

Final Report to City of St. Clair Shores

PCB Contaminant Profile in a Sediment Core
from the Lange and Revere Canals St. Clair Shores

May 20, 2003

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Executive Summary

In an effort to establish a deposition time frame for the PCBs contaminating the Lange and Revere canals in St. Clair Shores, Macomb County, through the City of St. Clair Shores, funded this project to investigate the PCB dumping. Therefore, this study seeks to establish through on-site sediment core sampling and subsequent laboratory analyses, a timetable for the PCB contamination of the Lange and Revere canals. Additionally, while not part of the project contract, characterizing the chemical nature of the PCBs makes it possible to suggest a potential contamination source. These data are not relevant for establishing an exposure assessment, however, or for correlating the PCBs present in the canals to health effects in people or animals residing in St. Clair Shores. This study was designed exclusively for delineating the time course of the PCB contamination, not for determining health effects, and in fact, the two cannot be correlated. The Michigan Department of Community Health issued a health assessment report that should be referred to for that purpose.

There is evidence of periodic mixing within the sediments in the canal, but a definite overall pattern of sediment layering which allowed us to determine a timetable for the PCB contamination. The data suggest a major PCB dumping dating to about 1983 plus or minus three years. A slightly lesser discharge dating to the mid 1960s corresponds to the known peak use of PCBs, prior to the regulatory ban in the early 1970s. We believe that there was not another release after 1983, and that the PCBs were stored to some degree in the drainage system (associated with sediments), and periodically released into the canals over time. Depending on the lake levels that ebb and flow between Lake St. Clair and the drainage system that feeds the Lange and Revere canals, movement of the contaminated sediments from the drainage system into the canals varied over time.

PCBs are ubiquitous in the environment, so we expect to find PCBs in sediments at background levels. Background concentrations need to be determined locally to distinguish between so-called, "normal" versus "contaminated" levels. We do not have local background PCB data, particularly historical data; however, background levels for Michigan have been reported at about 1 to 3 ppm total PCBs in sediments from urban areas. The past manufacture, use, and disposal of PCBs contributes to the continuous cycling of PCBs between air, water, soil, and sediments in the Great Lakes region. Based on these reports and our own research on PCBs in sediments in Michigan, we would expect to see no more than 5 ppm in sediments in the St. Clair Shores area. In the Lange and Revere canals, however, the levels of PCBs have been above this expected concentration for a long time, possibly since 1956.

Aroclors are commercial mixtures of PCBs. Different Aroclors were used for different applications, so we can examine the types of Aroclors to possibly give us information relating to the source of the contamination. Our assessment suggests that the PCBs dating to the 1980s and 1960s are mainly a mixture of Aroclors 1242, 1254 and traces of 1260. This combination of Aroclors was used in transformers, indicating a transformer source.

Analysis of the core samples shows that PCBs were detected in the canal sediments to a layer corresponding to 1927 ± 3 years. The manufacture of PCBs in the US started in 1927. In 1930, transformer oil (then called Askarel instead of Aroclor) contained about 70% PCBs. This early PCB use predates the canals. However, prior to the canals construction, there was a drainage ditch known to be present there since the early 1900's. Therefore, it is possible that PCBs leaking or dumped in the vicinity could have made their way into the sediments that now line the Lange and Revere canals. We do not know the historical use of PCBs in this area. An analysis of the PCB congeners and Aroclor patterns suggest that the PCBs deposited prior to the 1960's may have undergone weathering (decomposition) and/or the original composition was different than the more recently deposited PCBs. Both possibilities are suggested by the data. Transformer oil manufactured prior to 1960 was of a different composition, consisting of a higher percentage of the heavier PCBs; these heavier PCBs were phased out because they were found to bioaccumulate more than the lighter PCBs.

Finally, since it appears that for many years PCBs had been consistently entering the canals, we recommend that discharges entering the canals be monitored and periodically tested for PCBs to validate that the cleaning of the Ten-Mile storm sewer drainage system was complete and that there are no other sources entering the system. We also recommend a process oriented study be conducted to investigate the fate and transport of contaminants that are present in the watershed. Such a study will help to identify ways to improve water quality of Lake St. Clair. Background levels of PCBs must be taken into account in determining what is meant by "clean."

1.0 INTRODUCTION

Testing of canal sediments prior to a dredging project in St. Clair Shores, Michigan, revealed high levels of polychlorinated biphenyls (PCBs). The US EPA provided emergency response clean-up of the Lange and Revere Canals and the drainage system that empties into them. The Michigan Department of Community Health stated that the PCBs had posed no apparent health hazard because any expected contact with the chemicals was expected to be infrequent. However, concern remained in the community regarding the length of time the PCBs had been present in the canals and prosecution of liable parties, if found. Therefore, the City of St. Clair Shores contracted with two university researchers for further analysis of the contaminated sediments.

The specific goals of this proposed investigation were twofold: a) to age date 3 sediment cores using the lead isotope (^{210}Pb) method to establish the chronology of sediment cores for the past 5 or more years; and b) to quantify PCB congeners in approximately 25 sediment samples, or as needed, from 3 cores to determine PCB contamination during at least the past 5 years. From the isotope and PCB measurements, the purpose was to identify when the PCB dumping was done in the study site under investigation. These data are not relevant for establishing an exposure assessment or for correlating the PCBs present in the canals to health effects in people or animals residing in St. Clair Shores. This study was designed exclusively for delineating the time course of the PCB contamination, not for determining health effects, and in fact, the two cannot be correlated.

