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New Jersey Marine Sciences Consortium

and

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Office of Maritime Resources

# MEASUREMENT OF PCB FLUXES TO THE ATMOSPHERE FROM STABILIZED DREDGED MATERIAL

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# 1.0 INTRODUCTION

This study consisted of a laboratory investigation, during which sediment from New Town Creek, N.Y. was collected and placed in a laminar flow wind tunnel in order to determine PCB fluxes from stabilized dredged material (SDM) to the atmosphere in a controlled laboratory environment. The presently reported work was conducted as Phase II of a study. Phase I was conducted to measure PCB fluxes from SDM in a landfill (Korfiatis et al. 2003). The experiments conducted during this phase of the project, analyzed various environmental and sediment conditions that could not be controlled in the field. These conditions included; the initial concentration of PCBs in the sediment, moisture content of sediment and air, temperature of the sediment and air, wind speed, and percent of cement used to stabilize the sediment. The effects that these conditions have on the flux of PCBs were evaluated to isolate the effect of stabilization on PCB fluxes from sediment.

The presently reported study was conducted in order to; (1) assess the accuracy of these measurements using laboratory PCB flux measurements, and (2) assess the effects of stabilization on the fluxes of PCBs from SDM. This report will present background information, including theory and a review of previously collected flux chamber PCB measurements, and then the laboratory investigation will be discussed. Subsequently, the results and conclusions made from this study will be discussed.

## 1.1 Theory

### *1.1.1 Sediment Air Flux Theory*

The flux of a substance from sediment to the air is a common process. It was first expressed by Dalton (1802) for the flux of water vapor from the ground into the air.

$$E = C(e_s - e_a) \tag{1}$$

E is the flux of water vapor, C is a mass transfer coefficient for water, and $e_a$ and $e_s$ are moisture contents of the soil and air respectively. This equation can also be used to describe fluxes of contaminants. This flux can be separated into two distinct processes; first the contaminant diffuses to the sediment surface, and second it is transported from the surface into the atmosphere. These two processes can be described by the following equation.

$$F = k_S(C_S - C_A^*) = k_A(C_A^* - C_A^{\infty}) \tag{2}$$

$k_S$ and $k_A$ are the mass transfer coefficients for the sediment and air sides respectively, and $C_S$, $C_A^*$, and $C_A^{\infty}$ are the sediment-air concentration, surface air concentration, and background air concentrations. Since the flux rate will be constant over both processes they can be combined to yield an expression for the determination of $K_T$ (Schwarzenbach et al 1993).

$$\frac{1}{K_T} = \frac{1}{k_{sed}} + \frac{1}{k_a} \tag{3}$$

It is evident from this equation that the total flux will be limited by the interface with the greatest resistance.

### *1.1.2 Air Side ResistanceTheory*

In laminar flow, particles are forced to move in parallel paths due to viscosity. Laminar flows are, in essence, predictable, given knowledge of the molecular properties of the fluid. Since the flow in the present wind tunnel experiments will be laminar, the only mechanism of transport out of the sediment was diffusion. An equation for the mass transfer coefficient from the surface can be derived using boundary layer theory. The boundary conditions state that the concentration in the sediment is $C_o$, the concentration in the air away from the surface is zero, and the flux rate at the surface is constant. Thus $k_a$ can be derived for laminar flow of a fluid over a sparingly soluble flat plate using boundary layer theory (Cussler, 1984).

$$\frac{k_a\, x}{D} = 0.323 \left( \frac{\rho\, v^0\, x}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho\, D} \right)^{1/3} \tag{4}$$

| | |
|---|---|
| $k_a$ | local mass transfer coefficient at position x |
| x | position along x-axis |
| D | Molecular diffusion coefficient of species being transferred |
| $\rho$ | Flowing fluid density |
| $\mu$ | Flowing fluid dynamic viscosity |
| $v^0$ | Flowing fluid average velocity |

The mass transfer coefficient ($k_a$) is a local mass transfer coefficient since it is a function of the x position along the x-axis. This x dependence, is expected because the hydrodynamic and concentration boundary layer thicknesses vary with x. Since the material balance is applied over the length of the plate, the mass transfer coefficient $k_{ma}$ is different from the local mass transfer coefficient $k_a$. Here, $k_{ma}$ is a length-averaged mass transfer coefficient defined as:

$$k_{ma} = \frac{1}{L} \int_0^L k_a\, dx \tag{5}$$

where L is the length of the sediment chamber. Substitution into the previous equation yields the following expression for $k_a$:

$$k_a = \frac{0.646 D}{L} \left( \frac{\rho\, v^0\, L}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho\, D} \right)^{1/3} \tag{6}$$

Knowledge of the mass transfer coefficient for the air side of the sediment air interface allows inferences to be made about the rate limiting step in the process of volatilization of PCBs from SDM.

### *1.1.3 Sediment Side Resistance Theory*

The process of release and transport of contaminants from sediment into the air can be thought of as a three part process. First, the contaminant adsorbed to the solid will exist in equilibrium with the concentration of contaminant in the pore water; this is governed by an equilibrium constant, $K_D$. Second there will also be an equilibrium relationship between the concentration in the pore water and the pore air. This ratio is governed by Henry's Constant. Henry's constant is equal to the concentration of contaminant in the gas phase divided by the concentration in the liquid phase when the two are in equilibrium.

$$H_c = C_A / C_L \tag{7}$$

And finally, the contaminant will be transported in the vapor phase through the sediment into the atmosphere which will be a function of the diffusivity, $D_E$.

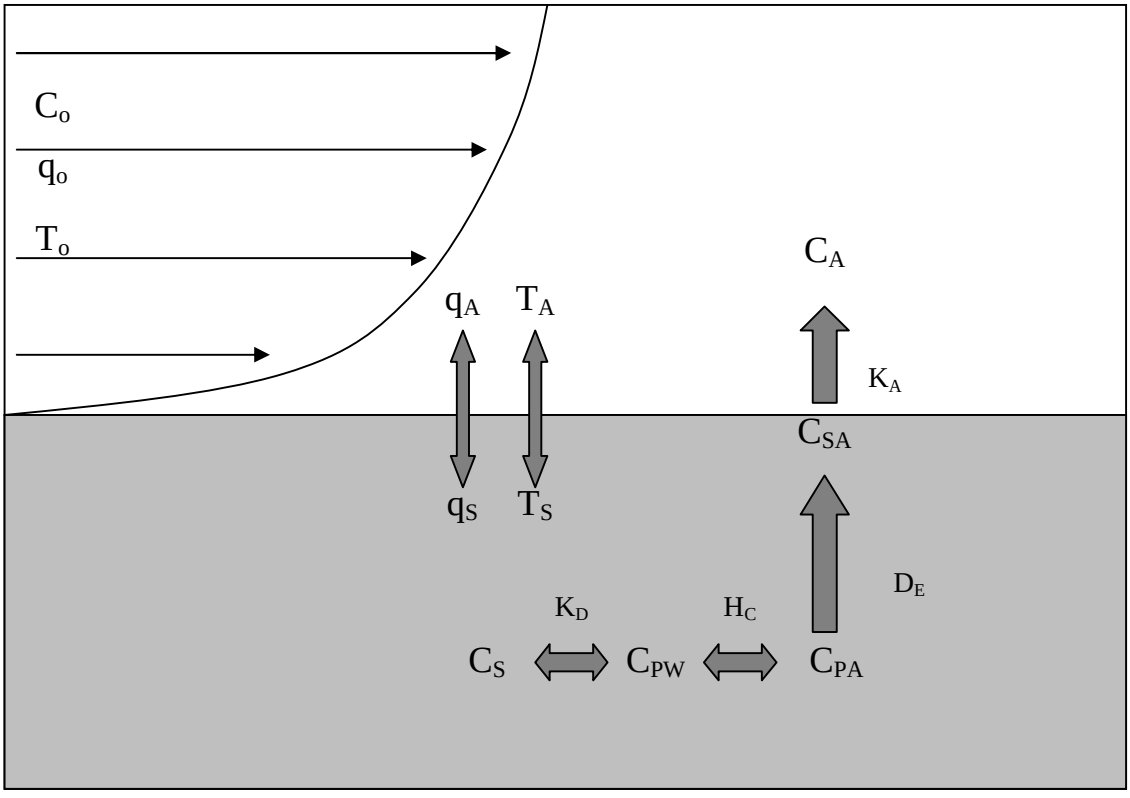


**Figure 1.** Conceptual Model of PCB Fluxes

The final step in this process is thought to be rate limiting (Dupont 1986). The largest effect on this rate limiting step will result from changing water content of the sediment.

### *1.1.4 Sediment Flux Models*

Various models have been developed to predict the volatilization of substances from soil. Several of these are discussed in the following section.

***Hartley Method (Hartley 1969)***

The Hartley Method is a model created to predict fluxes of contaminant from soil to air in terms of the heat balance between the contaminant and the air. The flux is expressed as:

$$F = \frac{\left(\rho_{\max} - \rho_{air}\right)}{\delta} \Bigg/ \left[ \frac{1}{D_V} + \frac{\lambda_V{}^2 \rho_{\max} M}{kRT^2} \right] \tag{8}$$

F = flux of compound
$\rho_{\max}$ = saturated vapor concentration at the temperature of the outer air
$\rho_{air}$ = vapor concentration of the outer air
$\delta$ = thickness of viscous sub-layer
$D_V$ = diffusion coefficient of vapor in the air
$\lambda_V$ = latent heat of vaporization
M = molecular weight
k = thermal conductivity of air
R = gas constant
T = temperature

The denominator in equation 8 is primarily the thermal component of the resistance to volatilization. It is only significant for water or other very volatile compounds. Thus, for less volatile compounds such as PCBs equation 8 becomes:

$$F = \frac{D_V\left(\rho_{\max} - \rho_{air}\right)}{\delta} \tag{9}$$

This is the film theory equation originally proposed by Nerst (1904). It proposed that the mass transfer coefficient is simply defined as $k=D/\delta$, where D is the molecular diffusion and $\delta$ is the width of the film. This model is useful because of its simplicity in determining the flux; however it does not take into account contaminant concentration and moisture content of the soil. It represents a situation where the contaminant is in abundant supply in the soil (unlike PCBs) and is only a function of the diffusivity and height of the viscous sub-layer.

***Valsaraj Method (Valsaraj et al 1997)***

In order to address the effect of soil moisture content, the model must be adjusted with a term that accounts for the effect that moisture will have on the flux of contaminant. This term is called a retardation factor, it is a function of the porosity, moisture content, Henry's constant, and the 'wet' or 'dry' sediment-air partition coefficient.

$$R_F = \varepsilon_a + \varepsilon_w / H_c + \rho_b K_{dw} \tag{10}$$

$\varepsilon_a$ = air filled porosity
$\varepsilon_w$ = water filled porosity
$H_c$ = Henry's constant
$\rho_b$ = sediment bulk density
$K_{dw}$ = 'wet' sediment-air partition coefficient

The diffusivity will also be affected by the reduction in air filled pores in the soil. As a result the effective diffusivity must be used. This is determined via the Millington Quirk expression.

$$D_e = D_A \varepsilon_a^{10/3} / \varepsilon_T^{2} \tag{11}$$

$D_A$ = chemical diffusivity in air
$\varepsilon_T$ = air filled porosity

The equation used to determine the concentration of a contaminant in a column of soil becomes:

$$\frac{\partial \rho_A}{\partial t} = \frac{D_e}{R_F} \frac{\partial^2 \rho_A}{\partial z^2} \tag{12}$$

$\rho_A$ = the mass concentration of contaminant A in the air in the sediment pore spaces. The boundary conditions are; (1) a lower boundary through which there are no fluxes of contaminant, (2) an upper boundary at which the flux of contaminant through the sediment equals the gradient of concentration between the surface and background air multiplied by an air side mass transfer coefficient, $k_a$. This mass transfer coefficient will largely be determined by the flow regime over the sediment. The initial condition states that at t=0 the concentration is constant throughout the soil column.

$$\begin{aligned} \frac{\partial \rho_A}{\partial z} &= 0 \text{ at z=0} \\ D_e \frac{\partial \rho_A}{\partial z} + k_a \left( \rho_A - \rho_A^{\infty} \right) &= 0 \text{ at z=H} \\ \rho_A(z,0) &= \rho_A^{0} \text{ at t=0, for all } z \in [0, H] \end{aligned} \tag{13}$$

The resulting flux is:

$$N(t) = 2 D_e \rho_A^{0} \frac{L^2}{H} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 T}}{L(L+1) + \alpha_n^2} \tag{14}$$

The terms L and T are defined by:

$$L = {k_a H}/{D_e} \tag{15}$$

$$T = {D_e t}/{R_{FW} H^2} \tag{16}$$

And $\alpha_n$ are the positive eigan values of:

$$\alpha_n \tan(\alpha_n L) = L \tag{17}$$

This model has the benefit of accounting for the effects of initial moisture content of the sediment. It has been used in several studies to monitor the flux rates of several PAHs from sediment with good results. The moisture content of the sediment is taken into account using the effective diffusivity and the retardation factor. The moisture content of the sediment changes, in order to account for the changing moisture content the authors of this model solved for a 'wet' condition and a 'dry' condition. The changing moisture was then accounted for by changing the ratio area of wet sediment to dry. The assumption is made that the moisture content varied horizontally but is constant vertically in the water column.

In a later study, Valsaraj *et. al*. (1999) proposed a simplified version of this model. The limiting factors were grouped into air-side resistance and sediment-side resistance.

$$\frac{C_A^{\,o}}{N_A} = \frac{1}{k_a} + \sqrt{\frac{\pi t}{D_e R_f}} \tag{18}$$

$C_A^{\,0}$ is the initial concentration of contaminant in the sediment pore air spaces. This equation is the normalized source concentration; the two terms on the right hand side are the air-side and sediment side resistances. The first term, $k_{a,}$ is the mass transfer coefficient on the air side of the interface. The second term is the sediment side resistance. This term is a function of time, as well as the moisture content of the sediment. This model assumes that the rate limiting step for the flux will be the rate at which the contaminant diffuses to the sediment surface.

Dry sediment will have large $D_e$ and $R_f$ values, thus increasing the resistance from the sediment side. Wet sediment will have large flux values due to lower resistance from the sediment side of the interface. Consequently, the contaminant flux rates are initially the maximum allowable by the air-side mass transfer coefficient. Over time, evaporation occurs, the sediment moisture drops, and the flux becomes limited by the diffusion rate out of the sediment.

### *1.1.5 Sediment Flux Measurements*

PCB fluxes are greatly influenced by the physical characteristics of the sediment. The water content, density, temperature, and organic content have to be taken into account

when attempting to model fluxes from sediment. Chiarenzelli *et al*. (1996) have conducted experiments to measure the effect of water content on the fluxes of PCBs from contaminated dredged sediment. Their study was conducted on PCB contaminated sediment from the St. Lawrence River. The samples were allowed to dry at ambient conditions, and PCB losses from the samples were determined. The sediment samples contained moisture contents ranging from 30%-99%. Filtered air was drawn through the 2 liter experimental chamber at 20 $cm^3$/sec. Average removal rates of PCBs from the sediment range from 2.1 – 184.2 ng/hr and increase with moisture content. An exponential correlation ($R^2$ = 0.932) was found between the amount of PCBs volatilized and the initial water content. When samples were effectively dry, PCB loss subsided. Analysis of the volatilized PCB congeners and those that remained in the soil, exhibited a great disparity in the amount of chlorination. Four, low molecular weight, ortho-chlorinated congeners represented 54%-76% of the PCBs volatilized. The low molecular weight congeners appeared to have a greater potential to volatilize from the sediment surface.

In another study, Chiarenzelli et al. (1996) dried PCB contaminated sediment samples using air of varied relative humidity. The amount of PCBs lost during drying was monitored. This study determined that PCB fluxes were large during drying of the soil; however, when the soil moisture reached equilibrium with the moisture content of the air, drying no longer occurred and the magnitude of PCB fluxes was greatly reduced. This study also focused on the PCB flux as a function of time. It was found that the fluxes decreased steadily over time, presumably due to the decrease in PCBs available for volatilization.

Thibodeaux et al (1989) conducted PCB volatilization studies in a flux chamber. The sediment was spread out very thin and air flow over it was laminar. Sediment from the New Bedford Harbor, MA superfund site was placed in the chamber and fluxes were monitored. The experiments were run under 'wet' (>4% w/w) and 'dry' (>1% w/w) conditions. During the 'wet' experiments the measured fluxes ranged from 12 to 62 $\mu g/m^2$/hr, and during the 'dry' experiments, the measured values from the sediment were 0.855 ± 0.432 $\mu g/m^2$/hr. The experiments were run using sediment with a concentration of 887 μg/g of Aroclor 1242. This study found a large dependence of the flux on moisture content of the soil, which in turn was the dominant factor in the sediment–air partitioning coefficient. These measured fluxes were compared to a model similar to the 'Valsaraj' method presented in the previous section. The predicted fluxes had a range of 36 to 113 $\mu g/m^2$/hr, The model was found to over predict the fluxes of Aroclor 1242 by 1.4 to 1.8 times.

Valsaraj *et al*. (1997) conducted experiments to measure Poly Aromatic Hydrocarbons (PAH) fluxes in microcosms designed to simulate the drying of sediment, and attempted to model the fluxes using the 'Valsaraj' method. Air was blown over the top of the sediment and sampled for PAHs.

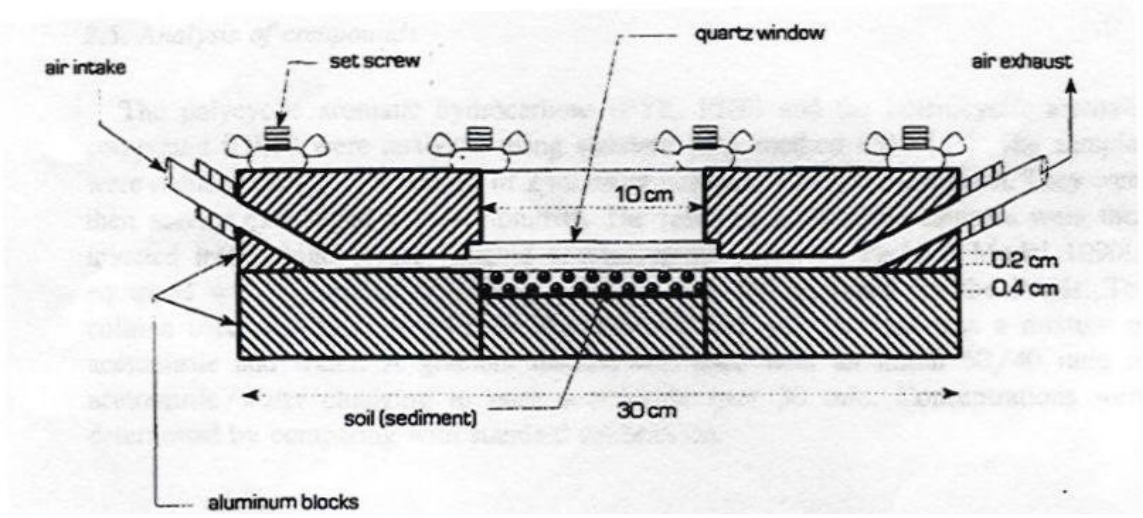


**Figure 2.** Volatilization Chamber (Valsaraj 1997**)**

The experimental microcosms had a sediment depth of 4mm and an air space of 2 mm. The exhaust air was pushed through XAD Resin and extracted to determine the PAH flux. This configuration allowed for a measurable moisture front in the sediment, thus they were able to quantify the flux as a sum of the flux from a wet section and a dry section. It was found that the 'wet' section dominated the flux value. This is due to the relatively small size of the sediment – air equilibrium coefficient as compared to Henry's constant. The experimental set-up included the use of sediment from three contaminated dredging sites and sediment spiked with the PAHs in the lab. The contaminant concentration, relative humidity, and soil moisture content were continually monitored.

The model was based on the idea that there are two rate determining resistances to the flux. The resistances were air-side and sediment-side. Depending on the environmental conditions, either may dominate the behavior of the flux. Experimental results from this study support the conclusion that the effect of the air-side mass transfer coefficient, $k_{a,}$ on the fluxes is only felt during the early stages of the experiment. Beyond this period, emissions are increasingly controlled by the sediment side. Further variations of the experiment included variations in the relative humidity, and remoistening of the soil.

Relative humidity was found to have a great influence on the flux values, by keeping the relative humidity at >99%, the flux rate dropped slowly from an initial rate. Using the same conditions but changing the influent air to 0% relative humidity, the flux rate decreased much more rapidly. When the relative humidity was alternated between >99% and 0%, the flux rates fell to very low values with dry air and increased when the humid air was reintroduced. The response to the change in relative humidity is expected; however the rate at which it occurred may be due to the fact that the experimental microcosm only had a thickness of 4 mm. This experiment shows the large dependence

on the water content of the air on the volatilization of contaminants. "Dry" sediments have a greater affinity for contaminant than do wet sediments because of the competition for space on the sediment with water. As the sediment particles in upper layers of the sediment dry, they not only hold the contaminant absorbed to them tighter, they will also absorb free contaminants that would otherwise diffuse to the surface, thus further increasing the sediment-side resistance. After flux values were determined for sediment, it was blended, and the experiment was rerun. The resulting fluxes were similar in magnitude to the values from the first cycle indicating that the change in the mass of contaminant present in the sediment is very small.

Price et al (1997) conducted a study using experimental microcosm similar to those in the previous studies. They noted the dependence of the flux on the air flow. The flow rates used corresponded to average velocities of 0.28 cm/sec, 2.78 cm/sec, and 27.78 cm/sec. The sediment was contaminated with PAHs. For the first 170 hours of the experiment the air velocity was 0.28 cm/sec. The fluxes were fairly constant and low, indicating that the air side resistance was controlling the flux. When the velocity was increased to 2.78 cm/sec, the flux rate increased approximately 7 times. When the velocity was increased again, no change in flux values was noted, most likely due to the fact that the sediment side resistance had become the rate limiting factor.

