VOLATILIZATION OF CONTAMINANTS FROM SUSPENDED SEDIMENT IN A WATER COLUMN DURING DREDGING

Raghunathan Ravikrishna, Kalliat T. Valsaraj, Louis J. Thibodeaux, Gordon A & Mary Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA, USA.
Cynthia B. Price, James M. Brannon, Environmental Laboratory, U.S. Army ERDC, Vicksburg, MS, USA.
Sally Yost, Dyn Tel Corporation, Vicksburg, MS, USA.

ABSTRACT
Remedial dredging of contaminated bed sediments in rivers and lakes results in the suspension of sediment solids in the water column. This can potentially be a source for volatilization of hydrophobic organic compounds (HOCs) associated with the sediment solids. An oscillating grid chamber was used to simulate the suspension of contaminated sediments and the measurements were recorded for evaporative flux, water concentration, total suspended solids and particle size distribution as a function of time. An unsteady state mathematical model was developed to describe contaminant desorption from sediment to water and evaporation from the water column. Comparison of the model and experimental data suggested that a realistic determination of the total suspended solids concentration that can be input into the model was the most critical parameter for predicting contaminant volatilization rates during dredging.

RÉSUMÉ
Le dragage à des fins de restauration des sédiments de lit contaminés des rivières et des lacs résulte dans la resuspension de particules dans la colonne d'eau. Ceci peut représenter une source potentielle pour la volatilisation des composés hydrophobes organiques (les HOCs) associés aux solides des sédiments. Une chambre de grille oscillante a été utilisée afin de simuler la resuspension de sédiments contaminés, les mesures enregistrées sont le flux évaporatif, la concentration en eau, les solides totaux et la distribution granulométrique des particules en suspension et en fonction du temps. Un modèle mathématique a été développé afin de décrire la désorption de contaminants des sédiments à l'eau et l'évaporation de l'eau de la colonne. La comparaison du modèle avec les données expérimentales suggèrent qu'une détermination réaliste de la concentration de solides en suspension rentrant dans le modèle était le paramètre le plus critique afin de prédire les taux de volatilisation du contaminant pendant le dragage.

1. INTRODUCTION

Contaminated sediments are a significant environmental problem in the United States and other countries around the world. Dredging "hot spots" of contaminated sediment is one of the active remediation options. The U.S. Army Corps of Engineers dredges large volumes of contaminated sediments annually in the United States. However, dredging leads to some degree of generation of suspended solids around the location of dredging. Compounds associated with the suspended sediment solids redistribute among the water, suspended solids, organic matter and suspended colloids in the water column. This may cause a portion of the aqueous contaminants to volatilize and pose an air pollution concern to both workers and nearby residents living along the shoreline. Currently, there is very little field monitoring or laboratory data that can be used to assess the air emissions resulting from dredging operations and to validate any mathematical model that can predict contaminant release at a dredge site (Price et al., 2001). An oscillating grid flux chamber was used in this study to simulate conditions of solids suspension near a dredge-head and to measure the volatilization rates of chemical associated with the suspended solids. This device has been used in past experiments in our laboratory to resuspend bed sediment using the energy generated by the oscillating grid, to the bed sediment (Valsaraj et al., 1997). In this study, the oscillating grid was used to provide the initial mixing force that may be present at a dredge-head. This simulates a scenario after the solids resuspension has occurred. The objectives were to study the dynamics of the suspended solids and the chemicals associated with them after the resuspending force is removed. In this manuscript, we report the air emissions of selected polynuclear aromatic hydrocarbons (PAHs) under different controlled suspended sediment concentrations using laboratory-inoculated and field-contaminated sediments in the oscillating grid flux chamber. This information can be valuable to evaluate predictive mathematical equations addressing chemical release to water and subsequent volatilization of the chemicals from the water column to air during dredging operations.