PCBs are a family of structurally and chemically similar, manmade compounds individually identified as congeners. PCBs were first manufactured near the beginning of the twentieth century. Because of their thermal stability, they were often used in electrical transformers and capacitors. PCBs first became commercially available for the electrical power industry (as insulators or heat transfer fluids) about 1929 under the generic name Askarel, produced by Swann Chemical Company (soon thereafter, bought by Monsanto). About 99% of PCBs (more than 1 billion pounds) used in the USA were manufactured by Monsanto in Sauget, Illinois. Production of PCBs increased in the 1960s and peaked around 1970. Between 1957 and 1970, 12 different types of Aroclors (PCB mixtures) were produced (ASTDR, 2000). In the US, open uses of PCBs (e.g.,

wire coatings, pesticide extenders) were initially banned in the early 1970s, and closed uses (e.g., in transformers and capacitors) were banned completely by 1979. Monsanto discontinued production in 1977.

PCBs in transformers were phased out in the 1980s due to the EPA PCB Electrical Use Rule (Federal Register, 1982) and the Transformer Fire Rule (Federal Register, 1985). The life expectancy of a transformer is over 30 years (ASTDR, 2000). Gaskets in old transformers can eventually fail, and the transformer can leak. Transformers were not just owned by electrical utilities; they were in industrial, private, and government buildings. EPA has a database containing the location and amount of PCBs in transformers across the US.

Due to the widespread manufacturing and use of PCBs in the Great Lakes region, background levels are high in Michigan. It is important to establish what background levels are in order to be able to say what is expected versus what can be considered as contamination (e.g., from a dumping event, illegal discharge, etc.). True background refers to PCBs that have been deposited from the atmosphere, and not from other sources. PCBs are ubiquitous in the environment due to their atmospheric transport, in spite of the fact that they are not very volatile. The main atmospheric source today is from contaminated sediments; PCBs cycle between sediment, water, air, and soil. Since PCBs were banned in the 1970's, the concentrations in air have been slowly decreasing. This is because older contaminated sediments are being buried, and the PCBs are in less contact with overlying water, and finally, air. In deposition zones (as opposed to areas of erosion and/or resuspension), background levels for surficial sediments will be lower than buried, undisturbed sediments.

The term background can also refer to the widespread average concentration of PCBs in sediments for a particular water body, not including a known contaminated site within that water body. It is known that background levels of PCBs in rivers that drain urban areas are typically ten times higher than rural areas (USGS 1998). We would expect a drainage area to have higher levels of PCBs than, say, in the middle of Lake St. Clair. Therefore, we should not be too concerned with PCBs concentrations that are slightly higher than reported background levels. Generally, concentrations above background and those that pose health or ecological concerns will drive cleanup

(remediation) efforts. Since the Lange and Revere canals are a receptacle for the Ten-Mile drainage system, which drains a large urban watershed, it should be expected that any sediments containing PCBs in the drainage system would continuously enter the canals to a level consistent with an urban background level. What exactly is this background number, has not been established. However, based on other reports on PCBs in sediments in Michigan, we expect this to be less than 5 parts per million (ppm). Our own testing of PCBs in sediments in the Clinton River, for example, routinely shows about 1 ppm.

2.0 EVALUATION OF SEDIMENT CORES - METHODOLOGY

There were two parts to this analysis, but they were conducted with close coordination. The objective was to determine when and how many PCB contamination events occurred in the Lange and Revere canals by analyzing at least 25 sediment samples from at least one good core. Dr. Mark Baskaran conducted the radiochemical dating of the sediment cores, and Dr. Linda Schweitzer evaluated the PCBs in the sediment cores. A total of 8 sediment cores were taken from the Lange and Revere canals. Dr. Ed van Hees of Wayne State University helped with the sampling and analysis. Dr. van Hees is a lecturer at Wayne State, and has worked as a field Geologist for over 10 years. Dr. van Hees used a ten-foot PVC pipe with a 4" diameter to construct a homemade coring device. The coring device had a trap on the bottom to contain the sediments after it was pushed into the sediments. The coring device was pushed and twisted into the sediments to a depth of approximately 8 feet deep, and pulled out with the help of two men. The pushing of the sediments compressed the cores to approximately half their original height in the coring device, or twice their original density. The cores were then transported immediately to Wayne State University and placed into a freezer. Once frozen, they were cut in one-inch increments with a diamond-coated metal blade electric saw down the entire length of the core. The one-inch hockey-puck shaped layers were broken up and divided between Wayne State and Oakland University. The outermost part of the sections that were in direct contact with the walls of the PVC coring device were not used in the analysis. Cores 2 and 7 were selected for

analysis. Core 2 was taken from just beyond the bridge south of Lange and Jefferson on November 16, 2002, and Core 7 was taken in the Lange Canal about half way between Jefferson and Lake St. Clair, on Jan 19, 2003. Subsequent analysis of Core 2 revealed that the sample did not adequately represent historic sedimentation, due to recently dredged material being deposited on top of the core (see Results and Discussion section), so Core 7 was the focus of this analysis.

