### Environmental Effects of Dredging Technical Notes

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### Sediment Organic Matter Quality Effects on Pore Water Contaminants

**PURPOSE:** This technical note examines the effect of sediment organic matter quality on pore water contaminants. Information obtained in the laboratory at the U.S. Army Engineer Waterways Experiment Station, and elsewhere, is included.

**BACKGROUND:** Over the past 10 years, the U.S. Environmental Protection Agency has pursued development of single-chemical sediment quality criteria (SQC). Equilibrium partitioning of neutral organic chemicals between the organic carbon fraction of bedded sediments and the interstitial water of the sediments provides the theoretical basis for the most popular approach to development of SQC. The solution phase of the chemical in equilibrium with the sediment is considered to represent the bioavailable fraction and to enable the conversion of existing water quality criteria (WQC) into SQC or sediment quality standards.

In this approach, sediment total organic carbon (TOC) is considered to be the primary sediment phase accounting for sorption of neutral organic chemicals, and concentrations of these chemicals are therefore normalized to the TOC fraction. A chemical-unique partition coefficient ( $K_{OC}$ ), applied to the TOC-normalized chemical concentration, is used to estimate the solution-phase concentration for calculation of the bioavailable fraction, which is then compared with WQC.

One assumption made when deriving SQC from equilibrium partitioning is that all organic carbon will exhibit consistent partitioning behavior. The implicit assumption is that all sediment organic carbon has the same composition, regardless of source.

The U.S. Army Corps of Engineers is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as the utility of equilibrium partitioning approaches for predicting toxicity. In the equilibrium partitioning approach, toxicity is assumed to be related to freely dissolved pore water concentrations of contaminants.

The study described in this technical note examined the assumption that all sediment organic carbon behaves similarly.

**INTRODUCTION:** Concentrations of truly dissolved organic contaminants in sediment pore water are regarded as the contaminant fraction available for organism uptake (Landrum and others 1985; Kukkonen, McCarthy, and Oikari 1990). If all sediment organic carbon does not exhibit comparable partitioning behavior for nonpolar organic contaminants, predicted pore water concentrations will not correspond to actual pore water concentrations.

Evidence suggests that  $K_{OC}$  values increase as the aromaticity of sediment organic matter increases (Garbarini and Lion 1986; Chiou and others 1987; Gauthier, Seitz, and Grant 1987; Grathwohl 1990; Murphy, Zachara, and Smith 1990; Zhou, Rowland, and Mantoura 1995).

Nonpolar organic contaminants such as polychlorinated biphenyls (PCBs) and polyclic aromatic hydrocarbons (PAHs) may also differ in partitioning behavior in the same sediment, depending upon the composition of the organic carbon. Kile and others (1995) reported much higher values of  $K_{OC}$  for sediments impacted by anthropogenic contamination than for pristine sediments. Dredged sediments, by virtue of their location, are almost always subject to anthropogenic inputs.

The  $K_{OC}$  values for a particular compound have been reported to vary widely between sediments (Schrap and Opperhuizen 1989; Brannon and others 1993, 1995a). Similar wide variations in  $K_{DOC}$  for sediment pore waters from different sediments have also been observed (Chin and Gschwend 1992, Brannon and others 1995b). These results imply that partitioning of nonpolar organic contaminants to sediments is much more complex than assumed in the SQC model. Both the form of the contaminant and the organic matter in the sediment have been shown to affect partitioning in ways that are not easily predicted based on sediment organic carbon and contaminant concentrations.

If organic matter quality differs between sediments and the differences affect partitioning, then many of the assumptions used in modeling interactions between nonpolar organic contaminants in sediment and pore waters in aquatic systems are invalid. This study was conducted to examine the impact that changes in sediment organic carbon functionality, including aromaticity, have on pore water concentrations of nonpolar organic contaminants.

**ORGANIC CARBON CHARACTERISTICS:** Partitioning, or distribution of a hydrophobic organic compound between sediment organic carbon and pore water at equilibrium, is mathematically described as follows:

$$C_{W} = C_{OC} / K_{OC}$$
(1)

where

 $C_W$  = truly dissolved aqueous phase concentration (mg/L)

 $C_{OC}$  = concentration of contaminant sorbed to the sediment organic carbon (mg/kg)

 $K_{OC}$  = distribution coefficient (L/kg)

This relationship forms the basis for equilibrium partitioning-based SQC (DiToro and others 1991).

Isolation of humic acids from soils and sediments, followed by <sup>13</sup>C nuclear magnetic resonance (NMR) (Davis 1993) or Fourier transform infrared (FTIR) analysis (Davis 1993, Brannon and others 1997), indicates that the aromatic character of soils and sediments varies by a factor of 2 or 3 (Table 1). The <sup>13</sup>C NMR method provides a measure of the percentage of aromatic functional groups, while the FTIR method coupled with the internal standard facilitates quantitative comparison of peak intensities between different humic sources. Other methods have also been used to estimate the aromatic character of isolated humic acids (Davis 1993, Johnston and others 1994), but the data presented in Table 1 are representative of the spread in aromatic carbon characteristics.

Table 1. Measures of aromatic carbon in soil and sediment organic carbon			
Method	Relative aromatic peak height	% Aromatic functional groups	Reference
<sup>13</sup> C NMR		23.6 - 47	Davis (1993)
<sup>13</sup> C NMR		20 - 34	Gauthier, Seitz, and Grant (1987)
FTIR peak height ratios <sup>1</sup>	2.21 - 5.76		Brannon and others (1997)
FTIR peak height ratios <sup>1</sup>	0.39 - 1.13		Davis (1993)

<sup>1</sup> Peak height ratios for humic substance aromatic carbon (1,600 cm<sup>-1</sup>) functional groups. Peak heights are normalized to the response of the internal standard (potassium thiocyanate, KSCN) at 2,050 cm<sup>-1</sup> and are in units of mg KSCN/mg humic C.

