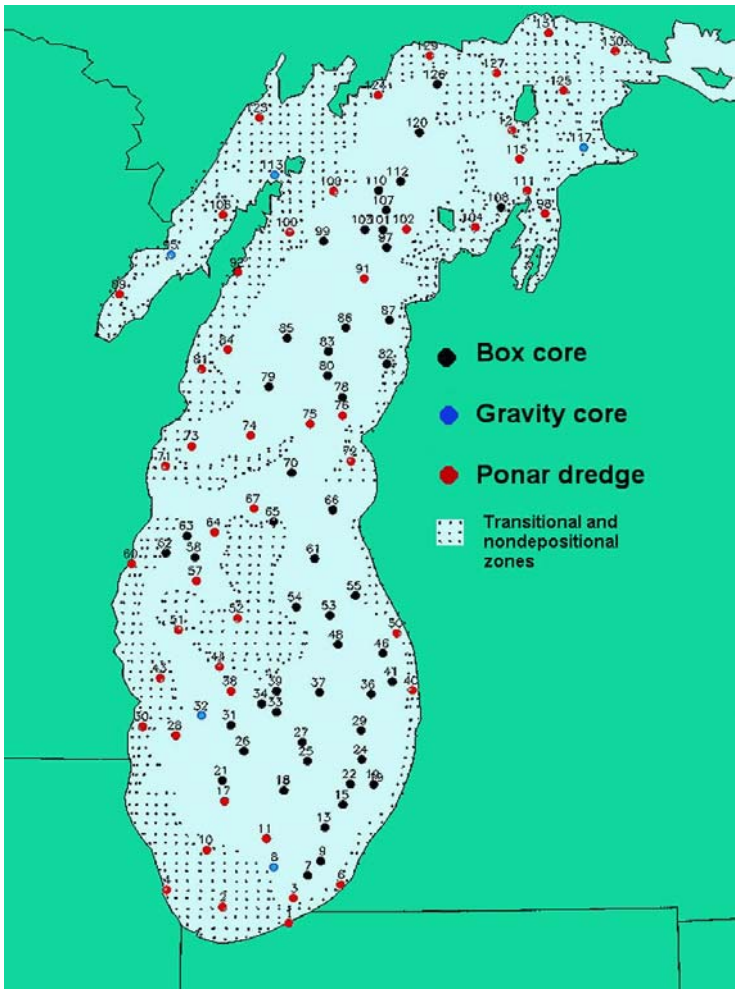
# Chapter 6
# PCBs/trans-Nonachlor in Sediment

## 6.1 Results

A total of 133 sediment samples were collected from 117 stations in Lake Michigan and 6 stations in Green Bay and analyzed for PCBs and *trans*-nonachlor. The samples were collected as described in Sections 2.2.4 and 2.5.4. Selection of sampling sites was based on prior information of the spatial distribution of sediment grain size, composition (e.g., organic carbon), sediment layer thickness, mixed layer depth, and $^{137}Cs$ and $^{210}Pb$ inventories. Emphasis was placed on sampling the more permanent accumulations of recent sediment in the depositional basins of the lake. Sediment samples were collected using three types of equipment: a box core, a Ponar dredge, and a gravity core.

The locations of the LMMB stations sampled by each of the three sampling methodologies are shown in Figure 6-1, along with the depositional classifications of Cahill (1981). Cahill developed the classifications of depositional, transitional and nondepositional zones in Lake Michigan from an examination of the physical description of sediment from 286 stations, grain size information, and echo-sounding tracks.

Figure 6-1. Sediment Sampling Stations




Recently deposited sediments were obtained from depositional basins through the use of a specially designed box corer. A modified Soutar box corer was used to retrieve cores approximately 60 cm in length, with extremely well preserved sediment-water interfaces. The 25- x 25- x 60-cm core was subsequently subcored with four 10-cm diameter butyrate tubes. Care was taken to preserve the interface and reduce distortion of the core upon insertion of the tube and during subsequent extrusion of the subcore. Two of the subcores were used for analysis of PCBs and *trans*-nonachlor, as well as to determine the organic carbon (OC) content of the sediment. A third subcore was used for analysis of radionuclides, trace elements, and biogenic components. The fourth subcore was archived. The sections of two cores from 0-1 cm were combined to allow for enough material for analysis of the PCBs and *trans*-nonachlor.

In transitional regions where recent deposits thinly overlie older glaciolacustrine clays, modern sediment is difficult to collect with a box corer. Therefore, a Ponar dredge was used at most transitional and nondepositional stations. However, this device does not collect modern sediment very efficiently, due to the bow wave's impact on the uppermost flocculent material. A gravity corer was used instead of a box corer at a few of the depositional stations, due to the lack of box coring capability of the vessel.

In addition to the core samples, sediment traps were deployed at eight locations (Figure 6-2), but the traps at two stations could not be recovered. Sample retrieval was successful at trap locations 1, 2, 5, 6, 7, and 8.

Figure 6-2. Sediment Trap Locations

As noted in Chapter 2, there are 209 possible PCB congeners and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. The investigators for the sediment portion of the study determined results for 105 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of the analytes:

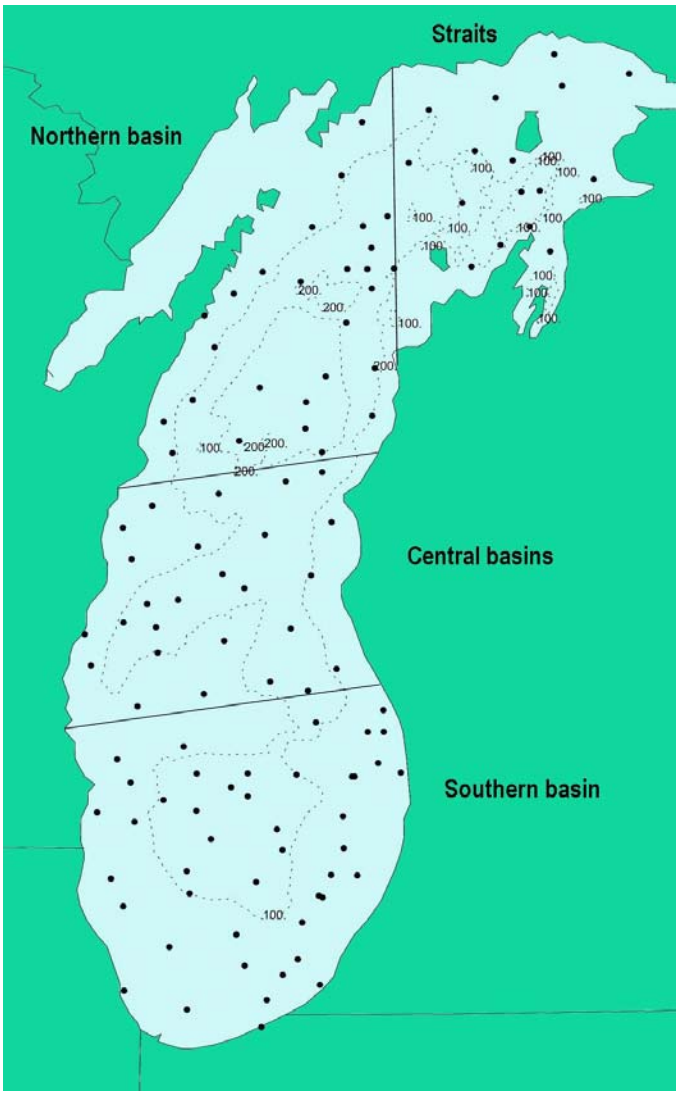
- The coeluting pair of PCB congeners 28 + 31 (2,4,4'-trichlorobiphenyl and 2,4',5-trichlorobiphenyl)
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

The PI for the sediment sample analyses focused on the coeluting pair 28 + 31 because of concerns that PCB congener 33 coeluted with the pesticide heptachlor. Based on matrix spike results for heptachlor and given the possibility that heptachlor was present in the sediments as a result of its historical use in the area around Lake Michigan, the PI flagged all of the PCB 33 results and presented data for PCB 28 + 31.

### 6.1.1 Geographical Variation

In addition to Cahill's three depositional zones, Lake Michigan can be divided into four geographical regions, based on characterizations of bottom morphology by the U.S. Department of the Interior (1967) (Figure 6-3):

Figure 6-3. Lake Michigan Basins




- The southern basin lies south of a line between Milwaukee and Muskegon. In this basin the bottom has a gentle relief and maximum depth of 180 m. The southern basin receives urban and industrial inputs of PCBs from Waukegan Harbor, IL, and the metropolitan areas of Chicago, IL, Gary, IN, and Milwaukee, WI.

- The divide area, located between the northern and southern basins, is bounded by two approximately east-west ridges. Two small depositional basins reside within the divide, the Grand Haven basin on the east side and the Milwaukee basin on the west side. For this study, the two basins' stations will be lumped together and referred to as the "Central basins."

