Non-target and target analyses of new compounds in Svalbard biota

Photo: E. Fuglei/NP

Heli Routti

Photo: H.Routti/NP

Outline

- Non-target screening of new chemicals in Arctic apex predators
- Screening of bisphenols, UV-filters and siloxanes in the Arctic
- Temporal trends of PFAS in Arctic apex predators

Environmental Science & Technology

October 2016

Article

pubs.acs.org/est

Environmental Chemicals Modulate Polar Bear (*Ursus maritimus*) Peroxisome Proliferator-Activated Receptor Gamma (PPARG) and Adipogenesis in Vitro

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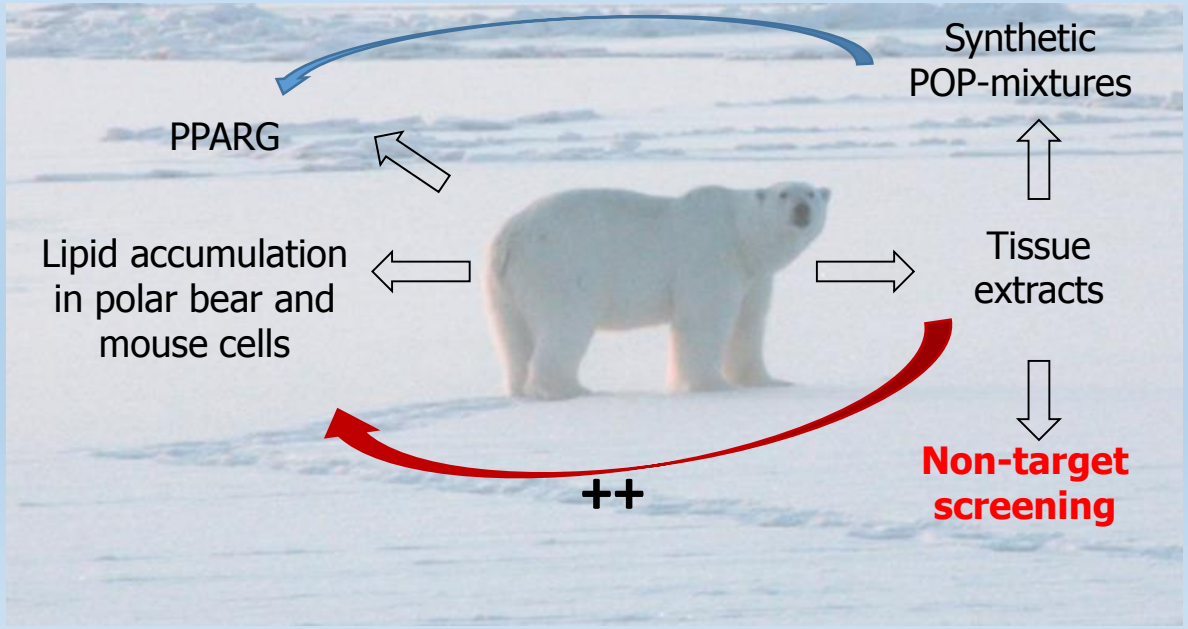
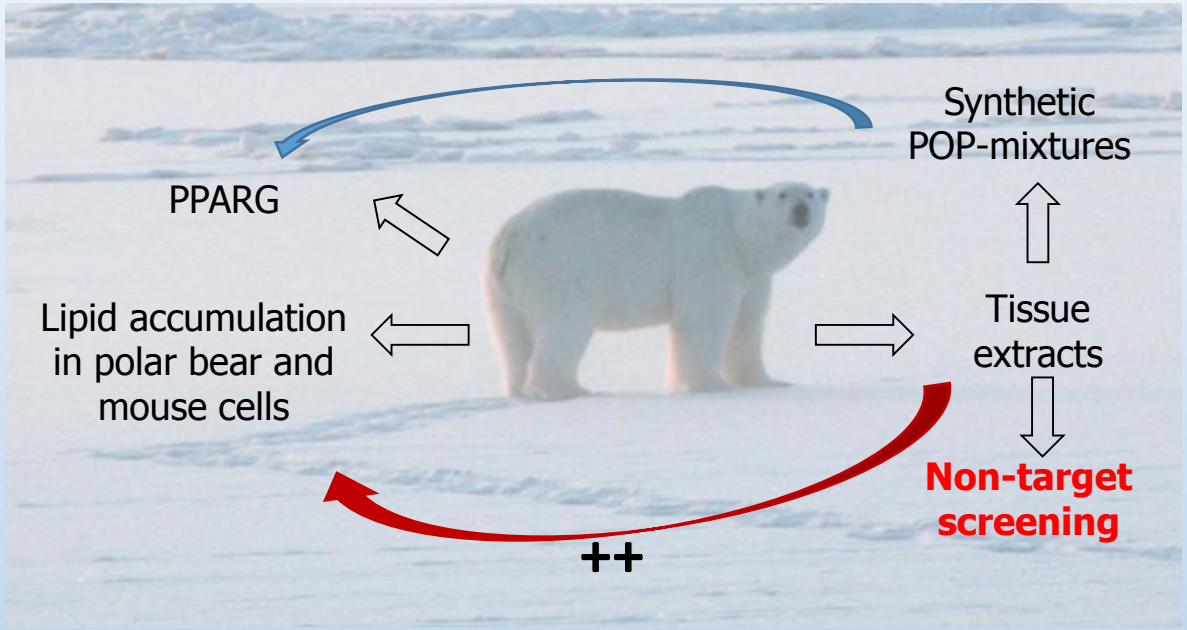


