

# Organochlorine Pesticides and Other Trace Organic Contaminants in the Upper Newport Bay Watershed

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## ABSTRACT

Upper Newport Bay (UNB), located at the base of the San Diego Creek and Santa Ana-Delhi Channel watersheds, is a valuable ecological and recreational resource. However, trace organic contaminants such as DDTs, PCBs, chlordanes, and PAHs are potentially threatening the ecological and recreational resources in UNB. The goals of this study were to: 1) link the sediment reservoir of these contaminants in the UNB and their input from the watershed via stormwater; and 2) identify the source of these contaminants in UNB sediment from a variety of land uses in the watershed. To accomplish these goals, six sites comprising residential, commercial/industrial, agricultural, and construction land uses, plus two mass emission sites located at the end of the San Diego Creek and Santa Ana-Delhi Channel watersheds, were sampled during three storm events in 2006. In addition, bedded sediments at four sites in UNB were sampled in July 2006 following the wet season. Laboratory analysis included gas chromatography-mass spectrometry (GC-MS), compound specific isotope analysis (CSIA), and chiral gas chromatography (CGC). Concentrations of trace organic contaminants in stormwater particles from both Santa Ana-Delhi Channel and San Diego Creek were greater than, or equal to, the concentrations of trace organic contaminants measured in UNB bedded sediments. These differences were statistically significant for total PAH and PCB ( $p < 0.05$ ), but not for total chlordane and DDT. This indicated that stormwater inputs are not diminishing, and could be adding to, the sediment contamination found in UNB. It was clear that some trace organic constituents were associated with some land uses more than others. For example, average stormwater particulate concentration of total DDT at agricultural land use sites ( $869 \pm 150$  ng/g) was an order of magnitude greater than any other land use examined ( $p < 0.01$ ). Similarly, the average stormwater concentration of total PCB at construction land use sites ( $681 \pm 535$  ng/g) was an order of magnitude greater than any other land use examined although this difference was not statistically significant. While residential and industrial/commercial land uses had substantially lower stormwater particulate concentrations of total DDT or total PCB (significantly different for PCBs;  $p = 0.042$ ), their average stormwater particulate concentrations of total PAH ( $1,550 \pm 462$  and  $26,100 \pm 35,200$  ng/g, respectively) were one to two orders of magnitude greater than either agriculture or construction land uses. Because of the large variability associated with the total PAH data, however, these differences were not statistically significant. These data were supported by CSIA analysis that indicated stormwater particulate concentrations from agricultural land uses had a different  $\delta^{13}\text{C}$  signature than other land uses. The CGC analysis demonstrated that chlordane enantiomeric fraction (EF) ratios in stormwater particulates were similar between construction, and to a lesser extent agricultural, land use sites and stormwater particulates from mass emission sites. Both the CSIA and CGC results were further supported by DDT/DDE and trans/cis chlordane ratios, respectively.

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## INTRODUCTION

Newport Bay is a valuable ecological and recreational resource. The lower portion of Newport Bay is one of the largest small craft harbors in California and the focus of an intensive recreational boating and fishing industry. Upper Newport Bay (UNB) is also one of the few remaining wetlands in southern California and the largest in the region (Dailey *et al.* 1993). It is a California State Ecological Reserve and serves as refuge, foraging areas, and breeding grounds for a number of threatened and endangered species. UNB is an important stop on the Pacific Flyway for 50,000 migratory birds each year. It also provides significant spawning and nursery habitats for commercial and non-commercial fish species (Allen 1976, Horn and Allen 1981). These diverse habitats make UNB an important ecosystem within the urban landscape of southern California.

Trace organic contaminants are potentially threatening the ecological and recreational resources in UNB. Organochlorine pesticides (OCP) such as DDT or chlordane were used historically in urban and agricultural applications throughout the bay's watershed, but were banned from use in the 1970's. Polychlorinated biphenyls (PCBs) had industrial applications prior to its removal from use in the 1970's. Polycyclic aromatic hydrocarbons (PAHs), most commonly associated with combustion of fossil fuels, continue to be a source to UNB even today. All of these potential trace organic contaminants are transported to the UNB through the municipal separate storm sewer system. Stormwater runoff, and the pollutants associated with land use based sources of these trace organic contaminants, enter the storm drainage system and are discharged to the UNB largely untreated whenever it rains.

As a result of OCPs and other contaminants, portions of UNB are currently listed as impaired waterbodies by the State of California (SWRCB 2001) due to elevated levels in both sediment and water column. Bay *et al.* (2004) observed sediment toxicity at multiple locations throughout the upper and lower portions of Newport Bay. Allen *et al.* (2004) found that many fishes in Newport Bay had bioaccumulated OCPs to levels above screening values for human or wildlife consumption; DDT was the most widespread contaminant.

Environmental managers are often faced with difficult choices with regard to the environmental problems in UNB linked to these trace organic contaminants. First, the listing of UNB as an impaired water body calls for mitigation measures to minimize the ecological impact of these contaminants on UNB. However, it is still unclear exactly where in the watershed the land-based source(s) occur and to what extent each individual source contributes to the inventory of trace organic contaminants in UNB. Factors such as imperviousness, land use activities, distance from UNB, and others complicate a manager's ability to differentiate sources and create best management practices to minimize inputs of OCPs. The objective of this study was to investigate the occurrence and distribution of OCPs, PCBs and PAHs in the stormwater of the UNB watershed and in the receiving water and sediment of UNB. Specifically, the goals of this study were to:

- 1) link the sediment reservoir of these contaminants in the UNB and their input from the

watershed via stormwater; and 2) identify the source of these contaminants in UNB sediment from a variety of land uses in the watershed.

Three different tools were used to achieve the goals of the study: 1) bulk concentration data from stormwater discharges and UNB sediments; 2) compound-specific isotope analysis (CSIA); and 3) chiral gas chromatography (CGC). Both CSIA and CGC yield concentration-independent chemical fingerprints. These new methods have been used with increasing frequency and sophistication in source identification and apportionment of trace organic compounds in the environment (Glaser *et al.* 2005, Phillips and Gregg 2003, Ruyken and Pijpers 1987, Schurig 2002, Wang *et al.* 1999). The utility of these methods lies in the fact that isotope ratios and chiral ratios of a chemical compound bear unique information on their origins, physical/chemical fractionations, and chemical/biological transformation and elimination processes. Therefore, these fingerprints can potentially be used to identify and/or discriminate different sources within a watershed and investigate post-release processes (Galimov 2006 and references therein, Schurig 2002).

## METHODS

The UNB watershed encompasses 98,847 acres (154 square miles) and includes all or portions of the cities of Irvine, Tustin, Costa Mesa, Newport Beach, Santa Ana, Laguna Hills, Lake Forest, Orange, and unincorporated Orange County (Figure 1). San Diego Creek is the largest tributary to UNB contributing 95% of the bay's freshwater input. (USEPA 2002). The Santa Ana-Delhi Channel is the second largest tributary to UNB contributing less than 5% of the bay's freshwater input. Currently, residential areas comprise the largest land use category (24%), followed by roads (16%), commercial/industrial (16%), and agricultural (5.2%) land uses (RWQCB 2000). The UNB watershed has changed dramatically over the past 50 years in land use and drainage patterns. The dominant trend has been the conversion of largely pervious agricultural lands, through construction, and into urban uses (residential, commercial/industrial); this trend is expected to continue for many years to come (RWQCB 2000, USACOE 2000, USEPA 2002).

### Sampling

Twelve (12) sampling sites were selected for this study (Figure 1). Eight of the sites were located throughout the UNB watershed for stormwater collection (A1, A2, C1, C2, R1, I1, M1 and M2), and the remaining four sites (S1-S4) were located in UNB for sediment and water column sampling. Six of the eight stormwater sites represented major land use types in the watershed. The commercial/industrial (I1) and residential (R1) sites were located in the City of Irvine. The agricultural sites included nursery/row crop (A1) and exclusively row crop (A2). The construction sites included completed grading (C1) and grading in process (C2). The two remaining "mass emission" stormwater sites were located at the base of the two major tributaries Santa Ana/Delhi Channel (M1) and San Diego Creek (M2) that were cumulative of all land uses in the watershed.

Three storms were sampled on February 18 (storm "a"), February 28 (storm "b"), and March 28, 2006 (storm "c"). Cumulative precipitation for these storms was 4.1, 11.9, and 18.3 mm, respectively, based on a rain gauge located at Newport Harbor (Figure 1).

Two sampling methods were used to collect stormwater. For mass emission sites, a depth-integrating water sampler containing a pre-cleaned (with detergent and tap water, followed by alternating rinses of double deionized water (DDIW) and methanol repeated three times) 1-gallon amber glass bottle and supported by a metal davit was lowered into the creek. After collection, the grab sample was poured into a 5-gallon pre-cleaned glass bottle through a stainless steel mesh (1.59 mm) to remove large debris. For each site, multiple grabs were made until 10 gallons (two 5-gal bottles per site) were collected. To minimize cross-contamination between samples, a new, pre-cleaned collection bottle was used. For land use sites, a pre-cleaned stainless steel bucket was cast into the open channel discharge and the sample was poured into a 5-gallon pre-cleaned glass bottle through a stainless steel mesh. All samples were kept on ice for transport to the laboratory and stored at 4°C until processing.

Surface sediment samples were collected on July 22, 2006, from stations S1-S4 in UNB (Figure 1). The top 5-cm sediment was taken using a Van Veen grab and transferred into precleaned 16-ounce glass jars. The sediment samples were placed on ice for transport, then stored in the laboratory at  $-20^{\circ}\text{C}$  until processing.

A total of 334 liters of surface water was collected at station S1 using an Infiltrax 100 in-situ pump system (Axys Technologies Inc., Sydney, BC, Canada) deployed at a depth of 2m from the bottom to minimize capture of resuspended bottom sediment. This collection was performed over a period of 4 days in July 2006. Water was continuously pumped through a stack of eight Whatman glass fiber filters (GF/F, 142-mm diameter,  $0.47\mu\text{m}$  effective pore exclusion diameter) and a single polytetrafluoroethylene (PTFE) column packed with XAD-II resin to extract dissolved organics. No surface water samples were collected from stations S2-S4. After sampling, the GF/Fs were placed in covered glass Petri dishes and the PTFE column wrapped with aluminum foil. Petri dishes and the PTFE column were placed in on ice during transport to the laboratory. The PTFE column was processed within 24 hours of collection and GF/Fs were stored at  $-20^{\circ}\text{C}$  until analysis (Zeng *et al.* 2002, Zeng *et al.* 1999)

### **Laboratory analysis**

A total of 81 individual trace organic constituents were targeted for this study (Table 1). These included total DDTs (p,p' and o,p' isomers of DDT, DDE, and DDD), total chlordanes (*cis* and *trans* isomers of chlordane and nonachlor, chlordene and oxychlordane), total PCBs (41 PCB congeners), and total PAH (28 different compounds).

### **Sample preparation**

Raw stormwater samples were filtered upon arrival at the laboratory using  $0.47\mu\text{m}$  GF/Fs. Dissolved phase organic contaminants were isolated by passing filtrates through Empore C-18 bonded disks (3M Corp., St. Paul, MN) using a vacuum pump. Target analytes were eluted from each C-18 disk with 30 ml of ethyl acetate followed by 30 ml of methylene chloride. Sediment samples were freeze-dried before extraction. PTFE columns with XAD-II resin were eluted with dichloromethane (DCM). GF/Fs containing suspended particulate matter (SPM) and sediment samples were extracted with DCM using a Dionex ASE300 Accelerated Solvent Extraction System. Extraction conditions were as follows: temperature –  $100^{\circ}\text{C}$ ; pressure – 1500 psi; stationary time – 5 minutes; 60% flushing volume. Three extraction cycles were carried out for each sample to ensure complete extraction.

Cleanup of sample extracts was performed using silica gel-alumina column chromatography. Both sorbents were pre-extracted three times using methylene chloride on the ASE300 system, dried and activated overnight at  $150^{\circ}\text{C}$  and  $250^{\circ}\text{C}$  for silica gel and alumina, respectively. Silica gel was subsequently deactivated using 3% (w/w) DDIW. After the sample extract was loaded, the first 20 ml of hexane eluent was discarded and a subsequent 40-ml aliquot of 30:70% DCM/hexane was collected. Spiked column calibration tests were performed to ensure that all target analytes were quantitatively eluted ( $\geq 70\%$ ) in this DCM/hexane (second) fraction.

After GC-MS measurements, the sample extracts were split 1:4 with 80% of the aliquot used for subsequent CSIA measurement and 20% for chiral analysis. Additional sample cleanup for isotope ratio measurement was carried out using column chromatography similar to the above procedure but with 3% deactivated silica gel as the sorbent phase. After discarding the first 20 ml of hexane eluent, 40 ml of hexane eluent was collected, followed by 20 ml of 95:5% hexane:DCM eluent. These two fractions were shown to contain all of the compounds of interest for isotopic analysis. When the chromatographic separation of target compounds was deemed not adequate by GC-MS analysis, silica gel chromatography was repeated with a higher resolution elution profile. After the first 20-ml hexane eluent was discarded, a total of three hexane fractions — two 10-ml aliquots followed by a final 20-ml aliquot — were collected. PCBs were targeted in the first fraction, lower MW PAHs (2-3 rings), DDD and DDEs were targeted in the second fraction, and heavier PAHs ( $\geq 4$  rings) and DDTs were eluted in the fraction three. All fractions were analyzed by GC-MS analysis for peak identification and semi-quantitation prior to GC-C-IRMS analysis.

Additional sample cleanup for chiral gas chromatography was also carried out using 3% DDIW-deactivated silica gel-alumina column chromatography. The column was layered with neutral alumina (3cm, 3.0g dry weight), neutral silica gel (21 cm, 8.0g dry weight), and anhydrous sodium sulfate (1cm). After loading the sample extract, the column was eluted with 35 ml of n-hexane (discarded), followed by collection of three fractions — 15 ml of n-hexane, 15 ml of n-hexane/methylene chloride (95:5, v/v), and 20 ml of n-hexane/methylene chloride (70:30, v/v) that were subsequently combined. The final extract was reduced to 100  $\mu$ l under a gentle nitrogen stream.

