Environmental Science & Technology

Article

pubs.acs.org/est

Calculating the Diffusive Flux of Persistent Organic Pollutants between Sediments and the Water Column on the Palos Verdes Shelf Superfund Site Using Polymeric Passive Samplers

Loretta A. Fernandez,*[,‡,†] Wenjian Lao,[§] Keith A. Maruya,[§] and Robert M. Burgess[‡]

[‡]U.S. Environmental Protection Agency, Atlantic Ecology Division, Narragansett, Rhode Island 02882, United States

[§]Southern California Coastal Water Research Project (SCCWRP), Costa Mesa, California 92626, United States

Supporting Information

ABSTRACT: Passive samplers were deployed to the seafloor at a marine Superfund site on the Palos Verdes Shelf, California, USA, and used to determine water concentrations of persistent organic pollutants (POPs) in the surface sediments and near-bottom water. A model of Fickian diffusion across a thin water boundary layer at the sediment-water interface was used to calculate flux of contaminants due to molecular diffusion. Concentrations at four stations were used to calculate the flux of DDE, DDD, DDMU, and selected PCB congeners from sediments to the water column. Three passive sampling materials were compared: PE strips, POM strips, and SPME fibers. Performance reference compounds (PRCs) were used with PE and POM to correct for incomplete equilibration, and the resulting POP concentrations, determined by each material, agreed within 1 order of magnitude. SPME fibers, without PRC corrections, produced values that were generally much lower (1 to 2 orders of magnitude) than those measured using PE and POM, indicating that SPME may not have been fully equilibrated with waters being sampled. In addition, diffusive fluxes measured using PE strips at stations outside of a pilot remedial sand cap area were similar to those measured at a station inside the capped area: 240 to 260 ng cm^{-2} y^{-1} for *p,p′*-DDE. The largest diffusive fluxes of POPs were calculated at station 8C, the site where the highest sediment concentrations have been measured in the past, 1100 ng cm^{-2} y^{-1} for *p,p′*-DDE.

INTRODUCTION

Much of the Palos Verdes Shelf (PVS) Superfund site, off of the coast of California, USA, is under more than 50 m of water. The water column and sediments at the site are contaminated with persistent organic pollutants (POPs), including dichlorodiphenyltrichloroethane (DDT), its breakdown products (e.g., dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD), and 1-chloro-4-[2-chloro-1-(4-chlorophenyl)benzene (DDMU)), and polychlorinated biphenyls (PCBs).[1−6] These contaminants are the legacy of industrial wastes produced throughout the mid-20th century and released through the wastewater outfall of the Joint Water Pollution Control Plant, operated by the Los Angeles County Sanitation Districts (LACSD).[7] Like other sites where industrial sources of environmental contamination have been controlled or eliminated, the sediments, originally a sink for contaminants, have become a continuing source of contamination to the water column.[8−12]

The flux of POPs between the sediment bed and water column may occur through many different mechanisms.[13] Compounds may desorb from sediment solids to the water column during resuspension events or as benthic organisms pump overlying water through their burrows (i.e., bioirrigation). In areas where groundwater discharges through sediments to the overlying water, contaminants can be carried in the advective flow either dissolved or sorbed to colloids.[14] An additional flux, due to molecular diffusion, occurs at the sediment-water interface, driven by the concentration gradient between sediment porewater and overlying water across a diffusion-controlled boundary layer.[15] Of these mechanisms, only molecular diffusion occurs in every sediment-water system. For this reason, it can be considered a conservative baseline for total flux. In addition, the gradient, which drives diffusive mass-transfer, may also be used to calculate the scale of other flux mechanisms such as bioirrigation and resuspension/desorption.

One remedial alternative that has been explored for the PVS is capping the most contaminated sediments (those near station 8C and the outfall) with a clean layer of sand. It is believed that this would have the effect of reducing contaminant flux during resuspension events as well as reducing flux due to bioirrigation by relocating benthic organisms to a cleaner sediment layer. In 2000, three 45-acre pilot sand caps (covering <0.5% of the contaminated sediment area) were installed on the PVS in

Received: October 7, 2013
Revised: February 20, 2014
Accepted: February 24, 2014
Published: February 24, 2014