Results from soil and sediment organic carbon characterizations are mirrored by results of adsorption experiments. Rutherford, Chiou, and Kile (1992) reported that the polarity effect of a sample of soil organic matter on the organic carbon-normalized partitioning of various nonpolar solutes can be measured by determining the partition coefficient of a single nonpolar solute, when compositional analysis of organic carbon is not available. These investigators reported that the calculated variation of organic carbon normalized partitioning was a factor of approximately 3, in agreement with the variability of the results reported in Table 1.

Studies that directly compared <sup>13</sup>C NMR and FTIR measures of organic carbon aromaticity to solute partitioning behavior showed that partitioning varied by a factor of 6 (Gauthier, Seitz, and Grant 1987) or a factor of 4 (Brannon and others 1997), for a roughly twofold variation in soil and sediment organic carbon aromaticity. Rutherford, Chiou, and Kile (1992) observed variability of approximately 3, for a roughly twofold change in aromatic carbon. These results indicate that measured values of organic carbon normalized partitioning can result in a three- to sixfold change, for a twofold change in organic carbon aromaticity. Therefore, pore water concentrations of nonpolar organic contaminant would differ markedly for sediments containing the same percentage of organic carbon but varying organic carbon aromaticity.

Results for organic carbon normalized partitioning are generally derived from adsorption studies (Gauthier, Seitz, and Grant 1987; Rutherford, Chiou, and Kile 1992; Davis 1993; Brannon and others 1997). It is becoming increasingly evident, however, that desorption of nonpolar organic contaminants from natural soils and sediments exhibits different behavior from that observed in adsorption studies. Fu, Kan, and Tomson (1994) reported that 30 to 50 percent of PAHs adsorbed by sediment resisted desorption. Desorption rates of PAHs were from 1 to 3 orders of magnitude smaller than previously predicted or measured by adsorption/desorption studies and could not be explained by kinetic models or artifacts of the procedure (Kan, Fu, and Tomson 1994).

The maximum concentrations resistant to desorption for one sediment were found to be 10 mg/kg for naphthalene and 0.36 mg/kg for PCB 52 (Kan and others 1997). These values can be expected

to vary from sediment to sediment, but are illustrative of the potential impact of the resistant fraction on desorption. The irreversibly adsorbed contaminant is apparently in an energetically more stable environment than that normally associated with adsorption of nonpolar organic contaminants (Kan and others 1997). This phenomenon will be present in sediments subject to anthropogenic inputs and will result in pore water contaminant concentrations lower than predicted by equilibrium partitioning theory even if the effect of organic carbon quality is not considered.

**OTHER ORGANIC CARBON SOURCES:** Dredged sediments are located in shipping channels and harbors and can be expected to contain organic carbon sources different from those in more pristine environments. Brannon and others (1991) reported finding coal in Red Hook sediment from the New York Bight. It is highly probable that this is not an isolated occurrence. Coal fines can be transported to receiving waters by storm events in high quantities, producing a coal-contaminated sediment system (Shorten, Elzerman, and Mills 1990). Coal contains substantial amounts of PAHs (Shorten, Elzerman, and Mills 1990), which may be measured in total sediment analyses but will exhibit markedly lower desorption than sediment-bound PAHs.

Equilibrium partitioning relationships developed for PAHs and sediment organic carbon are based on adsorption studies in which all the contaminant added was available for partitioning (DiToro and others 1991). However, Burford, Hawthorne, and Miller (1993) found that none of the spiking procedures they investigated was able to accurately represent the native analytes, which were normally bound much more strongly by the environmental matrices than were the spiked analytes.

Puschel and Calmano (1995) reported that, even for sorption, individual PAH compounds behaved differently, displaying behavior that could not be explained by organic carbon normalization or by the use of a reference compound. With time, contaminants added to soils become increasingly more resistant to biodegradation and extraction (Hatzinger and Alexander 1995). The fraction of contaminant in soils and sediments that is resistant to desorption can constitute half or more of the total contaminant concentration (Pavlostathis and Jaglal 1991, Carroll and others 1994).

A growing body of evidence shows that a large fraction of the total PAH concentration in sediments is unavailable for partitioning into pore water due to PAH inclusion in combustion-derived particles (McGroddy and Farrington 1995; McGroddy, Farrington, and Gschwend 1995; Maruya, Risebrough, and Horne 1996). In a field study in San Francisco Bay, Maruya, Risebrough, and Horne (1996) reported that the presence of soot and combustion-derived PAHs, together with substrate heterogeneity, invalidated or at best limited the utility of simple equilibrium models used to develop quantitative SQC for accurate prediction of bioavailable PAH concentrations. McGroddy and Farrington (1995) reported that only 0.2 to 5 percent of sediment phenanthrene concentrations appeared to be readily available to partition into pore water. Sediment pyrene was more variable, but the amount available for partitioning into pore water ranged from 5 to 70 percent (McGroddy and Farrington 1995). These results indicate that pore water concentrations of these PAH compounds predicted by equilibrium partitioning would be greatly overestimated because sediment analysis includes forms of the contaminant that are unavailable for partitioning.

Development of a method for quantification of soot carbon (SC) in sediment has facilitated evaluation of SC impacts on PAH partitioning. Gustafsson and others (1997) found that in a freshwater lake sediment, SC constituted between 1.8 and 6.4 percent of sediment organic carbon,

while SC constituted approximately 12 percent of sediment organic carbon from Boston Harbor sediment. Addition of a SC term to the partition model quantitatively explained the elevated PAH  $K_D$  values (a result of lower pore water PAH concentrations) of two marine sediment-pore water systems (Gustafsson and others 1997). The authors were of the opinion that the influence of PAH-soot associations was so large that the effects of such associations on the bioavailable fraction should be taken into account in the establishment of SQC. Gustafsson and others (1997) proposed the equation

$$K_{\rm D} = f_{\rm OC} K_{\rm OC} + f_{\rm SC} K_{\rm SC} \tag{2}$$

where

 $K_D$  = partition coefficient (L/kg<sub>sediment</sub>)

 $f_{OC}$  = weight fraction of organic carbon in the sediment

 $f_{SC}$  = weight fraction of soot carbon in the sediment

K<sub>SC</sub> = chemicals soot-carbon-normalized partition coefficient

Application of this equation to pore waters from Boston Harbor sediment has shown close agreement with measured in situ partitioning coefficients (Gustafsson and others 1997). These results clearly demonstrate the importance of SC in controlling partitioning of PAHs to pore waters and the impact that such partitioning will exert on SQC. Incorporation of the  $f_{SC}K_{SC}$  term into SQC would result in greatly increased values of PAH SQC because of the impact that sediment SC has on lowering the partitioning of PAHs to pore water.

