

Final Report

On:

Congener-Specific Characterization and Source Identification of PCB Input To Los Angeles Harbor

To:

Shirley Birosik

California Regional Water Quality Control Board
Los Angeles Region
101 Centre Plaza Drive
Monterey Park, California
91754-2156

Under Standard Agreement
No. 7-184-140-0

From:

Robert Eganhouse, Richard Gossett and G. Patrick Hershelman

Southern California Coastal Water Research Project
646 West Pacific Coast Highway
Long Beach, California
90806

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EXECUTIVE SUMMARY

In 1988 a study was initiated to evaluate the extent of PCB contamination in Los Angeles Harbor and to investigate possible sources of PCBs to harbor waters and sediments. Surficial sediments (0-2 cm) were collected from 18 locations within the inner harbor. In addition, materials were collected from the Hugo-Neu-Proler metal recycling facility, and water samples (microlayer, subsurface water) were obtained from the East Turning Basin during periods when scrap metal was being loaded onto ships and when loading was not occurring. Water samples were filtered to isolate the suspended particulate matter for subsequent analysis. These samples were analyzed for a variety of constituents including PCBs, total extractable organic matter, total organic carbon, total nitrogen, total suspended solids (water samples only) and iron.

The highest degree of PCB contamination in surficial sediments from the inner harbor is found along Consolidated Slip, near Todd Shipyards (Wharf A/B) and adjacent to the Hugo-Neu-Proler facility. Concentrations of Σ PCB at these locations reach 1.5, 1.9 and 11.4 $\mu\text{g dry g}^{-1}$, respectively. Concentrations of Σ PCB in other areas of the harbor (e.g. East Turning Basin, Main Channel, West Basin) generally fall within 0.05-0.30 $\mu\text{g dry g}^{-1}$, approximately one to two orders of magnitude lower than the highest concentrations found in the harbor. The compositions of the PCBs are variable, but at most locations the distributions are dominated by the more highly chlorinated isomers ($\geq \text{Cl}_5$). Harbor sediments collected from the loading area adjacent to Hugo-Neu-Proler, particularly those deposited immediately below the metal conveyor, appear to be an exception to this rule. These sediments contain greater quantities of the lower chlorinated species (i.e. $< \text{Cl}_5$). They also exhibit high concentrations of extractable organic matter, organic carbon and iron.

Examination of debris deposited beneath the conveyor (on land) at the the Hugo-Neu-Proler site indicates that this material is heavily contaminated with PCBs (22-39 $\mu\text{g dry g}^{-1}$). The composition of the PCBs is dominated by the lower chlorinated species (i.e. $< \text{Cl}_5$) and no DDT was detected in this material. The debris is also characterized by relatively high concentrations of organic carbon, extractable organics and iron. Because the subtidal sediments deposited near the Hugo-Neu-Proler facility exhibit anomalously high Σ PCB/ Σ DDT ratios and concentrations of iron, extractable organic matter, TOC and Σ PCB compared with other harbor sediments, it is apparent that the contamination at this site is attributable to loss of shredded metal debris from the conveyor, primarily during loading operations. The similarity of the PCB compositions of the conveyor debris and the sediments deposited beneath the conveyor and their dissimilarity to sediments from other parts of the harbor further support this hypothesis.

Results obtained for the microlayer samples taken during loading and non-loading conditions indicate that the Hugo-Neu-Proler facility is contributing PCB-bearing particulates to harbor waters. The Σ PCB concentrations found in replicate microlayer samples collected during the loading of scrap metal were 21.1 and 58.4 $\mu\text{g dry g}^{-1}$. These concentrations are similar to those found in the Hugo-Neu-Proler conveyor debris, and they agree with measurements made by Cross *et al.* (1987) in a previous study at this same location (also during loading conditions). The PCB compositions of the microlayer particles are dominated by lower chlorinated species (i.e. $< \text{Cl}_5$), and the patterns closely resemble those of the conveyor debris. In addition, no DDT metabolites were observed in these samples, and the iron and total organic carbon contents of the suspended particles were essentially identical with those of the conveyor debris. These facts combined with the visual observation of an extensive

brown slick generated by the loading operation, clearly indicate that losses of scrap metal debris are contributing to contamination of harbor waters. The concentrations of all constituents were lower in the suspended particles isolated from both the subsurface water samples and the samples collected during non-loading conditions. However, the absence of DDT in the non-loading microlayer sample and similarities between PCB composition of this sample and that of the Hugo-Neu-Proler site material indicate that PCBs are probably being introduced to the harbor on a chronic basis. This must result from atmospheric transport of aerosols generated at the metal processing site.

In summary, sediments of the harbor are contaminated with PCBs when compared with more pristine coastal sites. Three possible sources of PCB to the harbor, Todd Shipyard, Consolidated Slip/Dominguez Channel and Hugo-Neu-Proler, have been identified. The latter of these is clearly a source of contamination to sediments deposited near the recycling facility. This is the area where shredded scrap metal is loaded onto ships. Our data indicate that contamination of both sediments and surface waters is occurring during the loading operations. In the case of the sediments, this can probably account for most of the PCB contamination at the site. However, it is clear that the Hugo-Neu-Proler facility may also represent a chronic source of PCBs to the harbor as evidenced by the presence (in the microlayer) of PCBs which are similar in composition to those found in the scrap metal debris.

INTRODUCTION

The Los Angeles/Long Beach Harbor complex contains one of the largest port facilities in the world. It is also an area that is highly industrialized and includes a U.S. Navy shipyard, fish canneries, chemical manufacturers, small boat docks, commercial fisheries and a host of other businesses. Unfortunately, one of the more persistent classes of environmental contaminants known to man, the polychlorinated biphenyls (PCBs), are associated with some of these industries.

A review of the published literature reveals that surprisingly few studies of PCB contamination have been undertaken in Los Angeles Harbor. Consequently, our knowledge of the sources of PCBs to the harbor environment and their distribution within it is limited. Mearns *et al.* (1990) summarize most of the available sources of data for both sediments and organisms collected from the harbor since ca. 1973. These consist largely of surveys conducted by SCCWRP scientists during the 1970s and more recent efforts by the California State Mussel Watch (SMW) program. The SMW program has existed since 1980 and seeks to identify PCB (and other contaminant) hotspots through the use of caged mussels.

Chen and Lu (1974) reported surficial sediment concentrations of total PCB ranging from 340 ng dry g⁻¹ in the Main Channel area to 3750 ng dry g⁻¹ at Consolidated Slip (see Figures 1,2). Similarly, Gossett (unpublished data) found a mean of 848 ng dry g⁻¹ (n=3) total PCB in sediments collected during 1985 from the East Basin. These concentrations exceed those typically found in pristine coastal (shelf) sediments by factors of 1 to 3 orders of magnitude (Word and Mearns 1979). However, they are significantly lower than (i.e. by a factor of more than 3) PCB concentrations reported for contaminated sediments collected near the Los Angeles County Sanitation Districts' outfall system off Palos Verdes in 1977 (Word and Mearns 1979). Unfortunately, outside of unpublished reports associated with environmental impact assessments (e.g. dredging permits), these are believed to be the only data on sediment concentrations of PCB from the inner harbor.

Young and Heesen (1974) reported concentrations of PCB 1254 in mussels (*Mytilus edulis*) indigenous to the inner harbor ranging from 140 to 440 ng wet g⁻¹. These concentrations are as much as an order of magnitude greater than those found in mussels collected from relatively pristine coastal sites (Young *et al.* 1978; Mearns *et al.* 1990). Although other anthropogenic products known to contain PCBs (e.g. hydraulic fluids, lubricants) were not investigated by Young and Heesen (1974), antifouling paints were identified as a potential source of PCB contamination in the harbor environment. Furthermore, a correlation between PCB concentrations in mussel tissues and those in nearby sediments led Mearns and Young (1978) to suggest that the sediments could be acting as a source of contamination to the indigenous biota.

The California State Mussel Watch occupies several stations within the harbor. Results obtained over the last five years have identified areas in the inner harbor where concentrations of PCB bioaccumulated by the caged mussels have been unusually high (greater than 100 ng wet g⁻¹ total PCB). In particular, mussels collected from the site located at Berth 211 (near Hugo-Neu-Proler; cf. Figure 1) have consistently exhibited the highest total PCB concentrations. Mean concentrations reported for the years 1985, 1986 and 1989 were 433, 374 and 500 ng wet g⁻¹, respectively. Other highly contaminated sites include Todd Shipyard at 131 ng wet g⁻¹ in 1989, Consolidated Slip at 136 ng wet g⁻¹ in 1989 and West Basin at 229 ng wet g⁻¹ in 1988. These data can be compared to the most contaminated monitoring site in San

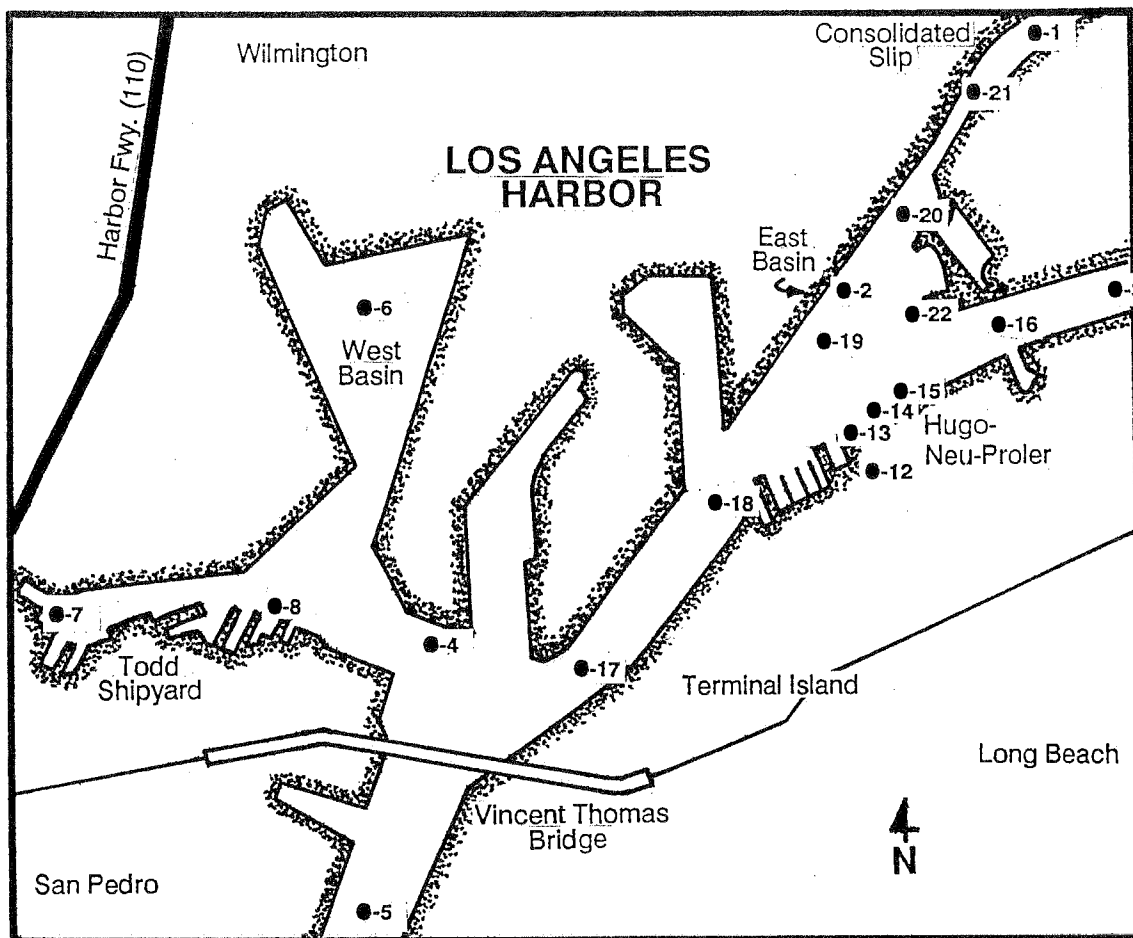


Figure 1. Map indicating sediment sample locations used in the Los Angeles Harbor study.

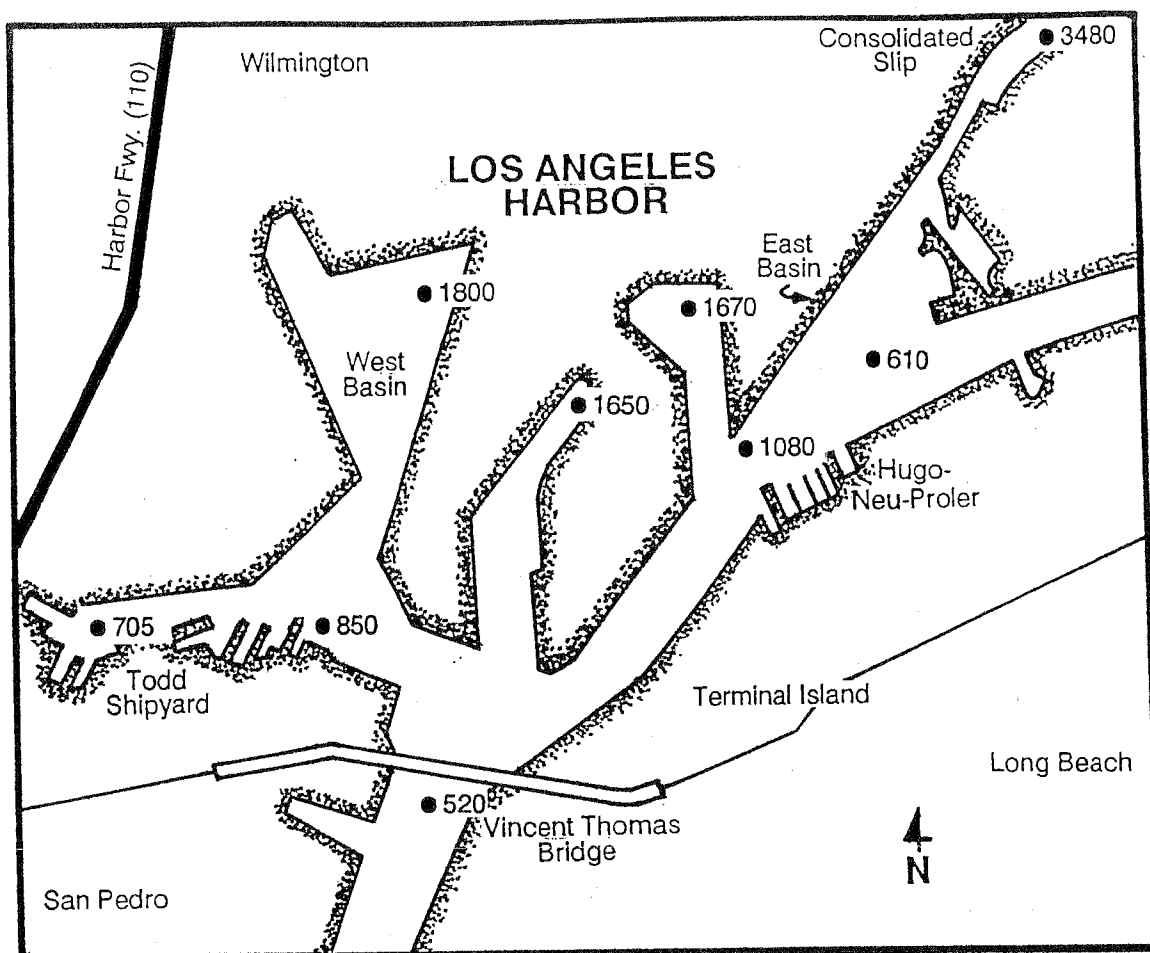


Figure 2. Concentrations (means; ng dry g^{-1}) of total PCBs in Los Angeles Harbor surficial sediments, 1973 (after Chen and Lu, 1974).

Diego Harbor (2740 ng wet g⁻¹) and Royal Palms, the site closest to the Los Angeles County Sanitation Districts' municipal wastewater outfall system (20.6 ng wet g⁻¹).

