IDENTIFYING REMEDIATION TECHNIQUES AND QUANTIFYING TMDL REGULATED POLLUTANTS FOR STORMWATER RUNOFF IN THE LOS ANGELES REGION

by

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Abstract

My research goals for Los Angeles and southern California water quality included evaluating the capture, treatment, and reuse of stormwater through groundwater infiltration; assessing the costs of stormwater quality control; monitoring virus numbers in stormwater; and developing improved methods for measuring pollutant concentrations.

The cost benefit analysis indicated that the treatment of larger regions as one watershed reduces the initial cost to employ the stormwater best management practices, that willingness to pay and value of ecological improvements vary and are difficult to quantify. The new cost estimated for both structural and non-structural BMPs was $12.6 billion, and the total benefit of the BMPs and improvement to the environment was $21.3 billion, for a net benefit of $8.7 billion.

The virus study was less conclusive, finding rather uniform virus counts in the tens of millions per milliliter. Previous research found human viruses in significantly smaller concentrations (1-100 per mL), suggesting that the total counts may reflect high background concentrations of non-human viruses from sources that are not coincident with sources of pollution.

Using two passive samplers, polyethylene devices (PEDs) and solid phase microextraction (SPME) fibers, hydrophobic organic contaminants (HOCs) were quantified and the samplers were compared. PEDs were calibrated for 16 model HOCs

(PCBs, PAHs, DDTs, and chlordanes) for both partitioning coefficients (K_{PEW}) and exchange rate kinetics (k_e). Triplicate PEDs and SPME fibers were exposed for 45 days to a concentration series of water spiked with nine model hydrophobic organic compounds. Model HOCs in SPME were higher than those in PEDs, with SPME measurements matching water concentrations more closely than PEDs for PCBs and chlorinated pesticides. For PAHs, PED and SPME measurements bracketed LLE water concentrations with no apparent bias. The number of detections using PEDs was greater for concentrations less than 0.1 ng/L, indicating that PEDs afford greater sensitivity than single SPME fibers. Researchers are continuing to investigate PEDs, including the use of pre-loaded reference compounds to quantify the "extent" of equilibrium vs. exposure time and possible variations due to polyethylene manufacturer and process.

Chapter One: Introduction

As one flies over the Los Angeles area, a distinctive characteristic is noticed: the abundance of concrete and impervious surfaces and the lack of green park space. Over 90% of rain water that falls in the Los Angeles region enters the Pacific Ocean untreated as it is quickly moved through an intricate system of storm drains and concrete channels. The Army Corp of Engineers channelized most of the rivers and streams in the region between the 1930s and 1960s to control flooding and enable development on the flood plains.

Stormwater pollution prevention and treatment is an important topic in southern California and the United States. The poor quality of stormwater runoff in Southern California is a result of two environmental alterations: the conversion of soils and other pervious surfaces to concrete, asphalt, buildings, and other impervious surfaces, and the release of pollutants from residential neighborhoods and industrial areas. Los Angeles County lacks open space and the larger percentage of impervious surfaces has made remediation of stormwater through infiltration basins, detention ponds, and constructed wetlands seem almost impossible; however, with multipurpose watershed management and park rehabilitation projects, such as that described in the Sun Valley Watershed Management Plan, these methods of stormwater remediation can be utilized.

1.1 Research Goals

This research is focused on water quality in Los Angeles, determining the presence of total maximum daily loads (TMDLs) regulated pollutants in stormwater, treatment options for the stormwater, and the associated costs and benefits of these treatment methods.

There are three main goals of this dissertation. The first is to define and identify suitable best management practices for treating stormwater runoff in the Los Angeles region. This included a cost benefit analysis of the BMPs that are suited to Los Angeles with a simple efficiency and effectiveness analysis.

The second goal was to determine whether a simple, inexpensive, method for quantifying viruses in stormwater could be used to trace pollution sources. This included three simple studies: a watershed contribution study in Ballona Creek, a land use contribution study in west Los Angeles, CA, and a virus accumulation study along the storm drain in a residential neighborhood in Long Beach, CA.

The final goal is to develop methods for quantifying hydrophobic organic contaminants (HOCs) in stormwater. In order to determine total maximum daily loads (TMDLs) and to provide cost-effective enforcement of standards, cheap and effective analytical techniques must be available. This research involved calibrating the passive samplers in the laboratory to quantify HOCs in Ballona Creek. The passive samplers employed are solid-phase microextraction and polyethylene devices. During the field study, the effectiveness of these two techniques was compared.

Chapter Two: Literature Review

Southern California and its beaches are unique recreational and economic resources because of the long coastline and year-round temperate climate. The safety of these beaches and ocean waters is a concern to the state and county health departments as well as to beachgoers.

This region is also one of the most densely populated coastal areas in the country. Population growth results in conversion of open land into impermeable surfaces, increasing the rate of runoff and impacting water quality through addition of sediment, toxic chemicals, microbial pathogens, and nutrients to the coastal ocean, all TMDL regulated pollutants (Jiang *et al* 2001). Research on southern California beaches and oceans has shown that for three days following a storm, contamination levels are high enough for the county health departments to issue warnings to avoid recreational water contact (Ackerman and Weisberg 2003). TMDL regulated microbial pathogens, which cause beach closures, and hydrophobic organic contaminants (HOCs), which may biomagnify in the ecosystem resulting in adverse effects in humans (Ross and Birnbaum 2003), are present in stormwater in the Los Angeles region (Ackerman and Weisberg 2003, Zeng *et al.* 2004).

2.1 Stormwater Mitigation and Control

Over the past three decades, urban runoff has been identified as a critical source of pollution in the United States. This runoff is now regulated under the Clean Water Act through National Pollutant Discharge Elimination System permitting, with pollution limits defined as total maximum daily loads. Urban and stormwater runoff are critical sources of contamination, particularly for waters near cities, which include the majority of the population. The United States Environmental Protection Agency (USEPA) ranks urban runoff and storm drain discharges as the second most significant source of water quality impairment to US estuaries, and the fourth most significant source of impairment to US lakes (NRDC 1999).

Stormwater pollution prevention and treatment is an important regulatory topic in southern California and the United States. The poor quality of stormwater runoff in southern California and elsewhere arises from two human alterations of the environment: the conversion of soils and other pervious surfaces to concrete, asphalt, buildings, and other impervious surfaces, and the release of pollutants from residential neighborhoods and industrial areas.

Since 1992, cities with populations over 100,000, certain industries, and construction sites over five acres have developed and implemented stormwater plans under Phase I of the National Pollutant Discharge Elimination System (NPDES) stormwater regulations. Since 1999, municipalities with populations of fewer than 100,000 people located in urbanized areas (where population density is greater than 1,000 persons per square mile) have been required to develop stormwater plans. Municipalities not in urbanized areas that have more than 10,000 residents and a population density greater than 1,000 persons per square mile must also develop stormwater plans if their state so designates (NRDC 1999).

Many everyday human activities, including driving vehicles, maintaining lawns and parks, disposing of waste and walking pets, can contribute to stormwater pollution, because these activities contaminate impervious surfaces with various pollutants. Common pollutants in stormwater and urban runoff include sediments, toxic metals, pesticides and fertilizers, oil and grease, pathogens, excess nutrients, and trash. These pollutants are washed from streets and roads, rooftops, and parking lots during rain events and are carried by the runoff to streams, rivers, and oceans (NRDC 1999).

The presence of pollutants and the increased velocity and volume of runoff affect the hydrology and water quality in the watershed, increasing flooding, degrading stream channels, damaging wildlife habitat, changing water temperatures, increasing erosion and sedimentation, and reducing water quality. This affects ecosystem function, biological diversity, public health, recreation, economic activity, and general community well-being. The environmental, aesthetic, and public health impacts of nonpoint pollution will not be eliminated until stormwater pollution is controlled (NRDC 1999).

2.1.1 Stormwater Regulation and Pollution Prevention in the United States

Decades after the passage of the Clean Water Act, urban stormwater continues to pollute water bodies in the US. The reason for this continued impairment is that, in most areas, urban stormwater receives little or no treatment before it enters a water body (NRDC 1999).

While the past few decades have seen much advancement in water pollution control technologies, most of these have been created for point source water discharges from facilities such as factories and sewage treatment plants. New technologies are needed to address the nonpoint source pollution from urban runoff (NRDC 1999).

2.1.1.1 Nonpoint Source Pollution

As defined by the United States Environmental Protection Agency (USEPA), a nonpoint source pollutant is any pollutant that comes from diffuse sources. Normally, nonpoint source (NPS) pollution is created through the migration of rainfall or snowmelt over and through the ground. NPS pollutants can be natural or anthropogenic; such pollutants common to the Los Angeles area include excess fertilizers, herbicides, and pesticides from lawns, oil, grease, and toxic chemicals from urban runoff and energy production, sediment from improperly managed construction sites, bacteria and nutrients from pet wastes and septic systems, and atmospheric deposition (USEPA 2004).

2.1.1.2 National Pollutant Discharge Elimination System Permits

Discharges into navigable waters from point sources are regulated by the National Pollutant Discharge Elimination System (NPDES), which was established by the Clean Water Act. This includes all municipal wastewater treatment plants or publicly owned treatment plants, municipal and industrial stormwater systems, industries and commercial facilities, and concentrated animal feeding operations

(USEPA 2004). This means that Los Angeles is required to have an operating and updated NPDES permit for stormwater discharge. This permit, entitled “Waste Discharge Requirements for Municipal Storm Water and Urban Runoff Discharges within the County of Los Angeles, and the Incorporated Cities Therein, Except the City of Long Beach” was prepared by the Los Angeles County Flood District, Los Angeles County, and the 84 municipalities within the Los Angeles County Flood Control District for the California Regional Water Quality Control Board, Los Angeles Region.

2.1.1.3 Total Maximum Daily Loads

The USEPA defines total maximum daily loads (TMDLs) as the maximum calculated amount of a given pollutant that a body of water can receive each day and still meet water quality standards (2005). Established by the Clean Water Act, section 303, a TMDL is the sum of the allowable loads of a single pollutant from all contributing point and nonpoint sources. This amount is then allocated to the pollutant’s sources, *i.e.* each known polluter on that water body is allowed to contribute a percentage of the total maximum daily load of that pollutant to the water body. The calculation must include a margin of safety to ensure that the water body can be used for the purposes the regulating State has designated and must also account for seasonal variation in water quality. The TMDLs for a water body include any nonpoint sources such as municipalities, construction sites, and agricultural areas, all of which contribute to stormwater runoff pollution. Water quality standards are set by the individual states, territories, and tribes, and identify the uses and scientific criteria for each body of water, *e.g.* drinking water supply, contact recreational activities such as swimming or boating, and supporting aquatic life (USEPA 2005).

2.1.2 Stormwater Best Management Practices

A Best Management Practice (BMP) is defined as a "device, practice, or method for removing, reducing, retarding, or preventing targeted stormwater runoff quantity, constituents, pollutants, and contaminants from reaching receiving water" (Strecker *et.al* 2001). In the 1990s, municipalities began to implement BMPs to treat and control the pollution of urban runoff and protect the receiving waters (Roesner *et.al.* 2001). The effectiveness of stormwater BMPs has been evaluated for the past twenty years by studies conducted in the United States, Europe, and other places in the world. These studies have created an abundance of literature on a myriad of practices and techniques.

The USEPA defines stormwater BMPs as techniques, measures, or structural controls that are used for a given set of conditions to manage the quantity and improve the quality of stormwater runoff in the most cost-effective manner. BMPs are classified as either structural BMPs, which are systems that are engineered and constructed, or nonstructural BMPs, which are pollution prevention techniques designed to stop pollutants from entering urban runoff (USEPA 1999).

One way to reduce the impacts of stormwater discharges is to limit the amount of rainfall that is converted to runoff. The USEPA recommends a series of on-site storage and infiltration facilities to reduce the amount of directly connected impervious surfaces, which reduces the amount of runoff generated from a site. Certain factors such as slope, depth to the water table, and geologic conditions can limit on-site infiltration (USEPA 1999).

When properly designed, BMPs can effectively remove a wide range of pollutants from urban runoff. Pollutant removal in stormwater BMPs can be accomplished through several physical and biochemical processes, including: sedimentation, filtration, floatation, infiltration, adsorption, biological uptake, biological conversion, and degradation. The pollutant removal efficiency of a BMP is dependent upon numerous site-specific variables, including the size, type and design of the BMP; the soil types and characteristics; the geology and topography of the site; the intensity and duration of the rainfall; the length of antecedent dry periods; climatological factors such as temperature, solar radiation, and wind; the size and characteristics of the contributing watershed; and the properties and characteristics of the various pollutants (USEPA 1999).

The EPA lists a number of designs that can greatly reduce the amount of stormwater runoff from a site. These designs include rain barrels, dry wells or infiltration trenches to capture rooftop and driveway runoff, vegetated open space, stream buffers and riparian corridors, porous pavement systems for parking lots and driveways, and grassed filter strips and vegetated swales to replace traditional curb-and-gutter type drainage systems. Development designs and construction features such as placing sidewalks on only one side of the street, limiting street widths, reducing frontage requirements and eliminating cul-de-sacs or reducing their radii to reduce the amount of impervious surface, reduces the amount of rainfall that is converted to runoff (USEPA 1999).

Structural BMPs are employed either at the point of generation, the source, or at the point of discharge, the storm sewer or the receiving water body. These include engineered and constructed systems designed to control the water quantity and quality in the stormwater runoff. Nonstructural BMPs are pollution prevention measures, education and public awareness, institutional, management, and the other practices designed to limit the amount of rainfall that is converted to runoff and to prevent contaminants from entering the runoff (USEPA 1999).

The four main categories of structural controls are velocity dissipation, sediment capture, and temporary and permanent stormwater management. As the velocity of the runoff increases, the quantity and size of the soil particles carried by the flow increases. Reducing stormwater velocity promotes infiltration, reduces the shearing forces exerted on the soil, and attenuates the volumetric runoff flow rate (Dodson 1999). Several structural BMP systems have been derived using the basic four mechanisms: infiltration systems, detention systems, retention systems, constructed wetland systems, filtration systems, vegetated systems and biofilters, minimization of directly connected impervious surfaces, and miscellaneous and vendor-supplied systems (USEPA 1999).

The effects of urban runoff on water quality are site-specific and local watershed and facility site characteristics should be considered when selecting BMPs (Barrett *et.al.* 1995). Particle-size distributions, solids fractions, hydrographic loadings, particle counts, and specific gravity are required to design infiltration systems or settling basins

(Sansalone *et al.* 1998). The selection of *in situ* treatment methods (*e.g.,* settling basins, granular media filtration systems, and other solids separation devices) is primarily determined by the site-specific particulate characteristics and loading rates. The selection of appropriate water quality and drainage measures requires identification of solid gradation, mass loading, surface area, and specific gravity of the soil at each site.

BMPs have become a common means for controlling runoff quality since the early 1990s and their effectiveness has been evaluated through studies conducted in the United States, Europe, and other places in the world (Roesner *et al.* 2001). The most common BMPs are listed in Table 2.1 along with their intended impacts.

Table 2.1 Best Management Practices and Their Intended Impacts[1]

BMP	Description	Intended Impacts
Constructed Wetlands	Upstream ponds with deep water and downstream wetland that imitates the function of a natural wetland that utilizes aerobic microorganisms, and anaerobic microorganisms to remove pollutants from water	Remove metal pollutants through plant uptake, neutralization by carbonates, adsorption to soils, metal adsorption and exchange onto algae layers, iron hydroxide formation and sulfates reduction through microbial dissimilation Remove pollutants through sedimentation, filtration, plant uptake, degradation, biological uptake and conversion
Infiltration Basins	Shallow depressions created by excavation or berming that capture stormwater and promote infiltration into soil (Figure 2.1), usually limited to roadway interchanges and large residual parcels of land and may not be suitable for dense urban areas	Have similar impacts as above with additional management of larger volumes of stormwater
Infiltration Trenches/ Ditches	Excavated trench lined and backfilled with stone to form subsurface basin (Figure 2.2) Most effective with pretreatment included in design, such as vegetated filter strips or grassed swales Ideal for small urban drainage areas	Divert and store runoff until it can infiltrate into soil, usually over a period of several days
Bioretention Areas	Conditioned soil layers containing a mixture of detritus, humus, and mineral and biological complexes in shallow depressed areas Small areas can be located in medians, parking lot islands, or grassy areas along streets, making these ideal for the constricted urban areas	Enhance filtration through soil layer and presence of microbes Remove constituents through the vegetation

Table 2.1 Best Management Practices and Their Intended Impacts (Continued)

BMP	Description	Intended Impacts
Water Quality Flotation Inlets	Settling and surface oil separation mechanisms and/or filtration, flotation, or vortex motion settling and separating mechanisms are utilized Oil and grease trap with a submerged outlet pipe allows contaminants to accumulate and to be removed	Settle out fine and coarse sediment Trap debris and trash Separate oil and grease from runoff Allow floatable materials such as styrofoam and other low-density materials to accumulate and be manually removed
Filtration Basins	Permanent pool with a sediment chamber through which stormwater flows	Remove solids and attached pollutants such as metals and nutrients
Underground Filters	A multi-chamber underground vault accessible by access holes or grate openings	Pretreat stored water in underground chambers through settling Collect filtered water in under drains and discharge into adjacent storm drains or natural channels
Sand Filters	A settling area and a filter, usually with a sand medium, An off-line facility can be used to provide additional capture and treatment of any water quality volume "Austin Filter" has a bypass chamber, sedimentation chamber for pretreatment, flow distribution cell, and a sand filter bed	Remove particulates from urban stormwater, and is often used to manage the first flush
Grassed Swales	Land surface is shaped to direct stormwater through in a broad, relatively flat grassed area Frequently located in medians or along the shoulders of roads	Remove sediments and increases infiltration

Table 2.1 Best Management Practices and Their Intended Impacts (Continued)

BMP	Description	Intended Impacts
Vegetated Strips	Evenly sloped vegetated areas similar to grassed swales (Figure 2.3) Commonly used as a pre-treatment BMP located upstream of other BMPs capable of greater pollutant removal rates or on roadway shoulders as a small treatment option	Remove sediments and increases infiltration
Detention Ponds	Ponding area that controls runoff from impervious area by storing and releasing at a slowed rate through an outfall (Figure 2.4)	Remove pollutants through settling, infiltration, nutrient uptake, adsorption, and physical filtration
Extended Detention Ponds	Longer, often coupled systems that facilitate longer detention times for optimal pollutant removal Detention time is a function of the size of the outflow opening with respect to storm event runoff volume	Provide water quality treatment of first flush runoff and some reduction of peak flows for small storm events Remove pollutants through settling, infiltration, nutrient uptake, adsorption, and physical filtration
Retention Ponds	One or more permanent pools of water that retain stormwater flow Pollutant removal efficiency is a function of pond depth, residence time, drainage area-to-pool volume ratio, and existence of aquatic vegetation	Enhance particulate settling by increasing residence time and provide conditions for growth of aquatic vegetation, thereby enhancing filtration, metal and nutrient uptake Enhance aesthetics and/or provide recreational benefits such as parks, soccer fields, and baseball fields
Porous Pavements	Porous asphalt and concrete and several types of lattice-type pavers Parking lots, emergency stopping areas, traffic islands, sidewalks, road shoulders, and low-traffic roads	Allow stormwater to percolate through pavement and infiltrate into soil Allow streets, parking lots, sidewalks, and other surfaces to retain their function for automobiles and pedestrians

Table 2.1 Best Management Practices and Their Intended Impacts (Continued)

BMP	Description	Intended Impacts
Green Roofs	Rooftop areas that support living vegetation Range from small gardens and planters to roofs that are completely covered by sod and plants Main layers include waterproofing and root barrier layer, an optional insulation layer, a drainage and filter layer, and the soil and plants	Reduce the size and cost of HVAC equipment on new and retrofitted buildings and a potentially reduce energy costs due to the insulating properties of most green roof systems
Rain Barrels	Water-tight barrel set next to a building with gutter downspout funneled into it	Collect and store rainwater so it can be used later to water lawns and gardens
Stream Buffers	Trees and grass areas planted next to streams to reduce runoff and erosion Function best when kept in a natural condition, but areas along rivers and streams can also be restored or replanted for effective buffers	Lock soil into place and reduce erosion and can also filter out sediment and other pollutants

1 – Based on Schueler 1987, Wieder 1988, Henrot and Wieder 1990, Schueler *et al.* 1992, Yu and Kaighn 1992, Wildeman *et al* 1993, Faulkner and Skousen 1994, USEPA 1999, NRDC 1999, Schueler 2000, FHWA 2003, Minnesota Metropolitan Council 2003, Menomenon Valley Partners 2005, Belan and Otto 2004, Devinny *et al.* 2004, USEPA 2004

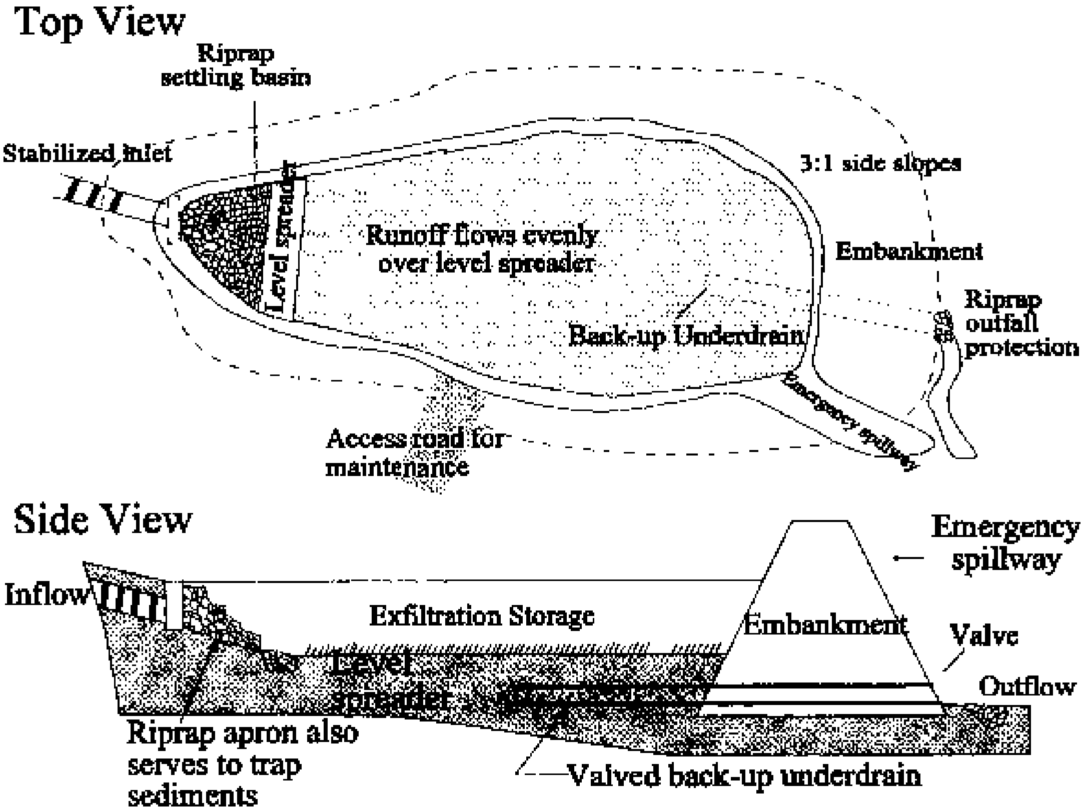


Figure 2.1 Schematic of Infiltration Basin (FHWA 2003, Young *et al.* 1996)

Figure 2.2 Infiltration Trench (Traver 2005)

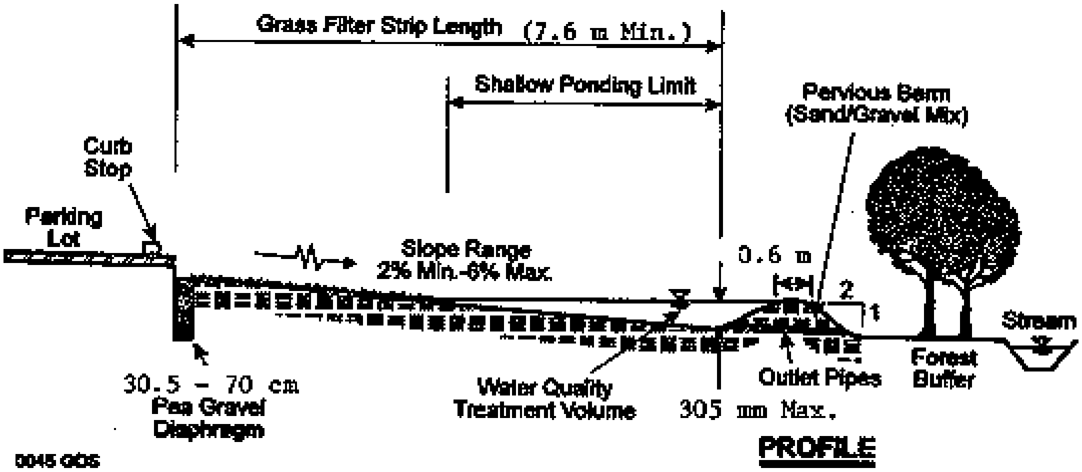


Figure 2.3 Profile View of Filter Strip (FHWA 2003)

Figure 2.4 Detention Pond (Traver 2005)

No one BMP can solve all stormwater problems. Each has limitations based on the drainage area served, available land, cost, desired pollutant removal efficiency, and site-specific factors such as soil type, slope, and depth of groundwater table. The advantages and disadvantages of common BMPs are presented in Table 2.2 and these factors should be carefully considered to select the appropriate BMP or group of BMPs for a particular location (USEPA 1999).

Table 2.2 Advantages and Disadvantage of Common BMPs[1]

Best Management Practice (BMP)	**Advantages**	**Disadvantages**
Constructed Wetlands	Provide peak flow control Serve large developments Provide vegetated habitat area and recreational benefits	Require more space than other common BMPs Require year-round water supply, which may limit use in semi-arid climates and/or require supplemental water
Infiltration Basins	Facilitate groundwater recharge Serve large developments Remove particulate and soluble pollutants Replicate predevelopment hydrology more than other BMPs Provide more habitat value than other infiltration systems	Fail frequently May contaminate groundwater May become an eyesore and a mosquito breeding ground with poor maintenance May clog in spite of regular maintenance activities Require permeable soil with sufficient depth of rock and water table
Infiltration Trenches/Ditches	Provide groundwater recharge Serve small drainage areas May be applied to medians, perimeters, and other unused open space areas Replicate the predevelopment hydrology by increasing dry weather baseflow and reducing bankfill flooding frequency	May contaminate groundwater Require significant maintenance Require appropriately permeable soil conditions

Table 2.2 Advantages and Disadvantage of Common BMPs (Continued)[1]

BMP	Advantages	Disadvantages
Infiltration Bioretention Areas	May fit in medians or grassy areas along streets and parking lots Remove pollutants through sedimentation, filtration, soil adsorption, microbial decay processes, and uptake by plants Provides habitat area for urban wildlife	Require modifications for arid watersheds Necessitate pretreatment to remove large debris, trash, and sand
Water Quality Inlets	Capture coarse-grained sediments and some hydrocarbons Require a minimal amount of land and can be fit to exiting small drainage areas and applicable to most urban areas Trap trash, debris, and other floatables,	Infeasible for drainage areas greater than one acre Remove little nutrients and organic matter May not control intense storms Requires high maintenance
Filtration Basins	Accommodate medium-size land areas May or may not recharge groundwater Provide peak volume control	Require settling pretreatment to prevent filter media from prematurely clogging
Underground Filters	Can be used in dense urban areas Require low maintenance Provide peak volume control Manage suspended solids effectively May be designed to treat a range of water quality volumes	Require sedimentation pretreatment to prevent filter media from prematurely clogging Require special disposal of fluids and sediment that may have high hydrocarbon fraction Require regular replacement of sand filter medium to ensure pollutants do not accumulate in the sediment
Sand Filters	Manage suspended solids Utilize to manage the first flush Remove particulates from stormwater effectively Utilize upstream as a pretreatment technique for sediment removal	Require large amount of land and cannot support secondary use such as park May not be suitable where hydrocarbon pollutants concentrations are high

Table 2.2 Advantages and Disadvantage of Common BMPs (Continued)[1]

BMP	Advantages	Disadvantages
Grassed Swales	Require minimal land Utilize in runoff conveyance systems for pretreatment Provide sufficient runoff control to replace curbs and gutters in low density housing and highway medians	May have low pollutant removal rates Require leaching culverts Require fertilization, which can increase concentrations of trace metals and nutrients Low treatment capacity
Vegetated Strips	Require little maintenance Utilize for runoff conveyance system pretreatment Reduce particulate pollutant levels in areas where runoff velocity is low to moderate Provide habitat for urban wildlife	May treat only low intensity rainfall events May not treat high-velocity flows Do not provide enough storage or infiltration to effectively reduce peak discharges to predevelopment levels Require regular repair, regrading, and sediment removal
Detention Ponds	Provide peak flow control Provide good particulate removal Serve large impervious areas	May not be suitable for areas with space limitations Require pretreatment to reduce clogging
Extended Detention Ponds	Provide peak flow control Provide good particulate removal Serve large impervious areas May not release warm water or anoxic water downstream Protect against downstream channel erosion May create valuable wetland and meadow habitat when properly landscaped	Require proper maintenance to prevent possible safety hazards, breeding of mosquitoes, undesirable odors, and nuisance eyesores May have low soluble pollutants removal rates
Retention Ponds (Wet Ponds)	Provide peak flow control Serve large developments or impervious area Enhance aesthetics and provide recreational opportunities Allow little ground water discharge Prevents scour and resuspension of sediments	Allow little ground water discharge (if groundwater recharge is important to the site) Require proper maintenance to prevent possible safety hazards, breeding of mosquitoes, undesirable odors, and nuisance eyesores

Table 2.2 Advantages and Disadvantage of Common BMPs (Continued)[1]

BMP	Advantages	Disadvantages
Retention Ponds (Wet Ponds) Continued	Provide moderate to high particulate and soluble pollutant removal	Require soil types "C" and "D" unless a liner is used May not be suitable for areas with space limitations
Porous Pavements	Retain the natural infiltration rate Facilitate groundwater recharge and maintaining base flows in urbanized streams Provide structural and functional use of paved surface Provide peak flow control Control water quality without additional land use	Require regular maintenance May not be suitable for areas with high traffic volume May pose a groundwater contamination risk May only be feasible where soil is permeable, there is sufficient depth to rock and water table, and there are gentle slopes
Green Roofs	May manage most or all of the runoff generated by a building's roof area Prolong the life of normal roofing materials by covering them and shielding them from wear Insulate a building, reducing cooling and heating requirements Reduce impervious surfaces Improve air quality by reducing dust and other airborne particles	May be costly to retrofit an existing building May leak which could pose substantial problems and costs to repair, even with electronic leak detectors Require maintenance which can be labor intensive
Rain Barrels	Provide easy method to collect and recycle rainwater for use on gardens and lawns, thus lowering water bills Reduce storm runoff discharges into sewers May be easily utilized by individual homeowners May be an aesthetically acceptable addition to gardens adjacent to houses	Provide minimal runoff mitigation for neighborhoods unless used by multiple homeowners Require proper installation and management to prevent insect growth

Table 2.2 Advantages and Disadvantage of Common BMPs (Continued)[1]

BMP	Advantages	Disadvantages
Stream Buffers	Reduce flooding Trap sediment, fertilizers, pesticides, pathogens, and heavy metals Reduce stormwater runoff velocity Reduce blowing soil in areas with strong winds, Protect wildlife from harsh weather, Provide connecting corridors that enable wildlife to move safely from one habitat area to another, Provide aesthetic border areas that can raise property values, Stabilize stream banks	May provide less effective pollutant removal and volume reduction on steep surfaces May be difficult to maintain widths in areas where land values are high

1 – Based on Schueler 1987, Wieder 1988, Henrot and Wieder 1990, Yu and Kaighn 1992, Schueler *et al.* 1992, Wildeman *et al* 1993, Faulkner and Skousen 1994, NRDC 1999, USEPA 1999, Schueler 2000, FHWA 2003, Minnesota Metropolitan Council 2003, Belan and Otto 2004, Devinny *et al.* 2004, USEPA 2004, Menomenon Valley Partners 2005

Pollutant removal in stormwater BMPs can be accomplished through several physical and biochemical processes, including sedimentation, filtration, floatation, infiltration, adsorption, biological uptake, biological conversion, and degradation. The pollutant removal efficiency is dependent upon numerous site-specific variables, including the size, type and design; the soil types and characteristics; the geology and topography of the site; the intensity and duration of the rainfall; the length of antecedent dry periods; climatological factors such as temperature, solar radiation, and wind; the size and characteristics of the contributing watershed; and the properties and characteristics of the various pollutants (USEPA 1999). The removal efficiencies of common BMPs for typical pollutants found in urban runoff are presented in Table 2.3.

Table 2.3 Percent Pollutant Removal Efficiencies for Common BMPs[1]

	TSS	NO_3-N	TKN	P	Total Copper	Total Lead	Total Zinc	Dissolved Copper	Dissolved Lead	Dissolved Zinc	Fecal Coliform
Underground Sand Filter	80	N/A	40	56	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sand Filter	82	N/A	47	50	58	86	86	24	36	78	76
Filtration Basin	74	49	42	48	67	79	72	66	75	62	N/A
Grassed Swales	52	N/A	10	37	N/A	13	38	N/A	N/A	N/A	N/A
Vegetated Strips	69	39	48	37	90	53	62	85	78	78	N/A
Wetlands	76	46	24	56	25	54	49	N/A	N/A	N/A	97
EDBs	72	8	17	39	58	72	73	76	74	84	N/A
Detention Basin	74	49	42	48	67	79	72	66	75	62	N/A
Water Quality Inlet	0	15	N/A	15	8	11	17	16	6	14	N/A
Infiltration Basin	84	65	38	69	65	58	60	N/A	N/A	N/A	100
Bioretention Areas	49	27	31	N/A	N/A	63	68	77	49	57	74
Infiltration Trench	84	N/A	55	60	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Porous Pavements	91	27	81	61	42	74	81	N/A	N/A	N/A	N/A

1 – Based on Yousef *et al.* 1985, Martin and Smoot 1986, Hogland *et al.* 1987, Schueler 1987, Yu and Benelmouffok 1988, City of Austin (1990, 1995), Kahn *et al.* 1992, Schueler *et al.* 1992, Yu and Kaighn 1992, Harper and Herr 1993, USEPA 1993, Yu *et al.* (1993, 1994), Bell *et al.* 1995, Horner and Horner 1995, Gain 1996, Young *et al.* 1996, USEPA 1999, FHWA 2003, California Department of Transportation 2004

2.1.3 Stormwater Systems Suitable for the Los Angeles Region

In order to serve the needs of the Los Angeles area, BMPs should be suitable for semi-arid watersheds and applicable to parks and urban open spaces. A stormwater management system that utilizes a system of native landscaping and vegetation to treat and convey stormwater in place of these conventional approaches allows natural infiltration to occur as close as possible to the original area of rainfall. By engineering terrain, vegetation, and soil features to perform this function, costly conventional conveyance systems can be avoided and the site's hydrologic characteristics can function in a more natural way (Menomenon Valley Partners 2005). Examples of stormwater park designs which included BMPs are presented in Table 2.4.

Through continued rapid growth and the spread of urbanization, the Los Angeles area has lost much of its open space and recreational park land. The Los Angeles Chamber of Commerce released the Olmsted Bartholomew Plan for Parks, Playgrounds, and Beaches for the Los Angeles Region in 1930. This plan, which integrated habitat conservation, watershed management, and recreation, was considered visionary and is still an epitome of regional planning, but was also deemed too expensive and was left ignored in the archives (Wolch *et al.* 2004).

Table 2.4 Stormwater Parks and Their Best Management Practices[1]

Park Description	Best Management Practice(s)	Desired Outcomes
Sun Valley District Sun Valley Watershed Management Plan Los Angeles, CA	Infiltration basin in park Tree planting and mulching Industrial reuse Permeable pavements Infiltration vaults under streets	Control floods – collect and infiltrate 50-year, 96-hour storm Create alternative to constructing storm drains
Stonehurst Park Sun Valley District Part of Sun Valley Watershed Management Plan Los Angeles, CA	Infiltration basin in park	Control floods – collect and infiltrate 50-year, 96-hour storm
Wentworth Park Sun Valley District Part of Sun Valley Watershed Management Plan Los Angeles, CA	Infiltration basin in park	Control Floods Collect and infiltrate 50-year, 96-hour storm
Taylor Yards Los Angeles, CA	Infiltration basin/soccer fields Grading for enhanced runoff velocity control Ox-bow retention pond	Control stormwater runoff Water quality management
San Diego Creek Watershed San Diego, CA	Natural treatment systems – Wetlands Detention ponds	Reduce in-stream TN concentrations to meet TMDLs Meet total phosphorus and fecal coliform TMDLs for all but wettest days Remove trash
Tule Pond Alameda, CA	Three treatment wetlands	Treat urban runoff
Treasure Island San Francisco Bay, CA	Treatment wetland	Control stormwater quality
Central Park Wet Ponds Austin, TX	Three stormwater quality wet ponds, plus recirculation system to keep oxygen in the water	Manage stormwater Control Floods Remove chemicals and debris from runoff Provide environmental, aesthetic, and economic benefits

Table 2.4 Stormwater Parks and Their Best Management Practices (Continued)[1]

Park Description	**Best Management Practice(s)**	**Desired Outcomes**
Edgewood Crossroads Nine Mile Run Pittsburgh, PA	Infiltration basin in park Permeable pavement Reforested slopes Tree canopies	Control floods Recharge groundwater Manage stormwater
Hunter Park Nine Mile Run Pittsburgh, PA	Woodland bioretention area Constructed wetland Stream daylighting	Restore hydrologic function to area surrounding headwater Manage and treat stormwater runoff Provide recreational opportunities to neighborhood
Villanova University Stormwater Best Management Demonstration and Research Park Villanova, PA	Wetlands Bio-infiltration traffic island Porous concrete Infiltration trench Rooftop garden (green roof)	Provide examples of successful implementation Provide research facility for performance quantification
Depot Park Restoration Project Gainesville, FL	Wet detention pond Infiltration basin in park	Manage stormwater and improve water quality Provide recreational opportunities to residents
Duck Pond Restoration Gainesville, FL	Stream daylighting Addition of wetland vegetation	Restore creek to return natural hydrologic function
Springhill Stormwater Park Gainesville, FL	Stormwater park Wet detention pond	Manage stormwater and improve water quality
Southwest Fifth Avenue Basin Gainesville, FL	Wet detention pond	Manage stormwater and improve water quality
Northeast Area Stormwater Demonstration Project Ann Arbor, MI	Wet pond Infiltration woodlands and floodplain area	Control floods Manage stormwater Remove pollutants, revegetate wildlife habitate, improve park aesthetics

1 – Based on Strecker *et al* 2002, Bachand 2003, City of Los Angeles Department of Recreation and Parks and California State Parks 2003, Fine 2003, Los Angeles County Department of Public Works 2003, Devinny *et al.* 2004, City of Austin 2005, Environmental Consulting and Technology Inc. 2005, Ferguson *et al.* 2005, Gainesville Creeks 2005, Traver 2005, Tule Ponds 2005

2.1.4 System Modifications for Semi-Arid and Arid Watersheds

Little consideration was given to the effect of climate and weather variations on the stormwater best management practices until recently. Not surprisingly, most BMPs require modifications for use in arid and semi-arid regions while others are considered unacceptable (Table 2.5). The watersheds in the Los Angeles basin are semi-arid and have distinctive wet and dry seasons. Previous studies, primarily those conducted in humid, eastern watersheds, did not consider such water constraints (Schueler 2000).

The Los Angeles area commonly receives 15 to 35 inches of rain during a short period in the winter. There are typically only 20 to 25 days of rain per year, although the storms are sometimes intense. Overall, the area has a very limited local water supply, and relies on an extensive system for water importation, which is costly in financial, environmental, and political terms. These conditions enhance the value of multiple use facilities, because infiltration will sustain or increase groundwater resources. The protection, management, and utilization of the local water resources are particularly advantageous for the abovementioned reasons.

Table 2.5 Modifications for BMPs in Arid and Semi-Arid Watersheds (from Schueler 2000)

BMP	Semi-Arid Watersheds	Arid Watersheds
Green Roofs	Preferred Recharge rooftop runoff onsite unless the land use is a hotspot	Preferred Recharge of residential rooftops through dry well design
Extended Detention Ponds	Acceptable Require a dry or wet forebay	Preferred Require multiple storm extended detention ponds, stable pilot channels, and a dry forebay
Constructed Wetlands	Limited Use Require supplemental water Use submerged gravel wetlands can help reduce water loss	Not Recommended Evaporation rates too great to maintain wetland plants
Sand Filters	Preferred Use mix of coarse and fine media to prevent premature clogging and ensure sufficient treatment	Preferred Require greater pretreatment Exclude pervious area
Grassed Swales	Limited Use Require irrigation Require rock berms and grade control to prevent erosion in open channels	Not Recommended Require rock berms and grade control for open channels to prevent channel erosion
Infiltration Basins	Major Modification No recharge for hotspot land uses Treat no pervious area Require multiple pretreatment	Major Modification No recharge for hotspot land uses Treat no pervious area Require multiple pretreatment Soil limitations
Bioretention Areas	Major Modification Use runoff to supplement irrigation Use xeriscaping plants Replace mulch with gravel	Major Modification Requires no irrigation Better pretreatment Treat no pervious area Xeriscape plants or no plants Replace mulch with gravel

These challenges of designing and operating BMPs in semi-arid environments may explain why so few systems have been proposed and/or implemented in the Los Angeles area. The government regulation of stormwater runoff quality and a commitment to reducing flood problems have brought more attention to BMPs in recent years.

Particular attention has been given to the Sun Valley project, which was funded by Los Angeles County to develop alternative approaches for flood control and runoff quality management for the Sun Valley district. This is an urbanized area with considerable industrial development that currently lacks storm drains and experiences frequent flooding. Four alternative plans that sought to: 1) maximize infiltration, 2) maximize water conservation and wildlife habitat, 3) maximize stormwater reuse by industry, and 4) emphasize conveyance to traditional storm drains were produced for this study (Los Angeles County Department of Public Works 2003, Devinny *et.al.* 2004). Notably, the alternative that maximized the use of onsite BMPs was rejected as too expensive; however, the components of the other plans included a variety of BMPs such as industrial reuse, infiltration basins in parks, tree planting and mulching, infiltration in parking lots, and infiltration in vaults beneath the streets. The project was undertaken to determine whether there was an approach to flood control other than simply building storm drains (Los Angeles County Department of Public Works 2003, Devinny *et.al.* 2004). Results indicated that a series of regional infiltration basins and wetlands, along side of standard regulatory, nonstructural source control BMPs, would be most economical and effective for the Los Angeles region. The highest cost estimate for treatment was $37 per capita per year for twenty years, with the benefits exceeding the costs (Devinny *et.al.* 2004).

2.2 BMP Cost Benefit Analysis for the Los Angeles Region

A cost-benefit analysis (CBA) for stormwater remediation in a highly urbanized area such as Los Angeles involves complex issues. In less densely urbanized areas, BMPs can be placed in green spaces and parks, and some runoff can be captured and treated at the wastewater treatment plant, requiring only an equalization basin or retention basin to capture excess runoff for treatment between rainstorms. Unfortunately, these treatment plants are not practical for handling stormwater in municipalities that currently have separate wastewater and stormwater sewers. (It may be possible to treat some dry weather flows in wastewater plants). Stormwater flows are extremely irregular, and the capacity necessary to treat peak flows is expensive (Gordon *et al.* 2002). Instead, it is likely that management will consist of a distributed system of "best management practices" (BMPs) in combination with vigorous source control.

One issue with integrating a system of stormwater parks and wetlands is that Los Angeles and its surrounding urban region have long been criticized for being a park-poor urban area compared to other cities, devoting only 7.8% of total area to parks and open space, and only 6.1 park acres per 1,000 residents. Albuquerque, NM has more than 25% of its land area devoted to public open space. Other cities allocating a large percentage of land to parks and open space include San Diego (22%), Washington, D.C. (19.7%), San Francisco (19.3%), and New York (19.1%). Jacksonville, Florida topped the acres per capita category with 126 acres of parkland for every 1,000 residents, and almost 98,000 acres of parks and preserves, including water preserves (Trust for Public Land 2006). In the Los Angeles area park assets are extensive, but they are unevenly distributed and are not always easily accessible to residents (Tables 2.6 and 2.7).

Table 2.6 Summary of Open Space in the Los Angeles Region (Sister *et.al.* 2007)

Type of Open Space	Number	Acres
Athletic Fields	1	13.41
Beach	29	4263.18
Golf Course	66	6654.73
Nature Preserve	6	1023.12
Open Space	5	2852.99
Parks	1289	95770.24
Recreation Areas	8	24909.41
Reserves	1	306.7
State Park Land	2	9850.29
Wilderness Area	4	38163.33
Wildlife Refuge	1	78.65
Misc	4	1215.65

Table 2.7 Open Space Distribution per Los Angeles Region (Sister *et.al.* 2007)

Area (Acres)	Metro LA	West LA	South LA	East LA	South Bay
Mean	53.7	250.4	12.8	25.1	20
Median	4.2	11.4	5.1	7	7
Ac/1000 cap	4.8	59.1	1.2	3.3	4
Ac/1000 youth	54.1	106.9	2.7	10.7	51.4

Cost Benefit Analyses (CBAs) in general have fallen short in estimating the benefits and values attributed to a healthy environment (in this case, treated stormwater runoff.) Most CBAs fail to incorporate an ecological sustainability criterion, and efforts to resolve the issue have only concluded with "how do we value the environment?" (Lekakis 2002.) Some suggested that philosophers are more capable of performing an accurate valuation of the environment and complex ecosystems, and would be able to determine which mix of ethical criteria should be used (Lumley 2002). However, when environmental benefits are excluded as "difficult to estimate" they are in effect taken as zero, introducing a substantial bias in the results.

An issue specific to the cost estimation of stormwater BMPs is that often these cost estimates do not include costs of pretreatment units, design or engineering fees, permit fees, land costs, or contingencies. The costs are usually reported based on watershed size or volume of water treated (water quality volume; Weiss *et.al.* 2007.)

Assessment of the costs and benefits of stormwater quality control requires evaluation of a host of elements. They range from quantitative factors, such as costs for construction of facilities, to intangibles such as the value of living near an unpolluted stream. Some of these have been moderately well examined, while for others, only approximate estimates are available.

The detailed literature used to prepare the cost-benefit analysis in this work are cited in that chapter.

2.3 Viruses in Stormwater Runoff

Viruses may be useful in source tracking studies because they are pathogens of interest (Noble *et al* 2005) and are known causes of waterborne disease, typically from ingestion of sewage contaminated water and seafood (Fogarty *et al* 1995). However, human virus detection and quantification has been used less than bacterial detection because the growth-based methods of detection (which were previously the only ones available) are much too slow and expensive to be effective source tracking tools. The use of human viruses to track sources has a low sensitivity and so is workable only where there are large human populations (Noble *et al.* 2003). Both viral and alternative bacterial indicators such as *Bacteroides* sp. have been shown to be potentially useful source tracking tools. Griffith *et al* (2003) concluded that gene-based methods, such as PCR, consistently provided the best information when attempting to conduct source tracking on mixed source samples. Enterovirus counts consistently and correctly detected human sewage when present, but had difficulty determining human sources when only one or a few likely uninfected individuals contributed fecal material. Because no method has all of the traits to be the consummate source tracking tool, a multi-tiered multi-indicator approach has been recommended by some investigators (Stewart *et al* 2003).

All of these methods remain experimental. Another method, chosen for its low cost and convenience, was tested in this work. Literature describing the specific techniques used in this study is reviewed in Chapter 4.

2.3.1 Case Studies

Ackerman and Weisberg (2003) studied the rainfall effects on beach water quality in southern California, stating that for three days following a storm, contamination levels are high enough for the county health departments to issue warnings to avoid recreational water contact. They examined the relationship between rainfall and beach indicator bacteria concentrations using five years of fecal coliform data taken daily at 20 sites in southern California, with the goal of enhancing the scientific foundation for these preemptive public health warnings. There was a countrywide increase in ocean bacterial concentrations associated with almost all storms larger than 6 mm and with every storm larger than 25 mm. Only for storms less than 2.5 mm was there no observable rainfall effect. Ackerman and Weisberg found that bacterial concentrations remained elevated for five days following a storm, although the concentrations returned to levels below state water quality standards within three days. The length of the antecedent dry period had a minimal effect on this relationship, probably reflecting a quickly developed equilibrium between the decay of older fecal material and the introduction of new fecal material to the landscape (Ackerman and Weisberg 2003).

