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# Historical record and fluxes of DDTs at the Palos Verdes Shelf Superfund site, California

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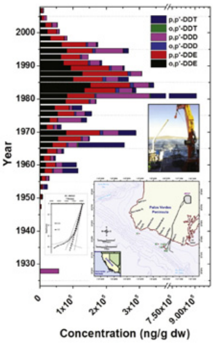
## HIGHLIGHTS

- Historical trends of DDTs at the Palos Verdes Shelf Superfund site were examined.
- Very high concentrations of DDTs were found in the sediment core 8C and adjacent cores.
- Peak concentrations of DDTs in sediment cores are linked to the discharge of these chemicals between the 1940s–1980s.
- The estimated total deposition of DDTs is fairly close to that reported for industrial wastewater discharge in this area.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Marine sediments at many locations in the world are contaminated with a wide range of persistent organic pollutants. The Palos Verdes Shelf (PVS) is located in the ocean off the coast of Los Angeles, California and has been listed as a Superfund site by the US EPA since 1997, because of heavy contamination of DDTs and PCBs. However, little is known about the historical trend in the deposition of DDTs as a result of decades-long discharge of wastewater effluents. In this study, sediment cores were taken from the PVS site and determined for DDT and its metabolites including DDE and DDD (denoted as DDTs). Individual DDTs were found in the majority (95%) of the samples analyzed. The highest $\sum$DDT concentrations were found in three cores along the 60-meter isobath with geometric means of 31300, 7490, and 5010 ng/g dw and medians of 82400, 17300, and 5200 ng/g dw, respectively. Among DDT congeners, *p,p′*-DDE, *o,p′*-DDE and *p,p′*-DDD were predominant, contributing to approximately 54%, 27%, and 14% of the ΣDDTs in sediment. The vertical profiles of concentrations of contaminants in the sediment cores were examined. For most of the cores, a steady increase in the concentrations of DDTs during 1940s to 1980s was observed, while the concentrations declined gradually toward the surficial layers. On the basis of the mass flux of DDTs calculated and the area of the PVS Superfund site, we estimated the total deposition amount of DDTs in sediment and the deposition amount of ΣDDTs in this region during 1947–1971 was 132 tons, which was fairly close to what was reported in earlier studies for industrial wastewater discharge in the PVS site (870–1450 tons). Our

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findings suggest that the elevated levels of DDTs in sediment from the PVS site are linked to the discharge of these contaminants between the 1940s–1980s.

## 1. Introduction

The Palos Verdes Shelf (PVS) site, located off the coast of Los Angeles, California, has been proposed as a typical Superfund site by the U.S. Environmental Protection Agency (US EPA) since 1997, due to heavy contamination by several persistent organic pollutants (POPs), specifically, dichlorodiphenyltrichloroethane (DDT) and its main degradation products dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) (denoted as DDTs), as well as polychlorinated biphenyls (PCBs) (Eganhouse and Pontolillo, 2008; Fernandez et al., 2012; Quensen et al., 2001; Venkatesan et al., 1996; Zeng and Venkatesan, 1999). Contamination of DDT in the PVS ocean floor is largely due to decades (1947–1983) of wastewater discharge via the outfall of the Joint Water Pollution Control Plant (JWPCP) operated by the Los Angeles County Sanitation District (LACSD) and disposal of residual DDT wastewater by Montrose Chemical Company, once the largest DDT manufacturer in North America (Stull et al., 1996; Venkatesan et al., 1996). It is estimated that over 44 $km^2$ of sediment in the PVS Superfund site is heavily contaminated with DDT and its metabolites DDE and DDD. High total concentrations of DDT, DDE, and DDD (up to 200 μg/g) in sediment samples collected from PVS have been reported (USEPA, 2009b, 2013).

