

Supplementary material

Particle aggregation, pH changes and metal behaviour during estuarine mixing: review and integration

Luke M. Mosley^{A,C} and Peter S. Liss^B

^ASchool of Biological Sciences, University of Adelaide Waite Campus, PMB 1, Glen Osmond, SA 5064, Australia.

^BCentre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK.

^CCorresponding author. Email: luke.mosley@adelaide.edu.au

Modelling description and input file parameters

The metal partitioning and speciation following mixing of river water with seawater in estuaries was simulated using the computer program Visual MINTEQ (G. P. Gustafsson, see <https://vminteq.lwr.kth.se>, accessed 22 August 2019). Visual MINTEQ is a geochemical model capable of computing equilibria among the dissolved, adsorbed, solid, and gas phases in water. The initial model input concentrations (pH, pe, alkalinity, major ions, dissolved organic carbon (DOC), dissolved oxygen, and <0.45- μ m metal concentrations), in the mixtures assumed conservative mixing of the river water and seawater end members (see below for end member concentrations). In each mixture, Visual MINTEQ was used to calculate the equilibrium concentration of dissolved inorganic, dissolved organic, and solid phases (Mosley *et al.* 2015).

The pH was fixed in the model based on the results of the inorganic carbon-pH model (see Fig. 2, Case 2). The modelling of metal binding to hydrous ferric oxide (HFO) was included in the model using the approach of Dzombak and Morel (1990) which is included in Visual Minteq. The modelling of metal complexation with organic ligands was assessed using the NICA–Donnan model (Kinniburgh *et al.* 1999) incorporated in Visual MINTEQ. A key rationale for using Visual MINTEQ has the ability to readily assess multi-site dissolved metal-organic matter complexation and HFO binding simultaneously (Mosley *et al.* 2015). The constants used in the NICA–Donnan model were the default ones from Milne *et al.* (2001) for all metals. As per Sjöstedt *et al.* (2010) the ratio of active dissolved organic matter (DOM) to DOC in Visual MINTEQ was 1.65 (assuming that DOM consists of 50% carbon by weight, the value of 1.65 implies that 82.5% of the DOM was ‘active’ with regard to proton and metal binding) with 100% of the active DOM/DOC considered to be fulvic acid. Considerable variation has been shown to exist in NICA–Donnan model parameters for various samples of fulvic acid (Groenenberg *et al.* 2010) and this creates some uncertainty in regard to using default values for predicting organic-metal complexation.

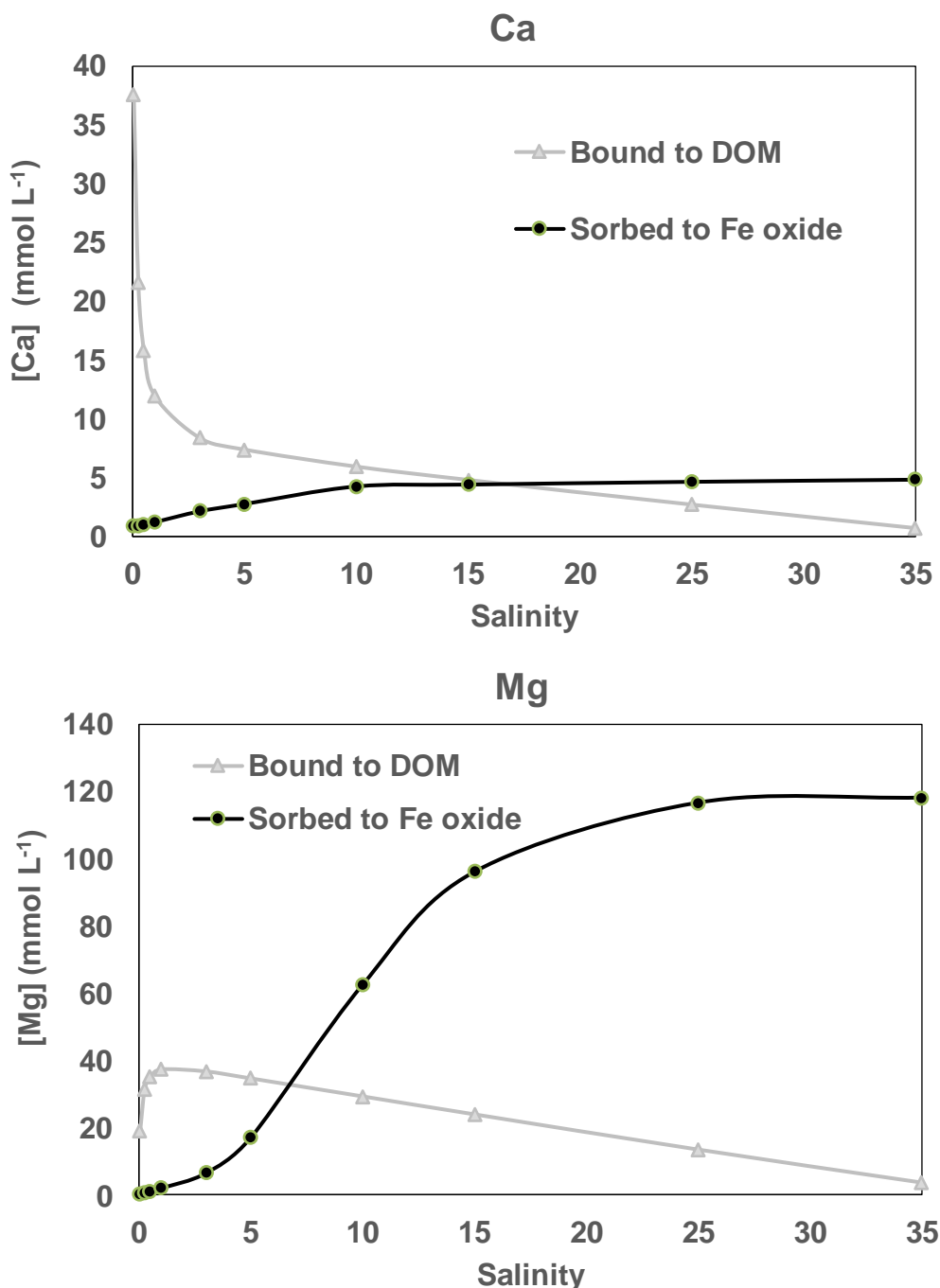


Fig. S1. Binding of calcium to dissolved organic matter and hydrous ferric oxide in the geochemical model.

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