Based on these findings, officials from the Los Angeles Regional Water Quality Control Board (M. Sowby, S. Birosik) approached SCCWRP in March of 1988 to request that an investigation be conducted to help better define the distribution of PCBs within the harbor and to identify potential sources of PCB contamination. The project was conceived as a preliminary survey of the sediments and several industrial sites in anticipation of possible regulatory/enforcement action. The premise of the study was that if discrete industrial sources of PCB were contributing to the contamination of the harbor and if these sources were unique with respect to PCB composition, an assessment of the relative importance of each source might be feasible. The technical approach we have used is based on the application of recently developed methods for "fingerprinting" PCB contamination. These "congener-specific" methods involve the identification and quantitation of 80 chromatographic peaks representing as many as 111 of the 209 possible PCB congeners.

In this Final Report we present findings of the preliminary study initiated in 1988. Owing to the scope of this project, our analysis of the data is relatively limited. However, we do intend to exploit this dataset through the use of multivariate statistical techniques. This should help establish differences between the PCB compositions of the harbor samples and increase our confidence in determining relations between potential sources and environmental sinks.

MATERIALS AND METHODS

Sampling Design

This study was conducted in two phases. In the first phase, we collected 8 surficial sediment samples from subtidal sites within the inner harbor including Todd Shipyard, Consolidated Slip and East Turning Basin on October 31, 1988 and November 8, 1988 (stations 1-8; Figure 1). This phase of the project was envisioned primarily as a reconnaissance effort to determine the PCB compositions (and concentrations) in harbor sediments and the extent to which materials at the Todd Shipyard and Hugo-Neu-Proler industrial sites might represent important, yet distinguishable, sources of PCB contamination. Also included in this preliminary survey were samples collected (on land) from the Hugo-Neu-Proler industrial site on December 7, 1988 (samples 9-12). Hugo-Neu-Proler shreds metal into small pieces that are loaded onto ships bound overseas for recycling. For this reason, ships dock adjacent to the harbor at Berth 211 on a periodic basis and are loaded by means of a conveyer belt. Large reservoirs of shredded (and unshredded) metal are maintained on site, and shredding operations would appear to be continuous. Three of the samples from this site (9-11) were collected from among the debris that is deposited below the ship-loading conveyer belt (collection made during non-loading conditions). The last sample (12) was obtained from soil in the northwest corner of the Hugo-Neu-Proler site (Figure 1).

Once the analyses of samples collected during phase 1 (stations 1-9, 12) had been completed, the data were examined, and it was decided that additional sediment collections were necessary. Although preliminary results indicated that Todd Shipyard had a unique PCB pattern, sampling within and near West Basin was not expanded to further delineate contamination gradients. This decision was based on the fact that Todd Shipyard is about to go out of business, and enforcement actions might not be fruitful. The Consolidated Slip (#1) sample had a relatively high concentration of Σ PCB suggesting that somewhere up the Dominguez Channel there could be a potential source (or sources) of PCB. However, adequately defining this source (or sources) would require an investigation, the scale of which was outside the scope of this study. The material collected from the Hugo-Neu-Proler site (below the conveyor belt) also proved to be quite contaminated with PCB, and the pattern appeared to be distinct from all of the other samples examined during phase 1. Therefore, we decided to concentrate our remaining effort on determining if PCBs from this site were making their way into the harbor environment.

To accomplish this, 10 additional sediment samples were taken on September 26, 1989 to determine how far into the harbor the Hugo-Neu-Proler PCB pattern could be detected and whether a (concentration) gradient of contamination could be established. This represented phase two of the study. On the basis of the high concentrations of total PCB found at station #9 (Hugo-Neu-Proler) and differences between the PCB composition of this sample and those collected near Dominguez Channel (#1) and the East Basin (#2), we decided to collect additional surficial sediment samples along a transect extending from the East Basin Channel into Consolidated slip (stations 17-21). In addition, we obtained sediments from the northeastern part of East Basin (#22) and within the Cerritos Channel (#16) as well as from below the docking area immediately adjacent to Hugo-Neu-Proler (stations 13-15). These latter samples collected on July 19, 1989 correspond to sediments deposited below the bow, stern and mid-ship areas of the scrap steel transport ships.

Visual observations indicated that one of the potential routes of transport of PCB from the Hugo-Neu-Proler site was a fine iron-rich dust blown onto the surface of the water during ship loading. Therefore, we decided to collect sea-surface microlayer and sub-surface water samples during both non-loading and loading periods (February 12, 1990

and July 11, 1990, respectively). These collections were made when the prevailing winds were onshore so that the probability of aeolian transport from Hugo-Neu-Proler to the harbor would be maximized. Finally, because of the obvious heterogeneity of the material deposited directly below the conveyor, we decided to investigate the distribution of PCBs among different size fractions of these samples (stns. 9-11). Because the finer size fractions of this material are most likely to be mobilized by winds, particularly during loading conditions, it is more realistic to compare the concentrations and composition of PCBs in the size-fractionated material with that found in the microlayer samples.

Sampling Methods

Surficial sediments (0-2 cm) were collected using either a 0.1 m² modified Van Veen grab sampler or a stainless steel Ekman dredge sampler. Upon retrieval of the grab sampler, the surface of the sediments was inspected to assure that a relatively undisturbed sample had been obtained. When these conditions were obtained, subsamples were taken using a 10 cm³ plastic barrel syringe with tip removed. Excess (sub-bottom) sediments were discarded, and the upper 2 cm were then extruded into a precombusted glass jar. The sediments were repeatedly subsampled in this manner from undisturbed portions of the grab sample until approximately 100 g of wet sediments had been collected. Then the jars were sealed with teflon-lined lids, labelled and immediately frozen. All sediment samples were maintained at -20°C until analyses could be performed.

Material from below the Hugo-Neu-Proler loading conveyor (stns. 9-11) as well as the soil from the northwest corner of the facility (stn. 12) were collected by hand (stainless steel spatula) directly into precombusted glass jars. All of these samples were immediately returned to the laboratory and frozen at -20°C until analyses could be performed.

Sea-surface microlayer samples were collected using a sampling device that consists of a motor driven rotating teflon drum (Cross *et al.* 1987) which adsorbs sea surface films (ca. 50 µm thick) onto the drum surface and collects it directly into a clean 1 gallon glass bottle. The subsurface water samples were obtained by submerging an organic-free 1 gallon glass bottle 10 cm below the air-sea interface and simply removing the cap to fill the bottle. The bottle was then resealed with a teflon-lined cap and brought to the deck. All liquid samples were immediately returned to the laboratory where they were filtered through pre-combusted Whatman GF/C glass fiber filters.

Chemical Analyses

Sample pretreatment.

The debris recovered from beneath the Hugo-Neu-Proler conveyor belt was separated into three grain size fractions, 1) > 2 mm, 2) 0.5-2 mm, and 3) < 0.5 mm, by dry sieving. No attempt was made to rinse the sieves following the particle size separations. Rather, each fraction was transferred quantitatively into teflon-sealed pre-combusted glass containers which were stored frozen (-20°C) until elemental and trace organic analyses could be performed.

In the case of the liquid samples, aliquots were taken for determination of suspended solids. This measurement was made by filtering ca. 1000 ml of water through a pre-combusted (i.e. 4 hours at 450°C), pre-tared 47 mm Whatman GF/C glass fiber filter (300 mm Hg), driving off excess water (at 60°C for one hour) and reweighing the filter using a Cahn C-31 microbalance. The filters were stored in pre-combusted petri dishes placed inside a vacuum dessicator prior to the taring and following the drying steps to insure that adsorbed water was not present during gravimetric analysis.

Filtrations of water samples (200-550 ml) for particulate iron were done using pre-tared Nuclepore 0.4 μ m polycarbonate filters. The filters were stored in petri dishes, one filter/dish, inside a vacuum dessicator until analyses could be performed.

Aliquots of the water samples to be used for particulate organic carbon and particulate nitrogen analyses (80-200 ml) were filtered through pre-tared, precombusted 25 mm Whatman GF/C glass fiber filters. These filters were dried and stored as described above for the suspended solids determination.

For the trace organic analyses, water samples were filtered using pre-combusted 47 mm GF/C filters as described above. Total volumes of approximately 1-2 liters were filtered by replacing the filters as needed when the first sign of clogging occurred. The filters (4-6) were directly transferred to a Soxhlet extraction apparatus. The concentration of solids on the filters was not determined directly. Instead, the measurements of suspended solids concentration and the volume of water filtered were used to estimate particle loading on the filters for the trace organic analyses. This was done to avoid drying of the filters prior to analysis. Such drying could result in volatilization of the low molecular weight PCBs.

Elemental analysis (C,N).

All sediment samples were subsampled for total organic carbon (TOC) and total nitrogen (TN) analysis. The sediments were thawed, mixed with a glass rod, and an aliquot of the wet sediments (ca. 20 g) was transferred to a precleaned, teflon-sealed jar. These sediments were dried in an oven at 60°C to constant weight after which they were homogenized with a glass rod. An aliquot (for CHN analysis) was then removed and reduced to a fine powder using an agate mortar and pestle. Approximately 20 to 30 mg portions of this powder were weighed into pre-cleaned, pre-tared silver boats using a microbalance (Cahn C-31). The samples were exposed to hydrochloric acid vapors inside an all-glass dessicator for 16 hours after which they were heated in an oven at 60 °C for about one hour to drive off HCl vapors and excess water. This acid vapor carbonate removal procedure is a modification of the method described by Hedges and Stern (1984). The silver boats were then placed inside tin boats and sealed prior to CHN analysis on a Carlo Erba EA1108 elemental analyzer.

Only one size fraction of the Hugo-Neu-Proler conveyor belt material was used for CHN analysis (<0.5 mm). This material was extremely fine. For this reason, it was directly transferred (with grinding) into the silver boats. These samples were acidified and processed using the same procedures as described above for the sediments.

Data were acquired using a Carlo Erba EAGER 100 data system which utilizes an IBM-compatible microcomputer. Instrument calibration was achieved using acetanilide. Analysis of National Research Council of Canada standard reference sediments, PACS-1, for total carbon yielded results that agreed with the certified value to within 3 %. Precision is estimated at <1 % based on replicate analyses of carbonate-free sediments. All data presented here are based on total sediment weight (i.e. including carbonate carbon).

Filters bearing suspended particles from the water samples were acid treated as described above by placing the petri dishes directly inside of the dessicator. The filters were then dried at 60°C and placed into tin boats. The instrumental analyses proceeded as described above. Precision for the filter procedure is estimated at <5% based on replicate analyses of wastewater effluent filtered from a single 24-hour composite.

Iron analysis.

Following homogenization of the oven-dried sediments by the glass rod (see above), an aliquot (1-2 g) was wet ashed with 20 ml of a 1:1 mixture of concentrated HNO_3 /deionized water. The contents of the beaker were heated to incipient boiling, and the liquid was reduced in volume to near dryness. The same procedure was repeated once again. Then a 20 ml solution of 1:3 HCl (conc.)/water was added to the residue and boiled for 20 minutes in order to reduce the liquid volume to about 10 ml. This material was cooled to room temperature and filtered through a Whatman # 40 filter paper. The volume of the filtrate was then adjusted to 50 ml with deionized water. This digest was aspirated into an air-acetylene flame for analysis on a Varian AA6 atomic absorption spectrophotometer at a wavelength of 248 nm (simultaneous background correction). Concentrations were determined by direct comparison with a calibration curve developed on the same day using freshly prepared standard solutions. Precision is estimated at <5%.

Water samples were processed as described above with the exception that the Nuclepore filters were reweighed and then placed directly into the beakers for digestion.

Trace organic analysis.

Extraction, fractionation. The sediment samples (and the conveyor belt material) were extracted at ambient temperature according to methods reported in Anderson and Gossett (1987). Sediments were thawed and homogenized, and a portion (10-30 g) was weighed into a clean centrifuge bottle. Pre-combusted anhydrous sodium sulfate (ca. 50 g) was added to the wet sediments and mixed in with a glass rod to facilitate adsorption of water. Then 100 ml of Burdick and Jackson distilled-in-glass dichloromethane and a small volume of recovery surrogate solution (PCB congeners 30, 112 and 198 in dichloromethane) were added, the bottles were sealed with a teflon-lined cap, and the bottles were agitated on a ball mill for 48 hours. The contents were centrifuged, and the supernatant was transferred to a round bottom flask. This procedure was repeated two times, with successive extracts being combined.

The extract was concentrated by rotary evaporation (<30°C, 600 mm Hg) and treated for sulfur removal using activated copper granules. The concentration of total extractable organics (TEO) was then determined by gravimetric analysis using a Cahn C-31 microbalance. Based on these results, a volume corresponding to no more than 25 mg of extractable material was transferred to a clean vial. The solvent was then evaporated to just dryness under a stream of nitrogen gas, and the residue was taken up in redistilled hexane for column chromatography.

Isolation of a fraction containing the PCBs was achieved by adsorption chromatography using a modification of procedures described in Eganhouse et al. (1987). This procedure employs a bed of alumina overlying silica gel (1:2) both deactivated with 3% water. The PCB fraction was concentrated under a stream of dry nitrogen gas to a measured volume of 50-250 μ liters and diluted by half with the internal standard solution (congener 207 in hexane).

Following filtration, the filters from the water samples were immediately placed into pre-extracted cellulose thimbles. Each sample was spiked with a small volume of recovery surrogate solution (see above), and the Soxhlet apparatus was sealed. Extractions were performed at a reflux rate of 3 cycles/hour for 48 hours using a dichloromethane/methanol mixture (9:1). The extracts were reduced to a volume of less than 1 ml using rotary evaporation (<30°C, 600 mm Hg) and diluted to ca. 2-4 ml with dichloromethane. All extracts were treated for sulfur removal by the addition of activated copper granules,

analyzed gravimetrically for TEO content and then cleaned up using adsorption chromatography as discussed above. Subsequent steps preceding instrumental analysis were identical to those used for the sediments.

Instrumental analysis. The analysis of the PCB-bearing fraction was accomplished using a Varian Vista 44 GC/ECD. Splitless injections at 55°C (6 min isothermal hold) were performed on a 0.25 mm ID J&W Scientific DB-5 fused silica capillary column (0.25 μ m film thickness, 30 m long) temperature programmed from 55°C to 100°C at 15°C/min and 100°C to 285°C at 3°C/min. These conditions conform to those described in Eganhouse *et al.* (1989). Detector calibration was carried out on a daily basis using a secondary calibration standard containing a 1:1:1:1 mixture of Aroclors 1242, 1248, 1254 and 1260. This standard has been characterized in detail as described by Eganhouse *et al.* (1989) and yields 96 peaks under the chromatographic conditions described here.

Data were acquired at a sampling rate of 2 Hz using a PE Nelson Model 900 series intelligent interface with downloading to an AST 386/20 MHz microcomputer. Peak identification and integration were performed with PE Nelson Turbochrom software. Each chromatogram and quantitation report was manually inspected to assure the accuracy of peak identifications. Quantitation was by the internal standard method (congener 207-internal standard). Although recovery surrogates were used (see Appendix A), the data presented here have **not** been recovery-corrected. Recoveries were generally high (>80%). However, it is difficult to accurately correct for recovery of a large number of analytes. Our use of surrogates is, therefore, primarily to monitor method performance. In addition, PCB congener #40, normally a minor constituent in environmental samples, has not been reported because it was found to be subject to occasional interference due to the incomplete removal of elemental sulfur from the extracts. Deletion of this PCB from the total PCB concentration would be expected to introduce a bias of no more than 1% (Schulz *et al.* 1989).

The data are presented in three formats: 1) individual peaks, 2) by chlorination level and 3) total PCB. The PCB composition of individual peaks is often indicated by more than one congener (cf. Appendix A). The compounds listed for such peaks are known to coelute under these chromatographic conditions (Eganhouse *et al.* 1989). While these congeners are present in the calibration standard, it is not clear that all of the listed congeners are, in fact, present in the samples. Consequently, the identifications of congeners in multicomponent peaks must be regarded as tentative assignments. In some cases, GC/MS confirmation can provide information on peak composition (i.e. when two congeners of different chlorination level coelute). However, no attempt has been made to indicate these cases. Another feature of the data is the coelution of DDT metabolites with specific PCB peaks. Whenever the apparent concentrations of the peaks in question exceeded those of other isomers (i.e. at the same chlorination level), it was assumed that interference was occurring. In some cases, GC/MS analysis provided confirmation of such instances. If either case obtained, however, the concentration of that peak was not included in the chlorination level summations or total PCB summations. The absence of these PCBs (in combination) from the summation of Σ PCB is expected to contribute a bias of no more than ca. 1.5% (worst case; Schulz *et al.* 1989).

