- \qquad \log\_k = 7.841 \tag{41}$$
$$Hg^{2+} + {PO_4}^{3-} + H^+ \longleftrightarrow HgHPO_4 \qquad \log\_k = 20.056 \tag{42}$$
$$Hg^{2+} + HS^- \longleftrightarrow HgS + H^+ \qquad \log\_k = 28.6 \tag{43}$$
$$Hg^{2+} + 2\,HS^- \longleftrightarrow {HgS_2}^{2-} + 2H^+ \qquad \log\_k = 24.73 \tag{44}$$
$$Hg^{2+} + 2\,HS^- \longleftrightarrow Hg(S_2)_2 \qquad \log\_k = 39.77 \tag{45}$$
$$Hg^{2+} + 2\,HS^- \longleftrightarrow {HgHS_2}^- + H^+ \qquad \log\_k = 39.77 \tag{46}$$
$$Hg^{2+} + HS^- \longleftrightarrow HgHS^+ \qquad \log\_k = 20.5 \tag{47}$$
$$Hg^{2+} + 5HS^- + 3H^+2O_2 \longleftrightarrow HgS_5 + 4H_2O \qquad \log\_k = 194.56 \tag{48}$$
$$Hg^{2+} + 10HS^- + 6H^+4O_2 \longleftrightarrow {Hg(S_5)_2}^{2-} + 8H_2O \qquad \log\_k = 352.0 \tag{49}$$
$$Hg^{2+} + 5HS^- + 2H^+2O_2 \longleftrightarrow HgS_5OH^- + 3H_2O \qquad \log\_k = 185.98 \tag{50}$$
$$Hg^{2+} + 2{S_2O_3}^{2-} \longleftrightarrow {Hg(S_2O_3)_2}^{2-} \qquad \log\_k = 29.48 \tag{51}$$
$$Hg^{2+} + 3{S_2O_3}^{2-} \longleftrightarrow {Hg(S_2O_3)_3}^{3-} \qquad \log\_k = 31.28 \tag{52}$$
$$Hg^{2+} + {SO_4}^{2-} \longleftrightarrow HgSO_4 \qquad \log\_k = 2.42 \tag{53}$$
$$Hg^{2+} + 2{SO_4}^{2-} \longleftrightarrow {Hg(SO_4)_2}^{2-} \qquad \log\_k = 3.48 \tag{54}$$

1.1.2 CH_4Hg^+ with Inorganic Species

$$CH_3Hg^+ + H_2O \longleftrightarrow CH_3HgOH + H^+ \qquad \log\_k = -4.557 \qquad (55)$$

$$2CH_3Hg^+ + H_2O \longleftrightarrow (CH_3Hg)_2OH^+ + H^+ \qquad \log\_k = -1.997 \qquad (56)$$

$$CH_3Hg^+ + {CO_3}^{2-} \longleftrightarrow CH_3HgCO_3^- \qquad \log\_k = 6.511 \qquad (57)$$

$$CH_3Hg^+ + {NH_4}^+ \longleftrightarrow CH_3HgNH_3^+ + H^+ \qquad \log\_k = -1.644 \qquad (58)$$

$$CH_3Hg^+{PO_4}^{3-} + H^+ \longleftrightarrow CH_3HgHPO_4^- \qquad \log\_k = 17.806 \qquad (59)$$

$$CH_3Hg^+ + {SO_4}^{2-} \longleftrightarrow CH_3HgSO_4^- \qquad \log\_k = 2.0 \qquad (60)$$

$$CH_3Hg^+ + HS^- \longleftrightarrow CH_3HgS^- + H^+ \qquad \log\_k = 7.0 \qquad (61)$$

$$2CH_3Hg^+ + HS^- \longleftrightarrow (CH_3Hg)_2S + H^+ \qquad \log\_k = 23.51 \qquad (62)$$

$$3CH_3Hg^+ + HS^- \longleftrightarrow (CH_3Hg)_3S^+ + H^+ \qquad \log\_k = 30.51 \qquad (63)$$