Cousins et al. (1997) conducted flux chamber experiments on sediment that was used to amend PCB contaminated sludge. The sludge was applied to the soil. Air with 100% relative humidity was passed over the sludge and through a poly-urethane foam filter. This filter was then extracted to remove the absorbed PCBs which where then analyzed to determine the flux of PCBs from the sludge. Cousins used the 'Jury Model' to predict fluxes, and then compared them to the values from their flux chamber. In addition to fluxes, the model was used to predict the values for the effective diffusion coefficient of individual congeners. The fluxes predicted by the model were relatively close to some of the experimentally determined values of the lighter congeners; however in other cases they varied by as much as an order of magnitude.

## 2.0 FLUX CHAMBER EXPERIMENT

Phase II of this experiment was conducted using laminar flow wind tunnel to evaluate the fluxes of PCBs from SDM. In order to eliminate the variability of site conditions at the landfill, a chamber was built in which these conditions could be controlled. Fluxes of PCBs from sediment were monitored to evaluate the accuracy of the landfill results and to get a greater understanding of the chemo-dynamics involved in the process. The following sections describe the underlying theory, methods, and the results from these experiments. Finally, the results will be analyzed to get a better understanding of the mechanisms that determine the magnitude of PCB fluxes.

### 2.1 Experimental Set-up

#### *2.1.1 Wind Tunnel Design*

The PCB flux experiments were conducted in a laminar flow wind tunnel designed and constructed at Stevens. The dimensions were 4 meters long, 0.50 meters wide and 0.1 meters deep. The test section is 2 meters long, and has a depth of 20 centimeters. Sediment was placed to a depth of 10 centimeters, and flattened to maintain a smooth channel. In front of the test section is 2 meter section with height of 10 centimeters. This section is for the establishment of a flow regime. The entrance cone of the wind tunnel was designed using a four to one reduction; the curve was designed to have a maximum adverse velocity gradient of 0.025 (Lighthill 1945).

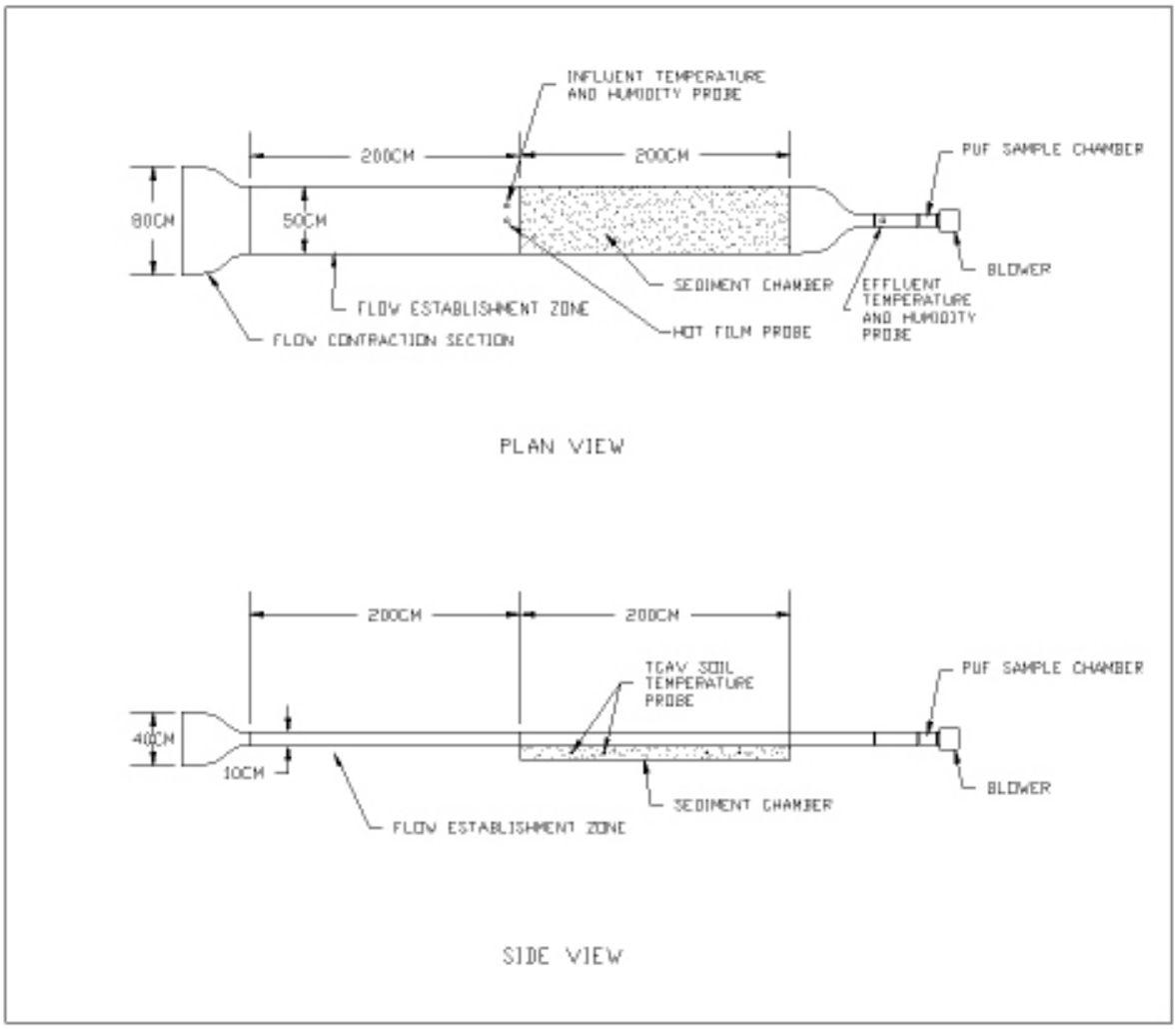


**Figure 3.** Wind Tunnel Plans

Several instruments were installed in the wind tunnel in order to directly measure various atmospheric and sediment characteristics. These characteristics included inlet and exit air temperature and moisture content, and SDM temperature. The temperatures were measured with chromel-constantan thermocouples with a diameter of 74μm. These thermocouples have a resolution of 0.006$^{o}$C with 0.1 μV rms noise. The vapor pressures were measured by pumping air through a cooled mirror, dew point hygrometer (Model Dew-10, General Eastern Corp., Watertown, MA). Air was drawn from both inlet and

outlet continuously. The hygrometer was equipped with a solenoid value that switched the air flow through the sensor between the two intakes for two minute intervals. The first minute of the interval was to clear the air from the previous interval, and the measurements were collected in the second. Air was drawn at a flow rate of 0.4 liters/minute with 2 liter mixing chambers to give a 5 minute time constant. The Dew-10 had a resolution of approximately ±0.01 kPa. The spatially averaged SDM temperature was measured with a TCAV (thermocouple averaging) probe. These data were compiled in a Campbell 23X Data logger (Campbell Scientific Inc. Logan, UT).

Sensible and latent heat flux appear to have a large effect on the flux of PCB from the SDM. The sensible heat flux is the amount of energy removed from the sediment through convective heat transport. It was calculated by taking the difference of influent and effluent temperatures, and multiplying this difference by the flow rate, Q, the air density, $\rho$, and the heat capacity of the air, $c_p$. The product was then divided by the surface area of the sediment, which was 1 $m^2$ for the wind tunnel.

$$H = \frac{\rho c_p (T_{out} - T_{in}) Q}{A_{surface}} \tag{19}$$

The units for the sensible heat flux are watts/$m^2$. The latent heat flux is calculated in much the same way. The difference of influent and effluent air moisture contents were multiplied by the flow rate, and the latent heat of vaporization, $\lambda$, then divided by the area of the sediment surface.

$$LE = \frac{\lambda (q_{out} - q_{in}) Q}{A_{surface}} \tag{20}$$

The units for the latent heat flux are also watts/$m^2$.

The average air flow rate for these experiments was 0.6 $m^3$/min. This yields an average flow rate of 20 cm/sec. Thus the Reynolds number is 1320. This is below the threshold value of 2000 for laminar flow in pipes. Experiments were conducted to determine the flow profile in the chamber. Precise calibration of the blower was required in order to determine the flow characteristics of the wind tunnel.

### *2.1.2 Wind Tunnel Calibration*

Characterization of the air flow through the wind tunnel was carried out in several steps, first, the blower was calibrated to determine the total air flow, then, a hot film probe was calibrated using the centerline velocity, and finally the vertical flow profile was measured with the hot film probe.

**Blower Calibration:**

The blower was removed from a Tisch Hi-Vol Sampler and installed at the effluent end of the wind tunnel. Calibrations were carried out using a Tisch Adjustable Orifice Calibrator at five known air flow rates, chosen to bracket field sampling flow rates. The

manometer readings were recorded at these flow rates and corrected for temperature and atmospheric pressure. A linear regression between the flow rate and effluent pressure measurements was used to calculate the flow rate. Regressions run with an $R^2 < 0.98$ were rejected and the calibration was repeated. The sampler's blowers were calibrated prior to and following each sampling run to ensure that flow measurements were accurate. . The effluent pressure readings and corresponding flow rates are shown in table 6.

**Table 1.** Wind Tunnel Blower Calibration

| Reading # | Flow Rate ($m^3$/min) | Effluent Pressure (Inches of oil) |
|---|---|---|
| 1 | 0.53 | 2.07 |
| 2 | 1.06 | 8.09 |
| 3 | 0.91 | 6.20 |
| 4 | 0.73 | 4.05 |
| 5 | 0.504 | 1.97 |
| No Flow | 0 | 0 |

Measurements were corrected for temperature and pressure, and linear regression was performed to create a calibration curve for the blower. The $R^2$ value for the calibration curve was 0.9996.

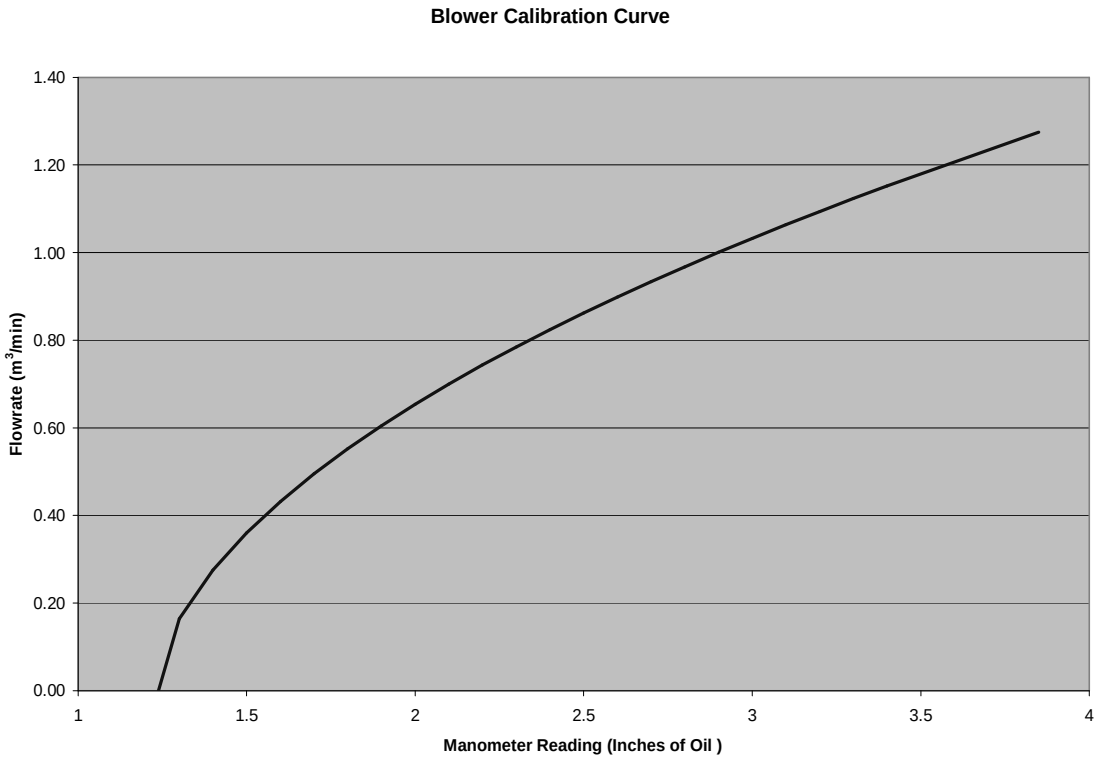


**Figure 4.** Wind Tunnel Blower Calibration Curve

**Hot Film Probe Calibration:**
A model 1218 Boundary Layer Hot Film Probe from TSI Incorporated (Shoreview, Minnesota) was used to measure the air velocity at various locations in the wind tunnel. The probe was calibrated by correlating the centerline velocity in the wind tunnel to the voltage reading of the probe. The centerline velocity was calculated as 1.75 x's the mean velocity for a rectangular duct with an aspect ratio of 5:1(Spiga and Morini, 1994). The probe was installed in the tunnel and the blower was started. The blower was run at several flow rates. These were recorded along with the voltage readings from the probe. The voltage readings and flow rates were then compared using King's law.

$$E = A + BU^{0.5} \tag{21}$$

E is the bridge voltage, U is the centerline velocity, and A and B are constants. A linear regression was performed to determine A and B. The $R^2$ value for this regression was 0.987. From this regression, a calibration curve for the Hot Film Probe was created.

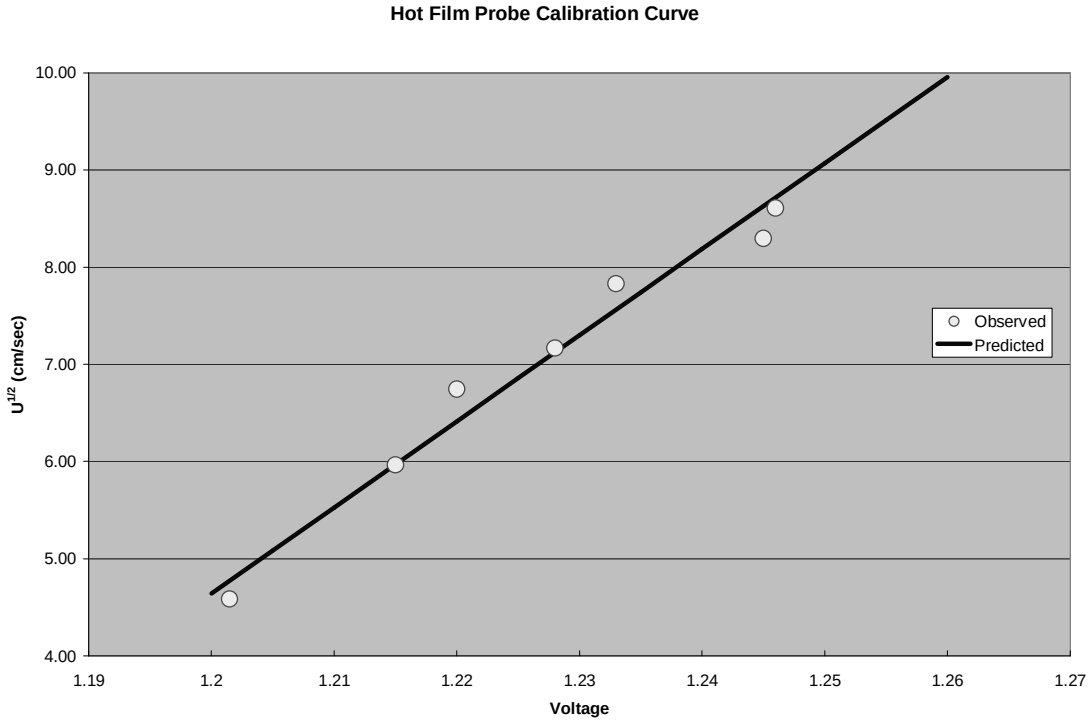


**Figure 5.** Hot Film Probe Calibration Curve

In order to determine the vertical flow profile in the wind tunnel, the probe was traversed from the center to the lower wall (0.5 cm from the surface) and velocity measurements were collected for each height. The velocity measurements gave a profile that was parabolic. The profile measured agrees well with theoretical values for a laminar flow profile (Spiga and Morini, 1994).

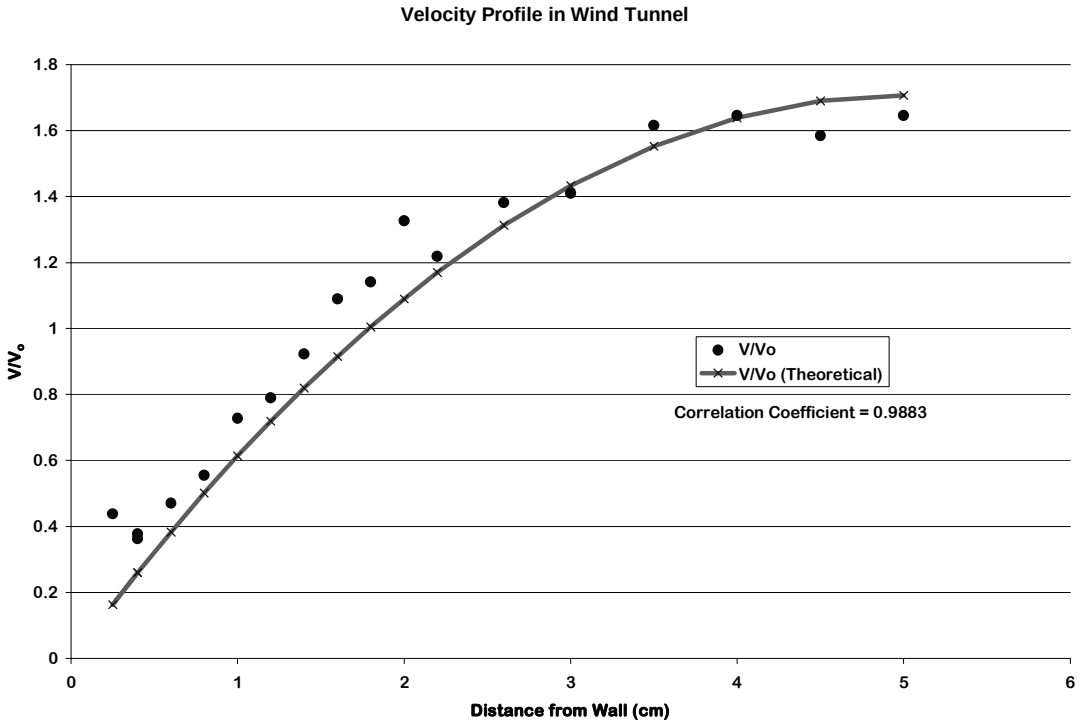


**Figure 6.** Vertical Velocity Profile

## 2.2 Methodology

### *2.2.1 Stabilization of Sediment*

The sediment used in this experiment was collected via a clamshell dredge on the US Army Corps of Engineer Vessel, Hayward, from New Town Creek, N.Y.

**Figure 7.** New Town Creek, N.Y. Sampling Location.

The sediment was collected in three batches; A, B and C. Each of these were homogenized on the deck of the Hayward, then placed into 30-gallon drums and labeled appropriately. The drums were then transported to the Stevens Institute of Technology, Center for Environmental Engineering (CES) and stored in a cold room at 4˚C. Each sediment drum was removed from the cold room and transported to the lab prior to the experimental run. Prior the first two experimental runs, the sediment was transported to the lab less than an hour before placement in the wind tunnel. Results from these runs indicated that the sediment was too cold, and should be allowed to equilibrate to the temperature of the laboratory prior to the experimental run. The sediment was brought to the lab two days in advance for the following eight experimental runs.

The sediment was homogenized in the drum using a power drill with a mixer head attachment. The appropriate amount of dry cement, if any, was then weighed out and added to the drum. Experimental, runs were completed with amounts of cement added that were equivalent to 0%, 4%, 6% and 8% of the total by weight. The sediment/cement was then blended until the mix was homogenous. The SDM was then shoveled into the wind tunnel and the surface was smoothed out as flat as possible.

