

FINAL REPORT

**PCB Study Using Semipermeable Membrane Devices in Torch Lake,
Houghton County
(MDEQ Project Number 05-25)**

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Michigan Department of Environmental Quality Water Bureau

Contract number: 071B1001643

Report Date: March 16, 2006

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INTRODUCTION

The Michigan Department of Community Health has issued a fish consumption advisory for several species of sport fish in Torch Lake in Houghton County, Michigan. The advisory was issued due to elevated levels of mercury and polychlorinated biphenyls (PCBs) in the fish. Mercury concentrations in Torch Lake fish are similar to levels measured in nearby waterbodies, including Lake Superior. In contrast, PCB concentrations are higher in Torch Lake fish than in fish from nearby inland lakes, and appear to be higher than concentrations measured in Lake Superior fish.

The Torch Lake region has historically been an area of heavy industry, primarily copper mining processing. Accidental spills or poor waste disposal methods by area industries may have introduced PCBs to the watershed; those potential sources have not been thoroughly investigated. Limited sediment sampling in Torch Lake has detected scattered low-level PCB contamination. No water column PCB concentration studies have been conducted.

The Michigan Department of Environmental Quality (MDEQ) contracted Great Lakes Environmental Center, Inc. (GLEC) to conduct a contaminant concentration study using semipermeable membrane devices (SPMDs) in Torch Lake, Portage Lake, and the Keweenaw Waterway in Houghton County, and Huron Bay in Baraga County. The intent of the study was to collect data for comparison of PCB residues at the various sites to determine if Torch Lake was a source of PCBs.

SPMDs are passive samplers that can be used as an alternative to the collection and analysis of water samples. An SPMD is a length of lay-flat low-density polyethylene tubing, essentially nonporous, but having transport cavities of less than 10Å in diameter. The interior surface of the tubing is coated with a thin film of pure, high-molecular weight neutral lipid (triolein) and sealed. When SPMDs are deployed in the water column, the transport cavities allow for the selective diffusion of hydrophobic organic compounds, which are then sequestered in the lipid (Huckins et al., 1993).

One advantage of SPMDs is that they isolate only the truly dissolved portion of these compounds from the water; compound that is adsorbed to particulates, and therefore not bioavailable, is excluded. SPMDs mimic the transfer of dissolved compounds across biological membranes (e.g., gills), effectively concentrating them and allowing the detection of compounds that may be present at concentrations below the analytical method detection level in water samples. At constant temperature and flow velocity, the amount of a particular compound absorbed by an SPMD is linearly proportional to the dissolved concentration of the compound in the water (Booij et al. 2003). The utility of SPMDs for monitoring aqueous residues of PCBs, as well as other low to moderate molecular weight nonpolar organic environmental contaminants, has been repeatedly demonstrated.

METHODS

Site Selection

Ten sites were identified by MDEQ (Figure 1), including five sites within Torch Lake, one site at the outlet from Torch Lake, one site each near the north and south entries to the Keweenaw Waterway, one site in Dollar Bay (Portage Lake), and one site in Huron Bay (Lake Superior). In Torch Lake, Sites 3, 4, and 5 were selected because they are near potential PCB sources. Site 1 was in an area without stamp sands, and was chosen to investigate whether stamp sands could be a PCB source. Site 2 in the Trap Rock River was chosen as an upstream reference site for Torch Lake and to determine if the river was a source of PCBs to the lake. Site 6 was chosen because it was the outlet for Torch Lake, and therefore representative of discharge from the entire watershed. Dollar Bay in Portage Lake (Site 7) was a suspected PCB source, as evidenced by abandoned equipment. Sites 8, 9, and 10 were chosen to demonstrate background levels of PCBs in the Keweenaw Waterway and Lake Superior.

Field Methods

GLEC purchased SPMDs and rented deployment canisters from Environmental Sampling Technologies, Inc. (EST). The SPMDs were standard size/weight (2.5 x 92cm, 4.5 g) and filled with 0.915g (1.0mL) ultra-high purity triolein. Four SPMDs were ordered per site, plus five SPMDs to be used as field blanks. The SPMDs were prepared by EST on October 13, 2005 and shipped in sealed cans to GLEC for arrival on October 14, 2005. Two SPMDs, each strung in a zig-zag pattern across a stainless steel “spider” carrier (Figure 2), were contained in each can. The cans were transported to the field unopened and at ambient temperature.

The deployment took place on October 19 (Sites 8 and 9), 20 (Sites 1, 4, 5, and 6), and 21 (Sites 2, 3, 7, and 10), 2005. At each site, two cans were opened and the four SPMD spider carriers were fitted into a stainless steel canister (Figure 3). One canister was buoyed in the water column near the sediment surface (i.e., within one-foot of the sediment, but not in contact with it) at each of the ten locations. The GPS coordinates, water depth, substrate type, and water temperature were recorded.

Field blanks were exposed at the time of deployment and retrieval at Sites 5, 7, 8, 9, and 10 to determine uptake of airborne PCBs by the SPMDs. Each blank was transported to the field individually in a sealed can. During the period that the investigative sample SPMDs were exposed to the air (i.e., while the field technician was placing them in a canister), the can containing the field blank was open (i.e., exposed to the ambient air). At the point that the canister was submerged in the water, the field blank can was sealed. The approximate elapsed time was recorded. The sealed field blank cans were held in a freezer (-10° C) until mobilization for retrieval of the SPMDs from the field.

After approximately 28-days of exposure, the canisters were retrieved and the spider carriers containing the SPMDs were removed from the canisters and sealed in labeled cans. During retrieval, the same field blank was exposed as was exposed during deployment. Water

temperature and approximate elapsed time of exposure to air were recorded. The retrieved SPMDs and field blanks were shipped in coolers on wet ice by Federal Express overnight service for delivery to EST on November 22, 2005.