PCB concentrations presented in terms of chlorination level were developed by summing all of the peaks containing congeners of the respective chlorination level (cf. Appendix A). Finally, the total PCB concentration represents the summation of all peak concentrations (excluding congener 40 and peaks suspected of interference). The method of quantitation used in this study has been tested in the SCCWRP laboratory against solutions of individual Aroclors and has been found to produce total PCB concentrations within 5 % of the gravimetrically determined amounts. Precision of the total PCB

concentration is estimated to be ca. 11% (coeff. of variation). The average precision for individual peaks is also ca. 11%. These estimates are based on analysis of replicate samples of lobster and clam muscle tissues (Eganhouse *et al.* 1989) which are generally much lower in concentration than the samples examined here.

Selected samples were confirmed for the presence of PCBs and DDTs using full scan or limited mass scan electron impact mass spectrometry on a Hewlett Packard 5790 GC/MSD. Full scan acquisition parameters were: 50-500 amu at 0.96 scans sec^{-1} , 70 eV. Limited mass scan parameters were: starting at 25 minutes of run time: 185.5-356.0 amu at 2.5 scans sec^{-1} for 20 min, 230.0-400.5 amu at 2.5 scans sec^{-1} for 10 min, and 300.0-470.5 amu for 20 min. Chromatographic conditions were identical with those described above for the GC/ECD analyses.

RESULTS AND DISCUSSION

Sediments

General constituents.

Table 1 summarizes data obtained for the sediment samples collected from Los Angeles Harbor. Data are plotted for the total PCB concentration at all 18 of the subtidal stations and one of the two land-based stations (#12) located on the Hugo-Neu-Proler site in Figure 3.

Examination of these data reveals that the concentration of total PCB in surficial sediments in the harbor range over more than two orders of magnitude ($50\text{--}11400\text{ ng dry g}^{-1}$). The highest concentrations are found near the Todd Shipyard sites (stns. 7 and 8), along Consolidated Slip (stns. 1, 2, 21 and 20) and in the immediate vicinity of the Hugo-Neu-Proler loading dock (stations 13-15). The cleaner areas correspond to the Main Channel (#5, 17) and to the northeast of Hugo-Neu-Proler in the vicinity of the Henry Ford Bridge (#3). Although the areal coverage of the sampling is not extensive, it would appear that if these three areas (Todd Shipyard, Consolidated Slip and Hugo-Neu-Proler) can be considered primary sources of PCB to harbor sediments, their effects on sediment contamination decline rapidly with distance.

For example, the concentrations of total PCB at the Hugo-Neu-Proler site decrease by more than an order of magnitude between the mid-ship station (#14) and the stern (#13), a distance of approximately 30-50 meters. The extent of contamination within Consolidated Slip would appear to be more extensive. Stations within the East Basin (#19, 22) exhibit relatively lower PCB concentrations suggesting a significant amount of dilution. The rather low concentrations observed at the Main Channel stations (#5, 17) and to the northwest of the Hugo-Neu-Proler site may also reflect dilution. However, these channels are dredged periodically and the sediments may not accurately represent contemporary releases from the contamination sources.

One difficulty in drawing many definitive conclusions about the transport and attenuation mechanisms that might be operating within the harbor is the fact that these sediments most likely represent residues that have accumulated over the last 40 years or more. Moreover, the harbor is a dynamic industrial area, and there have been numerous dredge and fill operations that have undoubtedly acted to homogenize and redistribute PCB-contaminated sediments. With these limitations in mind, it is, nevertheless, useful to compare the present results with those reported by Chen and Lu (1974) based on samples collected in 1973.

Figure 2 indicates the concentrations of total PCB reported by Chen and Lu (1974). Although the sampling sites in the present study do not coincide exactly with those of Chen and Lu (1974), the Σ PCB distribution patterns within the harbor are reasonably similar. The major exception to this statement is that the West Basin sediments we analyzed are relatively less contaminated with respect to other areas of the harbor than those investigated by Chen and Lu (1974). If these differences do not simply reflect spatial heterogeneity, one might conclude that mitigation activities at the Todd Shipyards have resulted in some improvements over this interim (1973-1989). It would also appear that in the early 1970s the harbor was generally more contaminated with PCBs than it is today. This conclusion must be tempered by the fact that Aroclor-based methods were used by Chen and Lu (1974) to determine PCB concentrations. These methods can suffer from a significant positive bias (i.e. the results may be too high) due to problems related to

Table 1. Summary of data for sediment samples collected in Los Angeles Harbor (1988-89)

STATION	Σ PCB (ng g ⁻¹)	Σ PCB/TOC (μ g g ⁻¹)	Σ DDT (ng g ⁻¹)	TEO (mg g ⁻¹)	TOC (%)	TN (%)	C/N ^a (%)	Iron (%)
1	1370	25.1	227	18.2	5.45	0.28	19.5	3.59
2	594	39.3	79.8	2.56	1.51	0.096	15.7	2.90
3	82.0	4.48	73.2	0.98	1.83	0.140	13.1	3.39
4	171	22.5	54.9	1.88	0.76	0.061	12.5	2.11
5	70.3	5.67	147	0.45	1.24	0.100	12.4	2.34
6	185	26.0	40.3	0.89	0.71	0.058	12.2	2.52
7	658	22.9	237	4.78	2.87	0.200	14.3	3.38
8	1870	101	52.7	5.66	1.85	0.087	21.3	2.51
9	30100	--	nd	63.7	--	--	--	--
12	660	114	77.7	1.95	0.58	0.043	14.5	2.00
13	491	39.3	65.0	2.65	1.25	0.096	13.0	2.91
14	11400	365	502	18.4	3.11	0.120	25.9	12.3
15	1360	88.3	234	3.70	1.54	0.130	11.8	2.88
16	134	12.8	79.9	0.50	1.04	0.081	12.8	2.78
17	49.1	13.5	51.2	0.46	0.36	0.030	12.0	1.50
18	228	17.7	69.6	2.64	1.29	0.093	13.9	3.32
19	228	18.1	492	2.00	1.26	0.094	13.4	3.22
20	1470	50.0	398	11.6	2.93	0.160	18.3	3.83
21	1260	42.3	1130	12.9	2.98	0.140	21.3	2.98
22	138	13.5	66.7	1.76	1.02	0.076	13.4	2.64

^a C/N ratio on mass, not atomic, basis.

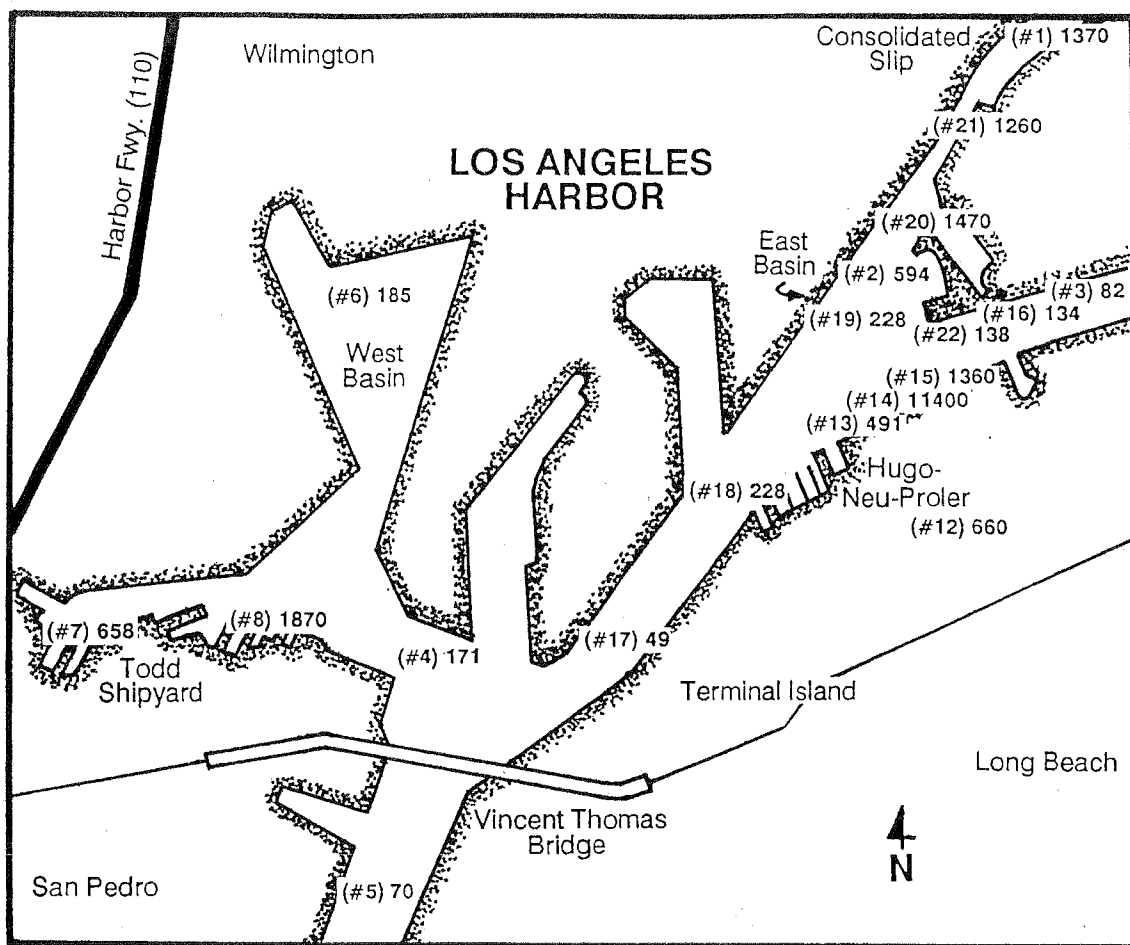


Figure 3. Concentrations (ng/dry g) of total PCBs in Los Angeles Harbor surficial sediments.

coelution of PCB congeners, variable ECD response and the co-occurrence of PCBs in various Aroclors (Eganhouse *et al.* 1990).

Additional information about the degree of sediment contamination and possible origins of the PCBs may be obtained from the data of Table 1. The concentration of total organic carbon ranges from less than 1% to 5.4%. The most organic-rich sediments are found at the mouth of the Dominguez Channel (stn. 1), and there would appear to be a trend of decreasing organic carbon content with distance down Consolidated Slip toward East Basin. Sediments near the Todd Shipyards (#7,8) and at the mid-ship station near Hugo-Neu-Proler are also enriched in organic carbon. These trends are probably partly due to grain size variations as the Consolidated Slip sediments were visibly more fine-grained than those collected from other parts of the harbor.

The concentration of solvent-extractable organic substances (TEO) show similar distribution patterns, with high concentrations at Todd Shipyard, Consolidated Slip and Hugo-Neu-Proler stations. Linear regression analysis reveals a significant relationship between TEO and TOC with a correlation coefficient (r^2) of 0.884 (Table 2). Similarly, the highest C/N ratios are found at stations within the same three areas. C/N ratios for natural marine sediments typically range from ca. 10-15. Consequently, the high C/N ratios observed in these harbor sediments (Todd = 14-21; Consolidated Slip = 18-21; Hugo-Neu-Proler = 26) are anomalous and may indicate the increased presence of carbon-rich substances such as hydrocarbons or hydrocarbon-based polymers. This would be supported by the higher TOC and TEO concentrations of sediments in these areas. The correlation between total extractable organics and Σ PCB is not strong ($r^2 = 0.678$) suggesting that if the extractable organic substances are largely petroleum hydrocarbons, their point of origin and transport is only weakly coupled to the PCBs. It would be useful to measure the total hydrocarbon content of these samples in order to see if the correlations improve.

When normalized to total organic carbon content, the Σ PCB concentration shows some interesting trends. Normalization to organic carbon helps differentiate between sediments that vary in grain size because grain size is inversely related to organic carbon content. The greatest contamination is found at station 14, near Hugo-Neu-Proler. High concentrations are also observed at station 8 (Todd) and at the Hugo-Neu-Proler soil site (#12). The sediments in Consolidated Slip exhibit relatively high concentrations, but it is clear that the heavily contaminated Hugo-Neu-Proler sediments are especially enriched with respect to PCBs. The generally poor correlation between TOC and Σ PCB ($r^2 = 0.395$) probably reflects differences in the sources of PCBs.

Sediments of the harbor contain iron in concentrations of 1.5 to 12.3%. Station 14 must represent an anomaly because all other sediments fall within a narrow range of 1.5-3.8%. This is consistent with results reported by Chen and Lu (1974) who found the iron content of inner harbor sediments to be within 1.8 to 3.8%. The unusually high iron concentration of the sediments at the mid-ship station adjacent to Hugo-Neu-Proler (#14) probably arises from inadvertent losses of particulate iron from the metal shredding facility. Under non-loading conditions inputs could occur by surface runoff (during rain events) or mobilization by winds. However, the majority of the iron is probably introduced during loading operations when material can escape the conveyor belt and fall to the sediments below. This hypothesis is supported by the iron content of sediments from the stern (#13) and bow (#15) stations which, although slightly greater than the mean iron concentration (mean = 2.82; excluding stn. 14), fall within the range of the other harbor sediments. If iron was being transported from the Hugo-Neu-Proler site to the harbor *via* the atmosphere alone, one would expect these sediments to be more enriched in iron than they are. It is probably reasonable to assume that the debris collected from beneath the conveyor belt (#9-11) is representative of materials lost to the harbor during loading

Table 2. Pearson correlation matrix for constituents measured in sediments of Los Angeles Harbor, 1988-89.

	Σ PCB	TEO	TOC	Iron	Σ DDT
Σ PCB	1.00				
TEO	0.678	1.00			
TOC	0.395	0.334	1.00		
Iron	0.957	0.633	0.417	1.00	
Σ DDT	0.531	0.579	0.437	0.618	1.00

operations. Unfortunately, this material was too heterogeneous to subsample for iron determination. Discussions to follow will consider data for the concentration of iron in the < 0.5 mm size fraction of these samples. (Particles of this size proved sufficiently homogeneous to permit analysis for iron content.)

Finally, the distribution of Σ DDT provides information on the effectiveness of transport processes within the harbor. Highest concentrations of DDT are observed in the sediments of Consolidated Slip (230-1130 ng dry g⁻¹). These concentrations are substantially higher than those found in other, apparently cleaner, areas of the harbor (#6=40 ng dry g⁻¹; #17=51 ng dry g⁻¹). The origin of these DDT compounds is from the Dominguez Channel which is known to have carried runoff from the Montrose Chemical Plant into the harbor (Chartrand 1986). The high relative abundances of the parent DDT compounds (i.e. *o,p'*-DDT and *p,p'*-DDT) compared with their respective metabolites (DDE, DDD) at certain stations (#19, 20, 12) suggests that if these are historical deposits, they were laid down with minimal degradation. The trends within the harbor are not distinct suggesting a patchiness with respect to DDT distribution. Of most interest, is the fact that the DDT compounds were not detected in the conveyor belt material. This suggests a possible means of differentiating between the PCBs originating within and/or upstream of the Consolidated Slip and those coming from the Hugo-Neu-Proler site. The presence of DDT in soils at the Hugo-Neu-Proler site (#12) is not surprising as this is believed to be fill dredged directly from the harbor (J. Wotherspoon, personal communication). The high relative abundance of parent DDTs in this sample again clearly indicates that these soils were contaminated either by direct application of DDT on-site or as a result of inadvertent release of industrial wastes (i.e. from Dominguez Channel). The former would seem to be an unlikely explanation.

The high concentrations of Σ DDT in the subtidal sediments near the Hugo-Neu-Proler loading area is another matter. Here, highest concentrations are observed at station 14, below the mid-ship area of the dock. Given the absence of DDT in all samples of debris collected from beneath the conveyor belt, it is difficult to explain the high DDT content of these sediments. Either they represent inputs that occurred earlier when debris from Hugo-Neu-Proler was releasing DDT-bearing materials or they have originated from the Dominguez Channel. The high relative abundance of *p,p'*-DDD in both of these sample suites and the absence of DDT + metabolites in the conveyor debris would appear to support the latter hypothesis.