- Extracts of polar bear tissues (1 male bear from 2010)
- Divided in 3 fractions
- Analyses: Agilent ultrahigh performance liquid cromatography coupled to high resulution quadruppole time-of flight mass spectrometer
- Data processing: Agilent Mass Hunter data processing platform

- Target analyses of POPs and their metabolites
- Non-target screening revealed:
  - Adipose tissue extract: 13 compounds
  - Liver neutral extract: 55 compounds
  - Liver MeSO2-extract: 23 compounds
  - Combination of liver neutral, $MeSO_2$ and OH-extracts: 109 compounds



- 14 different structures identified in the extracts by non-target analysis were structurally similar to compounds that disrupt lipid metabolism based on literature

Compounds identified in polar bear tissue extracts by suspect/non-target screening.

Numbers refer to confidence level (range 1-5,
1= structure is confirmed by a reference standard.
2: probable structure based on a library match and diagnostic evidence)

CAS	Name	Molecular formula	Adipose all fractions	Liver neutral fraction	Liver $MeSO_2$ fraction	Liver all fractions
1506-02-1	Tonalide	C18H26O	1			
117-84-0	Di-n-octylphthalate	C24H38O4	1			
6422-86-2	Bis(2-ethylhexyl)terephthalate	C24H38O4	1			
117-81-7	Bis(2-ethylhexyl) phthalate	C24H38O4	1			
84-74-2 / 84-69-5	Dibutyl / diisobutyl phthalate	C16H22O4	2	3	2	3
26761-40-0	Diisodecyl phthalate	C28H46O4	2	2		3
84-76-4	Dinonyl phthalate	C26H42O4	2	2		2
28553-12-0	Diisononyl phthalate	C26H42O4	2	2		2
85-68-7	Butyl benzene phthalate	C19H20O4		2		2
104-40-5	4-nonylphenol	C15H24O		2		
84-66-2	Diethyl phthalate	C12H14O4			2	

- Extracts made from one individual → presence should be confirmed by target analyses in more individuals

Compounds found in polar bear liver/adipose tissue:

- Tonalide:
  - A highly lipophilic synthetic musk used in consumer products (7-acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene (AHTN))
  - Not previously detected in polar bear liver (Vorkamp et al. 2004 NERI-report, Kannan et al. 2005 Chemosphere)

- Phthalates:
  - Extensively used in plastics
  - Previously detected in polar bear liver and Arctic seawater and air (Vorkamp et al. 2004 NERI-report; Xie et al. 2007, EST)

- 4-nonylphenol
  - Biodegradation product of nonylphenyl ethoxylate, an industrial chemical, and a component of produced water from the petroleum activity in the North Sea and Norwegian Sea
  - Previously detected in polar bear plasma (Simon et al. 2013, EST)

