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#### Review

# Recent advances in the field measurement of the diffusion flux of hydrophobic organic chemicals at the sediment-water interface

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#### ARTICLE INFO

ABSTRACT

Keywords: Benthic chamber Chemical-concentration gradient Diffusion flux Hydrophobic organic chemical Mass-transfer resistance Passive sampling Sediment porewater Sediment-water interface Sorbent-water interface Two-point measurement We describe and discuss recent advances in measurement of the diffusion flux of chemicals at the sediment-water interface. We analyze the key factors influencing diffusion flux (e.g., chemical-concentration gradient, mass-transfer resistance, sediment composition, hydrodynamics and temperature). We then discuss two main approaches to measure diffusion flux – two-point (i.e. chemical concentrations in sediment porewater and overlying water), and the traditional benthic chamber that can directly measure chemical-diffusion flux from sediment, but the measurement is done at the sorbent-water interface rather than the sediment-water interface. Finally, we present a recently-designed passive sampling device, which derives chemical-diffusion flux at the sediment-water interface from measured concentration profiles in overlying water and sediment porewater. Future work should be directed toward accurate determination of the chemical-diffusion coefficient in overlying water, which is still required for the new sampling device.

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#### 1. Introduction

Sediment could be a gigantic reservoir of various hydrophobic organic chemicals (HOCs) [1,2] [e.g., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs)], which may stem from a variety of routes (e.g., atmospheric dry/ wet deposition, wastewater discharge, and solid-waste disposal) [3]. When exogenous inputs are effectively controlled, contaminated sediment may become a secondary source of contamination to adjacent aquatic eco-environments [4], releasing once-buried contaminants through molecular diffusion, colloidal transport, particle resuspension, gas ebullition, and bioirrigation/bioturbation [5–7]. Among these processes, molecular diffusion is generally the slowest, but it is active all year round, whereas other processes are sporadic and short lived. In addition, molecular diffusion is driven by the difference in freely-dissolved concentrations of a target chemical between sediment porewater and overlying water [8,9], which can be clearly defined and quantitatively characterized.

Measurement of sediment-water diffusion fluxes of chemicals is significant for assessing the environmental fate of chemicals and the quality of aquatic systems. First, the direction and the magnitude of sediment-water molecular diffusion, one of the most important processes in geochemical cycling of chemicals, can be used to discern whether sediment acts as a source or a sink of chemicals. With the help of source apportionment and constituent analysis, it can also be used to examine the spatial distribution of diffusion fluxes and the dominant factors governing regional environmental fate [7,10,11]. Second, measuring molecular diffusion fluxes is crucial for ecological risk assessment, because the freely-dissolved fraction of a chemical is considered mostly bioavailable so it may cause health hazards to wildlife and perhaps humans through aquatic food-web transfer [12]. Numerous studies have also found that the extent of bioaccumulation in aquatic organisms is proportional to the amount of chemicals releasing from sediment rather than the total amount in sediment [13,14]. Third, diffusion flux is a key reference index in the framework of remedial actions for contaminated sediment and can be used to evaluate the effectiveness of *in-situ* remediation. For example, it can be used to select suitable capping materials and layer thickness in capping-amendment programs, and to estimate the magnitudes of reduction in porewater concentrations and releasing fluxes [1]. Consequently, there is an increasing need to quantify diffusion fluxes and to recognize their implications for aquatic quality.

This article presents a short but critical overview of available techniques/methods for determining sediment-water diffusion fluxes of chemicals, focusing on the key factors influencing sediment-water fluxes, the availability of currently available technologies and their main drawbacks, and introduction of a new passive sampling device that we developed for diffusion-flux measurements. With increasing levels of environmental pollution throughout the globe, we expect this review to provide useful information for conducting *in-situ* sediment remediation and ecological risk assessment.

## 2. Key factors influencing diffusion flux at the sediment-water interface

#### 2.1. Chemical-concentration gradient

By Fick's First Law of Diffusion, molecular diffusion flux is proportional to the chemical-concentration (or activity) gradient between sediment porewater and overlying water. In most cases, chemical concentrations are greater in sediment porewater than in overlying water. For example, Booij et al. [15] found a range of 1.2–44 times greater concentrations of PAHs in porewater than in overlying water in Harlingen Harbor, and Cornelissen et al. [16] observed up to 200 times greater concentrations of 2,3-ring PAHs in contaminated sediment in Oslo Harbor.

Sediment often acts as a significant source of chemicals, thereby exerting a release flux out of sediment (designated as "positive flux"). However, there are also exceptions {e.g., higher levels of PCB-52 and PCB-66 in overlying water than in sediment porewater in Dorchester Bay [17], and also PCB-153 and PCB-180 in Ijmuiden Harbor [9]}. In this case, sediment often acts as a sink of chemicals, thereby exerting a settlement flux into sediment (designated as "negative flux"). Also, there are cases where chemical concentrations were nearly identical in sediment porewater and overlying water {e.g., polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) in the Baltic Sea [18] and hexachlorobenzene (HCB) in Delfzijl Harbor [15]}, so that no net diffusion flux was observed.

#### 2.2. Mass-transfer resistance

Although chemical-concentration gradient is the driving force for molecular diffusion, the magnitude of diffusion flux is dictated by the mass-transfer coefficient ( $K_m$ ), the reciprocal of which is defined as total transfer resistance. In a sediment-water system, mass-transfer pathways include in-bed diffusion and overlying water transport [9,13]. Therein, overlying water transport is associated with the chemical-diffusion coefficient in water ( $D_w$ ) [19]:

$$D_{\rm w} = 0.01326/(\eta^{1.4}v^{0.589})$$

with  $\eta$  and v being the water viscosity and molar volume of the target chemical, respectively.

Similarly, in-bed diffusion is related to the chemical diffusion coefficient in porewater  $(D_s)$  [20,21]:

$$D_{\rm s} = D_{\rm w}/[1+3(1-\phi)]$$
 or

$$D_{\rm s} = D_{\rm w}/\theta^2$$

with  $\varphi$  and  $\theta$  being the sediment porosity and tortuosity, respectively.  $K_{\rm m}$  is therefore a comprehensive parameter integrating various physicochemical properties of the sediment-water system, and it can be obtained with laser-Doppler velocimeter, dissolved oxygen microprobe [22,23], alabaster-determined DBL-thickness [24,25] and other empirical formulas [10,13].

#### 2.3. Sediment composition

Chemical concentrations in sediment porewater are largely governed by the distribution of chemicals between solid and aqueous phases, so sediment composition has been recognized as a main factor for phase-distribution patterns [26,27]. In particular, black carbon (BC), with stronger affinity to HOCs than amorphous organic carbon by a factor of 10-100 [28,29], is the most dominant sorbing substance in sediment. Sequestration of chemicals by BC limits chemical desorption from sediment, decreasing porewater chemical concentration or increasing in-bed resistance to diffusion. Thus, a generic organic carbon-water distribution coefficient is inappropriate for predicting porewater-chemical concentrations; in some cases, up to two orders of magnitude higher concentrations than measured values were predicted [14,25]. Although BC generally takes up only a small fraction of sediment composition {e.g., 0.6% in Boston Harbor [30], 0.3% in New York Harbor [30], 0.25-0.4% in Oslo Harbor [16], and 0.09-0.27% in Baltic Sea [18]}, it may sequester up to 90% of chemical constituents in sediment [18]. Apparently, BC content is an essential factor controlling chemical-diffusion fluxes.

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