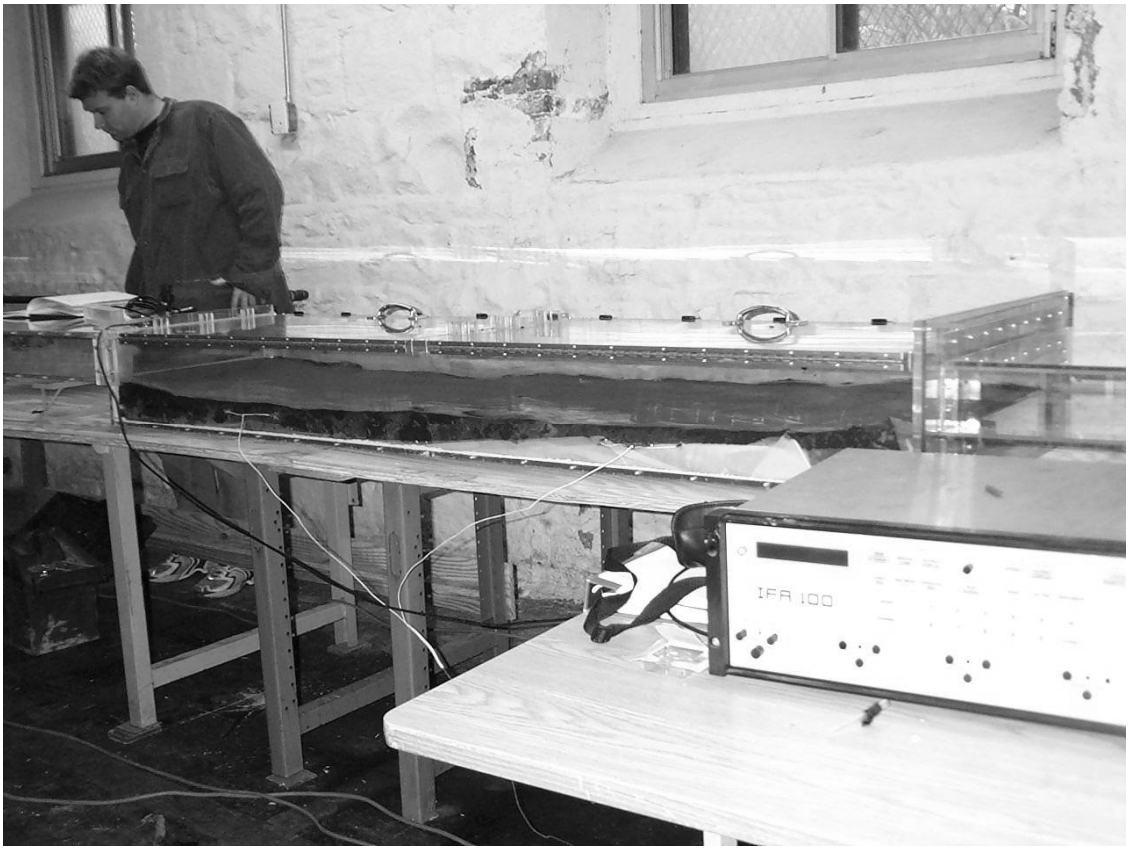

**Figure 8.** Wind Tunnel filled with Sediment

### *2.2.2 Wind Tunnel Operation*

The wind tunnel was closed and locked down when ready for the start of a sampling run. A PUF sample matrix was installed in the sample chamber of the wind tunnel and the background sampler. The sample chambers were then connected into the two sampling apparatuses. The blowers were turned on, and the start time and flow rates were recorded. The wind tunnel ran for the appropriate length of time. At the end of the sampling interval, the end time and flow rates were recorded. The PCB volatilization flux, $F_{PCB}(t)$ through the chamber was calculated with the total mass of PCB's captured by the PUF sampler in a given time interval using the equation:

$$F_{PCB}(t) = \frac{(C_{EFF} - C_{INF})Q_{AIR}}{A} \quad (21)$$

$\boldsymbol{C_{EFF}}$ = Concentration of PCBs in Effluent air stream

$\boldsymbol{C_{INF}}$ = Concentration of PCBs in Influent air stream (Background)

$\boldsymbol{Q_{AIR}}$ = Flow rate through the wind tunnel

A = Area of the SDM-air interface ($m^2$)

### *2.2.3 PCB Analysis*

The PUF filters from the experimental runs were extracted using the method described in section 2.1.5 of Korfiatis *et al.* (2003). The sample extracts were analyzed with a Varian 3800 Dual Column Gas Chromatograph with two Electron Capture Detectors at the Center for Environmental Systems at Stevens Institute of Technology (CES). The samples were analyzed for the congeners included in the Supelco PCB Congener Mixes 1 and 2. The methods used for analysis of the samples are included as Appendix 1. These methods include 1) the sample analysis method which includes the injection procedure, temperature program, and detector settings; 2) the recalculation method for quantification of the congeners included in PCB Congener Mix 1; 3) the recalculation method for quantification of the congeners included in PCB Congener Mix 2; and 4) the recalculation method for quantification of the surrogate spikes.

The quality control procedures for PCB analysis included matrix spike, blank spike, laboratory blank, and extraction blank preparation and analysis. The operating procedures were developed in the CES and are based on EPA Method 8082. Prior to initiation of the experiments, an equipment blank was collected in order to determine adsorption to the walls of the enclosure. This was completed by taking advantage of the fact that there are ample PCBs in the ambient air in our region. Two air samples were collected simultaneously; an ambient air sample, and an ambient air sample pulled through the empty flux chamber. The two PCB sample masses collected on the PUFs were then compared to determine if there is a sink of PCBs in the chamber. No significant difference between these samples was found.

### *2.2.4 Extraction Efficiency*

An experiment was conducted to evaluate the efficiency of the extraction procedure. Five clean PUFs were spiked with a mixture of six PCB congeners ranging in chlorination number from 3 to 8 and a pesticide surrogate. The samples were then subjected to the extraction procedure and analyzed. The recovery of the pesticide spike in all samples was used as a reference for the PCB extraction efficiency. The mass of PCB congeners recovered varied by chlorination number. The lower weight congeners had the highest recovery while the high weight congeners exhibited relatively poor recovery. The recoveries were used to create correction factors for the experimental samples. Table 2 shows the percent recovered for each of the samples. These samples were run on two separate days in order to account for temporal variations from the analysis equipment and different calibration runs.

**Table 2.** Extraction Efficiency Results

| | *Sample* | | | | |
|---|---|---|---|---|---|
| | ***ISR_1*** | ***ISR_2*** | ***ISR_3*** | ***ISR_4*** | ***ISR_5*** |
| **Pest. Surrogate (ppb)** | **146** | **130** | **123** | **183** | **130** |
| **Percent Recovery** | **73.01%** | **65.18%** | **61.58%** | **91.50%** | **65.00%** |
| **Congener Recovery** | | | | | |
| **14** | **96.88%** | **101.34%** | **99.63%** | **100.39%** | **99.49%** |
| **30** | **88.65%** | **93.78%** | **88.70%** | **94.57%** | **91.84%** |
| **23** | **68.42%** | **72.98%** | **68.10%** | **77.21%** | **63.94%** |
| **65** | **52.55%** | **57.46%** | **52.92%** | **59.07%** | **42.79%** |
| **166** | **17.82%** | **28.76%** | **15.12%** | **34.80%** | **23.26%** |
| **204** | **16.62%** | **26.45%** | **13.17%** | **31.30%** | **20.77%** |

The mean recovery efficiency for each congener and the standard deviation are presented in Table 3. The mean recovery efficiencies were then used to correct the PCB concentrations for loss of mass during the extraction procedure.

**Table 3.** Extraction Efficiency Correction Values

| | **Percent Recovery** | **Standard Deviation** |
|---|---|---|
| **14** | **99.44%** | **1.61%** |
| **30** | **91.40%** | **2.63%** |
| **23** | **70.04%** | **4.94%** |
| **65** | **52.89%** | **6.27%** |
| **166** | **23.91%** | **7.95%** |
| **204** | **21.63%** | **7.26%** |

The PUF filters collected during sampling runs seven through ten were spiked with 200 µL of a 700 ppb solution containing the six congeners used in the extraction efficiency experiment, as well as the pesticide surrogate spike. The recovery of these congeners was corrected by the recovery of the pesticide spike and the percent recovery was determined. The values for percent PCB congener recovered were very similar to the results presented in table 3.

The extraction efficiencies for the dichlorinated, trichlorinated and tetrachlorinated homologues range from 99.5% to 52.9% with standard deviations that range from 1.3% to 6.2%. The extraction efficiencies found for the heavier homologues are ~22% with a standard deviation of ~7.5%. The lack of extraction efficiency and high standard

deviation are a significant source of error in the concentrations measured for the high molecular weight homologues. As a result, for the presently reported study only the dichlorinated, trichlorinated and tetrachlorinated homologue concentrations will be presented.

## 2.3 Results

Ten experimental runs were completed for this phase of the project. They included; four runs of unammended dredged sediment, and two each of run stabilized with 4% portland cement, 6% portland cement, and 8% portland cement. The first three runs were completed using sediment from one scoop of the clam shell dredge labeled sample A, the next three were from sample C, and the final four were completed using the four drums that comprised sample B. During each of these runs, PCB concentrations, temperature, and humidity at the influent and effluent were measured. Additionally, the moisture content of the sediment was measured periodically throughout the run. The results from these experimental runs are summarized below. The Chromatograms for each sample are included in Appendix 2.

### *2.3.1 Run 1*

The first experimental run was conducted using unammended dredged sediment from sample A. The experiment was run from December 17, 2003 to December 23, 2003. The initial water content was 77% by weight (weight of water/weight of dry sediment) and fell to 70% after approximately 8 days. The first background sample was collected for the length of the first three wind tunnel samples. The background samples were combined because it was believed that there would not be sufficient mass collected in a background during the relatively short initial sampling intervals. Analysis of the samples revealed that this was not the case, and for the remainder of the study, a background sample was collected for each wind tunnel sample interval.

The temperature of the air and sediment, varied greatly during this experiment. The sediment was spread out in the chamber approximately one hour after being removed from the refrigerated storage room. As a result, the sediment temperature was initially 5˚C and rose to 15˚C by the end of the first day. The air temperature exhibited a large variance between day and night. There was a slight increase in the temperature of the sediment over the final six days of the experiment.

Measurements of influent and effluent temperature and humidity were used to determine the sensible heat flux and the latent heat flux from the sediment. These values are presented in units of watts/ $m^2$. The latent heat flux started out negative when the sediment was very cold and became positive as the temperature increased after 24 hours. It became relatively steady for the remainder of the run at approximately 10 watts/$m^2$. The sensible heat flux was approximately zero with small positive and negative fluctuation occurring throughout the experimental run. These measurements indicate that over this experimental run the relatively cool sediment and influent air combined to create a condition where there was very little convective heating or cooling of the

sediment, and a small but steady moisture flux from the sediment after the initial warming of the sediment.

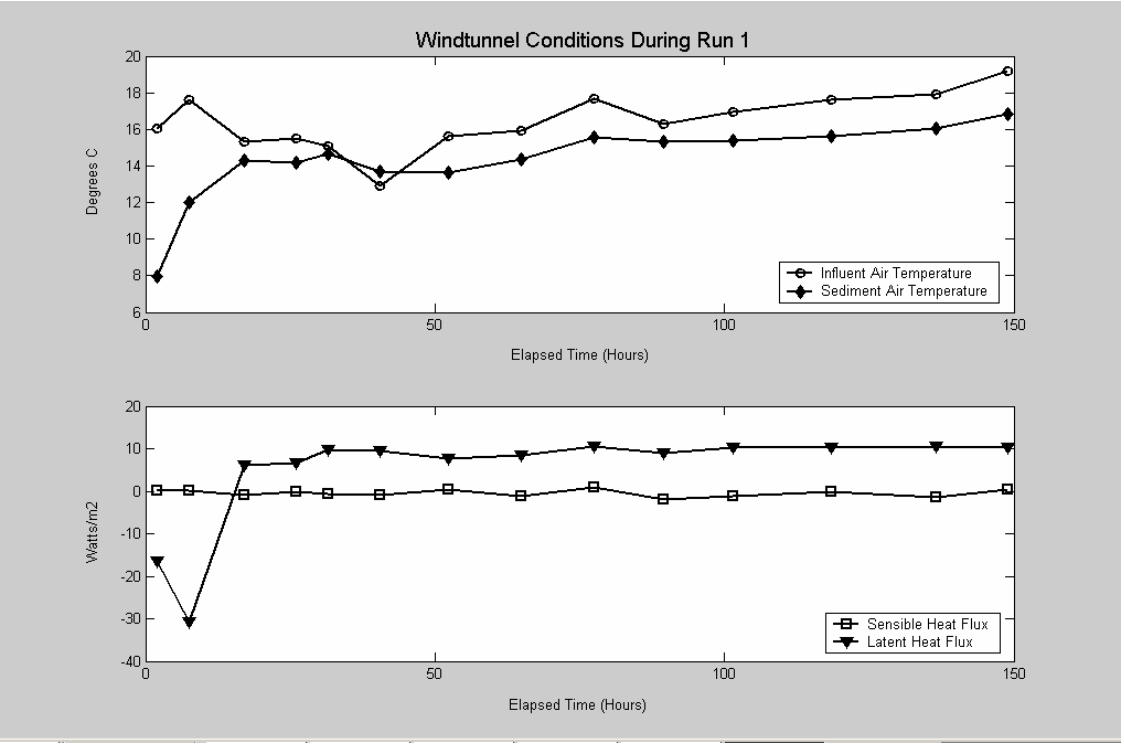


**Figure 9.** Wind tunnel Conditions During Run 1

The PCB fluxes measured over the first run show a large variance. Reasons for the variance include, the low temperature of the sediment at the time of placement, and the low air temperature in the laboratory. The values for the trichlorinated and tetrachlorinated homologues start off at approximately 80 ng/$m^2$/hr and decrease over the first 40 hours and reach zero. The fluxes then increase towards the end of the run at 95 hours. This increase corresponds to a large rise in temperature. The dichlorinated homologue is presented on a much larger scale (right axis). The flux measurements increase over the first three intervals then start to decline. There is a strong diurnal variation (>100 ng/$m^2$/hr), with large fluxes during the day and much smaller during the night. Later in the run there is a large spike in the measured flux at about 85 hours. Despite the high variability in the measure flux values it is observed that both the trichlorinated and tetrachlorinated homologues indicate an elevated initial flux and a decline throughout the run. The dichlorinated homologue has a similar pattern duing the first 60 hours of the run.

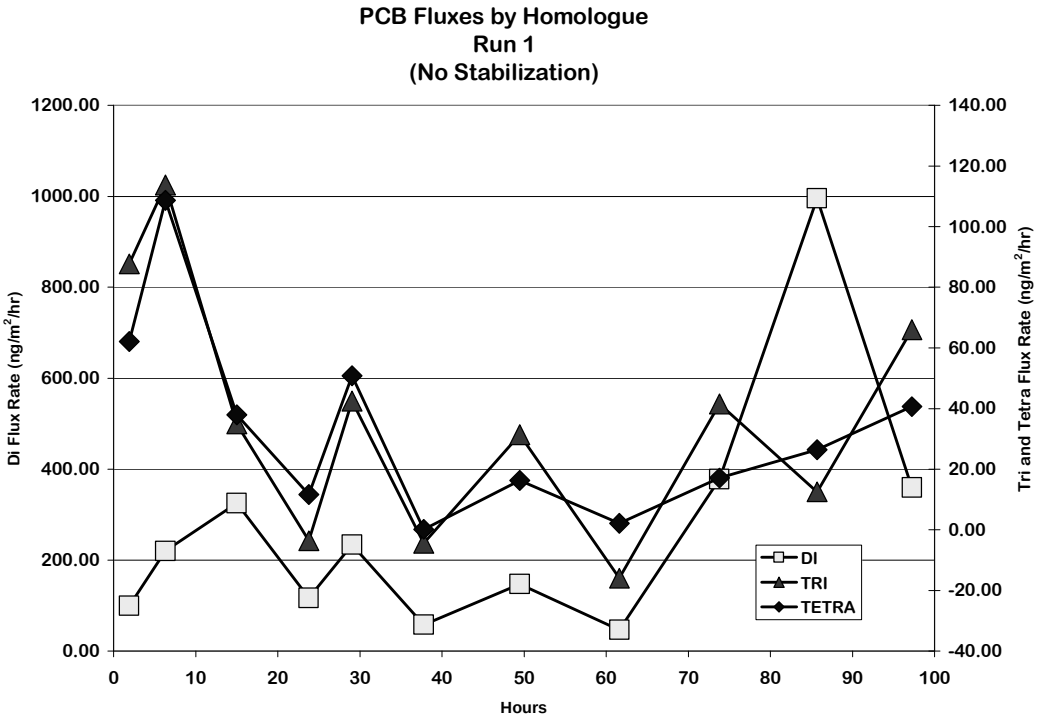


**Figure 10.** PCB Fluxes by Homologue, Run 1

### *3.3.2 Run 2*

The second experimental run was conducted January 5, 2004 to January 9, 2004. The sediment was stabilized with 8% Portland cement by weight. Prior to stabilization, the moisture content was 75% and after stabilization it was 67%. The moisture content decreased to 45% at the end of the experimental run. Stabilization and placement were completed while the sediment was still cold from storage. The temperature increased from 8 ˚C to 18 ˚C within a day. The sediment temperature was then approximately the same as the air temperature. The moisture flux during this experimental run was initially low and then reached a peak that coincided with a peak in the sediment temperature. After this point the moisture flux remained relatively constant. The day/night temperature fluctuations of the air temperature were approximately 3.5˚ C.

The initial latent heat flux measured was 4 watts/$m^2$. As the temperature of the sediment increased the latent heat flux also increased. At the same time, the sensible heat flux was very close to zero, and although there is a peak it was very small relative to the latent heat flux. After reaching a peak 25 hours into the experiment, both the latent and sensible heat fluxes decreased slightly. At the end of the run there was a latent heat flux out of the sediment of 11 watts/$m^2$ and a sensible heat flux into the sediment at approximately -2.5 watts/$m^2$.

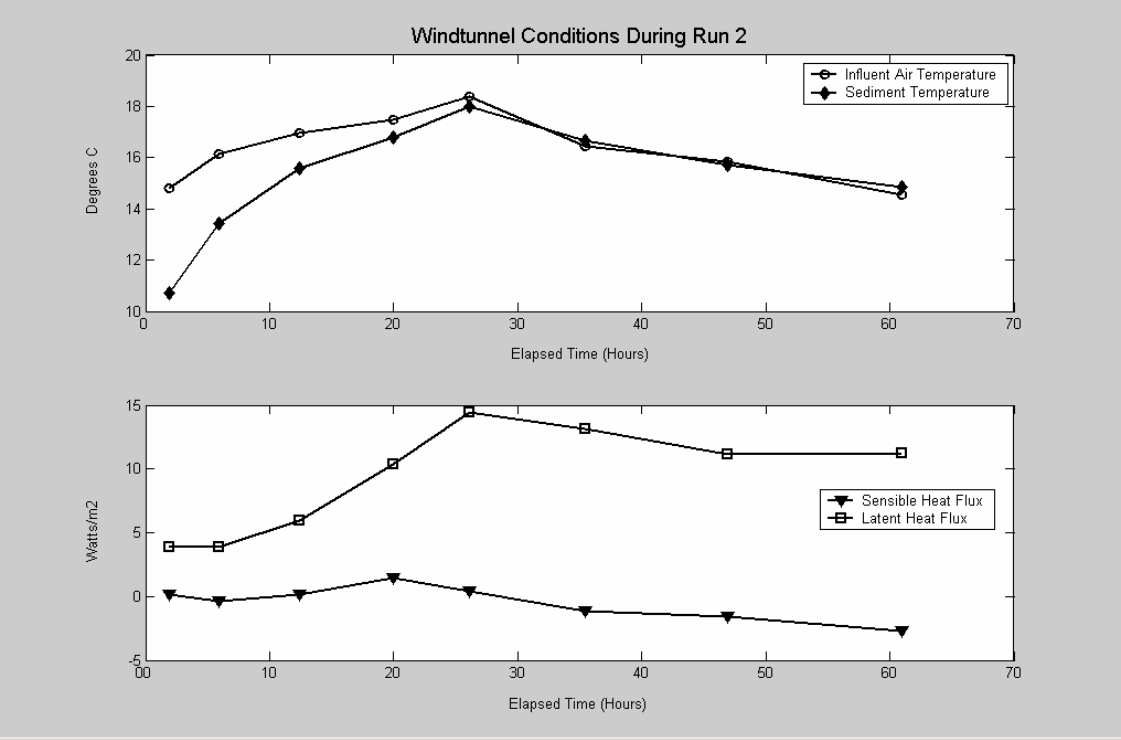


**Figure 11.** Wind tunnel Conditions During Run 2

PCB fluxes measured during the second experimental run for trichlorinated and tetrachlorinated homologues were high and then decreased rapidly over the subsequent sampling intervals. There was an increase between 11 and 19 hours into the run. This increase occurred in the interval that stretched over midday on the second day when the temperature in the laboratory increased. After this interval the fluxes decreased to approximately zero, until the final measurement. The fluxes measured during this interval were small and directed out of the sediment. This run, like the previous, exhibited a spike in the measured fluxes centered around midday when the temperature was highest. Fluxes of the dichlorinated homologue were very high relative to the other homologues. The initial measured flux was 993 ng/m$^2$/hr. Twenty hours into the experimental the measured fluxes stabilized at approximately 500 ng/m$^2$/hr. The measured values exhibit a pattern of elevated initial fluxes that quickly fall off and approach a minimum value. Variations in this pattern arise from the highly variable temperature conditions in the laboratory. During the subsequent experimental runs attempts were made to reduce or eliminate these sources of variance.

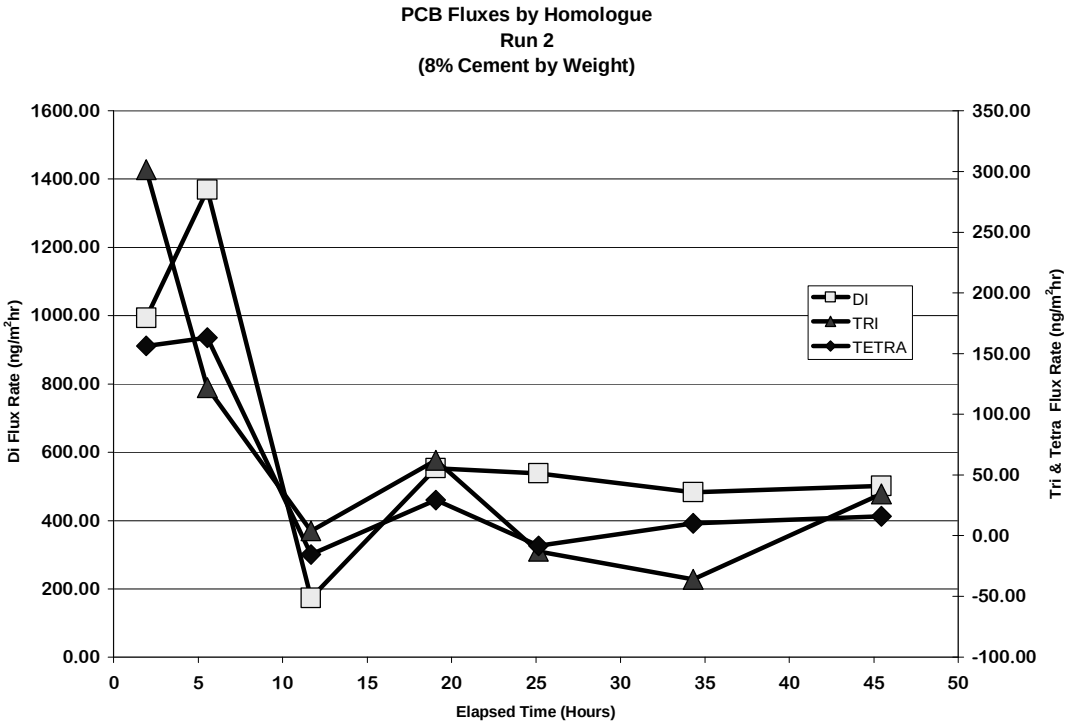


**Figure 12.** PCB Fluxes by Homologue, Run 2

### *2.3.3 Run 3*

The third run was carried out February 10, 2004 until February 12, 2004. The sediment for the first two runs was placed in the wind tunnel cold, approximately one hour after removing it from the cold storage room. In an attempt to have the sediment at a constant temperature throughout the experimental run, the sediment was removed from cold storage two days prior to the initiation of the experimental run and allowed to equilibrate to the air temperature in the laboratory. The sediment was stabilized with 4% portland cement by weight. Prior to stabilization, the moisture content was 81% and after stabilization it was 75%. By the end of the experiment it was down to 53%. The initial temperature of the sediment was 17˚C and rose slightly after being placed. The sediment cooled down over the remainder of the day and into the night, but increased the following day due to warmer influent air. The following night the air and sediment cooled down again.

