TRANSFER KINETICS OF PERFLUOROOCTANE SULFONATE (PFOS) FROM THE AQUATIC ENVIRONMENT TO A MARINE BENTHIC FISH

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Introduction

Bioaccumulation of perfluorooctane sulfonate (PFOS) in fish is of interest because PFOS is expected to accumulate in the aquatic environment[1,2]. Consumption of fish can be a major source of human exposure to PFOS[3]. Understanding the uptake and depuration kinetics of PFOS in fish is essential for predicting PFOS concentrations in fish in the environment. Because PFOS is present as an anion in ambient water[1], its kinetics may differ from those of neutral chemicals[4]. There has been a limited number of kinetic studies of PFOS in fish at environmentally relevant levels of exposure[5] or dealing with respiratory uptake efficiency.

In the aquatic environment, bottom and suspended sediments may play an important role as sources of chemicals for aquatic organisms[6,7]. In fish, only chemicals in the dissolved phase are considered to be taken up accompanying respiration[8]. Potential uptake of these chemicals from bottom and suspended sediments has been investigated[6,9], but quantitative kinetic evaluation of such uptake is limited, particularly in fish.

The objective of this laboratory study[10] was to determine the uptake and depuration kinetics of PFOS in a marine benthic fish, the marbled flounder (*Pseudopleuronectes yokohamae*). We focused particularly on uptake efficiency via the respiratory surfaces, kinetic contribution of PFOS in suspended or bottom sediment to the body burden of fish, and potential mechanisms responsible for this contribution.

Materials and methods

Setup of the experiment

We used marbled flounder (two-year old, average 46 g-wet) held in a flow-through system of filtered seawater (average water quality: 17.3 °C; 7.5 mg-O_2/L) for the experiment. There were control, water (WA), bottom-sediment (BS), and suspended-sediment (SS) treatments (T) (control and WAT: no sediment; BST: spiked BS; SST: no BS). Three exposure treatments (WAT, BST, and SST) were established to expose the fish to PFOS dissolved in water, associated with suspended sediment particles in water, or associated with bottom sediment. Only the WAT received spiked seawater (93 ng/L nominal). Spiked field-collected BS had been laid in the BST and was not renewed during the experiment. SS was also present in the BST due to the activity of the fish. The SST received effluent from the BST. Water was well-mixed in all treatments owing to aeration.

An 84-d depuration period followed a 28-d exposure period (only exposure period for SST). At the end of the exposure period, fish in each exposure treatment were moved to a new tank, which contained no sediment and received non-spiked seawater during the depuration period. The fish were fed commercial fish food.

Sampling and chemical analysis

The flounder, water, and sediment samples were taken regularly. The fish body surface, gills, and inside of gut were washed to remove particles. The sediment interstitial water was sampled immediately after the sediment sampling by centrifugation. The concentration of PFOS in the samples was determined according to previously reported methods with modifications[2,10]. The QA/QC results were satisfactory[10].

Kinetic model and uptake efficiency

We analyzed the uptake and depuration by the fish based on a first-order kinetic of concentration[9,11]. To assess the potential role of suspended and bottom sediments in the uptake of PFOS by fish, three models (A–C) were employed, that differed in terms of the exposure medium being considered.

A: $$\frac{\mathrm{d}C'_{\mathrm{b}}(t)}{\mathrm{d}t} = k_{\mathrm{tot}}C'_{\mathrm{tot}}(t) + k_{\mathrm{sed}}C'_{\mathrm{sed}}(t) - k_{\mathrm{d}}C'_{\mathrm{b}}(t)$$

B: $$\frac{\mathrm{d}C'_{\mathrm{b}}(t)}{\mathrm{d}t} = k_{\mathrm{dis}}C'_{\mathrm{dis}}(t) + k_{\mathrm{par}}C'_{\mathrm{par}}(t) + k_{\mathrm{sed}}C'_{\mathrm{sed}}(t) - k_{\mathrm{d}}C'_{\mathrm{b}}(t)$$

C: $$\frac{\mathrm{d}C'_{\mathrm{b}}(t)}{\mathrm{d}t} = k_{\mathrm{dis}}C'_{\mathrm{dis}}(t) - k_{\mathrm{d}}C'_{\mathrm{b}}(t)$$

where C_{b} is the concentration of PFOS in the fish as a function of time t, C_i is the concentration in an exposure medium i, k_i is the rate constant for uptake from the exposure medium, and k_{d} is the rate constant for collective depuration (elimination, metabolic transformation, and growth dilution). The suffixes 'dis', 'par', 'tot' and 'sed' indicate the dissolved phase, particulate phase, sum (total) of the concentrations in the dissolved and particulate phases in water, and sediment, respectively, and a prime symbol indicates subtraction of the control value. Both the water column and bottom sediment were considered as exposure media in models (A) and (B), whereas only the dissolved phase was considered in model (C). Model (A) used the total concentration in the water column, whereas the other models distinguished the dissolved phase from the particulate phase. The contribution of food to the body burden of PFOS in fish, if any, was cancelled out in all models by subtracting the concentrations in the control treatment.

