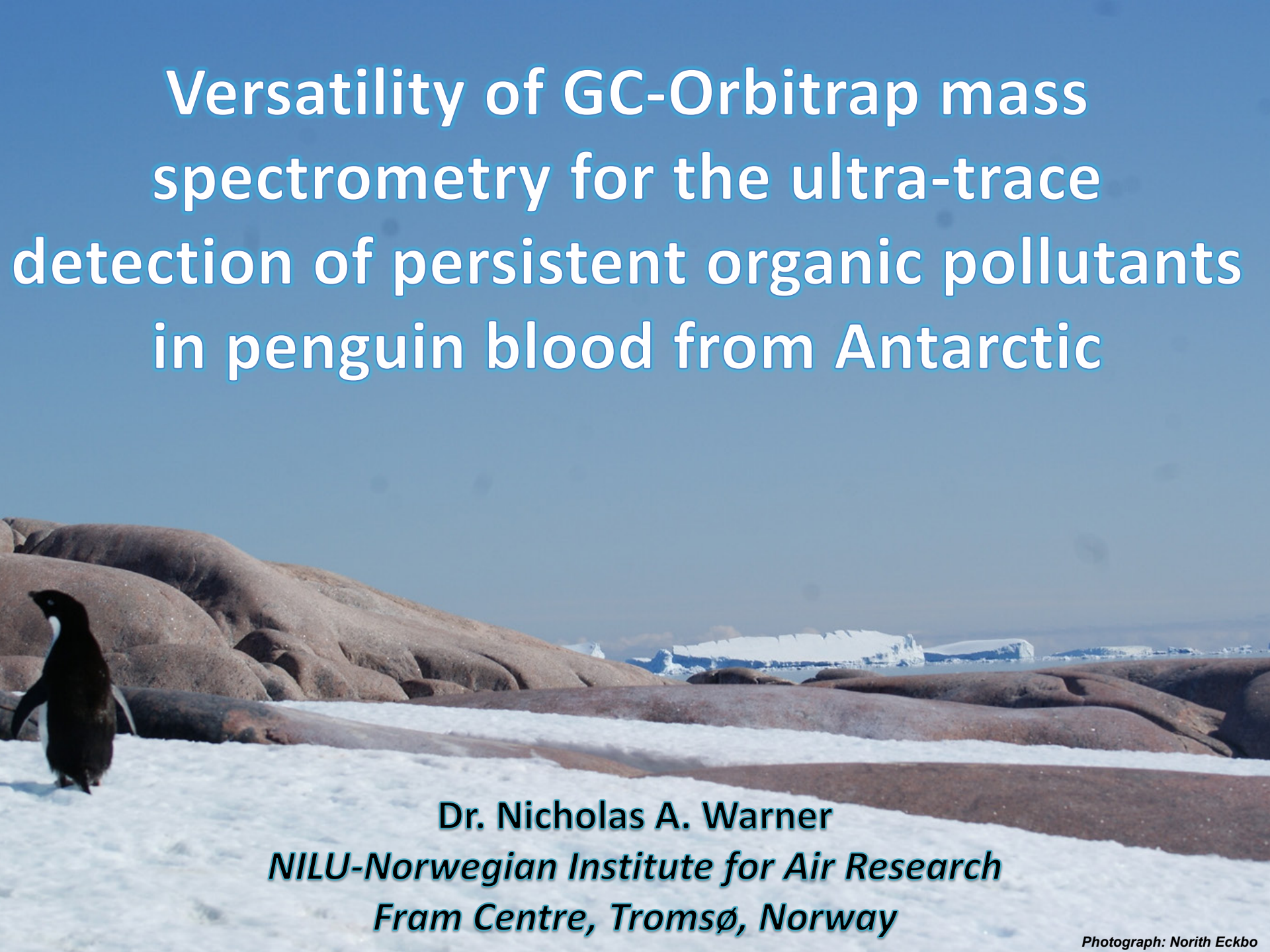
Versatility of GC-Orbitrap mass spectrometry for the ultra-trace detection of persistent organic pollutants in penguin blood from Antarctic



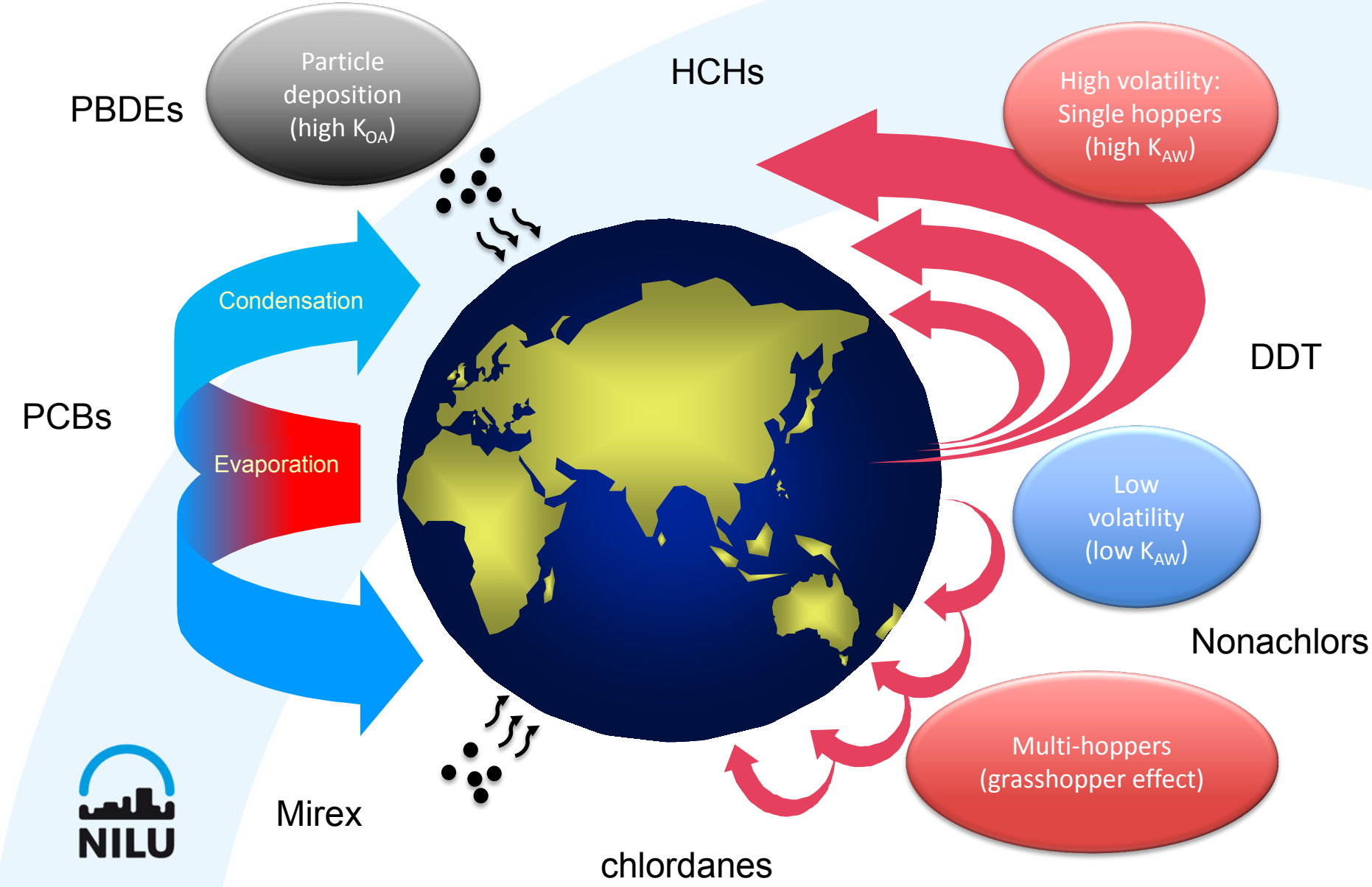
Dr. Nicholas A. Warner

NILU-Norwegian Institute for Air Research

Fram Centre, Tromsø, Norway

Photograph: Norith Eckbo

Contaminants in Polar Regions



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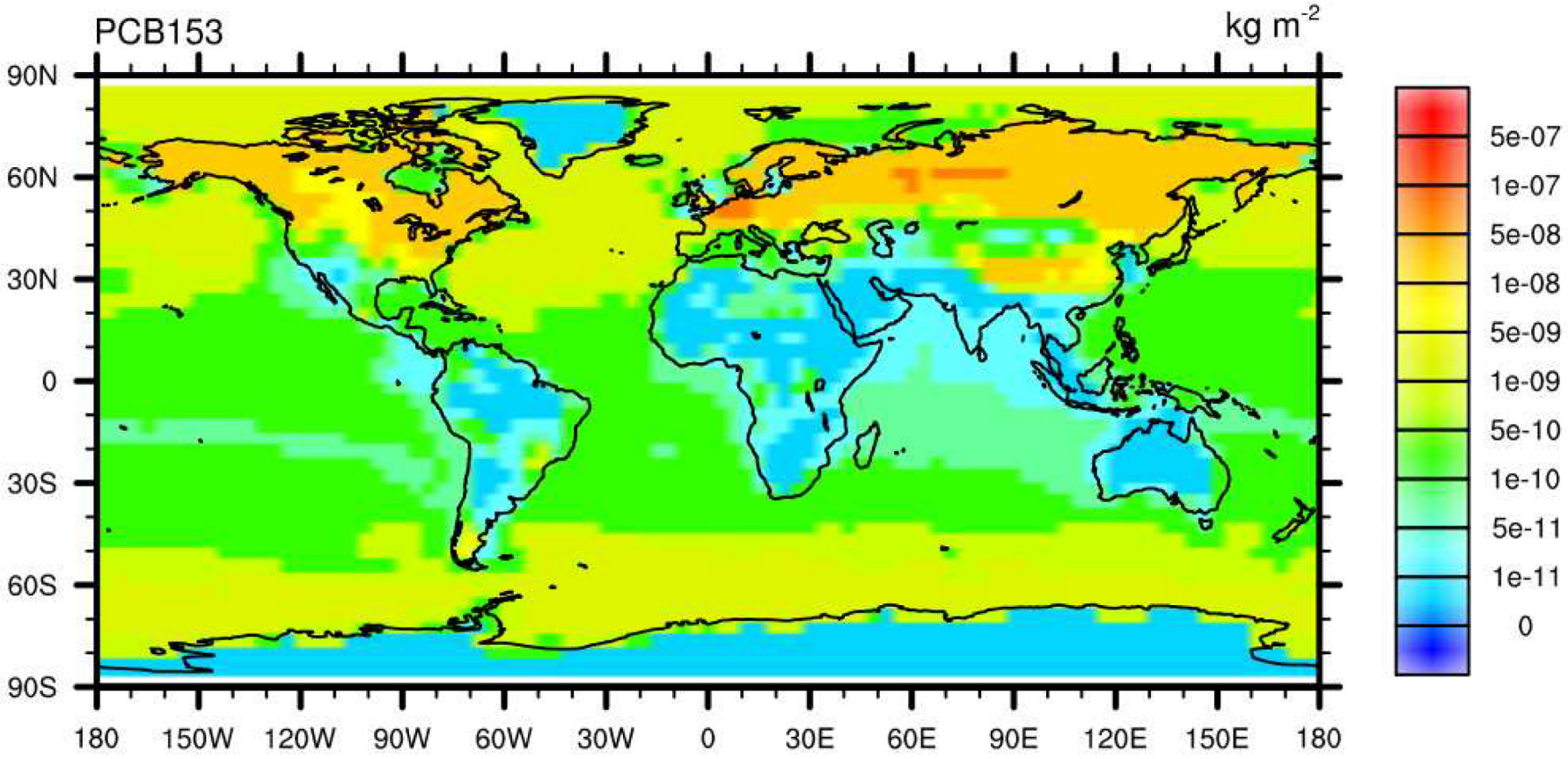
Arctic vs. Antarctic