Characklis *et al* (2005) studied the degree to which microbes in the water column associate with settleable particles, which has implications for microbial transport in receiving waters, as well as for microbial removal via sedimentation from stormwater through BMPs such as detention ponds and wetlands. Characklis *et al* (2005) examined the partitioning behavior of bacterial, protozoan, and viral indicator organisms in three urban streams under wet and dry weather conditions. They then estimated the fraction of organisms associated with settleable particles in stormwater through a centrifugation procedure that was calibrated using suspensions of standard particles. The fraction of organisms associated with settleable particles varied by microbe type, and the partitioning behavior was dependent on dry weather and storm conditions, with higher association with storm conditions. Bacterial indicator organisms such as fecal coliforms averaged 20 - 35% of organisms associated with these particles in dry weather samples and 30 - 55% in storm samples. Clostridium perfringens spores had the highest average level of particle association, 50 - 70%. Total coliphage partitioning in samples were more variable, with 20 - 60% associated with particles during storms (Characklis *et al* 2005).

Field *et al* (1993) assessed the bacterial indicators of human fecal contamination in recreational waters, accounting for indicator bacteria that originated from soils, vegetation, and animal feces. Stormwater runoff can contain high densities of the nonhuman indicator bacteria and epidemiological studies of recreational waters receiving stormwater runoff have found little correlation between indicator densities and swimming-related illnesses. They found that a number of non-enteric pathogens in stormwater runoff are linked to respiratory illnesses and skin infections and are not assessed by the present fecal indicators, which make these indicators inaccurate in assessing the receiving water's total illness-producing capacity. The intermittent and irregular nature of stormwater discharges causes unique disinfection requirements which were discussed in connection with present practices and developments. Field *et al* recommended epidemiological studies to assess the risk from nonhuman and non-enteric pathogens (1993).

Yousefi *et al* (2001) assessed the ability of wetlands and ponds to remove disease-causing viruses from stormwater using f-specific RNA bacteriophages (fRNA) as indicators for removal potential in two stormwater treatment systems. They collected samples at the inlets and outlets of each system and determined the concentrations of fRNA bacteriophages over a five-month period. Bacteriophages were detected in six wetland inlet samples, eight pond inlet samples and five pond outlet samples but were never present at the wetland outlet, indicating that the virus removal in the constructed wetland was more effective than the detention pond system. Results from this study suggest that the treatment systems provided conditions that were conducive to the removal of bacteriophages and perhaps enteric viruses from stormwater through the attachment of the bacteriophages to suspended particles that settle out.

2.4 Hydrophobic Organic Contaminants

The Clean Water Act mandated that TMDLs for toxic pollutants must be instituted for 303(d) listed watersheds. The Los Angeles Regional Water Quality Control Board is actively working to set these limits for all watersheds within the Los Angeles region, including Ballona Creek. The toxic pollutants researched for this TMDL effort include hydrophobic organic contaminants (HOCs) such as polycyclic aromatic hydrocarbons (PAHs), and the legacy contaminants DDT, polychlorinated biphenyls (PCBs), and chlordanes. These organic pollutants partition onto sediments (Karickhoff *et al.* 1979) and accumulate in the fatty tissues of aquatic organisms (Muir *et al.* 2003). Their water column phase, such as dissolved and suspended particulate forms, determines their potential for transport and detrimental biological effects. Moreover, their toxicity is measured against water quality criteria, which in turn are typically based on aqueous phase concentrations (LARWQCB 2005). Even ultra-low levels of HOCs in the water column play an important role in contaminant fate, effects and management scenarios. One of the objectives of this work was to test a new sampling method for stormwater runoff.

2.4.1 Passive Samplers

Effective management of toxic pollutants in urban waterways such as Ballona Creek, requires characterization of the relative contribution of dissolved and particulate pollutants in stream sources and the direction of contaminant flux between bedded sediments and the water column. This has been problematic to date in that conventional methods for measuring low level dissolved phase HOCs are expensive, time consuming and relatively insensitive. Historically, scientists have used biomonitors such as bivalves (in the "Mussel Watch" program) that concentrate waterborne chemicals by several orders of magnitude as surrogates for water quality (Farrington *et al.* 1983). However, this approach suffers from measurement variability from changes in biological or biochemical activities of the indicator organism. Samplers based on passive partitioning of HOCs into a solid phase were developed to eliminate these biological sources of variability.

2.4.1.1 Polyethylene Devices (PEDs)

Polyethylene devices (PEDs) are simply strips of low-density polyethylene that absorb contaminants when they are exposed to water. After exposure, they are returned to the laboratory so the contaminants can be extracted and characterized. HOCs exhibit strong affinity for PEDs, so that absorbed concentrations are much higher and more easily measured that those in the water (Adams, 2003). In addition, PEDs are time-integrative in nature (Adams 2003; Vinturella *et al.* 2004, Figure 2.5). Initial research using PEDs indicates that less than 1 ng/L (= parts per trillion) DDT can be measured (Adams 2003).

PEDs are inexpensive, can be easily created from a few pieces of plastic purchased at any hardware store. However, PEDs require a minimum of three days post deployment clean up and are prone to biofouling.

Figure 2.5 A Polyethylene Device Ready for Field Deployment (Sayre 2006)

2.4.1.2 Solid Phase Microextraction (SPME)

Arthur and Pawliszyn (1990) introduced solid phase microextraction (SPME) for the concentration of organic chemicals onto chemically modified fused silica fibers followed by thermal desorption directly into an analyzing instrument, such as gas chromatograph, mass spectrometer (GC-MS).

The SPME is a very efficient analytical method for the extraction of organic compounds of environmental significance covering a wide range of polarities and hydrophobicities. SPME uses a short piece of polymer coated, fused silica fiber, which acts as a solid, stationary phase. This fiber is attached inside a device resembling the needle of a syringe. During transport, storage, and manipulation, the fiber is retracted into the needle of the device. During extraction and desorption of the analytes, the fiber is exposed. Analytes partition onto the polymer until equilibrium is reached. The fiber is retracted back into the needle and transferred to the heated injection port of a gas chromatograph, where the analytes are thermally desorbed (Poerschmann *et.al* 2000).

A SPME-based sampler developed at the Southern California Coastal Water Research Project (SCCWRP) has recently shown promise in measuring less than 1 μg/L of DDT in coastal seawater (Zeng *et al.* 2004, Figure 2.6). Although SPME minimizes post-collection sample processing, small sorbing phase volumes limit measurement sensitivity and the fibers manufactured are relatively fragile.

Figure 2.6 A SPME Being Prepared for Field Deployment (Sayre 2006)

2.4.1.3 Semi-Permeable Membrane Devices

Huckins *et al.* (1990) developed lipid-containing polyethylene tubes known as semipermeable membrane devices (SPMDs) to passively monitor the concentration of HOCs dissolved in water. SPMDs have been designed to imitate the process that takes place in these aquatic organisms. Thus, they can be used to monitor low levels of waterborne pollutants. They are constructed of a tubular polyethylene membrane that lies flat and is filled with a thin film of triolein, a lipid (fat or fat-like substance) commonly found in aquatic organisms (Figure 2.7). The polyethylene membrane acts like a biological membrane by allowing only certain organic compounds to penetrate. When working in the marine environment, scientists deploy SPMDs in protective stainless-steel canisters. These canisters protect the SPMD from damage and also provide a solid structure for anchoring it in the water column. SPMDs may be deployed for periods ranging from one week to several months (National Oceanographic and Atmospheric Administration (NOAA) 2006).

SPMDs, with a much larger sorbing reservoir, provide excellent sensitivity, but are cumbersome, prone to damage and leakage and require substantial laboratory workup prior to analysis.

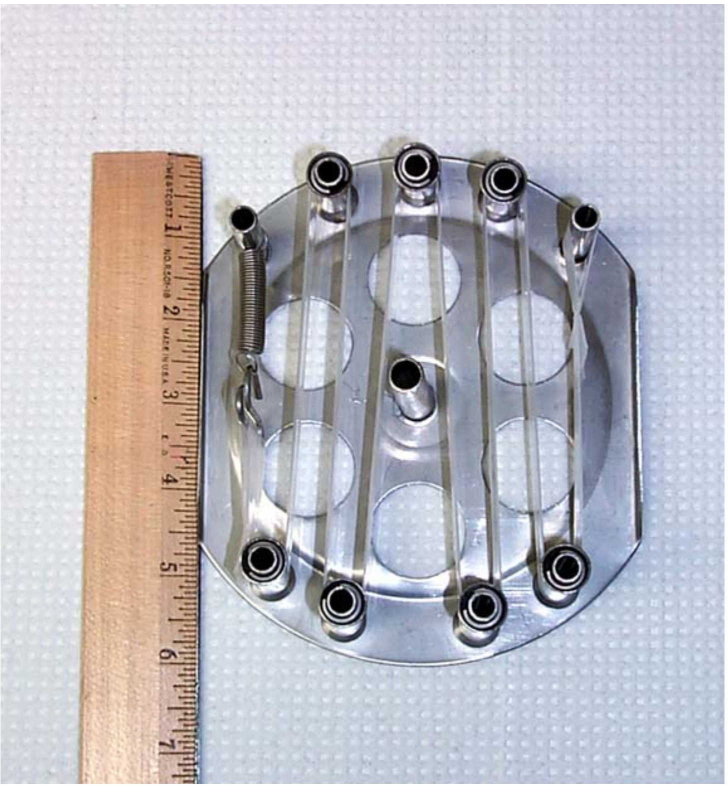


Figure 2.7 SPMD (NOAA 2006)

Chapter Three: Cost Benefit Analysis for Southern California Regional Stormwater Best Management Practices

As the percentage of impervious surface within a watershed increases, the amount of stormwater runoff increases. The stormwater carries pollutants that might otherwise have been adsorbed or degraded in soils. In southern California and Los Angeles, stormwater and dry-weather runoff water is not treated and flows directly into receiving waters and Pacific Ocean. Treatment plants like those used for wastewater are not practical for handling stormwater in municipalities like those in Los Angeles County. Stormwater flows in southern California are extremely irregular, and the capacity necessary to treat peak flows would be very expensive (Gordon *et.al.* 2002). A distributed system of BMPs in combination with vigorous source control is likely to be a more effective form of stormwater management.

To treat TMDL regulated pollutants in stormwater, BMPs such as those presented in Chapter 2, must be employed. The costs and benefits of these BMPs are important components of stormwater treatment as is the public's willingness to pay. Willingness to pay can be a determining factor in the extent of the treatment of stormwater. This chapter will correct and expand an existing study by Devinny *et.al* (2004) and present new, current costs and benefits of stormwater treatment.

3.0.1 The Initial 2004 Study

Devinny *et.al* (2004) reviewed low-cost approaches to stormwater quality control, including facilities that maximized secondary benefits. Systems that improve water quality while at the same time promoting groundwater replenishment, providing recreational opportunities and neighborhood improvement, or improving wildlife habitat were preferred.

For the 2004 study, the researchers found that the assessment of the costs and benefits of stormwater quality control required evaluation of a host of elements, ranging from quantifiable factors, such as costs for construction of facilities, to intangibles such as the value of living near an unpolluted stream. Some of these have been moderately well examined, while for others, only approximate estimates are available. BMPs were divided into "source control" (nonstructural) measures and "structural" measures. The first category refers to techniques for keeping pollutants out of the stormwater, while the second refers to techniques for collecting and treating stormwater (Devinny *et.al.* 2004).

In the 2004 study, structural BMPs were identified that were likely to be employed in future efforts to control stormwater quality. A literature search was done to find case study reports of best management practices that included the watershed area served by the facility and the cost of constructing the facility.

For the Cost Benefit Analysis chapter, a greater, more in-depth literature search was conducted to eliminate any gaps in information and include data published after the report was written. The initial study results suggested that two technologies – infiltration basins and treatment wetlands – are likely to be most economical when used to solve a regional problems in Los Angeles, but that the primary disadvantage with these approaches is that they require a great deal of land in a region where the land is occupied by other economically valuable applications. However, infiltration basins can be used as recreational parks, ball fields, schoolyards, and wildlife habitat. Wetlands serve as wildlife habitat and recreational parks. This approach is particularly appropriate in the Los Angeles area, which receives rainfall on only about 22 days per year (Gordon *et.al.* 2002). While conversion of significant amounts of land solely to the purpose of stormwater quality control might be difficult, creation of habitat, parks and ball fields that will be used for stormwater control during less than 10% of the year is likely to be economically and politically feasible. The cost-benefit estimation therefore assumes that these two technologies will be used over most of the study area (Devinny *et.al.* 2004).

Five percent of the total area of the City of Los Angeles is devoted to open space and park land (Wolch *et.al.*2002). The runoff from adjacent developed areas could be moved to parks, increasing the volume of runoff to the parks by a factor of 20. Assuming the runoff coefficient for the developed areas is 0.5, and designing for a storm of ¾ inches of rain, which would flood the parks to a depth of 7.5 inches. This was a third of the depth assumed for the stormwater parks planned in the Sun Valley project, a nearby community in Los Angeles County. Thus this crude calculation indicates that this approach should be feasible on a large scale in terms of the amount of land required.

The costs of stormwater BMPs are usually reported along with the corresponding watershed size and/or the water quality volume for which the stormwater BMP was designed. This is the volume of runoff that the BMP is designed to store and treat. Most often the reported costs of stormwater BMPs do not include the costs of land (Devinny *et.al.* 2004).

To evaluate the possible alternatives for stormwater control, the study conceptually divided the 3,100-square-mile region that is under the jurisdiction of the Los Angeles Regional Water Quality Control Board into four parts: 1000 square miles is estimated to be of “low density”, requiring some runoff BMP treatment, but having sufficient land for development of treatment wetlands or infiltration systems. 1,000 square miles is estimated to be “high density” requiring infiltration systems but excluding wetlands. 50 square miles is estimated to be extremely dense downtown development, requiring some more sophisticated BMP treatment system. The remainder of the region is considered rural, and it is presumed that the only cost is for source control outreach and enforcement. These definitions and numbers are approximate, but there is also flexibility in the applicability of the various technologies. In order to capture the range of uncertainty in the calculations, it was assumed that control will require, at a minimum, a set of source control measures implemented over 2050 square miles of developed area, and at a maximum, the source control measures and structural BMPs over the developed area. These two scenarios were considered to represent a lowest likely cost and a highest likely cost for the remediation.

Control achieved by structural BMPs should be sufficient to capture runoff from a ¾” storm. (85% of the storms in the Los Angeles area are this size or smaller, and it is presumed that the “first flush”, which will be treated during the first portion of larger storms, contains most of the pollutants.) Costs were reduced to present worth for comparison on the presumption of a 3% discount rate, appropriate for the time the report was written (Devinny *et.al.* 2004).

3.0.2 Methods for Modifying the Initial 2004 Report

Since publication of 2004 report, additional information and critical comments have become available. The purpose of this chapter is to update the report with new literature and cost data, add some more sophisticated analysis including a sensitivity analysis, and adjust cost data and analysis for inflation. This chapter will review literature describing cost estimates for appropriate stormwater BMPs, first from examples nationwide, then from local examples. This is followed by further explanations of nonstructural, source control BMPs. The reviewers' comments on the 2004 report were addressed, including correcting cost data for inflation and conducting the cost analysis based on appropriate local and national population data. An updated cost analysis and a sensitivity analysis were performed. The discount rate was adjusted from 3% to 7%, as literature suggested. The sensitivity analysis included adjusting costs using 5% and 9% discount rates.

3.1 New Literature and Cost Data

3.1.1 Examples of Stormwater Parks in the United States

The work for this chapter included review of currently operating facilities for which there were data on the capacity and cost.

3.1.1.1 Central Park Wet Ponds, Austin, Texas

In Austin, Texas, Central Park is the ten acre park space set aside as part of the 39-acre mixed-use development. The park includes a hiking trail, picnic areas, and a flood detention basin containing a series of three stormwater quality wet ponds constructed in 1998, which were funded by the City of Austin. The Central Park ponds provide environmental, aesthetic, and economic benefits. The environmental benefits include beneficial stormwater management. Stormwater enters the ponds, where it is detained to reduce downstream flooding and to allow removal of pollutants. The most common pollutants in the stormwater are chemicals and debris from the urban neighborhoods and streets that are in the 164-acre watershed. The ponds have been designed to hold and treat runoff from smaller storms for about two weeks, before the water is displaced by polluted stormwater. Runoff from larger storms may fill the entire basin, but will be released over the course of a few hours in order to limit flooding downstream. A recirculation system helps keep oxygen in the water by providing flow over two waterfalls. The effluent water is released into the Hemphill Branch of Waller Creek and eventually into Town Lake (City of Austin 2005).

The City of Austin estimates that the ponds capture the following amounts of pollutants every year:

- 36,400 to 50,000 pounds of total suspended solids
- 55 to 275 pounds of total nitrogen
- 55 to 2,000 pounds of total phosphorus
- 5 to 50 pounds of lead

- 10 to 150 pounds of zinc

The pond also provides wildlife habitat for a variety of birds and animals. Mosquito larvae-eating fish live in the pond to keep mosquito problems to a minimum. This park naturally filters stormwater before it reaches the creek, with a cost of $584,000). Keeping the area unpaved also minimizes erosion and flood problems for those downstream. A sign near the entrance of Central Park gives a cross-section of the pond and explanation of how it works to improve water quality. The sign also serves as an educational tool to teach people about how we affect our watersheds everyday. Water year-round provides beautiful scenery filled with birds, water plants, and wildlife. The hiking trail adds recreational benefits for residents and shoppers alike (City of Austin 2005).

3.1.1.2 Nine Mile Run, Pittsburgh, Pennsylvania

The City of Pittsburgh developed the 6.5-mi.^{2} watershed of Nine Mile Run in central Allegheny County, and proposed a remediation system capable of offering immediate benefit, and decades into the future, using all appropriate technically and financially feasible approaches to restore the watershed's natural processes and to revitalize its ecological communities. The model, the Nine Mile Run, presents a "restorative redevelopment" approach to the sewers, ecosystem, and communities of the Pittsburgh region. This model includes retrofit and redevelopment projects to improve the value and livability of the city while effectively restoring the watershed's natural functions. The City looked to integrate infrastructure improvements, community development desires, and ecosystem needs. The total cost of this series of stormwater parks is $7.7 million (Ferguson *et.al*. 2005).

3.1.1.2.1 Hunter Park

Hunter Park is located near the headwaters of the Nine Mile Run watershed. It is a neighborhood park in Wilkinsburg, Pennsylvania. This is a low income area, with neighborhood streets and sidewalks in poor condition. The park's ball field, wading pool, basketball courts, and small playground are in disrepair, although all are heavily used in season. The park collects drainage from an area of 59 acres. Sediment clogs most drainage inlets; some drainage pipes are broken. Some grass swales in the park improve water quality to a degree but are undersized even for the small amount of water they carry. Concentrated runoff from nearby impervious surfaces has eroded some of the park's drainage swales and steep sideslopes (Ferguson *et.al*. 2005).

The proposed design filters, detains, and infiltrates runoff. Specific features include a woodland bioretention area consisting of sand and soil mixtures planted with native plants; a constructed wetland; and swales to mediate overflow drainage from the wetlands and runoff from the fields. The plan comprises a reopened once-culverted stream and stream bank restoration. Bioengineering techniques will stabilize and protect the banks of the stream during two-year and 10-year storms (Ferguson *et.al.* 2005).

3.1.1.2.2 Edgewood Crossroads

Edgewood Crossroads is located near the center of the watershed and is the public center of the Borough of Edgewood, where a historic train station fronts on busy Swissvale Avenue and would treat 73 acres of the Nine Mile Run area. The design for the Edgewood Crossroads integrates the following community issues: reinforcing the social and physical sense of community, preserving public open spaces, reinforcing pedestrian access, eliminating street flooding, and bringing Edgewood into compliance with federal water-quality standards by separating storm drainage from the sanitary sewer system (Ferguson *et.al.* 2005).

The small community park facing the train station has become a public greenway developed as the new transit corridor. Stormwater solutions and public education with urban design are integrated at this prominent stormwater restoration facility. The center is a depressed bowl, which diverts floodwaters off the street and the surrounding plaza; it fills during a storm and the water infiltrates in two days. On dry days, the plaza and the bowl serve for communal gathering and play; the wall around the bowl functions for sitting. Other BMP technologies employed in the park include permeable unit pavers, reforested steep slopes to increase infiltration, and tree canopies to adsorb some rainfall before it reaches the ground (Ferguson *et.al.* 2005).

3.1.1.2.3 Tree Value

The Nine Mile Run Watershed Association (NMRWA) gathered residents to inventory all the trees within the watershed. The inventory included recording the location of each tree, the tree size, determined by its diameter at breast height, and the general condition of the tree, assessed by the conditions of the crown and the trunk. The data were then entered into the data base of iTree STRATUM (Street Tree Resource Analysis Tool for Urban Forest Managers), a software package from the USDA Forest Service that performs a cost benefit analysis of the trees in a community to help the residents understand the value created by their trees. STRATUM calculated a dollar value benefit for the trees based on six categories: Energy, a measure of the reduction in heating and cooling bills due to shade and insulation created by the trees; Stormwater, a measure of the reduction of annual stormwater runoff due to trees; Air Quality, a measure of air pollutants (*e.g.* O_3, NO_2[3], SO_2[4], and PM_{10}) deposited on tree surfaces and the reduction of power plant emissions due to reduced electricity use; Carbon Dioxide, a measure of reduction in atmospheric CO_2; and Aesthetic/Other, a measure of tangible and intangible benefits of trees that are reflected in increased property values. In the watershed community of Edgewood, PA had an average annual savings per tree of $218, each tree capturing an annual average of 3318 gallons of stormwater. Swissvale, PA had an annual average savings of $159 per tree and an annual average of 2081 gallons captured per tree. Wilkinsburg, PA had an average annual savings of $172 per tree, with 2341 gallons of stormwater captured per tree (Shanahan 2007).

3.1.1.3 Northeast Area Stormwater Demonstration Project, Ann Arbor, Michigan

The Northeast Area Park Demonstration Project in Ann Arbor, Michigan, is a park planning project to develop both active and passive park usage areas integrated with progressive stormwater management, with a total cost of $249,900. Northeast Area Park consists of a total of 56 acres, which includes a 7.2-acre pond and approximately 1,300 feet of Traver Creek, with approximately 14.25 acres of woodlands and floodplain areas. The park design incorporated a variety of stormwater management techniques to provide management of stormwater volumes, while providing ecological benefits, which include removal of pollutants from water, revegetation for wildlife habitat, and improved park aesthetics (ECT Inc. 2005).

3.1.1.4 Minneapolis, Minnesota

The City of Minneapolis, Minnesota, employed three constructed wetlands to treat urban runoff: the Cedar Lake watershed wetland/pond, the Lake Harriet Sub-surface flow wetland, and the Standish-Ericsson Neighborhood Association (SENA) wetland.

3.1.1.4.1 Cedar Lake Watershed Wetland/Pond System

Cedar Lake watershed wetland/pond system, which cost $591,000, acts as a regional pond/wetland system. At Twin Lakes, the pond is 1.3 acres and the wetland is 11.2 acres, and the system drains 1788 acres. The pool area to total drainage area ratio is 0.007 (the wetland/pond takes up 0.7% of contributory watershed area).

The Cedar Meadows pond is 1.5 acres and the wetland is 3.1 acres, and the system drains 116 acres. The pool area to total drainage area ratio is 0.04 (the wetland/pond takes up 4.0% of contributory watershed area).

The Cedar Lake watershed pond is 2.6 acres and the wetland is 14.3 acres, and the system drains 1904 acres. The pool area to total drainage area ratio is 0.009 (the wetland/pond takes up 0.9% of contributory watershed area).

3.1.1.4.2 Lake Harriet Sub-Surface Flow Wetland

Lake Harriet Sub-surface flow wetland, which cost $ 60,500, is a submerged gravel wetland with a total area of 0.258 acres. It drains 24 acres of the contributing watershed area and has a pool area to total drainage area ratio of 0.1 (the wetland/pond takes up 1.1% of contributory watershed area).

3.1.1.4.3 Standish-Ericsson Neighborhood Association (SENA) Wetland

Standish-Ericsson Neighborhood Association (SENA) wetland, which cost $67,700, is a regular shallow marsh system with a total area of 0.205 acres. It drains 53 acres of the contributing watershed area and has a pool area to total drainage area ratio of 0.004 (the wetland/pond comprises 0.4 % of the watershed area).

3.1.2 Previous Studies in Los Angeles

3.1.2.1 Cost Benefit Analysis for Ballona Creek

Kalman *et.al.* (2000) conducted a benefit-cost analysis (BCA) for Ballona Creek, in Los Angeles, California. The preliminary BCA was used as a screening method for a maximum extent practicable (ME) analysis, through which promising management practices and societal and economic tradeoffs for local stormwater problems were identified. The authors chose Ballona Creek because it represented the economic limits of stormwater management in an urban area. It also proved that coordinated, basinwide management was more valuable than uncoordinated management by individual landowners. Their results suggested that in urban areas, stormwater quality improvements would be best if they included comprehensive redesign of the drainage networks and neighboring land uses. The authors outlined their method for conducting the BCA:

1. Identify receiving water reaches
2. Identify beneficial uses of receiving water reaches
3. Identify pollutants originating in stormwater that affect beneficial uses
4. Establish pollution concentration thresholds
5. Establish current pollution concentrations
6. Eliminate currently unimpaired receiving waters and unimpaired beneficial uses
7. Estimate economic values for unimpaired beneficial uses
8. Estimate pollution concentrations with each management practice implemented
9. Estimate improvement in beneficial use economic value
10. Estimate overall alternative benefit value
11. Estimate costs to implement the alternative
12. Compare estimated total benefit and cost values.

Kalman *et.al.* suggested that the stormwater be treated by one of three levels – Level 1 was detention with screening and removal of total suspended solids, Level 2 was filtration with disinfection, and Level 3 was advanced treatment with reverse osmosis. The results of the BCA for Ballona Creek led the authors to believe that the treatment of storm flows into the creek was not economical and that there were no apparent changes in the analysis assumptions that would have resulted in a recommendation of the stormwater treatment options examined (2000).

3.1.2.2 TREES Project

Trans-Agency Resources for Environmental and Economic Sustainability (TREES) developed a series of BMPs for industrial sites, commercial buildings, schools, and single family homes. TREES project managers determined that strategic planting of trees and green spaces, other tree planting, tree maintenance, mulching, cistern installation, dry well installation, graywater system installation, and pavement removal were the most applicable and cost effective BMPs. The TREES goal was to identify and design retrofit areas that cost-effectively reduced the impacts of urbanization. TREES created a single-family residence demonstration site which employed several of the BMPs including a cistern collection system, redirection of roof-top runoff, vegetated swales, and retention grading to reduce runoff pollution and capture all runoff from the site, while reusing some for irrigation and returning the rest to the groundwater. The project proposes four additional demonstration sites: a multifamily housing site, a commercial site, an industrial site, and a public site such as a school (TreePeople 2008).

Most of the BMPs were relatively inexpensive and most were such that the average homeowner could install. The two cistern tanks at the Hall House were prototypes requiring custom manufacturing and installation. With widespread application of the technology, a do-it-yourself design, and mass production, the cost was expected to be approximately 50-cents per gallon (NRDC 1999).

The objective of the TREES project is to show the environmental, economic, and social benefits of cooperative approaches to designing and managing the urban landscapes as functioning mini-watersheds (TreePeople 2008).

3.1.2.3 Summarized Local and National Results

The Devinny *et. al.* (2004) study was performed to determine which structural BMPs were likely to be employed in future efforts to control stormwater quality. The literature collected are summarized below (Table 3.1). To strengthen this summary, additional literature was collected and reviewed (Table 3.1). Literature presented in previous chapters was strengthened through the cost analysis (Table 3.1). The literature reviews include case study reports of best management practices with the watershed area served by the facility and the cost of constructing the facility. Because of great variation in local conditions and specific designs, no effort was made to determine the effectiveness of the installations. The cost data reflect the cost for an individual facility

("Cost, \$M" and "Cost, \$M/mi^2") and the drainage area served, referred to as the "Unit Size".

Table 3.1 Summary of Case Study Project Costs

Project	**I or D[1]**	**Description**	**Unit Size, square miles**	**Cost, \$M**	**Cost, \$M per square mile**
Infiltration Systems					
Fresno Metropolitan Flood Control District Regional Infiltration Basins (NRDC, 1999; Dave Pomaville, 2003)	I	130 turfed or unturfed infiltration basins serving residential areas. Treats or infiltrates 98% of runoff over area of 120 square miles	1		2.5 to 3.7
Study of Stormwater Regulations Cost (Herrerra Environmental Consultants, 2001)	D	Hypothetical calculation of costs for new residential development	0.016	.24	15
Study of Stormwater Regulations Cost (Herrerra Environmental Consultants, 2001)	D	Hypothetical calculation of costs for new commercial development	0.0016	0.28 to 0.57	175 to 356

Table 3.1 Summary of Case Study Project Costs (Continued)

Project	I or D[1]	Description	Unit Size, square miles	Cost, $M	Cost, $M per square mile
Wet Ponds					
Central Park, Austin, Texas	I	Ten acre park, flood detention basin containing a series of three stormwater quality wet ponds	0.061	0.58	2.2
Wetlands					
Cedar Lake system, Minneapolis, Minnesota	I	Series of 3 wetland/pond systems, draining stormwater from a total of 3808 acres	5.95	0. 59	0. 099
Lake Harriet wetland, Minneapolis, Minnesota	I	Sub-surface flow wetland is a regular submerged gravel wetland draining stormwater from 24 acre watershed	0.0375	0.06	1.61
Standish-Ericsson Neighborhood Association (SENA) wetland Minneapolis, Minnesota	I	A regular shallow marsh system draining a 53 acre	0.081	0.068	0.82
Wetland/ Stormwater Park, West Valley City, Utah	I	Preserve used for wetland enhancement, restoration, creation, and possibly banking	0.58	0.31	0.54
Tule Pond, Alameda (Wetzig, 1999)	I	Stormwater treatment pond for urban runoff	0.8	0.36	0.45
Treasure Island, San Francisco Bay (NRDC, 1999: Galvanis, 2003)	D	Wetland treatment system for local runoff	0.65	0.8 to 1.1	1.2 to 1.7

Table 3.1 Summary of Case Study Project Costs (Continued)

Project	I or D[1]	Description	Unit Size, square miles	Cost, $M	Cost, $M per square mile
Long Lake Retrofit, Littleton, Mass. (Roy et al., 2003)	I	Swales, constructed wetlands, bioretention cells, outreach	1.5	0.63	0.42
San Diego Creek Natural Treatment System Master Plan (Strecker et al., 2003)	D	Network of open-water ponds and wetlands in Newport Bay drainage, 120 square mile area	2.7	<60	<0.5
Murray City, Utah (NRDC 1999: Hill, 2003)	I	Golf course and wetlands treat runoff from 4.5 miles of I-215 and the city	9.5	1.0	0.11
Dover Mall, Delaware, (NRDC 1999)	I	Wetland installed on mall grounds drains 30 acres of 100% impervious cover	0.048	0.17	3.5
Sun Valley Project, Los Angeles County	D	Combination of various measures for flood and quality control in L.A. Basin	4.4	172 to 297	39 to 68
BMP Treatment Processes					
Oakland Park, Fla, industrial area (NRDC 1999)	I	Oil, grease, sediment, and trash removal by sedimentation and absorbance	0.008	0.261	33
Clear Lake Packed Bed Wetland Filter System (NRDC 1999: FHWA, 2003)	I	Oil, grease, nutrients, trace metal removal for water entering Clear lake	0.2	0.92	4.6
Compost Filter Facility, Hillsboro, Or. (FHWA, 2003)	I	Oil, grease, removal and filtration for highway runoff	0.12	0.12	0.11
Alexandria, Va, airport parking lot	I	Sand filters installed along the borders of a 1.95-acre parking lot	0.003	0.04	12.9

Table 3.1 Summary of Case Study Project Costs (Continued)

Project	**I or D**[1]	**Description**	**Cost, $Million per square mile**
Bioretention Areas, FHWA cost estimate	D	Areas of highly permeable soil planted with trees and other vegetation	6.2
Underground Sand Filters	D	Porous medium filters placed in underground vaults, appropriate for highly urban areas	8.7
Dry Swales	D	Broad, shallow vegetated drainways covered with vegetation, usually grass	0.93
Surface Sand Filters	D	Porous medium filters installed at the surface	2.1
Filter Strips	D	Flat vegetated drainways covered with vegetation, usually grass	1.2
Port of Seattle container area cleanup	I	High quality street sweeping with sediment trap catch basins	3.1

[1] I or D refer to Implemented or Designed

The cost equations found on the Federal Highways Administration Ultra Urban BMP website, which have been commonly cited in the literature (Thurston *et.al.* 2003, Sample *et.al.* 2003) are presented in Table 3.2.

Table 3.2 Cost Formulas from Federal Highways Administration (2003)

Infiltration trenches, FHWA cost estimate	Gravel-filled trenches. Infiltration eliminates runoff discharge.	$C_{mi2} = C_A/A$ $= (1/A)\times 1317\times V^{(0.63)}$ $= 1.2\times 10^6\times A^{(-0.37)}$
Infiltration basins, FHWA cost estimate	Open basins, dry at most times, store and infiltrate runoff. Infiltration eliminates runoff discharge.	$C_{mi2} = C_A/A$ $= (1/A)\times(V/0.02832)^{(0.69)}$ $= 204{,}000\times A^{(-0.31)}$
Detention and retention wetlands, FHWA cost estimate	Wetlands used for treating stormwater, with storage capacity available	$C_{mi2} = C_A/A$ $= (1/A)\times 168\times V^{(0.699)}$ $= 324{,}000\times A^{(-0.301)}$
Detention vaults, FHWA cost estimate	Underground reservoirs for storage of runoff to reduce peak flows	$C_{mi2} =$ $(1/A)$ $\times 38.1\times(V/0.02832)^{(0.6816)}$ $= 690{,}000\times A^{(-0.3184)}$

3.1.3 Willingness to Pay and Benefit to the Environment

It is difficult to determine the economic benefit of a healthy environment through stormwater management and water quality control (Loomis 2000, Bockstael *et.al.* 2000, Kramer and Eisen-Hecht 2002, Shabman and Stephenson 2000). Some efforts to place a dollar value on these benefits have been made by the EPA (1999) and others (Kramer, 2003; Soderqvist, 2000; Whitehead, et al., 2000).

The APWA study estimated costs for a nationwide treatment program for five scenarios for stormwater quality control. One estimate was for a system of detention basins and wetlands. The APWA study estimated that the system would cost $91 million, an estimated $0.35 per capita, 260 million people in the United States in 1992, at the time of the APWA study. Adjusted for inflation (rate of 46.6%) and population growth (303.5 million (United States Census Bureau 2008)), the current estimation for a nationwide system is $134 million, approximately $0.44 per capita. For the 9.95 million people in the Los Angeles area (US Census 2006), this would be about $4.4 million. The APWA anticipated maintenance costs for detention and retention basins at about 1% of the construction cost per year. Expressed as present worth, this increases the total cost by 33%, or $1.5 million. APWA numbers thus indicate a total cost of $5.9 million. This estimate is again similar to those developed on the basis of watershed size or needed retention capacity.

In the USA, the average cost per capita for stormwater management is $36 and $21 of this goes to nonstructural controls (Taylor and Fletcher 2007). This estimate translated to $10.9 billion for total stormwater management nationwide and $6.4 billion for nonstructural controls nationwide; in Los Angeles, this totaled $358 million for stormwater management and $209 million for nonstructural.

Devinny *et.al* (2004) reviewed the willingness to pay literature and data and concluded that it was difficult to determine the economic benefit of a healthy environment through stormwater management and water quality control (Loomis 2000, Bockstael *et.al.* 2000, Kramer and Eisen-Hecht 2002, Shabman and Stephenson 2000). Some efforts to place a dollar value on these benefits have been made by the EPA (1999) and others (Kramer 2003; Soderqvist 2000; Whitehead *et al.* 2000). Soderqvist determined that the residents of Stockholm were willing to pay a one-time payment between $54 and $90 per person to reduce eutrophication of the nearby ocean. The effects of oceanic eutrophication are relatively subtle – less obvious than floating trash or debris washed up on the beach (Soderqvist 2000). Whitehead *et al.* (2000) investigated willingness to pay for the reduction of eutrophication of the Neuse River Basin in North Carolina, which was about $76 each for the water quality improvement. Kramer (2003) investigated people in the Catawba River area in North and South Carolina and determined that they would pay about $139 for improved water quality.

The EPA conducted a survey to determine what people in the US were willing to pay and found that they would pay $210 per household for improvement of water quality sufficient to support boating, $158 for the further improvement sufficient to support fishing, $177 for further improvement sufficient to allow swimming, and $158 for improvement sufficient to support natural aquatic life, a total of $703. Only 67%, or $471, was ascribed to local water quality improvement. The average household in the US has 2.59 people (US Census 2008), which equates to a willingness to pay of approximately $182 per person for local freshwater improvements (USEPA 1999). This value, $182, was similar to the estimate by Kramer for the Catawba River.

Devinny *et.al* (2004) chose the EPA estimate for freshwater improvements: the higher estimate seemed reasonable because freshwater resources in the LA area are generally in very poor condition and substantial improvement is possible. Adding this to a mid-range value of the Soderqvist estimate for improvements in ocean water quality produces a result of $260 per person. This seems reasonable in comparison to what people are willing to pay to visit the ocean or to live near it. About 9.95 million people live in the Los Angeles region, so this value indicates a total willingness to pay, based solely on the value of living in a region of clean and esthetically pleasant waters, of about $2.5 billion.

Larsen and Lew (2003) surveyed California residents and determined that the average willingness to pay for removing all impairments from bodies of water in the state was $15.46 per month per household. With 2.59 persons per household, that was $5.97 per person per month. Assuming there are 9.95 million people in the Los Angeles area, this translates to $59.4 million. This included removing all impairments – wastewater pollution, shoreside development, pollution from boats, and others. This number is much lower than the one estimated by Devinny *et.al.* (2004), by almost two orders of magnitude; however, both values are greater than the APWA cost estimation for stormwater treatment for the Los Angeles region, $5.9 million.

General support for these numbers was found in a survey conducted for the Packard Foundation by Mark Baldassare (Weisse, 2003). He determined that seventy percent of Californians are concerned about the decline in coastal resources. Sixty-nine percent said the condition of the coastline is very important to their quality of life, and 75% visit the coast at least several times each year. Seventy-two percent favor reducing stormwater pollution, even if the cost leads to higher utility bills.

3.1.4 Dollar Value of the Environment

TREES and TreePeople determined that an accurate dollar value can not be applied to the environment. Their suggested alternative to this conundrum was to evaluate the dollar value of enhanced ecological performance. They employed available direct costs. For cases when there were no actual costs available they used the costs of mitigating similar environmental impacts, concluding that their approach was conservative compared with most experts who attempt to ascertain similar costs of environmental degradation (Table 3.3) (TreePeople 2008).

Table 3.3 Cost-Benefit Matrix (From TreePeople 2008)

Issue	**Amount changed**	**Unit**	**Estimated value/year**	**Estimated value/30 year period**	**Estimated 30 year value/acre**
Water for Irrigation	80% reduction	Per dwelling unit	$219.00	$6,570.00	$52,560.00
Water for Domestic Consumption	40% reduction	Per dwelling unit	$264.00	$7,920.00	$63,360.00
Flood Management	Hold three inches of water during flood emergency	Per acre	$1,000.00 (r.e. parapet walls)	$10,000.00	$10,000.00
Water Pollution	Bio-remediate all first-flush water on site	Per acre	$522.00	$15,660.00	$15,660.00
Air Pollution	Strategic shade for structures, general planting for heat island	Per acre, 20 trees strategically placed @ 52.90/tree	$1,058.00	$31,740.00	$31,740.00
Green Waste	Recycle all green waste on site	Per dwelling	$81.00	$2,430.00	$19,440.00
Total value of all remediation strategies to apply to construction and maintenance per acre					**$192,760.00**

TreePeople estimated the costs and values of the environment and valued imported water at $0.01 per gallon. They determined that an 80% reduction in off-site water imported for irrigation would be worth about $219 per year per dwelling unit. A 40% reduction in the volume of water imported for domestic consumption produces an additional benefit of about $264 per dwelling unit. TREES and TreePeople demonstrated how retrofitting individual urban sites as functioning mini-watersheds would help to solve the Los Angeles region's environmental problems. Some small suggestions for stormwater remediation and decreased water consumption (as well as decreased dry weather flows) include the planting of native plants, which, once established, can easily withstand the long summer dry season (TreePeople 2008).

Cost effectiveness of on-site flood management strategies can be very difficult to calculate. TreePeople suggested using on-site storage systems to reduce peak urban run off rates during storm events by 30% and estimated that there are about 250,000 acres in individual sites in the urban portion of the Los Angeles River watershed. They estimated that the on-site stormwater holding systems (*i.e.* rain barrels and cisterns) could reduce public flooding costs by approximately $1,000 per acre, or $250 million in public savings (2008).

TreePeople and TREES estimated that the cost of treating stormwater in facilities would be close to the cost of treating sanitary waste. The cost of treating sanitary waste is approximately $1.37 per 100 cubic feet. TreePeople and TREES assumed an average run off coefficient of 0.7, creating 38,088 cubic feet of water discharge per one acre of urban land into the storm system per year. This equals approximately $522 per acre per year, if treated in a central facility with sanitary waste. TreePeople estimate that by 2020, without treating and controlling this discharge, the beaches of Santa Monica Bay to be unswimmable on more than half of the days following storms and on 15% of dry days (two to three months per year total) (2008).

TreePeople estimated the value of trees in the Los Angeles region. Tree planting served two benefits: the reduction of pollution and the reduction of energy demand for heating and cooling. Mature urban trees reduce the amount of carbon dioxide (CO_2) in the air by about 115 pounds per year through photosynthesis, and by providing shade which lowers the amount of CO_2 released into the atmosphere by power plants through the reduction of the demand for electricity. The California Energy Commission has estimated that reduced CO_2 emission has a dollar value of $920 per year. TreePeople used STRATUM to determine the tree value in Los Angeles Region. The Trees Value suggested that each tree has a yearly value of $52.90, or a "lifetime" value over a thirty-year "amortization period" of $1,587. This value is far in excess of the cost of installing a shade tree. Los Angeles Mayor Villaraigosa launched the Million Trees Initiative in an effort to plant trees on almost 16,000 acres in Los Angeles. TreePeople is conducting a tree census to inventory the number, location, condition, and size of the trees in Los Angeles; however, assuming a total of 1,000,000 trees in Los Angeles equals an annual value of $52.9 million for trees alone (2008).

3.2 Modifications Made to 2004 Study

3.2.1 New Costs for BMPs

3.2.1.1 Costs for Structural BMPs

The literature on the costs for certain classes of BMPs, either from the report by Devinny, *et. al.* (2004) (21 cases) or added in this work (35 cases) with the operation and maintenance costs converted to present value based on a discount rate of 7%, are presented in Table 3.4. Outliers in the cost data and literature exist; therefore, the high, low, and mean are presented to indicate the range of costs found for BMPs.

Table 3.4 Summary of BMP Costs

BMP		Capital Costs	O&M Costs
Constructed Wetland	**Mean**	$15,230,000	$310,000
	High	$143,700,000	$2,875,000
	Low	$9,500	$200
Infiltration Basin	**Mean**	$5,790,000	$ 3,800
	High	$22,430,000	NA
	Low	$37,000	NA
Infiltration Trench/Ditch	**Mean**	$ 23,090,000	$3,300
	High	$ 44,560,000	NA
	Low	$1,620,000	NA
Bioretention Area	**Mean**	$24,120,000	$3,400
	High	$ 45,470,000	NA
	Low	$8,390,000	NA
Underground Filter	**Mean**	$ 5,250,000	$1,200
	High	$ 11,780,000	$1,700
	Low	$905,000	$ 550
Sand Filter	**Mean**	$ 4,660,000	$ 3,600
	High	$ 13,420,000	NA
	Low	$ 1,270,000	NA

Table 3.4 Summary of BMP Costs (Continued)

BMP		Capital Costs	O&M Costs
Porous Pavements		$ 714,000	$250
Green Roofs	**Mean**	$17.50/square foot	NA
	High	$20/square foot	NA
	Low	$15/square foot	NA
Austin Sand Filter	**Mean**	$26,320,000	$1500
	High	$ 87,960,000	$3,600
	Low	$341,000	$1200
Grassed Swales	**Mean**	$ 80,660,000	$3,400
	High	$ 341,000,000	NA
	Low	$1,290,000	NA
Detention Ponds	**Mean**	$485,000	$3,300
	High	$677,000	NA
	Low	$381,000	NA
Extended Detention Ponds	**Mean**	$38,590,000	$ 3,300
	High	$59,680,000	NA
	Low	$16,840,000	NA
Retention Ponds	**Mean**	$3,120,000	$400
	High	$5,850,000	$600
	Low	$381,000	$150

A sensitivity analysis was performed on the discount rate, with an initial discount rate of 7% and a sensitivity range of 5% and 9% (Table 3.5). To perform the sensitivity analysis, additional literature was reviewed and costs were added to the initial BMP cost data from the Devinny study. These data were compiled in an Excel spreadsheet. The maximum, minimum, and average costs were determined (Table 3.4). The operation and maintenance (O&M) costs of most BMPs are an annual cost;

therefore, the discount rate was applied. Initially, Devinny *et.al*. (2004) calculated this amount based on a 3% discount rate, but a review of current literature indicated that a better choice would be 7% with a sensitivity analysis on 5% and 9% (National Center for Environmental Decision-Making Research 2008). This was used to convert estimated annual maintenance costs to a single present value. The cost spreadsheet was designed to update all calculations based on the cell with the discount rate; therefore, a sensitivity analysis could be easily manipulated in the spreadsheet for 5%, 7%, and 9% discount rates. The change of this discount rate did not have a large impact on the mean cost of each type of structural BMP. Effects were small for the infiltration basin, infiltration trench, bioretention area, sand filter, grassed swales, extended detention ponds, porous pavements, and green roofs.

Table 3.5 Sensitivity Analysis on BMP Costs

BMP	Discount Rate	Capital Costs	O&M Costs (present value)
Constructed Wetland	**5%**	$15,490,000	$434,000
	7%	$15,230,000	$310,000
	9%	$15,080,000	$241,000
Infiltration Basin	**5%**	$5,790,000	$5,320
	7%	$5,790,000	$3,800
	9%	$5,790,000	$2,960
Infiltration Trench/Ditch	**5%**	$ 23,090,000	$4,620
	7%	$ 23,090,000	$3,300
	9%	$ 23,090,000	$2,570
Bioretention Area	**5%**	$24,120,000	$4,760
	7%	$24,120,000	$3,400
	9%	$24,120,000	$2,640
Underground Filter	**5%**	$ 5,250,000	$1,680
	7%	$ 5,250,000	$1,200
	9%	$5,240,000	$950
Sand Filter	**5%**	$ 4,660,000	$5,040
	7%	$ 4,660,000	$3,600
	9%	$ 4,660,000	$2,800
Austin Sand Filter	**5%**	$26,320,000	$2,100
	7%	$26,320,000	$1,500
	9%	$26,310,000	$1,170
Grassed Swales	**5%**	$ 80,660,000	$4,760
	7%	$ 80,660,000	$3,400
	9%	$ 80,660,000	$2,640
Detention Ponds	**5%**	$485,000	$4,620
	7%	$485,000	$3,300
	9%	$483,000	$2,570
Extended Detention Ponds	**5%**	$38,590,000	$4,620
	7%	$38,590,000	$3,300
	9%	$38,590,000	$2,570

Table 3.5 Sensitivity Analysis on BMP Costs (Continued)

BMP	**Discount Rate**	**Capital Costs**	**O&M Costs (present value)**
Porous Pavements	**5%**	$ 714,000	$ 350
	7%	$ 714,000	$ 250
	9%	$ 714,000	$ 200
Green Roofs	**5%**	$17.50/square foot	NA
	7%	$17.50/square foot	NA
	9%	$17.50/square foot	NA
Retention Ponds	**5%**	$3,120,000	$ 560
	7%	$3,120,000	$ 400
	9%	$3,110,000	$ 320

3.2.1.2 Costs for Nonstructural BMPs

An estimate of costs for source control BMPs has been prepared by the American Public Works Association (APWA 1992). Their analysis includes ten source control measures with cost data, which have been adjusted for inflation and current 2008 rates (Table 3.6). Their cost data did not include engineering, administration, land acquisition, or permitting costs, which could increase the capital costs by 30 to 50 percent (APWA 1992).

