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Hydrophobic Organic Contaminants in Urban-Impacted Coastal Marine Sediments

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Science

by

Allison Reine Taylor

December 2019

Dissertation Committee:
Dr. Jay Gan, Chairperson
Dr. Daniel Schlenk
Dr. Samantha Ying

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The Dissertation of Allison Reine Taylor is approved:

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Committee Chairperson

University of California, Riverside

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ABSTRACT OF THE DISSERTATION

Hydrophobic Organic Contaminants in Urban-Impacted Coastal Marine Sediments

by

Allison Reine Taylor

Doctor of Philosophy, Graduate Program in Environmental Sciences
University of California, Riverside, December 2019
Dr. Jay Gan, Chairperson

Hydrophobic organic contaminants (HOCs) are anthropogenic compounds that have been used for many decades in a wide range of applications. Due to human activities and improper disposal, many HOCs have been deposited into aquatic environments where they strongly sorb to hydrophobic matrixes like bed sediments and can pose risk to aquatic organisms. Therefore, understanding the processes and factors that influence the bioavailability of HOCs is important for predicting and refining risk assessments, particularly for coastal marine sediments where contamination from adjacent urban centers is expected while relatively much less is known. Here we evaluated the bioavailability of aged DDTs and PCBs in historically contaminated sediment from the Palos Verdes Shelf Superfund Site. Total HOC concentrations remain as high as 41,000 mg/kg. However, these aged HOC residues had dramatically reduced bioaccessibility; the

bioaccessible fraction was generally <20%, and biota-sediment accumulation factor (BSAF) values ranged from 0.11-29. Therefore, it is important to consider the history and bioavailability of HOCs when conducting risk assessments. A subsequent study evaluated the use of different types of black carbon as an amendment to enhance sequestration and immobilization of HOCs. All amendment materials decreased C_{free} and bioaccumulation, with C_{free} ranging from nd-1.34 ng/L, and BSAFs from nd-0.024. Although the PAC resulted in significantly higher sequestration, the relative reductions were small, and the limited changes were likely due to the sediment's high organic matter content (5.4 %) and that the HOCs already had reduced bioavailability due to extensive aging. Therefore, the use of black carbon amendments may not be ideal for remediation of sediments with aged contaminants. The last study evaluated the distribution and source of urban-use insecticides in marine sediments off the coast of Los Angeles. Pyrethroids and a fipronil degradate, fipronil sulfide, were frequently detected across the PV Shelf in concentrations that may pose toxicity (nd-170 μg/kg). Some of these insecticides were attributed to WWTP effluent emission, while the rest were associated with nonpoint sources. These findings highlight the need for more systematic studies on toxicity of legacy and current-use HOCs for marine organisms and development of strategies to minimize their emission into the coastal environment.

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Abbreviations

HOC- Hydrophobic Organic Contaminant

DDT- Dichlorodiphenyltrichloroethane

DDE- Dichlorodiphenyldichloroethylene

DDD- Dichlorodiphenyldichloroethane

OP- Organophosphate

PCB- Polychlorinated Biphenyl

AC- Activated carbon

PAC- Powdered activated carbon

GAC- Granular activated carbon

BFT- Bifenthrin

FPT- Fenpropathrin

λ-CYH- λ-Cyhalothrin

CYP- Cypermethrin

PMT- *cis*-Permethrin

CYF- Cyfluthrin

FIP- Fipronil

DSF FIP- Desulfinyl Fipronil

FIP SFO- Fipronil Sulfone

FIP SFD- Fipronil Sulfide

Chapter 1 Introduction

1.1 HOC Contamination in the Environment

Hydrophobic organic contaminants (HOCs) have been in production and use in human society for many decades, and have made their way into the environment around the world (Anderson et al., 2012; Bettinetti et al., 2016; Zhang et al., 2002). For example, the chlorinated compound dichlorodiphenyltrichloroethane, or DDT, was first synthesized in 1874 and began use as a pesticide on farms in 1939, about 80 years ago (Sparling, 2016). In areas where malaria still heavily impacts the population, such as South America, India, and Africa, DDT is still in use, as it is highly effective at reducing mosquito populations (Sparling, 2016). However, due to the widespread effects DDT had on the environment, the use of DDT was banned in the United States in 1972 (U.S. EPA, 2009). Contaminants like DDT can enter into the environment in various ways, but the primary mechanism is generally through their use or in the case of pesticides, application on fields, landscaping, or in homes. Their transport through the environment, however, depends upon the properties of the chemical itself. HOCs are hydrophobic in nature, meaning that they strongly sorb to other hydrophobic matrixes, such as soil or sediment particles, organic matter, or the lipid tissues of organisms exposed to these contaminants (Ewald and Larsson, 1994). Frequently, HOCs are found in the highest concentrations in soils or sediments that have the highest organic matter contents (Wania, 1999). Although many contaminants residing in the environment are considered “legacy” contaminants due to their historical use, newer synthetic organic contaminants, such as pesticides like pyrethroids and fipronils, have also made their way into soils, sediments, and surface

waters (Delgado-Moreno et al., 2011; Lao et al., 2010; 2011; Richards et al., 2016; Weston et al., 2004; Weston and Lydy, 2010).

Once man-made chemicals were determined to have significant environmental risks, many were banned for use. To fill the void left by their phase-out, new alternatives are introduced. In the history of pesticide use, for example, to replace organochlorine pesticides (OCs) like DDT, organophosphates (OPs) were introduced (Amweg et al., 2005; Lao et al., 2010; Weston et al., 2013). OPs are much less persistent than OCs, but many exhibit greater acute toxicity to a wide range of non-target organisms, including humans (Amweg et al., 2005; Lao et al., 2010), and consequently, many Ops were also phased out. To fill the void left by the banning of OPs, pyrethroids and fipronil, which have low mammalian toxicity, were introduced into the market. Pyrethroids and fipronil have been widely used for pest management in both agricultural applications and in urban neighborhoods and landscaping (Amweg et al., 2006; Hainzl et al., 1998).

Both pyrethroids and fipronil have high potency to the target pests (such as ants, termites, fleas, and ticks), but they have been shown to have acute toxicity to aquatic organisms, especially aquatic invertebrates (Lao et al., 2010; Maul et al., 2008; Weston et al., 2004). For example, cypermethrin was shown to be highly toxic to *Hyallela azteca*, with an LC_{50} of only 0.4 μg/g organic carbon (Maund et al., 2002). Many other studies have demonstrated the high toxicity of pyrethroids to aquatic invertebrates at levels found in the environment (Ensminger et al., 2012; Weston and Jackson, 2009). Fipronil and its degradates, i.e., fipronil sulfone, fipronil sufilde, and disulfonyl fipronil, are also acutely toxic to a variety of aquatic species, including various benthic organisms (Chandler et al.,

2004; Lao et al., 2010; Schlenk et al., 2001). In particular, crustaceans are highly sensitive to these compounds, with reproductive effects observed at levels (fipronil) as low as 0.16 μg/L (Chandler et al., 2004; Goff et al., 2017). There has also been evidence that marine organisms may be even more sensitive to these insecticides because of their increased partitioning into the sediment due to increased salinity; however few studies have considered the actual toxicities of these current-use insecticides to marine organisms (Goff et al., 2017; Hasenbein et al., 2018; Saranjampour et al., 2017).

As many urban regions use pyrethroids and fipronil for structural and nuisance pest management, including indoor uses, there is the potential for these compounds to make their way into the environment (Gunasekara et al., 2007; Li et al., 2017; Richards et al., 2016). Large cities and urban centers where current-use insecticides are used, like Los Angeles, San Diego, are also located near large waterways and the coasts, allowing for these insecticides to enter urban waterways, streams/rivers, and ultimately, oceans (Delgado-Moreno et al., 2011; Hernandez-Guzman et al., 2017; Supowit et al., 2016; Weston and Lydy, 2012; Weston et al., 2010; 2013). When used indoor, e.g., for ant and cockroach control, or tick eradication on pets, current-use insecticides may enter sewer systems; and at wastewater treatment plants (WWTPs), are not completely removed and therefore trace amounts of insecticides were found in WWTP effluents (Hernandez-Guzman et al., 2017; Supowit et al., 2016; Weston et al., 2013). The urban-use insecticides have been found in estuarine sediments, at concentrations high enough to have negative impacts on the benthic communities (Lao et al., 2010; Walse et al., 2004). WWTP effluents are often discharged into the ocean, which, when coupled with surface

runoff, presents the potential for the transport of current-use insecticides to deeper ocean sediments, posing a cause for concern about their risks to marine benthic organisms in these ecosystems.

1.2 History of Palos Verdes Shelf

From the 1950s up until the 1970s, when the use of DDT was banned in the United States, Montrose Chemical Company discharged their waste into the Los Angeles County sewer system. Montrose was the world's largest DDT manufacturing company, and produced upwards of 800,000 tons of DDTs during the 35 years it was in operation (U.S. EPA, 2009). Unfortunately, at the time there was little treatment required for such industrial wastes, and approximately 1000 metric tons of DDTs were discharged into the Pacific Ocean along with the waste from other industrial sources containing PCBs, contaminating what is now approximately 44 km^2 of ocean sediment (US EPA, 2009). Ocean currents close to the seafloor have moved contaminants and contaminated sediment from the deposition site, located close to the 8C sampling location, northwest up the coast of California and around the Palos Verdes Peninsula, as shown in Figure 1.2 (Drake et al., 1994; Hickey, 1993; U.S. EPA, 2009). Due to this widespread contamination, the Palos Verdes (PV) Shelf was listed as a Superfund Site on October 4, 1989. The PV shelf sediment is over 45 m below the sea level and therefore is not in direct contact with humans, but due to the tendency of these contaminants to bioaccumulate, there are many health warnings for fish caught from this area (U.S. EPA, 2010). The steep slope also prevents the use of traditional methods of remediation for this

site, as gravel or sand caps may be easily eroded (U.S. EPA, 2009). Currently, the EPA has decided to use the monitored natural recovery (MNR), or attenuation, method as the remediation strategy for this Superfund site (US EPA, 2009). Due to the constant monitoring of this location and the proximity to a highly populated area like Southern California, the PV shelf is an ideal location to study what factors influence bioavailability of legacy contaminants like DDTs and PCBs, and what new contaminants, like current-use insecticides, may be entering coastal marine ecosystems.

1.3 Bioavailability of HOCs

Bioavailability is defined in several ways in science, dependent upon the context of the field. In toxicology and pharmacology, bioavailability is defined as the systemic availability of a xenobiotic in its unaltered state once it has been taken up into an organism (Shen, 2008). In environmental sciences, bioavailability is a more ambiguous term that can be typically defined in two different ways. Both are based upon Equilibrium Partitioning Theory, in which the chemical is at equilibrium between the sediment or soil organic matter, water, and biota, as shown in **Figure 1.1** (Di Toro et al., 1991). The first measure of bioavailability is the freely dissolved concentration, or C_{free}, in surface water, groundwater, or other pore water in sediments and soils (Reichenberg and Mayer, 2006). C_{free} is influenced by the compound's chemical activity or the potential for it to partition into organisms when the system is at equilibrium (Di Toro et al., 1991; Reichenberg and Mayer, 2006). The chemical activity of a contaminant refers to the contaminant's energetic state, and it quantifies the potential for spontaneous physicochemical processes

to occur (Di Toro et al., 1991). At equilibrium, the chemical activity of the contaminant is the same in each environmental matrix (i.e., the soil/sediment, water, biota, organic matter), and therefore the concentrations of the contaminant in each of these matrices are proportional to each other (Di Toro et al., 1991; Reichenberg and Mayer, 2006).

The second measure of bioavailability is commonly referred to as bioaccessibility, or the desorbable fraction of the contaminant from the sediment or soil. Bioaccessibility is a measurement of the weakly held or reversibly sorbed fraction of a contaminant from sediment or soil, and typically this measurement encompasses the fraction that rapidly desorbs, F_{rapid}, or F_r (**Equation 1.1**), into the aqueous phase (Cornelissen et al., 2005; Ehlers and Luthy, 2003; Reichenberg and Mayer, 2006).

$$\frac{S_t}{S_0} = F_r e^{-k_r t} + F_s e^{-k_s t} + F_{vs} e^{-k_{vs} t} \qquad (1.1)$$

Due to the unique properties of each contaminant and the measurement methods used to estimate F_r, the bioaccessible fraction can have more than one value, unlike C_{free} (Cornelissen et al., 2005; Ehlers and Luthy, 2003; Reichenberg and Mayer, 2006).

1.4 Aging of HOCs in the Environment

C_{free} and bioaccessibility are both strongly influenced by aging. As contaminants remain in the environment, they undergo a process called aging, in which they are usually rendered less bioavailable (White et al., 1999). Some of the first studies to note that the bioavailability of contaminants decreased in the environment over time observed that field aged pesticides were less bioavailable than those that were freshly applied (Scribner et al., 1992; Steinberg et al., 1987). Contrary to what would be expected based upon

equilibrium partitioning theory, BSAFs of the oligochaetes *Limnodrilus hoffineisteri*, *Tubifex tubifex*, and *Lumbriculus variegatus* exposed to multiple HOCs were lower in samples where these sediments were likely to be more highly sequestered, or aged (Kraaij et al., 2002). In a study by Hatzinger and Alexander (1995), the bioavailability to bacteria of two HOCs decreased with increased contact time in soils. Other studies also showed similar results, where increased contact time with a soil or sediment in the environment led to decreased bioavailability to organisms like bacteria or earthworms, and as a result they exhibited lower toxicities and body burdens (Landrum et al., 1992; Umbreit et al., 1986; Varanasi et al., 1985). Due to these decreases in bioavailability with increased contact time with the sediment or soil matrix, the use of bulk contaminant concentration in the sediment or soil to predict risk came under question. Many studies found that the use of bioavailable or bioaccessible concentrations is more accurate for estimating risk and the use of bulk concentrations will overestimate risk (Ahmad et al., 2004; Alexander, M., 2000; Morrison et al., 2000). Ehlers and Luthy (2003) further suggested that site-specific measurements of bioavailable concentrations should be used for risk assessment, as environmental conditions also influence how contaminants are sequestered.

1.5 Bioavailability Measurement Methods

1.5.1 Measuring C_{free}

In 1990, Huckins et al. introduced the use of semi-permeable membrane devices (SPMDs) for measuring C_{free}. These devices consist of a low density polyethylene film filled with a lipid (i.e., natural lipids or the model lipid triolein) that can passively

accumulate HOCs in the environment, which then can be extracted with solvent in the laboratory and measured (Huckins et al., 1990). These devices have very good correlations with bioaccumulation of HOCs into organisms because they resemble lipid tissues, but due to high extraction efficiencies, they can only be used in large volume samples (Hofelt and Shea, 1997; Zimmerman et al., 2004). Other limitations of SPMDs include their long equilibrium times and the potential loss of lipids before extraction (Hofelt and Shea, 1997; Leppanen and Kukkonen, 2006).

Some less complex devices, such as polyethylene devices (PEDs) and polyoxymethylene samplers (POMs), do not have a lipid phase, making them much simpler to use. Both can be deployed *ex situ* and *in situ*, allowing for more flexibility (Cui et al., 2013). PEDs were originally developed for use in water (Adams et al., 2007; Booij et al., 2003), but were then further applied to measure C_{free} and estimate bioavailability of HOCs in sediments (Cornelissen et al., 2008; Friedman et al., 2009). POMs were introduced to determine partitioning coefficients of HOCs from sediment into water by Cornelissen et al. (2008) and Hawthorne et al. (2009). Due to a polar group within the polymer, these devices have an improved sensitivity for more polar contaminants (Endo et al., 2011). Their smooth and hard surface relative to other samplers also decreases biofouling or particle trapping that may occur during sampling (van der Heijden and Jonker, 2009). However, both of these devices have similar limitations; they need large sample volumes to prevent depletion, and they can take weeks to a month to reach equilibrium (Cui et al., 2013). However, the use of performance reference compounds (PRCs) can circumvent the requirement for long equilibrium time, and help reduce in situ

sampling times (Adams et al., 2007; Tomaszewski and Luthy, 2008). More recently, thin polymer films are being used to measure C_{free}. Like PEDs, POMs, and SPME fibers, these films are easier to deploy as they lack a liquid lipid layer, and can be used with PRCs to eliminate long equilibrium times (Cui et al., 2013). These films are also less fragile and more sensitive than solid-phase microextraction (SPME) fibers due to larger contact areas and polymer volumes and can be used and optimized for a variety of contaminants (Bao et al., 2013; Beckingham and Ghosh, 2013; Burgess et al., 2015; Hawthorne et al., 2009). Thin films are commonly used as passive samplers and were developed for deployment in both surface waters and sediments to monitor for environmental contaminants (Hale et al., 2009; Wang et al., 2018). For example, polyethylene or PE films were determined to be the best for sampling pyrethroids in surface waters out of 4 types that were tested (PE, PU, POM, and PMMA) (Xue et al.; 2017).

As these devices are difficult to use with small sample sizes, solid-phase microextraction, initially developed by Arthur and Pawliszyn (1990) as an analytical tool, was adapted to measure C_{free} of HOCs in environmental samples. The SPME fibers are thin glass or metal rods covered in a thin polymer layer often in different thicknesses (Mayer et al., 2003; ter Laak et al., 2008). The most common polymer used for HOCs is polydimethylsiloxane (PDMS), and the small sorbent volume suggests that the sampling is usually non-depletive, meaning that they can be used in small size samples, such as those used for toxicity or bioaccumulation assays in small test vessels (Jonker et al., 2007; Leslie et al, 2002; Mayer et al., 2003; Potter and Pawliszyn, 1994; You et al., 2007;

Zhang et al., 2010). There are two types of SPME fiber configuration commonly used for sampling. The first is called injector-type SPME, where these fibers can be directly injected into a gas chromatograph without the need for any solvent extraction (Bondarenko and Gan, 2009). Bondarenko and Gan (2009) also used these fibers with an automated sampler for a gas chromatograph coupled with a mass spectrometer (GC/MS), further reducing sample processing times and improving reproducibility of analysis. Due to their small size, these fibers can be used for both *ex situ* and *in situ* deployment (Maruya et al., 2009; Xu et al., 2007; Zeng et al., 2005). The second type of configuration of SPME is the disposable fibers, where fibers themselves are directly used (Mayer et al., 2000; ter Laak et al., 2006). Many studies have shown close relationships between fiber concentrations of HOCs and bioconcentration factors (BCFs) and biota-sediment accumulation factors (BSAFs), making them reliable for estimating bioavailability via C_{free} (Cui et al., 2011; Jia et al., 2014; Mayer et al., 2000; van der Wal et al., 2004; Yang et al., 2009). Due to their small size, these fibers have been used in small-scale bioassays to measure C_{free} during the time of exposure, allowing for direct comparisons between C_{free} and BCFs or BSAFs (Hunter et al., 2009; Trimble et al., 2008; You et al., 2006; 2007). Other studies have used SPME fibers to look for changes in bioavailability of HOCs during remediation in under laboratory simulated or field conditions (Jia et al., 2016; Jonker et al., 2007; Yang et al., 2009).

1.5.2 Measuring Bioaccessibility

There are many ways to measure the bioaccessible fraction of a contaminant in sediment or soil (Cui et al., 2013). One of the earlier methods was mild solvent extraction – the use of a mild organic solvent such as methanol or a mixture of a solvent and water. There are many types and combinations used depending upon the compound of interest (Cui et al., 2013). Studies showed that the amount of HOCs given by the mild solvent extraction was proportional to bioaccumulation (Kelsey et al., 1997). However, the performance of this approach depends closely on experimental conditions (Cui et al., 2013). Another type of extraction process-based method is cyclodextrin extraction, typically using hydroxypropyl-β-cyclodextrin, or HPCD (Dean, 2007). These extractions are primarily used for polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and other HOCs (Cuypers et al., 2002; Reid et al., 2000; Stroud et al., 2009; Wong and Bidleman, 2010). This procedure is very similar to mild solvent extractions, where the solvent (HPCD) is added to the solid matrix, and then the extract is analyzed (Kelsey et al., 1997; Lei et al., 2006). HPCD extractions give good predictions for bioavailability of HOCs to smaller trophic level organisms (nearly 1:1 correlations between extracted concentrations and availability to microbes), but for higher-level organisms like earthworms and benthic invertebrates, this relationship is not as strong (Reid et al., 2000; Hickman and Reid, 2005; Barthe and Pelletier, 2007). Like with mild solvent extractions, cyclodextrin extraction performance is highly dependent upon experimental conditions and the species of interest. In addition, extraction-based methods cannot be used *in situ*, limiting their use (Cui et al., 2013).

Another common method to measure bioaccessibility of HOCs is to use a sorption sink, like Tenax, to capture the readily desorbable fraction. Tenax beads are made of a resin that has a high affinity for HOCs, are easy to use in various environmental compartments, and have an additional benefit over solvent extractions in that the beads are reusable (Cornelissen et al., 1997). There are two methods based on Tenax desorption (Cui et al., 2013). The first is sequential Tenax desorption, which determines desorption of a contaminant from a soil or sediment sample as a function of time. This is shown in **Equation 1.1** (above) and **1.2**:

$$F_{\mathrm{r}} + F_{\mathrm{s}} + F_{\mathrm{vs}} = 1 \qquad (1.2)$$

where F_{r}, F_{s}, and F_{vs}, are the rapid, slow, and very slowly desorbing fractions of a contaminant from the sediment or soil, respectively (Cornelissen et al., 1997; Kukkonen et al., 2003; Xu et al., 2008). From the sequential extractions, desorption curves can be created and fit of the data to Eq. (1) generates F_{r}, F_{s}, and F_{vs}, the sum of which equals to 1 (Eq. 2) (Cornelissen et al., 1997). However, the significant drawback of the sequential desorption method is that it is very time consuming and takes a long time (Cui et al., 2013; Xu et al., 2008). The second Tenax extraction-based method is the single-point desorption measurement that uses one time interval, such as 6 h or 24h, and the desorbed fraction is used to approximate F_{r} (Cornelissen et al., 2001; Jia et al., 2014; 2016). Compared to the sequential desorption method, the single-point desorption method is faster and much less labor-intensive. The estimated desorption fraction, $F_{6\mathrm{h}}$ or $F_{24\mathrm{h}}$, is used to approximate F_{r} (Cornelissen et al., 2001; Jia et al., 2014; 2016; Lydy ey al., 2015; Nutile et al., 2017; Yang et al., 2008). Single-point desorption measurements to estimate

bioaccessibility have been frequently used over sequential desorption, and have been validated with bioaccumulation in invertebrate species like *Neanthes arenaceodentata*, *Lumbriculus variegatus*, and *Eisenia fetida* (Jia et al., 2014; You et al., 2006; Wang et al., 2018). However, like with solvent extractions, these Tenax extraction-based methods cannot be used *in situ*, limiting their use for projects requiring field deployment (Cui et al., 2013). These detection methods are also useful for assessing the effectiveness of remediation efforts

1.6 Black Carbon Amendment

1.6.1 Natural and Anthropogenic Black Carbon in the Environment

Black carbon refers to the carbon found in the environment that has undergone incomplete combustion of either vegetation or fossil fuels, through natural means, like wildfires, or through artificial ones, like purposeful creation of charcoal or biochars (Goldberg, 1985). The exposure to high temperatures changes organic carbon, particularly in the formation of charcoals, by increasing the sorption capacity and the hydrophobicity of the carbon (Ghosh et al., 2011). Due to their high sorption capacities, black carbon materials are often used to remediate sediments and soils contaminated with HOCs (Cornelissen et al., 2005; Ghosh et al., 2011; Gustafsson et al., 1997; Patmont et al., 2014). There are several types of these materials that are commonly used, including activated carbon and biochars.

Activated carbon (AC) is created when either coal or biomass is treated at a very high temperature that greatly increases the porosity and sorption capacity of the carbon

(Ghosh et al., 2011). It is currently used in many forms of drinking water treatment, as the high sorption capacity removes many contaminants, and for poison control in humans (Ghosh et al., 2011). Often AC is sold and used in a powdered form, which allows for its use in many formats, but it is produced in a granulated form (granular activated carbon, GAC) that can be added to a medium and recovered later through sieving (Rakowska et al., 2013).

Biochars are typically made from a plant material that has been pyrolyzed at a range of temperatures, which heats the biomass in the absence of oxygen to produce a char (Lehmann, 2007). This process converts biomass that would otherwise break down quickly into a more stable form of carbon, and can be used as a soil amendment (Baldock and Smernik, 2002). Many studies show that biochar amendment improves the productivity of soil, and the production of biochars from excess biomass is also being considered as a carbon sequestration method to offset the impact of fossil fuel burning and climate change (Lehmann, 2007; Liang et al., 2006).