- The northern basin is bounded by a line between Manitowoc and Manistee and another line from Frankfort to Manistique. Bottom topography of the northern basin is much more complex than the southern basin. A steep grade defines this basin resulting in a maximum depth of 282 m. The northern basin receives lower inputs from industrial and urban centers relative to the southern basin. However, the extent to which PCB-laden Green Bay sediments contribute to the northern basin's inventory is unknown.

- The straits area, including Grand Traverse Bay, has a very irregular bottom with isolated depressions where sediments accumulate. Its morphology is more similar to that of northern Lake Huron than northern Lake Michigan.

Green Bay samples were not included in this analysis, because only six stations were visited, and these stations were not the focus of the LMMB Study.

The summary statistics for the four basins are provided in Table 6-1.

Table 6-1. Summary Statistics for Surficial Sediments

| Analyte | Basin | N | Mean (ng/g) | Range (ng/g) | Std. Dev. (ng/g) |
|---|---|---|---|---|---|
| Organic Carbon* | Southern | 50 | 22.634 | 0.440 - 42.620 | 14.346 |
| | Central | 22 | 22.755 | 0.930 - 49.920 | 17.280 |
| | Northern | 32 | 21.479 | 0.430 - 41.490 | 15.999 |
| | Straits region | 16 | 12.172 | 1.560 - 46.070 | 16.042 |
| PCB 28+31 | Southern | 50 | 4.593 | 0.0490 - 16.486 | 3.841 |
| | Central | 22 | 2.563 | 0.110 - 11.558 | 2.855 |
| | Northern | 31 | 1.879 | 0.0111 - 4.010 | 1.466 |
| | Straits region | 16 | 0.405 | 0.0625 - 1.640 | 0.493 |
| PCB 118 | Southern | 50 | 3.271 | 0.0130 - 9.840 | 2.608 |
| | Central | 22 | 2.668 | 0.0404 - 7.190 | 2.478 |
| | Northern | 31 | 2.176 | 0.00653 - 4.940 | 1.709 |
| | Straits region | 16 | 0.404 | 0.0655 - 1.660 | 0.493 |
| PCB 180 | Southern | 50 | 1.562 | 0.00740 - 4.783 | 1.318 |
| | Central | 22 | 1.223 | 0.00570 - 3.512 | 1.179 |
| | Northern | 31 | 1.070 | 0.00299 - 2.400 | 0.873 |
| | Straits region | 16 | 0.175 | 0.0264 - 0.745 | 0.238 |
| Total PCBs | Southern | 50 | 69.724 | 0.545 - 219.288 | 53.114 |
| | Central | 22 | 50.541 | 1.240 - 149.390 | 49.406 |
| | Northern | 31 | 41.599 | 0.138 - 91.220 | 33.102 |
| | Straits region | 16 | 7.271 | 1.056 - 28.600 | 9.187 |
| *trans*-Nonachlor | Southern | 49 | 0.599 | 0.00250 - 2.830 | 0.522 |
| | Central | 21 | 0.638 | 0.00576 - 2.243 | 0.644 |
| | Northern | 32 | 0.560 | 0.00661 - 1.200 | 0.456 |
| | Straits region | 16 | 0.168 | 0.0296 - 0.681 | 0.217 |

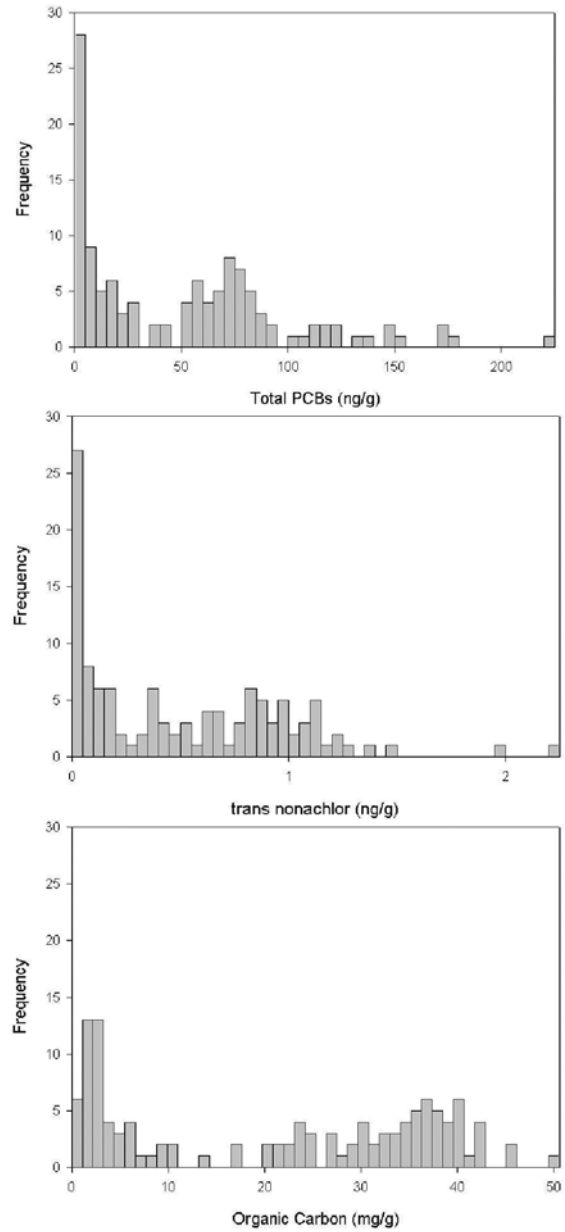
* Units for organic carbon content are mg/g.

The mean concentrations of the PCB congeners and total PCBs in Table 6-1 exhibit a general trend of decreasing concentrations from south to north, with the lowest concentrations in the Straits region. In contrast, the mean concentrations of *trans*-nonachlor, while lowest in the Straits region, exhibit no south to north trend. The organic carbon content data exhibit a pattern similar to that for *trans*-nonachlor.

### 6.1.2 Frequency Distributions

Frequency distributions of total PCBs, *trans*-nonachlor and organic carbon (OC) content for surficial sediment samples from Lake Michigan are shown in Figure 6-4. These data are not normally distributed. It should also be noted that these distributions are biased as a result of our emphasis on sampling the depositional regions of the lake, especially in the southern basin.

**Figure 6-4. Frequency Distributions of Total PCBs, *trans*-Nonachlor, and Organic Carbon**




Total PCBs exhibit a wide range in concentration. Although not a true bimodal distribution, two distinct groups are evident within the total PCB distribution. The first group of samples, from nondepositional and transitional stations, has very low concentrations that exponentially decline in number with increasing concentration (0 - 30 ng/g). The second group of samples taken mainly from depositional sites (35 - 225 ng/g) is more normally distributed, though tailing toward higher levels is evident.

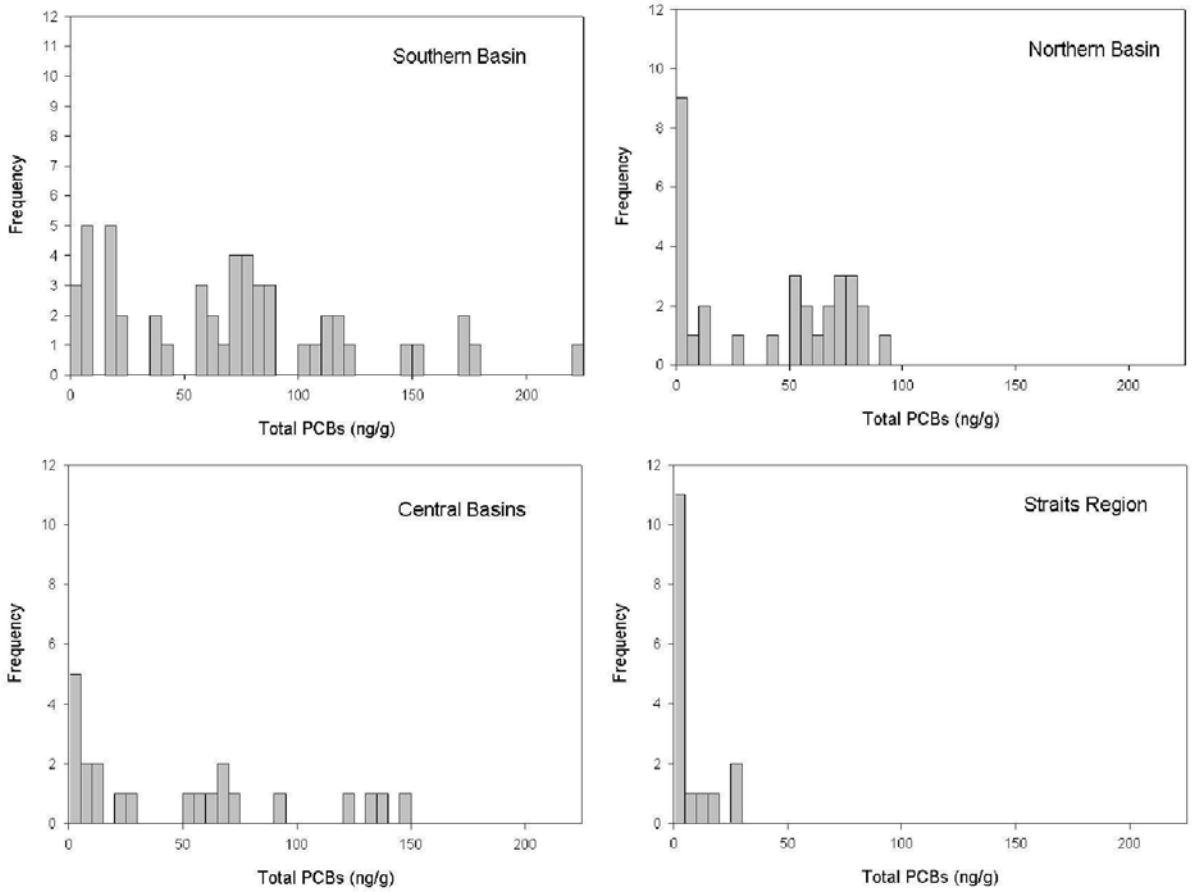
While the distribution of *trans*-nonachlor also is skewed toward lower concentrations in nondepositional and transitional regions (0 - 0.2 ng/g), this compound's distribution in the depositional region (0.25 - 2.25 ng/g) differs from PCBs by being more evenly distributed. The distribution of OC more closely resembles a bimodal distribution with the first peak representing nondepositional and transitional stations (0 - 11 mg/g), and the second peak representing depositional stations (20 - 51 mg/g).

