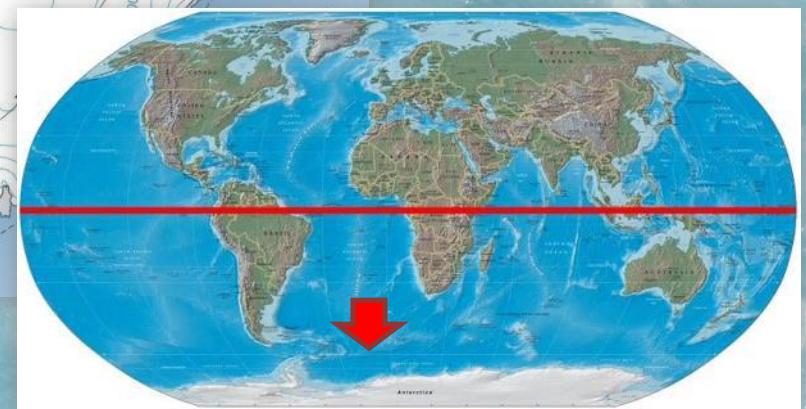


La metrología en los estudios de biomonitorización de la contaminación ambiental por contaminantes orgánicos emergentes en la Antártida

Motas M, Jerez S, Corsolini S, Guerranti C, Pozo K, Estellano VH, Diaz J, Benzal J, Barbosa A



1. Introduction

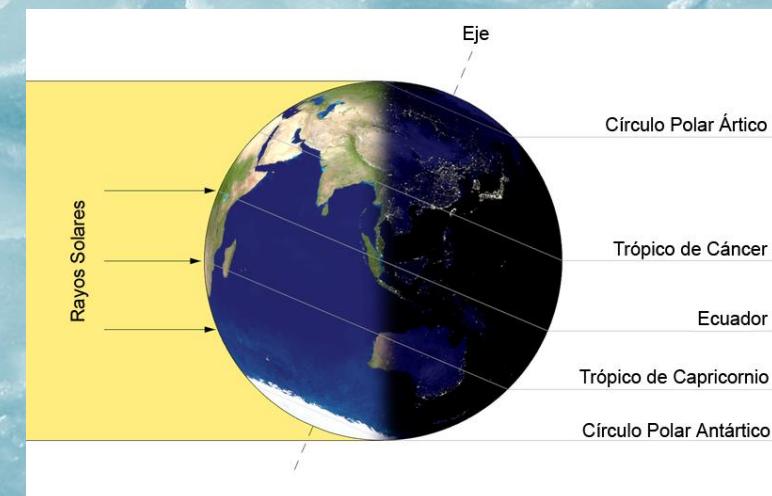
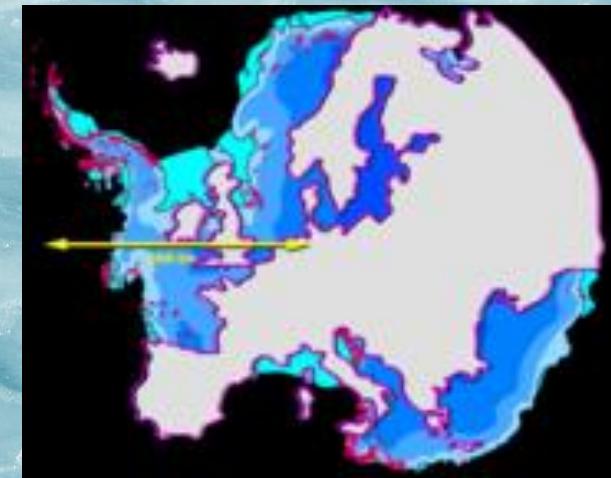
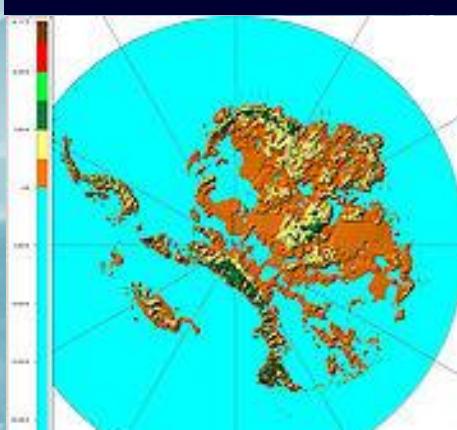
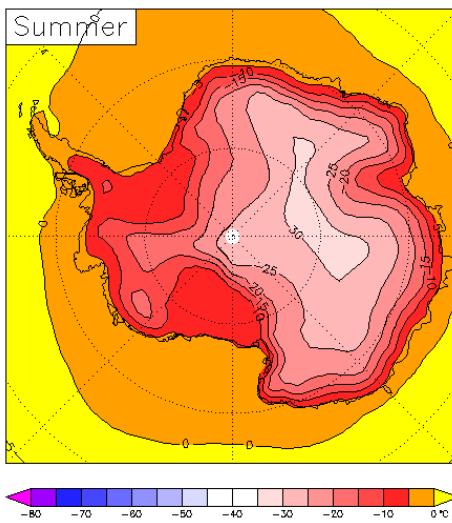
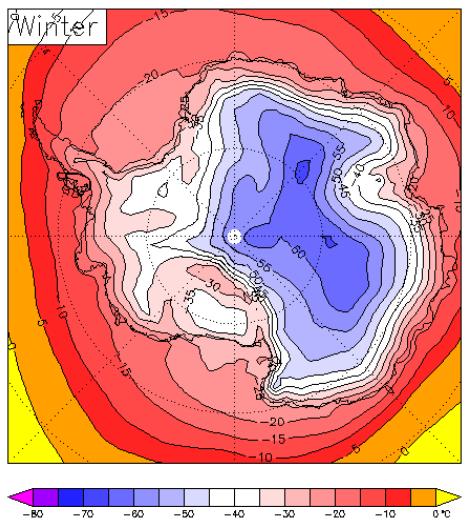


14 mill. Km²

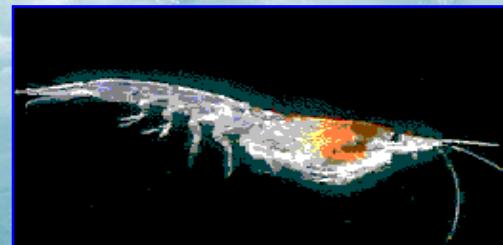
2% ice-free land at the coast, T^a < -80 °C



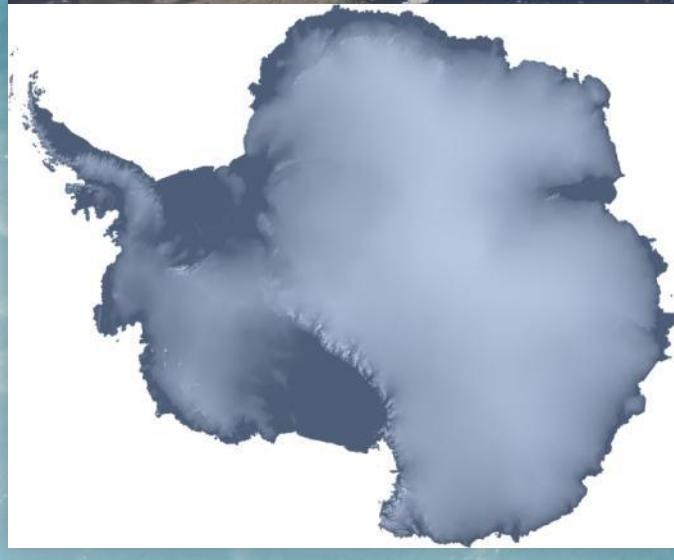
1. Introduction







The idea of an untouched region....



...versus the influence of local and global pollution





- Penguins as sentinels -

GENERAL ADVANTAGES

- Wide distribution.
- Easy identification.
- Essential components of the aquatic ecosystems.
- Sensitive to changes in the environment.
- Potential accumulation of bio-available forms of pollutants.
- Levels several orders of magnitude above the environmental levels.

PARTICULARITIES

- Numerous populations and exclusively localized in Antarctica.
- High position on the food web (potential magnification of pollutants).
- Long-lived species (potential bioaccumulations of pollutants during their life time).
- Permanent ecological niche.
- Dominate the avifauna biomass.