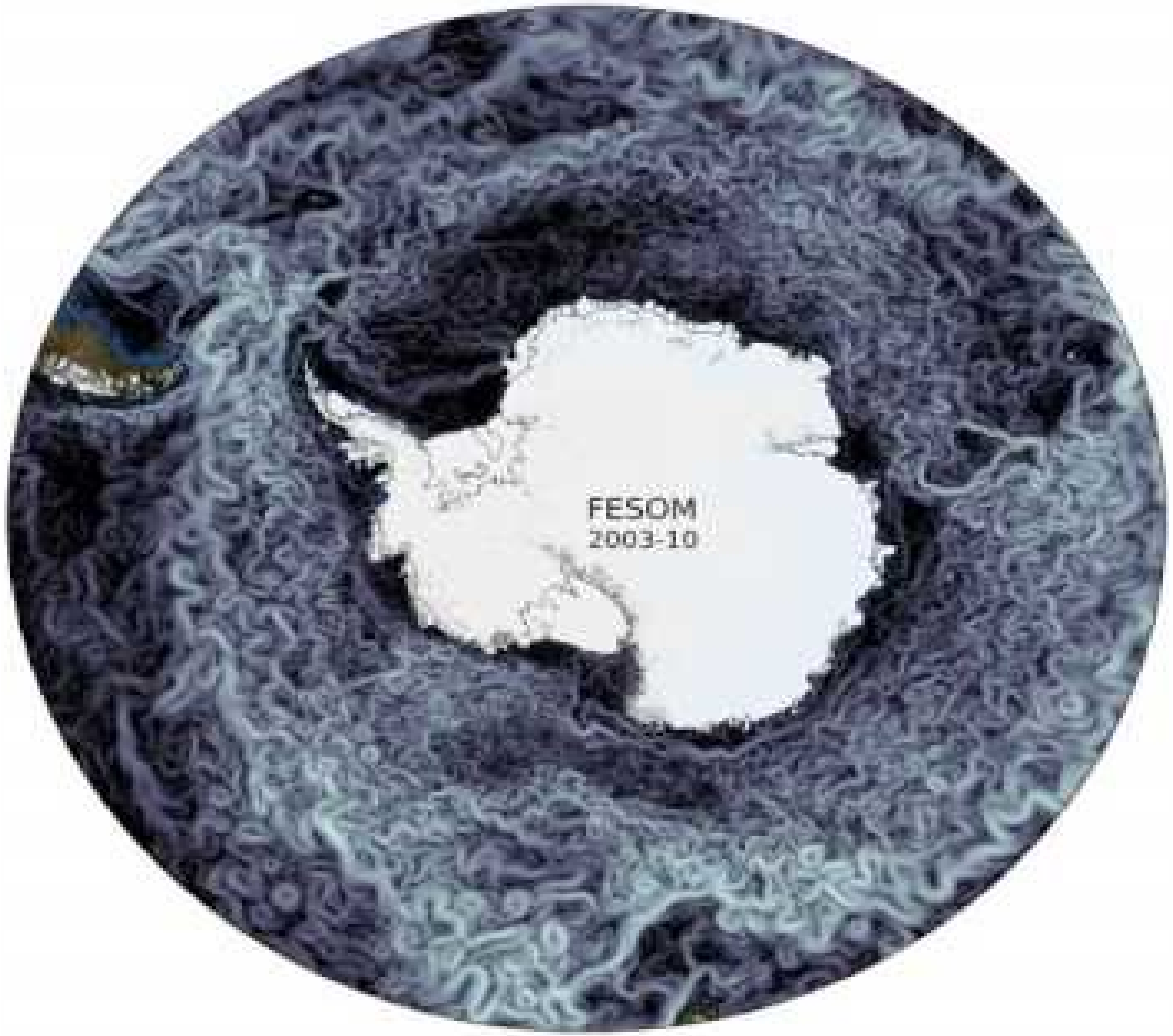
Predicted global distribution of total PCB 153 environmental burden (2010)

(Lammel and Stemmler. Atmos. Chem. Phys. 2012)



Arctic vs. Antarctic

Antarctic Circumpolar Current



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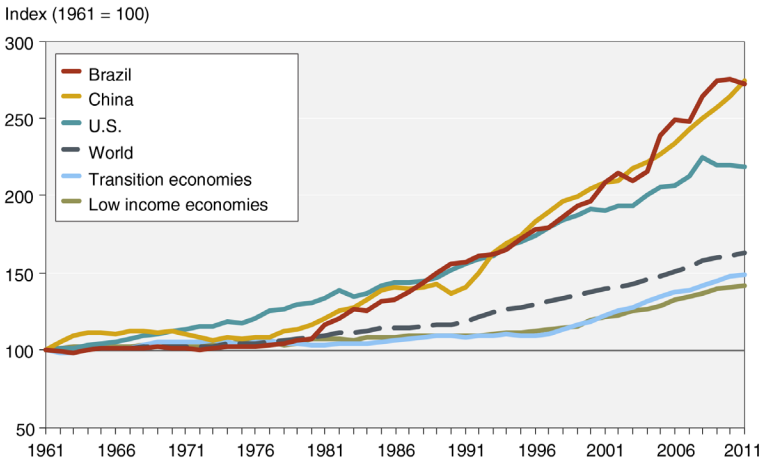
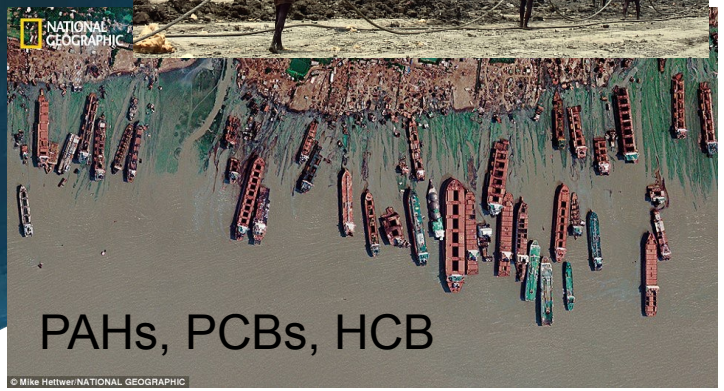
Exposure risks to Antarctica?

Agricultural productivity (measured as total factor productivity) growth for selected countries/country groups, 1961-2011



Note: Total factory productivity (TFP) takes into account all of the land, labor, capital, and material resources employed in farm production and compares them with the total amount of crop/livestock output. If total output is growing faster than total inputs, we call this an improvement in TFP.
Source: USDA, Economic Research Service, International Agricultural Productivity data product.

OC compounds detected in:
air, soil, biota



Contaminant monitoring needed to assess impacts of increased emission sources in Southern Hemisphere on Antarctic environment

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POLAR-ECOTOX project

«To quantify temporal changes in contaminants to identify climatic, ecological, and anthropogenic drivers affecting exposure in Antarctic wildlife"

- King penguin blood (2000-2017)

- Reside within and rely on the circumpolar current
- Provide a baseline to assess temporal changes in OC contaminant exposure

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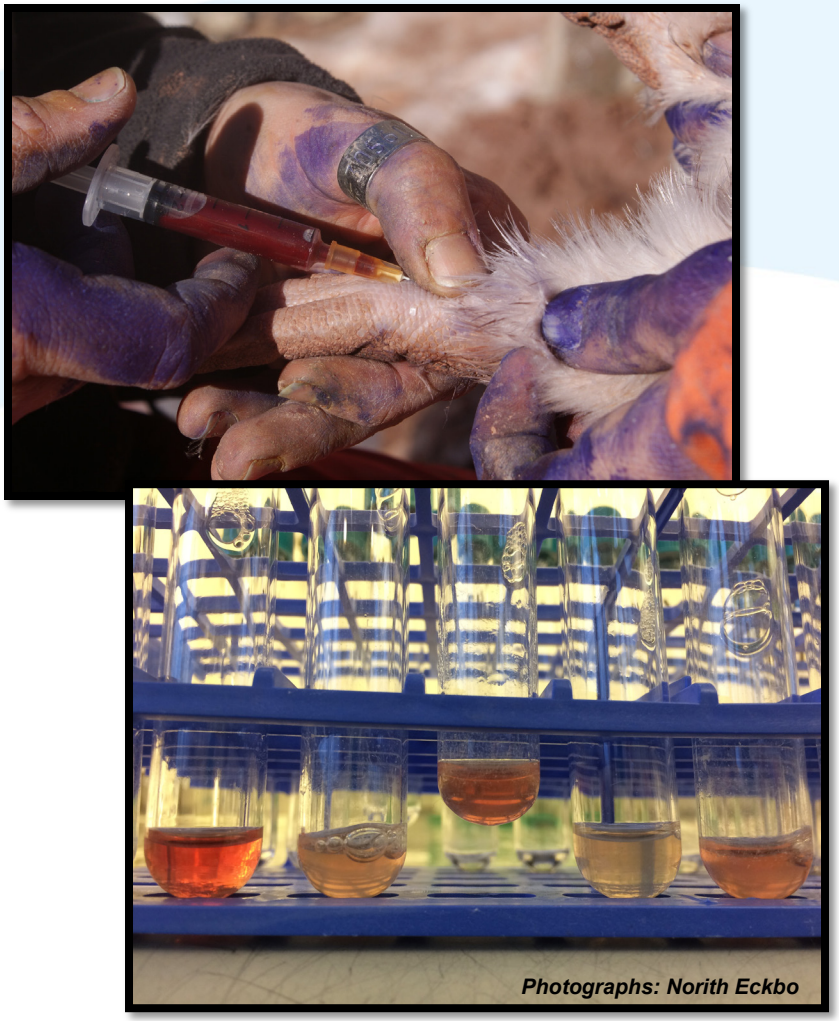
Challenges

- Sample material
  - non-destructive sampling
  - Limited material
- Low concentration levels
- Sample processing minimized to avoid analyte losses



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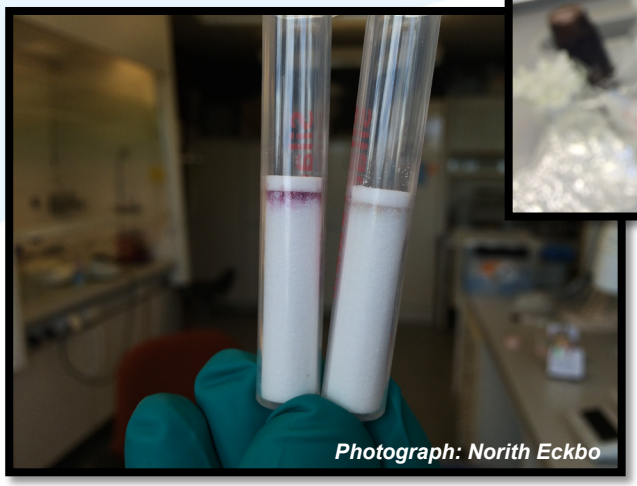
Sample preparation and analysis

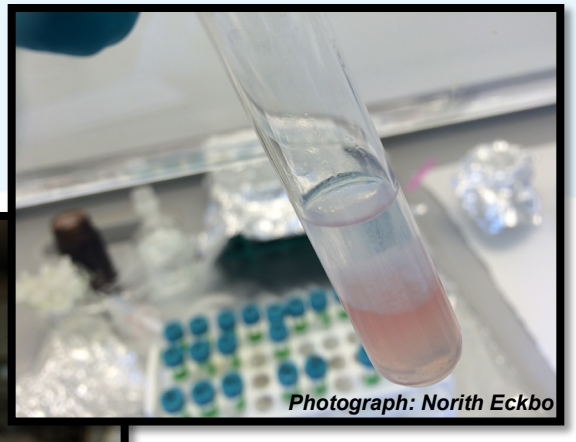
Liquid-liquid extraction
50% EtOH$(NH_4)_2SO_4$):Hexane

Automated SPE clean-up
using activated Florosil

Concentrated extract (50 µL) analyzed using GC-Orbitrap HRAM

- Full scan
- Targeted SIM





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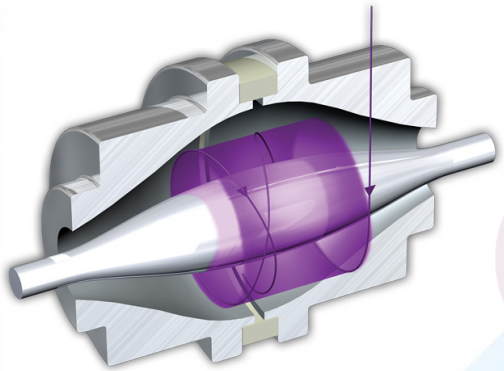
GC-Q-Exactive



120K mass resolution FWHM (routine at 60K)