1.6.2 Remediation Applications

Traditional methods of sediment remediation, including dredging and capping, are destructive to benthic communities and often very costly (Ghosh et al., 2011). Black carbon materials have been successfully used to reduce exposure and risk of contaminants, as bioavailability is determined by how strongly contaminants are bound to sediment particles (Cornelissen et al., 2005; Ghosh et al., 2000; Luthy et al., 1997; The National Research Council, 2003). The addition of black carbon materials to sediments

reduces exposure to HOCs by sequestering them efficiently through enhanced sorption (Cornelissen et al., 2005; Ghosh et al., 2000). Amendments, like activated carbon, have been shown to be very effective in laboratory simulated studies (Cornelissen et al., 2006; Hale et al., 2009; Hale and Werner, 2010; Janssen et al., 2010; McLeod et al., 2004, Sun et al., 2007; 2009; Werner et al., 2006; 2010), and in some field trials (Abel and Akkanen, 2018; Beckingham and Ghosh, 2013; Cornelissen et al., 2011; 2012). Under field conditions, there is the possibility that contaminated sediments may cover AC caps, reducing effectiveness (Ghosh et al., 2011). GAC has also been successfully used as an amendment to reduce contaminant bioavailability, as it provides the potential to sequester contaminants deeply into the pellet, and the granules may be removed from the sediment for offsite disposal (Parsons and Anchor QEA, 2012; Rakowska et al., 2013; Shimabuku et al., 2017).

The use of biochars to amend sediment is a relatively new practice, although biochar has been considered in many studies related to soil (Glasser et al., 2002). Many studies have shown biochars to be effective sorbents for many HOCs and metals, with some out-performing even AC (Cao et al., 2011; Wang et al., 2011). They are also seen as a more sustainable alternative to AC produced from anthracite, as biochar derived from plant biomass will also help to sequester and remove carbon from the global carbon cycle (Sparrevik et al., 2011). Biochars also are not "activated" during production, thus requiring less energy to produce (Ahmad et al., 2014). However, in general, biochars tend to have lower sorption capacities than AC, and in some studies only pore water HOC concentrations were reduced, not BAFs (Gomez-Eyles et al., 2013; Wang et al., 2011).

Although the use of AC and biochars as remediation amendments seems promising, their effectiveness over the long-term is relatively not well understood. The long term effectiveness is important, as aging changes their sorption properties and influences the biogeochemistry of the surrounding environment (Cheng et al., 2008; Ghaffar et al., 2015). For example, in a study by Ren et al. (2018), after 2.5 yr, amendment capacity was reduced in a soil contaminated with HOCs to the level of the untreated soil.

1.7 Research Objectives

There were three main objectives for this dissertation research. They were to (1) assess the role of aging on the bioavailability of legacy HOCs in historically contaminated marine sediments; (2) examine the influence of black carbon amendment on HOC sequestration and bioavailability in a historically contaminated marine sediment; and (3) evaluate the occurrence of current-use insecticides in urban-impacted coastal marine sediments and potential ecotoxicological implications.

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Figures

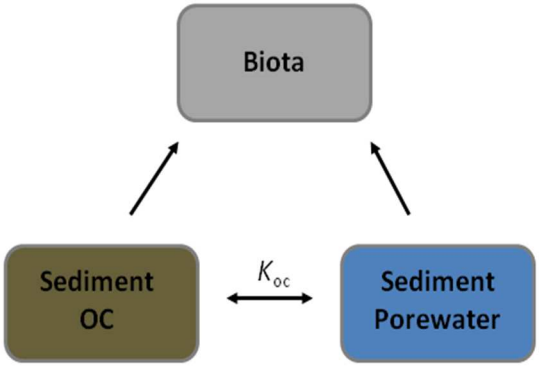

Figure 1.1. Modified diagram from Di Toro et al. (1991), showing the contaminant exposure route to an organism from the sediment. K_{OC} refers the partitioning coefficient between the sediment organic carbon (OC) and the pore water.

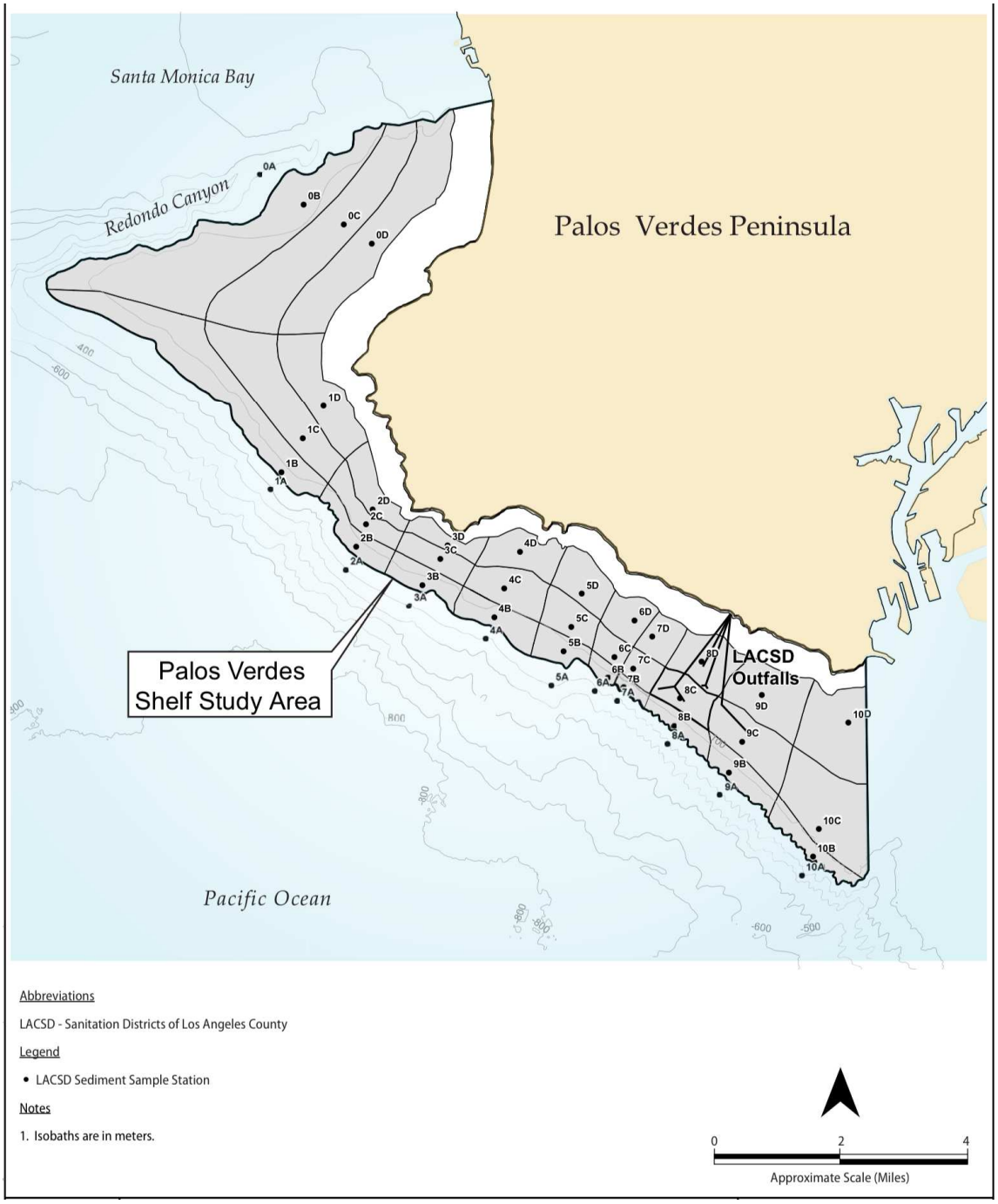

Figure 1.2. Location of sampling sites (U.S. EPA, 2009).

Chapter 2 Effect of Aging on Bioaccessibility of DDTs and PCBs in Marine Sediment

2.1 Abstract

Hydrophobic legacy contaminants like dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs) were banned almost half a century ago. While their residues still remain in many environmental compartments, they have undergone extensive aging and likely have lower bioaccessibility (the available fraction) compared to fresh residues. However, risk assessment relies heavily on the use of total chemical concentration, rather than accounting for age-diminished bioaccessibility, likely leading to overestimated risks. In this study, we used 24-h Tenax desorption to measure the potential bioaccessibility of DDTs and PCBs in two sediment cores taken from the Palos Verdes Shelf Superfund site in the Pacific Ocean. The total concentrations of DDTs and PCBs from the core located at the sewage outfall (8C) were as high as 41,000-15,700 mg/kg (dry weight, dw) and 530-2600 mg/kg dw, respectively, while those from a location 7 km northeast of the outfall (3C) were 2-3 orders of magnitude lower. Bioaccessibility estimated by 24-h Tenax-aided desorption (F_{24h}) decreased in the order of DDD > DDE > DDT for DDT derivatives, and PCB 52 > PCB 70 > PCB 153 for PCB congeners, showing a negative correlation with their log K_{ow}. Due to the extensive aging, F_{24h} values were <20% of the total chemical concentration for most contaminants and <5% for DDT, DDE and PCB 153, suggesting that aging greatly diminished their bioavailability. However, a quantitative relationship between F_{24h} and sediment age along the vertical profile was not found, likely because the contaminant residues had undergone

aging before their offsite transport and deposition onto the ocean floor. BSAFs for *Neanthes arenaceodentata* ranged from 0.11 to 1.6 in the topmost sediments of the cores, also indicating lowered bioavailability of aged DDT residues. Bioaccumulation also mirrored our bioaccessibility results, as BSAFs found for DDD>DDE, and with all other compounds below limits of quantification or not detected. As the use of man-made chemicals such as DDT and PCBs was discontinued in the U.S. many decades ago, the reduction in their bioavailability due to aging may be universal and should be taken into consideration to avoid overly conservative risk predictions or unnecessary mitigation interventions.

2.2 Introduction

The use of many hydrophobic legacy compounds such as DDT and PCBs was phased out in the 1970s, however their residues are still found in soil and sediment in many parts of the world (Anderson et al., 2012; Bettinetti et al., 2016; Zhang et al., 2002). One prominent example is the Palos Verdes Shelf off the coast of Los Angeles, California, where 44 km^2 of ocean floor sediment contains approximately 110 tons of DDT and 10 tons of PCBs due to wastewater discharge from a DDT manufacturer and other industries during the 1950-70s (U.S. EPA, 2009). Levels of DDT (and metabolites) up to 200 mg/kg were found at some locations (U.S. EPA, 2009). As these compounds are highly hydrophobic in nature, they have a strong tendency to remain in the bed sediment, where their natural degradation is extremely slow, with reported half-lives ranging from 2 to 25 years (Augustijn-Beckers et al., 1994; U.S. EPA, 1989; Luthy et al.,

1997; Cornelissen et al. 2005). Currently, the Palos Verdes Shelf is listed as a Superfund site, as the contamination threatens marine wildlife due to potential bioaccumulation of DDT and PCBs. The contamination is also a significant concern to local residents due to potential exposure to these chemicals via fish consumption (U.S. EPA, 2010).

As a contaminant has remained in the sediment (or soil) over decades, it has likely become less bioavailable through a biogeochemical process commonly referred as "aging" (White et al. 1999). Aging of contaminants may be due to several environmental factors, but the predominant theory is that bioavailability decreases through a reduction in a compound's bioaccessibility, which includes the freely dissolved and easily desorbed fractions of a contaminant (Alexander, M. 2000). Once the contaminants have reached phase equilibrium, molecules may slowly diffuse into the fine micropores in the sediment and organic matter aggregates, rendering them less accessible for organisms (Ehlers et al., 2003; White et al., 1999). However, although the effect of aging on contaminant bioavailability is often anticipated, there have been few experimental evaluations of this phenomenon when considering long-term aging in natural sediment, limiting the consideration of aging effect in risk assessment of contaminated sites or evaluation of the need for remediation (White et al. 1999).

Conventional risk assessment and management of contaminated sites rely almost exclusively on the use of bulk or total contaminant concentration (C_T) (Reichenberg et al., 2006; Sormunen et al., 2010). Tenax desorption is a well-established method to quantify bioaccessibility of hydrophobic compounds such as PAHs and PCBs in soil or sediment (Cornelissen et al., 2001; Jia et al., 2014; Nutile et al., 2017; Zhao and

Pignatello, 2004). The use of Tenax desorption as a measurement for potential bioaccessibility has been validated with direct bioaccumulation assays in benthic invertebrates such as *Neanthes arenaceodentata* and *Lumbriculus variegatus* and the earthworm *Eisenia fetida* (Jia et al., 2014; You et al., 2006; Wang et al., 2018).

In this study, we aimed to characterize the effect of aging on the potential bioaccessibility of DDTs and PCBs in the bed sediment from the Palos Verdes Shelf by using 24-h Tenax desorption and a bioaccumulation experiment with *Neanthes arenaceodentata*. We hypothesized that due to the long residence time, these contaminant residues have undergone extensive "aging" in the sediment and should exhibit limited bioaccessibility. We further hypothesized that the decrease in bioaccessibility should depend on the sediment age that is related to its burial depth along the sediment profile.

2.3 Materials and Methods

2.3.1 Chemicals and Sediments

A total of 9 hydrophobic organic compounds (HOCs), including six DDT analogues, i.e., (1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (*o,p'*-DDT), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT), 1,1-dichloro-2,4-bis-(chlorophenyl)ethylene (*o,p'*-DDE), 1,1-dichloro-2,2-bis(chlorophenyl)ethylene (*p,p'*-DDE), 1,1-dichloro-2,4-bis(chlorophenyl)ethane (*o,p'*-DDD), and 1,1-dichloro-2,2-bis-(chlorophenyl)ethane (*p,p'*-DDD)), and three PCB congeners, i.e., (2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,3',4',5-tetrachlorobiphenyl (PCB-70), and 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153)), were targeted for analysis. Their standards were

purchased from AccuStandard (New Haven, CT). Stable isotope labeled analogues ^{13}C-*o,p′*-DDD and ^{13}C-PCB-153 were purchased from Cambridge Isotope Laboratories (Tewksbury, MA), while deuterated standards PCB-52-d_3, PCB-70-d_3, *p,p′*-DDE-d_8, o,*p′*-DDE-d_8, *p,p′*-DDD-d_8, *o,p′*-DDT-d_8, and *p,p′*-DDT-d_8 were purchased from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Anhydrous sodium sulfate and Florisil (10-60 mesh) were purchased from Fischer Scientific (Pittsburgh, PA) and Acros Organics, respectively (Morris Plains, NJ). Before use, sodium sulfate was dehydrated at 400 °C and Florisil was activated at 130 °C. Empty 20 mL SPE cartridges were purchased from Supelco (Bellefonte, PA) and all organic solvents were of HPLC grade and were purchased from Fischer Scientific.

Sediments used in this study were taken from the Palos Verdes Shelf Superfund Site, located off the coast of Los Angeles, California. Sediment cores were taken in 2007 from two monitoring stations located on the shelf, and were kindly provided by the Los Angeles County Sanitation District. The 8C core was retrieved at a location at the sewer system outfall and may be considered as the hotspot of contamination. The 3C core was taken further northwest of 8C, about 7 km from 8C (**Figure 2.1**). The 8C and 3C sediments were approximately 70 m and 60 m, respectively, below the ocean surface, and the cores were taken using a gravity core sampler.

Upon collection, the sediment cores were sectioned into 2-cm increments, and were stored frozen until analysis. To measure the total organic carbon content (TOC), a small aliquot of each sediment section was placed in aluminum tins, dried at 70 °C for 24 h, and ground to a fine powder. An aliquot of the dried sediment sample was analyzed on

a Carbon/Nitrogen Flash Elemental Analyzer EA1112 (CE Elantech, Lakewood, NJ) to determine TOC. The particle size distribution was measured according to Gray et al. (2010). Approximately 0.25 g (wet weight) of sediment was taken from the same 5 representative sections of each sediment core used in the Tenax desorption experiment and added to a tall 250 mL glass beaker. Then, 100 mL of 30% hydrogen peroxide was added and samples were soaked for 24 hours. After this, the samples were heated on hot plates set to 70 °C and the hydrogen peroxide was evaporated to less than 5 mL. Any large organic particles that remained were removed with clean forceps and 60 mL of DI water was added. Samples were heated on a hot plate at 150 °C and the water was diluted to less than 5 mL. This step was repeated a second time before samples were transferred to 20 mL plastic liquid-scintillation vials containing 0.1 g of sodium hexametaphosphate to act as a dispersant. The samples were then placed on a horizontal shaker at 50 rpm for 24 h before analysis on a Beckman-Coulter LS 13-320 (Beckman Coulter Inc., Fullerton, CA, USA). The detailed results can be found in **Table 2.1**.

Artificial seawater was created in the laboratory by adding 32 g of Instant Ocean salts (Blacksburg, VA, USA) to 1 L of deionized water to recreate a ratio of 32‰. Electrical conductivity was also measured with each batch for quality control.

2.3.2 Sediment Core Dating Using ^{210}Pb

To determine the approximate age of the sediment in each section, aliquots were dated using ^{210}Pb by the constant initial concentration model (CIC) (Liao et al., 2017; Nittrouer et al., 1979). The use of 210Pb dating is common for sediments dated up to

100-150 years old because of the half-life (22.3 years) of the radioactive isotope. Well type intrinsic germanium detectors were used to conduct radiometric measurements of ^{210}Pb and ^{226}Ra via low-background gamma counting, with 137Cs activity used as a marker for the peak in atmospheric fallout from 1962 to 1963 (Nittrouer et al., 1979; Schelske et al., 1994). The age of each sediment section was determined using the mean sedimentation rate (MSR), which was calculated by dividing the ^{210}Pb decay constant (-0.031) by the slope of the regression of the natural log of unsupported ^{210}Pb (total ^{210}Pb activity – ^{226}Ra activity) versus the mid-depth cumulative mass in g/cm^2 (Nittrouer et al., 1979). Figures of these activities are shown in the SI. For these sediments, age corresponded well with depth in the core (R^2 = 0.61 and 0.65 for the 3C and 8C core, respectively, with $P < 0.01$). The results from this analysis are shown in **Figure 2.2**.

2.3.3 Total Concentration Analysis

To determine the total chemical concentration C_T, a 0.5 g aliquot (dry weight basis) of sediment was taken from every other section of the cores and dried by homogenization with sodium sulfate. Each sample was then spiked with stable isotope labeled analogues of DDTs and PCBs as recovery surrogates. The sediment samples were extracted twice using 40 mL of methylene chloride and acetone (1:1, v:v), and the extracts were combined and concentrated to <1 mL. The extracts were then loaded onto a 2 g Florisil cartridge for cleanup. Each sample was eluted with 20 mL of hexane and acetone (9:1, v:v), and the eluate was collected and concentrated to 1 mL. All samples were analyzed in triplicate on a Varian 3800 gas chromatograph equipped with a Varian

1200 triple quadrupole mass spectrometer (GC/MS-MS) for structural identification and quantification of the target analytes.

2.3.4 24h Tenax Desorption Test

In this study, a single interval desorption using Tenax resin was used to estimate the bioavailability of DDT and PCB residues in several sections of the aged sediment cores. Tenax resin beads are frequently used to measure contaminant bioaccessibility, either via sequential desorption or single interval desorption. Sequential desorption is used to determine desorption rates, which can be separated into a compound's rapid (F_r), slow (F_s), and very slow (F_{vs}) desorption fractions of a three-phase model (**Equations 2.1-2**).

$$F_r + F_s + F_{vs} = 1 \qquad (2.1)$$

$$\frac{S_t}{S_0} = F_r e^{-k_r t} + F_s e^{-k_s t} + F_{vs} e^{-k_{vs} t} \qquad (2.2)$$

Once these rates are determined, single interval desorption can be used to predict bioaccessibility, with the time chosen for this interval that encompasses the rapidly desorbing fraction and is available for uptake and poses the largest risk to organisms (Jia et al., 2014). However, sequential desorption is extremely tedious, time, and resource consuming. Previous studies have shown that a single interval desorption is able to approximate the rapid desorption fraction, F_r, of other HOCs, and predict bioaccessibility (Jia et al., 2014; You et al., 2006, Wang et al., 2008). For DDTs and PCBs, a 24 h desorption interval can be used to determine their bioaccessibility by accounting for the

entire rapidly desorbing fraction, and has been verified using bioassays (Cornelissen et al., 2001; Jia et al., 2016; Xu et al., 2008).

To determine F_{24h}, aliquots (1.0 g, dry weight basis) of sediment from 5 fairly similar depths (5, 13, 25, 37, 49 cm for the 8C core, 9, 17, 25, 37, 45 for the 3C core) along the sediment profile were placed in a 50-mL centrifuge tube and followed by the addition of 0.1 g Tenax resin beads (Scientific Instrument Services, Ringoes, NJ) and artificial seawater (35 ‰) containing sodium azide at 200 mg/L at a 1:10 (w/w) sediment to water ratio. The samples were shaken at 60 rpm for 24 h, and after the sediment slurry was centrifuged at 670 g for 30 min. The Tenax beads at the surface of the supernatant were collected by filtration and added to a 20 mL glass scintillation vial before being extracted 3 times for 5 min with 3 mL of acetone and hexane (1:1, v:v) using a Fisher Sonic 550 ultrasonic dismembrator. The extracts were combined and concentrated to <1 mL and reconstituted in acetone and hexane. All samples were prepared in triplicate and internal standards were added before being analyzed on the Varian GC/MS-MS.

The bioaccessible fraction given by the 24-h Tenax aided desorption fraction, F_{24h}, was calculated using the following equation:

$$F_{24\mathrm{h}} = \frac{C_{24\mathrm{h}}}{C_{\mathrm{T}}} \qquad (2.3)$$

where C_{24h} is the concentration of chemical desorbed from the sediment over 24 h, which equaled to the amount trapped by Tenax divided by the sediment mass, and C_T is the total chemical concentration in the sediment (Jia et al., 2016).

2.3.5 Bioaccumulation in *Neanthes arenaceodentata*

To investigate whether age and depth have an effect on bioaccumulation, a bioaccumulation experiment was conducted using *Neanthes arenaceodentata*, a marine benthic invertebrate found on that Palos Verdes Shelf. Laboratory-cultured *N. arenaceodentata* were purchased from Aquatic Toxicology Support (Bremerton, WA). Sediment from a core near the 8C location was split into three sections to represent three time periods: before contaminant deposition (60-76 cm depth), during deposition (38-54 cm), and after deposition (0-14 cm). The bioaccumulation test for sediments from the Palos Verdes Shelf was modified from 28 d to 96 h in order to prevent toxicity and death of exposed organisms (Jia et al.; 2014). In a 1 L beaker, 10 worms were added to approximately 200 g (dw) of sediment and the overlaying water was refreshed daily to reduce ammonia. Three replicates were used for each sediment section, including a control containing no DDT and PCB residues. After 96 h, worms were removed from the sediment and placed in Petri dishes without sediment for 24 h and allowed to depurate. The worms were then frozen and freeze dried before extraction.

Before extraction, surrogate standards were added to assess recovery. Each sample was extracted three times with 40 mL of a dichloromethane:acetone mixture (1:1, v:v), and the extracts were combined in a 60 mL glass ASE tube and concentrated to 10 mL. 2 mL of this extract was separated for lipid analysis, while the remaining 8 mL was concentrated to near dryness and reconstituted with 1 mL of a mixture of acetone and hexane (1:9, v:v) before cleanup. To remove any remaining lipids, samples were filtered through a 2 g florisil cartridge and eluted with 20 mL of the same acetone:hexane mixture

into a glass test tube. Samples were then concentrated to 100 µL and an internal standard was added before analysis on GC/MS-MS.

Total concentrations of these composite sediments were also extracted and measured in the same manner as the biota (aside from the lipid analysis), and analyzed on GC/MS.

2.3.6 Chromatographic Conditions

A Varian 3800 gas chromatograph (GC) coupled with a Varian 1200 triple quadruple mass spectrometer (MS/MS) was used to analyze all target analytes (Varian Instruments, Sunnyvale, CA); and 1 µL aliquots of all samples were injected into the inlet at a temperature of 250 °C. A DB-5MS Ultra Inert capillary column measuring 60 m x 0.25 mm x 0.25 µm was used for separation (Agilent, Wilmington, DE). Helium (99.999% purity) was used as the carrier gas at a flow rate of 1 mL/min, while 99.999% argon was used as the collision gas. The GC oven temperature was set initially at 80 °C (held for 1 min), then raised to 210 °C at 15 °C/min, and finally raised at 5 °C/min to 300 °C (held for 15 min). The transfer line temperature was 300 °C and the ionization source temperature was 250 °C. The MS/MS was operated in electron ionization mode at -70 eV with multiple reaction monitoring. Calibration standards were prepared in n-hexane on the same day of analysis.

2.3.7 Quality Assurance and Quality Control

To ensure and maintain quality assurance and quality control, several steps were taken. Blanks were included in every batch of samples to check for potential contamination and to ensure that no contamination was present in laboratory materials. Surrogate standards were added to all samples prior to extraction to quantify extraction recoveries and internal standards were added before injection to correct for instrumental drift during analysis. The limits of detection of the nine analytes were set at a value of three times the background noise, and ranged from 0.05 to 0.5 ng/mL. Calibration standard curves were prepared on the same day of analysis and were only used when the regression coefficient was greater than 0.99. The statistical significance was determined using Pearson's correlation coefficient with SigmaPlot 12.0 (Systat Software, Inc., San Jose, CA) and statistical analysis for particle size distribution was done using Gradistat software (Blott and Pye, 2001).

