ELSEVIER

Chemosphere 61 (2005) 1734–1739

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Short Communication

How accurately do semi-permeable membrane devices measure the bioavailability of polycyclic aromatic hydrocarbons to *Daphnia magna*?

Catherine Gourlay [a,*], Cécile Miège [b], Aurélien Noir [b], Corinne Ravelet [b], Jeanne Garric [b], Jean-Marie Mouchel [c]

[a] *Cemagref, Unité de Recherches Hydrosystèmes et Bioprocédés, Parc de Tourvoie, BP 44, 92163 Antony Cedex, France*
[b] *Cemagref, 3bis, quai Chauveau, CP 220, 69336 Lyon Cedex 9, France*
[c] *ENPC-CEREVE, Cité Descartes, 77455 Marne La Vallée Cedex 02, France*

Received 4 January 2005; received in revised form 23 March 2005; accepted 9 April 2005
Available online 15 June 2005

Abstract

Semi-permeable membrane devices (SPMDs) are passive samplers that have been designed to sample the bioavailable fractions of hydrophobic organic compounds in aquatic ecosystems. This study aims at evaluating the ability for SPMD to sample polycyclic aromatic hydrocarbons (fluoranthene, pyrene and benzo[*a*]pyrene) that are actually bioavailable to *Daphnia magna*. For that purpose, the SPMD-available fraction and the bioavailable fraction to *D. magna* are compared in controlled media with Dissolved Organic Matters (DOMs) from various origins and at different concentrations. The presence of all but one DOM reduces the accumulation of PAHs in SPMD or in *D. magna*. Moreover, this comparative laboratory study shows that in 10 cases on 13, the SPMD-available fraction is close to the available fraction to *D. magna*. When significant differences are observed between SPMD-available and bioavailable fractions, they remain less than 50% at DOM concentrations below 10 mg/l DOC, which corresponds to a maximum DOC concentration usually found in temperate rivers. This study confirms the suitability of the SPMD technique to monitor readily bioavailable hydrophobic contaminants in aquatic environments containing DOM from various origins and characteristics.

Keywords: Semi-permeable membrane device; Bioavailability; Bioaccumulation; Dissolved organic matter; Partitioning coefficient; K_{DOC}

1. Introduction

Various passive samplers have been recently designed in order to assess micro-contaminants in the environment. Their great interest is their ability to concentrate contaminants from the media. Some recent developed techniques also aim at estimating bioavailable organic and metallic contaminants in the environment, which

* Corresponding author. Tel.: +33 1 40 96 61 63; fax: +33 1 40 96 61 99.
E-mail address: catherine.gourlay@cemagref.fr (C. Gourlay).

0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.04.039

is of major issue for ecological risk assessment (for example Huckins et al., 1990; Davison and Zhang, 1994; Pörschmann et al., 1998). In this perspective, semi-permeable membrane devices (SPMD) have been developed in the 90s in order to sample hydrophobic organic contaminants (HOCs) in aquatic ecosystems (Huckins et al., 1990).

A SPMD consists in a tubular layflat low density polyethylene membrane containing a thin film of a high-molecular weight lipid (triolein). When placed in water, SPMDs passively accumulate non-ionic HOCs, the passive sampling being driven by membrane–lipid–water partitioning. HOCs can cross the polyethylene membrane since random thermal motion of polymers create transient cavities. The maximal cavity diameter is about 10 Å (or 1000 D), therefore only truly dissolved HOCs are supposed to be accumulated in SPMDs (Huckins et al., 1990).

It is also usually supposed that only truly dissolved HOCs can cross biological membranes and consequently be bioconcentrated in living organisms (Hamelink et al., 1994). Opperhuizen et al. (1985) estimated that the molecular cut-off of biological membranes was about 10 Å. Because of the similar cut-off of the membranes and the lipid content, SPMDs are usually supposed to sample the bioavailable HOCs in the environment (Huckins et al., 1990). Several studies have tested the ability for SPMD technique to evaluate the bioavailability of HOCs. In this perspective, SPMDs have been compared to biomonitoring techniques, generally using fishes (Verweij et al., 2004), or bivalves (Peven et al., 1996; Richardson et al., 2001; Huckins et al., 2004). Many reasons can explain the discrepancies between accumulations in organisms and in SPMDs. First, some processes may occur in biological organisms that the SPMD is not expected to represent: uptake of contaminants via food, or biotransformation and depuration of contaminants; the importance of processes depends on the molecules and the organisms. Second, the lack of similarity of the membrane transport properties for SPMD and biological membranes would lead to a poor representation of SPMD. This problem would be a more basic failure of SPMD and it should be carefully assessed.

Dissolved organic matter (DOM) is one of the major factors reducing the bioconcentration of HOCs to organisms in the aquatic environment (Haitzer et al., 1998). The generally accepted assumption is that bound HOCs are not available for bioconcentration, due to the polarity and steric hindrance of the HOC–DOM complex (Landrum et al., 1985). For similar reasons, DOM also reduces the accumulation of HOCs in SPMDs. Therefore, DOM addition was chosen as a relevant mean to modify environmental conditions in batch reactors, and to check the reliability of the response of SPMDs compared to that of organisms. *Daphnia magna* was chosen as a test organism. Three polycyclic aromatic hydrocarbons (PAHs) were tested, as well as several representative DOM samples.

2. Materials and methods

2.1. Water, chemicals and organic matters

Solutions of benzo[*a*]pyrene (BaP), pyrene and fluoranthene in methanol were prepared in the laboratory from solid PAH powder (purity: 98%, Aldrich, Steinheim, Germany). Mineral water (Evian, France) was used both for experiments and daphnid culture.

Seven DOMs from different rivers were used. They were extracted on XAD8 and XAD4 columns, following the IHSS protocol (Leenheer et al., 2000). From the rivers Suwannee (USA), Gartempe (France) and Appremont (France), only the hydrophobic fraction of DOM (retained in the XAD8 column) was used. For the Marne and the Seine rivers (France), the hydrophobic fraction (''HPO'') and the transphilic fraction of DOM (''TPH'', retained in the XAD4 column) were used separately. Commercially available Aldrich Humic Acids (Aldrich, Steinheim, Germany) and a commercially available mixture composed of meat and vegetal extracts and sugars (Viandox, Rueil Malmaison, France) were also used. Viandox was chosen as a model for anthropogenic DOM, since its major chemical characteristics are close to those of domestic wastewaters (Gourlay et al., 2005).

DOM stock solutions were prepared in mineral water prior to experiments by dissolution and filtration. DOM concentrations were measured as Dissolved Organic Carbon (DOC) using a Carbon Analyzer (O.I. Analytical, College Station, TX, USA).

2.2. Experimental set-up

The analysis and quantification of the effect of DOM on the bioaccumulation in *D. magna* and the accumulation in SPMD are briefly described below. They are detailed elsewhere (Gourlay et al., 2003; Miège et al., 2005).

Small SPMDs (5 cm long, 2.5 cm wide, 50 mg of triolein) were obtained from Exposmeter (Tavelsjo, Sweden). Sub-adult daphnids (5–7 d old) were obtained from a culture maintained in the lab.

For each DOM and each PAH, exposure media with different DOM concentrations were prepared by diluting the DOM stock solution in mineral water. One reference medium did not contain any organic matter. All media were spiked with one PAH at a uniform concentration (0.5–25 μg/l depending on experiment and the PAH). Exposure media were allowed to settle for 1 h in the dark before introducing the daphnids (1 per 10 ml maximum) or the SPMD (1 per 500 ml). SPMD and