The latent and sensible heat fluxes behaved much differently during run three than the two previous runs because of the conditions created when the sediment is warmer than the air and vice versa. The variability in the latent heat flux can be seen to correspond very closely to the pattern of sediment temperature versus air temperature. When the sediment was warmer, there was enhanced latent heat flux, and conversely, when the air temperature was greater than the sediment temperature, the latent heat flux appeared to shut down. The sensible heat flux also exhibits a similar pattern; however over the run, the peaks in the latent heat flux appear to reduce while the peaks in the sensible heat flux are increasing. This behavior is presumably due to the drying of the sediment.

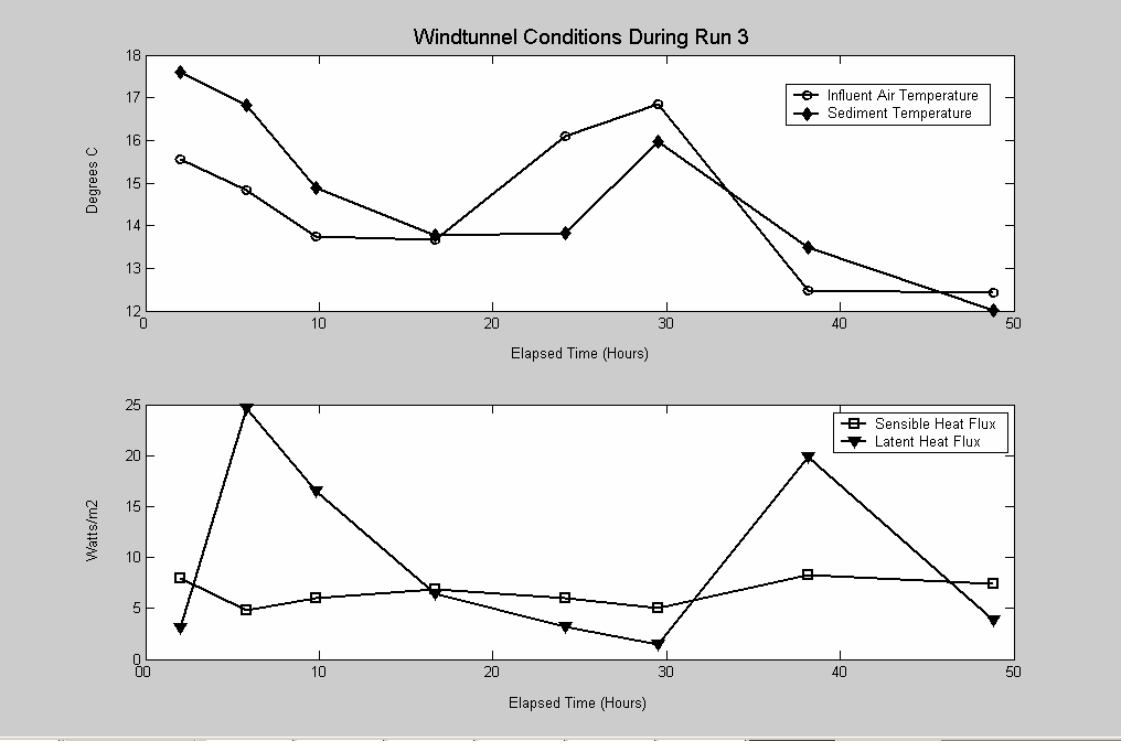


**Figure 13.** Wind tunnel Conditions During Run 3

PCB fluxes measured during run three for dichlorinated, trichlorinated, and tetrachlorinated chlorinated homologues exhibit large initial fluxes that drop off quickly. There is a slight increase corresponding to the period on the second day when the temperature was elevated; after which the fluxes appear to shut down completely. It is important to notice the scale of the initial measured fluxes compared to the previous experimental run. These are 2.5 times as large for the dichlorinated homologue, and 5 times as large for the tetrachlorinated homologue. The increase results from the high temperature of the sediment at the onset of the run relative to the previous experimental runs. During the rest of the experimental runs, the sediment was allowed to equilibrate with the laboratory temperature.

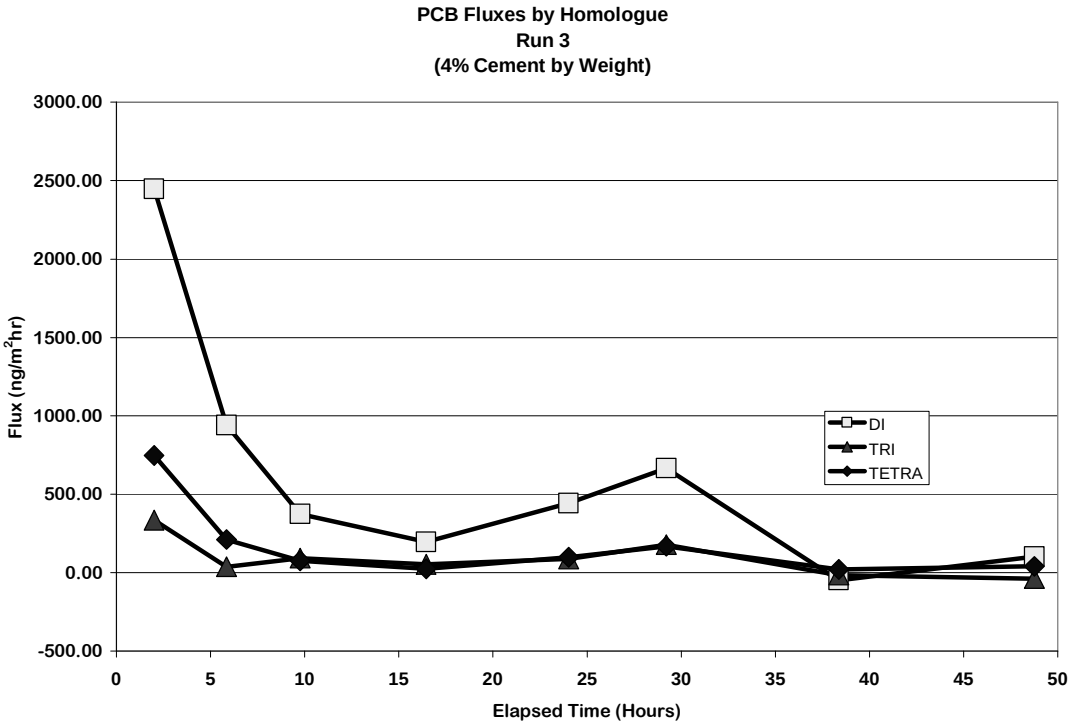


**Figure 14.** PCB Fluxes by Homologue, Run 3

### *2.3.4 Run 4*

The fourth run was completed March 8, 2004 until March 10, 2004. The sediment used during runs 4, 5, and 6 was from sediment sample C. The sediment had a much higher moisture content than the sediment used in the previous three runs. The sediment was removed from cold storage two days prior to the initiation of the experimental run. In order to regulate the laboratory temperature space heaters with thermostats were used in laboratory and set to 19˚C. The sediment was stabilized with 8% Portland cement by weight. Prior to stabilization the moisture content was 184% and after stabilization it was 130%. By the end of the experiment it was down to 117%. The initial temperature of the sediment was 21˚C and fell throughout the experimental run to 17.5˚C. The influent air temperature remained relatively steady at 19˚C with a small increase at midday on the second and third days of the experimental run.

The latent heat flux values measured during this experimental run were relatively small. The initial measurement was zero. The latent heats flux then rose for the first seven hours of the experimental run while the sediment temperature was greater than the influent air temperature. When the air temperature rose to that of the sediment, the latent heat flux decreased until it reached zero, one day into the experimental run. The sensible heat flux was initially 3.5 watts/$m^2$, then dropped to a minimum at ten hours. It then increased on the second day of the experiment to a peak value at midday equal to the initial value. Following this peak there is a slight decrease overnight and subsequently another increase at midday the following day.

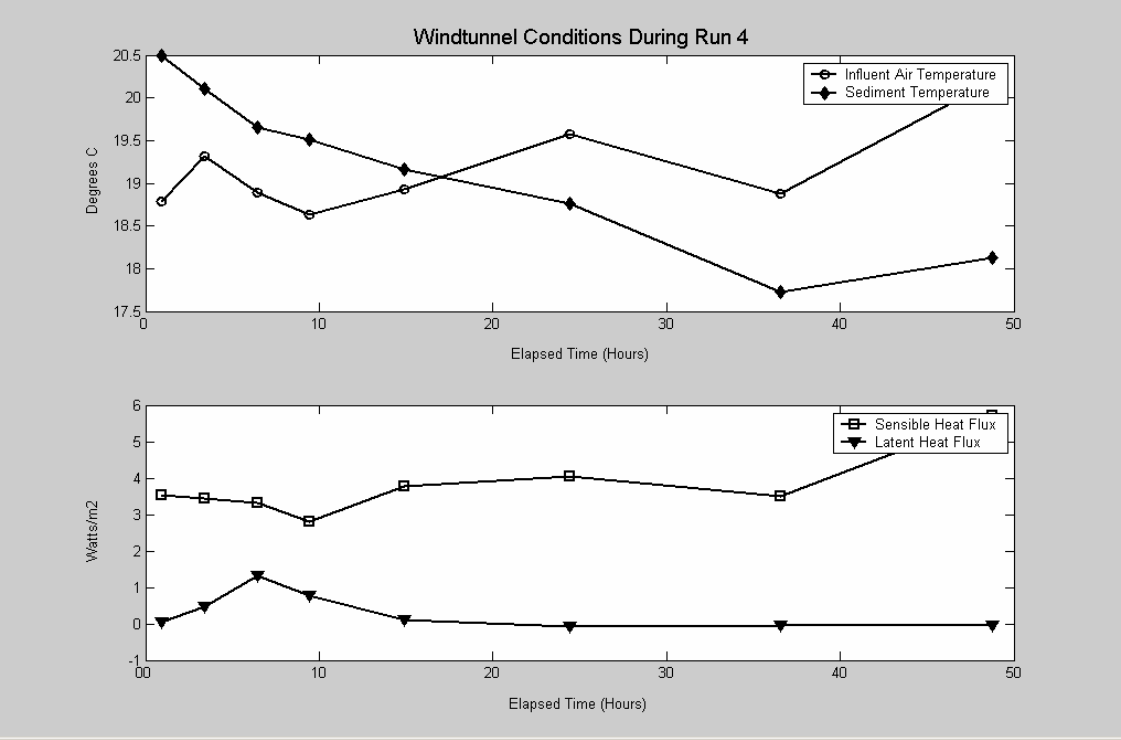


**Figure 15.** Wind tunnel Conditions During Run 4

PCB fluxes measured during run four of dichlorinated, trichlorinated, and tetrachlorinated homologues exhibited large initial flux measurements that dropped off quickly during the two subsequent sampling intervals. This was followed by a large increase at around 7 hours into the run. Subsequently, the dichlorinated and trichlorinated homologue flux measurements decreased, however the tetrachlorinated homologue flux measurement increased. During the interval centered around 15 hours, the flux measurements for the three homologues decreased significantly, and for the rest of the experimental run they showed a gradual decrease towards zero. The large spike in measured PCB fluxes corresponds directly with a minimum of sensible heat flux and a peak in latent heat flux. The scale of the fluxes was different than for the first three experiments and the distribution of PCB homologues also appeared to be different. The greatest flux was from the tetra-chlorinated homologue group in contrast to the runs conducted with sediment from sample A which had large fluxes from the dichlorinated homologues. The initial flux values for the two runs at 8% stabilization exhibit a five fold increase from sample A to sample C in terms of tetrachlorinated homologues, while the dichlorinated fluxes exhibit a three fold decrease and the trichlorinated homologue fluxes remain relatively constant.

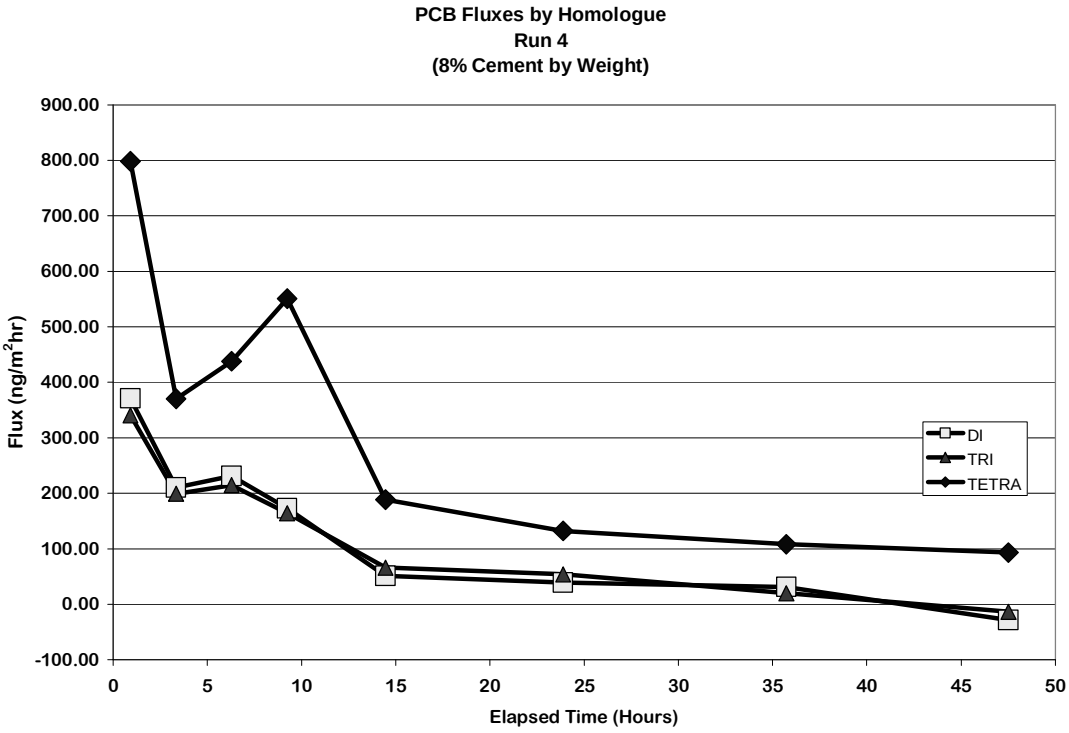


**Figure 16.** PCB Fluxes by Homologue, Run 4

### *2.3.5 Run 5*

The fifth run was conducted from March 15, 2004 to March 17, 2004. The sediment was stabilized with 4% Portland cement by weight. Prior to stabilization, the moisture content was 184%, and after stabilization it was 147%. At the end of the experimental run it was down to 131%. The initial temperature of the sediment was 19˚C and it rose for the first three hours of the experimental run to 20.5˚C. During the remainder of the run, it decreased. The influent air temperature followed a similar pattern reaching a peak of 22.2˚C at 3 hours. After 20 hours it stabilized at 19.5 ˚C.

The sensible heat flux during this experimental run reached a peak at approximately 3 hours into the run. This corresponds to the peaks observed in sediment and influent air temperatures. Subsequent to this peak, the sensible heat flux dropped to 4 watts/$m^2$ and remained steady for the remainder of the experimental run. The latent heat flux was initially 11 watts/$m^2$ and dropped for the following 20 hours. At 29.8 hours into the run there is a small increase, subsequent to this small peak, the latent heat flux continues to drop to a value close to 2 watts/$m^2$ at the end of the run (~50 hours).

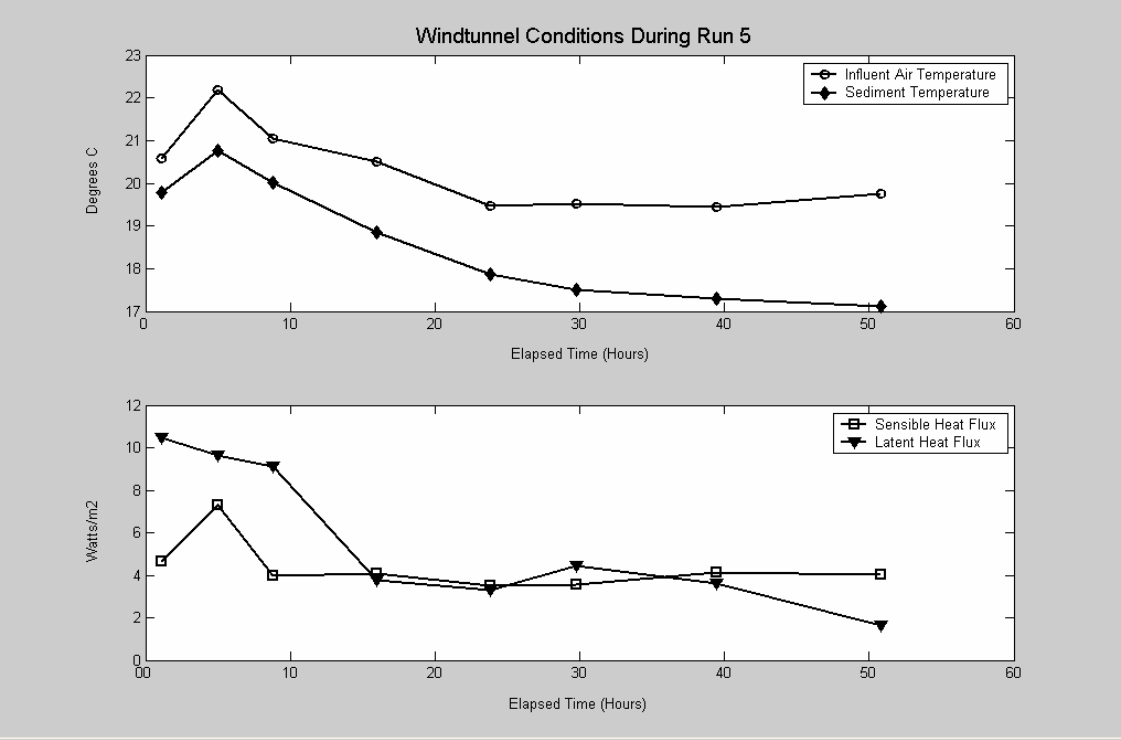


**Figure 17.** Wind tunnel Conditions During Run 5

The measured PCB fluxes during this experimental run, for dichlorinated, trichlorinated, and tetrachlorinated homologues exhibit an increase from the first interval to the second. The increase in PCB flux measurements coincides with an increase in both the influent air and sediment temperatures. The values for the second interval were similar to the initial flux values measured during the previous run. The measured fluxes then decreased significantly during the following intervals. The dichlorinated homologue exhibits a peak at 23.8 hours and remains elevated during the subsequent sampling interval centered around 29.8 hours. The trichlorinated and tetrachlorinated homologues exhibit a peak at 29.8 hours. These peaks coincide with the small peak in latent heat flux measured at 29.8 hours. These sampling intervals were centered around 9:10 and 15:10 on the second day of the run. The samples were changed at 12:00. Although the temperature of the room varied by less that a degree, there was an increase in humidity and the sun shone through the laboratory's windows directly on the sediment. Presumably, the sunlight warmed the sediment surface, which in turn resulted in an increase in moisture and PCB fluxes. After this peak the flux measurements decreased overnight and appear to have been increasing when the experimental run was ended. It is important to note that the increase in fluxes measured on the second day (~50 hours) are significantly less than those measure on the previous day.

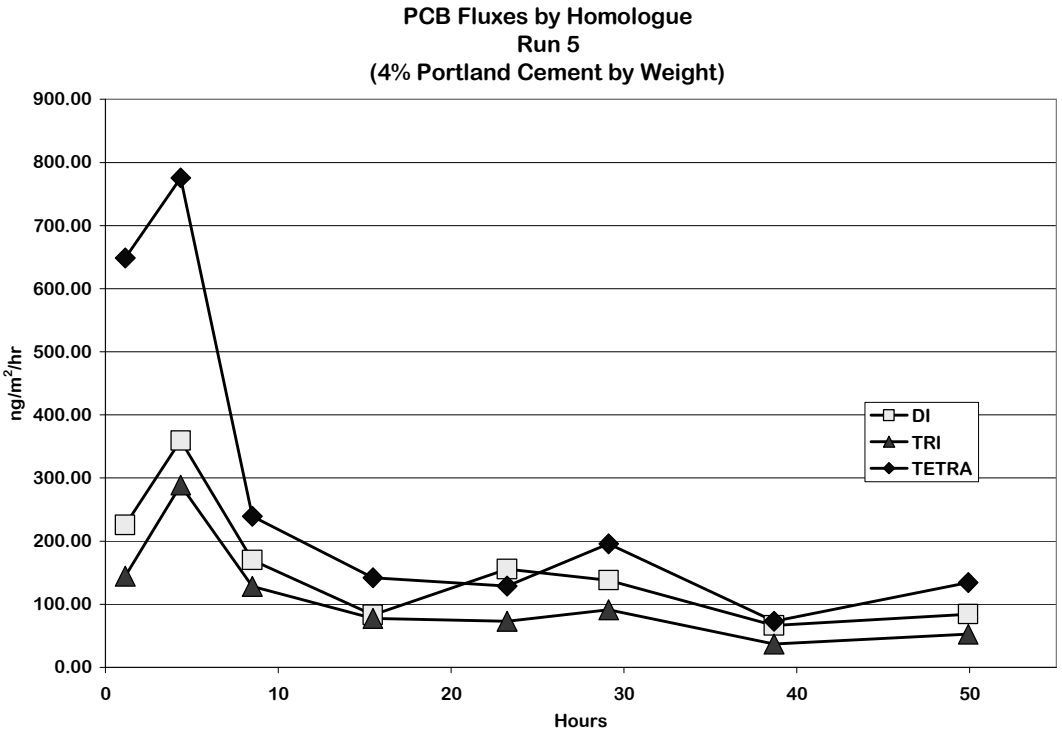


**Figure 18.** PCB Fluxes by Homologue, Run 5

### *2.3.6 Run 6*

The sixth run was completed March 23, 2004 to March 29, 2004. The sediment was not stabilized. The initial moisture content was 184%. At the end of the experimental run it decreased to 154%. The influent air temperature was initially 20.5˚C. It dropped for the next two sampling intervals to a minimum value of 19˚C. After reaching the minimum,, there was a steady increase until it reached a peak value of 21.5˚C at 28 hours. At the same time there was a sharp increase in the sediment temperature. Following the peak, there was a decline in temperature overnight, which in turn was followed by another increase the following day. The initial temperature of the sediment was 15˚C and it increased to approximately 18˚C through the experimental run. The sediment temperature increased steadily during the run with the exception two periods of sharper increase. The first was the initial increase from the relatively low temperature of the sediment in the drum, and the second corresponded to the peak in air temperature at 28 hours.

