Supporting Information for:

Stability of Metal-Glutathione Complexes During Oxidation by Hydrogen Peroxide and Cu(II)-Catalysis

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Figure S1. Oxidation of 5.0 μM GSH in the presence of Ag (○), 2.5 μM Hg (△) or without metals (×). **(a)** Oxidation by 100 μM H_2O_2, pH 7.8; **(b)** Oxidation by 0.2 μM Cu(II), pH 7.7. (Same data as in Figure 1; x-axes are extended to 100-150 hr.)

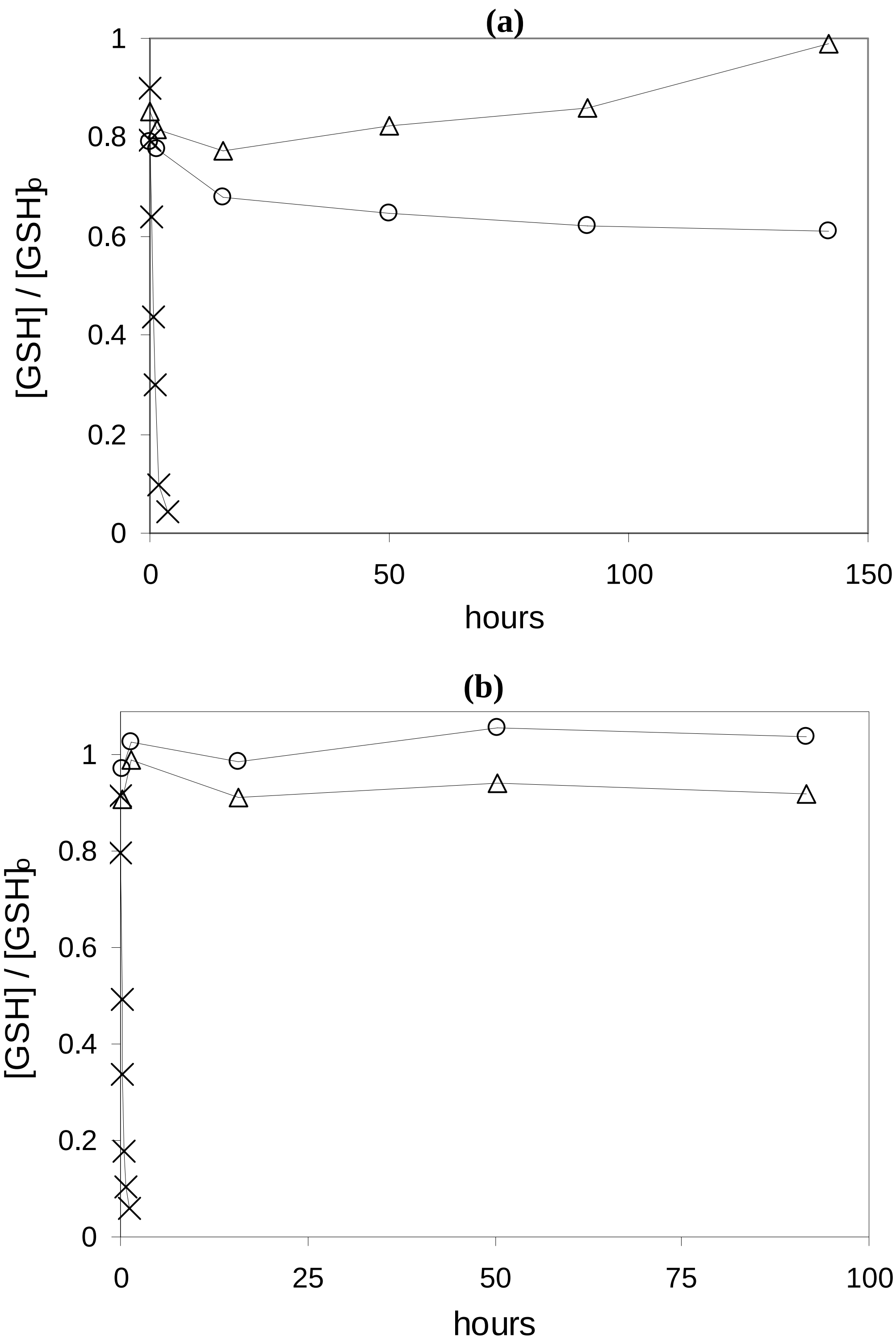

Figure S2. Total glutathione (GSH and GSSG) recovered during oxidation of 5.0 μM GSH in the presence of 5 μM Cd, Zn, Pb, or no metals. **(a)** Oxidation by 100 μM H_2O_2, pH 7.9-8.0; **(b)** Oxidation by 0.2 μM Cu(II), pH 7.7-7.8.

