

# Thermodynamic modelling of heterogeneous sorption of trace metals onto synthetic and natural non-stoichiometric Mn oxides

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Recent research highlighted the intricate relationships between solubility of Mn oxides and trace metal sorption in stratified marine and lacustrine water columns (see abstract by Kersten *et al.*). Existing speciation, solubility and surface complexation models taken separately are insufficient in rationalising such processes. This paper presents a new multi-site multi-surface thermodynamic model combining metal adsorption/ ion exchange with solubility of non-stoichiometric Mn oxide ( $\delta$ -MnO<sub>x</sub>). The model can account for both particle- and solution- concentration effects on trace metal partitioning in suboxic natural environments.

Gibbs energy minimisation (GEM) approach (see abstract by Kulik) implemented in Selektor-A 3.2 code was used for all calculations. The code can solve aqueous equilibria involving 'sorption nano-phases' composed of surface complexes arranged on up to six surface types on a solid-solution carrier of non-zero specific surface area *A*. The built-in thermodynamic dataset was extended for surface species using REACDC format of Selektor-A database. TLM (Hayes) was used for amphoteric surface types; non-electrostatic model (NEM) for ion exchange surface.  $\delta$ -MnO<sub>x</sub> was represented by MnO<sub>2</sub>-MnOOH ideal solid solution (see abstract by Kersten *et al.*).

Single-site TLM fits of  $\delta$ -MnO<sub>x</sub> surface acidity yield  $\text{pH}_{\text{PZC}} < 2.5$ ,  $C_1 > 2 \text{ F}\cdot\text{m}^{-2}$ ,  $\text{pK}_{\text{a}2} < 6.0$  and outer-sphere  $\text{pK}_{\text{Cat}}$  around 3.0 (Catts and Langmuir, 1986). However, Tamura *et al.* (1996) found  $\text{pH}_{\text{PZC}}$  between 3.76 and 4.72 by titration of synthetic  $\gamma$ -MnO<sub>x</sub> samples. Healy *et al.* (1966) reported  $\text{pH}_{\text{PZC}} < 2.0$  for  $\delta$ -MnO<sub>x</sub>, but  $\text{pH}_{\text{PZC}} = 5.5 \pm 0.2$  for  $\gamma$ -MnO<sub>2</sub>. Microscopic studies reveal energetically different sites for cation binding on surfaces of Mn oxides, probably responsible for solution-concentration effects in adsorption data for  $\delta$ -MnO<sub>x</sub> causing large scatter of fitted  $\text{pK}_{\text{ads}}$ . Moreover, the ion exchange is potentially significant on synthetic and natural birnessites/buserites with formal CEC  $\leq 0.3$  (Silvester *et al.*, 1997). All this suggests that MnO<sub>x</sub>

phases may act as heterogeneous sorbents (cf. Westall, 1995), for which the single-site TLM may be inadequate because of neglecting site heterogeneity effects and contribution of ion exchange.

## Model calculations

To assess this inadequacy, we modelled surface acidity and Zn adsorption data by Catts and Langmuir (1986) with a single-site GEM model based on their set of TLM parameters for 6.75 and 67.5 mg L<sup>-1</sup> of total MnO<sub>2</sub> and ionic strength  $I = 0.1$  and 0.01 *m*. Total Zn was 10<sup>-5</sup> *m*. Redox conditions were set by atmospheric  $p(\text{O}_2)$ . At  $\text{pH} < 4.5$ , MnO<sub>x</sub> solid solution dissolved, hence kinetic constraints on end-members were set such that  $\text{Mn}_{\text{aq}} < 10^{-6}$  *m*. Good fits of surface charge, similar for NaNO<sub>3</sub> and NaCl electrolytes, were obtained, but at  $\text{pH} > 6$  only with competitive site density  $\Gamma_{\text{max}} = 4 \text{ sites nm}^{-2}$ . However, we could not fit adsorbed Zn fraction at all  $\text{pH}$  from 2 to 8. Outer-sphere Zn complexes, even made 2 pK units stronger, were out-competed by  $>\text{O-Na}^+$  species at  $\text{pH} > 5$ . Replacement of outer-sphere by inner-sphere Zn complexes resulted in under-prediction at  $\text{pH} < 6.5$  and over-prediction at  $6.5 < \text{pH} < 8.0$ . Better fits obtain when both inner- and outer-sphere Zn species included, but such model still under-predicts at  $\text{pH} < 4.5$ .

Next, a multi-site- multi-surface TLM + ion exchange model was constructed and applied to the same experimental data. We assumed 100% protonation of ion exchange X surface (30% area) at  $I \leq 0.1$  *m* and  $\text{pH} < 2.5$ , completely deprotonated by exchange with Na<sup>+</sup> and/or Zn<sup>2+</sup> ions at  $\text{pH}$  6 to 7. Properties of the amphoteric surface type 1 (69% area) were assumed similar to that of crystalline  $\gamma$ -MnO<sub>2</sub> or TiO<sub>2</sub>, hence selection of TLM1  $\text{pH}_{\text{PZC}}$ ,  $\Delta\text{pK}_{\text{a}}$ ,  $\text{pK}_{\text{Na}}$  and  $\text{pK}_{\text{ads}}$  for outer- and inner-sphere Zn species. To account for site heterogeneity effects at low  $\text{Zn}_{\text{aq}}$ , a competitive TLM2 surface type (1% area) with 2 pK units stronger inner-sphere Zn complexes was included. In addition, Type 3  $>\text{OZn}^+$

