PART II. THE MODELING EFFORT: Louis Thibodeaux

This HSRC project is divided into two interrelated parts. The Rice University group is conducting the laboratory test aimed at simulating key elements fo the metal release process following dredging resuspension of bed-sediment residing solid particles. The LSU group is attempting to develop a theory-based simple and practical model to track the metal release process kinetics. Data generated by the Rice University group will be utilized by the LSU group in model development, refinement and testing. The overall product will be an algorithm to estimate metal concentrations in solution emanating from the mud clouds produced during dredging. Being able to predict the concentrations of metals is key in evaluating aquatic organism exposure levels and uptake quantities both in the water column and in the bed-sediment surface layers..

APPROACH TO MODEL DEVELOPMENT

A bi-phasic empirical model for organic chemicals released from suspended particles, first proposed by Karickhoff in 1980, has been successfully used by numerous investigators to interpret the release fractions and kinetics. A theory-based version of the bi-phasic model referred to as the "Hockey Stick Model" was developed and is being used in interpreting the empirical one. This HS model is a lumped-parameter version of the more complex model being developed by Center researchers Reible-Fleeger. The progress achieved in development and testing of the Hockey Stick model is presented as a meeting poster (Birdwell/Thibodeaux) and a manuscript is in the final stages of preparation(Birdwell, et al.2003). Much is known about the aquatic chemistry behavior of HOCs; they are suspected to have simple and traceable desorption kinetics and thermodynamics of release. A model based on this suite of compounds provides a basis upon which to build a metal release kinetic process. The latter is suspected to be much more complex for the individual metals and to vary considerably between metals.

Based on published material an extensive data-base exist for the desorption kinetics on numerous HOCs and application or the empirical bi-phasic model. Detailed results of the analysis of these data are presented in the Birdwell/Thibodeaux poster.

Key findings are:

1. The range of numerical values of the fast and slow desorption rate constants are very different numerically but remarkably uniform. They appear to be independent of the sediment particle sizes and chemical K_{OC}:
2. The fraction desorbed that is loosely bound or tightly bound appears to be very sediment specific.

Key developments of the "Hockey Stick Model" are as follows:

1. A two adsorbent patch chemical release model based of adsorbate diffusion correctly mimics the general shape of the bi-phasic model.
2. Both solid phase diffusion and porewater diffusion mechanism seemed to be involved in the release kinetics process. Their relative role and the importance of the equilibrium desorption is still under investigation.

Taken together these combined findings suggest that although the kinetic parameters for the slow and fast fractions may be estimated a priori, because the quantities are limited numerically and have a theoretical base, the fraction of each in the sediment organic matter must be obtained by experimental testing

At this juncture it appears that the organic chemical release model will provide a base upon which to commence to build a metals release one. However, based on the lab results it seems clear that three versions of the model will be needed. The categories are 1) Mn, Zn, Ni, Co, 2) Fe, Pb, As, and 3) Cu. These categories are based on the results of the DRET developed by the USACE for simulating chemical release during dredging operations. It involves solid-to-water ratios, typically 4 to 10g per liter in aerated and N_2 purged reaction vessels. The test simulates the short-term and long-term release process. The short-term captures the dredge head generated mud cloud while the long-term captures the redeposited down current surficial layer release and other fate(i.e., degradation, co-precipitation, etc.) process. Changes in pH and Eh at the reaction time of 24 hours seem to define the short and long term time periods. Clearly, the overall release is very complex and needs to be studied in a systematic approach considering the time, personnel, and economic constraints.

The plan for year 03 is to focus on the short-term release process. The following goals will be pursued:

1) Apply the HS model to the kinetic data for the # 24 hour time period when pH remains fairly uniform and conditions are aerobic. A working hypothesis at this juncture is that the quick release/mixing of

particles and water near the dredge head and in the departing mud cloud maintains near constant (i.e., background water) pH and O_2 conditions. Data for anionic conditions will be factored in as well. The outcome of using this data will be more or less, a "litmus test" for the appropriateness of the HS model for use in metals release. However a review of the available short-term release data appears to support the general HS model approach.

2) In conjunction with Rice University group the development of a modified DRET test will be explored. The build-up of the "chemical soap" in the DRET test solution does not truly mimic the continuing mixing/dilution of freshwater with the particle mass. In other words dilution occurs with time as the mud cloud moves downstream; it does not in the DRET experiment. Providing an infinite metal co-ion/counter ion sink by introducing an ion exchange resin into to the DRET protocol may mimic this dilution process and yield more realistic release kinetics while maintaining a fixed solids-to-water source strength ratio. This control of this s/w parameter is key for an unambiguous interpretation of the release kinetics.

Beyond year '03 the LSU PI's will becoming involved with the USACE in another research project having to do with collecting field data at environmental dredging sites. The focus of this Dredging Operations Environmental Research (DOER) project is on the emissions of organic chemicals to air generated by the dredging operations and related processes, however the water column concentration data is a key observable. The chemical release kinetics, particles-to-water, are needed as well for the DOER work so that the objectives of acquiring field data on metal concentrations in water for the HSRC project in Years 03 and 04 may dove-tailed nicely into the DOER project plans.

Current Project Amounts and periods:

LSU group year '01	$23,651.00
LSU group year '02	$29,400.00

Future project request and period:

LSU group year '03	$30,000.00