PCB composition.

Concentrations of the PCBs according to chlorination level are tabulated in Appendix A. These data are also illustrated in the form of bar diagrams in Figures 4-6. Figure 4 shows distributions for samples taken at the head of Consolidated Slip (#1) along a transect terminating at the East Basin Yacht Anchorage (#22). Figure 5 consists of a series of stations originating at the Henry Ford Bridge (#3) and including the Cerritos Channel (#16), the Hugo-Neu-Proler subtidal stations (#13-15) and the station to the southwest of H-N-P (#18). Figure 6 includes the Todd Shipyard stations (#7,8) and West Basin (#6), Fuel Dock (#4) and Main Channel stations (#5,17).

Referring to Figure 4, sediments from station 1 (Consolidated Slip) are dominated by the tetrachlorobiphenyls with relative abundances of the >Cl₄ isomers greatly exceeding the <Cl₄ isomers. By contrast, most of the samples taken along this transect show a maximum at Cl₆, the lone exception being station 19 which has a maximum at Cl₅. It would appear that stations 3 (Henry Ford Bridge), 18 (E. Turning Basin, Berth 215) and 19 (E. Turning Basin, Mid-channel) bear the greatest resemblance (cf. Figures 4 and 5), all maximizing at Cl₅ and exhibiting roughly normal distributions with respect to chlorination

Figure 4. Distribution of PCBs according to chlorination level: Consolidated Slip to East Basin.

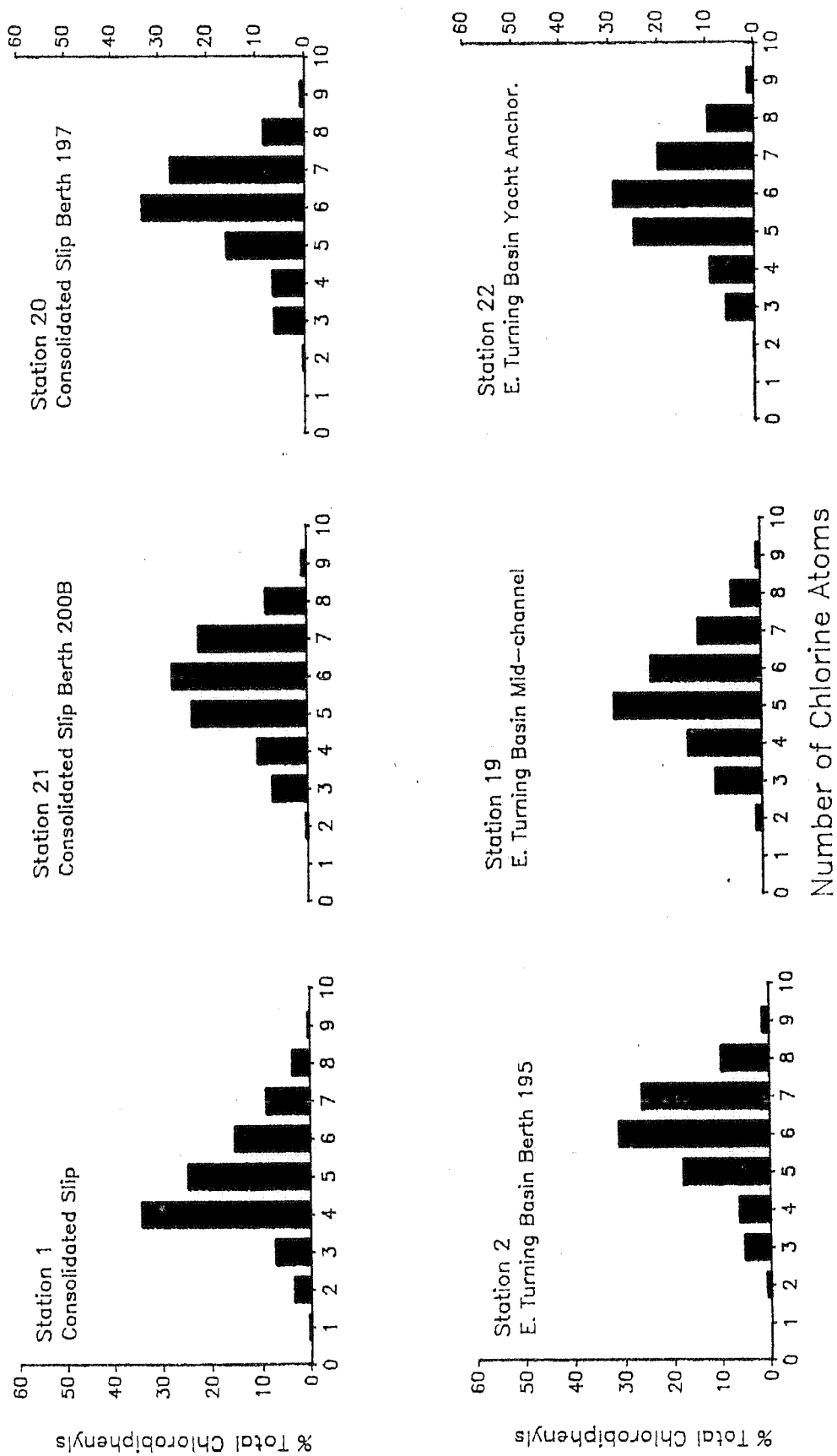


Figure 5. Distribution of PCBs according to chlorination level: Henry Ford Bridge to Hugo-Neu-Proler.

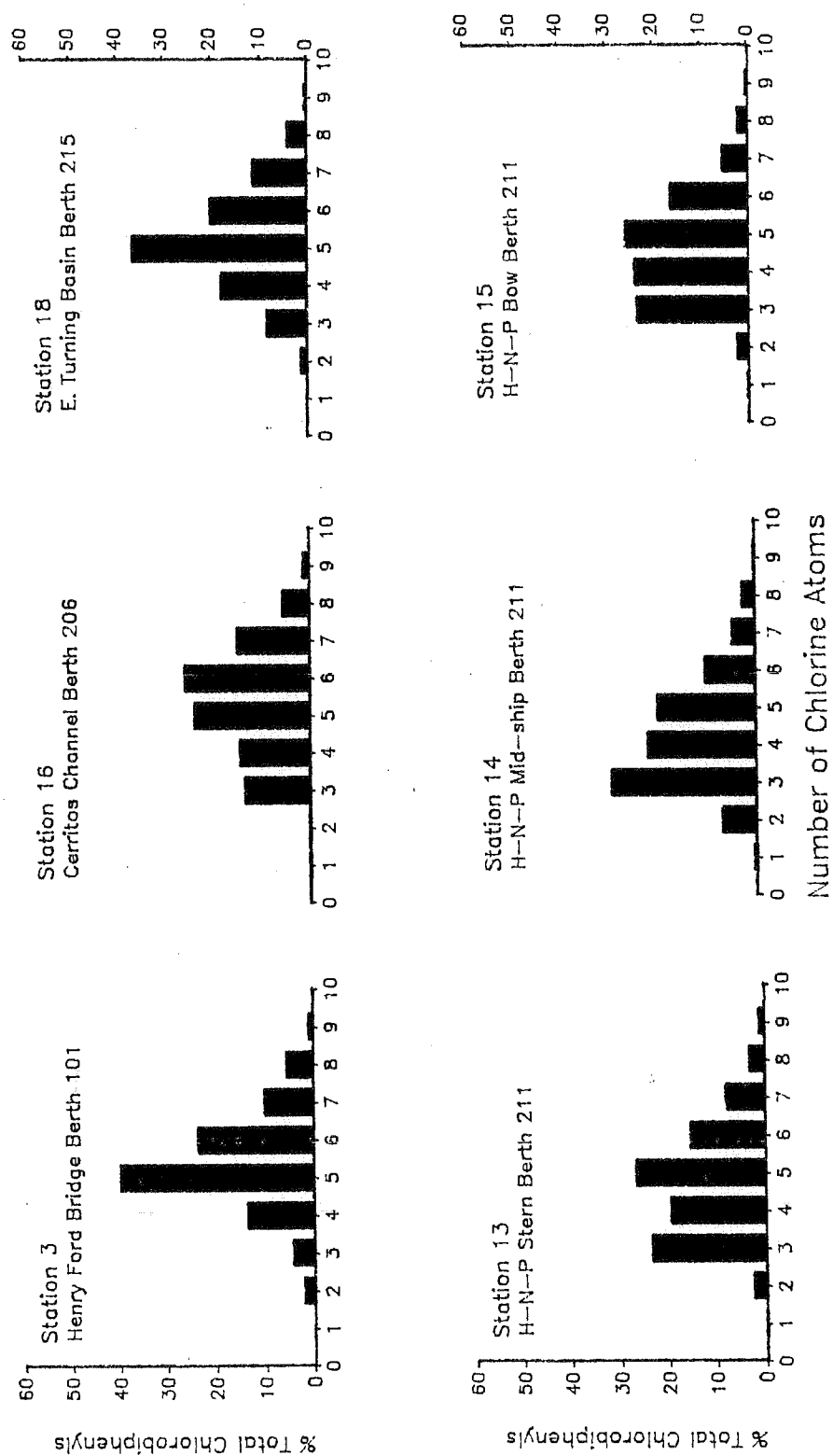
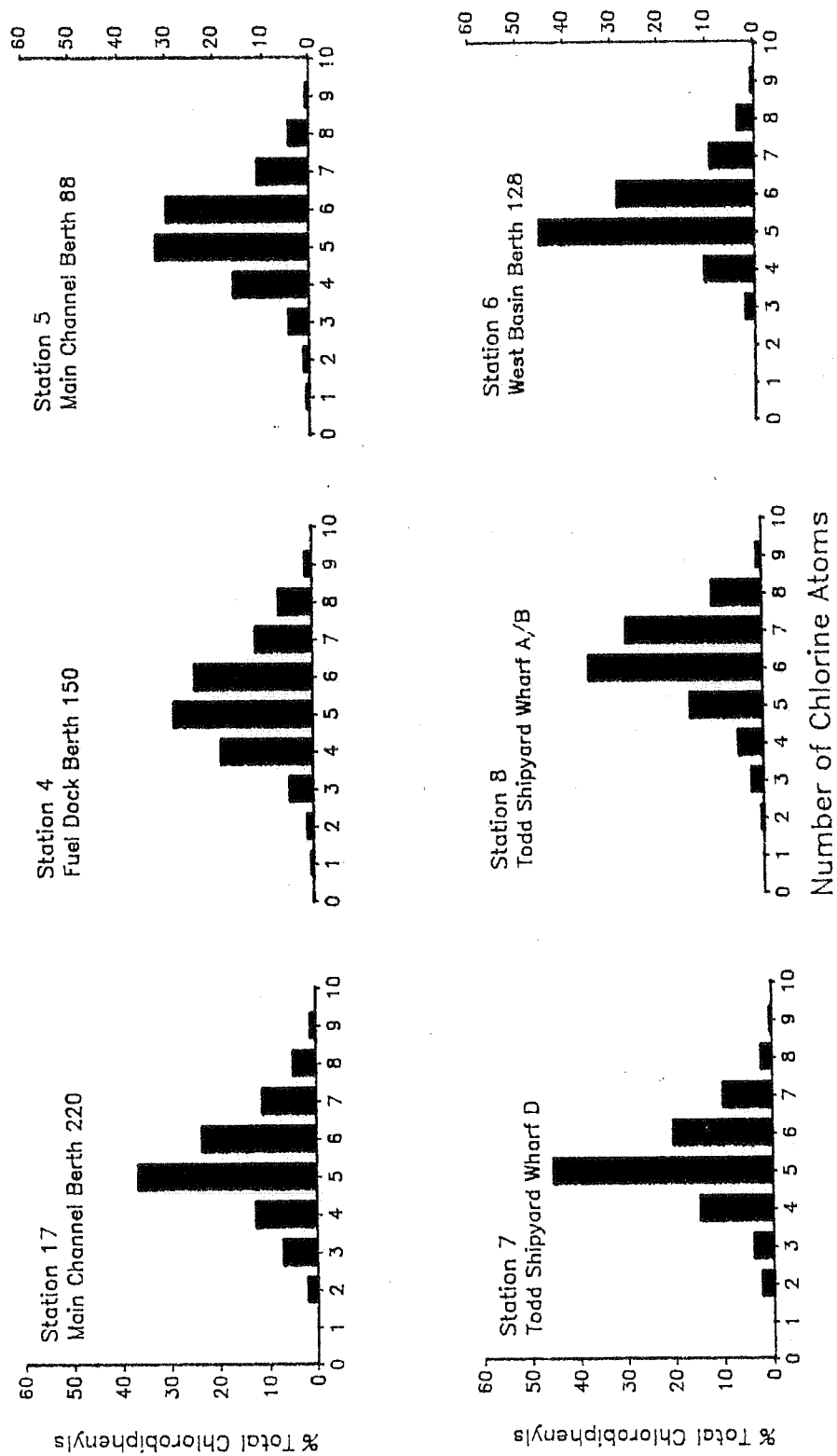


Figure 6. Distribution of PCBs according to chlorination level: West Basin and Main Channels.



level. Stations located at the Hugo-Neu-Proler loading dock (#13-15; Berth 211) exhibit large or dominant Cl_3 and Cl_5 abundances and the concentrations of isomers $<\text{Cl}_5$ greatly exceed those with more than five chlorines. This is apparently unique within the harbor as no other sediments examined here show these features. The patterns at these stations are not surprising as the Hugo-Neu-Proler site material (9-11) is strongly dominated by the tri- and tetrachlorobiphenyls (to be discussed below). This suggests that the PCBs at stations 13-15 are either weathered residues of material transported from Hugo-Neu-Proler (i.e. lowest chlorinated isomers were lost during early diagenesis) and/or a mixture of the H-N-P-derived material and PCBs from other sources. As shown earlier, the harbor sediments away from Hugo-Neu-Proler appear to be enriched in the more highly chlorinated species (Figure 4). The latter hypothesis is more consistent with the DDT data discussed earlier.

The diagnostic value of the Cl_3 maximum at the Hugo-Neu-Proler stations (13-15) is supported by trends apparent in the $\Sigma\text{PCB}/\Sigma\text{DDT}$ ratio (Table 3). Although this ratio incorporates a large amount of data, it is evident that most sediments in the harbor exhibit ratios within a relatively small range (i.e. 0.5-6). By contrast, ratios for sediments from the Hugo-Neu-Proler stations (13-15) are in the range 5.8-22.7. Given the apparent absence of DDT from the H-N-P site material, these high ratios indicate that the sediments underlying the loading area are heavily influenced by materials released from Hugo-Neu-Proler. Examining the PCB distributions at a finer scale, one observes that the relative abundances of specific PCB congeners show systematic variations.

Table 3 lists the concentration ratio of congeners 66,95:18. These peaks appear as prominent constituents in almost all of the sample chromatograms. Lowest ratios are found for the Hugo-Neu-Proler sediments (12-15; 0.3-2.6), whereas all of the other sediments fall in the range of 3.6-10.2 (excluding stn. 16). The low ratio seen at station 16 may indicate an influence from the Hugo-Neu-Proler site. For comparison, the conveyor belt site materials (9-11) show ratios of 0.7, 0.7 and 2.5. Thus, the enrichment of iron, the dominance of Cl_3 chlorobiphenyls, the low 66,95/18 ratios and the high abundance of total PCBs (especially relative to DDT) all indicate significant contamination of the sediments at Berth 211 by Hugo-Neu-Proler.

Figure 6 illustrates the chlorination distributions for stations within the West Basin, near Todd Shipyards and at two main channel locations. The sediments from these locations all show maxima at Cl_5 with the exception of station 8 (which maximizes at Cl_6). The reason for the unique pattern at station 8 is unknown. However, examination of Tables 1 and 3 clearly shows that this location probably was and may still be a significant source of PCB to the harbor. Given the relatively low $\Sigma\text{PCB}/\Sigma\text{DDT}$ ratios at stations only a short distance from station 8, it seems that the area influenced by this source is restricted.