Resolving power useful to remove co-extracted matrix/chemical inteferences

Detection sensitivity at ppt levels using full scan

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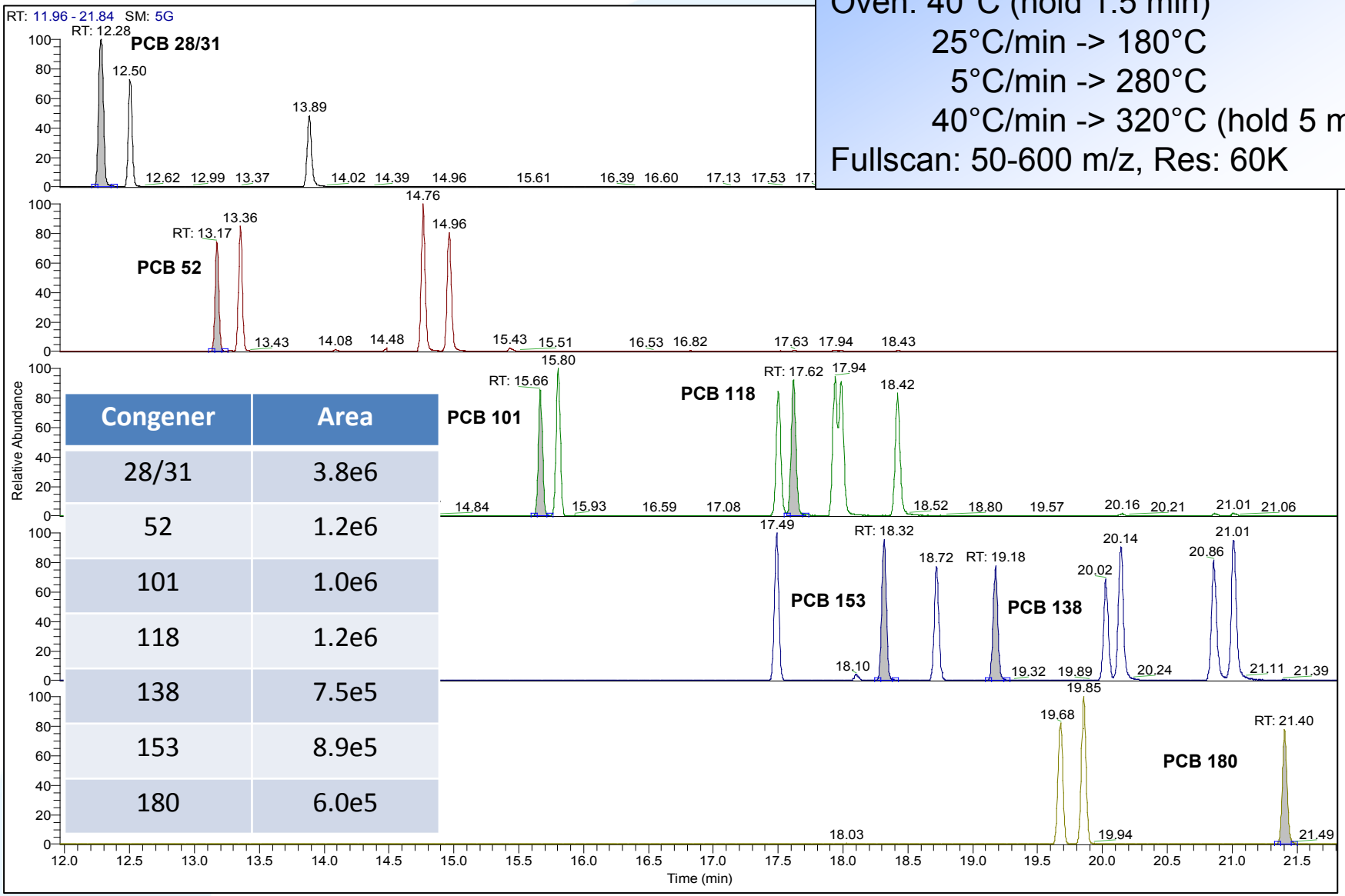
PCB standard (7 pg/µL)

Method details

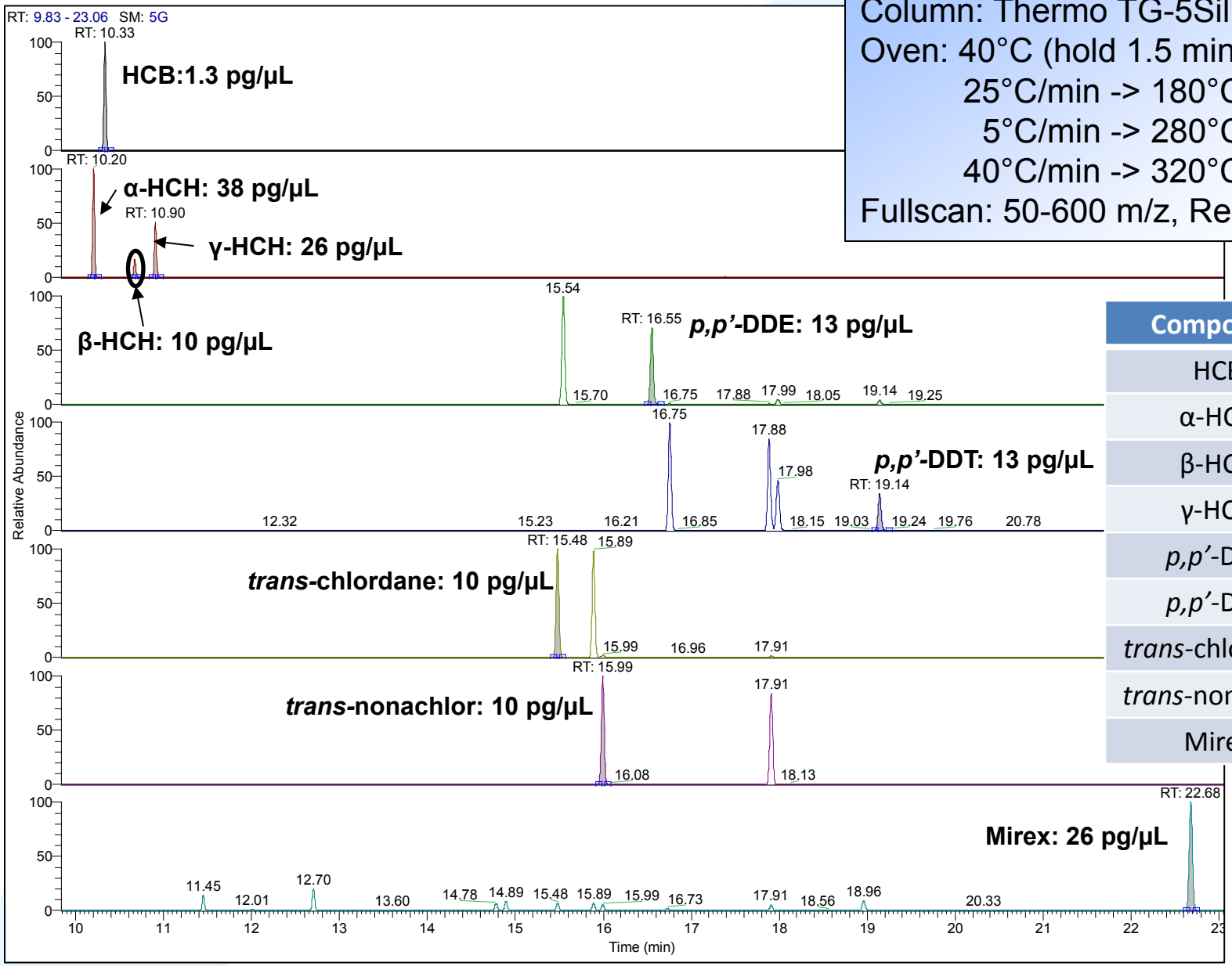
1 µL injection (SSL injector, 250°C)
Splitless time: 1.5 min
Column: Thermo TG-5Sil MS
Oven: 40°C (hold 1.5 min)
25°C/min -> 180°C
5°C/min -> 280°C
40°C/min -> 320°C (hold 5 min)
Fullscan: 50-600 m/z, Res: 60K



Congener	Area
28/31	3.8e6
52	1.2e6
101	1.0e6
118	1.2e6
138	7.5e5
153	8.9e5
180	6.0e5

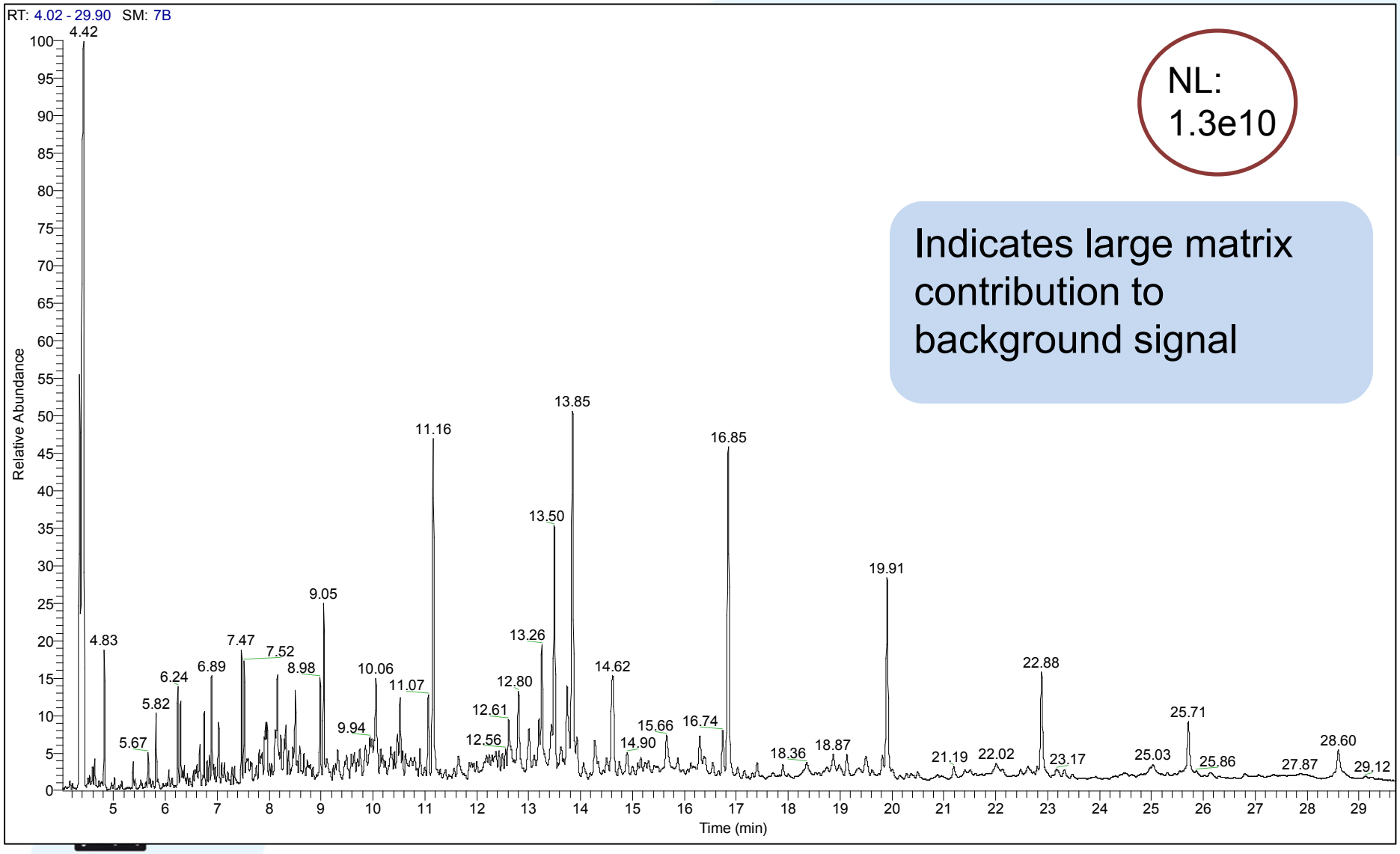
Pesticide standard

Method details
1 µL injection (SSL injector, 250°C)
Splitless time: 1.5 min
Column: Thermo TG-5Sil MS
Oven: 40°C (hold 1.5 min)
25°C/min -> 180°C
5°C/min -> 280°C
40°C/min -> 320°C (hold 5 min)
Fullscan: 50-600 m/z, Res: 60K



Compound	Area
HCB	4.8e5
α-HCH	1.0e7
β-HCH	1.8e6
γ-HCH	5.5e6
p,p'-DDE	4.3e6
p,p'-DDT	1.7e6
trans-chlordane	1.3e6
trans-nonachlor	1.4e6
Mirex	7.4e6

Antarctic penguin blood sample (full scan)