Table 3.6 Source Control Costs from APWA (1992) Adjusted for Inflation

Source Control	Description	Capital Cost	O&M Cost (present value)
Public education	Billing inserts, news releases, radio, school programs, pamphlets	$276,900	$355,800
Litter Control	Controls household and restaurant paper, plastics, and glass	$27.71/trash receptacle	$22.15/acre/trash
Recycling Programs	Controls household and restaurant paper, plastics, and glass	$277,100	$484,600/300,000 per capita
No Littering Ordinance	Prohibits littering, Controls household and restaurant paper, plastics, and glass	$27,700	Potential to be self-supporting through fines
Pooper Scooper Ordinance	Requires owners to clean up after their animals and properly dispose of waste, controls coliform bacteria and nitrogen/urea	$27,700	Potential to be self-supporting through fines
Spill Response Plan	Works to prevent pollutants from entering storm drains by controlling hazardous and harmful chemicals, oil, and grease	$27,700	N/A
Vacant Lot Clean Up	Prevents debris from accumulating on lots and eliminates sources of hazardous waste	N/A	Self-supported by fines to lot owners
Prohibit illegal and illicit connections and dumping into storm drains	Reduces pollutant load from entering the storm drains	$2.77/acre	Self-supported by fines

Table 3.6 Source Control Costs from APWA (1992) Adjusted for Inflation (Continued)

Source Control	Description	Capital Cost	O&M Cost (present value)
Identify, locate, and prohibit illegal or illicit discharges into storm drains	Halt hazardous and harmful discharges, whether intentional or negligent	$2.77/acre (1 monitor every 5 square miles)	$69.27/acre/year
Street Sweeping	Reduce potential for clogging storm drains with debris with potential for oil and grease control	N/A	$1.15/acre/year

The APWA defines five levels of BMPs that might be workable, with the appropriate level depending on the stringency of discharge requirements and the success of the individual measures. Level 1 is the institutional and non-structural controls. BMP Level 2 is a combination of Level 1 and increased maintenance of existing minor and moderate structural source controls (which primarily were constructed for flood control). BMP Level 3 is a combination of BMP Level 2 and construction of additional minor and moderate structural source controls. BMP Level 4 is a combination of BMP Level 3 and construction of detection basins or wetlands. BMP Level 5 is a combination of BMP Level 4 and construction of advanced treatment processes to remove metals, microorganisms, and nutrients. Therefore the capital costs of stormwater BMPs could range from $2 to $8,800 per capita and the operation and maintenance costs could range from $24/year to over $11,500/year per capita (APWA 1992). The capital and operation and maintenance (O&M) costs for these five levels for EPA Rainfall Zone 6, which includes Los Angeles, are presented in Table 3.7. The cost values have been adjusted for inflation since the publication of the study and the present value was calculated with current 2008 interest rates.

Table 3.7 APWA BMPs Costs for EPA Rainfall Zone 6 (Los Angeles)

Best Management Practice	**Capital Cost**	**O&M Cost (present value)**
BMP Level 1		
Institutional Source Controls		
No Littering Ordinance	$548,000	$822,000
Pooper Scooper Ordinance	$548,000	$822,000
Chemical Use/Storage Ordinance	$548,000	$822,000
Recycling Programs	$5,480,000	$9,590,000
Public education	$5,480,000	$7,040,000
Vacant Lot Clean Up	$548,000	$822,000
Spill Prevention Ordinance	$548,000	$822,000
Non-structural Source Controls		
Program to prevent illicit discharges	$13,700,000	$171,000,000
Street Sweeping	$0	$2,840,000
Increased cleaning of storm drains	$0	$71,700,000
TOTAL	$27,400,000	$266,000,000
BMP Level 2		
BMP Level 1	$27,400,000	$266,000,000
Minor Structural Controls		
Improve Diversion Channels	$0	$41,000,000
Improve Grass Swales	$0	$41,000,000
Improve Natural Channels to Reduce Erosion	$0	$10,200,000
Plant Vegetative Controls on Exposed Soils	$0	$854,000,000
Minor Structural Discharge Elimination Methods		
Increase Maintenance for Recharge Areas	$0	$5,120,000,000
Increase Maintenance for Porous Pavements	$0	$68,300,000
Moderate Structural Controls for Floatables/Oils Removal		
Increase Maintenance for Parking Lot Oil/Grease Separators	$0	$683,000,000

Table 3.7 APWA BMPs Costs for EPA Rainfall Zone 6 (Los Angeles) (Continued)

Best Management Practice	**Capital Cost**	**O&M Cost (present value)**
Increase Maintenance for Parking Lot and Rooftop Runoff Storage with Outlet Protection	$0	$751,000,000
TOTAL	$27,400,000	$7,840,000,000
BMP Level 3		
BMP Levels 1 & 2	$27,400,000	$7,840, 000,000
Moderate Structural Controls for Floatables/Oils Removal		
Construct Parking Lot Oil/Grease Separators	$6,150, 000,000	$6,150, 000,000
Construct Parking Lot and Rooftop Storage with Outlet Protection	$13,800,000,000	$6,760,000,000
TOTAL	$20,000,000,000	$20,700,000,000
BMP Level 4		
BMP Levels 1, 2, & 3	$20,000,000,000	$20,700,000,000
Major Structural Controls for Floatables/Oils Removal		
Construct Detention Basin with Outlet Protection	$446,000,000	$382,000,000
Construct Wetlands Treatment Area	$0	$0
TOTAL	$20,400,000,000	$21,100,000,000
BMP Level 5		
BMP Levels 1, 2, 3, & 4	$20,400,000,000	$21,100,000,000
Major Structural Controls for Floatables, Metals, Microorganisms, and Nutrient Removal		
Add Lime Precipitation, Filters, and Chlorination/Dechlorination to Detention Basins	$30,000,000,000	$68,400,000,000
Add Lime Precipitation, Chlorination/Dechlorination to Wetlands	$0	$0
TOTAL	$50, 500,000,000	$89,500,000,000

3.2.2 Cost Analysis

The cost data found in the literature demonstrated that the larger the watershed treated the smaller cost per square mile to treat the watershed. For example, constructing a wetland to treat one acre of watershed (0.002 square miles) cost approximately $40,500 (USEPA 1999), but constructing a wetland to treat almost 1800 acres (2.79 square miles) cost $591,000, an average of $330 per acre served ($212,000 per square mile treated) (Minneapolis Park and Recreation Board 2002). In the following figures, all the cost data are presented as Cost per Square Mile, in millions of dollars, versus Watershed Size, in square miles. The data presented in the figures includes the BMP data from the ASCE BMP database presented in Table 3.1, the cost values from the FHWA cost equations presented in Table 3.2, and the mean costs presented in the literature (Table 3.4).

All the data are presented in Figure 3.1. Figure 3.2 shows only points below $20 million dollars per square mile and for watersheds smaller than two square miles. Figure 3.3 shows only points below $10 million dollars per square mile and for watersheds smaller than 0.5 square miles. These more detailed views are presented to demonstrate how quickly the cost per square mile of watershed treated decreases. Figure 3.3 includes approximately 90% of the data collected through the literature.

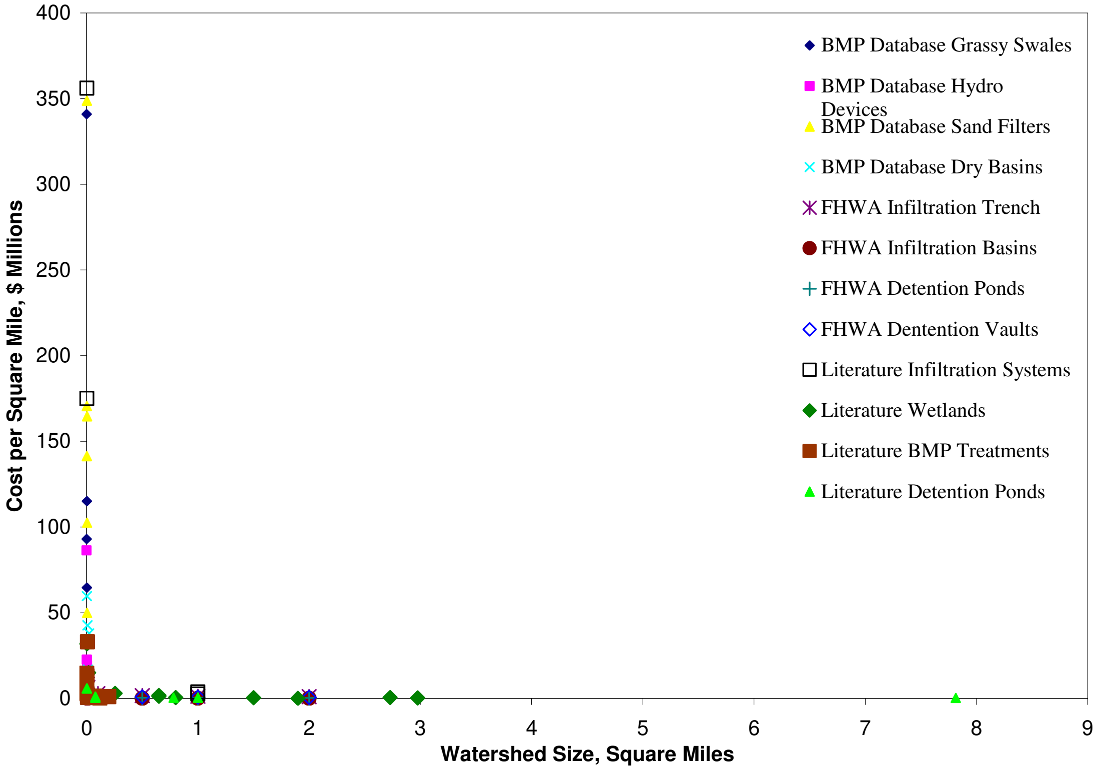


Figure 3.1 Literature Based Cost Analysis (All)

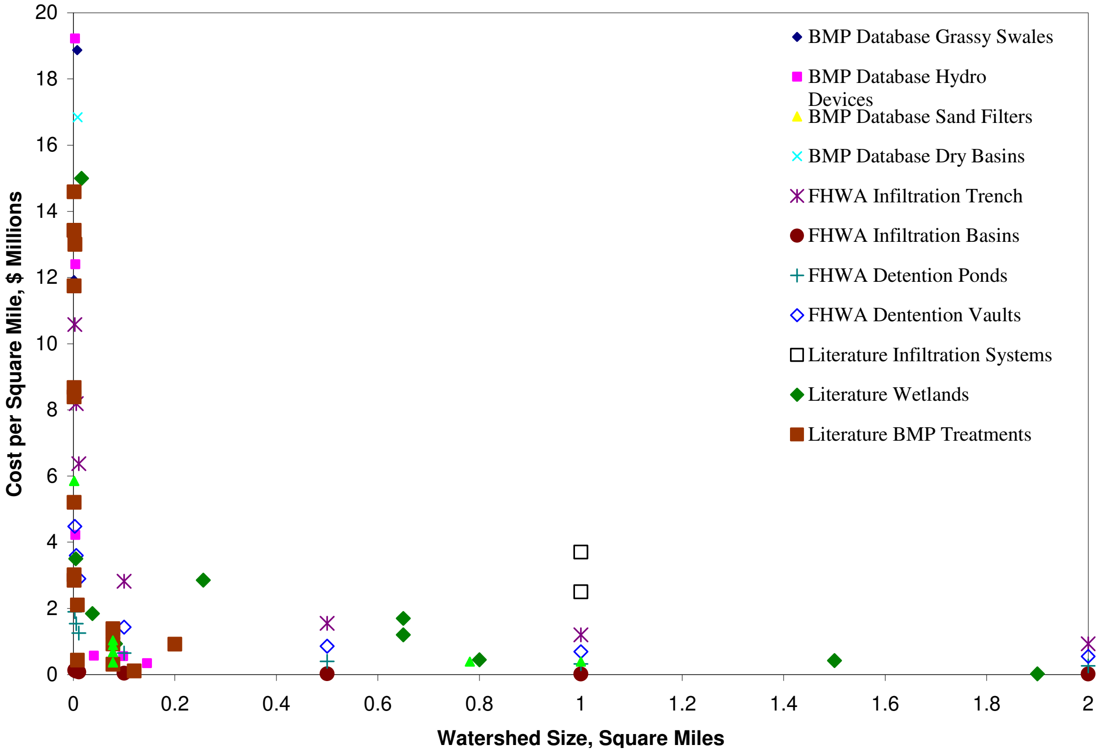


Figure 3.2 Literature Based Cost Analysis (Limited to $20 million and 2 Square Miles)

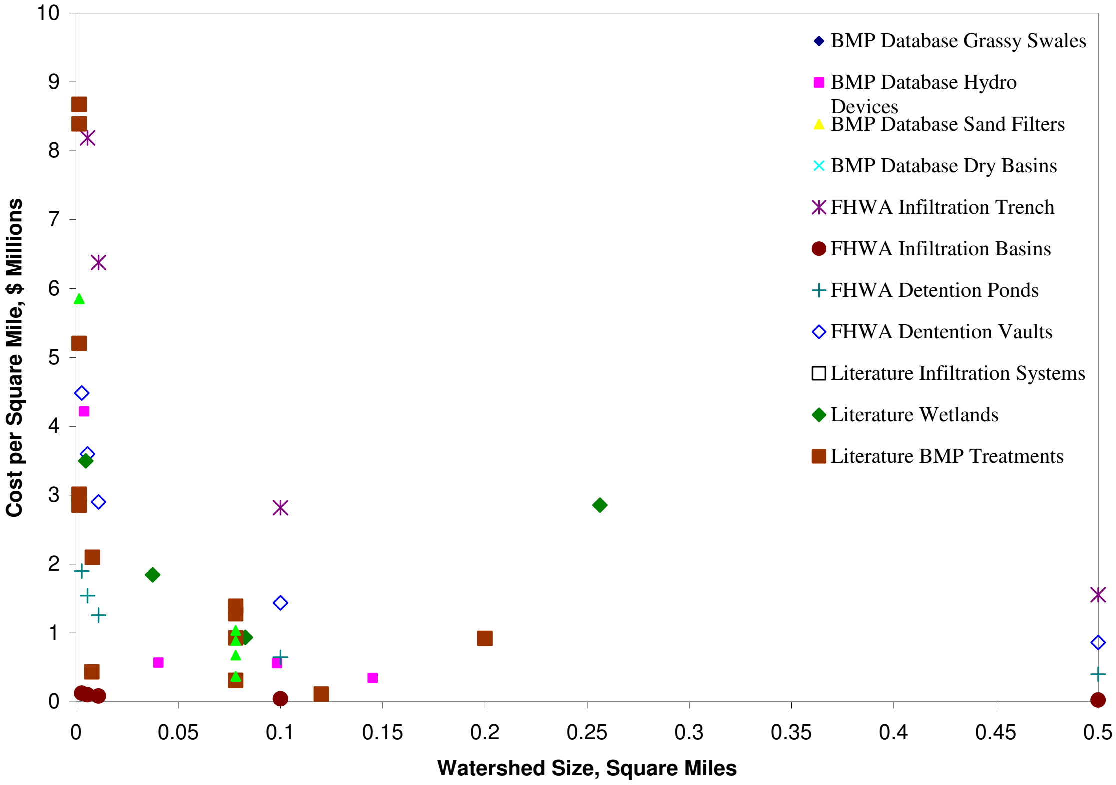


Figure 3.3 Literature Based Cost Analysis (Limited to $10 Million and 0.5 Square Miles)

Table 3.8 presents the estimated costs and benefits. Three estimates are included. In the first, source control BMPs are presumed to be the only measures employed. These costs are based solely on the values presented in Table 3.7, the APWA source control BMPs cost estimates for the Los Angeles area. These values have been adjusted for inflation from the 1992 values in their report. The Present Worth calculation is based on the discount rate of 7%, as presented in Table 3.5, and is the Capital Cost plus the Operation and Maintenance Cost divided by this discount rate.

In the second set of estimates, structural BMPs are assumed, and the costs are estimated on a cost-per-square-mile basis. The BMPs are based on the urban density, it was assumed that wetlands and detention ponds would be used in lower density areas, and treatment trains and underground filters would be used extremely high density areas. These costs estimates were based on current literature collected for this updated cost benefit analysis as well as values presented in Devinny *et.al.* (2004). The values from the literature were corrected for inflation based on the year of publication. The second estimate also presumes implementation of source control BMPs, except for storm drain cleaning (which is presumed unnecessary where structural BMPs are installed). The third set of estimates is based on the benefits of implementing BMPs and preserving the environment. Benefits differ because implementation of source control BMPs does not produce property value increases associated with greenspace, does not significantly increase groundwater supply, and does not reduce harbor sedimentation. These values are based on the numbers estimated in Devinny *et.al.* (2004) and have been adjusted for inflation. Based on these estimates, the implementation of source and structural BMPs would cost $12,600 million. The added benefits for implementing these BMPs would be approximately $21,100 million. This translates to an additional value of $8,400 million for implementing the BMPs. This value does not include cost estimation for tree value.

Table 3.8 Overall Cost Estimate for Stormwater Quality Control for Los Angeles

Costs	Capital	O&M	Present Worth	Sq Mile	Area
Non-Structural BMPs	**(million)**	**(million)**	**(million)**	**(million)**	**(million)**
No Littering Ordinance	$0.55	$0.82	$12		$15
Pet Waste Ordinance	$0.55	$0.82	$12		$15
Chemical Use and Storage	$0.55	$0.82	$12		$15
Public Education	$5.48	$7.04	$110		$110
Vacant Lot Clean Up	$0.55	$0.82	$12		$15
Spill Prevention Ordinance	$0.55	$0.82	$12		$15
Program to prevent illicit discharges	$14	$170	$ 2,400		$ 2,400
Street Sweeping		$2.80	$41		$40
Increased cleaning of storm drains		$72	$1,020		$1,020
Total N-S BMPs			$ 3,630		$ 3,630
Structural BMPs					
Rural (1050 sq.mi)					0
Lower density residential, industrial (C=.4) (1000 sq.mi.)					
Average Detention Pond Cost				1.76	$880
Average Wetland Cost				7.39	$3,700
High Density (C=.6) (1000 sq.mi.)					
Average Detention Pond Cost				2.16	$720
Average Swale cost				9.39	$3,100
Average Infiltration Area Cost				0.59	$200
Extremely Dense (C=1) (50 sq mi)					
Average Cost Surface Filter				4.67	$80
Average cost for Underground Filter				5.40	$90
Treatment trains				9.15	$150
Total Costs for Structural BMPs					***$9,150***
Total Costs for BMPs					***$12.600***
Benefits					
Flood Control					$440
Greenspace/property values					$5,500
Clean Ocean Esthetics					$ 2,700
Clean Streets Esthetics					$1,040
Additional Water Resources					$8,700
Improved beach tourism					$110
Preservation of ocean ecosystems					$2,200
Reduced harbor sedimentation					$360
Million Trees Benefit					$183
Improved Health					Significant
Total Benefits, LA Region					***$21,300***
Added Value					***$8,700***

The total cost of the BMPs, both structural and non-structural, were $12,600 million, while the total benefit of the BMPs and improvement to the environment were $21,300 million. This creates an added benefit of $8,700 million for treating the stormwater in the Los Angeles area. A sensitivity analysis performed on the estimated costs for the operation and maintenance of the BMPs determined that a discount rate of 5% would yield a total cost for BMP implementation (source and structural) of $12,800 million and an added benefit of $8,500 million. Using a discount rate of 9%, the implementation cost was approximately $12,500 million, with an additional benefit of $8,800 million.

The structural BMPs are redefined and cost estimates are made on a per-acre-foot-detention basis. The second and third estimates also presume implementation of the source control BMPs, except for storm drain cleaning (which is presumed unnecessary where structural BMPs are installed). Again, this estimate is lower than the benefits the BMPs created: $4,200 million for the structural BMPs, $3,630 million for the source control BMPs, a total cost of $7,830 million for implementation. Benefits of this implementation are approximately $21,100 million, an added benefit of $13,270 million.

Table 3.9 Calculated Costs Based on Land Use Type and Runoff

	Area	**Runoff**	**Total flow 3/4 storm**	**Cost per ac-ft.**	**Cost, ea area** (million)
Rural	1050				0
Lower density residential, industrial (C=.4)	1000	0.4	16,000	0.053	$850
High Density (C=.6)	1000	0.6	24,000	0.098	$2,400
Extremely Dense (C=1)	50	1	2,000	0.470	$940
Total Cost					***$4,200***

3.3 Conclusions

After adjusting the cost data for inflation, basing the calculations on appropriate population data for Los Angeles and the nation, and conducting the cost analysis based on a 7% discount rate, instead of a 3% rate, the values were significantly larger than those predicted in the 2004 Study. The 2004 Study concluded that the source control BMPs would cost $2.6 billion, while structural systems would cost between $5.7 billion and $7.4 billion, without discussing the offsets of the benefits, a total of $18 billion, making the minimum net benefit $10 billion.

The current study estimated both structural and non-structural BMPs at $12.6 billion, while the total benefit of the BMPs and improvement to the environment were $21.3 billion. This creates an added benefit of $8.7 billion for treating the stormwater in the Los Angeles area. The 2004 Study calculated a greater net benefit for stormwater treatment, because the inflation correction, the newer, the higher 7% discount rate, and the higher population numbers used raised the estimate of costs more than it raised the estimate of benefits.

The 1992 APWA Study BMP treatment levels for southern California indicated that a Level 4 treatment, which includes implementing non-structural controls, increased maintenance of existing minor and moderate structural source controls (which primarily were constructed for flood control), construction of additional minor and moderate structural source controls, and construction of detection basins or wetlands, is most similar to the treatment recommended here and in the 2004 Study. However, there is one major difference in both the final estimated cost from the 1992 APWA Study and the 2004 Study and this update. The 1992 APWA Study estimated the cost for a Level 4 treatment in southern California, corrected for inflation, to be $20.4 billion in capital costs, with an extra $21.1 billion in operation and maintenance costs. The 2004 Study estimated total costs to be $10 billion and this current study estimated total costs to be $12.6 billion. The difference between the Level 4 treatment proposed by the 1992 APWA Study and these two more recent studies is the elimination of Level 3 – major structural controls for floatables/oils removal, which the APWA defined as the construction of parking lot and rooftop storage with outlet protection (a cost of $13.8 billion capital, $6.76 billion operation and maintenance, making the APWA estimate for this amount of treatment $6.6 billion in capital, $14.3 billion in O&M.)

While TreePeople and TREES argue that it is economically justified to treat every site in the Los Angeles region as a mini watershed and feel that the benefit to the region may be far greater than the cost (2008), the analysis done here demonstrated the opposite. The larger the region that can be treated as one watershed, the lower the initial cost to employ the stormwater best management practice. Conducting a complete and comprehensive cost benefit analysis for a region the size of Los Angeles County is an undertaking that requires resources unavailable at the time of this analysis; however, what this analysis looked to achieve was to determine the cost of various BMPs that could be employed in an area such as Los Angeles, how much that might cost, and how much people would be willing to spend. The amounts vary: Devinny *et.al.* (2004) estimated that people in the Los Angeles region would be willing to pay about $2.5 billion, while Larsen and Lew (2003) determined that the amount was much lower, around $59.4 million. Both values are greater than the APWA cost estimation for stormwater treatment for the Los Angeles region, $5.9 million. In other words, it is difficult to determine how much people would be willing to pay for stormwater treatment anywhere, including the Los Angeles Region. Some analyses, such as that conducted by TreePeople, which moves the stormwater treatment into the hands of the individual, could alter these values. The Sun Valley model, also through TreePeople, is another valuable method for treating stormwater runoff – a series of BMPs to treat stormwater runoff.

Chapter Four: Numeration of Viruses in Stormwater

Viruses, which are the most abundant biological entities in marine and freshwater environments (Fuhrman 1999), are a fundamental concern in aquatic microbiology and in the control of human disease. Historically, human virus detection and quantification has been slowed by reliance on methods requiring culturing and have been much too slow to be effective source tracking tools. Counting human viruses in natural waters in order to track their sources also requires large human populations to meet detection limits (Noble *et. al.* 2003).

New, highly effective methods for counting viruses have recently been developed. For approximately three decades, epifluorescence microscopy has been the standard method for counting planktonic prokaryotic cells collected on blackened polycarbonate filters. SYBR Green I (a proprietary dye from Molecular Probes–Invitrogen) is frequently used in the enumeration of microorganisms. It is a cyanine-based fluorescent dye that binds to double-stranded DNA (dsDNA) and RNA. It is commonly used for nucleic-acid gel staining because of its high sensitivity, super-bright fluorescence and low background, and is considered a less-mutagenic alternative to ethidium bromide. SYBR Green I has recently been used in epifluorescence-microscopy of viruses (Patel *et.al* 2007).

The new virus enumeration method employing SYBR Green I stain and epifluorescence-microscopy represents an inexpensive and quick way to determine the presence of viruses in stormwater, and might enable faster and easier source tracking.

This chapter will test the applicability of this counting method for detecting viruses and tracking viral sources in urban stormwater.

4.1 Virus Study

The purpose of the study was to determine whether a simple, inexpensive method for quantifying viruses could be useful for identifying viral sources in stormwater and contribute to the effort to eliminate sources of contamination. The method had been confirmed effective for other applications (Patel *et.al* 2007); the goal of this study was to determine if this method would lead to an overall pattern.

This analysis included the collection of three sets of stormwater samples for three purposes. The first study entailed sampling from seven locations in the Ballona Creek watershed (Study 1), including the main watershed outlets, main tributary confluences (Sepulveda Channel and Centinela Creek) and the headwaters to determine virus concentration variation within the watershed and locate viral sources. This was to provide a longitudinal profile, demonstrating how the virus concentrations change as the stormwater passes through the collection system.

The second study was a comparison between neighborhoods supporting differing land uses (Study 2). This work was done at various sites in Los Angeles.

In the third effort, samples were taken from streetside gutters in Long Beach, California, residential area over a total distance of a few hundred meters from the initiation of flow to a storm drain (Study 3). It was to observe how rapidly viruses accumulated in the flow. These same data were also used for comparison between Los Angeles neighborhoods.

4.2 Reconnaissance and Sampling Sites

The locations of the sampling sites for Study 1, Ballona Creek Watershed, are in West Los Angeles, Playa del Rey, and Marina del Rey, California (Table 4.1, Figures 4.1 and Figure 4.2).

Table 4.1 Study 1, Watershed Contribution

Site	Water Body	Location
1	Ballona Creek	Pacific Avenue Bike Bridge
2	Centinela Creek	Centinela Blvd Bridge
3	Ballona Creek	Inglewood Avenue Bridge
4	Sepulveda Channel	Braddock Street Bridge
5	Ballona Creek	Overland Avenue Bridge
6	Sepulveda Channel	Sawtelle and Palms Bridge
7	Ballona Creek	Duquesne Bridge

Figure 4.1 Ballona Creek at Duquesne Street Bridge under Dry (Left) and Wet (Right) Weather Conditions

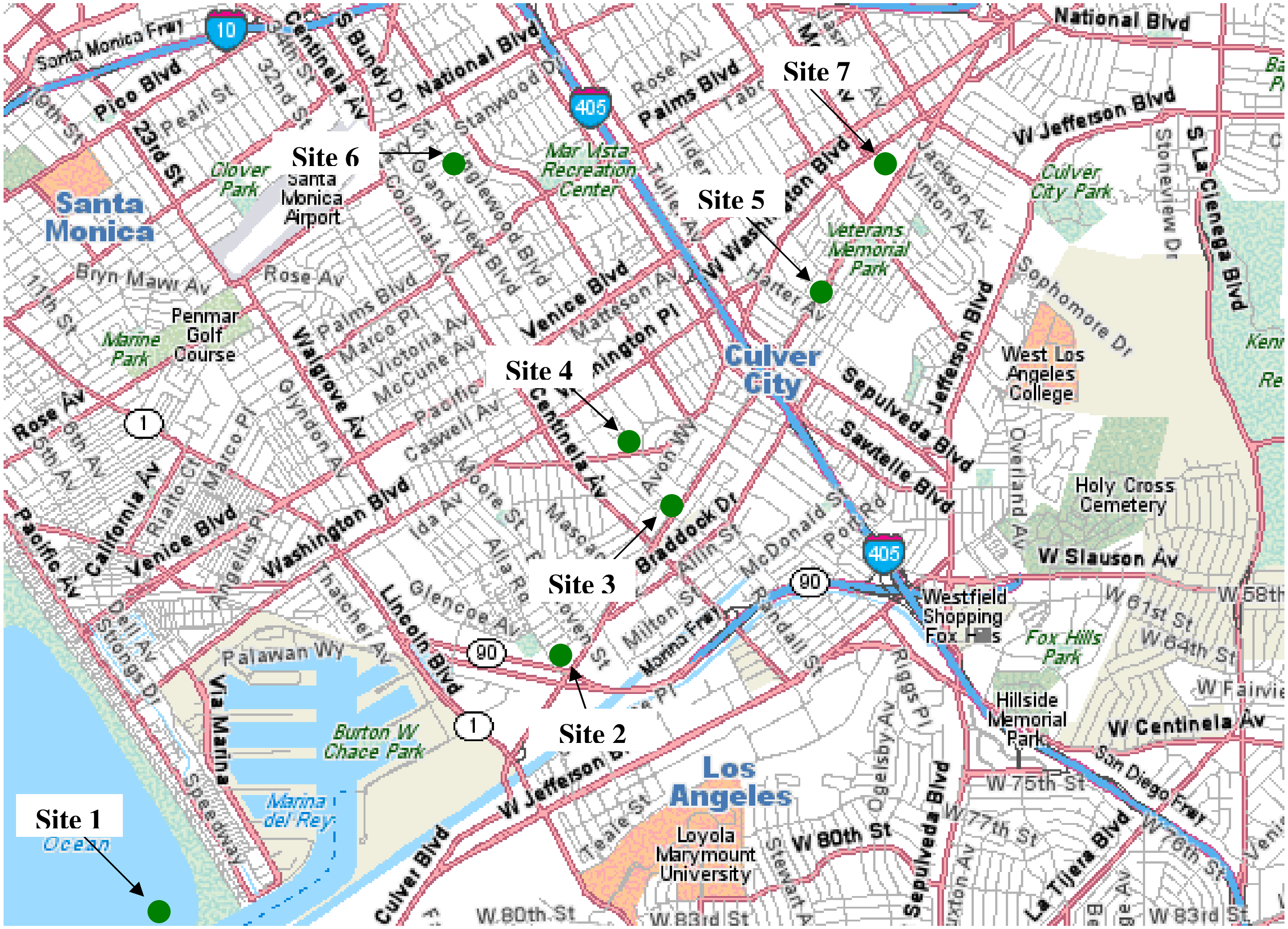


Figure 4.2 Sampling Site Locations for Study 1: Watershed Contribution (Rand McNally and Company 2007)

The sampling sites for Study 2, the land use contribution study, are presented in Table 4.2 and Figure 4.3. All Study 2 sites are located in west Los Angeles, California.

Table 4.2 Study 2, Land Use Contribution

Site ID	Land Use	Location
1	Multi-Family Residential (apartments and houses)	LA – Palms/Overland area – Lawler Street
2	Education (Palms Elementary school)	LA – Palms/Overland area – Glendon/Lawler Streets
3	High Density Single Family Residential (apartments and condominiums)	LA – Palms/Overland area – Glendon Street
4	Commercial/Retail (strip mall including a grocery store, restaurants, and dry cleaners)	LA – Palms Blvd – east of Sepulveda Blvd
5	Transportation (intersection of Palms Blvd and Sepulveda Blvd)	LA – Palms Blvd
6	Park/Open space	LA – Marvista Park – Sawtelle Ave and Palms Blvd

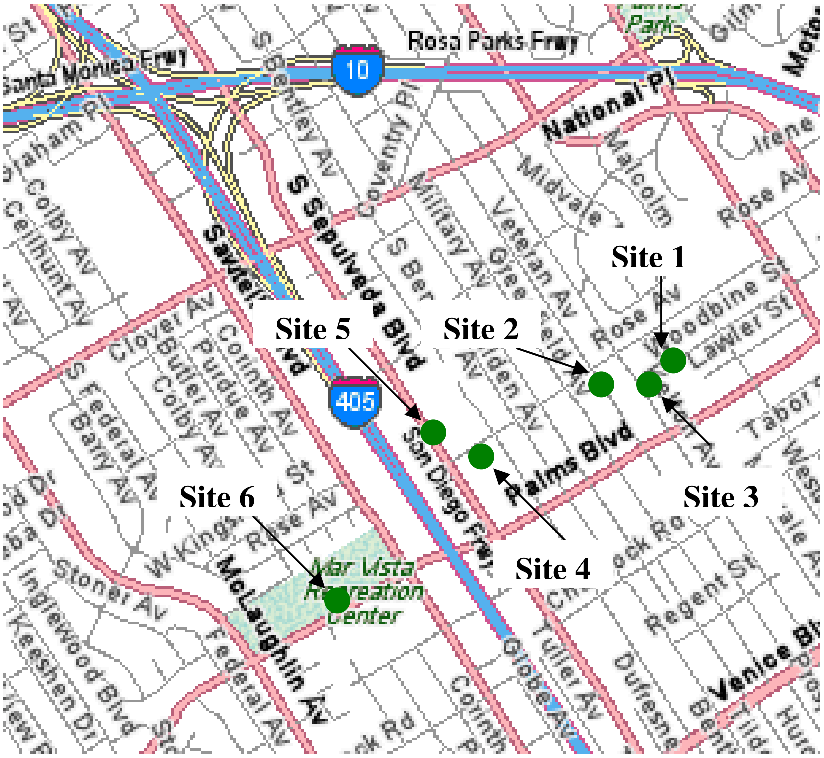


Figure 4.3 Sampling Site Locations for Study 2: Land Use Contribution (Rand McNally and Company 2007)

The sampling sites for Study 3, accumulation of viruses along the storm drain in a residential neighborhood, are presented in Table 4.3 and Figure 4.4. All are located in Long Beach, California.

Table 4.3 Study 3, Virus Accumulation in Residential Area

Site ID	Land Use	Location
1	Single Family Residential (houses with yards)	Long Beach – Country Club and Pacific Avenue
2	Single Family Residential (houses with yards)	Long Beach – Country Club and Cedar
3	Single Family Residential (houses with yards)	Long Beach – Cedar and 37th Street
4	Single Family Residential (houses with yards)	Long Beach – Cedar and Bixby
5	Single Family Residential (houses with yards)	Long Beach – 36th and Pacific
6	Single Family Residential (houses with yards)	Long Beach – 3720 Cedar

Figure 4.4 Sampling Site Locations for Study 3: Virus Accumulation (Rand McNally and Company 2007). Site 5 was at a high point, and received flow only from adjacent homes.

4.3 Materials and Methods

4.3.1 Sampling Procedure

The virus sampling method required 10 mL of sample water. Samples were collected in 50-mL sterile centrifuge tubes. The tubes did not require pre-washing, but were rinsed with the sample water three times in the field prior to collecting the sample for laboratory analysis. The samples were preserved by adding 0.02 µm filtered formalin to a final concentration of 2% (1:49). The samples can be preserved overnight or up to 3 days at 4 ^{o}C; however, samples were filtered as soon as possible to prevent loss of viruses.

4.3.2 Filtering and Counting Procedure

The virus counts were performed by epifluorescence microscopy following SYBR-Green staining in accordance with Noble and Fuhrman (1998). Materials required were Anodisc filters (0.02 µm pore size, 25 mm diameter), AA Millipore mixed-ester membrane filters (0.8 µm pore size, 25 mm diameter), Millipore-type glass filter holders (25 mm diameter, 15-mL funnel), plastic Petri dishes, pipette with tips, SYBR 1 solution from Molecular Probes, and Antifade mounting solution (50% glycerol, 50% PBS – 120 nM NaCl, 10 mM NaH_2PO_4 with a of pH 7.5, and 0.1% phenylenediamine).

A stock solution of SYBR was created by diluting 1:10 of the original concentration with deionized water, which had been filtered at 0.02 µm. From this, a 2.5% working solution was created just prior to use. An Anodisc filter was placed over a pre-wetted 0.8 µm Millipore filter in the glass filter unit. A vacuum was used to moisten and hold the Anodisc in place. The filter was flat and smooth without air bubbles. A 100-uL drop of SYBR (2.5-µL of 1:10 stock with 97.5-µL of water) was placed on the bottom of a Petri dish. The Petri dish held 4 filters; therefore, four spots were prepared with the diluted SYBR. The sample was filtered through the Anodisc at approximately 20 kPa. The filter funnel was removed immediately after the sample was filtered and the vacuum was left on while the filter was removed with sterile tweezers. Any water on the back of the Anodisc filter or top rim was blotted with a Kimwipe or paper tissue to ensure the filter was uniformly dry and looked opaque when held to the light. The Anodisc filters were placed sample side up on the drops of the staining solution and the Petri dishes were placed in a dark area for 15 minutes. After staining the filter, forceps or tweezers were used to lift the filter from the dish, leaving most of the stain on the dish. The remaining stain was carefully wiped away with a Kimwipe. The filter looked opaque when held to the light. The dried filter was placed on a glass slide; a 30-µL drop of antifade mounting solution was added to a 25 mm slide cover slip and the cover slip was inverted over the filter. The cover slip was pushed onto the slide to ensure the mounting solution filled the square space under the cover slip. The slide was viewed under blue light excitation (Figure 4.5). Viruses were counted in no less than 10 fields for a total of at least 200 viruses. The field sizes for viruses were small, perhaps three squares from a typical 100-square grid. The bottom of the filtration surface was dried with a Kimwipe. The microscope lens was cleaned to prevent fish eye (Figure 4.6). Samples with high suspended solids concentrations required pre-filtering through a filter with larger pore sizes to prevent dirt and debris from obscuring viruses (Figure 4.7). Viruses were identified by their "starlike" appearance and bacteria were identified by their "planetlike" appearance. Under blue excitation, no other light sources were expected.

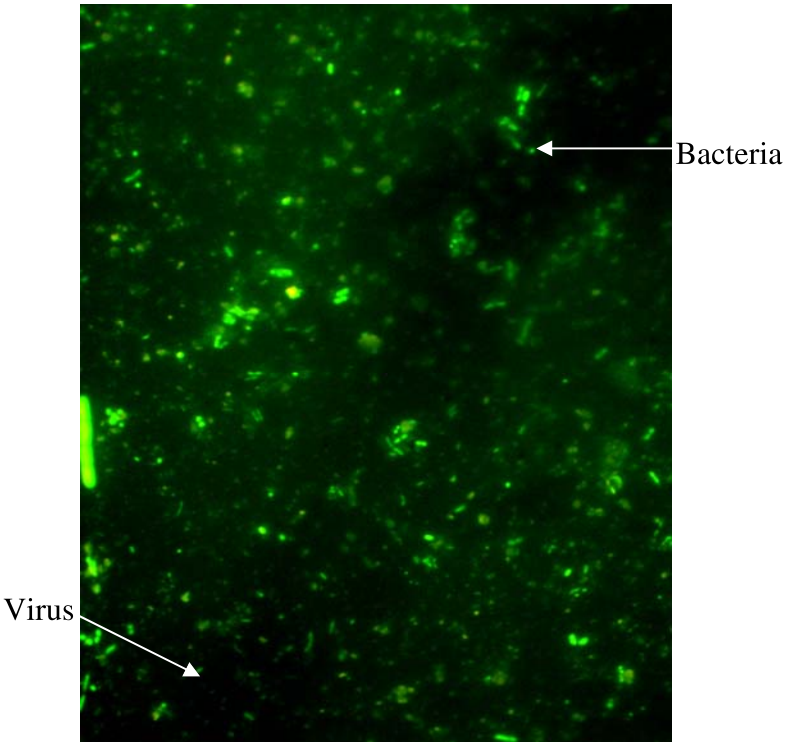


Figure 4.5 Viruses and Bacteria under Blue Excitation

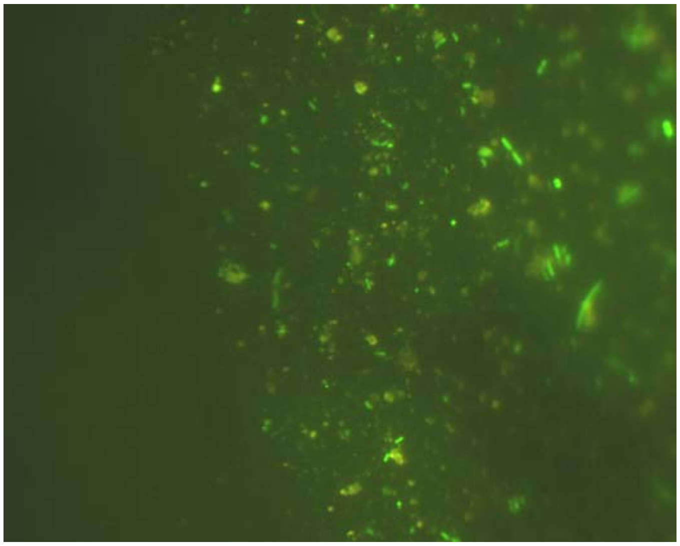


Figure 4.6 Dirty Microscope Lens

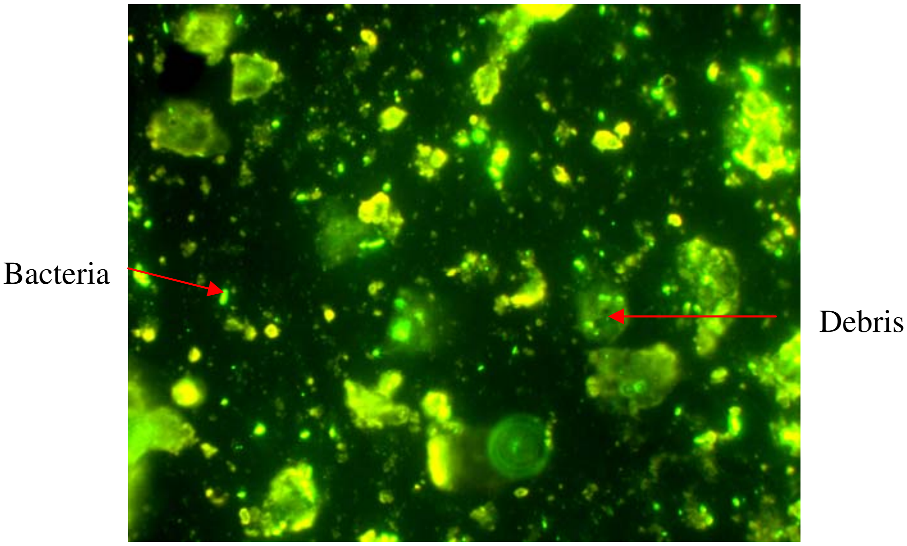


Figure 4.7 Filter with Dirt and Debris (Large Bright Globes are Bacteria)

4.4 Results

Virus concentrations for Study 1, Watershed Contribution, in Ballona Creek are presented in Table 4.4.

Table 4.4 Study 1 Results, Watershed Contribution

Site	Distance Upstream (km)	Site Name	# Viruses/mL
1	0.3	Pacific Avenue Bridge	2.08E+07
2	4.7	Centinela Creek & Bridge	2.12E+07
3	5.4	Inglewood Bridge	2.17E+07
4	6.3	Sepulveda Channel - Braddock	2.21E+07
5	7.4	Overland Bridge	2.48E+07
6	9.0	Sepulveda Channel - Sawtelle	2.21E+07
7	9.2	Duquesne Bridge	2.44E+07

The results of Study 2, the virus counts for the land use contribution, are presented in Table 4.5.

Table 4.5 Study 2 Results, Land Use Contribution

Site	Site Name	# Viruses/mL
1	Multi Family Res - 10740 Lawler Street	3.71E+07
2	Education - Lawler Street	3.94E+07
3	HDSF - Glendon/Palms	3.86E+07
4	Commercial/Retail – Strip mall	2.51E+07
5	Transportation	1.74E+07
6	Park	1.51E+07

The results of Study 3, the accumulation of viruses along the storm drain in a residential neighborhood, are presented in Table 4.6.

Table 4.6 Study 3, Virus Accumulation in the Storm Drain

Site	Site Name	# Viruses/mL
1	Country Club & Pacific	3.71E+07
2	Country Club & Cedar	3.65E+07
3	Cedar and 37th	3.27E+07
4	Cedar & Bixby	3.40E+07
5	36th & Pacific	2.76E+07
6	3720 Cedar	2.56E+07

The virus concentrations for Study 1 showed surprisingly little variation, ranging only from 20 to 25 million per milliliter sample (Table 4.4). In general, higher concentrations were found inland, and the lowest concentration was found at the mouth of the harbor (Figure 4.9). This might suggest inland viral sources whose concentration is being diluted by stormwater as the flow approaches the coast. However, this relationship could not be demonstrated quantitatively. Figure 4.8 is a plot of the virus concentrations in Ballona Creek versus the distance upstream in miles. There is no statistically significant correlation.

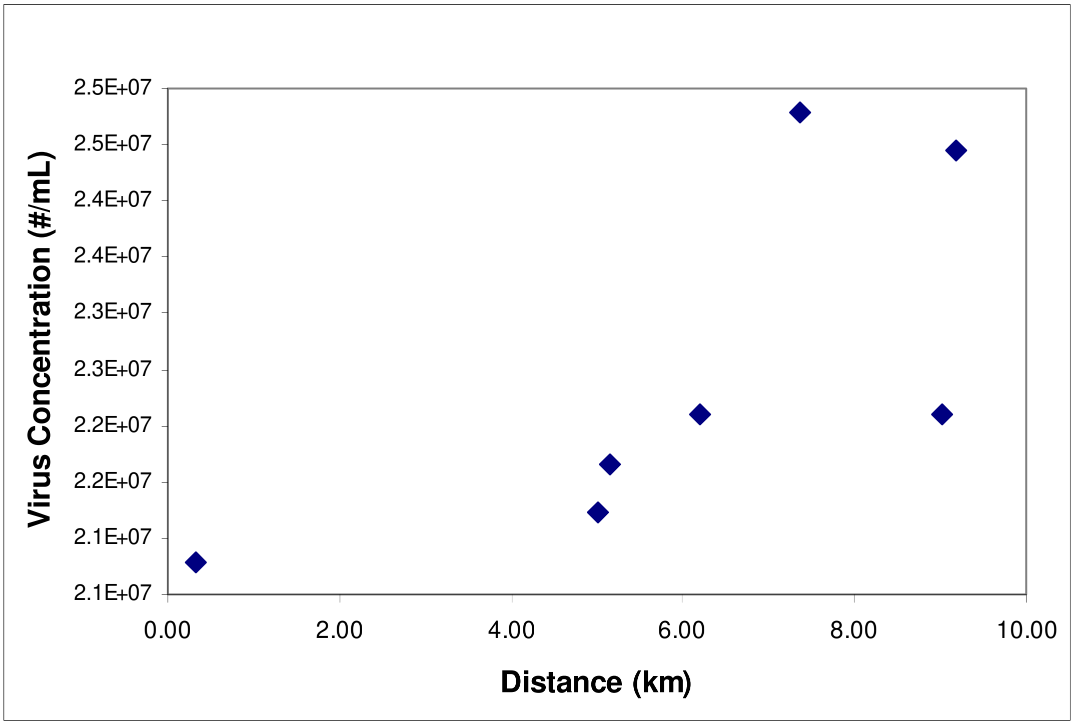


Figure 4.8 Virus Concentration as a Function of Distance (km)

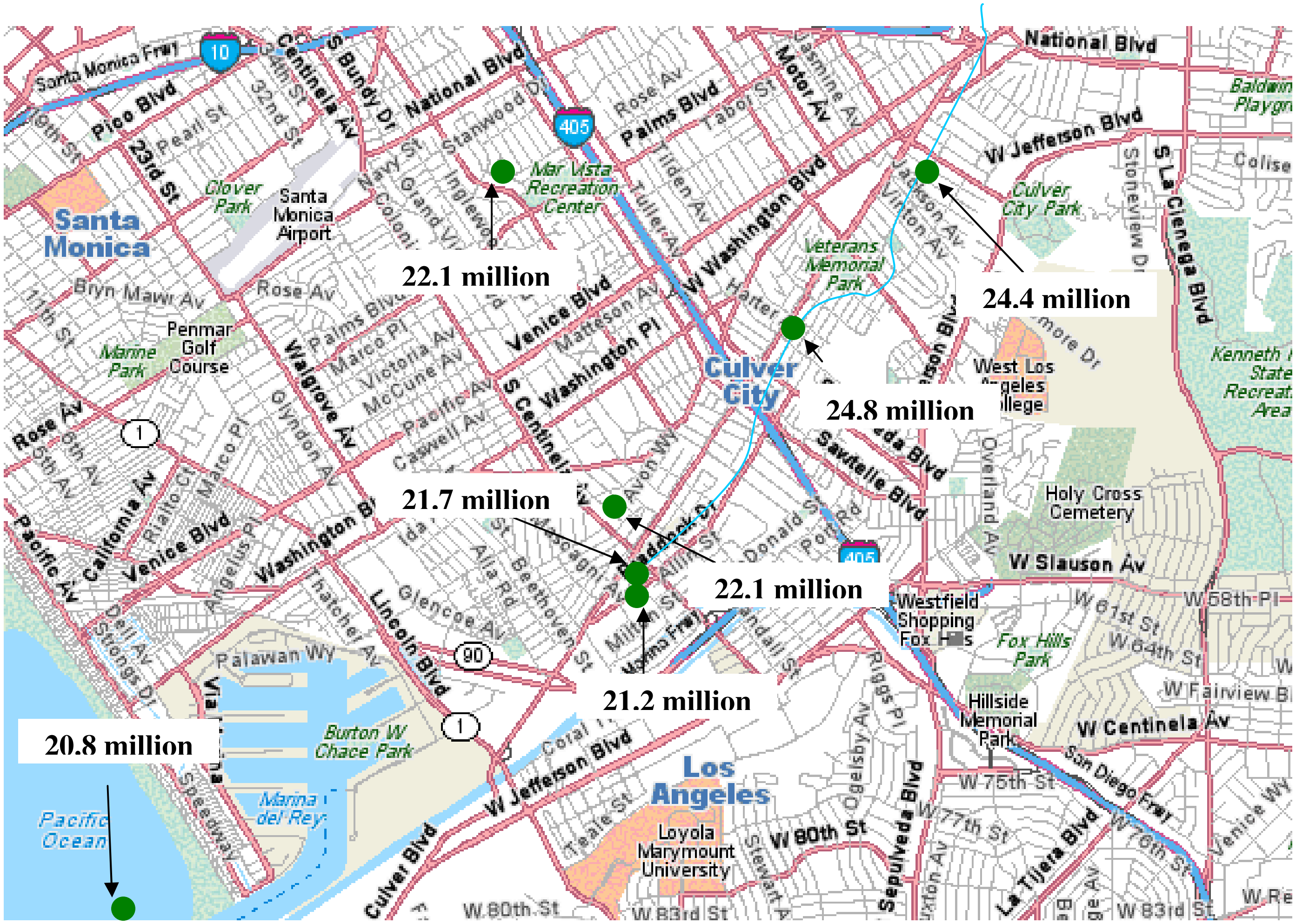


Figure 4.9 Map of Ballona Creek Sampling Sites and their Virus Concentrations (#Viruses/mL) (Rand McNally and Company 2007)

The results from Study 2, the land use contribution, indicated that the education and residential areas produced the highest virus counts, while the sample collected near the park had the lowest. Virus concentrations were between 15 and 40 million per milliliter sample. A simple Student's t-test, assuming 2-tailed distribution and a test on two samples of unequal variance provided a p-value of 0.02, indicating that the differences between the residential areas and the other land uses (transportation, commercial, and park) in Study 2 are statistically significant.