Hugo-Neu-Proler site material

Size fractionation/mass balance

As noted earlier, the debris obtained from beneath the conveyor belt at the Hugo-Neu-Proler site was extremely heterogeneous. Metal shards, bolts, fibers and fine dust were all present in the material collected into the three jars (stns. 9-11). We were concerned about the problem of obtaining a representative sample for analysis at this location and, therefore, decided to fractionate the materials from each of the three samples into three size fractions. The reasoning behind this was twofold. First, we wanted to compare PCB concentrations and compositions among the three samples in a manner that would reduce the bias due to sample heterogeneity. Second, we wanted to look at different size fractions because particles of different size could follow different paths into and through the harbor. For example, the finer particles are more likely to reside for a

Table 3. Σ PCB/ Σ DDT and 66,95/18 ratios for samples taken in Los Angeles Harbor, 1988-89.

Station	Description	Σ PCB/ Σ DDT	66,95/18
1	Consolidated Slip, Berth 200G	6.03	6.47
2	E. Basin, Berth 195	7.44	7.69
3	H. Ford Bridge	1.12	6.33
4	Fuel Dock, Berth 150	3.11	---
5	Main Channel, Berth 88	0.48	6.37
6	West Basin, Berth 128	4.59	---
7	Todd Shipyard, Wharf D	2.78	4.94
8	Todd Shipyard, Wharf A/B	35.5	3.63
9	Hugo-Neu-Proler Conveyor	---	0.47
9 ^a	Hugo-Neu-Proler Conveyor	---	0.69
10 ^a	Hugo-Neu-Proler Conveyor	---	0.70
11 ^a	Hugo-Neu-Proler Conveyor	---	*2.47
12	H-N-P, NW corner soil	8.49	0.26
13	H-N-P, Stern Berth 211	7.55	2.34
14	H-N-P, Mid-ship Berth 211	22.7	0.99
15	H-N-P, Bow Berth 211	5.81	2.56
16	Cerritos Ch., Berth 206	1.68	0.58
17	Main Channel, Berth 220	0.96	7.20
18	E. Basin, Berth 215	3.28	6.38
19	E. Basin, Mid-channel	3.69	5.86
20	Consolidated Slip, Berth 197	3.69	10.2
21	Consolidated Slip, Berth 200B	1.12	6.60
22	E. Basin, Yacht Anchor.	6.15	8.30
23	Subsurface SW Non-loading	---	---
24	μ layer Non-loading, Rep. 1	---	0.90
25	Subsurface SW Loading	---	1.81
26	μ layer Loading, Rep. 1	---	0.56
27	μ layer Loading, Rep. 2	---	0.83

a These data are "synthesized" from mass balance calculations.

b Dashes indicate that the constituent in the denominator was not detected.

significant period at the air-water interface due to their lower densities (see below) and smaller particle size. On the other hand, larger less oxidized particles are more likely to sink rapidly and accumulate in nearby sediments without being advected away from the source.

Table 4 lists data corresponding to >2 mm, 0.5-2 mm and <0.5 mm fractions. One fact is immediately apparent: the three samples differ with respect to their particle size distribution. In general, the <0.5 mm size fraction comprises from 20-56% by weight of the total, whereas the 0.5-2 mm and >2 mm size fractions make up 12-27 and 26-67%, respectively.

In order to examine the distribution of PCBs among particles of different size, we performed extractions of all three fractions. Samples 9 and 11 showed similar patterns of increasing Σ PCB concentration with decreasing particle size (Table 4). Sample 10, however, contained the highest concentration of Σ PCB in the >2 mm size class. The differences between these samples are difficult to rationalize, but it would appear on the basis of this limited sampling that particle size alone does not control the concentration of PCBs. Comparison of the Σ PCB concentration data with TEO concentrations suggest that other factors may be involved. There is a weak correlation between the total PCB concentration and TEO concentration ($r^2 = 0.594$). Such a correlation may mean that the coating of hydrocarbons and other extractable organics on the debris may act as a carrier for the PCBs. Under these conditions, the degree to which particles of different size are coated with hydrocarbons could well be related more to the origin of the particles than their propensity for binding them.

Another aspect of interest is whether a mass balance for Σ PCB and individual PCBs can be achieved. We applied the mass fractions that each size class represented to the concentration of PCB associated with each size class to compute a "synthetic" PCB concentration. The only sample for which analyses were performed on both the bulk (i.e. unfractionated) material and the individual size fractions was station 9. In this case, we obtained a Σ PCB concentration of $30.1 \mu\text{g g}^{-1}$ for the bulk material and $34.6 \mu\text{g g}^{-1}$ for the "synthesized" material. The agreement between these concentrations is good (within 15%), indicating that the "synthetic" Σ PCB concentration is a reasonable approximation of the concentration of the bulk material. Comparison of the concentrations of individual peaks which represent more than 1% of the Σ PCB in these samples yields an average difference of 25%. That such good agreement is obtained is even more remarkable in view of the difficulty of adequately subsampling this material for analysis.

General constituents.

Comparison of the "synthesized" Σ PCB concentrations computed for the three samples shows that stations 9 and 10 are quite similar (i.e. 34.6 vs. $40.1 \mu\text{g g}^{-1}$), whereas material from station 11 is less contaminated ($22.4 \mu\text{g g}^{-1}$). Given the heterogeneity of the material, the difficulties of subsampling and the assumptions being made in computing the "synthetic" Σ PCB concentrations, the variability is quite low. These results confirm that the high concentrations of Σ PCB measured in sample 9 are not unusual for the conveyor material. It is interesting to note that when normalized to TOC, the Σ PCB concentrations of the <0.5 mm fractions are similar to those found for sediments at station 14 just beneath the conveyor.

The total extractable organic matter concentration of the conveyor debris is very high (30 - 92 mg g^{-1}). Total organic carbon and iron concentrations were determined on only the <0.5 mm size fraction because of the extreme heterogeneity of the bulk material, the need for relatively small samples for analysis and the high concentrations of organic

Table 4. Concentrations of various constituents in the conveyor belt debris on the Hugo-Neu-Proler site.

Stn.	Size Fraction (mm)	Mass Fraction	Σ PCB ($\mu\text{g g}^{-1}$)	Σ PCB/TOC ($\mu\text{g g}^{-1}$)	TEO (mg g^{-1})	TOC (%)	C/N ratio	Iron (%)
9	<0.5	0.205	59.9	422.	70.5	14.2	52.4	19.9
	2-0.5	0.121	49.4		68.4	-- ^a	--	
	>2	0.674	25.1		30.1	--	--	
10	<0.5	0.371	42.5	310.	69.1	13.7	50.3	16.7
	2-0.5	0.267	30.2		69.9	--	--	
	>2	0.362	45.8		92.0	--	--	
11	<0.5	0.565	25.7	211.	49.7	12.2	39.7	18.9
	2-0.5	0.180	19.0		35.7	--	--	
	>2	0.255	18.5		40.5	--	--	

^a Dashes indicate size fractions not analyzed.

carbon and iron. Nevertheless, it is clear from the data in Table 4 that these particles have a high organic carbon content (12-14%) and that a significant part of this organic carbon may be hydrocarbons or other nitrogen-poor organic matter (C/N=40-52). Comparison of TOC and TEO concentrations indicates that most of the TOC does not come from extractable material. It is presumed that some of the non-extractable TOC originates from the many fibers and plastic particles (i.e. cellulose or synthetics) that can be observed under the microscope. Organic enrichment of the conveyor debris is consistent with the fact that most of the metal that is shredded at this facility comes from automobiles. The high TEO and organic carbon content of the conveyor debris is also consistent with the elevated concentrations found in nearby sediments (stn. 14). Assuming the TOC concentrations measured in samples 9-11 are representative of the material entering harbor waters at station 14, that this organic carbon is refractory and that simple dilution accounts for the observed concentration of TOC at station 14, it would appear that the conveyor debris is diluted to a **minimum** of about 2.5.

The iron content of the <0.5 mm fraction ranges from 17-20% by weight. Clearly, a significant fraction of this dust arises from oxidation of iron parts and particles as evidenced by the red-orange color of the material and its ferromagnetic properties. These particles are less than twice as iron-rich as the subtidal sediments underlying the conveyor (stn. 14). This may be due in part to mobilization of iron from the sediments under reducing conditions or preferential deposition of rapidly settling particles (in the larger size ranges). Larger particles would presumably exhibit higher iron concentrations than the fine particles because less of their mass would be oxidized. We have no data other than visual observations with which to test these hypotheses at this time.

PCB composition.

Distributions of the PCB among different chlorination levels for the station 9 bulk material, the three size fractions and the "synthesized" distribution are given in Figure 7. Figure 8 presents a comparison of the chlorination level distribution plots for the "synthesized" data for stations 9-11. Tabulations of the data shown in these figures can be found in Appendix A.

It is clear that the distribution of isomer group abundances among particles of different size is essentially identical (Figure 7). This, is borne out for the other samples taken at the site (Appendix A) indicating that the PCB compositions are uniform among different particle size groups. Comparison of the PCB distributions among the three samples collected from beneath the conveyor belt, however, indicates that there may be some variation in composition within the debris. The chlorination plots obtained for samples 9 and 10 are virtually indistinguishable and are characterized by high concentrations of Cl_{3,5} isomers with a maximum at Cl₃. The higher chlorinated species are in much lower abundance. Sample 11 exhibits a somewhat different chlorination distribution with maximum at Cl₅. Again, however, the lower chlorinated species predominate over the Cl₅ PCBs. This points out the fact that there may be some heterogeneity of the debris with respect to PCB composition. Comparison of the plots shown in Figure 7 with those in Figure 6 for station 13-15 indicate a linkage between the debris and the sediments underlying the loading dock area.

Water Samples

General constituents.

Table 5 lists concentrations of the constituents measured in the subsurface seawater and microlayer samples collected under loading and non-loading conditions near the Hugo-

Figure 7. Distribution of PCBs according to chlorination level: Hugo-Neu-Proler conveyor debris.

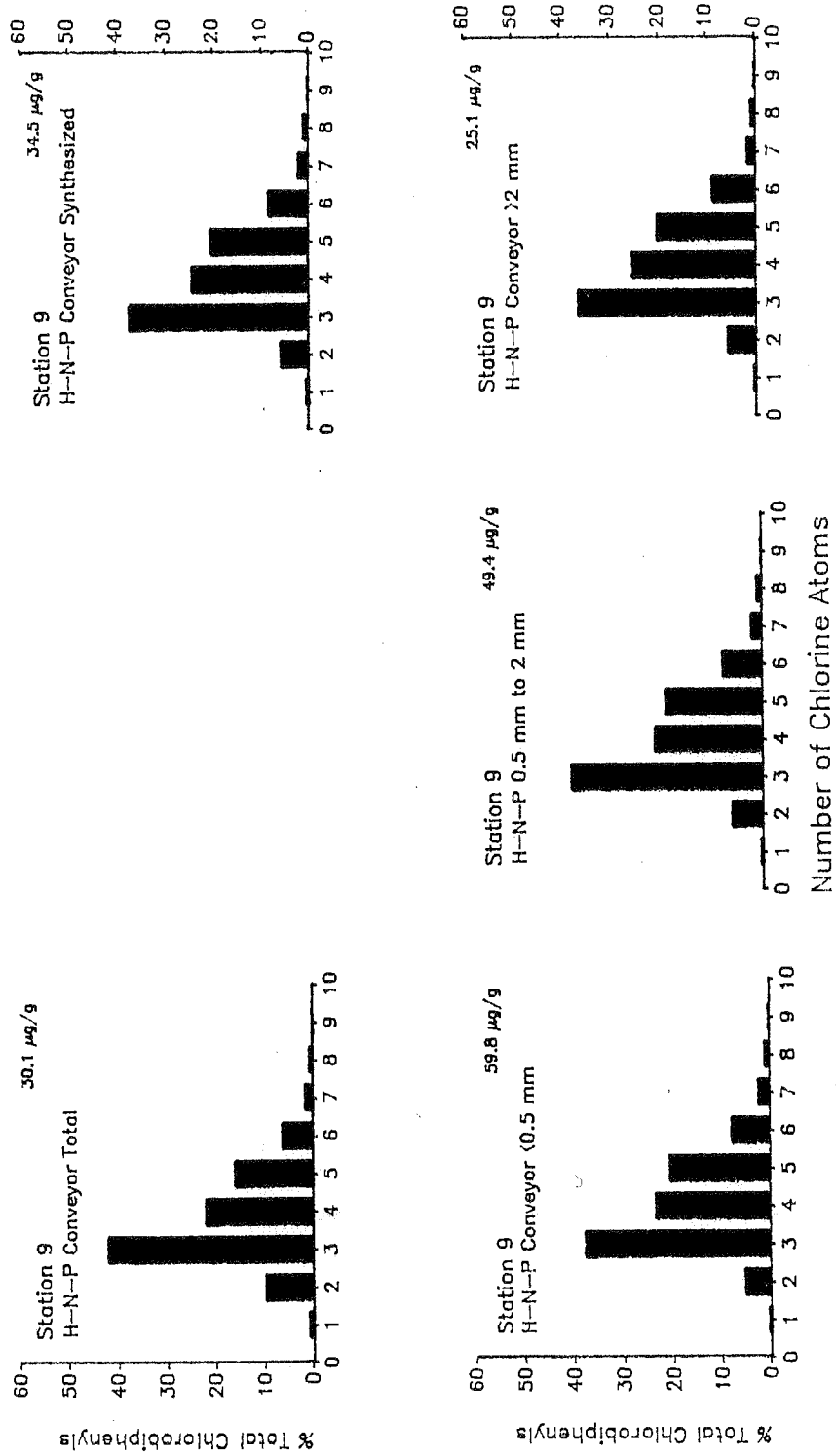


Figure 8. Distribution of PCBs according to chlorination level: Comparison of stations 9-11 "synthesized" PCB distributions.

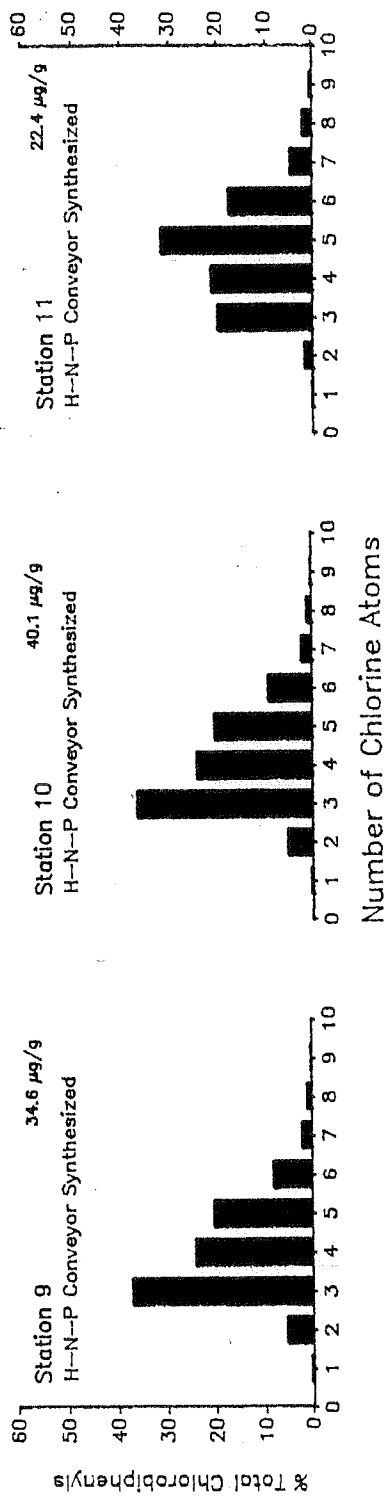


Table 5. Concentrations of various constituents in subsurface seawater (10 cm below air-sea interface) and microlayer samples collected near the Hugo-Neu-Proler site during loading and non-loading conditions, 1990.

Stn.	Sample Type	Conditions	ΣPCB ($\mu\text{g g}^{-1}$)	$\Sigma\text{PCB/TOC}$ ($\mu\text{g g}^{-1}$)	TEO (mg g^{-1})	TOC (%)	Iron (%)
24	microlayer	non-loading	5.50	54.4	193	10.1	4.66
23	subsurface	non-loading	0.71	71.0	-- ^a	1.0	3.81
26	microlayer	loading	21.1	205	33.7	10.3	24.8
27	microlayer	loading	58.4	517	235	11.3	22.8
25	subsurface	loading	0.39	7.5	228	5.2	3.61

^a Dashes indicate samples not analyzed.