Sample Processing and Analysis Methods

Upon arrival at EST, the condition of the SPMDs was checked and recorded, and any biofouling was removed with acetone, isopropyl alcohol, 1N hydrochloric acid, and hexanes. The SPMDs were stored frozen until they could be processed. On December 14 and 15, 2005, dialysis of the SPMDs in hexane was initiated in order to extract the compounds of interest. Prior to dialysis, one of the four SPMDs from each site, and each field blank SPMD, was spiked with 0.025 μ g 2,2',4,4',6,6'-hexabromobiphenyl (polybrominated biphenyl (PBB)-155) as a surrogate compound. Following dialysis, the sample extracts were concentrated using Kuderna-Danish (K-D) apparatus followed by a stream of ultra-high purity (UHP) nitrogen to a volume of approximately 0.5mL. The concentrated extracts were filtered through glass fiber filters using methylene chloride as the transfer solvent, and cleaned-up using size-exclusion gel permeation chromatography (GPC). The cleaned-up extracts were concentrated under UHP nitrogen, and solvent exchanged into hexane. At this point, the extracts from the four SPMDs exposed at one site were composited, concentrated to a volume of 1mL, and transferred to ampules. The ampules were chilled in isopropyl alcohol/dry ice, sealed using an acetylene/oxygen torch, and shipped for arrival on January 11, 2006 at the Michigan Department of Community Health (MDCH), Chemistry and Toxicology Division Laboratory for PCB analysis.

At the MDCH laboratory, the extracts were prepared for analysis by fractionation using fully activated silica gel 60 and elution with hexane followed by benzene. This procedure produced four distinct fractions, theoretically containing the following compounds if they were sample components: Fraction 1) mirex, octachlorostyrene, and hexachlorobenzene; Fraction 2) PCBs, PBBs, and up to 40% of DDE; Fraction 3) the remainder of the DDE, DDT, DDD, the technical chlordanes, cis- and trans-nonachlor, and toxaphene-like compounds; and Fraction 4) dieldrin. Fraction 2 of each extract was concentrated and analyzed for PCB congeners between January 24 and 26, 2006 on a Varian 3800 gas chromatograph equipped with an electron capture detector (GC/ECD) using Varian's Star software for data processing. The PCB congeners were separated on a JW DB-5 60-meter column with a 0.25ID, and a 0.25 μ m film thickness. In the extracts, 73 possible chromatographic peaks, representing 83 PCB congeners (Table1), were identified based on retention time and quantified based on the response of the peak compared to the calibration curve.

Quality Assurance and Quality Control Procedures

Quality assurance (QA) and quality control (QC) procedures were implemented to ensure that data of documented quality were generated. Standard Operating Procedures, submitted to MDEQ as part of the QAPP, were followed throughout the project.

In an effort to assess the precision of field sampling and analytical procedures, replicate SPMDs were exposed at each site. To assess accuracy, five field blanks were used to determine the uptake of airborne PCBs during deployment and retrieval of the sample SPMDs.

At EST, several quality control procedures were followed. The micropipettor used to add the triolein to the SPMDs was calibrated. A dialysis blank sample was processed along with the samples to assess potential contamination from solvents, glassware, and equipment. The GPC used to clean-up the samples was calibrated to accurately determine the appropriate fraction collection time.

At the MDCH laboratory, routine procedures were followed to ensure quality. All organic solvents were of the highest purity available, and were lot-tested to demonstrate the absence of interfering contaminants. The accuracy of laboratory balances was verified. Most samples processed as part of MDCH's routine QC program, such as procedural blanks, duplicate samples, and various control samples, could not be incorporated into this study because MDCH did not perform the sample extractions. However, a reagent blank sample was processed along with the investigative samples, field blanks, and dialysis blank. The GC/ECD was initially calibrated using a five-point calibration curve of solutions containing 15 PCB congeners, and continuing calibration verification was performed using rotating concentrations. Surrogate (PBB-155) recovery was determined in each extract.

RESULTS AND DISCUSSION

The field portion of the study was completed according to the Work Plan (WP) and Quality Assurance Project Plan (QAPP). The deployment, retrieval and transport of the SPMDs were all successful. SPMDs at Sites 2, 3, 7, 8, 9, and 10 were retrieved after 28-days of exposure; and SPMDs at Sites 1, 4, 5, and 6 were retrieved after 29-days. None of the canisters appeared to have been disturbed during the exposure period. Descriptions of the locations, and the conditions at the time of deployment and retrieval, are presented in Table 2. Field notes are included in Appendix A.

The SPMDs were received at EST in very good condition (Chain of Custody Records are included in Appendix B), although a few irregularities were reported. Of the 45 SPMDs, ten (one from each site) had light biofouling on the exterior which was easily cleaned. Two SPMDs had possible holes, which were sealed; no loss of triolein or uptake of water was visible. The dialysis and GPC clean-up of the SPMDs was completed successfully. Loss of approximately 10 percent of the extract from one of the four Site 8 SPMDs, due to technician error, was reported. Additionally, EST reported a concern that the surrogate compound may not have been collected along with the sample during the GPC clean-up, but rather may have been wasted along with the high-molecular weight sample components. This concern arose from their review of the ultra-violet detector output. (EST's narrative and data sheets are included in Appendix C.) None of these irregularities significantly impacted the final analytical data.

One variation from the WP/QAPP did affect the results. The WP/QAPP stated that the extracts from each of the four SPMDs exposed at each site would be analyzed individually. A contingent was included that would allow the extracts to be composited (two, three or four) by the MDCH laboratory in the event that the analytical results were largely below the quantitation limit. However, due to a misunderstanding, EST composited the four extracts from each site. The result was that no data could be generated to estimate the variability in the uptake of SPMDs within a site.

