

AIR EMISSIONS FROM EXPOSED, CONTAMINATED SEDIMENTS AND DREDGED MATERIAL

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ABSTRACT

Contaminated sediments in confined disposal facilities (CDF) are exposed to air leading to the emission of organic compounds, among many others. Laboratory flux experiments were conducted to measure the flux of tracer PAHs and the various physical factors that influence the emission. Continuing this effort, this document describes the effect of sediment reworking on PAH flux. A pilot-scale simulation of a CDF was performed at Waterways Experiment Station, Vicksburg, Mississippi. The experimental design and preliminary results of the pilot-scale field simulation are also presented in this work.

Key words: *contaminated sediment, flux, reworking, PAHs*

INTRODUCTION

Contaminated sediment at various sites in the United States contains volatile and semi-volatile hydrocarbons along with varying degrees of oil and grease. The U.S. Army Corps of Engineers (USACE) has the responsibility to maintain navigation. The dredged material may be stored on shore in confined disposal facilities (CDFs). The various pathways of contaminant transport from these CDFs have been reviewed extensively. Polynuclear aromatic hydrocarbons (PAHs) are one class of sediment contaminants that are of interest, owing to their suspected carcinogenic nature. When airborne, these compounds may pose a significant health hazard. Quantitative data and models are needed to predict volatile emissions from CDFs and evaluate control strategies to manage contaminated sediments. Characterizing the processes in the sediment and air that controls the volatile emissions from sediments can help identify proper contaminated sediment management practices.

Sediment in a CDF undergoes changing physical conditions in response to changing atmospheric conditions. Of particular significance to volatile emissions is the moisture content of the dredged material. The volatilization of hydrophobic organic compounds is strongly affected by the sediment moisture. Significant drying and shrinkage occurs during an extended dry period and swelling occurs after rewetting during a precipitation event (rain, fog). Diurnal changes in relative humidity also affect the sediment surface moisture content. Studies illustrate this behavior for various types of surfaces and organic compounds. Recent studies in our laboratory have focussed on the volatilization of PAHs from sediment surfaces under controlled conditions. Both laboratory-spiked and field sediments were used in the laboratory work. The effect of sediment moisture content and air relative humidity have been studied along with the use of capping to control these emissions.

Mathematical models were developed to validate the experimental findings and also to extend them to the field as valuable predictive tools. These experiments, the mathematical validation, and the discussion are presented in recently published work (Valsaraj et al., 1997; Valsaraj et al., 1999; R. Ravikrishna et al., 1998). A pilot-scale field simulation of a CDF was conducted at the U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg. A brief description of the setup and some preliminary results are presented in this work.

EXPERIMENTAL

Field sediments from two sources were used in the reworking effect study. These were from the Grand Calumet River and the Indiana Harbor Canal. The pilot-scale field verification was performed using sediment from Indiana Harbor Canal. The sediment is homogenized and used in the experiments. The properties of materials, experimental procedures, and analysis are described in an earlier work (Valsaraj et al., 1999).

The pilot-scale field verification setup is described in Figure 1. The sediment is loaded into a wooden box, which is placed inside the ground. There are pipes leading from the bottom and top of the box to closed drums placed under the ground to collect the leachate and runoff, respectively. The flux chambers used in this case are slightly different from those used in the laboratory experiments. The bottom of chamber is removed and the downward edges of the four walls are sharpened in order to allow easy placement in the sediment. During a measurement, the flux chamber is kept in place by an aluminum framework to prevent it from sinking into the sediment. The other difference in these experiments is in the air supply. Air is drawn across the sediment surface through the flux chamber by the use of a vacuum pump. The air exiting the chamber goes through a PAH trap, an XAD-2 resin bed, and then through a flow meter and on to the vacuum pump. A weather station is placed close to the sediment surface. The weather station records meteorological information and sediment temperature data in a datalogger attached to it. The weather data can give us information about any possible correlation between the flux and the atmospheric conditions.

During a run, the flux chamber is placed on a selected area on the surface and a fresh PAH trap bed is attached to the outlet. The vacuum pump is turned on and the flow rate is increased to about 1700 ml/min in small steps. The sampling intervals are typically 24 - 72 hours. The analysis methods are referred to earlier in this section. Samples of sediment were taken from the CDF at the beginning of the experiment and analyzed for PAHs, total recoverable petroleum hydrocarbons, fraction organic carbon, particle size, and moisture content. Sediment cores are removed after a few months of sampling to check for the PAH loss from the sediment.

After three months of sampling, a rainfall event was simulated (Price et al., 1998). Flux measurements were taken before and after the event. The sediment was reworked after three more months and the response of emission recorded. Reworking was performed by mixing the sediment, disturbing the surface, and bringing up new layers of sediment from below the original surface.