It could be inferred that these higher virus counts are a result of human activity or dog walking, or that the larger grassed natural area of the park removed the viruses. While such a small study cannot be definitive, there is indication that this approach might be useful in determining those neighborhoods that are the greatest contributors to the stormwater viral loads.

In Study 3, accumulation of viruses along the storm drain in a residential neighborhood, the viral concentration range was even smaller – 25 million to 37 million – with the highest point experiencing the lowest concentration. While the data suggested a trend of increasing viral concentrations as the stormwater flowed downstream, variation in the data was high and no statistically significant correlation between the virus concentration and the distance along the gutters was established (Figure 4.10).

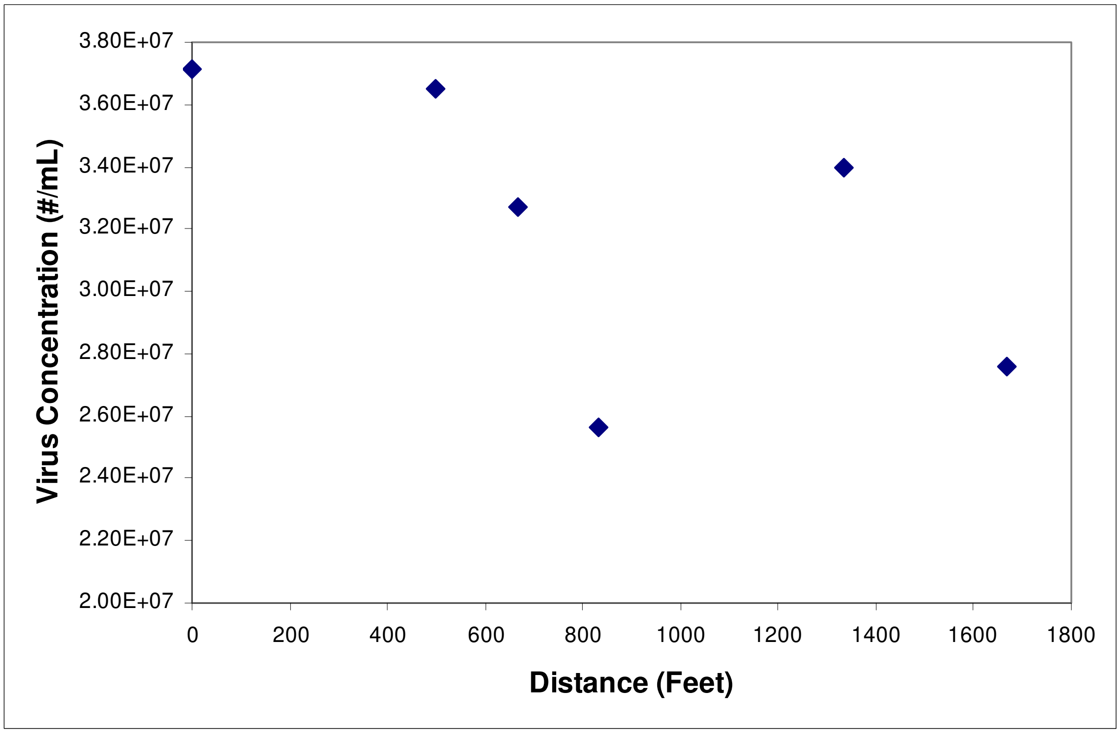


Figure 4.10 Virus Concentration as a Function of Distance Upstream from Site 1 (Feet)

4.4.1 Comparison with QRTPCR

The numerical viral counts method had not been employed in urban stormwater runoff or creek samples. However, Quantitative Reverse Transcriptase Polymerase Chain Reaction (QRTPCR) had been used by Noble *et.al.* (2005), which found evidence of fecal contamination and enteroviruses, in 44% of the sites they sampled in Ballona Creek (Table 4.7).

Table 4.7 Number of Enterovirus Genomes (per 100-mL) detected (Noble *et.al.* 2005)

Distance Upstream (km)	**Time of Day**					
	9:00	**10:00**	**11:00**	**12:00**	**1:00**	**2:00**
6.3	106*	71*	93*	708	67*	
5.4		41*	19**	25*		
4.7		17*		113*	51	
2.6				79*		
1.5				13*		39
0.0						

*Human Bacteroides marker also detected

** PCR reaction for human Bacteroides marker inconclusive due to inhibition

Enterovirus concentrations determined by QRTPCR were between 10 and 700 viruses per 100-mL, or 0.1 to 7 viruses per milliliter. The virus concentrations determined by DNA staining and counts were between 20 and 30 million per milliliter, indicating that human enteroviruses comprised an extremely small percentage of viruses in stormwater samples. This does not account for other human viruses which may be present, such as rotaviruses, hepatitis A viruses and noroviruses; however, these viruses are found in lower concentrations than enteroviruses (Noble *et.al.* 2005). In general, virus counts found in this study were about a million times higher than the enterovirus counts found by QRTPCR by Noble *et.al.* (2005).

4.5 Conclusions

The virus counts found in this study were high, in the tens of millions per ml. There were some suggestions of trends in the results – virus seemed to decline with distance downstream in the first study, there were more viruses in residential and educational neighborhoods in the second study, and there was a suggested (non-statistically significant) increase downstream in the third study. However, the counts were surprisingly uniform, varying by less than a factor of ten throughout the entire study in all three areas. Further, the patterns seen were all indistinct or of marginal statistical significance. Overall they did not provide a strong indication of the sources of the viruses.

The data provided by QTRPCR from the Noble *et.al.* study suggested that human viruses are found in significantly smaller numbers than the concentrations determined in this study. This suggests that the total counts determined here may reflect high background concentrations of non-human (or non-mammalian) viruses from sources that are not coincident with sources of pollution. It is also possible that sources of pollution are so dispersed that tracking is not possible.

It was concluded that the methods developed here are not likely to be useful in tracking pollutant sources in urban stormwater.

Chapter Five: Quantification of Organic Pollutant Concentrations in Impaired Urban Waterways

The concentrations of pollutants in water can be determined using integrative passive samplers. These consist of an organic solid that absorbs and concentrates the contaminant during extended deployment in the environment. It is returned to the lab for extraction and instrumental analysis. The objective for the work described in this chapter was to calibrate Polyethylene Devices (PEDs) used to determine the concentrations of waterborne organic pollutants, to compare the PEDs with the Solid Phase Microextraction Devices (SPMEs) in a controlled laboratory experiment, and to co-deploy the samplers for comparative testing in Ballona Creek. To accomplish this, a series of laboratory experiments using TMDL-regulated hydrophobic organic contaminants (HOCs) was performed to quantify HOC-specific polyethylene-water partition coefficients (K_{PEW}) and to characterize compound-specific exchange rate constants (k_e).

Use of the polyethylene device required determination of the partition coefficients and equilibration times prior to deployment *in situ*. Previous calibrations of PEDs have been done for chlorinated benzenes, PAHs and PCBs (Booij *et.al.*. 2003; Adams 2003). These experiments calibrated the PEDs for other TMDL-regulated HOCs, DDTs and chlordanes and for additional PAHs and PCBs. HOC reference compounds were added (Booij *et.al.*. 1998; 2002) to allow for the correction of nonequilibrium conditions.

The partition coefficients for the SPME have been researched extensively by the Southern California Coastal Water Research Project (SCCWRP) scientists and K_f values have been calculated (Maruya *et.al.* 2009, Yang *et.al.* 2007, Yang *et.al.* 2006, Zeng *et.al.* 2005).

The PED experiments (K_{PEW} and k_e) plus all prep work for PED deployment were conducted at Loyola Marymount University (LMU) under the supervision of Rachel Adams, whose PhD research at the Massachusetts Institute of Technology was on the development of the PED. The K_{PEW} experiment was conducted to determine the partitioning of the selected TMDL-regulated HOCs.

All chemical analyses (GC-MS and GC-ECD) were completed at SCCWRP using their instruments. I ran the GC-MS and GC-ECD, and Wenjian Lao and Jian Peng provided instrument support and helped with set up.

The PED/SPME comparison study was conducted at SCCWRP using equipment from both LMU and SCCWRP. I designed the experiment, set up the experiment, and supervised the experiment. On the final day of this experiment, liquid-liquid extraction support was provided by SCCWRP employees Wenjian Lao, David Tsukada, and Xiang-Zhou Meng. Mr. Tsukada also provided support with the concentrating of the water and PED samples from this experiment.

For the PED/SPME field deployment in September 2007, I prepared the PEDs for field deployment – cut and cleaned them, preloaded them with reference compounds, and threaded them onto cleaned copper wire – at LMU under the supervision of Dr. Rachel Adams. I deployed the PEDs in Ballona Creek with

SCCWRP employees David Tsukada and Dario Diehl, who deployed the SPMEs and Infiltrex *in situ* pump.

5.1 Analytical Methods

5.1.1 Instrumental Techniques

5.1.1.1 GC-MS Analysis

Sample extracts were analyzed using a Varian 3800 gas chromatography (GC)/Saturn 2000 ion trap mass spectrometry (MS) system (Varian, Walnut Creek, CA). The injector temperature was programmed to go from 100 to 280°C at ~100°C/min with a 40-minute hold time at the maximum temperature. The carrier gas was ultra high purity helium with a flow rate of 1.0 mL/min. Chromatographic separations were made with 60 m long, 0.25 mm-id (0.25-mm film thickness) DB-5MS columns (J&W Scientific, Folsom, CA) temperature-programmed from 80°C (held for 1 min) to 176°C at 8°C/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 minute hold time). A six-point calibration curve (*i.e.* 50, 100, 250, 500, 1000 and 2000 ng/mL) was used with an internal standard to calculate an RRF (relative response factor).

5.1.1.2 GC-ECD Analysis

A Hewlett Packard HP5890 Series II plus gas chromatograph (Palo Alto, CA, USA) with a DB-5MS capillary column (60m × 0.25 mm i.d., 0.25 um film thickness), equipped with an electron capture detector (ECD-63Ni) and a 7683 autosampler were employed for analysis of PCB and chlorinated pesticide samples. Helium and nitrogen were used as carrier and makeup gas, respectively. The carrier gas flow rate was 1.5 mL/min. The injector and detector temperature were 280˚C and 300˚C, respectively. The injection was splitless mode. The split valve of injector was opened at 2 minutes, and closed at 20 minutes. The column temperature was set at 170 ˚C for 20 minutes, increased to 290 ˚C at 4 ˚C / minutes, and held at 290˚C for 20 minutes. A 2-µL sample was injected into the GC. The external standard method was used for quantitation via multi-point calibration curve. The standard solutions included 1, 2, 5, 10, 25, 50, 100, 250, and 500 ng/mL solutions.

5.1.1.3 Calibration Curve for GC-MS Determinations

A six point calibration curve was used with an internal standard to calculate a relative response factor (RRF). A six-point calibration curve has six standards of various concentrations (*i.e.* 50, 100, 250, 500, 1000 and 2000 ng/mL) within a predetermined range.

The RRF is calculated as:

$$RRF = \frac{(A_{CS})(C_{IS})}{(C_{CS})(A_{IS})} \quad 5.1$$

where the A_{CS} is the peak area of the calibration standard, C_{CS} is the concentration of the calibration standard, C_{IS} is the concentration of the internal standard, and A_{IS} is the peak area of the internal standard. In the calibration curve, we know the concentration of the calibration standard and the internal standard, the GC-MS gives us the peak area of these; therefore, the RRF is determined.

Once the RRF is determined, the samples can be run, spiking each sample with 500 ppb (ng/mL) of internal standard. The GC-MS gives the peak area of the target analyte and the internal standard, and the concentration of the internal standard is known,; therefore, the concentration of the target analyte can be calculated.

$$RRF = \frac{A_{unk} / C_{unk}}{A_{IS} / C_{IS}} \tag{5.2}$$

where the A_{unk} is the peak area of the unknown analyte, C_{unk} is the concentration of the unknown analyte.

Rearranging terms:

$$C_{unk} = \frac{(A_{unk})(C_{IS})}{(RRF)(A_{IS})} \tag{5.3}$$

5.1.1.4 Recovery Surrogate Correction Method

We are able to calculate the recovery-corrected concentrations and masses using the recovery surrogate and sample peak areas and volumes.

$$RC = \frac{(\mathrm{A}_{\mathrm{Su}_{\mathrm{sam}}})(\mathrm{V}_{\mathrm{sam}})}{(\mathrm{A}_{\mathrm{Su\,std}})(\mathrm{V}_{\mathrm{surr\,added}})} \tag{5.4}$$

where RC is the recovery correction, $A_{su(sam)}$ is the peak area of the recovery surrogate in the sample, V_{sam} is the volume of the sample, A_{su} is the peak area of the recovery surrogate in the recovery surrogate standard, and $V_{surr\ added}$ is the volume of the recovery surrogate added to the sample.

Then the unknown analyte in the sample can be recovery-corrected as follows:

$$C_{ukn} = \frac{(\mathrm{A_{ukn}})(\mathrm{C_{IS_{ukn}}})}{(\mathrm{RRF})(\mathrm{RC})(\mathrm{A_{IS_{ukn}}})} \qquad 5.5$$

where C_{ISCs} is the concentration of the internal standard in the sample, and A_{ISunk} is the peak area of the internal standard in the sample. This equation can be modified to calculate mass of the unknown analyte as follows:

$$M_{ukn} = \frac{(\mathrm{A_{ukn}})(\mathrm{V_{ukn}})(\mathrm{C_{IS_{ukn}}})}{(\mathrm{RRF})(\mathrm{RC})(\mathrm{A_{IS_{ukn}}})} = \frac{(\mathrm{A_{ukn}})(\mathrm{V_{ukn}})(\mathrm{C_{IS_{ukn}}})}{(\mathrm{RRF})(\mathrm{A_{IS_{ukn}}})} \frac{A_{IS_{CS}}}{C_{IS_{Cs}}} \qquad 5.6$$

where M_{ukn} is the mass of the unknown analyte in the sample and V_{ukn} is the volume of the unknown analyte in the sample.

5.1.2 Theory

The partition coefficient, K_{PEW}, is the ratio of the concentration of chemical in the polyethylene at equilibrium (infinite time; $C_{PE\infty}$; mol/kg_{PE}) to the amount of chemical in the water ($C_{w\infty}$; mol/V_W), expressed in moles of chemical in polyethylene per mass of polyethylene (kg_{PE}) per moles of chemical in water per volume of water (V_W):

$$K_{PEW} = \frac{C_{PE\infty}}{C_{W\infty}} \qquad 5.7$$

Sorption/desorption rates can be measured using reference compounds impregnated within the PEDs. Assuming first order kinetics, the exchange rate constant, k_e can be calculated according to the following:

$$k_e = \ln\left(\frac{C_{PE0,r} - C_{PE\infty,r}}{C_{PEt,r} - C_{PE\infty,r}}\right) \cdot t^{-1} \qquad 5.8$$

where $C_{PE0,r}$ is the initial concentration of the reference compound in the PED, $C_{PE\infty,r}$ is the equilibrium concentration of the reference compound in the PED, and $C_{PEt,r}$ is the concentration of the reference compound measured in the PE at time t. $C_{PE\infty,r}$ is calculated according to the following equilibrium expression:

$$C_{PE\infty,r} = \frac{K_{PEW} \cdot C_{PE0,r} \cdot M_{PE}}{V_W + K_{PEW} \cdot M_{PE}} \qquad 5.9$$

where M_{PE} is the mass of the polyethylene. In a field or infinite bath case, Equation 5.8 becomes:

$$k_e = \ln\left(\frac{C_{PE0,r}}{C_{PEt,r}}\right) \cdot t^{-1} \qquad 5.10$$

Assuming that the sorption and desorption rate constants are equal, the $C_{PE\infty}$ for the chemical of interest can be calculated as:

$$C_{PE\infty} = \frac{\left(C_{PEt} - C_{PE0} \cdot e^{-k_e t}\right)}{\left(1 - e^{-k_e t}\right)} \qquad 5.11$$

where C_{PEt} is the concentration of the chemical of interest at time t and C_{PE0} is the concentration of the chemical of interest initially. Combining Equations 5.7 and 5.11 and assuming no initial HOC contamination in the PED initially yields:

$$C_{W\infty} = \frac{C_{PEt}}{\left(1 - e^{-k_e t}\right) \cdot K_{PEW}} \qquad 5.12$$

K_{PEW} values are presented here and can be measured in the laboratory. The exchange rate constant k_e can be determined using reference compounds as explained above, and C_{PEt} is measured in the PED.

Calculation of the water concentration of a compound with SPME data, under equilibrium conditions, is as follows:

$$K_f = \frac{C_f}{C_w} \qquad 5.13$$

Rearranging Equation 5.13 yields:

$$C_w = \frac{n_f}{K_f V_f} \qquad 5.14$$

where C_f and C_w are equilibrium concentration on fiber and in water, respectively; V_f and is volume of fiber coating; n_f is mass (pg) on fiber determined by GC-MS. The K_f values used for this study were those determined by Yang *et.al.* 2006 and Maruya *et.al.* 2009.

5.1.3 Materials

The analytes were from Ultra Scientific, each manufactured under ISO 9001 and ISO GUIDE 25 quality systems. All solution solvents were of the highest quality available. Ultra Scientific gravimetrically prepares all solutions to a precision of ±0.5%. Analytes included were PCB 52, PCB 70, PCB 101, PCB 110, PCB 153, PCB 180, phenanthrene, pyrene, chrysene, benzo[a]pyrene, benzo[ghi]perylene, DDT 4,4', DDE 4,4', heptachlor epoxide, *cis* chlordane, and *trans n*onachlor.

The low-density polyethylene was produced by Carlisle Plastics, Inc. of Minneapolis, MN. Polyethylene used in the K_{PEW} experiment was 51 µm thick. Polyethylene used in the k_e and SPME-PED comparison experiments was 30 µm thick. Prior to use, the PE was cut into 3-inch by 3-foot strips, pre-cleaned. The PE strips were stored in clean water until use.

Methanol (MeOH), acetone, dichloromethane (DCM), and hexane solvents were all JT Baker Ultra-resi-analyzed (Phillipsburg, NJ).

All water was clean water from a Milli-Q, Millipore water purification system with total organic carbon removed to less than 6 µg/L and a resistance of 18 MΩ. The Milli-Q water purification system filters the TOC from the water and continuously analyzes the level of TOC.

5.1.4 Analytes of Interest

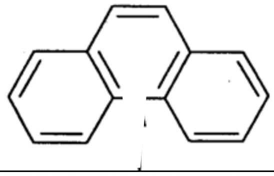
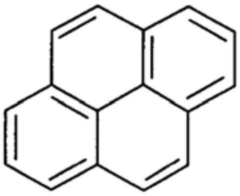
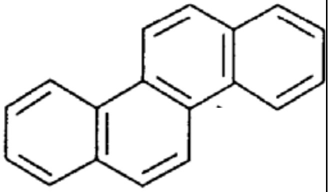
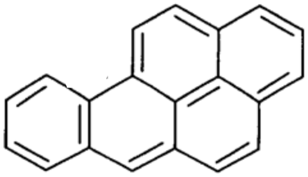
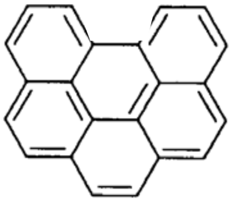
The analytes were selected based on their prevalence in the environment and molecular weight. A range of various molecular weight PAHs and PCBs is desirable because this produces a range of octanol-water partitioning coefficients (K_{OW}). A linear regression analysis between partitioning coefficients for PEDs and SPMEs (K_{PEW} and K_f) versus K_{OW} was done to help predict the partitioning for HOCs not studied in the lab.

5.1.4.1 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. PAHs are usually found as part of a mixture containing many compounds, such as soot. Pure PAHs usually exist as colorless, white, or pale yellow-green solids. PAHs are found in coal tar, crude oil, creosote, and roofing tar, but a few are used in medicines or to make dyes, plastics, and pesticides.

Studies indicate that PAHs cause reproductive problems and birth defects in mice. Some PAHs may reasonably be expected to be carcinogenic (United States Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR) 1995). The chemical properties of the PAHs selected for laboratory study are presented in Table 5.1.

Table 5.1 PAHs Selected for Study (ATSDR 1995)

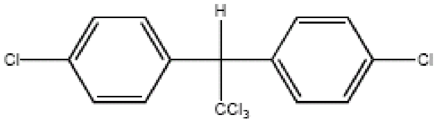
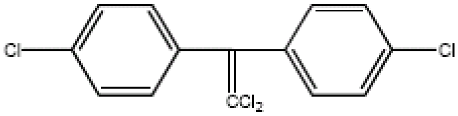
Compound	Molecular Shape	Molecular Formula	Molecular Weight	K_{OW}
Phenanthrene		$C_{14}H_{10}$	178.20	4.57
Pyrene		$C_{16}H_{10}$	202.30	5.13
Chrysene		$C_{18}H_{12}$	228.30	5.81
Benzo[a]pyrene		$C_{20}H_{12}$	252.30	6.13
Benzo[ghi] perylene		$C_{22}H_{12}$	276.34	6.58

5.1.4.2 DDTs

DDT (dichlorodiphenyltrichloroethane) is a pesticide once widely used to control insects in agriculture and insects that carry diseases such as malaria. DDT is a white, crystalline solid with no odor or taste. Its use in the U.S. was banned in 1972 because of damage to wildlife, but it is still used in some countries (ATSDR 2002). In the Los Angeles region, legacy DDT produced by Montrose Chemical Corporation was discharged off White Point on the Palos Verdes Shelf in the Pacific Ocean (USEPA 2007).

DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane) are chemicals similar to DDT that contaminate commercial DDT preparations. DDE has no commercial use. DDD was also used to kill pests, but its use has also been banned. One form of DDD has been used medically to treat cancer of the adrenal gland (ATSDR 2002). The chemical properties for DDT and DDE, both examined in the laboratory, are presented in Table 5.2.

Table 5.2 Chemical Properties of DDT and DDE (ATSDR 2002)

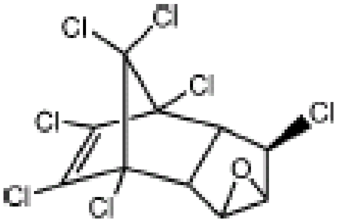
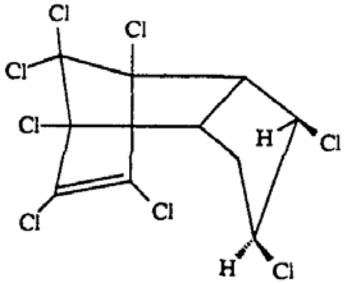
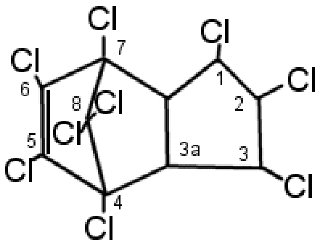
Compound	**Molecular Shape**	**Molecular Formula**	**Molecular Weight**	***K$_{OW}$***
DDT		$C_{14}H_9Cl_5$	318.00	6.91
DDE		$C_{14}H_8Cl_4$	354.50	6.96

5.1.4.3 Chlordanes

Chlordane is a manufactured chemical that was used as a pesticide in the United States from 1948 to 1988. It is a thick liquid whose color ranges from colorless to amber. Chlordane has a mild, irritating smell. Some of its trade names are Octachlor and Velsicol 1068. Until 1983, chlordane was used as a pesticide on crops such as corn and citrus and on home lawns and gardens. Because of concern about damage to the environment and harm to human health, the Environmental Protection Agency (EPA) banned all uses of chlordane in 1983 except control termite control. In 1988, EPA banned all uses (ATSDR 1994, ATSDR 2007).

Chlordane affects the nervous system, the digestive system, and the liver in people and animals. Headaches, irritability, confusion, weakness, vision problems, vomiting, stomach cramps, diarrhea, and jaundice have occurred in people who breathed air containing high concentrations of chlordane or accidentally swallowed small amounts of chlordane. Large amounts of chlordane taken by mouth can cause convulsions and death in humans (ATSDR 1994, ATSDR 2007). The chemical properties of the chlordanes examined in the laboratory are presented in Table 5.3.

Table 5.3 Chemical Properties of Chlordanes (ATSDR 1995)

Compound	Molecular Shape	Molecular Formula	Molecular Weight	K_{OW}
Heptachlor Epoxide		$C_{10}H_5Cl_7O$	389.32	4.91
***cis* Chlordane**		$C_{10}H_6Cl_8$	409.78	6.10
***trans* Nonachlor**		$C_{10}H_6Cl_9$	444.23	6.35

5.1.4.4 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are mixtures of up to 209 individual chlorinated compounds (congeners). Many commercial PCB mixtures are known in the U.S. by the trade name Aroclor. PCBs have been used as coolants and lubricants in transformers, capacitors, and other electrical equipment because they don’t burn easily and are good insulators. The manufacture of PCBs was stopped in the U.S. in 1977 because of evidence that they are subject to bioaccumulation and can cause harmful health effects. Products made before 1977 that may contain PCBs include old fluorescent lighting fixtures and electrical devices containing PCB capacitors, and old microscope and hydraulic oils (ATSDR 2000).

PCBs share the same molecular shape (Figure 5.1). The PCB congeners differ in the number and location of chlorine substituents (Table 5.4).

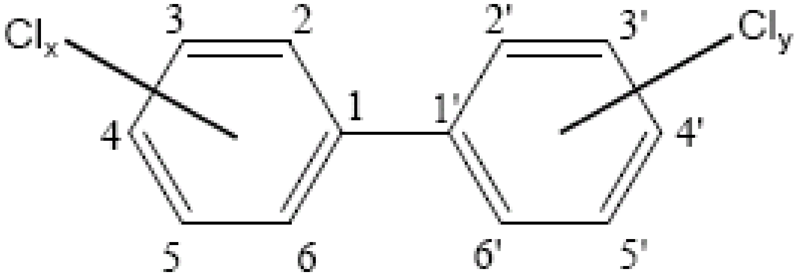


Figure 5.1 Molecular Shape of A PCB (ATSDR 2000)

Table 5.4 Chemical Properties of PCBs (ATSDR 2000)

Compound	**Molecular Shape**	**Molecular Formula**	**Molecular Weight**	***K_{OW}***
PCB 52	2,2',5,5' tetrachlorobiphenyl	$C_{12}H_6Cl_4$	292.00	6.09
PCB 70	2,3',4',5 tetrachlorobiphenyl	$C_{12}H_6Cl_4$	292.00	6.20
PCB 101	2,2',4,5,5' pentachlorobiphenyl	$C_{12}H_5Cl_5$	326.40	6.36
PCB 110	2,3,3',4',6 pentachlorobiphenyl	$C_{12}H_5Cl_5$	326.40	6.48
PCB 153	2,2',4,4',5,5' hexachlorobiphenyl	$C_{12}H_4Cl_6$	360.90	7.15
PCB 180	2,2',3,4,4',5,5' heptachlorobiphenyl	$C_{12}H_3Cl_7$	395.40	7.36

5.2 K_{PEW} Experiment

The objective for the work described in this section was to calibrate the Polyethylene Devices (PEDs) to determine the concentrations of waterborne organic pollutants. The polyethylene device required determination of HOC-specific partition coefficients and equilibration times prior to deployment *in situ*. Previously calibrated HOCs for PEDs include chlorinated benzenes, PAHs and PCBs (Booij *et.al.* 2003; Adams 2003, Adams *et.al.* 2007). This experiment calibrated the PEDs for other TMDL-regulated HOCs: DDTs and chlordanes as well as additional PAHs and PCBs.

5.2.1 Methods

The PED K_{PEW} experiment exposed a number of PEDs to contaminated water. PEDs were removed from the experimental vessels and the absorbed contaminants were extracted on designated days (t=1, 3, 10, 30, 44, 45, 46, and 47) to develop a time-to-equilibrium curve and establish that the polyethylene had reached equilibrium with the water. The analytes included were PCBs (52, 70, 101, 110, 153, and 180), PAHs (phenanthrene, pyrene, chrysene, benzo[a]pyrene, and benzo[ghi]perylene) and chlorinated pesticides (DDT 4,4', DDE 4,4', heptachlor epoxide, *cis* chlordane, and *trans* nonachlor).

The analyte solution was created by adding calculated volumes of the concentrated stock solutions to ten liters of clean water, gently mixing, and allowing the carrier solution solvents (*e.g.* methanol and acetone) to volatilize overnight.

Eleven one-liter round-bottom flasks were solvent-rinsed for the experiment. The procedure for solvent rinsing was as follows: the glassware was cleaned in a 10% Extran solution for 24 hours, dried, rinsed with approximately 15 mL methanol, then rinsed with approximately 15 mL DCM, and finally rinsed with 15 mL hexane. Nine round bottom flasks contained PED pieces (approximately 0.6 mg), which were anchored with three inches of copper wire. One flask was a control that contained the analytes of interest but had no PED. One flask was a blank that contained a PED and clean water, but no analytes of interest. The final flask held a thermometer and was gently mixed to monitor the temperature of the experiment. Glass stir bars were employed to minimize adsorption of HOCs. Each round bottom-flask was covered with three thicknesses of paper bags to minimize photodegradation of PAHs (Figure 5.2).

Figure 5.2 K_{PEW} Experimental Set-Up

An experimental control was created by filling a one-liter round bottom flask with 1050 mL of the compound solution. It was stirred for the full length of the experiment. This was to determine whether any losses occurred during the experiment due to volatilization or adsorption on glassware. The glassware from the control was extracted to determine the magnitude of a worst-case scenario HOC adsorption loss.

An experimental blank was prepared by submerging a PED piece on a copper wire in a one-liter round bottom flask filled with 1050 mL of clean water. The blank was stirred with a glass stir bar for one week and then the PED and water were extracted.

A thermometer was secured in a one-liter round-bottom flask that was prepared with clean water with a stirring bar agitating the water to observe whether the constant stirring of the solution increased the temperature.

Two recovery surrogate spiking solutions were prepared, in acetone for the water extraction and in hexane for the PED extraction. The recovery surrogates were created at a concentration of 200 µg/mL and included phenanthrene$_{d10}$, pyrene$_{d10}$, chrysene$_{d12}$, PCB 50, PCB 143, and PCB 189.

PEDs were removed from one of the round bottom flasks on days 1, 3, 10, 30, 44, 45, 46, and 47, to measure the concentration of HOCs in the water and PED phases to follow the time course of absorbtion.

The PED and the water were extracted as follows. The PED and copper wire were removed from the round-bottom flask with tongs and the time was recorded. The PED was separated from the copper wire with tweezers and placed into a 15-mL amber vial. The copper wire was preserved in foil and labeled with the date and flask number. Approximately 5 mL of hexane and 1 mL of the recovery surrogate were added to the amber vial. An additional 8 to 9 mL of hexane were added to the amber vial. The PED was extracted in hexane in a closed hood for 24 hours. The hexane was decanted from the 15-mL amber vial into a 40-mL amber vial, which was labeled and stored in the freezer. Ten to fifteen mL of hexane were again added to the 15-mL amber vial and the PED was extracted in a closed hood for 24 hours. The process was repeated once more for a total of three extractions. All glassware, tweezers, and tongs were solvent rinsed prior to use.

The water was liquid-liquid extracted as follows: 200 μL of the recovery standard (in acetone) were added with a small dial pipette. The round bottom flask was poured into an Extran-cleaned, solvent-rinsed 2-L separatory funnel, which was held upright by a ring stand. 150 mL of dichloromethate (DCM) were poured into the round bottom flask, the flask was rinsed, and the DCM was poured into the separatory funnel. The funnel was shaken for three minutes. The DCM was released from the separatory funnel into a 500-mL round bottom flask, and the procedure was repeated two more times, adding 150-mL of DCM each time. Na_2SO_4 (combusted at 400°C) was added to the DCM extract and the extract was stored in the freezer. All glassware, tongs, and tweezers were solvent rinsed prior to use.

The glassware from flask 9, the control with no PED, was rinsed three times with DCM and decanted into a solvent-rinsed 40-mL amber vial. Round bottom flask 9 was selected because it was the control and would present a worst case should HOCs be adsorbing to the glassware.

The samples were rotary-evaporated to approximately 10 mL and then a gentle nitrogen gas stream was used to evaporate the samples to 3 mL and then they were transferred into a solvent-rinsed conical vial (nitrogen blowdown). Prior to GC-MS analysis, the PED samples were concentrated to 500 µL and the water samples were concentrated to 100 µL. GC-MS analysis was as described below.

The masses of phenanthrene, pyrene, and heptachlor epoxide in the water samples were greater than the calibration standard curve, causing the GC-MS sensor to overload. The higher molecular weight compounds, PCB 153 and PCB 180, were close to detection limits. To remedy this, the water samples were separated into two parts: 90% of the original sample was concentrated to 100 µL (Water A), while the remaining 10% was diluted to 500 µL (Water B).

5.2.2 Calibrations

The GC-MS data for the PED and water extracts were processed using an internal standard and six point calibration curve. The response factor percent relative standard deviations (% RSDs) were typically between 3% and 15%, and always less than 25% (% RSDs = 11%±5.2%).

5.2.3 Data

To evaluate the kinetics, it was presumed that the measured value of the partition coefficient approached the infinite time value (K_{PEW}) asymptotically:

$$K_{part} = K_{pew} - (K_{pew} - K_{part0})e^{-k_e t} \qquad 5.15$$

A least-squares fit of this equation to the measured data was done to determine the best values for K_{PEW} and k_e (Table 5.5).

Table 5.5 Least-Squares Fit for K_{PEW} and k_e

	K_{PEW}	k_e	log K_{PEW}
PCB 52	$3.85 \text{x} 10^5$	0.80	5.59
PCB 70	$7.33 \text{ x} 10^5$	0.68	5.87
PCB 101	$1.37 \text{ x} 10^6$	0.82	6.14
PCB 110	$1.46 \text{ x} 10^6$	0.54	6.16
PCB 153	$5.07 \text{ x} 10^6$	0.57	6.70
PCB 180	$6.28 \text{ x} 10^6$	0.54	6.80
Phenanthrene	$3.79 \text{ x} 10^4$	1.21	4.58
Pyrene	$1.01 \text{ x} 10^5$	3.33	5.01
Chrysene	$6.74 \text{ x} 10^5$	1.47	5.83
Benzo[a]pyrene	$6.31 \text{ x} 10^6$	0.14	6.80
Benzo[ghi]perylene	$1.91 \text{ x} 10^6$	0.12	6.28
DDT	$9.25 \text{ x} 10^5$	0.20	5.97
DDE	$1.92 \text{ x} 10^6$	0.43	6.28
Heptachlor epoxide	$1.28 \text{ x} 10^4$	15.25	4.11
***cis* Chlordane**	$2.93 \text{ x} 10^5$	1.10	5.47
trans Nonachlor	$7.13 \text{ x} 10^5$	0.49	5.85

5.2.4 Results

Using Equation 5.7, the equilibrium constants, K_{PEW}s, were calculated for each of the HOCs of interest. To determine whether equilibrium was achieved for each compound, log (C_{PE}/C_W) was plotted versus the time of extraction (Figures 5.3 – 5.6.) The best-fit equations were plotted with the data from the experiment (Figure 5.3).

The higher molecular weight PCBs (153 and 180) took longer to reach equilibrium (approximately 45 days) and had higher log $K_{PEW}s$. The lower weight PCBs (52 and 70) reached equilibrium fastest (between 30 and 44 days). All PCBs reached equilibrium within the time of the experiment (t=47 days).

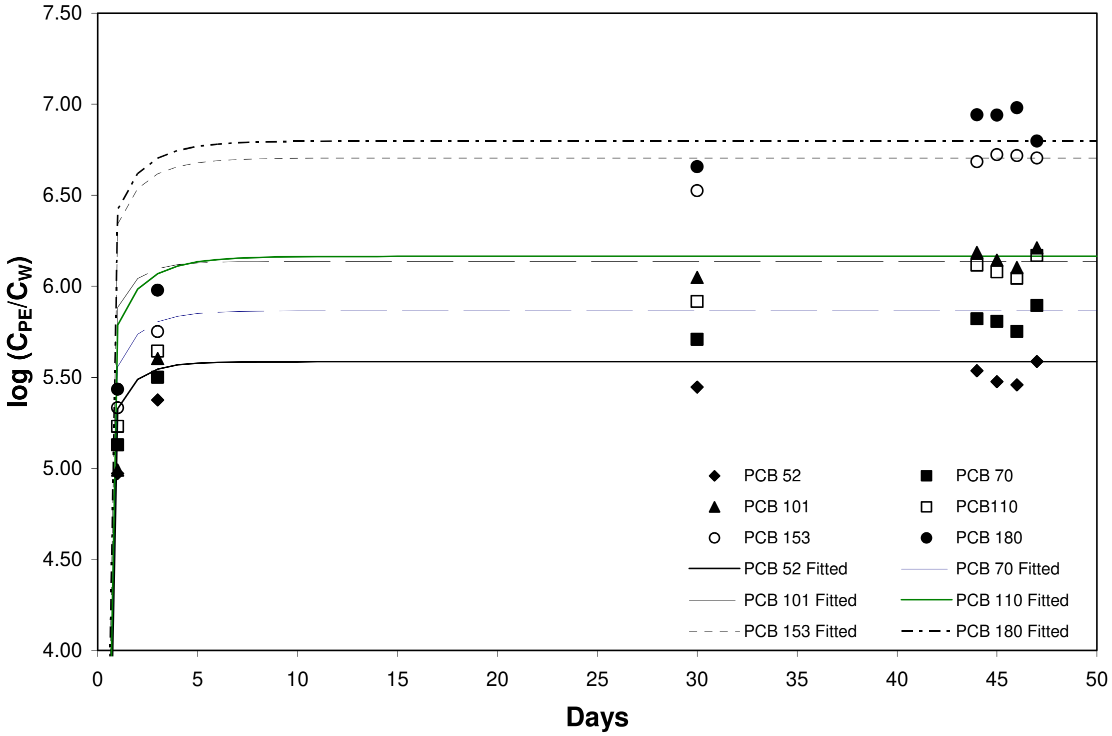


Figure 5.3 Log (C_{PE}/C_W) versus Time for PCBs of Interest

The higher molecular weight PAHs (benzo[a]pyrene and benzo[ghi]perylene) took longer to achieve equilibrium (approximately 45 days) and had higher log K_{PEW}s (Figure 5.4). The lower weight PAHs (phenanthrene and pyrene) reached equilibrium fastest (by t = 30). All PAHs reached equilibrium within the time of the experiment (t=47 days).

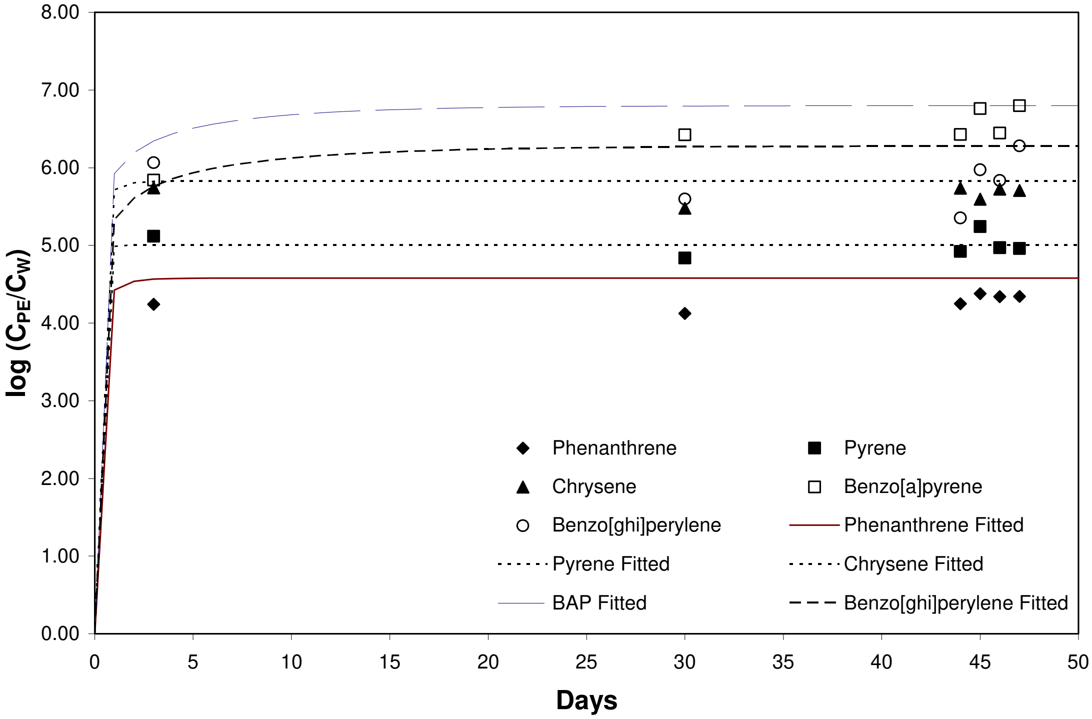


Figure 5.4 Log (C_{PE}/C_W) versus Time for PAHs of Interest

DDE took longer to achieve equilibrium (approximately 45 days) and had a higher log K_{PEW} than DDT, even though DDT has a higher molecule weight than DDE (Figure 5.5). This relationship has also been seen in octanol-water partitioning experiments (Pontolillo and Eganhouse 2005). Both DDT and DDE reached equilibrium within the time of the experiment (t=47 days).

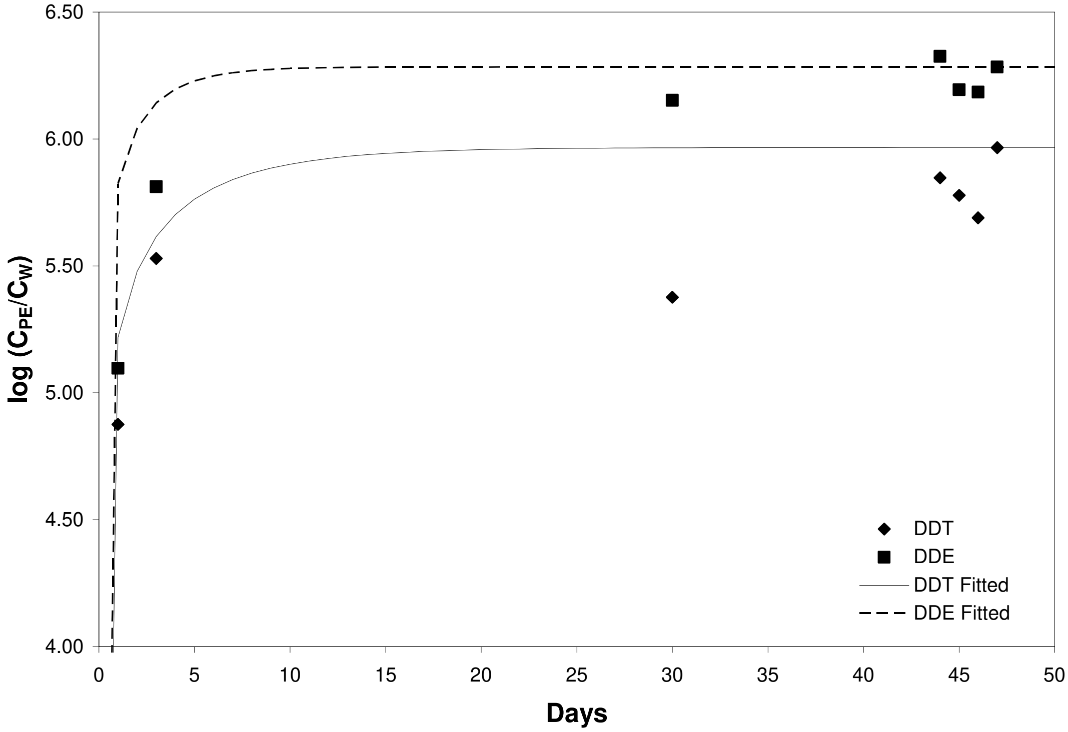


Figure 5.5 Log (C_{PE}/C_W) versus Time for DDT and DDE

The chlordanes responded similarly to the PCBs and PAHs – the higher the molecular weight of the compound, the longer it took to achieve equilibrium (approximately 45 days) and the higher the log K_{PEW}s (Figure 5.6). All chlordanes reached equilibrium within the time of the experiment (t=47 days).