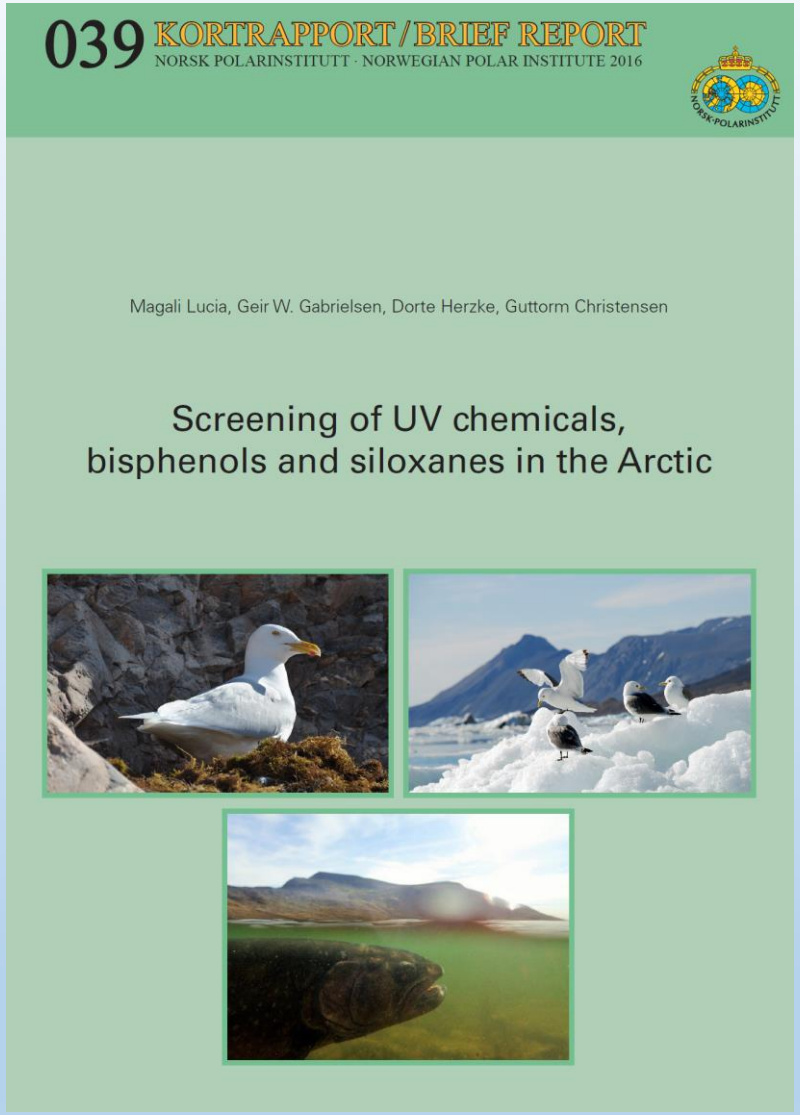
Conclusions of non-target analyses

- Study on polar bears, glaucous gulls and white whales revealed only few current used chemicals

→We cover quite well chemical exposure with target analyses

- Study on polar bear extracts → current used chemicals found!
- Different analytical software

- Challenges:
- Work-demanding and expensive
- Both non-target and target analyses needed to confirm the presence of the compounds
- Lack of target methods to analyze new compounds



- **Samples:** eggs from kittiwakes (*Rissa tridactyla*) and glaucous gulls (*Larus hyperboreus*), as well as Arctic chars (*Salvelinus alpinus*) from Svalbard.

- **Organic UV filters**
  - Sunscreen, cosmetics, plastics, and varnish
  - orthohydroxy benzotriazole UV stabilizers (UV-320, UV-326, UV-327, UV-328, UV-329), Benzophenone-3 (BP3), 2-ethylhexyl-4-dimethylaminobenzoate (ODPABA), Ethylhexylmethoxycinnamate (EHMC) and octocrylene (OC).