The kinetic models were fitted by nonlinear fitting assuming common rate constants among the treatments. Visual inspection of the overall fit and adjusted residual sum of squares (adjRSQ = RSQ/($n - 2p$), where RSQ is the squared sum of the residuals, n is the number of data, and p is the number of parameters)[12] were used as the criteria for model selection. In the present study, $C_i(t)$ was approximated during the interval $t_k \leq t < t_{k+1}$ by using the average of the two sample values at times t_k and t_{k+1}, and we adopted a general form of integration of the kinetic equation[11] to account for changes in the PFOS concentrations in the exposure media.

An uptake rate constant (k_i) can be expressed as the product of the fish-mass-specific medium exposure rate (e_i) and the corresponding uptake efficiency ($\alpha_{\mathrm{PFOS},\,i}$) of PFOS from the exposure medium: $k_i = e_i\,\alpha_{\mathrm{PFOS},\,i}$. Regarding the uptake of PFOS from the respiratory surfaces, the mass-specific ventilation rate (e_{resp}) was deduced from the mass-specific oxygen (O_2)-consumption rate of the fish at the kinetic experiment (r_{e}): $e_{\mathrm{resp}} = r_{\mathrm{e}}/(DO\;\alpha_{\mathrm{O2}})$, where DO is the dissolved O_2 concentration, α_{O2} is the uptake efficiency of O_2 at the respiratory surfaces and r_{e} was estimated using the measured O_2 consumption rate of marbled flounder[10,13] and based on an allometric relationship[14,15]. These two equations yield the uptake efficiency of PFOS relative to that of O_2 (α^*)[16]: $\alpha^* = \alpha_{\mathrm{PFOS,\,resp}}/\,\alpha_{\mathrm{O2}} = k_{\mathrm{resp}}\,DO/r_{\mathrm{e}}$. Regarding the uptake from the gut, e_{sed} is the mass-specific ingestion rate of sediment, and was conservatively assumed to equal the daily feeding rate of 0.5%. The gut uptake efficiency of PFOS from sediment is: $\alpha_{\mathrm{PFOS,\,gut}} = k_{\mathrm{sed}}/e$.

Results and discussion

The PFOS concentrations in the fish are shown in Figure 1. Dissolved and particulate PFOS concentrations in the WAT in the exposure period were relatively constant and averaged 74 and 18 ng/L, respectively. Those in the BST or SST were comparable and peaked on day 1 or 3 at 50–100 ng/L and then decreased. PFOS concentration in the BST sediment decreased during the 28 days from 110 to 15 ng/g-dry. PFOS concentrations were negligible in the water in the control and in the exposure treatments during the depuration period (average: WAT, 0.66 ng/L; BST, 0.37 ng/L), and in the control fish (average, 0.04 ng/g-wet). PFOS was not detected in the food (< 0.15 ng/g). Average suspended-solid concentrations (mg/L) were 7.3, 9.3, 224, 8.2, and 174, in the control, WAT, BST (exposure period), BST (depuration period), and SST, respectively.

The estimated rate constants are shown in Table 1. The curves predicted by models (A) and (B) were similar and were almost identical for the WAT and BST (Figure 1). Model (C) apparently over-predicted and under-predicted the PFOS concentrations in the WAT and BST fish, respectively. The adjRSQ values for models (A) and (B) were comparable and approximately 40% better than the adjRSQ value for model (C) (Table 1). The kinetic models successfully represented the observed PFOS concentrations in fish, including the decrease in the BST after day 14 and the plateau at the same time in the SST, patterns that reflected the decrease in the PFOS concentrations in the water and sediment. Because the wet mass of the fish showed no statistically significant trend with time in any treatment, no growth correction was applied in the kinetic analysis.

We consider the value of the uptake rate constant from the dissolved phase (k_{dis}) obtained from model (B) to be most representative of the respiratory uptake of PFOS among the k_{dis} values obtained in the present study. This interpretation was supported by the identical k_{dis} value obtained from model (C) applied only to the results from the WAT (Results not shown). The values obtained for the kinetic parameters (Table 1) were comparable to those previously reported for PFOS in other fish species (common carp (*Cyprinus carpio*)[17], bluegill (*Lepomis macrochirus*)[18], and rainbow trout (*Oncorhynchus mykiss*)[5]).

The obtained respiratory uptake efficiency of PFOS was comparable to efficiencies estimated for PFOS in other fish species and was lower than those typically reported for neutral hydrophobic compounds in fish[4, 13]. Uptake efficiency provides a better comparison of uptake kinetics between compounds or species because the uptake rate constant depends on the ventilation rate, which depends on the size and species of fish. There are few reported respiratory uptake efficiencies for PFOS[19]. Therefore we analyzed the literature data in carp[17] and bluegill[18] by using literature respiration data. These analysis yielded an estimate for α^* of approximately 0.007 to 0.095, which were all comparable in magnitude to our result (0.032).

