

Perfluoroalkyl acids in Arctic Caribou and Reindeer

Gamberg M¹, Muir DCG², Lind, Y³, Karrman A⁴, Cuyler C⁵, Rigét F^{5,6}, Bossi R⁶, Carlsson P⁷, Roos A^{3,5}

¹Gamberg Consulting, 708 Jarvis St., Whitehorse, Yukon, Canada, Y1A 2J2

²Environment and Climate Change Canada, 867 Lakeshore Road, Burlington, Ontario, Canada, L7S 1A1

³Swedish Museum of Natural History P.O. Box 50007 5-104 05 Stockholm, Sweden

⁴MTM Research Centre, School of Science and Technology, Örebro University, 701 82 Örebro, Sweden

⁵Greenland Institute of Natural Resources Box 570 3900 Nuuk, Greenland

⁶Aarhus University, Dep of Environmental Science, Arctic Research Centre, Frederiksborgvej 399, 4000 Roskilde, Denmark

⁷NIVA, Gaustadalléen 21, NO-0349 Oslo, Norway

Introduction

Per- and polyfluoroalkyl substances (PFASs) are fluorinated, anthropogenic chemicals. They are both oil and water repellent and are or have been used in a number of different consumer applications such as aqueous firefighting foams, in grease-proofing paper, textile stain and soil repellents, processing aids in fluoropolymer manufacturing, grease- and oil-resistant packaging for food products, nonstick cook-ware etc. [1, 2]. PFAS is the generic name on a large group of compounds incorporating perfluoroalkyl acids (PFAAs) and precursor compounds to PFAAs. Of highest concern are the perfluoroalkyl carboxylic acids (PFCAs) and the perfluoroalkane sulfonic acids (PFSAs).

Wild caribou and semi-domestic reindeer (*Rangifer tarandus spp.*) are an important food resource around the Arctic and are an integral part of traditional culture for many people in the north.

Materials and methods

As part of Canada's Northern Contaminants Program, liver of animals from six caribou herds from the Canadian Arctic have been analyzed for PFASs. Animals from one herd were analyzed annually for four years. These data were compared with data from Greenland, Svalbard, and three areas in northern Sweden sampled by the Swedish Museum of Natural History as a part of Sweden's National Monitoring Program.

Data from 193 samples have been compiled within this study. Caribou from Canada were collected from herds in Yukon Territory (Porcupine, Klaza), Northwest Territories (Bathurst, Bluenose West) and Nunavut (Dolphin & Union, Qamanirjuaq) (n=96, 2002-2015). In Greenland, reindeer (n=10) were sampled from southern Greenland in 2012. Greenland caribou were taken from two sites in western Greenland in 2008 and 2009: Akia-Maniitsoq (Akia; n=10) and Kangerlussuaq (n=10). The latter were animals in close proximity to the largest international airport in Greenland. The Svalbard caribou (n=7) were sampled in autumn 2012. From northern Sweden in 2002 and again in 2011, reindeer (n=60) were sampled from three sites. In this comparative study, four chemical laboratories, from Canada, Denmark, Norway and Sweden, have been involved. When previously published data is involved, we include the descriptions of those analytical methods used [3,4].

Within this study, we assessed eight PFCAs (PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFTeDA and PFHpA), and four PFSAs (PFHxS, PFOS, PFDS and the precursor FOSA). Statistical analyses were performed for

PFAS that had less than 25% MDL (Minimum Detection Level) in the sample set under consideration. Values below the MDL were replaced by $MDL/\sqrt{2}$ prior to statistical treatment [5]. Prior to statistical analysis concentration values were log-transformed in order to approach the assumptions of normal distribution and variance homogeneity. P-values below 0.05 were considered statistically significant. All chemical labs but Örebro University in Sweden reported total-PFOS (PFOS). Örebro University reported only linear-PFOS (L-PFOS). For the Canadian liver data from 2015 both PFOS and L-PFOS were available (n=40). For these data the amount of L-PFOS was ca 64% (SD=0.06, range (0.46-0.77) of total PFOS). This mean ratio was used to convert the Swedish Örebro University L-PFOS data to permit comparisons between areas.

