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Accumulation of perfluorooctane sulfonate (PFOS) in the food chain of the Western Scheldt estuary: Comparing field measurements with kinetic modeling

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Abstract

The environmentally persistent perfluorooctane sulfonate (PFOS) is a perfluoroalkylated acid (PFA), which has been found to accumulate and biomagnify through food webs all over the world. In the present investigation, the accumulation kinetics of PFOS was explored using the bioaccumulation model OMEGA. As accumulation behavior of PFOS may show similarities to fatty acids as well as to neutral organic compounds, different modeling approaches were used. Accumulation kinetics of PFOS was modeled similar to (1) moderately and (2) highly hydrophobic compounds, (3) metals and (4) as a combination of hydrophobic compounds and metals. Modeled elimination and uptake rate constants were compared to empirical rate constants from literature. Subsequently, model predictions were compared to field-based biota-suspended solids accumulation ratios (BSAF) in the estuarine food chain of the Western Scheldt, The Netherlands. Results show that uptake of PFOS is comparable to moderately hydrophobic compounds and elimination is best described by elimination kinetics of metals. These observations indicate that the accumulation behavior of PFOS is comparable to that of short and medium chained fatty acids.

Keywords: Perfluorinated compounds; Surfactants; Bioaccumulation; Kinetics; Uptake; Elimination

1. Introduction

Perfluoroalkylated acids (PFAs) are a class of perfluorinated alkylated substances that are characterized by a perfluoroalkyl chain and a terminal sulfonate or carboxylate group (Hekster et al., 2003; Beach et al., 2006). Perfluorinated alkylated substances have been manufactured for over 50 years and have found widespread use in a variety of applications ranging from carpet protection to fire-fighting foams. They can degrade to the environmentally persistent perfluorooctane sulfonate (PFOS) and perfluorooctanoic

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acid (PFOA) (Hekster et al., 2003; Prevedouros et al., 2006). PFOS and its potential precursors are of increasing interest as they have been found to accumulate and biomagnify through food webs all over the world (Van de Vijver et al., 2003; Tomy et al., 2004; Kannan et al., 2005; Houde et al., 2006a, b). However, the toxic mode of action of PFOS and its effect on the overall health of organisms are still under investigation (Van de Vijver et al., 2003; Ankley et al., 2004; Newsted et al., 2006). The growing awareness of the possible environmental risks of perfluorinated alkylated substances has lead to a reduction of global emissions between 1999 and 2004 (Prevedouros et al., 2006). This reduction has not yet been detected by temporal trend studies in biota (Houde et al., 2006a, b).

PFOS is a surface-active agent whose physical properties are governed by a hydrophilic head group and a tail that is both hydrophobic and oleophobic (Key et al., 1997; Beach et al., 2006; de Voogt and Saez, 2006). PFOS has a low acid dissociation constant (Kissa, 2001) and is expected to dissociate almost completely to PFOS anions at environmental conditions. Because of its tendency to aggregate at surface interfaces, the octanol–water partition coefficient (K_{ow}) of PFOS cannot be determined (OECD, 2002; 3M Company, 2003). The structure of PFOS and its behavior within the body of organisms is comparable to fatty acids (Martin et al., 2003a; Beach et al., 2006). Similar to fatty acids, PFOS binds to the protein albumin, which is mainly present in blood, liver and eggs (Martin et al., 2003b; Kannan et al., 2005). Complexation with biotic proteins has also been reported for metals (Hendriks and Heikens, 2001) and organotins (Veltman et al., 2006).