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2.1 Methods of Radiochemical Dating Work:

Radionuclides: Sample Preparation and Analysis

The water content of sediments was determined after drying at 80°C. Porosity was then calculated using the equation $\phi = f_w / [f_w + (1 - f_w) \rho_w / \rho_s]$ where, ϕ is the porosity, f_w is the fraction of water in wet sediment (1- dry weight / wet weight); ρ_w is the density of pore water (assumed to be 1.0 g cm⁻³) and ρ_s is the density of dry solids (assumed to be 2.5 g cm⁻³). The cumulative mass depth (M) was determined using the following equation from Baskaran and Naidu (1995): $M = \sum (1 - \phi_i) \rho_D \times \delta x$ where, ϕ_i is the porosity at depth i and δx is the thickness of the sediment layer (i.e., 1 cm). Activities of ¹³⁷Cs, ²¹⁰Pb and ²²⁶Ra (for the determination of parent-supported ²¹⁰Pb) were determined by a non-destructive gamma-counting method (Baskaran and Naidu 1995). Each section was measured for ²²⁶Ra (via its granddaughter ²¹⁴Pb, ²¹⁰Pb, and ¹³⁷Cs at photopeak energies of 352, 46 and 661.6 keV, respectively). The gamma counting system was calibrated with a fly-ash sediment standard obtained from the former U.S. National Bureau of Standards.

2.2 Methods of PCB Analysis

Aroclor and Individual Congener Analyses

EPA Method 3562 was used for extracting PCBs by supercritical fluid extraction (SFE). Extracts were trapped onto a C18 solid phase cartridge, eluted with hexane, and concentrated by the Kuderna-Danish method (blowed down to 1.0 ml with nitrogen gas). EPA Method 3660B was used to remove interfering sulfur with copper powder.

Addition of surrogates to sediment samples (in a solvent) constitutes what is called a modifier in SFE, and lowers the extraction efficiency of PCBs that are part of the sample matrix, which are best extracted with pure CO₂ gas. Therefore, our quality control is based on the recoveries of a standard reference material (SRM). The extraction efficiency of spiked surrogates is usually much higher than chemicals that have been in contact with the sample matrix for a long period of time. This has been demonstrated in many inter-laboratory comparison studies. Therefore, the precision and accuracy of extraction is much better demonstrated by evaluating SRMs. Duplicate sample extraction and analysis was also conducted on more than 10% of the samples as a quality control measure. Laboratory blanks (celite extracts) were evaluated as a quality control measure. Hexane analytical blanks were run every 5 samples as a quality control measure.

The PCB analysis was quantified on 4 different Aroclors (1242, 1248, 1254, and 1260) by EPA Method 8082, and quantified on 28 individual select congeners (NIST/WHO/NOAA recommended congeners) by GC/dual ECD with a Shimadzu (Columbia, MD) GC 17A, using two different capillary columns 30 m x 0.25 mm ID - DB-5 and DB 1701 equivalents. Peak assignments for individual congeners were also confirmed qualitatively by GC/MSD (Hewlett Packard 6890 series GC system, 5973 mass selective detector) using a 30 m x 0.25 mm ID DB-5 column.

3.0 RESULTS AND DISCUSSION

3.1 *¹³⁷Cs and ²¹⁰Pb Profiles*

The vertical profiles of excess ²¹⁰Pb and ¹³⁷Cs are given in Figures 1-4. A total of 63 split sections from 2 sediment cores (SCS-2 and SCS-7) were analyzed and the results are given in a spreadsheet. These profiles indicate the following:

- a) In sediment core SCS-2, there is wide scatter in the concentrations of radiocesium and Pb-210;
- b) The presence of Cs-137 in SCS-2 all the way to the bottom, indicate all the sediments are less than 50 years old;

- c) There are multiple sources of sediment to the site where SCS-2 core was collected and this was not a completely depositional environment;
- d) It appears that there was some deposition that took place in SCS-2 core;
- e) The Cs-137 concentration in SCS-7 indicates there was peak Cs-137 corresponding to the year 1963. Using this layer, we get a sedimentation rate of 0.9-1.0 cm/year (~2.5 year for every inch);
- f) The excess Pb-210 profile in SCS-7 shows considerable scatter, and using the linear-best-fit line of the natural log of the excess Pb-210 activity with depth, we estimate the sedimentation rate to be ~0.9 cm/year.

We hypothesize that several inches of dredge material were deposited onto the sediments from which we collected Core 2. Also, there appeared to be other disturbances in those sediments. Therefore, we did not use Core 2 to date the contamination event(s). After doing the initial analysis on Core 2 and determining these disturbances, we then collected new cores, including Core 7, farther away from the dredging activity. The profiles of ^{137}Cs and ^{210}Pb were as expected, but a bit more noisy than what would be seen in a core from a depositional zone that has not seen disturbances or inputs of older sediments. In our best professional judgment, we have stated a level of uncertainty of approximately 3 years based on the sedimentation rate range of 0.9-1.0 cm/year. Sedimentation rates are conventionally assigned in the units of cm/yr, but our cores were cut in inches, hence the conversion to an average of 2.5 year per inch. Note that the Pb-210 and Cs-137 both correspond to approximately 0.9 cm/year sedimentation rate.

