

EMISSION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM CONTAMINATED SEDIMENTS

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ABSTRACT

Contaminated sediments contain a variety of volatile and semi-volatile hydrocarbons, which are released into the air, when these sediments are stored in confined disposal facilities (CDFs). Polycyclic aromatic hydrocarbons (PAHs) are one class of sediment contaminants that of great interest, since they are carcinogenic and pose a significant health hazard. Hence quantitative data and models are needed to predict the volatile emissions from CDFs and evaluate control strategies to manage contaminated sediments.

Previous investigations conducted at the U.S. Army Engineer Waterways Experiment Station (WES) with New Bedford Harbor sediment showed high VOC emissions when the material was disturbed and exposed to air. Until recently, flux data obtained from field sediments have not been available to develop models to accurately predict emissions under various environmental conditions, such as moisture content, sediment characteristics and temperature. Sediment physical characteristics, such as aging, porosity and percent oil and grease can significantly impact the volatile emissions.

In this paper, experimental data on air emissions will be presented for two contaminated sediments and a mathematical model that incorporates sediment characteristics will be presented. Experimental data obtained by other researchers will also be analyzed using our models and the effectiveness of the model to quantify air emissions from contaminated sediments will be presented.

INTRODUCTION

Approximately one-eighth to one-quarter of National Superfund Priority list sites include contaminated subaquatic sediment (1). Approximately 14-28 million cubic yards of contaminated sediments are managed annually (2). Confined disposal facilities (CDFs) are used by the U.S. Army Corps of Engineers to dispose contaminated dredged material from shipping channels and harbors in Great Lakes, along the Atlantic and Gulf coasts, and to some extent along the Pacific coast. CDFs are mostly above ground, and are primarily designed to contain the sediment during storage. However, increasing attention is being directed toward the natural pathways for chemicals to leave the CDF and enter the air and water environments (3). For most volatile and semi-volatile contaminants, the primary pathway is volatilization into the atmosphere.

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds consisting of two or more fused aromatic rings. They represent the largest group of compounds that are mutagenic, carcinogenic, and teratogenic and are included in the U.S. EPA priority

pollutants lists. In recent years, increasing attention has been drawn to PAH contamination in aquatic sediments. High concentrations of PAHs have been reported in various sediments from urbanized as well as pristine environment (Fernandez et al., 1999; Ghosh et al., 2000; Li et al., 2001; van Metre et al., 2000; Yunker et al., 1996).

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and pose a significant health hazard. Hence quantitative data and models are needed to predict the volatile emissions from CDFs and evaluate control strategies to manage contaminated sediments. Previous investigations conducted at the U.S. Army Engineer Waterways Experiment Station (WES) with New Bedford Harbor sediment showed high VOC emissions when the material was disturbed and exposed to air. Until recently, flux data obtained from field sediments have not been available to develop models to accurately predict emissions under various environmental conditions, such as moisture content, sediment characteristics and temperature. Sediment physical characteristics, such as aging, porosity and percent oil and grease can significantly impact the volatile emissions.

MATERIAL AND METHODS

Two marine sediments from different sites of Seattle Harbor and two soils from different location in New Jersey will be used in this research. The overlaying water at the sampling site is also collected for preparing sediment. All the sediment, which is unused is stored in sealed plastic buckets at 4 °C. Pebbles, shells woods and other vegetable matter were removed from the sediments before loading them into the reactors. Sediments were homogenized by sieving using 2 mm mesh sieve in the water. Both sediments were characterized. Samples of sediment were sent to a commercial soil analysis laboratory (AGVISE Laboratories, Northwood, North Dakota) to determine the following physical and chemical properties of the sediment: moisture content, organic matter and carbon content, pH, cation exchange capacity, nitrogen, phosphorous, sulfur, soluble salts, sulfate, particle size distribution, and metals (Fe, Mn, Hg, Pb, Cu, Cr).

