



Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web

Marianne Haukås^{a,b,*}, Urs Berger^{c,d}, Haakon Hop^a, Bjørn Gulliksen^b,
Geir W. Gabrielsen^a

^a Norwegian Polar Institute, NO-9296 Tromsø, Norway

^b Norwegian College of Fishery Science, University of Tromsø, NO-9037 Tromsø, Norway

^c Norwegian Institute for Air Research, NO-9296 Tromsø, Norway

^d Department of Applied Environmental Science (ITM), Stockholm University, SE-10691 Stockholm, Sweden

Received 15 February 2006; received in revised form 4 September 2006; accepted 9 September 2006

The first comprehensive survey of fluoroorganic contamination in an European Arctic marine food web.

Abstract

The present study reports concentrations and biomagnification potential of per- and polyfluorinated alkyl substances (PFAS) in species from the Barents Sea food web. The examined species included sea ice amphipod (*Gammarus wilkitzkii*), polar cod (*Boreogadus saida*), black guillemot (*Cepphus grylle*) and glaucous gull (*Larus hyperboreus*). These were analyzed for PFAS, polychlorinated biphenyls (PCBs), dichloro-diphenyltrichloroethanes (DDTs) and polybrominated diphenyl ethers (PBDEs). Perfluorooctane sulfonate (PFOS) was the predominant of the detected PFAS. Trophic levels and food web transfer of PFAS were determined using stable nitrogen isotopes ($\delta^{15}\text{N}$). No correlation was found between PFOS concentrations and trophic level within species. However, a non-linear relationship was established when the entire food web was analyzed. Biomagnification factors displayed values >1 for perfluorohexane sulfonate (PFHxS), perfluorononanoic acid (PFNA), PFOS and $\Sigma\text{PFAS}(7)$. Multivariate analyses showed that the degree of trophic transfer of PFAS is similar to that of PCB, DDT and PBDE, despite their accumulation through different pathways.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: PFAS; PFOS; Trophic level; Biomagnification; European Arctic

1. Introduction

Chemicals produced to make industrial products more resistant against degradation or fire, possess properties that make them potentially harmful to organisms when they leak into the environment. Among such chemicals are halogenated organic synthetics, which are only slowly broken down in

nature and thus defined as persistent organic pollutants (POPs) by the Arctic Monitoring and Assessment Programme (AMAP) (de Wit et al., 2004). Legacy AMAP POPs such as the hydrophobic polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethanes (DDTs, including metabolites) accumulate and biomagnify in marine food webs due to their molecular stability (Borgå et al., 2004). As a result, upper trophic level organisms are exposed to relatively high levels of contaminants. Magnification factors, describing the magnitude of trophic transfer of such pollutants, can be estimated by relating ratio of stable isotopes of nitrogen ($\delta^{15}\text{N}$) to the chemical concentrations (Fisk et al., 2001; Hop

* Corresponding author. Present address: Norwegian Institute for Air Research, Instituttveien 1, NO-2027 Kjeller, Norway. Tel.: +47 63 89 82 50; fax: +47 63898050.

E-mail address: m.haukaas@nilu.no (M. Haukås).

et al., 2002). Knowledge of the biomagnification potential of persistent man-made compounds is essential in environmental management and protection.

Per- and polyfluorinated alkyl substances (PFAS) are a group of anthropogenic chemicals, some of which have been manufactured for more than 50 years. These fluorinated organic compounds are used in the production of stain repelling agents, fluoropolymers, pesticides, lubricants, paints, medicines and fire-fighting foams (Key et al., 1997; Prevedouros et al., 2006). The exceptional properties that make fluoroorganics so attractive for industrial applications also make them potentially hazardous to organisms and ecological systems. These chemicals repel both water and lipids, and are extremely resistant towards degradation (Faithfull and Weers, 1998). In contrast to chlorinated organic substances, the environmental fate and influence of PFAS have hardly gained any attention during the last decades of the 20th century, mainly due to difficulties with regard to their quantitative characterization. Recently, however, the development of a new method sequence for analysis (Hansen et al., 2001) revealed relatively high levels of PFAS in the environment. Two of the main groups of PFAS, perfluorinated sulfonates (including perfluorooctane sulfonate – PFOS) and perfluorinated carboxylic acids (PFCAs), were found to be widely distributed over the northern hemisphere, including remote areas such as the Arctic (Bossi et al., 2005; Giesy and Kannan, 2001; Verreault et al., 2005). The physico-chemical properties of PFAS suggest that these compounds are poor candidates for long-range atmospheric transport. Worldwide dissemination of perfluorinated compounds must therefore occur either by way of airborne neutral precursors such as fluorotelomer alcohols (FTOHs), by oceanic transport as dissolved or by long-range transport as bound to particles in water or air (Prevedouros et al., 2006; Simcik, 2005). Unlike legacy POPs, the amphiphilic PFAS have not been shown to accumulate preferentially in adipose tissue. They rather bind to blood proteins and accumulate in the liver of exposed organisms (Jones et al., 2003; Vanden Heuvel et al., 1991a,b). Experimental effect studies have demonstrated the toxicity of a number of perfluorinated substances through impedence of cell-to-cell communication and peroxisome proliferation, which are both mechanisms for hepatocarcinogenesis (Berthiaume and Wallace, 2002; Hu et al., 2002; Upham et al., 1998). Moreover, some PFAS are also suggested to affect lipid metabolism and reproduction (Haugom and Spydevold, 1992; Lau et al., 2003; Thibodeaux et al., 2003).

Despite being amphiphilic, PFAS demonstrate bioaccumulation tendencies due to their ability to bind to proteins. Their degree of bioaccumulation generally increases with perfluoroalkyl chain length (Martin et al., 2003a,b) and trophic position (Van de Vijver et al., 2003). Quantification of bioaccumulation potential has primarily been developed for lipid soluble substances. Consequently, their modelling estimations are based on octanol–water partitioning ($\log K_{ow}$) properties (Collander, 1951). However, $\log K_{ow}$ is not measurable for most PFAS (Golovanov and Tsygankova, 2001), and quantification of bioaccumulation based on empirical data is therefore essential to

understand the fate of PFAS and their impact on marine ecosystems. Field studies from the Canadian Arctic have indicated biomagnification of PFOS in aquatic food webs (Kannan et al., 2005; Martin et al., 2004; Tomy et al., 2004a). However, no research on food web bioaccumulation of PFAS has so far been conducted in the European Arctic.

The present study is an assessment of four selected species from the Barents Sea ice edge food web. The investigated species included the ice-associated (sympagic) amphipod *Gammarus wilkitzkii*, polar cod (*Boreogadus saida*), black guillemot (*Cepphus grylle*) and glaucous gull (*Larus hyperboreus*). The main objective was to assess whether PFAS show similar bioaccumulative behaviour as lipid soluble POPs in the selected species, particularly emphasizing the potential for biomagnification.

2. Materials and methods

2.1. Sampling procedures and sample preparation

All organisms were collected in the Barents Sea east of Svalbard (77–79°N, 30°E) in May–July 2004. Mass samples of the ice amphipod *G. wilkitzkii* were collected from ice-floes with an electrical suction pump operated by SCUBA divers (Lønne, 1988). Only specimens >20 mm (≥ 2 years) were kept for analysis. Polar cod ($n = 50$) were collected with a Campelen 1800 bottom trawl deployed from R/V *Jan Mayen*. Adult black guillemots ($n = 18$) and glaucous gulls ($n = 9$) (based on plumage) were sampled using a shotgun. All organisms were weighed and wrapped in aluminum foil before storage at -20°C . In addition, fish fork-lengths were measured; they ranged from 11.5–17.0 cm corresponding to 1–4-year-old (Falk-Petersen et al., 1986), which is within the size-range eaten by black guillemot and glaucous gull in the Barents Sea (Brikstad, 1990; Mehlum and Gabrielsen, 1993). In the lab, wing length, bill + head length and tarsus length were recorded for the seabirds before dissection. For both seabirds and fish, liver and muscle samples were obtained from each specimen for analyses of contaminants and stable isotopes, respectively. Furthermore, the stomach content was analyzed and sex was determined. All organisms used in the study appeared in good nutritional condition.

Prior to extraction, whole livers were homogenized using a blender (Ultra-turrax T 25, Janke & Kunkel, IKA Labortechnik, Staufen, Germany). Due to the small size of the polar cod liver, samples from three fish of similar length (two female and one male) were pooled ($n = 16$) for the analyses. The amphipods (whole body) were pooled ($n = 6$) according to length to gain homogenized samples of at least 1 g.

2.2. Analysis of PFAS

All liver samples of polar cod, black guillemot and glaucous gull, as well as whole amphipods, were analyzed for fluorinated compounds according to the method described by Berger and Haukås (2005). In short, approximately 1 g of sample homogenate was spiked with 20 ng of internal standard (ISTD) (7H-PFHpA; Table 1), before 3 mL of 2 mM ammonium acetate in methanol:water (1:1, by volume) was added. The sample was allowed to extract for 30 min in an ultrasonic bath. After extraction, the mixture was first filtrated through Kleanex on the tip of a Pasteur-pipette, and the resulting solution was filtrated further through a Microcon YM-3 centrifugal filter (14 000 rpm, ~ 30 min). The final extract was transferred to an autoinjector vial, weighed, and 2 ng recovery standard (3,5-BTPA; Table 1) was added.