#### *Total suspended solids, total organic carbon, and total nitrogen*

Total suspended solids (TSS) in stormwater was measured by filtering a 25- to 3000-ml aliquot of the sample through a tared 25 mm dia 0.45  $\mu$ m Whatman GF/F filter. After drying in an oven set at 60°C for 24 hours, the loaded filter was weighed to the nearest mg. Total organic carbon (TOC) and total nitrogen (TN) in sediment samples and stormwater particles were analyzed using a Carlo Erba 1108 CHN Elemental Analyzer equipped with an AS/23 autosampler. An aliquot of each dried sample was acidified with HCl vapors to remove inorganic carbon. The acidified sample was dried, packed in a tin boat and crimped prior to CHN analysis. The precision for TOC and TN measurement were estimated to be 0.05% and 0.005%, respectively.

#### *Gas chromatography-mass spectrometry (GC-MS).*

Sample extracts were analyzed using Varian 3800 gas chromatography (GC)/Saturn 2000 ion trap mass spectrometry (MS) system (Varian, Walnut Creek, CA). The injector temperature was programmed from 100 to 280°C at  $\sim 100^\circ\text{C}/\text{min}$  with a 40 min hold time at the maximum temperature. Carrier gas was ultra high purity helium ( $>99.9995\%$ ) with a flow rate of 1.0 ml/min. Chromatographic separations were made with 60 m  $\times$  0.25 mm i.d. (0.25- $\mu$ m film thickness) DB-5MS columns (J&W Scientific, Folsom, CA) temperature-programmed from 80°C (held for 1 min) to 176°C at  $8^\circ\text{C}/\text{min}$ , followed by a

ramp to 230°C at 1.5°C/min, and a final increase to 290°C at 5°C/min (21 min hold time). Mass spectra were acquired from  $m/z$  100 to 504 with a scan rate of 0.7 scans per second and an emission current of 15  $\mu$ A. Quantitation of individual analyte concentrations was by the internal standard method using a 6-point (25 to 2000 ppb) calibration curve. Extracts were diluted and/or concentrated accordingly to bring analyte concentrations into the calibration range. The internal standards 2-fluorobiphenyl-d14, p-terphenyl-d14, PCB30, and PCB205 were added to each sample extract prior to GC analysis to determine the relative response factors for and quantify concentrations of target analytes. Acenaphthylene-d10, phenanthrene-d10, perylene-d12, benzo(g,h,i)perylene-d12, tetrachloroxylene (TCX), PCB65, and PCB209 were fortified into each sample prior to extraction to monitor sample-specific surrogate recovery. Mean surrogate recoveries were 80% for stormwater particulate, UNB sediments and in situ pump samples, and 60% for stormwater dissolved phase samples. Sample concentrations were not corrected for surrogate recovery. The mean percent difference for project target analytes with reported certified concentrations in NIST SRM1941b (marine sediment), analyzed using identical protocols described herein, was 21.6%.

### *Compound-specific isotope analysis (CSIA)*

A Thermo Trace gas chromatograph (GC) coupled to a Delta<sup>plus</sup> XP isotope ratio mass spectrometer (IRMS) via a GC/C II/III gas interface was used to measure the compound-specific isotope ratios for selected target compounds. After injection of the sample extract, target compounds were first separated by the GC, then combusted with copper oxide at 940°C into gas phase CO<sub>2</sub> pulses, and finally analyzed by IRMS to obtain relative amounts of <sup>12</sup>C and <sup>13</sup>C. The isotope ratio ( $\delta^{13}\text{C}\%$ ) of each compound was calculated using the following equation:

$$\delta^{13}\text{C}_{\text{spl}\%} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{spl}} - (^{13}\text{C}/^{12}\text{C})_{\text{std}}}{(^{13}\text{C}/^{12}\text{C})_{\text{std}}} \times 1000\% \quad (1)$$

where subscripts spl and std represent sample and calibration standard with known  $\delta^{13}\text{C}$  values, respectively. In this notation, more negative  $\delta^{13}\text{C}$  values indicate that the sample was isotopically ‘lighter’, or more ‘depleted’ in <sup>13</sup>C relative to other samples.

The GC oven for the CSIA method was programmed as follows: hold at 80°C for 5 minutes, increase to 250°C at 8°C/min, and a final ramp to 300°C at 4°C/min. The splitless injection was carried out with a 50 psi pressure surge for two minutes. The carrier gas flow was programmed to increase from 0.5 ml/min to 1.5 ml/min within the first two minutes. Injection volume varied from 1 to 3  $\mu$ L depending on measured target analyte concentration. For larger, higher signal/noise ratio (S/N) chromatographic peaks (>50 mV intensity and S/N >>5), the isotope ratio was calculated automatically by the ISODAT 2.0 software. For less prominent peaks (<50 mV, S/N  $\geq$ 5), manual integration was performed using a dynamic background correction with a 35-second backtracking time.

Based on Equation (1), the isotope ratios were calibrated against multiple certified and/or reference materials, including an ultra-high purity (99.9999%) CO<sub>2</sub> standard gas (Scott Specialty Gas, Plumsteadville, PA) and a straight-chain alkane mixture donated by the Isotope Geochemical Laboratory at Indiana University (Bloomington, IN). Based on the alkane standards, secondary calibration standards (PCB congeners and deuterated normal alkanes) were calibrated and served as isotopic internal standards, which were spiked into the sample extracts before injection. To determine the precision of CSIA, each extract was injected at least three times, with the uncertainty reported as standard deviation for the replicate injections (averaging 0.7%).

### *Chiral gas chromatography (CGC)*

Extracts were analyzed using an Agilent 6890N GC-electron capture detector (ECD) system outfitted with a BGB-172 column (20% tert-butyldimethylsilyl-β-cyclodextrin dissolved in 15% diphenyl- and 85% dimethyl-polysiloxane, 30 m x 0.25 mm id, 0.25 μm film from BGB Analytik (Adlisil, Switzerland). Injections were splitless (260°C) and the GC oven was programmed as follows: 70°C (2 minute hold), ramp to 200°C at 1°C/min (80 minute hold); ramp to 240°C at 10°C/min (30 minute hold). The ECD temperature was maintained at 310°C and nitrogen (60 ml/min) was the detector makeup gas. The elution order of the four enantiomers of cis- and trans-chlordane (CC and TC, respectively) was (+) TC, (+) CC, (-) CC, and (-)TC. The distribution of enantiomers was expressed as the enantiomer fraction (EF), using Equation 2:

$$EF = \frac{(C_+)}{(C_+ + C_-)} \quad (2)$$

where C<sub>+</sub> and C<sub>-</sub> are concentrations of (+) and (-) enantiomers, respectively; and equal concentrations of enantiomers constitute a racemic EF (= 0.50), whereas enrichment of the (+) or (-) enantiomer yields EF >0.50 and <0.50, respectively (Harner *et al.* 2000).

Average EF values for repeated injections of racemic standards were 0.500 ±0.0005 for TC and 0.500 ±0.0003 for CC. The analytical variability of 0.003 for EFs (both isomers) was determined by repeated (*n* = 5) injection of the same sample extract. The variability in EFs among samples from the same site (sd = 0.004) was afforded via analysis of extracts from the SADC (M1) site. The relative standard deviation for TC/CC was 5.92%. Detection limits for chlordane enantiomers in water and sediment ranged from 0.061 to 0.122 ng/L and 0.245 to 0.986 ng/g dry weight, respectively.

Enantiomer peak purity for CC and TC was maximized by eliminating coeluting (non-target) interferences via extensive cleanup and fractionation of sample extracts and optimization of chromatographic separation. Interfering analytes were subject to removal by repeated silica gel-alumina column chromatography (see *Sample preparation*). No evidence of coeluting peaks was noted by GC-MS analysis after the initial cleanup. Although additional peaks were observed on the chiral ECD chromatogram, the gradual (1°C/min) oven temperature ramp utilized for chiral separation resulted in clear baseline

separation of the four peaks corresponding to *cis*- and *trans*-chlordane, with no observed peak shoulders and/or peak shape irregularities

## Data analysis

The data obtained in this study included the concentrations, isotopic ratios, and chiral ratios of trace organic contaminants (DDTs, chlordanes, PCBs and PAHs; Table 1) for UNB sediment, stormwater particles, and in situ pump particles. The general approach for the data analysis for this study was four-fold. First, concentrations of physicochemical parameters were examined to assess general characteristics of each storm/site event combination. For example, concentrations of TSS, TOC, TN, and C/N ratios were compared to rainfall quantity or land use type.

Second, concentrations of trace organic contaminants in stormwater particles from the mass emission sites were compared to UNB sediment contaminant concentrations. A parallel analysis examined the concentrations of trace organic contaminants in stormwater particles from land use sites relative to UNB sediments. Selected student *t*-tests were performed on untransformed concentration data to determine the statistical significance of differences between mean concentrations. All *t*-tests were one-tailed assuming equal variance with a significance threshold of 0.05. All applicable data points were included in the tests, i.e., no data was excluded. The enrichment or depletion of total DDT, PCBs, chlordane, or PAH from stormwater particulates was assessed relative to concentrations in UNB.

Third, carbon isotope ratios ( $\delta^{13}\text{C}$ ) of individual contaminants on stormwater particulates were compared among land use sites, mass emission sites, and UNB sediments. The  $\delta^{13}\text{C}$  signatures were only evaluated for those compounds with sufficient mass for analysis. These compounds included: *p,p'*-DDT and *p,p'*-DDE; PCB congeners 18, 28, 49 and 52; and the PAHs phenanthrene and pyrene. Values of  $\delta^{13}\text{C}$  were classified as different if the ranges of uncertainty based on replicate analysis of a single sample did not overlap. These data were supplemented with DDT/DDE ratios from GC-MS results.

Fourth, TC/CC ratios and enantiomeric fractions (EFs) of CC and TC were compared among land use sites, mass emission sites and UNB sediments. Pair-wise values of EFs were classified as different if their ranges of uncertainty based on replicate analysis of a single sample did not overlap. Fully racemic (equal) mixtures of chiral compounds have  $\text{EF} = 0.5$ . The TC/CC ratio of technical grade chlordane was reported to be 1.17 (Jantunen *et al.* 2000).

## RESULTS

Lack of flow at some sites prevented collection of stormwater samples from all stations during each of the three storm events (Table 2). Flow was observed and sampled from the most impervious land use sites (residential and industrial/commercial). Despite more than four inches of cumulative rainfall for the wet season, flow from the most pervious land uses (agricultural and construction) did not occur until the last storm. Samples were collected from every storm at the mass emission sites on Santa Ana-Delhi and San Diego Creek sites.

In general, TSS concentrations and C/N ratios increased with increasing rainfall at the mass emission sites (Table 2). For example, TSS concentrations increased from 21 to 550 mg/L at site San Diego Creek (M2), commensurate with increases in rainfall from 0.16 to 0.72 across the three storm events sampled at this site. Across the same three events, C/N ratio doubled from 6.5 to 12.9. In direct contrast, TOC and TN decreased with increasing rainfall. For example, organic content decreased from 20.8% to 3.8% TOC and nitrogen content decreased from 3.2 to 0.3% TN as rainfall increased at San Diego Creek. While the monotonically increasing trend in TSS with increasing rainfall was less strong at Santa Ana-Delhi Channel (M1), the monotonic trend in TOC, TN, and C/N was similar to San Diego Creek.

The construction land use sites had the greatest TSS concentrations of all land uses and storm combinations sampled, averaging 2,480 mg/L in stormwater. The second greatest TSS concentrations were observed at the agricultural land use averaging 541 mg/L in stormwater. Industrial and residential land uses had the lowest TSS concentrations averaging 165 and 34 mg/L in stormwater, respectively. In contrast to TSS, industrial and residential land uses had the greatest organic content in stormwater particles averaging 10.3% and 16.4% TOC, respectively. Agricultural land uses had intermediate organic content in stormwater particles averaging 5.2% TOC. Construction land uses had the least organic content in stormwater particles averaging 0.8% TOC.

Dissolved phase DDTs, chlordanes, and PCBs were below detection limits in all stormwater samples from the mass emission sites (Table 3). Conversely, concentrations were always above detection limits for the particulate phase. Total PAH was the only contaminant class that was detected in both phases for both mass emission sites. However, the mean dissolved phase concentrations for total PAH represented less than 10% of the corresponding particulate phase concentrations. In contrast to stormwater, compounds within all classes of organic contaminants were detected in both the dissolved and particulate phases of the UNB water column sample collected during the dry weather season. Concentrations of DDTs, chlordanes, PCBs and PAHs in the UNB water column were 1.73, 0.04, 0.10, and 4.60 ng/L, respectively. Lower detection limits for the UNB water column sample was due to larger volume of this sample (ca. 334 vs. 10 L).

Average total chlordane concentrations of stormwater particles from San Diego Creek were roughly one third of those from Santa Ana-Delhi Channel (Table 4). However, average total DDT concentrations of stormwater particles at San Diego Creek were twice

the average concentration at Santa Ana-Delhi Channel. Concentrations of total PCB and total PAH of stormwater particles were roughly similar between the two mass emission sites. None of these comparisons were statistically significant ( $p > 0.05$ ).

Average total PAH and total PCB concentrations in stormwater particles from either Santa Ana-Delhi Channel or San Diego Creek were roughly an order of magnitude greater than UNB bedded sediments (Table 4). Differences for total PAH and PCB for the combined mass emissions site data versus UNB sediments were both statistically significant ( $p = 0.019$  and  $0.040$ , respectively). In contrast, average total DDT and total chlordane concentrations in stormwater particles from either Santa Ana-Delhi Channel or San Diego Creek were roughly similar to UNB bedded sediments ( $p > 0.05$  for both). In no case were average concentrations of any constituent greater in UNB sediments than stormwater particles.

The average concentration of total DDT in stormwater particles at agricultural land use sites was one to two orders of magnitude greater than those representing the other specific land uses (Table 5). This difference was statistically significant ( $p = 0.005$ ). Moreover, average total DDTs from the two agricultural sites were an order of magnitude greater than the corresponding mean for mass emission sites. Further, the ratio of p,p'-DDT to p,p'-DDE measured in stormwater particles was dissimilar for agricultural sites and other land use sites (Figure 3;  $p = 0.046$ ). For example, the DDT/DDE ratios in stormwater particles at construction sites were less than 0.2 while DDT/DDE ratios at agricultural sites were greater than 0.7. The DDT/DDE ratio in stormwater particles at the mass emission site was intermediate between construction and agricultural land use sites (ca. 0.36).