2. MATERIALS AND METHODS

2.1 Sediments and Contaminants

Two sediments were used in the study one - a local uncontaminated sediment from the University Lake (UL) , Baton Rouge and two - an aged field contaminated sediment obtained from the Indiana Harbor Canal (IHC). The UL sediment was inoculated with phenanthrene (PHE), and pyrene (PYR) at concentrations of 54 and 50 mg/Kg respectively. The field IHC sediment contained a variety of

2nd International Symposium on Contaminated Sediments
2ième Symposium International sur les Sédiments Contaminés

Physical Characterization / *Caractérisation physique*

PAHs at various concentrations, but phenanthrene (PHE) with a concentration of 51 mg/Kg, is the only tracer shown in this paper. The physical properties of the sediments and the chemicals are given elsewhere (Ravikrishna et al., 2002).

2.2 Oscillating Grid Flux Chamber

The oscillating grid flux chamber, used in this study, was a hollow cubical container 50 cm on each side, constructed of ¾" Plexiglas. The "oscillating" grid consisted of an 8 x 8 mesh made of 1.27-cm square aluminum bars with a bar length of 49 cm. The spacing between the bars was 6.25 cm. A motor attached to the grid shaft controlled vertical oscillation frequencies of the grid from 60 to 600 rpm. A vacuum pump pulled air through the flux chamber, across the water surface and through a bed packed with XAD-2 resin (from SUPLECO®) at the chamber outlet. The flow of air across the water surface was directed through a perforated Teflon tube placed 1.5 cm above the surface of the water. Sampling ports were provided on the front of the chamber at three different heights, for the collection of aqueous samples.

2.3 Experimental Design

After the oscillating grid was set in motion, sediment was introduced into the chamber filled with about 95 liters of water, in the form of a slurry. The grid oscillation was stopped after two hours and quiescent conditions were maintained for the rest of the experiment. Two experimental runs were performed with University lake sediment, each with the same amount of sediment but with two different airflow rates (12 and 7 L/min). Airflow was provided continuously throughout the experiment except for during the times of sample collection. Three experimental runs were performed with the Indiana Harbor Canal sediment, each with a different sediment mass resulting in different initial suspended solids concentrations but with the same air flow rate (12 L/min).

2.4 Air and water samples

Contaminant flux from water to air were measured by desorbing the PAHs trapped in the XAD-2 resin (Supelco Inc., PA) bed attached to chamber exit with acetonitrile. These traps were replaced every air sampling interval. The flux was computed from the mass of contaminants desorbed, the surface area and the time interval of sampling. Water samples collected were split into different sub-samples to determine the total suspended solids (TSS) concentration (EPA Standard Method 148-A), PAH concentrations (EPA Standard Method 8270), particle size distribution of suspended solids using a optics based Particle Size Analyzer (Microtrac®) and dissolved organic carbon (DOC) using a Shimadzu® TOC analyzer.

3 RESULTS AND DISCUSSION

3.1 Total Suspended Solids (TSS)

The TSS values for the UL sediment decreased from 498 and 270 mg/L after 15 and 60 minutes of mixing and eventually to 63 mg/L after 144 hours of quiescent settling. In the IHC experiments, when 960 g of sediment was added, the TSS declined from 2900 mg/L after 2 hours of mixing to 390 mg/L at the end of 144 hours of quiescent settling. For IHC-2, with lesser sediment mass input, the TSS value was 415 mg/L after 2 hours of mixing and decreased to 40 mg/L after 144 hours of quiescent settling. The University lake and Indiana harbor canal sediments have average particle diameters of 106 μm and 27 μm respectively based on their particle size distributions. Particle size distribution of the suspended sediment solids and the measurement of total settled sediment solids showed that about 90% of the solids introduced into the water column had settled within the first 30 minutes. The very fine sediment solids are retained in the water column for a substantially longer period of time.

