Simulating the Stability of Colloidal Amorphous Iron Oxide in Natural waters

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Nov. 4, 2009

Disclaimer: although this work was reviewed and approved for presentation by the U.S. Environmental Protection Agency, it does not necessarily represent official agency policy.

Acknowledgments: the authors wishes to acknowledge previous discussions with members of the U.S. EPA OSP OPPTS Manufactured Nanomaterial Physical Chemical Properties workgroup and the OECD Steering Group 4 of the Working Party on Manufactured Nanomaterials. The author also acknowledges the value of comments by reviewers of this work and previous work in this area.

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Existing EPA and OECD standardized procedures for measuring manufactured chemical aqueous solubilities and octanol/water partition coefficients are unlikely to be applicable to insoluble nanomaterial aqueous suspensions…

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When the repulsive energies dominate, a relatively stable aqueous suspension is formed; when attractive energies dominate, a suspension aggregates and becomes immobilized.

Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory of Colloidal Particle Stability

The Critical Coagulation Concentration (CCC) is the minimum ionic strength (or dissolved salt content) needed to induce rapid aggregation of a colloidal suspension in water.

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DLVO theory yields procedures for estimating the Critical Coagulation Concentration (CCC).

$$CCC = \frac{3.84\times10^{-39}\gamma^4}{A^2z^6}\ mol\ dm^{-3}$$ (Shaw, 1992)

$$CCC = \frac{8.74\times10^{-39}\gamma^4}{A^2z^6}\ mol\ dm^{-3}$$ (Ross and Morrison, 1988)

$$CCC = \frac{8.1\times10^{-39}\gamma^4}{A^2z^6}\ mol\ dm^{-3}$$ (Overbeek, 1952)

$\gamma = (EXP(ze\Psi/2kT)-1)/(EXP(ze\Psi/2kT)+1)$
k = Boltzmann constant
e = charge of the proton
A = Hamaker constant

Ψ = zeta potential
T = absolute temperature
z = counterion valence

To calculate a minimum ionic strength needed to induce rapid aggregation of any colloidal suspension in water (CCC), one needs estimates of:

1) The temperature and valence of the counterion in water

2) The Hamaker constant (A)

3) The zeta potential (ψ_ζ)

ψ_ζ can be experimentally estimated from electrophoretic mobilities or can be assumed to equal or be less than the diffuse layer potential (ψ_d) obtained from geochemical speciation models.

Due to the availability of data, colloidal amorphous iron oxide was selected as a test substrate.

- representative water chemistry data and Hamaker constants for iron oxides are available in the literature

- datasets can be generated for conducting MINTEQA2 geochemical speciation model predictions of diffuse layer potentials with both the MIT Diffuse Layer Model and the Triple Layer Model.

Methods

Chemical properties of natural waters (moles/liter)

	Rain (Rothert, 1999)	*GW (Pope-Reid, 1985)*	*0.1 M SW*	*0.7 M SW*	*River (Hem, 1970)*
Ca^{++}	2.6×10^{-6}	1.81×10^{-3}	1.47×10^{-3}	1.03×10^{-2}	7.50×10^{-4}
Mg^{++}	8.6×10^{-7}	1.39×10^{-3}	7.54×10^{-3}	5.28×10^{-2}	3.40×10^{-4}
Na^{+}	3.9×10^{-6}	2.32×10^{-3}	6.70×10^{-2}	4.69×10^{-1}	2.70×10^{-4}
K^{+}	4.6×10^{-7}	1.25×10^{-4}	1.46×10^{-3}	1.02×10^{-2}	5.90×10^{-5}
$SO_4^{=}$	1.1×10^{-5}	3.02×10^{-3}	4.03×10^{-3}	2.82×10^{-2}	2.30×10^{-4}
Cl^{-}	4.2×10^{-6}	1.67×10^{-3}	7.80×10^{-2}	5.46×10^{-1}	2.20×10^{-4}
Nominal IS	*0.0000332*	*0.014498*	*0.09931*	*0.6952*	*0.0029*

Literature reported Hamaker constants for amorphous iron oxide

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1.9×10^{-19} J	Visser (1972)
1.0×10^{-19} J	Phenrat et al. (2007)
1.35×10^{-19} J	Mosley et al. (2003)