PAHs that do not partition into pore water are not available for uptake by organisms. This limitation on PAH bioavailability was demonstrated by McFarland and Ferguson (1994), who found that the biota/sediment accumulation factors (BSAFs) of PAH compounds in shellfish exposed to contaminated sediments were about 20-fold lower than the BSAFs reported for chlorinated compounds. These findings demonstrate that organic carbon normalization used to calculate SQC cannot accurately predict pore water PAH concentrations in sediments containing combustion-derived PAHs. Use of SQC in such sediments will greatly overestimate the impacts of sediment PAHs on biota.

**CONCLUSIONS:** The quality of organic carbon as reflected by aromaticity varies by a factor of 2 to 3. For a twofold change in soil and sediment aromaticity, partitioning behavior of nonpolar organic contaminants varies by a factor of 4 to 6. Therefore, pore water concentrations of nonpolar organic contaminants would differ markedly for sediments containing the same percentage of TOC but varying by a factor of 2 in organic carbon aromaticity.

Sediments also contain other organic phases, such as coal and soot, that markedly lower partitioning of PAHs into pore water (Table 2). The influence of PAH-soot associations on pore water partitioning is so pronounced that alternate equations incorporating the effects of soot on PAH partitioning have been proposed for SQC. Equilibrium partitioning models based on the assumption

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Table 2. Factors affecting prediction of sediment pore water nonpolar organic           contaminant concentrations predicted by equilibrium partitioning			
Factor	Reference		
Organic carbon aromaticity	Gauthier, Seitz, and Grant 1987; Davis 1993; Brannon and others 1997		
Irreversible adsorption	Kan, Fu, and Tomson 1994; Fu, Kan, and Tomson 1994; Kan and others 1997		
Coal	Shorten, Elzerman, and Mills 1990; Brannon and others 1991		
Combustion-derived PAHs	McGroddy and Farrington 1995; McGroddy, Farrington, and Gschwend 1995; Maruya, Risebrough, and Horne 1996; Gustafsson and others 1997		

that the sorption behavior of all sediment organic carbon is equivalent predict erroneous pore water concentrations of nonpolar organic contaminants.

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### Volatile Losses from Exposed Sediment

**PURPOSE:** This technical note describes laboratory investigations conducted to obtain flux data for the emission of volatile organic chemicals (VOCs) from sediment exposed to atmosphere. These investigations are being used to develop and validate predictive volatile emissions models. Laboratory experimental techniques and results obtained during these investigations are described.

**BACKGROUND:** Contaminated sediments and dredged materials are potential sources of volatile compound emissions, many of which exist in high concentration in these materials. The loss of volatile contaminants from dredged sediments is an environmental problem that is receiving increasing attention.

Previous laboratory investigations conducted at the U.S. Army Engineer Waterways Experiment Station (WES) with New Bedford Harbor, Massachusetts, sediment showed large amounts of VOCs emitted when the material was disturbed and exposed to air. The factors affecting volatile losses are largely unknown. Dredging and storage operations in confined disposal facilities (CDFs) can increase the opportunity for VOC emissions. Methods for predicting volatile losses from sediments during different aspects of dredging and disposal operations are needed to develop guidelines for controlling possible contaminant volatile emissions. Presently, neither field data nor models exist to accurately predict VOC emissions from sediments under different environmental and operational conditions.

**INTRODUCTION:** Dredging and disposal of contaminated sediments can pose significant environmental problems. During dredging operations and storage of sediments in CDFs, there is increased opportunity for VOCs to be emitted from contaminated dredged materials. Exposed sediments are a primary volatile contaminant pathway (Figure 1). In a CDF, sediments undergo cyclic "wet/dry" conditions, variations in the relative humidity of the air above the sediment, and temperature fluctuations. Moisture content has also been shown to affect the sorptive capacity of sediments for VOCs (Valsaraj and Thibodeaux 1988).

Mathematical models have been proposed to estimate the air emission rates of various volatile organic compounds from sediments (Thibodeaux 1989). These models are currently being tested using data generated at the WES Environmental Laboratory and the Louisiana State University (LSU) Department of Chemical Engineering, in laboratory investigations using both laboratory spiked and field sediments. Laboratory procedures developed at the WES, in coordination with LSU, were used in all experiments (Price and others 1996).

#### **MATERIALS AND METHODS:**

• Sediment. Two sediments were used in the experiments described here. The first sediment was obtained from University Lake (UL) in Baton Rouge, LA. Two separate experiments



Figure 1. Pathways for release of volatile emissions from dredged material

were conducted with UL sediment to determine polycyclic aromatic hydrocarbon (PAH) flux from sediments with initial moisture contents of 48 and 25 percent. The sediment was spiked with three PAHs: pyrene, phenanthrene, and dibenzofuran. Testing and analysis of UL sediment was conducted at LSU. The second sediment investigated was contaminated sediment obtained from Indiana Harbor Canal (IHC). This sediment contained several organic contaminants, including PAHs, polychlorinated biphenyls (PCBs), and inorganic compounds of concern, such as ammonia and hydrogen sulfide. The IHC sediment contains 0.9 percent oil and grease. Volatile emission testing for PAHs, total recoverable petroleum hydrocarbons (TRPHs), PCBs, ammonia, and hydrogen sulfide was conducted with the IHC sediment at WES for the Corps' Chicago District. For experimental purposes and model validation, only three PAH compounds were evaluated for emission comparisons between the two sediments. PAHs were chosen as representative VOCs due to their prevalence in contaminated sediments. The physical and chemical properties of both sediments are summarized in Table 1.