Pygoscelid penguins

Order *Sphenisciformes*, Family *Pygoscelidae*, Genus *Pygoscelis*

Gentoo penguin – *P. papua*



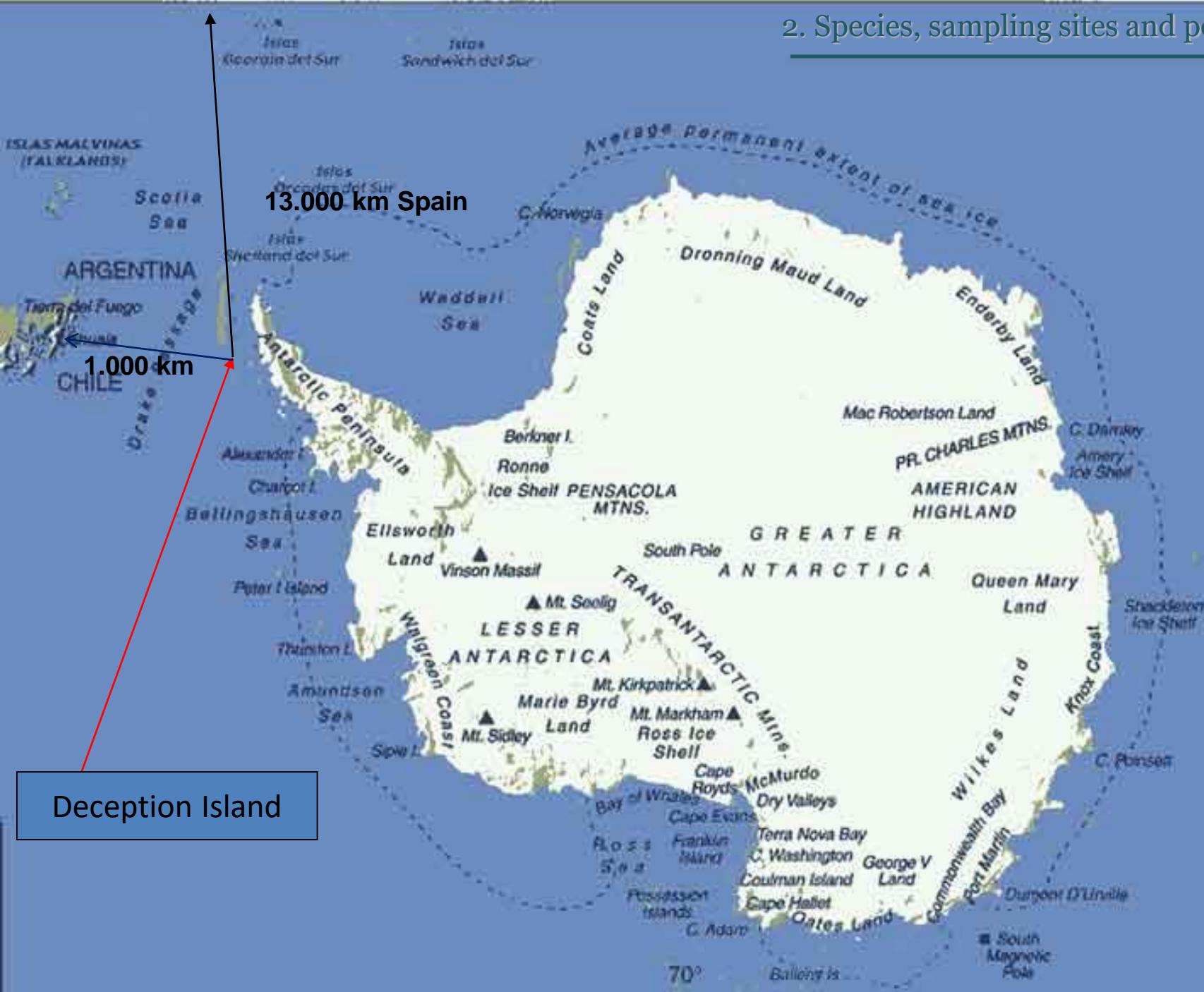
Chinstrap penguin – *P. antarctica*



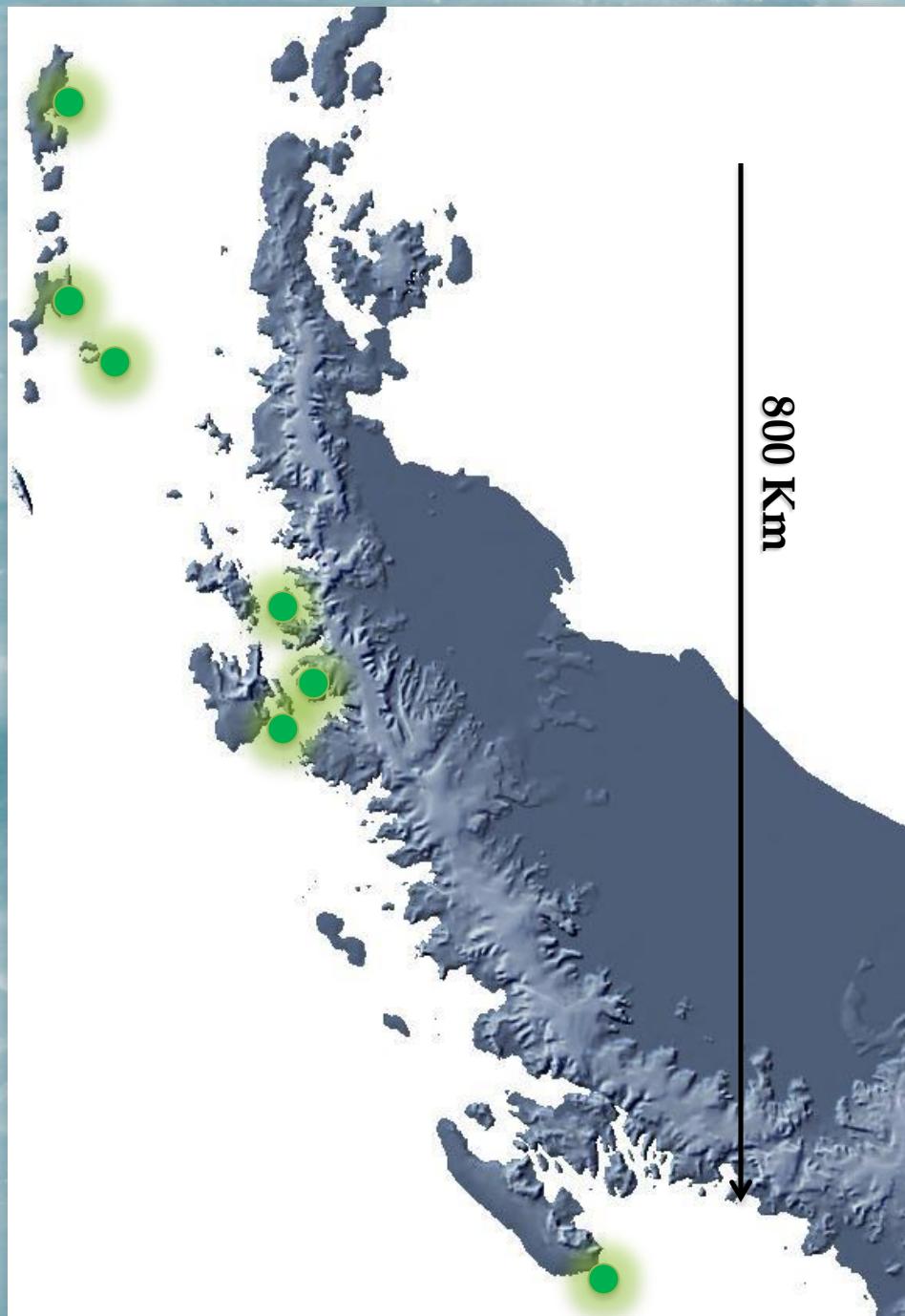
Adélie penguin – *P. adeliae*



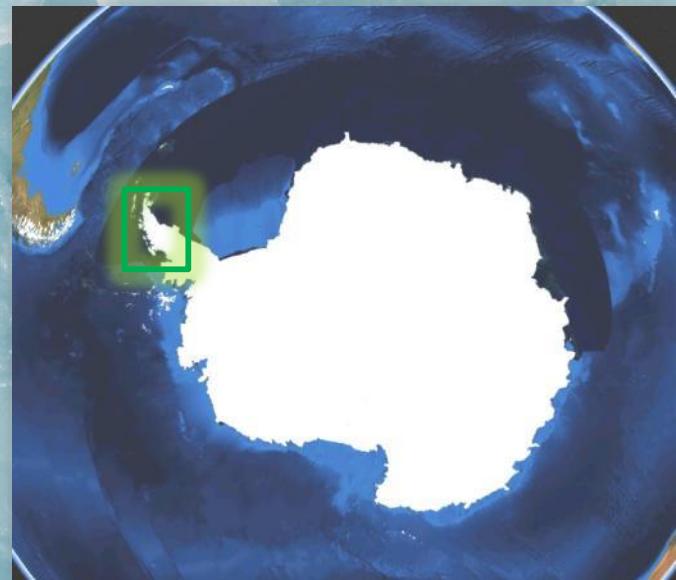
2. Species, sampling sites and pollutants