3.2 Measurements with University Lake Sediment

Figure 1 shows the flux and aqueous concentration of two PAHs inoculated into UL sediment at at the end of several time intervals and for two different air flow rates. The behavior of the fluxes in both these cases is similar - high flux in the beginning and decreasing with time and the magnitude of fluxes decreasing with increasing hydrophobicity and decreasing Henry's constant. Aqueous phase concentration measurements were obtained after correcting for the dissolved organic carbon present in the filtered samples. . The DOC for the filtered UL samples varied between 13 and 17 mg/L. The qualitative observations from the experimental results of the flux and aqueous concentration were that, higher air flow rates resulted in higher evaporation rates. The calculated experimental average mass transfer coefficients (k_{WA}) for the 12 L/min UL experiment were 0.24 cm/hr and 0.02 cm/hr for PHE and PYR respectively. For the 7 L/min experiment, the values of k_{WA} were 0.063 cm/hr and 0.007 cm/hr for PHE and PYR respectively. The overall mass transfer coefficients were calculated by dividing the measured flux by the measured aqueous phase concentrations.

3.3 Measurements with Indiana Harbor canal sediment

Figure 2 displays the flux and aqueous phase concentration of PHE during and after mixing of the IHC sediment. The figure shows that higher suspended solids concentrations caused higher aqueous phase concentrations which resulted in higher air emission fluxes. The qualitative trend is similar to that displayed in the UL sediment measurements. The average experimental mass transfer coefficient was 0.24 cm/hr for PHE. This k_{WA} was found to

2nd International Symposium on Contaminated Sediments
2ième Symposium International sur les Sédiments Contaminés
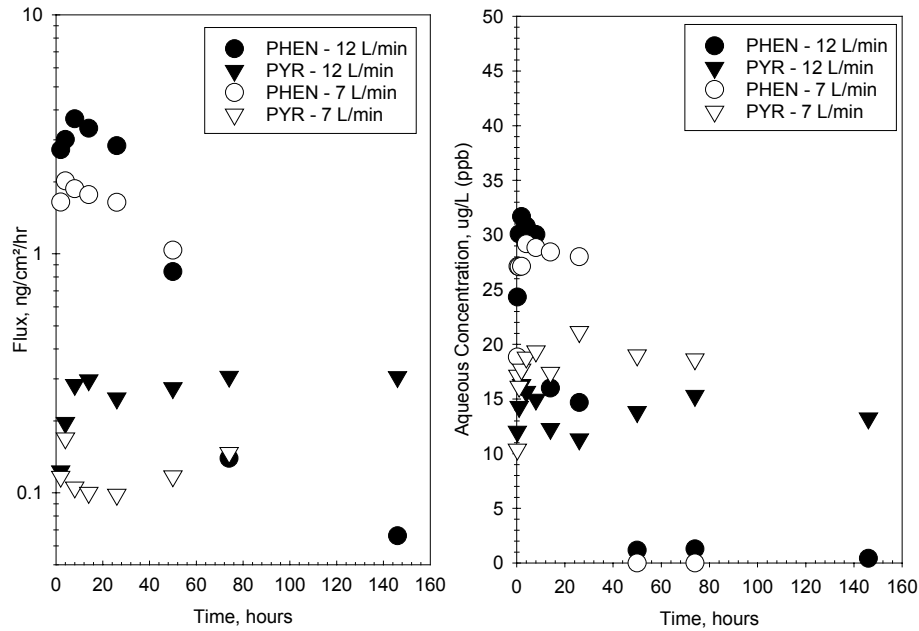
Physical Characterization / *Caractérisation physique*