MIT DLM stoichiometry	log(K)	Site/Reference
$>FeOH \leftrightarrow >FeO^- + H^+$	-8.93	Dzombak & Morel, 1990
$>FeOH + H^+ \leftrightarrow >FeOH_2^+$	7.29	Dzombak & Morel, 1990
$>FeOH + H^+ + Cl^- \leftrightarrow >FeOH_2Cl$	8.64	Loux, 2008
$>FeOH + Na^+ \leftrightarrow >FeONa + H^+$	-8.37	Loux, 2008
$>FeOH + Ca^{2+} \leftrightarrow >FeOH\ Ca^{2+}$	4.97	1/Dzombak & Morel, 1990
$>FeOH + Ca^{2+} \leftrightarrow >FeOCa^+ + H^+$	-5.85	2/Dzombak & Morel, 1990
$>FeOH + Mg^{2+} \leftrightarrow >FeOMg^+ + H^+$	-4.6	2/Dzombak & Morel, 1990
$>FeOH + SO_4^{2-} + H^+ \leftrightarrow >FeSO_4 + H_2O$	7.78	Dzombak & Morel, 1990
$>FeOH + CO_3^{2-} + H^+ \leftrightarrow >FeCO_3^- + H_2O$	13.862	1,2/Dzombak & Morel, 1990
$>FeOH + CO_3^{2-} \leftrightarrow >FeOHCO_3^{2-}$	6.415	1,2/Dzombak & Morel, 1990

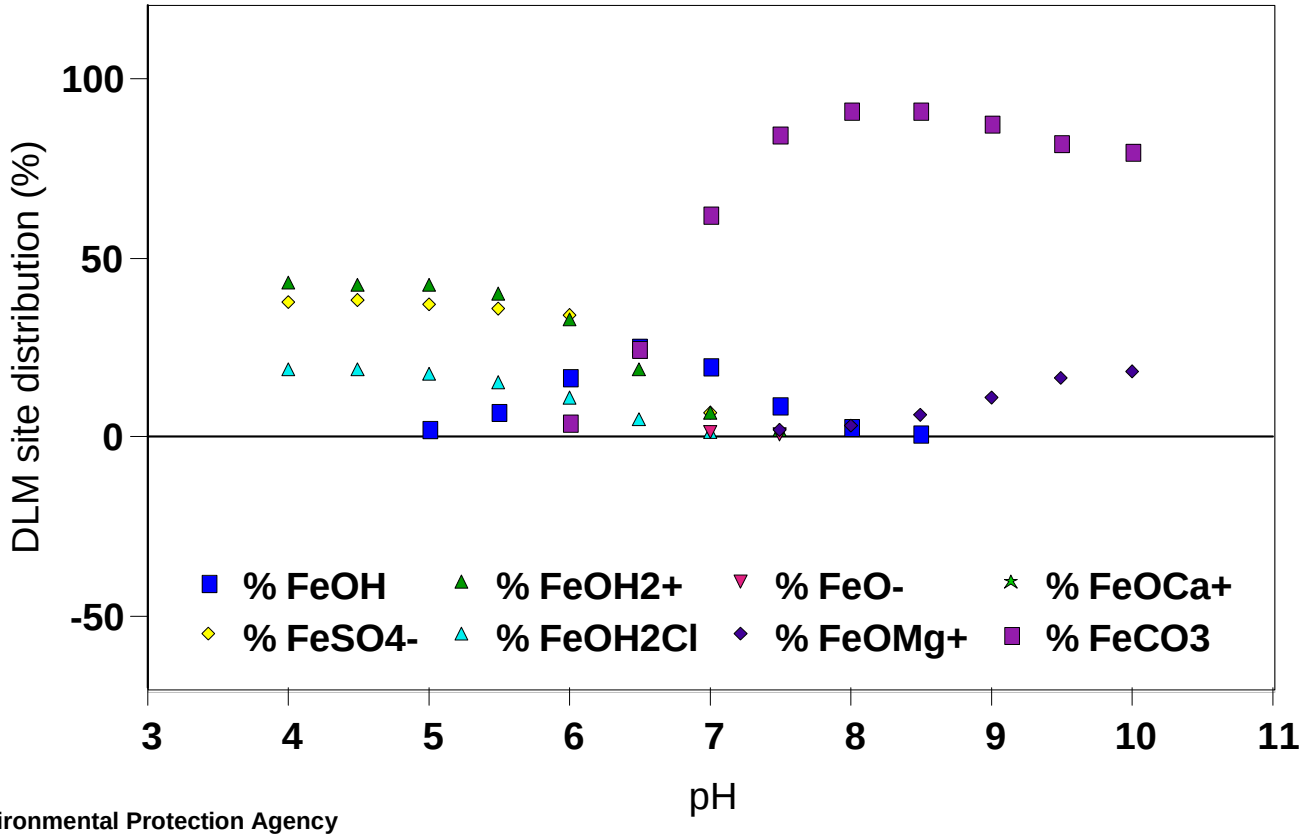
$2.31 sites/nm^2$ (Dzombak and Morel, 1990)