Total chlordane was detected in stormwater particles at construction and agricultural land use sites. In contrast, no detectable chlordane was observed for industrial/commercial and residential land use sites (Table 5). The average concentrations of total chlordane in stormwater particles from agricultural and construction land use sites was an order of magnitude greater than those representing the other land uses (Table 5). Moreover, the average concentration of total PCB in stormwater particles at construction and agricultural land use sites were one to two orders of magnitude greater than the average concentration of total PCB in stormwater particles at residential and industrial/commercial land uses. This difference was statistically significant ( $p = 0.042$ ). In contrast, the average concentration of total PAH in stormwater particles at residential and industrial/commercial land use sites were two to three orders of magnitude greater than the average concentration of total PAH in stormwater particles at construction and agricultural land use sites. Due to the high variability (and small sample sizes) associated with these mean values, however, these differences were not statistically significant ( $p = 0.12$ ).

The patterns of contaminant enrichment in UNB bedded sediments relative to stormwater particles from land use contributions mimicked the relationship observed with mass emission sites. For total DDT, stormwater particles from agricultural sites exhibited enrichment relative to UNB sediments, while stormwater particles from the residential,

industrial/commercial and construction sites were all depleted relative to UNB sediments (Figure 4). Although fewer data were available for chlordanes due to levels that were below/near detection limits, results for agricultural sites also suggested enrichment. For total PCB, the agricultural and construction sites exhibited enrichment relative to UNB sediments, while the industrial/commercial sites were depleted relative to UNB sediments (Figure 5). In fact, the difference in enrichment/depletion between land uses was more pronounced for total PCB than for total DDT. In contrast to total PCB, the agricultural and construction sites exhibited consistent depletion of PAHs in stormwater particles relative to UNB sediment, whereas enrichment was consistently observed for stormwater particles from residential and industrial/commercial sites relative to UNB sediments (Figure 6).

### CSIA and CGC analysis

Differences in CSIA signatures between land use sites, mass emission sites, and UNB sediments were only moderate in magnitude. The  $\delta^{13}\text{C}$  values for p,p'-DDE, the single most abundant pesticide analyte in stormwater particulates, ranged from -25 to -27% with an average uncertainty of 0.7% (Figure 7). The values for mass emission sites and UNB sediments were indistinguishable from those representing the construction and agricultural sites (A1-b and A2-b). In contrast, site and storm specific  $\delta^{13}\text{C}$  values for p,p'-DDT exhibited a wider range (~-20 to -27.5%). The difference between  $\delta^{13}\text{C}$  values for p,p'-DDE and p,p'-DDT were site-specific, with the two construction sites exhibiting a "heavier" (i.e., enriched in the heavier  $^{13}\text{C}$  isotope) ratio for p,p'-DDT. The most pronounced difference was for site/storm combination C1-c, where the difference between  $\delta^{13}\text{C}$  for the two DDT compounds was greater than 5%.

The  $\delta^{13}\text{C}$  values for PCB congeners 18, 28, 49 and 52 were obtained based upon peak abundance and purity (Figure 8). The range of  $\delta^{13}\text{C}$  values for these congeners was -25% to -30%, similar to the range as observed by Horii *et al.* (2005) and Drenzek *et al.* (2002) for Aroclors. In part due to the larger uncertainty associated with these measurements (up to 1.5%), differences in stormwater particles among land use categories could not be discerned. Except for PCB28, the values for UNB sediment at site S3 appeared lighter (i.e., depleted in the heavier  $^{13}\text{C}$  isotope) than the stormwater particle samples.

The  $\delta^{13}\text{C}$  values for one of the most abundant PAHs, phenanthrene, exhibited some source-specific CSIA signatures (Figure 9). The site and storm specific range of  $\delta^{13}\text{C}$  values for phenanthrene was -22% to -30% with precision of 0.5%. Carbon isotopic ratios of phenanthrene for the three samples representing C1-c, C2-c and I1-b were lighter by as much as 5% than the San Diego Creek mass emission site (M2) and all four UNB sediment samples.

There was a difference in the ratio of trans- to cis-chlordane concentrations (TC/CC) in stormwater particulates from the different land use and mass emission sites (Figure 10). The TC/CC ratio in stormwater particulates for construction, agricultural, and the industrial/commercial site were all near or less than unity. This ratio is less than the theoretical value for unmodified technical chlordane, which is almost 1.2. These TC/CC

ratios were also similar to the TC/CC ratios observed in stormwater particles from both the Santa Ana-Delhi Channel and San Diego Creek mass emission sites. Stormwater particles sampled from the residential site, however, had a TC/CC ratio of 1.3. This was similar to the TC/CC ratio observed in bedded sediment samples from Upper Newport Bay.

The enantiomer fraction (EF) for cis-chlordane uniformly exceeded the racemic value (0.50), whereas the opposite held true for trans-chlordane (Figure 11). Even though the absolute differences among these EFs were small, ranging from a low of ~0.46 (R1) to a maximum of ~0.57 (C2), the precision of these measurements are ~0.02 and the variability between storms was <0.05 (M1).

## DISCUSSION

It appears that stormwater runoff may be an ongoing contributor of some trace organic contaminants to UNB. Particulates in stormwater runoff from San Diego Creek and Santa Ana-Delhi Channel had concentrations that were greater than, or equal to, concentrations of total PAH, total PCB, total chlordane, or total DDT in sediments from UNB. At a minimum, the input of particles at these concentrations does not dilute existing sediment concentrations levels. Obviously, there are a large number of complicating factors including settling/resuspension, degradation/volatilization, and mixing/burial/dredging, but the ongoing contributions from stormwater do not help to diminish levels of these constituents in bedded sediments of UNB.

It is also apparent that land use properties played a role in the watershed wide contributions of trace organic contaminants. Specifically, there were two land use properties that were observed in this study; source emissions and imperviousness. Based on the data, certain trace organic constituents were associated with some land uses more than others. For example, agricultural land use average stormwater particulate concentrations of total DDT were an order of magnitude greater than any other land use examined. Similarly, construction land use average stormwater particulate concentrations of total PCB were an order of magnitude greater than any other land use examined. While residential and industrial/commercial land uses had substantially lower stormwater particulate concentrations of total DDT or total PCB, their average particulate concentrations of total PAH were one to two orders of magnitude greater than either agriculture or construction land uses.

The second land use property that played a role in watershed wide contributions of trace organic contaminants was imperviousness. Imperviousness played a role in runoff flows and volumes. In this study, flows were difficult to sample from the most pervious land use sites (e.g., agricultural and construction) because much of the rainfall infiltrated and did not runoff into surface waters. This was especially true at construction sites where best management practices were targeted towards retaining runoff on site and flows did not occur until the largest of storm events. Hence, large concentrations may not necessarily translate into large sources of mass emissions if flows are minimal.

Land use perviousness also played a role in sequestering trace organic contaminants in the watershed. This study, as have others (Cross *et al.* 1993), showed that trace organic contaminants were largely associated with stormwater particulates. In fact, concentrations of organochlorine constituents were never quantified in dissolved stormwater. It was also apparent that the largest TSS concentrations arose from the most pervious land uses. That is, where loose soil was available, such as plowed agricultural fields or graded construction sites, high stormwater TSS concentrations followed. The top three stormwater TSS concentrations, all greater than 1g/L, were from agricultural and construction land use sites. Ackerman and Schiff (2003), reviewed stormwater data from all of southern California and found identical results.

One interpretation is that legacy pesticides, such as total DDT and total chlordane, have been sequestered in soils at these previous land use types. When new soil is exposed, such as plowing or grading, historically applied organochlorine pesticides can be re-mobilized as “new” inputs when particles are washed offsite during a storm event. This interpretation is bolstered by DDT/DDE ratios in stormwater particulates that runoff from different land use types. Since DDE is a degradation product of DDT, larger ratios represent undegraded “newer” inputs, whereas smaller ratios represent degraded “older” inputs (Eganhouse *et al.* 2000). Thus, not only were total DDT concentrations in stormwater particles an order of magnitude greater at agricultural sites compared to construction sites, but DDT/DDE ratios in stormwater particles from agricultural sites were also five- to ten-fold greater than construction sites (Figure 3).

Land use also played a role in potential contributions from ongoing sources of trace organic contaminants. Specifically, total PAH concentrations in stormwater particles were greatest from urban land uses including residential and industrial/commercial sites. Total PAH derive largely from the combustion of fossil fuels, such as automobiles. Interstate 405, which runs through the watershed just upstream of UNB, averaged between 250,000 and 300,000 vehicles per day in 2005 (Caltrans 2006). Urban land uses have amongst the greatest imperviousness in any watershed (Ackerman *et al.* 2005), and this enhances the entrainment and transport of total PAH particulates because so little rainfall infiltrates. Instead, more rainfall runs off of these urban surfaces carrying urban associated trace organic contaminants, like total PAH, to receiving waters. This phenomenon does not appear to be unique to UNB. The total PAH concentrations in stormwater measured at different land uses in the Los Angeles area were similar in magnitude to those observed in this study (Stein *et al.* 2007). Moreover, sediments located at the mouth of other urban watersheds also suffer from total PAH contamination (Menzie *et al.* 2002, Hoffman *et al.* 1984).

Compound-specific isotopic analysis can potentially differentiate among source materials, or similar source materials that undergo differential transformation and degradation, for single compounds (e.g. p,p'-DDE) in the environment (Galimov, 2006; Hayes *et al.* 1990, Horii *et al.* 2005, Phillips and Gregg 2003, Wang *et al.* 1999, Drenzek *et al.* 2002). The CSIA played a helpful, but not definitive role in determining potential land use sources of trace organic contaminants to UNB. For example, the CSIA signatures for p,p'-DDE, the most common constituent in the total DDT group, showed limited differentiation between land uses, mass emission, or UNB sediment samples. This indicated that there was either a common source of p,p'-DDE, that all of the sources had undergone similar degradation, or both. However, CSIA signatures for p,p'-DDT were different among land uses. Values of  $\delta^{13}\text{C}$  from the two construction land use sites were less negative (“heavier”) for p,p'-DDT relative to the agricultural land use site suggesting differential rates and/or extents of transformation had occurred. Other explanations, including different original DDT sources, and the role of sorption and volatilization are also consistent with these data. However, in situ transformation rather than volatilization is supported by the low DDT/DDE ratio (Figure 3) for the construction sites, as DDT is less volatile than DDE (Spencer and Cliath 1973).

In a similar fashion, CSIA was able to partially distinguish source signatures for the PAH phenanthrene. The values of  $\delta^{13}\text{C}$  for San Diego Creek and UNB sediments were all similar linking San Diego Creek to the contaminated sediments in the Bay. However, the  $\delta^{13}\text{C}$  values for three land use sites (C1, C2 and I1) indicated a lighter signature for phenanthrene suggesting that other watershed contributors of PAHs with heavier isotopic signatures exist. The range of isotope ratios (-23% to -29%) of phenanthrene in this study was comparable to that of O'Malley *et al.* (1996; -25% to -29%) where the isotope signature in the receiving water was heavier than those of possible sources (car soot, fireplace soot and engine oil). The key to successfully utilizing CSIA for this application, however, is intimately tied to the magnitude of differences in individual source signatures ( $\delta^{13}\text{C}$ ), *i.e.*, the larger the difference, the more likely source contributions can be quantified. In two previous studies on PAH soil contamination, these differences were overwhelming for a highly degraded point source (McRae *et al.* 2000), but much less so for PAHs associated with highway runoff (Glaser *et al.* 2005). Characterization of compound-specific  $\delta^{13}\text{C}$  values for additional sources (see below) is needed for a more complete assessment of this technique.

The use of chiral gas chromatography is also a new tool that helped distinguish between land use sources of chlordane. Because enantiomers of chlordane or other chiral pesticides degrade at different rates, EFs have been used to "date" the age of residues (Bidleman *et al.* 2004). Since enantiomers are found in equal proportions in unmodified technical mixtures, increasing deviation from the racemate (*i.e.*, an EF of 0.50) indicates a higher degree of degradation. This is reflected in the different chlordane EFs observed among the land use sources in this study. With proper sample preparation, a high degree of analytical precision can be achieved with this technique, enhancing its utility for differentiating among source signatures.

While stormwater was the focus of source identification in this study, it is not the only source of trace organic contaminants to UNB. Specifically, atmospheric deposition is a potential source that could produce substantial impact to the bay. Many of the trace organic contaminants examined herein have been found in air including PAHs, PCBs, and to a lesser extent DDTs and chlordanes. For example, atmospheric deposition of PAHs has been measured in Orange County (unpublished data). Deposition of PAHs in other watersheds has led to contamination of receiving waterbodies (Gigliotti *et al.* 2005). Atmospheric deposition of other contaminants, such as nitrogen and sulfate species, has also been measured in and around UNB (French *et al.* 2005). Limited data from atmospheric samples near UNB show that EFs for chlordane are very similar to the EFs observed in UNB sediments (unpublished data). Based on this information, investigation into additional sources appears warranted.

Regardless of our inability to define exact sources of trace organic contaminants, it is apparent that UNB currently suffers from impaired water and sediment quality. For example, dissolved water column measurements of DDE and chlordanes exceed water quality criteria (CTR 2000). While no sediment quality criteria currently exist, both total DDT and total chlordane exceeded sediment quality guidelines developed by NOAA (Long *et al.* 1995). Moreover, other investigators have measured sediment

contamination, toxicity, and impaired benthic communities in UNB. This provides unique challenges to environmental managers and source tracking tools like CSIA and CGC may provide further confidence in mitigation/remediation strategies.