Although PFOS does not accumulate in fat tissue like neutral organic compounds, hydrophobic interactions may play a role in bioaccumulation of PFOS. The accumulation of PFAs in biota and their sorption to sediment was shown to be dependent on length of the perfluorinated tail (Martin et al., 2003a, 2003b; Van Roon et al., 2007). Long-chain fatty acids may cross membranes by means of transport proteins, while short and medium chain fatty acids probably enter cells by diffusion (Kamp and Hamilton, 2006). Also the binding of fatty acids to albumin is mainly driven by hydrophobic interactions (Spector 1975). Furthermore, Tolls and Sijm (1995) found that hydrophobicity strongly influences bioconcentration of surfactants. Accumulation behavior of PFOS may thus show similarities to fatty acids as well as to neutral organic compounds.

The aim of this study is to investigate the bioaccumulation behavior of PFOS. We use different modeling approaches in the bioaccumulation model OMEGA (Hendriks et al., 2001) to explore possible mechanisms underlying the accumulation of PFOS. Accumulation kinetics of PFOS is studied by comparing modeled rate constants with rate constants from literature. Additionally, the different modeling approaches are compared to accumulation data of PFOS from an estuarine food chain of the Western Scheldt, the Netherlands.

2. Methods

2.1. OMEGA

The model OMEGA (optimal modelling for ecotoxicological assessment) (Hendriks et al., 2001) has been developed for risk assessment purposes and allows assessment of many substances and species at different locations and periods. OMEGA combines classical fugacity theory with allometric regressions, in order to predict chemical accumulation in food chains. It has been successfully applied to estimate accumulation of priority substances, i.e. organic chemicals (Hendriks et al., 2001; Veltman et al., 2005) and metals (Hendriks and Heikens, 2001) in aquatic and terrestrial communities. The model has been extensively described before in Hendriks et al. (2001) and Hendriks and Heikens (2001). Here, a brief explanation of OMEGA is given (all equations and parameters used are provided in the Supplementary data).

The mass of organisms results from three basic flows: absorption and excretion of water, ingestion and egestion of food and (re)production of mass and mortality of tissues. Each of these flows may carry toxicants into and out of an organism. OMEGA calculates steady-state chemical residues in biota as the sum of influx via water (absorption) and uptake of food (assimilation) divided by the sum of elimination rates (Eq. (1)).

$$C_{i,x} = \frac{k_{0,x,\mathrm{in}} \times C_{0,w,x} + k_{1,x,\mathrm{in}} \times C_{i-1,x}}{\sum k_{j,x,\mathrm{out}}} \quad (1)$$

$C_{i,x}$ = concentration in biota (μg kg^{-1} wet weight)

$k_{0,x,\mathrm{in}}$ = rate constant for absorption (μg kg^{-1} wet weight/μg l^{-1} d^{-1})

$C_{0,w,x}$ = dissolved concentration in water (μg l^{-1})

$k_{1,x,\mathrm{in}}$ = rate constant for assimilation (μg kg^{-1} wet weight/μg kg^{-1} d^{-1})

$C_{i-1,x}$ = concentration in food (μg kg^{-1} wet weight)

$\Sigma k_{j,x,\mathrm{out}}$ = rate constants for elimination, i.e. excretion (d^{-1})

egestion and growth dilution

The different rate constants depend on resistances that substances encounter in the water and lipid layers of organisms and on metabolic flows that carry substances into and out of these organisms. These resistances and delays have been related to basic properties of chemicals and to the size and trophic level of the species. The adjacent coefficients and exponents needed to determine the various rate constants have been calibrated on hundreds of rate constants from laboratory studies (Hendriks et al., 2001) (Table A, Supplementary data).

Accumulation was here defined as the net process by which the chemical reaches a concentration in an organism as a result of chemical uptake through all possible routes of exposure (water and food) and elimination from all possible routes compared to the concentration in solids (biota-solids accumulation factor, BSAF). BSAFs were calculated by dividing the whole-body wet weight concentration in the

organism by the dry weight concentration in suspended solids. Biomagnification was here defined as the net process by which the chemical concentration in an organism achieves a level exceeding that in the organisms diet, as a result of chemical uptake through all possible routes of exposure (Gobas, 2000). The organism-food concentration ratio (biomagnification factor, BMF) is mainly determined by the assimilation efficiency of food in an organism. BMFs were calculated by dividing the whole-body wet weight concentration in the organism by the wet weight concentration in its food. As OMEGA takes into account all possible routes of uptake and elimination, calculated BSAFs and BMFs can be compared with field values.

