

## SEDIMENT-WATER PARTITIONING OF PCBs IN TRIBUTARIES OF NEWARK AND RARITAN BAYS, NEW JERSEY, U.S.A

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### Introduction

As part of ongoing harbor restoration efforts, a study was initiated to determine the sources and concentrations of organic contaminants and sediment to Newark Bay and the Hudson River Estuary system. This work is being conducted by the U.S. Geological Survey (USGS) in cooperation with the New Jersey (NJ) Department of Environmental Protection and the New York State Department of Conservation. As part of this study, the USGS determined concentrations of dissolved and sediment-bound organic contaminants in samples from the major freshwater tributaries (the Rartian, Passaic, Elizabeth, Rahway, and Hackensack Rivers) that flow into Newark and Raritan Bays. The measurement of specific congener concentrations of polychlorinated biphenyls (PCBs) and other organochlorine compounds in co-existing phases allows for the detailed examination of the partitioning of these chemicals, which yields insight into the fate and transport of organochlorine compounds in natural systems. This information also will be used in a mass-balance model that is being developed for the Harbor Estuary system. This paper describes the partitioning of PCBs between sediment and water collected from rivers in New Jersey.

### Methods

The sampling and analytical methods are detailed in previous publications<sup>1,2</sup>. Briefly, river water and sediment were collected during periods of base-flow and during storms using a sampler depicted in Figure 1. To collect suspended sediment and dissolved compounds, water is drawn into the sampler, filtered through a glass-fiber canister and a flat filter, and then passed through two columns of XAD-2 resin.

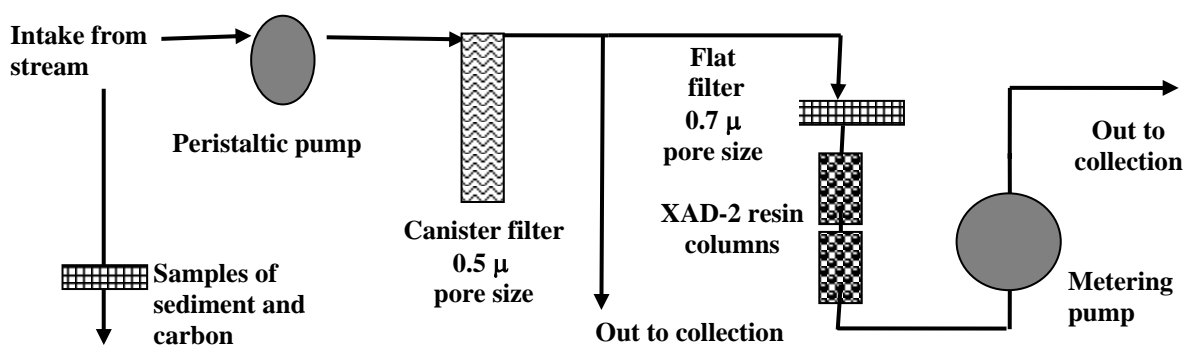


Figure 1. Schematic of sampler used for base-flow sampling

The base-flow partitioning data presented here were generated from samples collected when discharge was less than the historic 90 percent exceedance level, and when flow remained relatively steady for the 6 hours needed to collect a sample. Samples were collected by passing approximately 50 liters (L) of water through the XAD columns at a rate of 100 to 150 milliliter per minute, and 500 to 800 L of water through the filters at 1 to 2 L per minute. At least four-1 L samples were collected throughout the 6 hour sampling period for analysis of suspended sediment (SS), and dissolved (DOC) and particulate organic carbon (POC). Samples for chemical analyses were collected during storms using the same sampling equipment as for the base-flow samples, except that flow weighted composited samples were collected during storms<sup>1,2</sup>. The filters and the resin were transferred directly to a Soxhlet vessel and extracted in hexane-acetone solvent for 24

hours. Extracts were analyzed for PCBs using HRGC/HRMS methods following EPA Method 1668A-modified<sup>3</sup>. Suspended sediment was determined gravimetrically, and POC and DOC samples were analyzed in triplicate using combustion and spectroscopy.