TLM stoichiometry	log(K)	Reference
$>FeOH \leftrightarrow >FeO^- + H^+$	-10.9 ± 0.5	Smith & Jenne, 1988
$>FeOH + H^+ \leftrightarrow >FeOH_2^+$	5.0 ± 0.5	Smith & Jenne, 1988
$>FeOH + H^+ + Cl^- \leftrightarrow >FeOH_2Cl$	6.2	Smith & Jenne, 1988
$>FeOH + Na^+ \leftrightarrow >FeONa + H^+$	-9.3	Smith & Jenne, 1988
$>FeO^- + Ca^{2+} \leftrightarrow >FeO^-Ca^{2+}$	4.3	Smith & Jenne, 1988
$>FeO^- + CaOH^+ \leftrightarrow >FeO^-CaOH^+$	7.9	Smith & Jenne, 1988
$>FeO^- + Mg^{2+} \leftrightarrow >FeO^-Mg^{2+}$	4.1	Smith & Jenne, 1988
$>FeO^- + MgOH^+ \leftrightarrow >FeO^-MgOH^+$	6.7	Smith & Jenne, 1988
$>FeOH_2^+ + SO_4^{2-} \leftrightarrow >FeOH_2^+SO_4^{2-}$	5.5	Smith & Jenne, 1988
$>FeOH_2^+ + HSO_4^- \leftrightarrow >FeOH_2^+HSO_4^-$	9.2	Smith & Jenne, 1988
$>FeOH_2^+ + HCO_3^- \leftrightarrow >FeOH_2^+HCO_3^-$	5.0	Smith & Jenne, 1988
$>FeOH_2^+ + H_2CO_3 \leftrightarrow >FeOH_2^+H_2CO_3$	-2.1	Smith & Jenne, 1988