2.2. Modeling accumulation of PFOS

Accumulation of PFOS was explored by using four different modeling approaches (Table 1). In the first two approaches it was assumed that PFOS enter cells by diffusion, similar to short and medium chain fatty acids. Accumulation of PFOS was supposed to occur through hydrophobic mechanisms, comparable to kinetics of neutral organic compounds in OMEGA (Hendriks et al., 2001). In OMEGA accumulation of neutral organic compounds is described as a function of the K_{ow} (SI). As the octanol–water partition ratio for PFOS has not been determined empirically, this value had to be estimated. Fatty acids of comparable chain lengths, i.e. 6–12 carbon atoms, have $\log K_{ow}$ values ranging from 1.9 to 4.6 while the structure-fragment distribution of PFOS suggests values of 6 or higher (NLM et al. visited 09/2006; EPIwin., 2007). Chemical parameters in OMEGA, i.e. resistances that substances encounter in water and lipid layers of organisms, were calibrated on thousands of absorption, assimilation and elimination rate constants for various organic chemicals and for various species (Hendriks et al., 2001). Results showed that accumulation kinetics of moderately hydrophobic compounds ($\log K_{ow} = 3$) is rather different from highly hydrophobic substances ($\log K_{ow} \geqslant 6$). Highly hydrophobic substances have higher absorption and lower elimination rates than moderately hydrophobic compounds. Therefore, the accumulation of PFOS was modeled twice, i.e. similar to a moderately and a highly hydrophobic compound.

Table 1
Four modeling approaches used in OMEGA to explore accumulation behavior of PFOS

	Uptake kinetics according to	Elimination kinetics according to	Assumed $\log K_{ow}$
1	Neutral organic compounds	Neutral organic compounds	6
2	Neutral organic compounds	Neutral organic compounds	3
3	Metals	Metals	–
4	Neutral organic compounds	Metals	3/–

In the third approach, it was assumed that PFOS anions are transported through protein channels, similar to long chain fatty acids. In OMEGA this uptake mechanism is used to model accumulation of metals. The uptake rate of metals is determined by the abundance of transport proteins relative to metal ions (Hendriks and Heikens, 2001). In OMEGA uptake rate constants of metals are therefore described as dependent of their exposure concentrations. Elimination of PFOS may be similar to elimination kinetics of those metals that show affinity for proteins. Chemical parameters in OMEGA were calibrated on hundreds of absorption and elimination rate constants for various metals and for various aquatic species (Hendriks and Heikens, 2001). Results showed that the affinity of metals for dry biomass, i.e. proteins, results in lower elimination rates compared to most hydrophobic organic substances. The binding of metals to proteins is incorporated in the model as a generic dry tissue–water distribution coefficient (K_{tw}, see Supplementary data).

The fourth approach was a combination of the second and the third. Uptake of PFOS was modeled similar to moderately hydrophobic compound and elimination similar to a metal. This approach may mimic the behavior of short and medium chain fatty acids.

2.3. Elimination and uptake rate constants obtained from literature

To test the validity of the four approaches, modeled elimination and uptake rate constants were compared to empirical rate constants from literature. Data on accumulation kinetics of PFOS were obtained from laboratory studies. To this end a literature search was performed using the ISI Web of Science publication database and the electronic public docket system of the Environmental Protection Agency (US EPA). PFOS was characterized as 'PFOS', 'perfluorooctanesulfonate', 'PFA', 'perfluor*' and 'fluorinated'. The subject was defined as 'accumulation', 'kinetics', 'uptake', 'absorption', 'assimilation' and/or 'elimination'.