The frequency distribution of total PCBs in each of the regions are shown in Figure 6-5. Even when divided by basin, the total PCB data are not normally distributed. It should also be noted that these distributions are biased as a result of our emphasis on sampling the depositional regions of the lake, especially in the southern basin. Because of this sampling bias, less discussion is devoted to a statistical comparison of basins. Instead, more emphasis is placed on descriptions of their lake-wide distribution (contour maps), and examining relationships of these chlorinated organic contaminants (COCs) with OC in later sections.

The total PCB data from all four basins are skewed toward lower concentrations. The large number of low PCB concentrations in these sediments is not unexpected, given the relatively large area of the nondepositional and transitional regions in Lake Michigan, which tend to have lower silt and clay content, and thus lower particle-associated contamination. The range in concentration is wider in the

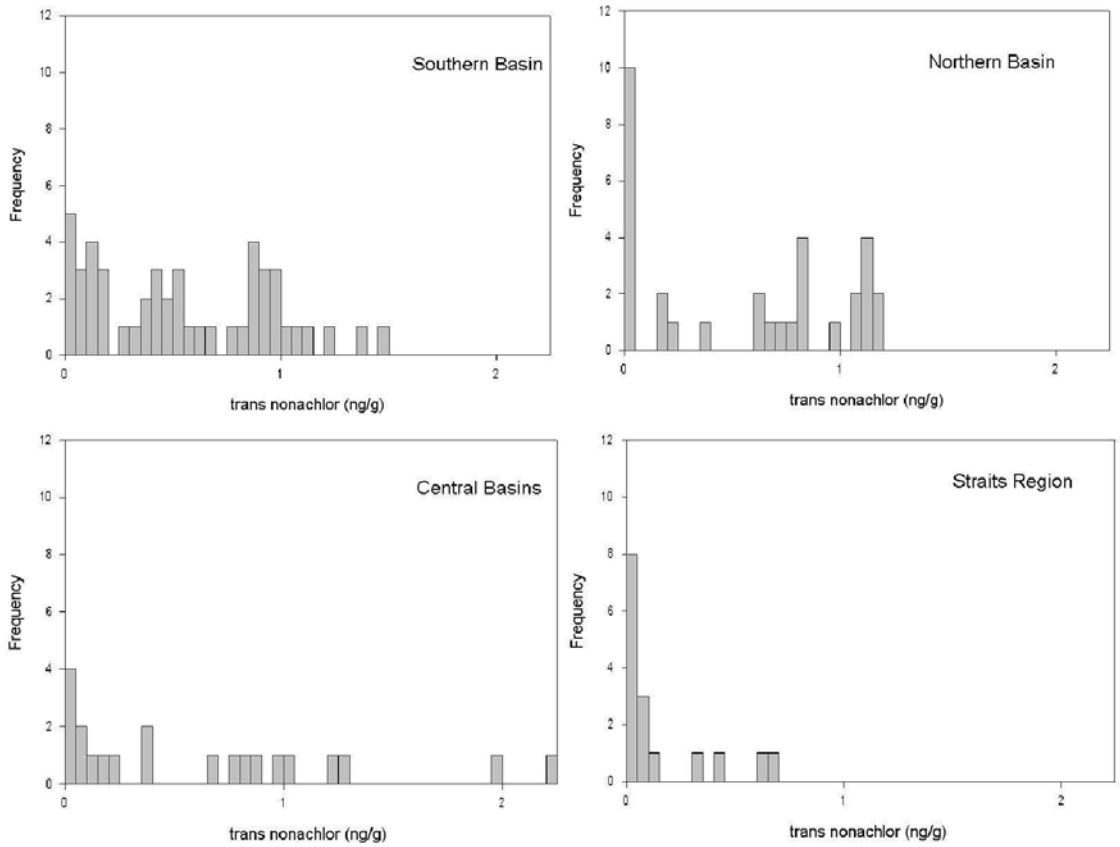
northern basin than straits region, while the southern and central basins have an even wider range due to a few stations with very high concentrations. Only in the southern and central basins did total PCBs exceed 100 ng/g, and only in the southern basin did total PCBs exceed 150 ng/g. The distribution of PCB would indicate that the accumulation of this contaminant is not evenly distributed throughout the lake but rather is preferentially collecting in depositional areas.

Figure 6-5. Frequency Distributions of Total PCBs by Basin




The distribution of *trans*-nonachlor for all basins is generally similar to that of total PCBs (Figure 6-6). One notable exception is the relative similarity of ranges between basins for *trans*-nonachlor.

Figure 6-6. Frequency Distributions of *trans*-Nonachlor by Basin




## 6.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the *Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of data quality issues for the sediment PCBs and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and *trans*-nonachlor monitoring in this study.

### 6.2.1 Sample Collection

The LMMB work plan indicated that 131 sediment sampling sites were to be visited. Field records indicated that only 117 stations were actually sampled. Of the eight sediment trap locations to be sampled, sample retrieval occurred at trap locations 1, 2, 5, 6, 7, and 8. Numerous attempts were made to retrieve samples from trap locations 3 and 4, but they were not successful.

The LMMB work plan specified that the sediment depth intervals to be sampled was from 0 to 1 cm. Actual intervals sampled and analyzed ranged from 0-0.5 to 0-1.5 cm, due to sporadic slanting at the top surface of the core after retrieval.

During examination of the field collection records for field duplicates, it was discovered that some field duplicates were not actually collected at the same time as the field sample due to equipment mobilization. Samples collected within five minutes of each other were considered field duplicates (FD1), and if more than five minutes elapsed, the samples were considered sequential field duplicates (SFD1). Separate labeling of these data points as FD1 and SFD1 was done in order to assess if precision differed based on the elapsed time.

### 6.2.2 Data Assessments

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 6-2 provides a summary of flags applied to the sediment PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. Compared to other matrices, the percentage of results that were qualified for these criteria is relatively small.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB results were corrected for the recoveries of the surrogates. The *trans*-nonachlor results were *not* surrogate-corrected. Only 0.5% of the PCB 28 +31 results, 2% of PCB 118 results, and 1% of the PCB 180 results were qualified for surrogate recovery problems (Table 6-2).

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. The results for the matrix spike samples were compared to the MQO for spike recoveries (50 - 125%). Analytical results associated with matrix spike samples with recoveries below the MQO limits were flagged with failed matrix spike and low bias flags and results associated with matrix spike samples that had recoveries higher than the MQO limits were flagged with failed matrix spike and high bias flags. Analytical results were considered invalid and flagged as such when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. No sediment *trans*-nonachlor samples failed the matrix spike MQOs. None of the results for PCBs 28+31 or 180 were flagged as failing the matrix spike MQOs. For PCB 118, 5% of the results were flagged as failing the matrix spike MQOs.

Field blanks were collected for PCBs and *trans*-nonachlor. When field blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with the failed field blank sample code (FRB). Field blanks were not collected at all stations, so potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sampling equipment, collection, processing, shipping, storing, and analysis can be evaluated based on the field blanks collected throughout the study. For PCB 28+31, 11% of the field samples were associated with a field blank in which this congener was reported above the sample-specific detection limit (Table 6-2). None of the field sample results for *trans*-nonachlor were qualified because of field blank results.

Field duplicates were to be collected at a frequency of 5%. Duplicate samples collected within 5 minutes of each other were considered field duplicates. However, an examination of the field collection records indicated that some of the planned field duplicates were not collected within that 5-minute time frame as a result of problems with equipment mobilization or the time required to pump the sample through the filter and resin cartridge. Those "duplicates" that were collected more than 5 minutes apart were considered "sequential field duplicates" and the data were labeled accordingly (e.g., SFD1 vs. FD1). Combining the field duplicates and sequential field duplicates, the actual rate of collection of duplicates was 5.5%.

