36901 PDF

MODELLING AIR EMISSIONS FROM CONTAMINATED DREDGED MATERIALS

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INTRODUCTION:

A confined disposal facility (CDF) is a diked area for gravity separation and dredged material solids. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals (VOCs) associated with the sediment to be released to the air. Sediments from the New Bedford Harbor (NBH) Superfund Site, MA, contain significant amounts of polychlorinated biphenyls (PCBs), some of which may be released to the air during evaporative drying in a CDF.

Models for evaluation of volatile emissions to air during dredged material disposal have been developed (Thibodeaux, 1989). These theoretical models may be applied to calculate potential PCB emissions from CDFs proposed for containment of NBH sediment. Four locales associated with a CDF operation were identified as separate volatile sources. These locales were: (1) the sediment (dredged material) relocation locale, (2) the exposed sediment locale, (3) the ponded sediment locale and, (4) the vegetation-covered sediment locale. The exposed sediment locale was ranked the highest. Field or laboratory emission data suitable for comparison to model predictions were not available for any of the locales. Brannon (1989) reported some preliminary data for locale 2 for the emission of Aroclor-1242 from a drying sediment exposed to air under laboratory conditions. This paper compares the experimental values against theoretical predictions.

METHODOLOGY:

A series of four experiments were performed with an emission isolation flux chamber. This apparatus was placed atop the sediment to collect the PCB vapors as air was passed over the sediment in the chamber for 1 hour. The vapors were trapped in fluorisil tubes and analyzed by gas chromatography. Two adsorption tubes, and an air rate of 900 cm^3/min were used. In general the experiments can be placed into two classes, wet and dry. The first three experiments were performed with sediment saturated with water; these are called *wet sediment experiments*. The last experiment showed significant cracking and drying of the surface sediment. The soil porosity decreased from 0.774 on day 1 to 0.103 on day 10, while the solid fraction increased from 0.33 to 0.88 during this period. The laboratory was maintained at $20 \pm 0.3\ ^{\circ}C$ and low relative humidity throughout the experiment. The experiment number 4 shall be termed the *dry sediment experiment*.

The following is a brief presentation of the model that applies for the exposed sediment locale. Contaminated sediment that is wet and exposed directly to air results in the highest VOC emission rates. VOCs sorbed on the particles at the soil surface have a relatively short pathway to the air. The top layers eventually become depleted of the chemical. Continuing losses will come from within the soil pores. The following equation applies for this transient volatilization rate

$$N_A = \frac{W_A K^* - C_a}{\left[\dfrac{\pi\ t}{D_{Aa}\left(1 + \dfrac{\rho_b}{\epsilon_a K^*} \right)} \right]^{1/2} + \dfrac{1}{k_A}} \qquad (1)$$

where N_A is the emission flux from the soil ($\mu g.m^{-2}.h^{-1}$), K^* is the air/soil partition constant ($g.m^{-3}$), W_A is the chemical concentration on soil ($\mu g.g^{-1}$), t is time (h), D_{Aa} is the diffusion constant of the chemical in the air-filled pores ($m^2.h^{-1}$), ρ_b is the soil bulk density ($g.m^{-3}$), ϵ_a is the air-filled porosity ($m^3.m^{-3}$), k_a is the air-side mass transfer coefficient ($m.h^{-1}$), and C_a is the chemical concentration in the background air ($\mu g.m^{-3}$). The above equation is for an

unsaturated (with respect to water) or dry sediment. As the sediment looses its water content by evaporation and drainage, the air-soil equilibrium partition constant changes. Three water content regimes exist and require as many partition constants. These are wet, damp and dry. Each can be expressed by the simple equilibrium expression, $C_a^* = K^* \, W_A$. The partition constant for the wet case is the ratio of Henry's constant to the soil-water partition constant, $K^* = \frac{H_c}{K_d}$, whereas for the dry case at soil loadings it is $K^* = \frac{p_A^* M_A}{B_1 RT \, W_A^*}$, where K_d is the soil-water equilibrium constant ($m^3.g^{-1}$), p_A^* is the chemical vapor pressure (atm), B_1 is the BET adsorption constant (dimensionless), M_A is the chemical molecular weight ($\mu g.mol^{-1}$), R is the gas constant (= 82 x 10^{-6} $atm.m^3.mol^{-1}.K^{-1}$), T is the temperature (K) and, W_A^* is the chemical loading on the sediment for a monolayer coverage ($\mu g.g^{-1}$).

RESULTS:

In the section in which the experimental data was reviewed it was noted that the experiments fall into two classes. These were the initial period with the wet sediment and the long-term run with the dry sediment. Equation (1) applies for both cases with the appropriate wet and dry equilibrium expressions given earlier.