Neu-Proler site. Under non-loading conditions no visible sheen related to the Hugo-Neu-Proler operations could be observed. Nevertheless, the abundance of suspended solids, Σ PCB (particulate) and particulate organic carbon were elevated over that observed for the subsurface water collected at the same time. Enrichment factors (i.e. $\text{concentration}_{\mu\text{layer}}/\text{concentration}_{\text{subs. sw}}$) for these constituents were: 2.2 (suspended solids), 7.71 (Σ PCB) and 10.1 (POC). In contrast, particulate iron concentrations were only marginally elevated ($\text{EF} = 1.22$) in comparison with the subsurface seawater. DDT metabolites were detected in the subsurface seawater. However, these compounds were not found in the microlayer sample, suggesting that the dominant source of PCBs to the sea surface, even under non-loading conditions, is the Hugo-Neu-Proler site. The observation of DDT in suspended particles below the sea surface is consistent with the hypothesis that these materials are, at least partly, derived from the harbor proper and have relatively long lifetimes compared with materials accumulating in the microlayer. Together, these data suggest that even during non-loading periods, the surface of the harbor is contaminated by materials originating at the Hugo-Neu-Proler site.

The data can be compared with recent results presented by Cross *et al.* (1987) for a microlayer sample collected in East Turning Basin (under loading conditions) at the same location occupied in this study. Cross *et al.* (1987) report concentrations for Σ PCB in bulk microlayer (i.e. particulate + dissolved) water samples of $38.8 \mu\text{g liter}^{-1}$. This datum reflects the summation of contributions from Aroclors 1242 and 1254 (based on Aroclor-based methodology). Converting the data given in Table 5 under non-loading conditions to equivalent volume-based units, we obtain $270 \text{ ng liter}^{-1}$ (microlayer) and 16 ng liter^{-1} (subsurface seawater). Even though the data from the present work does not include PCBs present in the "dissolved" phase, it is obvious that the sea surface microlayer was significantly more contaminated during the Cross *et al.* (1987) study. Cross *et al.* (1987) also report concentrations of total extractable organics (chloroform extraction) and particulate iron. Their data were: $21.8 \text{ mg liter}^{-1}$ (TEO) and $11.1 \text{ mg liter}^{-1}$ (iron). The data developed here under non-loading conditions are: $9.46 \text{ mg liter}^{-1}$ (TEO-microlayer); $0.84 \text{ mg liter}^{-1}$ (Fe-subs. sw), $2.28 \text{ mg liter}^{-1}$ (Fe-microlayer). Again, the concentrations determined for samples collected under non-loading conditions are lower than those found under loading conditions by Cross *et al.* (1987).

When samples were collected during loading operations at the Hugo-Neu-Proler site (# 25-27) a large brown slick extending across the entire channel was observed. A similar phenomenon was noted during the studies of Cross *et al.* (1987; personal communication). Examination of the data for microlayer samples collected under "loading" conditions in 1990 (Table 5) shows that the Σ PCB, Σ PCB/TOC and iron contents of the suspended particulate matter were markedly elevated (by factors of 4 to 60) when compared with the samples collected under non-loading conditions. However, the TOC contents of the suspended particles collected under the different conditions do not differ much. There is apparently a significant amount of variability in the concentration of Σ PCB of the suspended particulates in microlayer samples collected within an hour of each other, but this is to be expected given the patchy nature of such slicks and the likelihood of non-uniform releases from the site itself. Nevertheless, these concentrations compare favorably with those obtained for the $<0.5 \text{ mm}$ size fractions isolated from the Hugo-Neu-Proler conveyor debris. The same can be said of the Σ PCB concentrations computed on a TOC-normalized basis (i.e. $200\text{-}500 \mu\text{g g}^{-1}$ for microlayer, $200\text{-}400 \mu\text{g g}^{-1}$ for the debris) and the particulate iron concentrations (i.e. 23-25% for microlayer, 17-20 for the debris). Thus, the particles in the microlayer are essentially identical to fine particles deposited below the conveyor with respect to PCB, organic carbon and iron content. The concentration of Σ PCB in the microlayer samples under loading conditions is approximately two orders of magnitude greater than that found in the subsurface seawater. Enrichment factors for suspended solids, POC and iron are approximately 50-110, 2 and 6.4, respectively.

If one computes the concentration of Σ PCB on a volume basis, the following is obtained: 40.2-53.3 $\mu\text{g liter}^{-1}$ (microlayer), 6.6 ng liter^{-1} (subsurface seawater). These concentrations are similar to those found by Cross *et al.* (1987) and support the observation of an extensive iron-rich slick across the East Turning Basin. Although Cross *et al.* (1987) report finding DDT in the East Turning Basin sample (Σ DDT = 442 ng liter^{-1}), the Σ PCB/ Σ DDT ratio for this sample was extremely high (88) when compared with sediments in the harbor (cf. Table 3). Consequently, it is unlikely that a significant fraction of the PCBs in the microlayer sample of Cross *et al.* (1987) came from resuspension of harbor sediments. By comparison, none of the DDT metabolites were detected in the microlayer samples we collected (loading or non-loading). Because of the pervasive occurrence of DDT in the harbor environment and its absence in the Hugo-Neu-Proler conveyor debris, the absence of DDT in the microlayer samples supports the hypothesis that the majority of the PCBs found at the surface of the harbor waters arise from Hugo-Neu-Proler.

PCB composition.

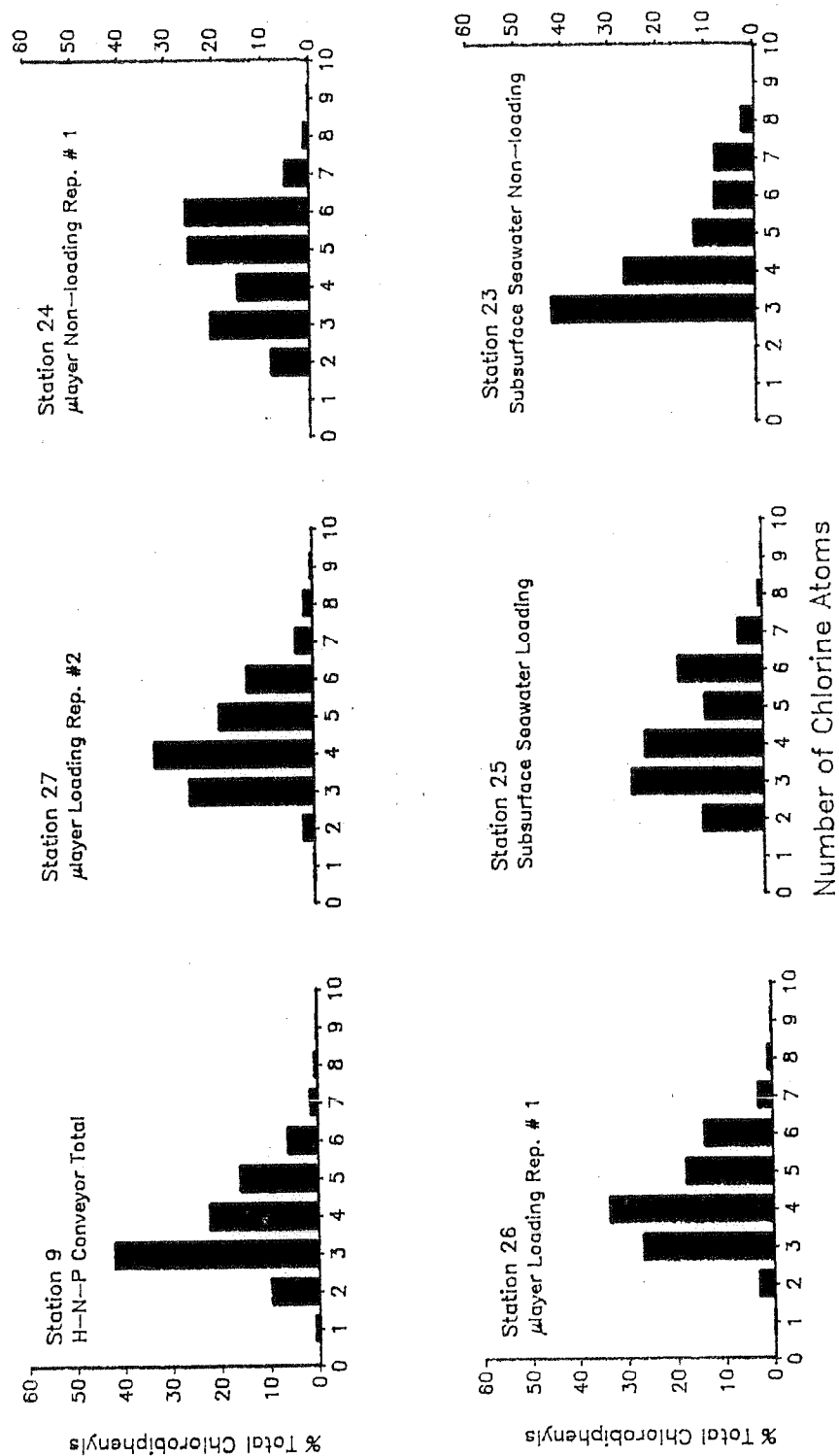
Figure 9 illustrates the distribution of PCBs by chlorination level in the Hugo-Neu-Proler conveyor debris (stn. 9) and the microlayer and subsurface seawater samples collected under both loading and non-loading conditions. Comparison of these diagrams with those obtained for the sediments (Figures 4-6) facilitates a discussion of potential PCB sources. Referring to Figure 9, it is clear that the two replicate microlayer samples obtained during loading conditions are dominated by the Cl_4 isomers with relative large quantities of Cl_3 isomers as well. These patterns bear a strong resemblance to that observed for the conveyor debris (Figures 7,8) in that they are dominated by the lower chlorinated PCBs. Moreover, these distributions are consistent with the results of Cross *et al.* (1987) who showed that 79% of the Σ PCB were present as Aroclor 1242 with the remainder made up by Aroclor 1254. The replicate samples taken during loading conditions have distributions that are essentially identical to each other suggesting that the PCBs originated from the same source or sources. By comparison, the microlayer sample obtained under non-loading conditions appears to have a bimodal distribution with maxima at Cl_3 and Cl_5 or Cl_6 . The bimodal pattern may indicate the presence of a mixture of materials derived from Hugo-Neu-Proler and other, as yet unidentified, sources. Examination of Figures 4-7 suggests that these sources could be sediments resuspended from almost any area of the harbor.

The subsurface seawater collected during loading conditions is also enriched in the Cl_3 isomers. However, the distribution is again bimodal with a second peak at Cl_6 . This suggests that possibly two (or more) sources of PCB are important contributors to the PCB burden of suspended particles below the air-water interface during loading. The lower chlorinated species may derive from Hugo-Neu-Proler debris, whereas the maximum at Cl_6 may represent materials from other parts of the harbor. It is interesting to note the strong dominance of the PCB distribution by the Cl_3 isomers in the non-loading subsurface seawater sample. This again shows an influence from the Hugo-Neu-Proler site. The surprisingly low 66,95/18 ratios (Table 3) exhibited by both microlayer and subsurface particles during loading and non-loading conditions further supports the hypothesis that the Hugo-Neu-Proler contributes PCB-bearing particles to harbor waters.

CONCLUSIONS

Los Angeles Harbor is a complex environment. There can be little doubt that the number of sources of PCB and their relative rates of input have varied over time. Moreover, it is highly likely that these materials have been redistributed throughout the harbor as a result of tidal flushing, shipping activities and dredge and fill projects. This

Figure 9. Distribution of PCBs according to chlorination level: Microlayer and subsurface seawater samples.



report presents strong evidence that Hugo-Neu-Proler, a scrap steel processing facility, is presently introducing PCB-bearing debris into the harbor, contaminating both surface waters and nearby sediments.

On the basis of our limited sampling of the harbor, and, in particular, the environment immediately adjacent to the Hugo-Neu-Proler site, the areal extent of severe contamination of sediments is restricted. In particular, the concentration of Σ PCB declines and other indicators of sediment contamination related to the loading operation (e.g. PCB isomer distribution, Σ PCB/DDT, Fe, TEO, TOC,) change rapidly within a short distance of the transfer point. Contamination of these sediments probably results mainly from release of relatively large, rapidly sinking solids during the loading of ships as opposed to more chronic input due to continuous mobilization of PCB-bearing aerosols into the atmosphere.

The analysis of microlayer and subsurface seawater samples under loading and non-loading conditions shows that the contamination of harbor waters is occurring. The absence of DDT in suspended particles collected both at the water surface and below the air-sea interface as well as the enrichment of low molecular weight PCB isomers ($\text{Cl}_{3,4}$) in these samples during non-loading conditions strongly suggests that Hugo-Neu-Proler is a **chronic** source of PCBs. The degree of PCB contamination of the sea surface microlayer, evidenced by visible iron-rich slicks during loading conditions, is approximately 100 times greater than during non-loading conditions. At these times concentrations of Σ PCB reach $21.1\text{-}58.4 \mu\text{g g}^{-1}$ or $40\text{-}53 \mu\text{g liter}^{-1}$ (particulate phase only). These high concentrations are in agreement with independent measurements made on samples collected from the East Turning Basin during similar loading conditions (Cross *et al.* 1987) . Moreover, the absence of DDT, the high particulate iron concentrations and the dominance of the PCB chlorination patterns by Cl_3 and Cl_4 isomers implicate the Hugo-Neu-Proler site as the source of these PCBs.

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APPENDIX A. Table containing a complete listing of all results obtained for the Los Angeles Harbor project. Results are presented in ng/dry g unless otherwise indicated.

STATION:	1	2	3	4	5	6	7	8	9	9a	9b	9c	10a	10b	10c
CONGENER	Consol. Slip	E.Turn Basin	H.Ford Bridge	Fuel Dock	Main Chan.	West Basin	Todd Ship.	Todd Ship.	HNP Conv.	HNP Conv.	HNP Conv.	HNP Conv.	HNP Conv.	HNP Conv.	HNP Conv.
NUMBER	Berth 200G	Berth 195	Berth 101	Berth 150	Berth 88	Berth 128	Wharf "D"	Wharf "A/B"	Total	>2mm	.5-2mm	<.5mm	>2mm	.5-2mm	<.5mm
Monochlorobiphenyls															
3	8.0	nd ^a	nd	1.0	0.5	nd	nd	nd	271	117	259	301	217	144	209
Dichlorobiphenyls															
10,4	49.6	5.1	1.7	2.4	0.9	nd	10.1	4.9	939	332	923	786	785	557	608
6	nd	nd	nd	nd	nd	nd	nd	nd	398	124	270	304	228	148	212
8,5	1.5	nd	nd	nd	nd	nd	6.2	7.1	1620	985	1920	2140	1680	1060	1440
Trichlorobiphenyls															
19	31.3	nd	nd	nd	nd	nd	nd	nd	244	115	376	211	211	150	186
18	3.2	2.6	0.6	nd	0.3	nd	4.8	13.7	2140	1450	2700	3060	2510	1540	2100
15,17	nd	2.2	0.4	nd	0.3	nd	nd	3.7	989	685	1310	1610	1190	804	1110
27	nd	nd	nd	nd	nd	nd	nd	nd	506	552	1150	1380	1050	735	1110
16,32	3.0	1.9	0.3	nd	0.4	0.4	1.6	4.0	1190	974	1810	2100	1650	1050	1410
23,29	11.9	4.5	nd	nd	0.4	nd	nd	nd	193	101	170	258	140	121	149
26	1.3	0.6	nd	nd	0.2	nd	0.7	1.9	334	226	452	499	374	247	370
25	21.0	3.9	0.6	1.8	0.3	0.8	10.9	3.9	428	267	562	616	439	300	428
31	5.8	nd	nd	3.4	0.9	1.7	nd	nd	1600	2140	2500	2870	2530	1420	2080
28	8.6	9.4	1.1	nd	nd	nd	3.9	13.6	2080	nd	3340	3980	2830	2070	2750
33,(53)	10.0	4.1	0.5	2.2	0.1	1.0	3.5	6.2	1590	1350	2630	3150	2440	1510	2090
(51),22	7.3	3.4	nd	1.3	0.2	nd	1.9	3.9	1380	1240	2360	2870	2200	1360	1900
Tetrachlorobiphenyls															
45	26.2	nd	nd	0.9	nd	nd	nd	nd	238	112	240	273	193	131	174
46	nd	1.5	nd	1.0	0.3	0.6	2.2	3.3	224	124	266	306	217	143	214
52,73	14.5	8.4	1.7	3.2	1.8	4.3	17.6	27.5	1130	1470	2500	3140	2670	1660	2440
49	208	4.8	1.0	nd	0.9	1.9	39.1	9.6	730	596	1060	1450	1130	688	985
47,75	80.2	4.0	0.7	12.0	0.6	0.9	1.9	5.1	566	634	115	518	341	88.9	88.7
44	5.0	3.5	1.0	1.8	1.0	2.4	7.1	13.3	889	887	1880	2550	2220	1770	2540
37,59,42	7.2	nd	nd	0.9	1.1	1.3	1.3	6.6	626	544	1020	1200	878	578	834

(Continued on next page)

APPENDIX A (cont.)