$$CH_3Hg^+ + F^- \longleftrightarrow CH_3HgF \qquad \log\_k = 1.71 \qquad (64)$$

$$CH_3Hg^+ + Cl^- \longleftrightarrow CH_3HgCl \qquad \log\_k = 5.39 \qquad (65)$$

$$CH_3Hg^+ + Br^- \longleftrightarrow CH_3HgBr \qquad \log\_k = 6.7 \qquad (66)$$

$$CH_3Hg^+ + I^- \longleftrightarrow CH_3HgI \qquad \log\_k = 8.71 \qquad (67)$$

$$CH_3Hg^+ + 2I^- \longleftrightarrow CH_3HgI_2^- \qquad \log\_k = 9.18 \qquad (68)$$

$$CH_3Hg^+ + {S_2O_3}^{2-} \longleftrightarrow CH_3HgS_2O_3^- \qquad \log\_k = 11.18 \qquad (69)$$

1.1.3 Hg^{2+} and CH_4Hg^+ with Organic Species

$$H^+ + DOM^{4-} \longleftrightarrow HDom^{3-} \qquad \log\_k = 10.0 \qquad (70)$$
$$Hg^{2+} + DOM^{4-} \longleftrightarrow HgDom^{2-} \qquad \log\_k = 21.4 \qquad (71)$$
$$H^+ + Rcoo^- \longleftrightarrow RcooH \qquad \log\_k = 4.5 \qquad (72)$$
$$Hg^{2+} + Rcoo^- \longleftrightarrow HgRcoo^+ \qquad \log\_k = 10.0 \qquad (73)$$
$$H^+ + Rs^- \longleftrightarrow RsH \qquad \log\_k = 10.0 \qquad (74)$$
$$Hg^{2+} + Rs^- \longleftrightarrow HgRs^+ \qquad \log\_k = 21.0 \qquad (75)$$
$$Hg^{2+} + 2Rs^- \longleftrightarrow HgRs_2 \qquad \log\_k = 28.7 \qquad (76)$$
$$CH_3Hg^+ + Rs^- \longleftrightarrow CH_3HgRs \qquad \log\_k = 14.0 \qquad (77)$$
$$H^+ + L^- \longleftrightarrow HL \qquad \log\_k = 10.0 \qquad (78)$$
$$Hg^{2+} + L^- \longleftrightarrow HgL^+ \qquad \log\_k = 21.27 \qquad (79)$$
$$Hg^{2+} + 2L^- \longleftrightarrow HgL_2 \qquad \log\_k = 34.04 \qquad (80)$$
$$CH_3Hg^+ + L^- \longleftrightarrow CH_3HgL \qquad \log\_k = 16.76 \qquad (81)$$
$$Ca^{2+} + L^- \longleftrightarrow CaL^+ \qquad \log\_k = 4.3 \qquad (82)$$
$$Mg^{2+} + L^- \longleftrightarrow MgL^+ \qquad \log\_k = 3.61 \qquad (83)$$
$$Zn^{2+} + L^- \longleftrightarrow ZnL^+ \qquad \log\_k = 9.69 \qquad (84)$$
$$Zn^{2+} + 2L^- \longleftrightarrow ZnL_2 \qquad \log\_k = 16.10 \qquad (85)$$
$$Cu^{2+} + L^- \longleftrightarrow CuL^+ \qquad \log\_k = 12.0 \qquad (86)$$
$$Cu^{2+} + 2L^- \longleftrightarrow CuL_2 \qquad \log\_k = 16.95 \qquad (87)$$
$$Ni^{2+} + L^- \longleftrightarrow NiL^+ \qquad \log\_k = 9.72 \qquad (88)$$
$$Ni^{2+} + 2L^- \longleftrightarrow NiL_2 \qquad \log\_k = 15.96 \qquad (89)$$
$$Cd^{2+} + L^- \longleftrightarrow CdL^+ \qquad \log\_k = 10.62 \qquad (90)$$
$$Cd^{2+} + 2L^- \longleftrightarrow CdL_2 \qquad \log\_k = 17.48 \qquad (91)$$
$$Pb^{2+} + L^- \longleftrightarrow PbL^+ \qquad \log\_k = 11.83 \qquad (92)$$
$$Pb^{2+} + 2L^- \longleftrightarrow PbL_2 \qquad \log\_k = 15.86 \qquad (93)$$
$$Co^{2+} + L^- \longleftrightarrow CoL^+ \qquad \log\_k = 10.62 \qquad (94)$$
$$Co^{2+} + 2L^- \longleftrightarrow CoL_2 \qquad \log\_k = 17.48 \qquad (95)$$
$${UO_2}^{2+} + 2L^- \longleftrightarrow UO_2L_2 \qquad \log\_k = 10.19 \qquad (96)$$
$$Fe^{3+} + L^- \longleftrightarrow FeL^{2+} \qquad \log\_k = 12.28 \qquad (97)$$
$$Fe^{3+} + 2L^- \longleftrightarrow {FeL_2}^+ \qquad \log\_k = 16.40 \qquad (98)$$