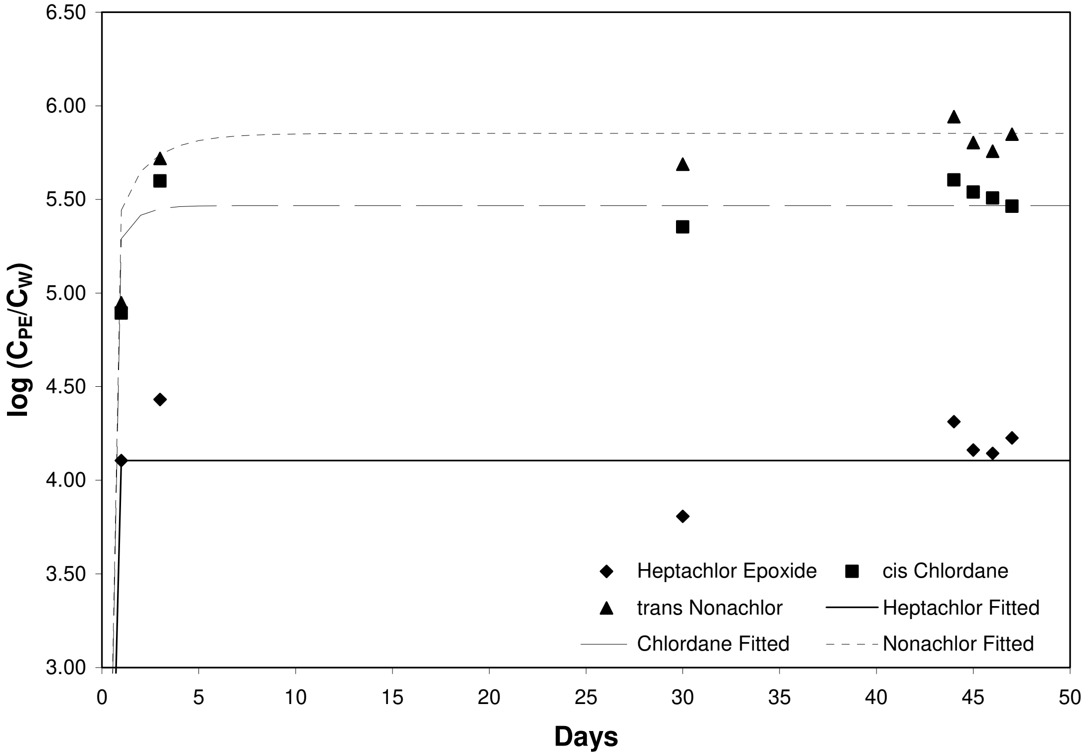


Figure 5.6 Log (C_{PE}/C_W) versus Time for Chlordanes of Interest

The calculated log K_{PEW} values from the experiment were compared with literature values for similar experiments (Table 5.6). The log K_{PEW}s were previously presented in Table 5.5. The log K_{PEW}s were similar to those found in the literature. K_{PEW}s have not previously been measured for PCB 180, DDT, DDE, benzo[ghi]perylene, heptachlor epoxide, *cis* chlordane, or *trans* nonachlor.

Table 5.6 Log K_{PEW} Results Compared with Literature Values

	Log K_{PEW}	**Adams *et.al* 2007**	**Huckins *et.al*1993**	**Muller *et.al* 2001**	**Booij *et.al* 2003**	**Log K_{ow}^{1}**
PCB 52	5.59	5.40	4.60		5.55	5.84
PCB 70	5.87	5.60				6.20
PCB 101	6.14	6.30				6.38
PCB 110	6.16	6.30			6.18	6.48
PCB 153	6.70	6.80				6.92
PCB 180	6.80					7.36
Phenanthrene	4.58	4.23	4.20		4.16	4.57
Pyrene	5.01	5.02		4.62	4.90	5.13
Chrysene	5.83	5.70			5.53	5.81
Benzo[a] pyrene	6.80	6.20			5.94	6.13
Benzo[ghi] Perylene	6.28					6.58
DDT 4,4'	5.97					6.91
DDE 4,4'	6.28					6.96
Heptachlor Epoxide	4.11					4.91
***cis* Chlordane**	5.47					6.10
***trans* Nonachlor**	5.85					6.35

1 – PCBs from Hawker and Connell 1988, PAHs from Schwarzenbach *et.al.* 2002, DDTs from De Bruijn *et.al.*1989, and chlordanes from Simpson *et.al.* 1995

K_{PEW}s measured in the laboratory are summarized in Table 5.6 and were found to correlate with octanol-water partition constants (Figure 5.7, log K_{PEW} = 0.88 log K_{OW} + 0.30, R^2 = 0.88, n=14, p=0.04). The findings suggested that the HOC accumulation in polyethylene correlates with well with the hydrophobicity of specific HOCs.

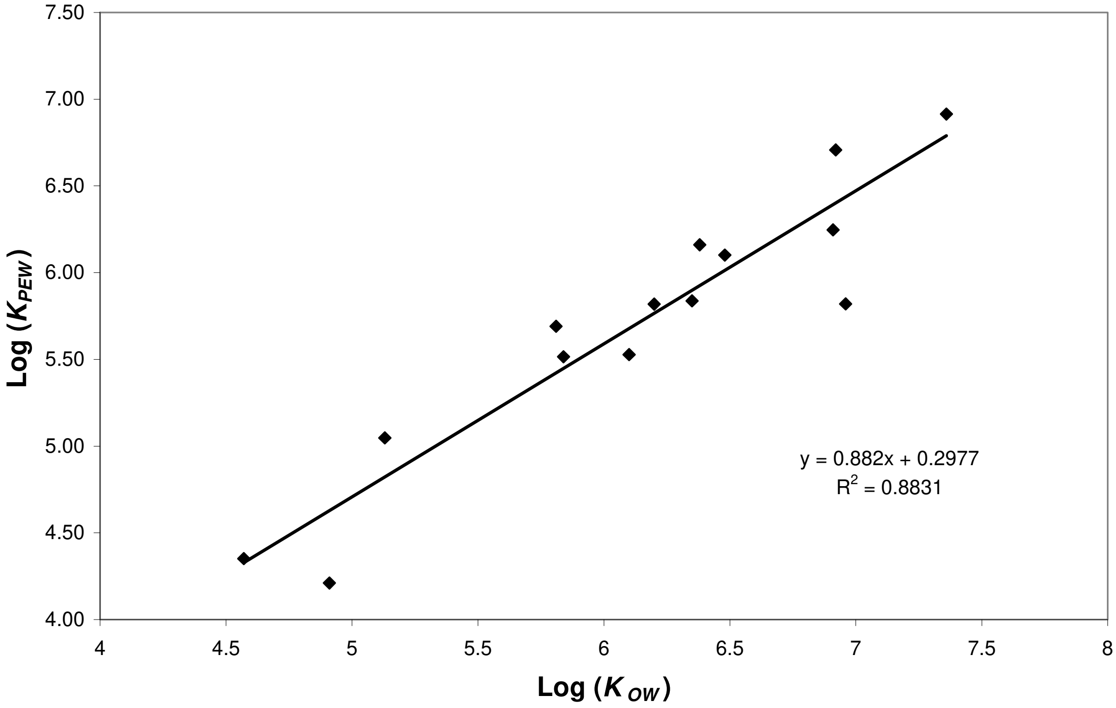


Figure 5.7 Positive Correlation between log K_{PEW} and log K_{OW}

Mean K_{PEW}s (days 44, 45, 46, 47) were positively correlated with octanol-water partition constants (K_{OW}). The Log K_{PEW} versus Log K_{OW}, the K_{PEW} can be estimated by regression:

$$\log K_{PEW} = 0.88 \log K_{OW} + 0.30 \quad 5.16$$

5.2.5 Discussion

The PED and water reached equilibrium by the end of the 45 day experiment, allowing calculation of the equilibrium partition coefficients, K_{PEW}. The log K_{PEW}s displayed a linear relationship with log K_{OW}s, which allows log K_{PEW}s to be estimated for contaminants not studied in this experiment. For example, if PCB 35 were found on the PED after field deployment, the linear relationship could be used to determine the log K_{PEW} from the log K_{ow}, which has been determined by Hawker and Connell (1988).

LMU researchers are currently studying the variation of K_{PEW}s based on thickness of the plastic and the manufacturing process. The PED method is labor intensive, and presents additional opportunities for human error. The slow approach to equilibrium of the PED creates some difficulties. The PED would be best applied without preloading reference compounds with the understanding that the PED-estimated water concentrations are within an order of magnitude of the actual water concentrations.

5.3 PED Exchange Rate Experiment

The objective for the work described in this section was to further investigate exchange rates for the PEDs in a controlled laboratory experiment using hydrophobic organic contaminants (HOCs). To correct for nonequilibrium conditions, preloaded HOC reference compounds were employed (Booij *et.al.*. 1998, 2002; Adams *et.al.* 2007).

5.3.1 Methods

An aqueous solution containing the PED target analytes described for the previous experiment was prepared in 90 L of clean water. The water was continuously stirred with a glass rod bent into a paddle powered by a drill motor controlled by a Variac (Figure 5.8). Reference compounds were preloaded on the PEDS. These compounds were either deuterated versions of the same compounds in the water (pyrene $_{d10}$, phenanthrene$_{d10}$, benzo[a]pyrene $_{d12}$) or compounds of similar characteristics and molecular weight (PCB 51, PCB 155 and PCB 185). This allowed simultaneous determination of adsorption and desorption rate constants, so that they could be compared. The reference compounds chosen were similar to those added in previous SPMD experiments (Booij *et.al.* 1998; Huckins *et.al.* 2002). They were added to the PEDs using an 80:20 methanol-water solution (Booij *et.al.* 2002) prior to exposure. Fifteen PED pieces (approximately 1.0 mg each) were preloaded with the reference compounds. The PEDs were cut approximately in half. Contaminants were extracted from one half to determine the initial preloaded reference compound concentration, and the other half was mounted on a copper wire and inserted into the stock pot. Triplicate PEDs were removed from the stock pot at 2, 7, 14, 30, and 45 days.

Figure 5.8 PED Exchange Rate Experimental Set-Up

One liter of the stock water was extracted on day 0 and day 45; 100 µL of recovery surrogate solution with a concentration of 2000 ng/mL was added to the water and the water was extracted in a 2-L separatory funnel with 150-mL of dichloromethane (procedure previously described). The procedure was repeated three times. Combusted Na_2SO_4 (combusted at 400°C) was added to the DCM extract and frozen overnight.

The PED was extracted in 15mL hexane and 100 µL of the recovery surrogate solution with a concentration of 2000 ng/mL was added (for this experiment the recovery surrogates were anthracene-$_{d10}$, chrysene $_{d12}$, perylene $_{d12}$, PCB 50, PCB 143, and PCB 189). The extraction took place in a hood for 24 hours and was repeated three times.

Procedure blanks for both the water and PED extractions were prepared. For the water extraction blank, clean water spiked with 100 µL 2000ppb recovery surrogates was extracted in a 2-L separatory funnel with 150 mL DCM three times. For the PED procedure blanks, a cleaned PED spiked with 100 µL 2000ppb recovery surrogates was extracted in 15 mL hexane for 24 hours three times, and 15 mL hexane was spiked with 100 µL 2000ppb recovery surrogates and the amber vial was extracted three times.

The samples were rotary-evaporated to approximately 10 mL and then a gentle nitrogen stream was used to evaporate the samples to 2 mL. They were transferred into a solvent-rinsed 2-mL amber micro vial. The PED samples were analyzed at 500 µL, the water samples at 1 mL and 100 µL. GC-MS analysis was as described previously.

5.3.2 Data

The samples were processed using GC-MS (Table 5.7). The PED samples had volumes of 500 µL, recovery surrogate standard concentration of 2000 ng/mL, and a recovery surrogate standard volume of 100 µL. Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

Table 5.7 PED Raw Data for Compounds Added to the Water (ng/mL)

Days	**2**			**7**			**14**		
Analytes	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**	**PED 7**	**PED 8**	**PED 9**
PCB 52	135	182	98.6	206	44.0	157	337	211	294
PCB 70	60.3	96.2	46.2	79.0	26.9	68.4	184	97.9	188
PCB 101	45.0	55.0	31.6	51.8	21.4	42.6	117	78.0	91.9
PCB 110	42.2	64.4	29.7	66.6	41.9	57.2	137	79.9	113
PCB 153	84.8	77.7	72.4	114	94.3	93.7	174	118	142
PCB 180	87.1	95.6	82.6	74.6	94.3	66.0	125	95.8	131
Phenanthrene	43.8	38.5	37.0	53.9	14.8	34.6	82.7	41.3	65.8
Pyrene	51.5	47.5	34.1	78.0	9.46	50.3	97.1	55.2	69.9
Chrysene	66.1	72.6	54.1	139	34.8	91.6	225	153	154
Benzo[a] pyrene	86.9	98.3	68.5	124	58.7	77.8	154	109	139
Benzo[ghi] perylene	81.3	85.5	72.2	124	232	101	175	117	122
DDT 4,4'	86.9	145	77.1	115	355	90.6	209	107	165
DDE 4,4'	62.2	62.6	61.9	108	54.5	91.3	176	140	145
Heptachlor Epoxide	48.7	67.0	37.8	51.4	20.7	41.0	86.8	51.3	82.3
cis Chlordane	28.7	34.6	20.4	33.2	16.3	28.5	52.7	41.7	45.8
trans Nonachlor	19.0	28.0	13.2	29.2	5.05	21.9	52.0	31.6	44.6

Table 5.7 PED Raw Data for Compounds Added to the Water (ng/mL) (continued)

Days	**30**			**45**		
Analytes	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
PCB 52	319	310	253	347	321	322
PCB 70	215	208	164	232	234	216
PCB 101	155	166	110	171	179	165
PCB 110	163	177	119	173	195	176
PCB 153	133	192	172	154	171	199
PCB 180	153	145	132	128	161	125
Phenanthrene	53.7	82.5	62.4	75.8	72.3	61.9
Pyrene	80.9	93.2	72.9	126	129	131
Chrysene	85.6	134	90.6	139	126	150
Benzo[a] pyrene	142	149	211	173	187	144
Benzo[ghi] perylene	191	181	116	189	226	175
DDT 4,4'	181	201	125	198	220	217
DDE 4,4'	167	165	118	177	152	115
Heptachlor Epoxide	118	111	103	127	120	142
***cis* Chlordane**	79.9	71.5	56.7	85.1	82.6	93.6
***trans* Nonachlor**	9.36	25.7	22.5	29.7	24.4	27.9

The kinetics of absorbtion were assumed to follow:

$$C_{PEt} = (C_{PE\infty})(1 - e^{-k_e t}) \qquad 5.17$$

A least squares fit of this equation to the data was performed to determine K_{PEW} and k_e absorb (Table 5.8).

Table 5.8 K_{PEW} and k_e Absorb Determined by Least Squares Fit

Analytes	**Log K_{PEW}**	**k_e**
PCB 52	5.51	0.293
PCB 70	5.68	0.093
PCB 101	5.97	0.056
PCB 110	5.97	0.072
PCB 153	6.21	0.241
PCB 180	6.43	1.48
Phenanthrene	4.51	0.503
Pyrene	5.00	0.211
Chrysene	5.72	0.291
Benzo[a]pyrene	6.21	0.229
Benzo[ghi]perylene	5.92	0.182
DDT 4,4'	5.51	0.255
DDE 4,4'	6.16	0.248
heptachlor epoxide	4.83	0.137
***cis* chlordane**	5.14	0.117
***trans* nonachlor**	4.75	0.983

Determinations and calculations were also made for the preloaded reference compounds to determine the desorption constants. The initial concentrations were determined by extraction and analysis of half-portions of the PEDs after preloading (Table 5.9). Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

The final concentrations were determined by extraction and analysis of half-portions of the PEDs after preloading and exposure to the contaminated water (Table 5.10). Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

Table 5.9 Concentrations in Extracts from the Preloaded Reference Compounds (Initial, ng/mL)

Initial	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{d10}$	225	262	261	294	254	252	222	247	247
Pyrene $_{d10}$	28.7	21.3	21.2	27.8	19.3	19.6	20.0	21.0	21.0
Benzo[a]pyrene $_{d12}$	59.6	44.4	58.3	84.6	68.4	70.3	52.0	63.4	63.4
PCB 51	42.6	43.3	44.7	54.1	50.7	45.0	35.7	45.8	45.8
PCB 155	19.0	16.7	13.9	17.4	19.6	20.3	22.9	17.5	17.5
PCB 185	83.7	77.5	62.1	84.9	83.1	75.9	80.7	79.1	79.1

Table 5.9 Concentrations in Extracts from the Preloaded Reference Compounds (Initial, ng/mL) (continued)

Initial	**10**	**11**	**12**	**13**	**14**	**15**
Phenanthrene $_{d10}$	247	247	222	234	247	247
Pyrene $_{d10}$	21.0	21.0	12.4	18.8	21.0	21.0
Benzo[a]pyrene $_{d12}$	63.4	63.4	51.8	80.8	63.4	63.4
PCB 51	45.8	45.8	61.3	34.5	45.8	45.8
PCB 155	17.5	17.5	11.9	16.0	17.5	17.5
PCB 185	79.1	79.1	93.8	70.3	79.1	79.1

Table 5.10 PED Final Concentrations of the Preloaded Compounds (ng/mL)

Final	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{d10}$	217	255	243	189	1633	198	171	202	211
Pyrene $_{d10}$	15.4	21.1	19.1	14.3	32.2	13.2	10.9	13.7	15.9
Benzo[a]pyrene $_{d12}$	39.3	39.5	40.5	28.9	425	33.5	25.2	46.8	52.1
PCB 51	40.4	38.9	43.0	43.0	120	34.6	25.1	39.2	28.6
PCB 155	15.4	10.6	13.2	12.8	29.3	14.4	13.0	17.1	12.2
PCB 185	67.6	69.6	40.5	35.6	257	44.2	32.9	37.1	24.8

Table 5.10 PED Final Concentrations of the Preloaded Compounds (ng/mL) (continued)

Final	**10**	**11**	**12**	**13**	**14**	**15**
Phenanthrene $_{d10}$	14.0	19.3	14.0	10.0	4.69	6.29
Pyrene $_{d10}$	12.6	7.17	6.08	6.57	5.40	4.79
Benzo[a]pyrene $_{d12}$	12.8	17.5	13.6	9.18	7.96	17.0
PCB 51	12.7	8.46	13.2	23.6	12.5	17.5
PCB 155	10.8	7.93	10.4	7.00	6.43	7.49
PCB 185	17.8	14.3	16.3	23.3	19.5	15.0

The desorption rate constant, k_e desorb, and K_{PEW} were determined by finding a least squares best fit between Equation 5.18 and the measured concentrations of the analytes on the polyethylene (Table 5.11).

$C_{PEt=2\ meas}$ (ng/mg) was the average of the chemical concentrations measured on the PEDs for Day 2, $C_{PEt=7\ meas}$ (ng/mg) was the average of the chemical concentrations measured on the PEDs for Day 7, etc. $C_{PEt\ calc}$ (ng/mg) was the calculated by the equation:

$$C_{PEt_{calc}} = C_{PEo}(e^{-k_e t}) + C_{PE\infty}(1 - e^{(-k_e t)}) \qquad 5.18$$

Table 5.11 k_e Desorb Using a Least Squares Fit

	ke
Phenanthrene $_{d10}$	0.154
Pyrene d_{10}	0.202
Benzo[a]pyrene $_{d12}$	0.435
PCB 51	0.191
PCB 155	0.401
PCB 185	0.489

5.3.3 Data Processing

Recovery surrogates were used for the water and the PED, both initial and final. The water extract recoveries were 82.4%±14.4%, 98.4%±16.1%, 88.1%±11.6%, 94.0%±16.3%, 97.8%±21.7%, and 93.8%±11.0% for PCB 50, 143, 189, anthracene $_{d10}$, chrysene $_{d12}$, and perylene $_{d12}$ respectively. Recoveries for the final PEDs (PEDs used in the experiment) were 81.7%±9.56%, 92.8%±9.65%, 93.4%±9.55%, 75.6%±8.02%, 95.1%±6.81%, and 88.5%±16.18%, for anthracene $_{d10}$, chrysene $_{d10}$, perylene$_{d12}$, PCB

50, PCB 143, and PCB 189, respectively. The recoveries for the initial PEDs (the PEDs extracted at the beginning of the experiment to test the preloaded compounds) were were 93.7%±11.7%, 89.4%±13.0%, 104.%±13.2%, 82.8%±7.35%, 106.%±8.11%, and 89.1%±13.8%, for anthracene $_{d10}$, chrysene $_{d10}$, perylene$_{d12}$, PCB 50, PCB 143, and PCB 189, respectively.

Procedure blanks were performed as extraction replicates, both PED and water extraction methods were tested without compounds of interest and with clean polyethylene. The results from these blanks indicated contamination from the laboratory or the procedure were negligible.

5.3.4 Results

The fitted curve for C_{PEt} for days 0 through 50 and the average measured values for each day were plotted (Figures 5.9 through 5.15). The standard deviations are presented as error bars. With the exception of a couple of outliers in the lower molecular weight compounds (PCB 52, phenanthrene, pyrene), the data matched the fitted line within one standard deviation.

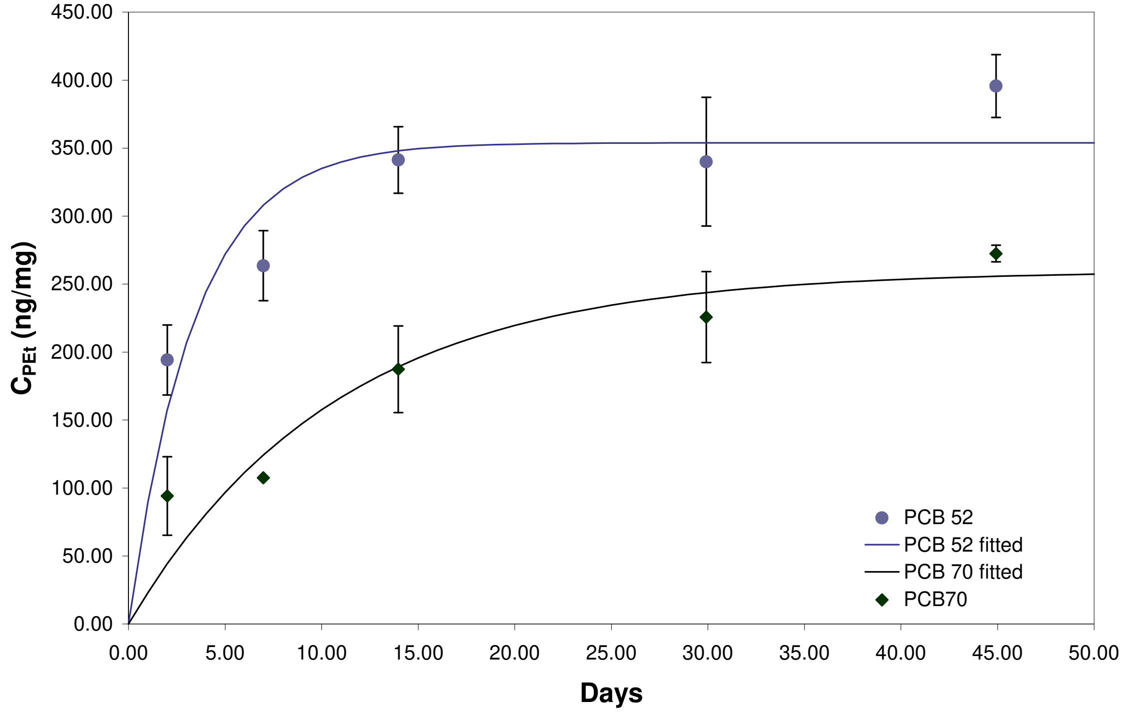


Figure 5.9 PCB 52 and PCB 70 with Fitted Lines

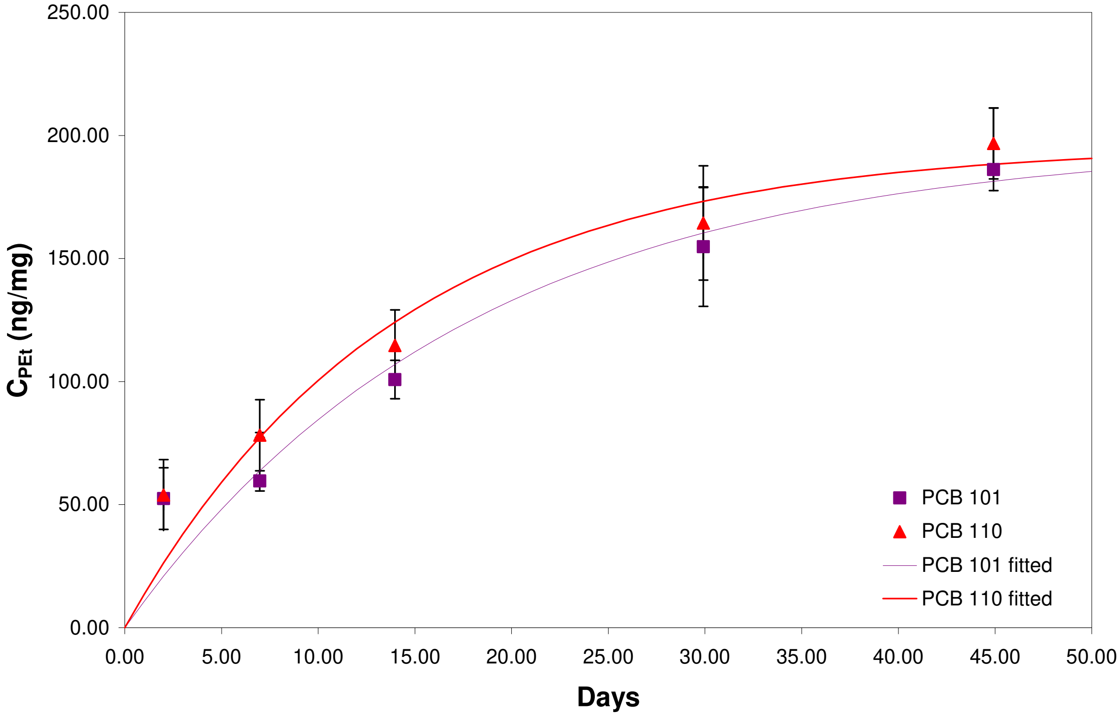


Figure 5.10 PCB 101 and PCB 110 with Fitted Lines

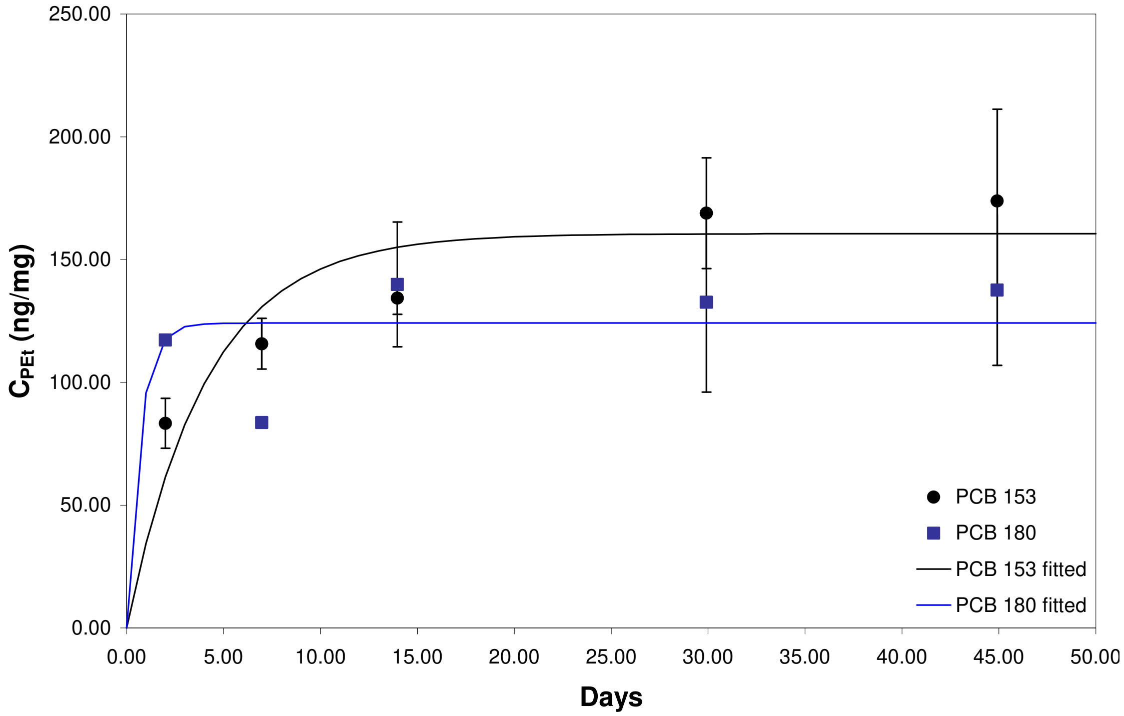


Figure 5.11 PCB 153 and PCB 180 with Fitted Lines

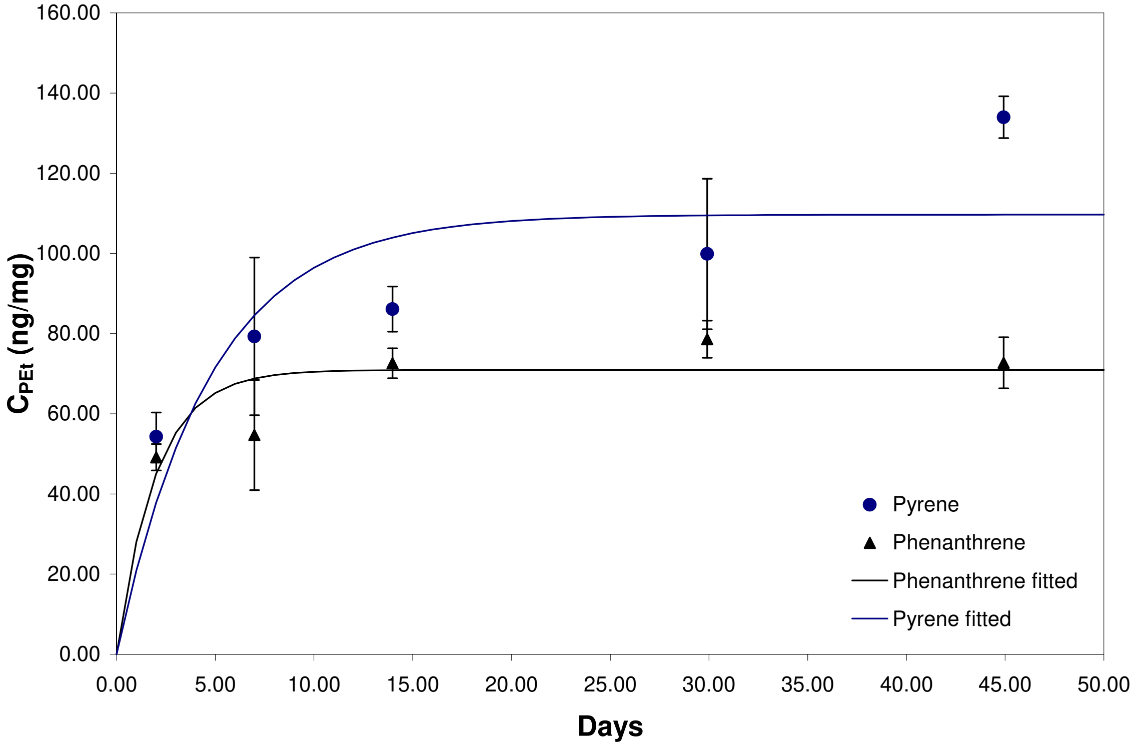


Figure 5.12 Phenanthrene and Pyrene with Fitted Lines

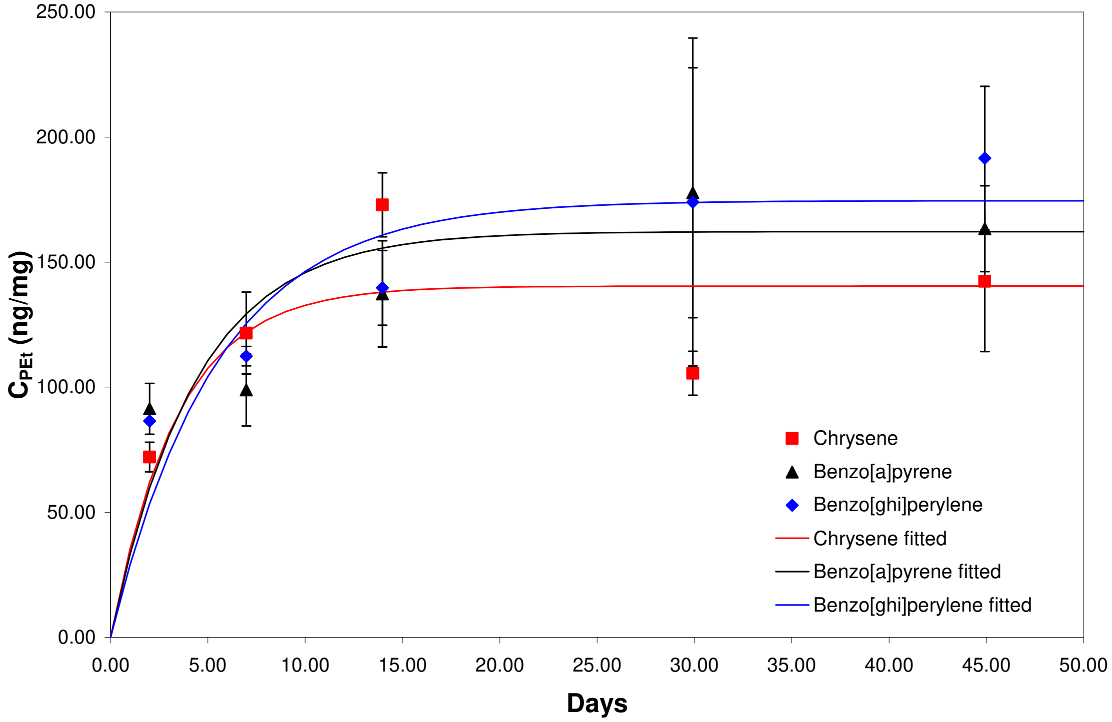


Figure 5.13 Chrysene, Benzo[a]pyrene, and Benzo[ghi]perylene with Fitted Lines

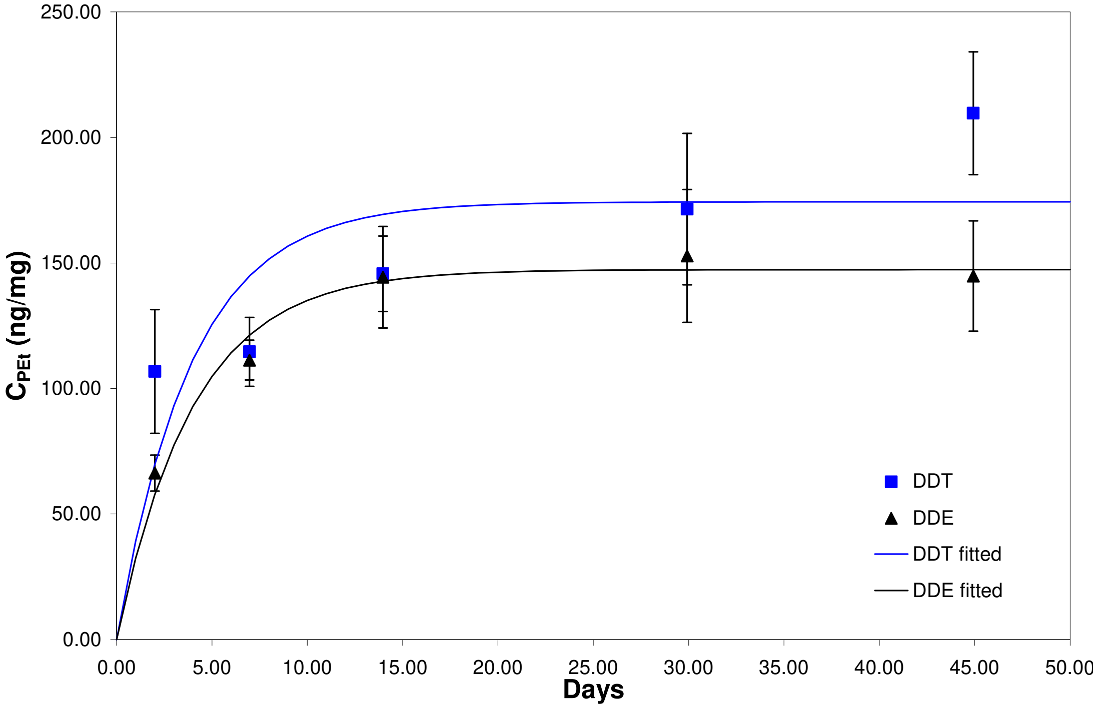


Figure 5.14 DDE and DDT with Fitted Lines

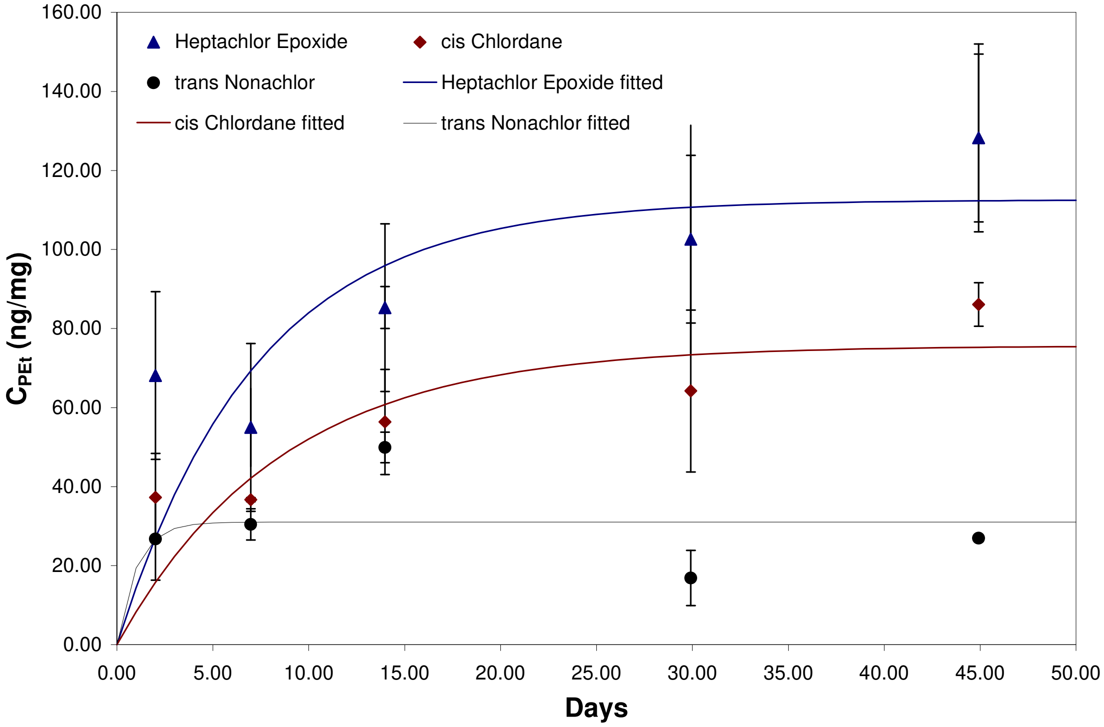


Figure 5.15 Heptachlor Epoxide, *cis* Chlordane, *trans* Nonachlor with Fitted Lines

The desorption rate constants were calculated using the equations and data presented above and were then compared to the absorption rate constants (Table 5.12).

Table 5.12 Comparison of the Absorption and Desorption Rate Constants

Preloaded Compound	k_e desorb	k_e desorb Plus St Dev	k_e desorb Minus St Dev	Compound of Interest	k_e absorb
Phenanthrene $_{d10}$	0.15	0.11	0.21	**Phenanthrene**	0.50
Pyrene $_{d10}$	0.20	0.13	0.28	**Pyrene**	0.21
Benzo[a]pyrene $_{d12}$	0.44	0.37	0.51	**Benzo(a)pyrene**	0.23
PCB 51	0.19	0.12	0.27	**PCB 52**	0.29
PCB 155	0.40	0.23	0.65	**PCB 153**	0.24
PCB 185	0.49	0.30	0.80	**PCB 180**	1.48

The desorption rate constants were within a standard deviation for all but two of the preloaded reference compounds (phenanthrene $_{d10}$ and PCB 185).

Another way of evaluating the dependability of the PEDs for measuring water concentrations is to determine the error likely if they are used to measure water concentrations. The desorption rate constants were used to calculate $1\text{-}e^{-kt}$ to correct for nonequilibrium conditions and calculate C_w (Table 5.13) as in Equation 5.12.

Table 5.13 The Estimated C_w (ng/L) Based on the Desorption Rate Constants

C_w (ng/L)	**$(1\text{-}e^{-kt})$**	**C_w Estimated**	**C_w Experimental**
Phenanthrene $_{d10}$	0.27	5756	2005
Pyrene $_{d10}$	0.33	1640	971
Benzo[a]pyrene $_{d12}$	0.58	102	106
PCB 51	0.32	1873	1045
PCB 155	0.55	93.9	98.2
PCB 185	0.63	69.1	54.8

The C_w values predicted by the desorption rate constants were greater than the C_w data measured in the laboratory experiment. However, conducting a similar calculation for the absorption rate constants demonstrates that these rates also overestimate the water concentrations (C_w ng/L) (Table 5.14).

Table 5.14 The Estimated C_w (ng/L) Based on the Absorption Rate Constants

C_w (ng/L)	**$(1\text{-}e^{-kt})$**	**C_w Estimated**	**C_w Experimental**
Phenanthrene	0.64	2413	2005
Pyrene	0.35	1579	971
Benzo[a]pyrene	0.37	161	106
PCB 52	0.45	1340	1045
PCB 153	0.38	135	98.2
PCB 180	0.95	45.6	54.8

It was thus determined that this method of kinetic correction for non-equilibrium cases typically overestimates water concentrations by a factor of two or less.

5.3.5 Discussion

Utilizing the kinetics assumptions presented in this section a first order kinetics equation can be used to calculate the exchange rate constant, k_e, for both desorption and absorption. The absorption and desorption rate constants were within plus or minus a standard deviation for all but two preloaded reference compounds (phenanthrene $_{d10}$ and PCB 185); therefore, the absorption and desorption rate constants can be assumed as equal and the $C_{PE\infty}$ for the chemical of interest can be calculated with Equation 5.11.

Alternatively, this equation was substituted for $C_{PE\infty}$ in the initial K_{PEW} equation. It was assumed that there was no initial HOC contamination of the preloaded compounds on the polyethylene. This yielded Equation 5.12.

The estimated C_W by both the absorption and desorption rate constants were within a multiple of two greater than the C_W measured in the laboratory experiment. This indicated that this method of correcting for non-equilibrium conditions was applicable to a reasonable approximation.

5.4 SPME/PED Laboratory Comparison Experiment

The objective for the work described in this section was to compare the PEDs with the Solid Phase Microextraction Devices (SPMEs) in a controlled laboratory experiment.

The PED/SPME comparison study was conducted at SCCWRP using equipment from both LMU and SCCWRP. I designed the experiment, set up the experiment, and supervised the experiment. On the final day of this experiment, liquid-liquid extraction support was provided by SCCWRP employees Wenjian Lao, David Tsukada, and Xiang-Zhou Meng. Mr. Tsukada also provided support with the concentrating of the water and PED samples from this experiment.

The goals of the PED/SPME comparison study were to determine the sensitivity and accuracy of the SPME (100 µm PDMS) and the PED (30 µm LDPE). First, the two samplers were compared in the laboratory under controlled conditions, with varying HOC concentrations, with known water concentrations. Then the samplers were compared in Ballona Creek (as described in the next section), with an Infiltrex 100 system deployed simultaneously, to determine which sampler exhibited greater sensitivity for low dissolved HOC concentrations.

5.4.1 Methods

The laboratory comparison was conducted in 5 20-L carboys. Four held a series of concentrations of the analytes of interest increasing by 1 order of magnitude at each step (Table 5.15), three PEDs (each weighing approximately 2 g), and 3 SPMEs. The fifth carboy served as a blank. The carboys were wrapped in foil and continuously stirred for 45 days (Figure 5.16). Temperature in the laboratory was monitored daily throughout the experiment.

Figure 5.16 PED/SPME Laboratory Comparison Experimental Set-Up

Table 5.15 Estimated Final Water Concentrations for Each Carboy

	Carboy 1	Carboy 2	Carboy 3	Carboy 4
PCB 52	0.01	0.1	1	10
PCB 101	0.01	0.1	0.1	1
PCB 153	0.001	0.01	0.1	1
PCB 180	0.001	0.005	0.01	0.05
Phenanthrene	0.1	1	10	100
Pyrene	0.01	0.1	1	10
Benzo[a]pyrene	0.001	0.01	0.1	1
DDE 4,4'	0.001	0.01	0.1	1
***cis* Chlordane**	0.01	0.1	1	10

Each PED was removed from the carboy, placed into a solvent-rinsed BOD bottle, and the time was recorded. Approximately 300mL of DCM was added to the BOD bottle, submerging the PED in DCM. Recovery surrogates were added – 500 pg/µL final concentration (anthracene-$_{d10}$, chrysene-$_{d12}$, perylene-$_{d12}$, PCB 50, PCB 143, and PCB 189). The PED was extracted twice for 24 hours. Depending on the concentrations in the carboy, the PED extracts were concentrated to different final volumes as follows:

- Carboy 1 (PEDs 1, 2, 3) – final volume 25 µL
- Carboy 2 (PEDs 4, 5, 6) – final volume 100 µL
- Carboy 3 (PEDs 7, 8, 9) – final volume 1 mL
- Carboy 4 (PEDs 10, 11, 12) – final volume 1 mL
    - concentrated to 1 mL then 100 µL of this was added to 900-µL hexane (10% of the concentration)
- Carboy Blank (PEDs 13, 14, 15) – final volume 25 µL

All PED extracts were injected in GC-MS. A procedure blank (no PED) was conducted and concentrated to 25 µL.

To determine concentrations in the water phase, for Carboy 1 (Concentration range 0.001 – 0.1* ng/L), all 20 L were extracted in 1.5-L increments (13 total), each increment was extracted three times with 150 mL of DCM, for a total of 450 mL DCM. The first three 1.5-L extracts were saved and concentrated to 25 µL. Each extract was manually injected into an electron capture detector (ECD) (4 µL required from each sample). The remaining 15.5 L were extracted and concentrated to 25 µL, which was combined with the 3 – 1.5 L extracts (21 µL each). This was concentrated to 25 µL, and manually injected in an ECD and a GC-MS. Recovery surrogates added were 10 µL of PCB 30 and 205 and 10 µL of anthracene $_{d10}$, chrysene $_{d12}$, and perylene $_{d12}$.

For the water phase of Carboy 2 (Concentration range 0.005 – 1 ng/L), three 1.5L extracts were made and concentrated to 25 µL. Each was manually injected into an

ECD (4 µL required from each sample). Each was also manually injected in the GC-MS (to possibly determine phenanthrene and pyrene). Recovery surrogates added were 125 µL of PCB 30 and 205, and 125 µL of anthracene-$_{d10}$, chrysene-$_{d12}$, and perylene-$_{d12}$.

For the water phase of Carboy 3 (Concentration range 0.01 – 10* ng/L), all 20 L were extracted, in 1.5-L increments (13 total). The first three 1.5-L extracts were saved and concentrated to 25 µL. Each was manually injected into the ECD (4 µL required from each sample). The remaining 15.5 L were extracted and concentrated to 25 µL, combined with 3 – 1.5 L extracts (21 µL each), concentrated to 25 µL, and manually injected into the ECD and the GC-MS. Recovery surrogates added were 125 µL of PCB 30 and 205, only to the first 3 extractions, and 10 µL of anthracene-$_{d10}$, chrysene-$_{d12}$, and perylene-$_{d12}$, added to all extracts.

For the water phase of Carboy 4 (Concentration range 1 – 100* ng/L), three 1.5-L extracts were made and concentrated to 25 µL. Each was manually injected into the ECD (4 µL required from each sample) and manually injected into the GC-MS. Recovery surrogates added were 125 µL of PCB 30 and 205, and 125 µL of anthracene-$_{d10}$, chrysene-$_{d12}$, and perylene-$_{d12}$.

For the water phase of Carboy 5, the blank, all 20 L were extracted, in 1.5-L increments (13 total) to determine whether there was any background concentration. The first three 1.5-L extracts were saved and concentrated to 25 µL. Each was manually injected into the ECD (4 µL required from each sample). The remaining 15.5 L were extracted and concentrated to 25 µL, combined with 3 – 1.5-L extracts (21 µL each), concentrated to 25 µL, and manually injected in the ECD and the GC-MS. Recovery surrogates added were 10 µL of PCB 30 and 205 and 10 µL of anthracene-$_{d10}$, chrysene-$_{d12}$, and perylene-$_{d12}$.

5.4.2 Data

5.4.2.1 SPME Data

SPME data were reported from the GC-MS as masses (pg) because the SPME fiber is injected directly into the GC-MS and the mass the GC-MS detects is all the mass that is in on the SPME fiber. The raw data from the laboratory SPMEs are presented in Table 5.16. Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

Three SPMEs were used in each carboy. The averages and standard deviations of the data from each SPME in each carboy are presented in Table 5.17.

