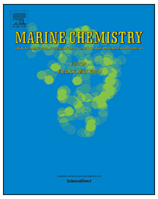
Marine Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem



DDT and related compounds in pore water of shallow sediments on the Palos Verdes Shelf, California, USA

Robert P. Eganhouse[a,*], Erica DiFilippo[a,1], James Pontolillo[a], William Orem[a], Paul Hackley[a], Brian D. Edwards[b]

[a] *U. S. Geological Survey, Reston, Virginia 20192, United States*
[b] *U. S. Geological Survey, Menlo Park, California 94025, United States*

ARTICLE INFO

Keywords:
DDT
Sediments
Pore water
Palos Verdes Shelf

ABSTRACT

For nearly two and a half decades following World War II, production wastes from the world's largest manufacturer of technical DDT (1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene) were discharged into sewers of Los Angeles County. Following treatment, the wastes were released via a submarine outfall system to nearshore coastal waters where a portion accumulated in shallow sediments of the Palos Verdes Shelf (PVS). An investigation of the pore-water geochemistry of DDT-related compounds (DDX) was undertaken in an effort to understand factors controlling the rate of reductive dechlorination (RDC) of the major DDT degradate, 4,4′-DDE (1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene). Equilibrium matrix-solid phase microextraction (matrix-SPME$_{eq}$) combined with automated thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) was used to determine freely dissolved concentrations of ten DDX analytes in sediment cores collected from three locations on the PVS (stations 3C, 6C, 8C, which are 7 km, 2 km, and 0 km, respectively, downcurrent from the outfall system). Pore-water concentrations (pM) of the principal DDX compounds involved in RDC were: **3C**-DDE: 6.0–24, DDMU (1-chloro-4-[2-chloro-1-(4-chlorophenyl)ethenyl]benzene): 11–160, DDNU (1-chloro-4-[1-(4-chlorophenyl)ethenyl]benzene): 1.8–68; **6C**-DDE: 5.6–170, DDMU: 5.6–177, DDNU: 1.7–87; **8C**-DDE: 27–212, DDMU: 31–403, DDNU: 5.5–89. Variations in the spatial distribution of DDX analytes in pore water reflect several factors including proximity to the outfalls, RDC reaction rates, and natural variability in sedimentation and post-depositional transport processes. A comparison of pore-water data produced using matrix-SPME$_{eq}$/TD-GC/MS and whole-core squeezing/solvent extraction/liquid injection-GC/MS indicates that the majority of the DDE in the upper sediment column ($\leq$ about 10 cm) is associated with dissolved/colloidal organic matter. Below that depth, freely-dissolved DDE predominates. The principal organic geochemical phase controlling sorption of DDE in PVS sediments are residual hydrocarbons, the vast majority of which originated from petroleum refinery wastes. Organic carbon-normalized sediment-water distribution coefficients (K_{OC}) were calculated from solid-phase and pore-water concentrations of DDX and organic carbon. Log K_{OC} values (L/kg) were relatively invariant across the shelf and with depth in the sediment column. Shelf-wide compound-specific coefficients (log K_{OC}) were: DDE: 7.5 ± 0.11, DDMU: 6.92 ± 0.13, DDNU: 6.37 ± 0.19. The spatial uniformity of K_{OC} means that biological exposure and availability of the DDX compounds can, in principle, be estimated from solid-phase chemical measurements.

1. Introduction

Shallow sediments on the Palos Verdes Shelf (PVS) are contaminated with the pesticide, DDT, and a variety of synthetic by-products and degradates. This resulted from introduction (ca. 1947–1971) of technical DDT production wastes to sewers of the Los Angeles County Sanitation Districts (LACSD). Following primary treatment, effluent containing DDT residues was discharged from a system of submarine outfalls terminating at water depths of 34–64 m off White Point (Fig. 1).

Contamination of sediments and biota on the PVS was first reported in the early 1970s (e.g., MacGregor, 1974; Southern California Coastal Water Research Project, 1973; Schmidt et al., 1971), but concerns over the effects of DDT on raptors and marine mammals continued to mount (see references in U.S. Environmental Protection Agency, 2007). In

---

[*] Corresponding author.
E-mail address: eganhous@usgs.gov (R.P. Eganhouse).
[1] Current address: S.S. Papadopulos & Associates, Bethesda, Maryland 20814, United States.

https://doi.org/10.1016/j.marchem.2018.05.003
Received 18 December 2017; Received in revised form 17 April 2018; Accepted 14 May 2018
0304-4203/ Published by Elsevier B.V.

Please cite this article as: Eganhouse, R.P., Marine Chemistry (2018), https://doi.org/10.1016/j.marchem.2018.05.003

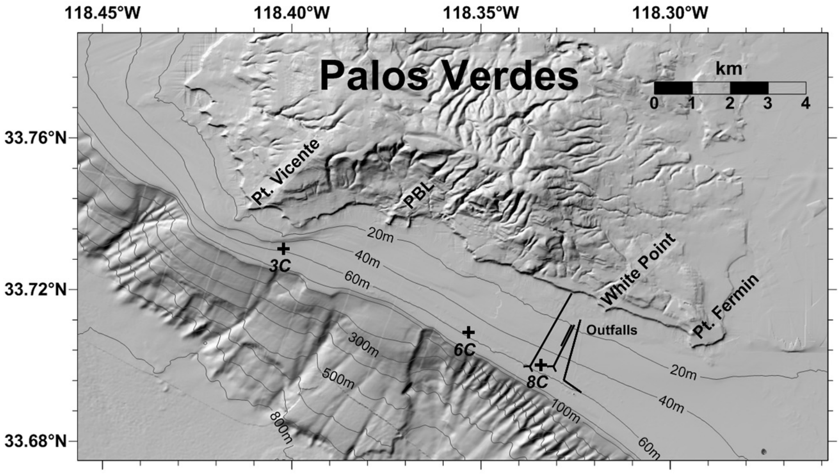


Fig. 1. Map showing stations on the Palos Verdes Shelf where sediment cores were collected. PBL = Portuguese Bend Landslide. Modified from Eganhouse et al. (2018).