NL:
1.3e10

Indicates large matrix contribution to background signal

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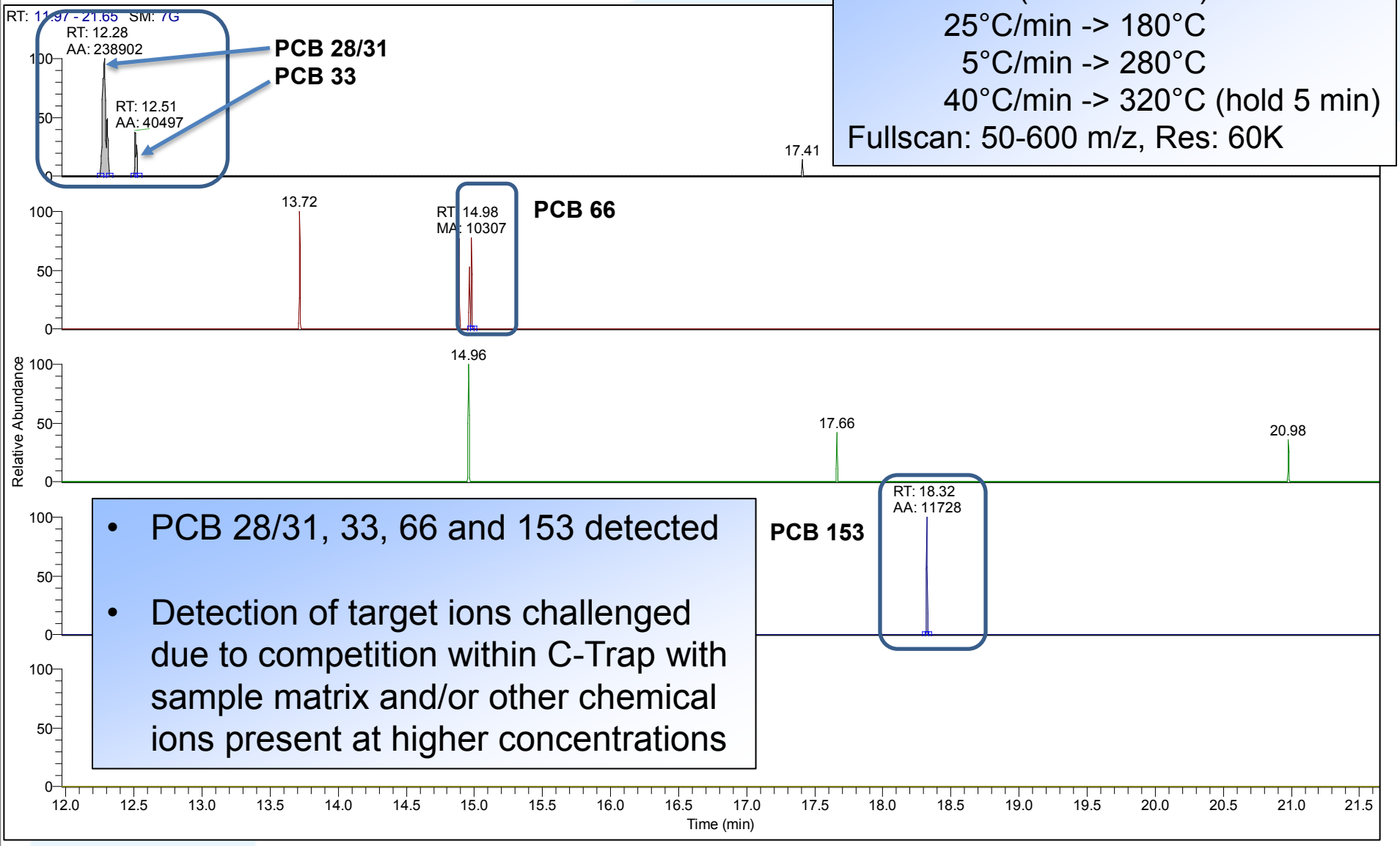
Antarctic penguin blood sample (PCBs)

Method details

1 µL injection (SSL injector, 250°C)
Splitless time: 1.5 min
Column: Thermo TG-5Sil MS
Oven: 40°C (hold 1.5 min)
25°C/min -> 180°C
5°C/min -> 280°C
40°C/min -> 320°C (hold 5 min)
Fullscan: 50-600 m/z, Res: 60K

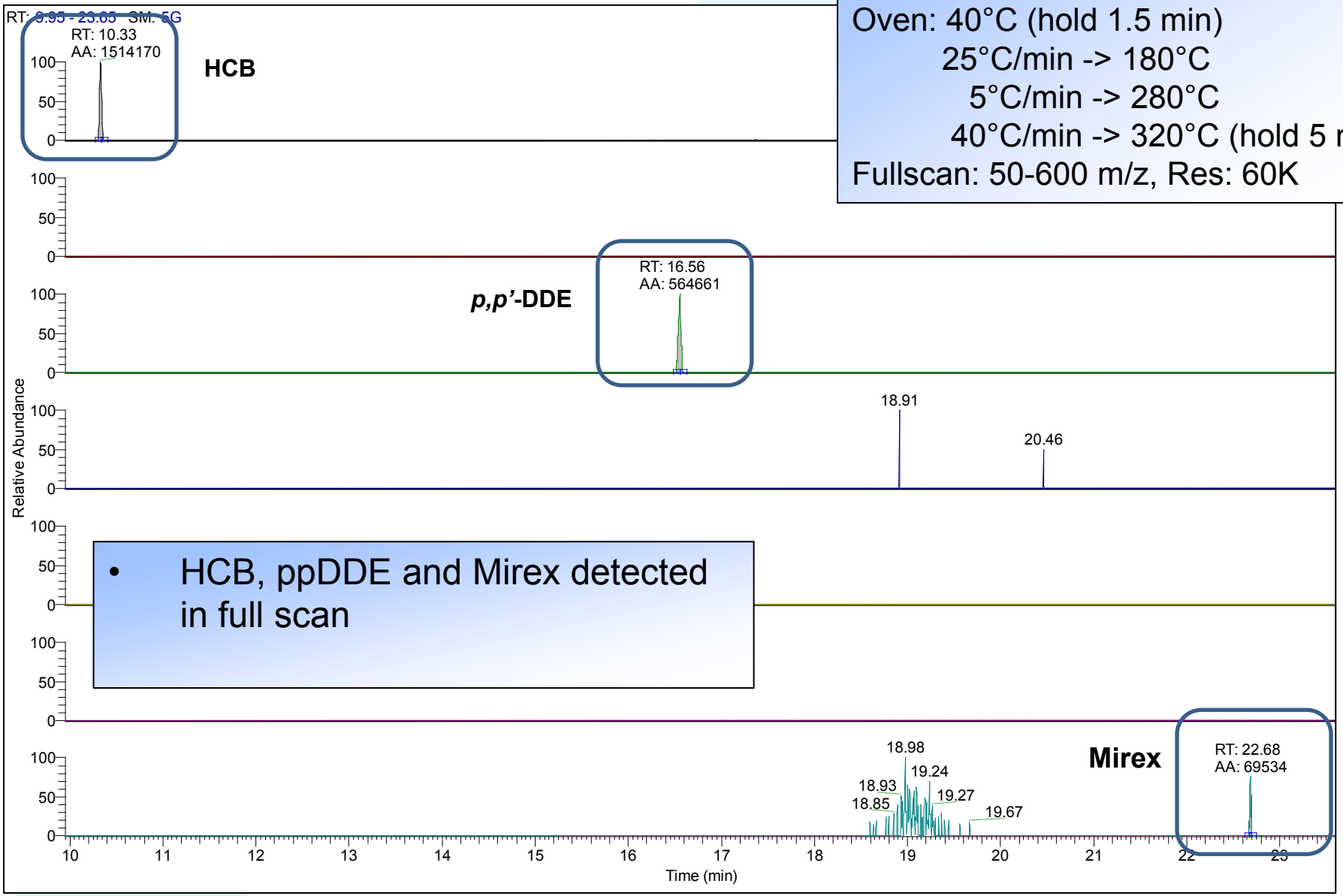


- PCB 28/31, 33, 66 and 153 detected
- Detection of target ions challenged due to competition within C-Trap with sample matrix and/or other chemical ions present at higher concentrations

Antarctic pengiun blood sample (pesticides)

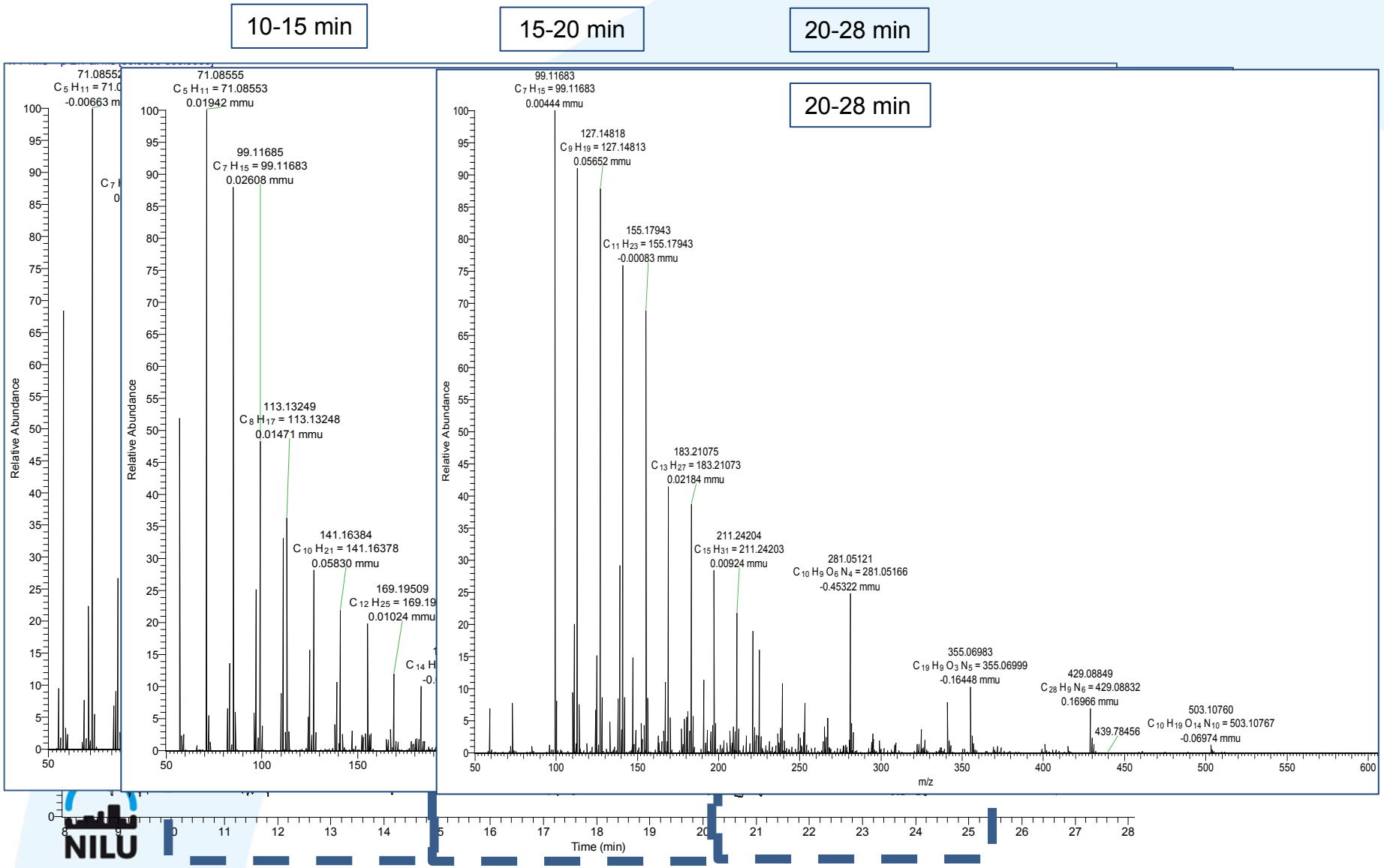
Method details

1 µL injection (SSL injector, 250°C)
Splitless time: 1.5 min
Column: Thermo TG-5Sil MS
Oven: 40°C (hold 1.5 min)
25°C/min -> 180°C
5°C/min -> 280°C
40°C/min -> 320°C (hold 5 min)
Fullscan: 50-600 m/z, Res: 60K