- **Bisphenols**
  - Consumer products, food containers
  - Endocrine-disrupting effects (bisphenol A)

- **Siloxanes**
  - Consumer and industrial products, (e.g. personal care products, medical devices).
  - Refers to organosilicon compounds including silicon, oxygen and alkanes:
  - D4: octamethylcyclotetrasiloxane, D5: decamethylcyclopentasiloxane, D6: dodecamethylcyclohexasiloxane, M3T(Ph): tris(trimethylsiloxy)phenylsilane)

Concentrations of UV-filters and siloxanes (ng/g ww)

Sample	Location	BP3	EHMC	OC	UV-320	UV-326	UV-327	UV-328	UV-329	ODPABA	D4	D5	D6	M3T(ph)
Char1	Ellasjøen	<3	31.7	<2	<1	<3	<1	<1	<2	<3	<3.11	<2.2	<10.4	<0.15
Char2		<2	30.7	<2	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char3		<5	11.6	<2	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char4		<3	39.3	<3	<1	<3	<1	<1	<1	<6	<3.11	<2.2	<10.4	<0.15
Char5		<3	8.0	<3	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char6	Erlingvatnet	<3	12.4	<2	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char7		<3	8.9	<2	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char8		<3	11.2	<2	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char9		<3	5.0	<2	<1	<3	<1	<1	<1	<5	<3.11	<2.2	<10.4	<0.15
Char10		<5	13.7	<4	<1	<3	<2	<2	<1	<5	<3.11	<2.2	<10.4	<0.15
Kit1	Kykkjefjellet	*	<20	<17	<2	<3	<1	<1	<2	<5	<2.78	<2.38	<8.01	<0.23
Kit2	Observasjonsholmen	*	<20	<17	<2	<3	<2	<2	<2	<10	<2.78	<2.38	<8.01	<0.23
Kit3		*	<20	<17	<2	<3	<1	<1	<2	<5	<2.78	<2.38	<8.01	<0.23
Kit4		*	<20	<17	<2	<3	<1	<1	<2	<5	<2.78	<2.38	<8.01	<0.23
Kit5		*	<20	<17	<2	<3	<1	<1	<2	<5	<2.78	<2.38	<8.01	<0.23
GG1	Kapp Guissez	*	<20	<17	<2	<3	<1	<1	<2	<5	5.77	3.37*	<8.01	<0.23
GG2		*	<20	<17	<2	<3	<1	<1	<2	<5	4.19*	11.6	<8.01	<0.23
GG3		*	<20	<17	<2	<3	<2	<2	<2	<5	3.54*	3.84*	<8.01	<0.23
GG4		*	<20	<17	<2	<3	<2	<2	<2	<5	<2.78	3.06*	<8.01	<0.23
GG5		*	<20	<17	<2	<3	<2	<2	<2	<5	<2.78	40.1	<8.01	<0.23

* denotes interferences

Photos: G. Christensen, GW Gabrielsen

Concentrations of bisphenols (ng/g ww)

Sample	Location	BPA	TBBPA	4,4'-BPF	2,2'-BPF	BPAF	BPBP	BPS	NOPHE4	OCPHE4	TOCPHE4
Char1		1.0	<1	<1	<1	<1.1	<3	<0.3	<1	2.8	<1.5
Char2		<2	<2	<1	<1	<1.1	<3	<0.3	<1	1.3	<1.5
Char3	Ellasjøen	<2	<2	<1	<1	<1.1	<3	<0.3	<1	1.4	<1.5
Char4		<2	<2	<1	<1	<1.1	<3	<0.3	82	2.3	<1.5
Char5		<2	<2	<1	<1	<1.1	<3	<0.3	<1	8.6	<1.5
Char6		<2	<2	<1	<1	<1.1	<3	<0.3	<1	5.9	<1.5
Char7		<2	<2	<1	<1	<1.1	<3	<0.3	<1	<2	<1.5
Char8	Erlingvatnet	<2	<2	<1	<1	<1.1	<3	1.3	<1	<2	<1.5
Char9		<2	<2	<1	<1	<1.1	<3	<0.3	<1	<2	<1.5
Char10		<2	<2	<1	<1	<1.1	<3	0.7	<1	<2	<1.5
Kit1	Krykkjefjellet	<1	1.0	<1	1.3	<1.1	<3	0.4	4.1	2.1	<1.5
Kit2		8.0	<1	7.4	<1	3.1	<3	1.0	<1	<2	<1.5
Kit3	holmen	<1	<1	<1	1.3	<1.1	<3	<0.3	<1	15.5	<1.5
Kit4		8.8	<1	7.5	<1	<1.1	<3	1.1	<1	<2	<1.5
Kit5		3.7	<1	<1	1.3	<1.1	<3	0.5	<1	4.8	<1.5
GG1		8.2	<1	<1	<1	3.1	<3	1.1	<1	<2	<1.5
GG2		7.0	<1	<1	<1	2.0	<3	1.0	<1	19	<1.5
GG3		6.3	<1	6.0	<1	<1.1	<3	0.5	<1	6.0	<1.5
GG4		7.1	<1	<1	<1	<1.1	<3	0.9	<1	3.8	<1.5
GG5		2.0	<1	2.0	<1	<1.1	<3	<0.3	<1	<2	<1.5

