

# Perfluoroalkyl acids in waters of the Canadian archipelago and Arctic Ocean

D.C.G. Muir<sup>1</sup>, S. Sturman<sup>2</sup>, A. Morris<sup>1</sup>, B.F. Scott<sup>1</sup>, C. Spencer<sup>1</sup>, X. Wang<sup>1</sup>, and H. Kylin<sup>3</sup>

<sup>1</sup>Environment Canada, Aquatic Ecosystem Protection Research Division, Burlington ON,

<sup>2</sup>Department of Environmental Biology, University of Guelph, ON, Canada, N1G 2W1

<sup>3</sup>Department of Environmental Assessment, Swedish University of Agricultural Sciences, PO Box 7050, SE-705 07 Uppsala, Sweden

## Abstract

Perfluoroalkyl acids (PFAs) have been shown to be ubiquitous contaminants of terrestrial, freshwater and marine environments. Previous work by Yamashita and co-workers, has shown that PFAs, in particular, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are present in the global oceans at concentrations ranging from <1 to 450 pg/L. However, no measurements have been made in the Arctic Ocean and only a limited number are from the adjoining northern seas. The Arctic Ocean is known to be influenced by inflows from the Pacific and Atlantic Ocean as well as from riverine inflows. Samples were collected from the Swedish research icebreaker Oden on a cruise across the Canadian archipelago to the Chukotka Peninsula in Russia in August-September 2005. Near shore samples were also collected near Nain, Labrador, in June and September 2006 and near Resolute (Nunavut) in June 2006 and 2007. PFOA concentrations ranged from 79-252 pg/L and PFOS from 12-107 pg/L. Higher concentrations were found in melt-water from the Arctic ice surface indicating that melt processes are a source of PFAs to upper Ocean layers and food webs



## Introduction

Previous work by Yamashita and co-workers (2005;2008), have shown that PFAs, in particular, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are present in the global oceans at concentrations ranging from <1 to 450 pg/L. Modelled predictions of PFOA concentrations in the Arctic Ocean (for 2005) range from 70 pg/L (Wania 2007) to 100 pg/L (Armitage et al. 2006) No measurements have been made in the Arctic Ocean and only a limited number are from the adjoining northern seas. Surface waters (2-200 m) of the Canadian archipelago are influenced by inflows of Pacific water via the Beaufort Sea. Baffin Bay and the northern Labrador Sea are influenced by Atlantic waters and the East Greenland current (Fig 1)

## Methods

### Sample collection:

Surface water (1L duplicates) was collected on the Swedish icebreaker Oden at 23 locations during a cruise through the Canadian Arctic archipelago in August 2005. Water was collected at 8 m depth from the inline seawater system in 1L polypropylene (PP) bottles (double capped) which were stored sealed in polyethylene bags and then held at 4°C until analysed. Depth profiles (0-100 m) were collected through the ice in Lancaster Sound in June 2007 with a Van Dorn sampler, in Anaktalak Sound near Nain (NL) in April 2007, by pumping. Depth profiles (0-2500 m) were collected from the Oden (using a Niskin bottle rosette) in the Chukchi and Beaufort Seas in Aug 2005. PP bottles were filled directly from the Niskin.

### Extraction:

Seawater (750 mL; 2 per site) was extracted using OASIS WAX cartridges. Prior to extraction these samples were spiked with isotopically C-labeled PFAs (C6, C8, C10, C11, C12, <sup>13</sup>PFHxS and PFOS) and with <sup>13</sup>C-labelled 8:2FTOH and deuterated perfluorooctane sulfonamides (d7-N-MeFOSE, d-N-MeFOSA), isotopically labeled PFNA (C9) was added to the samples before injection. All extractions were conducted in a clean room (carbon and HEPA filtered air; positively pressured) to minimize contamination. A second subset consisting of the combined remaining sample from each site (500 mL) was analysed later to confirm the results for the first batch of samples. These samples were spiked only with the <sup>13</sup>C-PFAs. Samples collected (1L) through the ice in 2007 were spiked only with the <sup>13</sup>C-PFAs and extracted as described