RESULTS AND DISCUSSION

Effect of Sediment Reworking

Figure 2a shows the effect of reworking in the field sediment on the flux of naphthalene from Grand Calumet River sediment simulated in a small laboratory flux chamber (Valsaraj et al., 1999). The open symbols represent the first cycle of the experiment. The value of naphthalene flux after 6 hours was 778 ng/cm².hr and dropped to 63 ng/cm².hr in 72 hours and to 2 ng/cm².hr in 168 hours. After the reworking, the flux, represented by the closed symbols, was 1480 ng/cm².hr after 6 hours, 176 ng/cm².hr after 24 hours and 7 ng/cm².hr after 72 hours. We observe that the flux follows almost the same path as for the first cycle. Figure 2b shows the flux of naphthalene from the Indiana Harbor Canal sediment. In the first cycle, before reworking, the flux was 46 ng/cm².hr after 6 hours, 1.8 ng/cm².hr after 48 hours, and 0.03 ng/cm².hr after 168 hours. After reworking, the flux was 56 ng/cm².hr after 6 hours, 7.7 ng/cm².hr after 24 hours, and 0.08 ng/cm².hr after 168 hours. Reworking exposes previously unexposed sediment to the surface. The resistance to mass transfer is primarily in air-side after this exposure and hence the high value. As the surface is depleted, the sediment-side resistance increases as the compound must diffuse in the vapor phase from the lower layers of sediment.

In a CDF, an enhanced emission from sediment reworking is significant because, from time to time, when new sediment is dumped, it disturbs the existing sediment. Also other agents like rain, storm water runoff, and macro fauna might cause sediment reworking.

Pilot-Scale Simulation

Figure 3 shows the flux of phenanthrene from the pilot-scale CDF at WES. The flux was 12.75 ng/cm².hr after 6 hours and quickly dropped to 0.13 ng/cm².hr after 68 hours. The flux was on the same order of magnitude for a long period of time. There was a rainfall event around 2100 hours after the start of the experiment. However, no perceptible effect was noticed because the sediment was already wet before the rainfall and the event did not cause any 're-wetting' of the sediment. The reworking event was performed at 4600 hours after start. The phenanthrene flux was 0.22 ng/cm².hr before the reworking and increased to 3 ng/cm².hr after the event and then decreased to 0.32 about 24 hours later. The behavior is similar to that observed in the laboratory experiments with field sediments. The model used for phenanthrene flux prediction, as shown in Figure 3, is described in an earlier work (Valsaraj et al., 1999). All the model parameters were derived from experimental measurements. The model fits the data satisfactorily and therefore represents a positive transition from the laboratory to the field.

CONCLUSIONS

Sediment reworking causes the air-emission flux to increase in laboratory experiments. This is reinforced in the pilot-scale field experiments. The model predicts the field data satisfactorily.

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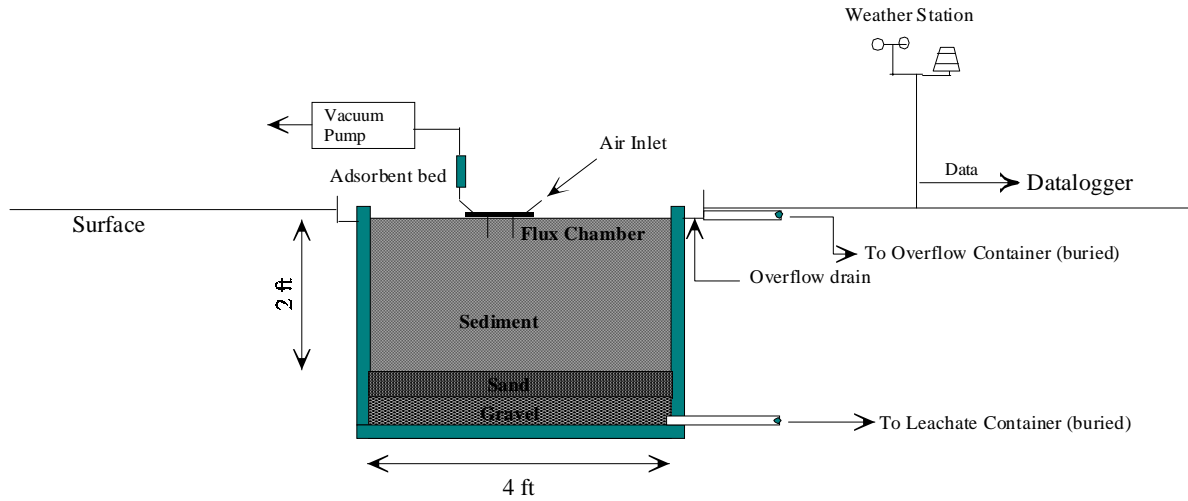


Figure 1. Pilot-scale field simulation setup.