2. Species, sampling sites and pollutants



Penguins were not sacrificed



2. Species, sampling sites and pollutants

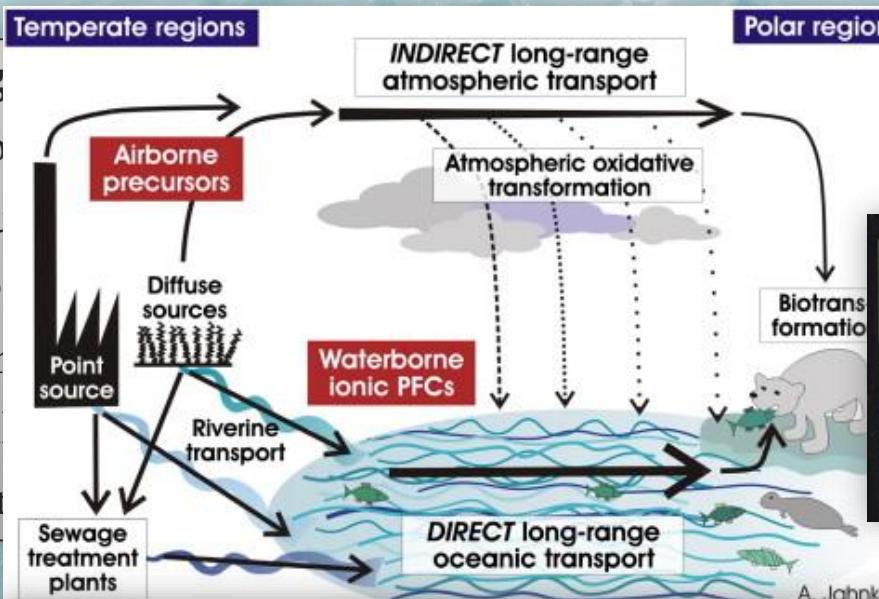




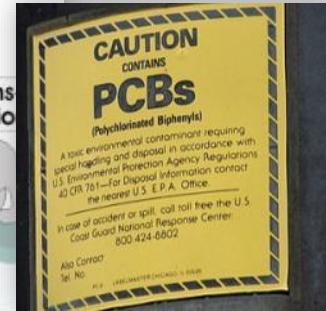
ORGANIC COMPOUNDS

PCBs

- 209 congeners
- High bioaccumulation
- Widely used
- **High ubiquity**
- Ingestion
- Accumulation
- Bioaccumulation

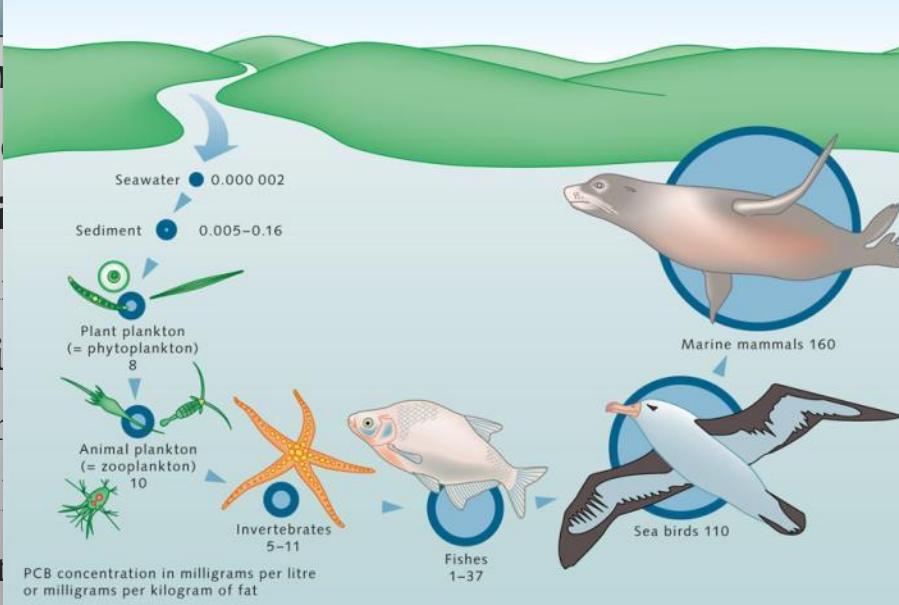


Only persistent



PFCs

- PFOS and PFOSA
- Highly resistant
- Present in all
- Several isoforms
- **Use limited**
- Ingestion
- Accumulation
- Bioaccumulation

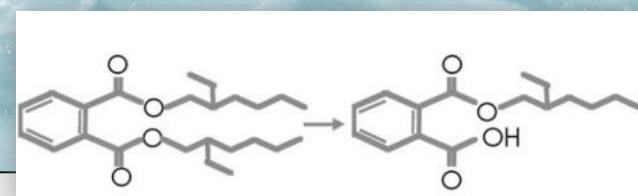


Only persistent

ORGANIC COMPOUNDS

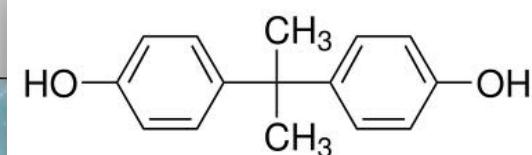
Phthalates

- DEHP and MEHP
- Widely used as plasticizers
- Use limitations
- Ingestion
- Rapidly metabolized and no-accumulated



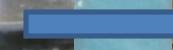
BPA

- Widely used and emitted to the environment
- Detectable levels in most of the studied individuals
- Different use limitations
- Ingestion
- Rapidly metabolized and no-accumulated



3. Analytical methodology and statistical analysis

PCBs



3. Analytical methodology and statistical analysis

PFCs



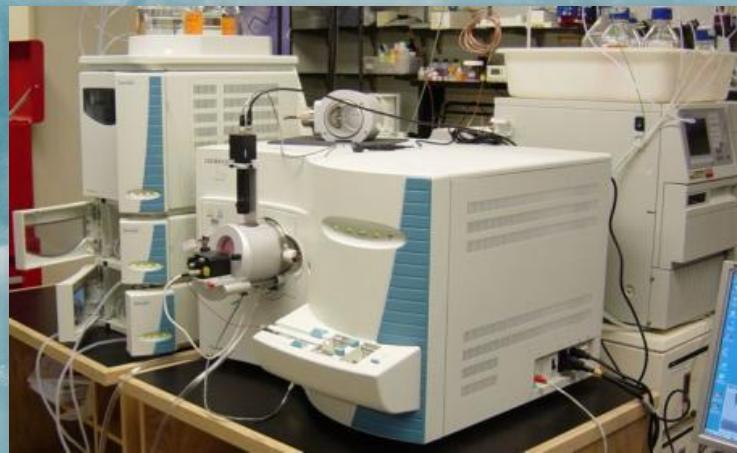
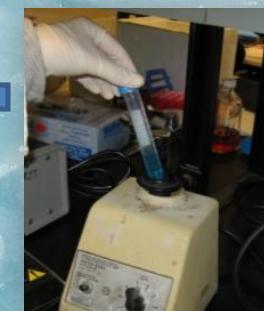
3. Analytical methodology and statistical analysis