STATION:

	1	2	3	4	5	6	7	8	9	9a	9b	9c	10a	10b	10c
64	6.7	3.7	0.9	2.5	1.0	1.6	5.0	8.0	772	593	1170	1510	986	711	1250
67	49.7	nd	nd	3.0	nd	nd	nd	nd	101	39.8	127	64.5	55.5	105	77
63	6.5	nd	nd	0.4	0.2	0.6	nd	4.5	65.4	41.6	79.6	106	78.5	44.8	73
61,74	6.7	2.9	0.7	1.7	0.5	1.4	11.3	nd	312	266	522	608	516	294	417
70,76	12.3	6.2	1.8	2.6	1.4	3.2	10.2	15.4	674	654	1270	1530	1190	732	957
56,60	47.6	3.6	3.4	2.6	2.3	1.2	2.5	4.5	360	400	772	914	712	427	637
Pentachlorobiphenyls															
66,95	20.7	20.0	3.8	6.5	3.4	8.4	23.7	49.8	998	959	1880	2220	1760	1080	1450
91	2.6	0.5	0.6	2.1	0.6	1.4	3.3	5.7	117	72.4	114	127	116	118	90
92,84	48.6	nd	nd	nd	nd	nd	nd	10.3	nd	66.8	147	196	157	102	137
89 ^b	(37.1)	(20.2)	(16.0)	(11.4)	(11.5)	(10.0)	(40.5)	(18.5)	168	166	345	376	304	195	298
101	20.2	20.6	3.9	6.4	3.7	11.4	29.4	67.3	564	592	1170	1490	1160	737	1100
99	146	nd	2.6	15.0	2.5	17.6	116	nd	618	244	513	643	479	376	562
83	4.5	12.9	9.2	nd	1.8	nd	18.4	11.1	87.8	66.4	172	181	118	122	144
86,97	4.2	4.1	1.1	1.7	1.4	3.2	7.9	16.1	178	158	291	391	291	182	316
87,115	11.7	6.8	1.6	2.5	1.4	5.4	14.3	25.2	297	314	597	752	575	390	574
85 ^b	(262)	(169)	(142)	(81.7)	(90.4)	(69.8)	(189)	(66.8)	179	165	128	311	133	323	298
110	37.4	24.9	3.0	8.4	1.5	14.2	38.4	61.8	615	567	1270	1580	1240	812	1200
82	7.9	nd	nd	0.5	nd	1.2	4.6	5.9	109	92.0	168	215	162	98.1	162
108,107	10.8	4.2	0.8	1.6	0.9	3.1	6.4	11.4	111	82.6	175	237	156	113	154
118	9.2	13.3	3.4	nd	2.8	9.6	19.3	nd	426	554	1060	1430	1050	705	1020
114,131 ^b	(30.4)	nd	nd	(3.8)	(49.8)	(3.9)	(53.2)	(9.0)	70.2	57.7	130	170	107	88.0	125
132,105	14.1	nd	2.7	4.5	2.5	7.9	17.9	15.7	312	939	1670	2080	1580	750	1530
Hexachlorobiphenyls															
136	14.0	12.1	nd	3.1	0.1	2.4	5.4	22.9	49.0	37.1	103	131	90.3	150	106
151	23.1	17.4	1.0	2.3	0.9	2.0	5.4	54.9	87.3	67.3	142	201	133	70.2	94.5
135,144	12.6	12.0	0.8	2.6	0.9	3.1	6.6	34.7	116	106	21.6	23.1	28.6	29.0	60.8
149	31.4	36.5	3.1	3.0	3.0	8.0	18.8	56.4	242	324	609	650	583	330	555
134 ^b	(492)	(222)	(27.9)	(49.2)	(46.4)	(36.0)	(164)	(75.3)	131	91.4	254	285	273	226	403
146,165	11.3	8.8	0.9	2.1	0.9	2.2	6.1	23.4	66.9	49.6	99.9	122	80.6	71.4	107
153	36.4	29.2	3.4	8.4	3.4	9.0	21.3	88.8	250	508	992	1120	967	577	854
141,179	7.5	11.5	0.8	1.9	1.0	2.5	6.4	89.2	61.9	744	172	167	129	82.1	120
137	nd	2.0	0.6	1.0	nd	2.2	4.6	12.1	88.2	57.3	171	260	155	121	219

(Continued on next page)

APPENDIX A (cont.)

STATION:	1	2	3	4	5	6	7	8	9	9a	9b	9c	10a	10b	10c
138	39.1	41.5	4.2	11.0	5.1	13.5	30.8	148	423	510	1030	1310	1020	666	1020
158	4.3	5.3	nd	1.3	0.7	1.6	4.6	17.6	58.5	67.2	147	196	119	91.2	158
129	8.0	nd	0.6	0.9	0.3	nd	nd	nd	91.2	35.3	83.9	13.6	53.7	37.7	39.8
166	nd	nd	nd	nd	nd	nd	nd	0.2	0.7	0.1	0.2	0.4	0.2	0.6	0.4
128,167	8.8	3.9	0.8	1.7	0.8	2.5	9.5	16.7	78.7	107	141	163	188	116	146
171,156	12.2	2.1	2.6	2.5	3.1	3.2	8.2	100	109	144	21.3	24.7	395	242	359
173,157	2.6	3.0	0.6	nd	0.7	1.1	5.8	17.0	29.5	27.1	7.8	79.4	63.6	4.8	9.9
Heptachlorobiphenyls															
176 ^b	(33.7)	(5.8)	(0.4)	(1.3)	(1.2)	(0.9)	(106)	(15.2)	53.6	32.7	92.2	123	47.1	66.9	129
178	5.8	20.9	1.8	nd	1.1	3.1	7.2	75.1	nd	nd	4.9	5.4	nd	3.8	3.2
187,182	19.3	22.5	1.1	3.8	1.1	2.0	5.5	62.3	61.6	69.9	139	181	170	93.2	149
183	13.3	14.0	0.7	2.5	0.7	1.4	4.2	42.4	42.0	37.5	97.5	122	97.3	59.0	90.1
185	8.0	7.8	0.6	1.1	nd	0.6	2.1	21.1	36.2	15.1	52.8	66.0	26.1	10.5	5.5
174,181	13.7	18.9	0.7	2.2	1.1	2.1	5.8	59.2	47.1	45.2	126	160	17.2	71.8	22.0
177	11.3	13.7	0.6	2.0	0.7	1.5	3.7	40.8	39.1	30.7	89.4	140	92.2	78.4	106
192,172	4.7	6.9	0.4	nd	0.4	0.7	17.2	23.0	16.6	24.0	16.0	33.3	74.5	29.1	58.1
180	36.6	36.0	1.7	5.6	1.7	3.7	14.0	137	127	144	273	353	362	183	259
193	nd	nd	nd	nd	nd	nd	nd	16.6	1.0	38.3	98.0	136	95.3	31.2	113
191	nd	0.2	nd	nd	nd	nd	nd	1.1	nd	0.1	0.6	0.2	0.3	0.2	0.4
170,190	12.6	15.7	0.7	3.2	0.9	1.9	6.2	55.4	52.9	36.0	131	178	141	94.8	37.2
189	nd	nd	nd	nd	nd	nd	nd	0.1	nd	nd	0.1	0.3	0.2	0.7	0.3
Octachlorobiphenyls															
199	2.7	3.7	0.2	0.7	0.2	0.4	0.9	13.7	9.6	3.7	2.5	8.63	21.0	10.9	3.4
201	12.5	13.1	0.8	3.1	0.7	1.5	4.0	36.9	48.0	77.8	164	215	214	99.3	75.9
196,203	14.8	15.8	1.0	3.0	0.9	2.0	4.0	63.3	67.9	90.3	192	261	224	86.5	185
195	12.6	11.1	0.8	3.3	0.7	1.5	3.1	35.9	43.7	3.4	55.6	27.9	82.7	21.4	49.9
194	10.4	15.9	1.7	2.1	0.6	1.1	2.7	43.6	43.2	75.9	139	177	166	81.6	113
Nonachlorobiphenyls															
206	7.7	8.8	0.7	2.5	0.5	1.3	2.8	22.0	54.9	73.4	130	200	132	56.0	140
TOTAL PCB ^c	1370	594	82.0	171	70.3	185	658	1870	30100	25100	49400	59800	47300	30700	43800

(Continued on next page)

APPENDIX A (cont.)

STATION: 1 2 3 4 5 6 7 8 9 9a 9b 9c 10a 10b 10c

RESULTS BY CHLORINATION LEVEL

Mono	8.0	nd	nd	1.0	0.5	nd	nd	nd	nd	271	117	259	301	217	144	209
Di	51.1	5.1	1.7	2.4	0.9	nd	16.3	12.0	2960	1440	3110	3230	2690	1760	2260	
Tri	103	32.6	3.5	8.7	3.1	3.9	27.3	50.9	12700	9090	19400	22600	17600	11300	15700	
Tetra	470	38.6	11.2	32.6	11.1	19.4	98.2	97.8	6670	6360	11000	14200	11200	7370	10700	
Penta ^C	338	107	32.7	49.2	22.5	83.4	300	280	4850	5100	9850	12400	9390	6190	9160	
Hexa ^C	211	185	19.4	41.8	20.9	53.3	134	682	1880	2210	4000	4750	4280	2810	4250	
Hepta ^C	125	157	8.3	20.4	7.7	17.0	65.9	534	477	470	1120	1500	1120	722	974	
Octa	53.0	59.6	4.5	12.2	3.1	6.5	14.7	193	212	251	553	690	707	300	427	
Nona	7.7	8.8	0.7	2.5	0.5	1.3	2.8	22.0	54.9	73.4	130	200	132	56.0	140	

SURROGATE RECOVERIES IN PERCENT

#30	92	121	105	85	125	74	94	75	57	63	88	70	70	70	68
#112	73	107	103	83	94	74	80	73	44	40	87	85	55	100	67
#198	61	101	94	93	85	75	85	84	55	30	88	92	62	81	78

OTHER CONSTITUENTS

<i>o,p'</i> -DDE	19.8	9.6	8.0	6.1	5.5	5.1	20.6	8.8	nd	nd	nd	nd	nd	nd	nd
<i>p,p'</i> -DDE	114	63.3	56.2	35.6	34.9	25.6	69.5	25.0	nd	nd	nd	nd	nd	nd	nd
<i>p,p'</i> -DDD	67.7	6.9	7.3	10.2	10.7	8.1	36.9	15.4	nd	nd	nd	nd	nd	nd	nd
<i>o,p'</i> -DDT	14.2	nd	nd	1.8	20.0	1.5	20.6	3.5	nd	nd	nd	nd	nd	nd	nd
<i>p,p'</i> -DDT	10.9	nd	1.7	1.2	76.1	nd	89.4	nd	nd	nd	nd	nd	nd	nd	nd
TOTAL DDT ^d	227	79.8	73.2	54.9	147	40.3	237	52.7	nd	nd	nd	nd	nd	nd	nd
Dry/Wet Ratio	0.44	0.60	0.52	0.63	0.56	0.61	0.37	0.59	0.97	N/A ^e	N/A	N/A	N/A	N/A	N/A
TEQ(mg/dry g)	18.2	2.56	0.98	1.88	0.45	0.89	4.78	5.66	63.7	30.1	68.4	70.5	92.0	69.9	69.1
% TOC	5.45	1.51	1.83	0.76	1.24	0.71	2.87	1.85	N/A	N/A	N/A	14.2	N/A	N/A	13.7
% Iron	3.59	2.90	3.39	2.11	2.34	2.52	3.38	2.51	N/A	N/A	N/A	19.9	N/A	N/A	16.7
SS(mg/L)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

- a nd = not detected; detection limit estimates given in Eganhouse *et al.* (1987).
b Results in parentheses indicate interference due to the presence of a DDT metabolite.
c These totals do not include congeners with DDT interference (numbers in parentheses).
d *o,p'*-DDD was not quantified because it is interfered with by PCB congener 110.
e N/A = Not Analyzed.

APPENDIX A (cont.)

STATION:	11a	11b	11c	12	13	14	15	16	17	18	19	20	21	22
CONGENER NUMBER	HNP Conv. >2mm	HNP Conv. .5-2mm	HNP Conv. <.5mm	HNP N.W. Corner	HNP Stern Berth 211	HNP Mid Berth 211	HNP Bow Berth 211	Cerrit. Chan. Berth 206	Main Chan. Berth 220	E.Turn Basin Berth 215	E.Turn Basin Mid Chan. Berth 215	Consol. Slip Berth 197	Consol. Slip Berth 200B	E.Turn Basin Yacht Anch.
Monochlorobiphenyls														
3	24.7	16.1	18.2	1.1	0.4	54.8	1.7	0.2	nd ^a	nd	nd	nd	nd	nd
Dichlorobiphenyls														
10,4	156	230	105	19.0	1.9	171	8.5	nd	0.9	nd	1.3	nd	4.4	nd
6	34.2	29.4	40.4	1.0	1.1	74.7	4.3	0.1	nd	0.3	0.2	2.7	0.9	0.1
8,5	228	205	280	4.2	9.0	564	20.1	0.2	0.1	2.5	1.6	4.6	1.4	nd
Trichlorobiphenyls														
19	31.5	29.7	37.6	5.6	1.3	61.5	5.1	nd	0.1	0.4	0.4	2.1	5.6	nd
18	324	323	485	14.7	18.1	700	43.0	2.6	0.5	2.6	2.8	6.2	9.2	1.0
15,17	188	194	269	8.9	8.6	381	26.1	1.5	0.3	1.2	1.2	34.6	5.1	0.4
27	157	159	242	8.4	7.9	275	20.5	1.9	0.2	1.2	2.1	4.4	7.6	0.6
16,32	242	268	364	12.6	10.5	350	24.8	0.7	0.2	1.5	1.8	4.9	6.0	0.5
23,29	40.8	47.1	56.6	6.7	1.4	49.8	6.9	5.0	0.6	2.2	1.4	15.6	19.3	0.8
26	81.0	90.1	135	2.9	1.6	95.0	7.2	0.3	0.1	0.4	0.3	1.4	1.9	0.2
25	96.8	161	183	3.9	1.7	131	14.3	0.8	nd	nd	0.6	nd	nd	0.3
31	450	512	706	nd	33.7	573	35.6	1.0	0.3	2.4	3.2	6.1	7.9	0.8
28	681	828	1120	nd	nd	nd	62.3	1.5	0.5	3.2	3.2	9.4	13.8	1.4
33,(53)	540	622	857	10.9	15.5	423	37.9	1.3	0.4	2.2	2.9	2.9	6.3	1.1
(51),22	492	582	819	10.5	15.5	403	35.4	1.5	0.3	2.0	2.4	6.5	10.7	0.9
Tetrachlorobiphenyls														
45	56.3	56.2	80.1	6.0	3.1	68.1	9.7	0.1	0.2	0.9	0.2	nd	nd	0.2
46	67.0	66.5	90.5	6.3	2.0	55.2	7.7	4.1	0.4	1.3	1.1	4.4	7.2	0.5
52,73	738	750	1090	33.7	21.4	469	47.1	2.8	1.0	4.9	4.6	11.9	17.8	2.0
49	352	321	503	17.8	10.8	325	35.5	nd	nd	8.8	6.2	nd	nd	nd
47,75	249	42.7	164	11.5	11.8	nd	41.5	nd	nd	3.6	2.7	15.1	19.5	nd
44	517	662	889	25.0	15.7	330	41.1	2.8	0.8	3.9	3.9	14.5	16.9	2.1
37,59,42	319	336	479	16.8	2.7	296	26.0	1.6	0.4	1.9	1.5	10.2	12.7	1.2

(Continued on next page)

APPENDIX A (cont.)