For the Qamanirjuaq herd from Canada, and at the three Swedish locations, samples were collected only twice and about 10 years apart. Qamanirjuaq caribou were sampled in 2008 and 2015 and reindeer from Sweden were collected from three areas in 2002/2003 and 2010/2011. These and the Canadian Porcupine caribou samples from 2005-2008 and 2015 allowed an examination of trends over time.

Results and discussion

The primary PFASs in Canadian caribou liver are the long chain PFCAs with 9, 10 and 11-carbon chains (PFNA, PFDA and PFUnDA). Concentrations of total PFCAs (with 9 to 12 carbon chains) and PFOS in the Porcupine and Qamanirjuaq herds appear to have declined by about 50% compared to earlier analyses in 2005 and 2008 [3].

PFOS was the most dominant PFAS in caribou/reindeer from Greenland and Sweden. Highest concentrations were found in two caribou populations from Greenland: Akia and Kangerlussuaq and at the three Swedish sites (See Figure 1). These five localities were statistically different from all other areas, but not each other. Highest concentrations were found in Kangerlussuaq caribou (range 6.0-28 ng/g ww, median 14), but the highest median concentration was found in Akia caribou (15 ng/g ww, range 7.2-19). PFOS constituted above 50% of PFAS in these herds. In Svalbard PFOS constituted ca 40% of PFAS and in the Canadian herds the proportion of PFOS was much lower, being only between 0-20%.

Concentrations of PFHxS were below MDL (<0.013 ng/g ww) in 49 animals: the Klaza and Bathurst herds, and 27 of 35 from the Porcupine herd (2005-2008). PFHxS was also below MDL in all animals from South Greenland, however here the MDL was higher (0.4 ng/g ww). Altogether 48% of the values of PFHxS analyzed were below the highest MDL of 0.4 ng/g ww. Thus, the results from statistical analyses must be treated with caution. Nevertheless, a clear pattern was apparent: Kangerlussuaq caribou stand out as having the highest concentrations, together with animals from Svalbard. As for the Qamanirjuaq and the three Swedish herds, all samples but except one were above MDL (0.01 ng/g ww). There was a significant or close to significant decrease in concentrations of PFHxS in Swedish reindeer from Västerbotten and Jämtland (ANOVA, $p<0.003$ and $p<0.06$ respectively). In contrast, there was a tendency to increase concentrations in the animals from the far north in Norrbotten (ANOVA, $p<0.07$). Reindeer from this remote site had higher concentrations than the other two Swedish herds. A decrease in concentrations of PFHxS was seen for the Qamanirjuaq caribou ($p<0.001$).

Concentrations of PFNA were above MDL in all samples and it was the dominant PFAS in the Canadian herds. The highest concentrations, (max 35 ng/g ww), were found in the Akia caribou from Greenland, and that herd was statistically separated from all other herds (Tukey post hoc text, $p<0.001$) but the Kangerlussuaq ($p<0.22$). The next highest concentrations were found in the Bathurst, Qamanirjuaq, Bluenose West and the three Swedish localities. They

were not significantly different (Tukey post hoc test, $0.10 < p < 0.96$). Lowest concentrations were found in the Klaza, Dolphin and Union, Porcupine, South Greenland and Svalbard herds. No indication of a time trend was found (ANOVA, $0.14 < p < 0.10$).

PFDA was found above detection limits in all but two animals, one from the Klaza herd (MDL= 0.008) and one from South Greenland (MDL= 0.1). Again, the Akia caribou stand out as having the highest concentrations of all herds (up to 17 ng/g ww), which was also significantly different from the adjacent Kangerlussuaq herd (Tukey post hoc test, $p < 0.007$). Concentrations of PFDA decreased in both Canadian herds (ANOVA, $p < 0.001$) but not in the three herds from Sweden (ANOVA, $0.06 < p < 0.71$).

PFUnDA was below MLD in only two samples. Here again, the Akia caribou exhibit the highest concentrations that were significantly different from all other herds (Tukey post hoc test, $p < 0.001$), including the Kangerlussuaq. PFUnDA decreased significantly in concentrations in the two Canadian herds, but no change was found in the herds from Sweden.

