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Uptake and depuration of PAHs and chlorinated pesticides by semi-permeable membrane devices (SPMDs) and green-lipped mussels (*Perna viridis*)

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Abstract

Semi-batch seawater experiments were conducted to follow the uptake and release of selected PAHs (anthracene, fluorathene, pyrene and B[*a*]P) and organochlorine pesticides (α-HCH, aldrin, dieldrin, *p*,*p*′-DDT) in semi-permeable membrane devices (SPMDs) and green-lipped mussels (*Perna viridis*). Mathematical models were applied to describe the uptake and elimination curves of the contaminants for SPMDs, and kinetic parameters, such as uptake rate constants, and equilibrium triolein/water partitioning coefficients were calculated. SPMD data showed a good fit to estimate rate constant and partition coefficient equations, but only those contaminants which partitioned mainly in the dissolved phase (α-HCH and dieldrin) were well explained for mussels. Poor conformity of the other contaminants indicated mussels uptake by routes other than diffusion, such as ingestion of algae. An apparent equilibrium state was only noted for α-HCH in mussels. Aldrin was not detected in mussels in the first few days of exposure, indicating potential metabolism of this compound. B[*a*]P was not detected in the triolein of SPMDs, which suggests that the membrane may act as a reservoir. Loss of spiked B[*a*]P from the triolein was evident in a depuration experiment, which may indicate transfer to the membrane. Rate constants for mussels were higher than those for SPMDs, but the reverse was true for partition coefficients. Overall, mussels and SPMDs had similar uptake rates for all compounds in this study, excluding *p*,*p*′-DDT and dieldrin. Contaminant elimination took place more rapidly in mussels, implying that SPMDs are better candidates for detecting episodic discharge of organic contaminants.

Keywords: Semi-permeable membrane devices; SPMDs; Mussels; *Perna viridis*; Trace organic contaminants

1. Introduction

In recent years there has been increasing awareness of the potential carcinogenic (Katiyar et al., 1993) and endocrine disrupting effects (Colborn et al., 1993; Sonnenschein and Soto, 1998) of organic contaminants such as PAHs and chlorinated pesticides. Pollution monitoring based on direct water measurement of these compounds is difficult, primarily because of the extremely low (but toxicologically relevant) levels in environmental waters. Ultra-clean, large-volume sampling ($\geqslant$50 L) is required for determining realistic concentrations as low as 1 ng/L, and the loss of such trace amounts of analytes through volatilization and glassware adsorption may be considerable. The problem has been alleviated to some extent by the use of bivalve shellfish as bioindicators of coastal pollution (Stegeman and Teal, 1973; Fossato and Canzonier, 1976; Goldberg et al., 1978). One of the key properties of shellfish in this regard is their ability to accumulate pollutants in body tissues at

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up to a million times that of water concentrations. An added advantage of employing mussels as bioindicators is that tissue residue concentrations offer the potential of reflecting an "integration" of contaminant levels in all bioavailable fractions of the water column (Phillips, 1983). In Hong Kong, the green-lipped mussel *Perna viridis* (Bivalvia: Mytilacea) is widely distributed from oceanic to estuarine waters (Huang et al., 1985), and its bioindication capability has been validated both locally (Phillips, 1985) and in other Asian countries, including Thailand (Siriwong et al., 1991; Ruangwises et al., 1994; Kan-atireklap et al., 1997) and India (Ramesh et al., 1990).

Semi-permeable membrane devices (SPMDs) are recently developed tools specifically for monitoring non-ionic, hydrophobic contaminants (Huckins et al., 1990a,b). The devices consist of lipid (triolein) spread into a thin film inside sealed polyethylene layflat tubing. Accumulation of organic chemicals in SPMDs is driven by passive membrane diffusion and thermodynamic partitioning between ambient water and triolein (via the polyethylene membrane). The bioaccumulation mechanism in shellfish is generally accounted for by the same diffusion-partitioning model (Mackay, 1982; Pruell et al., 1986; McLeese and Burridge, 1987). In addition, the diffusion phenomenon of non-polar organic compounds through polymer matrices such as polyethylene (Lieb and Stein, 1969), as well as the size exclusion limit (10 Å) of the SPMD membrane, are similar to those of biomembranes (Opperhuizen et al., 1985). Consequently, the utility of SPMD-derived data in providing bioavailability information has been suggested (Huckins et al., 1990a,b; Petty et al., 2000).