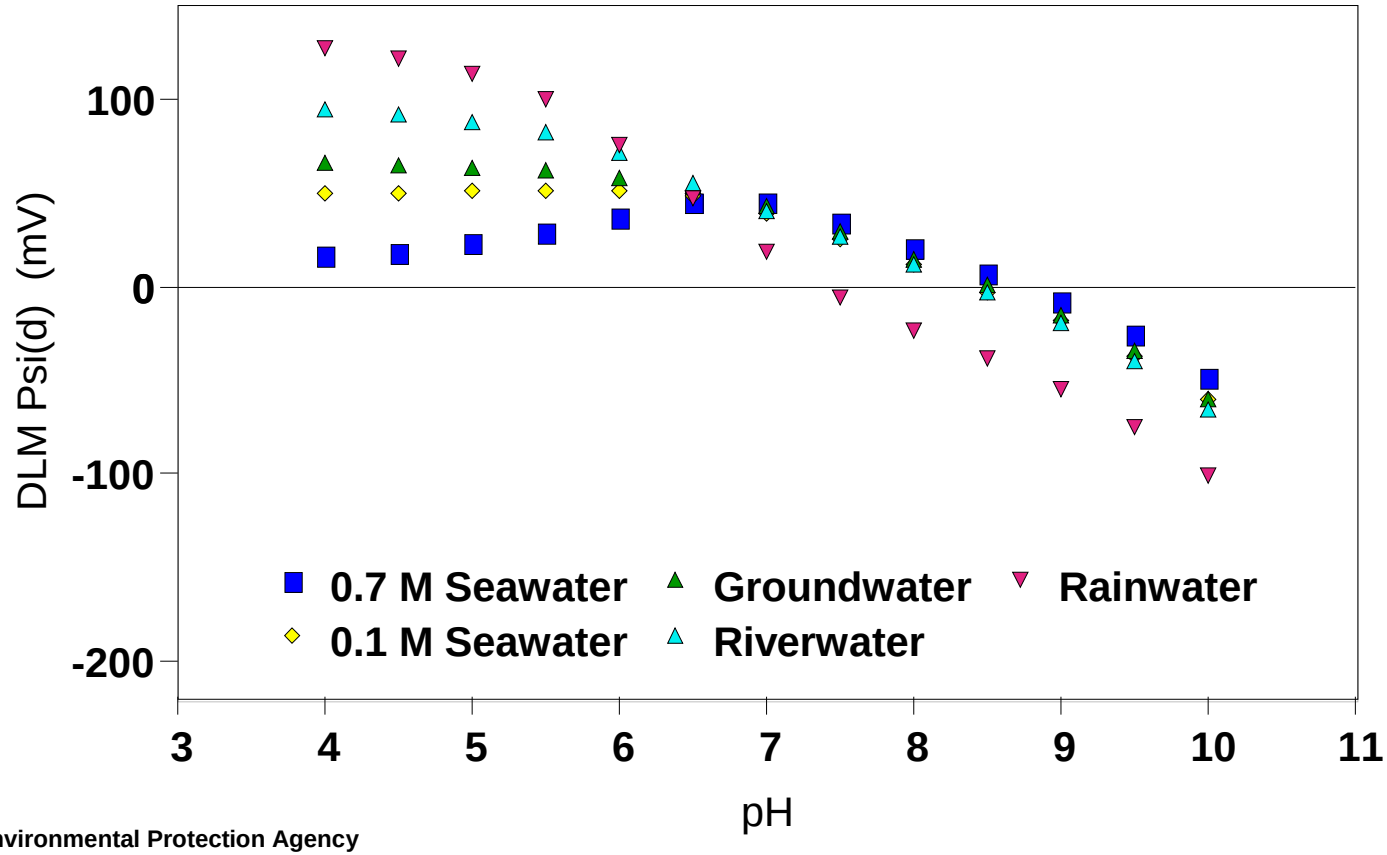
TLM site density = 9.89 sites/nm² (Davis and Leckie, 1978); C_1 = 1.4 F/m²; C_2 = 0.2 F/m² (Yates, 1975; Davis et al., 1978,: Davis and Leckie, 1978; Goldberg and Johnson, 2001; Goldberg, 2005)