Sample	Location	BPB	BPZ	BPAP	BPE	BPFL	BPP	BPM	BPG	BPTMC	2,4'-BPF
Char1		<3	<3	<1.5	<1.5	<2	<2	<3	<2	<2	<1.5
Char2		8.8	23	1.5	<1.5	<2	2.4	<3	17	<2	<1.5
Char3	Ellasjøen	6.0	<3	<1.5	<1.5	<2	10	<3	84	<2	<1.5
Char4		9.5	<3	4.8	<1.5	<2	7.8	<3	94	<2	<1.5
Char5		8.3	78	5.1	12	<2	19	<3	61	<2	<1.5
Char6		<3	142	<1.5	<1.5	<2	20	<3	29	<2	<1.5
Char7		6.9	96	<1.5	<1.5	<2	<2	<3	35	6.3	<1.5
Char8	Erlingvatnet	<3	32	2.0	<1.5	<2	14	<3	49	<2	<1.5
Char9		<3	114	8.9	<1.5	<2	<2	<3	42	<2	<1.5
Char10		14	98	5.2	<1.5	<2	33	<3	73	4.3	<1.5
Kit1	Krykkjefjellet	<3	<3	<1.5	<1.5	<2	<2	<3	15	<2	<1.5
Kit2		2.0	<3	<1.5	<1.5	1.3	<2	<3	<2	<2	0
Kit3	Observasjonsholmen	<3	<3	<1.5	<1.5	<2	<2	<3	<2	3.2	5.4
Kit4		11	<3	<1.5	<1.5	<2	<2	<3	<2	<2	<1.5
Kit5		<3	6.3	<1.5	<1.5	<2	<2	<3	<2	3.5	<1.5
GG1		6.0	<3	<1.5	<1.5	2.4	<2	<3	<2	<2	<1.5
GG2		2.0	<3	<1.5	<1.5	<2	<2	<3	<2	3.0	<1.5
GG3	Kapp Guissez	8.0	<3	<1.5	<1.5	<2	<2	<3	<2	<2	<1.5
GG4		11	<3	<1.5	<1.5	<2	<2	<3	<2	5.0	<1.5
GG5		<3	<3	<1.5	<1.5	<2	<2	<3	<2	<2	<1.5

Conclusions:

Seabird eggs:

- D5 (siloxane), bisphenol A and B
- Glaucous gulls > kittiwakes

Arctic char:

- EHMC (UV-filter), bisphenols G, P, Z

Levels are generally low

Photos: G. Christensen, GW Gabrielsen

Temporal trends of PFAS in Arctic apex predators

PFOS and related compounds

- Volunteer phase out since 2000 by 3M, the major producer
- Listed under the Stockholm Convention in 2009
- Extensive manufacturing in China since early 2000s (Wang et al., 2014; Xie et al., 2013)