Table 5.16 Mass of Contaminant on SPMEs (From GC-MS) (pg)

n_f	**Carboy 1**			**Carboy 2**			**Carboy 3**		
Phenanthrene	0.00	0.00	0.00	31.8	38.4	36.9	223		203
Pyrene	0.00	0.00	0.00	11.5	8.87	14.9	59.9		52.6
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	55.0		54.2
PCB52	0.00	0.00	0.00	49.9	64.6	68.7	510		467
PCB101	0.00	0.00	0.00	31.8	20.7	24.5	180		157
PCB153	0.00	0.00	0.00	0.00	0.00	0.00	441		457
PCB180	0.00	0.00	0.00	0.00	0.00	0.00	109		91.2
***cis* Chlordane**	0.00	0.00	0.00	94.7	92.7	110	699		639
DDE	0.00	0.00	0.00	59.9	45.7	46.6	328		301

Table 5.16 Mass of Contaminant on SPME (From GC-MS) (Continued) (pg)

n_f	**Carboy 4**			**Carboy 5 Blank**		
Phenanthrene	1524	1524	1398	0.00	0.00	0.00
Pyrene	410	396	345	0.00	0.00	0.00
Benzo[a]pyrene	395	342	255	0.00	0.00	0.00
PCB52	3352	3592	3453	0.00	0.00	0.00
PCB101	517	459	421	0.00	0.00	0.00
PCB153	791	975	730	0.00	0.00	0.00
PCB180	112	237	94.8	0.00	0.00	0.00
***cis* Chlordane**	4253	5048	4401	0.00	0.00	0.00
DDE	857	1386	814	0.00	0.00	0.00

Table 5.17 SPME Predicted Water Concentrations (ng/L)

ng/L	**Carboy 1**	**Carboy 2**	**Carboy 3**	**Carboy 4**
Phenanthrene	0.00	8.71 ± 0.85	52.0 ± 3.54	361 ± 17.8
Pyrene	0.00	0.94 ± 0.24	4.48 ± 0.41	30.5 ± 2.72
Benzo[a]pyrene	0.00	0.00	0.26 ± 0.00	1.59 ± 0.34
PCB 52	0.00	0.37 ± 0.06	2.97 ± 0.18	21.0 ± 0.73
PCB101	0.00	0.10 ± 0.02	0.67 ± 0.07	1.85 ± 0.19
PCB153	0.00	0.00	0.32 ± 0.01	0.59 ± 0.09
PCB180	0.00	0.00	0.08 ± 0.02	0.09 ± 0.05
***cis* Chlordane**	0.00	0.81 ± 0.08	5.48 ± 0.34	37.4 ± 3.46
DDE	0.00	0.07 ± 0.01	0.41 ± 0.02	1.32 ± 0.41

5.4.2.2 PED Data

The raw PED data are presented in the Table 5.18. The PAHs were processed using GC-MS. The PCBs, DDTs, and chlordanes were processed using GC-ECD. Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

Three PEDs were used in each carboy. The averages and standard deviations of the data from each PED in each carboy are presented in Table 5.20.

Table 5.18 PED Raw Data (ng/mL)

	Procedure	Carboy 1			Carboy 2		
ng/mL	**PED Blank**	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**
Phenanthrene	0.00	658	622	632	926	869	994
Pyrene	0.00	44.9	45.6	37.6	430	281	365
Benzo[a] pyrene	0.00	50.3	45.1	46.7	1073	1007	1226
PCB52	0.00	387	399	327	1432	921	1234
PCB101	0.00	266	295	276	547	317	187
PCB153	0.00	822	804	847	1914	1234	1995
PCB180	0.00	704	663	866	1779	1566	1514
***cis* Chlordane**	0.00	342	250	250	1280	706	1099
DDE	0.00	60.9	41.9	51.0	754	447	711

Table 5.18 PED Raw Data (ng/mL) (continued)

	Carboy 3			Carboy 4			Carboy 5 Blank		
ng/mL	**PED 7**	**PED 8**	**PED 9**	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
Phenanthrene	682	567	535	4162	4314	3895	0.00	0.00	0.00
Pyrene	289	278	264	2092	2515	2765	0.00	0.00	0.00
Benzo[a] pyrene	1008	775	779	7552	9013	8257	0.00	0.00	0.00
PCB52	1055	964	920	8967	5800	4752	0.00	0.00	0.00
PCB101	361	309	318	3148	3451	2690	0.00	0.00	0.00
PCB153	1597	1187	1457	10246	15682	8827	0.00	0.00	0.00
PCB180	325	282	199	1918	1482	1241	0.00	0.00	0.00
***cis* Chlordane**	883	794	762	8099	4997	7000	0.00	0.00	0.00
DDE	570	473	497	4938	4827	4393	0.00	0.00	0.00

Table 5.19 The Estimated C_W (ng/L) Calculated from the PED Concentrations

ng/L	**Carboy 1**			**Carboy 2**		
Compound	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**
Phenanthrene	0.39	0.40	0.37	2.29	2.61	2.52
Pyrene	0.01	0.01	0.01	0.27	0.21	0.23
Benzo[a]pyrene	0.00	0.00	0.00	0.02	0.03	0.03
PCB52	0.02	0.02	0.01	0.27	0.21	0.23
PCB101	0.00	0.00	0.00	0.02	0.02	0.01
PCB153	0.00	0.00	0.00	0.02	0.02	0.02
PCB180	0.00	0.00	0.00	0.01	0.01	0.01
***cis* Chlordane**	0.01	0.01	0.01	0.23	0.15	0.20
DDE	0.00	0.00	0.00	0.03	0.02	0.03

Table 5.19 Cont, The Estimated C_W (ng/L) Calculated from the PED Concentrations

ng/L	**Carboy 3**			**Carboy 4**			**Carboy 5 Blank**		
Compound	**PED 7**	**PED 8**	**PED 9**	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
Phenanthrene	16.2	13.6	13.9	108	112	114	0.00	0.00	0.00
Pyrene	1.74	1.69	1.75	13.8	16.6	20.6	0.00	0.00	0.00
Benzo[a] pyrene	0.20	0.15	0.17	1.64	1.96	2.02	0.00	0.00	0.00
PCB52	1.88	1.73	1.80	17.5	11.3	10.4	0.00	0.00	0.00
PCB101	0.14	0.12	0.14	1.35	1.49	1.30	0.00	0.00	0.00
PCB153	0.17	0.12	0.17	1.16	1.79	1.13	0.00	0.00	0.00
PCB180	0.02	0.02	0.02	0.16	0.12	0.11	0.00	0.00	0.00
***cis* Chlordane**	1.52	1.38	1.45	15.3	9.47	14.9	0.00	0.00	0.00
DDE	0.19	0.16	0.18	1.82	1.79	1.83	0.00	0.00	0.00

Table 5.20 Average and Standard Deviation of PED-Predicted Water Concentrations (ng/L)

ng/L	Carboy 1	Carboy 2	Carboy 3	Carboy 4
Phenanthrene	0.39 ± 0.02	2.47 ± 0.16	14.6 ± 1.41	112 ± 3.07
Pyrene	0.01 ± 0.00	0.24 ± 0.03	1.72 ± 0.03	17.0 ± 3.40
Benzo[a]pyrene	0.00 ± 0.00	0.02 ± 0.00	0.17 ± 0.02	1.87 ± 0.21
PCB 52	0.02 ± 0.00	0.24 ± 0.03	1.80 ± 0.07	13.1 ± 3.83
PCB101	0.00 ± 0.00	0.02 ± 0.01	0.13 ± 0.01	1.38 ± 0.09
PCB153	0.00 ± 0.00	0.02 ± 0.00	0.15 ± 0.02	1.36 ± 0.37
PCB180	0.00 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.13 ± 0.02
***cis*-Chlordane**	0.01 ± 0.00	0.20 ± 0.04	1.45 ± 0.07	13.2 ± 3.27
DDE	0.00 ± 0.00	0.02 ± 0.00	0.18 ± 0.02	1.81 ± 0.02

5.4.2.3 Water Data

The water was extracted using a liquid-liquid extraction as described above. The PAHs were manually injected on the GC-MS and the PCBs and chlorinated pesticides were manually injected on the GC-ECD. To test the recoveries, the first three 1.5-L extracts of each carboy were saved individually, concentrated to 25 μL, and manually injected on the GC-ECD; therefore, triplicate data were averaged. The average and the standard deviation of the PCBs and chlorinated pesticides (from GC-ECD) and the PAH data (from GC-MS) are presented in Table 5.21. Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

As described previously, each carboy was treated differently depending on the expected concentrations in the carboys. All 20 L of carboys 1, 3, and the blank were extracted, with the first three 1.5-L extracts saved individually, concentrated to 25 μL, and manually injected on the GC-ECD. Three 1.5-L extracts were extracted from carboys 2 and 4, concentrated to 25 µL, and manually injected on GC-ECD and GC-MS. On the PAH side, all extracts were combined and concentrated to 25 µL, including the three 1.5-L extracts of carboy 2, except for carboy 4 – only one 1.5-L extract (concentrated to 25 µL) was manually injected on the GC-MS. The total concentration (ng/L) in the carboy was calculated by multiplying the concentration of the sample (from either GC-MS or GC-ECD) by the volume of the sample (25 µL) divided by the total volume extracted (in liters) (Table 5.22).

The PEDs were preloaded with reference compounds selected to represent the suite of analytes of interest – deuterated compounds for the PAHs (pyrene-$_{d10}$, phenanthrene-$_{d10}$, benzo[a]pyrene-$_{d12}$) and reference PCBs for the PCBs and chlorinated pesticides of similar molecular weight and structure (PCB 51, PCB 155, and PCB 185). The average of the upper and lower molecular weights was used to correct PCBs and chlorinated pesticides of molecular weights between the molecular weights of the reference PCBs. In other words, for PCB 101, the average of PCB 51 and PCB 153 was used as a correction factor. To determine the initial concentration of the preloaded reference compounds, a small rectangle of the PED is cut off and extracted prior to the start of the experiment. The initial concentrations of the preloaded reference compounds are presented Table5.23.

Table 5.21 Contaminant Concentrations in Water (ng/mL)

	Carboy 1	Carboy 2	Carboy 3	Carboy 4	Carboy Blank (5)
Phenanthrene	572	469	10760	16200	6.65
Pyrene	45.4	16.35	2470	2150	0.00
Benzo[a]pyrene	10.9	4.80	541	451	0.00
PCB 52	3.04 ± 0.98	11.1 ± 1.20	166 ± 8.69	1722 ± 83.1	0.50 ± 0.02
PCB 101	0.97 ± 0.01	6.49 ± 0.42	22.6 ± 3.37	158 ± 16.8	0.56 ± 0.02
PCB 153	0.55 ± 0.22	2.94 ± 0.60	11.6 ± 4.62	117 ± 2.13	0.07 ± 0.04
PCB 180	0.12 ± 0.21	0.00 ± 0.00	2.75 ± 2.39	30.7 ± 4.46	0.00 ± 0.00
***cis* Chlordane**	9.96 ± 2.29	76.9 ± 3.28	538 ± 29.3	4460 ± 264	0.06 ± 0.01
DDE	1.38 ± 0.34	6.04 ± 1.32	34.28 ± 0.88	312.00 ± 2.72	0.14 ± 0.07

Table 5.22 Measured Water Concentrations (ng/L)

ng/L	Carboy 1	Carboy 2	Carboy 3	Carboy 4
Phenanthrene	0.78	3.09	15.0	269
Pyrene	0.06	0.11	3.43	35.8
Benzo[a]pyrene	0.02	0.03	0.75	7.51
PCB 52	0.08	0.18	2.78	28.7
PCB101	0.04	0.11	0.38	2.64
PCB153	0.01	0.05	0.19	1.95
PCB180	0.00	0.00	0.05	0.51
***cis* Chlordane**	0.20	1.28	8.97	74.3
DDE	0.01	0.10	0.57	5.20

Table 5.23 Initial PED Concentrations of the Preloaded Compounds (ng/mL)

Initial concentration	PED 1	PED 2	PED 3	PED 4	PED 5	PED 6
Phenanthrene $_{d10}$	161	141	126	107	163	99
Pyrene $_{d10}$	1056	849	947	755	1404	905
Benzo[a]pyrene $_{d12}$	176	134	154	167	230	125
PCB 51	1051	841	990	932	1263	806
PCB 155	1016	657	753	509	546	501
PCB 185	2860	2510	2558	2242	3624	2384

Table 5.23 Initial PED Concentrations of the Preloaded Compounds (ng/mL) (continued)

Initial concentration	PED 7	PED 8	PED 9	PED 10	PED 11	PED 12	PED 13	PED 14	PED 15
Phenanthrene $_{d10}$	147	161	114	171	195	283	202	212	218
Pyrene $_{d10}$	1237	1407	1137	1097	1005	2047	1303	1236	1190
Benzo[a]pyrene $_{d12}$	169	146	134	236	278	394	205	200	233
PCB51	1598	1568	1373	1549	1532	2324	1303	1205	1264
PCB 155	642	674	635	852	1157	1286	1064	1126	975
PCB 185	3350	3762	2824	3713	3752	4694	3961	4315	4488

The high solid-to-water ratio in each chamber produced a $C_{PE\infty,r}$ that was within a standard deviation of the average $C_{PEt,r}$ for each compound. In many non-infinite or finite bath cases, Equation 5.7 is valid; however, in cases with a high solid-to-water ratio, as the PEDs approach equilibrium, the concentration at time infinity and the concentration at time t (45 days) are essentially equal (Adams *et.al* 2007), so that Equation 5.7 becomes unsolvable (Table 5.24), indicating that the PEDs were at equilibrium.

$$k_e = \ln\left(\frac{C_{PE0,r} - C_{PE\infty,r}}{C_{PEt,r} - C_{PE\infty,r}}\right)\cdot t^{-1} = \ln\left(\frac{X}{\sim 0}\right)\times 45^{-1} \qquad 5.19$$

Table 5.24 $C_{PE\infty,r}$ (ng/g) and $C_{PEt,r}$ (ng/g)

	Carboy 1		**Carboy 2**		**Carboy 3**		**Carboy 4**		**Carboy 5 Blank**	
	$C_{PEt,ravg}$	$C_{PE\infty,r}$	$C_{PEt,ravg}$	$C_{PE\infty,r}$	$C_{PEt,ravg}$	$C_{PE\infty,r}$	$C_{PEt,ravg}$	$C_{PE\infty,r}$	$C_{PEt,ravg}$	$C_{PE\infty,r}$
Phenanthrene $_{d10}$	237	259	248	275	225	261	177	270	231	244
Pyrene $_{d10}$	2000	1986	2409	2387	2399	2413	1860	1958	2122	2095
Benzo[a]pyrene $_{d12}$	219	218	235	234	239	239	469	468	240	239
PCB51	1815	1868	2190	2306	2470	2733	2479	2579	1661	1730
PCB 155	1388	1397	1021	1034	1144	1149	2061	2057	1744	1741
PCB 185	5378	5370	6541	6510	6414	6422	7322	7362	6718	6729

5.4.3 Data Processing

Recovery surrogates were used for the PED, water, and Infiltrex extracts. Recoveries for the laboratory experiment were as follows. The water extract recoveries were 86.7%±20.0%, 89.2%±10.2%, 69.76%±30.7%, and 107.4%±7.5%, for PCB 30, 205, anthracene $_{\mathrm{d10}}$, and chrysene $_{\mathrm{d12}}$, respectively. Concentrations were corrected for recoveries less than 70%. Recoveries for the PEDs were 104.4%±15.1%, 80.9%-±12.2%, 89.6%±17.8%, 94.3%±17.0%, 91.4%±15.7%, and 96.1%±17.6%, for anthracene $_{\mathrm{d10}}$, chrysene $_{\mathrm{d10}}$, perylene$_{\mathrm{d12}}$, PCB 50, PCB 143, and PCB 189, respectively.

Procedure blanks were performed and a blank carboy (carboy without compounds of interest) underwent the same experimental and extraction procedure as the spiked carboys. The PED extraction method was tested without compounds of interest and with clean polyethylene. The results from these blanks indicated contamination from the laboratory or the procedure were negligible.

5.4.4 Results

In general, the SPME-determined water concentrations were higher than the PED-determined water concentrations and the measured water concentrations. The PEDs exhibited a greater sensitivity for the lower concentrations and had a higher number of detections across the experiment (31 of 36, or 86%, including 4 of the lowest concentrations); the SPME was unable to detect any of the lowest concentrations (Carboy 1) and overall detected 67% (24 of 36, Table 5.25).

Table 5.25 Ranges and Number of Detections For SPMEs and PEDs for Lab

Compound	Range of Water Concentrations (ng/L)	Range of SPME Determinations (ng/L)	SPME # Detects	Range of PED Determinations (ng/L)	PED # Detects
Phenanthrene	1.68 – 269	8.71 – 362	3/4	0.39 – 112	4/4
Pyrene	0.06 – 35.8	0.94 – 30.5	3/4	0.01 – 17.0	4/4
Benzo[a]pyrene	0.02 – 7.51	0.26 – 1.59	2/4	0.02 – 1.87	3/4
PCB 52	0.08 – 0.18	0.37 – 21.0	3/4	0.02 – 13.1	4/4
PCB 101	0.04 – 2.64	0.10 – 1.85	3/4	0.02 – 1.38	3/4
PCB 153	0.01 – 1.95	0.32 – 0.59	2/4	0.02 – 1.36	3/4
PCB 180	0.05 – 0.51	0.08 – 0.09	2/4	0.01 – 0.13	3/4
***cis*-Chlordane**	0.20 – 74.3	0.81 – 37.4	3/4	0.01 – 13.2	4/4
4,4' DDE	0.01 – 5.20	0.07 – 1.32	3/4	0.02 – 1.81	3/4
		Total	24/36	**Total**	31/36

The measured water concentrations, the SPME calculated concentrations, and the PED calculated concentrations are presented in Table 5.26.

Table 5.26 Measured Water Concentrations and Water Concentrations Predicted from PEDs and SPMEs Determinations

Carboy 1			
ng/L	**Water**	**SPME**	**PED**
Phenanthrene	0.78	0.00	0.39 ± 0.02
Pyrene	0.06	0.00	0.01 ± 0.00
Benzo[a]pyrene	0.02	0.00	0.00 ± 0.00
PCB 52	0.08	0.00	0.01 ± 0.00
PCB101	0.04	0.00	0.00 ± 0.00
PCB153	0.01	0.00	0.00 ± 0.00
PCB180	0.00	0.00	0.00 ± 0.00
***cis* Chlordane**	0.20	0.00	0.01 ± 0.00
DDE	0.01	0.00	0.00 ± 0.00

Table 5.26 Measured Water Concentrations and Water Concentrations Predicted from PEDs and SPMEs Determinations (Continued)

Carboy 2			
ng/L	**Water**	**SPME**	**PED**
Phenanthrene	3.09	7.35 ± 0.71	2.49 ± 0.17
Pyrene	0.11	0.94 ± 0.24	0.19 ± 0.02
Benzo[a]pyrene	0.03	0.00	0.02 ± 0.00
PCB 52	0.18	0.30 ± 0.05	0.21 ± 0.03
PCB101	0.11	0.03 ± 0.01	0.01 ± 0.01
PCB153	0.05	0.00	0.02 ± 0.00
PCB180	0.00	0.00	0.01 ± 0.00
***cis* Chlordane**	1.28	0.69 ± 0.07	0.17 ± 0.03
DDE	0.10	0.06 ± 0.01	0.02 ± 0.00
Carboy 3			
ng/L	**Water**	**SPME**	**PED**
Phenanthrene	14.98	43.86 ± 2.99	14.67 ± 1.42
Pyrene	3.43	4.50 ± 0.41	1.38 ± 0.03
Benzo[a]pyrene	0.75	0.14 ± 0.00	0.11 ± 0.01
PCB 52	2.78	2.41 ± 0.15	1.58 ± 0.06
PCB101	0.38	0.23 ± 0.02	0.12 ± 0.01
PCB153	0.19	0.41 ± 0.01	0.15 ± 0.02
PCB180	0.05	0.13 ± 0.02	0.02 ± 0.00
***cis* Chlordane**	8.97	4.66 ± 0.29	1.27 ± 0.06
DDE	0.57	0.35 ± 0.02	0.15 ± 0.01

Table 5.26 Measured Water Concentrations and Water Concentrations Predicted from PEDs and SPMEs Determinations (Continued)

Carboy 4			
ng/L	**Water**	**SPME**	**PED**
Phenanthrene	269.44	304.91 ± 14.98	112.40 ± 3.10
Pyrene	35.80	30.70 ± 2.74	13.60 ± 2.72
Benzo[a]pyrene	7.51	0.82 ± 0.18	1.18 ± 0.13
PCB 52	28.70	17.10 ± 0.59	11.43 ± 3.35
PCB101	2.64	0.63 ± 0.07	1.24 ± 0.08
PCB153	1.95	0.76 ± 0.12	1.31 ± 0.35
PCB180	0.51	0.19 ± 0.10	0.11 ± 0.02
***cis* Chlordane**	74.34	31.84 ± 2.95	11.56 ± 2.85
DDE	5.20	1.13 ± 0.35	1.55 ± 0.02

For the PCBs studied, the SPME-determined water concentrations were generally greater than the measured water concentrations, with the exception of a few points. The PED-determined water concentrations were lower than the actual water concentrations, but were within an order of magnitude (Table 5.26, Figure 5.17). Agreement between the PED-determined water concentrations and the actual water concentrations increases with concentration for PCB 101 and 153; however, it decreases with increasing concentration for PCB 180. The agreement between the SPME-determined water concentrations and the PED-determined water concentrations decreased with decreasing actual water concentration, which would be expected as the sensitivity of the samplers declines with lower concentrations. A stronger agreement within the calculated water concentrations was observed for the lower molecular weight compounds, particularly PCB 52.

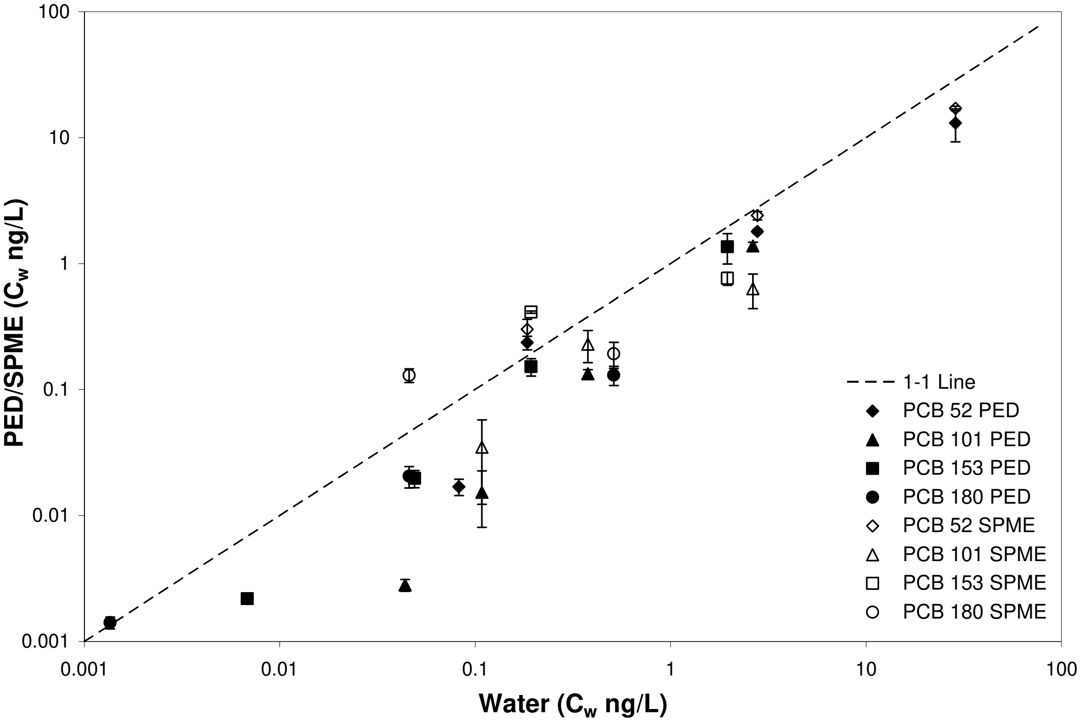


Figure 5.17 PED and SPME-Determined concentrations versus measured water concentrations for study PCBs. SPME points are open. PED points are filled.

The SPME-determined water concentrations were greater than the actual water concentrations for phenanthrene and pyrene, but were consistently low for benzo[a]pyrene. PED-determined water concentrations were less than the actual water concentrations for the PAHs studied, but were well within one order of magnitude (Table 5.26, Figure 5.18). Phenanthrene was within a multiple of two. Again, the accuracy of the calculated water concentrations for the PAHs decreased with decreasing actual water concentration.

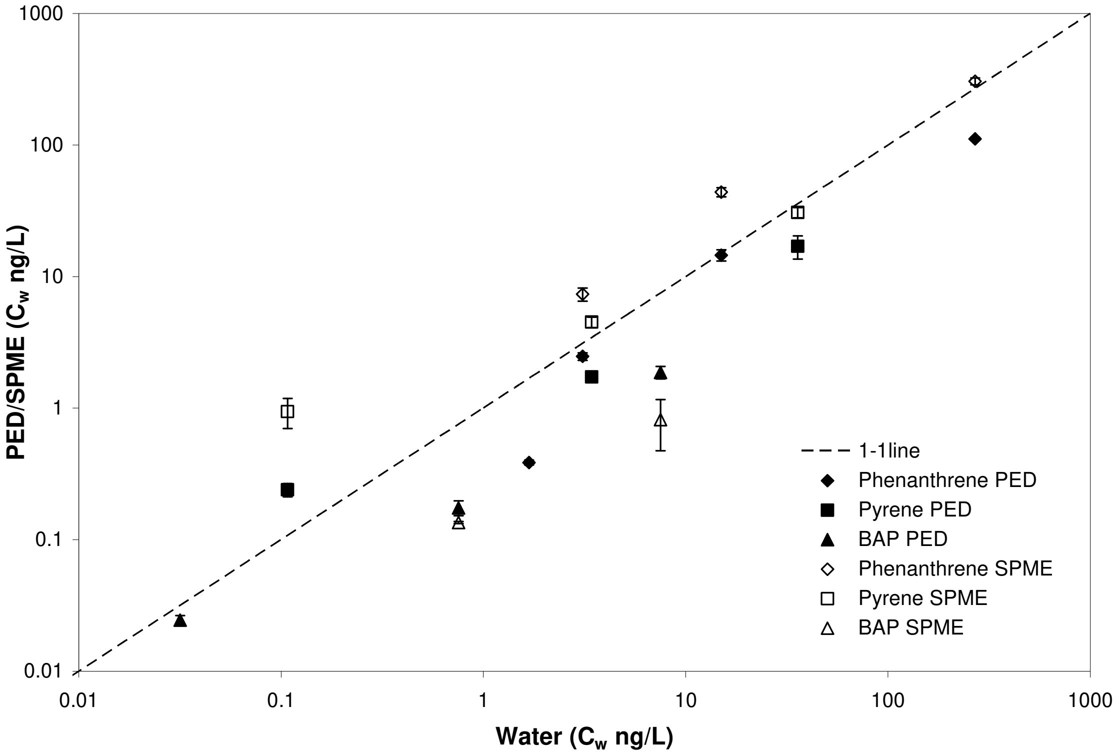


Figure 5.18 PED and SPME calculated concentrations versus measured water concentrations for study PAHs. SPME points are open. PED points are filled.

SPME concentrations were higher than the PED concentrations; both were below the actual water concentrations for *cis* chlordane, but were within an order of magnitude (Table 5.26, Figure 5.19). The agreements observed between the calculated water concentrations for the samplers did not hold true for *cis* chlordane. Similarly, SPME concentrations were higher than the PED for 4,4' DDE, with both samplers calculating water concentrations lower than those observed in the laboratory. Again, all SPME and PED concentrations were within an order of magnitude, all within a multiple of five (Table 5.26, Figure 5.19).

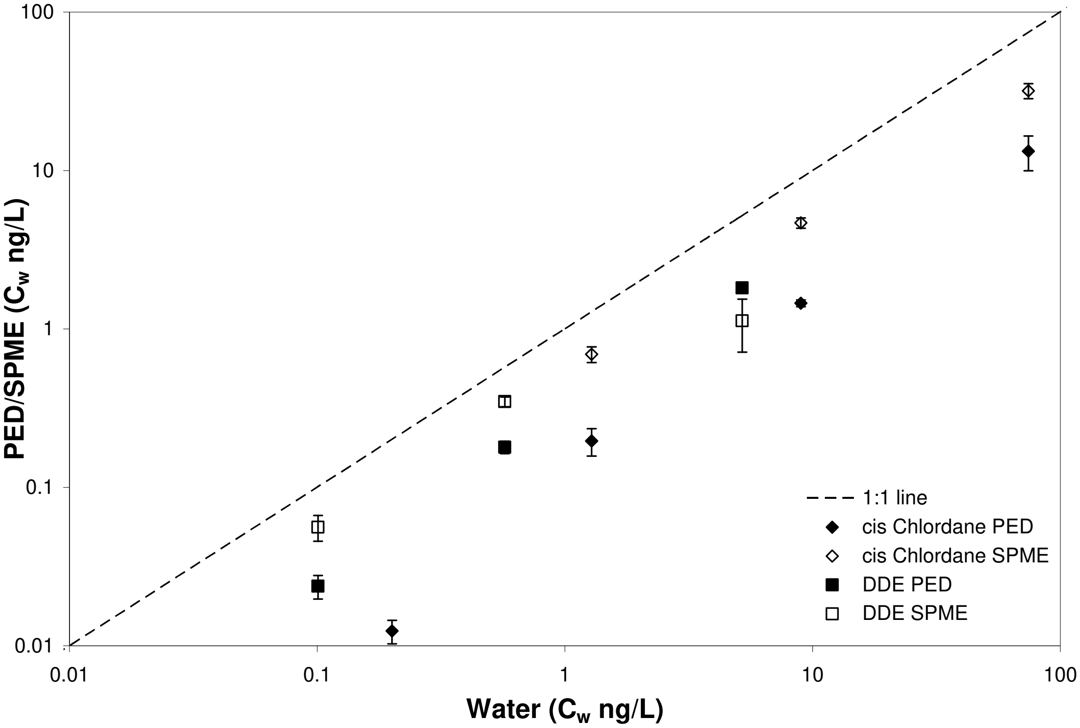


Figure 5.19 PED and SPME calculated concentrations versus measured water concentrations for *cis* Chlordane and 4,4'DDE. SPME points are open. PED points are filled.

The discrepancies between the SPME-determined water concentrations and the PED concentrations indicate that several factors may be affecting the results. SPME K_f values may be biased low, which would cause the SPMEs to over-predict water concentrations, as observed experimentally. PED K_{PEW} values may be biased high, which would cause the PEDs to under-predict the water concentrations, which was also observed. The K_{PEWs} used to calculate the water concentrations in the experiment were determined using low density polyethylene with a thickness of 51 μm. The thickness of the polyethylene used in this experiment was 30.3 ± 0.4 μm. Further investigation is underway to determine whether the difference in polyethylene thickness affects the partitioning. Another variation with the polyethylene is the manufacturer and manufacturing processes, which is concurrently being investigated.

5.4.5 Discussion

The comparison study showed neither sampler to be clearly superior. While the SPME was less labor intensive than the PED, requiring minimal handling, no extraction, and with the capacity to inject directly into the GC-MS, the PED extractions allowed for multiple injections. SPME fibers are reusable, but are extremely fragile. Three of 25 SPME fibers deployed were lost in the field. Two fiber injections were lost to instrument malfunction. PED extracts can be loaded into the GC-MS or GC-ECD and allowed to run overnight. In cases of instrument malfunction, the extracts can be rerun. However, comparatively, the extraction process is much longer, requiring two full days for solvent extraction, with a possible third day for silica column cleanup. PEDs are much less expensive than SPMEs and readily available--the polyethylene can be purchased at any hardware store. However, partitioning may be dependent on the manufacturing process employed and polyethylene thickness. This is currently being investigated by LMU researchers.

In the laboratory experiment, the SPME-determined water concentrations were generally higher than actual water concentrations, but more accurate than PED-determined water concentrations, which were typically lower than actual water concentrations. However, the PEDs displayed a greater sensitivity for lower HOC concentrations, including detections which were an order of magnitude or more less than those observed with SPMEs. This was proven in field study, as the PED detected 95.2% of the HOCs of interest.

The PED is labor intensive, presenting additional opportunities for human error, and the low exchange rate of the PED creates unnecessary difficulties, as seen in the SPME-PED bench comparison study.

5.5 SPME/PED Field Comparison Study

A field study was performed to determine the sensitivity and accuracy of the SPME (100 μm) and the PED (30 μm). The samplers were deployed in Ballona Creek, in Los Angeles, California. An Infiltrex 100 system was also deployed. The objective was to determine which sampler exhibited greater sensitivity for low dissolved HOC concentrations (less than 1 ng/L) and to allow comparison with a traditional measurement system under realistic operating conditions.

For the PED/SPME field deployment, I prepared the PEDs – they were cut and cleaned, preloaded with reference compounds, and threaded onto cleaned copper wire (procedure explained in greater detail below) – at LMU under the supervision of Dr. Adams. I deployed the PEDs in Ballona Creek with SCCWRP employees David Tsukada and Dario Diehl, who deployed the SPMEs and Infiltrex *in situ* pump. Dario Diehl piloted the research vessel.

5.5.1 Methods

In September 2007, PEDs and SPMEs were co-deployed in Ballona Creek at 6 sites (Figure 5.20) (Table 5.27).

PEDs were preloaded with reference compounds similar to those added in previous SPMD experiments (Booij *et.al.* 1998; Huckins *et.al*. 2002; *e.g.*, pyrene-$_{d10}$, phenanthrene-$_{d10}$, benzo[a]pyrene-$_{d12}$, PCB 51, PCB 155, and PCB 185) using an 80:20 methanol-water solution (Booij *et.al.* 2002) prior to exposure following the same procedure used in the PED/SPME laboratory comparison.

Figure 5.20 Locations of PED/SPME Sampling Sites (USGS TerraServer USA 2005)

Table 5.27 Locations of PED/SPME Sampling Sites

Site #	Site Description	SPME	PED	Notes
1 surface (up)	Buoy #2 inside Marina del Rey	136, 24	7	
1 bottom	Buoy #2 inside Marina del Rey	143, 84, 213(7µm)	8	PED 8 was missing, ripped off mooring
2 surface (up)	Buoy #1 end of pier between Ballona Creek and Marina del Rey	21, 59	9	Not recovered – tangled around buoy
2 bottom	Buoy #1 end of pier between Ballona Creek and Marina del Rey	127, 132, 204(7µm)	10	Not recovered – tangled around buoy
3 surface (up)	Outer location in Ballona Creek	135, 100	1	
3 bottom	Outer location in Ballona Creek	101, 97, 217(7µm)	2	SPME 97 missing from casing
4 surface (up)	Middle location in Ballona Creek	112, 152	3	
4 bottom	Middle location in Ballona Creek	113, 144, 214(7µm)	4	SPME 113 missing from casing
5 surface (up)	Pedestrian Bridge Ballona Creek	94, 134	11, 12, 13	
5 bottom	Pedestrian Bridge Ballona Creek	130, 99, 211(7µm)	14, 15, 16	SPME 99 damaged, fiber broken
6 surface (up)	Upper Ballona Creek, near pipes	92, 86	5	Excess debris tangled on line
6 bottom	Upper Ballona Creek, near pipes	88, 141, 216(7µm)	6	

During deployment of PEDs and SPMEs, a blank PED was exposed to the air during the same period while the deployed PEDs were exposed to determine whether any atmospheric interference was present. Triplicate PEDs were deployed at Site 5, the Pedestrian Bridge at Pacific Avenue. Two SPMEs with fiber thickness of 100µm were deployed at each site, at the surface and the bottom. One SPME fiber with 7µm thickness was deployed at each bottom site (Figure 5.21). One SPME fiber with 7µm thickness was deployed at each bottom site. SPMEs were housed in a 15 x 1.5 cm copper casing with 8-mm holes, which allow water to circulate around the fiber, while the casing protected against physical damage and slowed biological fouling. Prior to field deployment, all copper casings were sonicated in a methylene chloride: methanol (1:1) mixture for 20 min and in hexane for another 20 min, dried at ambient temperatures, and wrapped in aluminum foil until assembled with SPME fibers. The assembled SPME samplers were wrapped in aluminum foil and stored at -20 °C (Zeng *et.al* 2004).

Immediately before deployment, each PDMS-coated fiber was extruded from its protective sleeve and immersed into hexane for final cleaning; the PEDs were woven accordion style onto solvent-cleaned 18 gauge copper wire and a small square (less than 0.05 g) was cut from the PED and extracted to determine the initial concentration of the preloaded compounds in the PED. The copper wire was threaded through the 6.4-mm twisted polypropylene rope and the ends were twisted together with pliers. The SPMEs were attached to the rope with stainless steel hose clamps. The whole mooring unit was anchored by chain links and suspended in the water column with a subsurface float (Zeng *et.al* 2004).

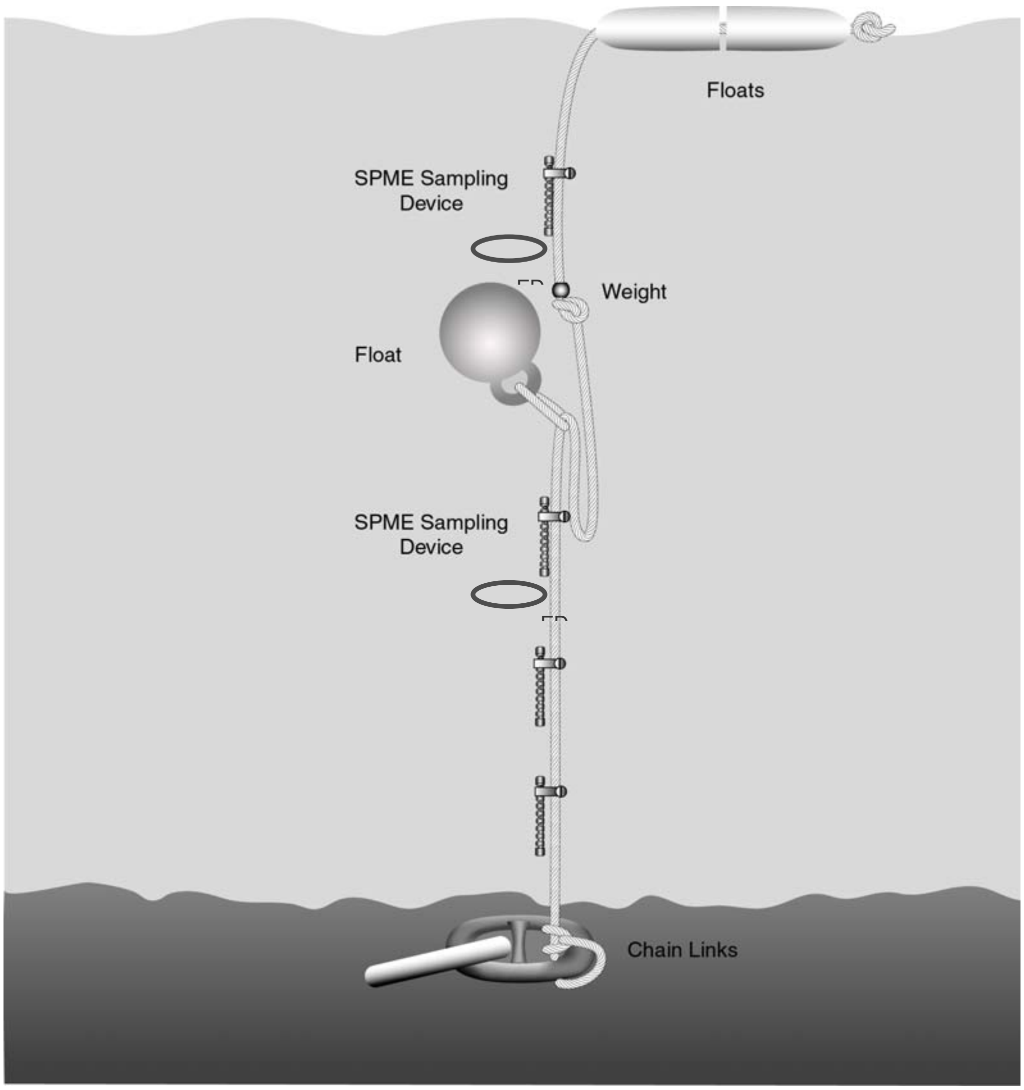


Figure 5.21 Depiction of SPME Water Column Mooring (from Zeng et al. 2004). PEDs are represented by the two ovals.

The Infiltrex 100 system *in situ* pump was deployed at Site 5 from September 27 through October 1, at 1.5 m from the sediment-water interface. 944 L of water were filtered during the five days of deployment. The Infiltrex housed eight Whatman GF/F glass fiber filters (142-mm diameter) to retain particles and one Telfon column packed with XAD-II resins to extract dissolved organics. Upon retrieval of each pump, the glass fiber filters were placed in glass Petri dishes and sealed. The Petri dishes and Teflon columns wrapped with aluminum foil were placed in an ice chest during transportation to the laboratory where the Teflon columns were processed within 24 h after arrival and the glass fiber filters in Petri dishes were stored at -20 °C until further treatment (Zeng *et.al.* 1999, 2002a, 2002b).

The Infiltrex 100 system collects both the particulate and dissolved phase materials. In this study, only the dissolved phase concentrations of the three samplers were compared. The XAD-II resin packed Teflon columns were spiked with surrogate standards and dissolved organic materials were eluted consecutively with 200 mL of methanol and methylene chloride at a flow rate of 5 mL/min. The methanol fraction was back-extracted three times with methylene chloride (50 mL each extraction) and the final extract was solvent exchanged to hexane and concentrated to 1 mL. Internal standards were added to final extracts before GC-MS analyses (Zeng *et.al.* 1999, Zeng *et.al.* 2004).

During PED and SPME retrieval, water samples were collected to determine the dissolved organic carbon at each site. Discrete temperature, specific conductivity, salinity, depth, pH, and turbidity data were collected at each site using a YSI data sonde.

The samples were retrieved – David Tsukada removed and stored the SPMEs and I removed and stored the PEDs. The SPMEs were removed from their copper casing, cleaned with DI water to remove any algae growth, retracted, placed in an amber vial, and transported on ice to facilities where they were stored in the freezer until injection on GC-MS. The copper wire supporting the PED was cut and the PED was removed from the wire, stored in a solvent-cleaned 120-mL amber jar, and transported on ice to LMU facilities where they were gently cleaned with Milli-Q Millipore clean water (TOC less than 6 µg/L and a resistance of 18 MΩ) to remove biofilm growth.

PEDs were spiked with recovery surrogates (anthracene-$_{d10}$, chrysene-$_{d10}$, perylene-$_{d12}$, PCB 50, PCB 143, and PCB 189) and twice extracted in DCM for 24 hours. The extract was decanted through a funnel packed with Na_2SO_4 (combusted at $400^{o}C$) to remove water. A silica column clean up followed to remove any excess algae or dirt in the sample that was not removed during the clean water clean-up.

5.5.1.1 Silica Column Clean Up

The PED field samples required silica column clean up, which took two days. Preparation of adsorbents was as follows: approximately 350 g of silica gel and 900 ml of redistilled methanol were added to a one-liter beaker. 500 g of alumina and 500 ml of redistilled methanol were added to another one-liter beaker. The mixtures were sonicated for 30 minutes. The methanol was decanted. The adsorbents were rinsed three times with 100 to 200 ml of methylene chloride. The methylene chloride was decanted. 500 ml of methylene chloride was added to each of the adsorbents and these were sonicated for 30 minutes. The methylene chloride was decanted. The adsorbents were allowed to dry in the hood overnight. The beakers were covered with aluminum foil with punctures to permit escape of vapors but prevent entry of particulate matter.

The silica gel at 180^{o}C and alumina at 250^{o}C were activated overnight. The adsorbents were transferred into glass-stopper 500 ml Erlenmeyer flasks and allowed to cool at room temperature. The weight of the adsorbents was recorded. Three percent by weight water was added to the adsorbents and the flasks were shaken vigorously. The flasks were allowed (covered with ground glass joint) to sit overnight to equilibrate. Dry hexane was added to the flasks.

The column was packed as follows: the glass column equipped with a Teflon stopcock was plugged with pre-combusted glass wool. The inner walls of the column were rinsed with 10 ml of dry hexane to remove glass fibers and any residual contaminants in the apparatus. This was allowed to run through the stopcock. The stopcock was closed and 5 ml of dry hexane were added. Silica gel was added to the column as a slurry to a height of 12 cm. The column was occasionally tapped with a plastic rod to pack the column and remove the bubbles. The walls of the column were continually rinsed with hexane to prevent build-up of dry silica gel during packing (always keeping the silica gel wet with solvent). Using a separate pipette, 6 cm of alumina slurry was added over the silica gel. The solvent level was lowered to just above the alumina surface and the stopcock was closed.

The column was cleaned and prepared with 30mL DCM by pouring the DCM into top of column and allowing it to filter through. Waste DCM was collected in a beaker. Solvent was kept on the column. DCM was followed by 30 mL hexane. Waste hexane was collected in a beaker. Once the 30mL of hexane has passed the top of the silica, approximately 2-3 mL more hexane were added and the stopper was closed. At least 1-2 cm hexane was maintained above the top of the silica column.

The sample was added. The sample vial was rinsed 3 times with approximately 0.5 mL hexane and added to the column. 15mL of hexane was added to the column. The decant was collected in a solvent-cleaned round bottom flask. 50 mL of 30:70 DCM:Hexane solution was added. The decant was collected in a solvent in a round bottom flask. The column drip was allowed dry into the round bottom flask. The sample was concentrated through rotovaping and N_2 blow down (as described in previous sections).

5.5.2 Data

5.5.2.1 SPME Data

SPME data are reported from the GC-MS as a mass in pg because the SPME fiber is injected straight into the GC-MS and the mass the GC-MS detects is all the mass that is in on the SPME fiber (Table 5.28).

Two SPMEs were deployed at each site. As noted (Table 5.27), not all SPMEs were retrieved from the field – some were either missing or damaged – and data were lost from two SPMEs due to GC-MS instrument faultiness. The averages of those sites for which duplicate data were available are presented in Table 5.29.

Table 5.28 Mass of Contaminant on SPMEs (pg)

pg	**1 bottom**	**1 bottom**	**1 up**	**1 up**	**3 bottom**	**3 up**	**3 up**	**4 bottom**
Compound	**143**	**84L**	**24**	**136L**	**101**	**100L**	**135**	**144**
Phenanthrene	2.40	2.48	16.6	1.40	10.2	8.95	9.08	8.17
Pyrene	7.80	9.09	20.9	20.0	20.2	0.00	27.3	29.9
Chrysene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 52	0.00	4.76	3.70	1.09	4.11	2.11	3.14	0.00
PCB 70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
***cis* Chlordane**	0.00	0.00	0.00	2.64	0.00	0.00	1.87	2.06
trans Nonachlor	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDE	5.23	5.73	0.00	15.4	12.0	37.7	15.3	23.6
DDT	365	662	68.9	213	15.4	37.2	340	206

Table 5.28 Mass of Contaminant on SPME (pg) (continued)

pg	**4 up**	**4 up**	**5 bottom**	**5 up**	**5 up**	**6 bottom**	**6 bottom**	**6 up**	**Site 6 up**
Compound	**152**	**112L**	**130L**	**134**	**94L**	**88**	**141L**	**92L**	**86L**
Phenanthrene	6.94	9.65	13.4	MS fault	17.7	86.6	102	24.7	26.9
Pyrene	25.6	34.9	15.0	No data[1]	54.2	107	123	71.9	81.4
Chrysene	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 52	0.00	8.25	3.78		2.98	0.00	2.10	8.14	0.00
PCB 70	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
***cis* Chlordane**	3.05	0.00	2.32		0.00	1.17	0.00	0.00	1.48
trans Nonachlor	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
DDE	17.9	27.4	15.9		7.84	6.38	20.0	9.73	20.7
DDT	208	268	172		77.7	201	217	42.7	137

[1] GC-MS Instrument failure, no data from this SPME fiber

Table 5.29 Average SPME Estimated C_w (ng/L)

C_w (ng/L)	1 bottom	1 up	3 bottom	3 up	4 bottom	4 up	5 bottom	5 up	6 bottom	6 up
Phenanthrene	0.59	2.19	2.48	2.20	1.99	2.02	3.26	4.32	23.0	6.29
Pyrene	0.67	1.63	1.61	1.09	2.38	2.41	1.19	4.31	9.17	6.10
Chrysene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 52	0.01	0.01	0.02	0.02	0.00	0.03	0.02	0.02	0.01	0.02
PCB 70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
***cis* Chlordane**	0.00	0.01	0.00	0.01	0.02	0.01	0.02	0.00	0.00	0.01
***trans* Nonachlor**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDE	0.01	0.01	0.02	0.03	0.03	0.03	0.02	0.01	0.02	0.02
DDT	1.46	0.40	0.04	0.54	0.59	0.68	0.49	0.22	0.59	0.26

5.5.2.2 PED Data

The PAH concentrations in the PEDS determined using GC-MS (Table 5.30). The PCBs, DDTs, and chlordanes were determined using GC-ECD. Additional data tables, including the calculations used to acquire the final results, are included in Appendix.