**Results**

Concentrations of PCB congeners were examined as individual congeners and as summed total PCBs for the dissolved and particulate phases. The total PCB concentrations in samples collected during base flow ranged from 383 to 7,820 picograms per liter (pg/L) for dissolved, and 10.2 to 3050 nanograms per gram (ng/g) for particulates. Suspended sediment concentrations ranged from 3.2 to 19 milligrams per liter (mg/L), POC ranged from 0.140 to 7.04 mg/L, and DOC ranged from 3.8 to 4.14 mg/L. To obtain these concentrations, volumes of water processed through the XAD columns ranged from 50.4 - 134.2 L, and 300 to 800 L through the filters, resulting in the capture of 1.6 to 5.9 grams of sediment. No relation was observed between concentrations of PCBs and concentrations of DOC or POC in the water, or sampling volume, or mass of sediment captured<sup>4</sup>.

The Passaic River base-flow data typify the congener patterns when plotted as percent by weight (Figures 2 and 3), found in all the rivers studied except the Elizabeth. The sediment concentrations (Figure 2) plot in a broad concave band with the highest concentrations in the penta through hexa homolog groups. This pattern may result from the higher abundance of these congeners in PCB Aroclor sources and possibly the greater number of coelutions that occur in these groups. The Elizabeth River sediment data plot as a band that increases to the middle congeners and then levels off. The relative percentage of dissolved congeners (Figure 3) plot in a broad band that decreases with increasing PCB number, which may reflect the ease with which the lower chlorinated congeners solubilize compared with higher chlorinated congeners. Similar patterns were observed for dissolved PCB concentrations in samples from the other rivers.

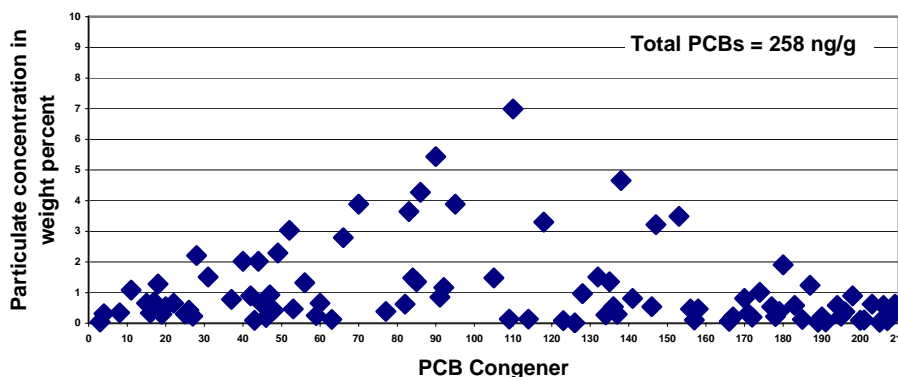


Figure 2. Concentrations of PCBs in sediment collected from the Passaic River, October 17, 2001

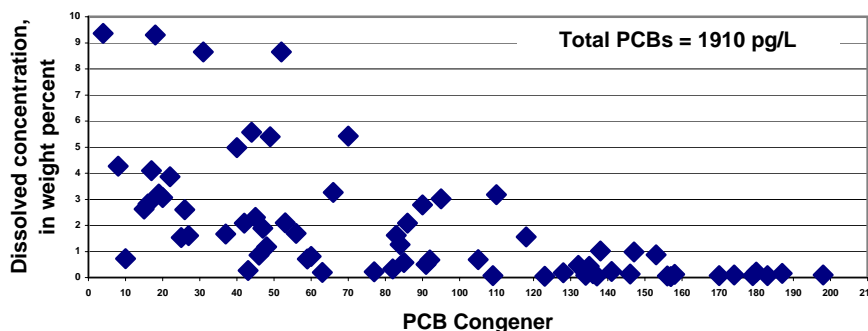


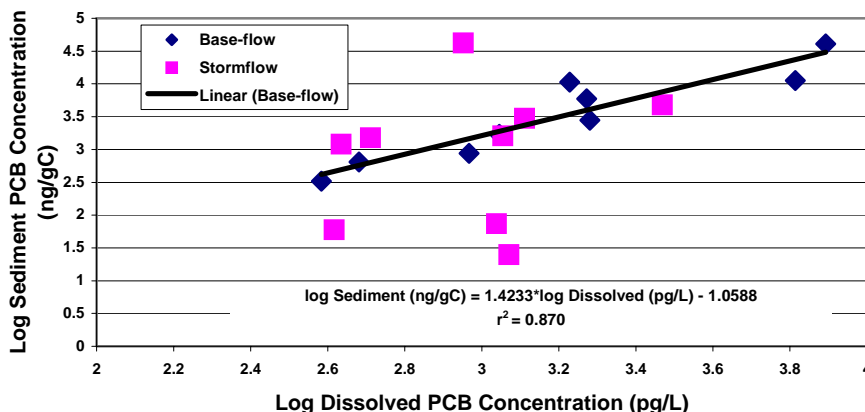
Figure 3. Concentrations of dissolved PCBs collected from the Passaic River, October 17, 2001