The latent and sensible heat fluxes during this experimental run remained relatively constant. The sensible heat flux was negative, indicating that the sediment was absorbing heat from the air passing over it. This is also indicated by the gradient of temperature between the influent air and sediment temperatures. The latent heat flux, despite a small spike early in the run remained relatively low and constant throughout the run.

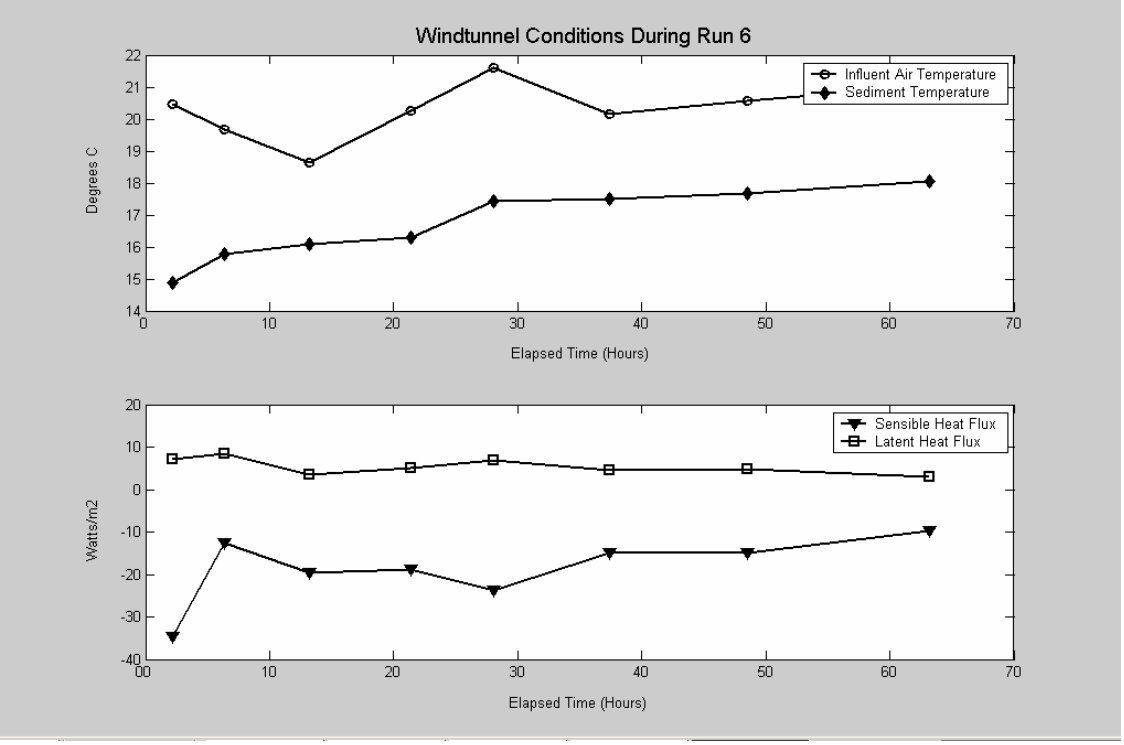


**Figure 19.** Wind tunnel Conditions During Run 6

The measured PCB fluxes for the dichlorinated, trichlorinated and tetrachlorinated homologues all exhibit similar behavior during this experimental run. They all have relatively high initial values then decrease for the first 12 hours of the run, then increase to a peak one day into the run. This peak is then followed by a decrease for the remainder of the run. The fluctuations observed in this experimental run appear to be directly related to the increase in temperature.

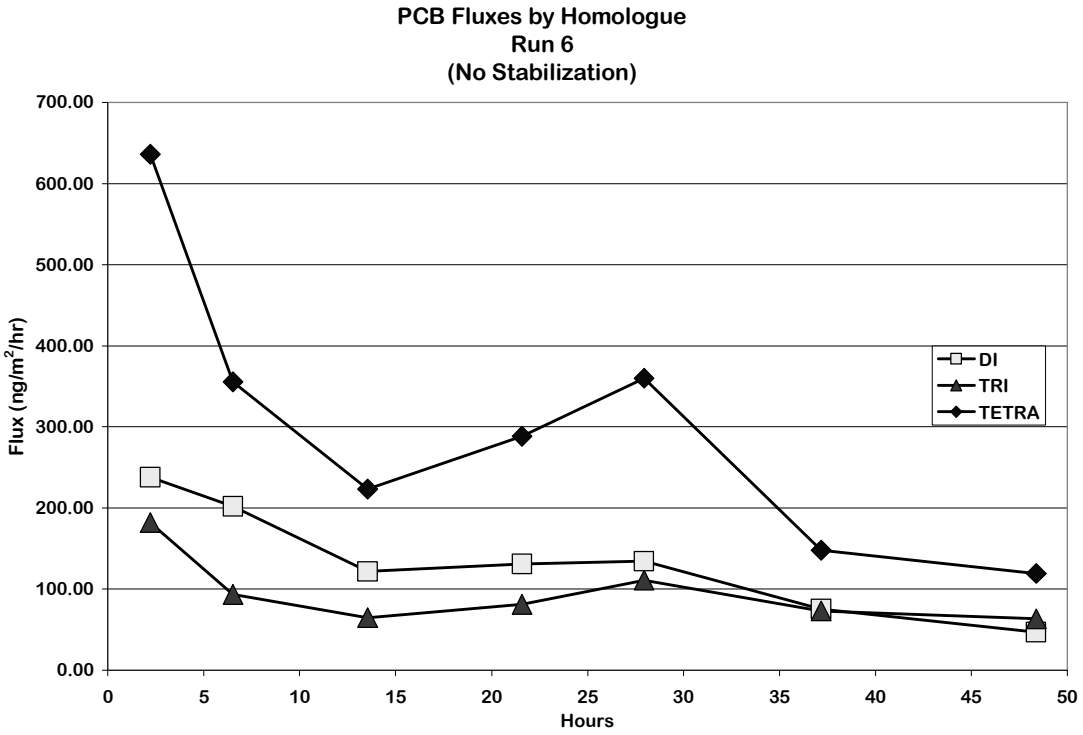


**Figure 20.** PCB Fluxes by Homologue, Run 6

### *2.3.7 Run 7*

Prior to the final four runs of the experiment, the first six were analyzed. It was determined that the fluctuations in temperature of as little as 3˚C were affecting the PCB flux measurements. In order to eliminate the effects of these temperature fluctuations, the equipment was transferred to a laboratory that had greater temperature controls. In order to confirm that the laboratory remained at a relatively constant temperature, the room temperature was recorded for nine days prior to the start of run seven. During these nine days the mean temperature was 23.52 ˚C with a standard deviation of 0.894 ˚C.

The final four runs were used to evaluate the effect of varying the airflow rate over the sediment. The four runs consisted of two non-stabilized runs, one at 15 cm/sec mean velocity and one at 20 cm/sec mean velocity (similar to runs 1-6), and two runs with 6% cement at the two speeds.

The seventh run was completed July 12, 2004 to July 14, 2004. The sediment used for this and the following three runs was taken from sediment sample B. The sediment was not stabilized. The mean velocity of the air flowing over the sediment was 15 cm/sec. The initial moisture content of the sediment was 131%. Over the course of the experiment there was no significant decrease in moisture content. The influent air temperature varied very little during this experiment (<2˚C). There was a small decrease the second half of the run. The sediment temperature was initially 20.7˚C and rose up to a peak 15.8 hours into the experimental run and then decreased slowly for the remainder

of the run. The latent heat flux measurements for this run were positive, however very close to zero, indicating a steady but very small evaporative flux. The sensible heat fluxes were also small, but negative, an indication that the sediment was absorbing a small amount of heat from the air. These measurements decreased as the temperature gradient between the sediment and air decreased during the second half of the run.

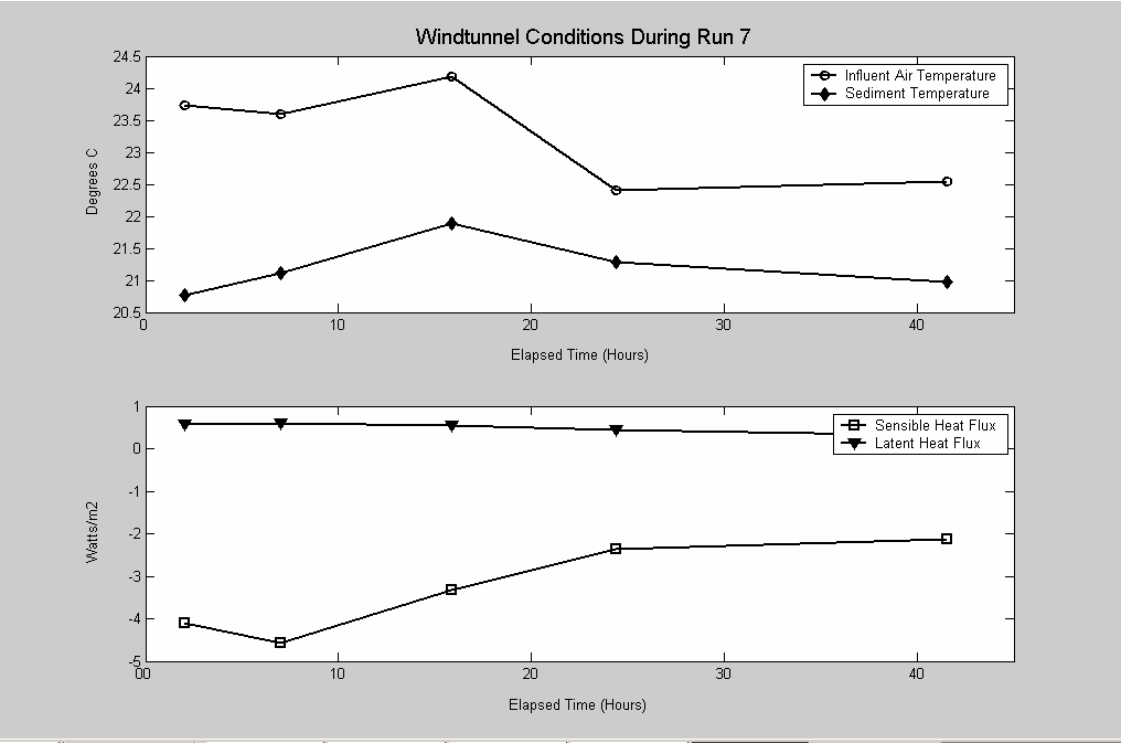


**Figure 21.** Wind tunnel Conditions During Run 7

The measured PCB fluxes for the dichlorinated, trichlorinated and tetrachlorinated homologues during this experimental run show a gradual decrease over the length of the experiment and do not appear to have any fluctuations due to temperature. The tetrachlorinated homologue has the highest flux rates measured during this interval similar to those fluxes measured during the runs carried out for sample C. When compared with run 6, (also not stabilized) the initial fluxes are similar. At the end of this experimental run (~40 hours), the dichlorinated and trichlorinated homologue flux measurements are very similar and the tetrachlorinated homologue flux measurement is slightly higher.

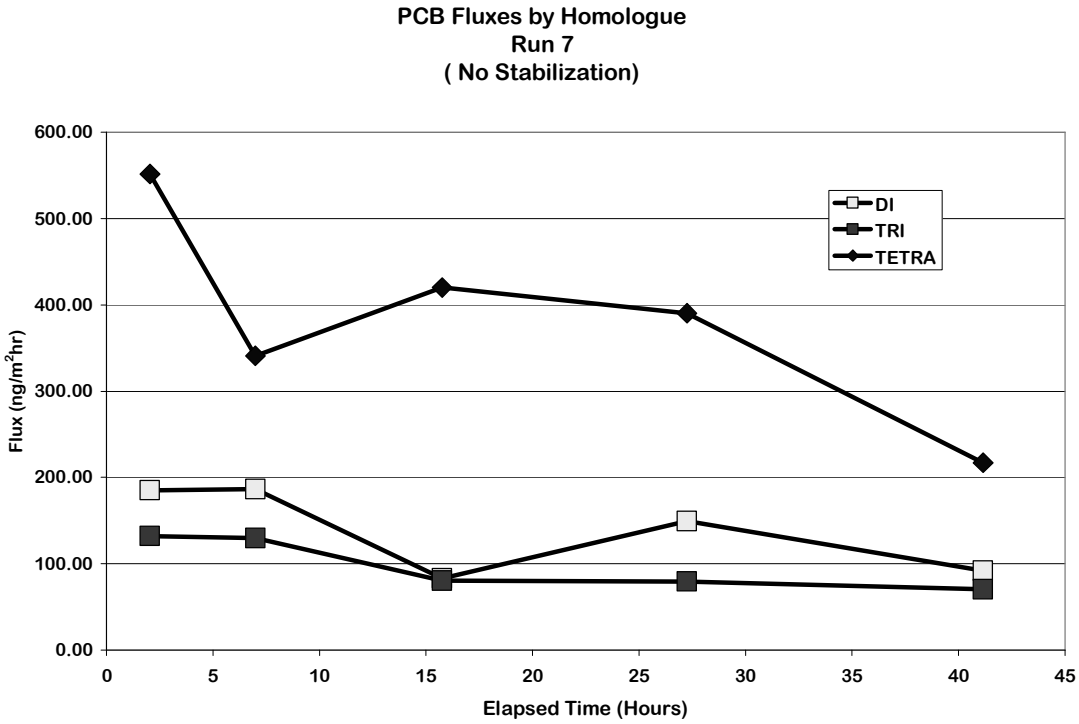


**Figure 22.** PCB Fluxes by Homologue, Run 7

### *2.3.8 Run 8*

The eighth run was completed July 19, 2004 to July 21, 2004. The sediment was stabilized with 6% Portland cement by weight. The mean velocity of the air flowing over the sediment was 15 cm/sec. The initial moisture content of the sediment was 121%. Over the course of the experiment the moisture content decreased to 106%. The influent air temperature varied very little during this experiment (<1.5˚C). Although the fluctuations were very small there appeared to be a pattern of peaks during the day and valleys at night. The sediment temperature did not appear affected by the variation in influent air temperature; instead it rose over the first 12 hours. The latent heat flux measurements, indicate a flux of moisture out of the sediment at 10-20 watt/$m^2$. The sensible heat flux is very similar to run 7, indicating a small flux of convective heat into the sediment at a fairly constant rate.

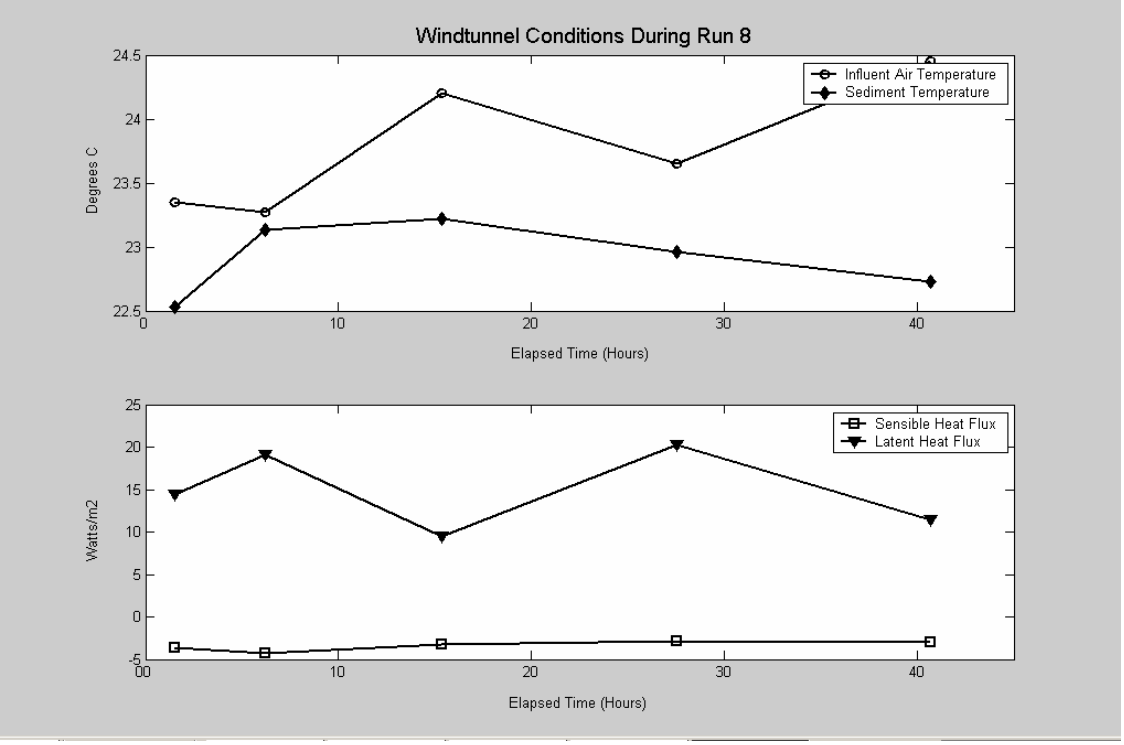


**Figure 23.** Wind tunnel Conditions During Run 8

The flux measurements for the dichlorinated, trichlorinated, and tetrachlorinated homologues were initially high and fell off rapidly. The initial flux values for the dichlorinated and trichlorinated homologues were approximately two times those measured during the previous run without stabilization, and the tetrachlorinated homologue flux was almost three. The decrease in fluxes was rapid and the final measured values were similar to those measured in the final interval of the previous run.

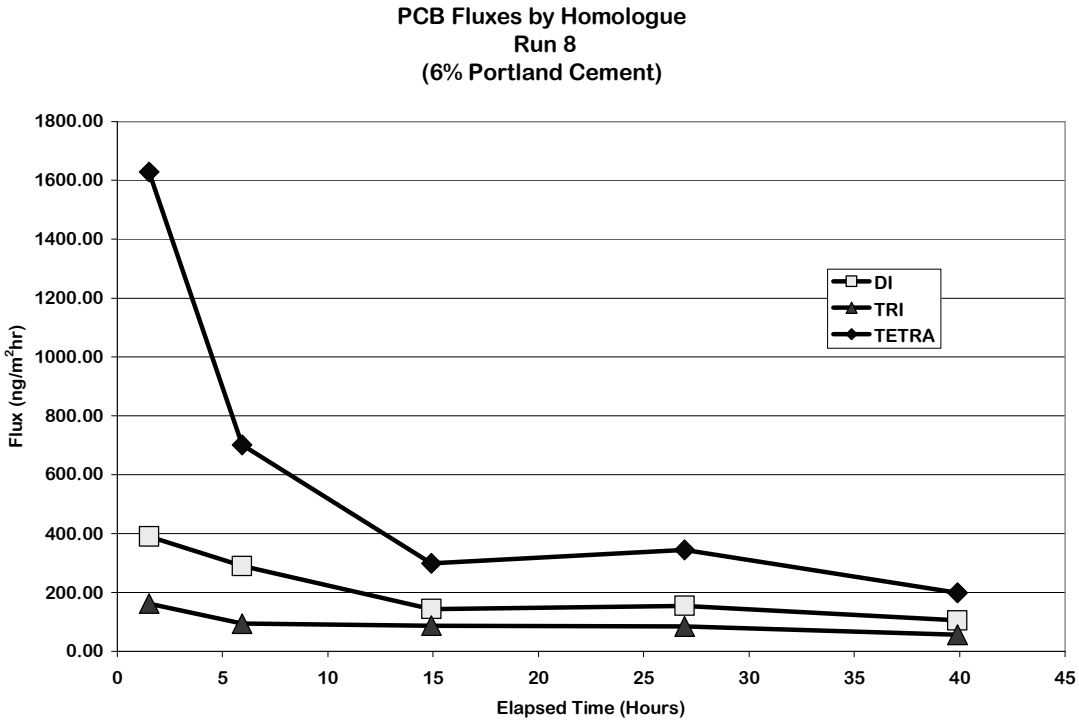


**Figure 24.** PCB Fluxes by Homologue, Run 8

### *2.3.9 Run 9*

The ninth run was completed July 26, 2004 to July 28, 2004. The sediment was not stabilized. The mean velocity of the air flowing over the sediment was 20 cm/sec. The initial moisture content of the sediment was 150%. Over the course of the experiment the moisture content did not change significantly. The influent air temperature varied very little during this experiment (<1.5˚C). Although the fluctuations were very small there appeared to be a pattern of peaks during the daytime and valleys at night. The sediment did not appear affected by the variation in influent air temperature; instead it rose steadily for the extent of this experimental run due to the warmer air blowing over it. The latent heat fluxes measured were close to zero, indicating little or no moisture flux from the sediment. The sensible heat was similar to the two previous runs indicating a small flux of convective heat into the sediment at a fairly constant rate.