1.1.4 Other Metals

1.2 Surface Complexation Reactions

1.3 Precipitation and Dissolution Reactions

2 Example Calculations

2.1 Hg^{2+} Speciation with Inorganic Ligands in EFPC Waters

Species and concentrations from Dong et al. (2010) are used in the calculations.

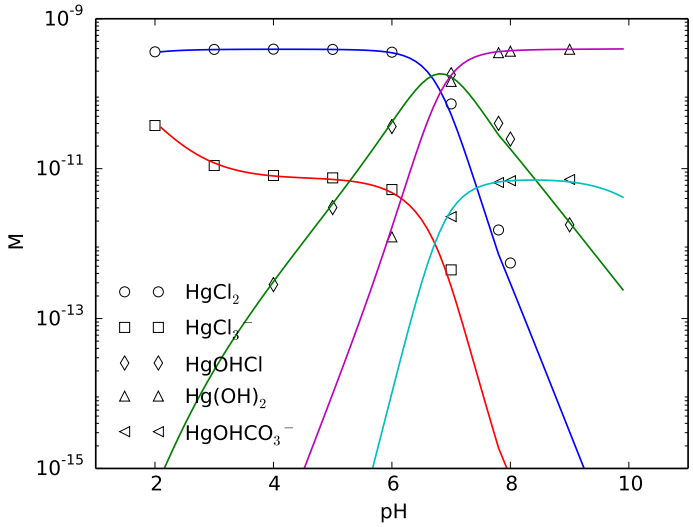

Figure 1: Hg^{2+} speciation with inorganic ligands in EFPC waters. Total Hg^{2+} = 0.4 nM. Other inorganic species and average concentrations from Dong et al. (2010) are used in the calculations. Curves = PHREEQC; Unfilled symbols = PFLOTRAN default (unit activity coefficient). PFLOTRAN and PHREEQC calculations are in general agreement.

2.2 Hg^{2+} Speciation with Organic Ligands in EFPC Waters

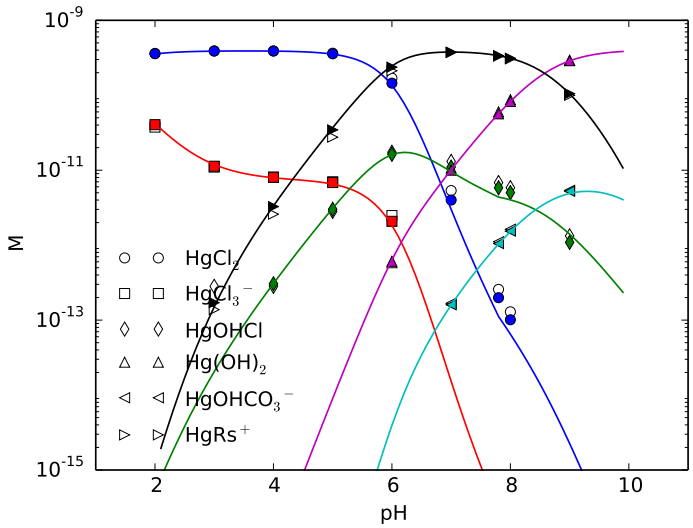

Figure 2: Hg^{2+} Speciation with organic ligands in EFPC waters. Based on inorganic species and concentrations in Fig. 1, 4 nM thiol sites (Rs^-) and 16 μM carboxyl sites ($Rcoo^-$) are added. Curves = PHREEQC; Unfilled symbols = PFLOTRAN default (unit activity coefficient); Filled symbols = PFLOTRAN + Debye-Huckel activity coefficient updated in each Newton Iteration. The results are quite different from Fig. 1 in Dong et al. (2010) probably because of different ways in fixing pH. In our calculations, HCl or NaOH is assumed to be added to a specified pH.