In conclusion, the results from the two Greenland herds are conspicuous compared to all other herds in our study. Greenland's Akia and Kangerlussuaq caribou had the highest concentrations of PFOS, PFHxS (only Kangerlussuaq), PFNA, PFDA, PFUnDA, PFDoDA (for the three latter only Akia had considerably higher concentrations). Both areas are relatively close to the international airport in Kangerlussuaq, while the range of the Akia caribou is adjacent to Greenland's capital city. These are possible reasons for the higher concentrations. However, the low concentrations of PFHxS in the Akia population challenge this viewpoint. Further, caribou from Svalbard showed elevated concentrations of PFHxS and that might be an effect by the airport in Longyearbyen. PFOS was the dominant PFAS in reindeer from Europe and Greenland but not from Canada where PFNA predominated. Concentrations in caribou/reindeer from remote areas most probably reflect atmospheric deposition, in combination with contamination from local hot spots such as airports, which could be a reason why the pattern is different among the countries in our study.

Acknowledgements

The analyses of caribou samples were funded by the Northern Contaminants Program, the Greenland Institute of Natural Resources and CARMA (Circum-Arctic Rangifer Monitoring & Assessment) through International Polar Year funding, the Danish Cooperation for Environment in the Arctic (DANCEA) and by the Swedish Environmental Protection Agency. We thank Mary Williamson (ECCC, Burlington ON) for the analysis of Canadian and the Kangerlussuaq and Akia samples from Greenland.

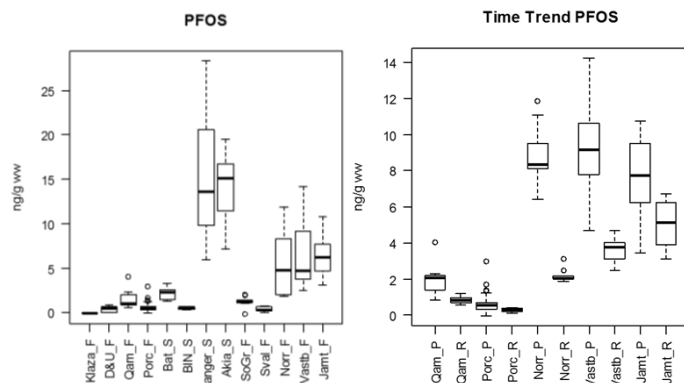


Figure 1. Box plots showing concentrations of PFOS in thirteen different herds. The horizontal thick lines show median values. The hinges represent the first and third quartile. The bars above & below roughly represent the 95% confidence interval for the median values. Outliers are shown in circles. Left figure: PFOS concentrations in caribou/reindeer from six Canadian herds (Klaza, Dolphin & Union (D&U), Qamanirjuaq (Qam), Porcupine (Porc), Bathurst (Bat), Bluenose West (BLN), three Greenland herds Kangerlussuaq (Kanger), Akia-Maniitsoq (Akia) and South Greenland (SoGr), one herd from Svalbard, Norway (Sval), and three locations in Sweden: Norrbotten (Norr), Västerbotten (Vastb) and Jämtland (Jämt). F indicates fall samples, and S spring samples. Right figure: PFOS in liver from animals in Qamanirjuaq and Porcupine (Canada) and Norrbotten, Västerbotten and Jämtland (Sweden). P is previous (i.e. the beginning of the time trend) and R is recent, i.e. 2010-2015.

References:

1. Kissa E. Fluorinated Surfactants and Repellents; Marcel Dekker: New York. 2001.
2. Sinclair E, Kim SK, Akinleye HB, Kannan K. Quantitation of Gas-Phase Perfluoroalkyl Surfactants and Fluorotelomer Alcohols Released from Nonstick Cookware and Microwave Popcorn Bags. *Environmental Science & Technology*. 2007;**41**(4):1180-5.
3. Müller CE, De Silva, A.O., Small, J., Williamson, M., Wang, X., Morris, A., Katz, S., Gamberg, M. and Muir, D.C.G. Biomagnification of Perfluorinated Compounds in a Remote Terrestrial Food Chain: Lichen–Caribou–Wolf. *Environmental Science and Technology*. 2011;**45**:8665-73.
4. Bossi R, Dam M, Rigét FF. Perfluorinated alkyl substances (PFAS) in terrestrial environments in Greenland and Faroe Islands. *Chemosphere*. 2015;**129**:164-9.
5. Loftis JCW, R. C.; Phillips, R. D. An Evaluation of Trend Detection Techniques for Use in Water Quality Monitoring Programs. U.S. Environmental Protection Agency, 1989.