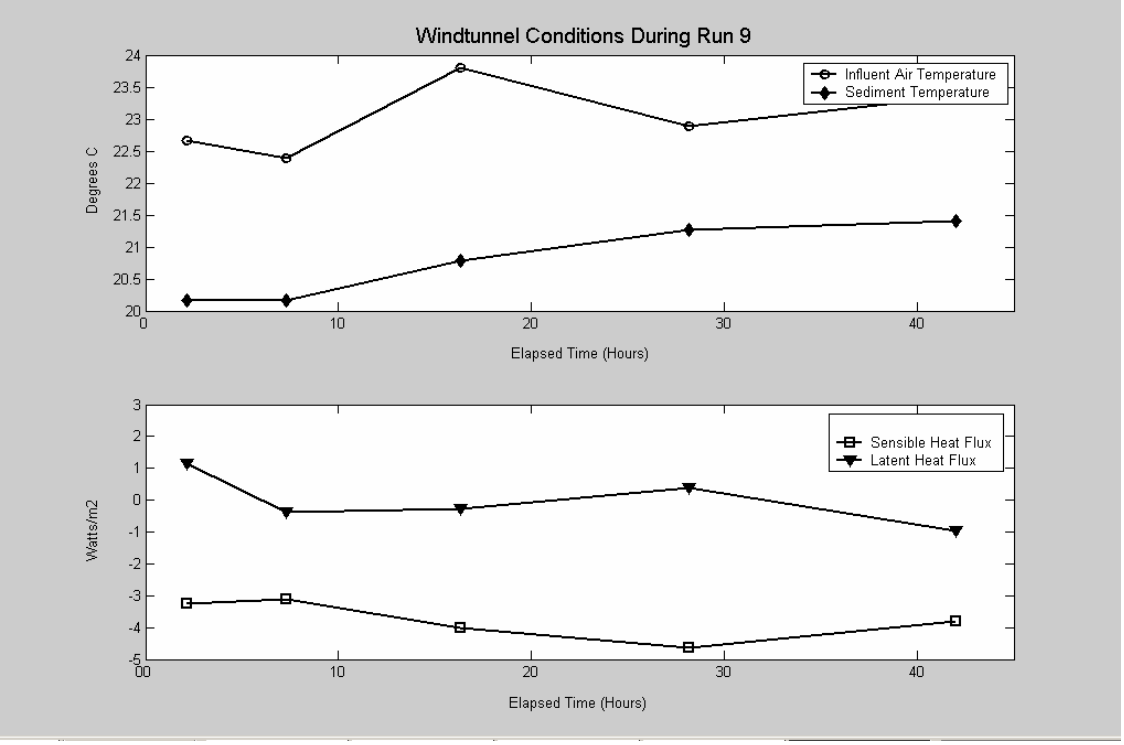


**Figure 25.** Wind tunnel Conditions During Run 9

Measurements for the third sampling interval in this run were not included because the PUF filter located in the effluent of the wind tunnel folded during the interval and a channel formed allowing the air to bypass the filter, thus the resulting concentrations were not accurate. The PCB fluxes measured in this experimental run were very similar to those measured during run 7. The increased speed compared to run 7 did not appear to have any effect on the measured fluxes.

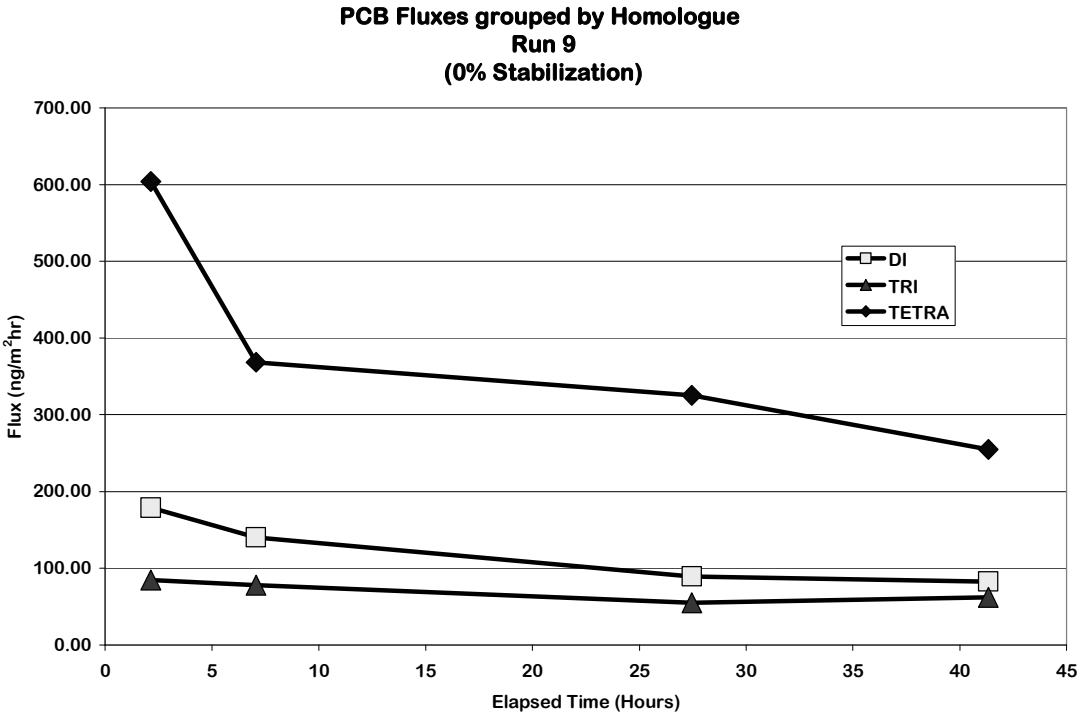


**Figure 26.** PCB Fluxes by Homologue, Run 9

### *2.3.10 Run 10*

The tenth run was completed July 31, 2004 until August 2, 2004. The sediment was stabilized with 6% portland cement by weight. The mean velocity of the air flowing over the sediment was 20 cm/sec. The initial moisture content of the sediment was 121%. Over the course of the experiment the moisture content decreased to 106%. The influent air temperature during this run increased due to the building's air conditioning shutting down during the second day of this run. The temperature reached as high as 27˚C. As a result of the very high air temperature the sediment also got extremely warm. The increase continued until it reached a peak six hours into the final sampling interval. The air conditioning in the room was restarted and the air temperature in the building dropped 2˚C. Since the values on the plot are averages, the final interval appears to have a lower temperature than the interval before it even though it was when the peak temperature occurred. The sediment followed the same pattern. The latent heat measurements indicate a flux of moisture out of the sediment at 10-20 watt/$m^2$, with the highest measurement occurring at the initial measurement when the sediment was warmer than the air. The sensible heat flux is very similar to the previous three runs, indicating a small flux of convective heat into the sediment at a fairly constant rate.

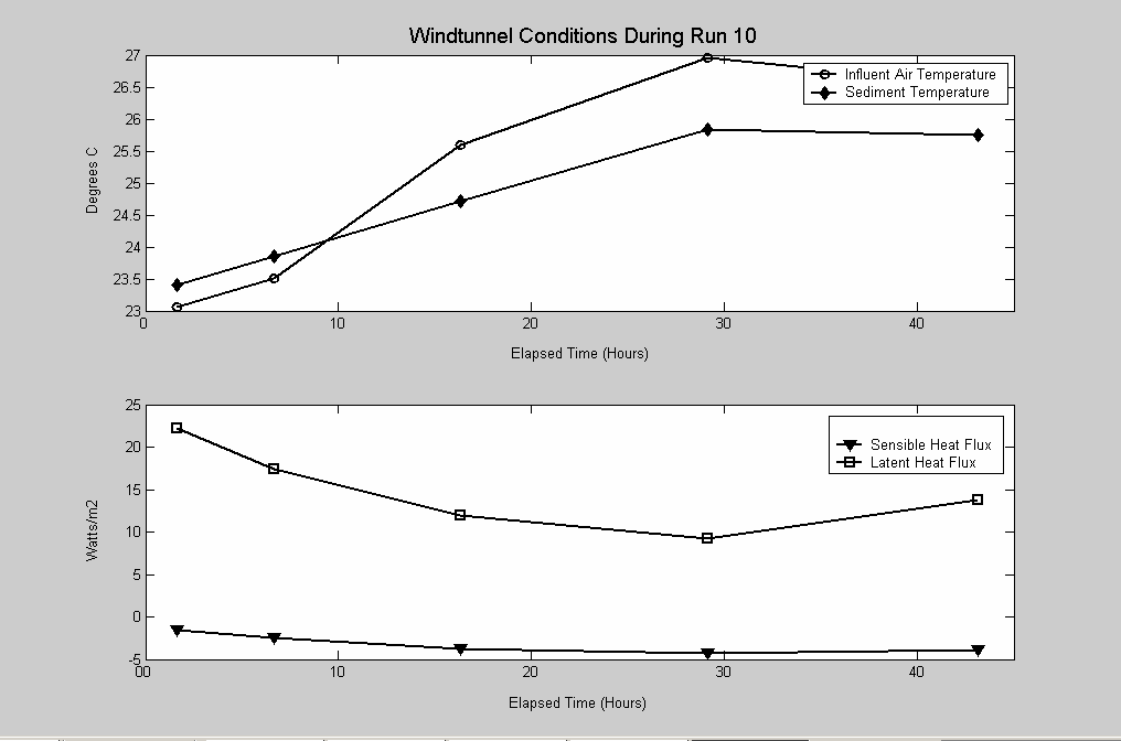


**Figure 27**. Wind tunnel Conditions During Run 10

The flux measurements for the dichlorinated, trichlorinated, and tetrachlorinated homologues indicate a high initial flux, that drops off quickly. The measure fluxes during this run exhibit a similar pattern to those collected during run 8, however the fluxes measured during run eight are much larger. The increase in temperature at the end of this run appears to have resulted in a small increase in the measured fluxes for the final sampling interval.

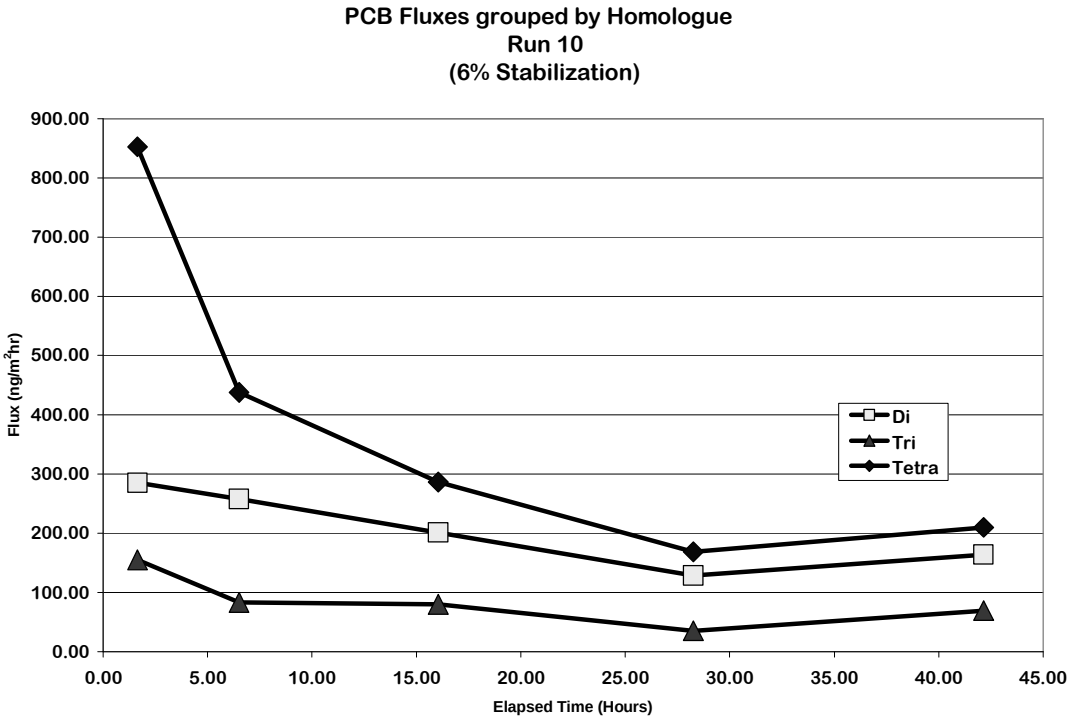


**Figure 28.** PCB Fluxes by Homologue, Run 10

### *2.3.11 Sediment Samples*

Sediment concentrations of PCBs were analyzed for the various samples. Two samples were analyzed for sediment samples A and C which were composited and analyzed. On the other hand, sediment from sample B was analyzed for each drum in the sample group. The results of these analyses show that there is a somewhat consistent distribution of PCBs in the various homologue groups although sediment analysis has a very high variance. The concentrations measured in sample A reveal that tetrachlorinated homologue is present in the highest concentrations in both A and C, and the value in C is about 1.5 time that found in A. The dichlorinated homologue is higher in A than C. These analyses are consistent with the flux measurements from sample A and C. Fluxes measured from A were dominated by the dichlorinated homologue and those measured from C were dominated by the tetrachlorinated homologue. .

**Table 4**. Sediment Sample Results: Samples A and C

| | ***Sediment Sample A (ppb)*** | | ***Sediment Sample C (ppb)*** |
|---|---|---|---|
| | **1A** | **2A** | **2C** |
| ***DI*** | *445.1* | *202.2* | *181.8* |
| ***TRI*** | *149.2* | *970.8* | *156.7* |
| ***TETRA*** | *908.4* | *802.2* | *1208.9* |

The measured concentrations for the samples C and B have a large range, but in general exhibit higher concentrations for the tetrachlorinated homologue. This is expected because the tetrachlorinated homologue dominates the fluxes measured from sediment samples B and C.

**Table 5**. Sediment Sample Results: Sample B

| | ***Sediment Sample B (ppb)*** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **7A** | **7B** | **8A** | **8B** | **9A** | **9B** | **10A** | **10B** |
| ***DI*** | *832.0* | *62.5* | *289.5* | *67.6* | *838.4* | *313.1* | *237.0* | *221.7* |
| ***TRI*** | *48.9* | *190.3* | *128.1* | *238.2* | *86.3* | *88.4* | *20.4* | *43.2* |
| ***TETRA*** | *993.1* | *338.8* | *286.0* | *386.2* | *688.3* | *1151.3* | *587.1* | *424.8* |

## 3.0 DISCUSSION

### 3.1 Time Dependence of PCB Fluxes

The evolution of the PCB flux after placement of SDM is a great concern, as are the effects of stabilization on that evolution. Each of the experimental runs conducted in the wind tunnel were carried out for at least forty eight hours. Several samples were collected during each run, in order to characterize the behavior of PCB fluxes as the sediment ages and the stabilizing agent cures. The pattern of fluxes with respect to time measured in both the field and laboratory investigations were analyzed to determine how the behavior of the fluxes was affected by the stabilization process. The PCB fluxes indicated a distinct pattern over time. The initial flux was high and it declined rapidly over the next 48 hours.

The fluxes measured for unammended dredged sediment show a similar pattern for samples B and C. Sample A (unammended) was run in the laboratory when it was very cold and the flux values were very low. There were two sampling runs completed on unammended sediment from sample B. These runs were conduced at two air velocities (~15 cm/s, and ~20 cm/sec) to investigate the effect of changing the velocity on the PCB flux. The fluxes measured during the two runs were very similar. The initial flux measurements of the dichlorinated homologue collected for samples B and C ( at ~2 hours) were 182 ± 5.6 ng/m$^2$hr and 243 ng/m$^2$hr respectively. These fluxes gradually declined over the sampling run to 88 ± 7.2 ng/m$^2$hr at ~41 hours for sample B, and 85 ng/m$^2$hr at ~37 hours for sample C. These measurements indicate a flux decrease of 52% and 65% for samples B and C with respect to dichlorinated homologues. The tetrachlorinated homologue exhibited similar behavior. The initial flux measurements for samples B and C ( at ~2 hours) were 581 ± 35.5 ng/m$^2$hr and 656 ng/m$^2$hr respectively. These fluxes gradually declined over the sampling run to 248 ± 8.4 ng/m$^2$hr at ~41 hours for sample B, and 198 ng/m$^2$hr at ~37 hours for sample C. These measurements indicate a decrease of 57% and 70% respectively for samples B and C with respect to tetrachlorinated homologues. The fluxes measured at approximately 37 hours for sample

C are slightly lower than those measured for sample B at a similar time; this is due to differences in the temperature. The temperature remained relatively stable during the two runs completed with sample B. Conversely, the temperature fluctuated greatly during the run completed with sample C. The sample was collected overnight and the temperature was lower than the samples before and after.

Several runs were completed with varying degrees of stabilization. Experimental runs with sediment samples A and C were conducted with 4% and 8% portland cement by weight. Two runs were completed with sediment sample B and stabilized with 6% portland cement. The sediment collected in sample A varied greatly in its amount and distribution of PCB congeners, as a result comparisons with the other samples are somewhat difficult.

The initial flux measurements for the fifth run in this experiment (sample C, 4% portland cement) were collected in the interval centered around1.14 hours. The fluxes measured during this interval appear to be extremely low. This may be due to the low initial sediment temperature or air by passing the PUF filter. As a result the second sampling interval will be analyzed for both 4% runs. This interval is centered around 4.35 hours for sample C and 5.85 hours for sample A. The dichlorinated homologue measurements collected during the experimental runs sediment stabilized with 4% portland cement for samples A and C ( at ~2 hours) were 941 ng/$m^2$hr and 369 ng/$m^2$hr respectively. These fluxes declined sharply to values of 198 ng/$m^2$hr, at ~16.47 hours for sample A, and 83 ng/$m^2$hr at ~15.8 hours for sample C. These represent a decrease of 77% and 82% for fluxes from samples A and C. The tetrachlorinated homologue measurements were 212 ng/$m^2$hr and 649 ng/$m^2$hr respectively. These fluxes declined sharply to values of 25 ng/$m^2$hr, at ~16.47 hours for sample A, and 142 ng/$m^2$hr at ~15.8 hours for sample C. These represent decrease of 79% and 88% for fluxes from samples A and C. The decrease in the flux rate from the sediment is larger in magnitude and shorter duration when the sediment is stabilized.

Two runs were completed with sediment that had been stabilized with 6% portland cement. These were run at two mean air velocities over the sediment (~15 cm/s, and ~20 cm/sec). Run eight was completed with an average air velocity of 15 cm/sec. The initial flux measurement of the dichlorinated homologue ( at ~1.5 hours) was 390 ng/$m^2$hr. This flux declined to 143 ng/$m^2$hr at ~15 hours and then decreased to 108 ng/$m^2$hr at ~40 hrs. The initial flux measurement of the tetrachlorinated homologue ( at ~1.5 hours) was 1629 ng/$m^2$hr. This flux declined to 299 ng/$m^2$hr at ~15 hours and then decreased to 198 ng/$m^2$hr at ~40 hrs. Run 10 was completed with an average air velocity of 20 cm/sec. The initial flux measurement of the dichlorinated homologue ( at ~1.5 hours) was 285 ng/$m^2$hr. This flux declined to 201 ng/$m^2$hr at ~15 hours and then decreased to 164 ng/$m^2$hr at ~40 hrs. The initial flux measurement of the tetrachlorinated homologue ( at ~1.5 hours) was 853 ng/$m^2$hr. This flux declined to 286 ng/$m^2$hr at ~15 hours and then decreased to 209 ng/$m^2$hr at ~40 hrs. The fluxes measured during the low velocity run were much higher those for the high velocity run; however they decreased quickly to values that were very similar.

Run 10 was completed at the same velocity as the remainder of the runs in order to compare the effect of varying amounts of stabilization. The initial fluxes were similar for both the dichlorinated and tetrachlorinated homologues, and they both decreased rapidly, however run 10 had an average sediment temperature of 24.7˚C and run 5 had an average sediment temperature of 18.7˚C. This discrepancy could explain why the fluxes at the end of the runs are much larger for run 10 even though more cement was used.

Two runs were completed using 8% portland cement by weight. The initial flux measured during run 4 was similar to that measured 4.35 hours into run 5 (sample C, %4 portland cement). The difference between the two runs can most easily be seen in the measurements of latent heat flux. In run five there is a positive moisture gradient out of the sediment. In run four however, there is no latent heat flux indicating that the sediment is essentially dry. The relatively low initial flux is most likely due to the loss of the PCBs during the stabilization process. Evidence for this loss of PCBs during stabilization is the background concentration during the initial sampling intervals.

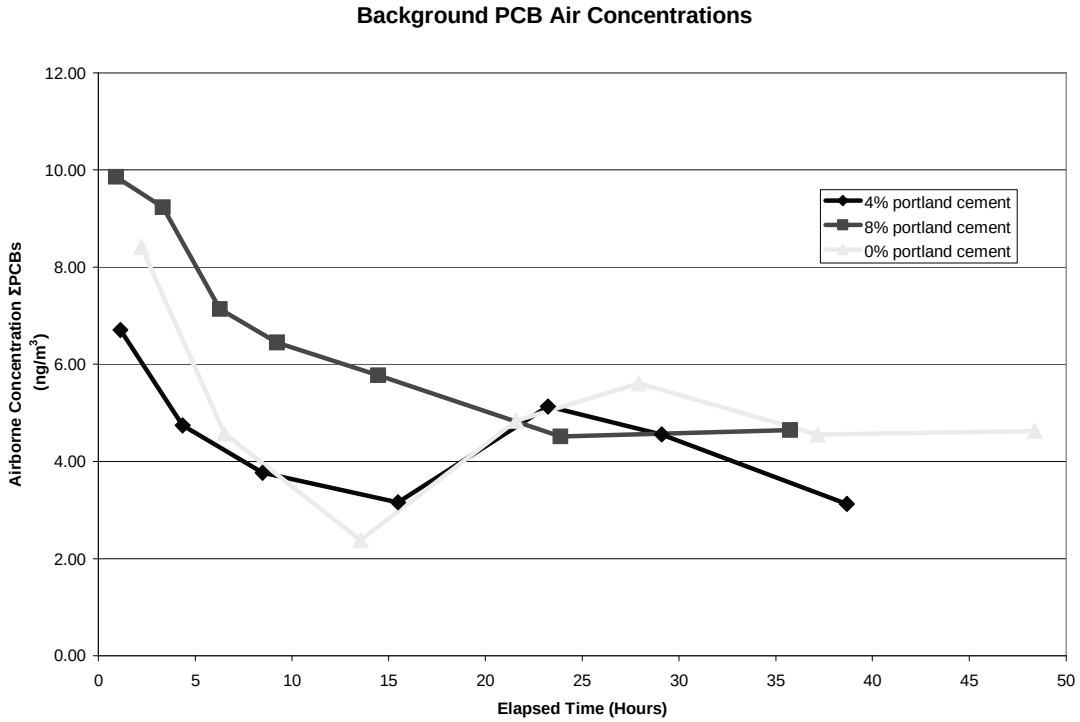


**Figure 29.** Background Laboratory PCB Air Concentrations

The run completed with 8% cement has a high background concentration which remains high through the first night when the concentrations typically decrease. After the first day the background concentrations return to normal for the laboratory.