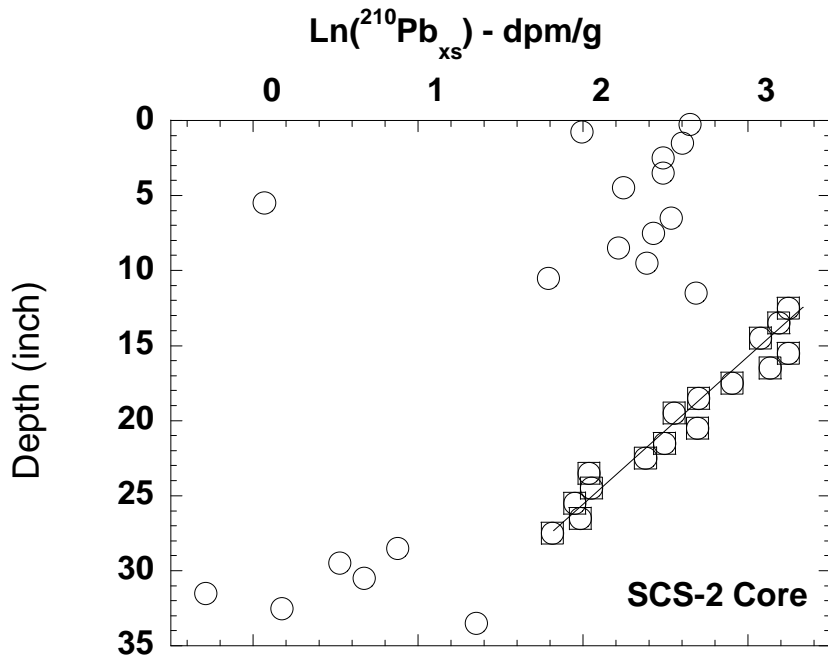


Figure 1: Plot of excess ^{210}Pb with depth.