2.4. Bioaccumulation factors derived from monitoring programs

Subsequently, model predictions were compared to field-based biota-suspended solids accumulation ratios of PFOS for the different trophic levels in the Western Scheldt estuary. Field data were obtained from two monitoring campaigns in the Western Scheldt estuary in 2001 and 2005, carried out by, respectively, the Dutch National Institute for Coastal and Marine Management RIKZ and the University of Antwerp (Hoff et al., 2003; Van de Vijver et al., 2003; Van de Vijver et al., 2005; Van den Heuvel-Greve et al., 2006). Sampling and analytical methods used by Van de Vijver and co-workers are described in Van de Vijver et al. (2003). In the RIKZ campaign, sediment, suspended matter, and biotic samples were collected in May–August 2005 in the Western Scheldt at location Middelplaat. The common

tern eggs ($n = 10$) were collected in June 2005 at the colony of Terneuzen. Samples were analysed according to a method published by Hansen et al. (2001). First, 2 g of homogenised sample was extracted three times with methyl-*tert*-butylether (MTBE) in the presence of the ion pairing agent tetra-*n*-butylammonium hydrogensulfate (TBA). The extracts were pooled and MTBE was evaporated to a final volume of 1 ml. In case of the biota samples, the following clean-up step was performed: lipids were removed from the extract by silica column chromatography (elution by 15 ml dichloromethane). The target compounds were subsequently eluted with 30 ml acetone. The acetone was removed by evaporation and replaced by 0.7 ml methanol, after which the extracts were ready for injection. The extracts were injected on a Thermo Electron Surveyer high pressure liquid chromatography (HPLC) system, coupled with an LCQ-Advantage ion trap mass spectrometric system (MS) and electrospray ionisation interface (ESI). For PFOS, the molecular ion m/z 499 was used for quantification. Ion trap MS is not capable of performing MS/MS on PFOS, and therefore more emphasis was put on the clean-up of the sample (as described earlier). The internal standard used was 7H-perfluorinated heptanoic acid (7H-PFHpA). Duplicate analysis were performed on four selected samples, and the precision was good (relative standard deviation 2–8%). Recovery experiments were conducted by spiking sediment and biota samples. The recoveries yielded 64–86%, which is very good at the time the study was conducted (if compared to the variable performance of a pool of laboratories in the first interlaboratory study on PFCs in environmental samples (Van Leeuwen et al., 2006)).

Biological samples used in present study were all from 'Terneuzen', as PFOS levels in suspended solids were only available for this location. PFOS concentrations in biota were presented on a wet weight basis. The role of organic matter as a partitioning phase for PFOS is unclear (Van Roon et al., 2007). Therefore, we expressed suspended solid concentrations on a dry weight basis.

OMEGA uses the concentration of toxicants in the water phase to calculate accumulation in biota. As dissolved concentrations of PFOS were not available from our data set, we used an empirically derived sediment-water partition coefficient of 52.5 l kg^{-1} dry weight (Van Roon et al., 2007) to calculate these from concentrations in suspended solids. Monitored organisms were classified into a food chain based on Veltman et al. (2005) and feeding preferences (FishBase. visited, 07/2006) (Table 2).

3. Results

3.1. Modeled rate constants versus empirical values

In Table 3 empirical rate constants for PFOS are compared to modeled values. Empirical absorption rate constants for PFOS are overestimated by model predictions for highly hydrophobic compounds by one order of magnitude. Estimations for moderately hydrophobic compounds are within the range of empirical values with deviations up to a factor of five. Model predictions for metals underestimate absorption; deviations are up to one order of magnitude. Modeled assimilation rate constants are similar for highly and moderately hydrophobic compounds, as assimilation efficiencies are independent from the $\log K_{ow}$ if its value is in the range of 2–7 (Hendriks et al., 2001). Both modeling approaches are in good agreement with empirical values for PFOS, i.e. deviations are up within a factor of two. Assimilation is underestimated by model predictions for metals by one order of magnitude.