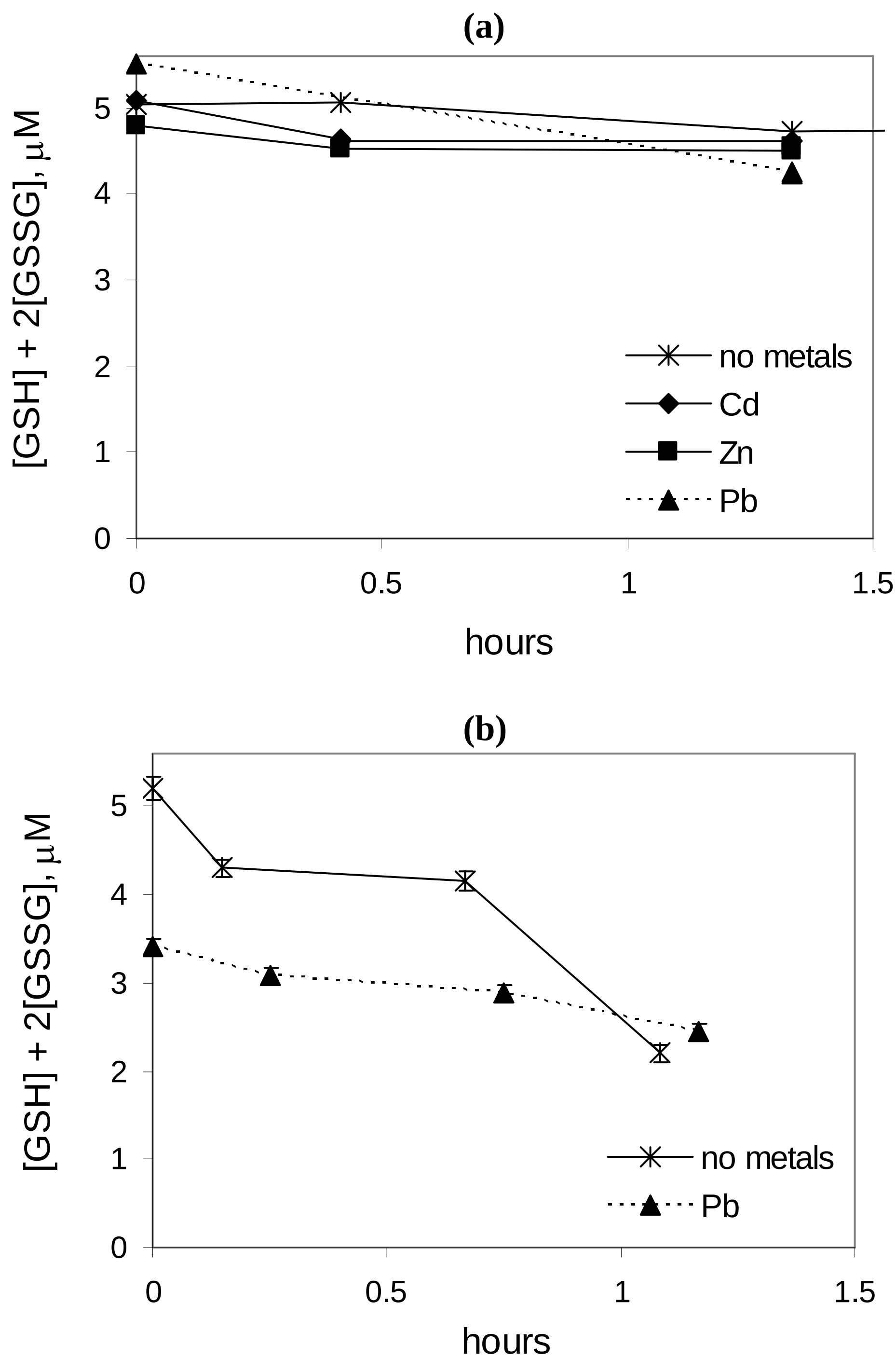

Table S1. Metal-GSH stability constants used for equilibrium calculations of initial GSH speciation in the experimental samples. Stability constants were adjusted to I = 0 using the Davies equation from values reported in references (*31*-*32*).