The separation and quantification method was based on high performance liquid chromatography (HPLC) in combination with time-of-flight mass spectrometry. Briefly, separation was performed on a C_{18} column employing a binary gradient of 2 mM ammonium acetate in both methanol and water. Electrospray ionization in the negative ion mode (ESI $^{-}$) was used applying an alternating cone voltage of 20 and 40 V. Mass spectra were recorded in

Table 1
Fluorinated analytes and standard compounds with abbreviations, high-resolution ion mass to charge ratio (*m/z*) used for quantification and method detection limits

Compound	Abbreviation	Quantification mass (<i>m/z</i>)	Method detection limit (ng g ⁻¹ wet weight)			
			Ice amphipod	Polar cod	Black guillemot	Glaucous gull
Perfluorobutane sulfonate	PFBS	298.94	0.20	0.16	0.14	0.18
Perfluorohexane sulfonate	PFHxS	398.94	0.03	0.04	0.15	0.06
Perfluorooctane sulfonate	PFOS	498.93	0.26	0.23	2.57	0.30
Perfluorodecane sulfonate	PFDS	598.92	>15	>15	>15	>15
Perfluorohexanoic acid	PFHxA	268.98	0.41	0.22	0.22	0.22
Perfluoroheptanoic acid	PFHpA	318.98	0.42	0.44	0.83	0.56
Perfluorooctanoic acid	PFOA	368.98	1.25	1.25	6.60	1.28
Perfluorononanoic acid	PFNA	418.97	0.33	0.24	2.69	1.00
Perfluorodecanoic acid	PFDA	468.97	2.40	0.32	>15	3.40
Perfluoroundecanoic acid	PFUnA	518.97	0.72	0.75	>15	>15
Perfluorododecanoic acid	PFDoA	568.96	>15	>15	>15	>15
Perfluorotetradecanoic acid	PFTeA	668.96	>15	>15	>15	>15
6:2 Fluorotelomer sulfonate	6:2 FTS	426.97	0.21	0.40	2.64	0.70
Perfluorooctane sulfonamide	PFOSA	497.95	0.77	5.59	3.22	9.80
7H-Perfluoroheptanoic acid ^a	7H-PFHpA	280.98	—	—	—	—
3,5-Bis(trifluoromethyl)phenyl acetic acid ^b	3,5-BTPA	227.03	—	—	—	—

^a Used as internal standard.

^b Used as recovery standard.

the full-scan mode. For quantification, the internal standard method was applied, using 7H-PFHpA as ISTD. For correction of matrix effect, external quantification standards were dissolved in an authentic matrix extract for each matrix. Integration was performed in extracted mass chromatograms using the high-resolution mass to charge ratios given in Table 1 and a typical mass tolerance of 0.06 u.

Method validation included method blanks, repeatability checks, recovery experiments, intra-lab method comparison and determination of the method detection limit (MDL) (Berger and Haukås, 2005). The MDL was defined as the higher value of the following two alternatives: (1) mean plus three standard deviations (SD) of a series of five blind extractions from *n*-hexadecane; (2) signal-to-noise ratio of three in the chromatogram of a sample extract from spiked liver calculated relatively to external standards diluted in the corresponding liver extract. Blank values were not subtracted due to relatively large variation in blank values and the fact that they were accounted for in the conservative MDL. Recoveries typically ranged from 60 to 115%.

MDLs for the screening method were in the range 0.03–1.3 ng g⁻¹ wet weight for most PFAS, except for the long-chain and less polar compounds (PFDS, PFUnA, PFDoA, PFTeA, PFOSA) which had MDLs > 15 ng g⁻¹ wet weight (Table 1). Some long-chain PFAS had lower recoveries than the ISTD (Berger and Haukås, 2005). Concentrations of these compounds may have been underestimated as no correction was performed for the differences in recoveries between the analytes and the ISTD. Some quantified values (given in Table 2) are thus lower than the MDL for the respective compound.

2.3. Analysis of organochlorines and organobromines

Pooled whole individuals of *G. wilkitzkii* (*n* = 6), and liver samples of polar cod (*n* = 9, pooled), black guillemot (*n* = 10) and glaucous gull (*n* = 9), were analyzed for organochlorine compounds (OCs) and polybrominated diphenyl ethers (PBDEs). Based on results from the PFAS analysis, the samples selected represented the whole range of PFAS concentrations. Prior to analysis, samples were extracted and prepared according to methods by Herzke et al. (2003). In short, sample homogenates were dried in a 10-fold amount of sodium sulfate, spiked with isotope labeled internal standards (see below) and subsequently extracted using cyclohexane/acetone (3:1; by volume). A fraction of the resulting extract was used to determine extractable organic matter gravimetrically. In order to remove lipids, gel permeation chromatography (GPC) was applied. An additional fractionation was carried out on a florisil column. A recovery standard (octachloronaphthalene) was added prior to quantification.

Sample extracts were analyzed using gas chromatography and low-resolution quadrupole mass spectrometry operated in the electron impact mode (GC/

EI-MS). Separations were performed on a 30 m DB5-MS capillary column as described by Herzke et al. (2005). The samples were analyzed for the content of polychlorinated biphenyls (PCB-28, -52, -99, -101, -105, -118, -153, -156, -180, -183, -187, -194), dichlorodiphenyltrichloroethane compounds (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *o,p'*-DDD) and polybrominated diphenyl ethers (PBDE-28, -47, -71, -77, -99, -100, -138, -153, -154, -183). Quantification was performed using the internal standard method, applying ¹³C-PCB congeners 28, 52, 118, 153 and 180 as ISTDs for the PCB and DDT analyses and ¹³C-PBDE congeners 28, 47, 99, 153 and 183 for the PBDE analyses. The quality of the method used is verified regularly in international inter-calibration studies (QUASIMEME, BROCC) and with certified reference materials. Method blanks were analyzed with every 10th sample. No background concentrations were detected in the blank samples, and the MDL was hence evaluated based on a signal-to-noise ratio of three in sample chromatograms. Recoveries of the ISTDs typically ranged from 40 to 80%.

Method detection limits for the chlorinated and brominated compounds ranged from 0.02 to 0.57 ng g⁻¹ wet weight for polar cod, black guillemot and glaucous gull. For the ice amphipod samples, MDLs ranged from 0.60 to 3.41 ng g⁻¹ wet weight.

2.4. Analysis of stable isotopes

Stable nitrogen isotope ratios were analyzed in muscle samples from polar cod (*n* = 11 pools), black guillemot (*n* = 18), and glaucous gull (*n* = 9), as well as whole specimen of *G. wilkitzkii* (*n* = 6). The analyses were performed at the Institute for Energy Technology, Kjeller, Norway as described by Hop et al. (2002). Stable isotope concentrations were expressed as:

$$\delta^{15}\text{N} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000, \quad (1)$$

where *R* is the corresponding ratio of ¹⁵N/¹⁴N, related to the standard values.

2.5. Trophic level and biomagnification factors

For each individual sample, the trophic level was determined using the relationship established by Fisk et al. (2001):

$$\text{TL}_{\text{consumer}} = 2 + \frac{(\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{C. hyperboreus}})}{3.8}, \quad (2)$$

where *TL*_{consumer} is the trophic level of the organism and ¹⁵N_{*C. hyperboreus*} is determined as 7.3 ± 0.2 (mean ± SE for the Barents Sea, May 1999)

Table 2

Concentrations in ng g⁻¹ wet weight of all analyzed contaminants (mean \pm SE, range and median) for whole ice amphipods, as well as liver of polar cod, black guillemot and glaucous gull