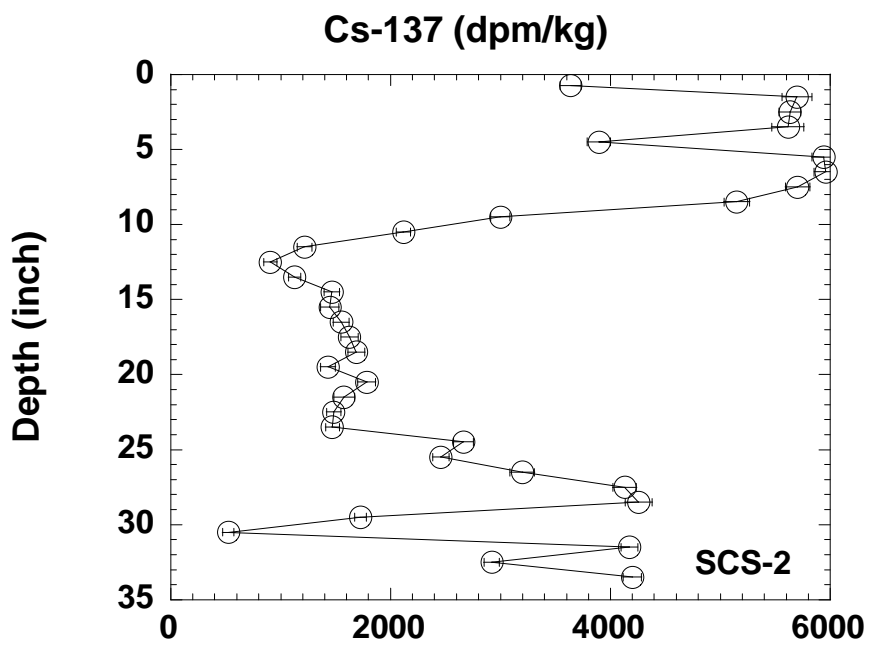


Figure 2: Vertical profile of ^{137}Cs

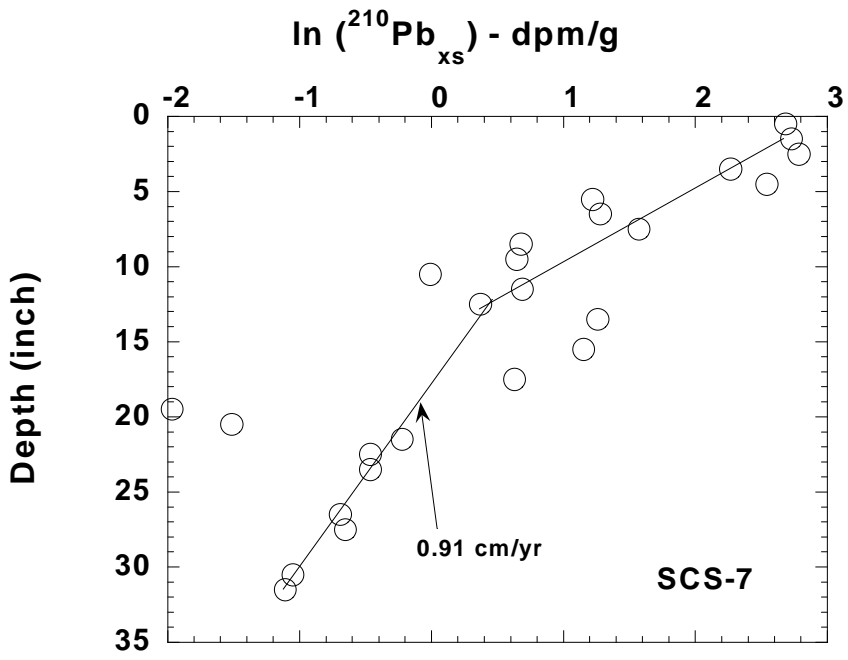


Figure 3: Vertical profile of excess Pb-210

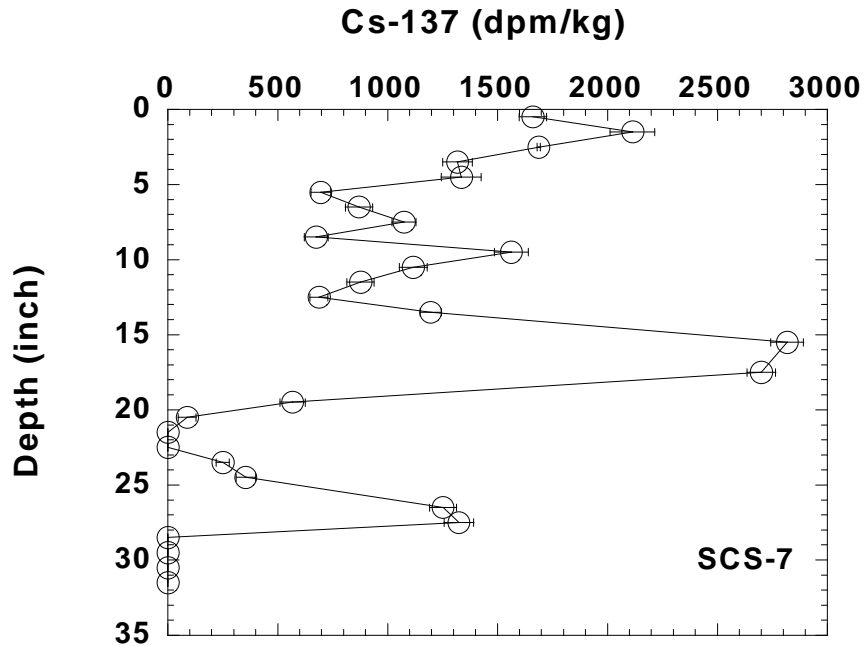


Figure 4: Vertical profile of Cesium-137

3.2 PCB Concentration Profiles

The vertical profile of PCBs in Core 7 is presented in Figure 5. The concentration of Aroclor 1242, only, is shown because the concentration of other Aroclors were lower, and the individual congener analysis confirms that the contamination mainly consists of Aroclor 1242. The concentrations of the individual congeners were not used to report the total PCB concentrations, because not all possible congeners were quantified. There are 209 theoretically possible congeners, but each Aroclor typically consists of about 60 congeners in the original commercial mixture. Only 28 select congeners were quantified to further characterize the PCB contamination, but approximately 45 were detected in any one sediment sample.

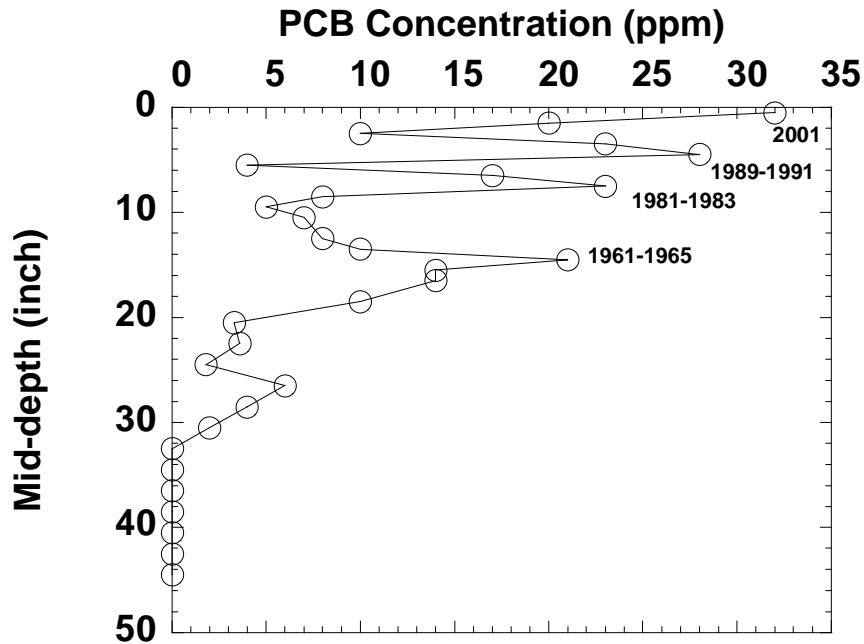


Figure 5: Vertical profile of PCBs (quantified as Aroclor 1242) in Core 7

The PCB concentrations were consistently elevated in the top of the core corresponding to the present date back to 1983. There was a slight exception in layer 5-6 inches, due to older sediments being deposited during that period (approximately, 1988). It could be interpreted that the increase in PCB concentration above 5 inches depth was due to a separate dumping event in approximately 1988. However, we feel that it is not likely, due to the sedimentation patterns. We postulate that the 1983 event was the source of PCBs in the top of the core, and that there was periodic mixing and deposition of older sediments on top of this layer, possibly from transport of fine particles from upstream where PCB concentrations were higher. There was another smaller peak in PCB concentration dating to about 1963, followed by a decline in PCBs with depth, which we interpret as an independent dumping event.

The reported peak usage of PCBs in the US was in the late 1960s. PCBs were banned in the 1970s (complete ban was 1979). Therefore, the peak we see corresponding to the

mid-1960's was as expected, with levels of PCBs in the canals decreasing before and after this peak, with the exception of the elevated levels near the top corresponding to the presumed dumping event. What was not expected, was that the concentrations were higher than predicted background levels throughout most of the core. For example, in 1970, we might expect to see a few parts per million PCBs, but in Core 7, the layer corresponding to that year was 21 ppm.