The analytical results for each site are presented in Table 3, and in Figures 4 through 13. Where no data are presented, the results were below the quantitation limit or the concentration could not be determined due to interference. MDCH's report of analytical data is presented in Appendix D.

PCBs detected at Sites 2, 5, 7, 8, 9, and 10 were very similar in concentration, congener pattern, and number of congeners. Total PCB concentrations at these sites ranged from 22 to 26 $\mu\text{g/L}$ (Table 4), with nearly identical congeners being detected. In fact, of the 13 to 16 congeners detected at these six sites, 12 were detected at all ten sites. Sites 2, 5, 7, 8, 9, and 10 were all located outside the main basin of Torch Lake. Site 2 was upstream of Torch Lake, in the Trap Rock River. Site 5 was in the southern basin of the lake, connected to the main basin by only a narrow strait, and partially fed by tributaries. Site 7 was located in Portage Lake. Sites 8 and 9 were in the Keweenaw waterway, and Site 10 was in Lake Superior. MDEQ selected Sites 5 and 7 to determine whether the stamp sands or the old mill near Site 5, and the abandoned equipment near Site 7, were sources of PCBs; the results from this study suggest that there were not. Sites 8, 9, and 10 were chosen to demonstrate background levels of PCBs in the Keweenaw waterway and Lake Superior. The similarity of PCB results for these six sites suggests that PCBs at Sites 2, 5, and 7 were also at background levels.

In contrast, the remaining sites within Torch Lake (Sites 1, 3, 4, and 6) had elevated levels of PCBs, with the highest concentrations and the greatest number of congeners found at Site 4 (Table 4). Sites 3 and 4 were selected because they were near potential PCB sources, which the results support. The fact that Site 1 (without stamp sands) had elevated levels of PCBs, and Site 5 (with stamp sands) had background levels of PCBs indicates that the stamp sands were not a source of PCBs. Site 6 was representative of the discharge from the lake. Overall, the results demonstrate that the main basin of Torch Lake is a source of PCBs.

Quality Assurance and Quality Control Results

All instrument calibrations were performed successfully:

- Ten trials of the micropipettor yielded a relative standard deviation of 0.052 percent (Appendix C).
- GPC calibration times were within the range of acceptability (Appendix C).
- GC/ECD calibration verifications were all within the acceptable criteria (Appendix D).

PCBs were detected in most of the QC samples. Although the field blank samples were only exposed to the air for 5 to 8 minutes during deployment of the SPMDs, and 3 to 5 minutes during retrieval (Appendix A), concentrations of 0.6 or 0.7 $\mu\text{g/L}$ PCB-174 were reported for each. PCB-174 was also detected in the dialysis blank sample at a concentration of 0.7 $\mu\text{g/L}$, indicating that this was likely a procedural contaminant. With the exception of the field blank from Site 8, no other PCB congeners were detected in the field blank samples. In addition to PCB-174, the Site 8 field blank had detectable levels of congeners 28, 31, 33, 37/42, 44, 49, 52, 66/95, and 70. PCB-28 was also detected in the dialysis blank sample. No PCB congeners were detected in the reagent blank sample prepared at the MDCH laboratory (Appendix D).

Recovery of the surrogate compound PBB-155, which was added to one of the four SPMDs from each site and to each of the field blank SPMDs prior to dialysis, ranged between 64.0 and 87.8

percent (Appendix D). Therefore, surrogate recovery met the criterion of being between 60 and 120 percent in every instance. EST's concern that the surrogate compound was not collected along with the sample fraction from the GPC was unwarranted.

The precision of the field sampling and analytical procedures could not be assessed in this study because the extracts from the four SPMDs exposed at each site were composited prior to analysis. However, less than 20 percent variability is generally expected for field-exposed SPMDs, with results for the more volatile compounds (e.g., polynucleated aromatic hydrocarbons and many chlorinated pesticides) showing higher coefficients of variation (CV) than PCBs. In a study conducted at the U.S. Geological Survey's Columbia Environmental Research Center, where the SPMD passive sampler technique was developed in the mid-1990s, CVs for PCBs averaged 14 percent (n=3) (Alvarez 2006). This level of variability cannot be separated from analytical method variability, which is often considered acceptable at less than 20 percent.

We suspect that many of the results would have been below the quantitation limit had the four SPMD extracts been analyzed individually (Table 5). Table 5 was developed from the data in Table 3. An assumption of no variability between SPMDs exposed at a single site was applied. The Table 3 data were adjusted by dividing each PCB congener concentration by four; resultant values below the quantitation limit were not included in the Table 5 totals. As Table 5 demonstrates, it is likely that the overall results of the study would not have been different had the SPMDs been analyzed individually rather than as composites. The results for the main basin Torch Lake samples would have shown higher PCB concentrations than the other samples.

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Table 1. PCB congeners quantified in the SPMD extracts and quantitation limits (QLs)