Analyte	Ice amphipod				Polar cod				Black guillemot				Glaucous gull			
	n	Mean \pm SE	Range	Median	n	Mean \pm SE	Range	Median	n	Mean \pm SE	Range	Median	n	Mean \pm SE	Range	Median
Lipid % ^a	6/6	5.39 \pm 0.45	3.69–6.60	5.54	9/9	41.8 \pm 1.39	35.9–48.1	41.5	10/10	6.79 \pm 0.91	4.01–13.3	5.93	9/9	6.20 \pm 1.05	3.24–14.1	5.5
6:2 FTS	3/6	0.48 \pm 0.24	n.d.–1.68	0.22	–	n.d.	n.d.	n.d.	1/18	–	n.d.–3.41	–	–	n.d.	n.d.	n.d.
p,p'-DDE	–	n.d. ^b	n.d.	n.d.	9/16	0.04 \pm 0.003	n.d.–0.07	0.04	17/18	0.17 \pm 0.02	n.d.–0.36	0.16	9/9	0.26 \pm 0.06	0.04–0.61	0.28
p,p'-DDT	5/6	3.85 \pm 1.17	n.d.–7.41	3.62	16/16	2.02 \pm 0.13	1.07–2.85	2.15	17/18	13.5 \pm 2.79	n.d.–43.8	11.2	9/9	65.8 \pm 22.4	8.49–225	38.4
p,p'-DDE	–	n.d.	n.d.	n.d.	16/16	2.22 \pm 0.34	0.64–5.38	2.06	3/18	–	n.d.–0.39	–	2/9	–	n.d.–1.55	–
p,p'-DDD	6/6	3.15 \pm 0.34	2.07–4.33	3.24	3/16	–	n.d.–1.88	–	5/18	–	n.d.–1.71	–	–	n.d.	n.d.	n.d.
p,p'-DDT	–	n.d.	n.d.	n.d.	14/16	0.20 \pm 0.02	n.d.–0.30	0.19	15/18	1.13 \pm 0.08	n.d.–1.60	1.28	8/9	1.90 \pm 0.42	n.d.–4.74	1.46
p,p'-DDT	–	n.d.	n.d.	n.d.	7/16	–	n.d.–0.44	–	–	n.d.	n.d.	n.d.	3/9	–	n.d.–9.43	–
p,p'-DDT	6/6	7.35 \pm 1.61	3.22–12.0	6.62	16/16	4.88 \pm 0.52	2.25–8.01	4.54	18/18	16.7 \pm 3.39	0.28–46.3	11.9	9/9	69.6 \pm 23.7	9.56–240	39.8
PCB-28	–	n.d.	n.d.	n.d.	9/9	2.64 \pm 0.15	1.88–3.26	2.66	10/10	1.25 \pm 0.17	0.58–2.14	1.04	9/9	8.24 \pm 2.23	2.48–24.6	6.84
PCB-52	–	n.d.	n.d.	n.d.	9/9	2.27 \pm 0.16	1.57–2.98	2.27	10/10	0.74 \pm 0.11	0.44–1.46	0.60	9/9	3.53 \pm 1.39	0.16–11.9	1.50
PCB-99	–	n.d.	n.d.	n.d.	9/9	1.90 \pm 0.18	1.23–3.03	1.97	10/10	4.31 \pm 0.58	1.95–7.13	3.86	9/9	122 \pm 25.0	44.7–286	109
PCB-101	–	n.d.	n.d.	n.d.	9/9	2.50 \pm 0.19	1.63–3.42	2.68	10/10	2.08 \pm 0.33	0.77–4.31	1.88	9/9	11.0 \pm 3.21	2.15–24.6	7.48
PCB-105	–	n.d.	n.d.	n.d.	8/9	0.66 \pm 0.09	n.d.–0.93	0.75	10/10	2.08 \pm 0.28	0.95–3.64	1.94	9/9	37.2 \pm 9.61	8.55–101	32.6
PCB-118	–	n.d.	n.d.	n.d.	9/9	2.56 \pm 0.23	1.74–3.83	2.74	10/10	7.36 \pm 1.03	3.11–12.5	6.53	9/9	184 \pm 42.0	50.1–456	166
PCB-138	–	n.d.	n.d.	n.d.	9/9	3.59 \pm 0.36	2.30–5.80	3.86	10/10	11.6 \pm 1.68	4.72–19.5	10.2	9/9	411 \pm 87.8	130–978	346
PCB-153	1/6	–	n.d.–1.63	–	9/9	3.65 \pm 0.36	2.36–5.76	3.93	10/10	12.0 \pm 1.78	4.87–21.8	11.0	9/9	510 \pm 103	183–1160	445
PCB-156	–	n.d.	n.d.	n.d.	9/9	1.41 \pm 1.08	0.18–10.0	0.34	10/10	0.53 \pm 0.10	0.21–1.26	0.38	9/9	2.2 \pm 5.38	6.56–53.8	17.0
PCB-180	–	n.d.	n.d.	n.d.	9/9	0.77 \pm 0.11	0.42–1.52	0.73	10/10	3.31 \pm 0.54	1.23–6.38	3.43	9/9	217 \pm 43.1	80.1–479	194
PCB-183	–	n.d.	n.d.	n.d.	7/9	0.22 \pm 0.04	n.d.–0.44	0.19	10/10	0.86 \pm 0.13	0.33–1.59	0.88	9/9	39.1 \pm 7.89	13.7–87.5	40.4
PCB-187	–	n.d.	n.d.	n.d.	9/9	0.78 \pm 0.09	0.39–1.20	0.80	10/10	3.11 \pm 0.47	1.35–5.87	3.03	9/9	88.7 \pm 18.2	30.1–175	85.9
PCB-194	–	n.d.	n.d.	n.d.	7/9	8.36 \pm 7.57	n.d.–68.9	0.75	9/10	0.25 \pm 0.05	n.d.–0.47	0.27	9/9	30.6 \pm 5.41	14.8–59.3	25.8
ΣPCB(13)	–	n.d.	n.d.	n.d.	9/9	31.4 \pm 9.96	14.9–110	24.4	10/10	49.5 \pm 7.02	21.0–83.5	43.6	9/9	1680 \pm 346	592–3890	1510
p,p'-DDT	–	n.d.	n.d.	n.d.	9/9	3.17 \pm 0.44	1.56–6.23	2.92	2/10	–	n.d.–0.50	–	2/9	–	n.d.–3.10	–
p,p'-DDT	–	n.d.	n.d.	n.d.	9/9	2.87 \pm 0.24	1.92–4.14	2.81	10/10	0.71 \pm 0.17	0.22–2.10	0.58	9/9	3.93 \pm 1.62	0.30–15.1	1.37
p,p'-DDE	2/6	–	n.d.–5.62	–	9/9	10.9 \pm 0.98	7.25–16.5	11.7	10/10	30.1 \pm 4.07	14.1–48.9	27.0	9/9	2370 \pm 341	867–3730	2640
p,p'-DDE	–	n.d.	n.d.	n.d.	9/9	0.59 \pm 0.04	0.42–0.72	0.61	–	n.d.	n.d.	n.d.	6/9	0.27 \pm 0.14	n.d.–1.33	0.17
p,p'-DDD	–	n.d.	n.d.	n.d.	9/9	3.30 \pm 1.38	1.41–14.2	1.84	10/10	0.35 \pm 0.08	0.17–1.06	0.26	1/9	–	n.d.–0.60	–
ΣDDT(5)	–	n.d.	n.d.	n.d.	9/9	20.8 \pm 2.62	12.7–39.6	19.7	10/10	31.3 \pm 4.28	14.5–52.5	27.6	9/9	2380 \pm 341	868–3740	2650
PBDE-28	–	n.d.	n.d.	n.d.	9/9	0.43 \pm 0.03	0.27–0.54	0.42	10/10	0.56 \pm 0.08	0.35–1.04	0.47	9/9	1.43 \pm 0.46	0.33–4.65	0.78
PBDE-47	–	n.d.	n.d.	n.d.	9/9	1.04 \pm 0.10	0.57–1.41	1.03	10/10	2.29 \pm 0.34	1.08–4.03	1.95	9/9	38.9 \pm 11.8	11.8–127	28.0
PBDE-71	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	9/9	0.70 \pm 0.20	0.17–1.82	0.49
PBDE-77	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	1/9	–	n.d.–0.08	–
PBDE-99	–	n.d.	n.d.	n.d.	1/9	–	n.d.–0.20	–	6/10	0.14 \pm 0.03	n.d.–0.31	0.08	9/9	4.98 \pm 1.06	1.84–12.3	4.60
PBDE-100	–	n.d.	n.d.	n.d.	1/9	–	n.d.–0.15	–	9/10	0.30 \pm 0.06	n.d.–0.61	0.28	9/9	6.86 \pm 2.00	1.78–21.5	4.62
PBDE-138	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.
PBDE-153	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	9/9	3.53 \pm 0.90	0.79–9.77	3.05
PBDE-154	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	5/10	0.18 \pm 0.04	n.d.–0.49	0.12	9/9	2.66 \pm 0.86	0.90–9.39	2.03
PBDE-183	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	–	n.d.	n.d.	n.d.	1/9	–	n.d.–0.41	–
ΣPBDE(10)	–	n.d.	n.d.	n.d.	9/9	1.50 \pm 0.15	0.88–2.24	1.50	10/10	3.45 \pm 0.54	1.55–6.33	2.91	9/9	59.1 \pm 17.2	19.9–186	41.4

Mean and median concentrations are given for compounds with sample detection ratio (*n*) \geq 0.50. Compounds only shown in Table 1 were not detected at their MDL.^a Percent extractable organic matter in the analyzed tissue.^b Not detected.

(Søreide and Hop, 2003). The used trophic enrichment factor of 3.8 was defined by Hobson and Welch (1992). Recent research, however, has suggested that a factor of 3.4 might better represent the Barents Sea marine food web (Søreide et al., 2006). Applying an adjusted diet-tissue fractionation of 2.4th for seabirds (Hobson and Welch, 1992; Mizutani et al., 1991), Eq. (2) can be modified, as described by Hop et al. (2002) to:

$$TL_{\text{bird}} = 3 + \frac{(\delta^{15}N_{\text{bird}} - 9.7)}{3.8} \quad (3)$$

The extent of biomagnification can be expressed in the form of biomagnification factors (BMFs). BMFs in the present study are compound-specific, trophic level-corrected factors of concentration increase from prey to predator, and were calculated by applying the following equation from Hop et al. (2002):

$$BMF = \frac{[CONT]_{\text{predator}}}{[CONT]_{\text{prey}} \cdot TL_{\text{predator}} - TL_{\text{prey}}} \quad (4)$$

where [CONT] is the contaminant's concentration. BMF values >1 indicate biomagnification.

2.6. Data analysis

For all compounds found in <50% of the samples of a given species, no statistics is presented. For the compounds included in statistical analyses, half detection limit for the respective compound replaced the samples below detection limit in order to avoid missing data in the computation. All inferential statistics were computed in R 1.9.1 for Windows, Statistica version 6 for Windows (StatSoft, Inc., Tulsa, OK, USA) and CANOCO 4.5 for Windows (Ter Braak and Šmilauer, 2002). The statistical significance level was set at $\alpha \leq 0.05$.