2.3 CH_3Hg Speciation in EFPC Waters

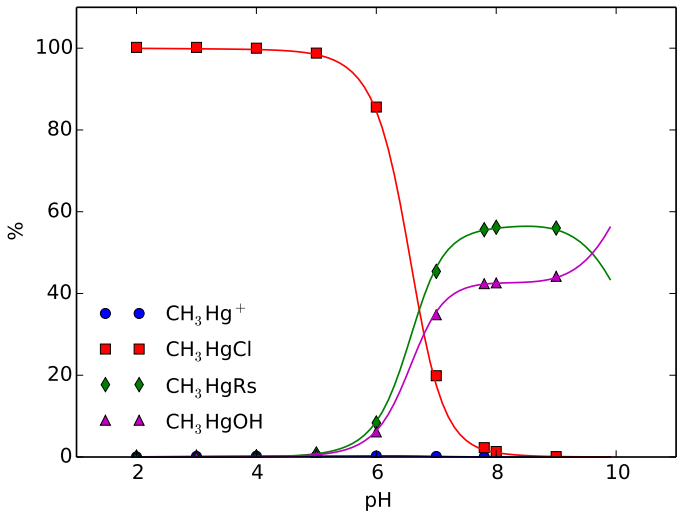

Figure 3: CH_3Hg speciation in EFPC waters. 5 pM CH_3Hg is added into the solutions as in Fig. 2. The results are in general agreement with Dong et al. (2010) Fig. 3a except that CH_3Hg concentrations are higher in the latter.