The results from the original field sample and the associated duplicate were compared on the basis of the relative percent difference (RPD). The RPD value for each PCB congener and *trans*-nonachlor was compared to the MQO for field duplicate precision. None of the field samples results for PCBs or *trans*-nonachlor were qualified because of the field duplicate precision (FFD) concerns (Table 6-2).

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 6-3 provides a summary of data quality assessments for several of these attributes for the sediment PCB and *trans*-nonachlor data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessment of the field duplicate results were divided into two concentration regimes. One measure of system precision was calculated for those results that were less than 5 times the sample-specific detection limit (SSDL) of the analyte and a separate measure was calculated for those results that were greater than 5 times the SSDL. However, none of the sediment sample results with corresponding field duplicates contained PCB 28+31, 118, or 180 at concentrations below the SSDL. The precision of the field duplicate results above the SSDL ranged from 19 to 24% for the PCB congeners in Table 6-3.

Three of the four field duplicate pairs contained *trans*-nonachlor below the SSDL and the mean precision of those pairs was 37%, compared to one field duplicate pair containing *trans*-nonachlor above the SSDL, with an RPD of 26%.

The variability of the laboratory measurement technique was assessed through the preparation and analysis of laboratory duplicate pairs. Eleven laboratory duplicate pairs were analyzed for the PCB congeners, and ten pairs were analyzed for *trans*-nonachlor. The laboratory duplicate precision ranged from 9 to 13% for the PCB congeners and *trans*-nonachlor (Table 6-3). As expected, the laboratory duplicate results are more precise than the field duplicate results.

Table 6-2. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in Sediment Samples

| Analyte | Flags | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sensitivity | | Contamination | Precision | Bias | | | | | | |
| | MDL | UND | FFR | FFD | FSS | FMS | LOB | HIB | INV | FBK | FDL |
| PCB 28 + 31 | 5% (11) | 0 | 11% (23) | 0 | 0.5% (1) | 0 | 0 | 0 | 0 | 0 | 0 |
| PCB 118 | 3% (6) | 0 | 0 | 0 | 2% (3) | 5% (10) | 0 | 0 | 0 | 0 | 0 |
| PCB 180 | 6% (13) | 0 | 0 | 0 | 1% (3) | 0 | 0 | 0 | 0 | 0 | 0 |
| *trans*-Nonachlor | 28% (54) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
UND = Analyte not detected (Analyte produced no instrument response above noise.)
FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
INV = Invalid.
FBK = Failed laboratory blank (Laboratory reagent blank result greater than the SSDL).
FDL = Failed laboratory duplicate

Table 6-3. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Sediment Samples

| Analyte/Number Field Samples | Parameter | Number of QC samples | Assessment |
|---|---|---|---|
| PCB 28 + 31<br>197 samples | System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL | 0 field duplicate pairs | — |
| | System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL | 9 field duplicate pairs | 16 % |
| | Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL | 11 lab duplicate pairs | 10% |
| | Analytical Bias - Mean Laboratory Matrix Spike Recovery (%) | 24 matrix spikes | 102% |
| | Analytical Sensitivity - Samples Reported as < SSDL (%) | - | 6% |
| PCB 118<br>189 samples | System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL | 0 field duplicate pairs | — |
| | System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL | 9 field duplicate pairs | 17% |
| | Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL | 11 lab duplicate pairs | 9% |
| | Analytical Bias - Mean Laboratory Matrix Spike Recovery (%) | 24 matrix spikes | 112% |
| | Analytical Sensitivity - Samples Reported as < SSDL (%) | — | 3% |
| PCB 180<br>196 samples | System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL | 0 field duplicate pairs | — |
| | System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL | 9 field duplicate pairs | 18% |
| | Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL | 11 lab duplicate pairs | 13% |
| | Analytical Bias - Mean Laboratory Matrix Spike Recovery (%) | 24 matrix spikes | 108% |
| | Analytical Sensitivity - Samples Reported as < SSDL (%) | — | 7% |
| *trans*-Nonachlor<br>185 samples | System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL | 8 field duplicate pairs | 25% |
| | System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL | 0 field duplicate pairs | — |
| | Analytical Precision - Mean Laboratory Duplicate RPD (%), > 5 * SSDL | 10 lab duplicate pairs | 12% |
| | Analytical Bias - Mean Laboratory Matrix Spike Recovery (%) | 22 matrix spikes | 88% |
| | Analytical Sensitivity - Samples Reported as < SSDL (%) | — | 28% |

RPD = Relative percent difference
SSDL = Sample-specific detection limit

Analytical bias was assessed using the results from matrix spike samples. The mean recoveries of the analytes were excellent for the PCBs, ranging from 102% to 112% for the PCB congeners in Table 6-3. The mean recovery for *trans*-nonachlor was very good, at 88%. Thus, these results demonstrate that the analytical techniques applied to the field samples introduce little or no bias into the PCB results, and a slight low bias into the *trans*-nonachlor results.

## 6.3 Data Interpretation

### 6.3.1 Comparison to Historical Studies

LMMB surficial sediment concentrations of total PCBs were compared to measurements made by Swackhamer and Armstrong (1988), Hermanson *et al.* (1991), and Golden (1994). Swackhamer and Armstrong (1988) collected 20 box cores from the southern and Grand Haven depositional basins in 1978-1980. Hermanson *et al.* (1991) collected five box cores from the northern, southern and Grand Haven basins in 1984. More recently, Golden (1994) collected four box cores from the northern and southern basins in 1991 and 1992. Only box cores taken from depositional regions were used for this comparison because of the lack of permanent sediment accumulation in the transitional and nondepositional regions.

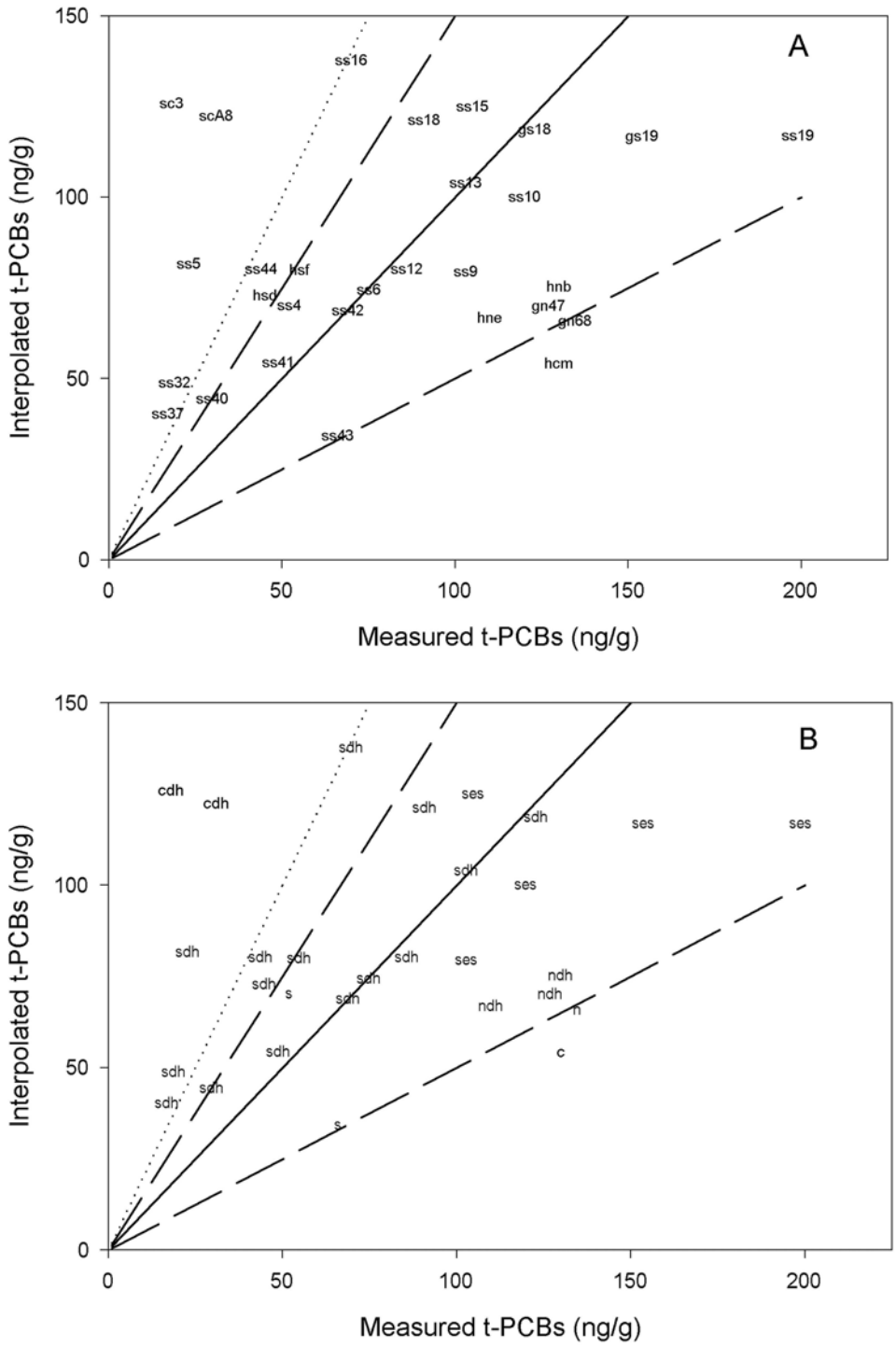
Swackhamer and Armstrong (1988) and Hermanson *et al.* (1991) used Aroclor analysis to quantify total PCBs. Aroclor analysis using COMSTAR, a multiple linear regression analysis program that provides the best fit to Aroclor composition, has been shown to compare favorably (90-95%) with total PCBs measurements using congener analysis (Burkhard and Weininger, 1987). Interpolated values from the contour map of LMMB surficial PCBs (1994-1995) were compared to the measured historical values. Plots of the interpolated versus measured total PCB values are shown in Figure 6-7.