2.4 Results and Discussion

2.4.1 ^{210}Pb Dating

The approximate ages for each section of the sediment cores is shown in **Figures 2.2** and **2.3** (Liao et al., 2017). **Figure 2.2** describes the decay rate, while **Figure 2.3** shows the age of each core. As mentioned previously, dates determined with the CIC model were used in all further analysis. Each core was accurately dated up to a 43 cm and 61 cm depth for the 3C and 8C core, respectively, and results were extrapolated to the deeper sections. The top of each core is dated to 2007, which is the same year these cores

were taken, and the 8C core goes back to approximately 1920, and the 3C core goes back to approximately 1848. For these sediments, age corresponded well with depth in the core (R^2 = 0.61 and 0.65 for the 3C and 8C core, respectively, with P <0.01).

2.4.2 Total Concentrations and Sediment Profiles of DDTs and PCBs

Elevated concentrations were observed in the 8C core for all the targeted analytes as compared to the 3C core (**Figures 2.4** and **2.5**). In the 8C core, the levels ranged from nd to 1530 µg/kg dw for PCB congeners (PCB 52, PCB 70, and 153) with a detection frequency of 96%. Even higher levels were found for DDT derivatives including *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, with concentrations ranging from 108 up to 90,850 µg/kg dw, with a 100% detection frequency. In comparison, in the 3C core, levels of PCBs ranged from nd to 209 µg/kg dw (detection frequency, 74%) and those of DDTs from nd to 10,007 µg/kg dw (detection frequency, 88%). The upper layers of the 8C core had generally higher concentrations than the bottom layers. The peak in concentration was very sharp in the 3C core, with the highest concentrations centering around the 1950s. The vertical distribution of contaminants in the 8C core was less focused, with high levels occurring throughout the top half of the core, spreading from 1970s to 2000s. This could be due to frequent resuspension of sediment at the 8C location because it was located at a sewage outfall, while at the 3C location the sediment was likely less disturbed. However, this resuspension was likely restricted to approximately 0.1 cm depths, so biological processes were likely more prevalent (Wiberg et al., 2002). Out of all DDTs, the compound found at the highest

concentrations in both cores was *p,p'*-DDE, followed by *o,p'*-DDE, and then *p,p'*-DDD, which are the main degradates of DDT (Chattopadhyay and Chattopadhyay, 2015). For PCBs, the compound found at the highest concentration was PCB 70 in both cores, followed by either PCB 52 or PCB 153.

These results were consistent with earlier studies using samples from the same site, showing elevated levels of DDEs and DDDs (*o,p'*- and *p,p'*) as compared to the concentrations of DDTs (U.S. EPA, 2009; Liao et al., 2017; Sanitation Districts of Los Angeles County, 2016). Several previous studies also considered the levels of DDTs and PCBs in sediments from this area, as extensive monitoring has been in place since the 1980s (Sanitation Districts of Los Angeles County, 2016). In a previous study, the geometric mean of total DDTs was 31,300 and 364 µg/kg dw in sediments from the 8C and 3C locations, respectively (Liao et al., 2017). The compound found at the highest concentrations was also *p,p'*-DDE. Previous studies reported elevated levels of total DDTs and PCBs in the surficial sediment from the 8C location than the 3C location, and the differences were 35-62 times (Sanitation Districts of Los Angeles County, 2016; U.S. EPA, 2009).

The ratio between DDT and its degradates, DDE and DDD, has been used to infer if there are new inputs of technical DDT (Guo et al., 2009). This ratio was calculated using the following equation:

$$\frac{\Sigma DDT}{\Sigma DDE+\Sigma DDD} \qquad (2.4)$$

where ∑ DDT is the sum of both *o,p'*- and *p,p'*-DDT, ∑ DDE is the sum of both *o,p'*- and *p,p'*-DDE, and ∑ DDD is the sum of both *o,p'*- and *p,p'*-DDD. A ratio >1 indicates recent

inputs of technical DDT, while a ratio <1 suggests degradation and hence aged DDT residues (Guo et al., 2009). The derived values of the ratio are shown in **Table 2.2**. The ratios ranged from 0.040-0.287 for the 8C core, and from 0.021-0.104 for the 3C core, suggesting an absence of new DDT input to the shelf and substantial residue aging. A similar ratio was also calculated using data reported in a previous study from the same area (Liao et al., 2017). The ratio for the surficial sediment taken from the 8C location was approximately 0.095, and it was 0.040 for the 3C core. As we anticipated, these ratios were in close agreement with those obtained in this study, even though sediment samples from multiple depths were considered in this study while only sediment samples at the surface were considered in the other study.

The ratio of $\sum$ DDE/$\sum$ DDD has also been used to infer whether the degradation is primarily aerobic or anaerobic transformations, and in places where aerobic degradation is predominant, the ratio of $\sum$ DDE/$\sum$ DDD is >1; whereas if anaerobic degradation is predominant, the ratio becomes <1 (Da et al., 2014; Wang et al., 2013). In the 8C core, this ratio was calculated to be 1.92 – 4.06, and it ranged from 9.40 to 18.4 in the 3C core. Therefore, it may be concluded that for these sediment sites, aerobic degradation was the predominant degradation pathway for DDT in the marine sediment, which affirmed similar findings in previous studies considering surficial sediments from the Palos Verdes Shelf (Fernandez et al., 2014; Jia et al., 2014).

2.4.3 Bioaccessibility of Aged DDTs and PCBs in Sediment

Extraction using Tenax beads has been frequently used to characterize bioaccessibility of hydrophobic contaminants in sediment or soil (Cornelissen et al., 2001; Jia et al., 2014; Jia et al., 2016; Nutile et al., 2017; Sormunen et al., 2010). The fractions derived from the 24 h Tenax desorption, F_{24h}, are shown in **Figure 2.6**. The F_{24h} values for ∑DDTs were nd-19.9% and nd-41.6% for the 8C core and 3C core sediment samples, respectively. For most of the individual compounds, F_{24h} was <20 % of the total sediment concentration, with the exception of only *o,p'*-DDD and PCB 52 in some samples. Among the DDT derivatives, the compound with the highest F_{24h} in both cores was *o,p'*-DDD (19.9% and 41.6%, in the 8C and 3C core, respectively), and the F_{24h} value decreased in the order of *p,p'*-DDD (5.67-14.3% in the 8C core; 8.96-13.2% in the 3C core), *o,p'*-DDE (3.95-5.95% in the 8C core; 8.03-10.1% in the 3C core), *p,p'*-DDE (2.70-4.36% in the 8C core; 5.09-9.29% in the 3C core), and *p,p'*-DDT (0.57-4.04% in the 8C core; nd-0.84% in the 3C core). This pattern generally coincided with the hydrophobicity of the DDT analogues. Among the DDT compounds, log K_{ow} was the smallest for *o,p'*-DDD (5.9), as compared to the other DDT derivatives (log K_{ow} 6.0, 6.0, 6.5, and 6.9 for *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, and *p,p'*-DDT, respectively) (U.S. Department of Health and Human Services, 2002).

The F_{24h} values for the ∑PCBs (PCB 52, PCB 70, and PCB 153) ranged from 0.38 to 26.6% and from nd to114.5% for the 8C core and 3C core, respectively. In the 8C core, F_{24h} values were 19.6-26.6% for PCB 52, 4.8-11.6% for PCB 70, and 0.4-1.5% for PCB 153. In the 3C core, F_{24h} values were nd-114.5% for PCB 52, 4.8-6.8% for PCB 70,

and 1.7-3.9% for PCB 153. For PCB 52, the exceedance of F_{24h} over 100% was likely due to experimental artifact induced by its very low concentration in the 3C core samples (**Figure 2.5a**). For both cores, PCB 52 appeared to be the most accessible, but the F_{24h} value decreased greatly for PCB 70, and further to only a small fraction for PCB 153. This trend also coincided with their relative hydrophobicity as indicated by their log K_{ow} values. The log K_{ow} of PCB 52 (5.8) is significantly smaller than that of PCB 70 (6.2) or PCB 153 (6.9) (Hawker and Connell, 1988; U.S. Department of Health and Human Services, 2002).

Other studies have shown similar trends in bioaccessibility of aged DDT and PCB residues, however these studies only looked at surface sediments, rather than along the sediment profile. In these studies, the bioavailable fraction for *o,p'*- and *p,p'*-DDE were also found to be < 20%, and sediment from the 8C location consistently had lower accessibility measurements than surface sediments from the other locations within the shelf (Jia et al. 2014, 2016). When comparing the F_{24h} values in this study between the 8C and 3C cores, the bioaccessible fraction was consistently smaller for both DDTs and PCBs from the 8C core, even though that the overall difference was not statistically significant. This was likely due to the higher organic matter content in the 8C core than that in the 3C core, as organic matter was considered to be the primary domain for binding hydrophobic contaminants (Wang et al., 2018). The TOC in the 8C sediment core was 2.5-2.9 times that in the 3C core for the same depths (**Table 2.3**). The difference was likely due to the fact that the 8C core was located at the sewer system outfall, while the 3C core was much further away, meaning that there was a greater amount of organic

material being deposited at the outfall and that the organic matter tended to remain close to the discharge point (U.S. EPA, 2009). Therefore, even though the vicinity of outfall point contained the highest levels of DDT and PCB residues, aging, along with the relatively high organic matter content, together rendered the contaminants less bioavailable.

The consistently very small F_{24h} values for the more biologically significant DDT derivatives (i.e., DDT, DDE) and more highly chlorinated PCBs (e.g., PCB153) suggested that due to aging, the majority of these contaminants were irreversibly sequestered in the sediment material. Aging therefore has rendered these contaminants marginally bioavailable to benthic organisms at this site. Although this study focused on how aging influenced relative bioaccessibility, as total concentrations varied between sediment core sections and locations, it is important to note that the actual mass of compound available would also vary. These concentrations are shown in the SI, and generally range between nd-2800 µg/kg for DDTs and PCBs in the 8C core, and nd-104 µg/kg for those in the 3C core. However, assuming F_{24h} is a good proxy for bioaccumulation potential, the use of total sediment concentration would result in overestimation of 10-100 times for DDT and DDE isomers, and 33-100 times for PCB153. The use of bioaccessibility values such as F_{24h} to estimate available concentrations therefore would contribute to improved risk assessment and likely minimize the need for overly protective management practices.

2.4.4 Relationship between Bioaccessibility and Sediment Depth/Age

An effort was further made to explore a quantitative relationship between F_{24h} and sediment depth, as sediment depth corresponds to sediment age. Contrary to our initial assumption, the correlation between F_{24h} and sediment depth and age appeared to be weak in both cores. In the 3C core, F_{24h} values for *o,p'*-DDD, PCB 52, and PCB 153 showed an apparent negative relationship with sediment age, with R^2 values of 0.55, 0.64 and 0.51, respectively, but the correlations were not significant statistically ($P > 0.10$). In the 8C core, F_{24h} values for *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT and PCB 70 also showed some dependence on the sediment age, with R^2 values of 0.57, 0.57, 0.53, and 0.62, respectively, but again the correlations were not significant statistically ($P = 0.12$-0.16). For the rest of compounds, the relationship between F_{24h} and sediment depth or age was even weaker.

The absence of a clear dependence of bioaccessibility of the legacy contaminants on sediment depth and age invalidated our second hypothesis and was also in contrast to the findings of several earlier studies. In soil or sediment, bioaccessibility and bioaccumulation of DDT and PAH residues generally diminished with time (Ahmad et al., 2004; Alexander, M., 2000; Kelsey et al., 1997; Hatzinger and Alexander, 1995; Morrison et al., 2000; Shor et al., 2003).When earthworms were exposed to aged and fresh soils contaminated with DDT and its metabolites, soils where the HOC residues had aged for approximately 50 years exhibited the lowest tissue concentrations as compared to soils that had aged 90 days or were freshly treated (Morrison et al., 2000). Aged residues of pyrethroids found in sediment also were resistant to desorption with Tenax

beads as compared to fresh residues, implying diminished potential bioavailability (Xu et al. 2008). Even a weakly sorbed pesticide, carbaryl, became less bioavailable as it aged in soils (Ahmad et al., 2004). However, in these studies, a quantitative analysis of the dependence of bioavailability on age of residues was not considered.

Findings from the current study suggested that the relationship between sediment age and the relative bioaccessibility of legacy contaminants may be influenced by factors other than the matrix age alone. Bioaccessibility may be influenced by sediment texture, especially organic carbon content (**Table 2.3**). However, the most probable cause for the lack of a quantitative dependence between F_{24h} and sediment depth or age was that DDT and PCB residues on the ocean floor of the Palos Verdes Shelf were transported offsite from terrestrial sources, and the residues may have already undergone extensive aging under terrestrial conditions before their deposition onto the shelf, meaning that the sediment may be younger than the contaminant residue (U.S. EPA, 2010).Therefore, sediment age under such conditions was not indicative of the age of these residues. As discharge and deposition of DDT and PCB residues at this site has continued till today, although at increasingly lower concentrations, even the freshest deposition at the bed surface may be assumed to have aged for several decades under terrestrial conditions.

The conclusion that bioavailability of legacy contaminants does not depend on the age of the matrix, determined by methods such as isotope dating, may be generally true for water bodies contaminated by such persistent pollutants as DDT, PCBs, and PBDEs. The disconnection is due to the fact that the contamination source is usually terrestrial, while only through offsite transport such as runoff and soil erosion the aged contaminants

have been moved into their terminal deposition site such as the sediment bed of lakes, estuaries, and coastal waters. Nevertheless, this and other studies together affirmed that aged residues of persistent organic pollutants are much less available as compared to that indicated by the total chemical concentration, and that the diminished bioavailability potential should be considered when evaluating the risk of contamination or designing management practices (Ahmad et al., 2004; Alexander, 2000; Hatzinger and Alexander, 1995; Kelsey et al., 1997; Morrison et al., 2000; Shor et al., 2003; Xu et al. 2008).

2.4.5 Bioaccessibility and Physicochemical Properties

In each core, the derived F_{24h} values were log transformed and further plotted against log K_{ow} values of the individual compounds to establish a semi-empirical model. Data from both cores were used in the simple linear regression analysis and one- way analysis of variance in SigmaPlot to derive the following relationship:

$$\log F_{24h} = 7.9 - (1.1 \times \log K_{ow}) \qquad (2.5)$$

The linear regression (R^2= 0.73) was statistically significant with $P < 0.001$(Figure S4). The semi-empirical Equation 3 was used to predict the bioaccessibility of DDTs and PCBs using their log K_{ow} values by solving the equation for $F_{24h.}$ This equation was capable of predicting F_{24h} values that were within the range of our measured values for most compounds. However, it overestimated the bioaccessibility for *o,p'*-DDE (**Table 2.4**). Out of the DDTs, the compound showing the largest bioaccessibility was *o,p'*-DDD,

which was followed by *o,p'*-DDE, *p,p'*-DDD, and then *p,p'*-DDE. For the PCBs, PCB 52 was the most bioaccessible, followed by PCB 70 and PCB 153. This analysis suggested that hydrophobicity played an important role in the bioaccessibility of aged persistent organic pollutants, with more hydrophobic compounds exhibiting less bioavailability. However, more data are needed to further refine the predictive model using log K_{ow} values for these and other HOCs, as this relationship may only be applicable for sites containing similar compounds that have undergone extensive aging.

When examining the relationships between sediment TOC and F_{24h} values of individual compounds, the results were mixed. No significant relationships between F_{24h} and TOC were found for most compounds, with the exception of DDTs in the 3C core. The derived F_{24h} of DDTs in the 3C core was negatively and significantly correlated with the sediment TOC (P= -0.94, $p< 0.05$), as shown in **Table 2.5**. This suggested that for DDTs in the 3C core, higher levels of TOC in the sediment led to potentially lower contaminant bioaccessibility. A weak negative relationship was also found between TOC and F_{24h} of PCBs in the 3C core, even though the relationship was not statistically significant. The inconclusive dependence of F_{24h} on the sediment TOC content implied that not only the quantity, but also the quality, of sediment organic matter affected the potential bioaccessibility of these HOCs. The organic matter in the bed sediment at the Palos Verdes Shelf originated primarily from the discharge of treated municipal wastewater effluent, which is also the source of these contaminants to the shelf (Shon et al., 2006). This concurrent discharge is likely why TOC did not have a clear relationship with bioaccessibility in sediments from this site. The treatment processes at the various

facilities likely have undergone progressive changes over the years as well, leading to the deposition of organic matter of different structures and characteristics. In addition, because the organic matter was derived mostly from municipal wastes, the organic matter lacks the aggregate structures typical of natural sediments or soils (Kukkonen et al., 2003). A direct correlation between sediment TOC and bioaccessibility may have also been masked by other factors, such as *in situ* degradation (You et al., 2006).

2.4.6 Bioaccumulation in *Neanthes arenaceodentata*

Concentrations of bioaccumulated DDTs in Neanthes arenaceodentata ranged from 130-290, 4600-12000, 190-320, and 960-1700 ng/g tissue dw for *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, and *p,p'*-DDD, respectively, with no DDTs detected in our control samples (**Figure 2.7**). The parent compound DDT was detected in the worm samples, but was below Limits of Quantification (LOQ). All PCB congeners tested were below detection limits in both our control and non-control samples. The compound found in the highest concentrations in the worms was *p,p'*-DDE, which was to be expected given that *p,p'*-DDE is also found in the highest total concentrations in the sediment. These trends were slightly similar to our concentrations sorbed to the Tenax, where average concentrations sorbed to the Tenax (C_{24h}) of *p,p'*-DDE and *p,p'*-DDD were the highest, while the *o,p'*- congeners were lower. This is likely because their total concentrations in these sediments are also higher than the *o,p'*- congeners. A one way ANOVA on Ranks was conducted, and there was no statistically significant difference ($P > 0.1$) between C_{24h} and C_b, indicating that C_{24h} reflects the concentrations that may accumulate in benthic

biota (C_b). The concentration of *p,p'*-DDE on worms exposed to sediment from the 0-14 cm section were statistically significantly different from those from other sections (38-54 and 60-76 cm), however there were no significant differences in total concentration of bioaccumulated DDTs for any other compounds or between any other sections. When compared with log K_{ow}, there was a highly statistically significant correlation, with the Pearson's correlation coefficient equaling 0.832 and p-value <0.001. This reflects how log K_{ow} is a driving force for the partitioning of HOCs into the sediment pore water, and subsequently into the lipid tissues of marine organisms.

Biota-Sediment Accumulation Factors (BSAFs) were calculated based upon this equation:

$$BSAF = \frac{C_b}{C_s} \quad (2.6)$$

where C_b is the total concentration of DDTs in biota, and C_s is the total concentration in the sediment. These values ranged from 0.11-29. The highest BSAFs were found in worms exposed to sediment from the 38-54 cm section (ranging from 4.2-29), while the lowest BSAFs were found in the 0-14 cm section (range: 0.11-1.6). Compounds with the highest BSAFs were *p,p'*-DDD, followed by *o,p'*-DDD, *p,p'*-DDE and finally, *o,p'*-DDE. This differs slightly with our F_{24h} results, as *o,p'*-DDD was predicted to be the most bioaccessible over *p,p'*-DDD, however it did accurately predict that DDDs are more accessible than DDEs and subsequently, DDTs. There were no significant differences in BSAFs between compounds (P>0.05), but there was a significant difference based upon depth (P=0.027). In particular, the BSAFs from the 0-14 cm section were significantly different from those in the 38-54 cm section (P=0.029). The extremely low BSAFs found

in the 0-14 cm section show how bioavailability has decreased significantly in many parts of these sediment cores. However, BSAFs increased in sections deeper in the core. This is due to the decrease in total concentrations in the sediment deeper into the core while concentrations in the biota were relatively similar to each other. These results clearly show that the use of total contaminant concentration is not a good indicator for actual risk, and bioaccessibility or bioavailability measurements are a better indicator of the actual concentrations that are taken up by exposed organisms.

2.5 Conclusion

Results from this study showed that even though DDTs and PCBs in the marine sediment at the Palos Verdes Shelf remained elevated, due to decades of aging, the potential bioavailability as estimated by Tenax-aided desorption was extremely low, especially for DDT and DDE isomers, and for PCB congeners with a higher degree of chlorination. For DDT, DDE and PCB 153, the bioaccessible fraction was generally predicted to be 5% or less. Aging effect therefore was more pronounced for contaminants with a higher log K_{ow} or stronger hydrophobicity, and log K_{ow} may be used to predict the potential bioavailability of aged legacy contaminants. The finding clearly highlighted the deficiency in the use of the total chemical concentration; for the Palos Verdes Shelf Superfund site, the use of total chemical concentrations would result in an overestimation of risk by a factor of 10 or greater, which may lead to overly protective regulations or unnecessary mitigation practices. The model developed in this study can be improved via the addition of more data from other locations with aged sediment and contaminant

residues, as the current model is site specific. An improved model may be useful for sites with these and other hydrophobic contaminants that have undergone extensive aging, as an estimation of bioaccessibility can help prioritize remediation efforts. Results from our bioaccumulation experiment highlight the reduction in bioavailability of the top and most accessible sediments on the shelf, emphasizing the importance of bioavailability based measurements for risk assessment. However, we found that there did not exist a quantitative relationship between the contaminant bioaccessibility and the age of sediment estimated by ^{210}Pb dating on the Palos Verdes Shelf. This was likely caused by a discrepancy between the age of matrix and that of residues, or that sediment matrix age does not always reflect the age of contaminants. For the Palos Verdes Shelf site, even the recent DDT and PCB residues had undergone extensive aging under terrestrial conditions before their deposition and burial in the bed sediment. This observation may be valid for other contaminated sites where the contamination is due to offsite movement of residues; however, evaluation of other contaminated sites is necessary to further validate this assumption. Therefore, the origin of the contaminant residues must be considered to better delineate the underlying causes for age-diminished bioavailability.

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Tables

Table 2.1. Detailed particle size distribution of samples from the 3C and 8C cores in %.

VF= very fine, VC= very coarse

Core	8C					3C				
Year	2002	1995	1984	1974	1962	1991	1974	1959	1937	1919
Coarse Sand	2.3	2.4	2.1	3.4	2.6	0.8	0.7	1.2	0.7	1.3
Medium Sand	4.9	3.6	4.4	6.3	6.9	2.6	2.3	1.7	3.3	3.3
Fine Sand	13.5	10.2	8.2	13.3	11.9	12.8	14.3	9.9	17.5	17.6
VF Sand	21.2	15.2	12.2	21.2	13.4	22.5	23.9	16.3	26.2	28.3
VC Silt	14.3	13.3	14.7	15.6	13.8	16.7	16.2	13.9	15.4	16.6
Coarse Silt	11.0	12.8	15.5	11.6	13.3	12.9	11.8	14.1	10.1	10.2
Medium Silt	9.3	12.6	13.5	9.2	11.5	9.6	8.9	12.2	7.5	7.0
Fine Silt	8.4	11.5	11.4	7.4	10.2	8.0	7.9	11.3	6.5	5.4
VF Silt	6.2	8.0	7.9	5.2	7.4	6.1	5.9	8.5	5.0	4.0
Clay	8.9	10.3	9.9	7.0	9.0	8.1	8.0	10.9	7.8	6.3

Table 2.2. Ratios of total DDTs to the sum of its metabolites DDE and DDD and the ratio between DDE and DDD.

Core	Depth (cm)	Year	DDT/(DDE+DDD)	DDE/DDD
8C	5	2002	0.29 ± 0.2	1.92 ± 1.1
	13	1995	0.06 ± 0.03	2.76 ± 0.8
	25	1984	0.04 ± 0.004	4.06 ± 0.2
	37	1974	0.14 ± 0.02	3.19 ±0.3
	49	1962	0.11 ± 0.02	3.13 ± 0.4
3C	9	1991	0.07 ± 0.03	12.8 ± 0.5
	17	1974	0.10 ± 0.1	10.8 ± 0.7
	25	1959	0.02 ± 0.001	18.4 ± 0.6
	37	1937	0.07 ± 0.1	9.46 ± 1.1
	45	1919	0.08 ± 0.1	9.40 ± 0.5

Table 2.3. Texture and total organic carbon content (TOC) of sediment samples from cores taken from the Palos Verdes Shelf Superfund site (%).

Core	Depth (cm)	Year	TOC	Particle Size Distribution		
				Clay	Silt	Sand
8C	5	2002	7.1	8.9	49.2	41.9
	13	1995	9.3	10.3	58.3	31.4
	25	1984	10.2	9.9	63.1	27.0
	37	1974	7.4	7.0	48.8	44.2
	49	1962	6.7	9.0	56.2	34.8
3C	9	1991	2.9	8.1	53.1	38.7
	17	1974	3.2	8.0	50.8	41.2
	25	1959	3.5	10.9	60.0	29.1
	37	1937	2.9	7.8	44.5	47.7
	45	1919	2.6	6.3	43.3	50.4

Table 2.4. Predicted and actual F_{24h} values using Equation 3.