Analysis of variance (ANOVA) was conducted to test for possible differences in contaminant concentration and lipid percentage between female and male seabirds. There were no differences in gender, and males and females in a species were accordingly treated as one group. When analyzing the differences in mean contaminant concentrations between species, ANOVA and Tukey's honestly significant difference (HSD) tests were employed. The possible influence of body weight, size and trophic level on the contaminant concentration was analyzed using linear regression and the generalized additive model (GAM). The Shapiro–Wilks' W test was used to test for normality. Linearity and constant variance were evaluated by the means of diagnostic plots. Log-transformation of variables was performed to obtain normality and reduce variance heterogeneity and skewness. Since the chlorinated and brominated organic substances are highly lipid soluble, their concentrations were lipid normalized before analysis.

Multivariate statistical analyses performed excluded the ice amphipod due to the low number of compounds detected in this organism. Principal component analysis (PCA) was performed to describe the main patterns of variation in contaminant concentration within species. Additionally, one PCA included

all three species (polar cod, black guillemot, glaucous gull) for each of the four contaminant groups separately: PFAS (3 compounds), PCBs (13), DDTs (2) and PBDEs (2). Every group was comprised only by analytes found in all three species (Table 2). In all the four PCAs, the first principal component axis (PC1) accounted for at least 95% of the variance in the contaminant concentrations. The PC1 sample scores representing each of the four contaminant groups were subsequently applied in a multivariate analysis of variance (MANOVA), a redundancy analysis (RDA) and in linear regression analysis. RDA is a direct (constrained) multivariate ordination analysis that was applied in order to relate contaminant concentrations to the explanatory variable trophic level (TL). The significance of all canonical axes was tested using Monte Carlo test with unrestricted permutations. Linear regression analysis was also conducted to test the relationships between trophic level and PC1 sample scores for each contaminant group.

3. Results

3.1. Concentrations and contribution of PFAS

PFOS showed the highest concentrations of the detected fluorinated compounds in all species studied, with values up to 225 ng g⁻¹ in glaucous gull (Table 2). In addition, PFOS was the only analyte found in all four species. Mean concentrations (ng g⁻¹ wet weight) of PFOS increased in the order polar cod (2.02) < ice amphipod (3.85) < black guillemot (13.5) < glaucous gull (65.8). 6:2 Fluorotelomer sulfonate (6:2 FTS), perfluorohexane sulfonate (PFHxS), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) were detected in at least two of the investigated species. Of these analytes, the highest concentration was found for PFOA in black guillemot (17.1 ng g⁻¹) followed by PFDA in glaucous gull (9.43 ng g⁻¹). In the ice amphipod, only the more hydrophilic 6:2 FTS and PFOA were detected in addition to PFOS.

PFOS had the largest relative contribution of the individual PFAS congeners and constituted 52, 41, 80 and 94% of all detected fluorinated compounds in ice amphipods, polar cod, black guillemot and glaucous gull, respectively (Fig. 1A). The relative contribution of "other PFAS" (congeners not detected in all species) decreased from fish and ice amphipods to birds (Tukey's HSD, $p < 0.05$). PFHxS and PFNA were detected in all species except for the ice amphipod. There was

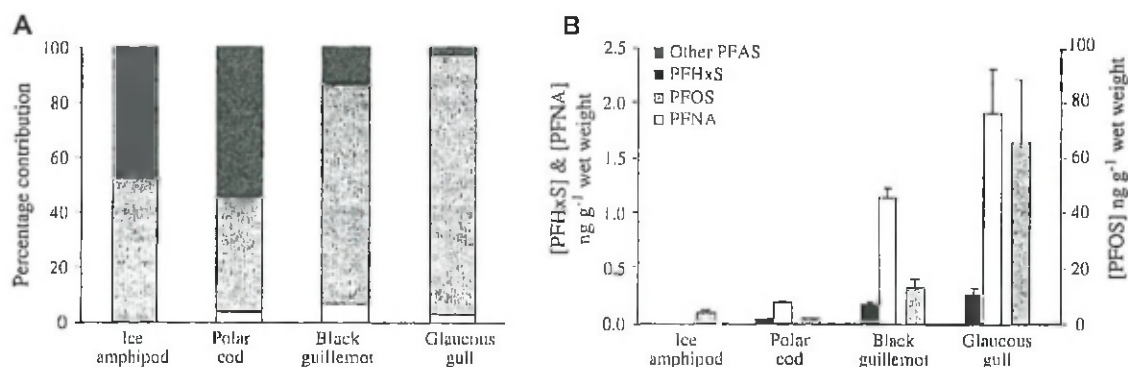


Fig. 1. Relative contribution to Σ PFAS(7) (A) and mean concentrations (\pm SE) in ng g⁻¹ wet weight (B) of PFHxS, PFOS, PFNA in ice amphipod, polar cod, black guillemot and glaucous gull. Concentrations are displayed on two different axes.

an apparent increase in concentrations of PFOS, PFHxS and PFNA from ice amphipod and/or polar cod via black guillemot to glaucous gull (Fig. 1B). However, concentrations of PFHxS and PFNA did not differ significantly between the birds, and PFOS levels were similar in polar cod and amphipods (Tukey's HSD, $p > 0.05$). No correlations were found between PFOS concentration and body weight/size of seabirds or between PFOS concentrations and body weight of polar cod. Nevertheless, there was a positive relationship between PFOS concentration and polar cod fork-length ($\beta_1 = 2.42$, adjusted $R^2 = 0.19$, $F_{1,14} = 4.62$, $p = 0.05$).

3.2. Concentrations and contribution of OCs and PBDEs

Probably due to the relatively high MDLs and low sample amounts, no chlorinated or brominated congeners were detected in *G. wilkitzkii*, except for PCB-153 in one sample, and *p,p'*-DDE in two samples (Table 2). The concentrations of chlorinated and brominated analytes showed highest values for PCB-138 and PCB-153, *p,p'*-DDE and PBDE-47 in all species analyzed. PCBs and DDTs were the most abundant of the analyzed contaminant groups, and contributed therefore most to the overall burden of contaminants (Fig. 2A). Although there were differences between individual analytes, the concentrations of OCs and PBDEs generally increased in the order polar cod < black guillemot < glaucous gull (Fig. 2B) (Tukey's HSD, $p < 0.05$).

3.3. Trophic level and transfer of PFOS

A wide range of $\delta^{15}\text{N}$ (6.7–16.7‰) was found in the investigated species. The ice amphipod represented the second trophic level (Fig. 3) (mean TL 2.0), whereas polar cod was intermediate between the third and the fourth level (mean TL 3.7). Black guillemot (mean TL 4.3) and glaucous gull (mean TL 4.5) represented trophic levels 4–5. All species differed significantly in mean trophic level, except for black guillemot and glaucous gull (Tukey's HSD, $p < 0.05$ for all but one pairwise comparison).

PFOS levels differed significantly among species (ANOVA, $F_{4,40} = 20.4$, $p < 0.001$) except between ice amphipods and polar cod (data from Table 2). There was an increase in PFOS concentration from amphipods and fish to black guillemot and glaucous gull (Tukey's HSD, $p < 0.05$ for all but one pairwise comparison). No correlation was found between PFOS concentration and trophic level within species. Nevertheless, a non-linear relationship was established when the entire food web was analyzed (Fig. 3) (ANOVA on GAM; $\text{d.f.} = 1.89$, Chi square = 18.7, $p < 0.001$). When excluding the ice amphipod samples from the model, the relationship between PFOS and trophic level was significantly linear ($\beta_1 = 2.68$, adjusted $R^2 = 0.48$, $F_{1,36} = 35.0$, $p < 0.001$).

3.4. Biomagnification factors

Biomagnification factors (BMFs) were based on predator–prey relationships inferred from literature and stomach content information, and corrected to unity for trophic level differences (Eq. (4)). BMFs based on presumed mixed diets were also calculated. The mixed diet comprised of 20% ice amphipods and 80% polar cod for black guillemot, and 20% ice amphipods, 50% polar cod and 30% black guillemot for glaucous gull. The mixed diet compositions represented one trophic level lower than the trophic positions for the birds in question. Mean contaminant concentrations (ng g^{-1} wet weight for PFAS and ng g^{-1} lipid weight for OCs and PBDEs) were applied in the calculation of the BMFs.

Biomagnification factors displayed values >1 for PFHxS, PFNA, PFOS and ΣPFAS in the majority of predator–prey relationships, except for polar cod–ice amphipods (Table 3). PFOS showed the highest BMF values of the fluorinated compounds. These values were comparable to lipid normalized BMFs for PCB-28, PCB-52, PCB-101, *o,p'*-DDT and PBDE-28 for most predator–prey relationships. The only quantifiable contaminants in the ice amphipod were PFOS and $\Sigma\text{PFAS}(7)$, and, consequently, these were the only two analytes for which the BMFs could be calculated based on the mixed diet. In both cases (PFOS, $\Sigma\text{PFAS}(7)$), the biomagnification factors deviated considerably from that of only one prey species.

