Concentrations of Dissolved and Particulate PCBs in the Saginaw River: As Determined by Filtration and XAD-2 Resin Extraction

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The Saginaw River and Saginaw Bay has been listed as one of 43 Areas of Concern in the North American Great Lakes. Development of the river shoreline includes industry, private marinas and public docks. The most recent previous study of PCBs in the Saginaw River found total concentrations of PCBs in water to range from 17.0-49.3 ng/L (ppt)[1]. Concentrations of PCBs in the water were closely linked with localized "hotspot" concentrations in the sediments. In October of 1986 the Saginaw River watershed experienced a 100 year flood event which may have significantly redistributed sediments to the lower portion of the river and Saginaw Bay. This is of interest due to increasing public pressure to "clean-up" Saginaw River and Saginaw Bay. This study determined loads of PCBs to Saginaw Bay from the Saginaw River and identified sources to assist in the selection of possible remediation alternatives. Concentrations of PCB were determined in the dissolved and particulate phases in the water column of the lower Saginaw River.

Material & Methods

The Saginaw River was divided into six equal distance segments with sampling transects across the river at the juncture of the segments. The downstream site was located near the mouth of the river (transect 6). The upstream boundary site was located 8 km up river from the mouth. 20 L water samples of water were collected at 3 locations along each transect with a high-volume submersible pump and composited into a single 60 L sample in glass carboys. The sample was

immediately transported to the field laboratory for partitioning into particulate and dissolved phases. Limnological parameters measured at each transect include among others, suspended particulate matter (SPM), particulate organic carbon (POC), and discharge rate. Sampling periods were selected to give a range of discharge conditions.

Samples were passed through a "Pentaplate" filtering system fitted with 29 cm GF/F Whatman filters. Pressure in the filter apparatus was less than 14 psi. The filtrate was acidified with HCl to pH < 2.0 and drawn through XAD-2 resin columns at a constant flow rate of 1 L/min (2,3). The filters were wrapped in aluminum foil and frozen. Resins were transferred to cleaned quart jars and stored at 4 °C.

GF/F filters and XAD-2 resin were extracted with a custom made large-volume Soxhlet extractor[2]. Acetone pre-extractions were used to remove excess water from the filters and XAD-2 resins. The XAD-2 resin and filters were extracted with refluxing acetone:hexane 325ml:275ml for 16 hr. The pre-extracts were back extracted with hexane and combined with the Soxhlet extracts. The samples were washed with water and dried on sodium sulfate columns. The PCBs were isolated using a reactive silica gel column, consecutive layers of silica gel, KOH treated silica gel, and 40% sulfuric acid on silica gel. PCBs were eluted from the column with 0.5% benzene in hexane. Extracts were spiked with PCB #30 as an internal standard and stored in iso-octane. PCBs were quantified using a Perkin Elmer 8500 series GC with ^{63}Ni electron capture detector, fitted with a DB-5 fused silica column, 30m X 0.25mm dia, 0.25μm film thickness (J&W Scientific). Total PCB concentrations were determined by summing the masses of all congeners. Two-way Analysis of Variance (ANOVA) was performed on the ranks of total PCB concentrations in the dissolved phase, particulate phase and total water column as a function of sample location and sampling period. The study design did not include site replication, therefore an interaction term could not be determined. The particulate fraction concentrations were normalized to POC and SPM.

Results & Discussion

Total concentrations of PCBs ranged from 7.42 to 34.48 ng/L in the particulate phase and 1.86 to 16.4 ng/L in the dissolved phase (Fig. 1). The mean percent difference between duplicate samples taken in the field ranged from 0% to 26%. Field blank concentrations ranged from 0.03 (<MDL) to 0.72 ng/L for particulates and 0.82 to 2.65 ng/L for the dissolved phase. The method detection limit (MDL) was 0.61 ng/L for the particulate phase and 1.70 ng/L for the dissolved phase. Concentrations of PCBs in blanks were less than the instrument detection limit (IDL). The average total concentrations of PCB were found to be progressively