• Flux chambers. All tests were conducted using VOC flux chambers designed by LSU and constructed at WES and LSU (Figure 2). The two-piece anodized aluminum chambers were devised to hold sediment at a depth of 10 cm with a surface area of 375 cm<sup>2</sup>. The top portion of the flux chamber was designed with channels to distribute airflow uniformly across the sediment surface. The chambers were sealed with an O-ring and threaded fasteners for an airtight fit.

Table 1. Physical and Chemical Properties of Sediments <sup>1</sup>			
	University Lake		
Property	High Moisture	Low Moisture	Indiana Harbor
Percent sand	3	3	45
Percent silt	41	41	46
Percent clay	56	56	8
Percent total organic carbon	4	4	2.6
Percent oil and grease	NA	NA	0.9
Porosity	0.7	0.44	0.79
Bulk density, g/cm <sup>3</sup>	0.67	1.7	0.6
Percent initial moisture (w/w)	48	25	54
Dibenzofuran, mg/kg	66	108	NA
Naphthalene, mg/kg	NA	NA	38
Phenanthrene, mg/kg	65	97	51
Pyrene. mg/kg	69	94	59
Total recoverable petroleum hydrocarbons, mg/kg	NA	NA	12,790

<sup>1</sup> Data obtained from Ravikrishna and others (in review).

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Contaminant-specific adsorbent-filled air sampling traps were attached to the chamber exit ports. PAHs/TRPHs and PCBs were trapped on XAD-2 resin enclosed in glass sample tubes (Orbo 44 from Supelco, Inc.). Traps were removed from the exit lines at the end of each sampling interval. Solvent was extracted and analyzed according to EPA method 8270 for PAHs/TRPHs and method 8081 for PCBs (U.S. Environmental Protection Agency 1982).

Contaminant flux, N(t), through the chambers was calculated using the equation

$$N(t) = \frac{\Delta m}{\Delta t A_c}$$

where

 $\Delta m = mass$  (ng) of compound collected on the trap in time  $\Delta t$  (hr)

 $A_c$  = area of the sediment-air interface,  $cm^2$ 

**EXPERIMENTAL DESIGN:** Flux chambers were filled with a known amount of homogenized sediment (wet weight) and sealed. Air was passed over the sediment surface at 1.7 L/min, and relative humidity was maintained by using an in-line bubble trap as needed to add moisture vapor. A thermohygrometer (Cole-Parmer) was connected to the exit port to monitor air temperature and relative humidity.

Experiments with IHC sediment were conducted to provide information on maximum contaminant fluxes expected under different air humidity, sediment moisture, and site management conditions that might occur during CDF operations. The sampling schedule consisted of five continuous runs simulating various environmental and operational scenarios.

Runs I and II gave maximum initial contaminant fluxes from wet sediment under dry and humid air conditions. In Run I, dry air was passed over the sediment surface for 2 weeks, after which the relative humidity of the air was increased to 98 percent and samples were taken over a 7-day period (Run II). Run III simulated a rainfall event in which the sediment was rewet to near field capacity and dry air was passed over the sediment surface for 14 days. Run IV represented the occurrence of mechanical mixing during CDF operations. The sediment was reworked in the chambers in glove bags equipped with sampling tubes to trap contaminants released during mixing. Dry air was then passed over the sediment for 7 days. The sediment was again rewet to near field capacity for Run V, and dry air was again passed over the sediment surface for a final 7 days. Air samples were taken as follows:

Run I	6, 24, 72, 168, 240, and 336 hr
Run II	6, 24, 72, and 168 hr
Run III	6, 24, 72, 168, 240, and 336 hr
Run IV	6, 24, 72, and 168 hr
Run V	6, 24, 72, and 168 hr

Testing of UL sediment conducted at LSU was designed to formulate comparisons of contaminant fluxes between a laboratory-spiked sediment and a naturally contaminated sediment. Experimental procedures were designed to determine the effects of changes in moisture content and relative air humidity on PAH emissions from each sediment (Ravikrishna and others, in press).

#### **RESULTS:1**

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- Moisture fluxes. Moisture fluxes were monitored during the course of all experiments. Water flux from the higher moisture UL sediment decreased from 0.006 to 0.005 g/cm<sup>2</sup>•hr in 48 hr and remained relatively constant for the duration of the test. Moisture content of the surface sediment and underlying layers did not vary significantly, indicating that the sediment surface remained relatively "wet" over the course of the test. Water flux from the lower moisture UL sediment was similar to that from the higher moisture sediment, but did decrease significantly after 400 hr. The water flux from the Indiana Harbor sediment remained at 0.005 g/cm<sup>2</sup>•hr throughout the experiment, with no difference between final surface and underlying sediment moisture contents.
- **Contaminant fluxes.** Experiments conducted with UL sediment were designed to determine and form comparisons of maximum initial contaminant fluxes from University Lake and Indiana Harbor sediments. The effects of different initial sediment moisture contents and relative air humidity conditions on PAH emissions were investigated.

For experiments conducted with UL sediment, dry air (0 percent relative humidity) was passed over the sediment surface for 568 hr. Within the first 48 hr of the experiment, dibenzofuran fluxes decreased from 32 to 12 ng/cm<sup>2</sup>•hr and from 111 to 10 ng/cm<sup>2</sup>•hr in the high- and low-moisture content UL sediment, respectively. During the first 48 hr, phenanthrene fluxes decreased from 7 to 3.5 ng/cm<sup>2</sup>•hr and from 13 to 3 ng/cm<sup>2</sup>•hr. Even though no decrease in sediment moisture flux or overall sediment moisture occurred in experiments run with IHC sediment, PAH fluxes sharply decreased within 168 hr after applying "dry" air over the sediment surface (Figure 3). This phenomenon may be due to the formation of a thin oil-film layer on the sediment surface, which would evaporate quickly resulting in the observed decline in flux (Ravikrishna and others, in press). Subsequent diffusion of contaminants from the sediment to the air would be significantly slower through the oil and grease within the sediments. This trend is in contrast to earlier investigations, where fluxes decreased significantly in conjunction with sediment surface drying decreasing the sediment sorptive capacity or retardation factor (R<sub>f</sub>) (Valsaraj and others 1997).

