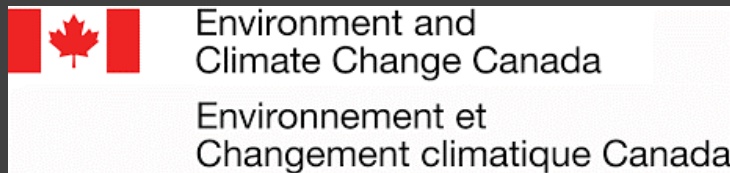




A Newly Developed Method for the Determination of Chlorinated Paraffins (Polychlorinated Alkanes) in Recent Hudson Bay Polar Bear Fat Samples

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NCP Project
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Introduction

- By the year 2020, approximately 33 million metric tons of polychlorinated alkanes (PCAs; also known as chlorinated paraffins (CPs)), were produced and used worldwide
- PCAs with the chemical formula $C_xH_{2x+2-y}Cl_y$, find extensive application in various industries as plasticizers, extreme-pressure additives, and flame retardants
- PCAs are available in a range of chain lengths, categorized as short- (PCAs- C_{10-13}), medium- (PCAs- C_{14-17}), and long-chain (PCAs- $C_{>17}$) alkanes, and often contain very-short-chain impurities (PCAs- C_{6-9})
- In the Arctic region, most PCA data are for PCAs- C_{10-13} with lesser emphasis for PCAs- C_{14-17} , and only minimal reports of PCAs- $C_{>17}$ in ecosystems and wildlife species including polar bears (*Ursus maritimus*)
- The polar bear, a marine-feeding apex predator on the Arctic, are affected by global warming and sea-ice loss and the resulting diet shifts may potentially be reflected in the bioaccumulation pattern of PCA congeners

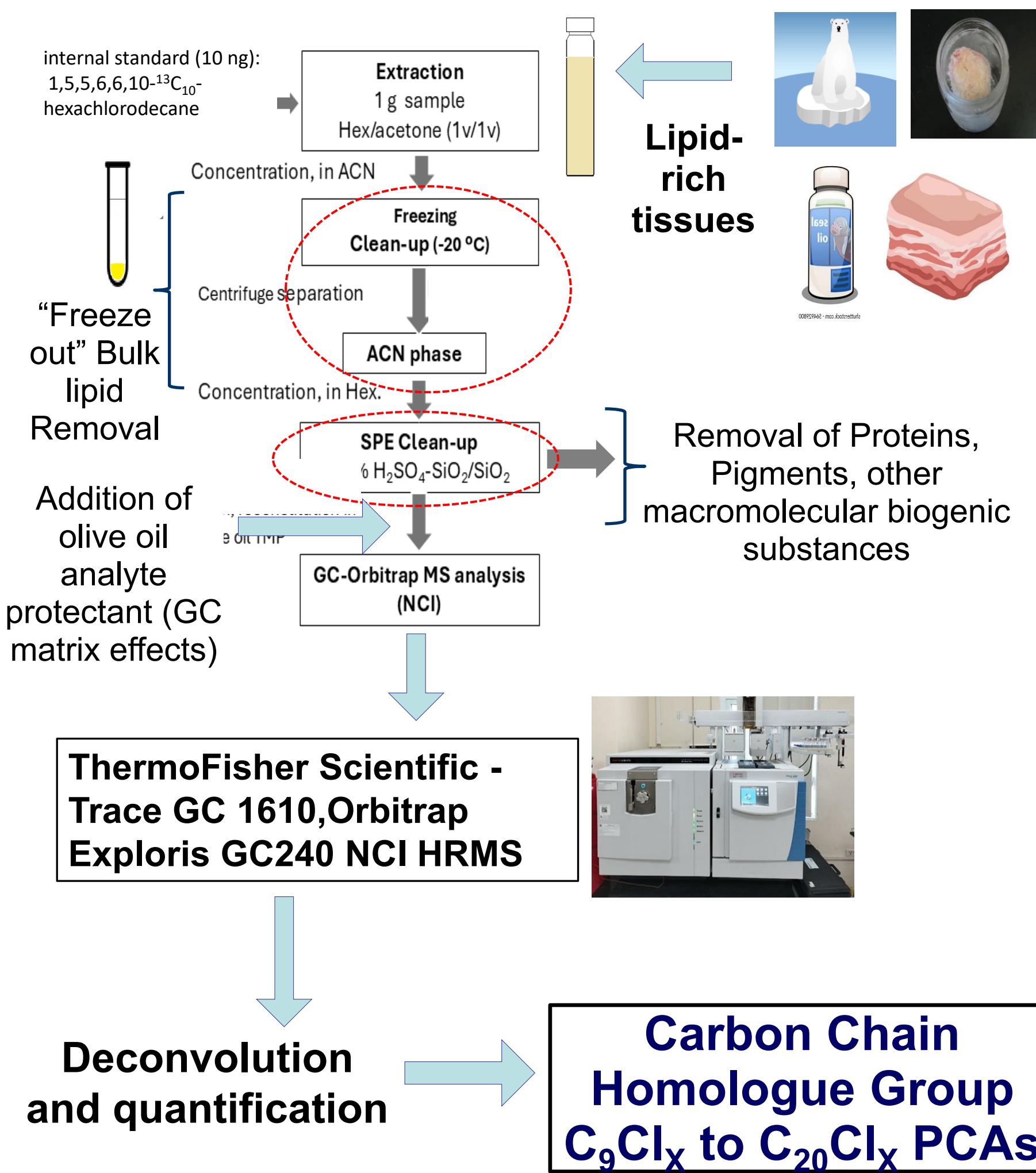
Objective:

Based on GC-Orbitrap-HRMS, to develop a robust, sensitive and reliable quantitative method to determine individual carbon chain homologue groups of PCAs (C_9Cl_x to $C_{20}Cl_x$) in lipid-rich biological samples focused polar bear fat

Methods

2023-2024 fat samples (all adult males):
Baffin Bay: n=5 Clyde River, n=5 Pond Inlet
Hudson Bay: n=5 Arviat, n=4 Rankin Inlet, n=10 Sanikiluaq

Sample Processing Flow Diagram



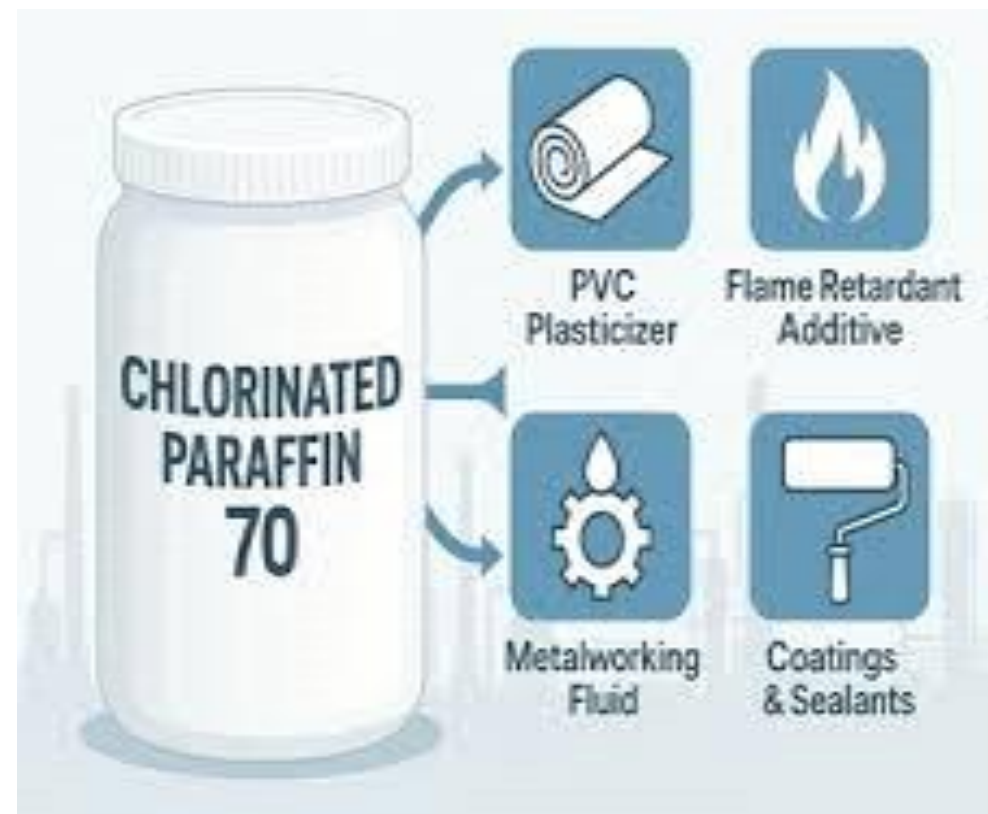
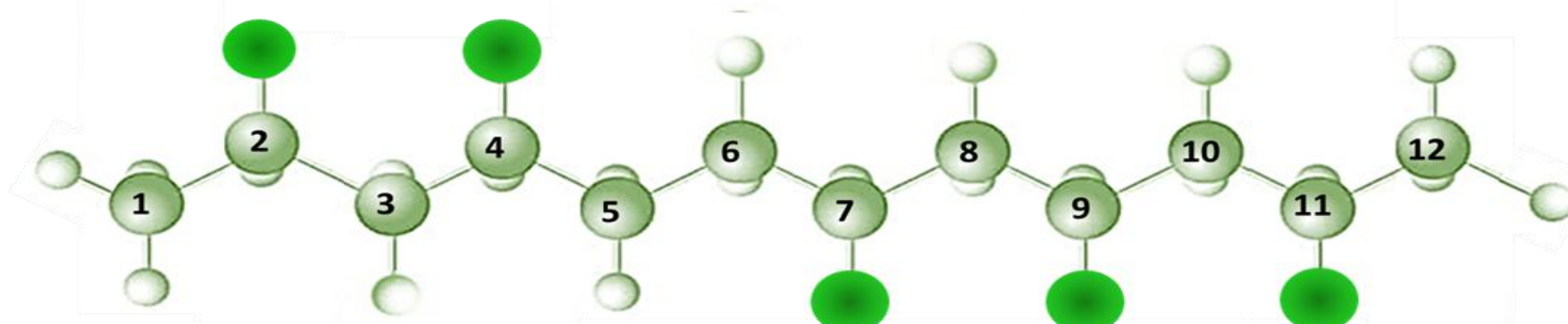
Results