During the initial phase of the experiment evaporation time is short (i.e, t ~ 0) and the sediment surface is wet. If the incoming air is also PCB free Equation (1) simplifies to

$$N_A = k_A \; W_A K^* \qquad \textbf{(2)}$$

where K^* is given by the equation for the wet case. At 25°C it is 0.132 $g.m^{-3}$. The air side mass transfer coefficient can be estimated using four different methods (Thibodeaux and Scott 1985). The estimates for Aroclor 1242 at 25°C range from 30 to 96 $cm.h^{-1}$. Based on the range of coefficients the predicted emission rates for A-1242 with a sediment loading of 887 $\mu g.g^{-1}$ ranges from 36 to 113 $\mu g.m^{-2}.h^{-1}$. The experimental values ranged from 12 to 62 $\mu g.m^{-2}.h^{-1}$. These values are shown in Figure 1. The fact that the predicted and experimental ranges substantially overlap each other suggests that the wet soil portion of the model is correct.

By the third day of the experiment the sediment was essentially dry. In this case, time is large and Equation (10 applies as written. The air-sediment partition constant should reflect the dry state of the sediment.

A procedure based on the theory of gas mixtures adsorbing competitively on a solid surface that extends the classical Brauner-Emmett-Teller (BET) model to account for water vapor was used to estimate K^* for Aroclor 1242 on dry sediment (Valsaraj and Thibodeaux, 1988). A key factor in the procedure is the surface area of the soil. In the case this was determined from the fractional organic matter and clay of the sediment. Together with the sediment surface area S ($m^2.g^{-1}$) so determined the monolayer coverage of Aroclor 1242 on the sediment W_A^* was computed. Other relevant parameters used were: B_1 = 20, 18.4% of S active for adsorption and Aroclor 1242 density was 1.5 $g.cm^{-3}$. All other Aroclor 1242 properties were from Thibodeaux (1989). Two estimates of K^* for the dry case were obtained; one for the estuarine composite sediment 0.056 $kg.l^{-1}$ and the other for the sediment from the hot spot 0.016 $kg.l^{-1}$.

The necessary information is available in Equation (1) to arrive at predicted values of the flux. The working form of Equation (1) is

$$N_A = \frac{887 \; K^*}{[\; 0.097(tK^*)^{1/2} + 3.29 \;]} \qquad \textbf{(3)}$$

with t in days, K^* in $g.m^{-3}$ and N_A in $\mu g.m^{-2}.h^{-1}$. The value of k_A was 0.304 $m.h^{-1}$, D_{Aa} was 0.035 $\epsilon_a^{4/3}$ in $cm^2.s^{-1}$, the soil bulk density was 0.69 $g.cm^{-3}$ and porosity ϵ_a was 0.774.

The predicted values for Aroclor 1242 flux assuming dry soil conditions appear in Figure 1. The experimental values are also given alongside. Comparison of predicted and measured flux values should be done for t ≥ 3 days, since the sediment was wet or damp before this time. The average measured fluxes for days 3 through 10 is 0.885 ± 0.432 $\mu g.m^{-2}.h^{-1}$, whereas the predicted

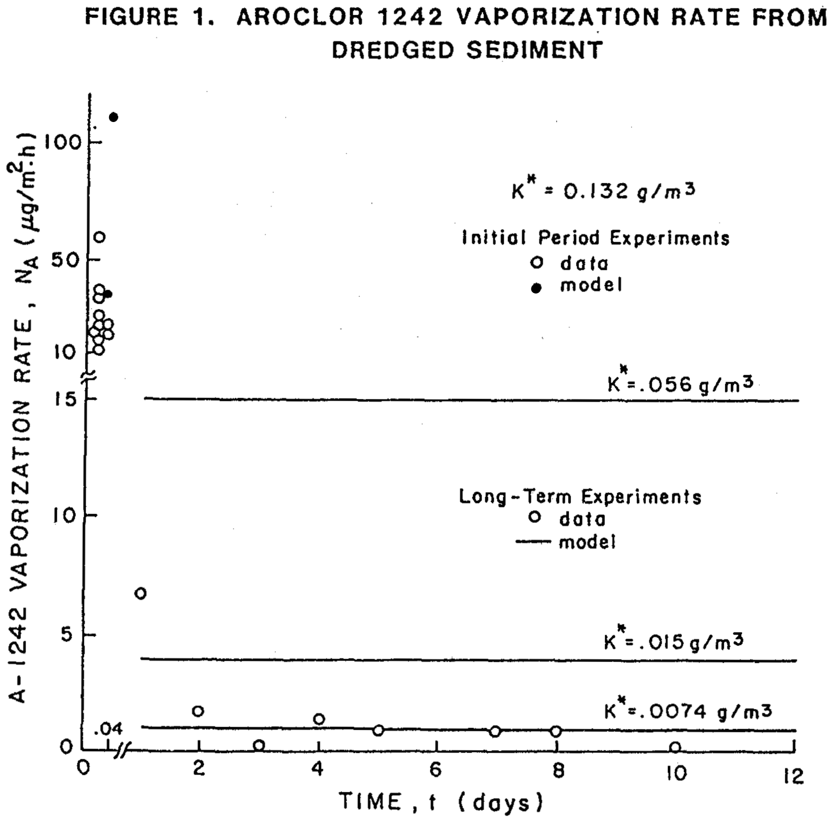

Figure 1. Aroclor 1242 vaporization rate from dredged sediment.