In experiments conducted with UL sediment, the relative humidity of the air was increased to 90 percent after 568 hr. No discernible increase in PAH fluxes was noted in the experiment

<sup>1</sup> Results reported herein summarize findings found in Ravikrishna and others (in press).



Figure 3. PAH fluxes from Indiana Harbor Canal sediment

conducted with the higher moisture content UL sediment. If the sediment surface was "dry," a noticeable increase in contaminant flux would have occurred. Although the water flux from the lower moisture UL sediment remained relatively constant during the first 400 hr of the test, a noticeable "drying front" formed on the sediment surface at the air inlet and progressed toward the exit port for the remainder of the experiment. In contrast to the higher moisture UL sediment, an increase in PAH flux rates occurred when the relative humidity of the air was increased. Dibenzofuran and phenanthrene fluxes increased to 50 and 10 ng/cm<sup>2</sup>•hr, respectively. An increase in relative air humidity after 336 hr did not result in any increase in PAH flux in the experiment run with IHC sediment. Sediment moisture flux did not change during the course of the test, which would account for the lack of an increase in PAH emissions. An increase in flux rates observed at test Run IV was possibly due to the formation and subsequent evaporation of another sediment surface oil-film layer during reworking of the sediment (Figure 3).

Ravikrishna and others (in press) found the predicted values for phenanthrene in good agreement with experimental values for the UL sediments, but the IHC sediment model predictions were orders of magnitude larger than for observed fluxes (Figure 4). Measured fluxes from the IHC sediment were lower than those from UL sediment. This suggests that a smaller concentration of phenanthrene was available for diffusion, probably due to irreversible binding through sediment aging involving sediment sorption and partitioning processes (Fu, Kan, and Tomson 1994; Kan, Fu, and Tomson 1994; Kan and others 1997).



Figure 4. Comparison of dibenzofuran flux from University Lake (UL) and Indiana Harbor canal (IHC) sediments

**CONCLUSIONS:** Results indicate that VOC fluxes depend upon several factors. Relative humidity can possibly affect flux rates, but its influence depends upon moisture content and sediment physical and chemical characteristics. Measured fluxes for Indiana Harbor sediment were orders of magnitude lower than model predictions and laboratory data collected in a comparable study conducted with laboratory spiked sediment (Valsaraj and others 1997). Sediment physical and chemical characteristics, such as contaminant aging, porosity, and percent oil and grease, probably decreased fluxes.

Comparison of the behavior of the IHC sediment to the laboratory-spiked UL sediment revealed important implications for estimating PAH air emission fluxes. PAH emissions can be overestimated if models developed through calibrations obtained from laboratory-inoculated sediments are used to predict fluxes from field-contaminated sediments. LSU is currently pursuing development of appropriate models for aged field-contaminated sediment in coordination with the WES.

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### Predicting Surface Runoff Water Quality from Upland Disposal of Contaminated Dredged Material

**PURPOSE:** The U.S. Army Engineer Waterways Experiment Station (WES) Rainfall Simulator/ Lysimeter System (RSLS) has been very effective in predicting surface runoff water quality from the upland placement of dredged material. However, this procedure is expensive and lengthy, and requires specialized equipment. The need for a simpler procedure has become evident.

In 1986, WES evaluated potential extraction procedures for use in predicting surface runoff water quality from dredged material. These experiments were conducted in conjunction with RSLS experiments on Indiana Harbor dredged material as reported in Environmental Laboratory (1987). Results of these investigations indicated that a simple laboratory extraction procedure could be used as a tool to provide initial engineering estimates and to screen contaminated sediments prior to conducting the RSLS procedure.

In fiscal year 1996, funding became available from the Long-term Effects of Dredging Operations Program to develop a simplified laboratory runoff procedure (SLRP) using other contaminated sediments and to compare the results with the RSLS procedure. The SLRP and RSLS procedures were conducted on five separate San Francisco Bay, CA, sediments for the U.S. Army Engineer District, San Francisco, and on one sediment from Black Rock Harbor, CT—representing the U.S. west and east coast, respectively. This technical note summarizes the results of this comparison.

**BACKGROUND**: The surface runoff water quality component of the Decisionmaking Framework for Management of Dredged Material (Lee and others 1991) evaluates the potential water quality problems that may result from discharges of storm water from contaminated dredged material placed in upland environments. Water leaving an upland confined disposal facility (CDF) must meet applicable State water quality standards for discharge into receiving waters. When dredged material is placed in a CDF, contaminant movement from the wet, unoxidized material will be mainly associated with suspended solids. As the material dries and oxidizes, suspended solids concentration may decrease while contaminants such as heavy metals may become more soluble. The RSLS predicts these effects so that restrictions or treatments, such as controlling movement of suspended solids or providing adequate mixing zones, can be incorporated into the CDF design.

The testing protocol for surface runoff water quality, described by Skogerboe, Price, and Brandon (1988), has been applied to dredged material from a number of locations including Black Rock Harbor, Indiana Harbor, Oakland Harbor, Everett Harbor, and New Bedford Harbor. Contaminants have included heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, organotins, and dioxins. The procedure uses a rainfall simulator/lysimeter system in the laboratory (Figure 1).



Figure 1. The rainfall simulator/lysimeter system in the laboratory

The RSLS has been field validated under the Field Verification Program (FVP) at the Black Rock Harbor CDF in Bridgeport, CT, using the portable RSLS (Figure 2).

The RSLS requires a minimum of eleven 208-L drums of sediment, representative of the proposed dredging site. After placing the sediment in a soil lysimeter, surface runoff experiments are conducted on the wet, unoxidized sediment. The lysimeter is then moved outside, covered with a ventilated top, and allowed to dry naturally for 6 months. The runoff experiments are then repeated on the dry, oxidized sediment.