| BZ# | QL (µg/L) | Compound names |
|------------|----------------------|---|
| 17 | 1.0 | 2,2',4-trichlorobiphenyl |
| 18 | 1.0 | 2,2',5-trichlorobiphenyl |
| 22 | 1.0 | 2,3,4'-trichlorobiphenyl |
| 25 | 1.0 | 2,3',4-trichlorobiphenyl |
| 26 | 1.0 | 2,3',5-trichlorobiphenyl |
| 28 | 1.0 | 2,4,4'-trichlorobiphenyl |
| 31 | 1.0 | 2,4',5-trichlorobiphenyl |
| 32 | 1.0 | 2,4',6-trichlorobiphenyl |
| 33 | 1.0 | 2',3,4-trichlorobiphenyl |
| 37 & 42* | 1.0 | 3,4,4'-trichlorobiphenyl & 2,2',3,4'-tetrachlorobiphenyl |
| 40 | 1.0 | 2,2',3,3'-tetrachlorobiphenyl |
| 44 | 1.0 | 2,2',3,5'-tetrachlorobiphenyl |
| 45 | 1.0 | 2,2',3,6-tetrachlorobiphenyl |
| 47 | 1.0 | 2,2',4,4'-tetrachlorobiphenyl |
| 49 | 1.0 | 2,2',4,5'-tetrachlorobiphenyl |
| 52 | 1.0 | 2,2',5,5'-tetrachlorobiphenyl |
| 56 & 60* | 1.0 | 2,3,3',4'-tetrachlorobiphenyl & 2,3,4,4'-tetrachlorobiphenyl |
| 63 | 1.0 | 2,3',4',5-tetrachlorobiphenyl |
| 64 | 1.0 | 2,3,4',6-tetrachlorobiphenyl |
| 66 & 95* | 1.0 | 2,3',4,4'-tetrachlorobiphenyl & 2,2',3,5',6-pentachlorobiphenyl |
| 70 | 1.0 | 2,3',4',5-tetrachlorobiphenyl |
| 71 | 1.0 | 2,3',4',6-tetrachlorobiphenyl |
| 74 | 1.0 | 2,4,4',5-tetrachlorobiphenyl |
| 77 & 110* | 1.0 | 3,3',4,4'-tetrachlorobiphenyl & 2,3,3',4',6-pentachlorobiphenyl |
| 82 | 0.5 | 2,2',3,3',4-pentachlorobiphenyl |
| 84 | 0.5 | 2,2',3,3',6-pentachlorobiphenyl |
| 87 | 0.5 | 2,2',3,4,5'-pentachlorobiphenyl |
| 90 & 101* | 0.5 | 2,2',3,4',5-pentachlorobiphenyl & 2,2',4,5,5'-pentachlorobiphenyl |
| 91 | 0.5 | 2,2',3,4',6-pentachlorobiphenyl |
| 92 | 0.5 | 2,2',3,5,5'-pentachlorobiphenyl |
| 97 | 0.5 | 2,2',3',4,5-pentachlorobiphenyl |
| 99 | 0.5 | 2,2',4,4',5-pentachlorobiphenyl |
| 100 | 0.5 | 2,2',4,4',6-pentachlorobiphenyl |
| 105 | 0.5 | 2,3,3',4,4'-pentachlorobiphenyl |
| 118 | 0.5 | 2,3',4,4',5-pentachlorobiphenyl |
| 126 & 178* | 0.5 | 3,3',4,4',5-pentachlorobiphenyl & 2,2',3,3',5,5',6-heptachlorobiphenyl |
| 128 | 0.5 | 2,2',3,3',4,4'-hexachlorobiphenyl |
| 130 | 0.5 | 2,2',3,3',4,5'-hexachlorobiphenyl |
| 132 | 0.5 | 2,2',3,3',4,6'-hexachlorobiphenyl |
| 135 & 144* | 0.5 | 2,2',3,3',5,6'-hexachlorobiphenyl & 2,2',3,4,5',6-hexachlorobiphenyl |
| 136 | 0.5 | 2,2',3,3',6,6'-hexachlorobiphenyl |
| 137 | 0.5 | 2,2',3,4,4',5-hexachlorobiphenyl |
| 138 & 163* | 0.5 | 2,2',3,4,4',5'-hexachlorobiphenyl & 2,3,3',4',5,6-hexachlorobiphenyl |
| 141 | 0.5 | 2,2',3,4,5,5'-hexachlorobiphenyl |
| 146 | 0.5 | 2,2',3,4',5,5'-hexachlorobiphenyl |
| 149 | 0.5 | 2,2',3,4',5,6-hexachlorobiphenyl |
| 151 | 0.5 | 2,2',3,5,5',6-hexachlorobiphenyl |
| 153 | 0.5 | 2,2',4,4',5,5'-hexachlorobiphenyl |
| 156 | 0.5 | 2,3,3',4,4',5-hexachlorobiphenyl |
| 157 | 0.5 | 2,3,3',4,4',5'-hexachlorobiphenyl |
| 158 | 0.5 | 2,3,3',4,4',6-hexachlorobiphenyl |
| 167 | 0.5 | 2,3',4,4',5,5'-hexachlorobiphenyl |
| 170 | 0.2 | 2,2',3,3',4,4',5-heptachlorobiphenyl |
| 171 | 0.5 | 2,2',3,3',4,4',6-heptachlorobiphenyl |
| 172 | 0.3 | 2,2',3,3',4,5,5'-heptachlorobiphenyl |
| 174 | 0.5 | 2,2',3,3',4,5,6'-heptachlorobiphenyl |
| 175 | 0.3 | 2,2',3,3',4,5',6-heptachlorobiphenyl |
| 177 | 0.3 | 2,2',3,3',4',5,6-heptachlorobiphenyl |
| 179 | 0.3 | 2,2',3,3',5,6,6'-heptachlorobiphenyl |
| 180 | 0.5 | 2,2',3,4,4',5,5'-heptachlorobiphenyl |
| 182 & 187* | 0.3 | 2,2',3,4,4',5,6'-heptachlorobiphenyl & 2,2',3,4',5,5',6-heptachlorobiphenyl |

Table 1. PCB congeners quantified in the SPMD extracts and quantitation limits (QLs)

| BZ# | QL (µg/L) | Compound names |
|------------|----------------------|--|
| 183 | 0.2 | 2,2',3,4,4',5',6-heptachlorobiphenyl |
| 185 | 0.2 | 2,2',3,4,5,5',6-heptachlorobiphenyl |
| 190 | 0.2 | 2,3,3',4,4',5,6-heptachlorobiphenyl |
| 193 | 0.2 | 2,3,3',4',5,5',6-heptachlorobiphenyl |
| 194 | 0.3 | 2,2',3,3',4,4',5,5'-octachlorobiphenyl |
| 195 | 0.2 | 2,2',3,3',4,4',5,6-octachlorobiphenyl |
| 196 & 203* | 0.3 | 2,2',3,3',4,4',5,6'-octachlorobiphenyl & 2,2',3,4,4',5,5',6-octachlorobiphenyl |
| 198 | 0.2 | 2,2',3,3',4,5,5',6-octachlorobiphenyl |
| 199 | 0.2 | 2,2',3,3',4,5,6,6'-octachlorobiphenyl |
| 201 | 0.3 | 2,2',3,3',4,5,5',6'-octachlorobiphenyl |
| 205 | 0.2 | 2,3,3',4,4',5,5',6-octachlorobiphenyl |
| 206 | 0.3 | 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl |

BZ# = identification numbers adopted by the International Union of Pure and Applied Chemists (IUPAC).