Results

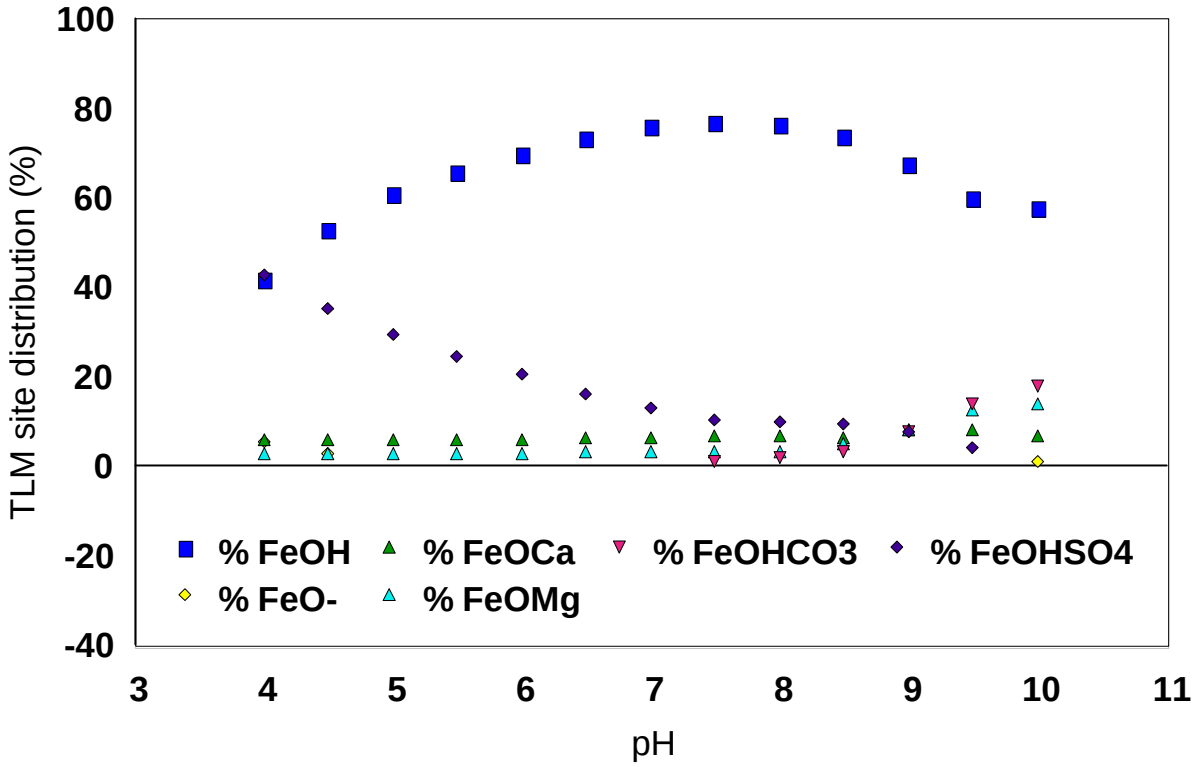
Simulated MIT DLM predictions of am. iron oxide site distributions in the groundwater environment over a pH range of 4 to 10.