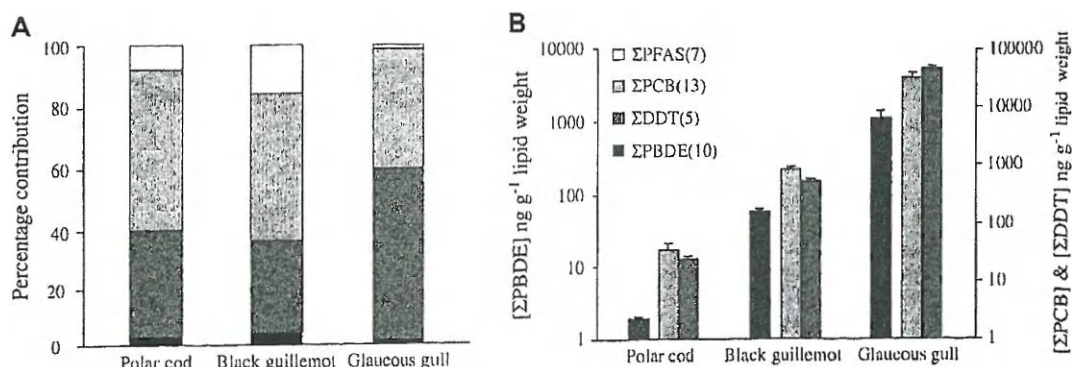


Fig. 2. Relative contribution to total contaminant burden (A), as well as mean concentrations ($\pm\text{SE}$) in ng g^{-1} lipid weight (B) of $\Sigma\text{PCB}(13)$, $\Sigma\text{DDT}(5)$, and $\Sigma\text{PBDE}(10)$ in polar cod, black guillemot and glaucous gull liver. Concentrations are displayed on two different logarithmic axes. Colour codes are similar for A and B.

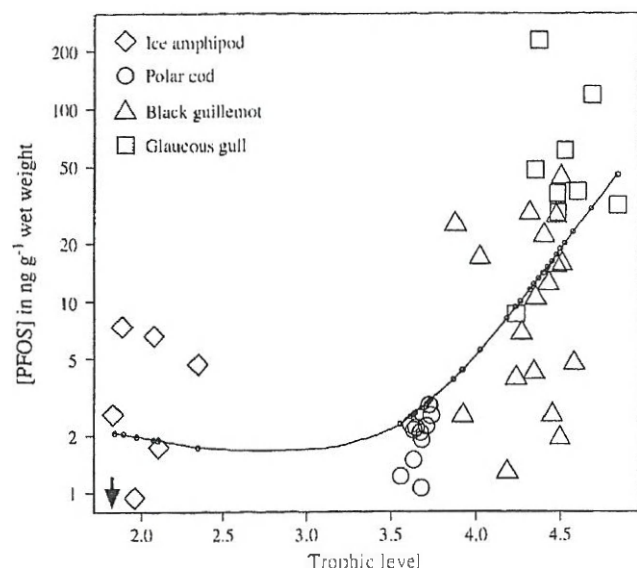


Fig. 3. Relationship between concentrations (ng g^{-1} wet weight) of perfluorooctane sulfonate (PFOS) and trophic level, quantified by $\delta^{15}\text{N}$, for the ice edge food web consisting of ice amphipod, polar cod, black guillemot and glaucous gull. The trendline follows predicted values (small dots) of a generalized additive model. The arrow illustrates that one amphipod sample (0.1 ng g^{-1} wet weight concentration) is outside the range of the logarithmical y-axis.

3.5. PFAS behaviour compared to lipid soluble POPs

Applying principal component analysis on concentrations of $\Sigma\text{PFAS}(7)$ together with $\Sigma\text{PCB}(13)$, $\Sigma\text{DDT}(5)$ and $\Sigma\text{PBDE}(10)$ in the three species (polar cod, black guillemot, glaucous gull) separately, the relationship between the four contaminant groups within each species could be determined through evaluation of correlation biplots (Fig. 4). In all three species, $\Sigma\text{PFAS}(7)$ displayed no significant correlation with $\Sigma\text{PCB}(13)$, $\Sigma\text{DDT}(5)$ and $\Sigma\text{PBDE}(10)$. Chlorinated and brominated compounds on the other hand, were positively correlated. Although, in polar cod only the correlation between $\Sigma\text{PCB}(13)$ and $\Sigma\text{DDT}(5)$ was statistically significant.

Concentrations of the four compound groups differed between species (MANOVA, approximately $F_{3,22} = 17.0$, $p < 0.001$). Redundancy analysis (RDA), using scores from PCA for each contaminant group, showed that 67.2% of the total variance in concentration of PFAS, PCBs, DDTs and PBDEs in the liver samples could be explained by trophic level (Fig. 5). Further, the RDA revealed a significant relationship between the variance in contaminant concentration and trophic level (TL) (Monte Carlo $F = 37.1$, $p = 0.002$). Despite the apparent differences in concentrations between the contaminant groups within species (Fig. 4), there were significant positive correlations between the four contaminant groups and trophic level when including all species (Table 4, Fig. 5).

Table 3
Species specific and trophic level-corrected biomagnification factors (BMF) for PFAS, PCBs, DDTs and PBDEs in the Barents Sea ice edge food web including ice amphipod, polar cod, black guillemot and glaucous gull

	Biomagnification factors (BMF)						
	P. cod/I. amph.	B. guill./I. amph.	B. guill./P. cod	G. gull/P. cod	G. gull/B. guill.	B. guill./mix diet ^a	G. gull/mix diet
$\text{TL}_{\text{predator}} - \text{TL}_{\text{prey}}^b$	1.62	2.28	0.66	0.84	0.18	1.00	1.00
PFHxS	—	—	6.00	7.20	8.49	—	—
PFOS	0.32	1.54	10.1	38.7	27.0	5.66	11.3
PFNA	—	—	8.76	11.6	9.34	—	—
$\Sigma\text{PFAS}(7)$	0.41	1.01	5.25	16.9	22.8	3.15	7.72
PCB-28	—	—	9.73	59.8	43.5	—	—
PCB-52	—	—	6.76	30.9	32.3	—	—
PCB-99	—	—	48.6	1270	185	—	—
PCB-101	—	—	17.4	86.8	35.3	—	—
PCB-105	—	—	66.1	1010	108	—	—
PCB-118	—	—	59.5	1310	155	—	—
PCB-138	—	—	69.0	2230	229	—	—
PCB-153	—	—	69.3	2710	277	—	—
PCB-156	—	—	9.62	354	260	—	—
PCB-180	—	—	88.3	5440	436	—	—
PCB-183	—	—	84.1	3560	299	—	—
PCB-187	—	—	82.6	2140	183	—	—
PCB-194	—	—	0.77	88.9	811	—	—
$\Sigma\text{PCB}(13)$	—	—	35.6	1100	219	—	—
<i>o,p'</i> -DDT	—	—	4.62	27.3	41.7	—	—
<i>p,p'</i> -DDE	—	—	58.5	4350	526	—	—
$\Sigma\text{DDT}(5)$	—	—	32.2	2320	509	—	—
PBDE-28	—	—	28.1	59.9	15.1	—	—
PBDE-47	—	—	45.0	686	108	—	—
$\Sigma\text{PBDE}(10)$	—	—	46.0	723	111	—	—

^a The composition of the mixed diet is described in the text.

^b Difference in trophic level (TL) between predator and prey.

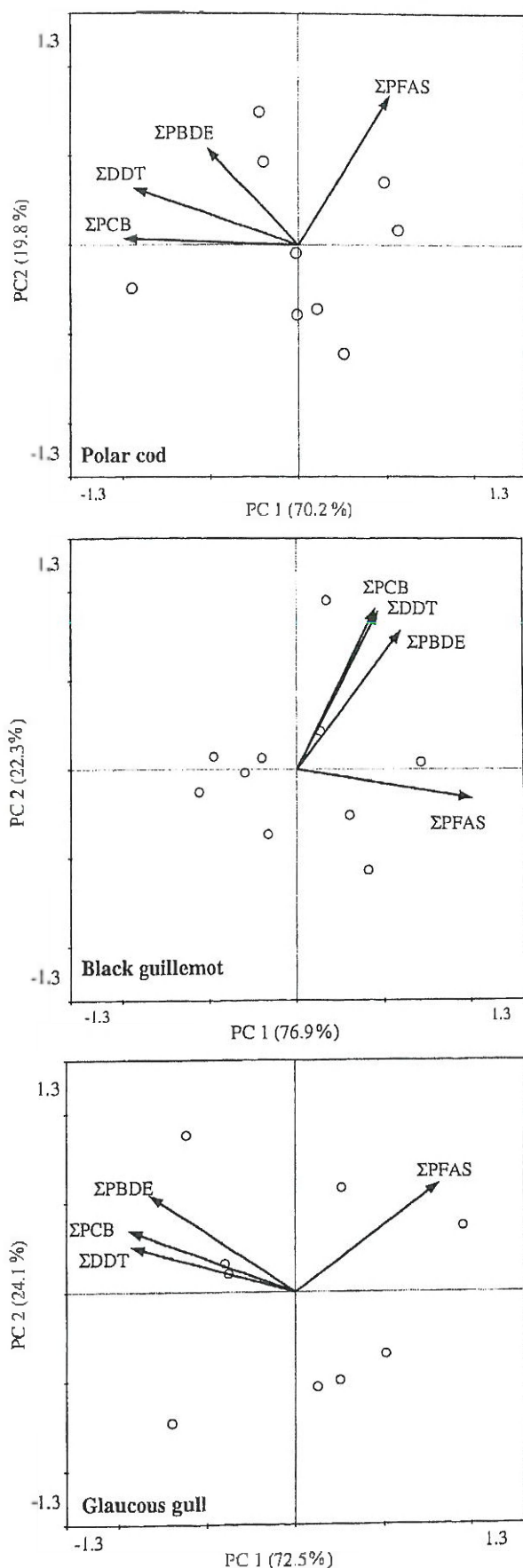


Table 4

Slope, adjusted R^2 , F -statistic with degrees of freedom and p -value for linear regressions between trophic level and PC 1-scores for the different contaminant groups

Group	Slope	R^2	$F_{1,23}$
PFAS	0.25	0.44	19.9
PCBs	0.31	0.64	43.1
DDTs	0.30	0.66	48.3
PBDEs	0.32	0.70	58.0

All slopes are significant at $p < 0.001$.