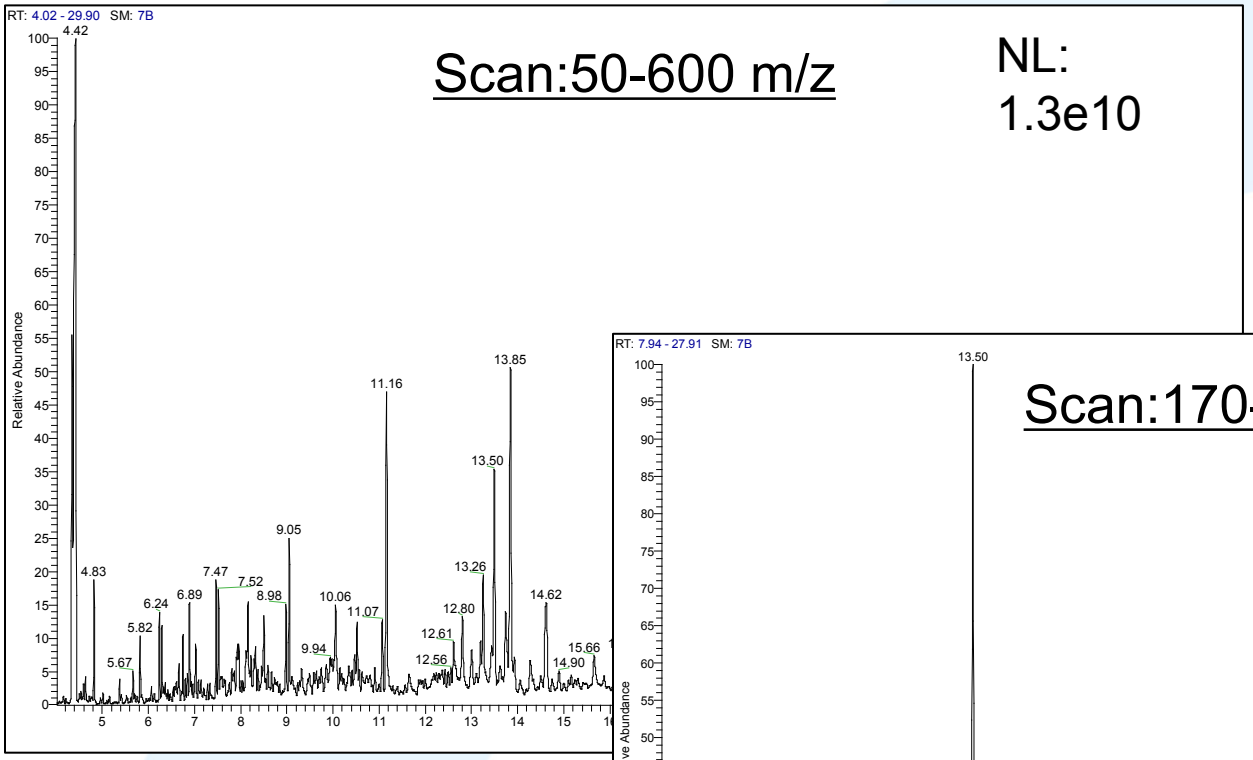


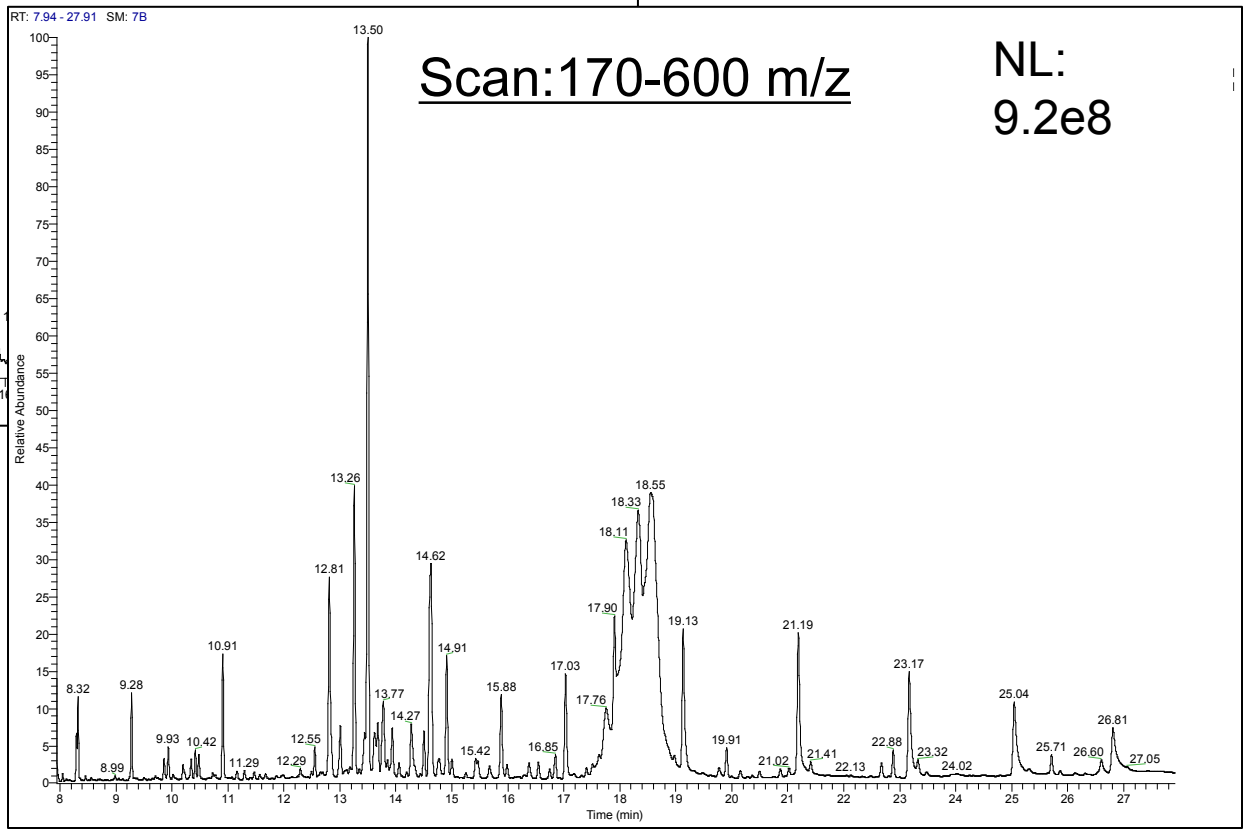
- HCB, ppDDE and Mirex detected in full scan

