# Metal Release from Contaminated Sediments during Resuspension Events

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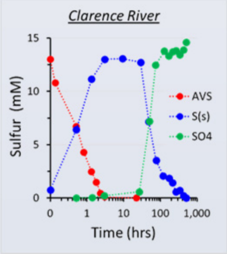
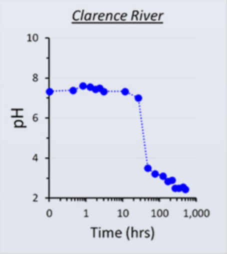
## ABSTRACT

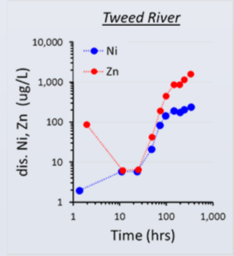
The presence of sulphides in sediments has been shown to play an important role in sequestering metals (e.g., Cd, Cu, Ni, Pb, Zn) and in limiting metal bioavailability. This effect has been considered in regulatory decision-making through static or “snap-shot” measures of simultaneously extractable metals (SEM) and acid volatile sulphide (AVS) ratios. A potential weakness in this approach is the oxidation of metal sulphides and associated changes in metal bioavailability that are likely to occur during sediment resuspension events (e.g., due to episodic storms, propeller-induced disturbances and dredging activities). A reactive-transport model was therefore developed using the TICKET framework and was applied in evaluating metal release during resuspension in laboratory chamber studies. Overall results show that the TICKET model provides an appropriate framework for evaluating the complexities of metal behaviour during resuspension events. Results also show that metal release and bioavailability during resuspension are intricately linked to metal sulphide oxidation rates, pH buffering, and metal binding to natural organic matter and oxide surfaces. Based on these findings, SEM/AVS, BLM and other regulatory assessment tools should be considered in a more dynamic framework to properly address the potential impacts of metals during sediment resuspension events.

## PRELIMINARY DATA EVALUATION

A number of laboratory chamber studies were performed to evaluate metal release during resuspension of anoxic sediments. Results from Burton et al. (2006, 2009) are given below.







*Short-term Response*: FeS(s) oxidation is fast; S(-II) is oxidized abiotically to the $S_8^0(s)$; pH remains relatively constant ; metal release is minimal.

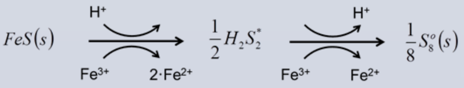
*Longer-term Response*: $S_8^o(s)$ is oxidize biologically to $SO_4^{2-}$ ; pH drops dramatically; increases in dissolved metal concentrations are typically associated with decreases in pH

## MODEL DEVELOPMENT

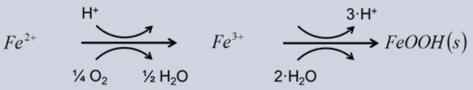
A coupled kinetic-equilibrium-transport model was developed to evaluate the potential impacts of metal release and toxicity associated with short-term resuspension events. The model is based on the TICKET computational framework (Farley et al., 2008) and includes:

- Metal sulfide oxidation kinetics (Schippers and Sand, 1999)
- Fe(II) oxidation kinetics (Stumm, 1992)
- Equilibrium descriptions for metal complexation and other precipitation/dissolution reactions (MINTEQA2 database)
- Metal binding to hydrous iron oxide (Dzombak and Morel, 1990)
- Metal binding to NOM (WHAM VII; Tipping et al., 2011)

*FeS(s) and MS(s) Oxidation: Polysulfide Mechanism (Schippers and Sand, 1999)*



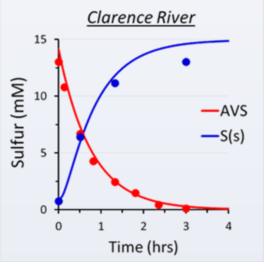
*$Fe^{2+}$ Oxidation (Stumm, 1992)*

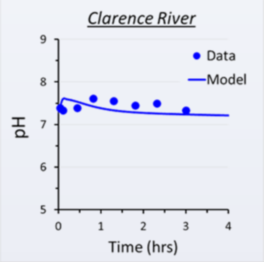


$Fe^{2+}$ oxidation kinetics are a function of $Fe^{2+}$ speciation ($Fe^{2+}$, FeOH, $Fe(OH)_2$, $(\equiv FeO)_2Fe^{II}$). Kinetic rate coefficients for $Fe^{2+}$ oxidation are taken directly from Stumm (1992).

## MODEL CALIBRATION

Model calibration for AVS oxidation was performed using Clarence River sediment (Burton et al., 2009).

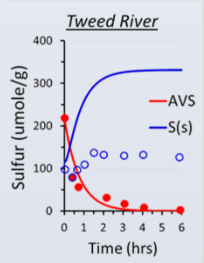


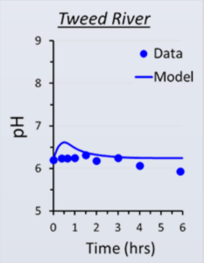


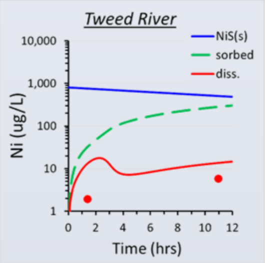
*Calibration Results*: $k_{FeS}$ = 1.3 / hr ; $k_{H2S2*}$ = 13 / hr; pH calculation was used as a final check of model performance; pH remains relatively constant at ~7.3 due to buffering by Siderite [$FeCO_3(s)$] precipitation / dissolution.

## MODEL VALIDATION

Model validation was performed using Tweed River sediment (Burton et al., 2006). $Fe^{2+}$ oxidation kinetics were again taken directly from Stumm (1992), FeS(s) oxidation kinetics were determined from model calibration (see Clarence River results above), and NiS(s) oxidation kinetics were taken as 0.042 / hr based on previous studies by Carbonaro et al. (2005).







*Validation Results*: Laboratory data for sulfur do not provide a closed mass balance; $S_8^0(s)$ data are therefore questionable; pH is again calculated to remain relatively constant but at pH of ~6.2 due to buffering by hydrous iron oxide (HFO) proton exchange reactions; dissolved Ni concentrations remain relatively low, however, NiS(s) is being oxidized and released Ni is largely sorbed to freshly precipitated HFO.

*Additional Modeling Studies*: Additional studies are being performed using laboratory resuspension data from the Anacostia River (USA), Lake DePue (USA) and Portland Harbor (USA).

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## ACKNOWLEDGEMENTS

This work is support by a grant from the U.S. Department of Defense, Strategic Environmental Research and Development Program (SERDP), and is being performed in collaboration with The University of Michigan and the U.S. Army Corps of Engineers Engineering Research and Development Center (ERDC).