*The two congeners co-elute on the GC column and are quantified together.

Table 2. Locations for exposure of SPMDs and conditions at the time of deployment/retrieval

| Watershed | Site # | Description | Lat. (N) Long. (W) | Water depth SPMD depth substrate | Water temperature (°F) | |
|-------------------|--------|--|-----------------------|--|------------------------|--------------|
| | | | | | At deployment | At retrieval |
| Torch Lake | 1 | East side, north of outlet in an area w/o mine waste piles | 47.16147 88.40175 | 3 ft 2 ft sand/gravel | 54 | 38 |
| | 2 | Trap Rock River between Sawmill Creek and river mouth | 47.19197 88.39360 | 4 ft 3 ft sand/mud/organics | 54 | 33 |
| | 3 | Near Lake Linden, north of public boat ramp in area near old pilings | 47.18835 88.40665 | 4 ft 3 ft firm sand | 53 | 42 |
| | 4 | Peninsula Copper Industries (PCI), in pilings near cooling water outfall | 47.17319 88.42579 | 4 ft 3 ft rock/sand | 54 | 42 |
| | 5 | Mason Sands, near old mill and roundhouse | 47.14265 88.46077 | 5 ft 4 ft firm sand | 54 | 42 |
| | 6 | Torch Lake outlet, in narrows | 47.15139 88.41246 | 7 ft 6 ft firm sand | 52 | 40 |
| Portage Lake | 7 | Dollar Bay, near old marina and equipment graveyard | 47.11911 88.49471 | 3 ft 2 ft mud/vegetation | 54 | 39 |
| Keweenaw Waterway | 8 | North Entry | 47.20833 88.61825 | 15 ft 14 ft rock | 54 | 42 |
| | 9 | South Entry | 46.98343 88.43620 | 15 ft 14 ft sand/mud | 54 | 41 |
| Huron Bay | 10 | South of Arum Township Park boat launch | 46.87061 88.23411 | 4 ft 3 ft sand | 54 | 37 |

Table 3. Concentrations of PCB congeners in SPMD extracts

| PCB BZ# Congener | Concentration (µg/L) | | | | | | | | | |
|---------------------|----------------------|--------|--------|--------|--------|--------|--------|--------|--------|---------|
| | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 | Site 8 | Site 9 | Site 10 |
| 17 | | | | 1.2 | | | | | | |
| 18 | | | 1.3 | 1.6 | | | | | | |
| 22 | | | | 1.0 | | | | | | |
| 25 | | | | | | | | | | |
| 26 | | | | | | | | | | |
| 28 | 2.5 | 2.6 | 3.3 | 4.4 | 2.4 | 2.8 | 2.1 | 3.0 | 2.9 | 2.3 |
| 31 | 1.7 | 1.9 | 2.4 | 3.2 | 1.7 | 1.9 | 1.5 | 2.2 | 2.2 | 1.7 |
| 32 | | | | | | | | | | |
| 33 | 1.4 | 1.4 | 1.9 | | 1.1 | 1.3 | 1.2 | 1.6 | 1.5 | 1.0 |
| 37 & 42 | 2.2 | 1.3 | 2.5 | 3.9 | 1.8 | 1.8 | | 1.8 | 1.5 | 1.3 |
| 40 | | | | | | | | | | |
| 44 | 3.0 | 1.5 | 2.7 | 5.9 | 1.3 | 2.4 | 1.0 | 1.6 | 1.5 | 1.1 |
| 45 | | | | | | | | | | |
| 47 | | | | 1.2 | | | | | | |
| 49 | 10.3 | 3.7 | 6.5 | 13.2 | 3.4 | 8.1 | 8.4 | 3.7 | 5.6 | 5.3 |
| 52 | 6.2 | 2.0 | 5.3 | 13.5 | 2.2 | 5.3 | 1.5 | 2.2 | 2.0 | 1.7 |
| 56 & 60 | 1.9 | | 1.1 | 2.4 | | | | | | |
| 63 | | | | | | | | | | |
| 64 | 1.4 | | 1.5 | 3.0 | | 1.2 | | | | |
| 66 & 95 | 5.9 | 1.8 | 5.2 | 12.0 | 1.8 | 5.1 | 1.3 | 1.8 | 1.8 | 1.5 |
| 70 | 2.9 | 1.3 | 2.8 | 6.3 | 1.2 | 2.8 | 1.1 | 1.3 | 2.3 | 1.3 |
| 71 | | | | 1.0 | | | | | | |
| 74 | | | 1.1 | 1.9 | | | | | | |
| 77 & 110 | 9.7 | 1.7 | 8.5 | 17.5 | 2.2 | 7.9 | 1.3 | 1.5 | 1.5 | 1.7 |
| 82 | | | | 0.7 | | | | | | |
| 84 | 1.5 | | 0.9 | 2.6 | | 0.7 | | | | |
| 87 | 2.3 | | 2.3 | 4.2 | 0.6 | 1.9 | | | | |
| 90 & 101 | 5.2 | 0.9 | 4.9 | 9.7 | 1.2 | 4.0 | 0.7 | 0.9 | 0.8 | 0.9 |
| 91 | 0.5 | | 0.6 | 1.4 | | | | | | |
| 92 | 1.5 | | 0.7 | 2.2 | | 0.7 | | | | |
| 97 | 1.5 | | 1.4 | 2.7 | | 1.2 | | | | |
| 99 | 2.3 | | 2.2 | 4.3 | | 1.8 | | | | |
| 100 | | | | | | | | | | |
| 105 | 1.2 | | 1.3 | 2.2 | | 0.9 | | | | |
| 118 | 3.4 | 0.6 | 3.6 | 5.8 | 0.8 | 2.7 | 0.5 | 0.5 | 0.5 | 0.7 |
| 126 & 178 | | | | | | | | | | |
| 128 | 0.5 | | 0.6 | 0.9 | | | | | | |
| 130 | | | | | | | | | | |
| 132 | 0.7 | | 1.0 | 1.5 | | 0.6 | | | | |
| 135 & 144 | | | | 0.9 | | | | | | |
| 136 | | | | | | | | | | |
| 137 | | | | | | | | | | |
| 138 & 163 | 2.9 | 0.5 | 3.3 | 5.1 | 0.7 | 2.5 | | 0.6 | | 0.6 |
| 141 | | | | 0.8 | | | | | | |
| 146 | | | | 0.6 | | | | | | |
| 149 | 0.6 | | 0.7 | 1.3 | | 0.5 | | | | |
| 151 | 0.9 | | 0.7 | 1.5 | | 0.7 | | 0.9 | | 1.5 |