Phtalates



3. Analytical methodology and statistical analysis

BPA



Organic compounds

Detection limits: Mean blank value + 3SD

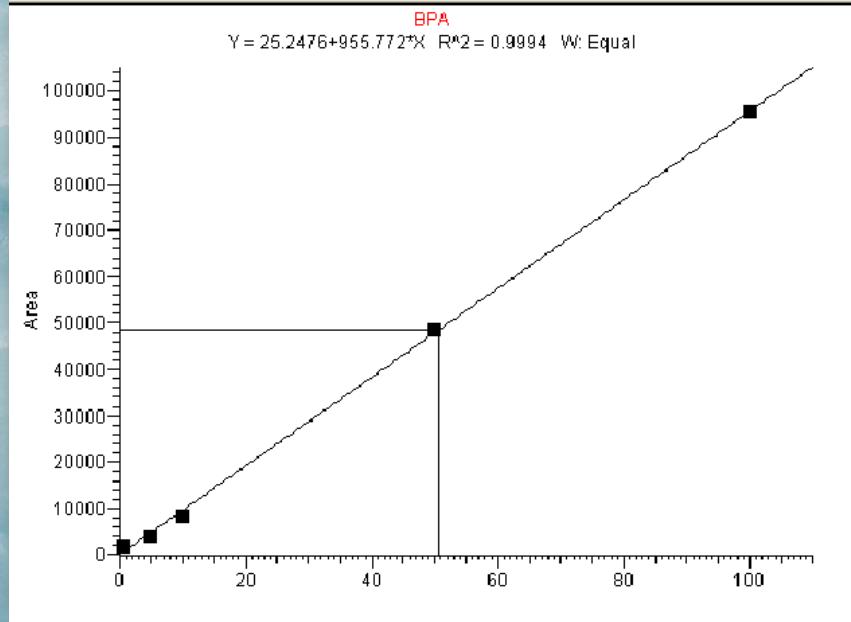
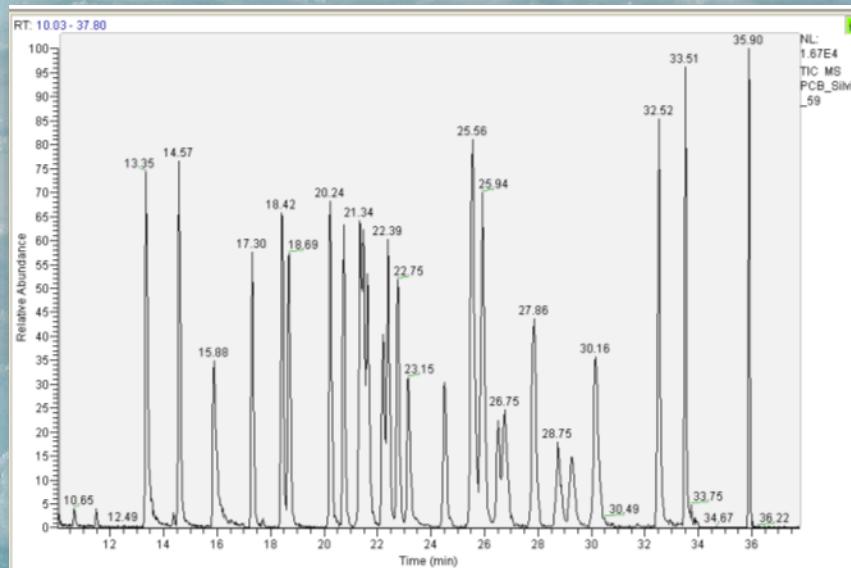
PCBs: 0.002-2.541 pg μl^{-1} (ppb)

PFCs and BPA: 0.50 ng g^{-1} (ppb)

MEHP: 2.00 ng g^{-1} , DEHP: 10.00 ng g^{-1}

Quality control:

- ✓ HPLC quality reagents.
- ✓ Double distilled and deionized water (Milli-Q system, Millipore, USA).
- ✓ Blanks every five samples, duplicate samples.
- ✓ Initial and periodic calibration standards.
- ✓ Internal standards, matrix spikes (recovery: 86-97% for PCBs, 87-92 % for PFOS, 85-91 % for PFOA and 85-90% for ftalatos and BPA).



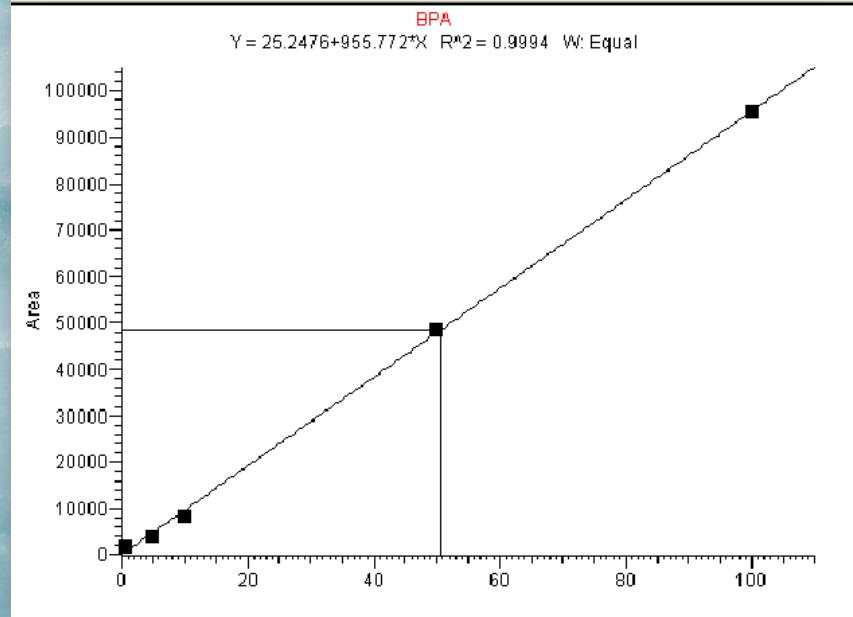
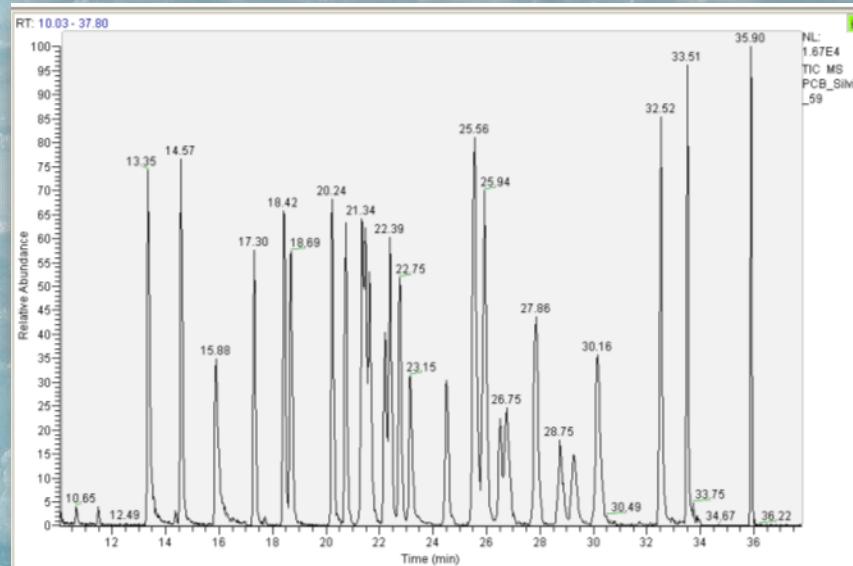
Organic compounds

Metrology:

- ✓ Para que los resultados obtenidos en biomonitorización tengan consistencia y puedan ser comparables a los obtenidos en otras investigaciones



- ✓ hay que dotarlos de trazabilidad metrológica mediante la utilización de materiales de referencia certificados (MRC), a ser posible, en las matrices en las que se realizan las determinaciones, siendo este el gran reto de la metrología en el campo de la biomonitorización.



