POLYCHLORINATED ALKANES IN FRESHWATER FISH

Anders R. Borgen[1], Martin Schlabach[1], Roland Kallenborn[2] and Eirik Fjeld[3]

[1]Norwegian Institute for Air Research, Instituttveien 18, P.O. Box 100, N-2027 Kjeller, Norway
[2]Norwegian Institute for Air Research, Polarmiljøsenteret, Hjalmar Johansens gt. 14, N-9296 Tromsø
[3]Norwegian Institute for Water Research, Brekkeveien 19, P.O. Box 173, Kjelsås, 0411 Oslo, Norway

Introduction

Polychlorinated alkanes (PCA), or chlorinated paraffins, are straight chained alkanes with varying degrees of chlorination. They have been produced since the 1930's to an extent of approximately 300 kilotons estimated for the western world[1]. PCA are mainly produced by direct chlorination of a petroleum fraction with molecular chlorine in the presence of UV-light[2].

PCA have been used as high temperature and pressure lubricants as well as secondary plasticisers and flame retardants in plastics and paints[1,4].

Based on their chainlength, PCAs are divided into the categories: short chained (C_{10}-C_{13}), medium chained (C_{14}-C_{17}) and long chained (C_{18}-C_{30}), and further by their degree of chlorination, low (<50%) and high (>50%)[4]. With their relatively high assimilation and accumulation potential, the short chained and highly chlorinated PCAs have been paid most attention to. Although PCA generally have shown low toxicity to mammals, the short chained PCAs have a carcinogenic potential in rats and mice[5]. In addition, recent dose-respons studies have shown that oral intake of PCA by mice results in an increase in liver weight, which is considerable compared to reference materials[12]. They have also shown to be toxic towards certain species in the aquatic environment[4, 6-7], although at concentration levels several orders of magnitude higher than for TCDD[7].

The fact that PCA is a mixture of several thousands of components, makes the analytical and quantitative methods a great challenge. The complexity of PCA results in different analytical approaches due to the disability of chromatographic separation[1-3, 5, 8-10].

In this study, short chained and highly chlorinated PCAs have been measured in trout, burbot and Arctic char from different locations in Norway.

Experimental

An HP5890 GC coupled to a VG AutoSpec, high resolution mass spectrometer was used for all of the analyses. The MS was operated in ECNI mode with methane at a pressure of 2×10^{-5} mbar as reagent gas. The GC was operated in constant flow mode, 1 mL/min, with a temperature program starting at 150°C, then ramping to 260°C by 7°C/min. The temperature was held at 260°C for 8 min and was then increased to 280°C by 10°C/min, holding that

temperature for 13 min. The injector temperature was 260°C. The quantifications were performed according to the method described by Tomy et al[3].
Previous PCA analyses had to be done using three injections for each sample. This was due to limitations in the AutoSpec software. A way around this problem is now found, and therefore the GC/MS program has been adapted to one injection analyses[14].

Results and Discussion
The results, shown in table 1, are reported as the sum of C_{10}–C_{13} PCAs with 5-10 Chlorine substitutions, together with the calculated average molar mass.

Table 1. Concentrations and calculated average molar masses of short chained and highly chlorinated PCAs in freshwater fish samples from different locations in Norway.