Table 1 Sediment and Soil Characterization

Label	Sediment 1	Sediment 2	Soil 1	Soil 2
Sand	96.1%	92.1%	77%	65%
Silt	1.1%	3.7%	18%	22%
Clay	2.8%	4.2%	5%	13%
Texture	Sand	Sand	Loamy Sand	Sandy Loam

Sediment and soil, which were homogenized, were sterilized by HgCl₂ solution. A capacity of 1 liter glass flask with 2 openings on the cover was used as a sediment container. Air flow was controlled at a flow rate of 0.25 LPM, to give an average gas residence time of about 4 to 5 minutes within the container. Cole Parmer thermo-hygrometer (Model CMM880) was used to monitor the temperature and relative humidity of air entering the sediment container. XAD-2, 20-60 mesh from Supelco was packed in a 3" long and 6mm diameter glass tube. Both ends were sealed with glass wool. Three different combinations of sediment and air in different environmental conditions were tested for PAHs air emission. a) dry air with dry sediment; b) dry air with wet sediment;

and c) dry sediment with 100% relative humidity air. Also, sediments at different oil and grease concentration were compared for PAHs air emission. Clean sediments artificially doped with PAHs for different aging time will be compared for PAHs air emission, later in this study. XAD-2 traps were replaced at the interval of 2 hours, 4 hours, 24 hours, 72 hours and 168 hours. The traps were extracted, washed and concentrated for analysis immediately.

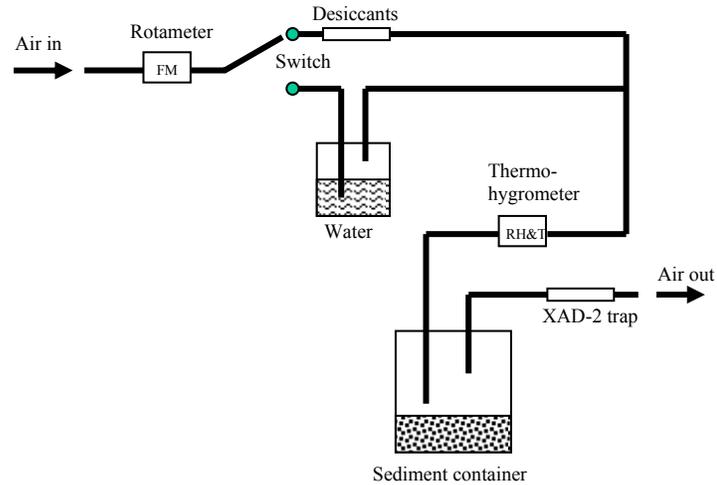


Figure 1 Schematic of PAH Air Emission Study Apparatus.

RESULTS AND DISCUSSION

Experimental studies of soil 1 under moisture percent of 20% and dry soil are shown below. PAHs that were non-volatile, which stayed within the soil and had no measureable air concentrations were not considered in this study.

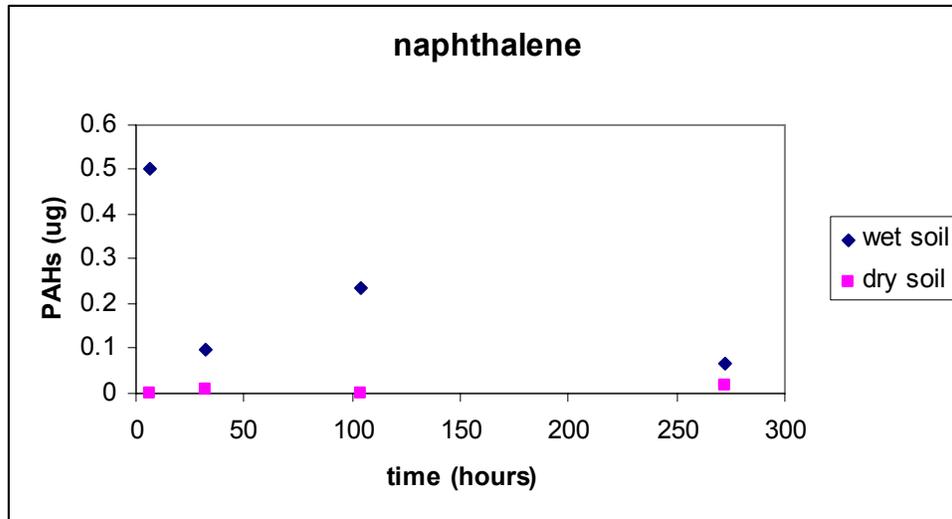


Figure 2 Sorption / desorption of naphthalene in soil #1 under different moisture contents