Although the RSLS is a very effective tool for predicting surface runoff water quality from an upland CDF, the procedure is expensive, time



Figure 2. Portable RSLS at field site

consuming, and can only be conducted at the WES. A need for a faster, less expensive response to surface water quality concerns prompted the development of a simple laboratory procedure that could be performed by any qualified laboratory with widely available equipment. The SLRP is designed to provide a less expensive, rapid-response screening evaluation of surface runoff water quality from upland CDFs.

A number of sediment-drying

and oxidation procedures were evaluated on Indiana Harbor sediment, and the results obtained were compared with the results from RSLS experiments on the same material (Environmental Laboratory 1987). A procedure using oven-drying and hydrogen peroxide was selected as the best sediment treatment to simulate the long-term effects of drying and oxidation. More recently, the SLRP has been applied to San Francisco Bay and Black Rock Harbor sediments, and the results were compared with RSLS results. The results from these two sediments, the purpose of this technical note, demonstrate the value of the SLRP as a screening procedure to determine the need for the more expensive RSLS procedure. After testing on other sediments and the further development of regression equations, the SLRP may eventually replace the RSLS completely.

#### **METHODS AND MATERIALS:**

• **Black Rock Harbor.** Black Rock Harbor (BRH) was the subject of the Field Verification Program conducted at the WES and Bridgeport, CT, from 1982 though 1986. Sediment was collected prior to dredging for chemical and physical characterization. During the actual dredging process, dredged material was placed in an upland and wetland CDF at the FVP site for subsequent testing and evaluation of laboratory methods. Both sediment from the proposed dredging cut and the actual dredged material from the upland CDF were tested using the RSLS. The rainfall simulations were also conducted on the CDF using the field portable RSLS. Rainfall simulations were performed on the wet, unoxidized and the dry, oxidized materials according to procedures described in Skogerboe and others (1987). Surface runoff quality experiments were first conducted on the BRH sediment and dredged material using the RSLS at the WES.

The portable RSLS was used at the CDF to field verify the laboratory results. Experiments were conducted on wet, unoxidized sediment before any significant drying had occurred. The sediment erodibility would be at its maximum level. The dry, oxidized sediment represented the period when heavy metal solubility was at maximum levels and no vegetation had yet been established. Surface runoff samples were collected and analyzed for total and dissolved cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn), PCBs, and PAHs.

Dredged material collected from the FVP wetland CDF in 1993 was used to conduct the SLRP experiment. The procedure for wet, unoxidized sediment utilized sediment:water ratios of 1:10, 1:100, and 1:1,000 or 100,000, 10,000, and 1,000 mg L<sup>-1</sup> suspended solids, respectively. For the dry, oxidized SLRP experiment, ratios were 1:100, 1:1,000, and 1:10,000 or 10,000, 1,000, and 100 mg L<sup>-1</sup> suspended solids. This represented the range of suspended solids previously measured in runoff from BRH sediment using the RSLS. After preparation of three replicate simulated runoff water samples, subsamples were analyzed for filtered and unfiltered (total and soluble) constituents. Results of the SLRP were compared to the RSLS data reported by Skogerboe and others (1987).

• San Francisco Bay sediments. Sediment was collected from five proposed dredging locations in San Francisco Bay and brought to the WES for surface runoff quality testing (Lee and others 1992a, 1992b; Lee and others 1993a, 1993b). These sediments included: (1) Inner Oakland Harbor, (2) Oakland Upper Turning Basin (3) Pinole Shoal, (4) West Richmond, and (5) Santa Fe Channel. The sediments were contaminated with varying concentrations of heavy metals, PCBs, PAHs, pesticides, and organotins.

Surface runoff quality experiments were first conducted on each of the five sediments using the RSLS in the laboratory as previously described for Black Rock Harbor. Surface runoff samples were collected and analyzed for total and dissolved heavy metals, and organotins. Next, each of the five sediments was tested using the simplified laboratory procedure. The simplified procedure for wet, unoxidized sediment utilized different ratios than described for Black Rock Harbor: 1:20, 1:200, and 1:2,000 (50,000, 5,000, and 500 mg L<sup>-1</sup> suspended solids) for the wet sediment and 1:200, 1:2,000, and 1:20,000 (5,000, 500, and 50 mg L<sup>-1</sup>)

suspended solids) for the dry. The ratios of sediment to water corresponded to the range of suspended solids previously measured in runoff from a number of sediments using the RSLS. The simplified laboratory procedure for dry, oxidized sediment also included oven drying and rapid oxidation with hydrogen peroxide. Samples were analyzed for total and dissolved arsenic (As), Cd, Cr, Cu, lead (Pb), mercury (Hg), Zn, PAHs, PCBs, pesticides, and organotins.

Results of the SLRP for the San Francisco Bay sediments along with sediment particle size and total organic carbon (TOC) concentrations were correlated to results of the RSLS. Multiple linear regression was used to develop equations to predict surface runoff quality from upland dredged material disposal sites (Winer 1971). The independent variables included heavy metal concentrations obtained from the simplified laboratory procedure, sediment percent sand, and sediment total organic carbon (TOC, mg kg<sup>-1</sup>). Heavy metal concentrations in surface runoff from the RSLS procedure were the dependent variables. Since actual disposal sites did not exist, results from the RSLS procedure were used for the dependent variable. Separate regressions were developed for wet, unoxidized sediment and for dry, oxidized sediment experiments.