2.4 Competition with Other Metal Ions for Complexation with Thiol Ligands

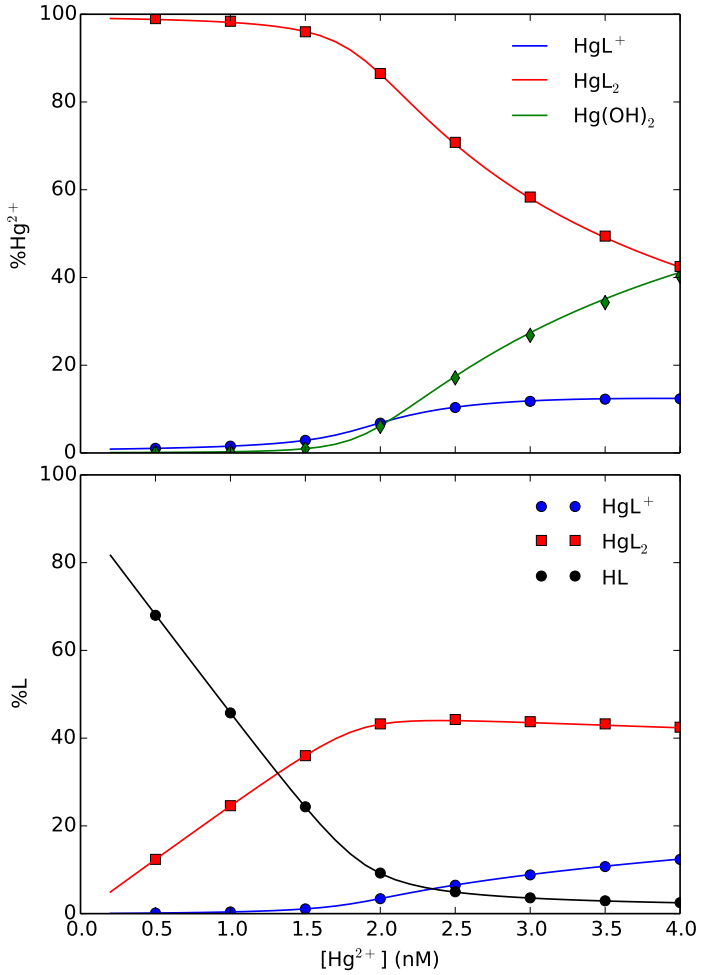

Figure 4: Without competition with other metal ions for complexation with thiol ligands (L), PFLOTRAN calculations are close to PHREEQC. The calculations are based on the same input files for Fig. 2 except that the 4 nM thiol sites (Rs^-) and 16 μM carboxyl sites ($Rcoo^-$) are replaced with 4 nM thiol sites represented by L (thiol group in Cysteine and Glutathione). For PHREEQC, CH_3Hg^+, Ni^{2+}, Cd^{2+}, Pb^{2+}, $UO_2{}^{2+}$, and Fe^{3+} are omitted from the solution to prevent the competition. For PFLOTRAN, the secondary species between these metals and L are not added in the input file to avoid the competition.

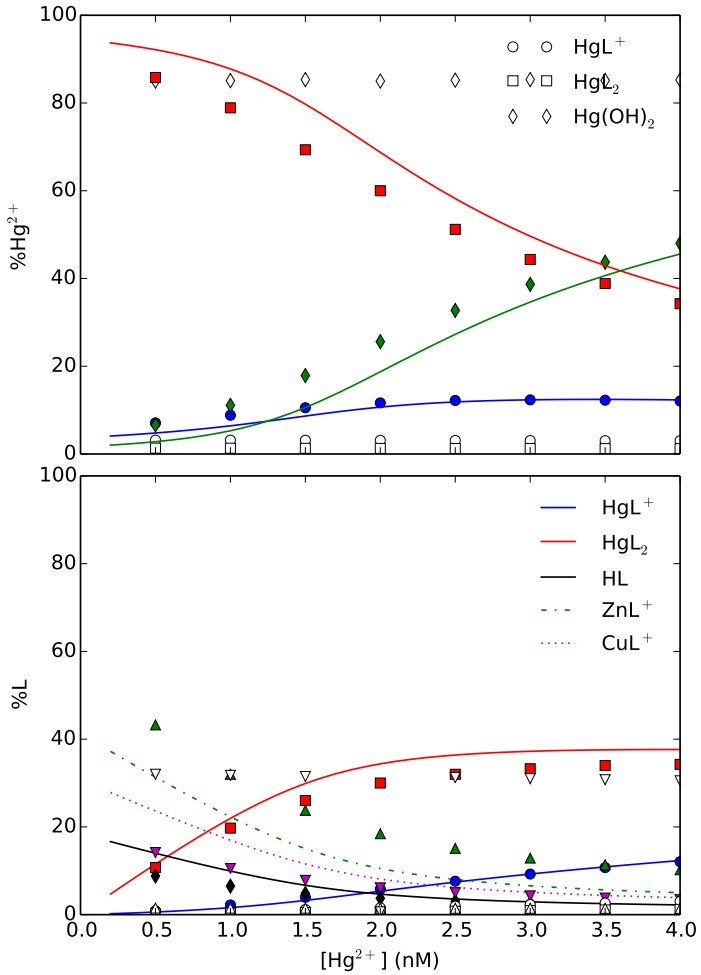

Figure 5: With competition with other metal ions for complexation with thiol ligands (L): PFLOTRAN calculations (add metal thiol complexation reactions to Fig. 4 case, empty markers) are different from PHREEQC (add metal species, curves). Adding secondary species $Fe(OH)_3(aq)$, $Fe(OH)^{2+}$, $Fe(OH)_4^-$, $Fe(OH)^{2+}$, FeF_2^+, and $Cu(OH)_2$ into PFLOTRAN input files gets the PFLOTRAN calculations (filled markers) closer to PHREEQC. Namely, without complexation reactions of Fe^{3+} and Cu^{2+} with OH^-, more L^- forms complex with Fe^{3+} and Cu^{2+}, and less L^- is available to form complex with Hg^{2+}.