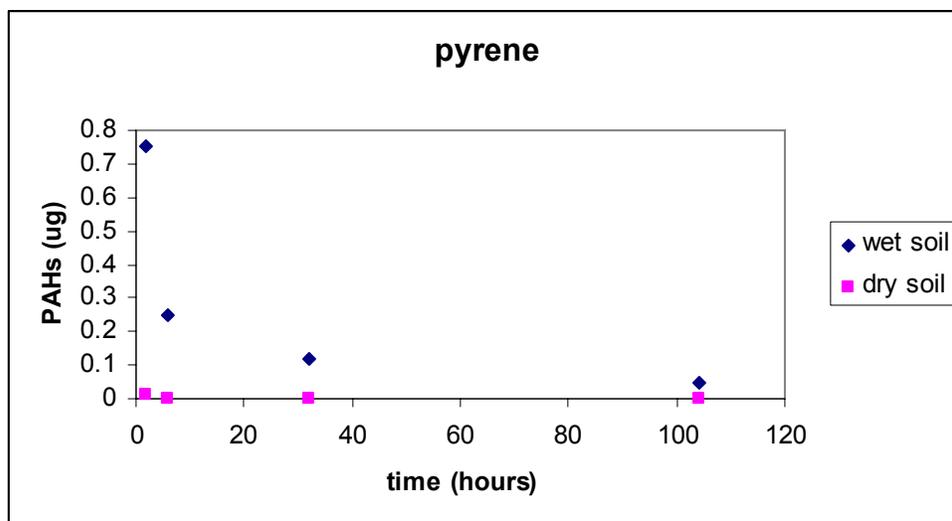


Figure 3 Sorption / desorption of pyrene in soil #1 under different moisture contents

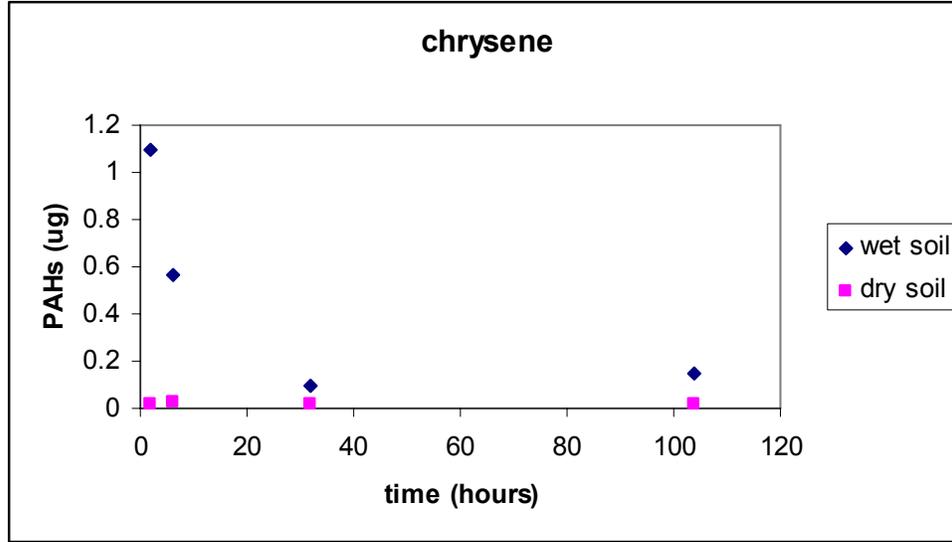


Figure 4 Sorption / desorption of chrysene in soil #1 under different moisture contents

From the figures above, we found the existence of moisture will improve air emissions. An explanation for this may be that water molecules in the soil matrix expands the soil pores, where PAHs or other contaminants are adsorbed. The expansion of the pores in the soil matrix will help PAHs diffusion.

Modeling of PAHs Air Emission Experiment

Slow-rapid adsorption model

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial z^2} + r_{sorp} + r_{reac} + S(C)_{source}$$

Assume the reaction and source terms can be neglected.

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial z^2} + r_{sorp}$$

Sediment PAHs desorption rate

$$\frac{C_s}{C_{s_0}} = \phi_s e^{-k_s t} + (1 - \phi_s) e^{-k_r t}$$

$$C_s = K_p C_{air}$$

$$\frac{C_{air}}{C_{air_0}} = \phi_s e^{-k_s t} + (1 - \phi_s) e^{-k_r t}$$

$$r_{sorp} = \frac{dC_s}{dt} = K_p \frac{dC_{air}}{dt}$$

$$r_{sorp} = K_p C_{air_0} [k_r (\phi_s - 1) e^{-k_r t} - k_s \phi_s e^{-k_s t}]$$

$$\frac{\partial C_{air}}{\partial t} = D_s \frac{\partial^2 C_{air}}{\partial z^2} + K_p C_{air_0} [k_r (\phi_s - 1) e^{-k_r t} - k_s \phi_s e^{-k_s t}]$$