Figure 1. PAH measurements in University lake sediment

be similar to that from the UL experiments. Naphthalene and acenapthene (not shown in the graphs) showed higher fluxes, aqueous concentrations and higher k_{WA} than PHE since these compounds are marginally more volatile than PHE. Volatilization from the surface is a two-step process – desorption from suspended solids to water and subsequent transport to air. The desorption rates are dependant on the hydrophobicity of the compound as measured by the organic-carbon normalized sediment/water partition constant (K_{oc}). For the compounds considered the K_{oc} are in the order PYR > PHE. The desorption rates are expected to be in the order PHE > PYR, if the solid phase concentrations are similar, and should be reflected in the aqueous concentration.
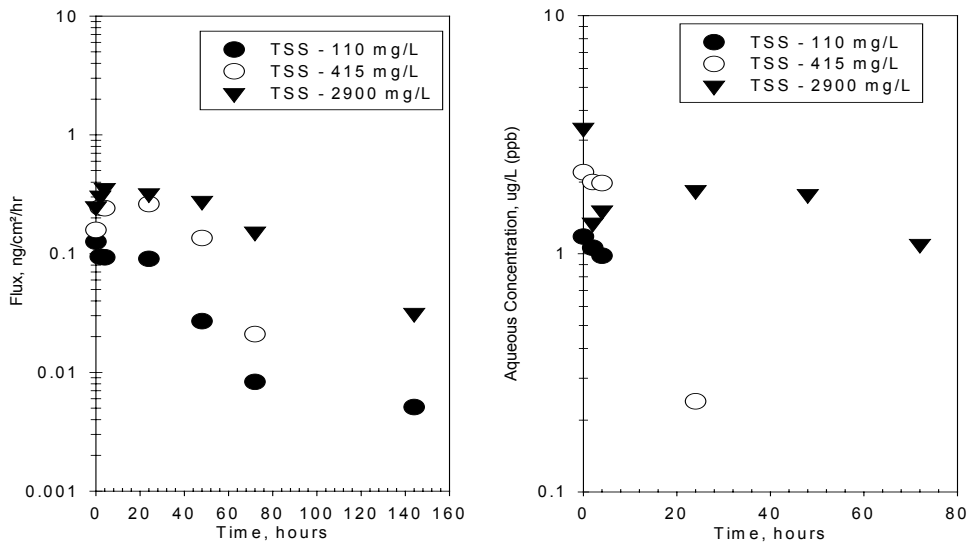

Figure 2. PAH measurements in Indiana Harbor canal sediment

4. MODEL COMPARISON

Evaporation of contaminants from the suspended sediment solids is modeled in two sequential processes - a) desorption from the suspended solids and b) evaporation from the water column and described by equations 1 and 2

Suspended Solids:

$$\frac{d}{dt}(W_S \rho_{SS}) = \frac{-6\rho_{SS}k_{SW}}{\rho_p d_p}(\frac{W_S}{K_d} - C_W) \qquad [1]$$

Aqueous Phase:

$$\frac{d}{dt}C_w = \frac{6\rho_{SS}k_{SW}}{\rho_p d_p}(\frac{W_S}{K_d} - C_W) - \frac{k_{WA}}{h}C_W \qquad [2]$$

where $W_s\rho_{ss}$, the dependent variable is the contaminant concentration associated with the solids; where W_s is the sediment loading (mg/kg) and ρ_{ss} is the total suspended solids concentration (mg/L). C_w is the 'free' aqueous concentration of the contaminant. The model assumes constant total suspended solids (TSS) and mean particle diameter in suspension and uniform aqueous phase concentration. Contaminant flux to air is given by $N_A(t) = k_{WA}(C_W - 0)$, assuming clean inlet air with the initial conditions of $C_W = 0$ (at time t = 0) and initial bed sediment loading (Ws = W_S^0). The desorption rate, k_{SW} is a function of