Table 5.30 Contaminant Concentrations in PED Blanks in ng/g

Concentration ng/g	**ng/mL ProcBLK**	**ng/g BLK 1**	**ng/g BLK2**	**ng/g BLK 3**	**ng/g BLK4**	**ng/g BLK5**	**ng/g BLK6**
Phenanthrene	1.62	1.60	1.18	0.12	0.51	1.37	0.00
Pyrene	1.23	0.00	0.00	0.00	0.00	2.04	0.72
Chrysene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[a] pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[ghi] perylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 52	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 70	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00
heptachlor epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00
***cis* Chlordane**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
***trans* Nonachlor**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDT	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 5.31 Contaminant Concentrations in PED Extracts for Field Study (ng/mL)

ng/mL	S1P7	S3P1	S3P2	S4P3	S4P4
Phenanthrene	119	42.8	32.1	40.2	44.7
Pyrene	204	287	117	263	435
Chrysene	183	147	115	349	298
Benzo[a] pyrene	185	72.9	57.0	354	383
Benzo[ghi] perylene	0.00	163	127	125	188
PCB 52	62.5	72.7	64.5	71.1	143
PCB 70	618	740	914	358	445
PCB 101	85.7	122	168	57.6	77.0
PCB 110	58.3	23.2	21.8	16.3	36.4
PCB 153	58.6	88.7	80.7	56.3	70.5
PCB 180	12.2	43.7	38.7	20.4	13.04
heptachlor epoxide	3.87	3.12	9.55	3.11	3.41
***cis* Chlordane**	40.6	59.6	48.7	35.3	54.3
***trans* Nonachlor**	26.4	36.5	26.2	21.9	30.7
DDE	108	122	104.1	68.4	106
DDT	84.6	96.9	99.3	68.6	84.8

One PED was deployed at each site, with the exception of Site 5, where triplicate PEDs were deployed. The average for this site for which triplicate data were available is presented in Table 5.32. The other values are from the single PEDs deployed at each site.

Table 5.31Contaminant Concentrations in PED Extracts for Field Study (ng/mL) (continued)

ng/mL	**S5P11**	**S5P12**	**S5P13**	**S5P14**	**S5P15**	**S5P16**	**S6P5**	**S6P6**
Phenanthrene	79.8	104	71.1	64.5	138	131	259	740
Pyrene	548	597	487	609	909	824	875	1144
Chrysene	533	1011	362	496	980	478	765	508
Benzo[a] pyrene	427	547	465	441	967	562	795	684
Benzo[ghi] perylene	0.00	433	55.8	0.00	0.00	0.00	272	112
PCB 52	202	125	206	165	146	169	343	223
PCB 70	642	345	270	1885	1514	1721	2391	2709
PCB 101	106	43.6	109	74.1	32.2	85.9	108	47.6
PCB 110	76.7	61.2	83.4	61.2	50.5	69.3	59.6	73.5
PCB 153	97.1	76.9	104	76.5	76.9	87.8	88.4	35.4
PCB 180	21.9	24.3	52.7	16.1	15.0	21.1	26.2	32.0
heptachlor epoxide	11.7	2.65	4.66	82.2	32.5	53.6	152	134
***cis* Chlordane**	89.9	70.9	99.6	70.1	47.4	82.2	138	58.3
***trans* Nonachlor**	56.0	38.3	61.7	46.8	31.1	51.2	85.5	37.6
DDE	163	134	187	129	105	149	161	69.2
DDT	132	110	171	112	94.3	116	158	68.3

Table 5.32 Average PED-determined Water Concentration (Average of Site 5 Up and Bottom)

Estimated C_w	**Averages**								
ng/L	**1 up**	**3 bottom**	**3 up**	**4 bottom**	**4 up**	**5 bottom**	**5 up**	**6 bottom**	**6 up**
Phenanthrene	1.07	0.31	0.37	0.37	0.54	1.09	0.76	5.34	2.22
Pyrene	0.36	0.23	0.50	0.75	0.75	1.65	1.01	1.71	1.53
Chrysene	0.07	0.05	0.06	0.11	0.21	0.29	0.27	0.16	0.29
Benzo[a] pyrene	0.01	0.00	0.00	0.02	0.03	0.04	0.03	0.03	0.04
Benzo[ghi] perylene	0.00	0.04	0.04	0.05	0.07	0.00	0.06	0.03	0.08
PCB 52	0.04	0.04	0.04	0.06	0.08	0.10	0.12	0.19	0.11
PCB 70	0.18	0.21	0.29	0.16	0.12	0.12	0.66	0.67	0.66
PCB 101	0.01	0.02	0.03	0.01	0.01	0.01	0.02	0.02	0.01
PCB 110	0.01	0.00	0.00	0.00	0.01	0.01	0.02	0.01	0.01
PCB 153	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.07	0.06	0.18	0.07	0.05	0.14	2.35	2.73	1.75
***cis* Chlordane**	0.03	0.05	0.05	0.04	0.04	0.09	0.12	0.12	0.04
***trans* Nonachlor**	0.01	0.02	0.01	0.01	0.01	0.03	0.04	0.04	0.01
DDE	0.02	0.03	0.02	0.02	0.02	0.03	0.05	0.03	0.01
DDT	0.03	0.06	0.05	0.06	0.04	0.07	0.11	0.09	0.02

The PEDs were preloaded with reference compounds selected to represent the suite of analytes of interest – deuterated compounds for the PAHs (pyrene-$_{d10}$, phenanthrene-$_{d10}$, benzo[a]pyrene-$_{d12}$) and reference PCBs for the PCBs and chlorinated pesticides of similar molecular weight and structure (PCB 51, PCB 155, and PCB 185). For PCBs and chlorinated pesticides of molecular weights between the molecular weights of the reference PCBs, the average of the upper and lower molecular weights was used to correct for nonequilibrium conditions. To determine the initial concentration of the preloaded reference compounds, a small rectangle of the PED was cut off and extracted prior to deployment. The initial concentration of the preloaded reference compounds is presented in Table 5.33.

The raw PED data for the preloaded compounds from the final PEDs from the field deployment are presented in Table 5.34.

The concentrations of the preloaded compounds in the PED, both initial and final, were normalized to ng/g (presented in Appendix). Using Equation 5.10, the average initial concentration of the preloaded compounds, the $\boldsymbol{k_e}$ (d^{-1}) was calculated (Appendix). Assuming that the sorption and desorption rate constants are equal, the $C_{PE\infty}$ for the chemical of interest can be calculated using Equation 5.11. The values for ($1\text{-}e^{-k_e t}$) were calculated (Appendix). The concentration in the water was then corrected for nonequilibrium cases using Equation 12 (Table 5.35).

Table 5.33 Initial PED Data Concentrations of the Preloaded Reference Compounds (ng/mL)

Initial concentration (ng/mL)	**PED13i**	**PED2i**	**PED11i**	**PED4i**	**PED16i**	**PED9i**
Phenanthrene $_{d10}$	8.34	16.2	16.7	21.6	1.64	3.15
Pyrene $_{d10}$	114.1	80.7	197	54.9	87.0	94.6
Benzo[a]pyrene $_{d12}$	189.3	254	67.5	92.3	49.3	70.9
PCB 51	272	389	394	343	286	135
PCB 155	140	217	206	142	133	76
PCB 185	5629	12728	11402	6446	6234	3100

Table 5.34 Final Concentrations in the Extracts from the Preloaded Contaminants in the PEDs (ng/mL)

Final Concentration	**S1P7**	**S3P1**	**S3P2**	**S4P3**	**S4P4**
Phenanthrene $_{d10}$	22.7	1.31	0.98	0.01	0.01
Pyrene $_{d10}$	135	88.2	66.2	180	182
Benzo[a]pyrene $_{d12}$	712	84.3	65.9	809	558
PCB51	153	88.5	18.5	36.2	82.2
PCB 155	6265	7327	5469	3075	4768
PCB 185	98589	177135	118438	99687	134346

Table 5.34 Final Concentrations in the Extracts from the Preloaded Contaminants in the PEDs (ng/mL) (continued)

Final Concentration	S5P11	S5P12	S5P13	S5P14	S5P15	S5P16	S6P5	S6P6
Phenanthrene $_{d10}$	0.01	0.01	2.75	0.01	6.64	2.31	12.78	0.01
Pyrene $_{d10}$	122	196	154	150	57.5	81.6	184	156
Benzo[a]pyrene $_{d12}$	971	846	639	592	1084	670	844	878
PCB 51	206	65.9	118	165	34.6	357	93.9	94.2
PCB 155	9640	7041	9011	6699	3601	9290	7065	5828
PCB 185	176491	92027	164615	132279	122702	164029	175826	129151

Table 5.35 Calculated C_w Corrected for Nonequilibrium (ng/L)

Calculated C_w	**Averages**								
ng/L	**1 up**	**3 up**	**3 bottom**	**4 up**	**4 bottom**	**5 up**	**5 bottom**	**6 up**	**6 bottom**
Phenanthrene	1.07	0.31	0.37	0.37	0.54	1.09	0.76	5.34	2.22
Pyrene	0.36	0.23	0.50	0.75	0.75	1.65	1.01	1.71	1.53
Chrysene	0.07	0.05	0.06	0.11	0.21	0.29	0.27	0.16	0.29
Benzo[a] pyrene	0.01	0.00	0.00	0.03	0.04	0.05	0.04	0.03	0.05
Benzo[ghi] perylene	0.00	0.04	0.04	0.07	0.07	0.00	0.08	0.03	0.10
PCB 52	0.04	0.04	0.04	0.06	0.08	0.10	0.12	0.19	0.11
PCB 70	0.18	0.21	0.29	0.16	0.12	0.12	0.66	0.67	0.66
PCB 101	0.01	0.02	0.03	0.01	0.01	0.01	0.02	0.02	0.01
PCB 110	0.01	0.00	0.00	0.00	0.01	0.01	0.02	0.01	0.01
PCB 153	0.01	0.01	0.01	0.01	0.00	0.01	0.02	0.01	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.10	0.10	0.28	0.10	0.07	0.28	4.90	4.66	5.51
***cis* Chlordane**	0.05	0.09	0.07	0.06	0.05	0.19	0.24	0.20	0.12
***trans* Nonachlor**	0.02	0.04	0.02	0.02	0.02	0.05	0.06	0.06	0.04
DDE	0.02	0.06	0.03	0.04	0.03	0.06	0.07	0.06	0.03
DDT	0.05	0.13	0.09	0.11	0.06	0.13	0.17	0.15	0.09

5.5.3 Data Processing

Recovery surrogates were used for the PED and Infiltrex extracts. Recoveries for the Infiltrex XAD-II resin were naphthalene $_{d8}$ 70%, acenaphthylene $_{d10}$ 94%, phenanthrene $_{d10}$ 98%, chrysene $_{d12}$ 107%, benzo[ghi]perylene $_{d12}$ 84%, TCX 90%, and PCB 65 96%. PED field recoveries were 89.5%±16.1%, 98.7%±13.4%, 98.1%±13.5%, 92.5%±11.1%, 83.9%±12.7%, and 85.1%±11.8% for anthracene $_{d10}$, chrysene $_{d10}$, perylene$_{d12}$, PCB 50, PCB 143, and PCB 189, respectively.

Field blanks were exposed during deployment of the PED. The results from these blanks indicated contamination from the laboratory or the procedure were negligible.

5.5.4 Results

The PEDs exhibited a greater sensitivity for the lower concentrations and had a higher number of detections (198 of 208 or 95.2 %, Table 5.36). PEDs detected all HOCs of interest at most sites; HOCs detected at all sites included phenanthrene, pyrene, chrysene, PCBs 52, 70, 101, 110, and 153, heptachlor epoxide, *cis*-chlordane, *trans* nonachlor, 4,4'DDE, and 4,4'DDT. The SPMEs (100 µm) detected contaminants at 89 of 255 sites (34.9 %, Table 5.36). SPME detects included phenanthrene, pyrene, PCB 52, 4,4' DDE, and 4,4'DDT. The SPME-determined water concentrations for 100 µm fibers were higher than the PED -determined concentrations, with the exception of PCB 52, which was less than the PED-determined concentrations; however, SPME-determined concentrations for PCB 52 were less than SPME detection limits (Zeng *et.al.* 2004), which suggests that these data may not be reliable.

Table 5.36 Ranges and Number of Detections For SPMEs and PEDs in the Field

Compound	**Infiltrex (ng/L)[1]**	**SPME Range (ng/L)[2]**	**SPME # Detects**	**PED Range (ng/L)**	**PED # Detects**
Phenanthrene	1.90	<=0.59 – 22.97	17/17	0.15 – 5.06	13/13
Pyrene	NA	0.67 – 9.17	15/17	0.06 – 2.40	13/13
Chrysene	NA	Below DL	0/17	0.03 – 0.28	13/13
Benzo[a]pyrene	0.15	Below DL	0/17	0.01 – 0.05	11/13
Benzo[ghi]perylene	NA	Below DL	0/17	0.02 – 0.10	8/13
PCB 52	0.02	<=0.01 – <=0.03	14/17	0.02 – 0.19	13/13
PCB 70	NA	Below DL	0/17	0.12 – 0.65	13/13
PCB 101	NA	Below DL	0/17	0.01 – 0.02	13/13
PCB 110	NA	Below DL	0/17	0.01 – 0.03	13/13
PCB 153	0.01	Below DL	0/17	0.004 – 0.01	13/13
PCB 180	0.00	Below DL	0/17	0.001 – 0.003	10/13
Heptachlor epoxide	0.00	Below DL	0/17	0.07 – 5.51	13/13
***cis* Chlordane**	0.07	<=0.01 – <=0.02	10/17	0.05 – 0.24	13/13
***trans* Nonachlor**	0.00	Below DL	0/17	0.02 – 0.07	13/13
4,4’DDE	0.09	<=0.01 – 0.03	16/17	0.02 – 0.10	13/13
4,4’DDT	0.03	0.04 – 1.46	17/17	0.05 – 0.21	13/13
		Total	89/255	**Total**	198/208

1 Infiltrex calculated dissolved water concentration in 944L of water at Site 5, Pedestrian Bridge at Pacific Avenue for 5 days.
2 <= represents detects that were below the detection limits (100 µm fibers)

The Infiltrex was deployed for five days in late September and early October, with detections of PCB 52 (0.02 ng/L), PCB 153 (0.01 ng/L), phenanthrene (1.90 ng/L), benzo[a]pyrene (0.15 ng/L), *cis*-chlordane (0.07 ng/L), 4,4’DDE (0.09 ng/L), and 4,4’DDT (0.03 ng/L). Triplicate PED samples were taken at Site 5, the Pedestrian

Bridge and a standard deviation was calculated. The PED-determined water concentrations for PCB 153, *cis* chlordane, 4,4'DDE, and 4,4'DDT from Site 5 were within one standard deviation of the concentrations determined from the *in situ* pump sampling (Figure 5.22). The SPME-determined water concentration for phenanthrene was above that measured by the Infiltrex; the PED was below, as observed in the laboratory experiment (Figure 5.20). This suggests that the K_f for phenanthrene is biased low and that the K_{PEW} is biased high. 4,4'DDT concentrations were higher in both the SPME and the PED. Although SPME-determined water concentration for PCB 52 was below detection limits, it matched the concentration measured by the Infiltrex; however, *cis* chlordane was much lower in the SPME than the Infiltrex, suggesting that the SPME measurements are below detection limits. The SPME-determined concentration of 4,4'DDE was lower than the Infiltrex concentration, but within one standard deviation of the PED concentration (Figure 5.22).

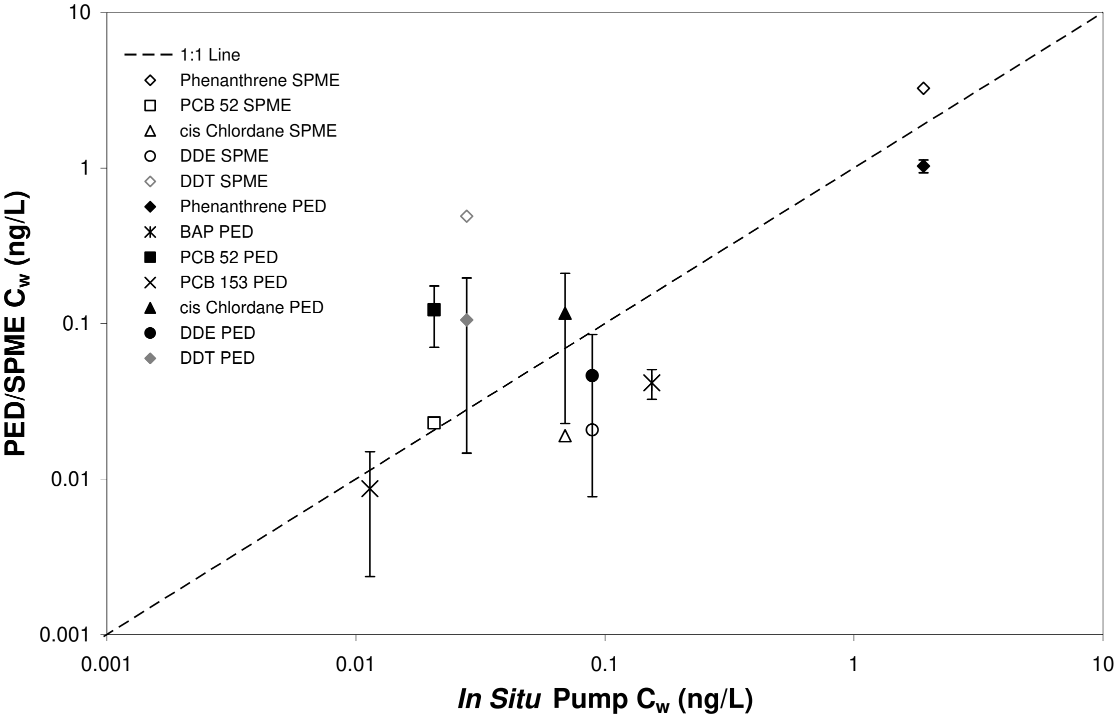


Figure 5.22 PED and SPME calculated concentrations versus Infiltrex *c*alculated water concentrations for Site 5, Pedestrian Bridge at Pacific Avenue. SPME points are open, PED points are closed.

Based on kinetic calculations from preloaded compounds in the PEDs (Equations 5.11 and 5.12), the lower molecular weight compounds (phenanthrene$_{d10}$, pyrene$_{d10}$, and PCB 51; 1-e^{-kt} greater than 0.95) are at equilibrium, while the higher molecular weight compounds (benzo[a]pyrene$_{d12}$, PCB 155, and PCB 185; 1-e^{-kt} 0.85, 0.60, and 0.54 respectively) had not reached equilibrium. The higher molecular weight HOCs of interest were corrected for non-equilibrium. Ballona Creek represents an infinite bath.

5.5.5 Discussion

PED preloaded compounds in the field indicated that higher molecular weight compounds (benzo[a]pyrene, PCB 155, PCB 185) had not reached equilibrium; therefore, it can be inferred that the higher molecular weight compounds have not reached equilibrium with the SPME in the field as well, particularly for the shorter exposure time in the field (23 days and infinite bath).

PEDs and SPMEs were slow to reach equilibrium. The higher molecular weight compounds had not reached equilibrium within the 23 days in the field for the PED. The SPME had a number of non-detects, which made it difficult to determine whether the problem was slow approach to equilibrium or detection limits of the sampler.

5.6 Conclusions

As demonstrated in the comparison studies, neither PEDs nor SPMEs were clearly superior. SPME has better agreement with conventional measures, likely because more mature calibration work is available. PEDs allow for lower detection limits, such as are typical in the dissolved water phase, but K_{PEW}s may be affected by thickness and/or processing differences for the material.

Use of the SPME was less labor intensive than the PED, requiring minimal handling, no extraction, and with the capacity to inject directly into the GC-MS. However, the PED extractions allowed for multiple injections. SPME fibers are reused, but are fragile and fiber injections can be lost to instrument malfunction. PED extracts can be loaded into the GC-MS or GC-ECD, run overnight, and rerun in cases of instrument malfunction. However, comparatively, the extraction process for PEDs is much longer, requiring two full days, with a possible third day for silica column cleanup. PEDs are much less expensive than SPMEs and readily available as the polyethylene can be purchased at any hardware store; however, partitioning may be dependent on the manufacturing process employed and polyethylene thickness.

LMU researchers are currently examining if partitioning into the polyethylene is effected by the polyethylene manufacturer or thickness. They are also investigating the effect these differences may have on the kinetic rate exchange.

As previously stated, the K_fs for the SPME have been extensively studied and reevaluated by SCCWRP researchers (Yang *et.al.* 2007, Yang *et.al.* 2006, Zeng *et.al.* 2005). Now that laboratory facilities at LMU are complete (GC-MS is installed and running, materials and glassware are purchased, and graduate students are involved), the K_{PEW}s and k_es should be reevaluated to a great degree to verify the values.

One disadvantage of both SPMEs and PEDs is that they are equilibrium based, meaning that they require time to measure the contaminant concentration. They do not provide a flow based nor a discrete measurement. Their results are composite based, over a length of time anywhere between two to three days to several weeks.

Both SPMEs and PEDs are applicable for research, monitoring, and regulatory applications. Depending on the need, one sampler would be recommended over the other. SPME should be considered more by municipalities and regulators, who may not have the labor force to invest in the extraction process of the PED, but could have the SPME fibers analyzed in house or by an outside facility. PEDs are more useful in academic research, where labor force is not as large an issue as funding can be. Lower water concentrations, such as in TMDL dissolved water phase monitoring, could be problematic for SPME, which has much higher detection limits than the PED. However, monitoring of slight variations of the water concentration could be problematic with the PED, until the K_{PEW}s are more refined.

Chapter Six: Conclusions

This dissertation had three main goals. The first was to identify suitable best management practices for treating stormwater runoff to meet TMDL goals of the Los Angeles County NPDES permit and to perform a cost benefit analysis of these BMPs. The following was determined through the cost benefit analysis:

- Treatment of larger regions as one watershed, reduces the initial cost to employ the stormwater best management practice
- This analysis determined the cost of various BMPs that could be employed in an area such as Los Angeles, how much that might cost, and how much people would be willing to spend.
- Willingness to pay varied:
    - Devinny *et.al.* (2004) estimated about $2.5 billion,
    - Larsen and Lew (2003) estimated around $59.4 million
    - These values were greater than the APWA cost estimation for stormwater treatment for the Los Angeles region, $5.9 million.
- The cost estimated for both structural and non-structural BMPs was $12.6 billion, and the total benefit of the BMPs and improvement to the environment was $21.3 billion, for a net benefit of $8.7 billion. The 2004 study calculated a greater net benefit for stormwater treatment, because the inflation correction, the newer, the higher discount rate, and the higher population numbers used increased the estimate of costs more than the estimate of benefits.

The second goal was to determine whether a simple, inexpensive, method for quantifying viruses in stormwater could be used to trace contaminant sources. This research determined the following:

- Virus counts for human viruses were high, in the tens of millions per milliliter. These numbers were typical for all viruses.
- Trends in the results were difficult to identify. The counts were rather uniform, varying by less than a factor of ten throughout the entire study in all three areas.
- QTRPCR data (Noble *et.al* 2005) found human viruses in significantly smaller concentrations than determined in this study, suggesting that the total counts determined here may reflect high background concentrations of non-human (or non-mammalian) viruses from sources that are not coincident with sources of pollution.
- The methods developed here are not useful in tracking pollutant sources in urban stormwater.

The final goal was to develop methods for quantifying hydrophobic organic contaminants (HOCs) in stormwater using two passive samplers (SPMEs and PEDs). The findings of these studies were as follows:

- Neither sampler was clearly superior.
- SPME was less labor intensive as the PED, requiring minimal handling, no extraction, with the capacity to inject directly into the GC-MS.

- PED extractions allowed for multiple injections. SPME fibers are reusable, but are extremely fragile.
- PEDs are less expensive than SPMEs and readily available as the polyethylene can be purchased at any hardware store; however, partitioning may be dependent on the manufacturing process employed and polyethylene thickness.
- SPME-determined water concentrations were typically higher than actual water concentrations, but more accurate than PED-determined water concentrations.
- PED-determined water concentrations were typically lower than actual water concentrations.
- PEDs had lower detection limits than SPME, over an order of magnitude in some cases.
- In the field study, PED detected 95.2% of the HOCs of interest.

SPMEs and PEDs are being further evaluated. LMU researchers are currently studying the K_{PEW}s of the polyethylene based on thickness and manufacturing process. The PED requires a labor intensive procedure that presents additional opportunities for human error. The slow rate of contaminant exchange for the PED creates unnecessary difficulties, as seen in the SPME-PED bench comparison study.

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Appendix

K_{PEW} Experiment

The dilution correction equation with sample calculation and the percent recovery equation with sample calculation for Water A (Table A.1) are presented in Equation A.1 and Equation A.2, respectively. The sample calculation is for phenanthrene:

$$\mathrm{C_{Adc}} = \mathrm{C_A}\ \frac{\mathrm{V_T}}{\mathrm{V_{TA}}} = 133.98 ng/mL \frac{1000 \mu L}{900 \mu L} = 148.87 ng/mL \qquad \text{A.1}$$

where C_{Adc} is the concentration of Water A after dilution correction, C_A is the concentration of Water A, V_T is the total initial volume of the sample prior to separation and dilution, and V_{TA} is the portion of the total initial volume in Water A.

$$\mathrm{Re}c = \frac{(\mathrm{C_{Adc}})(\mathrm{V_A})}{(\mathrm{C_{Su}})(\mathrm{V_{Su}})} = \frac{(148.87 ng/mL)(0.1 mL)}{(200 ng/mL)(0.1 mL)} = 74.4\% \qquad \text{A.2}$$

Where Rec is the percent recovery, C_{Adc} is the concentration of Water A after dilution correction, C_{Su} is the concentration of the recovery surrogate added, V_A is the volume of the Water A sample during analysis, and V_{Su} is the volume of the recovery surrogates added. Dilution corrections were done in a similar manner for Water B. The recovery surrogates in Water B were either below detection limits or too close to detection limits to produce reliable results due to baseline interference, (Table A.2); therefore, the percent recoveries calculated for Water A were used for Water B as well.

The percent recovery equation with sample calculation for the PED (Table A.3) is presented in Equation A.3. Sample calculation is for PED 1 phenanthrene:

$$\mathrm{Re}\,c = \frac{(\mathrm{C_{PED}})(\mathrm{V_{PED}})}{(\mathrm{C_{Su}})(\mathrm{V_{Su}})} = \frac{(38.0ng/mL)(0.5mL)}{(200ng/mL)(0.1mL)} = 95.0\% \qquad \text{A.3}$$

where C_{PED} is the concentration of the chemical extracted from the PED and V_{PED} is the volume of the PED sample during analysis.

Table A.1 Percent Recovery Calculation Results for Water A

Water A (ng/mL)	Initial	1	2	3	4	5	6	7	8	9	10 Blank	
Phenanthrene-$_{d10}$	11.4	48.2	134.	97.3	187.	262.	299.	252.	247.	309.	292.	
Pyrene-$_{d10}$	12.7	80.0	141.	91.0	181.	221.	260.	247.	245.	243.	226.	
Chrysene-$_{d12}$	13.8	95.2	160.	86.1	179.	243.	268.	235.	202.	192.	216.	
PCB 50	N/A	N/A	96.6	42.3	155.	202.	239.	206.	218.	180.	213.	
PCB 143	94.8	69.9	146.	66.9	213.	264.	303.	274.	290.	203.	307.	
PCB189	N/A	N/A	251.	98.5	280.	320.	345.	312.	326.	225.	356.	
Dilution Correction (ng/mL)												
Phenanthrene-$_{d10}$	12.7	53.6	149.	108.	208.	292.	332.	280.	275.	344.	324.	
Pyrene-$_{d10}$	14.1	88.9	157.	101.	201.	246.	288.	274.	272.	270.	251.	
Chrysene-$_{d12}$	15.4	105.	178.	95.6	199.	270.	297.	261.	225.	214.	240.	
PCB 50	N/A	N/A	107.	47.0	172.	224.	266.	229.	243.	200.	237.	
PCB 143	105.	77.6	162.	74.3	237.	293.	337.	305.	322.	226.	341.	
PCB189	N/A	N/A	279.	109.	311.	356.	383.	346.	362.	250.	396.	
Percent Recovery												**Average**
Phenanthrene-$_{d10}$	6.3%	26.8%	74.4%	54.1%	52.1%	72.9%	83.0%	69.9%	68.6%	86.0%	81.0%	66.9%
Pyrene-$_{d10}$	7.0%	44.5%	78.6%	50.6%	50.2%	61.4%	72.1%	68.6%	68.0%	67.4%	62.9%	62.4%
Chrysene-$_{d12}$	7.7%	52.9%	88.9%	47.8%	49.7%	67.6%	74.3%	65.4%	56.2%	53.4%	60.1%	61.6%
PCB 50	N/A	N/A	53.7%	23.5%	43.0%	56.1%	66.5%	57.3%	60.6%	50.0%	59.2%	52.2%
PCB 143	52.7%	38.8%	81.0%	37.2%	59.2%	73.4%	84.3%	76.2%	80.4%	56.4%	85.2%	67.2%
PCB189	N/A	N/A	139.4%	54.7%	77.7%	88.9%	95.9%	86.5%	90.5%	62.5%	99.0%	88.4%
Average PCB 50/ PCB 143	26.3%	19.4%	67.3%	30.3%	51.1%	64.8%	75.4%	66.8%	70.5%	53.2%	72.2%	

Table A.2 Percent Recovery Calculation Results for Water B

Water B (ng/mL)	**Initial**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10 Blank**
Phenanthrene-$_{d10}$	25.3	8.97	9.72	7.98	9.49	11.9	10.8	8.87	8.76	1.44	0.00
Pyrene-$_{d10}$	30.0	0.0	119	32.1	0.0	0.0	0.0	0.0	0.0	2.2	0.0
Chrysene-$_{d12}$	34.2	0.0	18.9	16.6	18.9	0.0	14.2	2.9	5.8	0.0	0.0
PCB 50	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PCB 143	23.8	0.0	89.6	0.0	0.0	12.9	12.2	11.7	12.0	0.0	0.0
PCB189	71.8	0.0	161.9	45.5	28.0	10.8	11.2	0.0	4.3	0.0	0.0
Dilution Correction (ng/mL)											
Phenanthrene-$_{d10}$	252.8	89.7	97.2	79.8	94.9	119.	108.	88.7	87.6	14.4	0.0
Pyrene-$_{d10}$	300.0	0.0	1190	321.	0.0	0.0	0.0	0.0	0.0	21.7	0.0
Chrysene-$_{d12}$	342.	0.0	189.	166.	189.	0.0	142.	29.3	58.0	0.0	0.0
PCB 50	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PCB 143	238.0	0.0	896.	0.0	0.0	129.	122.	117.	120.	0.0	0.0
PCB189	718.	0.0	1620.	455.	280.	108.	112.	0.0	43.3	0.0	0.0
Percent Recovery											
Phenanthrene-$_{d10}$	632%	224%	243%	100%	119%	149%	135%	111%	110%	18%	0%
Pyrene-$_{d10}$	750%	0%	2972%	402%	0%	0%	0%	0%	0%	27%	0%
Chrysene-$_{d12}$	854%	0%	472%	208%	236%	0%	177%	37%	72%	0%	0%
PCB 50	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
PCB 143	595%	0%	2240%	0%	0%	162%	153%	146%	150%	0%	0%
PCB189	1794%	0%	4048%	568%	350%	135%	141%	0%	54%	0%	0%

Table A.3 Percent Recovery Calculation Results for the PEDs

PED (ng/mL)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**10 Blank**	
Phenanthrene-$_{d10}$	38.0	130	19.0	31.6	260	274	272	285	202.	
Pyrene-$_{d10}$	39.5	130	22.1	36.5	282	316	341	340	260.	
Chrysene-$_{d12}$	40.1	96.5	24.1	29.8	209	383	243	244	217.	
PCB 50	N/A	144	19.0	35.2	330	344	357	346	274.	
PCB 143	50.8	183	28.1	50.2	375	414	390	419	332.	
PCB189	N/A	164	32.9	49.1	298	327	353	404	284.	
Percent Recovery										**Average**
Phenanthrene-$_{d10}$	95%	65%	5%	79%	65%	68%	68%	71%	50%	66.7%
Pyrene-$_{d10}$	99%	65%	6%	91%	71%	79%	85%	85%	65%	77.3%
Chrysene-$_{d12}$	100%	48%	6%	75%	52%	96%	61%	61%	54%	63.8%
PCB 50	N/A	72%	5%	88%	83%	86%	89%	87%	68%	81.8%
PCB 143	127%	92%	7%	125%	94%	104%	98%	105%	83%	100.0%
PCB189	N/A	82%	8%	123%	74%	82%	88%	101%	71%	88.7%
Average PCB 50/ PCB 143	127%	81.7%	5.9%	106.8%	88.2%	94.8%	93.4%	95.7%	75.7%	

Correction to Recoveries:

Equation A.2 represents the initial calculation of the recoveries for Water A, Water B, and the PED. To correct the recoveries according to the results for the surrogate compounds, the assumed concentration of the recovery surrogate is multiplied by the ratio of the area of the recovery surrogate peak to the area of the calibration standard peak.

$$\mathrm{Re}c = \frac{(\mathrm{C_{Adc}})(\mathrm{V_A})}{(\mathrm{C_{Su}})(\mathrm{V_{Su}})} \qquad \text{A.4}$$

Where Rec is the percent recovery, C_{Adc} is the concentration of Water A after dilution correction, C_{SuC} is the corrected concentration of the recovery surrogate added, V_A is the volume of the Water A sample during analysis, and V_{Su} is the volume of the recovery surrogates added. The corrected concentration of the recovery surrogate added is calculated using Equation A.5.

$$C_{SuC} = C_{Su}\frac{(\mathrm{A_{Su}})*10}{(\mathrm{A_{SG}})} = 200ng/mL\frac{(10)(2011)}{(22614)} = 177.85ng/mL \qquad \text{A.5}$$

Where C_{SuC} is the corrected concentration of the recovery surrogate added, A_{Su} is the area of the recovery surrogate peak at 200 ng/mL (or 0.2 ppm), and A_{SG} is the area of the Sea Grant calibration standard peak at 2,000 ng/mL (of 2 ppm). Therefore, the area of the recovery surrogate peak must be multiplied by a factor of 10 to account for this concentration difference (Tables A.4 and A.5).

$$\mathrm{Re}c = \frac{(\mathrm{C_{Adc}})(\mathrm{V_A})}{(\mathrm{C_{SuC}})(\mathrm{V_{Su}})} = \frac{(148.87ng/mL)(0.1mL)}{(177.85ng/mL)(0.1mL)} = 83.7\% \qquad \text{A.6}$$

Table A.4 Surrogate-Corrected Recoveries for Water A

Water A	**Initial**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9 Control**	**10 Blank**	**Average**
Phenanthrene-$_{d10}$	7.1%	30.1%	83.7%	60.8%	58.5%	82.0%	93.3%	78.6%	77.2%	96.7%	91.1%	75.2%
Pyrene-$_{d10}$	9.3%	58.4%	103.2%	66.4%	65.9%	80.6%	94.7%	90.1%	89.4%	88.5%	82.6%	82.0%
Chrysene-$_{d12}$	10.4%	71.7%	120.6%	64.9%	67.5%	91.7%	100.8%	88.7%	76.2%	72.5%	81.5%	83.6%
PCB 50	0.0%	0.0%	74.5%	32.6%	59.6%	77.9%	92.2%	79.5%	84.1%	69.3%	82.1%	72.4%
PCB 143	62.8%	46.3%	96.6%	44.4%	70.6%	87.6%	100.6%	91.0%	96.0%	67.3%	101.7%	80.2%
PCB189	0.0%	0.0%	173.5%	68.2%	96.8%	110.7%	119.4%	107.8%	112.7%	77.9%	123.3%	110.0%
Average PCB 50/ PCB 143	31.4%	23.2%	85.5%	38.5%	65.1%	82.7%	96.4%	85.2%	90.1%	68.3%	91.9%	

Table A.5 Surrogate-Corrected Recoveries for PED

PED	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**10 blank**	**Average**
Phenanthrene-$_{d10}$	106.8%	73.1%	5.3%	88.7%	73.0%	77.0%	76.4%	80.1%	56.8%	75.0%
Pyrene-$_{d10}$	129.8%	85.4%	7.3%	119.9%	92.6%	103.7%	112.0%	111.7%	85.3%	101.5%
Chrysene-$_{d12}$	136.1%	65.5%	8.2%	101.1%	71.0%	130.0%	82.3%	82.9%	73.6%	86.6%
PCB 50	0.0%	99.6%	6.6%	122.2%	114.6%	119.3%	124.0%	120.1%	94.9%	113.5%
PCB 143	151.5%	109.3%	8.4%	149.8%	111.9%	123.7%	116.4%	125.1%	99.2%	119.3%
PCB189	0.0%	102.1%	10.2%	152.8%	92.7%	101.8%	110.0%	125.7%	88.4%	110.5%
Average PCB 50/ PCB 143	75.8%	104.4%	7.5%	136.0%	113.2%	121.5%	120.2%	122.6%	97.0%	

Total Mass Extracted:

The equation and calculation for the total mass extracted from the Water A samples (Table A.6) is presented in Equation A.7. This includes a correction for dilution.

$$\mathrm{M_{Adc}} = (\mathrm{C_A})\,(\mathrm{V_A})\,\frac{\mathrm{V_T}}{\mathrm{V_{TA}}} = (5410 ng/mL)(100 \mu L)\frac{1000 \mu L}{900}\left(\frac{1 mL}{1000 \mu L}\right) = 601 ng \qquad \text{A.7}$$

Where $\mathrm{M_{Adc}}$ is the total mass extracted from Water A after dilution correction, $\mathrm{C_A}$ is the concentration of Water A, $\mathrm{V_A}$ is the volume of Water A, $\mathrm{V_T}$ is the total initial volume of the sample prior to separation and dilution, and $\mathrm{V_{TA}}$ is the portion of the total initial volume in Water A.

The equation and calculation for the total mass extracted from the Water B samples (Table A.7) is presented in Equation A.8. This includes a correction for dilution.

$$\mathrm{M_{Bdc}} = (\mathrm{C_B})\,(\mathrm{V_B})\,\frac{\mathrm{V_T}}{\mathrm{V_{TB}}} = (254. ng/mL)(500 \mu L)\frac{1000 \mu L}{100 \mu L}\left(\frac{1 mL}{1000 \mu L}\right) = 1268. ng \qquad \text{A.8}$$

Where $\mathrm{M_{Bdc}}$ is the total mass extracted from Water B after dilution correction, $\mathrm{C_B}$ is the concentration of Water B, $\mathrm{V_B}$ is the volume of Water B, $\mathrm{V_T}$ is the total initial volume of the sample prior to separation and dilution, and $\mathrm{V_{TB}}$ is the portion of the total initial volume in Water B.

The calculation for the total mass extracted from the PED samples (Table A.8) is presented in Equation A.9.

$$\mathrm{M_{PED}} = (\mathrm{C_{PED}})\,(\mathrm{V_{PED}}) = (85.71 ng/mL)(500 \mu L)\left(\frac{1 mL}{1000 \mu L}\right) = 42.85 ng \qquad \text{A.9}$$

Where M_{PED} is the total mass extracted from the PED, C_{PED} is the concentration of the chemical on the PED, and V_{PED} is the volume of PED sample.

The recovery correction equation and calculation for the total mass extracted of the chemical from Water A (Table A.9) is presented in Equation A.10. Recovery corrected masses for Water B are presented in Table A.10.

$$\mathrm{M}_{\mathrm{Adc\,Rec}} = \frac{\mathrm{M}_{\mathrm{Adc}}}{\mathrm{Rec}} = \frac{600.80ng}{53.7\%} = 1119.4ng \qquad \text{A.10}$$

Where $M_{Adc\ Rec}$ is the recovery corrected mass for Water A, M_{Adc} is the mass of chemical in Water A, and Rec is the percent recovery.

The recovery correction equation and calculation for the total mass extracted of the chemical from the PED (Table A.11) is presented in Equation A.11.

$$\mathrm{M}_{\mathrm{PED\,Rec}} = \frac{\mathrm{M}_{\mathrm{PED}}}{\mathrm{Rec}} = \frac{42.85ng}{126.9\%} = 33.76ng \qquad \text{A.11}$$

Where $M_{PED\ Rec}$ is the recovery-corrected mass, M_{PED} is the mass of chemical on the PED, and Rec is the percent recovery.

Table A.6 Total Mass Extracted from Water A (Corrected for Dilution)

(ng)	**Initial**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10 Blank**
PCB 52	227	226	601	163	429	557	770.	651	600.	734	0.53
PCB 70	246	213	537	170	345	434	579	505	468	631	0.34
PCB 101	260	228	544	99.1	258	311	458	420	373	781	0.62
PCB 110	266.	233	553	120	304	357	520	478	422	778	0.00
PCB 153	28.3	30.7	64.8	7.78	15.8	18.1	25.9	21.8	24.2	63.6	0.00
PCB 180	30.2	32.0	63.4	8.08	14.2	14.5	19.4	14.0	19.6	51.0	0.00
Phenanthrene	378.	1760	6075	2390	5120	7570	8380	7310	7480	9320	15.0
Pyrene	571.	3087	10290	3550	8590	10970	14300	13600	12700	14500	21.3
Chrysene	20.8	74.7	248	91.7	215	262	299	278	220.	309	0.12
Benzo[a]pyrene	21.0	51.0	97.5	13.1	38.1	35.9	41.6	54.1	24.7	356	0.00
Benzo[ghi]perylene	24.7	47.7	109	73.8	353	414	208	227	61.7	180.	0.00
DDT 4,4'	148.	153	229	361	328	180	286	306	213	444	0.00
DDE 4,4'	1490	975	2730	885	1270	1520	2160	1900	1600	3090	2.74
Heptachlor epoxide	3557	4140	13000	2700	10200	12900	17800	15810	14900	12400	12.9
cis Chlordane	1460	1210	3270	1250	2450	3130	3460	2990	3080	2860	3.60
trans Nonachlor	1630	1189	3350	1110	2260	2820	3860	3450	3050	4140	4.13

Table A.7 Total Mass Extracted from Water B (Corrected for Dilution)

(ng)	Initial	1	2	3	4	5	6	7	8	9	10 Blank
PCB 52	424	518	1270	572	808	951	1050	923	905	773	0.00
PCB 70	556	515	1510	596	667	794	850	787	719	639	0.00
PCB 101	520	595	1280	466	544	590	690	630	599	889	0.00
PCB 110	704	717	1660	635	702	749	831	815	743	872	0.00
PCB 153	225	83.6	916	176	102	50.7	68.5	58.3	50.5	51.0	0.00
PCB 180	327	0.00	989	249	67.8	27.4	0.00	0.00	0.00	32.1	0.00
Phenanthrene	4190	5570	11800	5790	8710	11200	11000	8440	9250	8870	0.00
Pyrene	6120	8500	14000	6650	10700	12470	13300	12000	12100	14000	0.00
Chrysene	392	93.8	381	49.7	273	272	222	179	0.00	190	0.00
Benzo[a]pyrene	194	0.00	0.00	0.00	121	0.00	0.00	0.00	0.00	268	0.00
Benzo[ghi]perylene	1490	0.00	0.00	0.00	585	396	0.00	139	0.00	63.8	0.00
DDT 4,4'	949	213	350	220	487	584	828	760	295	3320	0.00
DDE 4,4'	2340	2370	4410	1890	2250	2580	2810	2570	2240	272	0.00
Heptachlor epoxide	4510	5770	14600	7160	11700	12800	15200	15400	14800	14700	0.00
cis Chlordane	1950	2420	5020	2560	3570	4420	5090	4840	4470	4780	0.00
trans Nonachlor	2130	2040	4800	2240	3260	3940	4230	4160	3680	4740	0.00

Table A.8 Total Mass Extracted from the PED

(ng)	1	2	3	4	5	6	7	8	10 Blank
PCB 52	42.9	141	13.7	184	233	174	186	195	0.00
PCB 70	58.0	168	27.2	272	352	281	283	310	0.00
PCB 101	45.2	197	37.9	450	543	470	476	489	0.00
PCB 110	80.0	220	39.9	393	530	459	474	502	0.00
PCB 153	13.4	30.7	8.5	84.0	93.1	98.6	92.8	94.4	0.00
PCB 180	17.6	26.3	5.1	76.4	88.4	84.4	86.8	81.0	0.00
Phenanthrene	94.1	133	45.4	132	147	127	114	125	0.70
Pyrene	915	1123	264	1002	993	1487	884	815	0.00
Chrysene	32.8	54.6	12.8	72.8	92.2	88.4	86.9	71.8	0.00
Benzo[a]pyrene	41.1	27.2	0.00	113	61.9	180	89.0	100	0.00
Benzo[ghi]perylene	17.9	51.0	0.00	157	60.0	147	91.8	75.9	0.00
DDT 4,4'	23.4	64.9	14.6	124	134	123	122	152	0.00
DDE 4,4'	247	827	141	2093	2704	2052	2000	2015	0.00
Heptachlor epoxide	107	153	7.64	77.6	185	128	143	165	0.00
cis Chlordane	192	566	32.8	652	873	597	624	591	0.00
trans Nonachlor	213	765	63.1	1306	1714	1227	1278	1418	0.00

Table A.9 Recovery-Corrected Mass for Water A

(ng)	Initial	1	2	3	4	5	6	7	8	9	10 Blank
PCB 52	361	487	807	500	719	715	834	819	713	1059	0.64
PCB 70	391	460	721	521	579	558	628	635	557	910	0.41
PCB 101	414	492	637	258	396	376	475	493	414	1144	0.68
PCB 110	424	502	646	311	467	432	539	561	469	1139	0.00
PCB 153	45.1	66.3	67.1	17.5	22.4	20.7	25.8	24.0	25.2	94.5	0.00
PCB 180	48.1	69.1	36.5	11.9	14.7	13.1	16.3	13.0	17.4	65.5	0.00
Phenanthrene	5303	5845	7258	3936	8743	9227	8983	9300	9687	9635	16.5
Pyrene	6170	5288	9974	5342	13027	13613	15089	15038	14191	16408	25.8
Chrysene	200	104	206	141	319	286	296	313	288	426	0.15
Benzo[a]pyrene	201	71.1	80.8	20.1	56.5	39.2	41.2	61.0	32.5	491	0.00
Benzo[ghi]perylene	237	66.5	90.3	114	523	451	206	256	81.0	248	0.00
DDT 4,4'	236	331	237	813	465	205	284	337	222	660	0.00
DDE 4,4'	2374	2105	1574	1299	1312	1376	1813	1767	1418	3969	2.22
heptachlor epoxide	5660	8930	7465	3966	10553	11658	14869	14670	13193	15869	10.4
cis chlordane	2322	2618	1885	1837	2527	2825	2902	2777	2735	3680	2.92
trans nonachlor	2594	2567	1933	1633	2337	2544	3238	3200	2706	5317	3.35

Table A.10 Recovery-Corrected Mass for Water B

(ng)	Initial	1	2	3	4	5	6	7	8	9	Blank
PCB 52	674	1118	1703	1757	1356	1221	1138	1161	1076	1115	0.00
PCB 70	885	1112	2022	1828	1119	1019	922	990	855	922	0.00
PCB 101	828	1285	1493	1430	913	758	748	792	712	1283	0.00
PCB 110	1121	1549	1946	1650	1078	905	862	956	825	1276	0.00
PCB 153	358	181	948	398	145	57.9	68.1	64.1	52.6	75.8	0.00
PCB 180	520	0.00	570	366	70.1	24.8	0.00	0.00	0.00	41.3	0.00
Phenanthrene	58787	18486	14129	9528	14876	13712	11785	10744	11990	9171	0.00
Pyrene	66157	14555	13527	10015	16177	15468	14038	13313	13506	15053	0.00
Chrysene	3764	131	316	76.6	405	296	220	202	0.00	262	0.00
Benzo[a] pyrene	1865	0.00	0.00	0.00	179	0.00	0.00	0.00	0.00	370	0.00
Benzo[ghi] perylene	14331	0.00	0.00	0.00	867	432	0.00	157	0.00	88.0	0.00
DDT 4,4'	1509	461	362	496	689	668	822	836	307	4935	0.00
DDE 4,4'	3718	5127	4561	4269	3187	2951	2789	2824	2331	404	0.00
heptachlor epoxide	7179	12452	8396	10508	12126	11576	12695	14258	13124	18849	0.00
cis chlordane	3101	5225	2895	3762	3691	3994	4264	4492	3968	6133	0.00
trans nonachlor	3397	4395	2765	3292	3366	3564	3541	3857	3268	6085	0.00

Table A.11 Recovery-Corrected Mass for PED

(ng)	1	2	3	4	5	6	7	8	10-Blank
PCB 52	28.3	142	208	151	204	146	150	163	0.00
PCB 70	38.3	169	414	222	307	236	228	258	0.00
PCB 101	29.8	189	507	331	480	387	396	399	0.00
PCB 110	52.8	211	533	289	468	378	394	409	0.00
PCB 153	8.83	28.1	101	56.1	83.2	79.7	79.7	75.5	0.00
PCB 180	11.6	25.7	49.7	50.0	95.3	82.9	78.9	64.4	0.00
Phenanthrene	88.1	182	851	148	202	165	150	156	1.24
Pyrene	704.81	1315	3630	836	1072	1434	789	729	0.00
Chrysene	24.1	83.4	157	72.0	130	68.0	106	86.6	0.00
Benzo[a] pyrene	30.2	41.6	0.00	112	87.3	139	108	121	0.00
Benzo[ghi] perylene	13.2	77.9	0.00	155	84.6	113	112	91.6	0.00
DDT 4,4'	15.4	59.3	174	82.9	120	99.6	105	121	0.00
DDE 4,4'	163	756	1678	1397	2418	1659	1718	1611	0.00
heptachlor epoxide	70.5	149	74.6	50.8	199	126	130	131	0.00
cis chlordane	127	554	320	427	942	587	567	470	0.00
trans nonachlor	141	750	616	855	1848	1206	1162	1128	0.00

Table A.12 PED Weight

PED #	1	2	3	4	5	6	7	8	10
Weight (mg)	0.65	0.78	0.59	0.79	0.87	0.61	0.67	0.62	0.73

Kinetic Exchange Experiment Data

To calculate the weight-based concentration in the PED, the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng) (Table A.13). Then this mass was divided by the PED weight to produce the concentrations in the PEDs (Table A.14).