STATISTICAL ANALYSIS

Data association (sample, species, sampling site, age)

Microsoft Excel 2007 and SPSS 15.0

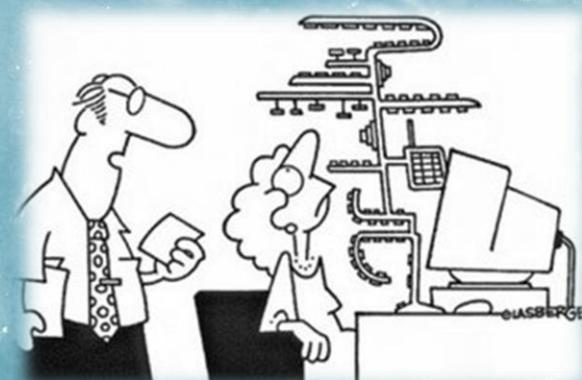
Kolmogorov-Smirnov normality test

Data log transformation

$$p < 0.05$$

Expected normal scores

- One-way ANOVA test, post hoc: Bonferroni
- Kruskal-Wallis test, post hoc: least significant difference between mean ranks
- Student's t-test
- Mann-Whitney U test
- Pearson's correlation coefficient
- Spearman's rank correlation coefficient



ORGANIC POLLUTANTS IN CHINSTRAP PENGUINS FROM DECEPTION ISLAND

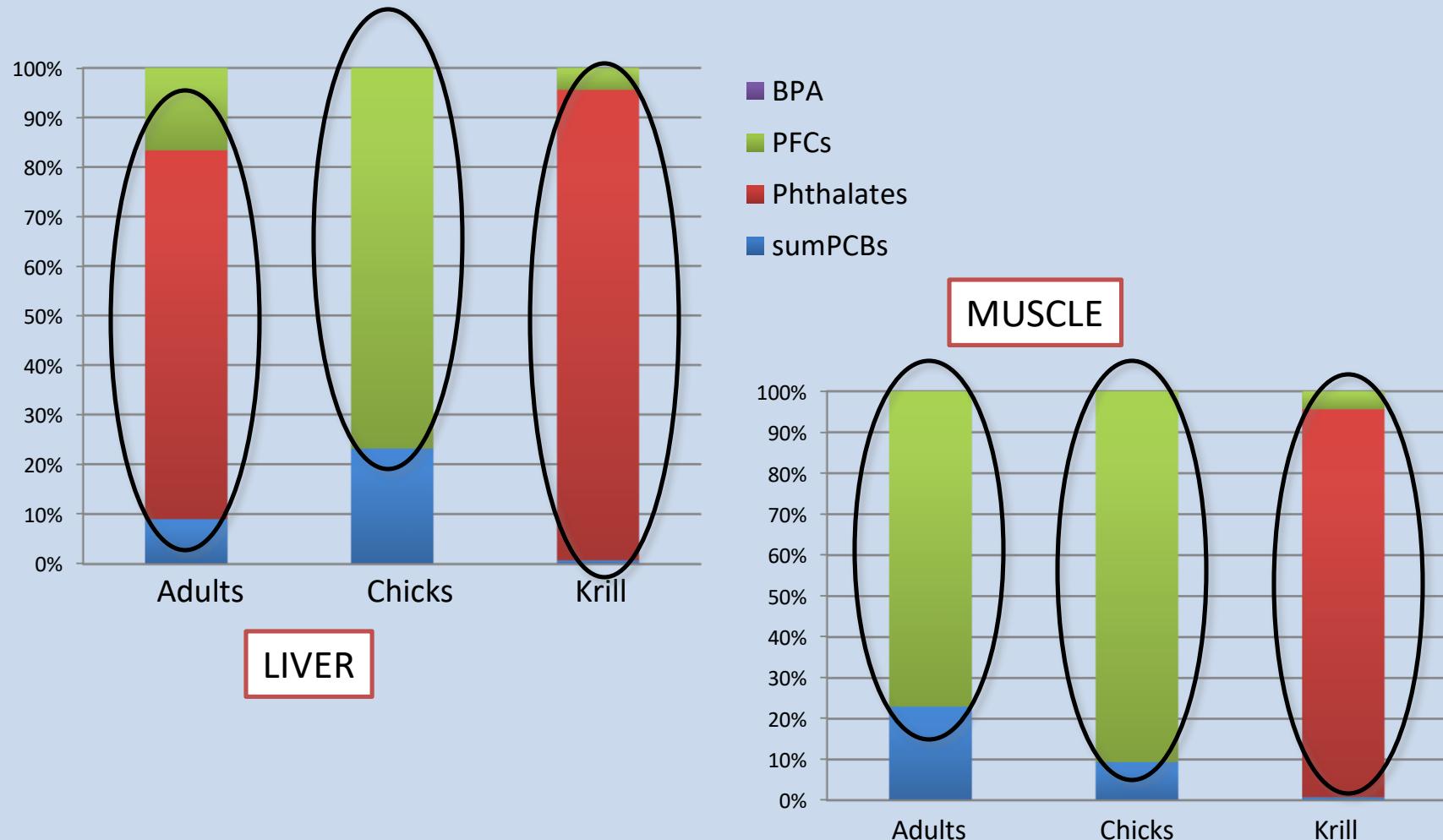
Samples <DL → DL/2

Results on wet weight and lipid basis

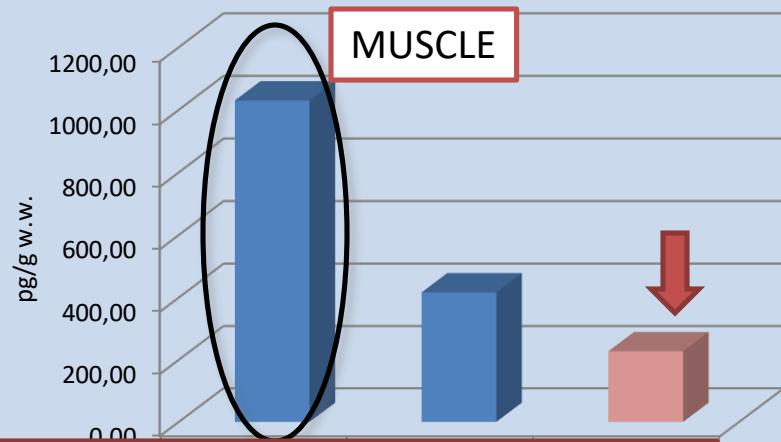
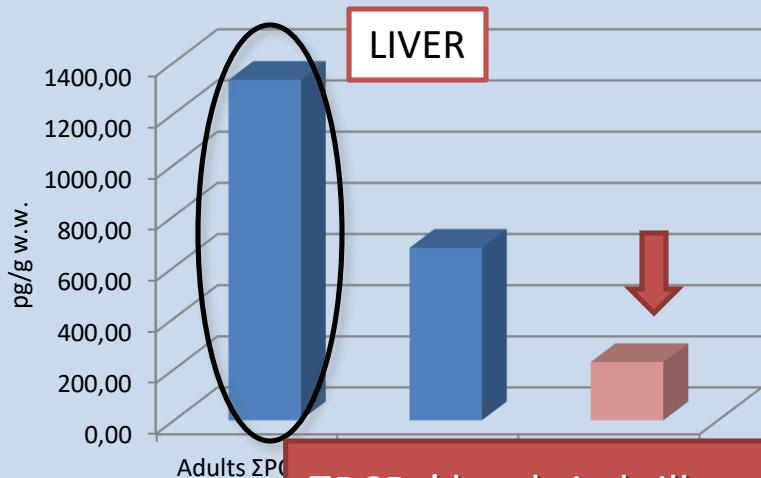
- ✓ Chinstrap penguins , the species less studied
- ✓ Deception Island, no previous data
- ✓ 35 samples (4 adults, 6 chicks)
- ✓ Liver, kidney, muscle, heart, brain, krill
- ✓ Accumulation patterns, fingerprints, class of isomers, age and prey-predator differences



