MEASUREMENT OF PCB FLUXES IN A LAMINAR FLOW FLUX CHAMBER FROM STABILIZED DREDGED MATERIAL

Executive Summary

Project Goals and Objectives

The goal of this project was to measure directly the volatilization of gas phase polychlorinated biphenyls (PCBs) from stabilized dredged material (SDM) in a laboratory scale flux chamber. This study complements earlier field observations (Phase I) to estimate PCB fluxes from SDM being applied to a landfill (Korfiatis *et. al.*, 2003, Miskewitz *et al*, 2004*)*. Phase I included measurements of the PCB concentration at two elevations above land-filled SDM and measurements of the required micrometeorological parameters to estimate the flux of PCBs from the land-fill surface using the aerodynamic gradient method. The variability of atmospheric and SDM characteristics at the landfill made quantification of the factors controlling rates of volatilization difficult. Phase II was initiated to measure PCBs volatilization from stabilized dredged material (SDM) under controlled laboratory conditions. In addition to controlling conditions, the Phase II experiments directly measured flux of PCBs using a mass balance approach rather than relying on an indirect method. PCB flux measurements were obtained for intervals of 2 to 12 hours over the length of each experimental run (typically 50 hours). During each experimental run air velocity, temperature and humidity, SDM temperature, and surface moisture content were monitored. The PCB flux measurements were then analyzed to determine their dependence on elapsed time, degree of stabilization, temperature, and soil or air moisture content.

Methods

Sediment was collected from Newtown Creek, NY, and sub-divided into ten 30-gallon containers. Each experimental run required about 25 gallons of sediment so therefore 10 experimental runs were conducted. For each of these, homogenized samples were stabilized with 0% (4 runs), 4% (2 runs), 6% (2 runs), or 8% (2 runs) Portland cement. The average PCB concentrations in the sediment for the di, tri, and tetra-chlorinated homologue were 338, 72, and 420 ppb, respectively.

The PCB flux experiments were conducted in a laminar flow flux chamber designed and constructed at Stevens Institute of Technology. Figure 1 is a picture of the flux chamber.