The flux rate for the 8% stabilized sediments decreases very steadily over the final four sampling intervals in both. Over the same period the fluxes measured from the 4% stabilized sediments fluctuate along with the air temperature. In addition, fluxes from

non-stabilized sediments have even larger fluctuation due to temperature. Thus it is apparent that temperature has a lesser affect on the fluxes from more highly stabilized sediment.

## 3.2 Temperature Dependence of PCB Fluxes

The effects of temperature fluctuations can be seen in some of the experimental runs. The two runs affected most by the fluctuations in temperature were runs 3 and 6.

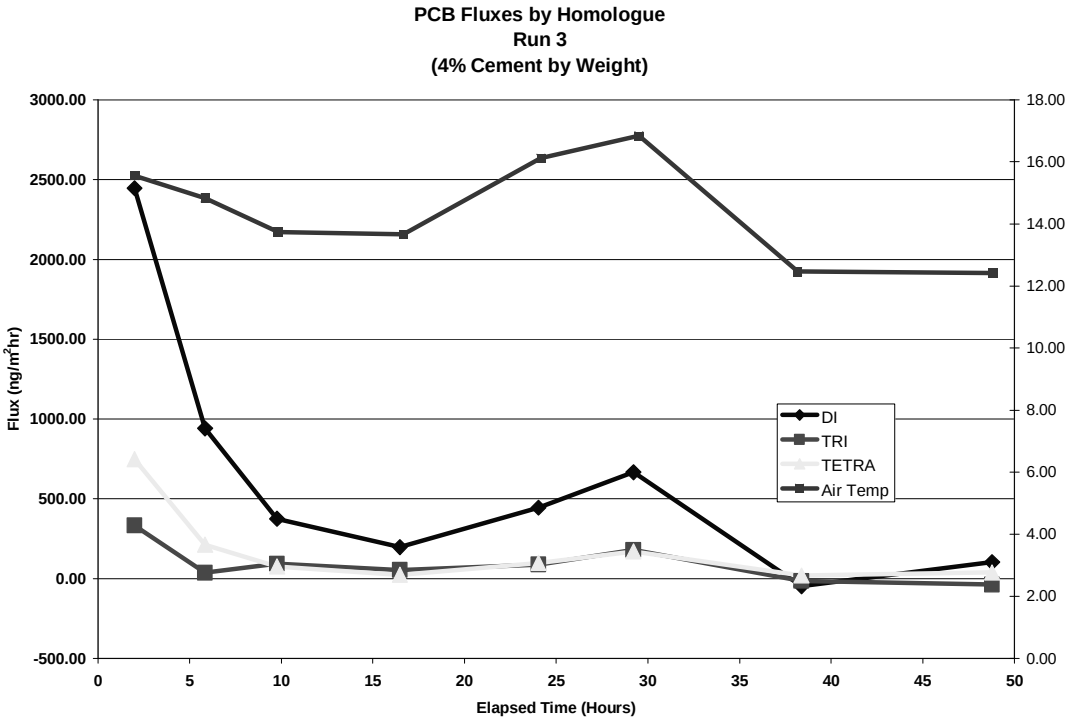


**Figure 30.** PCB Homologue Fluxes and Air Temperature, Run 3

It can be seen from this figure that spike in temperature that occurred between 24 and 30 hours induced a spike in the PCB fluxes.

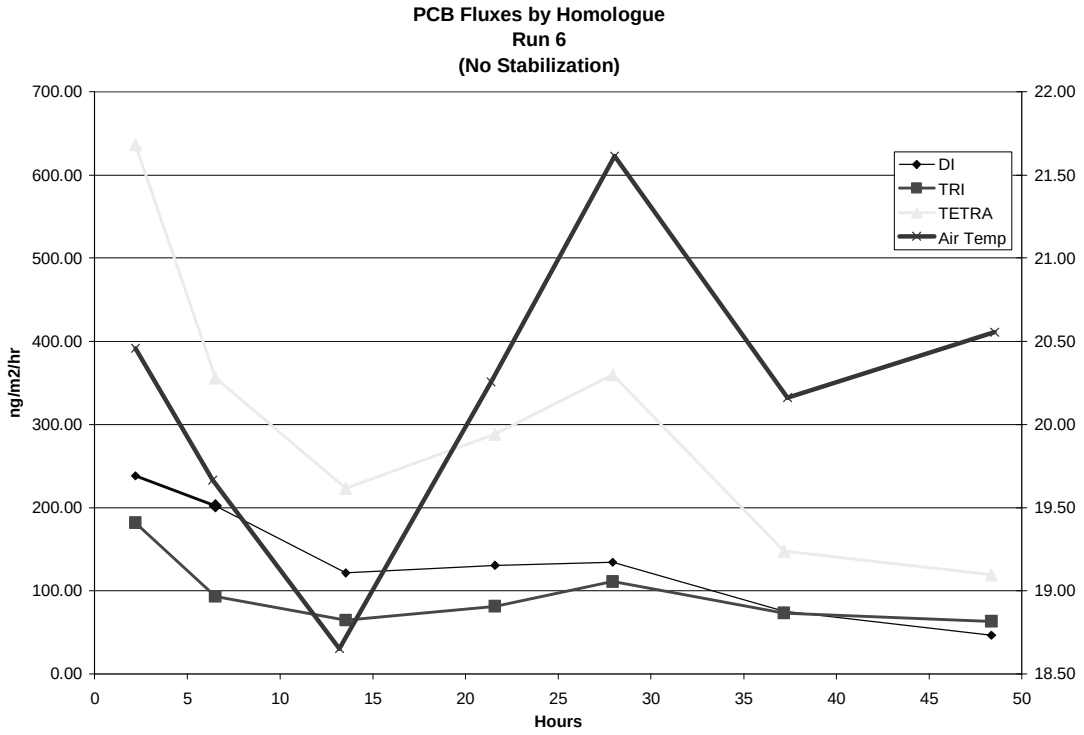


**Figure 31.** PCB Homologue Fluxes and Air Temperature, Run 6

This plot of run six also shows the influence that temperature fluctuations had on the PCB fluxes. This plot shows that as well as increasing the flux on a temperature peak, there is also a depression in the PCB flux measurements during colder conditions.

The relationship between temperature and the concentrations of PCBs measured in the laboratory background air as well as in the wind tunnel was investigated using a least squares regression of the natural log of the PCB concentration to the reciprocal of the temperature, (1/˚K), to yield a Clausisus Clapyeron-like equation. The background PCB concentrations were highly variable. The $R^2$ values for these relationships are relatively low. Temperature fluctuations in the laboratory account for approximately 40-50% of the variance in PCB concentrations. The background measurements of PCB concentration vary a great deal.

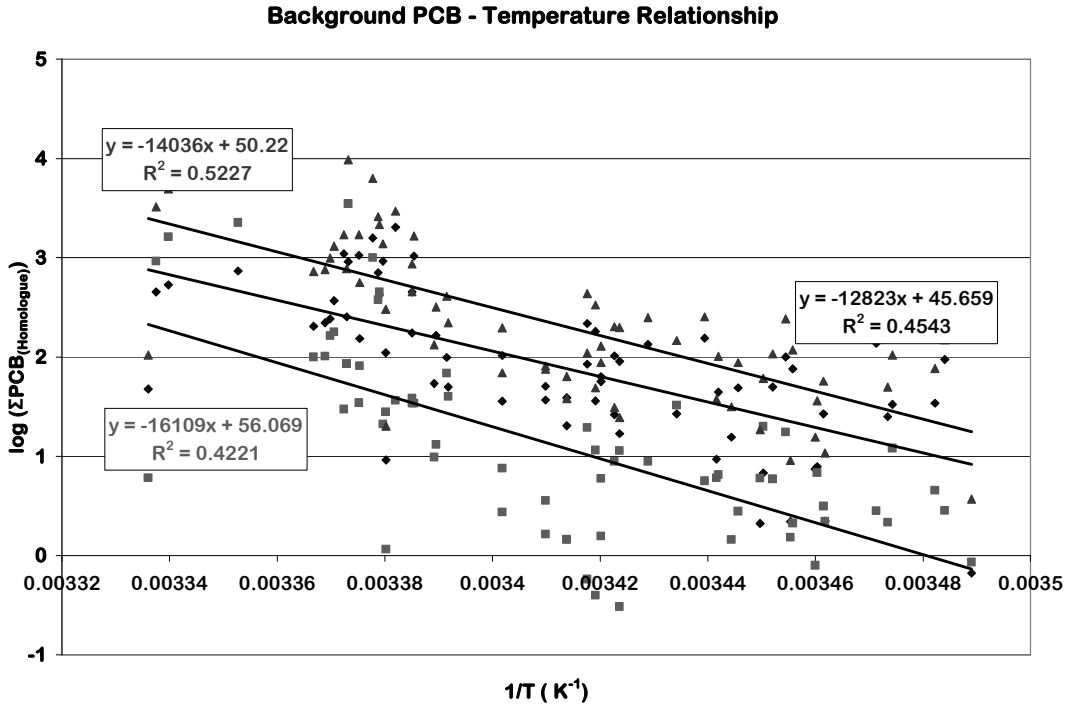


**Figure 32.** Laboratory Temperature versus PCB Concentration

The relationship shown in the figure above was determined over all of the experimental runs. As a result there is a large amount of variance due to stabilization, initial PCB concentration of the sediment, and initial moisture content. In order to eliminate these variables, each run was investigated separately. The temperature – PCB concentration relationships were then used to correct the measured concentrations in the wind tunnel and background air. Only regressions with an $R^2$ value greater than 0.5 were used. In addition, the first measurement of PCB concentration was not used due to a consistent large flux observed during the initial sampling interval for each experimental run. Predicted concentrations based solely on temperature were calculated for each time interval. PCB fluxes were calculated using the difference of the predicted concentrations, the flow rate, and the surface area of the dredged material. After the predicted fluxes were calculated, the mean was determined and subtracted out. The remaining values represented the fluctuations in PCB fluxes due to temperature. These were then subtracted from the measured fluxes, the resulting 'corrected' flux values represented the fluxes from the sediment over the length of the experimental run ,with the temperature held constant at the mean temperature measured during the run. This procedure was completed for runs three and six because of the strong influence of temperature. The equations of the regression lines and fit statistics are presented in Table 11.

**Table 6**. Temperature - PCB Concentration Relationships

| | | Equation | $R^2$ |
|---|---|---|---|
| Run 3 | Wind Tunnel | $\ln(C_{di}) = -20486 \times (1/T) + 73.143$ | 0.59 |
| | | $\ln(C_{tri}) = -31863 \times (1/T) + 111.22$ | 0.53 |
| | | $\ln(C_{tetra}) = -30968 \times (1/T) + 108.03$ | 0.86 |
| | Background | Background concentrations exhibit $r^2<0.5$ when regressed versus temperature, as a result the measured background concentrations were used. | |
| Run 6 | Wind Tunnel | $\ln(C_{di}) = -17523 \times (1/T) + 61.077$ | 0.68 |
| | | $\ln(C_{tri}) = -29705 \times (1/T) + 102.41$ | 0.82 |
| | | $\ln(C_{tetra}) = -27136 \times (1/T) + 94.271$ | 0.74 |
| | Background | $\ln(C_{di}) = -18447 \times (1/T) + 63.274$ | 0.62 |
| | | $\ln(C_{tri}) = -32755 \times (1/T) + 111.61$ | 0.64 |
| | | $\ln(C_{tetra}) = -24889 \times (1/T) + 85.228$ | 0.56 |

Figures 33 and 34 are plots of the measured, predicted, and ‘corrected’ tetrachlorinated PCB fluxes for runs 3 and 6.

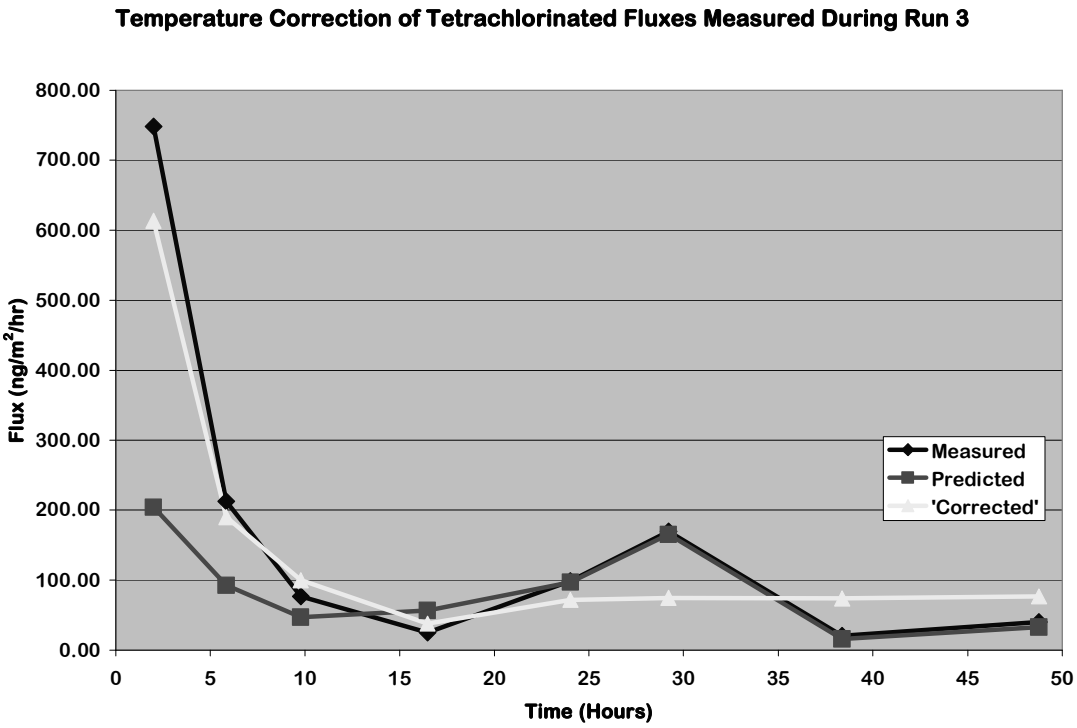


**Figure 33.** Temperature 'Corrected' PCB Fluxes, Run 3

Run 3 was stabilized with 4% portland cement. This reaction creates heat; as a result the 'corrected' flux is lower than the measured. For the rest of the run fluctuations due to temperature are removed and the tetrachlorinated PCB flux remains steady at ~75 ng/$m^2$/hr.

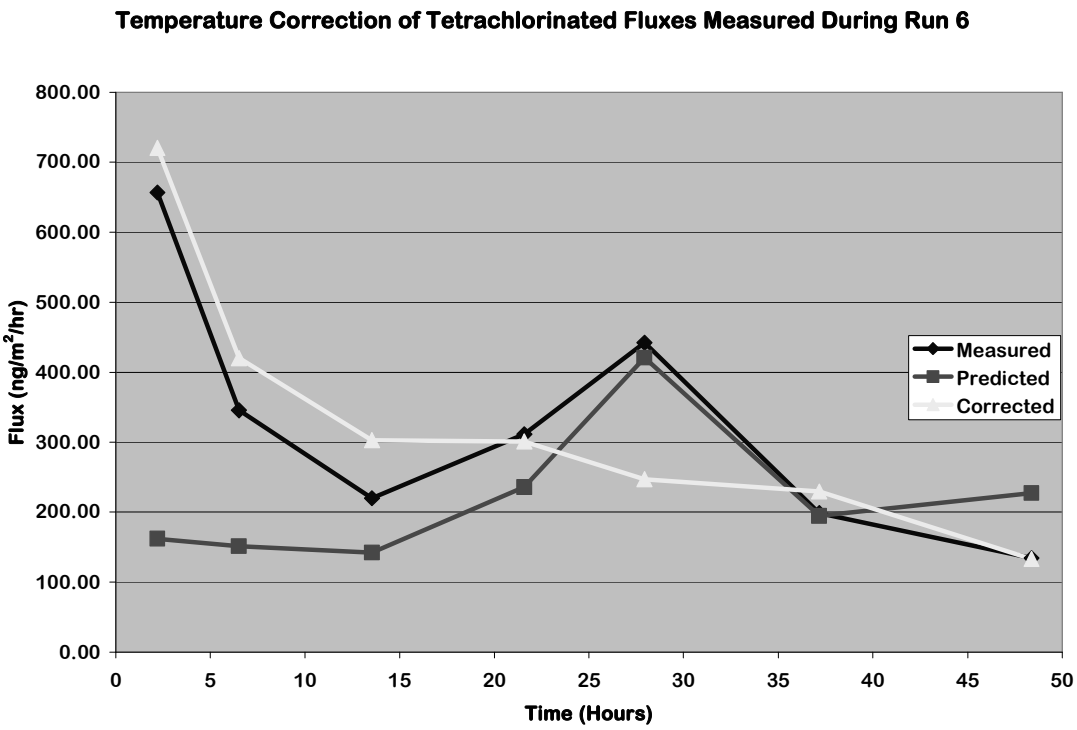


**Figure 34.** Temperature 'Corrected' PCB Fluxes, Run 6

The sediment used during run 6 was not stabilized. As a result the initial flux occurs at a relatively low temperature and when corrected, increases. The fluxes steadily decrease from the initial value and the peak in temperature on the second day is successfully removed.

### 3.3 Modeling of PCB Flux Measurements

Several models described in a previous section were evaluated in order to simulate the laboratory measurements. Though several were promising the main confounding variable was the vertical moisture profile. It was determined that a bulk approach would be the most effective method of modeling the data. This approach assumes that the concentration of PCB available to volatilize in the sediment follows a first order 'kinetic'. The initial equation is:

$$\frac{\partial C}{\partial t} = -\alpha C \tag{22}$$

$\frac{\partial C}{\partial t}$ is the change in concentration over time, $\alpha$, is a pseudo-first order volatilization rate constant, and C, is the concentration of PCBs in the sediment. When this is integrated with and initial condition that C=C˚ (the initial concentration in the sediment) at t=0, the result is:

$$C = C^{\circ} e^{-\alpha t} \quad (23)$$

This equation can then be substituted into the Nerst equation presented earlier in the description of the Hartley model. It represents the flux as the concentration gradient between the pore air and the free stream concentration of the air, $C^{\infty}$, multiplied by the overall mass transfer coefficient, k.

$$F = k\left(C - C^{\infty}\right) \quad (24)$$

Since PCBs are in extremely low concentrations in the atmosphere, for modeling purposes it can normally be assumed that $C^{\infty}$ is equal to zero, ($C^{\infty} = 0$), the resulting equation is

$$F = kC^{\circ} e^{-\alpha t} \quad (25)$$

Thus the flux of contaminant is the product of the mass transfer coefficient, the sediment concentration, and the volatilization rate. Taking the natural log of both sides of this equation and plotting them yields a linear relationship between ln(F) and $\alpha$. The intercept is the natural log of the product of the mass transfer coefficient at t=0 and the initial sediment concentration. The overall mass transfer coefficient at t=0 is approximately equivalent to the air side mass transfer coefficient because when freshly placed the sediment is moist, and resistances to PCB fluxes are not yet present in the sediment. As time passes, the resistances in the sediment will build up and the flux will be increasingly sediment-side controlled. Since the intercept in the model represents the flux at t=0 the air side mass transfer coefficient can be substituted for the overall mass transfer coefficient. This model was applied to the PCB flux measurements made during this study. The results are presented in Table 7.

## Model Results

| | | Dichlorinated Homologue | | | Trichlorinated Homologue | | | Tetrachlorinated Homologue | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ***slope*** | ***Intercept*** | ***$R^2$*** | ***slope*** | ***Intercept*** | ***$R^2$*** | ***slope*** | ***Intercept*** | ***$R^2$*** |
| ***Unammended*** | ***Run_1*** | NA | NA | NA | -0.0256 | 4.2465 | 0.4281 | -0.0317 | 4.2347 | 0.458 |
| | ***Run_6*** | -0.0384 | 5.3604 | 0.7534 | -0.0099 | 5.118 | 0.1144 | -0.0238 | 6.034 | 0.434 |
| | ***Run_7*** | -0.0152 | 5.374 | 0.3903 | -0.0114 | 5.0638 | 0.5922 | -0.016 | 6.185 | 0.6259 |
| | ***Run_9*** | -0.0211 | 5.0393 | 0.9265 | -0.0114 | 4.0063 | 0.6985 | -0.0167 | 6.0242 | 0.7598 |
| ***4%*** | ***Run_3*** | -0.0478 | 7.0855 | 0.5562 | NA | NA | NA | -0.0472 | 5.5207 | 0.4086 |
| | ***Run_5*** | -0.0382 | 5.3008 | 0.5847 | -0.0459 | 5.5221 | 0.8047 | -0.0455 | 5.9867 | 0.6117 |
| ***6%*** | ***Run_8*** | -0.0316 | 5.977 | 0.8385 | -0.0224 | 4.9206 | 0.7347 | -0.0428 | 6.9732 | 0.7626 |
| | ***Run_10**** | -0.0301 | 5.7849 | 0.9875 | -0.0488 | 4.9952 | 0.898 | -0.0565 | 6.6441 | 0.9364 |
| ***8%*** | ***Run_2*** | -0.0219 | 7.0018 | 0.7145 | -0.0428 | 5.3151 | 0.8203 | -0.0635 | 5.0758 | 0.8423 |
| | ***Run_4*** | -0.1562 | 5.7157 | 0.8685 | -0.1247 | 6.0095 | 0.9586 | -0.0547 | 6.2314 | 0.8857 |
| | ***May-02*** | -0.0481 | 7.1973 | 0.7537 | -0.0465 | 7.3381 | 0.6495 | -0.039 | 6.9107 | 0.6727 |

** Measurement at 42 hours removed due to large temperature spike*

*NA = $R^2$ value >0.05*

**Table 7**. Temperature versus PCB Concentration Relationships

The dichlorinated homologue fluxes exhibit a trend of slopes that are increasingly negative with respect to the amount of portland cement added. The exception to this trend is the 6% stabilized measurements. It is believed that the relatively high temperatures result in slightly increased fluxes even when the sediment is essentially dry, thus reducing the rate of decay of the flux. The intercepts, which are the initial concentrations multiplied by the air side mass transfer coefficients, appear to increase with the amount of cement added. The unammended sediment runs for samples B and C have lower intercepts than those measured for runs with the same samples that have been stabilized. This is presumably due to the increased temperature resulting from the exothermic reaction between the moisture in the sediment and the portland cement. The measurements collected during landfill study of dichlorinated homologue fluxes are very similar to the measurements for Run 3 (4% cement).