**Table 1. List of targeted constituents.**

<b>Compound Groups</b>	<b>Individual Compounds</b>
DDTs	<i>o,p'</i> -DDD, <i>p,p'</i> -DDD, <i>o,p'</i> -DDE, <i>p,p'</i> -DDE, <i>o,p'</i> -DDT, <i>p,p'</i> -DDT
Chlordanes	chlordene, oxychlordane, <i>cis</i> -chlordane, <i>trans</i> -chlordane, <i>cis</i> -nonachlor, <i>trans</i> -nonachlor,
PCBs <sup>1</sup>	18, 28, 37, 44, 49, 52, 66, 70, 74, 77, 81, 87, 99, 101, 105, 110, 114, 118, 119, 123, 126, 128, 138, 149, 151, 153/168, 156, 157, 158, 167, 169, 170, 177, 180, 183, 187, 189, 194, 200, 201, 206
PAHs <sup>2</sup>	Naphthalene (N), 2-Methylnaphthalene (2MeN), 1-Methylnaphthalene (1MeN), Biphenyl (BP), 2,6-Dimethylnaphthalene (DMN), Acenaphthylene (Acey), Acenaphthene (Ace), 2,3,5-Trimethylnaphthalene (TMN), Fluorene (Flu), Phenanthrene (Pb), Anthracene (An), 2-Methylphenanthrene (2MePh), 1-Methylphenanthrene (1-MePh), 3,6-Dimethylphenanthrene (DMPh), Fluoranthene (Fla), Pyrene (Py), Benz[a]anthracene (BaA), Chrysene (Chry), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[e]pyrene (BeP), Benzo[a]pyrene (BaP), Perylene (Peryl), 9,10-Dyphenylanthracene (DphA), Indeno[123- <i>cd</i> ]pyrene (I123cdP), Dibenzo[ <i>a,h</i> ]anthracene (DbahA), Benzo[ <i>g,h,i</i> ]perylene (BghiP)

<sup>1</sup> International Union of Pure and Applied Chemistry (IUPAC) nomenclature

<sup>2</sup> Acronyms of PAHs are shown in parentheses

**Table 2. Total suspended solids (TSS), total organic carbon (TOC), total nitrogen (TN) and carbon/nitrogen ratio (C/N) for stormwater particulate and Upper Newport Bay sediment samples. The estimated measurement error for TOC and TN measurements were 0.05% and 0.005%, respectively.**

Station Type Station ID (n*)	Storm a (2/18/2006)				Storm b (2/28/2006)				Storm c (3/28/2006)			
	0.16" precipitation				0.47" precipitation				0.72" precipitation			
	TSS (mg/L)	TN (%)	TOC (%)	C/N	TSS (mg/L)	TN (%)	TOC (%)	C/N	TSS (mg/L)	TN (%)	TOC (%)	C/N
<b>Land Use</b>												
R1 (2)	12.9	0.83	19.9	24.1	54.6	0.5	12.81	25.7	ns	ns	ns	ns
I1 (2)	253	0.49	8.63	17.7	76.9	0.38	12	31.9	ns	ns	ns	ns
A1 (1)	nf	nf	nf	nf	1490	0.26	2.16	8.2	ns	ns	ns	ns
A2 (2)	58.3	1.17	6.83	5.83	76.1	0.68	6.55	9.66	ns	ns	ns	ns
C1 (1)	nf	nf	nf	nf	nf	nf	nf	nf	3310	0.07	0.6	9.02
C2 (1)	nf	nf	nf	nf	nf	nf	nf	nf	1650	0.08	0.96	11.5
<b>Mass Emission</b>												
M1 (3)	156	1.02	13.19	12.9	227	0.66	12.15	18.3	171	0.59	11.3	19.3
M2 (3)	21.3	3.2	20.8	6.51	155	1.05	15.12	14.4	550	0.29	3.79	12.9
<b>Bay Sediment**</b>												
S1	na	0.09	0.96	10.23								
S2	na	0.14	1.7	11.8								
S3	na	0.12	1.22	10.02								
S4	na	0.11	1.202	11.34								

nf - no flow

ns - no sample collected

\*: numbers within the parentheses indicate sample size

\*\*collected on 7/21/06 (dry weather conditions)

na - not applicable

**Table 3. Mean ( $\pm$  sd) dissolved and particulate concentrations (ng/L) of organic contaminants in stormwater at the mass emission sites.**

	<b>Matrix</b>	<b>Santa Ana-Delhi Channel</b>	<b>San Diego Creek</b>
Total DDTs	Dissolved	< 13.1	< 13.1
	Particulate	10.5 $\pm$ 4.38	27.3 $\pm$ 12.1
Total Chlordanes	Dissolved	< 12.6	< 12.6
	Particulate	3.81 $\pm$ 4.68	1.55 $\pm$ 2.10
Total PCBs	Dissolved	< 63.0	< 63.0
	Particulate	149 $\pm$ 211	227 $\pm$ 209
Total PAHs	Dissolved	81.8 $\pm$ 22.4	93.4 $\pm$ 77.1
	Particulate	834 $\pm$ 88.0	1160 $\pm$ 1350

**Table 4. Mean ( $\pm$  sd) concentrations of organic contaminants (ng/g) in stormwater particulates at the Santa Ana-Delhi Channel (M1) and San Diego Creek (M2) mass emission sites, and Upper Newport Bay (UNB) water column particulates and bedded sediment.**

	Santa Ana-Delhi Channel		San Diego Creek		UNB Water Column Particulates <sup>1</sup>		UNB Sediment <sup>2</sup>	
Total DDTs	57.0	$\pm$ 23.8	113	$\pm$ 50.0	134	$\pm$ 65.2	122	$\pm$ 65.2
Total Chlordanes	20.6	$\pm$ 25.3	6.40	$\pm$ 8.69	3.84	$\pm$ 3.50	5.70	$\pm$ 3.50
Total PCBs	804	$\pm$ 1140	939	$\pm$ 865	59.2	$\pm$ 76.4	41.3	$\pm$ 76.4
Total PAHs	4510	$\pm$ 476	4780	$\pm$ 5560	163	$\pm$ 213	645	$\pm$ 213

<sup>1</sup> site S1 ( $n = 1$ ; see Fig. 1)

<sup>2</sup> sites S1-S4 ( $n = 4$ ; see Fig. 1)

**Table 5. Mean ( $\pm$  sd) concentrations of organic contaminants (ng/g) in stormwater particulates from sites representing different land use categories in the San Diego Creek watershed. (see also Figure 1 for site locations)**

	<b>Agricultural</b>	<b>Construction</b>	<b>Industr./Comm.</b>	<b>Residential</b>	<b>Mass Emission<sup>1</sup></b>
Total DDTs	869 $\pm$ 150	48.3 $\pm$ 1.49	31.7 $\pm$ 7.69	< 2.24	85.1 $\pm$ 46.7
Total Chlordanes	10.0 $\pm$ 17.3	4.18 $\pm$ 0.554	< 0.48	< 2.31	13.5 $\pm$ 18.6
Total PCBs	218 $\pm$ 51	681 $\pm$ 535	17.6 $\pm$ 20.4	< 3.45	872 $\pm$ 907
Total PAHs	216 $\pm$ 133	72.4 $\pm$ 58.5	26100 $\pm$ 35200	1550 $\pm$ 462	4640 + 3520

<sup>1</sup> site M2 (Fig. 1)

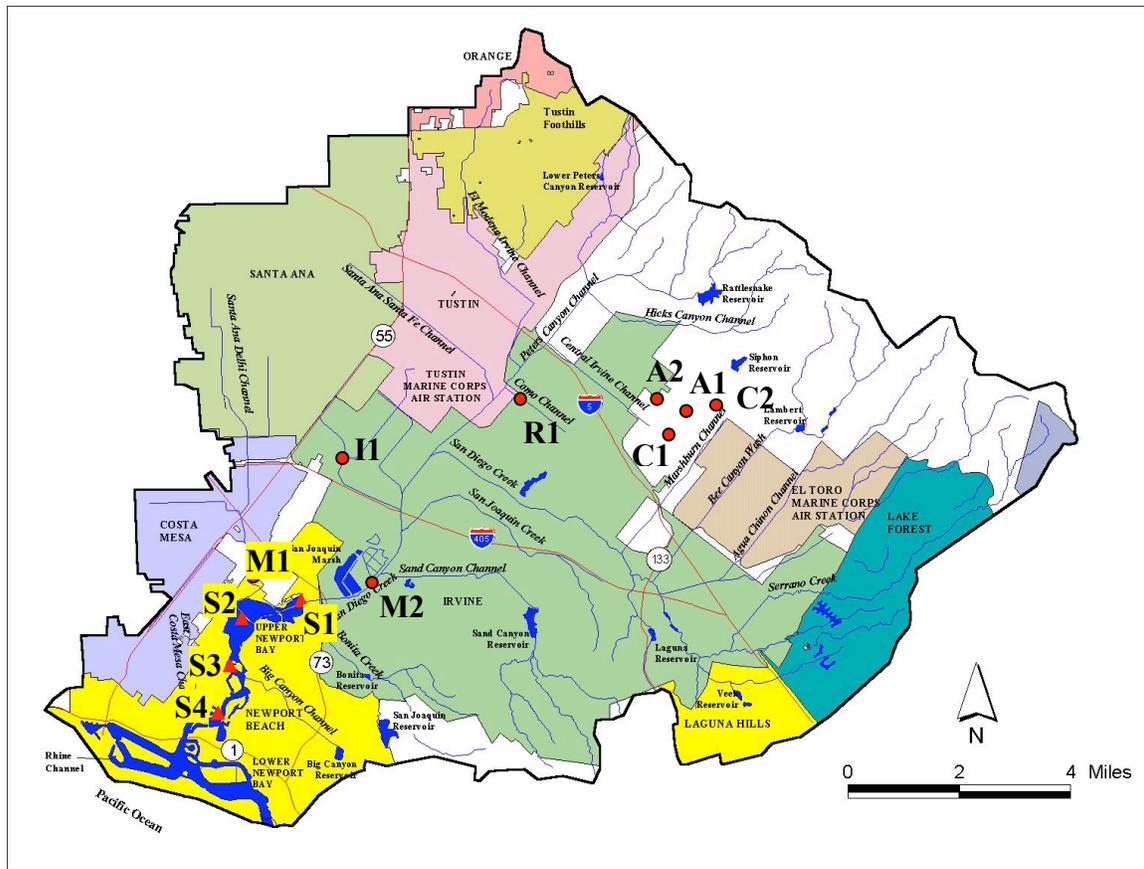


Figure 1. Stormwater and sediment sampling sites in the Upper Newport Bay watershed. Land use categories are agricultural (A1, A2), construction (C1, C2), industrial/commercial (I1) and residential (R1). Santa Ana-Delhi Channel (M1) and San Diego Creek (M2) are sub-watershed mass emission sites. Sediment/water column sites (S1-S4) are in upper Newport Bay.

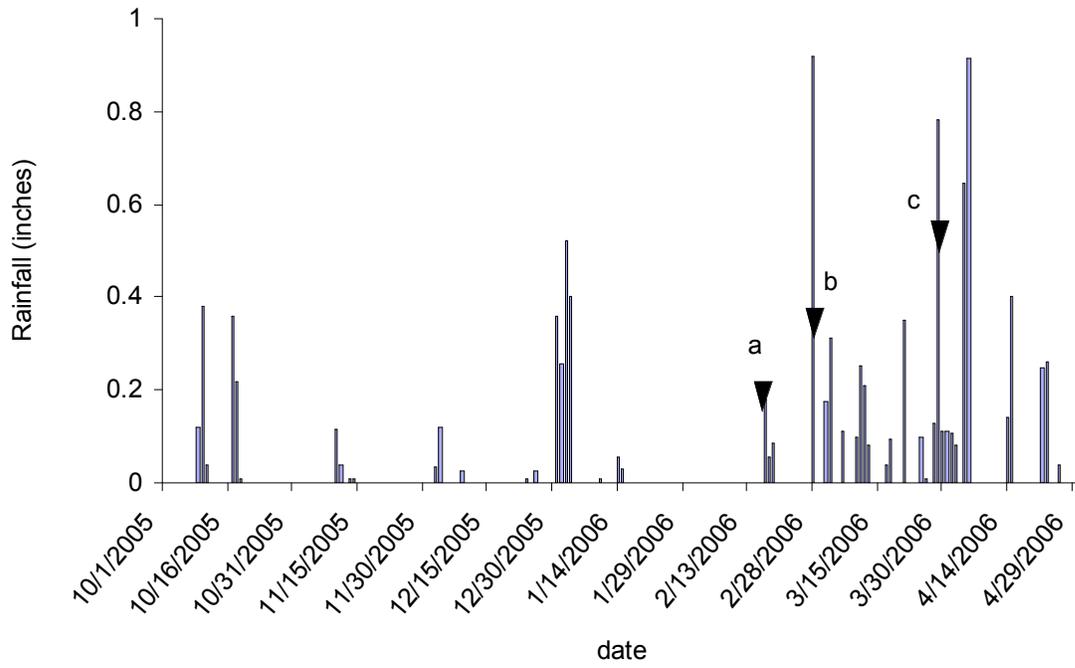
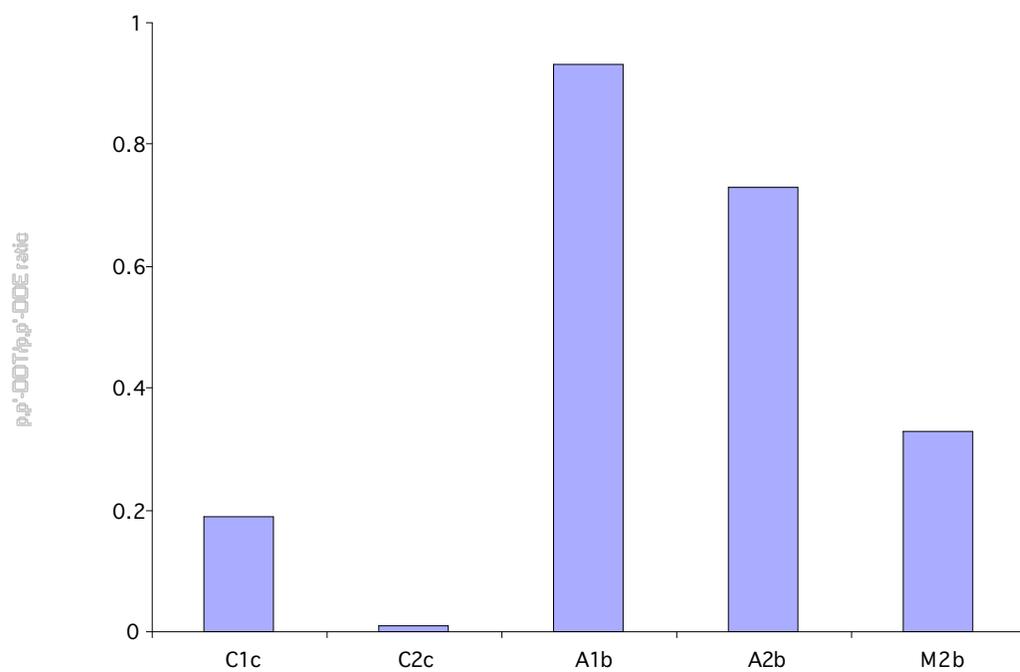
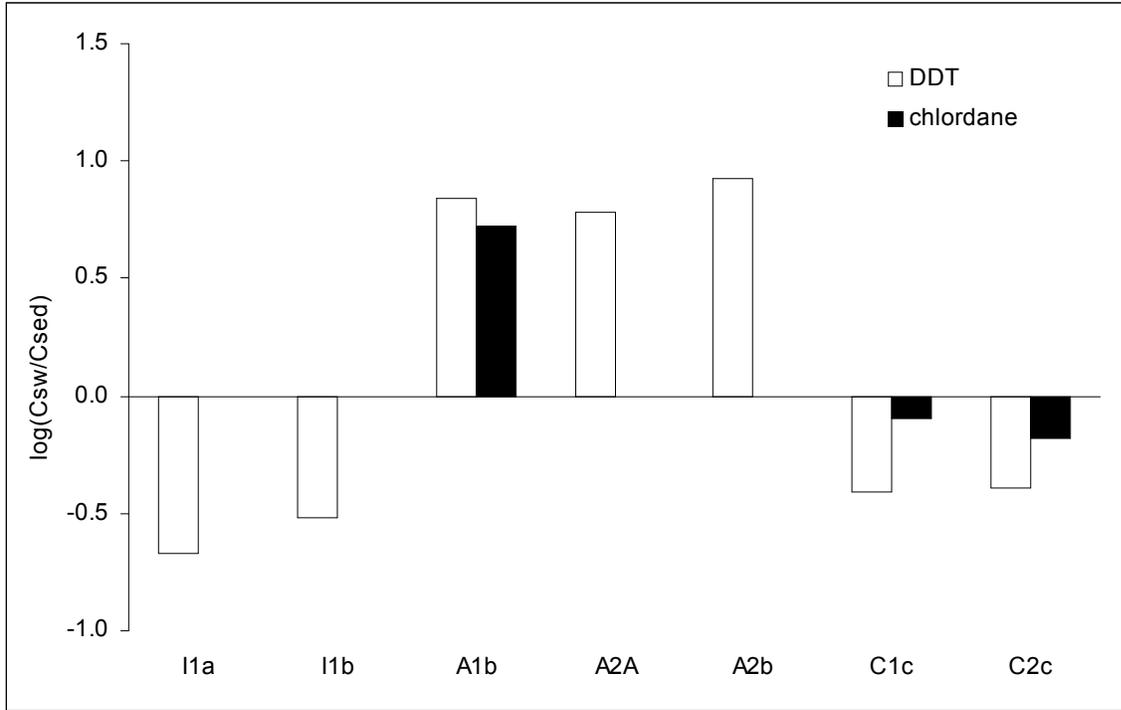