Relative contributions of different contaminant families to Σ POPs

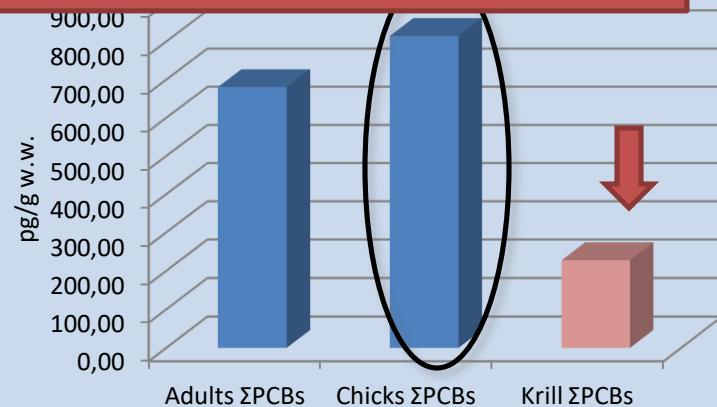
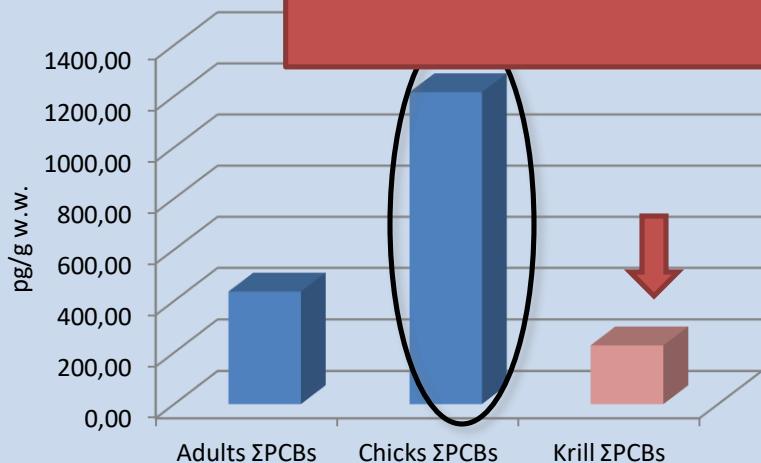


PCBs: age and prey-predator differences

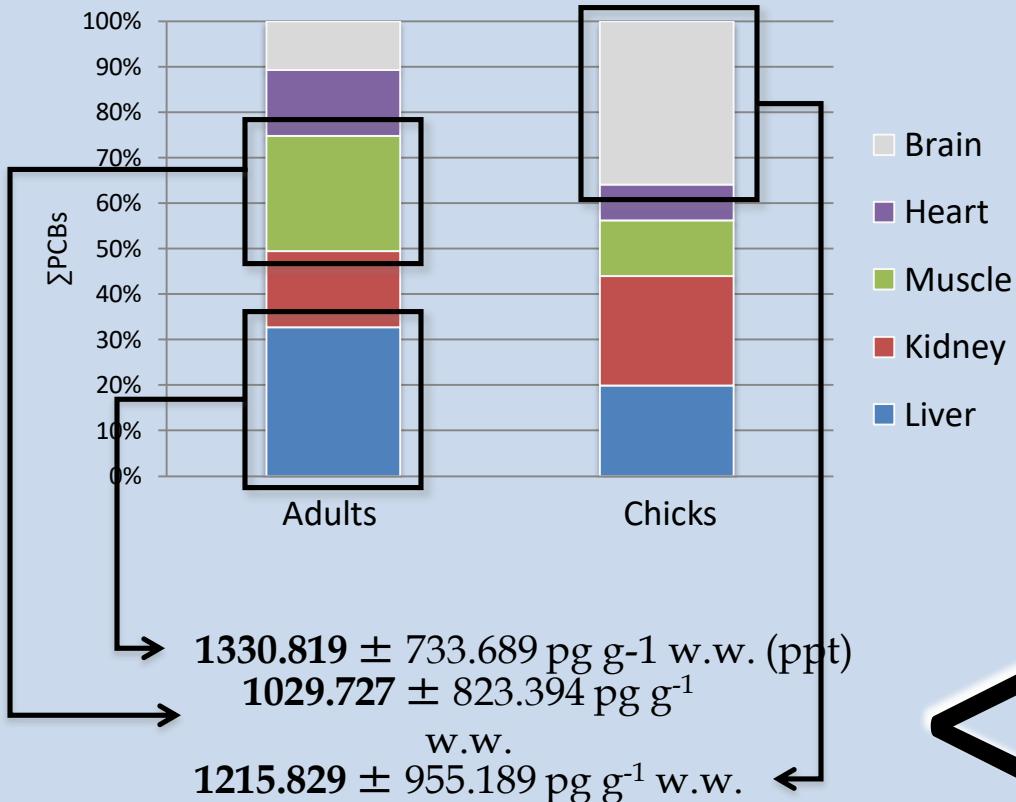


Σ PCBs' levels in krill were 14 - 83% lower than levels in penguins

BMF = 5.85



PCBs: Accumulation pattern



Specimens from the nearby
King George Island



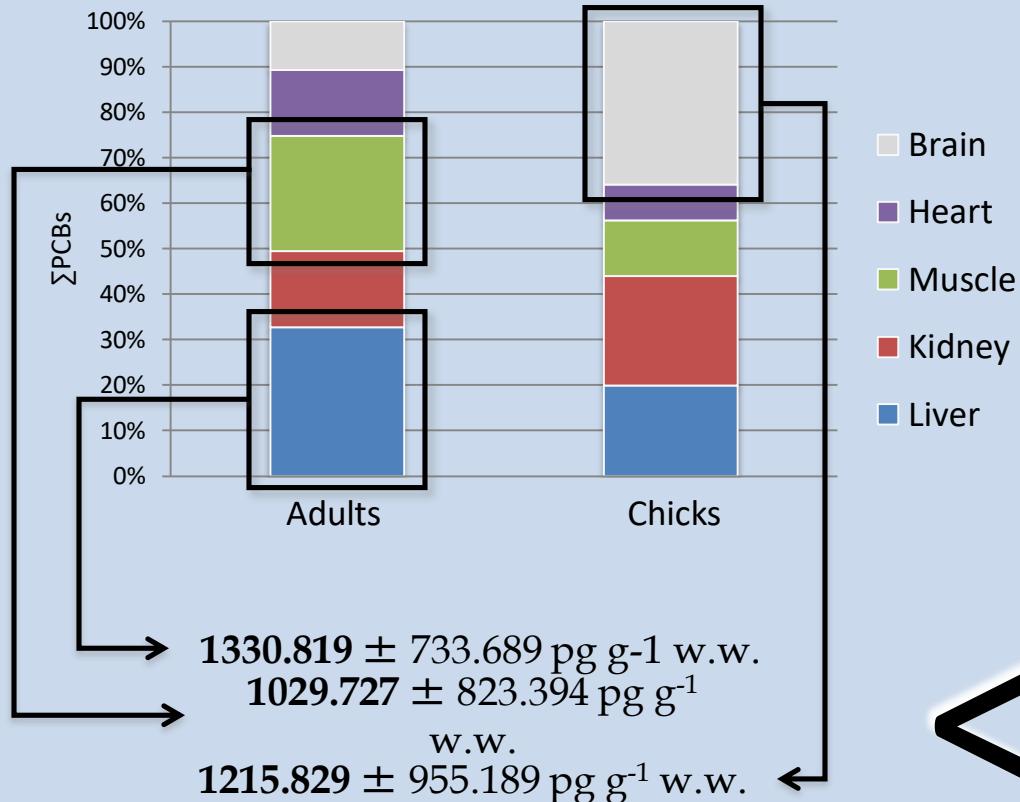
Blood: $4500 \text{ pg g}^{-1} \text{ w.w.}$
(Corsolini et al., 2007)

Egg: $6000 \text{ pg g}^{-1} \text{ w.w.}$
(Schiafone et al., 2009a)

Egg: $26000 - 37300 \text{ pg g}^{-1} \text{ w.w.}$
(Cipro et al., 2010)

Liver, muscle, heart, brain:
 $2474 - 23074 \text{ pg g}^{-1} \text{ w.w.}$
(Gesi, 2009)

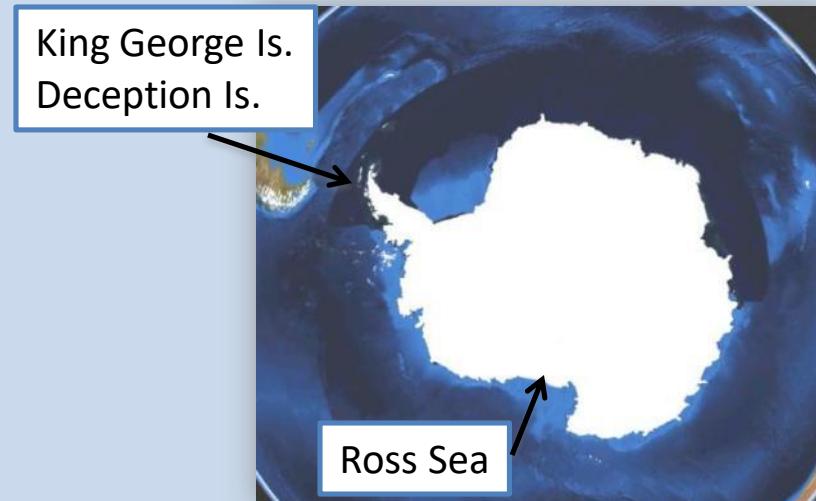
PCBs: Accumulation pattern



Liver: $11150 \text{ pg g}^{-1} \text{ w.w.}$
(Corsolini et al., 2002)

