Ecotoxicology and Environmental Safety 149 (2018) 284–290

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Refining uptake and depuration constants for fluoroalkyl chemicals in *Chironomus riparius* larvae on the basis of experimental results and modelling

Delphine Bertin[a,1], Benoît J.D. Ferrari[a,b], Pierre Labadie[c], Alexandre Sapin[a,2], Débora Da Silva Avelar[a], Rémy Beaudouin[d], Alexandre Péry[e,f], Jeanne Garric[a], Hélène Budzinski[c], Marc Babut[a,*]

[a] IRSTEA, UR MALY, 5 rue de la Doua, 32108 CS 20244, F-69625 Villeurbanne, France
[b] Swiss Centre for Applied Ecotoxicology Eawag-EPFL (C entreEcotox), EPFL-ENAC-IIE-GE, Station 2, CH-1015 Lausanne, Switzerland
[c] CNRS, UMR 5805 EPOC (LPTC Research group), Université de Bordeaux, 351 Cours de la Libération, F-33405 Talence, France
[d] Unité Modèles pour l'Ecotoxicologie et la Toxicologie (METO), Institut National de l'Environnement Industriel et des Risques (INERIS), BP2, F-60550 Verneuil en Halatte, France
[e] AgroParisTech, UMR 1402 INRA-AgroParisTech EcoSys, F-78850 Thiverval-Grignon, France
[f] INRA, UMR 1402 INRA-AgroParisTech EcoSys, F-78850 Thiverval-Grignon, France

ARTICLE INFO

Keywords:
Per- and polyfluoroalkyl substances
Perfluorotridecanoic acid
Chironomus riparius
Bioaccumulation
Uptake rate
Concentration-dependency

ABSTRACT

The aims of this study were to determine depuration rates for a range of per- and polyfluoroalkyl substances (PFASs) using *Chironomus riparius,* and to test a concentration-dependency hypothesis for the long-chain perfluorotridecanoic acid (PFTrDA) for this species. Midge larvae were exposed to field sediments collected downstream of a fluorotelomer plant, and to the same sediment spiked with PFTrDA. Elimination kinetics results indicated complete elimination of all PFASs by chironomids after 42 h. These data were used to develop two PFTrDA bioaccumulation models accounting for chironomid growth and for compound concentration dependency or not. There was much better agreement between observed and simulated data under the concentration-dependency hypothesis than under the alternative one (passive diffusion). The PFTrDA uptake rate derived from the concentration-dependency model equaled 0.013 ± 0.008 g_{oc} g_{ww} h^{-1}, and the depuration rate 0.032 ± 0.009 h^{-1}.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are compounds of emerging interest; their numerous uses and specific properties induce their global distribution in the environment (Houde et al., 2011, 2006; Prevedouros et al., 2006). The physicochemical properties of PFASs differ substantially from those of other persistent organic pollutants (POPs). While the perfluoroalkyl moiety is hydrophobic and lipophobic (Bhhatarai and Gramatica, 2011), the functional group increases the solubility in water, and per- and polyfluoroalkyl acids are thus amphiphilic. These complex properties make it difficult to predict their bioaccumulation, even though it seems that the bioaccumulation of longer-chain PFASs is partly driven by their increasing lipophilic character (Greaves et al., 2013). Several studies have shown the presence of PFASs in sediment (Ahrens et al., 2009; Bao et al., 2009, 2010; Higgins et al., 2005; Labadie and Chevreuil, 2011; Myers et al., 2012; Zushi et al., 2010), whereas other studies have suggested the importance of sediment as a PFAS source for biota (e.g., Martin et al., 2004). However, PFAS transfer from sediment to biota is poorly understood. Only a few experimental studies have provided evidence of bioaccumulation from sediment by benthic invertebrates, namely in the oligochaete worm, *Lumbriculus variegatus* (Higgins et al., 2007; Lasier et al., 2011; Prosser et al., 2016), in insect *Chironomus riparius* (Bertin et al., 2014) and *Hexagenia* spp. larvae (Prosser et al., 2016), and in an amphipod, *Gammarus* spp. (Bertin et al., 2016). Two contamination routes were identified for *C. riparius*: food was the main route of exposure for perfluorinated carboxylic acids (PFCAs) with a fluorinated chain from C_{11} to C_{14}, and perfluorooctane sulfonamide (FOSA). For