4. Discussion

4.1. Concentrations and contribution of PFAS

The concentrations of PFOS found in polar cod and black guillemot were comparable to those reported from the Canadian Arctic (Tomy et al., 2004a) and Greenland (Bossi et al., 2005), respectively. The liver levels of PFOS in glaucous gull are the highest reported so far in any Arctic seabird species. No previous studies have reported PFAS concentrations in *G. wilkitzkii*. The detection of PFHxS, PFOS and PFNA in most of the liver samples can be explained by the strong persistence of these compounds and relatively high environmental concentrations. The presence of the more hydrophilic PFOA and 6:2 FTS in ice amphipods may be due to partitioning of contaminants directly with the surrounding water. The relative contribution of PFOS compared to PFHxS, PFNA and the other detected compounds, increased from ice amphipods and fish to seabirds. This demonstrates the high biomagnification potential of PFOS.

Biological factors that may have influenced the concentration pattern of PFAS in the target species include biotransformation, feeding ecology, migration and size/age. The high relative contributions of PFOS in seabirds may be a result of retention of this compound. However, it may also be due to an ability to biotransform and excrete other less persistent fluorochemicals. More effective elimination through increased metabolic rate might explain the relative decrease of "other compounds" from ice amphipods and fish via black guillemot to glaucous gull (Livingstone et al., 1992). In addition, it has been suggested that biotransformation of perfluorooctane sulfonamide (PFOSA) and similar precursors to PFOS may affect the concentration pattern in marine organisms by increasing the relative amount of PFOS (Tomy et al., 2004a,b). Feeding ecology might also influence the bioaccumulation of fluorinated compounds. Greater feeding rates in homeotherms

Fig. 4. Correlation biplots based on principal component analysis (PCA) of pollutant concentrations (Σ PFAS(7), Σ PCB(13), Σ DDT(5), Σ PBDE(10)) in polar cod, black guillemot and glaucous gull. Circles represent individual samples, and the arrows point in the direction of steepest increase of the respective pollutants. The angles between descriptors in the biplot reflect their covariances or correlations. The percentage of pollutant concentration variance explained by each axis is given in brackets.

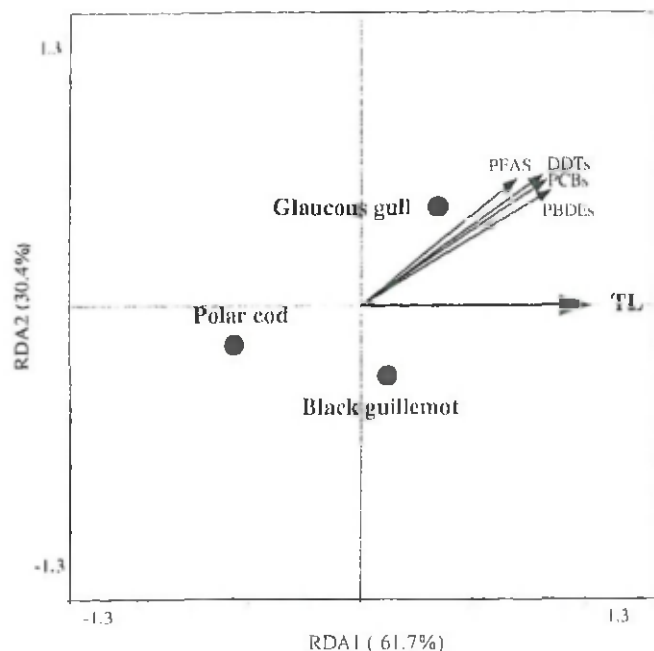


Fig. 5. Ordination diagram based on redundancy analysis (RDA) of the relationship between trophic level (TL, calculated from $\delta^{15}\text{N}$) and the contaminant concentration in polar cod, black guillemot and glaucous gull. Black circles are mean scores of samples per species, whereas thin and bold arrows are continuous response variables (scores of PFAS (3 compounds), PCBs (13), DDTs (2) and PBDEs (2) from PCA) and predictor (TL) variables, respectively. The fraction of unconstrained variance accounted for by each axis is given in brackets.

compared to poikilotherms may result in higher levels in seabirds than in fish and amphipods (Braune and Norstrom, 1989; Fisk et al., 2001; Hop et al., 2002). Migration to northern industrial areas, which are generally more exposed to per- and polyfluorinated contamination than the Arctic, may also contribute to elevated PFAS levels in seabirds. This is consistent with the high PFAS concentration found in the migrating glaucous gull compared to the resident black guillemot. Furthermore, age may have an effect on the obtained level of PFAS in organisms. For adult seabirds, however, there are no methods currently available to determine age. Nevertheless, Bustnes et al. (2003) showed that in glaucous gulls, age explained very little of the variation in OC levels. Based on their work, Borgå et al. (2004) suggested that the trophic level of birds rather than the age determines the contaminant burden. In the present study, however, a positive relationship was found between size and PFOS concentration in polar cod, indicating the effect of age on the contamination level in this species. Another important factor that may influence the concentrations of PFOS in organisms is the amount of available binding sites of proteins in the analyzed tissues, but qualitative and quantitative determinations of this are still lacking.

4.2. Concentrations and contribution of OCs and PBDEs

PCB and DDT concentrations in polar cod, black guillemot and glaucous gull were comparable to previously reported

levels from the Barents Sea and Svalbard (Borgå et al., 2001, 2005; Gabrielsen et al., 1995; Herzke et al., 2003). Moreover, recent Arctic studies of brominated compounds have documented similar concentrations of PBDEs as the current project in polar cod, black guillemot and glaucous gull (Herzke et al., 2003; Sørmo et al., 2006; Vorkamp et al., 2004). Even though hardly any chlorinated and no brominated compounds were detected in the ice amphipods, earlier studies have shown that *G. wilkitzkii* from the Barents Sea contains significant amounts of OCs and PBDEs (Borgå et al., 2002; Hop et al., 2002; Sørmo et al., 2006).

During the last 20 years, ecotoxicological studies have shown that many chlorinated and brominated compounds biomagnify in aquatic food webs. Uptake rates of most lipid soluble organohalogenes are similar among species (see Drouillard and Norstrom, 2000). It is the elimination rate that determines whether a chemical biomagnifies or not (Borgå et al., 2004). Slow elimination prevents the chemical concentration in an organism from reaching equilibrium with that in the food, and biomagnification occurs. Generally, our results support that there is biomagnification of the lipid soluble analytes in the investigated food web.

Based on wet weight in liver samples, the concentrations of $\Sigma\text{PCB}(13)$ and $\Sigma\text{DDT}(5)$ were ranging 3–24 and 2–34 times higher than $\Sigma\text{PFAS}(7)$, respectively. $\Sigma\text{PBDE}(10)$ levels, on the other hand, were consistently lower than $\Sigma\text{PFAS}(7)$. Even though these comparisons do not take into account the amount of lipids in the liver relative to the amount of potential protein binding sites for PFAS, the differences in the order of magnitude may give some indication of the accumulation potential.

4.3. Trophic level and transfer of PFOS

The calculated trophic levels for each of the species studied are comparable to those reported from similar studies in the Barents Sea (Hop et al., 2002). It is noteworthy that *G. wilkitzkii* is 1.5 trophic levels lower than polar cod, which may reflect the generally lower levels of the ^{15}N isotope in sympagic fauna relative to pelagic zooplankton given on a food base dominated by ice algae versus phytoplankton (Tamelander et al., 2006). The polar cod included in the current study were caught near the ice edge in May after the onset of melting. Even though they may have been partly influenced by the sympagic system, the gap in trophic level between *G. wilkitzkii* and polar cod could be a result of different nitrogen sources (Søreide et al., 2006). The direct transfer of contaminants from *G. wilkitzkii* to polar cod in the present study is most probably insignificant considering their diet patterns and different habitats (Lønne and Gulliksen, 1989; Poltermann, 2001). This may explain the comparable concentrations of PFOS in these two species, rather than an increase from *G. wilkitzkii* to polar cod. Increased exposure to PFOS in the sympagic environment might result from adhering of contaminants to the surface of the ice or release of contaminants from melting sea ice. The concentration of PFOS in ice amphipods relative to polar cod in the present study may, however, also reflect the use of different matrices in the chemical analyses.