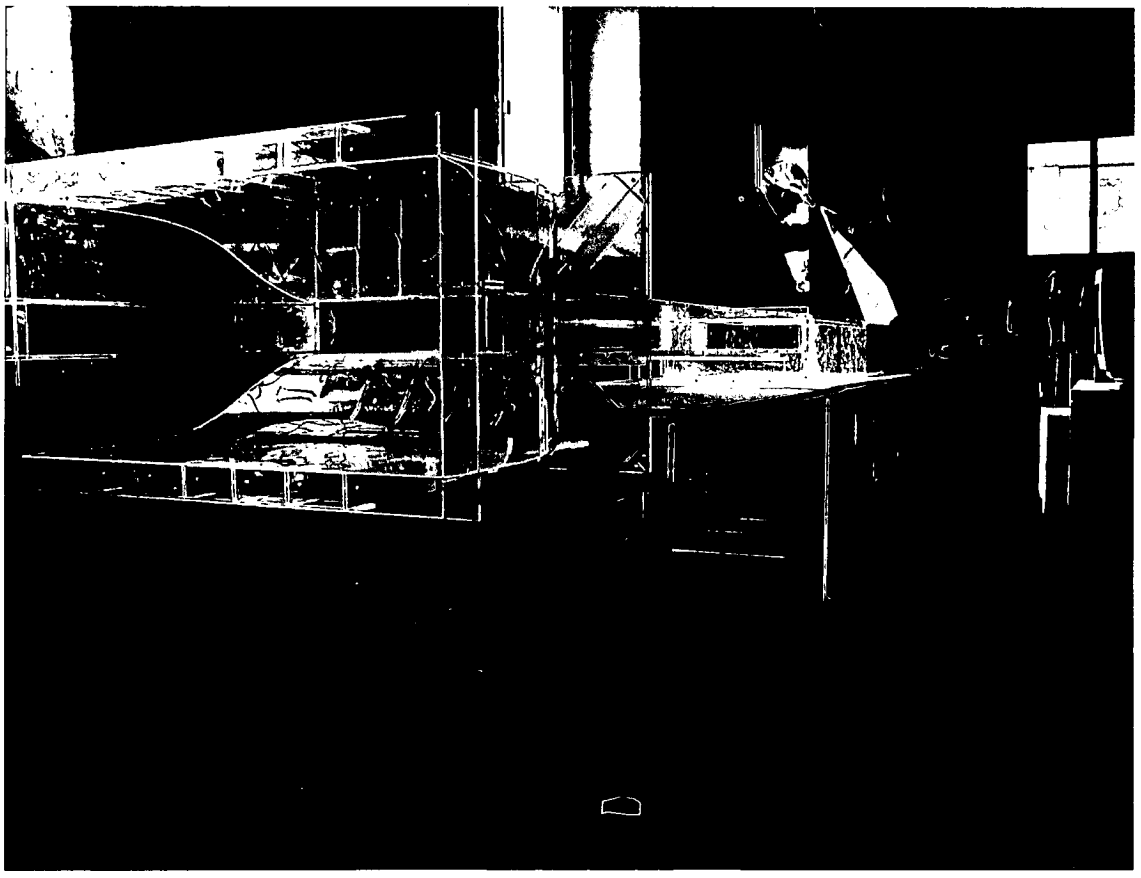

Figure 1. Laminar Flow Flux Chamber

This chamber consisted of a *once-through* wind tunnel with a test section that allowed for placement of SDM in a 10 cm deep layer with an area of one square meter exposed to the laminar air flowing over it. Figure 1 is a sketch of this chamber. All air flowing over the exposed sediment was subsequently passed through a polyurethane foam filter or PUF, which served to adsorb PCBs in the air stream. A second PUF sample was taken simultaneously with the one in the chamber to determine the average PCB concentration in the room air entering the flux chamber. A minimum sampling time of two hours was needed to collect sufficient mass of PCBs in the ambient room sample for subsequent analysis. The difference between the mass flux of ambient PCBs in the airflow into the chamber and the mass flux in the outflow is the contribution of PCBs volatilized from the 1.0 m^2 area of exposed SDM in the chamber.