#### **RESULTS AND DISCUSSION**

• Black Rock Harbor—comparison of SLRP with RSLS laboratory and field results. Results of the wet, unoxidized SLRP test were compared with the wet, unoxidized RSLS data as reported in Skogerboe and others (1987). The 10,000-mg L<sup>-1</sup> SLRP (SLRP 1:100) suspended solids concentration was within the range determined from the three RSLS tests (range: 9,247 to 12,296 mg L<sup>-1</sup>). The laboratory RSLS test on BRH sediment (RSLS-SED) generally overestimated total concentrations of Cd, Cr, Cu, Ni, and Mn compared with the RSLS results for dredged material in the laboratory (RSLS-DM) and on the CDF (RSLS-CDF), while Mn was not significantly different. The SLRP total metals correlated well with laboratory and field RSLS results on dredged material for all total metals and for soluble Cr, Cu, Ni, and Zn. Figure 3 compares the SLRP 1:100 with the RSLS results for chromium. As with most other metals, chromium was not very soluble in the wet, unoxidized material.



Figure 3. Comparison of SLRP chromium to RSLS tests on wet BRH sediments

On the dry, oxidized material, the SLRP 1:100,000 sediment:water ratio was more closely aligned with the RSLS suspended solids (range 320 to 151 mg L<sup>-1</sup>). Although suspended solids were reduced nearly 2 orders of magnitude, the soluble fraction of all metals tested increased. Concentrations in the SLRP 1:100,000 ratio were not significantly different from all three RSLS tests for Cr, Cu, and Ni. The SLRP and RSLS laboratory tests underestimated actual Zn and Mn concentrations determined in the CDF. The SLRP estimates for Cd were not significantly different from the

CDF results, although the results were more variable than for the other metals. Results of total and dissolved chromium are shown in Figure 4.

Results of laboratory RSLS tests showed total PCBs and PAHs to be closely associated with suspended solids in the wet material, but near or below detection limits in the dry material. Based on these results, no analysis was conducted for the SLRP.

San Francisco Bay sediments

 development of prediction equations. Heavy metal concentration ranges and means from the wet, unoxidized RSLS test were most closely approximated by the 1:200 SLRP test. Good correlations existed between the simplified labo 



Figure 4. Comparison of SLRP chromium to RSLS tests on dry BRH sediments

ratory test concentrations of As, Cd, Cr, Cu, Pb, and Zn and their respective RSLS test concentrations for the wet, unoxidized sediment. Heavy metal concentration means from the dry, unoxidized RSLS test were between the means of the 1:200 and the 1:2,000 SLRP tests. The SLRP 1:200 ratio was also selected for the dry, oxidized sediment because the sediment-to-water ratio, mean concentrations, and concentration ranges were closest to the RSLS test, and the correlation (R2) values were highest. The process of oxidation and drying did increase metals solubility, and the SLRP simulated that process effectively. Statistically significant correlations existed between SLRP test concentrations and the RSLS test concentrations for Cd, Cr, Cu, Pd, and Zn. Because mercury concentrations were mostly below detection limits, no statistically significant relationships could be determined. The same was true for PAHs, PCBs, pesticides, and organotins.

- Total organic carbon, percent sand, and suspended solids data. Soil erosion and resulting suspended solids (SS) concentrations in surface runoff have been shown to be affected by the soil particle size and the organic matter content (Wischmeier, Johnson, and Cross 1971). The percent sands in sediments from this study varied by a factor of 20 (Table 1), and sediment TOC varied by a factor of 2 to 3. Suspended solid concentrations were also highly variable in surface runoff samples from the RSLS tests, although suspended solids were mostly higher in surface runoff samples from wet, unoxidized sediments with low sand and high TOC levels.
- **Prediction equations**. Using the data obtained from the San Francisco Bay sediments, regression equations were developed to predict each heavy metal concentration in surface runoff using the SLRP, the percent sand, and TOC. Heavy metal concentration data from the 1:200 SLRP test were entered into the regression equations, and the predicted concentrations

were compared with those observed from the RSLS test. Correlations ( $R^2$ ) and prediction equations for wet, unoxidized sediment are shown in Table 2.

Table 1. Summary of Sand and TOC in Sediments and Suspended Solids in Runoff           (RSLS Tests)						
Sediment	Sand, percent dry weight	TOC, mg kg <sup>-1</sup>	SS, mg L <sup>-1</sup> wet sediment	SS, mg L <sup>-1</sup> dry sediment		
Inner Harbor	66.8	3,364	4,447	1,686		
Turning Basin	3.2	6,450	9,140	970		
Pinole Shoal	25.0	2.634	1,500	618		
West Richmond	55.5	2.292	3,290	2,340		
Santa Fe Channel	18.4	4,900	6,240	2,130		

 Table 2. Regression Equations for Predicting Heavy Metal Concentrations in Surface

 Runoff from Wet, Unoxidized Sediment Using the Simplified Laboratory Test

Motal	SLRP:RSLS	Prediction Equation <sup>1</sup>
Arsonic	0.87	In (As <sup>2</sup> ) = -1.30268 + 0.87958 * In(AS <sup>2</sup> ) + 0.03072 * (% Sand) + 0.00021 * (TOC)
Cadmium	0.42	In (Cd) = -3.95989 + 0.85419 * in(CD) + 0.04350 * (% Sand) + 0.00062 * (TOC)
Chromium	0.71	In (Cr) = -2.70912 + 0.87328 * In(CR) + 0.01744 * (% Sand) + 0.00040 * (TOC)
Copper	0.83	In (Cu) = -3.48731 + 1.38320 * In(CU) + 0.01230 * (% Sand) + 0.00030 * (TOC)
Lead	0.96	In (Pb) = -4.02897 + 1.44986 * In(PB) + 0.02320 * (% Sand) + 0.00018 * (TOC)
Zinc	0.93	In (Zn) = -1.63788 + 1.07703 * In(ZN) + 0.00533 * (% Sand) + 0.00028 * (TOC)

<sup>1</sup> Heavy metal concentrations are expressed in micrograms per liter; TOC concentrations are in milligrams per kilogram.

<sup>2</sup> "As" is the predicted surface runoff concentration, and "AS" is the measured concentration from the simplified laboratory test. Similar forms are used for all parameters.

In the wet sediment, arsenic showed good agreement ( $R^2 = 0.87$ ) between concentrations calculated by the regression model (predicted), and the actual concentrations that resulted from RSLS test.