### Instrumental analysis:

PFAs were analysed by LC-tandem MS using an Agilent 1100 LC coupled to an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, (Foster City, CA) operated in the electro-spray ionization mode with multiple reaction monitoring. PFAs were chromatographed on a Security Guard C18 guard column (2 mm i.d. X 4 mm, 5 µm) connected to a Luna column (2 mm i.d. x 50 mm, 3 µm) using a 0.01M ammonium acetate solution in water (as solvent A) and MeOH (as solvent B) as the mobile phase. Column temperature was 35°C. Injection volumes were 10 µL -100 µL. PFAs were quantified using a 8-point calibration curves from just above the quantification limit to 100 x this value.

### QA

Laboratory blanks consisting of SPE extracted HPLC grade water were spiked with the same <sup>13</sup>C-surrogates and analysed for every 10 samples. Travel blanks consisted of SPE extracted HPLC grade water. For the Oden cruise samples a robust blank based on nine laboratory blanks was calculated and used for blank correction. Method Detection Limits (3\*SD of the blank) ranged from 56 pg/L for PFOA to 8.7 pg/L for PFOS for 750 mL samples.

## Results and Discussion

### Quality assurance

Elevated blanks due to native <sup>13</sup>C-PFAs in <sup>13</sup>C-FTOH and deuterated FOSE standards were found during the analysis of the 750 mL samples. All samples were rerun by combining the remaining 250mL into a single sample – without the FTOH and FOSE ISs. This resulted in much lower blanks and improved MDLs especially for PFOA and PFNA. Comparable results were obtained from both procedures (Table 1). Results for PFAs were >2x the MDL except for C9 (PFNA)

**Table 1.** Comparison of concentrations (pg/L) for major PFAs in 26 sea water samples along a transect from Greenland to the Chukchi Sea