PFCA

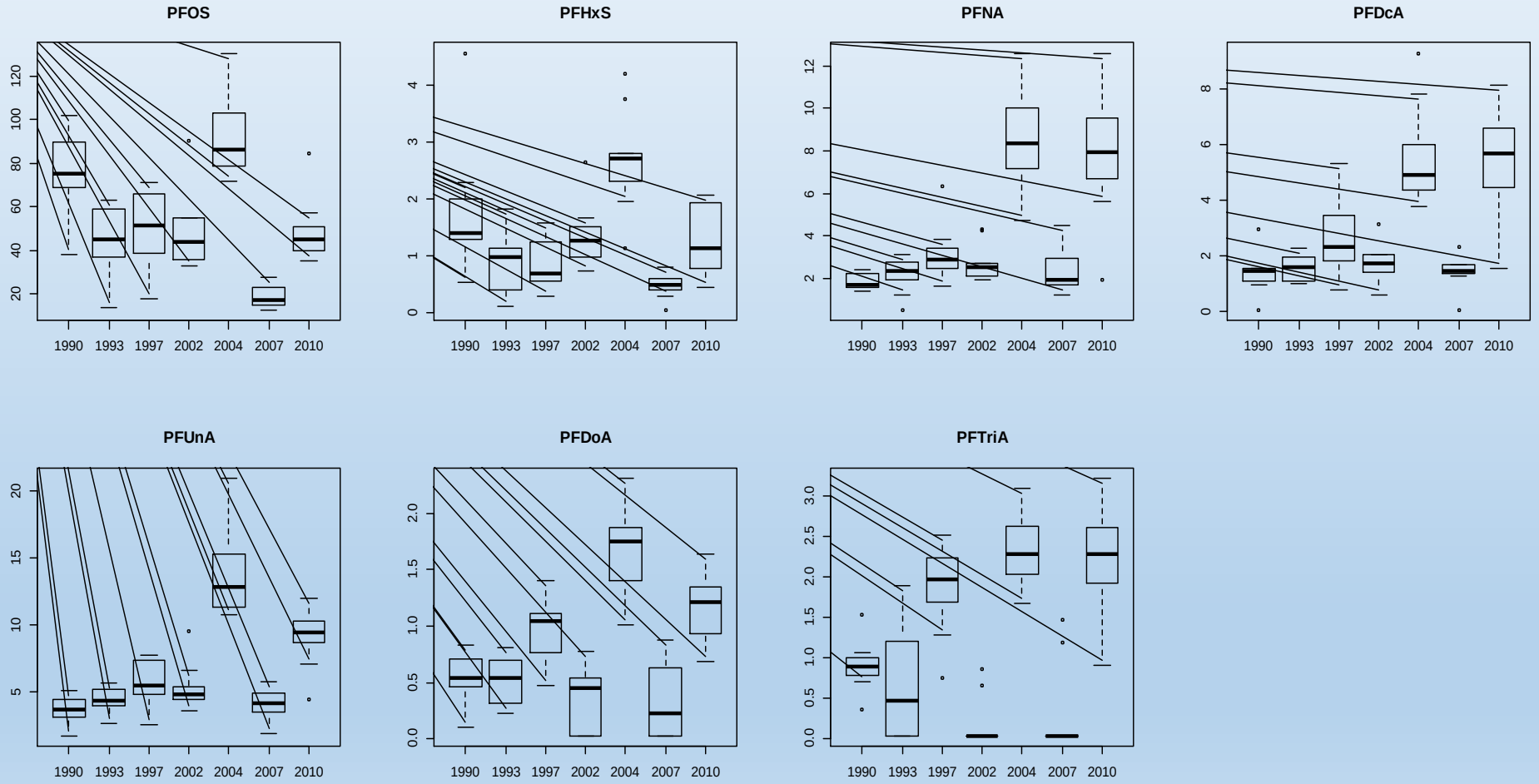
- Perfluorooctanoate (PFOA) and its higher homologues with >8 carbons gradually phased out in the US.
- Release of PFCAs has also decreased in production sites in Western Europe and Japan since 2000 (Wang et al., 2014).
- Today, PFCAs with ≥8 carbons considered in the candidate list of “substances of very high concern”by EHCA
- PFOA and its precursors are proposed for listing under the Stockholm Convention
- Production of PFCAs and their precursors increased in China and other developing Asian economies since 2002 (Wang et al., 2014).