4.4. Biomagnification factors

Estimated biomagnification factors (BMFs) for PFOS in the Barents Sea food web were similar or higher than the BMFs found for PFOS in the Canadian Arctic marine food web (Tomy et al., 2004a). The present study displays BMFs >1 for all the statistically analyzed PFAS in the majority of predator–prey relationships, which implies biomagnification of these compounds. Calculated BMFs for PCBs and DDTs were similar or higher than those previously reported for the Barents Sea food web (Borgå et al., 2001; Hop et al., 2002). However, for substances that partition differentially to liver tissue, the liver weight to whole amphipod body weight ratio might be a questionable BMF estimate. Regarding BMFs for all compounds, it should also be taken into consideration that the predator–prey relationship between polar cod and *G. wilkitzkii* may be somewhat unrealistic. Furthermore, pelagic polar cod and adult black guillemot only make a partial contribution to the glaucous gull diet. BMFs calculated relative to one prey species and not to a mixture of species may be difficult to interpret, as few Arctic marine predators are specialists. Variable food availability in the Arctic marine system supports a diet of mixed items for BMF calculation. The BMFs based on a mixed diet corresponding to approximately one trophic level lower than the predator should be quite representative when regarding the actual trophic transfer of PFAS.

4.5. PFAS behaviour compared to lipid soluble POPs

PFOS and PFCA concentrations in Arctic biota have been shown to display similar trends as PCB concentrations in analogous species-specific samples (Martin et al., 2004; Smithwick et al., 2005). The current project is the first to report and compare individual tissue-specific levels of lipid soluble POPs and PFAS in an Arctic marine food web. Levels of lipid soluble POPs are known to correlate among individuals of the same species due to similar mode of bioaccumulation, that is, comparable rate of uptake, distribution, storage, biotransformation and excretion (Livingstone et al., 1992). In the present study, this was supported through positive relationships between the chlorinated and brominated compounds within species. No correlations were found between the lipid soluble POPs and PFAS. This demonstrates the differences between these contaminant groups in compound-specific physicochemical properties such as lipid solubility and binding affinity to proteins. The fluorinated compounds are thus not accumulated through the same physiological pathways as PCBs, DDTs and PBDEs.

Despite the lack of correlation between lipid soluble POPs and PFAS within species, redundancy analysis including all three species (polar cod, black guillemot, glaucous gull) showed that there were significant correlations between the lipid soluble compound groups and fluorinated substances in the degree of biomagnification in the food web. PFAS, PCBs, DDTs and PBDEs were all increasing significantly with trophic level and displayed similar slope values. Assuming that wet weight in liver is a reliable measure of an

organism's burden of fluorinated compounds, PFAS appear to accumulate through the food web to the same extent as the lipid soluble POPs.

4.6. Challenges in the quantification of bioaccumulation and biomagnification of PFAS

Wet weight concentrations in liver have been a customary measure for estimating biomagnification of PFAS (Kannan et al., 2005; Martin et al., 2004; Tomy et al., 2004a). However, quantifying bioaccumulation and biomagnification of PFAS based on wet weight is intricate due to the lack of knowledge about the binding sites of these compounds. For lipid soluble compounds, the variation in lipid content among tissues and species is accounted for by expressing concentrations on a lipid weight basis. With regard to fluorinated compounds, the deviation in amount of protein binding sites between tissues and species cannot be corrected for. It is therefore difficult to determine if the increase in concentrations of PFAS with trophic level is in fact food web accumulation or a result of enhanced binding to proteins and, hence, different retention abilities. Variable protein content can be related to the amount of blood present in the tissues analyzed. PFOS and the structurally analogous PFAS retained in blood plasma have been shown to bind via the sulfonate group or the hydrophobic alkyl chain to the protein albumin (Jones et al., 2003). Martin et al. (2003b) and Verreault et al. (2005) have reported that plasma levels of PFOS in rainbow trout (*Oncorhynchus mykiss*) and glaucous gull seem to be higher than liver levels in these species. These findings establish the potential importance of blood content in the analyzed tissue. Hence, the detected concentration of PFOS in an organ or organism may depend upon the amount of blood in the respective matrix analyzed. A direct comparison between wet weight based biomagnification factors for the fluorochemicals and lipid normalized biomagnification factors for the PCBs, DDTs and PBDEs would thus be difficult to interpret. In view of the abovementioned aspects of uncertainty around the quantification for PFAS, their binding affinity to proteins and the mechanism of accumulation should be assessed in future studies.

5. Conclusions

The present study is the first comprehensive survey of perfluoroorganic contamination in a Norwegian Arctic marine food web. Significant amounts of per- and polyfluorinated compounds were found in seabirds, fish and ice amphipods from the Barents Sea food web. Perfluorooctane sulfonate (PFOS) displayed the highest concentrations, with values up to 225 ng g^{-1} wet weight in glaucous gull liver. These are the highest values reported so far for any Arctic seabird species. A significant increase in liver wet weight concentrations of PFOS with trophic level was found in the investigated food web. Liver based magnification factors displayed values >1 for PFHxS, PFOS, PFNA and Σ PFAS in the majority of predator–prey relationships, which suggests biomagnification of these compounds. Redundancy analysis (RDA) showed that

the degree of trophic transfer of PFAS is similar to that of the lipid soluble contaminants PCBs, DDTs and PBDEs, despite accumulation through different pathways.

Acknowledgements

The authors thank Even Jørgensen, Hans Wolkers, Dorte Herzke, Helèn Terese Kalfjøs and Nigel Gilles Yoccoz for practical, chemical and statistical help. This study received financial support from the Norwegian Research Council (project no. 153740/720), the European Union (PERFORCE project NEST-508967), the Norwegian Polar Institute and the Amundsen Centre at the University of Tromsø.

References

- Berger, U., Haukås, M., 2005. Validation of a screening method based on liquid chromatography coupled to high-resolution mass spectrometry for analysis of perfluoroalkylated substances in biota. *Journal of Chromatography A* 1081, 210–217.
- Berthiaume, J., Wallace, K.B., 2002. Perfluorooctanoate, perfluorooctanesulfonate, and *N*-ethyl perfluorooctanesulfonamide ethanol: peroxisome proliferation and mitochondrial biogenesis. *Toxicology Letters* 129, 23–32.
- Borgå, K., Fisk, A.T., Hoekstra, P.F., Muir, D.C.G., 2004. Biological and chemical factors of importance in the bioaccumulation and trophic transfer of persistent organochlorine contaminants in Arctic marine food webs. *Environmental Toxicology and Chemistry* 23, 2367–2385.
- Borgå, K., Gabrielsen, G.W., Skaare, J.U., 2001. Biomagnification of organochlorines along a Barents Sea food chain. *Environmental Pollution* 113, 187–198.
- Borgå, K., Gabrielsen, G.W., Skaare, J.U., 2002. Differences in contamination load between pelagic and sympagic invertebrates in the Arctic marginal ice zone: influence of habitat, diet and geography. *Marine Ecology Progress Series* 235, 157–169.
- Borgå, K., Wolkers, H., Skaare, J.U., Hop, H., Muir, D.C.G., Gabrielsen, G.W., 2005. Bioaccumulation of PCBs in Arctic seabirds: influence of dietary exposure and congener biotransformation. *Environmental Pollution* 134, 397–409.
- Bossi, R., Riget, F.F., Dietz, R., Sonne, C., Frauser, P., Dam, M., Vorkamp, K., 2005. Preliminary screening of perfluorooctane sulfonate and other fluorinated chemicals in fish, birds and marine mammals from Greenland and Faroe Islands. *Environmental Pollution* 136, 323–329.
- Braune, B.M., Norstrom, R.J., 1989. Dynamics of organochlorine compounds in herring gulls: III. Tissue distribution and bioaccumulation in Lake Ontario gulls. *Environmental Toxicology and Chemistry* 8, 957–968.
- Bustnes, J.O., Bakken, V., Skaare, J.U., Erikstad, K.E., 2003. Age and accumulation of persistent organochlorines: a study of Arctic-breeding glaucous gulls (*Larus hyperboreus*). *Environmental Toxicology and Chemistry* 22, 2173–2179.
- Coffander, R., 1951. The partitioning of organic compounds between higher alcohols and water. *Acta Chimica Scandinavica* 5, 774–780.
- Drouillard, K.G., Norstrom, R.J., 2000. Dietary absorption efficiencies and toxicokinetics of polychlorinated biphenyls in ring doves following exposure to Aroclor (R) mixtures. *Environmental Toxicology and Chemistry* 19, 2707–2714.
- Erikstad, K.E., 1990. Winter diet of four seabird species in the Barents Sea after a crash in the capelin stock. *Polar Biology* 10, 619–627.
- Faithfull, N.S., Weers, J.G., 1998. Perfluorocarbon compounds. *Vox Sanguinis* 74, 243–248.
- Falk-Petersen, I.-B., Frivoll, V., Gulliksen, B., Haug, T., 1986. Occurrence and size/age relations of polar cod *Boreogadus saida* (Lepechin), in Spitsbergen coastal waters. *Sarsia* 71, 235–345.
- Fisk, A.T., Hobson, K.A., Norstrom, R., 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwest Polynya marine food web. *Environmental Science and Technology* 35, 732–738.
- Gabrielsen, G.W., Skaare, J.U., Polder, A., Bakken, V., 1995. Chlorinated hydrocarbons in glaucous gulls (*Larus hyperboreus*) in the southern part of Svalbard. *Science of the Total Environment* 160/161, 337–346.
- Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science and Technology* 35, 1339–1342.
- Golovanov, I.B., Tsygankova, I.G., 2001. Structure-property correlation equation: VII. Some properties of perfluorinated organic compounds. *Russian Journal of General Chemistry* 6, 839–844.
- Hansen, K.J., Clemen, L.A., Ellefson, M.E., Johnson, H.O., 2001. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environmental Science and Technology* 35, 766–770.
- Haugen, B., Spydevold, Ø., 1992. The mechanism underlying the hypolipemic effect of perfluorooctanoic acid (PFOA), perfluorooctane sulphonic acid (PFOSA) and clofibrate acid. *Biochimica et Biophysica Acta* 1128, 65–72.
- Herzke, D., Berger, U., Kallenborn, R., Nygård, T., Vetter, W., 2005. Brominated flame retardants and other organobromines in Norwegian predatory bird eggs. *Chemosphere* 61, 441–449.
- Herzke, D., Gabrielsen, G.W., Evensen, A., Burkow, I.C., 2003. Polychlorinated camphenes (toxaphenes), polybrominated diphenylethers and other halogenated organic pollutants in glaucous gulls (*Larus hyperboreus*) from Svalbard and Bjørnøya (Bear Island). *Environmental Pollution* 121, 293–300.
- Hobson, K.A., Welch, H.E., 1992. Determination of trophic relationships within a high Arctic marine food web using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis. *Marine Ecology Progress Series* 84, 9–18.
- Hop, H., Borgå, K., Gabrielsen, G.W., Kleivane, L., Skaare, J.U., 2002. Food web magnification of persistent organic pollutants in poikilotherms and homeotherms from the Barents Sea food web. *Environmental Science and Technology* 36, 2589–2597.
- Hu, W., Jones, P.D., Upham, B.L., Trosko, J.E., Lau, C., Giesy, J.P., 2002. Inhibition of gap junctional intercellular communication by perfluorinated compounds in rat liver and dolphin kidney epithelial cell lines in vitro and Sprague–Dawley rats in vivo. *Toxicological Sciences* 68, 429–436.
- Jones, P.D., Hu, W., de Coen, W., Newsted, J.L., Giesy, J.P., 2003. Binding of perfluorinated fatty acids to serum proteins. *Environmental Toxicology and Chemistry* 22, 2639–2649.
- Kannan, K., Tao, L., Sinclair, E., Pastva, S.D., Jude, D.J., Giesy, J.P., 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. *Archives of Environmental Contamination and Toxicology* 48, 559–566.
- Key, B.D., Howell, R.D., Criddle, C.S., 1997. Fluorinated organics in the biosphere. *Environmental Science and Technology* 31, 2445–2454.
- Lau, C., Thibodeaux, J.R., Hanson, R.G., Rogers, J.M., Grey, B.E., Stanton, M.E., Butenhoff, J.L., Stevenson, L.A., 2003. Exposure to perfluorooctane sulfonate during pregnancy in rat and mouse. II: postnatal evaluation. *Toxicological Sciences* 74, 382–392.
- Livingstone, D.R., Donkin, P., Walker, C.H., 1992. Pollutants in marine ecosystems: an overview. In: Walker, C.H., Livingstone, D.R. (Eds.), *Persistent Pollutants in Marine Ecosystems*. SETAC Special Publishing Series. Pergamon Press, Oxford, UK, pp. 235–263.
- Lønne, O.J., 1988. A diver-operated electric suction sampler for sympagic (=under-ice) invertebrates. *Polar Research* 6, 135–136.
- Lønne, O.J., Gulliksen, B., 1989. Size, age and diet of polar cod, *Boreogadus saida* (Lepechin 1773), in ice covered waters. *Polar Biology* 9, 187–191.
- Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003a. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). *Environmental Toxicology and Chemistry* 22, 189–195.
- Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003b. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environmental Toxicology and Chemistry* 22, 196–204.
- Martin, J.W., Smithwick, M.M., Braune, B.M., Hoekstra, P.F., Muir, D.C.G., Mabury, S.A., 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environmental Science and Technology* 38, 373–380.