Differences between LMMB values and historical measurements are compared to gains/loss lines (solid line, 0% change; dashed lines, 50% gain or loss; dotted line, 100 % gain). In Figure 6-7A, the author, basin, and station are designated for each data point (s= Swackhamer and Armstrong [1988]; h=Hermanson *et al.* [1991]; g=Golden [1994]). In Figure 6-7B, the stations are divided into basins (n=north, c=central, s=south) followed by areas within basins (dh=deep hole, es=eastern side).

It appears that in the southern deep hole (sdh) and central deep hole (cdh) regions, total PCB levels have either increased (35 → 100%) or remained un-changed since they were measured in 1978-1984. In contrast, 4 of 5 stations on the eastern side of the southern basin (ses) exhibited reductions in PCB concentrations.

In the northern basin, surficial sediment total PCBs appear to have declined significantly (~40%) since Hermanson's 1984 collection, and even over the 3-year period since Golden's 1992 collection. It is possible that the northern basin's complex topography results in a very heterogenous distribution of total PCB sediment concentrations. Thus, comparisons of historical data with recent interpolated values could be misleading. There is other evidence, however, that a significant decline in total PCB levels is occurring in the northern basin. A core profile of total PCBs at LMMB station 103 indicates that a 33% decline in PCB concentrations has occurred since the early 1980s. Looking at Golden's sediment core profiles, a loss of only 1-9% was noted for two northern cores between about 1984 and 1992. However, a 30% loss was noted between about 1980 and 1992.

Figure 6-7. Comparison of Measured Historical Total PCB Results in Surficial Sediment and Interpolated Total PCB Results from Contours of the 1994-1995 LMMB Collections




0% change — 50% gain or loss ..... 100% gain

See text for the key to the letter designations of each data point.

Since PCBs were banned from use in North America in 1979 and loadings to the Great Lakes have decreased (Eisenreich *et al.*, 1989; Rapaport and Eisenreich, 1988), reductions in surficial sediment PCB content are expected. Decreasing sediment PCB concentrations have been observed in Lakes Ontario and Superior (Golden *et al.*, 1993). The lack of a decline in sediment PCB content in the southern basin of Lake Michigan may result from sediment focusing processes that redistribute the PCB inventory, and/or continued external source inputs.

### 6.3.2 Other Interpretations and Perspectives

#### *6.3.2.1 Relationship of PCB Congeners and trans-Nonachlor with Sediment Organic Carbon*

Concentrations of PCBs and *trans*-nonachlor in surficial sediments increase with increasing organic carbon (OC) content. The correlations of these two variables, however, were not very strong on a linear scale ($r^2$ = 0.25 - 0.67). The spread in the data suggest that the southern basin stations were significantly higher in contamination. Dividing the stations into groups, based on basin morphology and regional inputs, may explain some of the variability and improve OC correlation.

Generally, the concentrations of PCB congeners and *trans*-nonachlor increased with sediment organic carbon content according to a power equation,

$$[PCB] = a \times [OC]^b$$

This power equation best described the relationship of PCB congeners and *trans*-nonachlor with sediment organic carbon in all four regions of Lake Michigan. Coefficients of the power relationship were obtained by log transformation of the data and fitting the linear relationship,

$$\log[PCB] = A + (B \times \log[OC])$$

Linear regressions for the four compounds in each of the four regions are shown in Figures 6-8 - 6-11. Coefficients for the relationships are listed in Table 6-4. The $r^2$ values for these relationships, ranged from 0.865 - 0.977, indicating a strong correlation between the two variables. This finding was expected as hydrophobic compounds are known to partition strongly to organic matter. The southern basin PCB relationships exhibited an additional feature not seen in other basins. A peak in PCB concentration was observed at ~25 mg/g OC for PCB 28+31 and at ~35 mg/g for PCB 118 and PCB 180 (Figure 6-8). *trans*-Nonachlor did not exhibit such a peak.

A comparison of coefficient results was used to discern any differences in compound behavior between basins, as well as differences between compounds within a basin. Congener-specific behavior within a basin was examined by comparing regression slopes (i.e., extent of association with OC). A slope greater than 1 suggests that enrichment of the compound is occurring with increasing OC content. A slope of 1 also indicates a linear relationship of contaminant content with OC content, while a slope of < 1 indicates a dilution of contaminant content with increasing OC content. Non-unity slopes may result from differences in OC composition or PCB loadings between nearshore sandier stations and offshore siltier stations.

Generally, slopes were >1 for all chlorinated organic contaminants in the southern, central and northern basins. An exception occurred for PCB 28+31 in the southern and central basins where the slopes ranged from 0.88 to 1. In the straits region, all compounds exhibited slopes <1.

Significant differences in slopes between compounds for a specific basin are designated by dissimilar superscripts in Table 6-4. For the southern and central basins, a difference in PCB congener behavior was

noted. Within these basins, the slopes of the more highly chlorinated congeners, PCB 118 and PCB 180 were significantly greater than those of the trichlorobiphenyls, PCB 28+31. In the northern basin, only congeners PCB 180 and PCB 28+31 were significantly different. For the straits region, no significant difference in slopes was observed between congeners.

The relationship of *trans*-nonachlor with OC did not follow the same pattern as any particular PCB congener. No significant differences between the slopes of trans-nonachlor and any of the PCB congeners were noted for the central basins and straits region. However, in the southern basin, the slope for *trans*-nonachlor was lower than that of PCB 180, while in the northern basin its slope was lower than the slopes for PCB 118 and PCB 180.

Figure 6-8. Relationships of PCB/*trans*-Nonachlor Concentrations and Organic Carbon Content for the Southern Basin

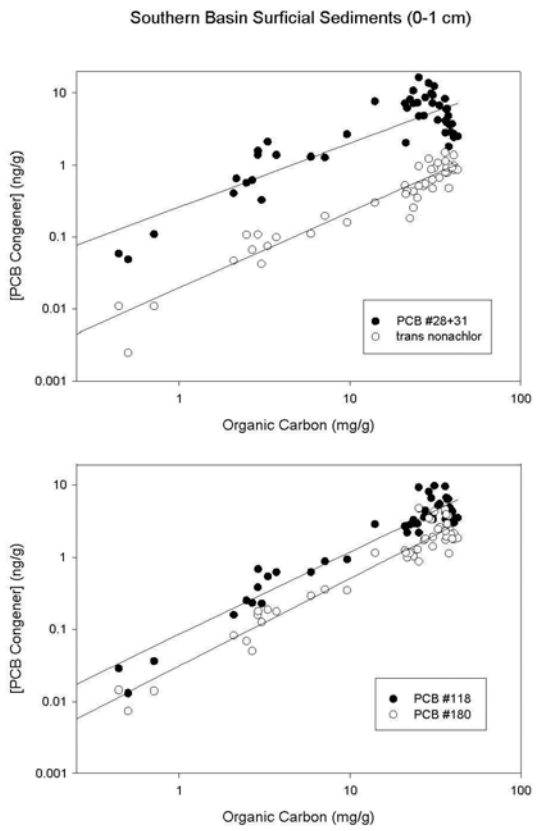



Figure 6-9. Relationships of PCB/*trans*-Nonachlor Concentrations and Organic Carbon Content for the Central Basins