Spatial and temporal trends of perfluoroalkyl substances (PFASs) in ringed seals from Svalbard

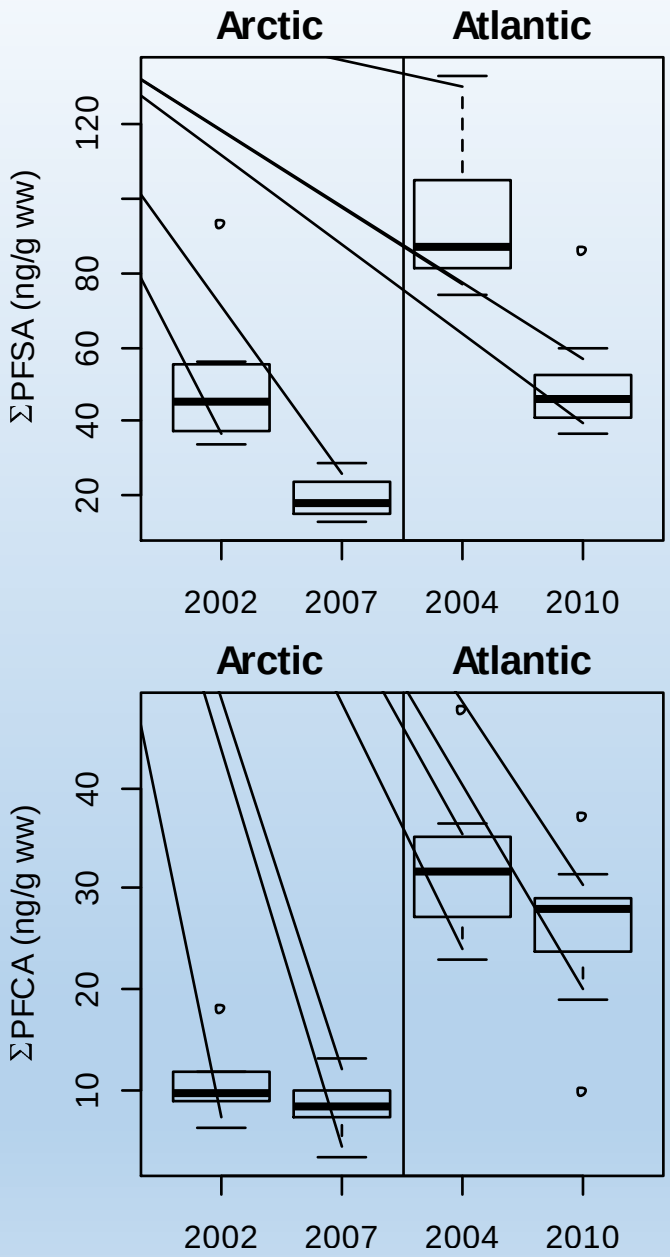
- 1990-2010
- 71 ringed seals
- 9-11 per year, 7 years
- Known sex, age, body condition

Routti, H., Gabrielsen, G.W., Herzke, D., Kovacs, K.M., Lydersen, C., 2016. Environmental Pollution 214, 230-238.