Estimations for elimination of highly hydrophobic compounds and metals are within the range of empirical rate constants for PFOS, deviations are up to a factor of eight

Table 2
Trophic levels in Western Scheldt food chain (Terneuzen) with representative species (FishBase. visited, 07/2006; Veltman et al., 2005)

Trophic level		Species	Common name	Sample	Sampling campaign
1	Suspended matter				
2	Herbi-detritivores	*Arenicola marina*	Lugworm	Whole-body	Van den Heuvel-Greve et al. (2006)
3	Primary carnivores	*Crangon crangon*	Brown shrimp	Whole-body Soft tissue	Van den Heuvel-Greve et al. (2006); Van de Vijver et al. (2003)
		Sprattus sprattus	Sprat	Whole-body	Van den Heuvel-Greve et al. (2006)
		Ammodytes sp.	Sandeel	Whole-body	Van den Heuvel-Greve et al. (2006)
3.5	Primary–secondary carnivores[a]	*Carcinus maenas*	Green crab	Soft tissue	Van de Vijver et al. (2003)
		Solea solea	Sole	Whole-body and filet	Van den Heuvel-Greve et al. (2006)
		Pleuronectes platessa	Plaice	Liver	Hoff et al. (2003)
		Trisopterus lucus	Bib	Liver	Hoff et al. (2003)
		Anguilla anguilla	Eel	Filet	Van den Heuvel-Greve et al. (2006)
		Dicentrarchus labrax	Seabass	Liver	Van de Vijver et al. (2005)
4	Secondary carnivorous birds	*Sterna hirundo*	Common tern	Eggs	Van den Heuvel-Greve et al. (2006)

[a] Carnivores that feed on both herbi-detritivores and primary carnivores.

Table 3
Modeled rate constants and assimilation efficiencies for PFOS compared to empirical values from literature

Species	Exposure conc.[a]	Empirical value	Modeled value			References
			OMEGA $\log K_{ow} \geqslant 6$	OMEGA $\log K_{ow} = 3$	OMEGA metal	
	(μg/l)	Uptake rate constants ($l\,kg^{-1}\,d^{-1}$)				
Leopard frog[b]	30	17	520	46	1.6	Ankley et al. (2004)
Blue gill[c]	86	8.5	670	59	2.6	OECD (2002)
Rainbow trout PFOS[b]	0.4	53	520	46	24	Martin et al. (2003b)
	(μg/g)	Assimilation efficiencies (%)				
Rainbow trout PFOS[b]	0.54	120	80	80	0.03	Martin et al. (2003a)
	(μg/l)	Elimination rate constants (d^{-1})				
Leopard frog[b]	30	0.059[d]	0.007[d]	0.77[d]	0.008[d]	Ankley et al. (2004)
Blue gill[c]	86	0.006[d]	0.012[d]	1.0[d]	0.013[d]	OECD (2002)
Rainbow trout PFOS[b]	0.4	0.048[e]	0.007[e]	0.77[e]	0.008[e]	Martin et al. (2003b)

[a] In OMEGA, uptake rate constants for metals are calculated dependent from the exposure concentration.
[b] Weight = 7.5 g.
[c] Weight = 2.7 g.
[d] Excretion/egestion rate constant.
[e] Total elimination rate constant, i.e. excretion/egestion and growth dilution.

and seven respectively. Model predictions for moderately hydrophobic compounds overestimate elimination by three orders of magnitude.

3.2. Field-based accumulation and magnification factors

Accumulation of PFOS in primary–secondary carnivorous fish, i.e. fish that feed on both herbi-detritivores and primary carnivores, is measured in samples of whole-body, liver and filet (Fig. 1). Accumulation in whole-body samples is a factor of two higher than in filet, but a factor of four lower than in liver.