Table 2 lists the typical values of three parameters in the above kinetic model. The time required to reach pseudo desorption equilibrium predicted by this model varies from 2 weeks (Cornelissen et al., 1998) to about 8 months. Figure 5 is a simulated desorption profile based on the typical values chosen from Table 2, i.e., $\phi_s = 0.7$, $k_s = 1.5 \times 10^{-3} \text{ day}^{-1}$, and $k_r = 0.2 \text{ day}^{-1}$. The difference in the kinetic rates between slowly desorbing and rapidly desorbing PAHs is evident. Figure 5 also implies that experiment duration commonly used in desorption studies (days to weeks) are inappropriate for PAHs when slowly desorbing fraction may be significant.

Table 2. PAH desorption rate parameters for the three-parameter biphasic first-order desorption model

Source:	ϕ_s	$k_s \text{ (day}^{-1}\text{)}$	$k_r \text{ (day}^{-1}\text{)}$
Ghosh et al. (2001)*	0.06	5.01×10^{-3}	0.80
Cornelissen et al. (1998) [†]	0.2-0.74	$1.92-4.56 \times 10^4$	19.2-67.2
Johnson and Weber (2001) [§]	0.69-0.736	$1.38-3.01 \times 10^{-3}$	0.134-0.362
Johnson et al. (2001) [§]	0.657-0.736	$1.38-2.63 \times 10^{-3}$	0.134-0.332

*Clay/silt (<63 μm); [†]2-4 ring PAHs; [§]Phenanthrene in a sediment containing 8.27% sediment organic matter. (Zhang, C., et al)

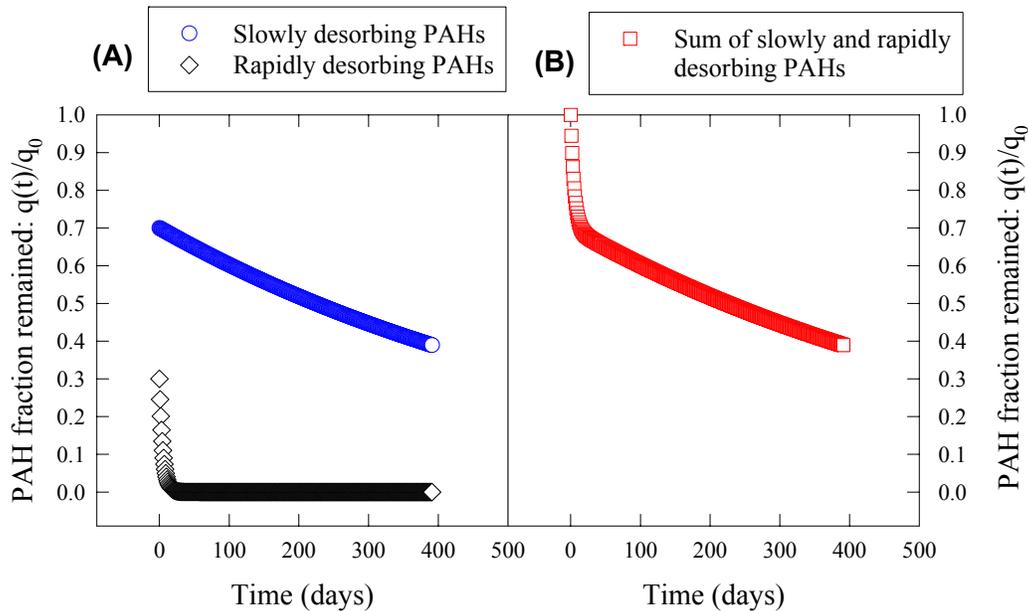


Figure 5. Simulated PAHs desorption profile from a contaminated sediment (Zhang, C., et al)

NOMENCLATURE

C_s : Concentrations of PAHs in the water phase or gas phase of the intraparticle pore in the sediment

K_p : partition coefficient

k_s : apparent 1st order rate constants for slowly desorbing fraction

k_r : apparent 1st order rate constants for rapidly desorbing fraction

r_{sorp} : the rate of sorption

r_{reac} : the rate of reaction

Φ_s : slowly desorbing fraction

$1 - \Phi_s$: rapidly desorbing fraction

$S(C)_{source}$: contaminants source

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