- Mehlum, F., Gabrielsen, G.W., 1993. The diet of high-Arctic seabirds in coastal and ice-covered, pelagic areas near the Svalbard archipelago. *Polar Research* 12, 1–20.
- Mizutani, H., Kabaya, Y., Wada, E., 1991. Nitrogen and carbon isotope compositions relate linearly in cormorant tissues and its diet. *Isotopenpraxis* 4, 166–168.
- Pottermann, M., 2001. Arctic sea ice as feeding ground for amphipods – food sources and strategies. *Polar Biology* 24, 89–96.
- Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. *Environmental Science and Technology* 40, 32–44.
- Simcik, M.F., 2005. Global transport and fate of perfluorochemicals. *Journal of Environmental Monitoring* 7, 759–763.
- Smithwick, M., Mabury, S.A., Solomon, K.R., Sonne, C., Martin, J.W., Born, E.W., Dietz, R., Derocher, A.E., Letcher, R.J., Evans, T.J., Gabrielsen, G.W., Nagy, J., Stirling, I., Taylor, M.K., Muir, D.C.G., 2005. Circumpolar study of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*). *Environmental Science and Technology* 39, 5517–5523.
- Søreide, J.E., Hop, H., 2003. Trophic plasticity in Arctic marine invertebrates. Poster at “Arctic–Alpine Ecosystems and People in a Changing Environment”. 23 February–1 March, 2003, Tromsø, Norway.
- Søreide, J.E., Hop, H., Falk-Petersen, S., Hegseth, E.N., Carroll, M.L., 2006. Seasonal food web structures and sympagic–pelagic coupling in the European Arctic revealed by stable isotopes and a two-source food web model. *Progress in Oceanography* 71, 59–87.
- Sørmo, E.G., Salmer, M.P., Jenssen, B.M., Hop, H., Bæk, K., Kovacs, K.M., Lydersen, C., Falk-Petersen, S., Gabrielsen, G.W., Lie, E., Skaare, J.U., 2006. Biomagnification of brominated diphenyl ether and hexabromocyclododecane flame retardants in the polar bear food chain in Svalbard, Norway. *Environmental Toxicology and Chemistry* 25, 2502–2511.
- Tameler, T., Renaud, P.E., Hop, H., Carroll, M.L., Ambrose Jr., W.G., Hobson, K.A., 2006. Trophic relationships and pelagic–benthic coupling during summer in the Barents Sea Marginal Ice Zone revealed by stable carbon and nitrogen isotope measurements. *Marine Ecology Progress Series* 310, 33–46.
- Ter Braak, C.J.F., Šmilauer, P., 2002. CANOCO Reference Manual and CanoDraw for Windows User's Guide: Software for Canonical Community Ordination (Version 4.5). Microcomputer Power, Ithaca, USA.
- Thibodeaux, J.R., Hansen, R.G., Rogers, J.M., Grey, B.E., Barbee, B.D., Richards, J.H., Butenhoff, J.L., Stevenson, L.A., Luu, C., 2003. Exposure to perfluorooctane sulfonate during pregnancy in rat and mouse. I: maternal and prenatal evaluations. *Toxicological Sciences* 74, 369–381.
- Tomy, G.T., Budakowski, W., Halldorson, T., Helm, P.A., Stern, G.A., Friesen, K., Pepper, K., Tittlemier, S.A., Fisk, A.T., 2004a. Fluorinated organic compounds in an Eastern Arctic marine food web. *Environmental Science and Technology* 38, 6475–6481.
- Tomy, G.T., Tittlemier, S.A., Palace, V.P., Budakowski, W.R., Braekvelt, E., Brinkworth, L., Friesen, K., 2004b. Biotransformation of *N*-ethyl perfluorooctanesulfonamide by rainbow trout (*Oncorhynchus mykiss*) in liver microsomes. *Environmental Science and Technology* 38, 758–762.
- Upham, L.B., Deccampo, N.D., Wurl, B., Trosko, J.E., 1998. Inhibition of gap junctional intercellular communication by perfluorinated fatty acids is dependent on the chain length. *International Journal of Cancer* 78, 491–495.
- Vanden Heuvel, J.P., Kuslikis, B.I., Van Rafeleghem, M.J., Peterson, R.E., 1991a. Tissue distribution, metabolism, and elimination of perfluorooctanoic acid in male and female rats. *Journal of Biochemical Toxicology* 6, 83–92.
- Vanden Heuvel, J.P., Kuslikis, B.I., Van Rafeleghem, M.J., Peterson, R.E., 1991b. Disposition of perfluorodecanoic acid in male and female rats. *Toxicology and Applied Pharmacology* 107, 450–459.
- Van de Vijver, K.I., Hoff, P.T., Das, K., Van Dongen, W., Esmans, E.L., Jauniaux, T., Bouquegneau, J.M., Blust, R., de Coen, W., 2003. Perfluorinated chemicals infiltrate ocean waters: link between exposure levels and stable isotope ratios in marine mammals. *Environmental Science and Technology* 37, 5545–5550.
- Verreault, J., Houde, M., Gabrielsen, G.W., Berger, U., Haukås, M., Letcher, R.J., Muir, D.C.G., 2005. Perfluorinated alkyl substances in plasma, liver, brain and eggs of glaucous gulls (*Larus hyperboreus*) from the Norwegian Arctic. *Environmental Science and Technology* 39, 7439–7445.
- Vorkamp, K., Christensen, J.H., Glasius, M., Riget, F.F., 2004. Persistent halogenated compounds in black guillemots (*Cephus grylle*) from Greenland levels, compound patterns and spatial trends. *Marine Pollution Bulletin* 48, 111–121.
- de Wit, C.A., Fisk, A.T., Hobbs, K.E., Muir, D.C.G., Gabrielsen, G.W., Kallenborn, R., Krahn, M.M., Norstrom, R.J., Skuare, J.U., 2004. AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic. Arctic Monitoring and Assessment Programme, Oslo, Norway, p. 309.