Field-based biota-suspended solids accumulation ratios (BSAF) for all trophic levels of the Western Scheldt food chain are greater than 1 (Fig. 2; Table B, Supplementary data). Accumulation ratios increase in the food chain. Magnification ratios increase in primary and primary–secondary carnivores (Table 4), however no biomagnification is observed from primary–secondary carnivores to *Sterna hirundo*.

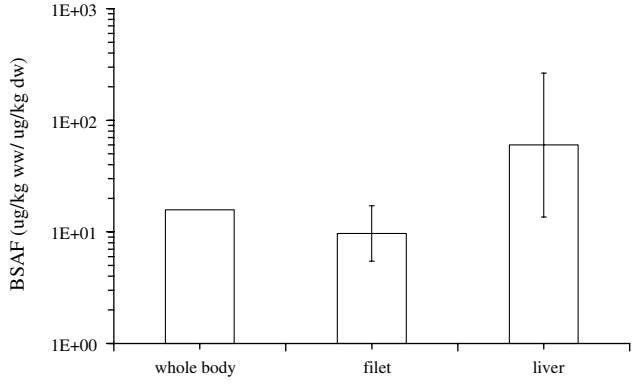

Fig. 1. Empirical biota-suspended solids accumulation factors (BSAF) (geometric mean ± standard deviation; μg kg^{-1} wet weight/μg kg^{-1} dry weight) for PFOS in different samples of primary–secondary fish of the Western Scheldt estuary. Sample sizes: whole-body $n = 1$, filet $n = 2$, liver $n = 19$.

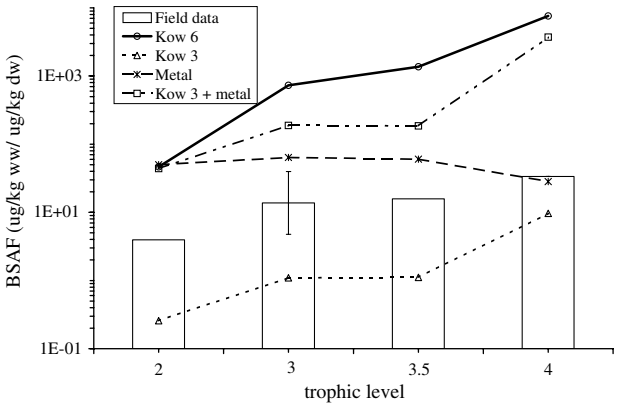

Fig. 2. Empirical and modeled biota solid accumulation factors (BSAF) (geometric mean ± standard deviation; μg kg^{-1} wet weight/μg kg^{-1} dry weight) for PFOS in the aquatic food chain of the Western Scheldt estuary. For primary–secondary carnivores only whole-body samples are used. Sample sizes: levels 2, 3, 5 and 4 $n = 1$, level 3 $n = 8$.

3.3. Modeled accumulation and magnification factors compared to field observations

BSAFs are overestimated by one to two orders of magnitude when PFOS is modeled as a highly hydrophobic compound (Fig. 2; Table B, Supplementary data). On the other hand, model estimations for moderately hydrophobic compounds underestimate accumulation by one order of magnitude. Model predictions for metals overestimate accumulation by a factor of four to thirteen, except for secondary carnivores, where observed and predicted BSAFs are in good agreement. Estimations of the combined modeling approach overestimate empirical BSAFs for trophic levels 2, 3 and 3.5 by one order of magnitude. Accumulation in secondary carnivores is overestimated by two orders of magnitude.