Although industrial releases of major contaminants, including DDTs, have ceased, sediments in the PVS Superfund site are continuously a source of contaminants to the adjacent water column, and biota living within and above the sediment, like many other Superfund sites (Friedman et al., 2011; Larsson, 1985; Zeng et al., 1999). By using a solid-phase microextraction-based sampling technique, a large-scale survey on DDTs in water column of the PVS and vicinity reported that the *p,p′*- and *o,p′*-DDE concentrations were in the range of <0.073 to 2.6 ng/L and <0.043 to 0.26 ng/L, respectively (Zeng et al., 2005), which was clearly higher than those found for other water column across the globe, e.g. the North Sea, Western Europe (*p,p′*-DDE: ~0.01 ng/L) (Bergqvist et al., 1998), the San Francisco Bay watershed, CA (*p,p′*-DDE: 0.0066–0.23 ng/L; *o,p′*-DDE: ND-0.019 ng/L) (San Francisco Estuary Institute, 1999), and the Pearl River Estuary, China (*p,p′*-DDE: 0.01–0.09 ng/L; *o,p′*-DDE: <0.008–0.02 ng/L) (Luo et al., 2004). Elevated DDTs were detected in surface sediments (0–15 cm) collected from the PVS site with concentrations as high as 25,100, 3350, 11,000, and 1850 ng/g dry weight (dw) for *p,p′*-DDE, *o,p′*-DDE, *p,p′*-DDD, and *o,p′*-DDD, respectively. A national survey on spatial distribution of DDTs in bivalves, collected from the coastal marine environments in the United States during 1986–2009, indicated that bivalves living in areas linked to areas of DDT production or heavy usage, including the southern California and San Francisco area on the west coast, contain elevated concentrations of DDTs in their tissues. For example, the $\sum$DDTs in bivalves from the PVS site was 731 ng/g dw (Sericano et al., 2014).

Elevated levels of DDTs in the sediment and water column not only pose risk to the marine environment, but also to invertebrates and microorganisms that live within or above the sediment, which in turn harm organisms at upper trophic levels, including bottom-feeding fish, fish-eating birds, marine mammals, and humans. Due to elevated DDT levels accumulated, fish consumption advisories and health warnings have been posted in the Southern California bight (Wolfe and Lowe, 2015). Given the high toxicities of DDTs, e.g., carcinogenicity, endocrine disrupting activity, reproductive and development and effects (Mrema et al., 2013; Rosner and Markowitz, 2013; Su et al., 2014), cleanup strategies and remedial options such as dredging, sand capping and in-situ sorbent treatment have been explored for Superfund sites to protect human and ecological health (USEPA, 2009a, 2005). Despite such attempts, the PVS site remediation is still a difficult task because the site comprises a large area which extends over 44 $km^2$ with sediment layer depth ranging from 150 to 300 ft (USEPA, 2009b).

In view of the potential for continuous release and high toxicity, determination of typical contaminants, including DDTs, in sediment cores and elucidation of sources of environmental pollution arising from anthropogenic activities are imperative to the assessment of risks and for the development of strategies to mitigate exposures. Little is known about the historical trends and chemical fluxes of DDTs at the PVS site, although some studies with respect to the spatial distributions of DDTs have been done in this area (Friedman et al., 2011; Zeng et al., 1999). The objectives of this study were: (i) to determine the concentrations of DDTs, including the *o,p′*- and *p,p′*-isomers of DDT, DDE, and DDD, in sediment core samples collected from the PVS Superfund site; (ii) to determine the composition profiles of contaminants to discuss the environmental behavior and fate of such chemicals in aquatic ecosystem; (iii) to evaluate the spatial distributions and temporal variations in concentrations of contaminants to reveal the current and historical contamination situation in this area of concern; (iv) to calculate the mass flux of contaminants to explore possible links between contamination and anthropogenic activities. Our study fills an important knowledge gap by identifying that industrial wastewater discharge between the 1940s–1980s is the main source for elevated levels of DDTs in the PVS site.

## 2. Materials and methods

### 2.1. Chemicals and materials

Six DDT compounds, including 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) and their metabolites 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), were purchased from AccuStandard (New Haven, CT). Deuterated compounds $d_4$-*p,p′*-DDE, $d_8$-*p,p′*-DDD, $d_8$-*o,p′*-DDT, and $d_8$-*p,p′*-DDT were purchased from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Anhydrous sodium sulfate (10–60 mesh; Fisher Scientific, Pittsburgh, PA) and florisil (10–60 mesh; Acros Organics, Morris Plains, NJ) were activated before use in an oven at 400 °C and 130 °C, respectively. Empty SPE cartridges (20 mL) were purchased from Supelco (Bellefonte, PA). All organic solvents, including dichloromethane (DCM), acetone and hexane, were of HPLC grade and purchased from Fisher Scientific. The stock solutions (1 mg/mL) of all target analytes and internal standards were prepared in acetone and stored at −20 °C. The working solutions were prepared from the stock solutions through serial dilution with hexane before use.

### 2.2. Sample collection and preparation

Marine sediment cores were collected in 2007 from six locations inside the PVS Superfund area off the coast of Los Angeles, CA (Fig. 1), stored in dry ice and transferred to freezers held at −20 °C in the JWPCP Marine Biology Laboratory for storage (LACSD, 2014). The length of these cores were 75, 71, 75, 77, 53, and 77 cm for cores 3C, 6C, 7.5CD,