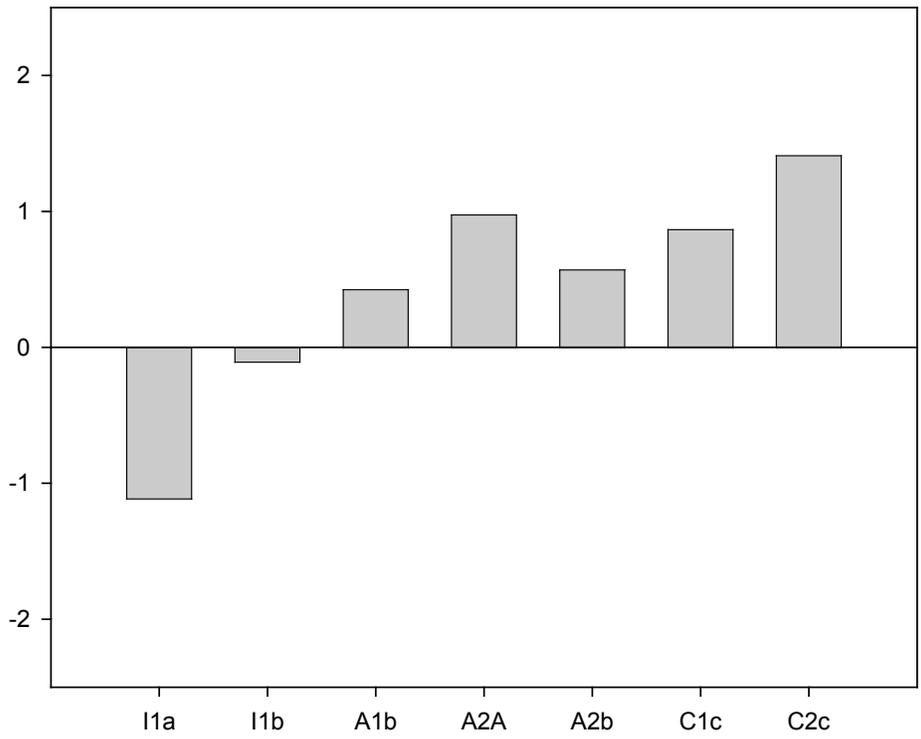
Figure 2. Cumulative daily rainfall at Newport Harbor for the three sampled storms (a, b, and c) and throughout the 2005-2006 wet weather season.



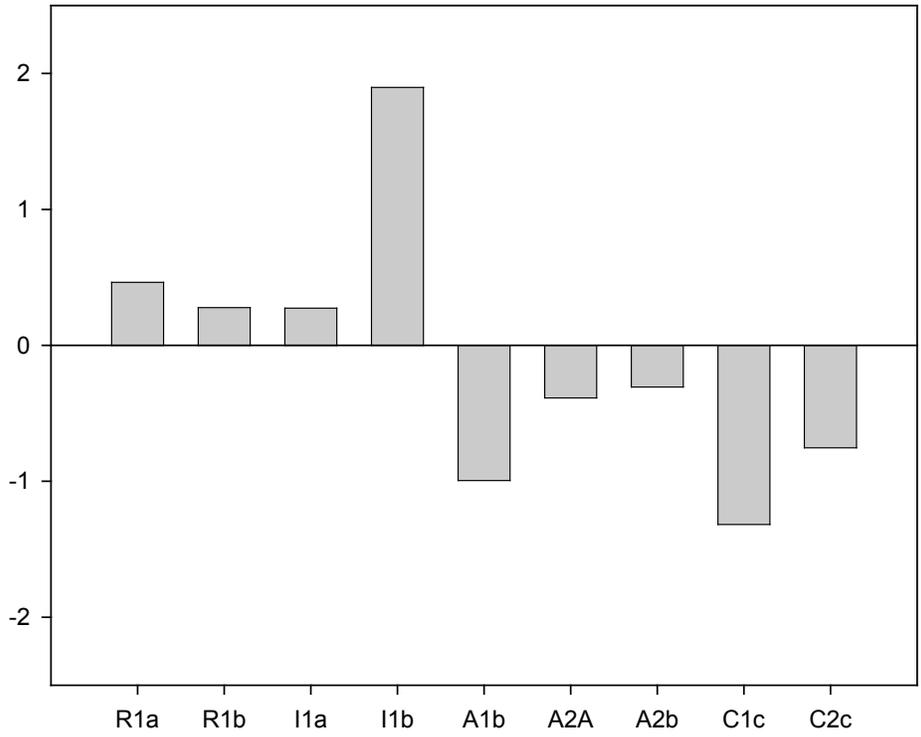
**Figure 3. Ratio of  $p,p'$ -DDT to  $p,p'$ -DDE in stormwater particulate matter for different site and rain event combinations (see Figure 1 and Table 2 for complete description).**



**Figure 4. Enrichment/depletion of DDTs and chlordanes in stormwater (C<sub>sw</sub>) relative to Upper Newport Bay sediment (C<sub>sed</sub>) for different site and rain event combinations (see Figure 1 and Table 2 for complete description).**



**Figure 5. Enrichment/depletion of PCBs in stormwater (Csw) relative to Upper Newport Bay sediment (Csed) for different site and rain event combinations (see Figure 1 and Table 2 for complete description).**



**Figure 6. Enrichment/depletion of PAHs in stormwater (Csw) relative to Upper Newport Bay sediment (Csed) for different site and rain event combinations (see Figure 1 and Table 2 for complete description).**

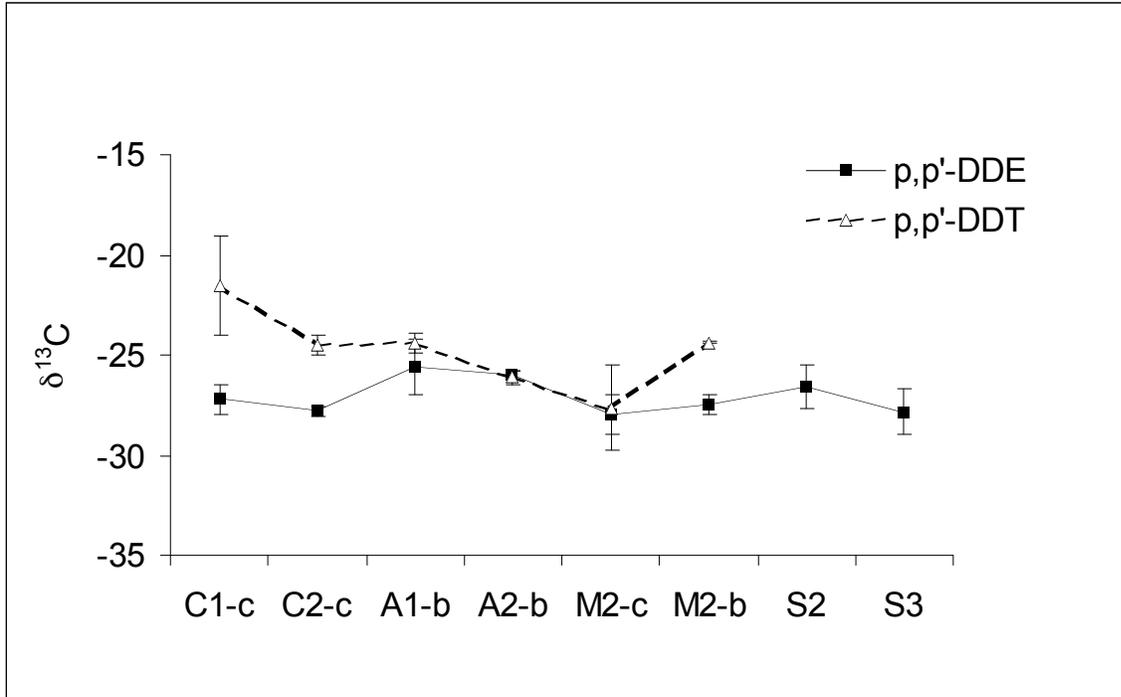


Figure 7. Stable carbon isotope ratios of DDT compounds in stormwater particulates and upper Newport Bay sediments for different site and rain event combinations (see Figure 1 and Table 2 for complete description).

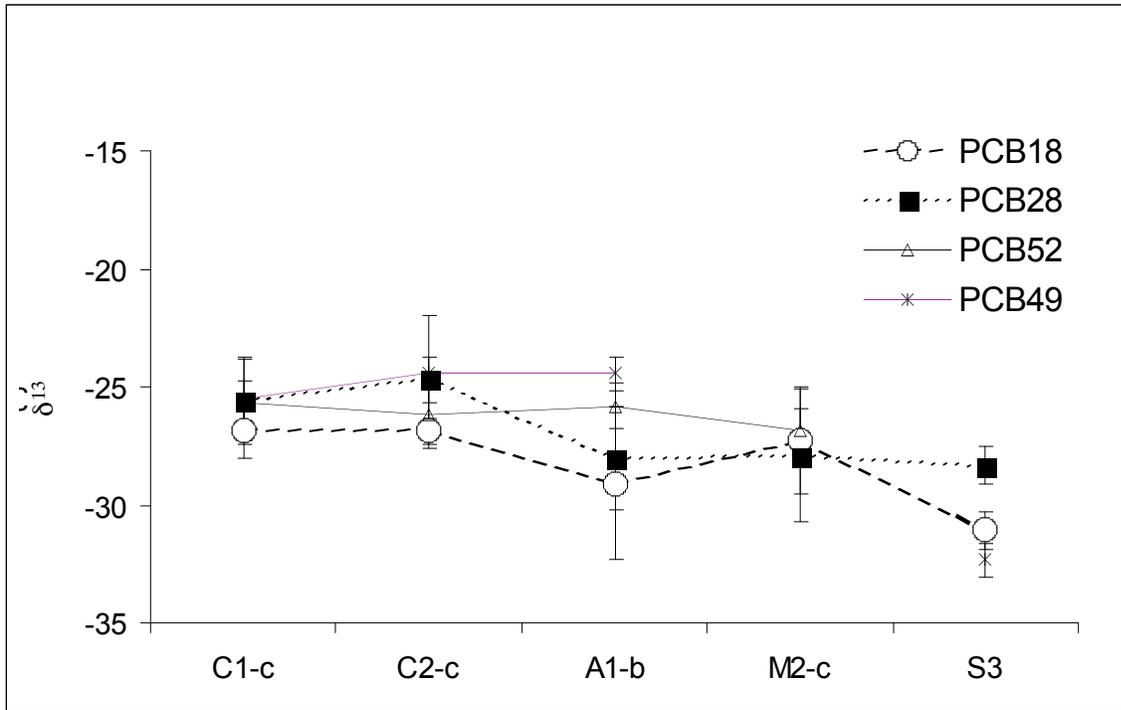


Figure 8. Stable carbon isotope ratios of PCB congeners in stormwater particles and upper Newport Bay sediments for different site and rain event combinations (see Figure 1 and Table 2 for complete description).