Antarctic penguin blood sample

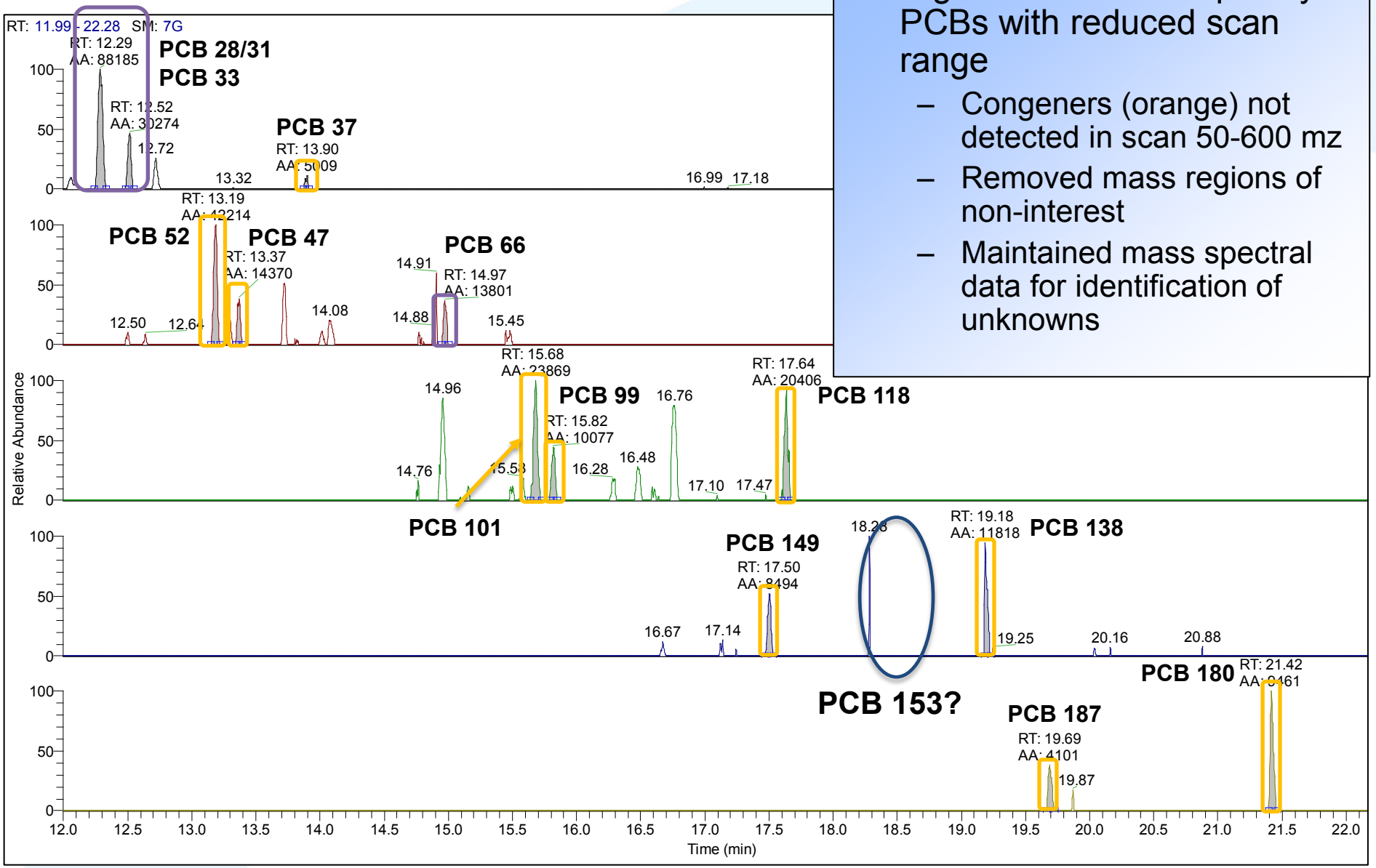


Full scan vs. reduced full scan



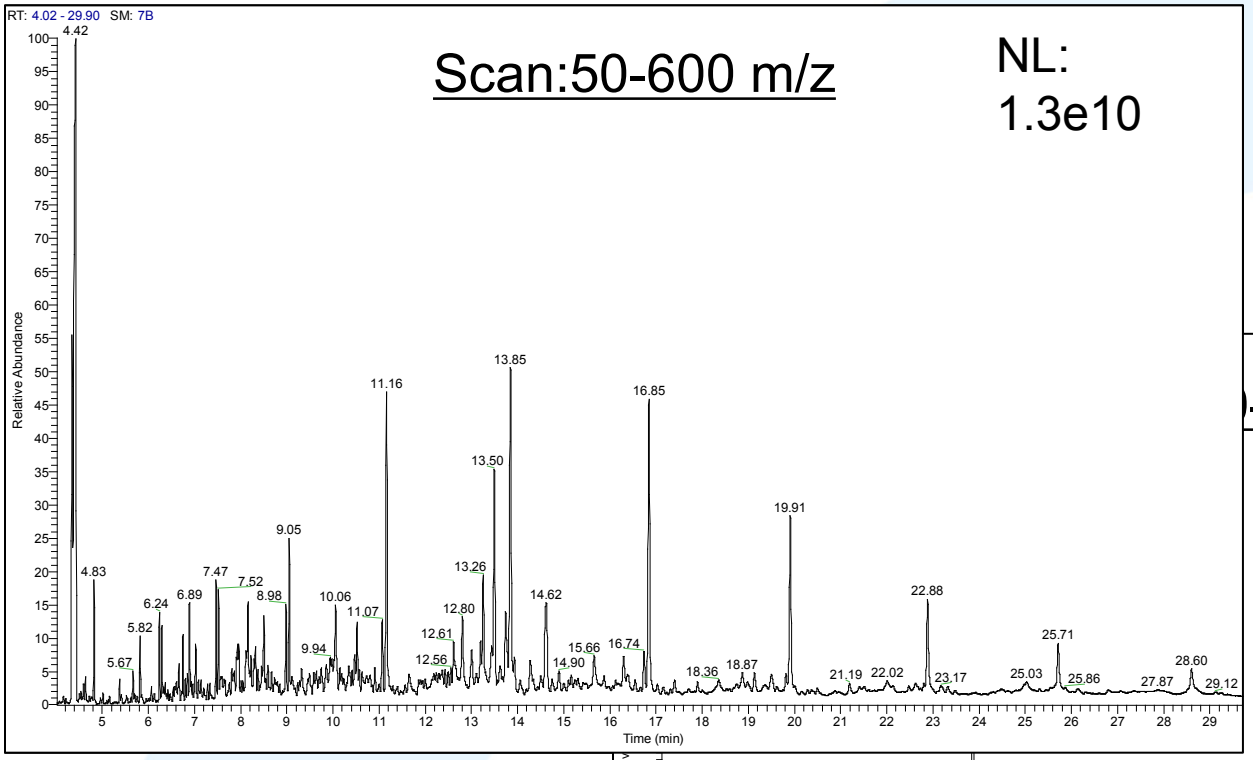


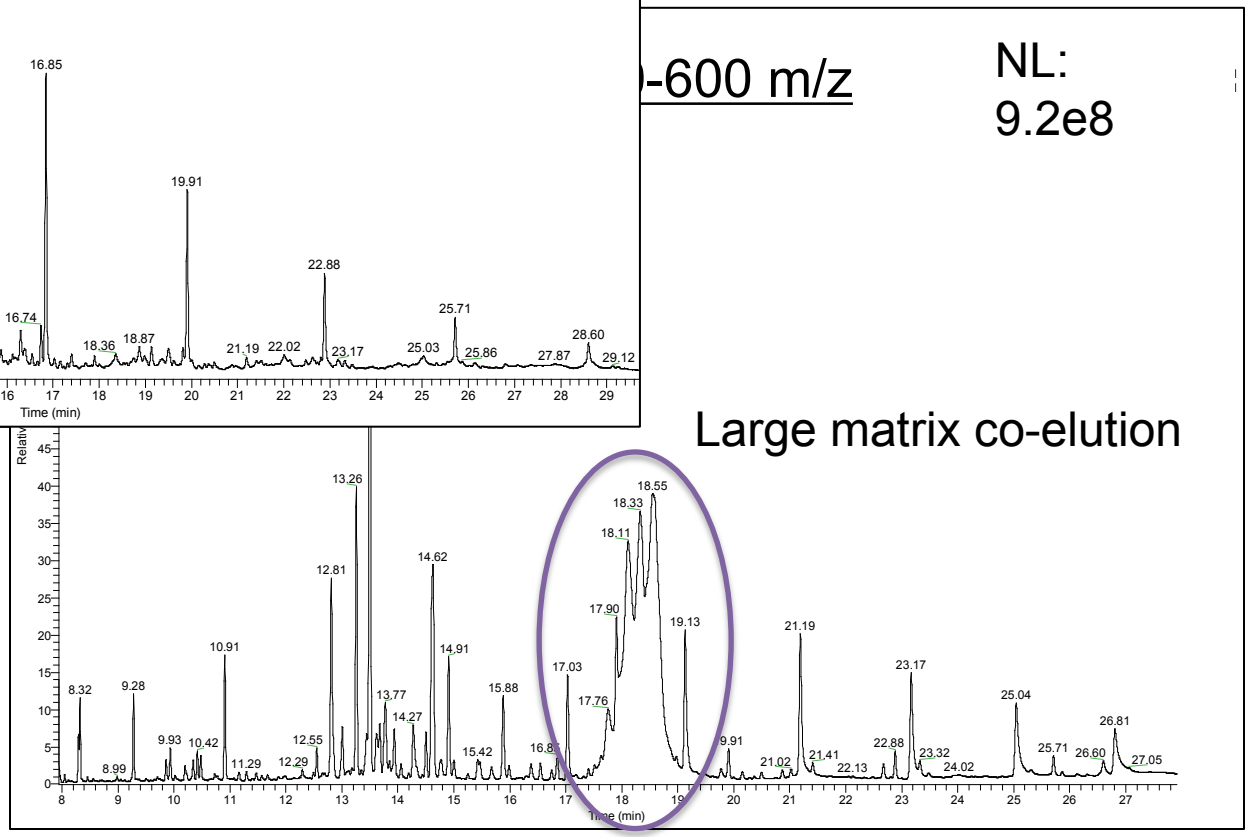
Antarctic penguin blood sample (PCBs, 170-600 mz)



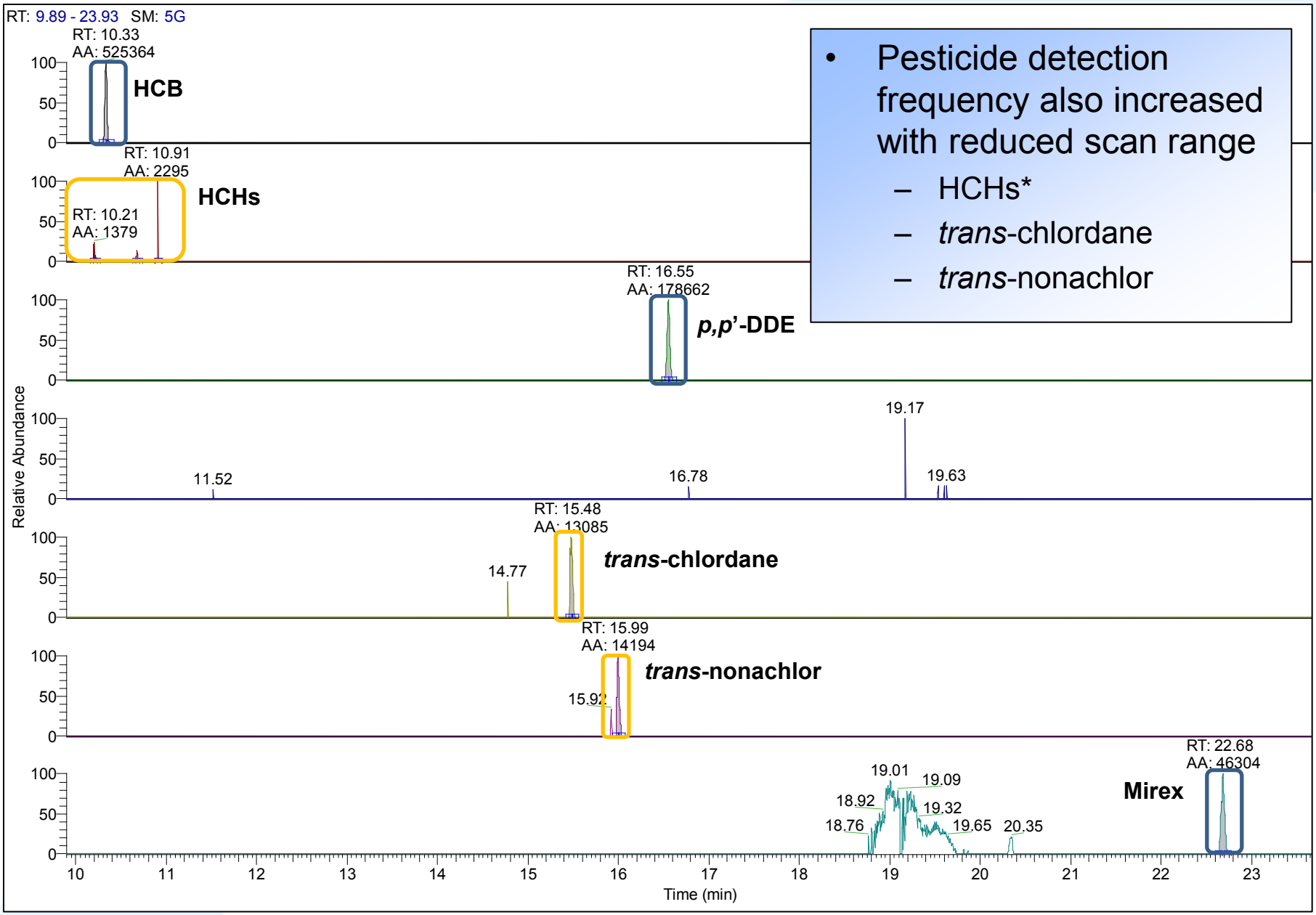
- Higher detection frequency of PCBs with reduced scan range
  - Congeners (orange) not detected in scan 50-600 mz
  - Removed mass regions of non-interest
  - Maintained mass spectral data for identification of unknowns

Full scan vs. reduced full scan





Antarctic penguin blood sample (pesticides, 170-600 mz)

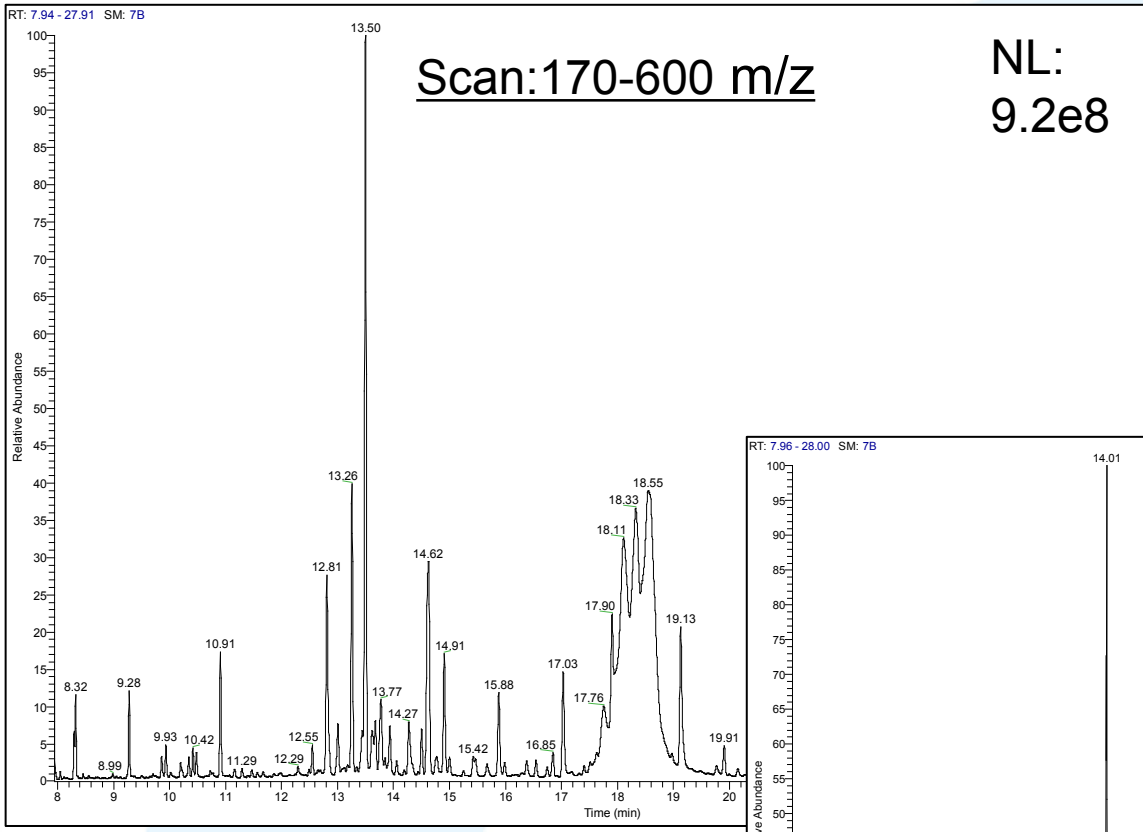


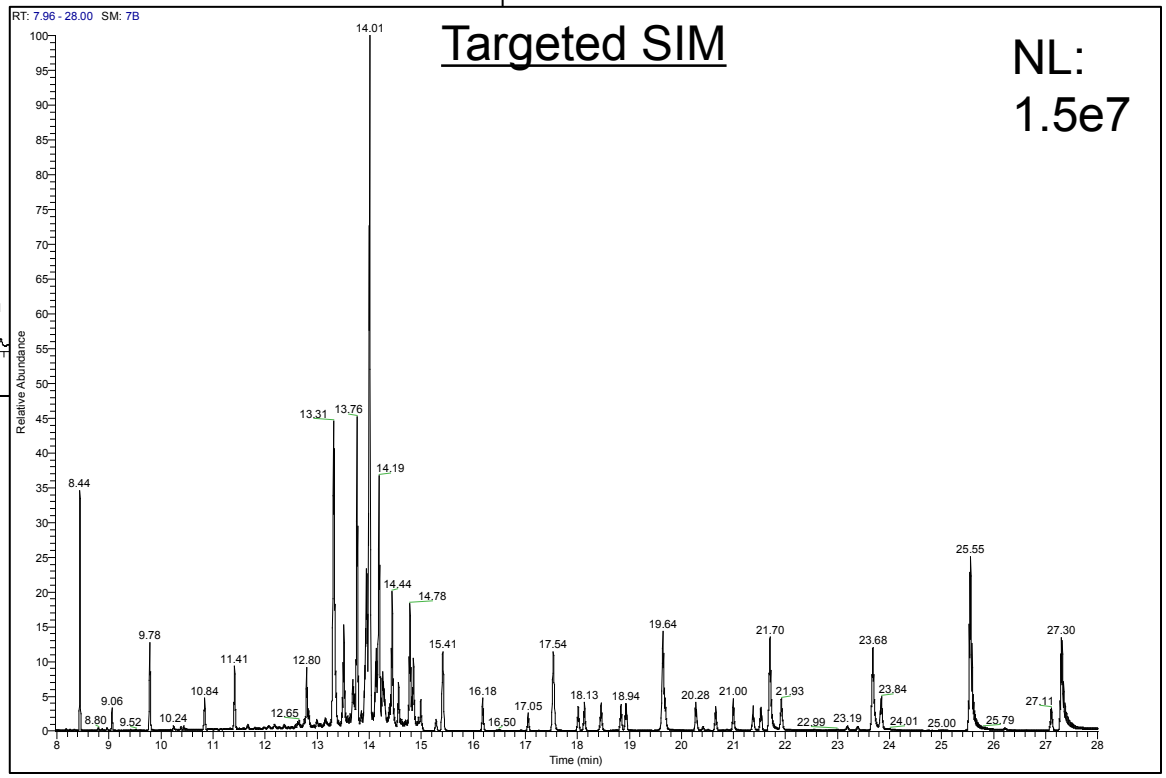
- Pesticide detection frequency also increased with reduced scan range
  - HCHs*
  - *trans*-chlordane
  - *trans*-nonachlor