Table 1: Concentrations of individual PCA carbon chain length homologues PCAs and instrument limits of detection (ILODs), method limits of detection (MLODs), method limits of quantitative (MLOQs) and PCA homologue group recoveries in spiked sunflower oil samples

	C_9Cl_x	$C_{10}Cl_x$	$C_{11}Cl_x$	$C_{12}Cl_x$	$C_{13}Cl_x$	$C_{14}Cl_x$	$C_{15}Cl_x$	$C_{16}Cl_x$	$C_{17}Cl_x$
ILOD (ng/mL)	2.8	0.4	0.4	0.4	0.3	0.5	0.4	0.5	0.9
MLOD (ng/g w.w.)	5.3	2.8	3.4	2.0	1.7	0.8	0.4	0.8	0.3
MLOQ (ng/g w.w.)	17.5	9.3	11.4	6.7	5.6	2.6	1.2	2.7	1.1
Recovery (%) *	106	110	102	106	105	127	120	99	116
STD	4	5	4	4	4	8	8	7	11
Recovery (%) *	130	140	119	121	108	160	129	122	115
STD	19	14	26	16	9	12	10	12	15

* 1 g of sunflower oil spiked with 50 ng each homologue group of PCAs.

** 1 g of sunflower oil spiked with 10 ng each homologue group of PCAs.



Highlights/Conclusions

- Developed GC-Orbitrap-HRMS based method ideal for determining individual PCA carbon chain homologue groups (C_9Cl_x to $C_{20}Cl_x$) in lipid-rich samples, e.g. polar bear fat (also other tissues?)
- Regardless of year, PCA homologue patterns for polar bears are MCCPs > SCCPs > LCCPs; PCA concentrations, WHB > SHB > BB subpopulations of bears (relation to production/emission changes?)
- Using the GC-Orbitrap-HRMS based method, more expansive PCA temporal trends underway with archived polar bear fat from Hudson Bay and for years ranging from 1983 to 2024

Acknowledgements

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Table 2: Concentrations of individual PCA carbon chain length homologues in free-ranging polar bear adipose and commercial seal oil from Canada (ng/g w.w.)

Sample name	Polar bear adipose						Harp Seal oil
Location	Rankin Inlet, NU, Canada	Whale Cove, NU, Canada	Arviat, Canada	Sanikiluaq, Canada	Pond Inlet, NU, Canada	Clyde River, NU, Canada	N/A, Canada
Lipid (%)	72.9-91.6	63.7	80.1-90.1	77.2-90.6	77.7-92.1	63.7-89.7	100
C_9Cl_x	ND-26.9	ND	ND-<17.5	ND	ND	ND-<17.5	<17.5
$C_{10}Cl_x$	ND-<9.3	ND	ND-<9.3	ND	ND-<9.3	ND	42.7
$C_{11}Cl_x$	ND-<11.4	<11.4	ND-<11.4	ND-<11.4	ND-<11.4	ND	17.3
$C_{12}Cl_x$	ND-7.4	<6.7	ND-6.9	ND-<6.7	ND-<6.7	ND-<6.7	8.9
$C_{13}Cl_x$	ND-<5.6	8.1	ND-<5.6	ND-<5.6	ND-<5.6	ND	140.0
$C_{14}Cl_x$	ND-19.1	11	8.6-29.5	ND-14.7	ND-13.4	ND-10.8	349.5
$C_{15}Cl_x$	ND-4.9	2.4	1.6-14.6	ND-3.5	ND-3.1	ND-2.4	47.3
$C_{16}Cl_x$	ND-<2.7	<2.7	ND-5.1	ND-<2.7	ND-3.0	ND-<2.7	21.2
$C_{17}Cl_x$	ND	ND	ND-<1.1	ND	ND-<1.1	ND	3.2
$C_{18}Cl_x$	ND	ND	ND-<3.3	ND	ND	ND-<3.3	<3.3
$C_{19}Cl_x$	ND	ND	ND	ND	ND	ND	ND
$C_{20}Cl_x$	ND	ND	ND	ND	ND	ND	ND
SUMs	16.8-48.2	30.8	13.2-38.2	ND-27.6	ND-27.4	ND-26.9	639.4
Mean	32.2	30.8	32.7	8.7	18.1	9.8	

Figure 1: extracted ion chromatograms (EICs) of homologue groups of PCAs (from C_9Cl_x to $C_{18}Cl_x$) detected in a polar bear adipose tissue