Predicted Cd concentrations with the poorest  $R^2$  (0.42) tended to overpredict concentrations at lower concentration levels and underpredict at higher levels. Cadmium concentrations were very near or below the detection limits, which caused more variability in the sample analysis. Predicted Cr concentrations mostly showed good agreement with the RSLS test data except for a couple of points at the highest concentration levels observed. Results for chromium are illustrated in Figure 5.

Predicted Cu, Pb, and Zn concentrations showed very good agreement with the concentrations observed from the RSLS data. Concentrations of Hg, PAHs, PCBs, pesticides, and organotins were near or below detection limits, and no statistical comparisons concerning these contaminants could be made.

Correlations and prediction equations for the dry, oxidized sediment are shown in Table 3. Predicted arsenic concentrations showed little agreement with the concentrations observed from the RSLS test. The actual range of values observed was very small (1 to 7 g L<sup>-1</sup>), so procedural variability was high compared to the data range. However, predicted Cd, Cr, Cu, Pb, and Zn concentrations all showed good agreement with the observed concentrations from the RSLS test. Predicted SLRP chromium and RSLS chromium concentrations for all SFB sediments are illustrated in Figure 6.



Figure 5. Comparison of SLRP predicted and RSLS measured chromium from wet SFB sediments.

## Table 3. Regression Equations for Predicting Heavy Metal Concentrations in Surface Runoff from Dry, Oxidized Sediment Using the Simplified Laboratory Test

Metal	SLRP:RSLS (R <sup>2</sup> )	Prediction Equation <sup>1</sup>	
Arsenic	0.21	In (As <sup>2</sup> ) = -0.81497 + 0.09659 * In(AS <sup>2</sup> ) + 0.01848 * (% Sand) + 0.00022 * (TOC)	
Cadmium	0.74	In (Cd) = -2.43298 + 0.99195 * In(CD) + 0.04305 * (% Sand) + 0.00017 * (TOC)	
Chromium	0.85	in (Cr) = -7.05319 + 1.55841 * In(CR) + 0.04971 * (% Sand) - 0.00017 * (TOC)	
Copper	0.87	In (Cu) = -3.28271 + 0.99471 * In(CU) + 0.04454 * (% Sand) + 0.00018 * (TOC)	
Lead	0.89	In (Pb) = -4.57752 + 1.23537 * In(PB) + 0.03942 * (% Sand) + 0.00036 * (TOC)	
Zinc	0.82	In (Zn) = 1.44438 + 0.52197 * In(ZN) + 0.01106 * (% Sand) + 0.00002 * (TOC)	

<sup>1</sup> Heavy metal concentrations are expressed in micrograms per liter; TOC concentrations are in milligrams per kilogram.

<sup>2</sup> "As" is the predicted surface runoff concentration, and "AS" is the measured concentration from the simplified laboratory test. Terms of similar form are used for all parameters.

**BENEFITS OF THE SLRP:** The simplified laboratory test is significantly less expensive than the RSLS test (Table 4). The SLRP can be conducted by almost any competent, certified laboratory in a much shorter period of time than required for the RSLS test. The SLRP provides the Corps with a valuable tool for conducting preliminary engineering estimates to evaluate surface runoff from proposed upland dredged material disposal sites. Sediments can be screened quickly and much more inexpensively for potential surface runoff quality problems. Sediments with obvious runoff quality



Figure 6. Comparison of SLRP predicted and RSLS measured chromium from dry SFB sediments

Table 4. Monetary Benefits of the SLRP							
	RSLS		SLRP				
Expense Item	Cost (\$)	Time (mo)	Cost (\$)	Time (mo)			
Sediment collection <sup>1</sup>	11,000	0.5	5,500	0.25			
Conduct test/report <sup>2</sup>	38,600	12.0	5,600	0.50			
Chemical analysis <sup>3</sup>	15,400	1.0	15,400	1.0			
Disposal of material <sup>1</sup>	5,000		500				
Total	70,000	13.5	27,000	1.75			

problems can be eliminated from further consideration for upland disposal or pinpointed for runoff quality improvement measures.

<sup>1</sup> For the Simplified Laboratory Test, 5 gal (19 L); for the RSLS, eleven 55-gal drums (2,290 L).

<sup>2</sup> RSLS test conducted by the WES and the SLRP test conducted by any certified laboratory.

<sup>3</sup> Twelve samples including extraction at \$1,000/sample plus quality analysis/quality control. Turnaround time by analytical laboratories is highly variable (1 to 6 months).

**CONCLUSIONS AND RECOMMENDATIONS:** The SLRP developed from this study accurately predicted most heavy metal concentrations in surface runoff from Black Rock Harbor and San Francisco Bay sediments. In cases where the SLRP could not predict the heavy metal concentrations accurately, concentrations were at or below detection limits. Predicted concentrations represent the worst-case scenarios for both the wet, unoxidized sediment stage and the dry, oxidized sediment stage. The conditions that the simplified laboratory test represents are those in which the sediment is most erosive and/or heavy metals are most soluble. The simplified laboratory test is approximately \$40,000/sediment less expensive than the RSLS test and may be completed in one tenth of the time. In addition, the simplified laboratory test requires only 5 gal (19 L) of sediment compared to eleven 55-gal drums (2,290 L) of sediment for the RSLS.

The hydrogen peroxide oxidation does reliably simulate the natural oxidation that occurs when sediment is placed in an upland environment. Comparisons of the results from the simplified laboratory test to selected water quality standards result in the same conclusions as those from the RSLS test.

The SLRP has been applied to San Francisco Bay, Black Rock Harbor, and Indiana Harbor sediments and is currently being applied to New York Harbor sediments. The results from the Black Rock Harbor, Indiana Harbor, and New York Harbor tests will be incorporated into the regression equations to increase the accuracy and nationwide use of the SLRP as a predictive tool. The SLRP requires more testing for general application to sediments throughout the United States as part of a regulatory process. Further testing should be conducted on contaminated marine sediments from the Gulf coast and on contaminated freshwater sediments from lakes and rivers.

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