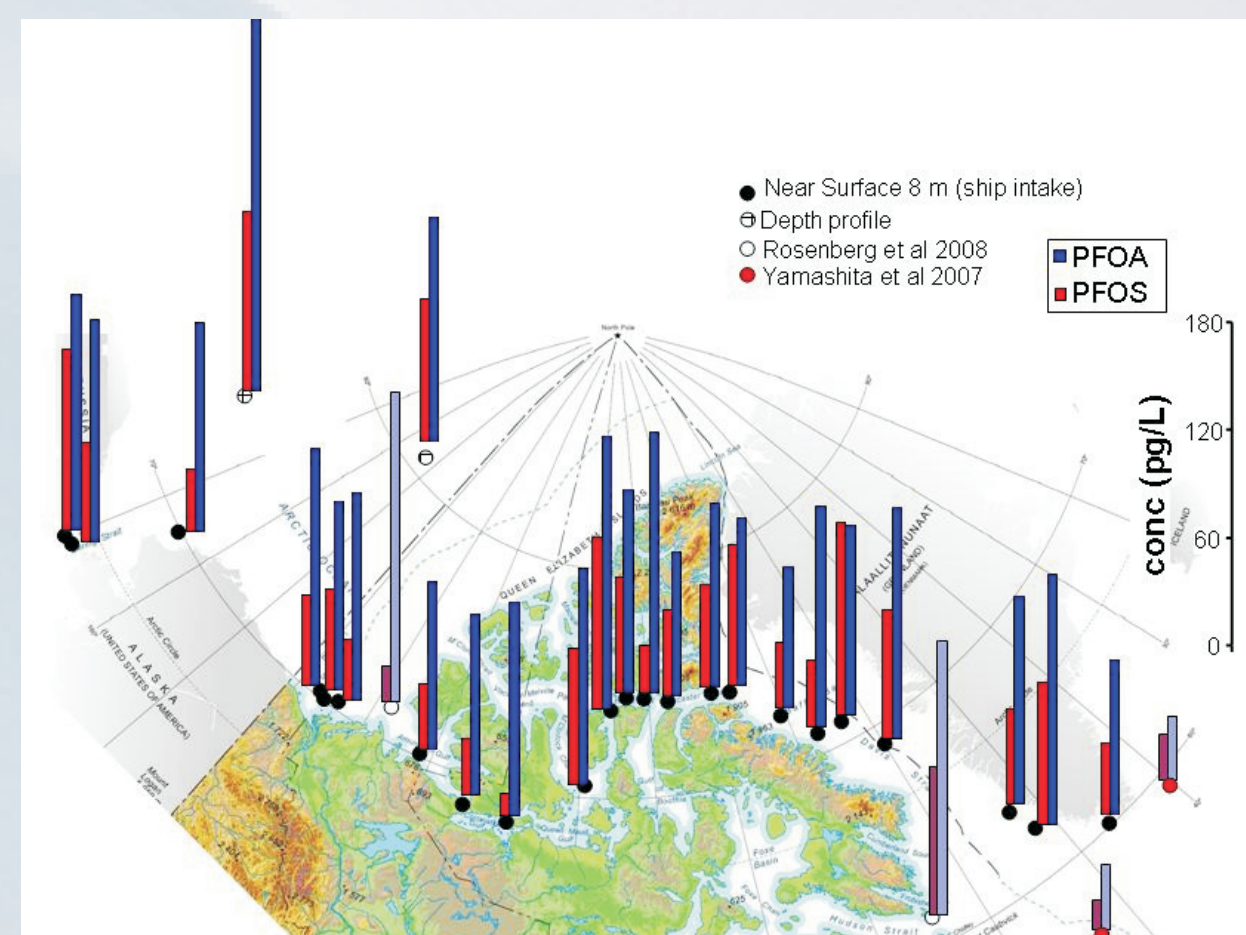
		N	C6	C7	C8	C9	C10	C11	C12	PFHxS	PFOS
		PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA			
750 mL samples	All-average	26	93.6	126	131	52.2	47.7	18.6	14.9	9.2	68.4
	SD		157	130	80.3	47.8	40.2	14.1	11.3	6.6	67.1
	MDL		58	66	56	123	9.6	2.1	2.9	2.4	8.7
750 mL samples	All-average	24	99.9	148	168	85.1	24.4	13.0	15.9	6.3	50.8
	SD		144	127	113	90.3	34.8	8.1	18.1	3.7	57.6
	MDL		18	4.2	12	2.3	28	2.4	3.1	3.6	18
500 mL samples	West <sup>1</sup>	11	59	111	109	42	43	18	13	11	58
	East	13	82	131	129	54	38	16	17	9	57
	Lancaster Sound <sup>2</sup>	6	78	44	122	93	10	3.7	nd	1.8	14
	Anaktalak Sound	6	32	25	47	21	3.0	1.2	nd	1.9	8

<sup>1</sup>West of 90°W longitude <sup>2</sup>Collected through the ice, June 2007, average 2, 4 & 6 m depth



## Spatial trends

PFOA and PFNA were the major PFAs averaging 168 and 85 pg/L, respectively. PFHxS and PFOS were the major PFSS averaging 6.3 and 51 pg/L, respectively. PFOA concentrations in samples taken from the sea ice in Apr-June 2007 in Lancaster Sound were comparable to ship based measurements (Table 2) Although average concentrations of PFAs were higher in the western samples (Canadian archipelago and southern Beaufort Sea) compared with eastern (Baffin Bay/Davis Strait) the differences were not statistically significant (t test, P>0.05) Concentrations of PFAs in seawater were generally higher than expected based on very limited previous measurements (Table 2). PFOS concentrations were comparable to results from the recent study by Rosenberg et al (2008) (Table 2) PFOA and PFOS concentrations were higher than reported for the Greenland and Norwegian Seas in an earlier study (prior to use of <sup>13</sup>C-PFA surrogates) (Caliebe et al. 2004;2005)