Both modeling approaches for neutral organic compounds show biomagnification in the food chain. Estimations for highly hydrophobic compounds overestimate

Table 4
Empirical and modeled biomagnification ratios (BMF) (μg kg^{-1} wet weight/ μg kg^{-1} wet weight) of PFOS in the Western Scheldt food chain

Predator	Prey	BMF (μg kg^{-1} wet weight/μg kg^{-1} wet weight)				
		Empirical	OMEGA $pK_{ow} \geqslant 6$	OMEGA $pK_{ow} = 3$	OMEGA metal	OMEGA pK_{ow} 3 + metal
Primary carnivores	Herbi-detritivores	3.5	16	4.3	1.3	4.3
Primary–secondary carnivores[a] (whole-body)	Herbi-detritivores	4.0	29	4.3	1.2	4.2
Primary–secondary carnivores[a] (whole-body)	Primary carnivores	1.1	1.9	1.0	0.9	1.0
Secondary carnivores	Primary carnivores	2.4	10	8.8	0.4	20
Secondary carnivores	Primary–secondary carnivores[a] (whole-body)	2.1	5.6	8.7	0.5	20

[a] Carnivores that feed on both herbi-detritivores and primary carnivores.

field BMFs, deviations are up to a factor of seven (Table 4). Model predictions for moderately hydrophobic compounds are in good agreement with field observations, except for secondary carnivores, where magnification is overestimated by a factor of four. Inorganic metals do not biomagnify in the food chain. Model estimations are up to a factor of five lower than field BMFs. Predictions by the combined modeling approach are in good agreement with field observations except for secondary carnivores, where magnification is overestimated by a factor of nine.

4. Discussion

4.1. Modeled rate constants versus empirical values

In our modeling approaches we used parameters that were developed and calibrated for neutral organic compounds and metals. The chemical properties used to describe the accumulation kinetics of these substances in OMEGA, i.e. the K_{ow} and K_{tw}, may not have been completely suitable for PFOS.

Results show that absorption rate constants of PFOS are most comparable to predictions for moderately hydrophobic compounds. This may indicate that PFOS cross biological membranes in a way that is similar to short and medium chained fatty acids, i.e. by diffusion (Kamp and Hamilton, 2006). It is not likely that uptake kinetics of PFOS is similar to metals, since both assimilation and absorption rate constants are substantially underestimated by model estimations for metals. Therefore, it does not seem probable that PFOS enters cells through a protein channel type of mechanism.

Elimination kinetics of PFOS is comparable to predictions for highly hydrophobic compounds and metals that bind to proteins. Elimination of these substances is determined by their affinity for lipids and proteins, respectively. As PFOS binds to proteins and does not accumulate in lipid tissue (Martin et al., 2003b; Kannan et al., 2005), its elimination may be more comparable to a metal type of kinetics. Furthermore, in their study on bioconcentration of surfactants Tolls and Sijm observed that elimination is independent of the K_{ow}. Elimination rate constants for surfactants in their study are all in the range of values observed for PFOS (Tolls and Sijm, 1995).

4.2. Field-based accumulation and magnification factors

The relatively high accumulation ratios observed in liver samples of primary–secondary carnivorous fish are in agreement with observations from other studies that PFOS accumulates in viscera (Martin et al., 2003b; Kannan et al., 2005). We did not include liver in the calculation of accumulation and magnification ratios, as they are known to be higher than ratios on a total body burdens basis (Houde et al., 2006a, b). We also excluded filet samples, as we expect residues in muscle to be below average accumulation. Martin and co-workers found that bioconcentration factors (BCF) in the carcass, i.e. the whole-body without viscera, of rainbow trout closely approximate the whole-body BCF (Martin et al., 2003b). Although PFOS binds to albumin in both blood and eggs (Kannan et al., 2005), the egg samples may not be fully representative of the whole-body concentration of *S. hirundo*.

To check whether accumulation ratios of Western Scheldt species are similar to those in related species from other areas, we compared the accumulation ratios obtained is the present study to those reported in literature (Table 5). Accumulation in the herbi-detritivore *Arenicola marina* in the Western Scheldt is a factor of four higher than in zooplankton in the Sarasota bay. This may confirm the suggestion that benthic organisms are exposed to higher concentrations of PFOS and precursors (Martin et al., 2004; Van de Vijver et al., 2003). On the other hand, Tomy et al. (2004) suggested that exposure concentrations are greater in the water column, as they observed higher concentrations in zooplankton compared to benthic invertebrates. BSAFs of primary carnivorous fish in the Western Scheldt are lower, while ratios for secondary carnivorous fish are within the range of values found in Charleston and Sarasota. Accumulation observed in the secondary carnivorous bird *S. hirundo* is two orders of magnitude lower than in secondary carnivorous mammals and is more comparable to primary and secondary carnivorous fish.