The results suggested that the PFOS in suspended or bottom sediment contributed to the observed body burden in the fish. The better fit of models (A) and (B) demonstrated that these models were most suitable to interpreting the experimental results, and that the PFOS in suspended and bottom sediments contributed to the observed body burden in fish. The values obtained for the uptake rate constant from these media were not trivial (i.e., k_{par} or k_{tot} of the same order of magnitude as k_{dis}, and k_{sed} corresponding to $\alpha_{PFOS,\ gut} > 100\%$) and were statistically significant (Table 1). Overestimating and underestimating PFOS concentration in fish in the WAT and BST, respectively, by model (C) suggested that the body burden of PFOS was not fully accounted for by the measured PFOS concentration in the dissolved phase (see Reference 10 for further discussion).

Several factors (including physiological mechanisms) not specifically considered in our calculations may have contributed to the observed uptake rate constants of PFOS from suspended and bottom sediments. We used the observed data and information in the literature to evaluate the possible contribution of these factors, which included sediment particles remaining in fish, changes in dissolved O_2 level and ventilation rate, uptake of PFOS from ingested sediment particles, water drinking, and cutaneous uptake. All these factors and physiological mechanisms played a minor role in the observed rate constants of the uptake of PFOS from suspended and bottom sediments, and other potential mechanisms responsible for the uptake need to be investigated.

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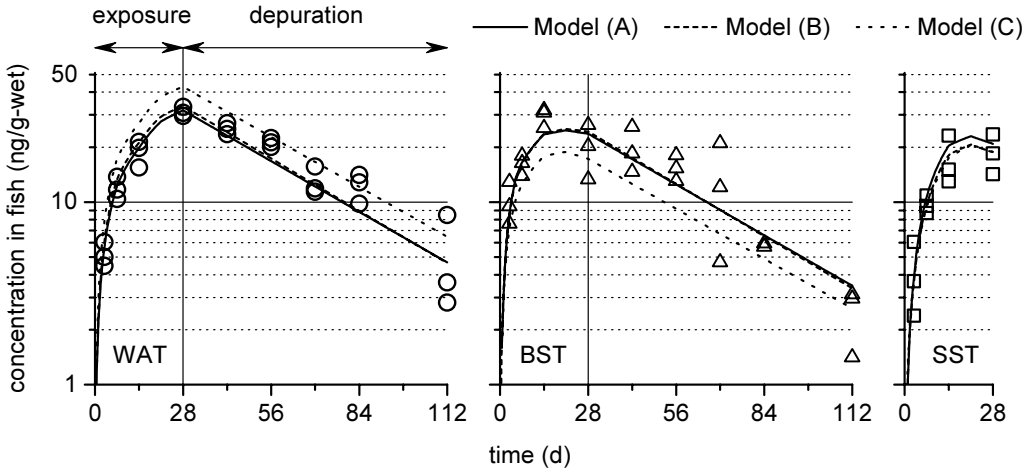

Figure 1. Time course of PFOS concentrations in fish and model prediction curves based on kinetic models. WAT = water exposure treatment; BST = bottom-sediment exposure treatment; SST = suspended-sediment exposure treatment.

Table 1. Rate constants of PFOS for whole body of marbled flounder estimated by kinetic models, corresponding uptake efficiency or half-life, and a measure of fit of each model.

Model	adjRSQ[a]	Rate constant[bc]		Uptake efficiency[b]	Half-life (d)[b]
A	0.099	k_{tot}	18 (17–20)	0.027 (0.024–0.030)[d]	
		k_{sed}	5.0 (1.2–9.0)	4.0 (0.85–7.1)[e]	
		k_d	0.023 (0.020–0.026)		30 (27–35)
B	0.099	k_{dis}	22 (18–26)	0.032 (0.026–0.038)[d]	
		k_{par}	11 (3.6–20)	0.016 (0.0039–0.028)[d]	
		k_{sed}	7.1 (2.1–12)	5.7 (1.9–9.5)[e]	
		k_d	0.024 (0.020–0.027)		29 (26–34)
C	0.16	k_{dis}	31 (27–35)	0.046 (0.040–0.052)[d]	
		k_d	0.023 (0.019–0.026)		31 (27–36)

[a] Adjusted residual sum of squares, as a measure of fit. adjRSQ = RSQ/(n − 2p), where RSQ is the squared sum of the residuals, n is the number of data, and p is the number of parameters.
[b] Values are presented as "point estimate (95% confidence interval)".
[c] Unit of the rate constant is (L/[kg d]) for k_{tot}, k_{dis}, and k_{par}; (g/[kg d]) for k_{sed}; and (1/d) for k_d.
[d] Uptake efficiency relative to that of oxygen assuming respiratory uptake.
[e] Gut uptake efficiency assuming sediment ingestion rate equal to that of food.