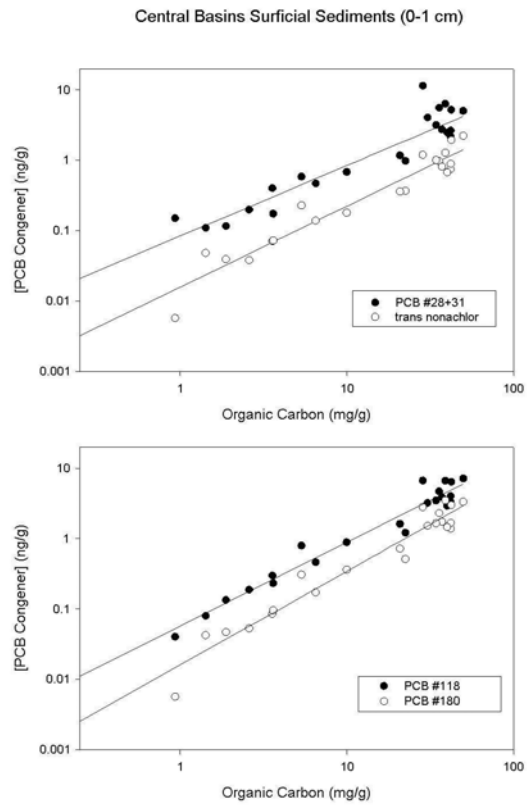


Figure 6-10. Relationships of PCB/*trans*-Nonachlor Concentrations and Organic Carbon Content for the Northern Basin

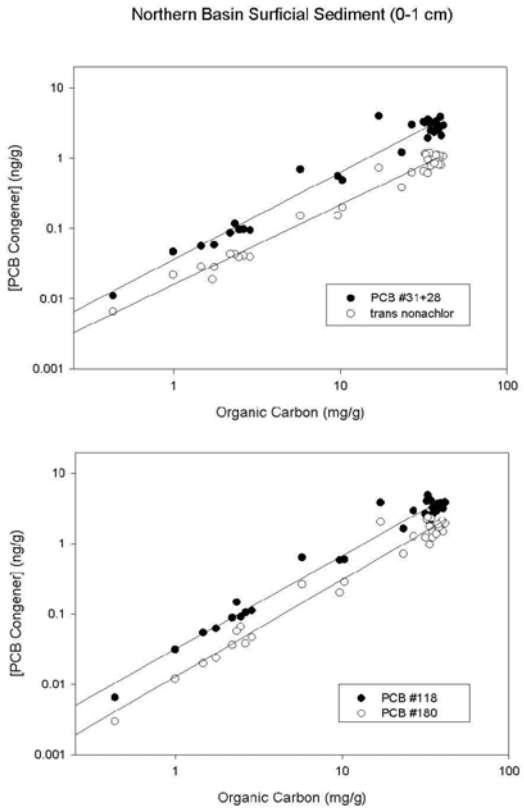



Figure 6-11. Relationships of PCB/*trans*-Nonachlor Concentrations and Organic Carbon Content for the Straits Region

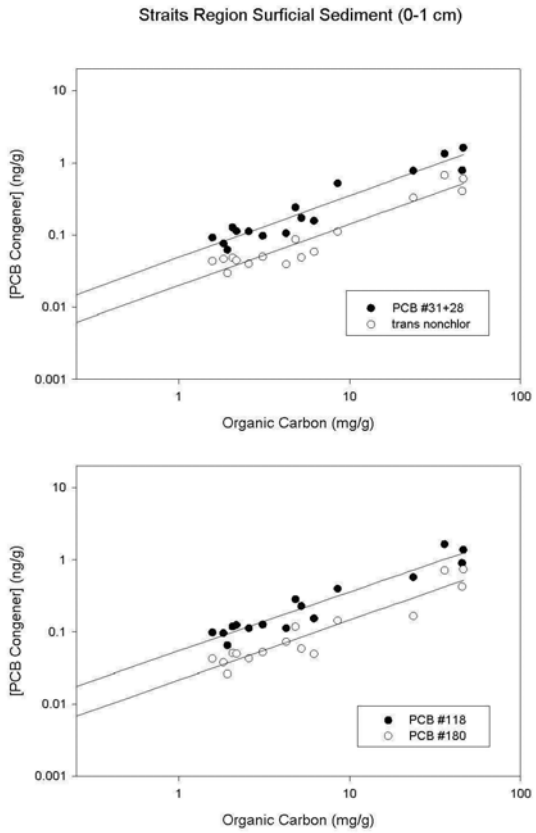


Table 6-4. Linear Regression Parameters of Log PCB and *trans*-Nonachlor versus Log OC Content in Surficial Sediments in Lake Michigan

| Basin | Parameter | PCB 28+31 | PCB 118 | PCB 180 | *trans*-Nonachlor |
|---|---|---|---|---|---|
| Southern | slope | 0.8809[a] | 1.1461[bc] | 1.2178[b] | 1.0761[c] |
| | intercept | -0.5799 | -1.0717 | -1.5113 | -1.7336 |
| | $r^2$ | 0.7329 | 0.9810 | 0.9370 | 0.9048 |
| | n | 50 | 50 | 50 | 48 |
| Central | slope | 1.003[a] | 1.1884[b] | 1.3326[b] | 1.1500[ab] |
| | intercept | -1.076 | -1.2402 | -1.7968 | -1.8006 |
| | $r^2$ | 0.9160 | 0.9562 | 0.9457 | 0.9278 |
| | n | 21 | 22 | 22 | 21 |
| Northern | slope | 1.2393[ac] | 1.3269[bc] | 1.3763[b] | 1.1341[a] |
| | intercept | -1.4384 | -1.4963 | -1.8870 | -1.7966 |
| | $r^2$ | 0.9611 | 0.9718 | 0.9691 | 0.9773 |
| | n | 31 | 31 | 31 | 32 |
| Straits | slope | 0.8587[a] | 0.8160[a] | 0.8307[a] | 0.8496[a] |
| | intercept | -1.3100 | -1.2589 | -1.6658 | -1.7002 |
| | $r^2$ | 0.9138 | 0.9189 | 0.8870 | 0.9095 |
| | n | 16 | 16 | 16 | 16 |
| Whole lake | slope | 1.091 | 1.2215 | 1.2945 | 1.0878 |
| | intercept | -1.0893 | -1.2938 | -1.7365 | -1.7645 |
| | $r^2$ | 0.7587 | 0.9024 | 0.9077 | 0.9300 |
| | n | 119 | 120 | 120 | 117 |

Dissimilar superscripts denote a significant difference ($p<0.05$) in slopes between compounds for a specific basin.

Several general observations can be made based on the relationships of organic carbon content and the chlorinated organic contaminants for each of the basins (Table 6-5). For the high molecular weight (HMW) congeners, PCB 118 and PCB 180, and *trans*-nonachlor, the straits region slopes were significantly lower than the other basins, and the northern basin slopes were higher than those of the southern basin (except for *trans*-nonachlor). For the low molecular weight (LMW) congeners, PCB 28+31, the northern basin slope was significantly higher than for all other basins. No significant difference was detected between slopes for PCB 28+31 in the central, southern and straits regions. Interestingly, the southern basin stations that had high OC content and lower than expected PCB concentrations were located in the basin's deep hole at >100 m depth; *trans*-nonachlor did not exhibit reduced concentrations at the deep-hole stations. If these stations are excluded from the regressions, then the slopes of the southern basin (1.11 for PCB 28+31, 1.23 for PCB 118, 1.27 for PCB 180) are not significantly different from those of the central and northern basins for all PCB congeners tested.

The intercept parameter is an indication of the level of contamination as a net result of loading and removal rates. For *trans*-nonachlor, the intercept was similar for all four basins, suggesting that regional inputs may be similar if removal rates are not significantly different between basins (Tables 6-7 and 6-8). At the other end of the spectrum, PCB 28+31 had higher intercepts in the southern and central basins relative to the northern basin and straits region. The HMW congeners, PCB 118 and PCB 180 had higher intercepts in the southern basin than the northern basin, while the intercepts in the central basins and straits region fell in between.

In summary, while it would appear at first glance that there is not much of a relationship of either PCB or *trans*-nonachlor concentration to the OC content of surficial sediments in Lake Michigan, strong power relationships resulted when the stations were divided into basin groups. The association between *trans*-nonachlor concentration and sediment OC does not vary throughout the lake's basins, except in the straits

region. For the PCB congeners, more variability in their associations with sediment OC was noted between basins. The variability appears to result, in part, from differences in regional source input functions. Other variables that control burial, such as sedimentation rate, residence time in the sediment mixed layer, sediment focusing processes, and compound hydrophobicity, may also influence PCB associations with particles and particulate OC in Lake Michigan.