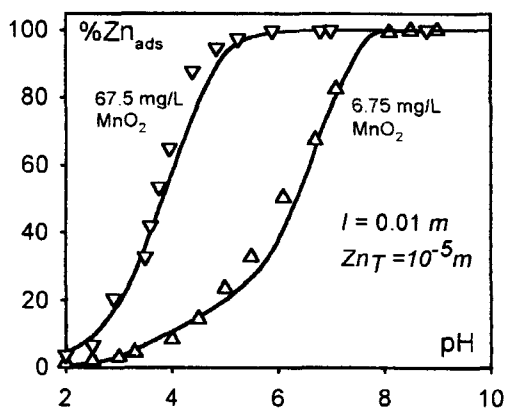


FIG. 1. Adsorption of Zn on  $\delta$ -MnO<sub>x</sub>. Points: experimental data (Catts and Langmuir, 1986). Lines: TLM - ion exchange GEM model (see text). Parameters of TLM 1 and 2 surface types:  $pK_{a1}^0 = 1.6$ ,  $pK_{a2}^0 = 8.0$ ,  $pK_{An}^0 = 2.6$ ,  $pK_{Na}^0 = 4.7$ ,  $C_1 = 2.4$ ,  $C_2 = 0.2 \text{ F m}^{-2}$ ,  $\Gamma_{\max} = 12.05 \text{ sites nm}^{-2}$ . TLM1 outer-sphere:  $pK_{Zn^{2+}}^0 = -2.0$ ,  $pK_{ZnOH^+}^0 = 6.0$ ; inner-sphere:  $pK_{OZn^+}^0 = 2.8$ ,  $pK_{OZnOH^0}^0 = 10.8$ ,  $pK_{OZn(OH)^{-}}^0 = 16.3$ ; Type 3 site:  $pK_{OZn^+}^0 = -1.2$ ; TLM2:  $pK_{OZn^+}^0 = 0.8$ ,  $pK_{OZnOH^0}^0 = 8.8$ ,  $pK_{OZn(OH)^{-}}^0 = 14.3$ ; Ion exchange X:  $pK_{XH^+}^0 = -8.3$ ,  $pK_{XH^+ - XNa^+}^0 = 3.0$ ,  $pK_{XH^+ - 2XZn^+}^0 = 2.5$ .

inner-sphere complex 4 pK units stronger was set on TLM1 surface, limited by a non-competitive  $\Gamma_{\max} = 0.03 \text{ sites nm}^{-2}$ . As a result, Good fit of surface acidity and Zn adsorption data (Fig. 1) was obtained at all pH values. Cation exchange capacity (CEC) was found to be  $680 \mu\text{mol g}^{-1}$  at  $\Gamma_{\max} = 4.7 \text{ sites nm}^{-2}$ . X-Zn<sub>0.5</sub> displayed moderate selectivity over X-Na<sup>+</sup>. The model is more sensitive to area fractions occupied by surface types than to particular values of inner-sphere  $K_{\text{ads}}$ . Removal of TLM1 outer-sphere Zn species resulted in bad fits at pH > 4.5.

Calculation of Zn adsorption isotherms at  $67.5 \text{ mg L}^{-1} \text{ MnO}_x$ ,  $I = 0.2 \text{ m NaCl}$ , pH 7.0 and 7.5 showed that the strongest Type 3  $>OZn^+$  species holds >99% of total Zn at  $Zn_{\text{aq}} \leq 10^{-9} \text{ m}$ . TLM2 surface gets saturated at  $10^{-6} \text{ m Zn}_{\text{aq}}$ ; but TLM1 saturation is not completed even at  $10^{-3} \text{ m Zn}_{\text{aq}}$ . 97% Zn is still

adsorbed at  $10^{-4} \text{ m Zn}_{\text{aq}}$ . While at  $I = 0.01 \text{ m}$  and  $10^{-5} \text{ m Zn}_{\text{aq}}$  zinc is bound mainly as outer-sphere and ion-exchange species, less than 3% Zn was held on X surface type at  $I = 0.2 \text{ m}$ .

## Discussion

It follows that composite GEM multi-site multi-surface models such as the one developed in this study can potentially account for particle- and solution- concentration effects of trace metal sorption on  $\delta$ -MnO<sub>x</sub> and similar phases in a wide range of solid, electrolyte and metal concentrations. In such cases, 'patches' of amphoteric surface may behave similar to surfaces of related simple oxides, e.g.  $\gamma$ -MnO<sub>2</sub> with properties, in turn, similar to that of TiO<sub>2</sub> (cf. Tamura *et al.*, 1996). If so, then  $pK_{\text{ads}}$  measured at high  $f(\text{O}_2)$  and low surface coverage on  $\gamma$ -MnO<sub>2</sub> and TiO<sub>2</sub> plus microscopic data for  $\gamma$ -MnO<sub>2</sub> surface can be directly used for predicting metal sorption on natural Mn oxides in both lacustrine and marine environments. Future experimental studies of surface acidity and metal sorption on the non-stoichiometric MnO<sub>x</sub> phases should focus on influence of redox conditions and on possible competition effects between adsorbed Mn<sup>2+</sup> and trace metals. Rigorous model interpretations of such experimental data should include explicit account for solid carrier solubility, site heterogeneity, ion exchange and outer-sphere complexation.

## References

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