From 1929 to the late 1970s, transformer oil contained a high percentage of PCBs. Transformer oil (and related heat-transfer fluids), is a dense nonaqueous phase liquid (DNAPL). DNAPLs are heavier than water, so they will sink in water. If transformer oil were released into the canal, the oil would sink along a trajectory from the point of release, the distance depending on the flow rate of the water in the canal at the time, and factors that contribute to the dispersal of the oil including the turbulence of the water, and the amount of suspended sediments and dissolved organic matter that could carry the PCBs. If globules of transformer oil dropped to the sediments, they could theoretically migrate down into the sediments as a DNAPL, especially since the sediments were very watery and not densely packed. However, once the transformer oil was dispersed and diluted as it moved down the canal, it would no longer be a DNAPL, and would not sink into the sediment column. Instead, the PCBs would stick to the surface layer of the sediments (i.e., at the sediment-water interface). For this reason, we believed that this would be unlikely in Core 7, the sampling site located down the canal about half-way between Jefferson and Lake St. Clair.

PCBs can diffuse within the sediment column through water trapped between sediment particles (i.e., sediment porewater) in all directions, but they will not diffuse very far because they have a strong tendency to sorb (adhere) to sediment particles. Therefore, by diffusion, the PCBs would not have moved down the sediment very far as long as the sediments were undisturbed. We know that there has traditionally been a lot of human activity in the canals, and when water levels were low, boats and swimmers may have disturbed the sediments. The sediments above the hard-packed clay layer are loosely packed and watery, but since the depth of these sediments is so deep, and the total mass of those sediments is so great, there would not be complete mixing at any one time. We expect that several inches of sediments could have been disturbed from human

activity at any time causing some local mixing. However, we determined that there was definite sedimentation (strata) built up in the canals; layering was visible in the cores, and the pattern of the dating was as predicted. The concentrations of radiotracers (Cs, Pb, etc.) and PCBs were not homogenous throughout the core. Had the sediments been completely mixed, these patterns would not have emerged, and the concentrations would have been more homogenous.

There were elevated levels of PCBs present in the Ten Mile drainage system that were subsequently removed in the initial stages of the cleanup. Since Aroclor mixtures of PCBs are oily and denser than water, and since they stick to sediments, the PCBs may have been trapped in sediments within the drainage system for a long time, and when there was sufficient turbulence caused by rapid, high flows of water, some of the sediments/oil could have been washed out of the drain and into the canals. The sediment transport from the drainage system to the canals may be a function of lake levels for Lake St. Clair. Lake levels reached record highs in 1986-1987, which could have transported sediments out of the drains and into the canals, which should result in increased PCB concentrations corresponding to those dates. This would imply that in Figure 5, the rising peak dating to 1989 could actually correspond to 1987, which is within the 3-year range of accuracy. Conversely, high flows could wash PCBs out of sediments into the water column, resulting in a decrease in PCB concentration in those sediments. In either case, the fluctuation in lake levels every few years may be responsible for the fluctuation in PCB levels in sediments from the time the PCBs were dumped to the present.

Fine-grained sediments and dissolved organic matter in the water will transport PCBs as well as suspended sediments. Newly deposited sediments that are not carrying PCBs will in effect dilute the PCB-laden particles. Therefore, it is feasible that concentrations coming out of the drain and into the canal could vary significantly over time due to the variation in natural sediment deposition. Additionally, recent disturbances upstream before Core 7 was collected may have caused mobility of PCBs into the water followed by deposition of PCB-laden particles onto the top of Core 7. This may explain why the very top inch of the sediment had a higher concentration of PCBs than the layers below it. We would have expected to see the highest concentration in the layer corresponding to the contamination/dumping event, just as is apparent in the profile

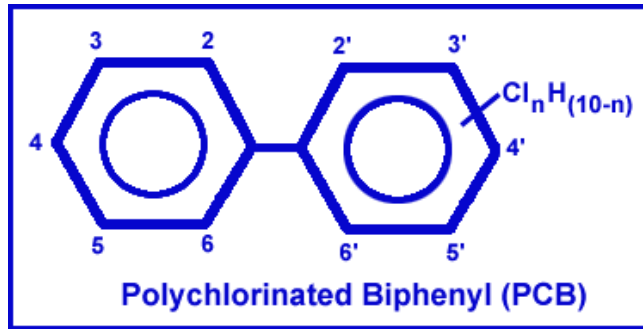
of the core between 10-20 inches. There should be a peak with decreasing concentrations above and below this peak. Therefore, there is some room for interpretation as to whether the release dating to 1983 was the last one, and whether resuspension of that release contributes to the contamination in the layers after 1983. We are hypothesizing that there was a one-time dumping event or source release that resulted in PCB discharges from early/mid 1980's to the present.

The radiochemical dating of Core 2 showed significant mixing, and showed that older sediments had been deposited at the surface of the sediment. Therefore, we cannot use this core to date the PCBs. We did evaluate concentrations of PCBs in Core 2, and found that there was a much higher concentration of PCBs at the very top of the core (over 300 ppm), just below which was about 50 ppm, and then decreased gradually by depth. The removal effort was being done in sections, and we collected Core 2 nearby that activity. We postulate that it may have been dredge material deposited on top, which was subsequently removed from the cleanup.

