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REPORT

PCB Desorption Kinetics Under Realistic Shear and Turbulence

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PCB Desorption Kinetics Under Realistic Shear and Turbulence

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Objectives

We hypothesize that the impact of PCB desorption from resuspended sediments depends upon the intensity of the resuspension (which scales to bottom stress in the absence of organisms), the rate at which each congener desorbs (which depends on the size and hydrophobicity of the chemical, the relative amount of 'labile' and 'resistant' forms, and the size distribution of the suspended particles), and the residence time of the particles in the water column (which depends on the time-variable water column turbulence regime and the particle settling velocities). In order to accurately quantify the impact of PCB desorption from Hudson River sediments, we are conducting experiments that realistically mimic bottom shear stress and water column turbulence and rapidly measure PCB congener release. The objectives of this study are to measure the kinetics of PCB congener desorption from Hudson River sediments under realistic bottom shear and water column turbulence conditions and to quantify the impact of shear stress and contaminant aging on PCB desorption kinetics. Specifically we are conducting experiments that will:

- Measure the rate at which PCB congeners are released from resuspended sediment under a constant shear stress.
- Determine the dependence of the desorption rate on the properties of the PCB congeners (size, K_{ow}) and the particles (carbon content, size, settling rates).
- Evaluate how changes in shear stress impact the above measurements and relationships.
- Examine the influence of particle reworking on the PCB desorption rate.
- Compare the desorption rate among sediment with different contaminant ageing histories.

These experiments are being conducted using surficial sediment from the Thompson Island Pool.

Field Sampling

On May 22, 2003 we collected sediment from the Hudson River for our experiments. Frank Estabrooks of the New York State Department of Environmental Conservation provided us with boat time and took us out onto the water. We collected 30 five-gallon buckets of sediment from two sites on the south side of Griffin Island. Upon returning to Solomons, the buckets were covered with black tarp and left to defaunate in the sun for twenty-four hours. After this defaunation period, five buckets of sediment were added to five Shear Turbulence Resuspension Mesocosm (STORM) tanks. The sediment in each STORM tank was mixed together and the surface of the sediment was smoothed to eliminate roughness in the sediment surface. The sediment depth in each tank was approximately five centimeters. The STORM tanks were then covered with black tarp and the sediment was left to consolidate for ten days. Preliminary experiments were then conducted in one of the STORM tanks to determine how the sediment would behave with applied shear stress. The actual experiments began on 6/20/03.

Experiment Design and Execution

Resuspension experiments were conducted in three of the STORM tanks and the fourth STORM tank served as a diffusion control. A tent made of Mylar was erected around the three-resuspension tanks and the experiments were conducted in the dark. The diffusion control tank was covered with a black tarp to keep out the light. A series of three-day resuspension events was conducted in the STORM tanks. The same bottom shear stress was applied to all three tanks resulting in similar water column turbulence

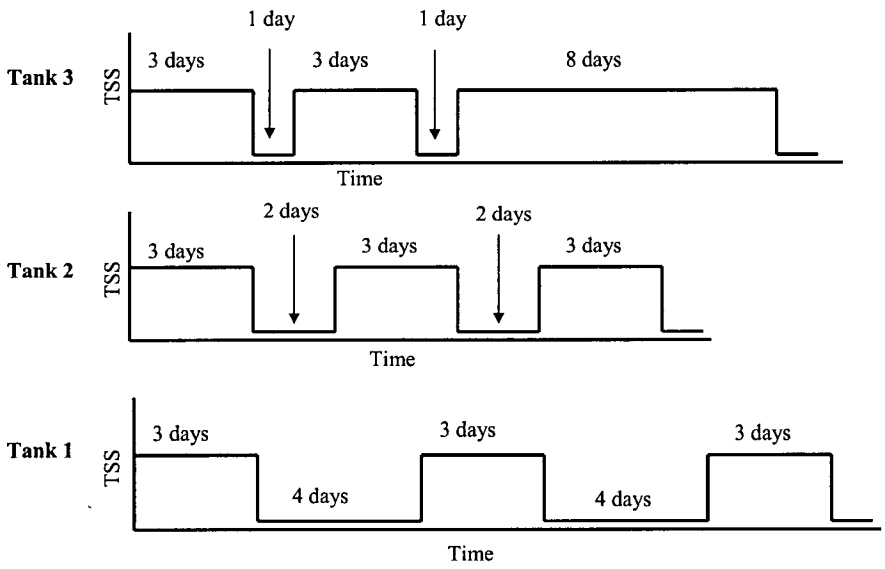

Figure 1: Schematic of resuspension experiments

and total suspended solids concentrations. The resting time between each resuspension event varied between the three tanks. Figure 1 shows a schematic of the resuspension

cycles in the tanks. The duration of the resuspension event was the same for each tank, but the resting time between events varied between the tanks. Triplicate resuspension events were conducted in each tank. The water in each tank was removed 12 hours after each resuspension event ended and not added back to the tank until 1 hour before the start of the next resuspension event. The last resuspension event in tank 3 was extended to analyze the impact of longer resuspension times on PCB desorption kinetics. This series of resuspension events ran from 6/20/03 to 7/7/03.