	log K (25°C, 1 atm)	ref.
$GSH^{3-} + H^+ \Leftrightarrow HGSH^{2-}$	8.88	(*32*)
$GSH^{3-} + 2H^+ \Leftrightarrow H_2GSH^-$	17.12	(*32*)
$GSH^{3-} + 3H^+ \Leftrightarrow H_3GSH^0$	20.40	(*32*)
$GSH^{3-} + 4H^+ \Leftrightarrow H_4GSH^+$	22.48	(*32*)
$Cd^{2+} + GSH^{3-} \Leftrightarrow CdGSH^+$	11.02	(*31*)
$Cd^{2+} + GSH^{3-} + H^+ \Leftrightarrow CdHGSH^0$	18.0	(*31*)
$Cd^{2+} + GSH^{3-} + H_2O \Leftrightarrow CdOHGSH^{2-} + H^+$	0.77	(*31*)
$Cd^{2+} + 2GSH^{3-} \Leftrightarrow Cd(GSH)_2^{4-}$	15.77	(*31*)
$Cd^{2+} + 2GSH^{3-} + H^+ \Leftrightarrow CdH(GSH)_2^{3-}$	26.07	(*31*)
$Cd^{2+} + 2GSH^{3-} + 2H^+ \Leftrightarrow CdH_2(GSH)_2^{2-}$	34.78	(*31*)
$Zn^{2+} + GSH^{3-} \Leftrightarrow ZnGSH^+$	9.41	(*31*)
$Zn^{2+} + GSH^{3-} + H^+ \Leftrightarrow ZnHGSH^0$	15.74	(*31*)
$Zn^{2+} + GSH^{3-} + H_2O \Leftrightarrow ZnOHGSH^{2-} + H^+$	0.49	(*31*)
$Zn^{2+} + 2GSH^{3-} \Leftrightarrow Zn(GSH)_2^{4-}$	14.01	(*31*)
$Zn^{2+} + 2GSH^{3-} + H^+ \Leftrightarrow ZnH(GSH)_2^{3-}$	24.25	(*31*)
$Zn^{2+} + 2GSH^{3-} + 2H^+ \Leftrightarrow ZnH_2(GSH)_2^{2-}$	32.02	(*31*)
$Pb^{2+} + GSH^{3-} \Leftrightarrow PbGSH^+$	11.44	(*31*)
$Pb^{2+} + GSH^{3-} + H^+ \Leftrightarrow PbHGSH^0$	18.49	(*31*)
$Pb^{2+} + 2GSH^{3-} \Leftrightarrow Pb(GSH)_2^{4-}$	15.42	(*31*)
$Pb^{2+} + 2GSH^{3-} + H^+ \Leftrightarrow PbH(GSH)_2^{3-}$	25.07	(*31*)
$Pb^{2+} + 2GSH^{3-} + 2H^+ \Leftrightarrow PbH_2(GSH)_2^{2-}$	34.40	(*31*)
$Hg^{2+} + GSH^{3-} \Leftrightarrow HgGSH^+$	27.36	(*32*)
$Hg^{2+} + GSH^{3-} + H^+ \Leftrightarrow HgHGSH^0$	33.92	(*32*)
$Hg^{2+} + GSH^{3-} + 2H^+ \Leftrightarrow HgH_2GSH^+$	37.22	(*32*)
$Hg^{2+} + 2GSH^{3-} \Leftrightarrow Hg(GSH)_2^{4-}$	34.06	(*32*)
$Hg^{2+} + 2GSH^{3-} + H^+ \Leftrightarrow HgH(GSH)_2^{3-}$	43.94	(*32*)
$Hg^{2+} + 2GSH^{3-} + 2H^+ \Leftrightarrow HgH_2(GSH)_2^{2-}$	54.49	(*32*)

Figure S3. Calculated equilibrium speciation of GSH in model solutions containing 5 μM GSH_T, 0.01 M KCl and a) 5.0 μM $Cd(II)_T$, b) 5.0 μM $Pb(II)_T$, c) 5.0 μM $Zn(II)_T$, and d) 2.5 μM $Hg(II)_T$. Calculations were conducted in MINEQL+ using stability constants listed in Table S1.