Table 5
Biota solids accumulation factors (BSAF) (suspended solids) for PFOS in the Western Scheldt food chain compared to BSAFs (sediment) from literature

Trophic level	BSAF ($\mu g\ kg^{-1}$ ww/$\mu g\ kg^{-1}$ ww)		
	Western Scheldt[a] geometric mean	Charleston, SC[b] (Houde et al., 2006a,b) range	Sarasota bay, FL[b] (Houde et al., 2006a,b) range
Herbi-detritivores	3.9		1
Primary carnivorous fish	14	75	16–29
(Primary–)Secondary carnivorous fish[c]	57	48–230	44
Secondary carnivorous bird	34		
Secondary carnivorous mammal		1700	2285

To allow a comparison between data from literature and the Western Scheldt.
[a] BSAFs from the Western Scheldt are expressed on a wet weight basis.
[b] BSAFs from Charleston and Sarasota are calculated from concentrations in organisms and sediment from the same location.
[c] Carnivorous fish that feed on both herbi-detritivores and primary carnivores.

Table 6
Biomagnification ratios (BMF) of PFOS in the Western Scheldt food chain compared to BMFs from literature

Predator	Prey	BMF ($\mu g\ kg^{-1}$ ww/$\mu g\ kg^{-1}$ ww)	
		Western Scheldt geometric mean	(Houde et al., 2006a,b) range
Primary carnivores	Herbi-detritivores	3.5	12–23[a]
Primary–secondary carnivores[c]	Herbi-detritivores	4.0	19[a]
Primary–secondary carnivores[c]	Primary carnivores	1.1	1.5–2.8[a]
Secondary carnivores	Primary carnivores	2.4	9.6–18[a]
Secondary carnivores	Primary–secondary carnivores[c]	2.1	1.2–2.6[b], 6.2–11[a]

[a] Sarasota bay, FL.
[b] Charleston bay, SC.
[c] Carnivores that feed on both herbi-detritivores and primary carnivores.

Generally, biomagnification in the Western Scheldt is lower than in Charleston and Sarasota (Table 6).

4.3. Modeled accumulation and magnification factors compared to field observations

Model estimations for highly and moderate hydrophobic compounds showed large deviations from field BSAFs. This is probably because these compounds are known to accumulate exclusively in lipid tissue (Hendriks et al., 2001), whereas PFOS binds to proteins. (Han et al., 2003; Kannan et al., 2005; Martin et al., 2003b; Van den Heuvel et al., 1992). Predictions based on a metal type of kinetics corresponded well to the field BSAFs. However, metals did not show biomagnification in the food chain, while this has been observed for PFOS in present study as well as in many other studies (Martin et al., 2004; Tomy et al., 2004; Kannan et al., 2005; Houde et al., 2006a,b). Of all modeling approaches, estimated accumulation and magnification factors based on a combined approach of moderately hydrophobic compounds and metals are most comparable to field observations.

4.4. Accumulation kinetics of PFOS

Results of this exploratory study show that accumulation kinetics of PFOS can not be described by a single modeling approach for moderately hydrophobic compounds, highly hydrophobic compounds or metals. A tentative conclusion is that uptake of PFOS is comparable to moderately hydrophobic compounds and elimination is best described by elimination kinetics of metals. Comparison with field accumulation factors also demonstrate that predictions based on a combined approach of moderately hydrophobic compounds and metals are most comparable to field observations. These observations indicate that the accumulation behavior of PFOS is comparable to short and medium chained fatty acids.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2007.08.038.

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