Table A.13 PED Weights (mg)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.48	0.54	0.45	0.49	0.32	0.45	0.65	0.41	0.51	0.44	0.65	0.41	0.52	0.49	0.48

Table A.14 PED Contaminant Concentrations (ng/mg)

Days	**2**					**7**				
Analyte	**PED 1**	**PED 2**	**PED 3**	**Average**	**Std Dev**	**PED 4**	**PED 5**	**PED 6**	**Average**	**Std Dev**
PCB 52	195	238	149	194	44.8	282	424	245	264	25.7
PCB 70	86.9	126	69.8	94.2	28.8	108	260	107	108	0.58
PCB 101	55.9	59.9	41.7	52.5	9.59	62.6	157	56.8	59.7	4.12
PCB 110	52.4	70.2	39.2	53.9	15.5	80.4	306	76.1	78.3	3.07
PCB 153	92.7	72.5	84.8	83.3	10.2	123	554	108	116	10.4
PCB 180	128	125	99.3	117	15.6	90.1	736	77.2	83.6	9.11
Phenanthrene	50.4	45.4	51.6	49.1	3.29	64.4	200	44.9	54.7	13.7
Pyrene	59.2	56.0	47.6	54.3	6.01	93.2	127	65.4	79.3	19.7
Chrysene	67.6	78.7	69.8	72.1	5.89	133	183	110	122	16.3
Benzo[a] pyrene	90.3	102	81.7	96.2	8.26	109	675	88.7	98.9	14.4
Benzo[ghi] perylene	84.5	88.7	86.2	86.5	2.13	110	2673	115	112	3.86
DDT 4,4'	95.0	135	90.3	107	24.6	124	2086	105	115	13.7
DDE 4,4'	68.0	58.5	72.5	66.3	7.16	117	320	106	111	7.93
heptachlor epoxide	71.4	87.5	45.5	68.1	21.2	62.0	162	48.0	55.0	9.90
cis chlordane	42.0	45.2	24.6	37.3	11.1	40.1	127	33.3	36.7	4.75
trans nonachlor	27.8	36.6	15.8	26.8	10.4	35.2	39.4	25.6	30.4	6.79

Table A.14 PED Contaminant Concentrations (ng/g) (continued)

Days	**14**					**30**				
Analyte	**PED 7**	**PED 8**	**PED 9**	**Average**	**Std Dev**	**PED 10**	**PED 11**	**PED 12**	**Average**	**Std Dev**
PCB 52	314	360	350	341	24.4	392	299	329	340	47.3
PCB 70	171	167	224	187	31.9	264	201	213	226	33.5
PCB 101	97.3	110	95.5	101	7.77	179	154	131	155	24.2
PCB 110	114	112	118	115	2.73	188	164	142	164	23.3
PCB 153	130	142	131	134	6.51	145	171	190	169	22.5
PCB 180	114	165	141	140	25.4	164	92.6	141	133	36.7
Phenanthrene	72.4	68.9	76.4	72.6	3.73	80.4	82.1	73.3	78.6	4.64
Pyrene	85.0	92.2	81.1	86.1	5.62	121	92.7	85.7	99.8	18.8
Chrysene	158	183	178	172.9	12.8	115	104	97.7	105.6	8.80
Benzo[a] pyrene	113	146	153	137.3	21.2	184	125	224	177.7	50.0
Benzo[ghi] perylene	128	157	134	139.7	15.0	248	151	123	174.0	65.6
DDT 4,4'	157	129	152	145.7	15.1	197	179	138	171.4	30.2
DDE 4,4'	132	168	133	144.3	20.2	182	147	130	152.8	26.5
Heptachlor Epoxide	79.2	88.2	88.6	85.3	5.31	127	70.7	110	102.6	28.8
cis Chlordane	48.1	71.7	49.4	56.4	13.3	86.2	45.7	60.7	64.2	20.5
trans Nonachlor	47.4	54.4	48.0	49.9	3.85	10.1	16.4	24.1	16.9	7.00

Table A.14 PED Contaminant Concentrations (ng/g) (continued)

Days	**45**				
Analyte	**PED 13**	**PED 14**	**PED 15**	**Average**	**Std Dev**
PCB 52	400	371	416	396	23.1
PCB 70	267	271	279	272	6.13
PCB 101	178	185	195	186	8.59
PCB 110	181	201	208	197	14.4
PCB 153	147	158	217	174	37.4
PCB 180	120	173	120	138	30.7
Phenanthrene	78.5	73.6	65.9	72.7	6.35
Pyrene	130	132	140	134	5.25
Chrysene	126	126	175	142	28.1
Benzo[a]pyrene	150	183	157	163	17.2
Benzo[ghi]perylene	163	221	191	192	28.8
DDT 4,4'	188	204	236	210	24.4
DDE 4,4'	168	141	125	145	22.0
Heptachlor Epoxide	119	129	136	128	8.38
cis Chlordane	79.8	88.7	89.7	86.1	5.49
trans Nonachlor	27.8	26.3	26.7	26.9	0.82

The water samples taken at day 0 and day 45 were spiked with 100 µL (0.1 mL) of 2000 ng/mL recovery surrogate standard. The estimated concentrations in the water were split into two ranges – one including the higher molecular weight analytes having smaller concentrations (less than 100 ng/mL) and a second including the lower molecular weight analytes having higher concentrations (greater than 500 ng/mL). The samples were analyzed on GC-MS at a volume of 1 mL and then concentrated to 100µL (0.1 mL) using a gentle Nitrogen gas (N_2) blow down. The raw data for the water samples, in ng/mL, are presented in Table A.15. Water A was the sample at 100 µL and Water B was the sample at 1 mL.

Table A.15 Raw Water Data for compounds added to the water (ng/mL)

	Water A (100 µL)		**Water B (1 mL)**	
Analytes	**Day 0**	**Day 45**	**Day 0**	**Day 45**
PCB 52	1509	1188	1008	1312
PCB 70	668	566	546	689
PCB 101	252	201	183	193
PCB 110	251	208	204	206
PCB 153	130	74.7	88.5	52.7
PCB 180	59.5	29.6	63.0	36.6
Phenanthrene	2263	1841	1832	2489
Pyrene	1226	988	888	1166
Chrysene	351	294	235	194
Benzo[a]pyrene	128	101	96.6	74.8
Benzo[ghi]perylene	224	238	189	199
DDT 4,4'	623	543	471	433
DDE 4,4'	129	97.9	92.3	77.2
heptachlor epoxide	1682	1684	1747	2057
cis chlordane	561	501	618	683
trans nonachlor	532	457	588	650

Determinations and calculations were also made for the preloaded reference compounds to determine the desorption constants. The initial concentrations were determined by extraction and analysis of half-portions of the PEDs after preloading (Table A.16)

Table A.16 Preloaded Reference Compounds Initial Concentrations (ng/mL)

Initial	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{d10}$	225	262	261	294	254	252	222	247	247
Pyrene $_{d10}$	28.7	21.3	21.2	27.8	19.3	19.6	20.0	21.0	21.0
Benzo[a] pyrene $_{d12}$	59.6	44.4	58.3	84.6	68.4	70.3	52.0	63.4	63.4
PCB 51	42.6	43.3	44.7	54.1	50.7	45.0	35.7	45.8	45.8
PCB 155	19.0	16.7	13.9	17.4	19.6	20.3	22.9	17.5	17.5
PCB 185	83.7	77.5	62.1	84.9	83.1	75.9	80.7	79.1	79.1

Table A.16 Preloaded Reference Compounds Initial Concentrations (ng/mL) (continued)

Initial	**10**	**11**	**12**	**13**	**14**	**15**
Phenanthrene $_{d10}$	247	247	222	234	247	247
Pyrene $_{d10}$	21.0	21.0	12.4	18.8	21.0	21.0
Benzo[a]pyrene $_{d12}$	63.4	63.4	51.8	80.8	63.4	63.4
PCB 51	45.8	45.8	61.3	34.5	45.8	45.8
PCB 155	17.5	17.5	11.9	16.0	17.5	17.5
PCB 185	79.1	79.1	93.8	70.3	79.1	79.1

To calculate the weight-based concentration in the PED, the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng) (Table A.19). Then this mass was divided by the PED weight presented above (Table A.17) to calculate a normalized mass per mass concentration (Table A.18).

Table A.17 Initial PED Weights (mg)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0.38	0.35	0.37	0.42	0.36	0.36	0.37	0.47	0.38	0.48	0.37	0.42	0.33	0.50	0.57	1.00

Table A.18 Normalized Initial PED Preloaded Concentrations (ng/mg)

Initial	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{d10}$	293	369	358	348	357	346	301	261	323
Pyrene $_{d10}$	37.4	30.0	29.1	32.9	27.1	26.9	27.1	22.2	27.5
Benzo[a]pyrene $_{d12}$	77.7	62.5	79.9	100	95.9	96.4	70.3	66.9	82.8
PCB 51	55.4	60.9	61.2	64.2	71.2	61.6	48.3	48.3	59.8
PCB 155	24.7	23.5	19.0	20.6	27.6	27.8	31.0	18.5	22.9
PCB 185	109	109	85.0	101	117	104	109	83.5	103

Table A.18 Normalized Initial PED Preloaded Concentrations (ng/mg) (Continued)

Initial	**10**	**11**	**12**	**13**	**14**	**15**
Phenanthrene $_{d10}$	256	337	267	356	248	217
Pyrene $_{d10}$	21.8	28.6	14.9	28.6	21.1	18.4
Benzo[a]pyrene $_{d12}$	65.6	86.2	62.3	122.7	63.4	55.4
PCB 51	47.4	62.2	73.6	52.4	45.8	40.1
PCB 155	18.1	23.8	14.3	24.3	17.5	15.3
PCB 185	81.9	108	113	107	79.2	69.2

Table A.19 PED Preloaded Masses (ng)

Initial	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene d10	112	131	131	147	127	126	111	124	124
Pyrene d10	14.4	10.7	10.6	13.9	9.7	9.8	10.0	10.5	10.5
Benzo[a]pyrene d12	29.8	22.2	29.1	42.3	34.2	35.2	26.0	31.7	31.7
PCB 51	21.3	21.6	22.4	27.1	25.4	22.5	17.9	22.9	22.9
PCB 155	9.49	8.35	6.93	8.70	9.82	10.15	11.46	8.76	8.76
PCB 185	41.9	38.7	31.0	42.4	41.6	37.9	40.3	39.6	39.6

Table A.19 PED Preloaded Masses (ng) (continued)

Initial	**10**	**11**	**12**	**13**	**14**	**15**	**Total**	**Average**
Phenanthrene d10	124	124	111	117	124	124	1856	124
Pyrene d10	10.5	10.5	6.2	9.4	10.5	10.5	158	10.5
Benzo[a]pyrene d12	31.7	31.7	25.9	40.4	31.7	31.7	475	31.7
PCB 51	22.9	22.9	30.6	17.2	22.9	22.9	343	22.9
PCB 155	8.76	8.76	5.95	8.00	8.76	8.76	131	8.76
PCB 185	39.6	39.6	46.9	35.1	39.6	39.6	593	39.6

Table A.20 PED Final Concentrations of the Preloaded Compounds (ng/mL)

Final	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{d10}$	217	255	243	189	1633	198	171	202	211
Pyrene $_{d10}$	15.4	21.1	19.1	14.3	32.2	13.2	10.9	13.7	15.9
Benzo[a]pyrene $_{d12}$	39.3	39.5	40.5	28.9	425	33.5	25.2	46.8	52.1
PCB 51	40.4	38.9	43.0	43.0	120	34.6	25.1	39.2	28.6
PCB 155	15.4	10.6	13.2	12.8	29.3	14.4	13.0	17.1	12.2
PCB 185	67.6	69.6	40.5	35.6	257	44.2	32.9	37.1	24.8

Table A.20 PED Final Concentrations of the Preloaded Compounds (ng/mL) (continued)

Final	**10**	**11**	**12**	**13**	**14**	**15**
Phenanthrene $_{d10}$	14.0	19.3	14.0	10.0	4.69	6.29
Pyrene $_{d10}$	12.6	7.17	6.08	6.57	5.40	4.79
Benzo[a]pyrene $_{d12}$	12.8	17.5	13.6	9.18	7.96	17.0
PCB 51	12.7	8.46	13.2	23.6	12.5	17.5
PCB 155	10.8	7.93	10.4	7.00	6.43	7.49
PCB 185	17.8	14.3	16.3	23.3	19.5	15.0

To calculate the weight-based concentration in the PED, the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng) (Table A.22). Then this mass was divided by the PED weight presented above (Table A.17) to calculate a normalized mass per mass concentration (Table A.21).

Table A.21 Final Normalized PED Preloaded Concentrations (ng/mg)

Final	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{d10}$	225	236	273	191	2563	222	131	244	209
Pyrene $_{d10}$	15.9	19.5	21.4	14.4	50.6	14.7	8.35	16.6	15.8
Benzo[a]pyrene $_{d12}$	40.7	36.7	45.4	29.2	667	37.5	19.3	56.7	51.5
PCB 51	41.9	36.1	48.2	43.4	189	38.7	19.2	47.6	28.3
PCB 155	16.0	9.82	14.8	13.0	46.0	16.2	9.96	20.7	12.0
PCB 185	70.0	64.6	45.4	36.0	403	49.4	25.2	44.9	24.5

Table A.21 Final Normalized PED Preloaded Concentrations (ng/mg) (continued)

Final	**10**	**11**	**12**	**13**	**14**	**15**
Phenanthrene $_{d10}$	16.0	14.9	17.3	9.64	4.77	6.58
Pyrene $_{d10}$	14.4	5.51	7.48	6.31	5.49	5.01
Benzo[a]pyrene $_{d12}$	14.6	13.5	16.8	8.82	8.10	17.8
PCB 51	14.5	6.51	16.3	22.6	12.8	18.3
PCB 155	12.3	6.10	12.8	6.72	6.54	7.83
PCB 185	20.3	11.0	20.1	22.4	19.8	15.7

Table A.22 Final PED Preloaded Masses (ng)

Final	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Phenanthrene $_{\mathrm{d10}}$	109	127	122	94.4	816	99.1	85.7	101	106
Pyrene $_{\mathrm{d10}}$	7.68	10.5	9.54	7.14	16.1	6.58	5.46	6.85	7.97
Benzo[a]pyrene $_{\mathrm{d12}}$	19.7	19.8	20.3	14.4	212	16.7	12.6	23.4	26.0
PCB 51	20.2	19.4	21.5	21.5	60.1	17.3	12.6	19.6	14.3
PCB 155	7.72	5.29	6.59	6.42	14.64	7.22	6.52	8.53	6.08
PCB 185	33.8	34.8	20.3	17.8	128	22.1	16.4	18.5	12.4

Table A.22 Final PED Preloaded Masses (ng) (continued)

Final	**10**	**11**	**12**	**13**	**14**	**15**	**Total**
Phenanthrene $_{\mathrm{d10}}$	7.02	9.66	7.02	5.02	2.34	3.14	1694
Pyrene $_{\mathrm{d10}}$	6.31	3.58	3.04	3.28	2.70	2.39	99.2
Benzo[a]pyrene $_{\mathrm{d12}}$	6.39	8.76	6.82	4.59	3.98	8.50	404
PCB 51	6.36	4.23	6.62	11.8	6.27	8.73	251
PCB 155	5.40	3.97	5.21	3.50	3.22	3.74	94.0
PCB 185	8.92	7.13	8.17	11.6	9.75	7.50	358

The desorption kinetics for the PEDs were calculated based on the following assumptions and calculations. The total PED weight for the initial PEDs (extracted prior to start of experiment) was 6.14 mg. The PED weight for the final PEDs (extracted at the end of the experiment) was 7.29 mg. Sample extract volume was 0.5 mL (500 µL). Recovery surrogate volume was 0.1 mL (100 µL) and concentration was 2000 ng/mL. C_{PE} (ng/mL) was from GC-MS traces. The total mass (M_T) of chemical was calculated by summing the mass of chemical on each PED – calculated for both Initial and Final PEDs. $C_{PE\,\sim}$ (ng/mg) (Table A.25) was calculated from the following equation:

$$C_{PE\infty} = \frac{K_{PEW} \cdot M_T}{V_W + K_{PEW} \cdot Mass_{PE}} \tag{A.12}$$

The modeling in this case was complicated by the fact that masses of contaminant were removed from the system each time a PED was removed. Thus $C_{PE\,o}$ (ng/mg) was calculated in two ways. For t=2 Days (Table A.23), the equation used was as follows:

$$C_{PEot=2} = \frac{M_T}{Mass_{PE}} \tag{A.13}$$

For t=7 days and the following days (Table A.23), the equation was as follows:

$$C_{PEot=7} = C_{PEt=2} \tag{A.14}$$

$C_{PEt=2}$ (ng/mg) was the average of the three chemical concentrations measured on the PEDs for Day 2, $C_{PEt=7}$ (ng/mg) was the average of the three chemical concentrations measured on the PEDs for Day 7, and so on.

The mass remaining in system (Table A.22), for t=2 days, was determined by $M_{Tt=2} = M_{Tinitial} - M_{t=2}$. For t=7 days, mass remaining was calculated by $M_{Tt=7} = M_{t=2} - M_{t=7}$.

Table A.22 Total Mass Remaining in the System on Each Day

Mass Remaining in System (ng)	**2**	**7**	**14**	**30**	**45**
Phenanthrene $_{d10}$	1498	1208	916	892	882
Pyrene $_{d10}$	130	109	89.2	76.2	67.9
Benzo[a]pyrene $_{d12}$	415	369	307	285	268
PCB 51	282	224	177	160	133
PCB 155	112	91.3	70.2	55.6	45.2
PCB 185	504	445	397	373	344

Table A.23 $C_{PE\sim}$ (ng/mg)

$C_{PE\sim}$ (ng/mg)	**log K_{PEW}**	**2**	**7**	**14**	**30**	**45**
Phenanthrene $_{d10}$	4.55	0.73	0.59	0.48	0.36	0.35
Pyrene $_{d10}$	5.05	0.19	0.16	0.14	0.11	0.09
Benzo[a]pyrene $_{d12}$	6.29	8.89	7.99	7.27	6.24	5.98
PCB 51	5.51	1.20	0.99	0.79	0.63	0.57
PCB 155	6.71	5.29	4.78	4.13	3.42	2.92
PCB 185	6.91	32.3	29.9	28.4	28.3	29.7

Table A.24 $C_{PE\infty}$ (ng/mg) Calculated from Equation A.12

$C_{PE\sim}$ (ng/mg)	**Phenanthrene $_{d10}$**	**Pyrene $_{d10}$**	**Benzo[a] pyrene $_{d12}$**	**PCB 51**	**PCB 155**	**PCB 185**
log K_{PEW}	**4.55**	**5.05**	**6.29**	**5.51**	**6.71**	**6.91**
2	0.73	0.19	8.89	1.20	5.29	32.3
7	0.59	0.16	7.99	0.99	4.78	29.9
14	0.48	0.14	7.27	0.79	4.13	28.4
30	0.36	0.11	6.24	0.63	3.42	28.3
45	0.35	0.10	5.98	0.57	2.92	29.7

SPME/PED Experiment

SPME DATA

The concentration in the water was calculated using the raw data and the following equation. The K_fV_fs (Yang *et.al.* 2006, Maruya *et.al.* 2009) used are presented in Table A.25. The concentrations in the water based on the SPME concentrations are presented in Table A.26.

Table A.25 K_fV_fs (Yang *et.al.* 2006, Maruya *et.al.* 2009)

Compound	K_fV_f
Phenanthrene	0.49
Pyrene	1.25
Benzo[a]pyrene	40.4
PCB 52	20.3
PCB 101	73.6
PCB 153	109
PCB 180	77.1
cis-Chlordane	14.4
DDE	90.5

Table A.26 Water Concentrations Calculated from SPME Determinations (ng/L)

ng/L	Carboy 1			Carboy 2			Carboy 3		
Phenanthrene	0.00	0.00	0.00	6.54	7.90	7.59	46.0	No Data[1]	41.8
Pyrene	0.00	0.00	0.00	0.92	0.71	1.20	4.80		4.21
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.14		0.13
PCB52	0.00	0.00	0.00	0.25	0.32	0.34	2.52		2.31
PCB101	0.00	0.00	0.00	0.04	0.03	0.03	0.24		0.21
PCB153	0.00	0.00	0.00	0.00	0.00	0.00	0.40		0.42
PCB180	0.00	0.00	0.00	0.00	0.00	0.00	0.14		0.12
alpha-Chlordane	0.00	0.00	0.00	0.66	0.65	0.77	4.87		4.46
DDE	0.00	0.00	0.00	0.07	0.05	0.05	0.36		0.33

[1] GC-MS malfunction during injection, data lost for this SPME

Table A.26 Water Concentrations Calculated from SPME Determinations (ng/L) (continued)

ng/L	Carboy 4			Carboy 5 Blank		
Phenanthrene	313	314	288	0.00	0.00	0.00
Pyrene	32.8	31.7	27.6	0.00	0.00	0.00
Benzo[a]pyrene	0.98	0.85	0.63	0.00	0.00	0.00
PCB52	16.5	17.7	17.0	0.00	0.00	0.00
PCB101	0.70	0.62	0.57	0.00	0.00	0.00
PCB153	0.73	0.90	0.67	0.00	0.00	0.00
PCB180	0.15	0.31	0.12	0.00	0.00	0.00
alpha-Chlordane	29.6	35.2	30.7	0.00	0.00	0.00
DDE	0.95	1.53	0.90	0.00	0.00	0.00

PED DATA

To calculate the weight-based concentration in the PED (Table 5.43), the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng). Then this mass was divided by the PED weight (Table A.27). The concentrations of the PED in ng/g are presented in Table A.28. The exception is the procedural blank, which was the full extraction procedure without a PED – starting with a BOD bottle with ~400 mL DCM and recovery surrogates.

Once the concentration in the PED (ng/g) was determined, the concentration in the water was calculated using Equation 5.7. The log K_{PEW}s were determined in the K_{PEW} experiment and are presented in A.29. The concentrations in the water based on the PED concentrations and Equation 5.7 are presented in Table 5.19.

Table A.27 PED Weights (g)

PED	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
(g)	1.97	1.81	2.00	1.88	1.55	1.84	1.97	1.95	1.79	1.80	1.79	1.59	1.95	1.75	1.73

Table A.28 PED Concentrations (ng/g)

ng/g	**Carboy 1**			**Carboy 2**		
Compound	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**
Phenanthrene	16.5	15.6	15.8	92.6	86.9	99.4
Pyrene	1.12	1.14	0.94	43.0	28.1	36.5
Benzo[a]pyrene	1.26	1.13	1.17	107	101	123
PCB52	9.67	9.97	8.18	143	92	123
PCB101	6.65	7.38	6.89	54.7	31.7	18.7
PCB153	20.6	20.1	21.2	191	123	199
PCB180	17.6	16.6	21.6	178	157	151
cis Chlordane	8.56	6.26	6.26	128	70.6	110
DDE	1.52	1.05	1.28	75.4	44.7	71.1

Table A.28 PED Concentrations (ng/g) (continued)

ng/g	**Carboy 3**			**Carboy 4**			**Carboy 5 Blank**		
Compound	**PED 7**	**PED 8**	**PED 9**	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
Phenanthrene	682	567	535	4162	4314	3895	0.00	0.00	0.00
Pyrene	289	278	264	2092	2515	2765	0.00	0.00	0.00
Benzo[a]pyrene	1008	775	779	7552	9013	8257	0.00	0.00	0.00
PCB52	1055	964	920	8967	5800	4752	0.00	0.00	0.00
PCB101	361	309	318	3148	3451	2690	0.00	0.00	0.00
PCB153	1597	1187	1457	10246	15682	8827	0.00	0.00	0.00
PCB180	325	282	199	1918	1482	1241	0.00	0.00	0.00
cis Chlordane	883	794	762	8099	4997	7000	0.00	0.00	0.00
DDE	570	473	497	4938	4827	4393	0.00	0.00	0.00

Table A.29 Log K_{PEW}s Used to Determine C_w (ng/L)

	Log K_{PEW}
Phenanthrene	4.35
Pyrene	5.05
Benzo[a]pyrene	6.61
PCB 52	5.51
PCB 101	6.16
PCB 153	6.71
PCB 180	6.92
cis-Chlordane	5.53
DDE	6.25

Table A.30 PED Weight for the Initial PEDs (g)

PED	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
(g)	0.27	0.19	0.20	0.16	0.25	0.16	0.23	0.25	0.21	0.20	0.21	0.31	0.25	0.25	0.27

Table A.31 Initial PED Concentrations of the Preloaded Compounds (ng/g)

Initial concentration	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**
Phenanthrene $_{d10}$	303	364	311	345	326	310
Pyrene $_{d10}$	1993	2185	2338	2428	2810	2845
Benzo[a]pyrene $_{d12}$	332	345	381	537	461	392
PCB 51	1984	2163	2442	2998	2529	2532
PCB 155	1916	1690	1858	1637	1093	1576
PCB 185	5395	6458	6313	7214	7253	7492

Table A.31 Initial PED Concentrations of the Preloaded Compounds (ng/g) (continued)

Initial concentration	**PED 7**	**PED 8**	**PED 9**	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
Phenanthrene $_{d10}$	315	319	272	420	466	460	409	423	408
Pyrene $_{d10}$	2661	2791	2719	2684	2410	3327	2635	2463	2221
Benzo[a]pyrene $_{d12}$	363	289	321	577	667	640	415	398	435
PCB 51	3437	3111	3286	3790	3671	3777	2635	2401	2360
PCB 155	1381	1337	1518	2085	2774	2090	2150	2244	1820
PCB 185	7205	7465	6755	9086	8993	7631	8009	8599	8379

Table A.32 Final PED Concentrations of the Preloaded Compounds (ng/mL)

PED	**Carboy 1**			**Carboy 2**		
Final Concentration	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**
Phenanthrene $_{d10}$	20427	13301	21330	4250	4068	4727
Pyrene $_{d10}$	151076	153277	157030	44472	42277	39385
Benzo[a]pyrene $_{d12}$	15934	16377	18191	4458	3658	4265
PCB 51	122057	139575	157093	46673	30895	38641
PCB 155	135661	77711	109350	22909	13366	18164
PCB 185	431770	411628	396765	114212	110688	118214

Table A.32 Final PED Data Concentrations of the Preloaded Compounds (ng/mL) (continued)

PED	**Carboy 3**			**Carboy 4**			**Carboy 5 Blank**		
Final Concentration	**PED 7**	**PED 8**	**PED 9**	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
Phenanthrene $_{d10}$	508	408	373	353	214	342	16772	16627	16689
Pyrene $_{d10}$	5079	4519	4114	3498	2387	3663	151166	155803	152668
Benzo[a]pyrene $_{d12}$	503	425	438	718	867	833	17688	17432	16931
PCB 51	5370	4574	4177	4380	4615	3856	128464	119276	113097
PCB 155	2377	2086	2065	3271	3890	3486	126067	143001	109164
PCB 185	12146	12720	11709	13621	14289	10196	543885	433308	484817

To calculate the weight-based concentrations in the PEDs, the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng). Then this mass was divided by the PED weight presented above (Table A.27). The concentrations of the PED in ng/g are presented in Table A.33.

Using Equation 5.8 and the average Initial concentrations of the preloaded compounds, the $\boldsymbol{k_e}$ (d^{-1}) was determined. $C_{PE\infty,r}$ is calculated according to Equation 5.9.

The $C_{PE\infty}$s calculated for this experiment are presented in Table A.34. Included in this table are the individual volumes for each carboy, the real time from start to finish for each batch experiment in days, and the M_T (ng), which was the summation of the masses of the preloaded reference compound in the three phases (water, SPME, PED) at the end of the experiment.

Table A.33 Final PED Concentrations of the Preloaded Compounds (ng/g)

	Carboy 1			Carboy 2		
Final Conc (ng/g)	**PED 1**	**PED 2**	**PED 3**	**PED 4**	**PED 5**	**PED 6**
Phenanthrene $_{d10}$	259	184	267	226	262	257
Pyrene $_{d10}$	1914	2122	1965	2360	2727	2139
Benzo[a]pyrene $_{d12}$	202	227	228	237	236	232
PCB 51	1546	1932	1966	2477	1993	2099
PCB 155	1719	1076	1369	1216	862	987
PCB 185	5470	5699	4966	6060	7140	6422

Table A.33 Final PED Data Concentrations of the Preloaded Compounds (ng/g) (continued)

	Carboy 3			Carboy 4			Carboy 5 Blank		
Final Conc (ng/g)	**PED 7**	**PED 8**	**PED 9**	**PED 10**	**PED 11**	**PED 12**	**PED 13**	**PED 14**	**PED 15**
Phenanthrene $_{d10}$	258	210	208	197	120	214	215	238	241
Pyrene $_{d10}$	2581	2320	2297	1948	1332	2301	1935	2227	2203
Benzo[a]pyrene $_{d12}$	255	218	244	400	484	523	226	249	244
PCB 51	2729	2348	2332	2439	2576	2422	1645	1705	1632
PCB 155	1208	1071	1153	1821	2171	2189	1614	2044	1576
PCB 185	6173	6530	6538	7585	7977	6403	6963	6193	6997

Table A.34 $C_{PE\infty}$s Calculated for Each Carboy for the Preloaded Reference Compounds

	Carboy 1		**Carboy 2**		**Carboy 3**		**Carboy 4**		**Carboy 5**	
Volume (L)		19.3		19.1		19.3		19.0		18.9
Time (days)		46.8		46.8		46.8		46.8		46.7
	M_T (ng)	$C_{PE\infty}$ **(ng/g)**	**M_T (ng)**	$C_{PE\infty}$ **(ng/g)**	**M_T (ng)**	$C_{PE\infty}$ **(ng/g)**	**M_T (ng)**	$C_{PE\infty}$ **(ng/g)**	**M_T (ng)**	$C_{PE\infty}$ **(ng/g)**
Phenanthrene $_{d10}$	1639	259	1599	275	1629	261	1540	270	1454	244
Pyrene $_{d10}$	11815	1986	13000	2387	14183	2413	10474	1958	11735	2095
Benzo[a] pyrene $_{d12}$	1263	218	1238	234	1366	239	2428	468	1301	239
PCB 51	10903	1868	12304	2306	15760	2733	13509	2579	9503	1730
PCB 155	8077	1397	5457	1034	6561	1149	10660	2057	9469	1741
PCB 185	31033	5370	34362	6510	36662	6422	38147	7362	36579	6729

The PED-determined water concentrations were consistently lower than the actual water concentrations, which suggest that the PEDs had not reached equilibrium. However, kinetic calculations from the preloaded compounds indicate the PEDs had reached equilibrium. Because of the small volume of water in the chambers (less than 20L in each) and the large mass of PED required for detections (approximately 6g in each), the solid-to-water ratio was extremely high. This nullifies the finite bath simplification in Equations 5.7 and 5.8.

The K_fV_fs (Yang *et.al.* 2006, Maruya *et.al.* 2009) used are presented in Table A.35.

Table A.35 K_fV_fs (Yang *et.al.* 2006, Maruya *et.al.* 2009)

Compound	K_fV_f
Phenanthrene	0.49
Pyrene	1.25
Chrysene	2.93
Benzo[a]pyrene	40.4
PCB 52	20.3
PCB 70	22.7
PCB 101	73.6
PCB 110	73.6
PCB 153	109
PCB 180	77.1
Heptachlor epoxide	1.85
cis-Chlordane	14.4
trans-Nonachlor	29.3
DDE	90.5
DDT	10.6

The concentration in the water (Table A.36) was calculated using the raw data and Equation 5.14.

Table A.36 Water Concentrations Calulated from SPME Determinations (ng/L)

Estimated C_w	**1 bottom**	**1 bottom**	**1 up**	**1 up**	**3 bottom**	**3 up**	**3 up**	**4 bottom**
Phenanthrene	0.49	0.51	3.41	0.29	2.09	1.84	1.87	1.68
Pyrene	0.62	0.73	1.67	1.60	1.62	0.00	2.19	2.40
Chrysene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 52	0.00	0.02	0.02	0.01	0.02	0.01	0.02	0.00
PCB 70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis-Chlordane	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.01
trans-Nonachlor	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDE	0.01	0.01	0.00	0.02	0.01	0.04	0.02	0.03
DDT	3.43	6.23	0.65	2.00	0.15	0.35	3.20	1.94

Table A.36 Water Concentrations Calculated from SPME Determinations (ng/L) (continued)

Estimated C_w (ng/L)	**4 up**	**4 up**	**5 bottom**	**5 up**	**5 up**	**6 bottom**	**6 bottom**	**6 up**	**6 up**
Phenanthrene	1.43	1.99	2.75	No Data	3.64	17.8	20.9	5.08	5.53
Pyrene	2.05	2.79	1.20		4.33	8.58	9.85	5.76	6.52
Chrysene	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
Benzo[a] pyrene	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 52	0.00	0.04	0.02		0.01	0.00	0.01	0.04	0.00
PCB 70	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
cis-Chlordane	0.02	0.00	0.02		0.00	0.01	0.00	0.00	0.01
trans-Nonachlor	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00
DDE	0.02	0.03	0.02		0.01	0.01	0.02	0.01	0.02
DDT	1.96	2.52	1.62		0.73	1.89	2.04	0.40	1.29

Table A.37 Concentration Determinations for PED Extracts for the Field Blanks

ng/mL	ProcBLK	BLK 1	BLK2	BLK 3	BLK4	BLK5	BLK6
Phenanthrene	1.62	4.96	3.74	0.52	1.41	2.66	0.00
Pyrene	1.23	0.00	0.00	0.00	0.00	3.96	2.53
Chrysene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[ghi]perylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 52	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 70	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 101	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 110	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 153	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00
heptachlor epoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00
***cis* Chlordane**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
***trans*-nonachlor**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DDT	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.38 PED Weights for Individual Blank PEDs (g)

ped	Blk 1	Blk 2	Blk 3	Blk 4	Blk 5	Blk 6
weight	1.55	1.58	2.13	1.39	0.97	1.77

Table A.39 PED Weights (g)

PED	S1P7	S3P1	S3P2	S4P3	S4P4	S5P11	S5P12	S5P13	S5P14	S5P15	S5P16	S6P5	S6P6
Weight	2.75	2.76	2.44	1.77	2.83	2.93	2.11	3.38	1.53	3.08	2.59	2.81	3.26

To calculate the weight-based concentration in the PED, the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng). Then this mass was divided by the PED weight (Table A.38). The concentrations in the PED in ng/g are presented in Table A.37. The exception is the procedural blank, which was the full extraction procedure without a PED – starting with a BOD bottle with ~400 mL DCM and recovery surrogates. A silica column clean up was preformed on the procedural blank as well.

To calculate the weight-based concentrations in the PEDs, the concentration (ng/mL) was first multiplied by the volume of the extract (0.5 mL) to get the mass in the extract from the PED (ng). Then this mass was divided by the PED weight (Table A.39). The concentrations of the PED in ng/g are presented in Table A.40.

Table A.40 Contaminant Concentrations in Field-Deployed PEDs (ng/g)

ng/g	**S1P7**	**S3P1**	**S3P2**	**S4P3**	**S4P4**
Phenanthrene	21.7	7.75	6.59	11.4	7.88
Pyrene	37.1	51.9	24.0	74.4	76.7
Chrysene	33.2	26.5	23.5	98.8	52.6
Benzo[a]pyrene	33.7	13.2	11.7	100	67.5
Benzo[ghi]perylene	0.00	29.4	26.1	35.4	33.2
PCB 52	11.4	13.2	13.2	20.1	25.2
PCB 70	112	134	187	101	78.4
PCB 101	15.6	22.0	34.4	16.3	13.6
PCB 110	10.6	4.19	4.47	4.60	6.43
PCB 153	10.7	16.04	16.5	15.9	12.4
PCB 180	2.21	7.90	7.93	5.77	2.30
heptachlor epoxide	0.70	0.56	1.96	0.88	0.60
***cis* Chlordane**	7.40	10.77	9.98	9.98	9.58
***trans*-nonachlor**	4.81	6.61	5.38	6.18	5.42
DDE	19.7	22.1	21.3	19.3	18.6
DDT	15.4	17.5	20.4	19.4	15.0

Table A.40 Contaminant Concentrations in Field-Deployed PEDs (ng/g) (continued)

ng/g	S5P11	S5P12	S5P13	S5P14	S5P15	S5P16	S6P5	S6P6
Phenanthrene	13.6	24.6	10.5	21.1	22.5	25.3	46.1	114
Pyrene	93.6	141	72.1	200	148	159	156	176
Chrysene	91.0	240	53.6	162	159	92.5	136	78.0
Benzo[a]pyrene	72.9	130	68.8	144	157	109	142	105
Benzo[ghi]perylene	0.00	103	8.26	0.00	0.00	0.00	48.4	17.2
PCB 52	34.4	29.6	30.5	54.0	23.7	32.7	61.1	34.2
PCB 70	110	81.9	40.0	617	246	333	426	416
PCB 101	18.1	10.3	16.2	24.3	5.23	16.6	19.2	7.31
PCB 110	13.1	14.5	12.3	20.1	8.21	13.4	10.6	11.3
PCB 153	16.6	18.2	15.3	25.1	12.5	17.0	15.7	5.44
PCB 180	3.74	5.77	7.80	5.28	2.43	4.07	4.67	4.91
heptachlor epoxide	2.00	0.63	0.69	26.9	5.29	10.4	27.0	20.5
***cis* Chlordane**	15.36	16.81	14.7	23.0	7.70	15.9	24.6	8.95
***trans*-nonachlor**	9.56	9.07	9.13	15.3	5.06	9.91	15.2	5.78
DDE	27.9	31.8	27.7	42.3	17.1	28.9	28.6	10.6
DDT	22.6	26.1	25.3	36.6	15.3	22.4	28.1	10.5

Table A.41 The Estimated C_W (ng/L) in the Field Calculated from the PED Concentrations

Estimated C_W	**1 up**	**3 up**	**3 bottom**	**4 up**	**4 bottom**
ng/L	**S1P7**	**S3P1**	**S3P2**	**S4P3**	**S4P4**
Phenanthrene	1.07	0.37	0.31	0.54	0.37
Pyrene	0.36	0.50	0.23	0.75	0.75
Chrysene	0.07	0.06	0.05	0.21	0.11
Benzo[a]pyrene	0.01	0.00	0.00	0.03	0.02
Benzo[ghi]perylene	0.00	0.04	0.04	0.07	0.05
PCB 52	0.04	0.04	0.04	0.06	0.08
PCB 70	0.18	0.21	0.29	0.16	0.12
PCB 101	0.01	0.02	0.03	0.01	0.01
PCB 110	0.01	0.00	0.00	0.00	0.01
PCB 153	0.00	0.01	0.00	0.00	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.07	0.06	0.18	0.07	0.05
cis-Chlordane	0.03	0.05	0.05	0.04	0.04
trans-Nonachlor	0.01	0.02	0.01	0.01	0.01
DDE	0.02	0.03	0.02	0.02	0.02
DDT	0.03	0.06	0.05	0.06	0.04

Table A.41 The Estimated C_W (ng/L) in the Field Calculated from the PED Concentrations (continued)

Estimated C_W	**5 up**	**5 up**	**5 up**	**5 bottom**	**5 bottom**	**5 bottom**	**6 up**	**6 bottom**
ng/L	**S5P11**	**S5P12**	**S5P13**	**S5P14**	**S5P15**	**S5P16**	**S6P5**	**S6P6**
Phenanthrene	0.64	1.16	0.50	0.99	1.07	1.20	2.22	5.34
Pyrene	0.91	1.41	0.70	2.00	1.41	1.54	1.53	1.71
Chrysene	0.19	0.52	0.11	0.35	0.33	0.19	0.29	0.16
Benzo[a] pyrene	0.02	0.04	0.02	0.05	0.05	0.03	0.04	0.03
Benzo[ghi] perylene	0.00	0.18	0.01	0.00	0.00	0.00	0.08	0.03
PCB 52	0.11	0.09	0.10	0.18	0.07	0.12	0.19	0.11
PCB 70	0.18	0.13	0.06	1.00	0.38	0.59	0.67	0.66
PCB 101	0.02	0.01	0.01	0.03	0.00	0.02	0.02	0.01
PCB 110	0.01	0.02	0.01	0.03	0.01	0.02	0.01	0.01
PCB 153	0.01	0.01	0.01	0.02	0.00	0.01	0.01	0.00
PCB 180	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptachlor epoxide	0.25	0.08	0.07	5.22	0.40	1.45	2.73	1.75
cis-Chlordane	0.09	0.10	0.07	0.21	0.03	0.11	0.12	0.04
trans-Nonachlor	0.03	0.03	0.02	0.07	0.01	0.03	0.04	0.01
DDE	0.03	0.03	0.03	0.09	0.01	0.04	0.03	0.01
DDT	0.07	0.06	0.07	0.21	0.04	0.07	0.09	0.02

Table A.42 PED Weight for the Initial PEDs (g)

PED #	**PED13i**	**PED2i**	**PED11i**	**PED4i**	**PED16i**	**PED9i**
Weight	0.068	0.123	0.062	0.044	0.057	0.037

Table A.43 Initial Concentrations of the Pre-Loaded Contaminants in the PEDs (ng/g)

Initial concentration	**PED13i**	**PED2i**	**PED11i**	**PED4i**	**PED16i**	**PED9i**	**Average**
Phenanthrene $_{d10}$	61.5	66.0	134	245	14.4	42.7	93.9
Pyrene $_{d10}$	841	329	1576	622	762	1281	902
Benzo[a]pyrene $_{d12}$	1396	1035	541	1046	431	961	902
PCB51	2008	1586	3154	3890	2504	1829	2495
PCB 155	1035	886	1647	1606	1165	1034	1229
PCB 185	41510	51907	91360	73089	54587	42006	59076

Table A.44 Final Concentrations of the Preloaded Contaminants in the PEDs (ng/g)

Final Conc (ng/g)	**S1P7**	**S3P1**	**S3P2**	**S4P3**	**S4P4**
Phenanthrene $_{d10}$	4.14	0.24	0.20	0.00	0.00
Pyrene $_{d10}$	24.5	15.9	13.6	50.9	32.1
Benzo[a]pyrene $_{d12}$	130	15.2	13.5	229	98.4
PCB 51	27.9	16.0	3.80	10.2	14.5
PCB 155	1140	1325	1121	870	841
PCB 185	17947	32037	24283	28198	23697

Table A.44 Final Concentrations of the Preloaded Contaminants in the PEDs (ng/g) (continued)

Final Conc (ng/g)	**S5P11**	**S5P12**	**S5P13**	**S5P14**	**S5P15**	**S5P16**	**S6P5**	**S6P6**
Phenanthrene $_{d10}$	0.00	0.00	0.41	0.00	1.08	0.45	2.28	0.00
Pyrene $_{d10}$	20.9	46.5	22.8	49.3	9.35	15.8	32.8	23.9
Benzo[a]pyrene $_{d12}$	166	201	94.6	194	176	130	150	135
PCB 51	35.1	15.6	17.4	54.2	5.63	69.0	16.7	14.5
PCB 155	1646	1669	1333	2195	585	1797	1258	895
PCB 185	30130	21820	24358	43333	19942	31730	31311	19827

Table A.45 Calculated k_e for the Pre-Loaded Contaminants in the Infinite Bath Field PEDs

k_e (d^{-1})	S1P7	S3P1	S3P2	S4P3	S4P4
Phenanthrene $_{d10}$	0.14	0.26	0.27	0.45	0.47
Pyrene $_{d10}$	0.16	0.18	0.18	0.12	0.14
Benzo[a]pyrene $_{d12}$	0.08	0.18	0.18	0.06	0.10
PCB 51	0.20	0.22	0.28	0.24	0.22
PCB 155	0.05	0.04	0.05	0.06	0.06
PCB 185	0.05	0.03	0.04	0.03	0.04

Table A.45 Calculated k_e for the Pre-Loaded Contaminants in the Infinite Bath Field PEDs (continued)

k_e (d^{-1})	S5P11	S5P12	S5P13	S5P14	S5P15	S5P16	S6P5	S6P6
Phenanthrene $_{d10}$	0.47	0.46	0.24	0.45	0.19	0.23	0.16	0.48
Pyrene $_{d10}$	0.16	0.13	0.16	0.13	0.20	0.18	0.14	0.16
Benzo[a]pyrene $_{d12}$	0.07	0.07	0.10	0.07	0.07	0.08	0.08	0.08
PCB 51	0.19	0.22	0.22	0.17	0.26	0.16	0.22	0.22
PCB 155	0.03	0.03	0.04	0.02	0.07	0.03	0.04	0.06
PCB 185	0.03	0.04	0.04	0.01	0.05	0.03	0.03	0.05

Table A.46 1-e^{-ket} For the Preloaded Contaminants in the Infinite Bath Field PEDs

(1-e^{-ket})	**S1P7**	**S3P1**	**S3P2**	**S4P3**	**S4P4**
Phenanthrene $_{d10}$	0.96	1.00	1.00	1.00	1.00
Pyrene $_{d10}$	0.97	0.98	0.98	0.94	0.96
Benzo[a]pyrene $_{d12}$	0.86	0.98	0.99	0.75	0.89
PCB 51	0.99	0.99	1.00	1.00	0.99
PCB 155	0.65	0.59	0.65	0.73	0.74
PCB 185	0.70	0.46	0.59	0.52	0.60

Table A.46 1-e^{-ket} For the Pre-Loaded Contaminants in the Infinite Bath Field PEDs (continued)

(1-e^{-ket})	**S5P11**	**S5P12**	**S5P13**	**S5P14**	**S5P15**	**S5P16**	**S6P5**	**S6P6**	**Average**
Phenanthrene $_{d10}$	1.00	1.00	1.00	1.00	0.99	1.00	0.98	1.00	0.99
Pyrene $_{d10}$	0.98	0.95	0.97	0.95	0.99	0.98	0.96	0.97	0.97
Benzo[a]pyrene $_{d12}$	0.82	0.78	0.90	0.78	0.80	0.86	0.83	0.85	0.85
PCB51	0.99	0.99	0.99	0.98	1.00	0.97	0.99	0.99	0.99
PCB 155	0.49	0.48	0.59	0.32	0.82	0.44	0.61	0.72	0.60
PCB 185	0.49	0.63	0.59	0.27	0.66	0.46	0.47	0.66	0.55