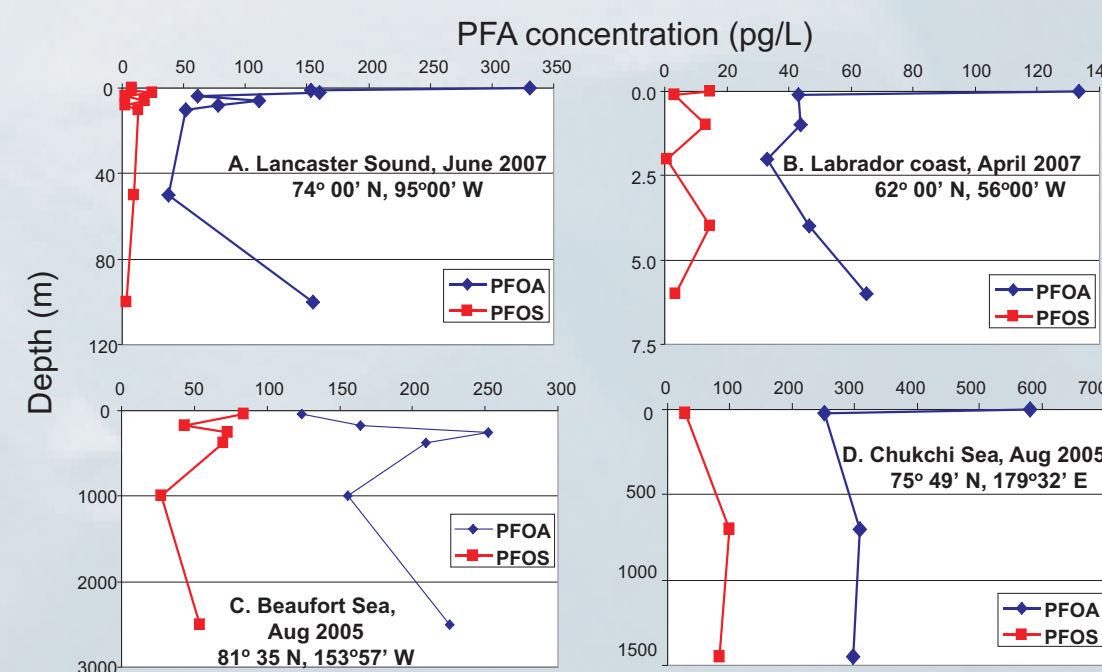


**Figure 1.** Spatial trends of PFOA and PFOS in surface (8 m) seawater along a transect from Greenland to the Bering Sea (Jul-Aug 2005). Results are compared with Yamashita et al (2008) for the northern Labrador Sea and Rosenberg et al (2008) for selected sites

**Table 2.** Comparison of PFA concentrations in surface and deep waters including Arctic waters

	PFOS	PFHS	PFNA	PFOA	Ref
Western Pacific Ocean	54-78	2.2-2.8	n.a.	136-142	[1]
Central to Eastern Pacific Ocean (surface water)	1.1-20	0.1-1.6	1.0-16	15-62	[1]
Central to Eastern Pacific Ocean (deep water; 4000-4400 m)	3.2-3.4	0.4-0.6	n.a.	45-56	[1]
North Atlantic Ocean	8.6-36	4.1-6.1	15-36	160-338	[1]
Mid Atlantic Ocean	37-73	2.6-12	n.a.	100-439	[1]
Labrador Sea (AO-1 deep water)	9-12	n.a.	n.a.	55-75	[2]
Labrador Sea (coastal)	24-73	2.3-10	<MDL	8-182	[3]
North Sea (at 60°N, 7°E)	-25	n.a.	n.a.	-300	[4]
Greenland Sea (75-80°N)	12-32	<2-20	n.a.	25-80	[5]
Norwegian Sea (72-75°N)	25-80	5-16	n.a.	45-60	[5]

[1] Yamashita et al 2005 ; [2] Yamashita et al. 2008 ; [3] Rosenberg et al 2008 ; [4] Caliebe et al 2004; [5] Caliebe et al. 2005



**Figure 2.** Depth profiles of PFOA and PFOS at 4 Arctic locations. A. Lancaster Sound under ice B. Labrador Coast near Nain, April 2007, C. Beaufort Sea, Aug 29 2005, D. Chukchi Sea Aug 26 2005.