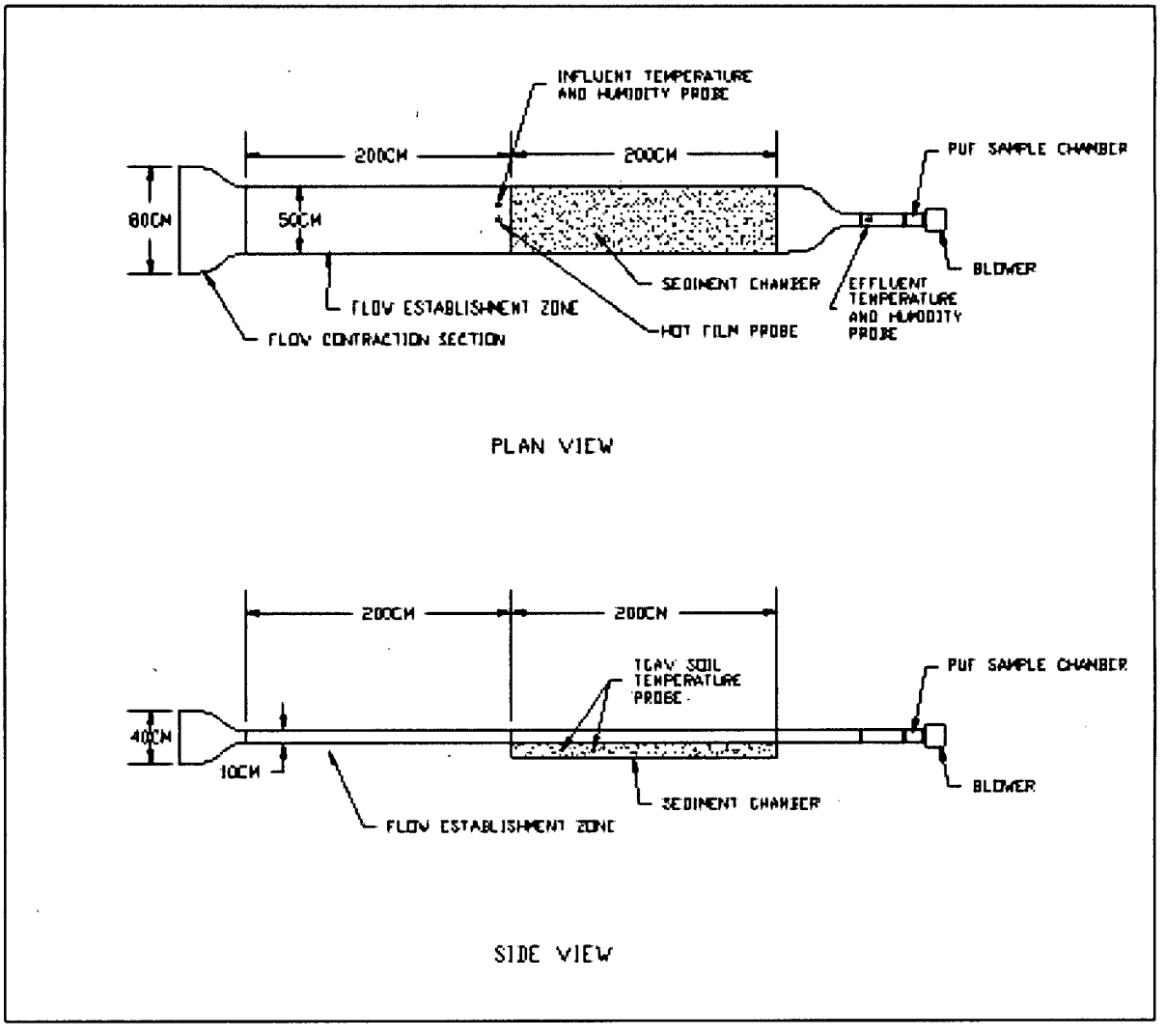

Figure 2. Design of the flux chamber.

The analysis for the PCBs adsorbed to the PUFs proceeded as follows: They were extracted using a standard accelerated solvent extraction technique. The extract, following a cleanup process, was analyzed using a gas chromatograph with electron capture detectors with the procedure based on EPA Standard Method 8082. The analytes were 62 congeners in 9 homologue groups. The analysis showed that the gaseous PCBs were dominated by the di-chlorinated, tri-chlorinated and tetra-chlorinated homologue groups. All subsequent analyses were focused on the fluxes of these three homologue groups.

Results

Temperature effects

It was clearly shown in the Phase I results that both the concentrations of gaseous PCBs over SDM and their fluxes were substantially reduced with reduction of ambient

temperatures. The same results were similarly evident in these Phase II results. For example, a small increase in room temperature (2-3 degree Celsius) was observed to produce an *increase* in the PCB flux for a given interval from what otherwise appeared to be an overall simple monotonic *decrease* of flux with time. In order to clarify the experimental results a model was developed to account for the variability arising from the ambient temperature fluctuations. If it is assumed that the temperature changes produce changes in PCB saturation vapor pressure then the PCB concentrations should follow a standard Clausius Clapyeron-like dependence on temperature. The compound-specific coefficients in this model were determined using a least squares fit to the measured concentrations in these flux chamber experiments. This model was then applied where needed to remove the dependence of the flux measurements on temperature variability.

PCB fluxes

A typical experimental result for the time history of PCB fluxes from untreated sediment is shown in Figure 2. There is a slow decay of the observed flux with increased time of exposure. If these results were to be modeled as a first order decay process, then the decay would be expected to follow an exponential decay. In such a model the time for the flux to decrease to 1/e or 0.368 of its initial value becomes a useful descriptive parameter and completely describes the distribution. For the results shown in Figure 2 this time is about 30 hours.