After this series of experiments ended, the salinity in two of the tanks was changed. One three-day resuspension cycle was carried out in each of the three tanks using water with different salinities (0, 1, and 2 ppt). In this experiment applied bottom shear stress was kept at the same level as before but the resulting total suspended solids concentration decreased due to salinity effects. After the salinity experiments ended, one additional experiment was done in the 0 ppt tank. The bottom shear stress in this tank was greatly increased to producing higher water column turbulence and higher total suspended solids levels. The conditions in this tank were designed to mimic the total suspended solids concentration that would be measured during a dredging event. Table 1 shows the day-by-day break down of the activity in each tank for all three experiments. All experiments ended on 7/22/03 and clean up of the tanks took one week.

During each resuspension event the dissolved phase PCB concentration was measured using non-equilibrium solid phase microextraction (SPME). SPME fibers were deployed into the water for 30-minute sampling periods. At the same time, the volume size distribution of particles was measured using Laser In-Situ Scattering Transmisometry (LISST). LISST data was collected 10 minutes into each SPME deployment, and captured a five-minute snapshot of the volume size distribution of the particles. Once the LISST was removed from the water column, water samples were collected to measure total suspended solids, dissolved organic carbon, particulate carbon, particulate nitrogen, and chlorophyll a levels. Particulate samples were also collect for PCB analysis. The sampling schedule was the same for each resuspension event. Before a resuspension event began, SPME, LISST and ancillary water samples were collected. The water column was sampled most intensely on day one of each resuspension event. During the first three hours of resuspension, as the total suspended solids concentration spun up to equilibrium, SPME fibers were deployed continuously every half hour. LISST data and ancillary water samples were collected once every half hour during this sampling period. After the first three hours, SPME, LISST and ancillary water was collected once an hour till 7 hours has passed. On day two and three of the resuspension events samples were collected once in the morning and once in the late afternoon. On day three, after the late afternoon sampling, resuspension was turned off. The LISST was left in the tank overnight to capture the size distribution of the particles as they settled through the water column. The next morning on day 4, an off sampling event occurred and SPME, LISST, and ancillary water samples were taken. After this final sampling event, the water was pumped out of the tank.

Data Analysis

We are currently analyzing and synthesizing data collected from this series of experiments. All *in situ* particle size, transmissometry, and temperature data have been

compiled and finalized. Suspended solids, chlorophyll-a, and particulate carbon measurements are completed. We are nearing completion of the complete characterization of the SPME calibration, and have verified that the SPME technique samples only dissolved PCB congeners without interference from particles or dissolved organic carbon. Four-point SPME calibration curves have recently been generated for each PCB congener, and we are nearly ready to begin quantification of dissolved PCBs in the resuspension experiment samples.

The project is on schedule for completion in late 2004.

Date	Day of Week	Exp. Day	Tank 1	Tank 2	Tank 3	Comment
20-Jun	F	1	On			
21-Jun	S	2	On		On	
22-Jun	S	3	S		On	
23-Jun	M	4	Off	On	S	
24-Jun	T	5	Off	On	Off	
25-Jun	W	6	Off	S	On	
26-Jun	T	7	Off	Off	On	
27-Jun	F	8	On	Off	S	
28-Jun	S	9	On	On	Off	
29-Jun	S	10	S	On	On	
30-Jun	M	11	Off	S	On	
1-Jul	T	12	Off	Off	On	
2-Jul	W	13	Off	Off	On	
3-Jul	T	14	Off	On	On	
4-Jul	F	15	On	On	On	
5-Jul	S	16	On	S	On	
6-Jul	S	17	S	Off	S	
7-Jul	M	18	Off	Off	Off	
8-Jul	T	19	Off	On	Off	Change salinity
9-Jul	W	20	On	On	Off	
10-Jul	T	21	On	S	On	
11-Jul	F	22	System down			
12-Jul	S	23	System down			
13-Jul	S	24	System down			
14-Jul	M	25	Off	On	Off	Redo salinity experiments
15-Jul	T	26	On	On	Off	
16-Jul	W	27	On	S	On	
17-Jul	T	28	S	Off	On	
18-Jul	F	29	Off	Off	S	
19-Jul	S	30	Off	On	Off	Spin lots no LISST
20-Jul	S	31	Off	On	Off	Dredging
21-Jul	M	32	Off	S	Off	
22-Jul	T	33	Off	Off	Off	

Table 1: Schedule of resuspension events in the three storm tanks. On means resuspension is occurring, off means no resuspension, and S means resuspension is shut off after afternoon sampling.