Compound	**log K_{ow}**	**Predicted F_{24h} (%)**	**Actual F_{24h} Range (%)**
o,p′-DDE	6.0	13	3.9-10.1
p,p′-DDE	6.5	3.4	2.7-9.3
o,p′-DDD	5.9	18	13-42
p,p′-DDD	6.0	12	5.7-14
p,p′-DDT	6.9	1.2	nd-4.0
PCB 52	5.8	19	nd-114
PCB 70	6.2	7.6	4.8-12
PCB 153	6.9	1.2	0.4-3.6

Table 2.5. Pearson's linear correlation between total organic carbon (TOC) and the total chemical concentration C_T and accessible fraction F_{24h}.

Core	Compounds	P(Total concentrations)	P (F_{24h})
8C	∑ DDTs	0.819****	0.344
	∑ PCBs	0.534****	0.618
3C	∑ DDTs	0.491***	-0.94*
	∑ PCBs	0.686****	-0.761

* $p<0.05$

** $p<0.01$

*** $p<0.005$

**** $p<0.001$

Figures

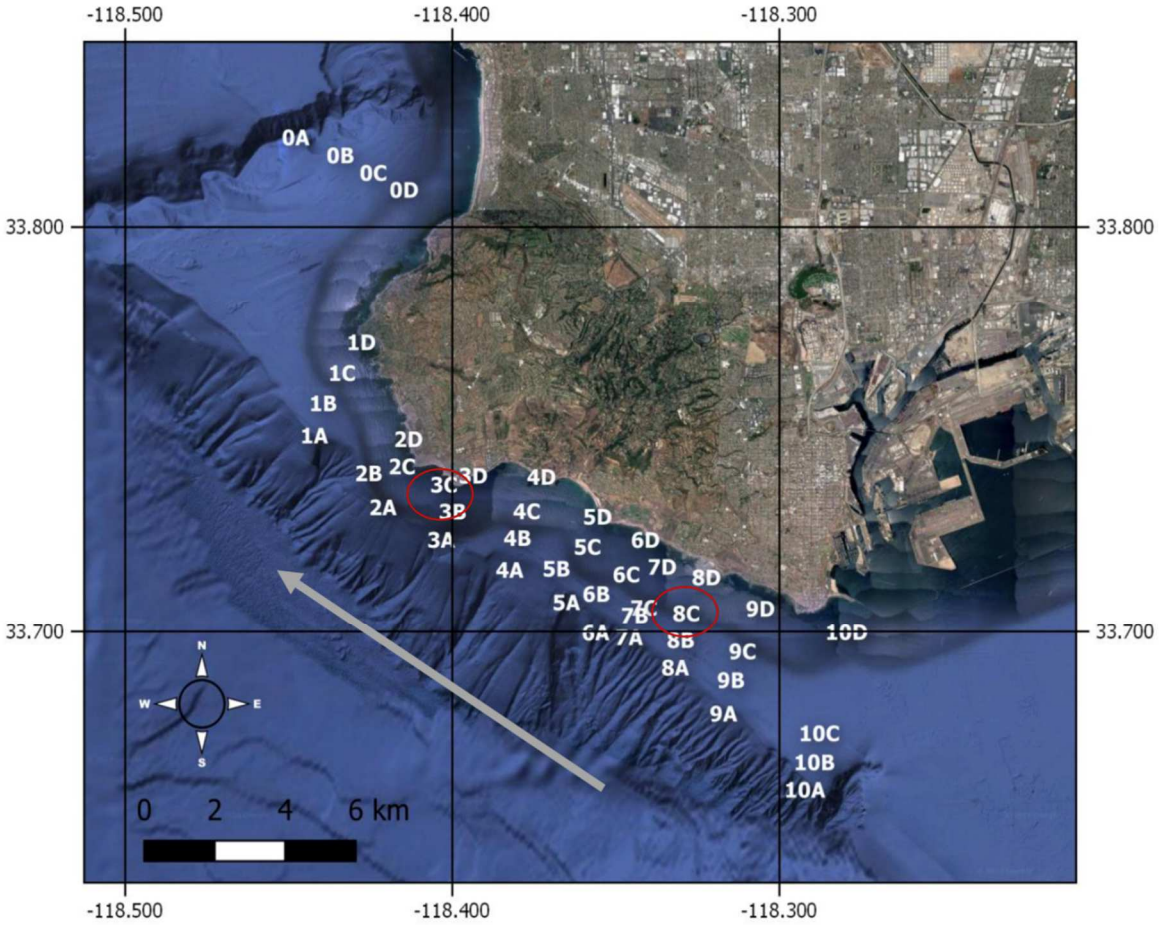

Figure 2.1. Locations of sampling site on the PV Shelf. 3C and 8C are highlighted inside the red rings.

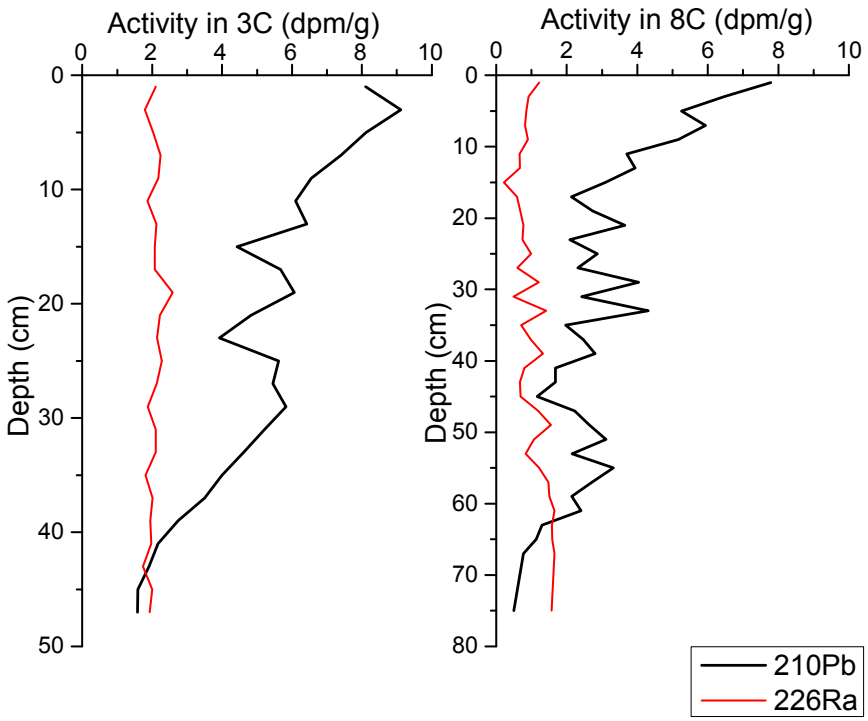

Figure 2.2. ^{210}Pb and ^{226}Ra activities in sediments.

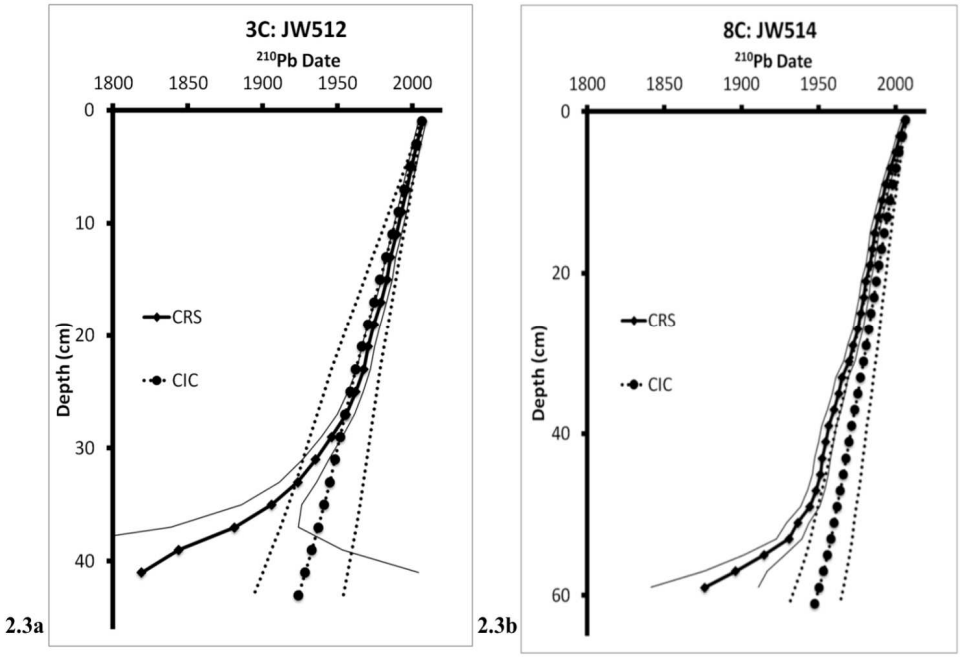

Figure 2.3. Approximate ages for each section of the (a) 3C core; and (b) 8C core taken from the PV Shelf.

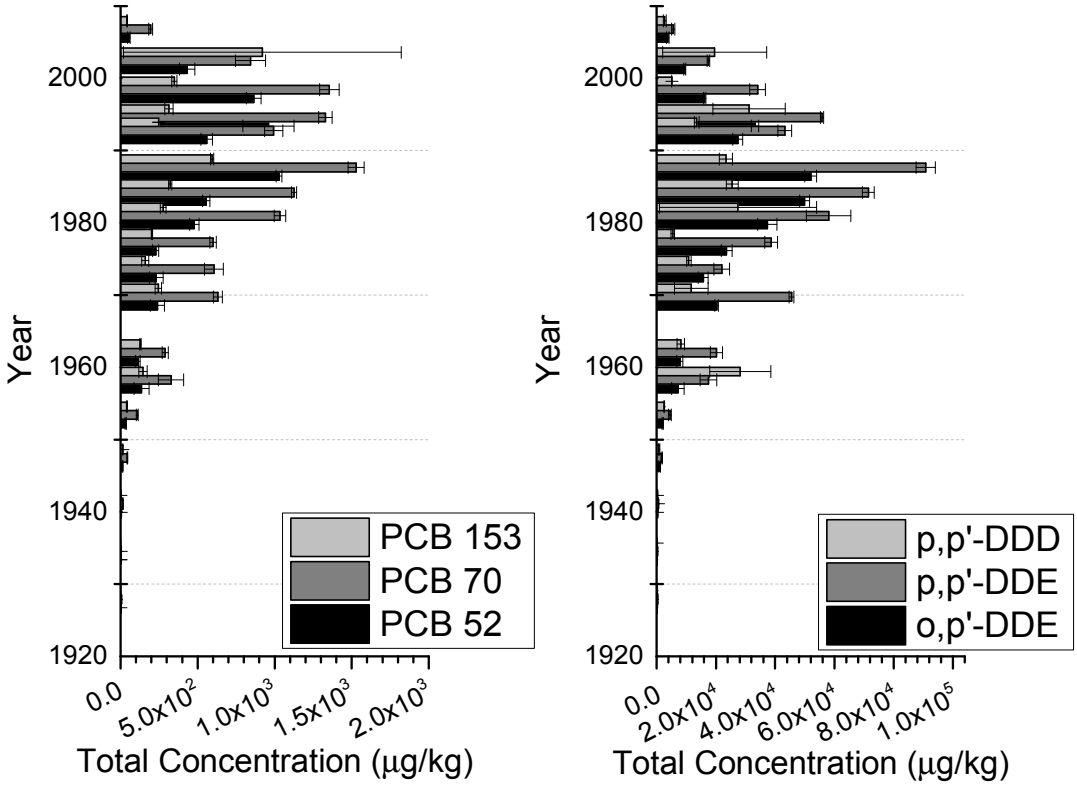

Figure 2.4. Total concentration profiles of PCBs and DDTs versus sediment age in the 8C core in µg/kg dry weight (d.w.) of sediment. Age corresponds with depth, with the youngest sediment at the top of the Y-axis.

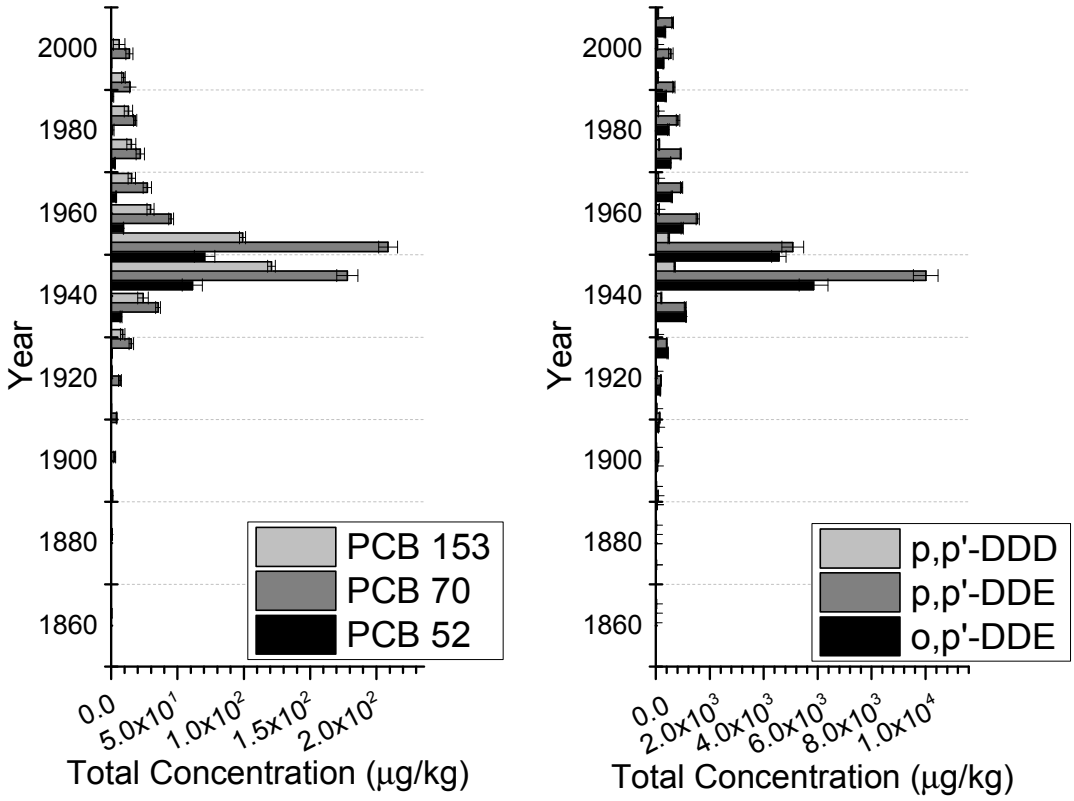

Figure 2.5. Total concentration profiles of PCBs and DDTs versus sediment age in the 3C core in µg/kg dry weight (d.w.) of sediment. Age corresponds with depth, with the youngest sediment at the top of the Y-axis.

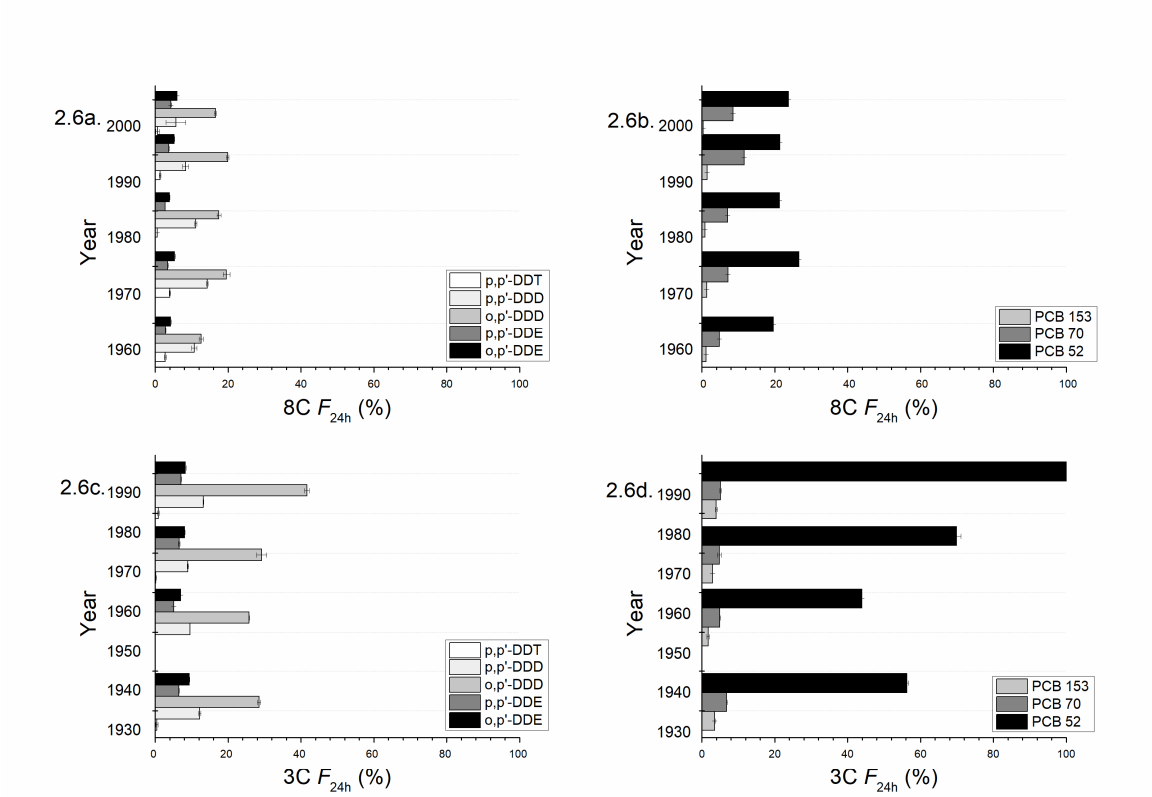

Figure 2.6. Average values of the 24-h desorbable fraction of HOCs (F_{24h}) from the 3C and 8C cores versus sediment age. Average values of F_{24h} were calculated using the average 24-h desorbable concentrations (S_{24h}) for each section and dividing that by the average total concentration (C_T). Error bars represent the first standard deviation from the mean.

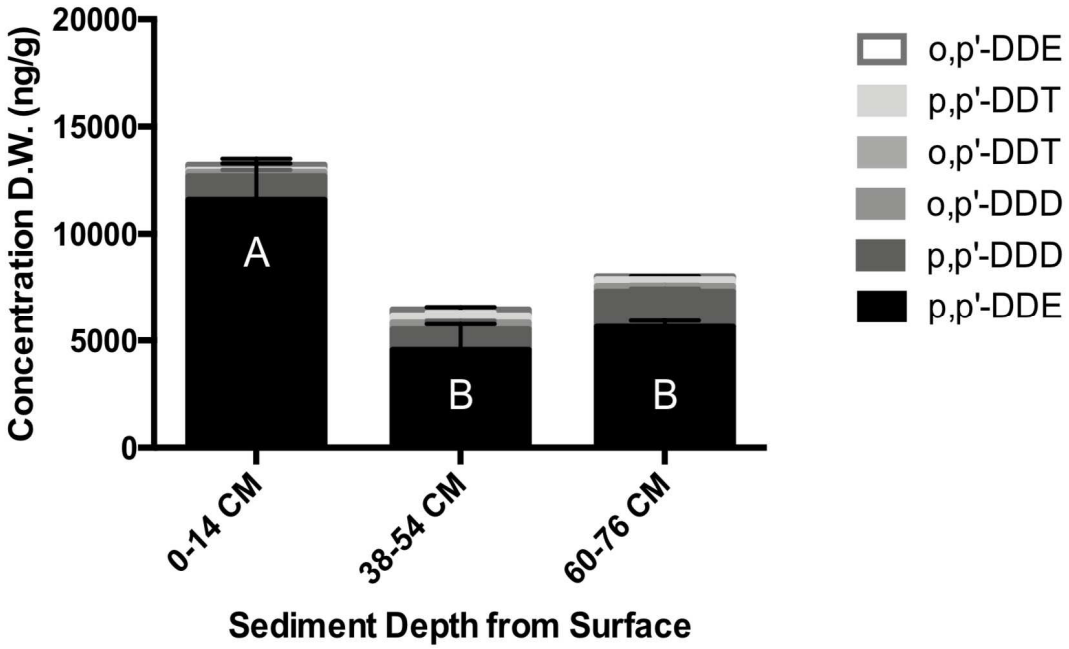

Figure 2.7. Concentrations of DDTs in *N. arenaceodentata* tissues (ng/g dw) from a core near the 8C location of the PV Shelf.

Chapter 3 Effectiveness of Different Black Carbon Materials in Sequestering HOCs in Historically Contaminated Sediments

3.1 Abstract

Black carbon is a common amendment used for remediation of soils and sediments contaminated with various contaminants, where the role of black carbon is essentially to immobilize contaminants and lower their availability. However, little is known about the effectiveness of different black carbons in sequestering HOCs in historically contaminated media, where the contaminants have undergone extensive aging. In this study, three different black carbon materials, i.e., a biochar, powdered activated carbon, and granular activated carbon, were used to amend a marine sediment that was contaminated with DDT residues (DDTs) several decades ago. The amended sediments were incubated for up to one year in seawater, and both the freely dissolved concentration, C_{free}, and the biota-sediment accumulation factors (BSAFs) were followed to assess the influence of black carbon amendment on sequestration of the DDTs at several time points. C_{free} decreased with time in all treatments compared to controls, and was closely correlated with C_b ($R^2 = 0.66$, $p < 0.0001$). BSAFs also decreased over time compared to controls, except for the GAC treatment. However both C_{free} and BSAFs were very small, even in the unamended control sediments, ranging from nd to 1.34 ng/L and from nd to 0.024, respectively. Addition of black carbon materials at 2% did not lead to significantly enhanced sequestration of the HOCs. The limited effectiveness of black carbon amendment was attributed to the very low HOC bioavailability in the sediment due to strong sorption to sediment organic matter and extensive aging. Therefore the use

of black carbon or other sorbents may not be an effective option for the remediation of sites historically contaminated with HOCs. Remediation operations using black carbon and other sorbents should take on-site contaminant bioavailability into consideration, and may not be suitable for sites with greatly diminished bioavailability.

3.2 Introduction

Hydrophobic organic contaminants (HOCs), including chlorinated pesticides, polycyclic aromatic hydrocarbons, and other halogenated industrial compounds, have been frequently found in water, sediment, and soil (Anderson et al., 2012; Bettinetti et al., 2016; Zhang et al., 2002). Pesticides like DDT were phased out many decades ago in the U.S. and many other countries, and yet their residues still remain in the environment due to their stability (U.S. EPA, 2009). Because of their strong hydrophobicity, HOCs in the environment are preferentially partitioned into the soil and sediment phases. Traditional remediation methods for contaminated sediments include dredging and capping (Ghosh et al., 2011). Over recent years, the use of black carbon materials as amendment has been shown as a promising strategy, as it avoids the high cost and some of the adverse consequences associated with sediment removal and *ex situ* treatment (Cornelissen et al., 2005; Ghosh et al., 2011; Luthy et al., 1997).

Black carbon is the carbon that has undergone incomplete combustion through either natural (i.e., wildfires) or artificial (i.e., biochar production) means using biomass or fossil fuel as the starting material (Goldberg, 1985). Exposure to high temperatures increases both the sorption capacity and hydrophobicity of the organic carbon, lending to

their desired property as a strong sorbent for HOCs (Cornelissen et al., 2005; Ghosh et al., 2011; Gustafsson et al., 1997; Patmont et al., 2014). Activated carbon and more recently, biochars, are common types of black carbon that can be used for soil or sediment remediation. Activated carbon (AC) is created from either coal or biomass "activated" by treatment at very high temperatures and is frequently used during drinking water treatment and for poison control in humans (Ghosh et al., 2011). It is most often used in a powdered form (PAC) that lends itself for easy use in many situations, while granular AC (GAC) can be added and subsequently removed from a contaminated soil or sediment via sieving, allowing for the removal of HOCs from a contaminated site (Rakowska et al., 2013). Biochars are another type of black carbon typically made from plant materials that have been pyrolyzed at a range of temperatures in the absence of oxygen (Baldock and Smernik, 2002; Lehmann, 2007).

The principal of black carbon amendment is based on the reduction in HOC availability due to strong sorption or sequestration (Cornelissen et al., 2005; Ghosh et al., 2000; Luthy et al., 1997; The National Research Council, 2003). Active carbon has been shown to be very effective in laboratory studies (Cornelissen et al., 2006; Hale et al., 2009; Hale and Werner, 2010; Janssen et al., 2010; McLeod et al., 2004, Sun et al., 2007; 2009; Werner et al., 2006; 2010), as well as in some field trials (Abel and Akkanen, 2018; Beckingham and Ghosh, 2013; Cornelissen et al., 2011; 2012). Studies have also found biochars to be effective sorbents for many HOCs and metals (Cao et al., 2011; Wang et al., 2011). Biochars are also seen as a more sustainable alternative, as conversion of plant biomass to biochars helps to remove carbon from the global carbon

cycle (Ahmad et al., 2014; Sparrevik et al., 2011). However, in general, biochars tend to have lower sorption capacities than activated carbon, and limited effectiveness was observed in some studies (Gomez-Eyles et al., 2013; Wang et al., 2011).