January 1990 an environmental lawsuit was filed by the U.S. Department of Justice and the State of California against the manufacturer of DDT (Montrose Chemical Corporation of California), its parent companies, and others.

Microcosm studies conducted in support of the defendants in the lawsuit demonstrated that the most abundant DDT degradation product in the sediments, 4,4′-DDE, previously regarded as recalcitrant in the marine environment, could be transformed to 4,4′-DDMU, through microbially-mediated reductive dechlorination (RDC; Deming and Carpenter, 2000; Quensen et al., 1998; Quensen et al., 2001). 4,4′-DDMU, in turn, is believed to be transformed to 4,4′-DDNU by the same RDC process (Eganhouse et al., 2016a). A significant finding of the microcosm experiments, subsequently confirmed by field studies (Eganhouse and Pontolillo, 2008a; Eganhouse et al., 2018), was that the rate of DDE RDC is spatially variable, with higher rates in sediments deposited farther from the outfalls than in the nearfield. However, the reason(s) for this pattern remain obscure.

The aforementioned observations resulted in an effort by the USGS (United States Geological Survey) with support from the USEPA (United States Environmental Protection Agency) to investigate factors controlling DDE RDC rates on the PVS. The purpose of this endeavor was to improve the ability to predict the course of natural recovery and, if possible, to identify a means of accelerating RDC. Because the current scientific paradigm is that microbial transformation of organic substances, such as DDE, occurs in the dissolved phase (Cornelissen et al., 1998), a major objective of the study was to measure the freely dissolved concentration of DDE and other DDT-related substances (hereafter referred to as DDX) in sediment pore water.

Prior to about 2000, classical methods of determining concentrations of hydrophobic organic compounds (HOCs) like DDT in porewater relied upon centrifugation or whole-core squeezing and filtration as a means of isolating what was believed at the time to be the dissolved phase (e.g., Brownawell and Farrington, 1986; Manchester, 1993; Socha and Carpenter, 1987). However, these approaches were incapable of separating freely dissolved HOCs from those associated with dissolved/colloidal organic matter (Burgess et al., 1996).

Passive sampling methods (Górecki and Namieśnik, 2002; Mayer et al., 2014; Mayer et al., 2003), in which a sampling material (usually a polymer) is directly exposed to an environmental medium (such as saturated sediments), allow partitioning of freely dissolved HOCs between the medium, in this case pore water, and the sampler. For best results, the sampler is exposed to the medium until equilibrium is established (Mayer et al., 2014). After thermal or solvent extraction of the HOC from the sampler, the analyte concentration is determined, and the freely dissolved concentration in the aqueous phase (in this case, pore water) can then be calculated by using the compound-specific sampler-water partition coefficient (cf., references in DiFilippo and Eganhouse, 2010). This approach has led to significant advances in our ability to measure freely dissolved HOCs at the very low concentrations (fM to pM) typically encountered in the field.

The present work is part of a multi-disciplinary study aimed at understanding the factors controlling DDE RDC rates (Eganhouse et al., 2016a; Eganhouse et al., 2016b). Equilibrium matrix-solid phase microextraction (matrix-SPME$_{eq}$; Mayer et al., 2000) was used to determine freely dissolved concentrations of ten DDX compounds in pore water of shallow sediments (0–46 cm) at three locations on the PVS. These data were combined with ancillary geochemical measurements to provide information on 1) the spatial variation in pore-water concentrations of DDX in PVS sediments, 2) the fraction of DDE associated with dissolved/colloidal organic matter, 3) the organic geosorbent phase(s) primarily responsible for controlling distribution of DDX between solid and aqueous phases, and 4) the spatial variation in organic carbon-normalized sediment-water distribution coefficients (K_{OC}) on the PVS. A previous publication presents RDC rate data for sediments at the PVS study site (Eganhouse et al., 2018).

2. Materials and methods

2.1. Materials

Glass-distilled solvents (dichloromethane, methanol, hexane) and high-purity chemical standards obtained from commercial sources (cf., Eganhouse and DiFilippo, 2015 for sources, purities, and IUPAC [International Union of Pure and Applied Chemistry] names) were used without further purification. Deionized water, polished with a Milli-Q® Advantage A10 water purification system, was used to prepare NaN$_3$-poisoned artificial seawater (Eganhouse, 2016) for sediment slurries in a dynamic ex situ fiber exposure experiment (**Dyn-TTE;** cf., Section 2.7.6.). Ten DDT-related compounds were targeted for determination: 4,4′-DDNS, 4,4′-DDNU, 4,4′-DDMU, 2,4′-DDE, 4,4′-DDMS, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, and 4,4′-DDT (see Eganhouse et al., 2018, Supplementary Data, for structures and IUPAC names of the DDX analytes). Quantitation was performed with one of three internal standards: 1,2,3,5-tetrachloro-4,6-dimethylbenzene, PCB 11, or PCB 207, whereas seven compounds (PCB 30, PCB 103, PCB 121, PCB 198, 4,4′-DDE-D8, 4,4′-DDD-D8, and 4,4′-DDT-D8); were employed in the **Dyn-TTE** experiment to verify attainment of equilibrium (cf., Section 2.7.6). Additional information on the materials and equipment used for analysis of the solid phase of sediments for DDX analytes, total organic carbon, total nitrogen, and 'black carbon' can be found in Eganhouse