* Corresponding author.
E-mail addresses: d.bertin@hotmail.fr (D. Bertin), asapin@rovaltainresearch.com (A. Sapin), dhezinha@gmail.com (D. Da Silva Avelar), marc.babut@irstea.fr (M. Babut).
[1] Present address: UMR 5023 LEHNA (E3S Research group), Université Claude-Bernard Lyon 1, 6 rue Raphaël Dubois, 69622 Villeurbanne, Cedex, France.
[2] Present address: Rovaltain Research Company BP 10 313, F-26958 Valence cedex 9, France.

https://doi.org/10.1016/j.ecoenv.2017.12.011
Received 19 July 2017; Received in revised form 4 December 2017; Accepted 7 December 2017

perfluoroundecanoic acid (PFUnDA), perfluorooctane sulfonate (PFOS), and 6:2 fluorotelomer sulfonic acid (6:2 FTSA), which are present in pore water (PW) and sediment, both uptake from water (i.e. respiration) and from food were involved. Accumulated concentrations in this species fit an exponential curve which could be supported by two models: (i) a classical partition model (Higgins et al., 2007), which assumes that the PFASs concentrations in organisms and sediment at steady state are proportional; and (ii) a concentration-dependency model (Liu et al., 2011), which hypothesizes that the uptake kinetics involves active transport through binding to specific sorption sites, such that these sites may become saturated at high exposure concentrations. To gain a more accurate understanding of the processes underpinning the PFAS uptake mechanisms for chironomids, and to refine the uptake and depuration constants, the models proposed must be tested to determine which is the most suitable.

The aims of the present study were therefore (i) to describe PFAS elimination kinetics for chironomids, and (ii) to test the concentration dependency of the PFAS bioaccumulation for a model compound, the perfluorotridecanoic acid (PFTrDA). A combined accumulation and depuration experiment involving field sediment was implemented to address the first objective. For the second one, we conducted combined accumulation and depuration experiments at different concentrations and applied a bioaccumulation model adapted to these compounds and species that could account for realistic kinetics constants.

2. Bioaccumulation modelling: theoretical background

Assuming that PFAS uptake and elimination depend on the organisms' surface, the dynamics of the PFAS load in the organism are defined as follows:

$$\frac{d(Q_{org})}{dt} = S_{org}.\ k_u.\ C_{sed-oc} - S_{org}.\ k_e.\ C_{org} \quad (1)$$

where Q_{org} corresponds to the quantity of PFASs in and/or on the organism, S_{org} the chironomids surface, k_u ($g.g_{ww}\,mm^{-2}\,d^{-1}$) and k_e ($mm^{-2}\,d^{-1}$) the uptake and elimination constants, respectively. $C_{sed\text{-}oc}$ ($ng\ g_{ocdw}^{-1}$) and C_{org} ($ng\ g_{ww}^{-1}$) indicate the PFAS concentrations in sediment adjusted to the f_{oc}, and in the organisms, respectively. As a consequence of growth during the test (Péry et al., 2002), the tissue concentration dynamics is described by Eq. (2) (details in SI):

$$\frac{d(C_{org})}{dt} = \left(\frac{1}{L}.\ k_u.\ C_{sed-oc} - \frac{1}{L}.\ k_e.\ C_{org}\right) - C_{org} \times \frac{d(V)}{dt} \times \frac{1}{V} \quad (2)$$

Where C_{org} is the internal concentration, L is the chironomids length (cm), and V is the chironomid volume (cm^3). Note that k_u and k_e in Eq. (2) are expressed in different units than in Eq. (1), namely $g_{oc}\,g_{ww}\,h^{-1}$ for k_u and h^{-1} for k_e.

PFAS uptake may or may not be concentration-dependent, i.e. this uptake could follow either first order kinetics or kinetics with saturation. In case of concentration-dependency, the accumulation can be viewed as an adsorption-like process, in which the chemical adsorb at binding sites, i.e. specific components of the organs where PFASs accumulate (Liu et al., 2011). The binding site saturation process progressively slows down the uptake, and the steady state is reached at a lower concentration than in the case of a first order kinetics. Both the concentration in the exposure media and the number of sites remaining free control the uptake rate. The S term was introduced in order to model these two cases:

$$S = \frac{1}{(1+C_{org}/C_{50})} \quad (3)$$

with C_{50} representing the half-saturation concentration, i.e. the internal concentration at which the uptake is one-half of its maximum rate. When C_{org} is low, S is close to 1, and the dynamics follow Eq. (2); conversely, when C_{org} increases and site binding occurs, S decreases and tends to 0, meaning that the uptake is lower or stopped. The final equation is:

$$\frac{d(C_{org})}{dt} = \left(\frac{1}{L}.\ k_u.\ C_{sed-oc}.\ S - \frac{1}{L}.\ k_e.\ C_{org}\right) - C_{org} \times \frac{d(V)}{dt} \times \frac{1}{V} \quad (4)$$

A half-life ($T_{1/2}$) can be derived from the model as the time necessary for a 50% decrease in the accumulated concentration.