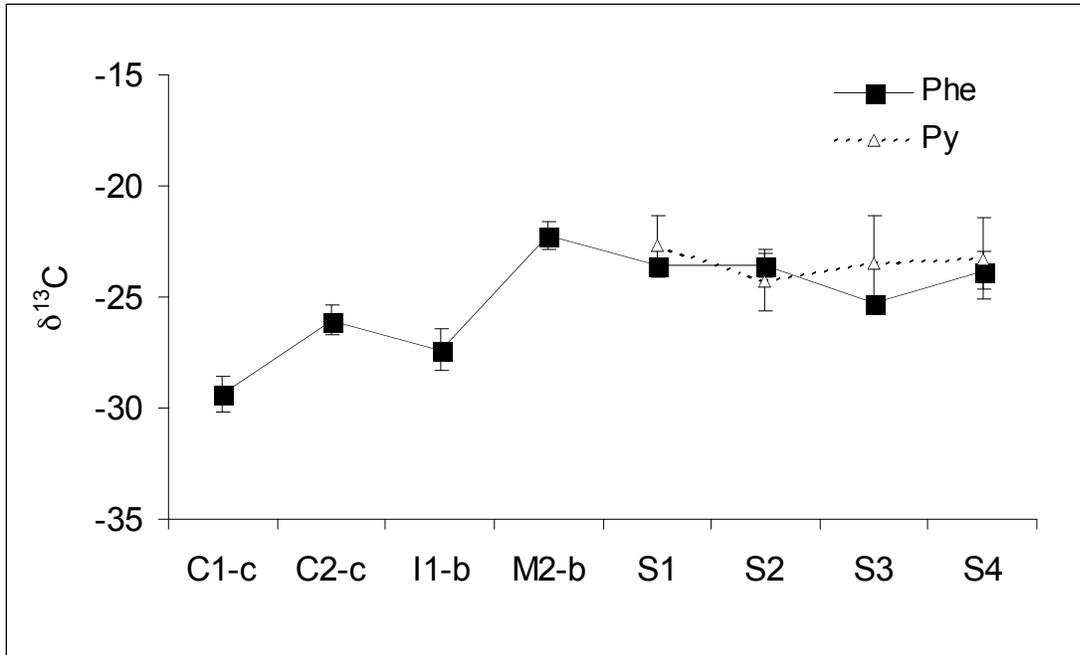


Figure 9. Stable carbon isotope ratios of phenanthrene (Phe) and pyrene (Py) in stormwater particles and upper Newport Bay sediments for different site and rain event combinations (see Figure 1 and Table 2 for complete description).

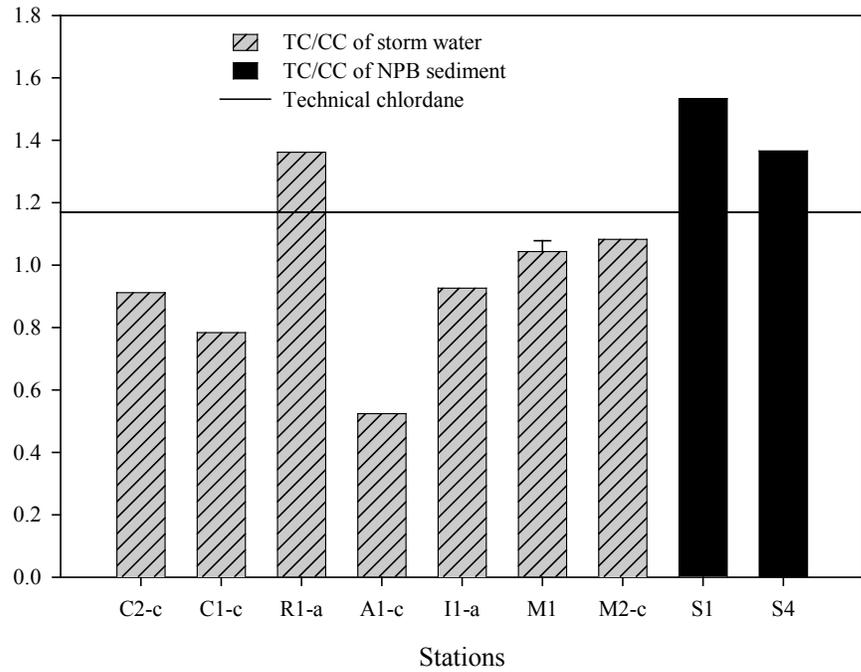
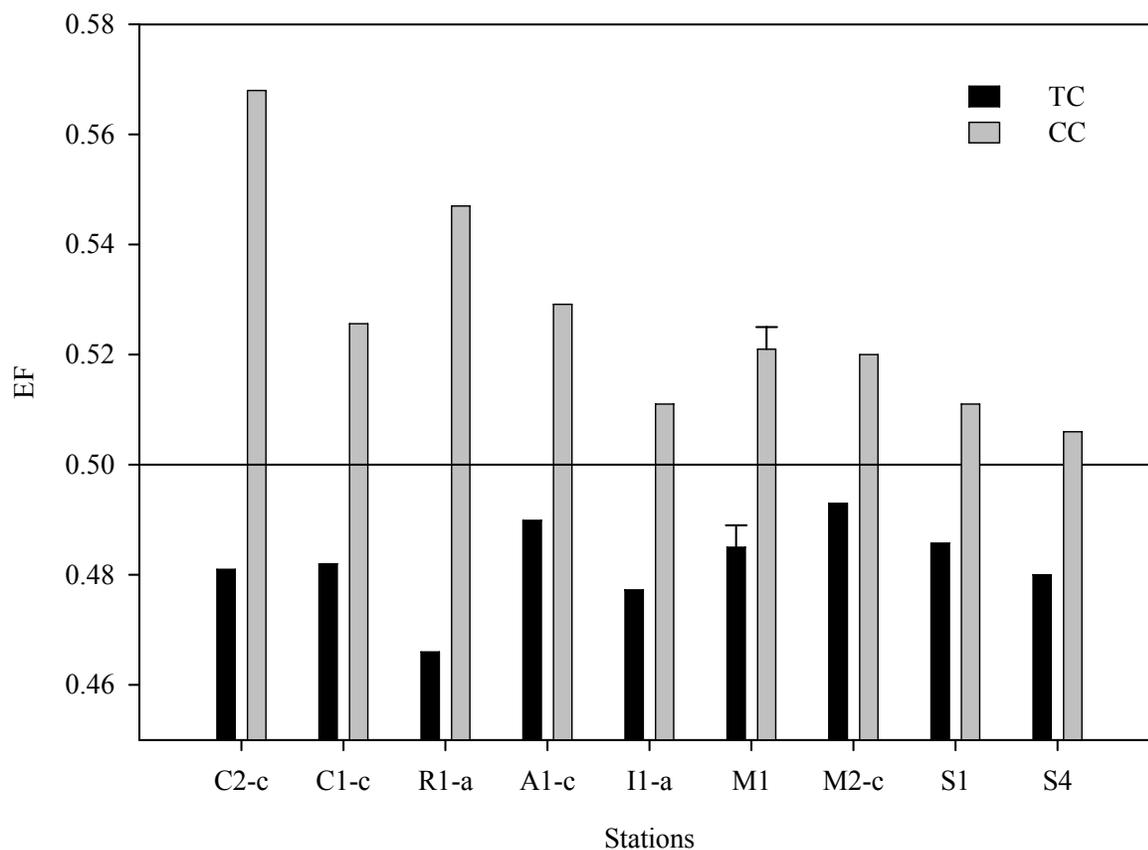


Figure 10. The ratio of *trans*- to *cis*-chlordane (TC/CC) concentrations in stormwater particles for different site and rain event combinations (see Figure 1 and Table 2 for complete description). The horizontal line represents TC/CC for technical chlordane (1.17). Error bar for M1 is the standard deviation for samples collected during the three sampling events ( $n = 3$ ).



**Figure 11. Enantiomer fractions (EFs) for *cis*- and *trans*-chlordane (CC and TC, respectively) in stormwater particles for different site and rain event combinations (see Fig. 1 and Table 2 for complete description). The horizontal line represents a completely racemic mixture (EF = 0.50). Error bars for M1 are the standard deviations for samples collected during the three sampling events ( $n=3$ ).**

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## APPENDIX A. SAMPLE-SPECIFIC CONCENTRATIONS OF TARGET ANALYTES

**Table A-1.** Stormwater Dissolved Phase PAHs (ng/L)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
N	5.26	9.05	10.6	44.0	12.6	8.83	8.78	4.72	6.30	13.7	18.8	11.2	6.27	25.3	10.2
2MeN	5.10	9.25	10.9	23.3	13.6	7.71	6.36	3.62	5.95	13.4	16.7	9.13	6.29	18.3	10.3
1MeN	2.59	4.32	6.41	13.1	6.45	3.39	3.18	<1.39	1.73	9.33	10.6	6.16	3.80	10.6	6.64
BP	<0.53	<2.14	3.11	7.85	<2.14	<2.14	<2.14	<2.14	<2.14	4.03	4.83	<2.14	<0.53	5.55	4.72
DMN	<0.61	2.53	5.31	4.95	4.77	<2.43	<2.43	<2.43	<2.43	6.05	8.21	4.00	2.50	4.42	4.49
ACY	<0.53	<2.11	<2.11	<2.11	<2.11	<2.11	<2.11	<2.11	<2.11	<2.11	<2.11	<2.11	<0.53	<2.11	<2.11
ACE	<0.35	<1.39	<1.39	35.11	<1.39	<1.39	<1.39	<1.39	<1.39	<1.39	2.14	<1.39	<0.35	15.47	<1.39
TMN	<0.39	<1.55	<1.55	<1.55	<1.55	<1.55	<1.55	<1.55	<1.55	2.72	<1.55	2.14	<0.39	<1.55	1.65
FLU	<0.25	3.66	3.60	46.1	4.89	<1.01	<1.01	<1.01	1.39	3.80	7.12	3.64	<0.25	23.1	5.44
Phe	<0.17	7.11	6.92	61.2	19.8	5.01	5.14	1.64	3.61	9.44	13.6	5.85	4.61	50.3	13.0
Anth	<1.55	<6.22	<6.22	7.60	<6.22	<6.22	<6.22	<6.22	<6.22	<6.22	<6.22	<6.22	<1.55	<6.22	<6.22
2MP	<1.02	<4.08	<4.08	4.80	<4.08	<4.08	<4.08	<4.08	<4.08	5.19	<4.08	<4.08	<1.02	<4.08	<4.08
1MP	<0.57	<2.27	<2.27	<2.27	<2.27	<2.27	<2.27	<2.27	<2.27	2.28	<2.27	<2.27	<0.57	2.47	<2.27
DMP	<0.50	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99	<0.50	<1.99	<1.99
Fla	<0.28	3.87	3.19	15.2	5.10	2.97	2.14	1.27	3.02	5.42	8.45	5.37	2.69	9.46	5.25
Py	<2.07	<8.29	<8.29	13.9	11.7	<8.29	<8.29	<8.29	<8.29	8.34	12.8	11.1	3.61	14.2	9.80
BaA	<0.92	<3.67	<3.67	<3.67	<3.67	<3.67	<3.67	<3.67	<3.67	<3.67	<3.67	<3.67	<0.92	<3.67	<3.67
Chr	<0.80	<3.22	<3.22	<3.22	<3.22	<3.22	<3.22	<3.22	<3.22	<3.22	<3.22	<3.22	<0.80	<3.22	<3.22

**Table A-1 (Continued).** Stormwater Dissolved Phase PAHs (ng/L)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
BbFla	<1.19	<4.76	<4.76	<4.76	<4.76	<4.76	<4.76	<4.76	<4.76	<4.76	<4.76	<4.76	<1.19	<4.76	<4.76
BkFla	<0.39	<1.56	<1.56	<1.56	<1.56	<1.56	<1.56	<1.56	<1.56	<1.56	<1.56	<1.56	<0.39	<1.56	<1.56
BeP	<1.52	<6.06	<6.06	<6.06	<6.06	<6.06	<6.06	<6.06	<6.06	<6.06	<6.06	<6.06	<1.52	<6.06	<6.06
BaP	<2.79	<11.1	<11.1	<11.1	<11.1	<11.1	<11.1	<11.1	<11.1	<11.1	<11.1	<11.1	<2.79	<11.1	<11.1
Pery	<3.50	<14.0	<14.0	<14.0	<14.0	<14.0	<14.0	<14.0	<14.0	<14.0	<14.0	<14.0	<3.50	<14.0	<14.0
DPA	<0.83	<3.31	<3.31	<3.31	<3.31	<3.31	<3.31	<3.31	<3.31	<3.31	<3.31	<3.31	<0.83	<3.31	<3.31
123cdP	<4.51	<18.1	<18.1	<18.1	<18.1	<18.1	<18.1	<18.1	<18.1	<18.1	<18.1	<18.1	<4.51	<18.1	<18.1
DahA	<3.09	<12.4	<12.4	<12.4	<12.4	<12.4	<12.4	<12.4	<12.4	<12.4	<12.4	<12.4	<3.09	<12.4	<12.4
BghiP	<4.65	<18.6	<18.6	<18.6	<18.6	<18.6	<18.6	<18.6	<18.6	<18.6	<18.6	<18.6	<4.65	<18.6	<18.6