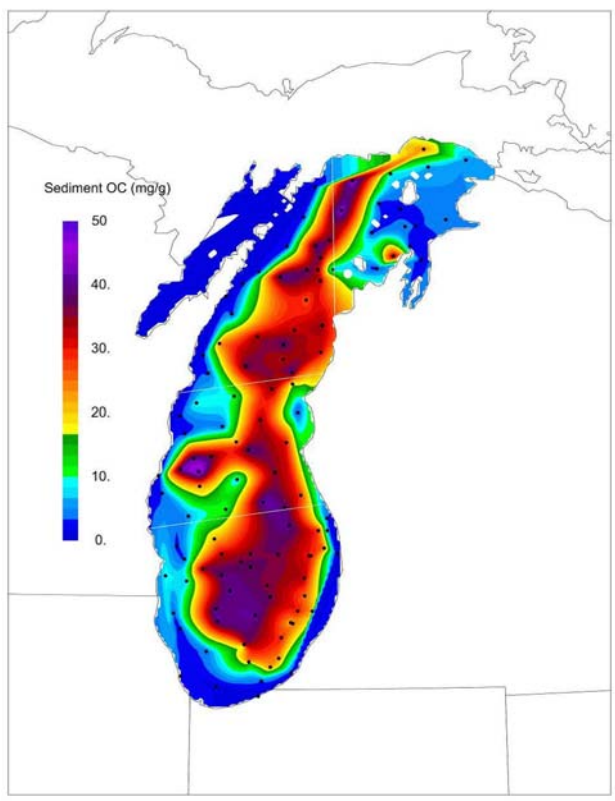
Table 6-5. Significant Differences between Linear Regression Parameters among Lake Michigan Basins for Log Analyte versus Log Organic Carbon

| Analyte | Regression Parameter | Significant Differences at $\alpha$ = 0.05 | | | |
|---|---|---|---|---|---|
| | | Southern (So) | Central (C) | Northern (N) | Straits (St) |
| PCB 28+31 | slope | N | N | C, St, So | N |
| | intercept | C, N, St | So, N, St | C, So | C, So |
| PCB 118 | slope | N, St | St | So, St | C, So, N |
| | intercept | N, St | N | C, So, St | N, So |
| PCB 180 | slope | N, St | St | So, St | C, So, N |
| | intercept | C, N | So | So, St | N |
| *trans*-Nonachlor | slope | St | St | St | C, So, N |
| | intercept | -- | -- | -- | -- |

### *6.3.2.2 Contour Maps*

The data for the 117 LMMB stations were used to create contour maps of surficial sediment concentrations for organic carbon, total PCBs, PCB 28+31, PCB 118, and PCB 180, and *trans*-nonachlor (Figures 6-12 - 6-17). Note that the contour maps for PCB congeners are normalized to the highest concentration measured in order to facilitate comparisons.

Figure 6-12. Contour Plot of Organic Carbon Content in Lake Michigan Sediments




High OC concentrations (20-50 mg/g) are associated with the accumulation of recent sediments in the depositional and transitional regions of Lake Michigan (Figure 6-12). In addition, the OC distribution in Lake Michigan generally tracks with the depth contours of the lake (Figure 6-18). Sediment OC concentrations > 30 mg/g are generally found at depths greater than 100 m. The other cluster of high OC content stations is located in the eastern portion of the southern basin. These sites are located at a depth range of 45 - 85 m and have OC contents of 20 - 33 mg/g. The cluster of low OC content stations (< 10 mg/g) includes those generally located at depths less than 100 m. Stations that do not fall within these three clusters are either located in transition areas, or located in the straits area. Stations in the straits region tend to have higher OC content than other stations located at similar depths.

PCBs are also accumulating in the depositional and transitional regions of Lake Michigan (Figure 6-13). In particular, PCBs accumulate at relatively high concentrations (> 100 ng/g) along the eastern side of the southern basin, as well as at a few of the deeper stations in the southern and central basins. Enrichment of most PCB congeners with increasing OC content in sediments was demonstrated by the slopes of greater than 1 for the relationship of log PCB versus log OC(except the straits region, Table 6-4). Localized input sources may contribute to the depositional pattern and explain the enrichment of PCBs relative to OC. Southern basin surficial sediment concentrations have a higher maximum, and greater areal coverage for the high Total PCB concentration range (>100 ng/g) than the northern basin. Additionally, focusing processes may be responsible for concentrating PCBs into select regions of the lake.

The contour maps of PCB 118 and PCB 180 exhibit similar distribution patterns to one another throughout Lake Michigan (Figures 6-15 and 6-16). The accumulation of these PCB congeners occurs in the depositional and transitional regions with the highest concentrations located in the deepest parts of the southern and central basins, and in the upper half of the eastern side of the southern basin. The straits region has some of the lowest concentrations of these two PCBs despite having some stations with relatively high levels of OC content.

The contour map for PCB 28+31 provides evidence of accumulation in the surficial sediments of the lake's depositional and transitional regions (Figure 6-14). Relative to PCB 118 and PCB 180, however, elevated concentrations of PCB 28+31 are found on the eastern side of the southern basin and for Station 55, in the Grand Haven basin. A plot of the concentrations of PCB 28+31 versus PCB 180 for stations in the southern and central basins illustrates the enhanced levels of this low molecular weight PCB congener on the eastern side of the southern basin (Figure 6-19). In contrast, depositional/transitional stations located in the rest of the lake, including the northern basin (not shown), are about a factor of four lower in their concentrations of PCB 28+31, for a given concentration of PCB 180. PCBs 15+17 (not shown) also demonstrated enrichment in this region, while PCB 101 (not shown) and PCB 118 had a one-to-one correspondence with PCB 180 (Figure 6-19). Other stations with elevated levels of PCB 28+31 relative to PCB 180 are located in nearshore nondepositional areas (< 25 km offshore) with low concentrations of PCBs: along the northern coast, and western coast of the southern and central portion of the lake. Note that Waukegan Harbor and Green Bay also have elevated levels of PCB 28+31 relative to PCB 180, due to point-source contamination of Aroclors 1242 and 1248 (Swackhamer and Armstrong 1988, and Manchester 1993).