3.3 Characterization and Weathering of PCBs

When PCBs are stored in sediments for a prolonged period of time, they are subject to biodegradation by bacteria. This process, along with other physiochemical processes that change the composition of the PCB congeners is called weathering. An Aroclor mixture contains about 60 or so individual PCBs called congeners. In these sediments sampled from the Lange and Revere canals, there were about 45 different congeners detected in any one sample. Some PCB congeners biodegrade faster than others. As an Aroclor is weathered, its composition of the individual congeners changes slightly. This can makes Aroclor identification and quantification difficult. However, the weathering of the Aroclor mixture can also give us clues as to how long the PCBs have been there. The longer they've been there, the more the composition will change, in a somewhat predictable pattern. For example, ortho substituted positions (in the 2 and 6 positions; i.e., 2,2',6, or 6') are not easily biodegraded. The meta (3,3',5,5') and para (4,4') positions are more readily biodegraded. The following schematic shows the basic structure of PCBs and the positions where chlorine (Cl) may be substituted in place of hydrogen (H):

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Congeners can decrease in concentration and percent composition by biodegradation. Between the sediment-water interface, PCBs can desorb from sediments into the water column. Near the water surface, they can volatilize into air. Congeners that cannot be biodegraded will appear to be enriched, meaning that there will be an increase in percent composition, but not in concentration. When a chlorine atom is removed from a PCB molecule by biodegradation, as long as there are still other chlorine atoms still attached to the molecule, it is still a PCB, but now it is a different congener. Congeners with two chlorine atoms are called *di*-chlorobiphenyls; three chlorines makes a *tri*-chlorobiphenyl; four chlorines is a *tetra*-; five is a *penta*-; six is a *hexa*-; seven is a *hepta*-; and 8 is an *octa*- chlorobiphenyl, respectively. For example, when a *tetrachlorobiphenyl* loses a chlorine, it becomes a *trichlorobiphenyl*. Therefore, when we say that PCBs break down, we don't mean completely. Half-lives for PCBs are on the order of years to decades, depending on how many chlorine atoms they start out with, and depending on site-specific conditions.

The rate of weathering depends on several factors including the concentration of PCBs, the temperature, oxygen level, and types of bacteria present. Pure transformer oil is very stable. High ppm levels of PCBs will readily biodegrade. Levels lower than 50 ppm may not biodegrade much at all. At high levels of PCBs, bacteria adapt to using the PCBs as fuel (i.e., food source). At low PCB levels, PCB biodegrading strains of bacteria are not stimulated/induced to biodegrade PCBs. Citations in the literature reporting short half-lives for PCBs, or significant biodegradation of PCBs, refers to bioremediation experiments done in laboratories under favorable conditions, particularly with anaerobic bacteria that have been stimulated to biodegrade PCBs. This information has contributed

to a common misconception that PCBs can rapidly biodegrade under anoxic conditions in the environment. While most sediments are anoxic within millimeters of the surface if not disturbed, the reason that PCBs are a problem in the environment years after being banned is due to their stability and persistence in the environment.

The PCBs in Core 7 were similar in composition in the top layers. Chromatograms of standard solutions of Aroclor 1242 and 1254 and extracted canal sediments are presented in the Appendix, Figures 1 and 2, for a visual representation of the PCB mixtures. Note that the composition of any Aroclor mixture was not completely consistent from lot-to-lot. Aroclor 1242 contained approximately 42% PCBs by weight. The individual congeners may have varied, since the composition of any Aroclor mixture was not consistent lot to lot, but the overall pattern should be recognizable. As well, there were certain congeners that were indicative of each Aroclor mixture. For this reason, we can state with fairly high certainty that the PCBs in most of Core 7 were comprised of mainly Aroclor 1242, with 1254, and possibly 1260 to a lesser extent. The chromatograms of sediment samples from the dumping event dating to about 1983 are very similar in pattern to the sediments dating to the 1960s and both are suggestive of transformer oil. The composition of PCBs in the deeper part of the core appears to be different. However, transformer oil was known to be of a different composition before the mid-1950s. So, the PCBs in the deeper part of the core could also be from local use and/or disposal of transformer oil, or perhaps from a different source.

The concentrations of individual select congeners are presented in the Appendix, Figure 5. The congeners are identified by their IUPAC number (a number assigned by the International Union of Pure and Applied Chemistry) as well as their chemical name. Congeners were identified by retention time by ECD on two columns, plus confirmed by GC/MS. However, the deep core samples could not be confirmed by GC/MS because they were below detection limits on that instrument. Therefore, some specific congeners may have been misidentified, but if so, could be interpreted as having about the same level of chlorination as the reported congener by GC/ECD-ECD. The congener profile data suggest that some weathering took place, and that the composition of the PCB contamination was different at the bottom of the core compared to the top and mid sections. Some of the changes in individual congeners appear to be more gradual, and

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Comment [B6]: What was detection limit?

some more sharp and distinctive. A distinctive change suggests a different source, whereas a gradual change may be due weathering. There is a gradual change in the composition of some of the PCB congeners in layers of Core 7 corresponding to the late 1950s/early 1960s. There was a slight change in the percentage of IUPAC 8 pertaining to 1953. At about the same time, there was a distinct increase in IUPAC 169, which appears to be enriched in the deep core samples. IUPAC 169 is expected to be present in Aroclor 1260, but not in 1242 or 1254. Overall, there were more higher-chlorinated congeners in the deep core sample than the surface or mid-depth of the core. At the same time, there were decreases in IUPACs 101, 105, and 118, suggesting weathering and a difference in composition, namely an increase in the percentage of Aroclor 1260 present in the deep core.