The measurements collected for the trichlorinated fluxes exhibit a pattern similar to the dichlorinated fluxes. The field event data has a very large intercept value compared to those measured during the laboratory studies. The model results for the tetrachlorinated results show the most consistent pattern of increasing decay of fluxes with increased cement added. The field data appears similar to the measurement made with sediment stabilized with 4% cement by weight.

The slopes of the various regression lines are dependent on the amount of cement used for stabilization and the chlorination of the various PCB homologues. It can be seen that increasing the amount of Portland cement used to stabilize the sediment will increase the rate at which the fluxes decay from an initial value.

Runs 4, 5, and 6, were completed under similar atmospheric and sediment conditions. These runs represent unammended, 4% , and 8% stabilization. The flux values have been normalized by the initial flux rate in order to eliminate the effects of varied concentration. The May 2003 field measurements were also included to compare the field measurements to the laboratory study. The value found at night during the field event was not included due to the high stability during that interval. The dichlorinated homologue fluxes appear to show a distinct pattern with the 8% Portland cement mix showing the steepest slope. The 4% and 0% appear to have the same slope as each other while the field event has a slope that is slightly more negative than the 4%.

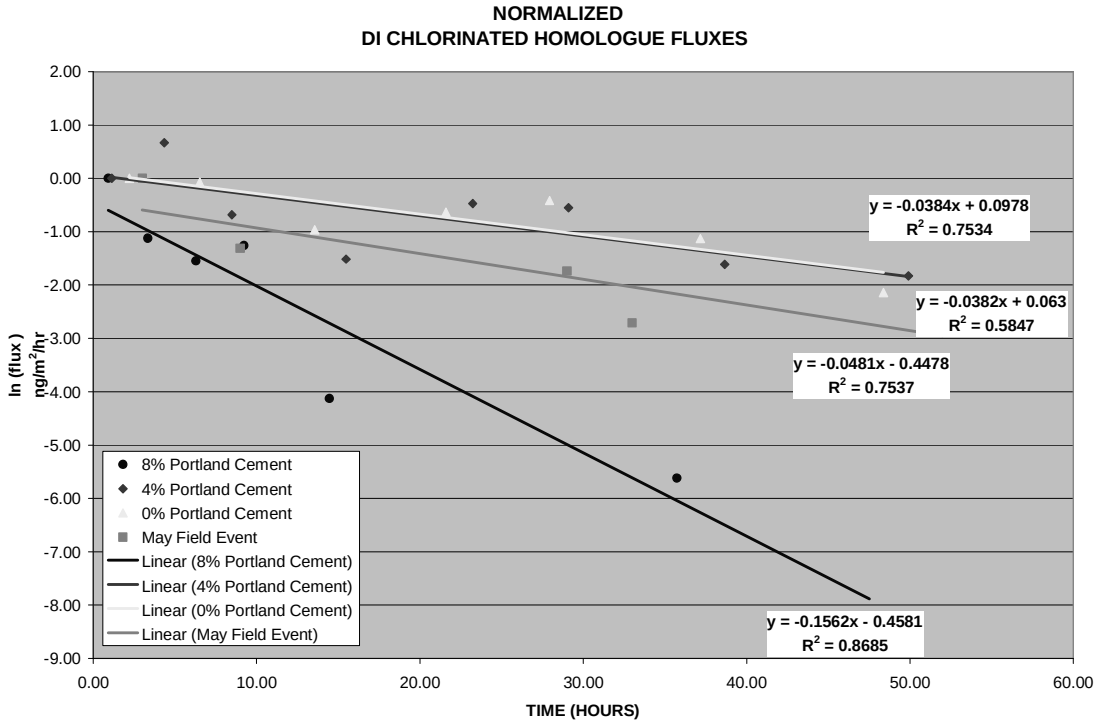


**Figure 35.** Di-Chlorinated PCB Fluxes

A similar pattern is observed in the trichlorinated homologues. The 4% has a steeper slope than the 0%, and the field event has a slightly more negative slope than the 4%. The 8% is still very steep compared to the less stabilized experimental runs and the field event.

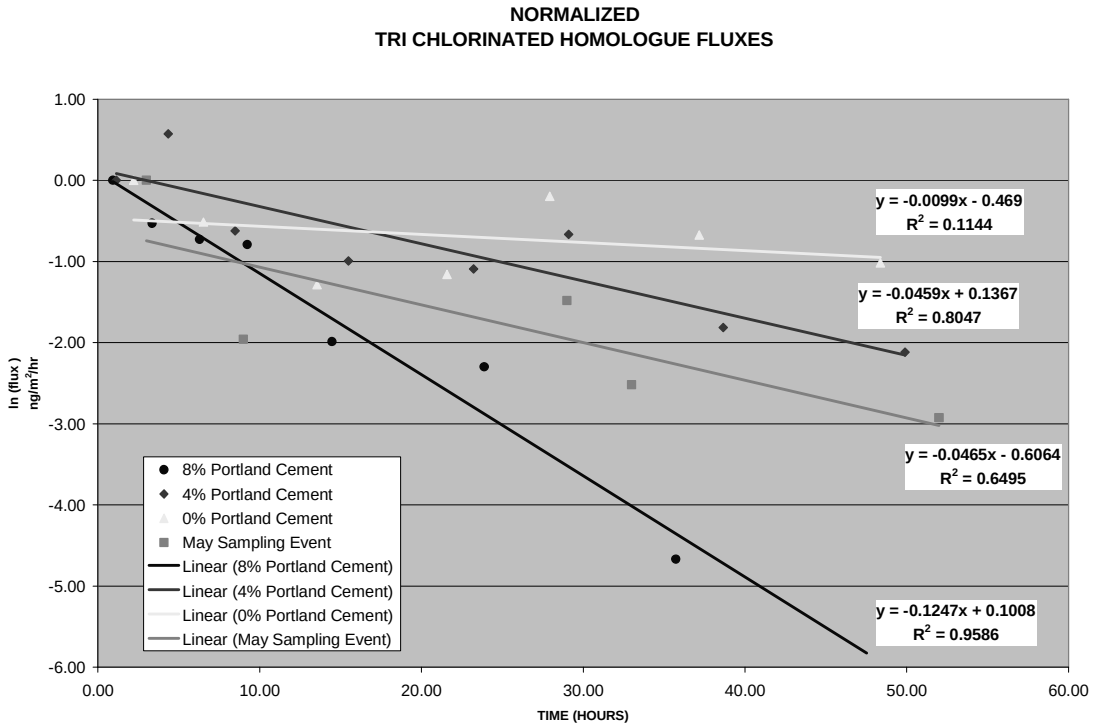


**Figure 36.** Tri-Chlorinated PCB Fluxes

The tetrachlorinated homologues also exhibited similar behavior. The slopes of all the trend lines are steeper than for the trichlorinated homologues. The 4% and field event are very similar to the 8% stabilized sediment.

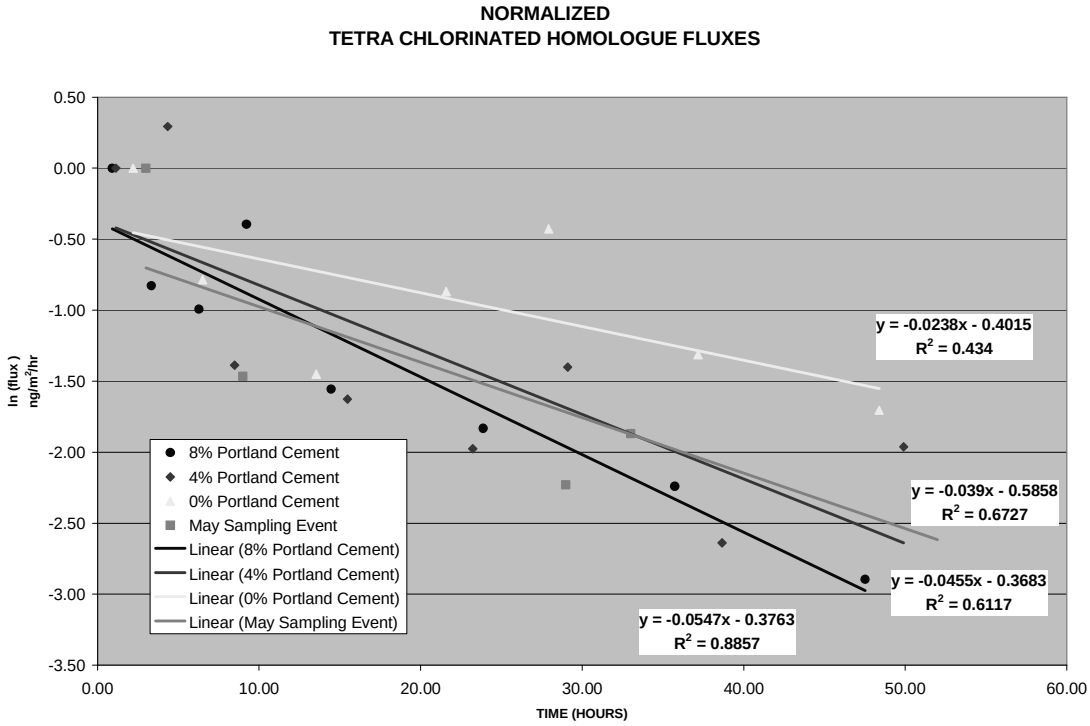


**Figure 37.** Tetra-Chlorinated PCB Fluxes

It is also apparent that the rate of decay of the fluxes is dependent on the molecular weight of the PCB. The decay is greatest for the tetrachlorinated and least for the dichlorinated homologue. Another apparent effect is that stabilization will affect the homologues differently. The 4% mix appears to have little effect on the decay rate while 8% has a large effect on the dichlorinated homologue. In contrast to this, for the trichlorinated homologue the 4% mix exhibits a slope approximately halfway between the 0% and 8% mixes. And finally for the tetrachlorinated homologue the decay rate for the 4% mix approached the 8% mix.

During the May 2000 field sampling interval, the sediment was stabilized with approximately 12% cement. When compared with the measurements collected for this study it matches closer to the behavior of sediment stabilized with 4% cement. The difference may be due to the sediment sampling method, physical properties of the sediment or meteorological factors (sunlight, wind, etc.).

## 4.0 CONCLUSIONS

Comparisons between the data collected from the field study at the Bayonne Landfill and the laboratory wind tunnel study were made to determine if the measurements from the laboratory study were a good representation of the field. In addition, these data were also compared to studies conducted by other researchers. In order to make these comparisons it must be noted that there were differences in initial PCB concentration, PCB congeners that were analyzed, and scaling differences. The average of the total PCB flux measured during the laboratory experiment was 577 ng $m^{-2}$ $hr^{-1}$ and they ranged in value from -155 to 4465 ng $m^{-2}$ $hr^{-1}$. These are well with the range of values measured during the field sampling experiments: 72 to 15,000 ng $m^{-2}$ $hr^{-1}$ with a mean value of 2050 ng $m^{-2}$ $hr^{-1}$ (Korfiatis et al., 2003). These values represent a sum of PCBs, although the sampling set is not the same they all have several of the same congeners represented.

Fluxes of PCBs from stabilized sediment are initially high and decrease rapidly as the sediment dries. Thus the high fluxes measured in the first few hours after placement may appear to represent the largest source of PCBs to the atmosphere. In reality the low magnitude, long term fluxes represent a more significant source. The fluxes measured during runs four and six are a good example of this. The sediment used for run four was stabilized with 8% portland cement. After placement, the initial flux of tetrachlorinated PCB congeners was 798 ng/$m^2$/hr, this was elevated due to an increase in temperature caused by the reaction of the cement and the water in the sediment. The sediment used in run six was not stabilized. The initial flux rate was 636 ng/$m^2$/hr. The sediment used for both of these samples was homogenized when it was collected so the initial concentrations in the sediment during both experimental runs were approximately the same. Although the initial flux rate increases with the addition of cement, the flux rate declines much faster over time due to the much lower moisture content of the sediment. When integrated over the length of the experimental run it was found that the non-stabilized sediment released 15 μg of tetrachlorinated PCB congeners to the atmosphere from one square meter of sediment while the stabilized sediment released only 11 μg. Thus it is apparent that stabilization will reduce the total amount of PCB released to the atmosphere.

**Table 8.** ΣPCBs Volatilized during Experimental runs

| Sediment Sample | Experimental Run | Stabilization | ΣPCBs Volatilized (µg) (per $m^2$ of sediment surface) | | |
|---|---|---|---|---|---|
| | | | Di | Tri | Tetra |
| *A* | *Run 1* | *0%* | *12.2* | *2.4* | *2.8* |
| | *Run 3* | *4%* | *22.9* | *3.2* | *6.4* |
| | *Run 2* | *8%* | *29.1* | *1.9* | *1.6* |
| *C* | *Run 6* | *0%* | *6.4* | *7.4* | *15.2* |
| | *Run 5* | *4%* | *7.3* | *5.2* | *12.4* |
| | *Run 4* | *8%* | *3.5* | *3.6* | *11.1* |
| *B* | *Run 7* | *0%* | *6.3* | *4.7* | *17.5* |
| | *Run 9* | *0%* | *4.7* | *2.1* | *13.7* |
| | *Run 8* | *6%* | *10.0* | *5.1* | *24.3* |
| | *Run 10* | *6%* | *3.7* | *0.9* | *12.6* |

This table shows that in general, the total mass of PCBs volatilizing from the sediment decreases with the amount of stabilization. Notable exceptions to this trend are Run 8 and Run 1. Run 8 exhibited extremely high measured fluxes while having the same pattern of decrease in the flux values as run 10. This could be the result of a higher concentration of PCBs in the sediment. Run 1 was completed with extremely cold sediment, the low temperature acted to restrict the flux of PCB. In both cases, if the experimental runs were extended it is believed that the ΣPCBs volatilized would fit into the pattern. When the fluxes for runs 7 and 8 are calculated using the models proposed in the previous section, the ΣPCBs volatilized from the non-stabilized sediment is equal to the 6% stabilized sediment from run eight, 108 hours after placement, and is larger as time passes.

The first order bulk transport model presented in the previous section can be used to predict PCB fluxes from sediment. The flux will be a function of the initial sediment concentration of PCBs, the decay rate and time.

$$F = C^{\circ} k_a e^{-\alpha t} \tag{26}$$

α is the volatilization rate, $k_a$ is the air-side mass transfer coefficient, and $C^{\circ}$ is the initial sediment concentration of PCBs. The volatilization rate was determined using the measured flux rates from the wind tunnel study. The reciprocal of the volatilization rate will be in units of hours, as a result it can be used as a time constant for the decrease in flux rate by one factor of e. It was found to be largely a function of the amount of portland cement used for stabilization of the sediment. The time constant for the decrease in the flux rate of PCBs is shown to decrease by more than 50% by the addition of 8% portland cement as compared to addition of none for the di, tri, and tetrachlorinated homologues.

**Table 9.** Time Constant in Hours (1/α) versus Stabilization

| | % Stabilization | | | |
|---|---|---|---|---|
| **Homologue** | **0** | **4** | **6** | **8** |
| **Di** | **53.2** | **27.8** | **22.4** | **18.8** |
| **Tri** | **74.6** | **25.6** | **19.3** | **15.5** |
| **Tetra** | **43.5** | **23.9** | **19.5** | **16.5** |

The values for C° can be predicted using the bulk sediment concentration, $C_{sediment}$, and the temperature of the sediment. To predict this value, the ratio of C° and $C_{sediment}$ were compared to the reciprocal of the temperature of the sediment.

$$\ln\left(\frac{C°}{C_{sediment}}\right) = a\left(\frac{1}{T}\right) + b \tag{27}$$

Where a and b are regression coefficients and T, is the sediment temperature in °K. The regression coefficients can then used in the model to predict the value for C° for each experimental run.

**Table 10.** Temperature – Concentration Regression

| *Homologue* | *Equation* | *Correlation* |
|---|---|---|
| *Di* | *y = -8978.4 (1/°K) + 31.771* | *R2 = 0.4496* |
| *Tri* | *y = -10085 (1/°K) + 34.733* | *R2 = 0.5351* |
| *Tetra* | *y = -15624 (1/°K) + 53.499* | *R2 = 0.7241* |

Using these expressions it is possible to predict fluxes of PCB for each homologue based upon the bulk sediment concentration, the temperature, the mass transfer coefficient, and the time of exposure.

$$F = C_{sediment}\left[e^{a/T+b}\right]k_a e^{-\alpha t} \tag{28}$$

This expression was evaluated for all of the experimental flux measurements collected in the wind tunnel.

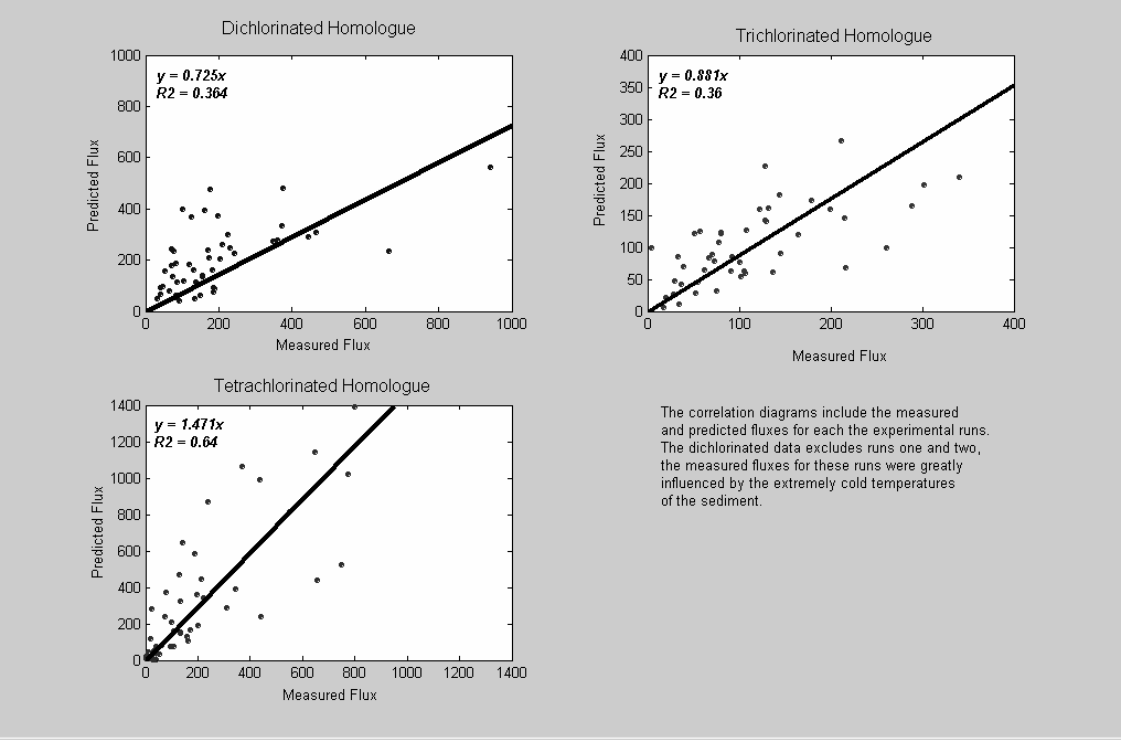


**Figure 38.** Model Correlation Results

The proposed model was found to under predict the dichlorinated and trichlorinated fluxes by 27.5% and 11.9% and over predict the tetrachlorinated fluxes by 47.1%. The correlation of predicted fluxes to measured fluxes is $r^2$=0.36 for both dichlorinated and trichlorinated homologue fluxes and $r^2$=0.64 for the tetrachlorinated homologue fluxes. The model was found to predict fluxes within a factor of 3 for over seventy percent of the fluxes measured in the wind tunnel. Divergences of the predictions from the measured fluxes are a result of variations in temperature over the length of an experimental run, and the equipment error inherent in the measurement of PCB concentrations from the air and sediment samples. This model was created with laminar flows, in a turbulent flow regime; the initial fluxes would be greater due to an increase in the value of $k_a$. In addition the values for α would also increase due to enhanced water loss from the sediment.

The presented studies were conducted in order to 1) create a viable, repeatable method for the field measurement of PCB fluxes from dredged sediment, 2) verify the field measurements with a bench scale experiment, and 3) produce a predictive model that can be used to assess the fluxes of PCB from dredged sediment. The field measurement technique described in the first section was used in four sampling intensive and yielded consistent results. The PCB fluxes measured using this technique were found to be comparable to fluxes measured in the laminar flow wind tunnel used in the bench scale laboratory experiments. These experiments yielded measurements that were then used to calibrate a model for the determination of fluxes of PCB from dredged sediment.

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