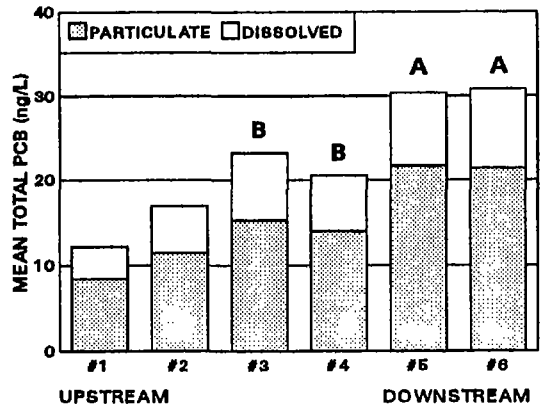

Fig 1. Mean total concentrations of PCBs in the water column, averaged over all sampling dates by transect. Letters denote means that are not significantly different from one another (ANOVA; Duncans Test, $\alpha = 0.05$)

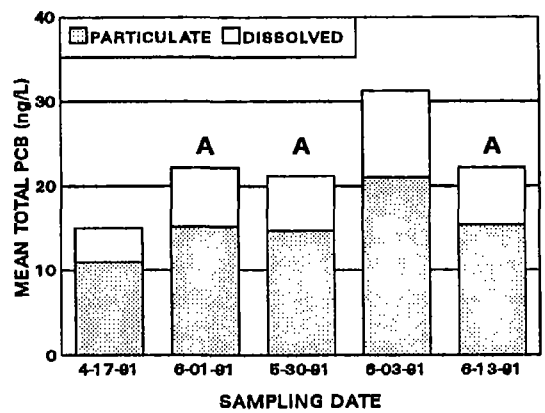

Fig 2. Mean total concentrations of PCBs in the water column, averaged over transects by sampling date. Dates are ordered by decreasing flow rate. Letters denote means that are not significantly different from one another (ANOVA; Duncans test, $\alpha = 0.05$)

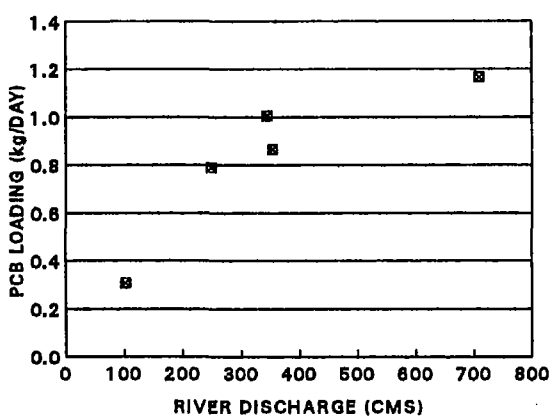

Fig 3. Loading of total concentrations of PCBs to Saginaw Bay from the Saginaw River, as a function of river discharge.

greater from the upstream-most sampling station to the downstream-most stations (Fig. 1). This was true, even though the concentrations which were measured on different dates, and discharges varied considerably. Thus, there seemed to be a trend of greater concentrations downstream. Total concentrations of PCBs increased two fold from upstream to downstream locations. This could be due to PCBs entering the water column from runoff, or from PCBs in the sediments. Because this trend persisted, even during the low-flow conditions of summer when runoff was at a minimum, it is likely that the source of PCBs are substantially from within the river.

The total concentrations of PCBs averaged across all locations within a period, varied seasonally (Fig. 2). Particulate concentrations of PCBs normalized to SPM is inversely related to SPM loads. Again, this indicates dilution of the concentration of PCBs in the river, due to runoff of uncontaminated sediments.

Loading of total masses of PCBs to Saginaw Bay was related to discharge (Fig. 3). In general, greater masses of PCBs were transported to the Bay during times of greater flow. However, since conditions of lesser flow were more usual, the greatest portion of the annual loading to the Bay occurs during these conditions.

Conclusion

The Saginaw River was estimated to transport approximately 125 kg/yr of PCB to Saginaw Bay. It is estimated that approximately 1/2 of the annual mass of PCBs discharged to Saginaw Bay by the Saginaw River seems to have originated in the lower 8 km of the river, in the vicinity of the more urbanized and industrialized areas. However, an equal portion of the total PCB loading originates from more upstream sources.

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