Best-fit linear regression equations were calculated using all base-flow sample data. These equations serve as sediment-water partitioning functions. Data collected during storms were not used to calculate these equations, but were compared to the predicted functions (Figure 4). Neglecting the stormflow data removes possible bias caused by the flow-weighted sampling techniques employed during storms. Regression equations calculated using normalized and log-normalized masses and carbon normalized sediment concentrations are listed in Table 1. Good correlations were obtained using the log-transformed data as shown by the high  $r^2$  values.

**Table 1. Best-fit regression equations using results from base-flow samples**

Characteristic	Equation	$r^2$
Sediment mass normalized	Sediment (ng/g) = 0.3509 * dissolved (pg/L)	0.874
Sediment mass normalized	Log sediment (ng/g) = 1.6553 * log dissolved (pg/L) - 2.8837	0.877
Carbon normalized	Log sediment (ng/gC) = 1.4233 * log dissolved (pg/L) - 1.0588	0.870
Fraction of organic matter	Log (sediment/water) = 1.1736 * log $f_{om}$ + 3.229	0.988

The partitioning between the concentrations of PCBs in the dissolved phase and the carbon normalized sediment are shown in Figure 4. Results from the base-flow samples plot linearly. Results from most stormflow samples plot near the regression line, but several fall below and above. The scatter in the stormflow data could be attributed to several factors, one of which might be the input of particulate-bound PCBs that have not yet equilibrated with the stream sediment. Overall, the regression line developed using results from the base-flow samples closely predicts the partitioning of PCBs.



**Figure 4. Sediment carbon-water partitioning of PCBs in NJ rivers**

The partitioning ratios for PCBs in the base-flow samples can be compared to the octanol-water partitioning ratios. The logarithm of the sediment-water ratio plotted against the chlorination level for the different PCB homolog groups is shown in Figure 5. The ratios are developed using the sum of all concentrations in each homolog group and are expressed as molar concentrations normalized to carbon. PCB concentrations in the water were not obtained for mono, deca, and the nona-homolog groups. The plotted line falls through the octanol-water partitioning ratios for each homolog group<sup>5</sup>. The ratios in the samples trend along a straight line ( $r^2 > 0.9$ ) near the octanol-water partitioning ratios. Results from the Raritan River sample plots slightly below, and the Elizabeth River sample plots slightly above the octanol-water partitioning line. These differences could reflect the low POC content in the Raritan River and the very high PCB content in the sediment in the Elizabeth River. Overall, the partitioning of PCBs between water and sediment in these rivers can be predicted using the octanol-water partitioning values.

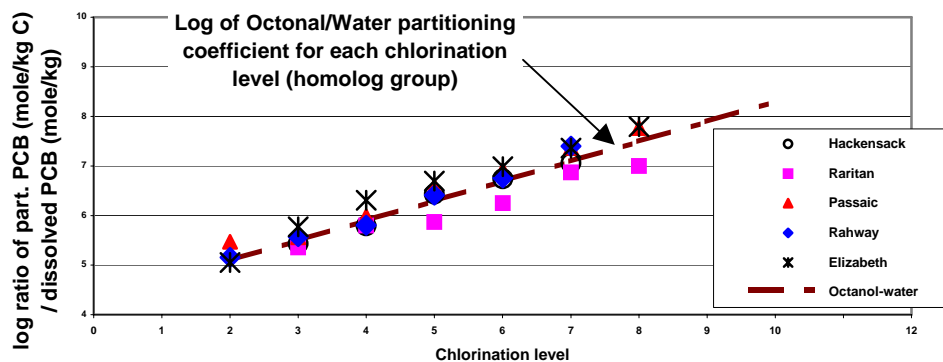


Figure 5. Sediment carbon -water PCB ratios in relation to octanol-water partitioning

### Conclusions

Samples of coexisting sediment and water provide information on the partitioning of PCBs in the freshwater tributaries flowing into Newark and Raritan Bays. Results from the samples collected during low-flow conditions produce logarithmic relations that accurately predict the distribution between sediment and water. The ratios of carbon normalized sediment and water concentrations of the samples closely agree with octanol-water partitioning ratios.

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