Although many studies have considered the effectiveness of black carbon amendment in sequestering HOCs in soils or sediments, to date little research has compared different types of black carbon under the same conditions, and even less on their comparative efficiency in immobilizing HOCs in historically contaminated sediments or soils (Cao et al., 2011; Hua et al., 2017; Thompson et al., 2016). In this study, we used a marine sediment collected from a Superfund site off the coast of Los Angeles, and three types of black carbon materials as amendment. Both chemical measurement and bioaccumulation assay were used to evaluate the effect of black carbon amendment on the bioavailability of DDT residues. Our hypotheses were: (1) the addition of black carbon materials increases sequestration of DDTs (*o,p'*- and *p,p'*-DDE and DDD) in a historically contaminated sediment; and (2) the type of black carbon used will determine the effectiveness of contaminant sequestration.

3.3 Materials and Methods

3.3.1 Chemicals, Sediments, and Black Carbon Amendment Materials

Standards of four DDT derivatives, i.e., *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, and *p,p'*-DDD, and 4 PCB congeners (PCB 30, 67, 80, and 191) were purchased from AccuStandard (New Haven, CT). The PCBs were used as internal standards (PCB 30 and

80) or as surrogate standards (PCB 67 and 191). A sheet of 25-μm thin polyethylene (PE) film was purchased from BBB Accredited Business (Cleveland, OH) and was cut into 1 × 2 cm long strips. The PE strips were pre-cleaned by sonication in *n*-hexane for 1 h and used for measuring the freely dissolved concentration C_{free}. Instant Ocean salts (Blacksburg, VA) were used to create artificial seawater for all experiments. Florisil was purchased from Acros Organics (Morris Plains, NJ) and cartridges used for sample cleanup (2 g) were packed in the laboratory. A powdered activated carbon (PAC) and a granular activated carbon (GAC) were purchased from Fisher Scientific (Hampton, NH), and the biochar was purchased from Biochar Supreme (Everson, WA). Each powdered product (PAC or biochar) was sieved (No. 100 mesh, ≤0.15 mm) before use. All other chemicals and solvents were of HPLC grade or higher.

The sediment used in this study was collected from the Palos Verdes Superfund Site off the coast of Los Angeles, near the wastewater effluent outfalls (8C), where high levels of DDT residues were documented. Between 1947-71, Montrose Chemical Company, the largest DDT manufacturer in North America at the time, discharged wastewater containing DDT into the Los Angeles County sewer system that flowed out of the White Point outfalls. An estimated 870-1450 tons of DDT was emitted and deposited onto the ocean sediment floor of the Palos Verdes Shelf (Eganhouse and Pontolillo, 2008; U.S. EPA, 2009; 2013). Consequently, approximately 44 km^2 of sediment floor has been contaminated, leading to the U.S. EPA to designate the shelf as a Superfund site in 1989 (U.S. EPA, 2009). The levels of DDT derivatives remain high at

present, with total sediment concentrations of DDT and its metabolites (DDE and DDD) in the range of 364-31,300 ng/g dry weight (dw) (Liao et al., 2017).

Since the DDT residues had remained in contact with the sediment for several decades, a recent study showed that DDT derivatives exhibited remarkably reduced bioavailability, likely due to contaminant aging (Taylor et al., 2019). The sediment was amended with 2% of either powdered activated carbon (PAC), granular activated carbon (GAC), or biochar, with an unamended sediment used as the control treatment. After amendment, sediments were incubated with a 2 cm layer of clean seawater up to 1 y. Sediments were removed after 1 d, 6 months, and 1 yr for the following analyses. The total concentrations of DDTs with or without amendments for this sediment were determined in preliminary experiments, and were 23900 ± 4232, 154904 ± 36100, 6390 ± 1869, and 25000 ± 13432 ng/g OC for *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, and *p,p'*-DDD, respectively.

3.3.2 Measurement of C_{free}

C_{free} was measured using methods developed previously for DDXs using PE film (Hale et al., 2009; Wang et al., 2018). A 2.0 g dw aliquot of sediment was mixed with 2 mL of clean seawater containing 200 mg/L sodium azide in a 10 mL liquid scintillation vial, and one 2 × 1 cm strip of pre-cleaned PE film was embedded into the slurry. Previous experiments showed that 28 d was sufficient for the PE film to achieve equilibrium (Hale et al., 2009), so samples were shaken for 28 d at 120 rpm on a horizontal shaker at room temperature. The PE film was removed, cleaned with deionized

water, and dried with a clean Kimberly® wipe. Each film was then placed into a 2 mL GC vial and extracted by 1 mL of hexane for 30 min via sonication, and an internal standard added just prior to analysis on GC-MS. C_{free} was then calculated using **Equation 3.1**:

$$C_{free} = \frac{C_{PE}}{K_{PE}} \quad (3.1)$$

where C_{PE} is the concentration in the PE film, and K_{PE} is the PE-water partitioning coefficient (Hale et al., 2009; Wang et al., 2018).

3.3.3 Bioaccumulation Assay

A marine polychaete, *Neathes arenaceodentata*, was purchased from Aquatic Toxicology Support (Bremerton, WA) and used as the exposure organism, as this species is native to sediments on the Palos Verdes Shelf and is an important source of food for larger bottom-feeding fish species like the California halibut, *Paralichthys californicus* (Anderson et al., 1998). The bioaccumulation test for sediments from the Palos Verdes Shelf was modified from 28 d to 96 h in order to prevent toxicity and death of exposed organisms (Jia et al., 2014). In a 500 mL jar, 10 worms were added to approximately 100 g (dw) of sediment and the overlaying water was refreshed daily to reduce concentrations of ammonia. Three replicates were used for each treatment, including a reference sediment containing no DDT residues. After 96 h, worms were removed from the sediment and placed in Petri dishes containing only seawater for 24 h to allow depuration before they were frozen at -80 °C and freeze dried prior to extraction.

Before extraction, surrogate standards were added to assess recovery rates. Samples were extracted three times via sonication in a 50 mL centrifuge tube with 40 mL of dichloromethane:acetone mixture (1:1, v:v), and all extracts were combined into a 60 mL glass tube and concentrated to 10 mL. An aliquot of 2 mL of this extract was removed for lipid analysis, while the remaining 8 mL was concentrated to near dryness and reconstituted in 1 mL of acetone-hexane (1:9, v/v). To remove residual lipids, samples were filtered through a 2 g Florisil cartridge and eluted with 20 mL of acetone-hexane mixture into a 20 mL glass test tube. Samples were then concentrated to 100 µL and an internal standard was added before analysis on GC/MS (Morrison et al., 2000; Wang et al., 2018).

The Biota-sediment Accumulation Factors (BSAFs) were calculated for each sample (**Equation 3.2**):

$$BSAF = \frac{C_b}{C_s} \quad (3.2)$$

where C_b is the concentration in the worm tissues (ng/g organic carbon (OC)), and C_s is the sediment concentration (ng/g OC) (U.S. EPA, 1995).

3.3.4 Instrumental Analysis

All samples were analyzed on an Agilent 6890N GC equipped with an Agilent 5975 mass spectrometry detector (MS or MSD) operating in electron ionization (EI) mode for structural identification and quantification of the target analytes. All samples were injected (2 µL) into the GC at 200 °C in splitless mode, and separation was conducted using a 30 m X 0.25 mm X 0.25 µm DB-5 fused silica capillary column

(Agilent, Wilmington, DE). The initial oven temperature was set at 80 °C (held 1 min), ramped to 210 °C at a rate of 10 °C/min, and then ramped once more to 300 °C at 5 °C/min and held for 5 min. The transfer line, ion source, and MS detector were set at 300 °C, 230 °C, 150 °C, respectively. The carrier gas (helium, 99.999 % purity) flow rate was 1.0 mL/min.

3.3.5 Quality Assurance and Quality Control

During this study, several steps were taken to ensure quality control. All samples had three replicates, and laboratory blanks were included for PE film, sediment, and tissue analyses, in which no target analytes were detected. Sediments containing no compounds of interest were also used as references. An external calibration curve was constructed using calibration standards prepared on the same day of analysis, and were used only when regression coefficients were ≥ 0.99. Recoveries of PCB 67 and PCB 191 ranged between 84.3 and 106 % for all sample media. Limits of detection were set at a value of three times the background noise and ranged from 0.05 to 0.1 ng/mL. Statistical significance and linear regression analysis were determined or calculated (i.e., via Pearson's correlation coefficients, 1-way Analysis of Variance (ANOVA), or Student's t-tests) using SigmaPlot 12.0 or Prism 6 (Systat Software, San Jose, CA and GraphPad©, San Diego, CA, respectively).

3.4 Results and Discussion

3.4.1 Carbon amendment and C_{free}

The addition of black carbon materials to the contaminated sediment generally decreased C_{free} of DDTs compared to the controls, but with exceptions. For example, for the ∑DDTs (*o,p'*- and *p,p'*-DDE, *o,p'*- and *p,p'*-DDD), the average values of C_{free} after 1 d of incubation were 1.48 ± 0.16, 1.28 ± 0.23, 0.71 ± 0.10, and 1.84 ± 0.31 ng/L for the control, biochar, PAC, and GAC treatments, respectively. Similarly, C_{free} values were 1.80 ± 0.34, 1.18 ± 0.16, 0.23 ± 0.09, and 1.18 ± 0.98 ng/L after 180 d of incubation, and 1.82 ± 0.31, 0.56 ± 0.25, nd, and 0.49 ± 0.72 after 365 d of incubation, for the control, biochar, PAC, and GAC treatments, respectively (**Figures 3.1 and 3.2**). When ∑DDTs was considered, both biochar and PAC treatments resulted in significant decreases in C_{free} compared to the unamended control, especially after 6 months or 1 yr of incubation. In comparison, GAC amendment did not lead to a significant reduction in C_{free} in comparison to the unamended control after 1 d or 6 months of incubation (**Figure 3.1**).

In the unamended sediment, *p,p'*-DDE showed the highest C_{free} values, followed by *o,p'*-DDE and *p,p'*-DDD, while *o,p'*-DDD was found in the lowest concentrations. The C_{free} values of the individual compounds corresponded to their bulk chemical concentrations in the sediment, and were influenced further by their physicochemical properties. When the evaluation was made on individual compounds, the effectiveness of each black carbon amendment depended upon the compound. Amendment with biochar or PAC significantly decreased the C_{free} of *o,p'*-DDE and *p,p'*-DDE after 6 months or 1 yr of incubation, with the relative reduction by PAC to be greater than the biochar. In

comparison, the amendment of GAC did not result in appreciable decreases in C_{free} (Table 3.1; Figure 3.2). A consistent or significant effect of the black carbon materials was not detected for *o,p'*-DDD or *p,p'*-DDD (**Table 3.1; Figure 3.2**). The general lack of an effect on the DDD derivatives was likely due to their relatively low hydrophobicity or moderate sorption by the black carbon materials. It must be noted that the initial C_{free} values were very small for *o,p'*-DDD, which may have contributed to the lack of a clear trend (**Figure 3.2**).

The reductions in C_{free} due to the addition of black carbon materials observed for some DDT derivatives and black carbon materials in this study were in agreement with findings from other studies. For example, powdered activated carbon and biochar decreased the C_{free} of DDTs in a contaminated soil by >90% (Wang et al., 2018). Other researchers also observed significant reductions in C_{free} in HOC-contaminated sediments (Cornelissen et al., 2011; Rakowska et al., 2013; Wang et al., 2011). The effect is typically attributed to the strong sorption capacities of black carbon materials, and differences between different amendment materials is considered to be controlled by their physical properties, such as specific surface area (Kleineidam et al, 2002; Millward et al., 2005). In this study, the powdered products had specific surface areas of 706.2 and 690.4 m^2/g for the PAC and biochar, respectively. For example, in a study by Jia et al. (2014), AC had much higher SSA than a biochar and correspondingly decreased C_{free} of PBDEs in freshwater sediments more effectively. In contrast, the pelleted form of GAC may have hindered its ability to reduce C_{free} of most HOCs examined in this study.

It is important to note that the sediment used in this study had very high total organic carbon (TOC) content (5.7%). Therefore, it may be assumed that DDTs were strongly sorbed to the sediment organic matter already before the black carbon amendment. For example, a study using a soil with lower TOC showed a reduction in C_{free} of DDTs by 94-96% with the addition of AC at 0.2%, and a further reduction at 2% amendment rate (Wang et al., 2018). Beckingham and Ghosh (2011) found that amending sediments at rates closer to the native TOC content was more successful at reducing PCB bioaccumulation into benthic invertebrates. In another study using sediments with higher TOC content (4.46 %), GAC was found to be effective at reducing sediment porewater concentrations of PAHs at a high amendment rate (4%) (Rakowska et al., 2013). Results from this and other studies suggested that the reduction in C_{free} after black carbon amendment depends on the ratio of the external carbon over the native organic carbon, and limited effectiveness may be expected for organic matter rich-sediment or soil with low black carbon amendment rate, especially for HOCs with moderate hydrophobicity.

3.4.2 Effect of black carbon amendment on bioaccumulation

Concentrations of DDTs in the tissues of *N. arenaceodentata* generally followed patterns similar to C_{free}, with the exception of the GAC treatment. When C_{free} and C_b values of individual compounds from all treatments were plotted, there was a significant linear relationship between C_b and C_{free} ($R^2 = 0.66$; $p < 0.0001$) (**Figure 3.3**). However, even though the correlation was significant, it is apparent that the data were highly

scattered, suggesting that other factors, in addition to C_{free}, may have also affected the accumulation of DDTs by the benthic invertebrate.

Biota-sediment accumulation factor (BSAF) was further calculated to assess the effectiveness of black carbon treatment in reducing bioaccumulation. The derived BSAF values were very small across all treatments and all compounds, including the unamended sediment (**Figure 3.4**). The amendment of black carbon did not result in a statistically significant reduction in BSAF as compared to the control for most of the compounds and time points. A significant decrease in BSAF was observed for each compound only in the PAC amended sediment after 365 d of incubation (**Table 3.2; Figure 3.4**). For the rest of target compounds, a discernible decreasing trend was absent (**Figure 3.4**). In fact, BSAFs unexpectedly increased at 180 d in the GAC amended sediment. However, it must be noted again that in general, the derived BSAFs were very small, which was not surprising given the low C_{free} values, suggesting again that after extensive aging, DDTs in the sediment had very limited bioavailability (Taylor et al., 2019; Wang et al., 2018). The very small BSAFs may be also related to the fact that the exposure time was only 4 d in this study. In Wang et al. (2019), the same sediment was exposed to *Lumbriculus variegatus* for 28 d, and the derived BSAFs for the unamended sediment were < 0.05, but generally higher than those seen in this study.

The increases seen in bioaccumulation of DDTs in the GAC amended sediment at 180 d were not anticipated. There has been research suggesting that the changing micro-environment created by the addition of a black carbon material may increase microbial activity or disturb sequestered contaminants, releasing previously sequestered HOCs

(Gregory et al., 2015; Kjellerup et al., 2014; Pignatello et al., 2017). Another probable cause could be that *N. arenaceodentata* ingested some GAC granules during the exposure assay at this time interval, which contributed to increased bioaccumulation. Therefore, when evaluated using BSAFs, amendment of black carbon to the historically contaminated marine sediment was largely ineffective at decreasing bioaccumulation, although differences existed between different DDT derivatives and among different types of black carbon materials.

3.4.3 Implications for contamination management

Most soil or sediment sites contaminated by legacy contaminants such as DDT are somewhat similar to the PV Shelf, where the contaminants have undergone prolonged aging since their initial deposition. The extensive aging has likely greatly decreased their bioaccessibility or bioavailability (Taylor et al., 2019; Wang et al., 2019). Remediation strategies suing black carbon or other sorbents works on the principle to enhance contaminant sequestration, therefore further decreasing the bioavailability of these HOCs (Luthy et al., 1997). Although the reductions in C_{free} or BSAFs were significant for specific DDT derivatives, black carbon types or incubation intervals, appreciable reductions were not consistently achieved. On the other hand, measurement of C_{free} and BSAFs clearly showed that due to contaminant aging and likely also the unique site characteristics (e.g., high TOC content), the majority of HOCs were not bioavailable. This conclusion was in contrast to studies where freshly spiked HOCs were considered. For example, in a study using spiked sediments, uptake of PBDEs into a passive sampling

device was reduced by 92-98% with the addition of only 0.5 % of AC (Jia et al., 2014). In another study, similar decreases in aqueous concentrations of DDTs were observed in a spiked sediment after addition of AC or multi-walled carbon nanotubes (Hua et al., 2017). This also suggests that using freshly spiked sediments or soils may overestimate the effectiveness of black carbon or other sorbent materials in remediation applications. For historically contaminated sites, the need and value of using black carbon or other sorbents should be evaluated using samples from the same site before initiating the actual remediation operation.

Aging of the black carbon materials themselves may also influence their sequestration capacities, particularly for black carbon generated from plant materials, such as biochar. Although the effectiveness of using biochar to immobilize contaminants has attracted broad attention, there have been several studies showing that time may change how contaminants are sequestered, and the sorbed contaminants may be even released again over time (Ghaffar et al., 2015; Kumar et al., 2018; Ren et al. 2018a; 2018b). For example, while aged biochars were shown to have increased rates of metal sorption due to changes in functional groups, another study suggested that aging of biochar would lead to decreased sorption capacities for HOCs (Kumar et al., 2018; Ren et al., 2018a; 2018b; Qian and Chen, 2014). Therefore, consideration of the properties and endurance of the amendment material is also important when selecting proper amendment materials for remediation.

The systematic research in this project highlighted that for contaminated sites where the contaminants have undergone extensive aging, like the PV Shelf, other

management options should also be considered. Aging, in combination with site-specific characteristics, may have already rendered the contaminant of interest to be largely non-bioavailable. Additional aging may be expected to further decrease the contaminant bioavailability and hence environmental risks. In this context, the so-called Monitored Natural Recovery (MNR) may be a better overall option to protect the environment while allowing time for the contaminated site to "self-cleanse" and recover. MNR requires the initial evaluation of a contaminated site for processes that will remove or sequester contaminants from a location without or in combination with other remediation techniques (Magar and Wenning, 2006). These processes include contaminant burial or transport from a site, reductions in contaminants mobility (i.e., reductions in bioavailability due to strong sorption to sediment organic matter), and chemical or biological transformation (Magar and Wenning, 2006). If these criteria are met, like with the aged DDT residues at the PV shelf, MNR can be the most cost-effective option. Due to this, MNR is already in effect for the PV Shelf (U.S. EPA, 2013). Therefore it is crucial to determine the actual risks of historically contaminated sites before an actual remediation operation, and bioavailability, as demonstrated through this research, could be highly valuable to refine the risk assessment and hence need for remediation .

3.5 Conclusion

This study evaluated the effect of black carbon amendment on the rate of sequestration of DDTs and compared the differences between different types of black carbon materials in a historically contaminated sediment. The addition of black carbon

materials to the sediment did not consistently reduce the bioavailability of DDTs, as shown through measurement of C_{free} and estimation of BSAFs of *N. arenaceodentata*. Among the three different black carbon materials, PAC appeared to be more effective than biochar or GAC at reducing the bioavailability of DDTs in the aged sediment. However, no appreciable reductions in bioaccumulation were found for most of the DDT compounds. The limited effectiveness of black carbon amendment in this study may be attributed to the high TOC content in the sediment and more importantly, the low bioavailability of DDTs in the sediment due to aging, prior to the amendment of black carbon. Therefore, the use of black carbon or other strong sorbents as amendment may be much less effective in historically contaminated sediments or soils. For contaminated sites with aged contaminant residues, options such as MNR should be considered over physical remediation approaches.

3.6 References

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Tables

Table 3.1. C_{free} (ng/L) in control, biochar, powdered activated carbon (PAC), and granular activated carbon (GAC) treatments at each sampling point.

Treatment	Day	*o,p′*-DDE	*p,p′*-DDE	*o,p′*-DDD	*p,p′*-DDD
Control	1	0.19 ± 0.05	1.03 ± 0.12	0.06 ± 0.02	0.19 ± 0.05
	180	0.26 ± 0.06	1.33 ± 0.22	0.06 ± 0.03	0.15 ± 0.03
	365	0.22 ± 0.03	1.34 ± 0.15	0.07 ± 0.06	0.18 ± 0.08
Biochar	1	0.16 ± 0.05	0.96 ± 0.12	nd	0.12 ± 0.03
	180	0.14 ± 0.03	0.91 ± 0.12	nd	0.11 ± 0.01
	365	0.04 ± 0.02	0.37 ± 0.07	nd	0.16 ± 0.18
PAC	1	0.06 ± 0.008	0.55 ± 0.06	nd	0.10 ± 0.04
	180	nd	0.18 ± 0.08	nd	0.05 ± 0.01
	365	nd	nd	nd	nd
GAC	1	0.24 ± 0.05	1.29 ± 0.15	0.11 ± 0.08	0.20 ± 0.07
	180	0.16 ± 0.14	0.87 ± 0.75	0.04 ± 0.03	0.11 ± 0.07
	365	0.14 ± 0.25	0.05 ± 0.04	0.07 ± 0.11	0.25 ± 0.39

Table 3.2. BSAFs in control, biochar, powdered activated carbon (PAC), and granular activated carbon (GAC) treatments at each sampling point.

	Day	*o,p′*-DDE	*p,p′*-DDE	*o,p′*-DDD	*p,p′*-DDD
Control	1	0.006 ± 0.0004	0.010 ± 0.0005	0.007 ± 0.0003	0.006 ± 0.003
	180	0.005 ± 0.0003	0.007 ± 0.0005	0.004 ± 0.0004	0.004 ± 0.002
	365	0.009 ± 0.001	0.011 ± 0.003	0.010 ± 0.002	0.013 ± 0.004
Biochar	1	0.006 ± 0.001	0.009 ± 0.001	0.003 ± 0.002	0.006 ± 0.001
	180	0.005 ± 0.0003	0.007 ± 0.0006	0.003 ± 0.0003	0.007 ± 0.0008
	365	0.004 ± 0.0004	0.007 ± 0.0007	0.0001 ± 0.0003	0.003 ± 0.0005
PAC	1	$0.005 \pm 7 \times 10^{-5}$	0.008 ± 0.0002	0.004 ± 0.001	0.003 ± 0.002
	180	0.004 ± 0.0002	0.005 ± 0.0004	0.0004 ± 0.0007	0.003 ± 0.0002
	365	0.002 ± 0.0003	0.004 ± 0.0005	0	0.001 ± 0.0003
GAC	1	0.004 ± 0.0002	0.007 ± 0.0002	0.003 ± 0.0009	0.005 ± 0.0004
	180	0.016 ± 0.004	0.024 ± 0.006	0.012 ± 0.004	0.018 ± 0.004
	365	0.005 ± 0.0003	0.010 ± 0.0009	0.006 ± 0.001	0.010 ± 0.002

Figures

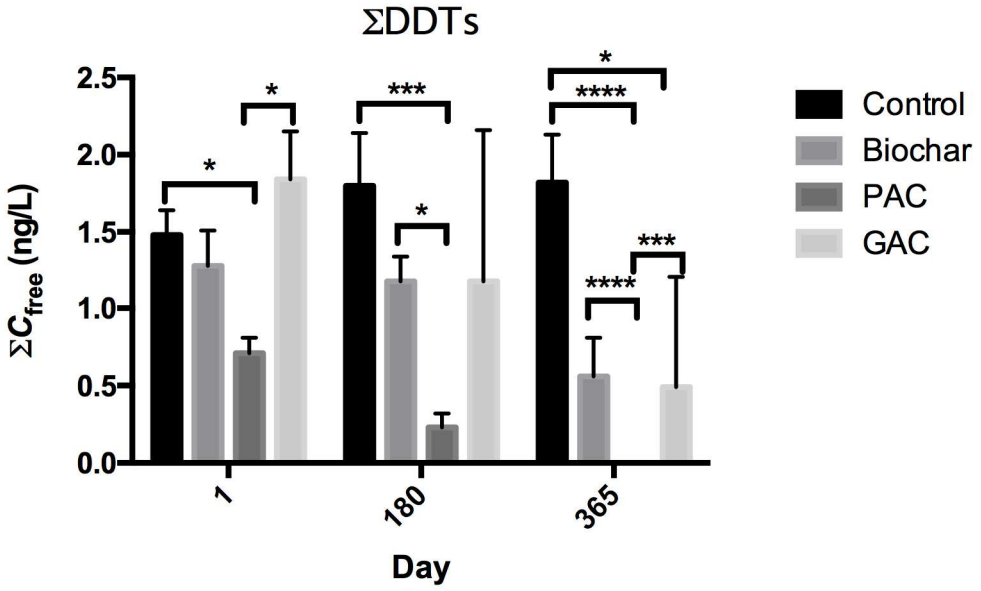

Figure 3.1. Sum of C_{free} (ng/L) in each treatment over time. Asterisks (*) refer to significant differences between treatments (* $p< 0.05$, ** $p< 0.01$, *** $p< 0.005$, **** $p< 0.001$).