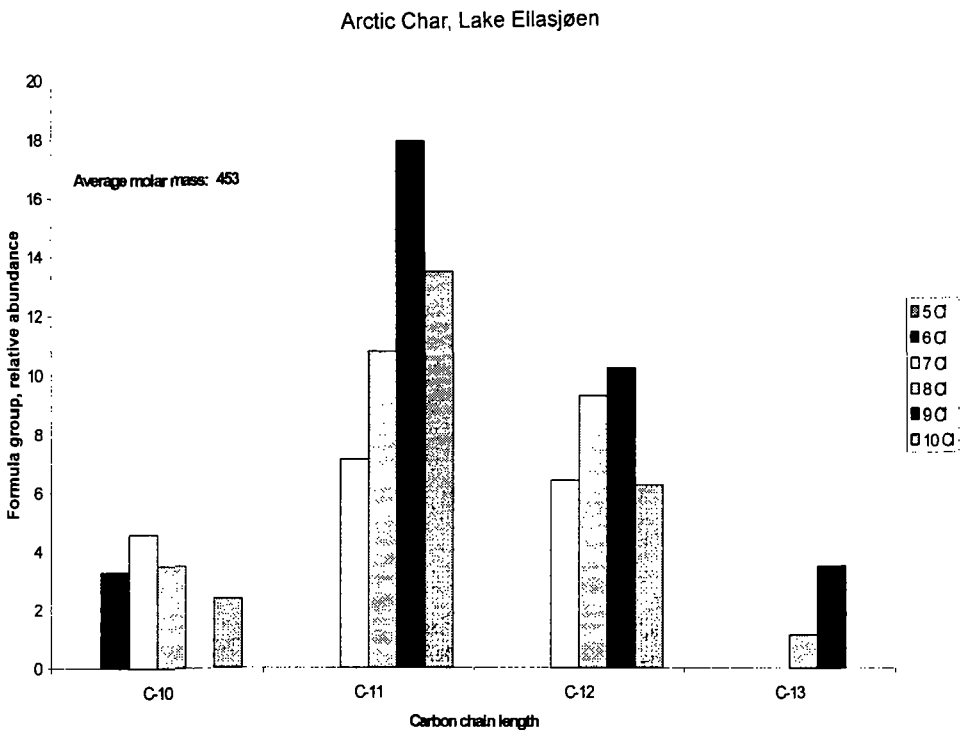
Location	*Sample type*	*ΣPCA in ng/g fat*	*Average molar mass, g/mole*
Takvatn	Trout, muscle	172	396
Fjellfrøsvatnet	Trout, muscle	545	378
Grunnvatnet	Trout, muscle	1 692	421
Store Raudvannet	Trout, muscle	108	411
Selbusjøen	Trout, muscle	436	389
Breimsvatn	Trout, muscle	923	427
Bogevatnet	Trout, muscle	1 414	395
Kalsjøen	Trout, muscle	178	394
Kalandsvatn	Trout, muscle	254	387
Vegår	Trout, muscle	263	407
Mårvann	Trout, muscle	256	415
Grindheimsvatn	Trout, muscle	733	394
Lygne	Trout, muscle	408	408
Ellasjøen	Arctic char, muscle	592	453
Velmunden	Arctic char, muscle	500	435
Grensefoss	Burbot, liver	741	435
Selbusjøen	Burbot, liver	226	421
Røgden	Burbot, liver	787	456
Røgden	Burbot, liver	1 152	422
Øgderen	Burbot, liver	695	417
Femsjøen	Burbot, liver	3 700	429
PCA 55,5 %	Standard		407

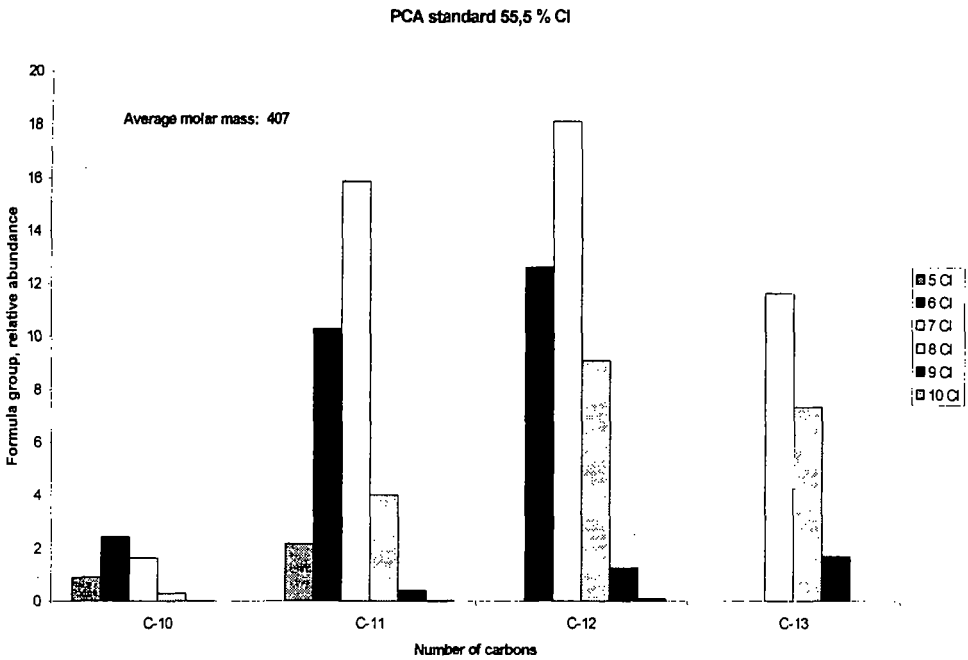
Generally the burbot liver samples contain PCA with a higher average molar mass than the trout muscle samples. This may be due to a higher rate of biotransformation in the liver, and the fact that PCAs with lower chlorine content is more easily metabolised than the higher chlorinated PCAs[5]. Another possible explanation is that the burbot generally is at a higher trophical level than the trout, but the size of the trout is also important for its predatory abilities. This may again be one of the explanations of the variations in the average molar mass of the trout samples.