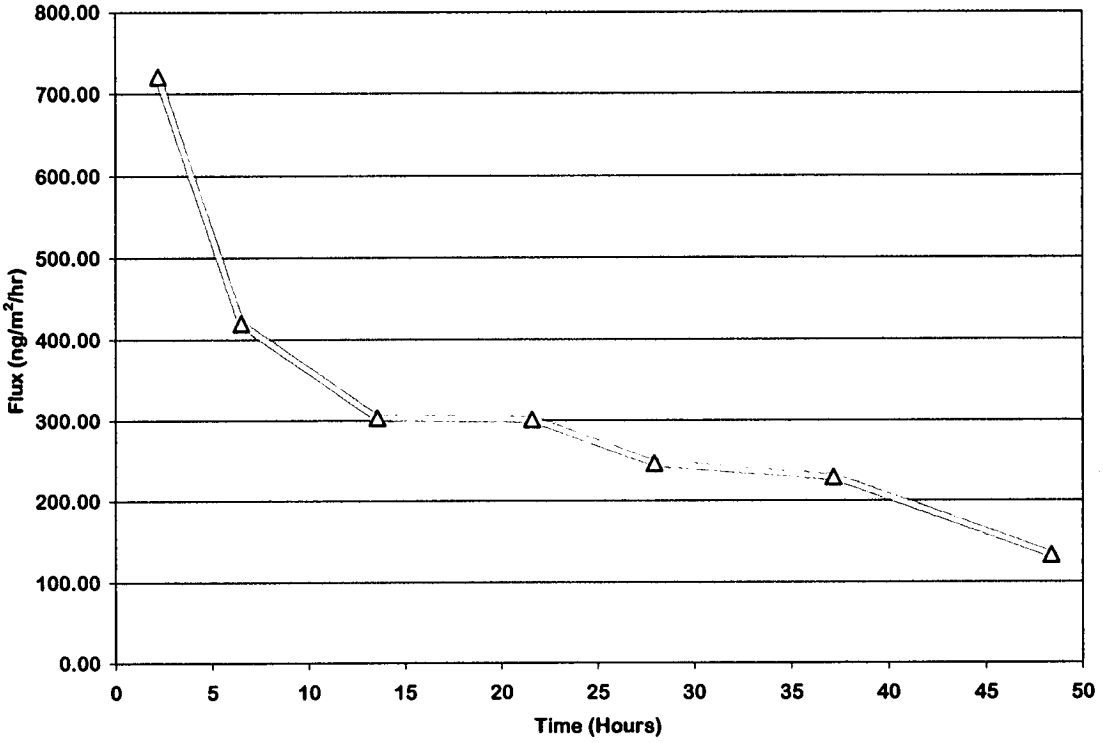

Figure 3. Temperature Corrected Flux of Tetra-chlorinated PCBs From Raw Newtown Creek Sediment

A similar result for sediment mixed with 4% portland cement is shown in Figure 3. It is evident that the decay rate is significantly faster with a 1/e decay time of about 6 hours.