3. Materials and methods

3.1. Chemicals

Standard PFAS solutions (PFC-MXA and PFS-MXA) were obtained from Wellington Laboratories (via BCP Instruments, Irigny, France): PFC-MXA contained perfluoro-*n*-butanoic acid (PFBA), perfluoro-*n*-pentanoic acid (PFPA), perfluoro-*n*-hexanoic acid (PFHxA), perfluoro-*n*-heptanoic acid (PFHpA), perfluoro-*n*-octanoic acid (PFOA), perfluoro-*n*-nonanoic acid (PFNA), perfluoro-*n*-decanoic acid (PFDA), perfluoro-*n*-undecanoic acid (PFUnDA), perfluoro-*n*-dodecanoic acid (PFDoDA), perfluoro-*n*-tridecanoic acid (PFTrDA), and perfluoro-*n*-tetradecanoic acid (PFTeDA), each at 2 ng μL^{-1} in methanol (MeOH). PFS-MXA contained perfluoro-1-butanesulfonate (PFBS) potassium salt, perfluoro-1-hexanesulfonate PFHxS) sodium salt, perfluoro-1-heptanesulfonate (PFHpS) sodium salt, n-perfluoro-1-octanesulfonate (PFOS) sodium salt and perfluoro-1-decanesulfonate (PFDS) sodium salt, N-Ethyl perfluorooctane sulfonamide (EtFOSA), N-Methyl perfluorooctane sulfonamide (MeFOSA), perfluorooctane sulfonamide (FOSA), N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA), N-Methyl perfluorooctane sulfonamidoacetic acid (MeFOSAA), and 6:2 Fluorotelomer sulfonic acid (6:2 FTSA), each at 2 ng µL-1 in MeOH. A working solution containing all analytes, each at approximately 0.05 ng μL^{-1}, was prepared in MeOH and stored at −18 °C. ^{13}C-labeled perfluorodecanoic acid (PFDA), PFOS, and perfluorooctane sulfonamide (FOSA), each at 50 ng μL^{-1} in MeOH, were supplied by Wellington Laboratories and used as internal standards (ISs). A working solution was prepared in MeOH, each containing IS at 0.1 ng μL^{-1} (Table S1 in supplementary information).

LC/MS-grade MeOH and acetonitrile (ACN) were purchased from J.T. Baker via Interchim (Montluçon, France). Sodium acetate buffer (99%, ACS Reagent), ammonium hydroxide (28–30% in water), 0.2-µm nylon centrifuge tube filters, and ENVI-Carb cartridges (6 cc, 250 mg) were obtained from Sigma-Aldrich (St Quentin Fallavier, France), whereas Strata XAW (6 ml, 200 mg) were purchased from Phenomenex (Le Pecq, France). Nitrogen (99%) was supplied by Air Liquide (Paris, France). Ultra-pure water was obtained using an Elix 10 purification system fitted with an EDS pack (Millipore, Guyancourt, France).

3.2. Testing strategy

Two experiments were conducted with *C. riparius*: an accumulation test with field and field-spiked sediment, and an elimination test with field and field-spiked sediment (Fig. S1 in SI). The decision to spike field sediment was made for testing the concentration-dependency hypothesis; spiking involved PFTrDA, the main PFAS among those detected in the field sediment used in the present study (Munoz et al., 2015). The elimination experiment was implemented in order to improve the accumulation kinetics modelling when concentration-dependency occurs (Bertin et al., 2014).

3.2.1. Field sediment

The study was conducted using sediment collected at Beurre Island (characteristics in SI). This site is a fluvial annex of the Rhone River (eastern central France, N45°28′17.0″E4°46′43.4″) located downstream of a fluoropolymer manufacturing plant. Since 1902, this industrial site has been used to produce hydrofluoric acid and a wide array of fluorine-based organics. Three PFAS production periods can be defined at this site: (i) polytetrafluoroethylene (PTFE) production from 1960 to