Antarctic penguin blood sample (Targeted SIM (TSIM))

Method details

1 µL injection (SSL injector, 250°C)
Splitless time: 1.5 min
Column: Thermo TG-5Sil MS
Oven: 40°C (hold 1.5 min)
25°C/min -> 180°C
5°C/min -> 280°C
40°C/min -> 320°C (hold 5 min)
Targeted SIM: 8 m/z scan window,
Resolution: 60K





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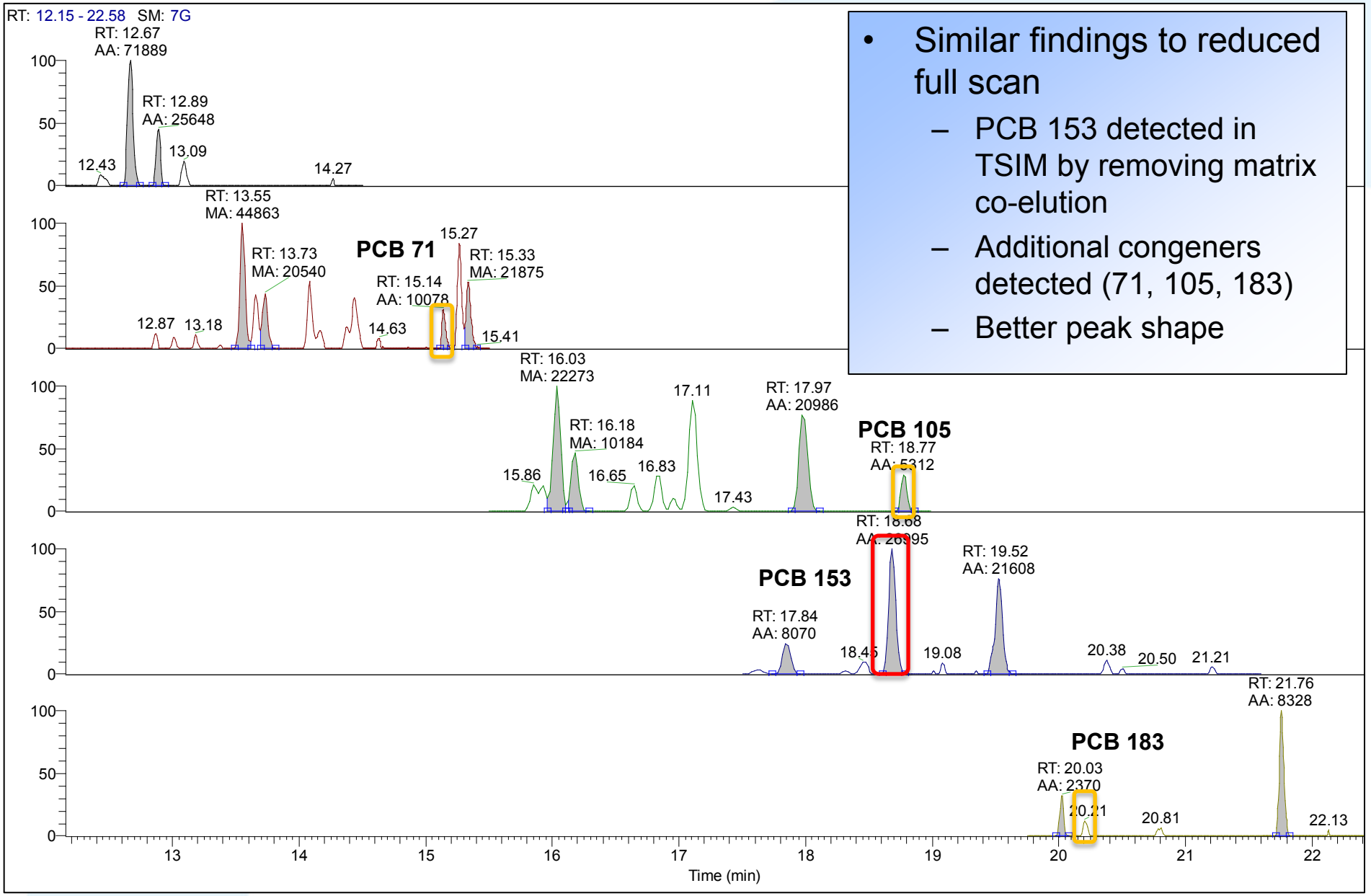
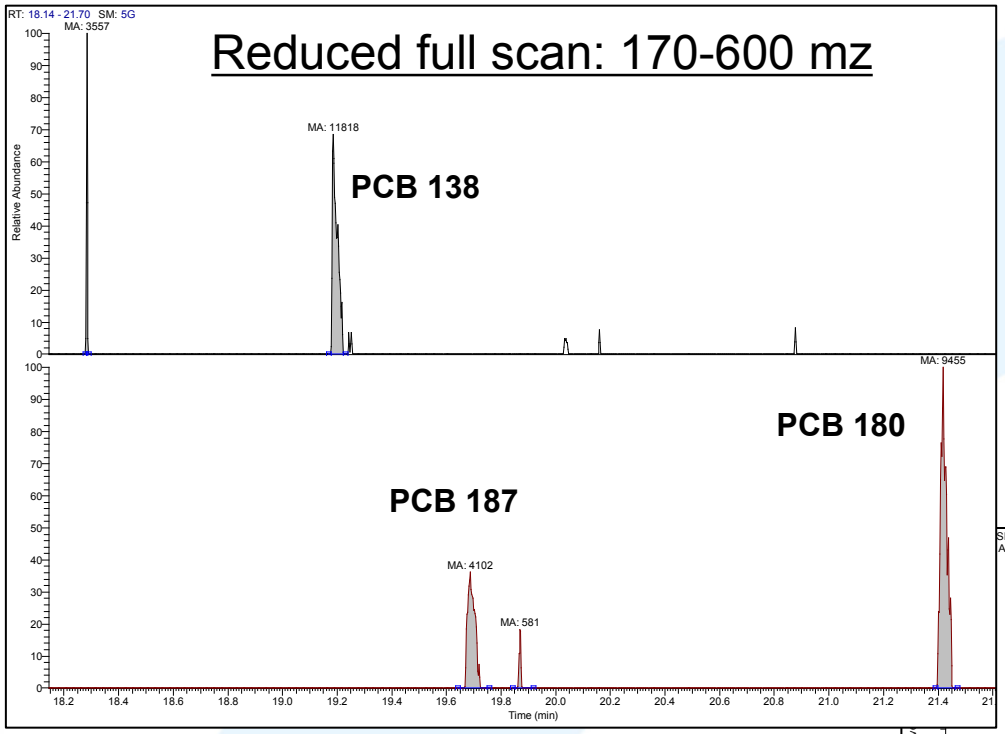
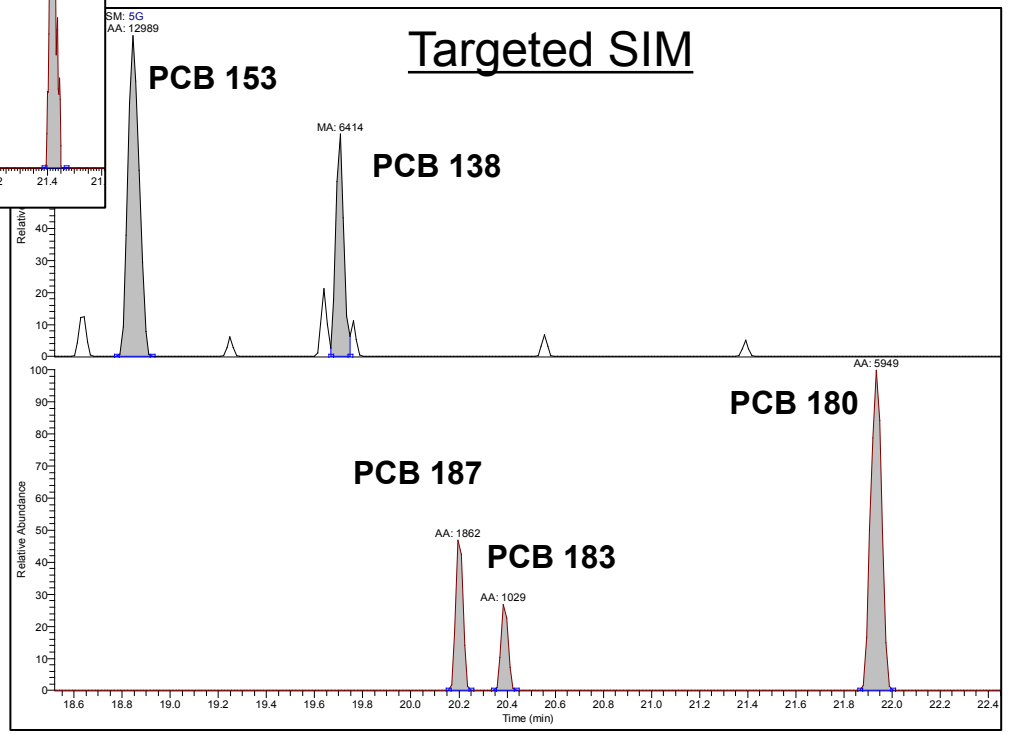
Antarctic penguin blood sample (PCBs, Targeted SIM)



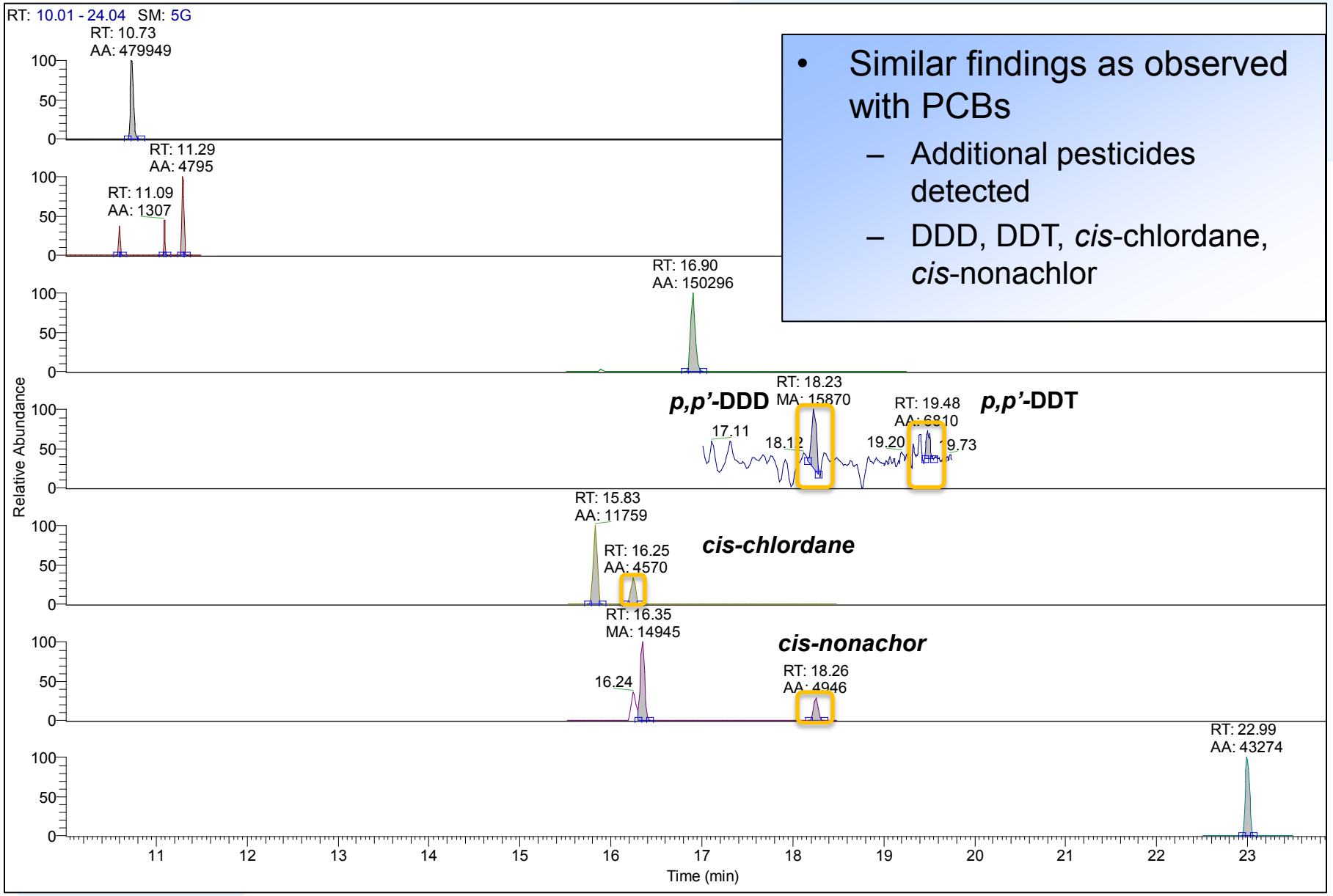
- Similar findings to reduced full scan
  - PCB 153 detected in TSIM by removing matrix co-elution
  - Additional congeners detected (71, 105, 183)
  - Better peak shape