**Table A-1 (continued).** Stormwater Dissolved Phase OCPs (ng/L)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
Diazinon	<0.80	<3.18	<3.18	<3.18	<3.18	<3.18	<3.18	<3.18	<3.18	<3.18	<3.18	<3.18	<0.80	<3.18	<3.18
Chlordene	<1.49	<5.96	<5.96	<5.96	<5.96	<5.96	<5.96	<5.96	<5.96	<5.96	<5.96	<5.96	<1.49	<5.96	<5.96
Chloropyrifos	<0.31	<1.24	<1.24	<1.24	<1.24	<1.24	<1.24	<1.24	<1.24	<1.24	<1.24	<1.24	<0.31	<1.24	2.42
Aldrin	<0.61	<2.45	<2.45	<2.45	<2.45	<2.45	<2.45	<2.45	<2.45	<2.45	<2.45	<2.45	<0.61	<2.45	<2.45
Oxychlordane	<1.01	<4.03	<4.03	<4.03	<4.03	<4.03	<4.03	<4.03	<4.03	<4.03	<4.03	<4.03	<1.01	<4.03	<4.03
o,p'-DDE	<0.23	<0.91	<0.91	<0.91	<0.91	<0.91	<0.91	<0.91	<0.91	<0.91	<0.91	<0.91	<0.23	<0.91	<0.91
□-Chlordane	<0.18	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.71	<0.18	<0.71	<0.71
□-Chlordane	<0.19	<0.76	<0.76	<0.76	<0.76	<0.76	<0.76	<0.76	<0.76	<0.76	<0.76	<0.76	<0.19	<0.76	<0.76
trans-Nonachlor	<0.13	<0.53	<0.53	<0.53	<0.53	<0.53	<0.53	<0.53	<0.53	<0.53	<0.53	<0.53	<0.13	<0.53	<0.53
p,p'-DDE	<0.08	<0.32	<0.32	<0.32	6.97	<0.32	2.37	4.81	<0.32	<0.32	<0.32	<0.32	<0.08	<0.32	<0.32
Dieldrin	<0.31	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	2.39	<1.25	<1.25	<1.25	<1.25	<0.31	<1.25	<1.25
o,p'-DDD	<0.43	<1.70	<1.70	<1.70	<1.70	<1.70	<1.70	<1.70	<1.70	<1.70	<1.70	<1.70	<0.43	<1.70	<1.70
Endrin	<1.20	<4.79	<4.79	<4.79	<4.79	<4.79	<4.79	<4.79	<4.79	<4.79	<4.79	<4.79	<1.20	<4.79	<4.79
cis-Nonachlor	<0.15	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.15	<0.59	<0.59
p,p'-DDD	<0.49	<1.97	<1.97	<1.97	<1.97	<1.97	<1.97	<1.97	<1.97	<1.97	<1.97	<1.97	<0.49	<1.97	<1.97
o,p'-DDT	<1.05	<4.19	<4.19	<4.19	<4.19	<4.19	<4.19	<4.19	<4.19	<4.19	<4.19	<4.19	<1.05	<4.19	<4.19
p,p'-DDT	<0.99	<3.96	<3.96	<3.96	<3.96	<3.96	<3.96	<3.96	<3.96	<3.96	<3.96	<3.96	<0.99	<3.96	<3.96



PCB99	<0.32 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <1.28 <0.32 <1.28 <1.28
PCB119	<0.26 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <1.04 <0.26 <1.04 <1.04
PCB87	<0.33 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <1.32 <0.33 <1.32 <1.32
PCB81	<0.40 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <1.62 <0.40 <1.62 <1.62
PCB110	<0.26 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <1.02 <0.26 <1.02 <1.02
PCB77	<0.46 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <1.85 <0.46 <1.85 <1.85
PCB151	<0.32 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <1.27 <0.32 <1.27 <1.27
PCB149	<0.30 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <1.20 <0.30 <1.20 <1.20
PCB123	<0.28 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <0.28 <1.13 <1.13
PCB118	<0.28 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <1.13 <0.28 <1.13 <1.13
PCB114	<0.20 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.79 <0.20 <0.79 <0.79
PCB153	<0.10 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.41 <0.10 <0.41 <0.41
PCB105	<0.31 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <1.25 <0.31 <1.25 <1.25
PCB138	<0.26 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <1.03 <0.26 <1.03 <1.03
PCB158	<0.22 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.87 <0.22 <0.87 <0.87

**Table A-1 (Continued).** Stormwater Dissolved Phase PCBs (ng/L)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
PCB187	<0.22	<0.88	<0.88	<0.88	<0.88	<0.88	<0.88	<0.88	<0.88	<0.88	<0.88	<0.88	<0.22	<0.88	<0.88
PCB183	<0.21	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.21	<0.86	<0.86
PCB128	<0.30	<1.21	<1.21	<1.21	<1.21	<1.21	<1.21	<1.21	<1.21	<1.21	<1.21	<1.21	<0.30	<1.21	<1.21
PCB167	<0.21	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.21	<0.84	<0.84
PCB177	<0.23	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.92	<0.23	<0.92	<0.92
PCB156	<0.26	<1.05	<1.05	<1.05	<1.05	<1.05	<1.05	<1.05	<1.05	<1.05	<1.05	<1.05	<0.26	<1.05	<1.05
PCB200	<1.18	<4.72	<4.72	<4.72	<4.72	<4.72	<4.72	<4.72	<4.72	<4.72	<4.72	<4.72	<1.18	<4.72	<4.72
PCB157	<0.26	<1.03	<1.03	<1.03	<1.03	<1.03	<1.03	<1.03	<1.03	<1.03	<1.03	<1.03	<0.26	<1.03	<1.03
PCB180	<0.17	<0.66	<0.66	<0.66	<0.66	<0.66	<0.66	<0.66	<0.66	<0.66	<0.66	<0.66	<0.17	<0.66	<0.66
PCB169	<0.27	<1.06	<1.06	<1.06	<1.06	<1.06	<1.06	<1.06	<1.06	<1.06	<1.06	<1.06	<0.27	<1.06	<1.06
PCB170	<0.25	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.25	<0.99	<0.99
PCB201	<1.48	<5.93	<5.93	<5.93	<5.93	<5.93	<5.93	<5.93	<5.93	<5.93	<5.93	<5.93	<1.48	<5.93	<5.93
PCB189	<0.25	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.99	<0.25	<0.99	<0.99
PCB194	<2.44	<9.74	<9.74	<9.74	<9.74	<9.74	<9.74	<9.74	<9.74	<9.74	<9.74	<9.74	<2.44	<9.74	<9.74
PCB206	<0.45	<1.80	<1.80	<1.80	<1.80	<1.80	<1.80	<1.80	<1.80	<1.80	<1.80	<1.80	<0.45	<1.80	<1.80

**Table A-2. Stormwater Particulate Phase PAHs (ng/g)**

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
N	142	29.2	45.2	126	1.84	21.4	11.6	1.91	6.02	55.3	73.0	70.9	61.2	39.2	15.3
2MeN	130	21.4	38.1	145	3.53	21.7	11.9	3.54	9.59	50.8	64.8	95.3	54.3	36.9	19.9
1MeN	61.3	11.6	18.5	87.0	1.62	9.92	6.59	<0.10	4.32	23.7	34.4	42.6	26.2	20.7	10.0
BP	45.0	<9.78	28.0	78.0	0.79	<9.16	<7.02	1.04	3.27	21.9	26.0	24.6	<25.1	20.7	7.05
DMN	19.6	18.5	43.2	94.9	1.48	20.3	<8.00	1.94	3.37	33.3	59.9	61.8	<28.6	34.4	24.6
Acey	<40.9	12.1	16.5	33.1	<0.35	<9.04	<6.93	<0.16	<0.32	23.9	28.8	19.6	<24.7	14.0	6.42
Ace	13.0	<6.36	15.9	933	<0.23	<5.96	<4.56	<0.10	<0.21	36.6	65.9	39.3	<16.3	138	<0.63
TMN	19.5	<7.12	15.8	33.4	0.56	<6.67	1.03	0.85	3.56	10.2	26.6	55.8	<18.3	6.45	11.8
Flu	<19.6	<4.62	31.2	1470	0.81	<4.33	<3.31	1.82	<0.15	36.7	31.0	8.42	<11.8	144	<0.46
Ph	304	251	363	13000	13.5	85.9	59.3	2.35	22.4	586	864	812	186	1930	155
An	17.1	<28.5	8.28	3230	<1.05	<26.7	<20.4	<0.47	<0.94	80.0	107	84.2	<73.0	322	7.27
2MePh	<79.0	119	138	830	6.85	<17.5	<13.4	<0.31	4.33	165	194	282	<47.8	171	45.5
1MePh	<44.0	31.2	70.5	434	2.97	<9.74	<7.46	1.77	4.78	85.9	129	136	<26.6	102	24.6
DMPH	20.2	27.9	17.5	145	<0.34	<8.55	<6.55	<0.15	1.15	42.2	112	78.8	<23.4	32.1	3.32
Fla	434	416	<1.09	12200	10.9	<4.73	62.8	5.52	9.08	1040	856	1350	252	1910	221
Py	662	268	361	10500	17.5	63.5	105	8.20	15.2	1230	1440	1400	347	1800	247
BaA	<71.2	<16.8	<3.62	3200	<0.62	<15.7	<12.1	<0.28	<0.56	264	<4.05	143	<43.1	771	<1.67
Chry	<62.4	<14.7	<3.17	4250	2.72	<13.8	<10.6	<0.24	5.99	592	<3.55	291	<37.8	1260	202
BbF	<92.2	<21.8	<4.69	133	<0.80	<20.4	<15.6	1.61	4.84	<7.61	<5.25	42.9	278	75.9	<2.16
BkF	<30.2	<7.13	<1.54	<5.06	<0.26	<6.68	<5.12	0.43	<0.24	<2.49	<1.72	<2.27	<18.3	548	36.6
BeP	<117	<27.8	<5.98	<19.7	<1.02	<26.0	<19.9	<0.46	<0.92	<9.70	<6.69	<8.85	<71.2	<9.77	<2.75
BaP	<216	<51.0	<11.0	<36.2	<1.88	<47.8	<36.6	<0.84	<1.69	<17.8	<12.3	<16.3	<131	<18.0	<5.06
Peryl	<272	<64.2	<13.8	<45.6	<2.36	<60.1	<46.1	<1.06	<2.12	<22.4	<15.5	<20.5	<165	<22.6	<6.37
DPhA	<61.1	<15.2	<3.26	<10.8	<0.56	<14.2	<10.9	<0.25	<0.50	<5.29	<3.65	<4.83	<38.8	<5.33	<1.50
I123cdP	<350	<82.7	<17.8	<58.7	<3.04	<77.4	<59.3	<1.36	<2.73	<28.9	<19.9	<26.3	<212	<29.1	148
DBahA	<239	<56.6	<12.2	<40.2	<2.08	<53.0	<40.6	<0.93	<1.87	<19.8	<13.6	<18.0	<145	1570	212
BghiP	<360	<85.1	<18.3	<60.5	<3.13	<79.7	<61.1	<1.40	<2.81	<29.7	<20.5	<27.1	<218	211	379

**Table A-2 (Continued).** Stormwater Particulate Phase OCPs (ng/g)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
Diazinon	<61.6	<14.6	<3.14	<10.3	<0.54	<13.6	<10.4	<0.24	<0.48	<5.09	<3.51	<4.64	<37.3	<5.12	<1.44
Chlordene	<116	<27.3	<5.88	<19.4	<1.00	<25.6	<19.6	<0.45	<0.90	<9.53	<6.58	<8.70	<70.0	<9.60	<2.71
Chlorpyrifos	<24.0	<5.66	<1.22	<4.02	5.29	<5.30	<4.06	<0.09	<0.19	<1.98	<1.36	<1.81	<14.5	<1.99	4.25
Aldrin	<47.4	<11.2	<2.41	<7.95	<0.41	<10.5	<8.03	<0.18	<0.37	<3.91	<2.70	<3.57	<28.7	<3.94	<1.11
Oxychlorthane	<78.1	<18.5	<3.98	<13.1	<0.68	<17.3	<13.2	<0.30	<0.61	<6.45	<4.45	<5.88	<47.3	<6.50	<1.83
o,p'-DDE	<17.7	<4.19	<0.90	<2.97	7.74	11.9	13.7	0.87	<0.14	<1.46	<1.01	<1.33	<10.7	4.85	<0.42
g-chlordane	<13.8	<3.26	<0.70	<2.31	9.00	<3.05	<2.34	0.95	<0.11	5.27	6.62	23.3	<8.34	<1.15	<0.32
a-chlordane	<14.8	<3.49	<0.75	<2.47	6.47	<3.26	<2.50	1.15	0.16	<1.22	<0.84	14.1	<8.93	10.8	<0.35
trans-nonachlor	<10.3	<2.44	<0.53	<1.73	10.4	<2.28	<1.75	1.32	3.63	<0.85	<0.59	12.3	<6.25	5.51	2.91
p,p'-DDE	<6.25	<1.48	26.3	37.1	376	536	488	35.6	48.4	37.4	50.0	83.5	101	66.0	112
Dieldrin	<24.3	<5.74	<1.24	<4.07	<0.20	<5.37	<4.12	9.22	<0.19	<2.00	<1.38	<1.83	<14.7	<2.02	<0.57
o,p'-DDD	<33.0	<7.80	<1.68	<5.54	5.47	<7.31	18.5	0.64	<0.26	<2.73	<1.88	<2.49	<20.0	<2.75	<0.77
Endrin	<92.8	<21.9	<4.72	<15.6	<0.80	<20.5	<15.7	<0.40	<0.72	<7.66	<5.28	<6.99	<56.2	<7.71	<2.17
cis-Nonachlor	<11.5	<2.71	<0.58	<1.92	4.13	<2.54	<1.94	1.14	<0.09	<0.95	<0.65	<0.86	<6.94	<0.95	<0.27
p,p'-DDD	<38.1	<9.01	<1.94	<6.39	59.2	<8.43	103	2.84	0.43	<3.15	<2.17	<2.87	<23.1	<3.17	11.2
o,p'-DDT	<81.2	<19.2	<4.13	<13.6	40.3	<18.0	52.5	0.41	<0.60	<6.70	<4.62	<6.11	<49.2	<6.75	10.8
p,p'-DDT	<76.7	<18.1	<3.90	<12.9	353	187	355	6.84	0.50	<6.33	<4.37	<5.78	<46.5	<6.38	34.0