Figure 6-13. Contour Plot of Total PCBs in Lake Michigan Sediments

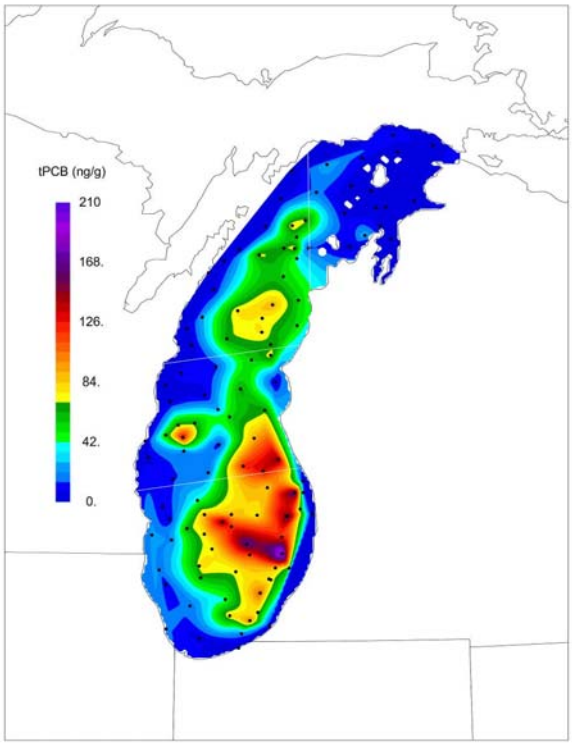



Figure 6-14. Contour Plot of PCB 28+31 in Lake Michigan Sediments

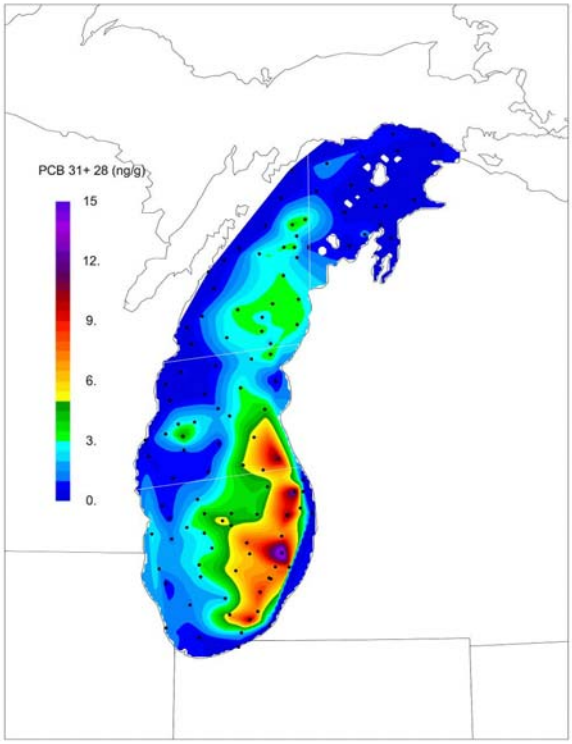



Figure 6-15. Contour Plot of PCB 118 in Lake Michigan Sediments

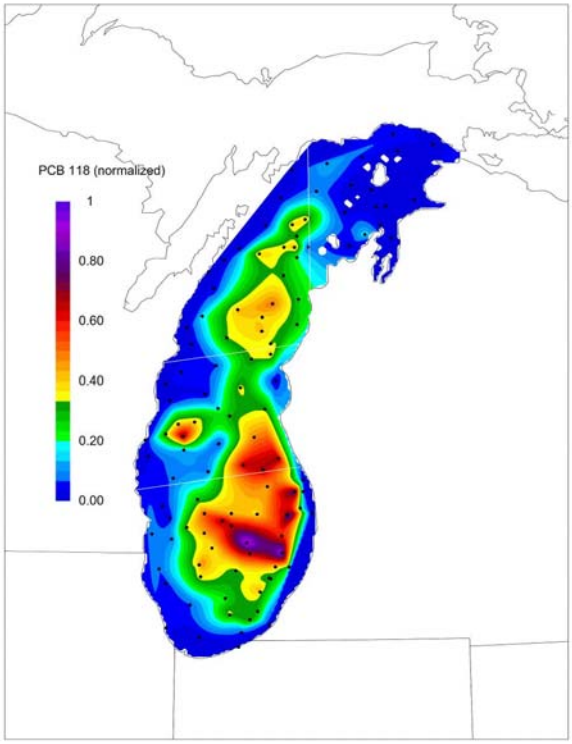
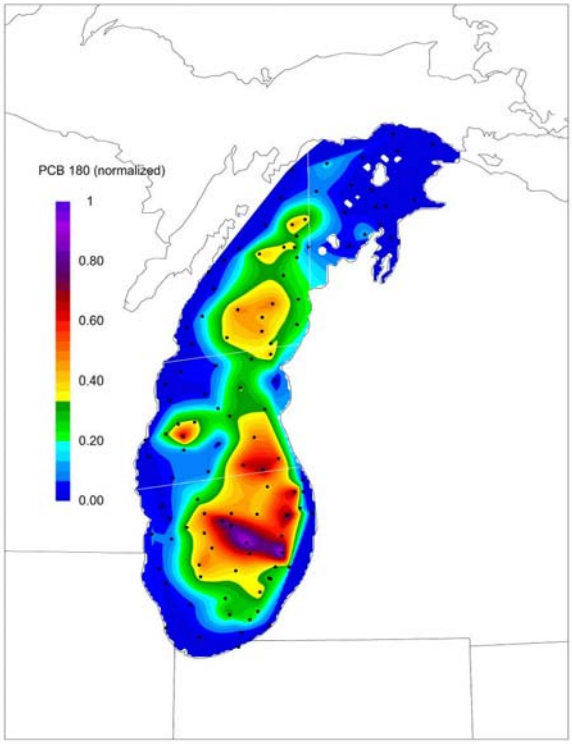



Figure 6-16. Contour Plot of PCB 180 in Lake Michigan Sediments



*trans*-Nonachlor is also accumulating in the depositional and transitional regions of Lake Michigan. Unlike PCBs, *trans*-nonachlor is not preferentially accumulating along the eastern side of the southern basin. Nor does *trans*-nonachlor have the elevated concentrations in the southern basin relative to the northern basin that PCBs exhibit. The log-log slope of 1.09 for *trans*-nonachlor and OC suggests more of a linear relationship and less of a power relationship with OC compared to PCBs.

Figure 6-17. Contour Plot of *trans*-Nonachlor in Lake Michigan Sediments

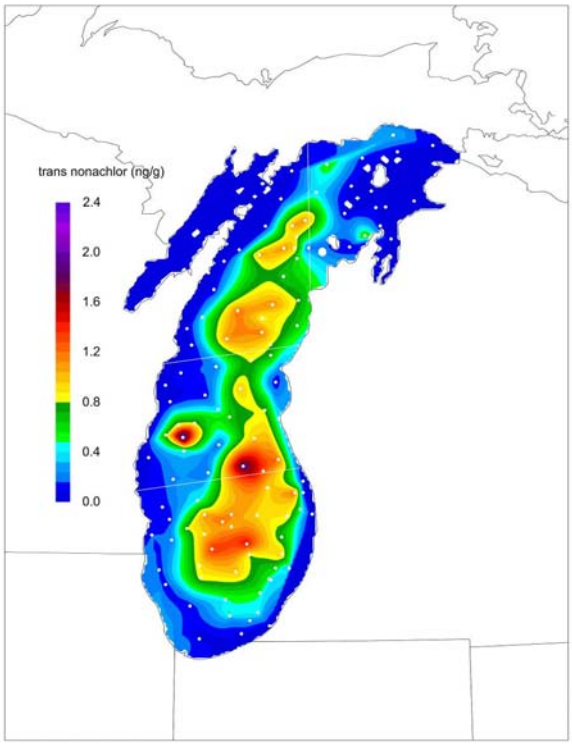



Figure 6-18. Organic Carbon Content versus Depth in Lake Michigan

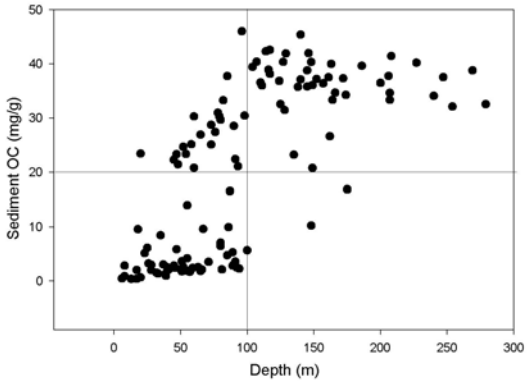
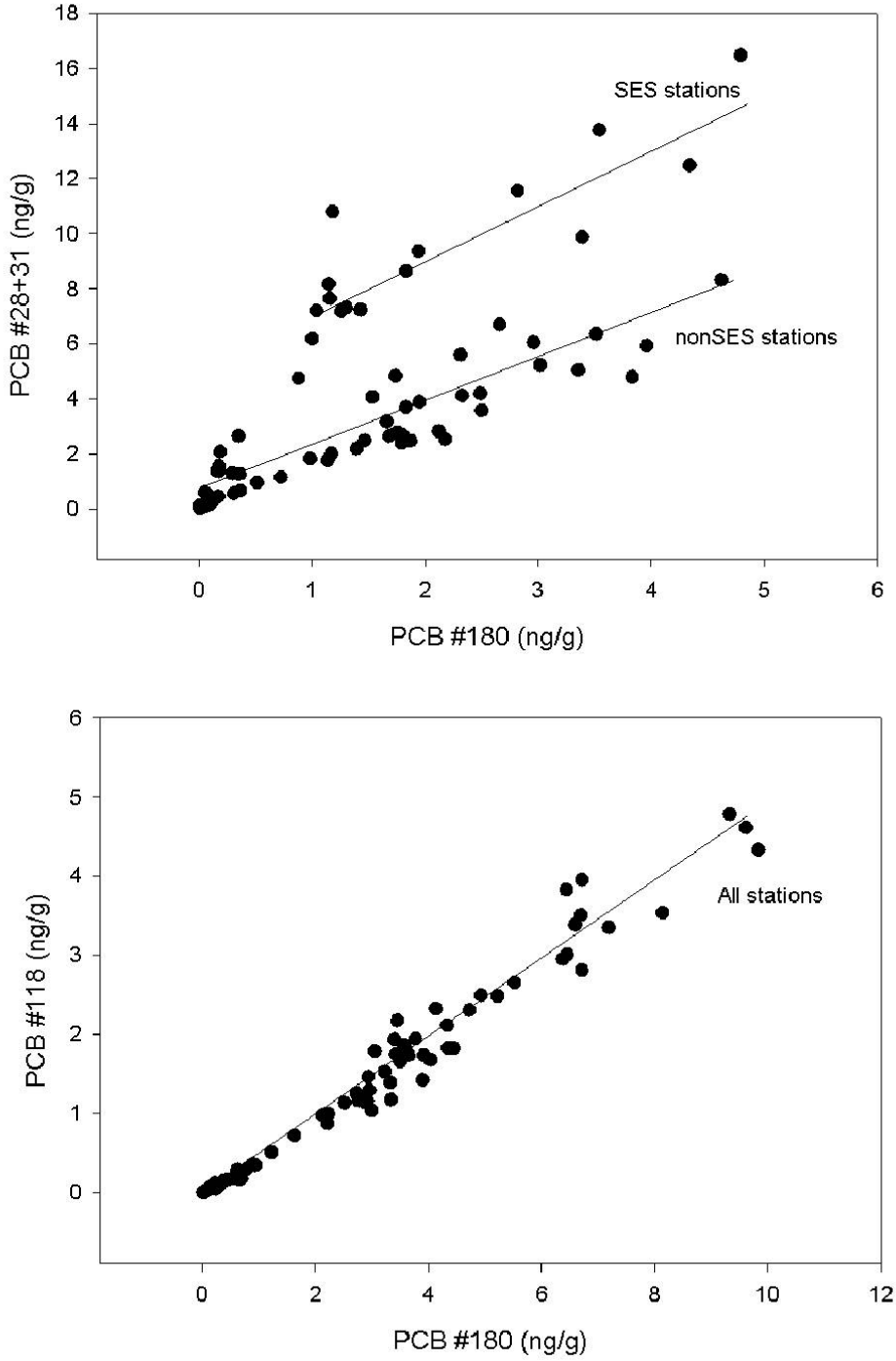



Figure 6-19. Plot of PCB 28+31 Concentrations versus PCB 180 Concentrations in Lake Michigan Sediments