Peak shape comparison



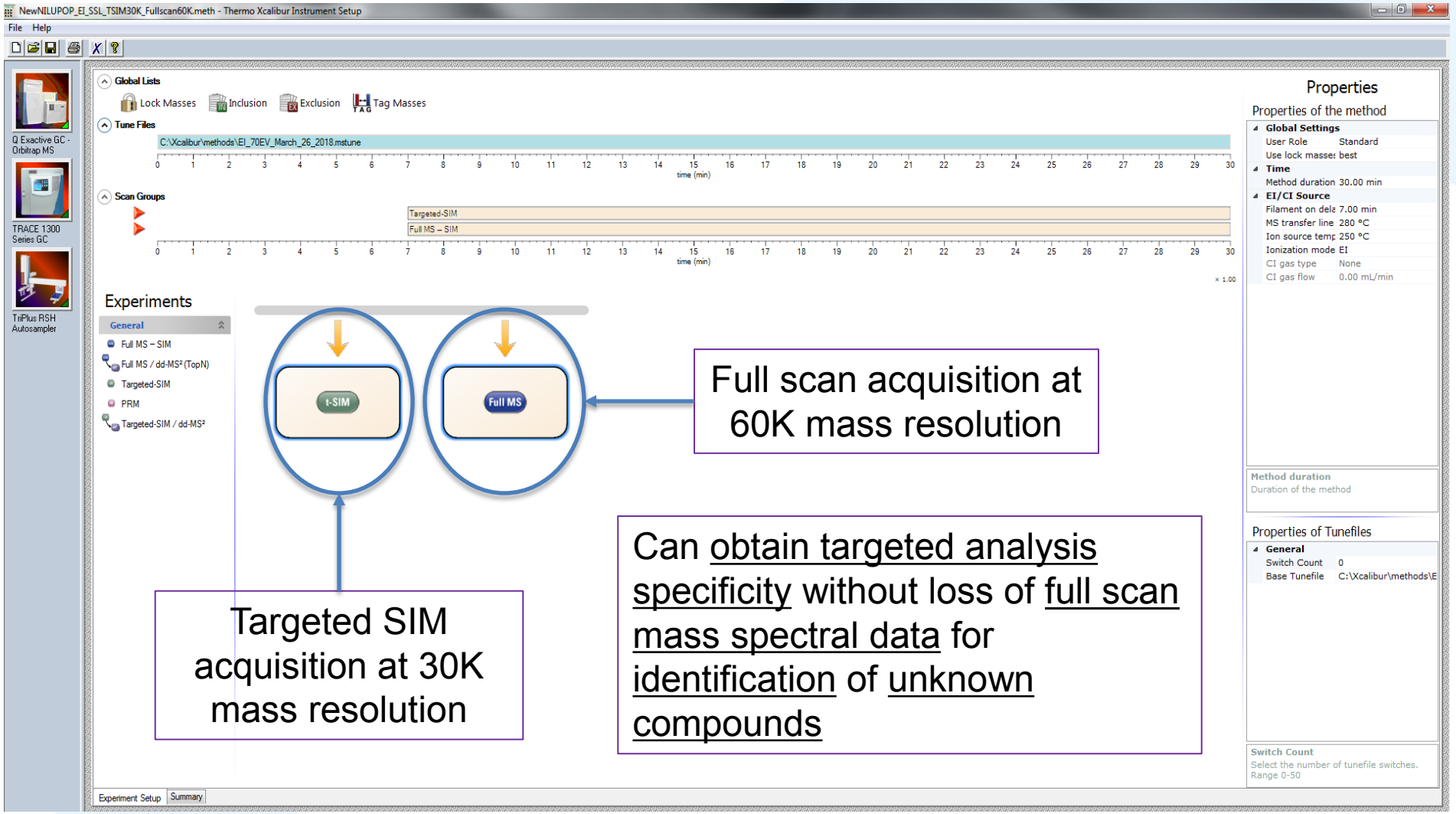


Antarctic penguin blood sample (pesticides, Targeted SIM)



- Similar findings as observed with PCBs
  - Additional pesticides detected
  - DDD, DDT, *cis*-chlordane, *cis*-nonachlor

Simultaneous full scan and targeted SIM



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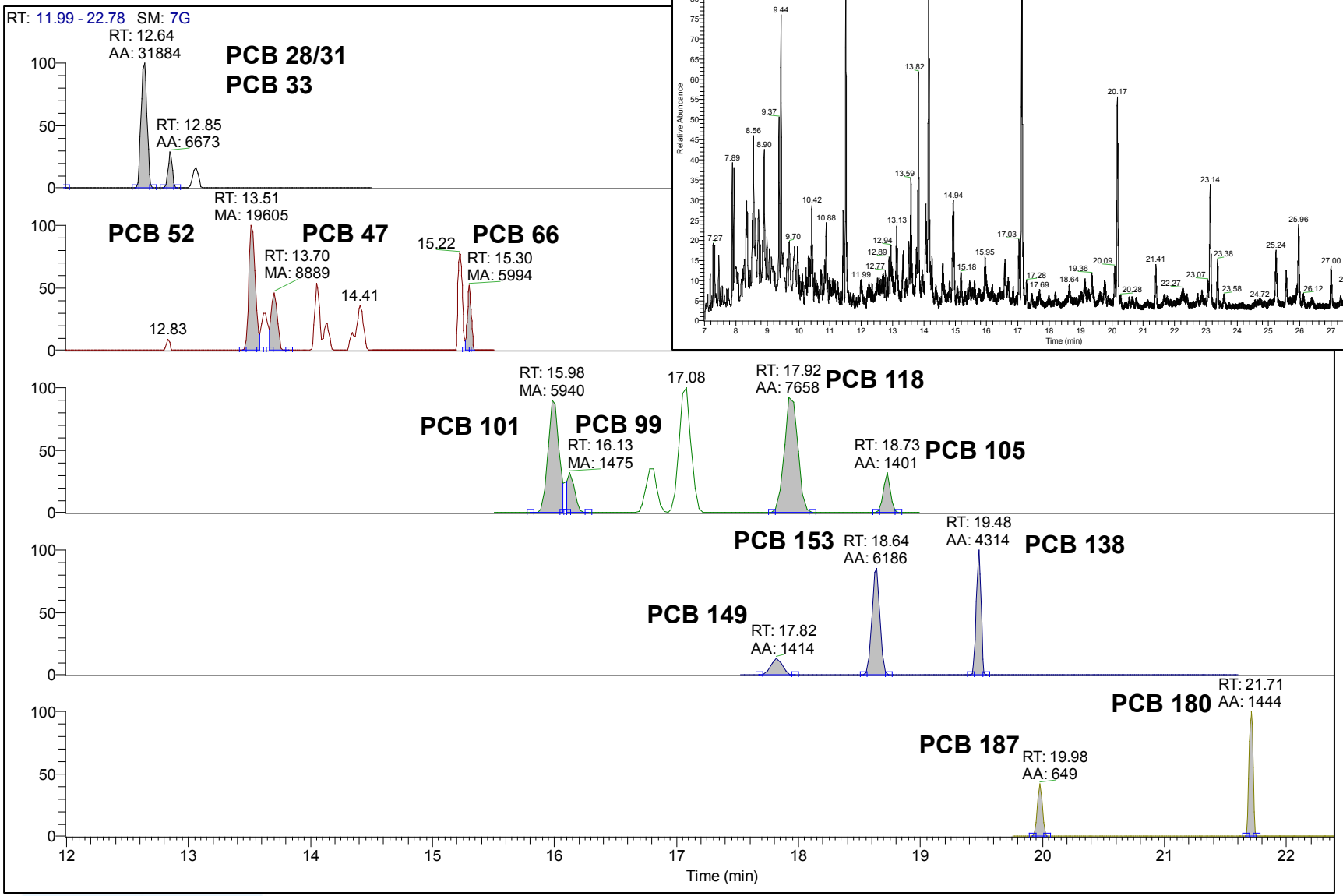
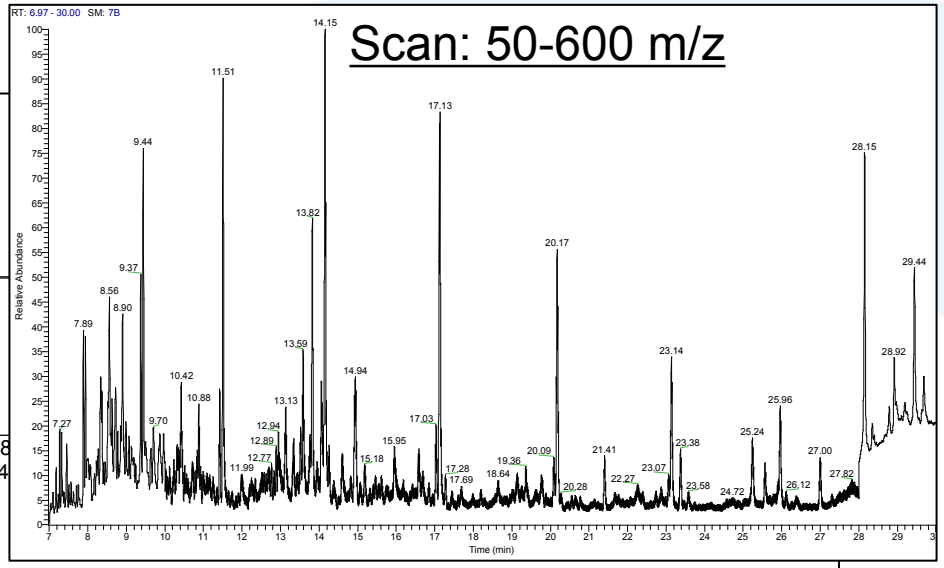
Antarctic penguin blood (Target SIM/Full scan)



Antarctic penguin blood (Target SIM/Full scan)



RT: 9.92 - 24.01 SM: 7G

RT: 10.70
AA: 248762
HCB

RT: 16.8
AA: 844
***p,p'*- DDE**

RT: 15.79
AA: 3894
***trans*-chlordane**

RT: 16.29
MA: 4425
***trans*-nonachlor**

RT: 18.20
AA: 2668
***cis*-nonachlor**

RT: 22.95
AA: 24364
Mirex

Relative Abundance

Time (min)

OC concentrations in penguin blood sample

PCB congener	Concentration (pg/g ww)
52	11.5
101	16.3
118	6.4
138	13.2
149	3.8
153	11.6
180	5.3
183	1.4
187	2.0

Pesticide	Concentration (pg/g ww)
HCB	290
aHCH	3.9
p,p'-DDT	1.38
p,p'-DDD	4.72
p,p'-DDE	101
trans-chlordane	11.7
cis-chlordane	3.5
trans-nonachlor	11.7
cis-nonachlor	0.9
Mirex	38

- Blank subtraction performed on sample results
- LOQ: 0.1 – 14.2 pg/g ww (compound dependent)

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GC-Q-Exactive provides excellent sensitivity for OC analysis in penguin blood

Sample matrix can hinder detection at ppt concentrations

PCBs and OC pesticides detected at ppt concentrations in full scan and TSIM

Targeted SIM can reduce influence of matrix ions in C-Trap

HCB, ppDDE, Mirex dominate in penguin blood

Full scan data acquired simultaneously without compromising targeted analysis

Photograph: Norith Eckbo

thermo scientific

APPLICATION NOTE 10623

Versatility of GC-Orbitrap mass spectrometry for the ultra-trace detection of persistent organic pollutants in penguin blood from Antarctica

Authors

Nicholas A. Warner[1] and Cristian I. Cojocariu[2]

[1]NILU-Norwegian Institute for Air Research, Fram Centre, Tromsø, Norway, [2]Thermo Fisher Scientific, Runcorn, United Kingdom

Goal

In this study, the performance of the Thermo Scientific™ Q Exactive™ GC Orbitrap™ mass spectrometer was evaluated for routine analysis of POPs within King penguin blood from Antarctica.

Introduction

Persistent organic pollutants (POPs) have been studied extensively over the past five decades due to their toxicity and environmental persistence

Acknowledgements

Cristian Cojocariu (Thermo Scientific)

Strategic Institute Funding grant (CleanArctic, NRC)

POLAR-ECOTOX project (NRC)

Thank you for your attention

Photograph: Norith Eckbo