Blood: $9000 \text{ pg g}^{-1} \text{ w.w.}$
(Bustnes et al., 2010)

PCBs levels in krill



DECEPTION ISLAND

227.384 pg g⁻¹ w.w. *This study*



KING GEORGE ISLAND

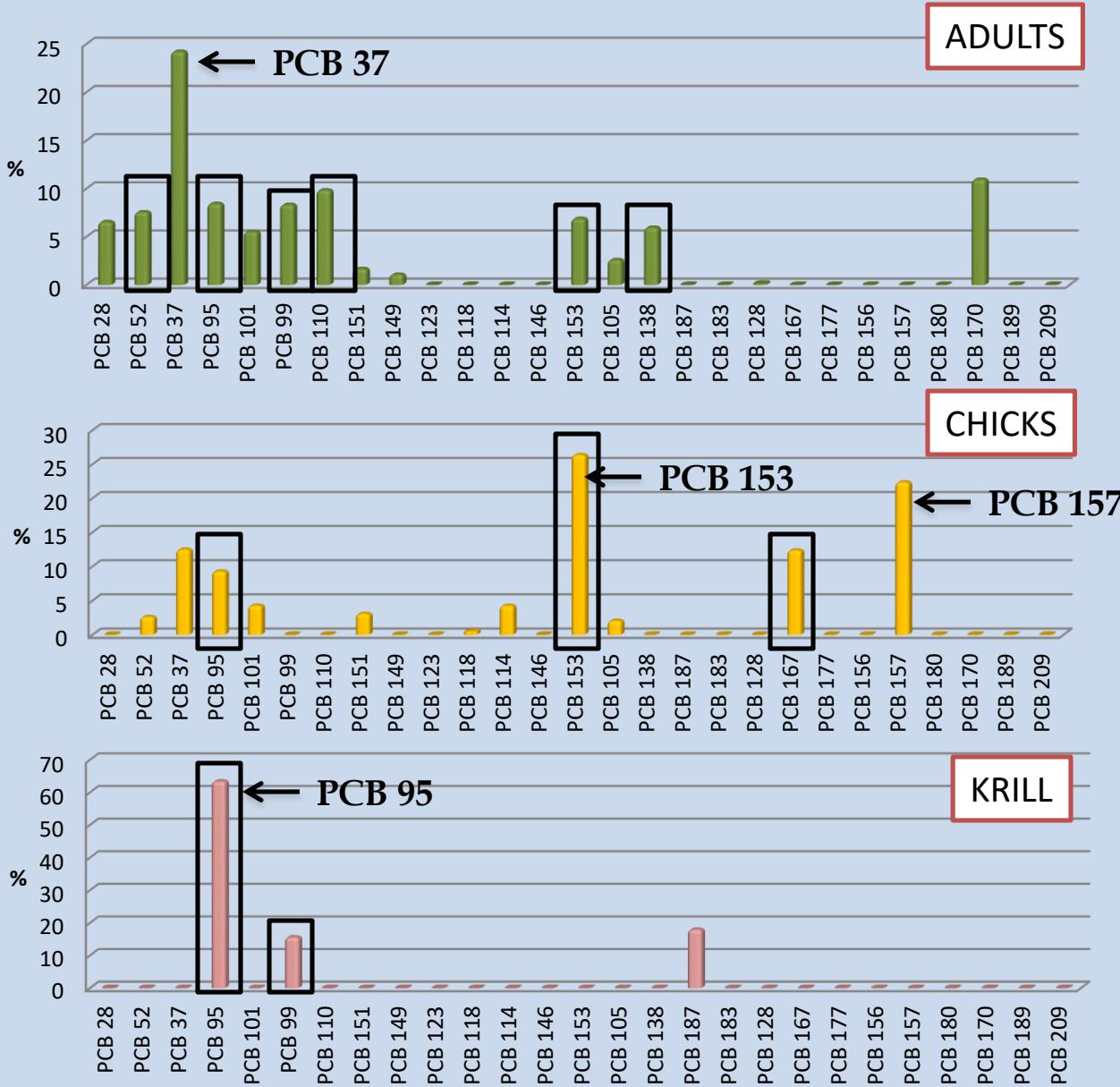
1129 pg g⁻¹ w.w. Maisano (2009)

12300 pg g⁻¹ w.w. Cipro et al. (2010)

ROSS SEA

1900 pg g⁻¹ w.w. Corsolini et al. (2002)

PCBs: fingerprints



Abundant
congeners in
Antarctic
seabirds

Gesi, 2009

Corsolini et al., 2007

Maisano, 2009

Focardi et al., 1995

Schiavone et al., 2009a

Coincidence among eggs
(Schiavone et al., 2009a),
chicks and adults →
a possible maternal
transfer

Coplanar PCBs and toxic equivalents (TEQs)

TEFs proposed by the WHO

LIVER OF ADULTS PENGUINS:

PCB 114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167, PCB 189 <DL

PCB 105

TEQ = 0.004 pg g⁻¹

BRAIN OF CHICK PENGUINS:

PCB123, PCB 156, PCB 189 < DL

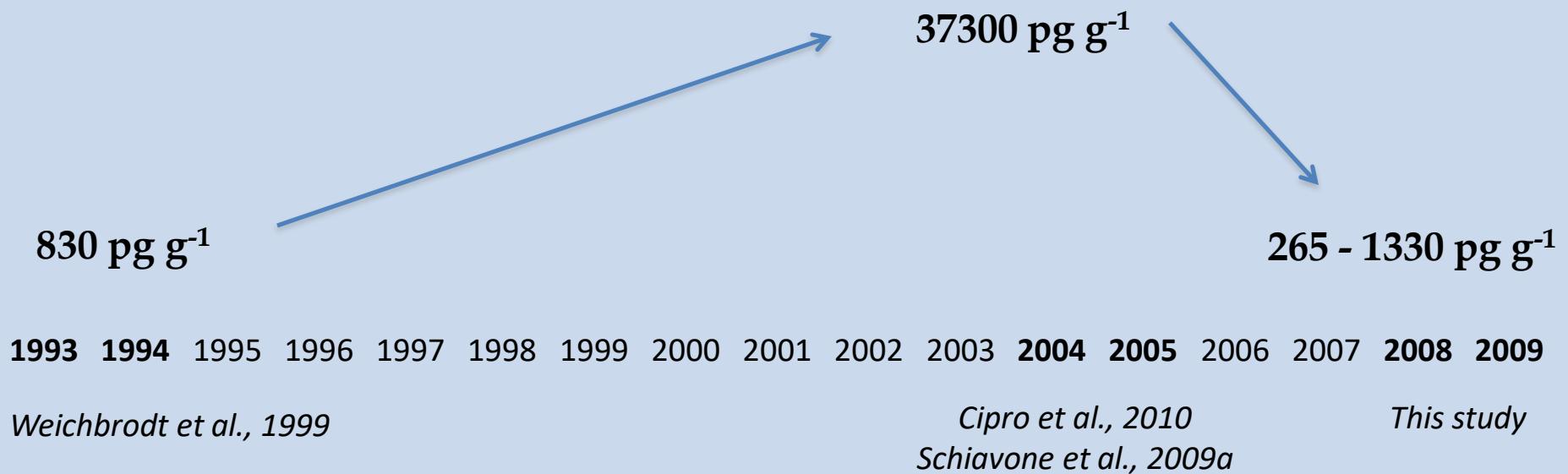
PCB 105, PCB 114, PCB 118, PCB 157, PCB 167

TEQ = 0.167 pg g⁻¹



> 0.01 pg g⁻¹ in blood of chinstrap penguins from
King George Island (Corsolini et al., 2007)

PCBs: temporal trends



A similar decreasing trend was earlier observed in Antarctic seabirds in high Antarctica change is a delay in the transport of blood and a different decrease of PO₂ levels