R, the particle size, K_d, the sediment-water partition constant, ρ_p, particle density, $D_{A,e}$ is the effective diffusivity. The overall water-air mass transfer coefficient was extracted from the experimental data for the university lake sediment (Ravikrishna et al., 2002). The model described by Equations (1) and (2) was compared with the experimental results obtained for PYR for 7 L/min air flow rate experiments with the University Lake sediment (shown in figure 3). The semi-empirical model treatment required adjustment of the initial TSS to fit the experimental data. When the sediment is suspended, the larger solids rapidly settle leaving the bulk of the smaller particles in suspension. It is well known that the hydrophobic organic chemicals sorb on to the organic matter. It is also known that these organic matrices are very small particles that may take a very long time to settle. Based on the above arguments, using a transient TSS based on settling velocities alone may not be sufficient to accurately predict contaminant concentrations associated with the suspended solids. It is important to estimate the contaminant concentration based on sediment solid size fractions. In terms of the model described in this manuscript, this translates to an 'effective' initial TSS value. Future developments of the model may include this aspect in the simulation of contaminant release from suspended solids occurring at a dredge site. The model comparison is discussed in detail in a recent publication (Ravikrishna et al., 2002).
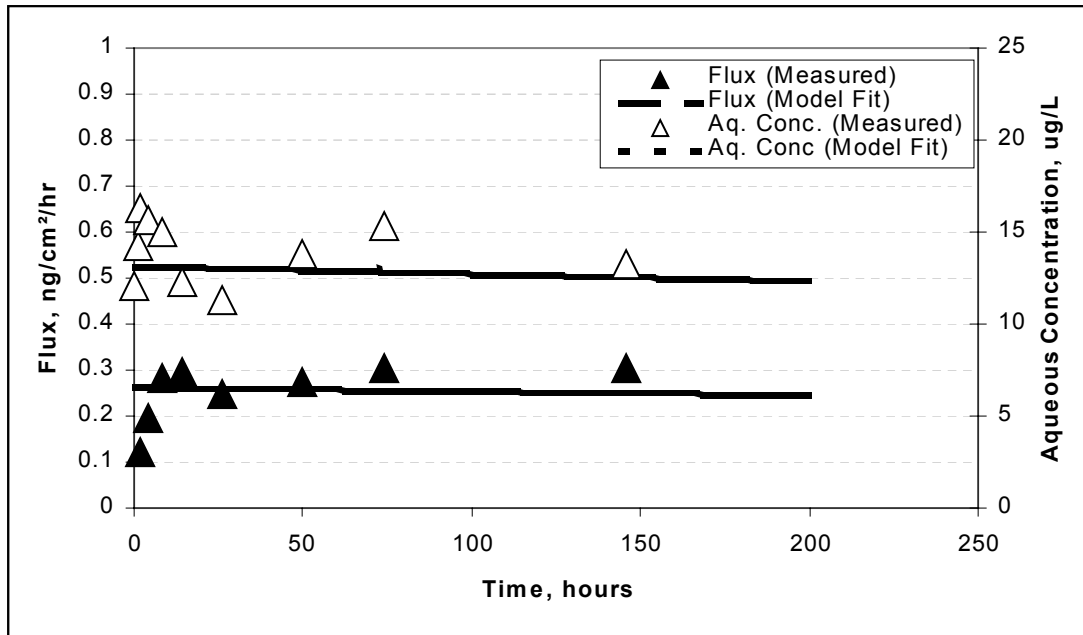

Figure 3. Comparison of experimental flux and aqueous concentration values to model fit estimates

REFERENCES

National Research Council. Contaminated Sediments in Ports and Waterways: Cleanup Strategies and Technologies. National Academy Press. Washington D.C. 1997

Price, C., Brannon, J., Yost, S., Sanchez, F., Thibodeaux, L., Valsaraj, K., Ravikrishna, R. Volatile Losses from Resuspended Dredged Material. Technical Note EEDP-02-30; U.S. Army Corps of Engineers Engineering Research and Development Center, Vicksburg, MS. 2001

Valsaraj, K. T.; Ravikrishna, R., Orlins, J. J.; Smith, J. S.; Gulliver, J. S.; Reible, D. D.; Thibodeaux., L. J. 1997. Sediment-to-air mass transfer of semi-volatile contaminants due to sediment resuspension in water. Advances in Environmental Research, Vol 1, pp. 145-156.

Ravikrishna, R., Yost, S., Price, C. B., Valsaraj, K. T., J. M. Brannon, Thibodeaux, L. J. 2002., Volatilization of contaminants from suspended sediment in a water column during dredging. Journal of the Air and Waste Management Association, Vol 52, pp. 1214-1228.