fluxes were 15 and 4 $\mu g.m^{-2}.h^{-1}$ for the two calculated values of K^*. At best the predicted values are 4.7 times larger than the measured values. The model predicts a very weak time dependance on the rate. At day 10 the soil-side mass tranfer resistance accounts for only 1.1% of the transport resistance for the organic. The measured values also seem to display a time dependance. This behavior may be due to several factors including cracking and other soil porosity changes with time. However, it appears that K^* is the primary factor that controls the flux in this set of measurements. A value of 0.0074 $g.m^{-3}$ in the model equation yields predicted fluxes in line with the experimental values. The model predicted and measured values appear in Figure 1. An overall mass balance indicates that 2.32 g of Aroclor 1242 were present initially in the isolation flux chamber. Using 1.7 $\mu g.m^{-2}.h^{-1}$ as the average evaporation rate yields 59 μg lost from the sediment in 10 days. This is 0.0026%, so the bulk of the original Aroclor 1242 remained in the soil and did not evaporate.

CONCLUSIONS:

The theoretical model does a satisfactory job in predicting the Aroclor 1242 emission rate from exposed sediment. The measured values for wet sediment averaged 26 ± 13 $\mu g.m^{-2}.h^{-1}$. The model yielded values of 36 to 113 $\mu g.m^{-2}.h^{-1}$ depending on the k_A values used. The measured values for the dry sediment averaged 0.855 ± 0.432 $\mu g.m^{-2}.h^{-1}$. The most sensitive parameter in the model was K^*, the air-sediment partition constant. In general, the theoretical model overpredicts the measured values by a factor of 1.4 to 18.

Additional experimental measurements are needed to reduce this range of uncertainty and explore the effects of cracking. These experiments should involve re-wetting the soil in order to observe any increase in flux. Field measurements at a CDF site should be performed with the isolation flux chamber or a similar method. Laboratory experiments should be performed and the air-sediment partition constant K^* measured for damp and dry conditions. This critical parameter has a very weak data base (Valsaraj and Thibodeaux, 1988).

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ACKNOWLEDGEMENT:

This work was supported by a grant from the US Environmental Protection Agency (Grant No: R 819165-01) to the Hazardous Substance Research Center (South and Southwest). Dr. Dale Manty is the Project Officer.

BIOREMEDIATION OF CONTAMINATED SEDIMENTS

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INTRODUCTION

Contaminants in bottom sediments have historically been considered to have minimal environmental impact because they are buried, sorbed or electrostatically bound to clay particles, or incorporated into humus. Physical and chemical conditions such as alkalinity, pH, and redox of the sediments also play a part in sequestering contaminants. (2,3) As long as the sediments are undisturbed, the contaminants are considered stabilized and not an immediate environmental problem. Resuspension of bottom sediments makes contaminants more available for dispersal into the marine environment. Events that can cause resuspension include storm surges, construction activity, and dredging.

A conceptual model of the effect of a resuspension event on contaminated sediments is shown in Figure 1. During resuspension, sediment particles move from an anaerobic to aerobic environment, changing their redox characteristics, and allowing the indigenous aerobic bacteria to grow and utilize certain classes of contaminants as energy sources. The contaminants are also more available for use because the mixing energy imparted to the particles during resuspension enhances mass transfer, allowing contaminants to enter the aqueous phase more rapidly.

The contaminants targeted in this research are polynuclear aromatic hydrocarbons (PAHs), a class of contaminant commonly found in bottom sediments near highly industrialized areas. A major source of PAH contamination is the combustion of fossil fuels. (8,5) Other sources are industrial wastewater effluents, petroleum spills and oilfield produced brine disposal into waterways. PAHs consist of multiple benzene rings fused in linear, angular, and cluster arrangements. PAHs are non-ionic and hydrophobic and as such, are lipid soluble and can be bioaccumulated in the food chain. Exposure to polycyclic compounds has also been associated with higher risks for cancer.

Previous research has shown that PAHs can be biodegraded. Size and structure, i.e., number and configuration of condensed rings, can affect compound disappearance. (4,7) PAHs of up to three condensed rings have been shown to serve as growth substrates. Compounds with more than three rings may be subject to cometabolic degradation.(1) Probably the most important parameter affecting biodegradation is the redox character of the sediment or sediment/water system. Studies of sediment slurries under various redox conditions have shown that rates of compound disappearance and mineralization increase with increasing redox potential. (3,6)

The focus of this research was to examine the relationship between resuspension and biodegradation of PAHs in lab scale slurry reactors. The rate and extent of contaminant release from the sediments into an uncontaminated water column was determined. Oxygen demand of initially anaerobic sediments were investigated. Then rate and extent of phenanthrene biodegradation was examined. Final partitioning of the phenanthrene, after the degradation test, was determined based on mass balance calculations made on the radiolabeled carbon in the tracer. Several factors which may influence the design or operation of bioreactors used for remediation of contaminated sediments were also evaluated.

METHODOLOGY

Sediments used in these experiments were collected from Dickinson Bayou, Galveston County, Texas. The natural environment is esutarine with total dissolved solids (TDS) of the water measuring