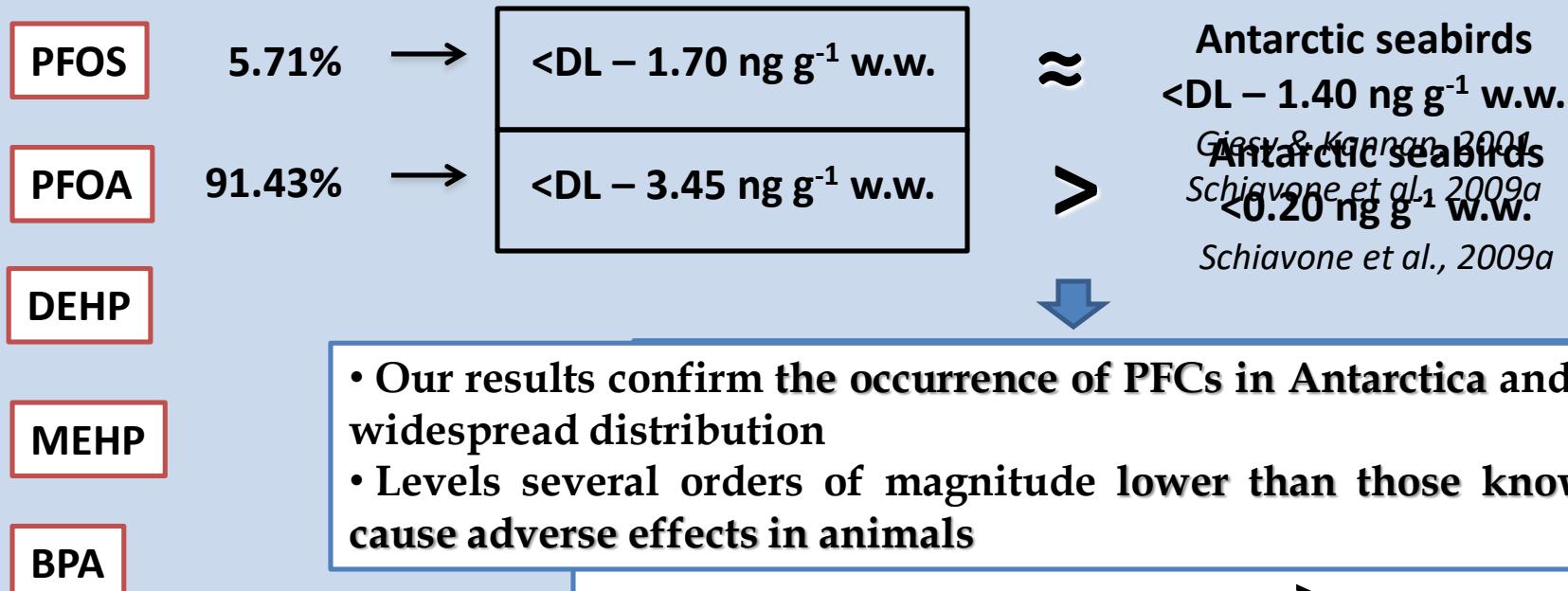
(Brauner et al., 2007; Çakmakçı, 2006; Ünal, 2011)

PFCs, phthalates and BPA

These contaminants have been very less studied in Antarctic organisms



It is difficult to establish temporal trends or look for geographical differences.



PFOA levels in Antarctic penguins $>$ Arctic seabirds

$<1 \text{ ng g}^{-1} \text{ w.w.}$

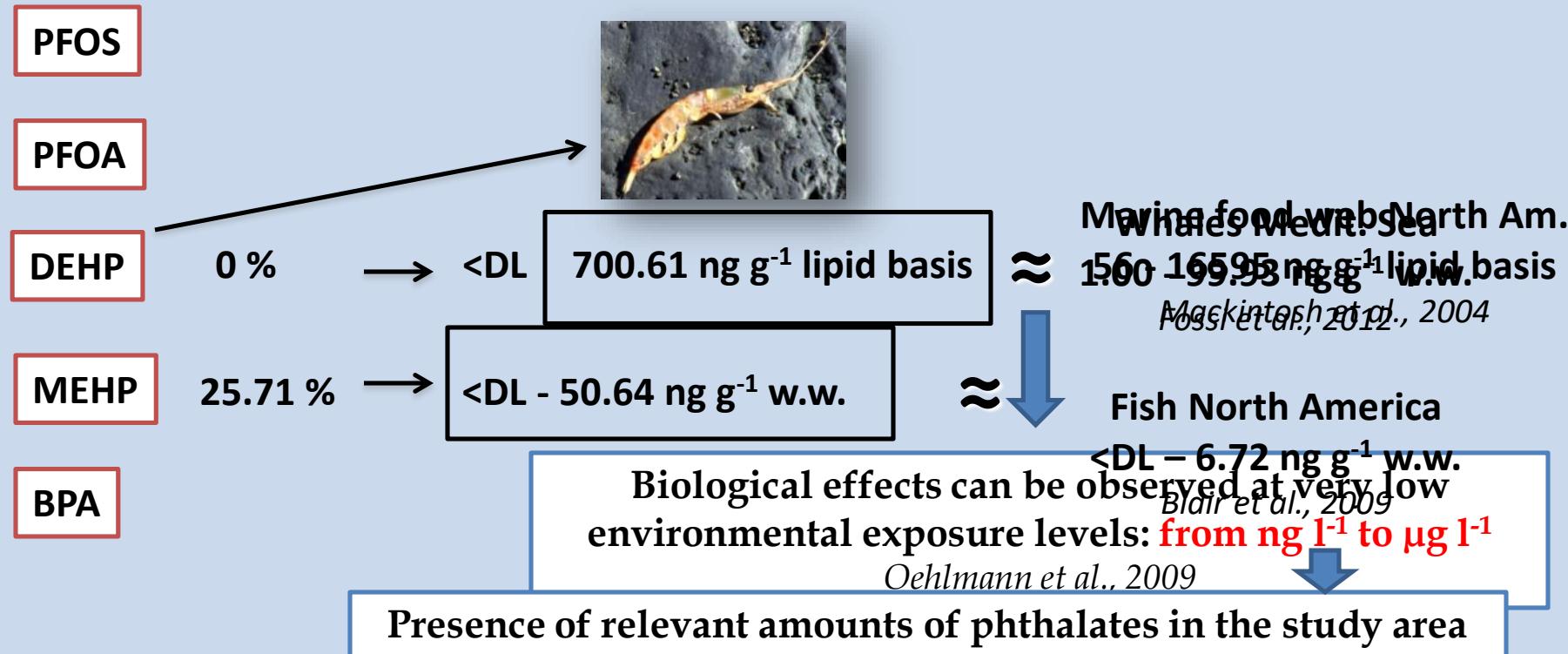
Bossi et al., 2005; Butt et al., 2007; Löfstrand et al., 2008

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PFOS

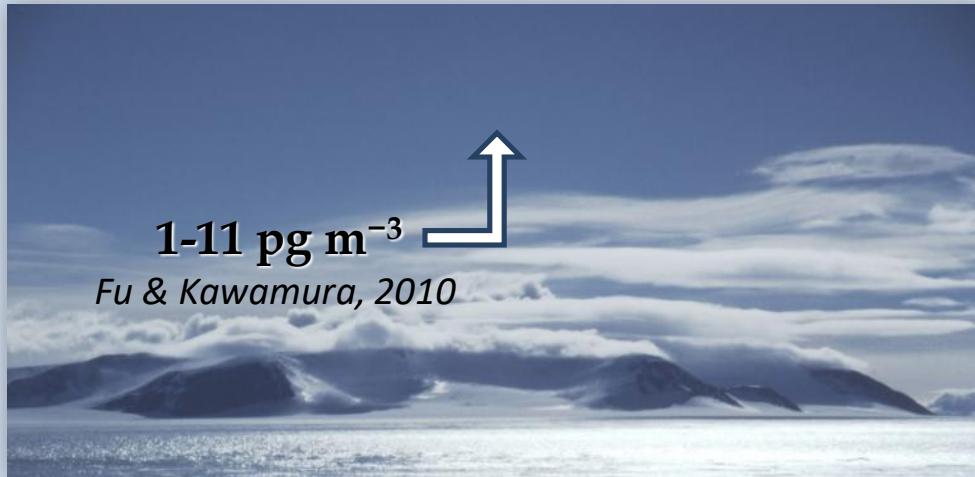
PFOA

DEHP

MEHP

BPA

→ < DL



The occurrence of this compound in Antarctic organisms
should be tested in future studies



GRACIAS