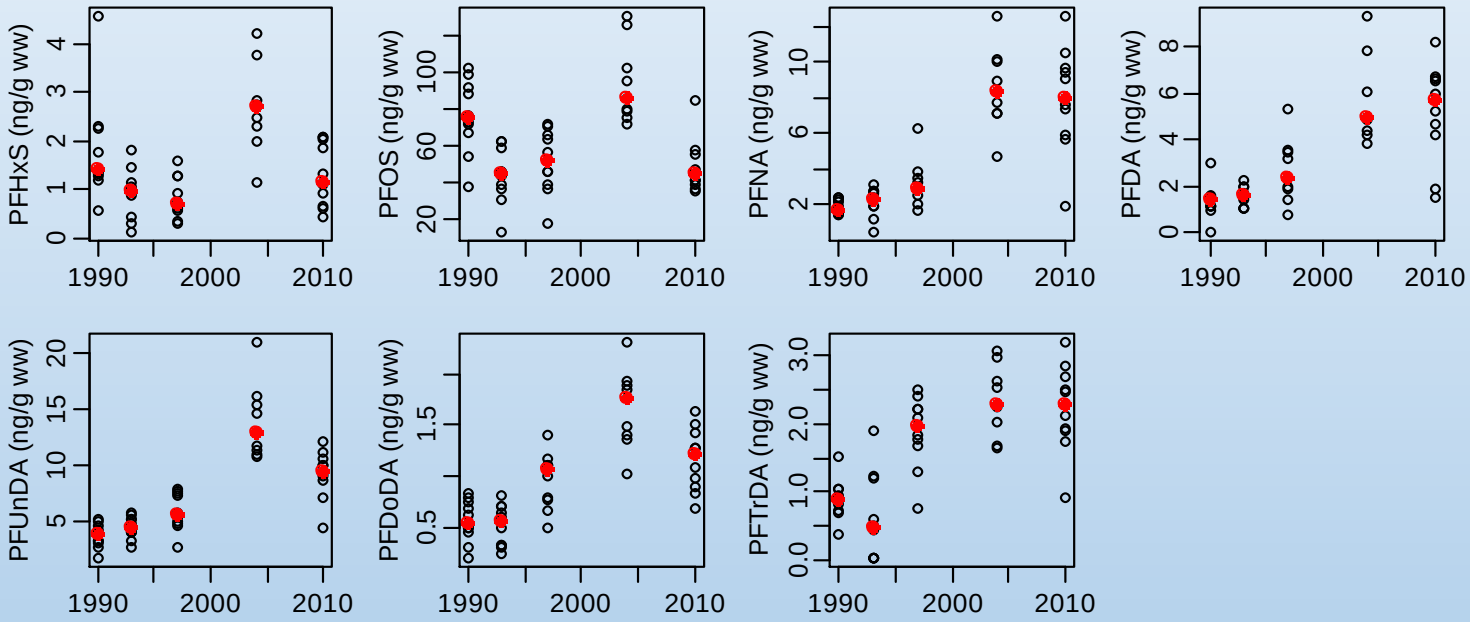
Temporal trends of PFASs in ringed seals from Svalbard



Kongsfjorden
Billefjorden
Tempelfjorden
Van Mijenfjorden
78°N
10°E
50 km
© Norwegian Polar Institute 2016


Arctic
Atlantic
ΣPFSA (ng/g ww)
20
40
60
80
120
2002
2007
2004
2010
Arctic
Atlantic
ΣPFCA (ng/g ww)
10
20
30
40
2002
2007
2004
2010

Temporal trends of perfluoroalkyl substances in ringed seals from Kongsfrorden



Red dots = annual median concentrations

	1990-2010 (n=51)	2004-2010 (n=20)
PFHxS	1.5 % [-1.2 , 4.3]	-12 % [-19 , -5.6]
PFOS	-0.18 % [-1.9 , 1.5]	-11 % [-14 , -7.3]
PFSA	-0.14 % [-1.8 , 1.6]	-11 % [-14 , -7.4]
PFNA	8.4 % [6.6 , 10]	-2 % [-8.1 , 4.6]
PFDA	8.5 % [5.7 , 11]	-2.2 % [-8.9 , 4.9]
PFUnDA	5.8 % [4.3 , 7.3]	-6.6 % [-10 , -2.9]
PFDoDA	5.3 % [3.6 , 7]	-5.9 % [-9.6 , -1.9]
PFTrDA	8.2 % [4.1 , 13]	-1.2 % [-5.7 , 3.5]
PFCA	6.8 % [5.3 , 8.3]	-3.9 % [-8.4 , 0.85]

Acknowledgements

- Non-target screening of new chemicals in Arctic apex predators
  - NILU: Mikael Harju, Pawel Rostkowski
  - NPI: Geir Wing Gabrielsen, Kit Kovacs, Christian Lydersen, Jon Aars

- Screening of bisphenols, UV-filters and siloxanes in the Arctic
  - NPI: Magali Lucia, Geir Wing Gabrielsen
  - NILU: Dorte Herzke
  - Akvaplan: Guttorm Christensen

- Temporal trends of PFAS in Arctic apex predators
  - NPI: Jon Aars, Eva Fuglei, Åshild Pedersen, Karen Lone
  - NILU: Linda Hansen
  - NMBU: Anuschka Polder
  - Univ. of Alaska: Jeffrey M. Welker
  - UiT: Nigel G. Yoccoz