The PCA pattern (figure 1) and the average molar mass of the sample from Lake Ellasjøen, located on Bjørnøya island (74° N), is quite high considering the location of this lake. With only long range transport by air, the average molar mass would be expected to be lower than in samples collected near PCA sources. Lake Ellasjøen is located in the catchment area of large nesting colonies of seabirds, and the result of the analysis of the Arctic char sample supports the theory of POPs being transported to Lake Ellasjøen by seabirds together with long range transport by air[13].

The concentration of PCA in the sample from Lake Femsjøen, located near the Swedish border in the south of Norway, is of the same order of magnitude as in an Arctic char sample collected in the south of Sweden[15].

The concentrations of PCA reported here, are about an order of magnitude lower than concentrations of rainbow trout samples collected in Lake Ontario, Canada[16].





Acknowledgement

Anders R. Borgen would like to thank The Research Council of Norway for financing this project.

References

[1] Fisk A.T., Cymbalisty C.D., Tomy G.T. and Muir D.C.G, Aquatic Toxicology, 43 (1998) 209-221.

[2] Kraemer W. and Ballschmiter K., Fresenius Z Analytical Chemistry (1987) 327:47-48, Detection of a new class of organochlorine compounds in the marine environment: the polychlorinated paraffins.

[3] Tomy G.T., Thesis, The mass Spectrometric Characterization of Polychlorinated n-Alkanes and the Methodology for their Analysis in the Environment.

[4] Gjøs N. and Gustavsen K. O., Analytical Chemistry 1982, 54, 1316-1318, Determination of Chlorinated Paraffins by Negative Ion Chemical Ionization Mass Spectrometry.

[5] International programme on chemical safety, Environmental health criteria 181, Chlorinated paraffins

[6] Rieger R., Ballschmiter K., Fresenius' J. of Analytical Chemistry (1995) 352:715-724, Semivolatile organic compounds-polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), biphenyls (PCB), hexachlorobenzene (HCB), 4,4'-DDE and chlorinated paraffins (CP) as markers in sewer films.

[7] Coelhan M., Saraci M., Parlar H., Chemosphere 40 (2000) 685-689, A comparative study of polychlorinated alkanes as standards for the determination of C10-C13 polychlorinated paraffins in fish samples.
[8] Fisk A.T ., Tomy G. T. and Muir D. C.G., Environmental Toxicology and Chemistry. Vol. 18. No. 12. pp. 2894-2902, 1999, Toxicity of C_{10}-, C_{11}-, C_{12}- and C_{14}-polychlorinated alkanes to japanese Medaka (*Oryzias Latipes*) embryos.
[9] Jansson B., Andersson R., Asplund L., Bergman Å., Litzén K., Nylund K., Reuthergårdh L., Sellström U., Uvemo U., Cajsa Wahlberg and Ulla Wideqvist, Fresenius' Journal of Analytical Chemistry (1991) 340:439-445, Multiresidue method for the gas-chromatographic analysis of some polychlorinated and polybrominated pollutants in biological samples
[10] Junk S.A. and Meisch H.-U., Fresenius' Journal of Analytical Chemistry (1993) 347:361-364, Determination of chlorinated paraffins by GC-MS.
[11] Coelhan M, Analytical Chemistry 1999, 71, 4498-4505, Determination of Short-Chain Polychlorinated Paraffins in Fish Samples by Short-Column GC/ECNI-MS.
[12] Osmundsen H, personal correspondance.
[13] Skotvold T, Wartena E. M.M. and Schlabach M, Organohalogen compounds 1998, Volume 39,411-414
[14] Borgen A.R., Schlabach M. and Organohalogen compounds 1998, Volume 39,411-414
[15] Tomy G.T., Fisk A.T., Westmore J.B. and Muir D.C.G., Rev Environ Contam, 1998, 158:53-128
[16] Bennie D.T., Sullivan C.A. and Maguire R.J., Water Qual. Res. J. Canada, 2000, Volume 35, No. 2, 263-281.