Table 4. Number of PCB analytes and total PCBs at each site

| Site # | Number of Analytes Detected* | Total PCB (ppb) |
|--------|------------------------------|-----------------|
| 1 | 30 | 78 |
| 2 | 15 | 23 |
| 3 | 33 | 75 |
| 4 | 42 | 151 |
| 5 | 16 | 24 |
| 6 | 28 | 63 |
| 7 | 13 | 22 |
| 8 | 16 | 25 |
| 9 | 14 | 26 |
| 10 | 16 | 24 |

*A total of 73 analytes, representing 83 congeners were determined.

Table 5. Adjusted^a Number of PCB analytes and total PCBs at each site

| Site # | Number of Analytes Detected ^b | Total PCB (ppb) |
|--------|--|-----------------|
| 1 | 10 | 51 |
| 2 | 0 | 0 |
| 3 | 10 | 44 |
| 4 | 17 | 116 |
| 5 | 0 | 0 |
| 6 | 8 | 38 |
| 7 | 1 | 8 |
| 8 | 0 | 0 |
| 9 | 1 | 6 |
| 10 | 1 | 5 |

^aAdjusted to show the probable results, had the four SPMD extracts from each site been analyzed individually.

^b A total of 73 analytes, representing 83 congeners were determined.



Figure 1. Sampling Locations



Figure 2. SPMD on a spider carrier



Figure 3. SPMD deployment canister

Figure 4. Site 1 PCBs

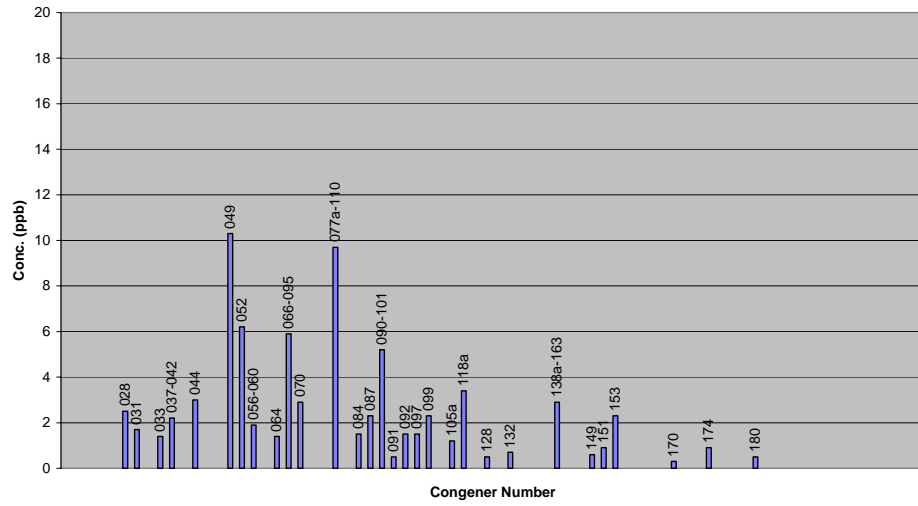