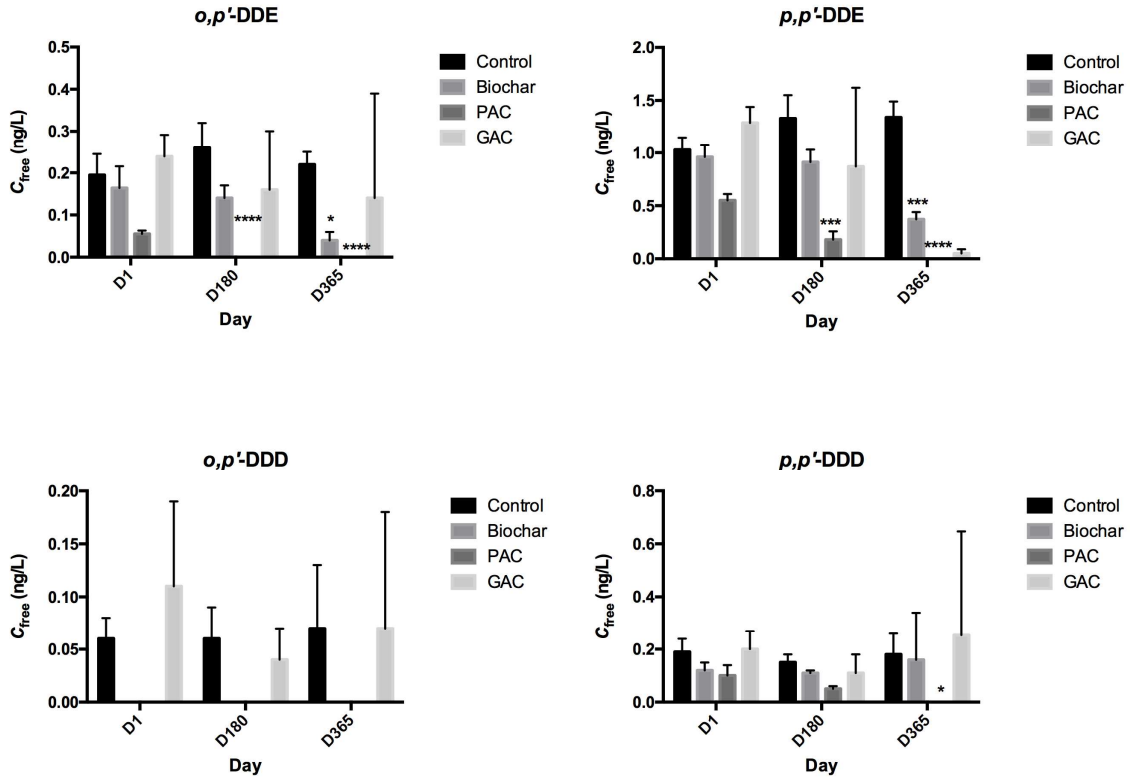

Figure 3.2. C_{free} (ng/L) of individual compounds in each treatment over time. Asterisks (*) refer to significant differences between treatments (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.005$, **** $p < 0.001$).

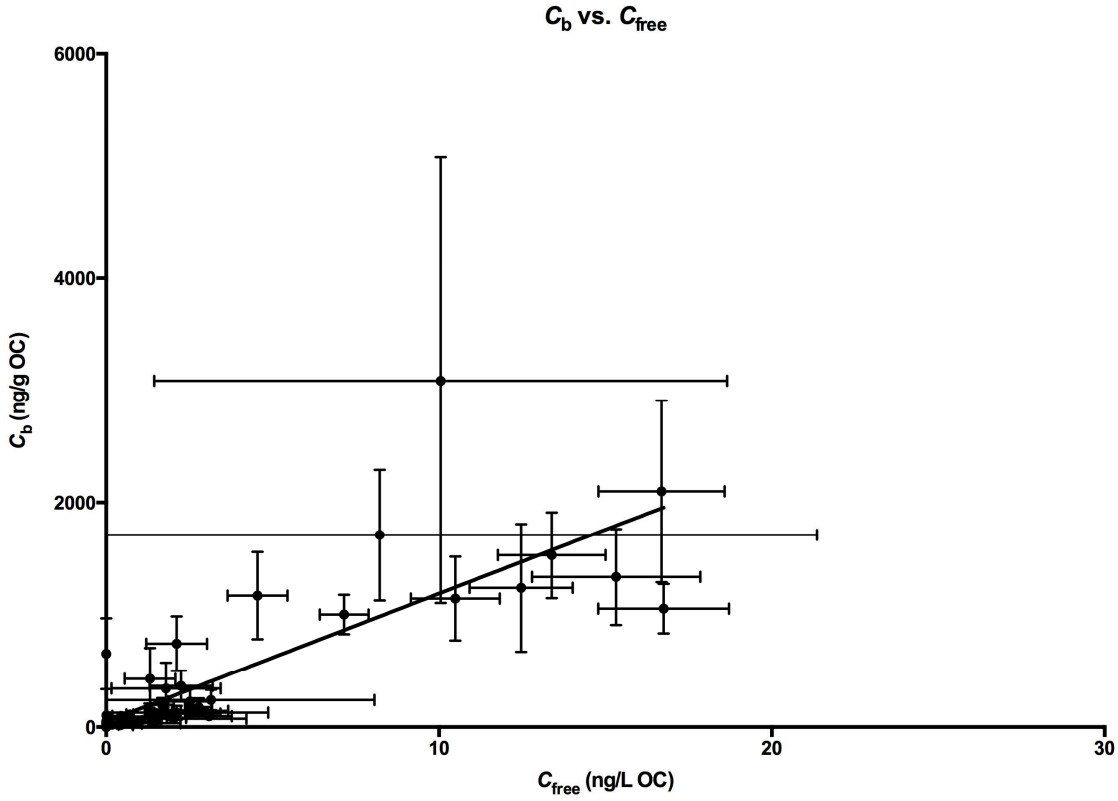

Figure 3.3. C_{free} (ng/L OC) versus C_b (ng/g OC). $R^2 = 0.66$, $p < 0.0001$.

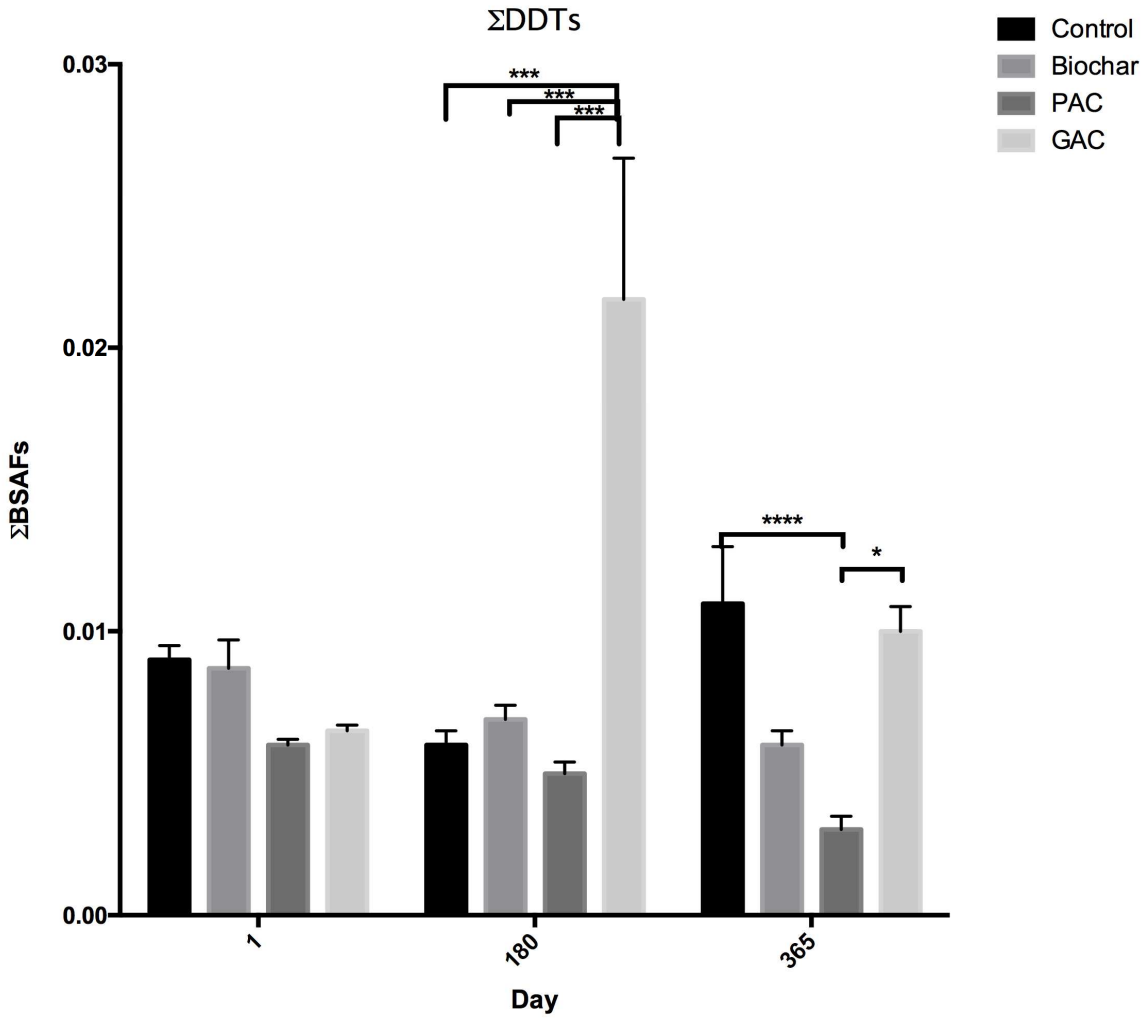

Figure 3.4. BSAFs for each treatment at each time point. Asterisks (*) refer to significant differences between treatments (* $p< 0.05$, ** $p< 0.01$, *** $p< 0.005$, **** $p< 0.001$).

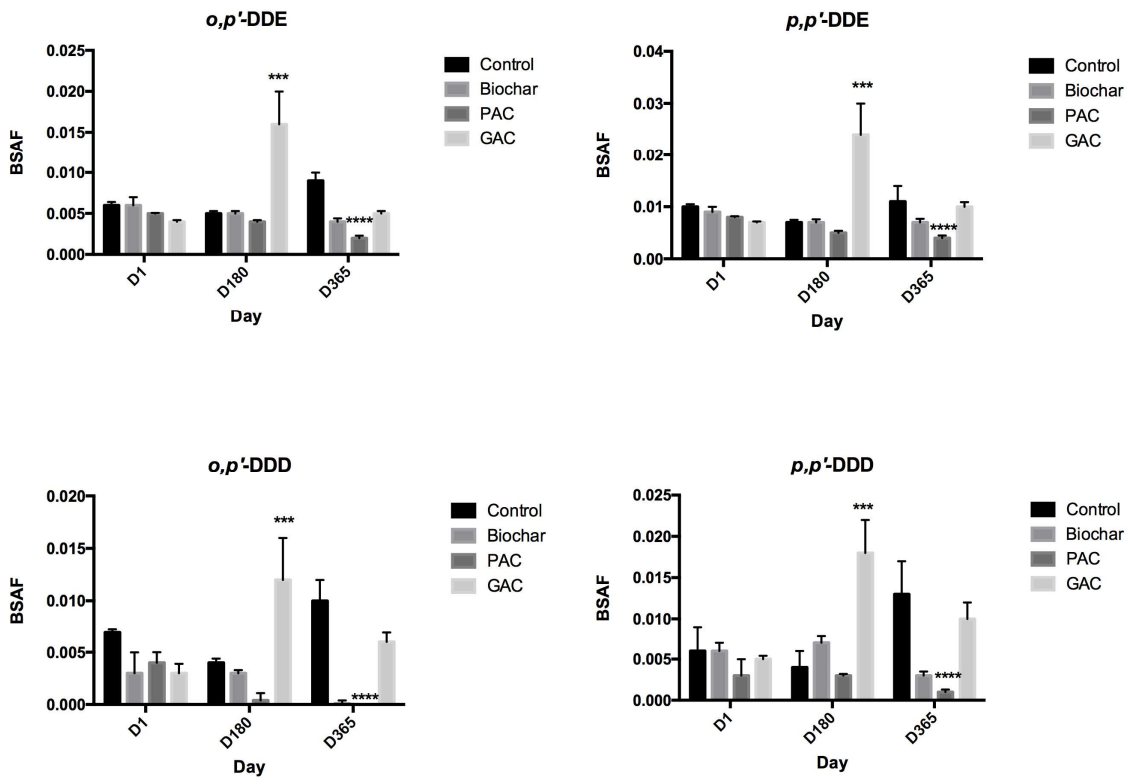

Figure 3.5. BSAFs of individual compounds in each treatment over time. Asterisks (*) refer to significant differences between treatments (* $p< 0.05$, ** $p< 0.01$, *** $p< 0.005$, **** $p< 0.001$).

Chapter 4 Occurrence and Probable Sources of Urban-Use Insecticides in Marine Sediments off the Los Angeles Coast

4.1 Abstract

Insecticides such as pyrethroids and fipronil are used in large amounts in both agricultural and urban settings and have the potential to elicit toxicity to nontarget aquatic organisms. In California, like in many other regions of the world, urban centers are located along the coast, and it is documented that urban-use insecticides enter the marine environment, where little is known about their occurrence and consequences. In this study, we measured the spatial distribution of pyrethroids and fipronil (and its metabolites) on the Palos Verdes Shelf off the coast of Los Angeles. Total pyrethroid levels ranged from nd to 170 μg/kg (dry weight), and fipronil sulfide levels ranged from 1.8 to 5.6 μg/kg. Two pyrethroids were traced to wastewater effluent discharge, while two others and fipronil sulfide were traced to surface runoff. Toxicity units (TUs) were estimated for benthic invertebrates, which ranged from no toxicity (nt) to 146 for total pyrethroids, and 0.09 to 1.6 and 4.2 to 75 for fipronil sulfide, depending on the indicator species. Therefore, near-shore deposition of urban-use insecticides due to wastewater discharge and surface runoff poses a significant risk to marine benthic invertebrates and highlights the importance of monitoring near-shore ocean environments and developing mitigation strategies to reduce seaward movement.

4.2 Introduction

Insecticides play an essential role not only in agricultural production but also in management of structural and landscape pests in urban environments. For example, large quantities of synthetic pyrethroids and fipronil are used in urban settings, both indoor and outdoor, for controlling insects such as ants, cockroaches, termites, and pet fleas and ticks; and the urban use is especially substantial in regions with large populations (Gunasekara et al., 2007; Li et al., 2017; Richards et al., 2016). Pyrethroids are the third most used group of pesticides worldwide (Li et al., 2017). In 2016, the total amount of pyrethroids and fipronil used by licensed applicators for structural and landscape pest control in cities of California was 526000 kg (a.i.), with fipronil comprising approximately 24% of this total. This amount was likely an underestimate, because many pyrethroid and fipronil products are available at retail stores and may be used by homeowners (CDPR, 2018).

Pyrethroids are extremely hydrophobic with log K_{ow} from 5.97 to 7.0, while fipronil and its biologically active metabolites (termed collectively as fiproles hereafter) are moderately hydrophobic with log K_{ow} of 3.68 to 4.77 (Gan et al., 2012; Spurlock and Lee, 2008; Walse et al., 2004). Due to their hydrophobicity, these compounds are associated predominantly with sediment in surface aquatic systems (Ensminger et al., 2013; Richards et al., 2016;Weston et al., 2004; Weston and Lydy, 2010). Surface runoff induced by rain and irrigation events and discharge of wastewater treatment plant (WWTP) effluent have been identified as the main routes of emission for these insecticides into urban streams (Hernandez-Guzman et al., 2017; Supowit et al., 2016;

Weston and Lydy, 2012; Weston et al., 2013a). Pyrethroids and fipronil in freshwater aquatic systems have been linked to sediment toxicity, especially toxicity to benthic invertebrates (Lao et al., 2010; Maul et al., 2008; Weston et al., 2004). Hydrophobic contaminants are known to have increased partitioning into the sediment phase with increasing salinity, which may lead to their increased occurrence and toxicity to benthic marine organisms (Hasenbein et al., 2018; Saranjampour et al., 2017). However, likely due to sampling challenges, to date, very little is known about the occurrence of these urban-use insecticides in near-shore marine environments.

Worldwide, many population centers are located along the coast. For example, in California, approximately 68% of its 39.6 million residents live in close proximity to the Pacific Ocean, and about 80% live in large metropolitan areas that are within 100 km of the coast, including the Greater Los Angeles area (18.8 million), the San Francisco Bay Area (9.7 million), and San Diego County (3.1 million) (Sievanen et al., 2013; U.S. Census Bureau, 2017; 2018; U.S. Office of Management and Budget, 2013). There are 57 WWTPs that discharge along the California coastal line, and the WWTP effluent is often directly or indirectly discharged into the Pacific Ocean (Hawkins et al., 2018). For example, effluent of WWTPs in Los Angeles County is discharged into the Pacific Ocean through two underwater pipes over 2 m in diameter, with the effluent released 2.4 km from the shore (Sanitation Districts of Los Angeles County, 2016). The continuous discharge has resulted in the formation of a large swath of heavily contaminated ocean floor on the Palos Verdes Shelf (U.S. EPA, 2009). Approximately 35% of water from precipitation near the coast is estimated to flow as surface runoff into the Pacific Ocean

(Hevesi and Johnson, 2016). Therefore, it may be hypothesized that pyrethroids and fipronil used in the coastal urban regions are susceptible to transport via WWTP effluent discharge and surface runoff and that given the hydrophobicity of these compounds, they accumulate in the coastal marine sediment.

This study aimed to understand the occurrence, spatial distribution, composition, and potential sources of urban-use insecticides in the marine sediment on the Palos Verdes (PV) Shelf off the coast of Los Angeles. Potential flux to the shelf was determined using the measured pesticide concentrations in sediment together with sedimentation rates. The results were further used to estimate the potential toxicity of these insecticides to marine benthic invertebrates.

4.3 Materials and Methods

4.3.1 Chemicals and Sediments

A total of 10 urban-use insecticides, including six pyrethroids (fenpropathrin, bifenthrin, *cis*-permethrin, λ -cyhalothrin, cypermethrin, and cyfluthrin) and four fiproles (fipronil and its primary degradates, i.e., desulfinyl fipronil, fipronil sulfide, and fipronil sulfone), were obtained from FMC (Princeton, PA), Bayer Crop Science (Kansas City, KS), Syngenta (Greensboro, NC), Valent (Mahomet, IL), and the U.S. EPA's National Pesticide Standard Repository (Fort Meade, MD). The chemical structures are shown in **Figures 4.1** and **4.2** in the Supporting Information (SI). Stable isotope labeled bifenthrin (bifenthrin-d_5) was purchased from Toronto Research Chemicals and used to determine recoveries (Toronto, Ontario, Canada). All solvents were of HPLC grade.

Florisil was purchased from Acros Organics (Morris Plains, NJ), and cartridges containing 2 g of Florisil were packed in the laboratory and used for extract cleanup.

Sediment samples were collected in 2014 from the Palos Verdes Shelf Superfund Site (PV Shelf) off the Palos Verdes Peninsula coast in north of Los Angeles, CA. More details about the PV Shelf site are described below. Sediment grab samples were collected using a 0.1 m^2tandem Van Veen grab in a grid format consisting of 44 locations, i.e., 0A through 10D, as shown in **Figure 4.3**. The top 2 cm sediment was carefully scraped off using spatula from each grab sample and transferred to a glass jar. Sample collection lasted over several days and the collected samples were frozen immediately on board the vessel upon collection (**Figure 4.3**). The sediment samples were stored as frozen in the dark until analysis. The total organic carbon contents (TOC) of these sediment samples may be found in **Table 4.1** based on data in a report by the LA County Sanitation District (Sanitation District of Los Angeles County, 2016).

4.3.2 Study Site

The PV Shelf site encompasses a large swath of sediment found on an 88 km^2 section of the continental shelf called the Southern California Bight, bordered by Santa Monica Bay and Channel Islands in the north and northwest and San Pedro Bay in the south (U.S. EPA, 2009). Discharge from the Joint Water Pollution Control Plant, which services the County of Los Angeles, is deposited onto the shelf via two sewer lines (2.44 and 3.66 m in diameter) and then deposited from the White Point outfalls that correspond to 8C among the sampling locations in **Figure 4.3**. The discharge operates

continuously, at an average rate of 1.34 billion liters per day (Sanitation District of Los Angeles County, 2016). Two other pipes are smaller and are operational only during heavy rains. During the 1950–70s, the Montrose Chemical Company operated the largest DDT manufacturing plant in the world, and approximately 10% of the waste effluent containing DDT and PCBs settled onto the PV Shelf near the outfall location, with currents leading northwest that carried sediment to the north, contaminating approximately 44 km^2 of sediment floor (U.S. EPA, 2009). This contamination led to the study location being designated as a Superfund Site in 1989 (U.S. EPA, 2009). Sediment samples used in this study came from the 44 sampling locations used by the LA County Sanitation District for monitoring, with locations 8A–9D near the White Point outfalls and 0A–1D as reference locations. These samples are located at depths from 20 to 200 m below the ocean's surface.

4.3.3 Sediment Concentration Measurement

To measure the levels of pyrethroids and fiproles, an approximately 1.0 g (wet weight) aliquot of sediment was added to a 50 mL centrifuge tube and dried with sodium sulfate. Water content was determined using a separate aliquot. A surrogate standard, bifenthrin-d_5, was added, and the sediment was extracted by mixing with 40 mL of dichloromethane and acetone (1:1, v:v) on a horizontal shaker at 120 rpm for 30 min. The extraction was repeated three consecutive times, and the combined extract was concentrated under nitrogen gas to near dryness. The residues were dissolved in 1.0 mL

of acetone and hexane (1:9, v/v). For cleanup, the extract was filtered through a 2 g Florisil cartridge and eluted with 20 mL of the acetone/hexane mixture into a glass vial. The eluate was concentrated under nitrogen gas to <1 mL, and an internal standard (50 ng of PCB 209) was added before analysis on an Agilent GC/MS.

4.3.4 Chemical Analysis and Quality Assurance/Control

The target insecticides were analyzed on an Agilent 6890N GC equipped with an Agilent 5975 mass spectrometer (MS) operating in electron ionization (EI) mode. Chromatographic separation was done using an Agilent 30 m × 0.25 mm DB-5 fused silica capillary column, with the injector temperature set at 250 °C. The carrier gas was at 1.0 mL/min. The oven temperature was initially set for 1 min at 120 °C, ramped to 220 °C at 30 °C/min and held for 1 min, ramped to 300 °C at 5 °C/min, and then held for 5 min. The ion source temperature, quadrupole, and transfer line temperatures were 230, 150, and 280 °C, respectively.

Several steps were used to ensure quality assurance and quality control. All measurements were made in triplicates, and method blanks were included to ensure that the detection of target insecticides was not due to laboratory contamination. The limits of detection were set as three times the background noise and ranged from 0.5 to 1 μg/kg for the 6 pyrethroids and 4 fiproles. Surrogate standards were added to determine recoveries, and internal standards were added before analysis to account for instrument drift. Recoveries for the sediment extractions were 84.2–102%.

4.3.5 Toxicity Unit Calculation

Toxicity Units (TUs) were calculated to estimate the potential toxicity that the target insecticides may have on benthic invertebrates. TUs were calculated using **Equation 4.1** (Lao et al., 2010),

$$TU = \frac{Sediment\ concentration\ (\frac{\mu g}{g}\ OC)}{LC_{50}\ (\frac{\mu g}{g}\ OC)} \quad (4.1)$$

However, benchmark values of these compounds for marine benthic invertebrates are scarce. In a previous study, other species were used to approximate the potential acute toxicity for marine benthic invertebrates (Lao et al., 2010). A similar approach was adopted by using LC_{50} values derived for other sediment-dwelling invertebrates. The LC_{50} values used included those from 10 d whole sediment toxicity assays on *Eohaustorius estuarius*, an estuarine amphipod, *H. azteca*, a freshwater amphipod, and *Chironomus tentans*, a freshwater midge. Reported LC_{50}values (based on OC) were 1.05 μg/g for bifenthrin for *E. estuarius*, 1.1, 0.445, and 0.4 μg/g for fenpropathrin, λ-cyhalothrin, and cypermethrin, respectively, for *H. azteca* (Amweg et al., 2005; Delgado-Moreno et al., 2011; Lao et al., 2010). For fiproles, the reported LC_{50} values were 0.16 and 7.7 μg/g for fipronil sulfide for *C. tentans* and *H. azteca*, respectively (Lao et al., 2010; Maul et al., 2008; Schlenk et al., 2001. These benchmark values from previous studies, along with the log K_{ow} values of the target insecticides, are listed in **Tables 4.2–3**.