## Depth profiles

Depth profiles through the ice during spring melt April in Labrador; June in Lancaster Sound) demonstrated that melt-water was injecting elevated PFA concentrations (Fig 2) Concentrations at 2 to 10 m depth were 3 to 4x lower than in surface or melt waters (Sturman et al. 2007) In the Beaufort and Chukchi Seas relatively high PFOA and PFOS concentrations were observed even in deep waters (1450-2500 m) Concentration profiles in the Canada basin were similar to observations by Yamashita et al (2008) with regard to presence of PFAs in deep waters he Niskin bottles were well flushed (used daily), but the possibility of PFA contamination of the Niskin bottles cannot be completely ruled out

## Conclusions

Relatively high concentrations of PFOA, other PFAs, PFOS and PFHxS were found in Arctic Ocean water samples Concentrations of PFOA were similar to model predictions (for 2005) which range from 70 pg/L (Wania 2007) to 100pg/L (Armitage et al. 2006) for the whole Arctic Ocean. No distinct geographical trends were seen in surface water concentrations across the Canadian archipelago PFA concentrations in the archipelago and Baffin Bay waters were higher than in nearshore Labrador waters (Sturman et al 2007; Rosenberg et al 2008) Concentrations in melt-waters were elevated compared with waters at 2-10 m depth indicating that melt processes are a source to upper Ocean layers and food webs

## Acknowledgements

We wish to extend thanks for community support during this project from Nancy and Peter Amarualik (Resolute Bay HTA) and John Lampe (Nunatsiavut Government). Appreciation is also extended to Dan Walsh for sample collections and Emma Lopez for sample extractions, Environment Canada, and ArcticNet provided project funding.

## References

- Armitage, J., I. T. Cousins, R. C. Buck, K. Prevedouros, M. H. Russell, M. MacLeod and S. H. Korzeniowski (2006). Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. *Environ. Sci. Technol.* 40: 6969-6975.
- Caliebe, C., W. Gerwinski, H. Hühnerfuss, N. Theobald (2004). Occurrence of Perfluorinated Organic Acids in the Water of the North Sea. *Organohalogen Compds* 66:4074-4078.
- Caliebe, C., W. Gerwinski, N. Theobald, H. Hühnerfuss (2005). Occurrence of perfluorinated 465 organic acids in the water of the North Sea and Arctic North Atlantic. Poster presented at Fluoros, Toronto, Canada.
- Rosenberg, B., J. DeLaronde, A. MacHutchon, G. Stern, C. Spencer, B. Scott, E. Lopez, D. Muir and G. Tomy (2008). Spatial and Vertical Distribution of Perfluorinated Compounds in Canadian Arctic and Sub-Arctic Ocean Water. *Organohalogen CompD* (Dioxin 2008) In press.
- Sturman, S., J. Small, J., C. Spencer, A. Morris, K. Solomon, D.C.G. Muir (2007) Presented at the Annual SETAC Meeting, Milwaukee WI Nov 2007. (WP 170)
- Wania, F. (2007). A Global Mass Balance Analysis of the Source of Perfluorocarboxylic Acids in the Arctic Ocean. *Environ. Sci. Technol.* 41(13): 4529-4535.
- Yamashita, N., K. Kannan, S. Taniyasu, Y. Horii, G. Petrick and T. Gamo (2005). A global survey of perfluorinated acids in oceans. *Mar. Pollut. Bull.* 51: 658-668.
- Yamashita, N., S. Taniyasu, G. Petrick, S. Wei, T. Gamo, P. K. S. Lam and K. Kannan (2008). Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. *Chemosphere* 70: 1247-1255.