Aroclor 1260 was used in transformers in the 1930s, but was being phased out after 1966 because it was discovered that the higher chlorinated congeners of Aroclor 1260 bioaccumulated and were very persistent in the environment. Unweathered Aroclor 1260 does not contain di-, tri-, or tetra- chlorinated congeners, which were found to be present in the deep core. Aroclor 1254 also should not contain any significant percentages of di- or tri-chlorinated congeners. Therefore, the deep core appears to contain some of the higher chlorinated congeners found in Aroclor 1260, and some lower chlorinated congeners either from the presence of other Aroclors and/or from substantial weathering of the original parent mixture.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Two cores were evaluated. The first one (Core 2) appeared to have older sediments deposited on top, and the sediments too disturbed to be dated. Core 2 was close to the ongoing dredging operation. The second evaluated core (Core 7) had radiochemical profiles that enabled the core to be dated. The PCB concentrations were high in the top several inches of the core dating back to early 1980's. The concentration decreased with depth for several inches, and then increased again, peaking at a layer corresponding to the early 1960's, and then decreased sharply with depth. The PCBs in the top and middle layers of the core appear to be similar in composition, with some

evidence of weathering with age. The PCB composition strongly resembles primarily Aroclor 1242 with 1254 and trace 1260 mixtures. This combination is consistent with transformer oils from these time periods. In the deeper part of the core dating back before the 1960's, there was a higher percentage of the higher chlorinated PCBs such as in Aroclor 1260, but also lower chlorinated PCBs suggesting a mixture of Aroclors and/or substantial weathering.

The differences in PCB composition in the core samples are consistent with what we know about the historical changes in composition of Aroclors used in transformers. It is possible that the PCB mixtures were used for something other than transformers, but the data suggest a transformer source. The PCB contamination in the Lange and Revere canals in St. Clair Shores appears to be due to improper disposal and/or leakage of PCBs, locally.

Although the drainage system feeding the canals has been cleaned, it drains a large urban watershed, and the Macomb County Public Works Office should consider having the drains and canals tested periodically for contamination. There is still a possibility that an old source could find its way into the system, and new types of contaminants could drain into the canals. The Public Works Office and other county authorities should address the sources of contaminants getting into the drainage system and canals and implement best management practices to reduce the probability of such contamination events from occurring. Finally, as scientists wanting to explore sources and causes of such events in order to provide solutions, we propose that a process-oriented study be conducted to identify sources of contaminants and to study their fate and transport. Routine monitoring and scientific studies can help implement improvements in water quality, and reduce the liability to fiduciary agencies.

APPENDIX

I. QUALITY CONTROL AND QUALITY ASSURANCE

The gamma ray detector was calibrated with NIST and IAEA spikes. The reproducibility was within 5-10%.

Duplicate Sample Analysis

The results of quantification of Aroclor 1242 for duplicate samples are presented below. Independent duplicate sediment samples were extracted and analyzed separately, and on different days.

Depth	Conc. (ppm)	Conc. (ppm)
4-5	28	23
5-6	4	5
6-7	17	19
7-8	23	20
14-15	21	21

Precision and Accuracy of Extraction and Analysis of Standard Reference Material (SRM)

The overall average recovery, calculated as the mean percent of the certified values was 88%. The precision of the four replicates was 19% variation. The SRM values were from soxhlet extractions, which inherently may yield different extraction efficiencies than supercritical fluid extraction (SFE).

Comparison of SFE values for 4 replicate extractions to SRM values
SRM 2978, NIST, Gaithersburg, MD

PCB Congener	IUPAC #	SRM Value (µg/kg)	SFE #1 (µg/kg)	SFE #2 (µg/kg)	SFE #3 (µg/kg)	SFE #4 (µg/kg)
2,2'5'-TCB	18	7	3.09	14.26	8.68	11.47
2,4'5' or 2,2,2,4'-TCB	31 or 17	21.4	9.2	13.54	11.37	12.46
2,2',5,5'-TeCB	52	17.7	22.47	37.62	30.05	33.83
2,2',3,5'-TeCB	44	11.8	2.1	1.54	1.82	1.68
2,2',4,5,5'-PCB	101	35.9	28.14	32.17	30.16	31.16
2,2',3,4,5,6'-HCB	144	17.9	15.92	17.73	16.83	17.28
2,3',4,4',5'-PCB	118	35.1	22.75	28.9	25.83	27.36
2,2',4,4',5,5'-HCB	154	56.9	12.18	31.84	22.01	26.93
2,2',3,4,4',5'-HCB	138	17.9	16.59	25.91	21.25	23.58
2,2',3,4,4',5,5'-HpCB	180	7.81	7.52	5.32	6.42	5.87

TCB = trichlorobiphenyl; TeCB = tetrachlorobiphenyl; PCB = pentachlorobiphenyl;
HCB = hexachlorobiphenyl; HpCB = heptachlorobiphenyl

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Figures Attached :

- 1. TIC Aroclor 1242** (annotated with PCB congeners by IUPAC #)
- 2. TIC Aroclor 1254** (annotated with PCB congeners by IUPAC #)
- 3. TIC Core 7 Depth 6-7''** (annotated with PCB congeners by IUPAC #)
- 4. Comparison of GC/dual ECD Chromatograms of top, mid, and deep core**
- 5. Profile of Select PCB Congeners in Core 7**