Studies undertaken to date comparing shellfish and SPMDs have focused mostly on field studies, with deployment at the same localities and collection at single time points (e.g. Prest et al., 1992, 1995; Hofelt and Shea, 1997; Moring and Rose, 1997; Axelman et al., 1999; Richardson et al., 2001). The deployment period for these studies has varied between 26 and 60 days, periods which were insufficient for most contaminants to attain equilibrium status in either matrix. A real-time field study on mussels and SPMDs has also been conducted in Dorcester Bay, Massachusetts (Peven et al., 1996). However, uptake profiles in this case suggested environmental conditions influenced accumulation kinetics, and ambient contaminant levels (which may fluctuate considerably) also provided an influence.

With the aim of precisely comparing the musselwatch technique and SPMDs under controlled conditions, a laboratory study of the uptake and release of organic contaminants by SPMDs and *P. viridis* was undertaken. Selected model contaminants included the USEPA priority pollutant PAHs anthracene, fluoranthene, pyrene and benzo[*a*]pyrene (B[*a*]P), and the chlorinated pesticides α-HCH, aldrin, dieldrin and *p*,*p*′-DDT. These compounds were selected on the basis that they are consistently measured at significant levels in sediments and mussels collected from Hong Kong coastal waters (Hong et al., 1995; Richardson and Zheng, 1999; Zheng and Richardson, 1999; Richardson et al., 2001).

2. Materials and methods

SPMD polyethylene layflat tubing (5 cm wide and 50 μm thick) was soaked in *n*-hexane for 24 h to remove impurities such as phthalates. After drying of residual solvent under a stream of nitrogen, 0.5 mL of triolein was added into the tubing to form a 23 cm long, continuous thin film. Double heat-sealing was applied at both ends, leaving 3 cm polyethylene overhangs. The resulting SPMDs had an effective surface area to volume ratio of 460 cm^2 per mL of triolein, and a lipid-to-membrane mass ratio of 0.29 (including the weight of membrane overhangs).

Mussels (*P. viridis*) of similar shell length (101 ± 5 mm) were collected from Sha Tau Kok, a relatively uncontaminated site in Hong Kong (Richardson and Zheng, 1999; Zheng and Richardson, 1999). A total of 100 mussels were acclimated for 7 days, during which time 250 L of clean seawater was exchanged daily, along with an algae supply. Only two mussels died during acclimation, and ten mussels were sampled at the end of this period to estimate the residual content of the test contaminants. Unicellular green algae (*Dunaliella tertiolecta*) were fed to the mussels daily at a constant initial density (2×10^6 cell/L) during acclimation, uptake and elimination periods. Natural seawater was collected from Ocean Park and Wong Shek Pier, which are known to be relatively clean sites within Hong Kong waters. Organic contaminants and suspended particles, if any, were removed by circulating the raw seawater for 24 h through a decontamination module containing activated charcoal and fine sand.

A stock solution containing PAHs (10 μg mL^{-1} each of anthracene, fluoranthene, pyrene, B[*a*]P) and pesticides (1 μg mL^{-1} each of α-HCH, aldrin, dieldrin, *p*,*p*′-DDT) was prepared in acetone. The stock solution was used to dose a fresh volume of decontaminated seawater daily during the uptake period so that initial concentrations in the experimental tank were 1 μg L^{-1} each for individual PAHs and 0.1 μg L^{-1} each for individual pesticides. The concentration of the carrier solvent (acetone) was 0.1 mL L^{-1}.

2.1. Laboratory exposure and depuration

Ten SPMDs and 88 mussels were exposed to 250 L of natural seawater spiked with PAHs and chlorinated pesticides in a 380 L fiberglass tank. The mussels were fed with *D. tertiolecta* at an initial density of 2×10^6 cells L^{-1}