STATION:

	11a	11b	11c	12	13	14	15	16	17	18	19	20	21	22
64	333	364	483	16.5	6.5	368	37.2	2.4	0.7	2.6	4.1	9.2	17.0	1.7
67	39.4	33.8	68.7	1.5	0.6	52.8	3.9	nd	nd	nd	1.7	nd	nd	nd
63	33.7	30.6	49.6	0.9	1.1	19.2	3.0	nd	0.1	0.2	0.1	0.5	0.8	0.2
61,74	212	228	316	4.4	9.4	175	16.2	1.4	0.6	4.4	2.1	7.4	7.5	1.1
70,76	520	580	786	12.5	2.5	257	33.5	2.2	0.9	4.7	4.0	13.8	16.0	1.9
56,60	368	400	563	6.3	9.2	174	23.9	2.0	1.2	3.4	2.8	11.0	12.3	1.8
Pentachlorobiphenyls														
66,95	777	860	1190	3.8	42.4	695	110	1.5	3.6	16.6	16.4	63.0	60.7	8.3
91	56.6	65.6	87.6	4.0	0.2	34.3	3.2	0.9	0.3	1.1	0.5	3.1	5.4	0.4
92,84	89.6	72.6	111	5.1	1.7	55.6	4.5	nd	nd	nd	nd	3.0	4.2	0.5
89 ^b	159	175	232	(10.4)	(13.2)	(174)	(20.0)	(8.2)	(3.5)	(19.0)	(11.1)	(38.2)	(51.3)	(5.0)
101	686	668	895	31.0	16.3	313	41.8	5.4	1.9	6.3	6.3	36.3	32.6	4.2
99	284	269	370	12.2	11.4	187	21.5	5.9	1.5	13.9	7.8	49.1	80.4	4.1
83	81.8	87.4	128	6.1	0.2	55.0	12.9	0.2	2.4	9.9	6.0	2.3	38.3	3.4
86,97	194	187	258	9.4	4.6	137	11.8	1.6	0.6	2.5	2.0	6.1	5.9	1.1
87,115	374	373	514	15.9	12.0	177	20.4	2.4	1.0	4.7	6.7	10.5	10.7	1.9
85 ^b	446	484	643	(33.1)	(23.9)	(269)	(178)	(100)	(42.9)	(77.4)	(47.5)	(478)	(391)	(50.6)
110	754	671	1080	37.7	17.3	256	50.4	3.1	2.1	10.9	12.1	28.7	18.1	2.5
82	104	51.7	148	5.3	nd	81.8	6.1	1.1	0.3	0.9	1.4	nd	2.9	0.5
108,107	129	115	182	5.9	3.0	55.3	7.6	1.5	0.6	2.2	0.4	10.7	4.0	1.3
118	819	680	1060	22.5	11.3	nd	33.9	4.5	1.7	5.9	5.6	21.6	18.1	3.8
114,131 ^b	95.0	59.5	152	(10.6)	(3.5)	(35.9)	(11.9)	(3.3)	(0.1)	(6.3)	(3.3)	(39.1)	(38.8)	(2.8)
132,105	1280	1070	932	18.8	11.1	303	27.3	3.8	2.1	8.2	4.2	nd	13.5	2.3
Hexachlorobiphenyls														
136	54.6	50.6	75.3	3.4	1.3	53.6	6.9	0.9	0.5	1.6	1.1	19.3	14.8	1.3
151	94.8	28.8	114	6.1	2.9	95.1	11.2	1.9	0.5	1.8	2.3	48.2	33.8	2.5
135,144	134	135	182	7.6	5.3	93.9	11.9	1.4	0.6	2.0	0.2	24.6	18.9	1.8
149	383	416	580	19.7	17.5	81.0	32.2	5.0	1.6	8.5	8.9	73.4	59.6	5.6
134 ^b	235	216	345	(41.1)	(40.0)	(515)	(109)	(32.3)	(17.9)	(161)	(84.4)	(856)	(957)	(40.3)
146,165	74.1	78.6	103	4.8	0.2	41.2	8.0	1.3	0.5	nd	1.6	17.8	12.8	1.6
153	777	824	876	20.7	16.3	211	38.1	6.2	2.0	7.7	11.1	92.1	69.8	7.3
141,179	114	114	149	5.9	4.0	81.8	9.0	1.4	0.5	2.0	2.3	24.3	18.4	1.8
137	138	170	150	6.8	2.3	53.4	6.2	0.9	0.4	1.0	1.6	3.8	3.3	0.8

(Continued on next page)

APPENDIX A (cont.)

STATION:

	11a	11b	11c	12	13	14	15	16	17	18	19	20	21	22
138	732	677	1010	32.8	15.1	207	55.9	8.0	2.8	14.4	14.7	97.7	74.2	8.3
158	98.7	120	140	4.6	2.1	60.5	5.9	1.0	0.3	0.9	0.9	9.4	6.7	0.9
129	63.0	74.4	93.8	19.6	3.5	19.6	12.0	1.8	0.7	1.9	2.8	32.6	22.6	2.8
166	0.3	0.4	0.6	nd	nd	0.1	0.1	nd	nd	nd	nd	0.2	0.2	nd
128,167	166	208	166	5.2	2.2	70.4	7.6	1.3	0.5	1.7	0.9	4.4	3.2	1.2
171,156	270	326	414	8.8	2.1	129	14.4	2.4	0.7	1.7	3.4	31.2	1.4	2.9
173,157	3.6	16.7	9.7	2.5	0.8	2.8	3.1	1.1	nd	0.3	0.5	11.2	5.4	1.2
Heptachlorobiphenyls														
176 ^b	69.6	75.8	45.5	nd	(1.8)	(21.6)	(3.0)	(0.1)	nd	(0.7)	nd	(6.8)	(5.6)	(0.7)
178	nd	nd	nd	nd	2.8	0.9	4.1	2.7	0.9	4.1	2.3	nd	nd	nd
187,182	92.3	113	152	5.3	6.2	83.3	13.2	2.8	0.8	3.3	1.1	59.4	43.1	4.4
183	64.9	85.2	99.9	4.1	3.3	60.8	8.5	1.7	0.5	2.0	2.9	34.2	24.4	2.6
185	34.1	22.2	38.8	2.0	0.2	25.5	4.2	0.7	0.2	1.1	1.2	18.3	12.6	1.3
174,181	77.2	106	117	4.6	5.4	90.5	10.6	2.0	0.6	2.9	3.3	44.4	29.9	2.9
177	64.6	80.1	109	3.7	4.1	57.5	9.3	1.7	0.5	2.2	2.6	36.0	22.6	2.4
192,172	31.7	46.3	67.3	2.0	2.0	33.7	5.3	1.5	0.3	0.9	1.5	24.8	13.8	1.9
180	222	281	382	9.1	8.3	106	2.3	4.2	1.2	5.9	10.2	128	89.6	7.3
193	39.0	23.0	99.9	nd	0.9	19.6	2.0	0.6	nd	0.1	0.5	12.6	9.4	1.3
191	nd	0.3	0.3	nd	nd	0.7	nd	nd	nd	nd	nd	0.4	0.2	nd
170,190	117	171	188	5.2	6.0	89.6	11.9	2.1	0.6	3.4	4.3	44.9	30.1	3.4
189	0.1	0.2	nd	nd	nd	0.2	nd	nd	nd	nd	nd	nd	nd	nd
Octachlorobiphenyls														
199	25.8	18.0	41.4	0.8	0.7	10.5	0.3	0.4	0.2	0.6	0.6	8.6	6.3	0.7
201	103	111	193	3.9	6.0	96.2	8.0	2.1	0.6	2.6	3.6	3.1	26.9	3.3
196,203	104	138	187	4.6	7.5	105	9.3	2.1	0.7	2.3	4.0	44.8	30.4	3.7
195	39.8	35.4	26.9	11.1	0.2	35.2	4.4	1.1	0.4	1.9	2.2	22.8	16.0	2.3
194	84.5	114	141	3.4	0.6	73.6	8.2	1.9	0.5	2.2	3.5	44.8	27.2	3.2
Nonachlorobiphenyls														
206	91.8	84.8	152	4.6	5.0	25.2	5.0	1.7	0.6	1.2	2.3	14.7	12.9	2.0
TOTAL PCB ^c	18500	19000	25700	660	491	11400	1360	134	49.1	228	228	1470	1260	138

(Continued on next page)

STATION:	11a	11b	11c	12	13	14	15	16	17	18	19	20	21	22
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[illegible]

#30	70	72	75	N/A ^e	64	88	80	96	87	112	90	75	78	45
#112	52	70	79	N/A	49	57	80	78	91	111	90	69	77	57
#198	59	66	69	N/A	64	30	98	121	138	104	94	112	97	94

[illegible]

^b Results in parentheses indicate interference due to the presence of a DDT metabolite.

^d o,p'-DDD was not quantified because it is interfered with by PCB congener 110.

(Continued on next page)

APPENDIX A (cont.)

STATION:	23	24	25	26	27
	Sea	Micro	Sea	Micro	Micro
	Water	Layer	Water	Layer	Layer
CONGENER	Non-Load	Non-Load	Loading	Loading	Loading
NUMBER	Rep #1	Rep #1	Rep #1	Rep #1	Rep #2
<hr/>					
Monochlorobiphenyls					
3	nd ^a	nd	nd	44.1	95.4
<hr/>					
Dichlorobiphenyls					
10,4	nd	400	13.6	99.6	240
6	nd	nd	3.9	87.4	208
8,5	nd	42.2	31.6	498	904
<hr/>					
Trichlorobiphenyls					
19	75.9	nd	nd	69.5	118
18	nd	116	8.0	1100	2370
15,17	nd	440	7.7	527	1070
27	nd	54.3	3.0	204	470
16,32	21.4	57.3	4.8	585	1520
23,29	137	72.2	9.9	106	211
26	7.7	3.3	2.3	234	521
25	35.0	38.4	6.7	266	660
31	2.7	78.0	11.6	971	3020
28	nd	94.5	19.9	nd	nd
33,(53)	nd	76.1	14.8	774	2210
(51),22	21.8	90.2	17.8	812	2690
<hr/>					
Tetrachlorobiphenyls					
45	nd	16.7	7.7	143	269
46	117	30.2	31.3	137	282
52,73	20.0	188	6.2	733	2140
49	23.2	45.1	5.8	617	1760
47,75	nd	284	nd	2550	4150
44	16.8	100	5.9	502	1760
37,59,42	nd	10.4	5.8	570	1660

(Continued on next page)

APPENDIX A (cont.)

STATION:

23

24

25

26

27

64	nd	5.3	6.7	725	2480
67	nd	nd	nd	30.4	1080
63	nd	5.7	nd	43.0	131
61,74	3.6	41.6	10.0	310	983
70,76	2.7	53.1	10.5	409	1470
56,60	9.1	40.2	5.6	321	1030

Pentachlorobiphenyls

66,95	20.0	104	14.5	618	1970
91	nd	15.9	1.0	33.2	166
92,84	nd	nd	nd	50.5	159
89 ^b	(14.5)	77.3	4.4	251	52.2
101	9.1	89.6	3.5	397	1200
99	17.3	115	5.4	303	986
83	nd	56.9	nd	44.6	147
86,97	4.5	20.4	1.4	154	424
87,115	nd	50.4	3.8	266	805
85 ^b	(49.1)	508	nd	79.6	356
110	10.5	32.9	6.4	367	1190
82	9.1	15.5	1.3	129	344
108,107	10.0	23.1	1.2	88.8	317
118	7.7	65.7	2.7	293	1020
114,131 ^b	(5.0)	121	nd	140	309
132,105	nd	77.3	0.9	586	1880

Hexachlorobiphenyls

136	6.8	2.2	1.6	39.5	80.5
151	8.6	22.4	nd	51.9	204
135,144	nd	27.3	1.6	96.7	315
149	12.7	73.7	4.1	340	1170
134 ^b	(41.8)	937	9.9	341	641
146,165	nd	13.3	2.5	37.7	136
153	10.0	116	2.3	293	962
141,179	5.5	2.0	0.7	73.2	294
137	nd	8.8	nd	60.7	336

(Continued on next page)

APPENDIX A (cont.)

STATION:

23 24 25 26 27

138	10.9	110	6.2	317	1090
158	nd	12.4	0.6	58.4	267
129	nd	nd	0.8	1.6	28.6
166	nd	nd	nd	0.1	1.2
128,167	3.2	22.9	0.7	88.4	227
171,156	nd	42.7	31.8	1170	2290
173,157	nd	5.3	5.2	1.9	12.9

Heptachlorobiphenyls

176 ^b	(5.5)	nd	4.5	34.6	159
178	nd	nd	nd	nd	nd
187,182	5.0	30.4	1.6	58.7	279
183	14.1	14.9	0.4	32.8	127
185	2.7	11.8	nd	8.3	34.2
174,181	4.1	26.9	1.2	67.1	256
177	5.9	20.4	0.6	56.7	262
192,172	nd	8.0	2.4	21.9	155
180	4.5	42.9	1.5	138	429
193	16.8	89.4	6.1	146	40.8
191	nd	nd	nd	0.1	2.6
170,190	3.6	30.8	1.0	85.8	440
189	nd	nd	nd	nd	0.2

Octachlorobiphenyls

99	6.4	3.5	nd	9.0	23.5
201	2.7	21.8	1.9	53.5	335
196,203	2.7	20.8	0.6	58.0	346
195	5.0	8.8	0.5	24.5	84.7
194	nd	13.1	0.5	47.6	333

Nonachlorobiphenyls

206	nd	12.7	0.9	53.2	254
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TOTAL PCB ^c	713	5500	389	21100	58400
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(Continued on next page)

APPENDIX A (cont.)

STATION: 23 24 25 26 27

RESULTS BY CHLORINATION LEVEL

Mono	nd	nd	nd	44.1	95.4
Di	nd	442	49.1	685	1350
Tri	302	1120	106	5650	14900
Tetra	192	820	95.5	7090	19200
Penta ^c	88.2	1370	46.5	3800	11300
Hexa ^c	57.7	1400	68.0	2970	8060
Hepa ^c	56.7	276	19.3	650	2180
Octa	16.8	68.0	3.5	193	1120
Nona	nd	12.7	0.9	53.2	254

SURROGATE RECOVERIES (IN PERCENT)

#30	130	163	120	115	59
#112	59	56	115	7	36
#198	66	65	112	241	129

OTHER CONSTITUENTS

<i>o,p'</i> -DDE	8.7	nd	nd	nd	nd
<i>p,p'</i> -DDE	59.1	nd	nd	nd	nd
<i>p,p'</i> -DDD	37.6	nd	nd	nd	nd
<i>o,p'</i> DDT	7.8	nd	nd	nd	nd
<i>p,p'</i> -DDT	3.0	nd	nd	nd	nd
TOTAL DDT ^d	116	nd	nd	nd	nd

Dry/Wet Ratio	N/A ^e	N/A	N/A	N/A	N/A
TEQ(mg/dry g)	N/A	193	228	33.7	235
% TOC	1.00	10.1	5.15	10.3	11.3
% Iron	3.81	4.66	3.61	24.8	22.8
SS(mg/L)	21.9	49.0	17.0	1896	913

a nd = not detected; detection limit estimates given in Eganhouse *et al.* (1987).

b Results in parentheses indicate interference due to the presence of a DDT metabolite.

c These totals do not include congeners with DDT interference (numbers in parentheses).

d *o,p'*-DDD was not quantified because it is interfered with by PCB congener 110.

e N/A= Not analyzed.