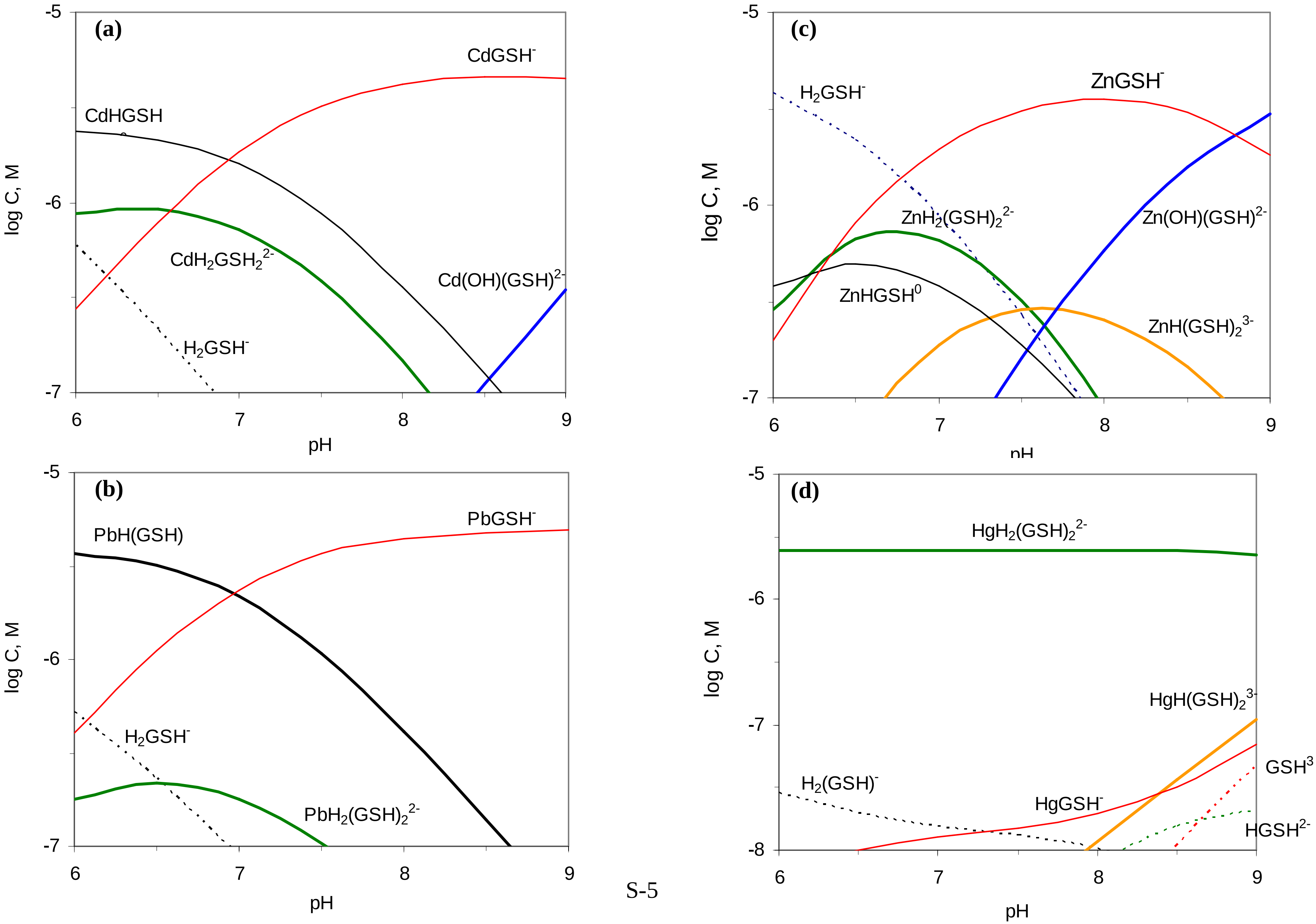

Figure S4. Equilibrium GSH^{3-} concentration in solutions containing 5 μM GSH_T and either 5 μM Cd_T, 5 μM Zn_T, 5 μM Pb_T, or 2.5 μM Hg_T (0.01 M KCl). Equilibrium calculations were conducted on MINEQL+ using stability constants listed in Table S1.