**Table A-2 (Continued).** Stormwater Particulate Phase PCBs (ng/g)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
PCB18	<27.2	<6.42	<1.40	21.7	36.3	127	47.6	56.5	332	50.4	40.3	618	386	6.72	640
PCB28	<32.1	<7.59	3.17	10.4	50.9	207	65.1	162	485	57.1	47.0	886	472	3.71	732
PCB52	<12.8	<3.02	<0.65	<2.15	9.51	35.5	11.6	33.6	97.7	22.0	14.5	212	144	<1.06	141
PCB49	<21.7	<5.13	<1.11	<3.64	7.96	20.7	23.5	28.1	78.2	15.8	<1.24	178	73.5	<1.81	113
PCB44	<25.1	<5.93	<1.28	<4.21	2.31	<5.55	5.60	7.01	22.5	4.29	<1.43	76.2	10.8	<2.09	36.6
PCB37	<51.1	<12.1	<2.60	<8.57	0.23	<11.3	<8.66	4.07	9.90	3.24	<2.91	10.1	<30.9	<4.25	8.01
PCB74	<23.0	<5.43	<1.17	<3.85	<0.20	<5.08	<3.89	<0.09	<0.18	3.15	<1.31	27.3	<13.9	<1.91	<0.54
PCB70	<23.3	<5.51	<1.19	<3.92	1.37	<5.16	<3.96	4.17	11.1	3.63	<1.33	29.7	<14.1	<1.94	19.1
PCB66	<26.9	<6.36	<1.37	<4.52	0.92	<5.96	<4.56	3.68	11.1	5.45	<1.53	22.2	<16.3	<2.24	14.5
PCB101	<23.6	<5.58	<1.20	<3.96	0.22	<5.22	<4.00	0.66	2.30	6.94	<1.34	38.2	<14.3	<1.96	6.17
PCB99	<24.8	<5.86	<1.26	<4.16	<0.22	<5.49	<4.21	2.23	6.78	<2.05	<1.41	17.2	<15.0	<2.06	10.9
PCB119	<20.1	<4.75	<1.02	<3.37	<0.17	<4.44	<3.40	<0.08	<0.16	<1.66	<1.14	<1.51	<12.2	<1.67	<0.47
PCB87	<25.5	<6.03	<1.30	<4.28	<0.22	<5.65	<4.33	<0.10	<0.20	<2.11	<1.45	<1.92	<15.5	<2.12	<0.60
PCB81	<31.3	<7.40	<1.59	<5.25	<0.27	<6.93	<5.31	<0.12	<0.24	<2.58	<1.78	<2.36	<19.0	<2.60	<0.73
PCB110	<19.8	<4.68	<1.01	<3.32	<0.17	<4.38	<3.36	1.13	3.99	14.0	<1.13	9.07	<12.0	<1.65	<0.46
PCB77	<35.9	<8.47	<1.82	<6.01	<0.31	<7.93	<6.08	<0.14	<0.28	<2.96	<2.04	<2.70	<21.7	<2.98	<0.84
PCB151	<24.5	<5.80	<1.25	<4.12	<0.21	<5.43	<4.16	<0.10	<0.19	<2.03	<1.40	<1.85	<14.9	<2.04	<0.58
PCB149	<23.2	<5.47	<1.18	<3.89	<0.20	<5.13	<3.93	0.48	<0.18	<1.91	<1.32	<1.74	<14.0	<1.93	<0.54
PCB123	<21.9	<5.16	<1.11	<3.67	<0.19	<4.84	<3.71	<0.09	<0.17	<1.80	<1.24	<1.65	<13.2	<1.82	<0.51
PCB118	<22.0	<5.19	<1.12	<3.68	<0.19	<4.86	<3.72	0.44	0.87	<1.81	<1.25	<1.65	<13.3	<1.82	<0.51
PCB114	<15.2	<3.60	<0.77	<2.55	<0.13	<3.37	<2.58	<0.06	<0.12	<1.26	<0.87	<1.15	<9.22	<1.27	<0.36
PCB153/168	<7.90	<1.87	<0.40	<1.32	<0.07	<1.75	<1.34	<0.03	<0.06	<0.65	<0.45	<0.59	<4.78	<0.66	<0.19

**Table A-2 (Continued).** Stormwater Particulate Phase PCBs (ng/g)

	R1a	R1b	I1a	I1b	A1b	A2a	A2b	C1c	C2c	M1a	M1b	M1c	M2a	M2b	M2c
PCB105	<24.1	<5.70	<1.23	<4.05	<0.21	<5.34	<4.09	<0.09	<0.19	<1.99	<1.37	<1.82	<14.6	<2.01	<0.57
PCB138	<19.9	<4.69	<1.01	<3.33	<0.17	<4.40	<3.37	<0.08	<0.16	<1.64	<1.13	<1.50	<12.0	<1.65	<0.47
PCB158	<16.8	<3.97	<0.85	<2.82	<0.15	<3.72	<2.85	<0.07	<0.13	<1.39	<0.96	<1.26	<10.2	<1.40	<0.39
PCB126	<23.5	<5.55	<1.19	<3.94	<0.20	<5.19	<3.98	<0.09	<0.18	<1.94	<1.34	<1.77	<14.2	<1.95	<0.55
PCB187	<17.1	<4.03	<0.87	<2.86	<0.15	<3.78	<2.89	<0.07	<0.13	<1.41	<0.97	<1.29	<10.3	<1.42	<0.40
PCB183	<16.6	<3.93	<0.85	<2.79	<0.14	<3.68	<2.82	<0.06	<0.13	<1.37	<0.95	<1.25	<10.1	<1.38	<0.39
PCB128	<23.4	<5.52	<1.19	<3.92	<0.20	<5.17	<3.96	<0.09	<0.18	<1.93	<1.33	<1.76	<14.2	<1.94	<0.55
PCB167	<16.2	<3.83	<0.82	<2.72	<0.14	<3.58	<2.75	<0.06	<0.13	<1.34	<0.92	<1.22	<9.81	<1.35	<0.38
PCB177	<17.8	<4.21	<0.91	<2.99	<0.15	<3.94	<3.02	<0.07	<0.14	<1.47	<1.01	<1.34	<10.8	<1.48	<0.42
PCB156	<20.3	<4.79	<1.03	<3.40	<0.18	<4.48	<3.44	<0.08	<0.16	<1.67	<1.15	<1.53	<12.3	<1.68	<0.48
PCB200	<91.4	<21.6	<4.65	<15.3	<0.79	<20.2	<15.5	<0.36	<0.71	<7.54	<5.20	<6.88	<55.4	<7.60	<2.14
PCB157	<20.0	<4.73	<1.02	<3.36	<0.17	<4.43	<3.39	<0.08	<0.16	<1.65	<1.14	<1.51	<12.1	<1.66	<0.47
PCB180	<12.8	<3.02	<0.65	<2.15	<0.11	<2.83	<2.17	<0.05	<0.10	<1.06	<0.73	<0.96	<7.75	<1.06	<0.30
PCB169	<20.6	<4.86	<1.05	<3.45	<0.18	<4.55	<3.49	<0.08	<0.16	<1.70	<1.17	<1.55	<12.5	<1.71	<0.48
PCB170	<19.2	<4.53	<0.98	<3.22	<0.17	<4.25	<3.25	<0.07	<0.15	<1.58	<1.09	<1.44	<11.6	<1.59	<0.45
PCB201	<115	<27.2	<5.85	<19.3	<1.00	<25.4	<19.5	<0.45	<0.90	<9.49	<6.55	<8.66	<69.6	<9.56	<2.70
PCB189	<19.1	<4.52	<0.97	<3.21	<0.17	<4.23	<3.24	<0.07	<0.15	<1.58	<1.09	<1.44	<11.6	<1.59	<0.45
PCB194	<189	<44.6	<9.61	<31.7	<1.64	<41.8	<32.0	<0.74	<1.47	<15.6	<10.7	<14.2	<114	<15.7	<4.42
PCB206	<34.8	<8.23	<1.77	<5.84	<0.30	<7.71	<5.90	<0.14	<0.27	<2.87	<1.98	<2.62	<21.1	<2.89	<0.82

**Table A-3. PAH Concentrations in UNB Sediment and Water Column**

	UNB Sediment				In Situ Pump	
	S1 ng/g	S2 ng/g	S3 ng/g	S4 ng/g	Dissolved ng/L	Particulate ng/g
N	4.24	5.16	2.95	3.75	0.34	10.6
2MeN	4.18	4.53	2.50	4.97	0.23	14.2
1MeN	1.74	1.75	1.21	1.90	0.12	6.53
BP	<1.42	1.68	<1.42	<1.42	<0.06	<3.50
DMN	9.45	7.64	7.48	6.39	0.14	31.1
Acey	<1.41	1.73	<1.41	<1.41	0.08	<3.46
Ace	<0.93	2.07	1.90	<0.93	0.10	<2.28
TMN	<1.04	1.68	1.50	1.71	0.17	<2.55
Flu	6.29	14.6	9.20	7.83	0.21	<1.65
Ph	22.0	34.4	24.0	25.5	0.77	27.8
An	4.89	7.65	4.91	<4.14	<0.19	<10.2
2MePh	8.66	13.1	6.42	5.95	0.37	8.28
1MePh	3.48	5.19	1.89	1.72	0.20	3.97
DMPH	3.74	1.16	5.28	5.05	0.10	<3.27
Fla	49.2	89.2	53.1	57.3	0.82	18.0
Py	88.8	152	92.3	96.2	0.91	29.2
BaA	29.1	46.2	34.2	35.3	<0.11	13.4
Chry	11.3	29.8	65.2	27.7	<0.10	<5.28
BbF	50.9	48.7	44.3	44.8	<0.14	<7.80
BkF	15.3	26.5	13.2	27.6	<0.05	<2.55
BeP	34.6	65.0	28.2	38.5	<0.18	<9.94
BaP	19.8	103	53.7	46.3	<0.33	<18.3
Peryl	20.5	104	33.3	46.7	<0.42	<23.0
DPhA	<2.21	<2.21	<2.21	<2.21	<0.10	<5.43
I123cdP	31.0	60.4	23.5	42.3	<0.54	<29.6
DBahA	<8.24	<8.24	<8.24	<8.24	<0.37	<20.3
BghiP	53.3	127	41.6	77.6	<0.56	<30.5

**Table A-3 (Continued).** OCP Concentrations in UNB Sediment and Water Column

	UNB Sediment				In Situ Pump	
	S1 ng/g	S2 ng/g	S3 ng/g	S4 ng/g	Dissolved ng/L	Particulate ng/g
Diazinon	<2.12	<2.12	<2.12	<2.12	<0.10	<5.22
Chlordene	<3.97	<3.97	<3.97	<3.97	<0.18	<9.77
Chloropyrifos	<0.82	<0.82	<0.82	<0.82	<0.04	<2.03
Aldrin	<1.63	<1.63	<1.63	<1.63	<0.07	<4.01
Oxychlordane	<2.69	<2.69	<2.69	<2.69	<0.12	<6.61
o,p'-DDE	0.55	3.79	1.82	5.07	<0.03	<1.50
gamma-Chlordane	1.01	4.02	1.17	1.08	<0.02	<1.17
alpha-Chlordane	1.10	2.77	1.07	0.99	0.04	1.57
trans-Nonachlor	0.94	2.71	1.92	1.73	<0.02	2.28
p,p'-DDE	23.5	117.3	74.1	110.9	0.34	82.2
Dieldrin	<0.84	<0.84	<0.84	<0.84	0.11	<2.05
o,p'-DDD	<1.14	1.77	<1.14	5.17	0.06	<2.80
Endrin	<3.19	<3.19	<3.19	<3.19	<0.14	<7.85
cis-Nonachlor	0.85	1.45	<0.39	<0.39	<0.02	<0.97
p,p'-DDD	9.26	54.4	34.6	42.8	1.33	52.2
o,p'-DDT	<2.79	<2.79	<2.79	<2.79	<0.13	<6.87
p,p'-DDT	<2.64	<2.64	3.58	<2.64	<0.12	<6.49

**Table A-3 (Continued).** PCB Concentrations in UNB Sediment and Water Column

	UNB Sediment				In Situ Pump	
	S1 ng/g	S2 ng/g	S3 ng/g	S4 ng/g	Dissolved ng/L	Particulate ng/g
PCB18	<0.93	3.7	<0.93	56.9	0.04	19.5
PCB28	<1.10	2.9	<1.10	65.3	0.06	28.1
PCB52	<0.44	2.4	0.6	15.0	<0.02	6.44
PCB49	<0.75	<0.75	<0.75	11.6	<0.03	5.22
PCB44	<0.86	<0.86	<0.86	3.6	<0.04	<2.21
PCB37	<1.76	<1.76	<1.76	<1.76	<0.08	<4.32
PCB74	<0.79	<0.79	<0.79	<0.79	<0.04	<1.94
PCB70	<0.80	<0.80	<0.80	1.5	<0.04	<1.97
PCB66	<0.93	<0.93	<0.93	<0.93	<0.04	<2.28
PCB101	<0.81	<0.81	<0.81	1.8	<0.04	<2.00
PCB99	<0.85	<0.85	<0.85	<0.85	<0.04	<2.10
PCB119	<0.69	<0.69	<0.69	<0.69	<0.03	<1.70
PCB87	<0.88	<0.88	<0.88	<0.88	<0.04	<2.16
PCB81	<1.08	<1.08	<1.08	<1.08	<0.05	<2.65
PCB110	<0.68	<0.68	<0.68	<0.68	<0.03	<1.68
PCB77	<1.23	<1.23	<1.23	<1.23	<0.06	<3.03
PCB151	<0.84	<0.84	<0.84	<0.84	<0.04	<2.08
PCB149	<0.80	<0.80	<0.80	<0.80	<0.04	<1.96
PCB123	<0.75	<0.75	<0.75	<0.75	<0.03	<1.85
PCB118	<0.76	<0.76	<0.76	<0.76	<0.03	<1.86
PCB114	<0.52	<0.52	<0.52	<0.52	<0.02	<1.29
PCB153/168	<0.27	<0.27	<0.27	<0.27	<0.01	<0.67
PCB105	<0.83	<0.83	<0.83	<0.83	<0.04	<2.04
PCB138	<0.68	<0.68	<0.68	<0.68	<0.03	<1.68
PCB158	<0.58	<0.58	<0.58	<0.58	<0.03	<1.42
PCB126	<0.81	<0.81	<0.81	<0.81	<0.04	<1.99
PCB187	<0.59	<0.59	<0.59	<0.59	<0.04	<1.44
PCB183	<0.57	<0.57	<0.57	<0.57	<0.03	<1.41
PCB128	<0.80	<0.80	<0.80	<0.80	<0.04	<1.98
PCB167	<0.56	<0.56	<0.56	<0.56	<0.03	<1.37
PCB177	<0.61	<0.61	<0.61	<0.61	<0.03	<1.51
PCB156	<0.70	<0.70	<0.70	<0.70	<0.03	<1.71
PCB200	<3.14	<3.14	<3.14	<3.14	<0.14	<7.74
PCB157	<0.69	<0.69	<0.69	<0.69	<0.03	<1.69
PCB180	<0.44	<0.44	<0.44	<0.44	<0.02	<1.08
PCB169	<0.71	<0.71	<0.71	<0.71	<0.03	<1.74
PCB170	<0.66	<0.66	<0.66	<0.66	<0.03	<1.62
PCB201	<3.96	<3.96	<3.96	<3.96	<0.18	<9.73
PCB189	<0.66	<0.66	<0.66	<0.66	<0.03	<1.62
PCB194	<6.49	<6.49	<6.49	<6.49	<0.29	<16.0
PCB206	<1.20	<1.20	<1.20	<1.20	<0.05	<2.95