4.3.6 Source Tracing and Statistical Analysis

Statistical analysis was carried out using both SigmaPlot 12 and SSPS 19.0. Principle component analysis (PCA) was used to cluster occurrence of pesticides and for source elucidation (Larsen and Baker, 2003; Li et al., 2018). In this study, population index and the natural log of the distance from the White Point outfall, combined with the TOC normalized concentrations, were used in the PCA analysis. Several different methods were initially tested to assess population index (PD) in this study (Li et al., 2006), and the final method used was

$$PD = \frac{\sqrt{P}}{D} \qquad (4.2)$$

where P is population of one of four nearby cities (Rancho Palos Verdes, Palos Verdes Estates, San Pedro, and Lomita, CA) and D is the distance in km between each city and the sampling locations. The final PD (**Table 4.4**) was calculated by summing the value for each city at each sampling location, and that value was used in the PCA analysis. For example, for sampling location 0A, this equation was used to calculate PD for one city using that city's population and distance from 0A, and similar calculations were made for the next three cities. Then the total PD for 0A was summed from those results. The PCA results give several factors that account for the variance within variables of interest that may be used to infer sources of contaminants in the environment. When analyzing the correlations among target pesticides and possible source properties, these variables were

grouped into two factors in this study (**Table 4.5**, **Table 4.6**). The two principal factors (F1 and F2) with eigenvalues greater than 1 represented ≥75% of the total variance.

4.4 Results and Discussion

4.4.1 Concentrations and Distribution of Insecticides in the PV Shelf Sediments

Synthetic pyrethroids commonly contain structural and/or stereoisomers, and isomers of the same pyrethroid may differ in biological activity. In this study, analytical standards were obtained from the primary manufacturers and used as received for quantitative analysis, without consideration of isomer profiles. For permethrin, only the *cis* isomer was targeted for analysis. Fipronil is known to degrade to fipronil sulfone, fipronil sulfide, and disulfonyl fipronil, and these metabolites also possess biological activity. Therefore, fipronil, along with its three metabolites, was targeted for analysis. Hydrolysis of some pyrethroids leads to the formation of 3-phenoxybenzoic acid that is known to have endocrine disruption activity. However, 3-phenoxybenzoic acid is highly water-soluble, and therefore it was excluded in the targeted analysis in this study due to its negligible partition into the sediment phase.

Total concentrations of pyrethroids varied widely across the PV Shelf, ranging from nondetectable (nd) to 170 μg/kg (dry weight), and the types of pyrethroids found at each location also varied greatly (**Figure 4.3**). Cyfluthrin was not detected in any of the sediment samples, and concentrations of individual compounds were: bifenthrin (nd-11.7 μg/kg, detection frequency 64.4%), fenpropathrin (nd to 50.4 μg/kg, 49.2%), *cis*-permethrin (nd to 59.7 μg/kg, 0.76%), λ-cyhalothrin (nd to 18.6 μg/kg, 23.0%), and

cypermethrin (nd to 74.9 μg/kg, 23.5%). In samples from 10A, 10B, and 10D (reference locations), no pyrethroids were detected, while *cis*-permethrin was the only pyrethroid found at 10C. The compounds found in the highest concentrations and detected at <25% of the time were cypermethrin and λ-cyhalothrin, and they were found primarily near the White Point outfall (8A–9D). Fenpropathrin was found in the next highest concentrations; however, it was more evenly distributed across the shelf. Bifenthrin was detected frequently (64.4%) but only in relatively low concentrations. However, it is important to note that bifenthrin generally exhibits an enhanced aquatic toxicity than the other pyrethroids and that low concentrations of bifenthrin do not necessarily suggest low or absence of toxicity (**Table 4.2**).

For cypermethrin and λ-cyhalothrin, the highest concentrations occurred near the wastewater outfall (8A–9D), suggesting that WWTP effluent might be their primary source into the marine environment. The highest numbers of contaminants per sample were also found in the sediments adjacent to the outfall (8A–9D). When normalized by the sediment OC content, these trends become slightly clearer (**Figure 4.4**). λ-Cyhalothrin and cypermethrin exhibited much higher concentrations around the outfalls than at locations from the rest of the shelf, with the exception of another peak in λ-cyhalothrin at the 3A and 3B locations. In comparison, fenpropathrin showed the highest concentrations at locations closest to the shoreline. Bifenthrin displayed one large peak at 5D, which was also close to the shoreline, while levels of bifenthrin were relatively homogeneous at the other locations. These patterns were reflected in the coefficients of variation in the PCA analysis for these compounds (**Table 4.6**), which were less than 1.5

for bifenthrin and fenpropathrin and above 1.5 for λ-cyhalothrin and cypermethrin, clustering these into two separate groups and suggesting different primary sources for contamination.

When comparing the detected concentrations to those from freshwater sediments in California, concentrations of bifenthrin were found to be similar to those in the Santa Clara and Calleguas Creek watersheds that had median sediment concentrations of 2 and 4 μg/kg during the dry and wet seasons, respectively (Delgado-Moreno et al., 2011). These concentration trends were different from those observed in the Ballona Creek sediments, where bifenthrin and permethrin were found in the highest concentrations, indicating the possibility of lower use near the PV Shelf (Lao et al., 2010). Permethrin was also frequently detected in high concentrations at these freshwater locations but not in the PV Shelf sediments in this study. The difference suggested that permethrin might be removed more effectively at WWTPs, due to more rapid degradation and/or greater adsorption to sludge. It was also possible that permethrin underwent more rapid degradation once deposited in the marine sediment bed, although the persistence of pyrethroids is largely unknown in marine sediments.

Surprisingly, total concentrations of fiproles in sediments were composed of only one fipronil degradate, fipronil sulfide, and the concentrations of fipronil sulfide ranged from 1.8 to 5.6 μg/kg. Fipronil sulfide was detected at all locations. The lack of parent compound suggested that fipronil was easily transformed in the environment either before or after its discharge into the study area. The formation of fipronil sulfide implied that fipronil had likely undergone reductive transformation in the marine sediment under

anoxic conditions (Gunasekara et al.; 2007). This could also be partially due to other mechanisms; for example, fipronil sulfide is slightly more hydrophobic than fipronil or its other degradates, suggesting that it might be better retained in the sediment, instead of dissipating into the overlaying water (Walse et al., 2004). In this study, the levels of fipronil sulfide were at least 8 times lower than those of pyrethroids, which may be again attributed to their lower hydrophobicity, more rapid degradation, and/or different emission loads. The ratio of concentrations of fiproles to pyrethroids in the PV Shelf was also similar to those found in other studies and may therefore reflect their use patterns (Gunasekara et al., 2007; Hintzen et al., 2009; Lao et al., 2010).

Unlike pyrethroids, there was limited variation among the different locations for fipronil sulfide, indicating that the source of fipronil sulfide might be primarily surface runoff and/or deposition of urban dust. The low concentrations of fiproles were similar to other freshwater locations, although the chemical compositions differed (Delgado-Moreno et al., 2011; Lao et al., 2010). Fipronil sulfone was commonly found in sediments from Ballona creek in southern California and a central Texas stream, but fipronil sulfide was more dominant in rice paddies in Louisiana (Demcheck and Skrobialowski, 2003; Hintzen et al., 2009; Lao et al., 2010). The difference was likely due to different redox conditions, as fipronil sulfone is an aerobic oxidation product while fipronil sulfide is a reduction product (Aajoud et al., 2003; Demcheck and Skrobialowski, 2003; Lin et al., 2008; Schlenk et al., 2001) . In previous studies, degradation of fipronil to fipronil sulfide was found to be very rapid under anaerobic conditions in aquatic systems and flooded soils (Aajoud et al., 2003; Biever et al., 2003). Although redox

potential of the marine sediment bed was not measured in this study, it may be expected that the depth, when coupled with the high content of organic matter, rendered the PV Shelf sediment anoxic or reduced. The prevalence of fipronil sulfide in the PV Shelf sediments may be partially attributed also to its longer half-life as compared to fipronil and its other degradates (Gan et al., 2012; Walse et al., 2004), although half-lives of fipronil and fipronil degradates in marine sediments are unknown.

4.4.2 Correlation with Sediment Organic Carbon Content

The sediment TOC values ranged from 0.21% (7D location) to 4.4% (8C location), and the higher TOC levels in areas close to the outfall affirmed that WWTP effluent was the main source of organic matter to the sediment bed. Pearson's correlation coefficients were calculated for the four pyrethroids detected at a frequency above 20% (bifenthrin, fenpropathrin, λ-cyhalothrin, and cypermethrin) and fipronil sulfide. There was no statistically significant correlation between sediment TOC and levels of fenpropathrin or fipronil sulfide; however, there was a significant correlation with the occurrence of bifenthrin, cypermethrin, or λ-cyhalothrin (0.475, 0.600 and 0.589, respectively; $P < 0.005$) (**Figure 4.5**). When the total pyrethroid levels were considered, the correlation with TOC was also significant (0.634, $P < 0.001$). This analysis showed that for compounds more widely distributed across the shelf, such as fenpropathrin and fipronil sulfide, the source of contamination may not be the same as the source of TOC. It may be also inferred that pyrethroids in general may be emitted at the same time as the

organic matter, likely through the discharge of WWTP effluent and underpinned by their strong hydrophobicity. The sole exception, fenpropathrin, was probably due to the fact that it has a lower hydrophobicity (log K_{ow}= 6.00, as compared to >6.40 for the other pyrethroids) (Laskowski, 2002). This may also explain why cyfluthrin was not detected, since it had the lowest reported use among the pyrethroids considered in this study (CDPR, 2014; 2015; 2016) as well as a relatively low K_{ow} (5.97) (Laskowski, 2002). The lack of a clear relationship between sediment TOC and fipronil sulfide distribution may be also attributed to its lower log K_{ow} compared to pyrethroids (Walse et al., 2007). While this may not preclude its origination from WWTPs, the inconclusive results merited further data analysis, as discussed below.

4.4.3 Potential Sources of Contamination

To discern the potential sources of pyrethroids and fiproles to the PV Shelf, principal component analyses (PCA) were conducted. Multivariate statistical techniques like PCA are powerful tools to identify sources contributing to observed contamination and have been often used to infer the factors that influence contaminant distribution in the environment (Larsen and Baker, 2003; Li et al., Li et al., 2006; Li et al., 2018). The two sets of factor scores created for each location and their spatial distributions were mapped for the entire shelf (**Figure 4.6**).

Factor 1 (F1) was the highest around the White Point outfalls, which was indicative of input of WWTP effluents, as it was highly negatively correlated with

distance from the discharge point (ln (D), −0.760). Therefore, samples from these locations likely had the WWTP discharge outfalls as the major source of contamination. Additional analysis suggested that the sources of λ-cyhalothrin and cypermethrin were particularly associated with the WWTP effluent, as F1 was highly correlated with these two compounds (0.819 and 0.904, respectively). Approximately, 3.87×10^{11} L of treated wastewater was discharged from the nearest large treatment plant facility, the Joint Water Pollution Control Plant in 2009, which when combined with discharge from the other facilities, emitted millions of cubic meters each day of WWTP effluent to the ocean surrounding the PV Shelf (Lyon and Sutula, 2011). Since pyrethroids and fiproles are not completely removed during wastewater treatment, this discharge contributed to sediment contamination (U.S. EPA, 2011). For example, λ-cyhalothrin and cypermethrin were previously detected in wastewater influent and λ-cyhalothrin was frequently found in WWTP effluent in northern California. Both λ-cyhalothrin and cypermethrin were detected in the effluent at one or more WWTPs throughout the state (Markle et al., 2014; Weston et al., 2013a). This, coupled with their relatively high log K_{ow}, may explain why they were more prevalent in areas close to the White Point outfalls.

Factor 2 (F2) was the highest at locations along the coastline and represented nonpoint source contamination to the shelf, such as urban surface runoff. Samples from these locations likely received contamination due to nonpoint sources rather than a significant input from the WWTP effluent, as F2 was highly correlated with population density (0.778). One exception was location 8D, which has high factor scores for both factors (1.7 and 1.8, for F1 and F2, respectively), indicating that both factors may have

contributed to the heavy contamination at this location. Nonpoint sources were likely the predominant contribution for fenpropathrin, fipronil sulfide, and bifenthrin in the PV Shelf, as their highest concentrations (normalized by sediment TOC) were found at the sample locations with the highest F2 scores (e.g., C and D locations for many sampling series); and these three compounds were highly correlated with F2 (0.757, 0.666, and 0.571, respectively). Fenpropathrin was previously found in streams of southern California that were impacted by residential runoff but not in WWTP influent or effluent (Markle et al., 2014; Weston et al., 2013a). Previous monitoring studies showed the ubiquitous occurrence of fiproles in surface runoff from residential homes, as fipronil is widely used for ant and termite control around structures (Gan et al., 2012). Although bifenthrin has been widely detected in WWTP influent, transport to the PV Shelf appears to be dominated also by nonpoint sources (Markle et al., 2014). This was likely due to both the removal of bifenthrin by partitioning into biosolids during wastewater treatment and its longer half-life in the environment compared to the other pyrethroids (Laskowski, 2002; Markle et al., 2014). The long persistence of bifenthrin likely allowed its sustained off-site movement from sites of application, such as homes, including emission into the ocean due to urban runoff.

4.4.4 Mass Fluxes of WWTP Associated Insecticides

The annual fluxes for λ-cyhalothrin and cypermethrin associated with WWTP effluent were estimated using **Equation 4.3:**

$$Flux = C_s \times MSR \quad (4.3)$$

where C_s is the average sediment concentration for each sampling location (ng/g) and MSR is the mean sedimentation rate (g/cm^2/yr) (Liao et al., 2017). The MSR was calculated for the 8C location to be 0.858 g/cm^2/yr by Liao et al. (2017). This rate was assumed to be similar for the other locations adjacent to the outfall, which were also the locations where λ-cyhalothrin and cypermethrin were most frequently detected in this study. The total fluxes to the area of the shelf with the heaviest contamination (44 km^2) of λ-cyhalothrin and cypermethrin for the year 2014 were estimated to be 64 and 77 kg/yr, respectively. As the usage for these two pyrethroids nearly doubled from 2012 to 2016, it may be expected that their emission flux to the shelf may have remained similar to those found in this study or may have increased in more recent years. It may be also assumed that the flux calculated here likely reflected the lower-end deposition for these insecticides, as current movements and in situ degradation would result in their dissipation from areas near the outfalls.

The contamination of WWTP influent and effluent by pyrethroids and fiproles is related primarily to their indoor use, such as the use of sprays and other formulations for ant and cockroach control, and the use of pet products (Markle et al., 2014); Teerlink et al., 2017; Weston and Lydy, 2010; Weston et al., 2013a). For example, when products containing fipronil were used for flea or tick control on dogs, washing of such pets resulted in contribution of fipronil to the contamination of WWTP influent (Teerlink et al., 2017). As the usage of pyrethroids and fipronil products has been increasing with

time, their presence in the marine sediment may pose potential acute toxicity to benthic marine organisms (Amweg et al., 2005; Delgado-Moreno et al., 2011; Lao et al., 2010).

4.4.5 Toxicity Unit (TU) Estimation for Benthic Invertebrates

To estimate the potential toxicity to marine benthic invertebrates, toxicity units (TUs) were calculated for pyrethroids found at a frequency above 20% and fipronil sulfide which was found at all sites. Several studies showed that *H. azteca* was approximately 2 times more sensitive than *E. estuarius* to pyrethroids, while *Chironomus tentans* was much more sensitive than *H. azteca* to fiproles (Lao et al., 2010; Maul et al., 2008). Therefore, calculated TUs above 2 using LC_{50}values based on *H. azteca* or *C. tentans* were considered toxicologically relevant for *E. estuarius*. However, it is important to note that these two species inhabit freshwater environments and were thus indirect estimates for marine benthic invertebrate species.

The derived TUs ranged from no toxicity (nt) to 15, nt to 51, nt to 60, and nt to 81 for bifenthrin, fenpropathrin, λ -cyhalothrin, and cypermethrin, respectively (**Figure 4.7**). As pyrethroids have similar mechanisms of action, we can assume that contributions to toxicity are additive for pyrethroids (Delgado-Moreno et al., 2011; Weston et al., 2004); thus, the total TUs for all detected pyrethroids ranged from nt to 146. In nearly all samples where pyrethroids were detected, total pyrethroid TU values were higher than unity (>1 for *E. estuarius*; > 2 for other species), indicating a potential for acute toxicity on benthic invertebrates. The large TUs suggest that there is a high likelihood for pyrethroids to exhibit toxicity to some benthic organisms in the PV Shelf sediment.

Among the different pyrethroids, fenpropathrin accounted for the majority of the estimated toxicity in most samples (44%), followed by cypermethrin (28%) and λ-cyhalothrin (11%), in contrast to the predominance of bifenthrin-associated toxicity in freshwater sediments (Delgado-Moreno et al., 2011; Ensminger et al., 2013; Lao et al., 2011). However, in sediment samples where cypermethrin was detected, it almost always contributed the most to the total toxicity, due to its low LC_{50} (**Table 4.2**).

The calculated fipronil sulfide TUs ranged from 0.09 to 1.6 if *H. azteca* was used as a proxy for *E. estuaries*. However, *H. azteca* was considered to be only moderately sensitive to fiproles, while *C. tentans* was comparatively more sensitive. If *C. tentans* was used as the proxy, the derived TUs ranged from 4.2 to 75 or approximately 47 times higher than that for *H. azteca* (**Table 4.7**). Therefore, depending upon the species used for estimating toxicity, TU values for fipronil sulfide showed either a low or high potential for acute toxicity. This highlights the species sensitivity of fipronil toxicity and also the urgency for deriving benchmark values for marine benthic invertebrates, especially those native to the study area. In this study, locations closest to the shoreline generally had the highest fipronil TUs, while those farther away from the coast were much lower. This suggested again that contamination of marine sediment by fiproles was mainly due to nonpoint sources such as surface runoff, which impacted near-shore locations much more than locations further away from the coast.

The large variations in TU values were similar to findings in freshwater waterways in the region, such as the Santa Clara River and Calleguas Creek watersheds, where total pyrethroid TUs to *H. azteca* were estimated to be 0.4–199.3, but the values

were greater than that found in Ballona Creek, which is about 48 km north of the Palos Verdes Peninsula (Delgado-Moreno et al., 2011; Lao et al. 2010). The TUs for fipronil sulfide in this study were similar to those found for fipronil and its degradates in freshwater streams and creeks from southern California, where TUs based upon mysid shrimp were above unity in approximately 74–88% of samples (Gan et al. 2012). For sediments from Ballona Creek, TUs of fiproles based upon *H. azteca* were all below unity (Lao et al. 2010). However, when *C. tentans* was used as the indicator species, approximately 50% of the sediment samples were above unity, indicating that Ballona Creek had a lower toxicity potential from fiproles than that in the present study (Lao et al. 2010).

Again, toxicity prediction in this study was handicapped by the fact that almost no LC_{50}values were available for marine benthic invertebrates for these chemicals. As salinity has the potential to increase toxicity due to increased partitioning into the sediment and likely other processes, it is possible that our TUs underestimate actual toxicity (Hasenbein et al., 2018; Saranjampour et al., 2017). It must be noted that in addition to acute toxicity, insecticides may also pose chronic effects to less sensitive organisms, including both developmental and reproductive impairments (Chandler et al., 2004; Cui et al., 2009; U.S. EPA, 1996). It is also possible that sensitive organisms could experience chronic toxicity, given that measured insecticide concentrations may not capture those below the detection limits (Brander et al., 2016; Stehle and Schulz, 2015). For example, trace levels of fiproles impaired development and reproduction of mysid shrimp and an estuarine copepod, *Amphiascus tenuiremis*, and showed endocrine

disruption in the blue crab *C. sapidus* (Chandler et al., 2004; Goff et al., 2017; U.S. EPA, 1996). Bifenthrin decreased the survival rate of *Daphnia magna* neonates, and at concentrations >0.04 μg/L, brood size decreased and the onset of reproduction was delayed (Cui et al., 2009). Additionally, when these compounds diffuse into the overlaying water column, they may also have the potential to affect the development of water-column invertebrates and fish (Haya, 1989; Jin et al., 2009; Yang et al., 2014). Organisms of the same species found in locations like the PV Shelf may also have developed resistance to contaminants in the environment due to their prolonged exposure to these contaminants, making them less sensitive than laboratory organisms. For example, wild *H. azteca* have lowered pyrethroid sensitivity versus laboratory raised organisms, again highlighting the uncertainties due to the lack of data for indigenous marine organisms (Clark et al., 2015; Weston et al., 2013b). Findings of this study therefore present an urgent need to establish threshold values for sensitive marine organisms for urban-use pesticides and further evaluate effects at the community level.

4.5 Conclusion

In this study, a survey of surficial sediment across a wide swath of marine floor next to the Los Angeles coastline showed the ubiquitous presence of urban-use insecticides including pyrethroids and fipronil sulfide. Spatial distribution and correlation analysis suggested that both discharges of WWTP effluent and surface runoff were responsible for the contamination, but the influence differed among the insecticides. The concentrations and numbers of pyrethroids detected were the highest in areas near the

White Point outfall, linking the contamination to WWTP effluent emission. Fipronil sulfide was found at low levels across the shelf, suggesting that fipronil was reductively transformed in the marine sediment bed. On the basis of the PCA results, the sources of cypermethrin and λ-cyhalothrin were attributed to WWTP effluent discharge, while nonpoint sources such as rain and irrigation-induced surface runoff likely contributed to the occurrence of bifenthrin, fenpropathrin, and fipronil sulfide in the near-shore sediments. Using toxicity thresholds previously derived for several freshwater and estuarine invertebrates, levels of pyrethroids and fipronil sulfide in the PV Shelf sediment were sufficiently high to cause acute toxicity, with the highest toxicity to be near the White Point outfalls or close to the shoreline. However, toxicity benchmarks for marine benthic invertebrates, including those native to the PV Shelf, are currently unavailable. It is imperative that the sensitivity of marine benthic species to these urban-use insecticides be determined for a better prediction of actual ecotoxicological impairments. While southern California represents a highly urbanized area, there are numerous other metropolises situated next to coasts around the globe. The emission of urban-use pesticides from these urban regions and the implications for the health of marine ecosystems merit heightened attention. Mitigation strategies should be developed to minimize emission of urban-use pesticides to the marine environment.

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Tables and Figures

Table 4.1. Percent total organic carbon (TOC) for each sample taken from Sanitation District of Los Angeles County, 2016.

Location	TOC (%)	Location	TOC (%)	Location	TOC (%)
0A	2.40	4A	1.40	8A	2.40
0B	1.50	4B	2.20	8B	2.70
0C	0.80	4C	1.30	8C	4.40
0D	0.56	4D	0.45	8D	0.48
1A	1.50	5A	1.70	9A	2.30
1B	0.70	5B	2.70	9B	1.80
1C	1.00	5C	1.50	9C	0.85
1D	0.66	5D	0.27	9D	0.63
2A	1.40	6A	1.40	10A	0.99
2B	1.00	6B	2.60	10B	0.74
2C	0.90	6C	1.90	10C	0.51
2D	0.42	6D	0.68	10D	0.48
3A	1.20	7A	1.20		
3B	1.10	7B	3.10		
3C	1.10	7C	0.94		
3D	0.62	7D	0.21		

Table 4.2. LC_{50} values (μg/g OC) and log K_{ow} for pyrethroids bifenthrin (BFT), fenpropathrin (FPT), λ-cyhalothrin (λ-CYH), cypermethrin (CYP), *cis*-permethrin (PMT), and cyfluthrin (CYF) for selected benthic invertebrate species.

Compound	BFT	FPT	λ-CYH	CYP	PMT	CYF
log K_{ow}	6.40	6.00	7.00	6.54	6.90	5.97
Species	LC50					
Eohaustorius estuarius	1.05					
Hyallela azteca		1.10	0.445	0.40	10.80	1.08

Table 4.3. LC_{50} values (µg/g OC) and log K_{ow} for fiproles fipronil (FIP), desulfinyl fipronil (DSF FIP), fipronil sulfone (FIP SFO) and fipronil sulfide (FIP SFD) for selected benthic invertebrate species.

Compound	FIP	DSF FIP	FIP SFO	FIP SFD
log K_{ow}	4.01	4.63	3.68	4.77
Species	LC50			
Procambarus clarkii (96-h, µg/L)		49.7		
Hyallela azteca	4.10		9.70	7.70
Chironomus tentans				0.16

Table 4.4. The latitude, longitude, distance (km) between sampling sites and the White Point outfalls, and the population density index for samples on the Palos Verdes Shelf, where P is the population, and D is the distance between sampling sites and four major cities.