Figure 5. Site 2 PCBs

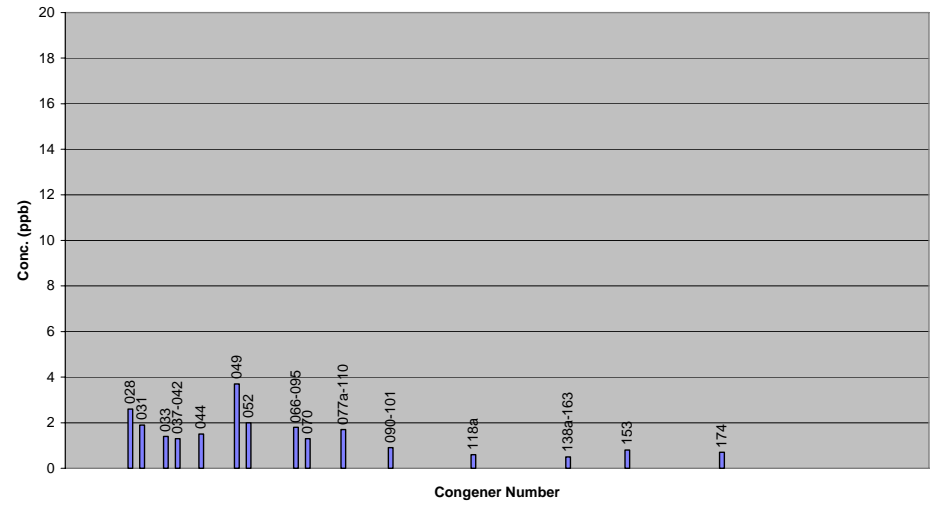


Figure 6. Site 3 PCBs

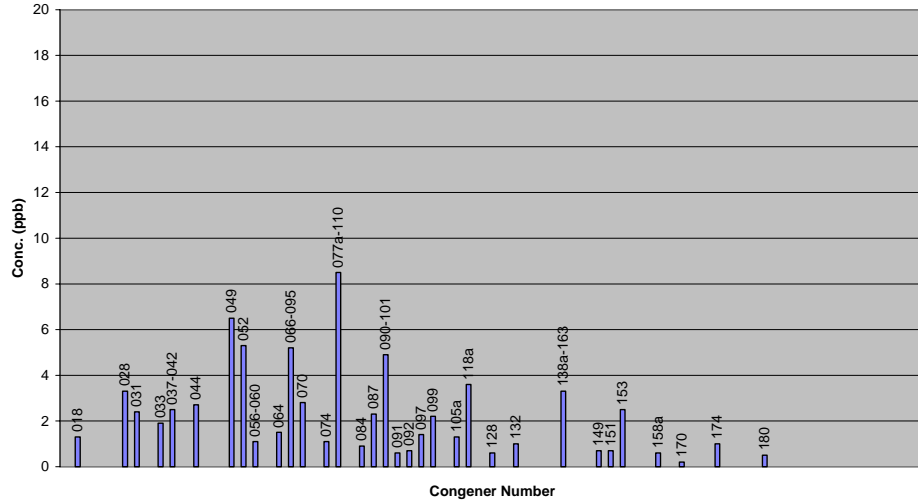


Figure 7. Site 4 PCBs

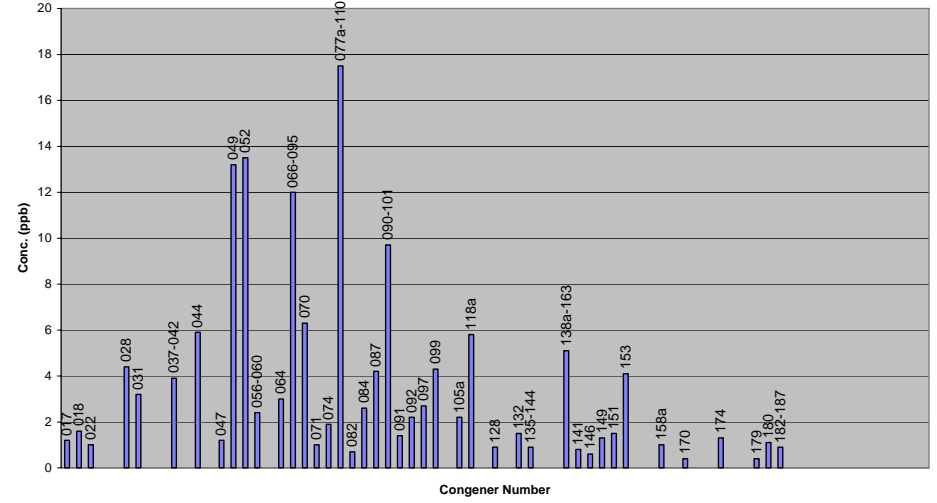


Figure 8. Site 5 PCBs

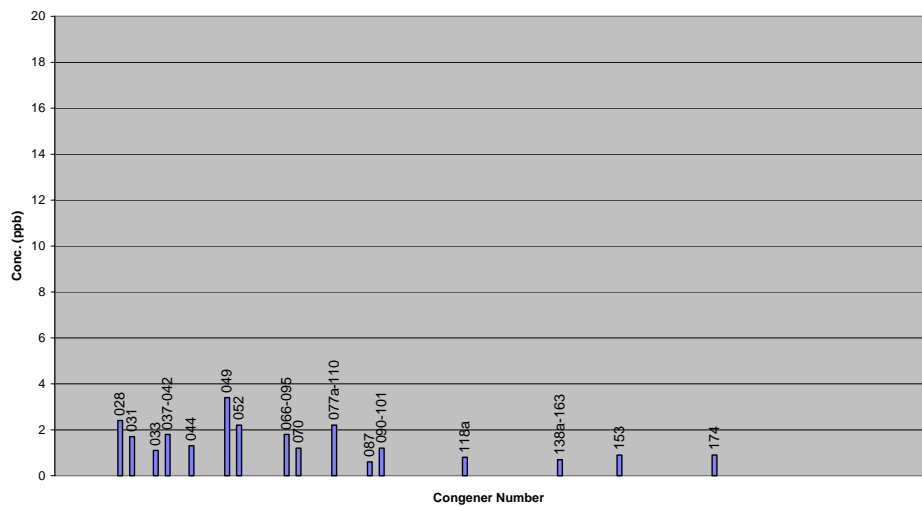


Figure 9. Site 6 PCBs

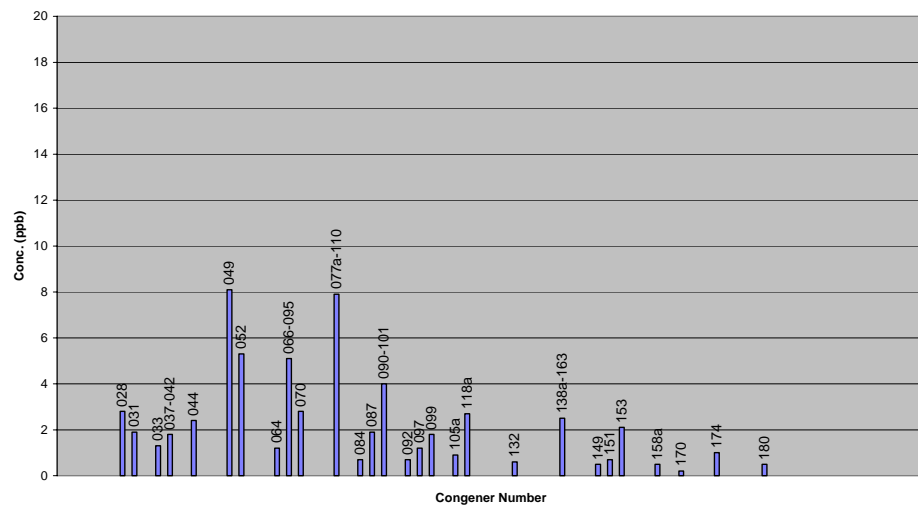


Figure 10. Site 7 PCBs

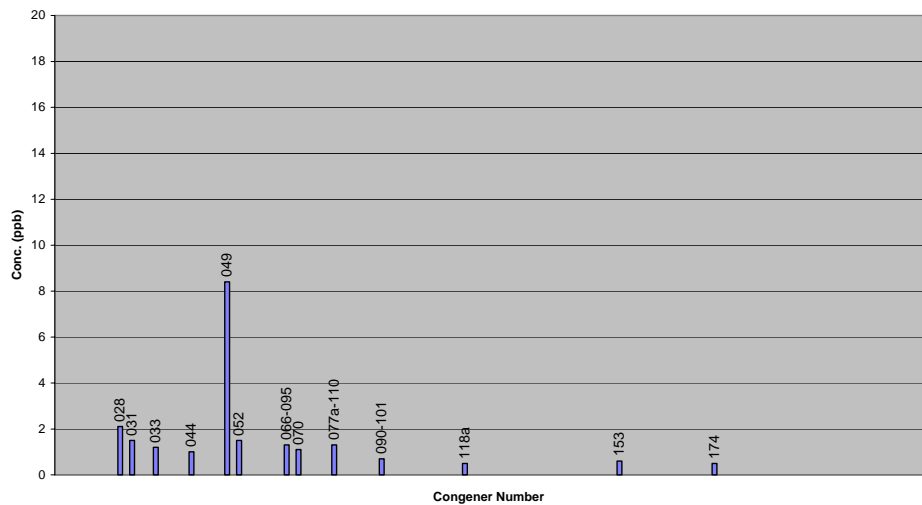


Figure 11. Site 8 PCBs

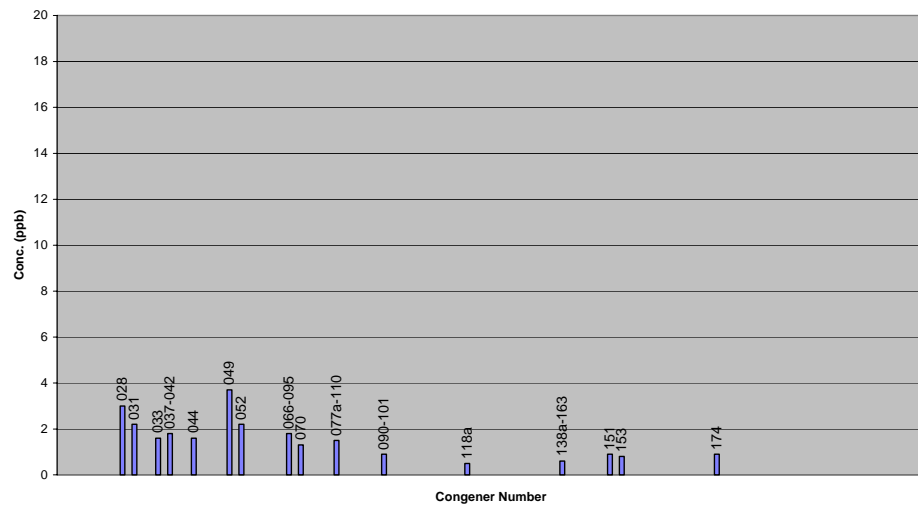


Figure 12. Site 9 PCBs

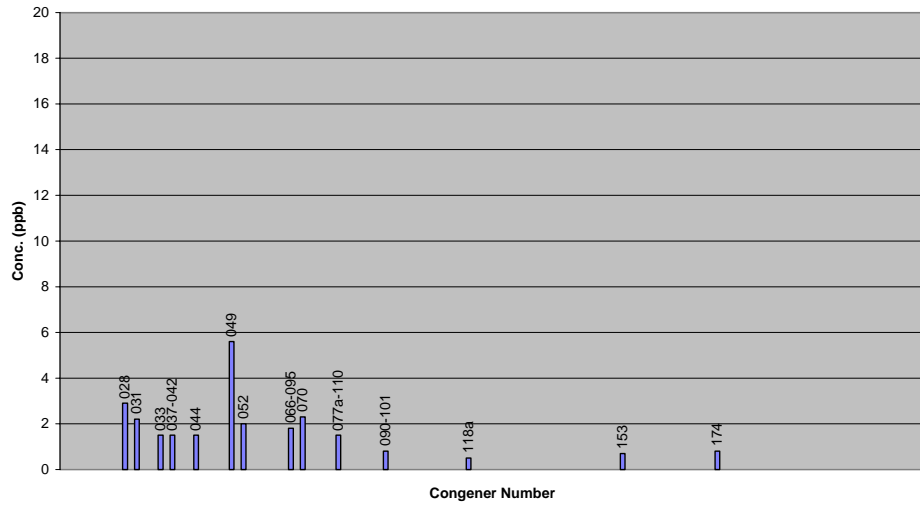


Figure 13. Site 10 PCBs