Simulated MIT DLM diffuse layer potentials for amorphous iron oxide in all systems over a pH range of 4 to 10.



Simulated TLM predictions of am. iron oxide site distributions in the groundwater environment over a pH range of 4 to 10.



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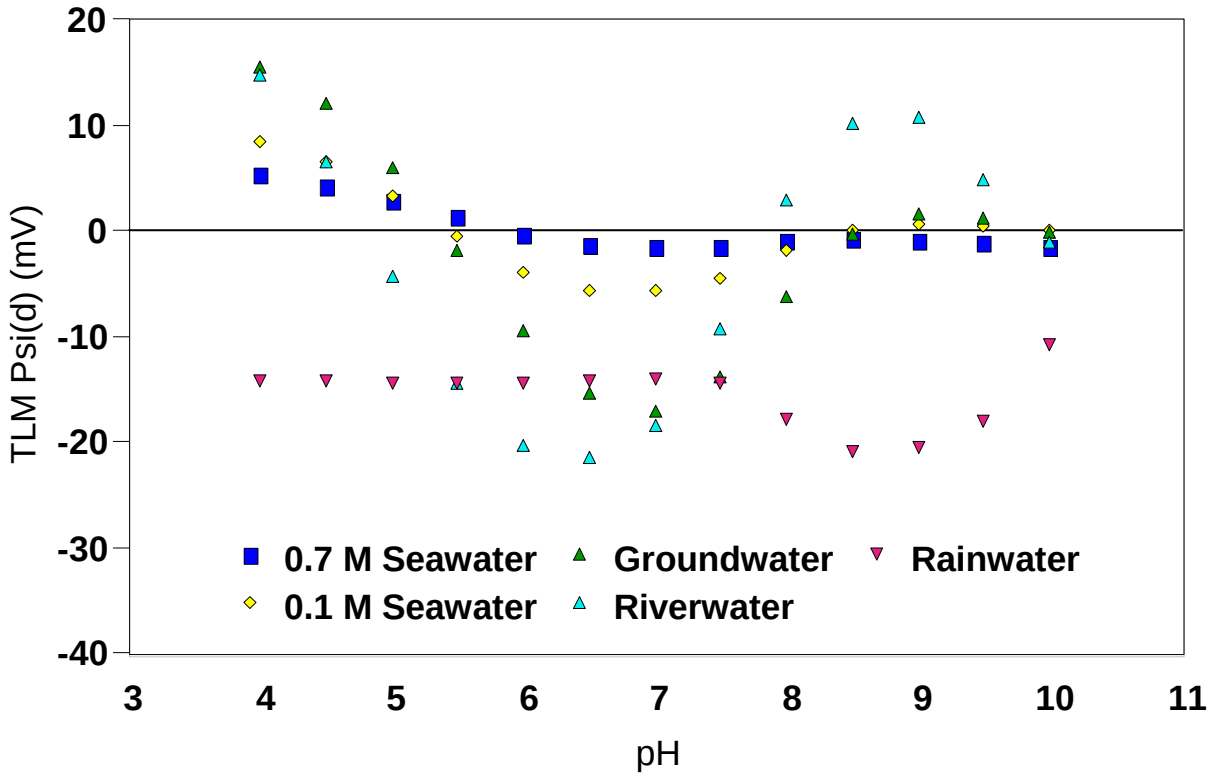
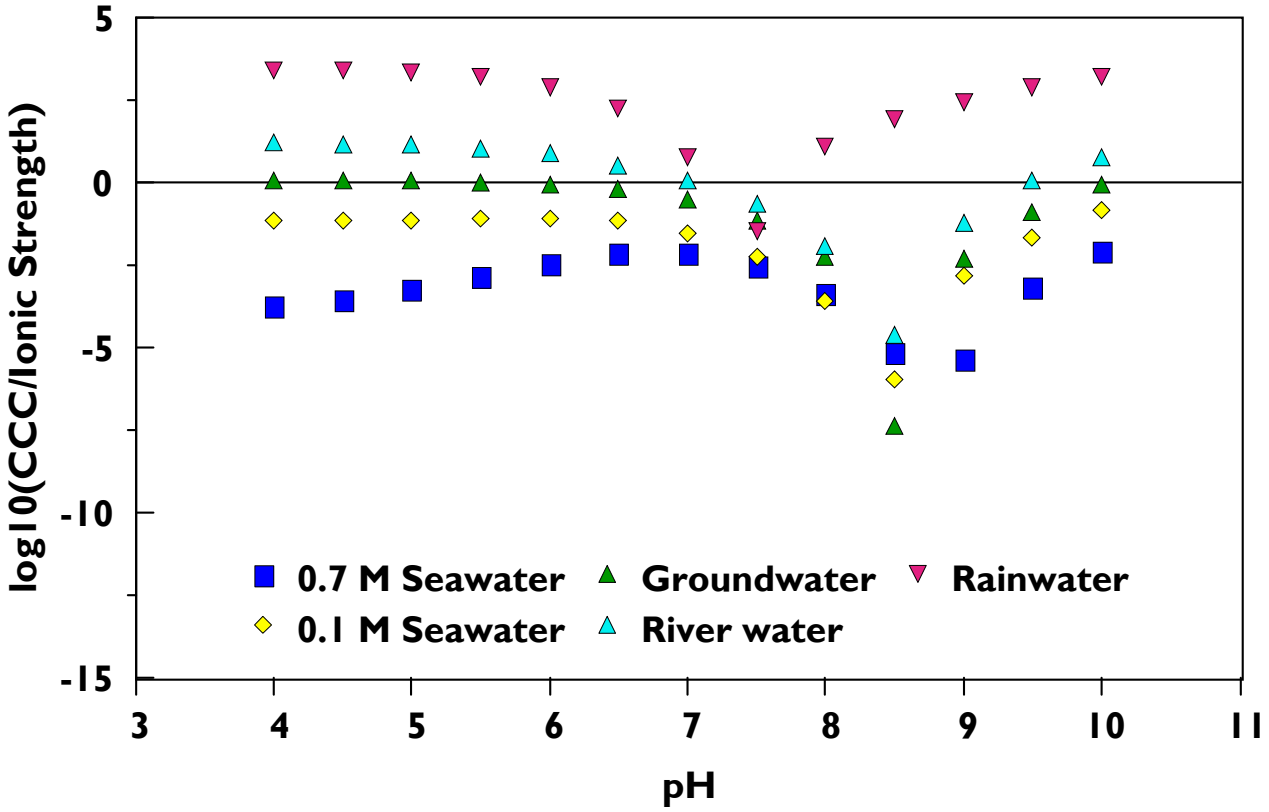


Predicting amorphous iron oxide colloidal suspension stability:

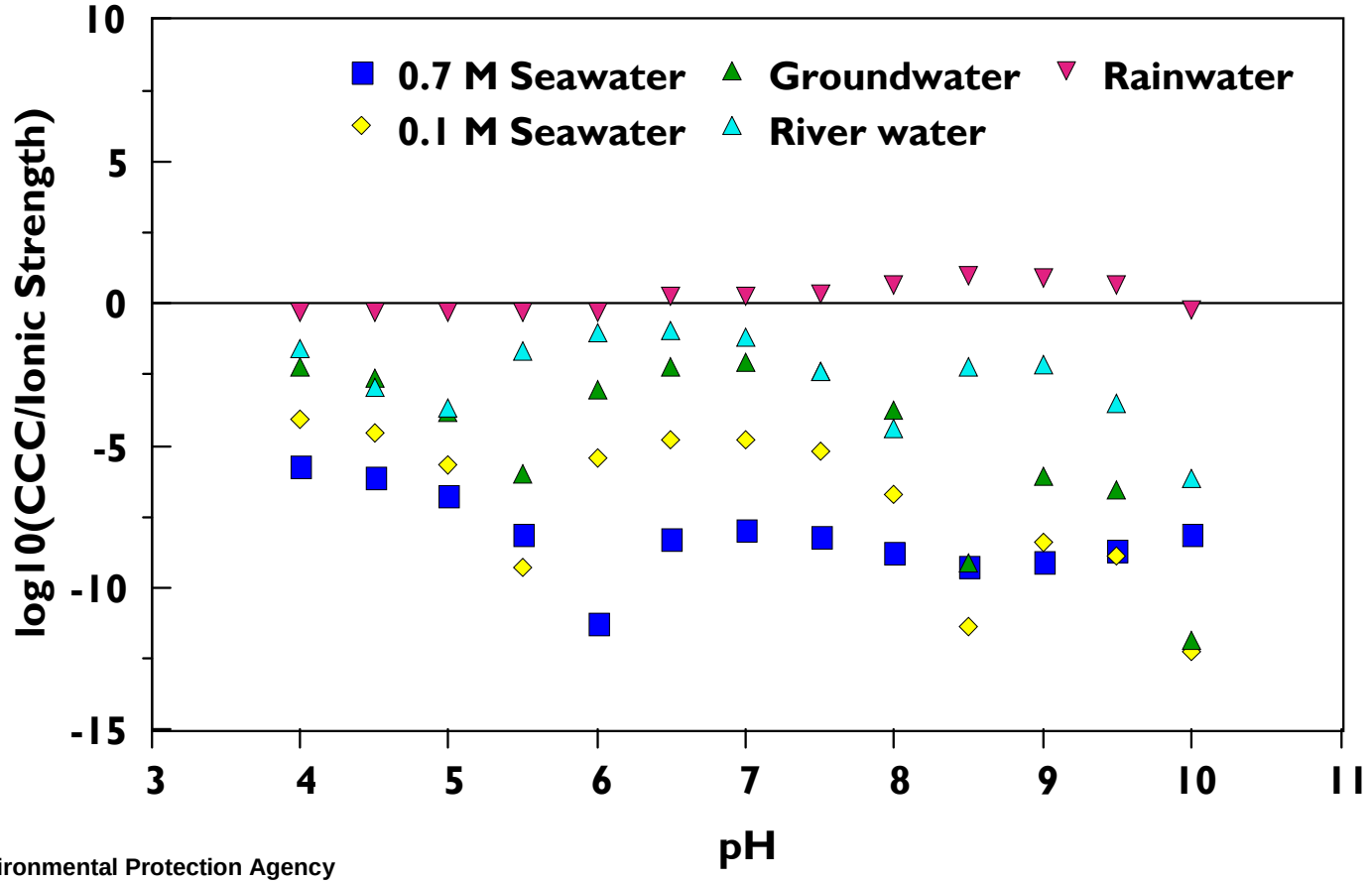
Stable suspension: $\log_{10}(CCC/IS) > 0$

Unstable suspension: $\log_{10}(CCC/IS) < 0$

Prediction of iron oxide colloidal suspension stability (MIT DLM)



Prediction of iron oxide colloidal suspension stability (TLM)



Source of variation		*Est. variation in $\log_{10}$(CCC/IS)*
Water chemistry contributions to Ψ_d		*~7*
Ψ_d (DLM) vs. Ψ_d (TLM) (seawater)		*~4*
Variations in Hamaker constant		*~0.6*
Variations in distance to plane of shear (DLM):	*~0.1/κ*	*~0.2*
	~0.2/κ	*~0.4*
	~0.7/κ	*~1.2*
CCC expression variation (eqns. 1-3)		*~0.4*

Conclusions

1) *Major ions will play a role in the electrokinetic properties of MNs in natural waters; aquatic chemistry is a dominant variable…*

2) *DLM predictions of Ψ_d likely overestimate Ψ_ζ and TLM predictions of Ψ_d likely underestimate Ψ_ζ*

3) *OM coatings will likely stabilize colloidal amorphous iron oxide suspensions*

4) *Given the large number of assumptions required in the simulations, extensive experimental datasets will likely be required in order to validate model predictions.*