Location	Latitude	Longitude	Distance	√P / D	Location	Latitude	Longitude	Distance	√P / D
0A	33.82	-118.45	18.4	44.9	2D	33.74	-118.42	7.91	88.1
0B	33.81	-118.44	17.43	53.6	3A	33.72	-118.41	5.87	80.5
0C	33.81	-118.43	16.91	63.6	3B	33.73	-118.4	5.76	95.5
0D	33.81	-118.42	16.83	74.9	3C	33.73	-118.4	5.73	130.7
1A	33.75	-118.45	10.46	55	3D	33.74	-118.4	5.82	167
1B	33.75	-118.44	10.47	57.3	4A	33.72	-118.39	4.73	79.5
1C	33.76	-118.44	10.42	61.8	4B	33.72	-118.38	3.78	90.7
1D	33.77	-118.43	10.59	65.8	4C	33.73	-118.38	4.29	114.1
2A	33.73	-118.43	7.8	68.1	4D	33.74	-118.38	4.37	159.1
2B	33.74	-118.42	7.76	75.3	5A	33.7	-118.37	1.9	65
2C	33.74	-118.42	7.85	82.8	5B	33.71	-118.37	1.81	73.6

Location	Latitude	Longitude	Distance	√P / D	Location	Latitude	Longitude	Distance	√P / D
5C	33.72	-118.36	2.03	79.6	8B	33.7	-118.33	0.1	62.6
5D	33.73	-118.36	2.56	88.5	8C	33.7	-118.33	0.05	68
6A	33.7	-118.36	0.74	64.4	8D	33.71	-118.33	1.15	80.2
6B	33.71	-118.35	0.94	67.4	9A	33.68	-118.32	0.58	53
6C	33.71	-118.35	0.8	71.8	9B	33.68	-118.32	0.15	56.9
6D	33.72	-118.35	1.73	79.9	9C	33.69	-118.32	0.81	63.8
7A	33.7	-118.35	0.41	63.6	9D	33.7	-118.31	2.31	78.9
7B	33.7	-118.35	0.61	66.4	10A	33.66	-118.3	3.28	43
7C	33.71	-118.35	0.73	70.3	10B	33.67	-118.3	3.15	44.9
7D	33.72	-118.34	1.52	78.5	10C	33.67	-118.29	2.74	48.4
8A	33.69	-118.34	0.66	58.9	10D	33.7	-118.29	3.4	71.3

Table 4.5. Correlation results for each factor score versus pyrethroids, fipronil sulfide, distance, and the population density index from Principle Component Analysis.

	Factor 1	Factor 2
Cypermethrin	**.904**	.078
λ-Cyhalothrin	**.819**	-.004
ln (D)	**-.760**	.240
√P / D	-.110	**.778**
Fenpropathrin	.175	**.757**
Fipronil sulfide	-.266	**.666**
Bifenthrin	-.014	**.571**

Table 4.6. Coefficients of Variation (CV) for 4 selected pyrethroids and fipronil sulfide.

Compound	CV
Cypermethrin	2.03
λ-Cyhalothrin	1.87
Fenpropathrin	1.11
Fipronil sulfide	0.71
Bifenthrin	1.44

Table 4.7. Fipronil sulfide (FIP SFD) toxicity units estimated using *H. azteca* and *C. tentans* for each sampling location.

	FIP SFD			FIP SFD			FIP SFD			FIP SFD	
	H. azteca	*C. tentans*		*H. azteca*	*C. tentans*		*H. azteca*	*C. tentans*		*H. azteca*	*C. tentans*
0A	0.17 ± 0.06	8.3 ± 2.7	2D	0.69 ± 0.3	33 ± 10	5C	0.35 ± 0.07	17 ± 3.5	8B	0.19 ± 0.03	9.1 ± 1.3
0B	0.26 ± 0.07	12 ± 3.3	3A	0.36 ± 0.2	17 ± 7.9	5D	1.5 ± 0.5	74 ± 20	8C	0.14 ± 0.01	6.9 ± 0.7
0C	0.46 ± 0.2	22 ± 9.1	3B	0.43 ± 0.2	21 ± 7.4	6A	0.30 ± 0.05	14 ± 2.6	8D	1.1 ± 0.05	53 ± 2.4
0D	1.3 ± 0.6	62 ± 30	3C	0.43 ± 0.03	21 ± 1.4	6B	0.17 ± 0.03	8.1 ± 1.0	9A	0.26 ± 0.02	12 ± 1.0
1A	0.41 ± 0.02	20 ± 1.0	3D	0.71 ± 0.2	34 ± 9.8	6C	0.16 ± 0.03	7.9 ± 1.3	9B	0.25 ± 0.05	12 ± 2.2
1B	0.70 ± 0.07	33 ± 3.3	4A	0.23 ± 0.09	11 ± 4.4	6D	0.35 ± 0.07	17 ± 3.3	9C	0.51 ± 0.07	24 ± 3.2
1C	0.40 ± 0.03	19 ± 1.5	4B	0.15 ± 0.02	7.3 ± 0.9	7A	0.47 ± 0.07	23 ± 3.1	9D	0.60 ± 0.1	29 ± 6.3
1D	0.61 ± 0.2	29 ± 8.9	4C	0.39 ± 0.3	19 ± 10	7B	0.09 ± 0.03	4.2 ± 1.2	10A	0.31 ± 0.1	15 ± 6.8
2A	0.42 ± 0.08	20 ± 4.0	4D	0.95 ± 0.1	46 ± 5.5	7C	0.44 ± 0.2	21 ± 9.6	10B	0.37 ± 0.1	18 ± 6.0
2B	0.45 ± 0.2	22 ± 7.5	5A	0.39 ± 0.1	19 ± 5.9	7D	1.6 ± 0.4	75 ± 20	10C	0.85 ± 0.2	41 ± 10
2C	0.56 ± 0.1	27 ± 4.7	5B	0.16 ± 0.05	7.5 ± 2.2	8A	0.18 ± 0.08	8.9 ± 3.9	10D	0.61 ± 0.09	29 ± 4.2

Figures

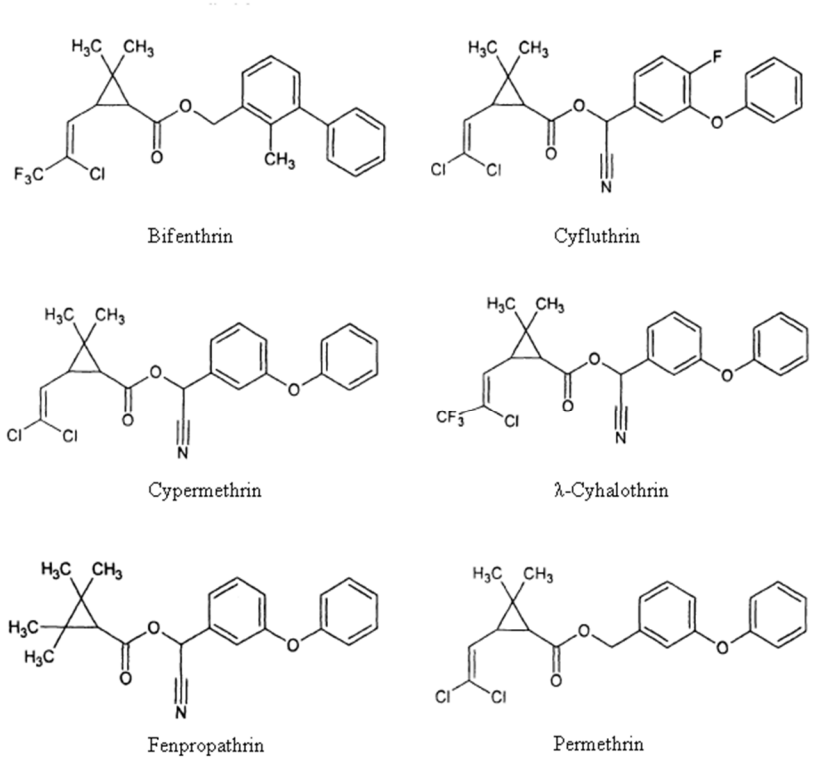

Figure 4.1. Chemical structures of 6 selected pyrethroids, modified from a table in Spurlock and Lee (2008).

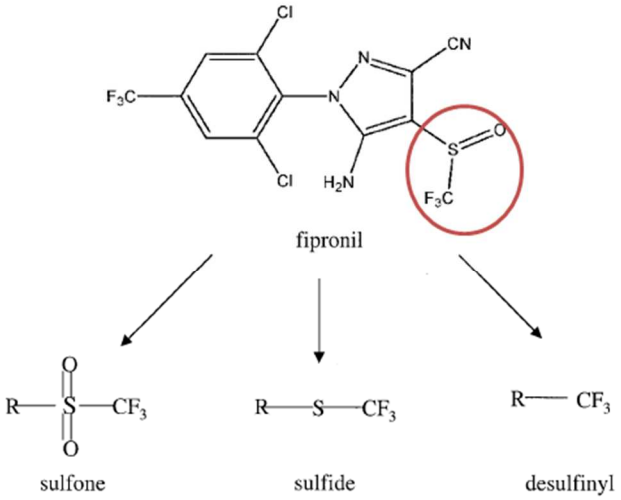

Figure 4.2. Chemical structures of Fipronil and its major degradation products, from Schlenk et al. (2001). The red circle indicates the functional group that changes during degradation.

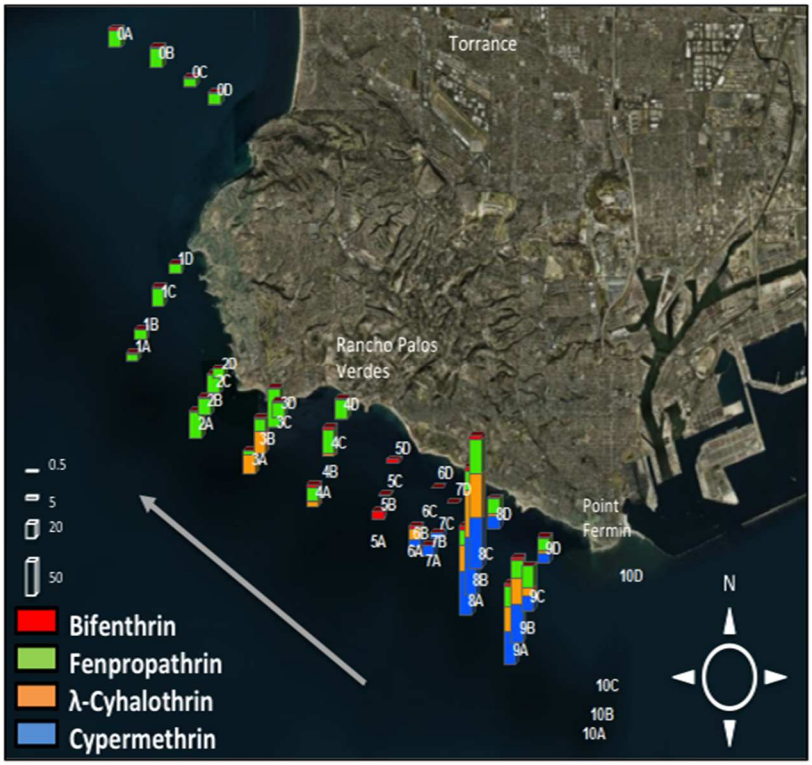

Figure 4.3. Sampling locations and spatial distribution (µg/kg) of total pyrethroids (ΣPYR= bifenthrin, fenpropathrin, λ-cyhalothrin, and cypermethrin) in sediment in the Palos Verdes Shelf. The gray line indicates the direction of currents, and 8A-9D points are located next to the White Point sewage outfalls.

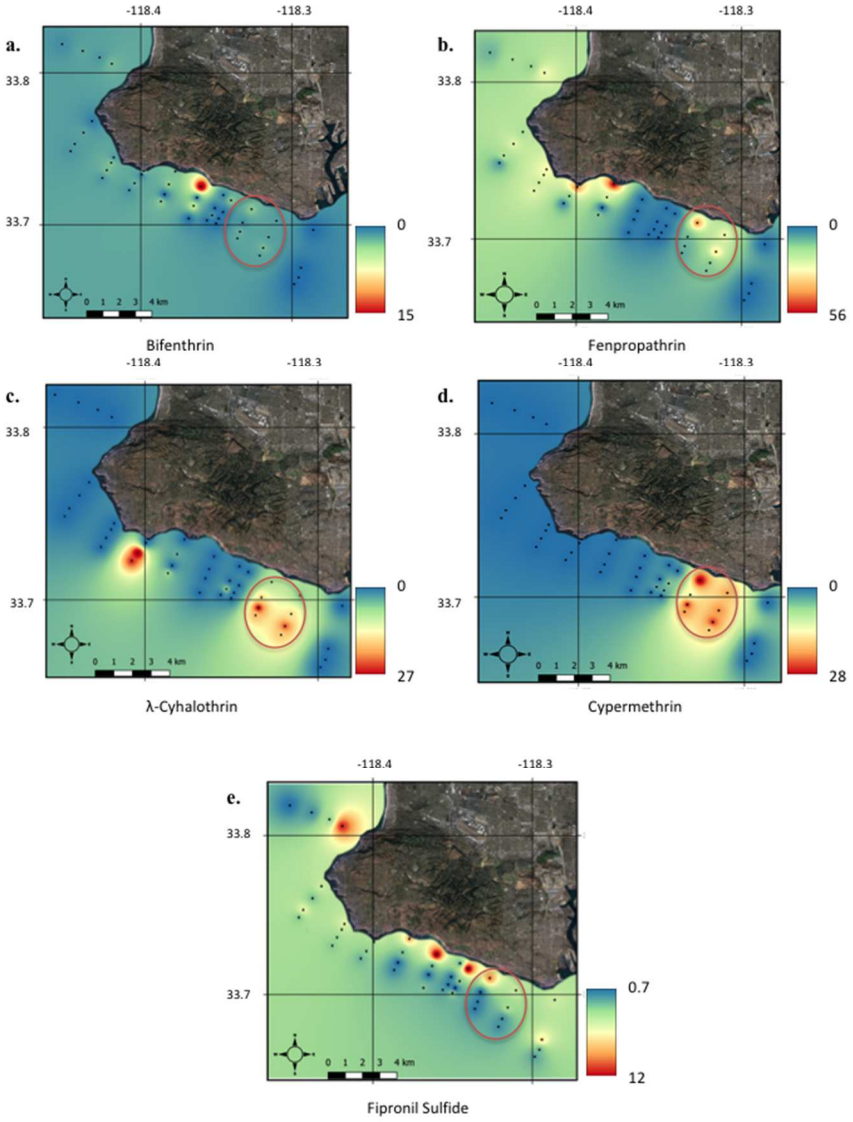

Figure 4.4. Spatial distribution (µg/g TOC) of (**a**) bifenthrin, (**b**) fenpropathrin, (**c**) λ-cyhalothrin, (**d**) cypermethrin, and (**e**) fipronil sulfide in the Palos Verdes Shelf sediment. The red circle highlights the sampling sites 8A-9D that are close to the White Point sewage outfalls.

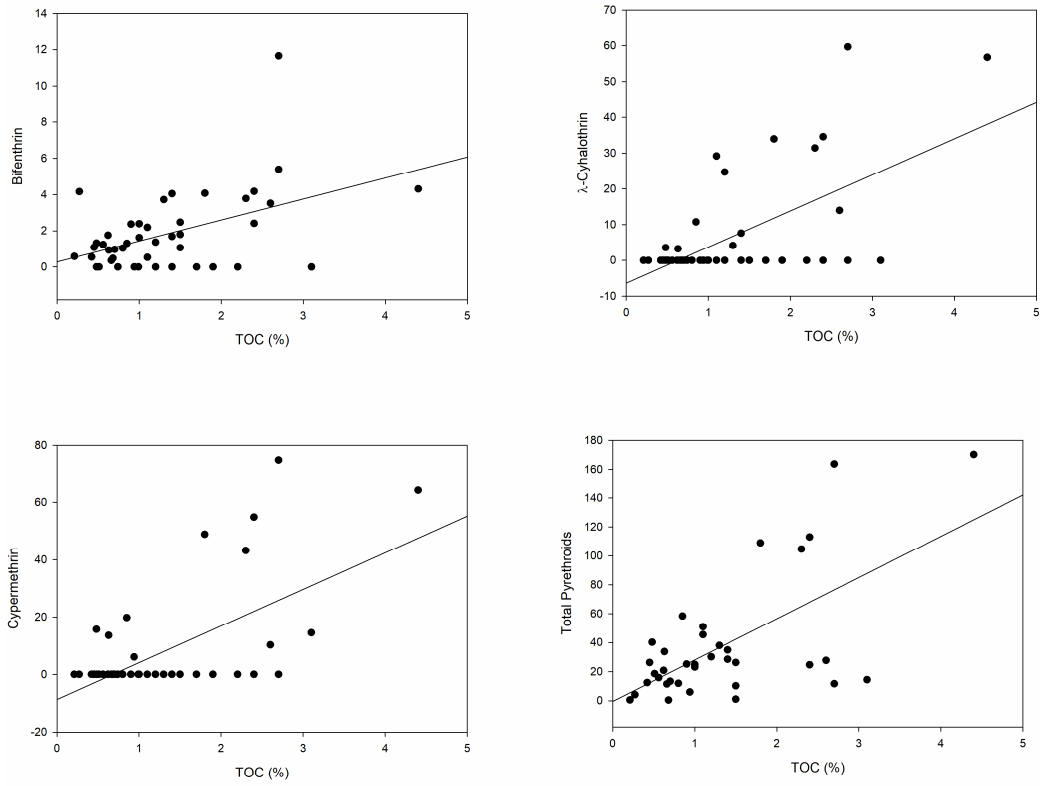

Figure 4.5. Correlations between (**a.**) Bifenthrin (BFT; µg/kg), (**b.**), λ-Cyhalothrin (λ-CYH; µg/kg), (**c.**) Cypermethrin (CYP; µg/kg), and (**d.**) total Pyrethroids (total PYR; µg/kg) versus total organic carbon (TOC; %). All are statistically significant, with $P<0.01$.

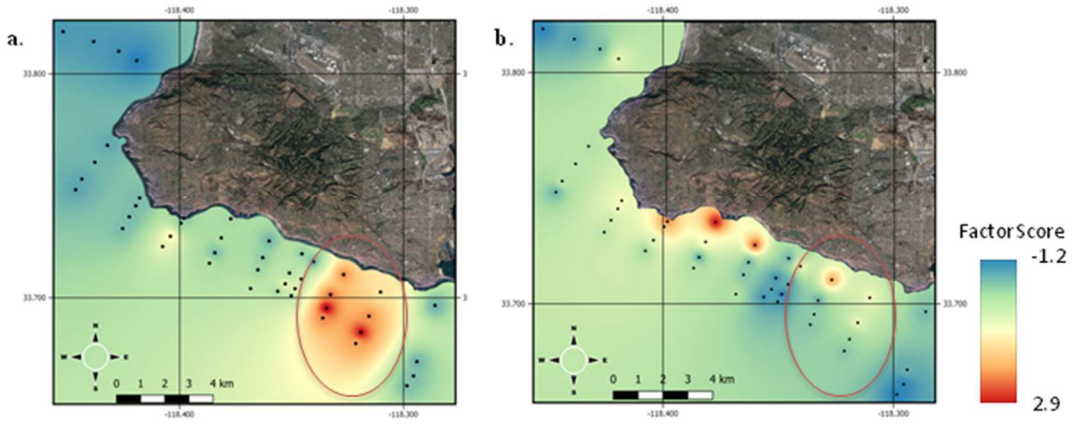

Figure 4.6. Spatial distribution of factor scores (**a**) F1 and (**b**) F2. F1 represents wastewater as the source of contamination to the PV Shelf, while F2 represents non-point sources. The red circle highlights the sampling sites 8A-9D that are close to the White Point sewage outfalls.

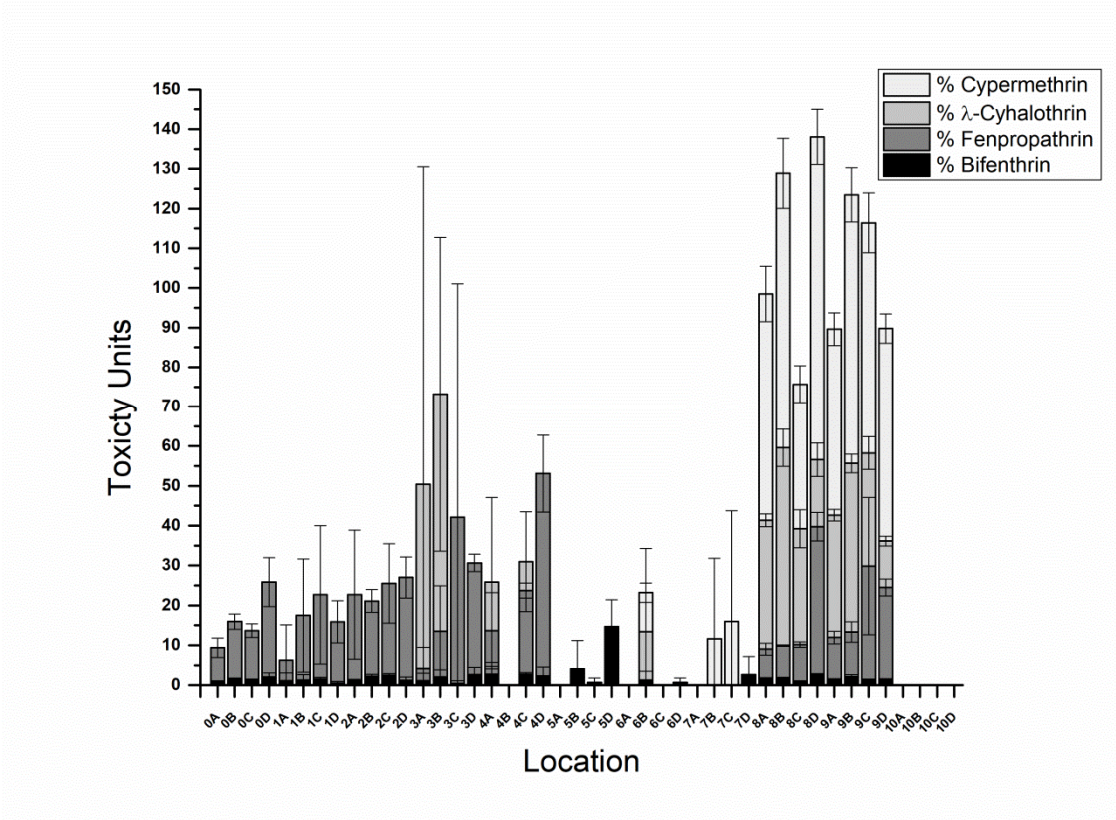

Figure 4.7. Distribution of total pyrethroid toxicity units at each sampling location.

Chapter 5 General Summary and Conclusions

Coastal environments, particularly those near major metropolitan areas, are heavily impacted by anthropogenic activities, where coastal marine sediments often serve as the repository of hydrophobic organic contaminants (HOCs). The bioavailability or bioaccessibility of HOCs in marine sediments is determined by many factors, including aging (or contact time) and sediment organic carbon content. In amendment-based remediation operations, bioavailability is intentionally suppressed by the addition of hydrophobic sorbents such as black carbon materials.

This project has a focus on marine sediments from the Palos Verdes Shelf Superfund Site, where the sediment was contaminated with DDT and PCBs decades ago. We first used chemically-based methods to evaluate the effect of aging or contact time on the bioavailability of DDTs and PCBs in sediment cores from the PV Shelf. After residing in the sediment for 50-70 years, the bioavailability of DDTs and PCBs as measured by Tenax desorption greatly decreased. Bioaccumulation tests using *N. arenaceodentata*, a marine benthic invertebrate native to the region, validated the reduced bioavailability. Therefore, extensive aging of contaminants like DDT in the marine environment decreases their risk to benthic organisms, due to enhanced sequestration and reduced bioavailability. Risk assessments must consider the extent and age of contaminant residues and their bioavailability, rather than relying only upon their bulk concentrations.

The role of black carbon in enhancing sequestration and minimizing bioavailability of HOCs was subsequently explored using a sediment sample from the PV

Shelf site. Bioavailability of DDTs in the aged sediment was measured using polyethylene film strips as a passive sampler and bioaccumulation into *N. arenaceodentata* after 4 d exposure after amending the sediment with three different black carbon materials – powdered activated carbon, granular activated carbon, and biochar. The different black carbon materials affected C_{free} differently, with the powdered activated carbon consistently exhibiting a reduction effect. Amendment of black carbon materials at 2% was largely ineffective at reducing bioaccumulation of DDT residues by *N. arenaceodentata.* The finding was in contrast to many previous studies, and the limited effectiveness of black carbon amendment was likely due to the fact that only a small fraction of DDTs in the marine sediment was bioavailable due to extensive aging and strong sorption to sediment organic matter. The observations highlighted the importance to consider bioavailability of legacy contaminants in sediment or soil before employing sorbent amendment as a remediation strategy. Other management options, such as monitored natural recovery (MNR), may be more cost-effective and protective of a contaminated area if the contaminant bioavailability is low.

Insecticides such as synthetic pyrethroids and fipronil are heavily used in urban environments for structural pest control and various indoor uses. These insecticides are known for their acute toxicity to aquatic species, especially invertebrates. In the last study, we analyzed residues of pyrethroids and fipronil degradates in surface sediments collected from the PV Shelf in 2014. Five pyrethroid compounds and fipronil sulfide were detected in the marine sediments, with variations in their spatial distribution. The origin of these insecticides was analyzed with PCA analysis, and the analysis showed that

several pyrethroids, including cypermethrin, were likely from wastewater effluent emission, while some other compounds were related with non-point source surface runoff. As the use of these insecticides is common in other urbanized regions along the coast, similar contamination routes may also contribute pesticide pollution to near shore coastal environmental contamination and degradation. However, relevant toxicity thresholds for marine benthic invertebrates are scarce, which hinders the accurate prediction of ecotoxicological impairments. Findings of this study highlight the need for more toxicity studies on marine organisms, and the development of management and mitigation strategies to minimize emission of urban-use insecticides into coastal environments.