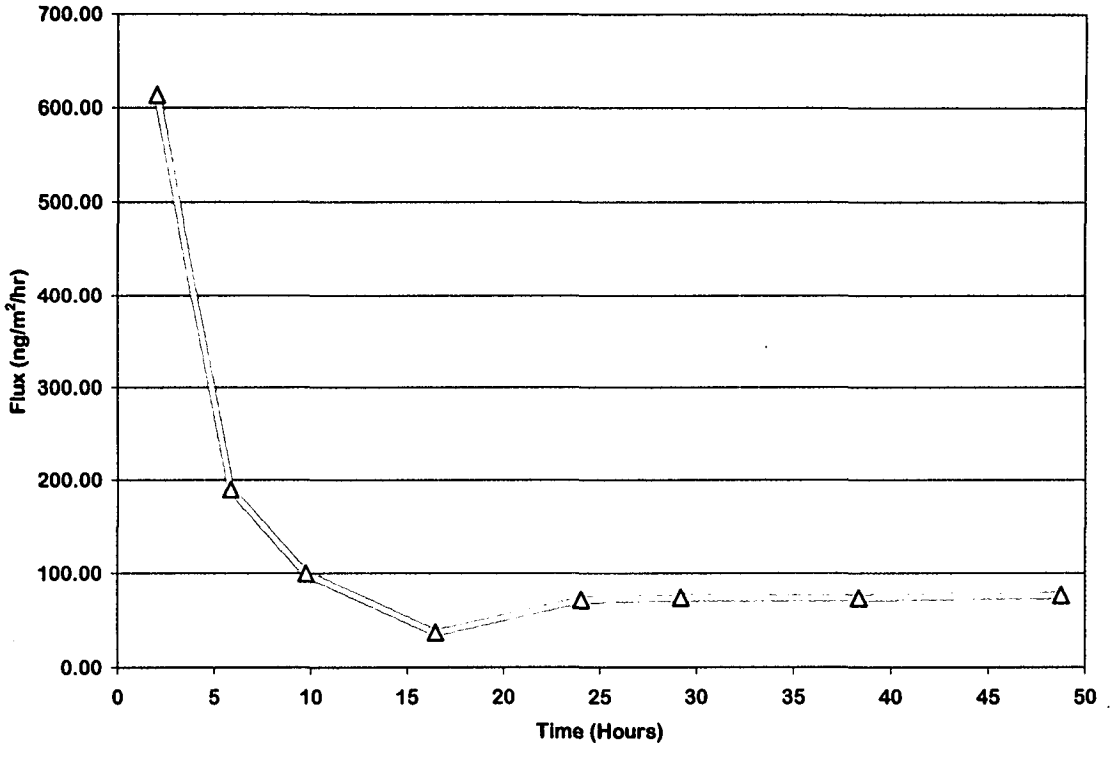

Figure 4. Temperature Corrected Flux from Stabilized (4% Portland) Newtown Creek Sediment.

A summary of the average 1/e decay times for all experimental runs is given in the following table:

Table 1. Average Time Constant in Hours (1/e decay time) as a Function of Stabilization

	Stabilization (% Portland by weight)			
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 effect of treating the sediment with Portland cement is a reduction in the decay time. Increasing the proportion of cement decreases the decay time.

A first order bulk transport model was proposed in order to predict fluxes of PCBs from SDM as a function of initial sediment concentration, elapsed time, degree of stabilization, and initial temperature. The model was calibrated using a least squares fit of the experimental data from this study. It was found to under predict the dichlorinated and

trichlorinated fluxes by 27.5% and 11.9% and over predict the tetra-chlorinated fluxes by 47.1%. The coefficient of determination is r^2=0.36 for both dichlorinated and trichlorinated homologue fluxes and r^2=0.64 for the tetra-chlorinated homologue fluxes. The model was found to predict fluxes within a factor of 3 for over seventy percent of the fluxes measured in the flux chamber. This model was created using laminar flow results. In a turbulent flow regime, the initial fluxes may be greater due to an increase in the value of the air-side mass transfer coefficient but the sediment-side may still dominate the overall transfer rate. Consequently, this model provides a useful initial screening for potential air quality effects of a dredged material management project.

Agreement with Previous PCB Flux Measurements

Comparisons between the data collected from the field study at the Bayonne Landfill (Phase I) and the laboratory flux chamber study were made to determine if the measurements from the laboratory study were similar to those obtained in the field. It should 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 within the range of values measured during the field sampling experiments. That range was from -1944 to 14870 ng m^{-2} hr^{-1} with a mean value of 1209 ng m^{-2} hr^{-1}. The total PCB concentration in the Newtown Creek sediment was approximately 1 ppm this is at least two times as high as the sediment dredged from navigational channels and placed in the Bayonne Landfill (Douglas, 2005).

Summary of Findings

- Fluxes of PCBs from sediment in the flux chamber are initially high and decrease rapidly over time, and the rate of decrease is dependent on the amount of Portland cement used in the stabilization process.

- The rate of volatilization of PCBs changes significantly with relatively minor temperature changes.

- In general, the total mass of PCBs released from the sediment over the length of the experiment decreased with increasing amounts of Portland cement used.

- The time it takes for the flux rate to decrease by a factor of 1/e decreases when the SDM is stabilized with increasing amounts of Portland cement.

- The flux of PCBs from sediment can be reasonably (within a factor of 3) modeled using a simple mass transfer model.

- Laboratory-measured PCB flux rates are in the same range as the PCB flux estimated in Phase I of this study.

Recommendations for further study

High resolution measurements of the SDM vertical moisture profile should be collected in order to assess the expected significant effects of moisture content on PCB fluxes.

PCB fluxes should be measured in turbulent flow conditions to assess stabilization effects for a far wider range of flow velocities than those used in Phase II. Although the air-side mass transfer coefficient will increase in a turbulent flow regime, the transition from air-side control to sediment-side control may occur more rapidly due to the accelerated loss of soil moisture due to an increased rate of volatilization. These turbulent flow experiments would provide a closer approximation to field conditions.

Laboratory and field studies of the emissions of PCBs from native (untreated), tidally exposed estuarine sediments are needed to quantify this potentially important part of the cycling of these contaminants. This would serve as a comparison between naturally exposed contaminated sediments and anthropogenic sources such as, for example, the Bayonne Landfill.

References

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Acknowledgements

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