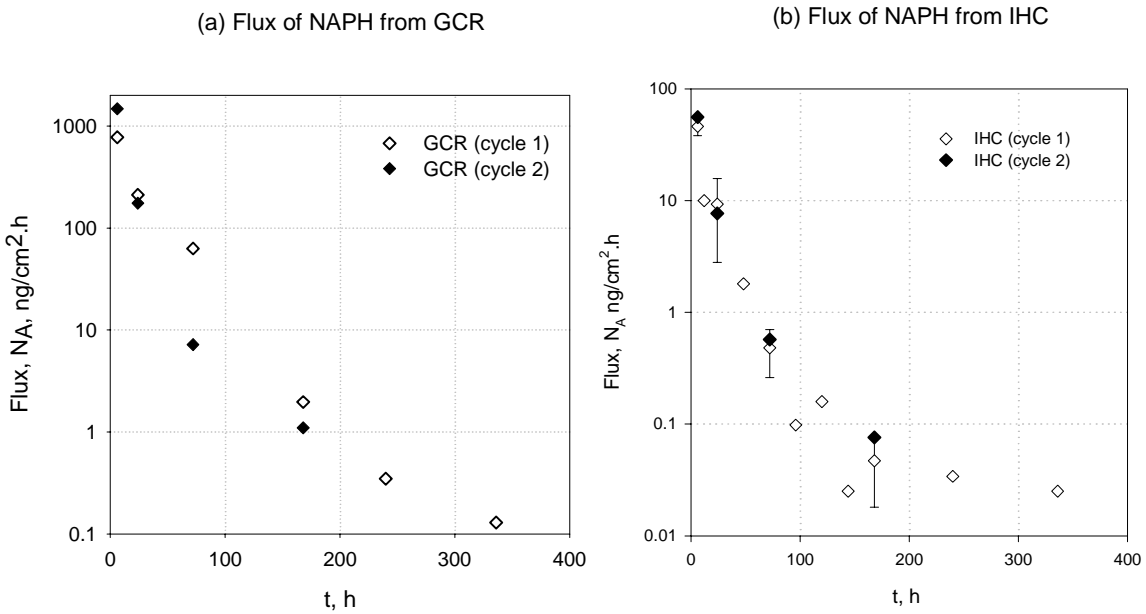


Figure 2. Field Sediments—Effect of reworking in small laboratory chambers.

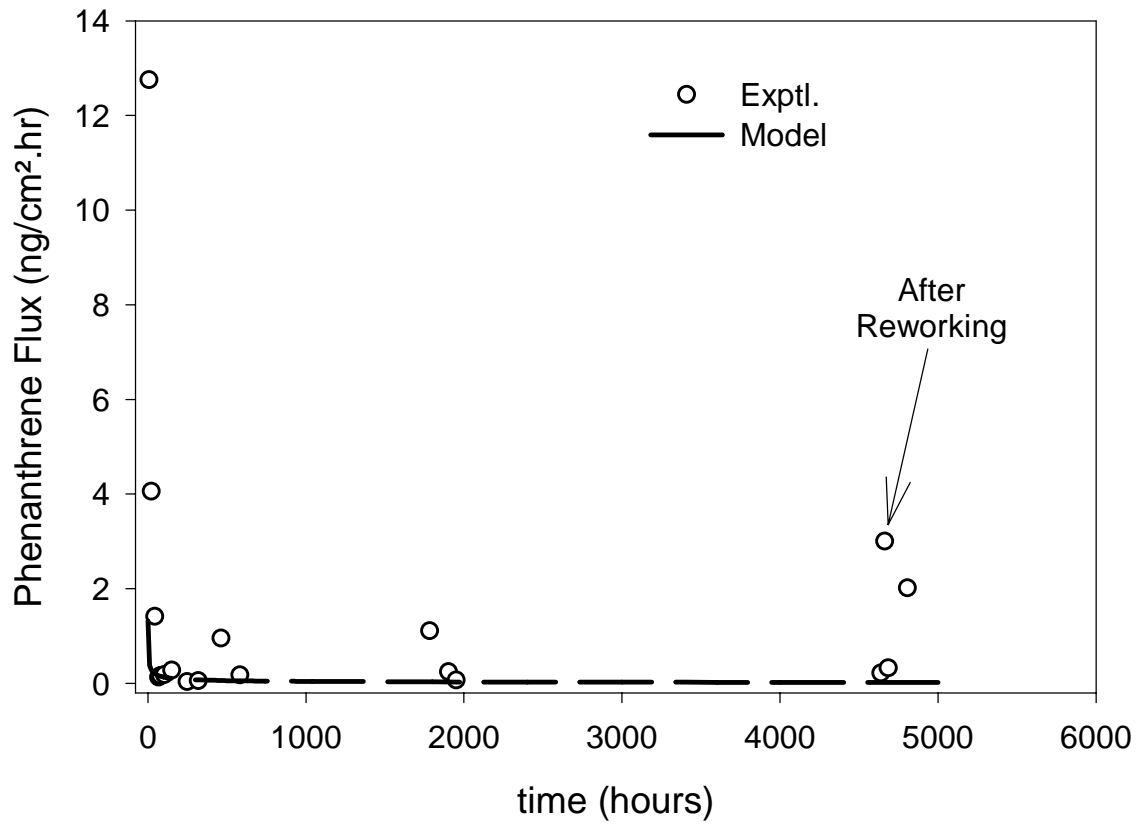


Figure 3. Pilot-scale field simulation—Phenanthrene flux.