HCH Isomers in Wildlife of Arctic Alaska and Other Regions

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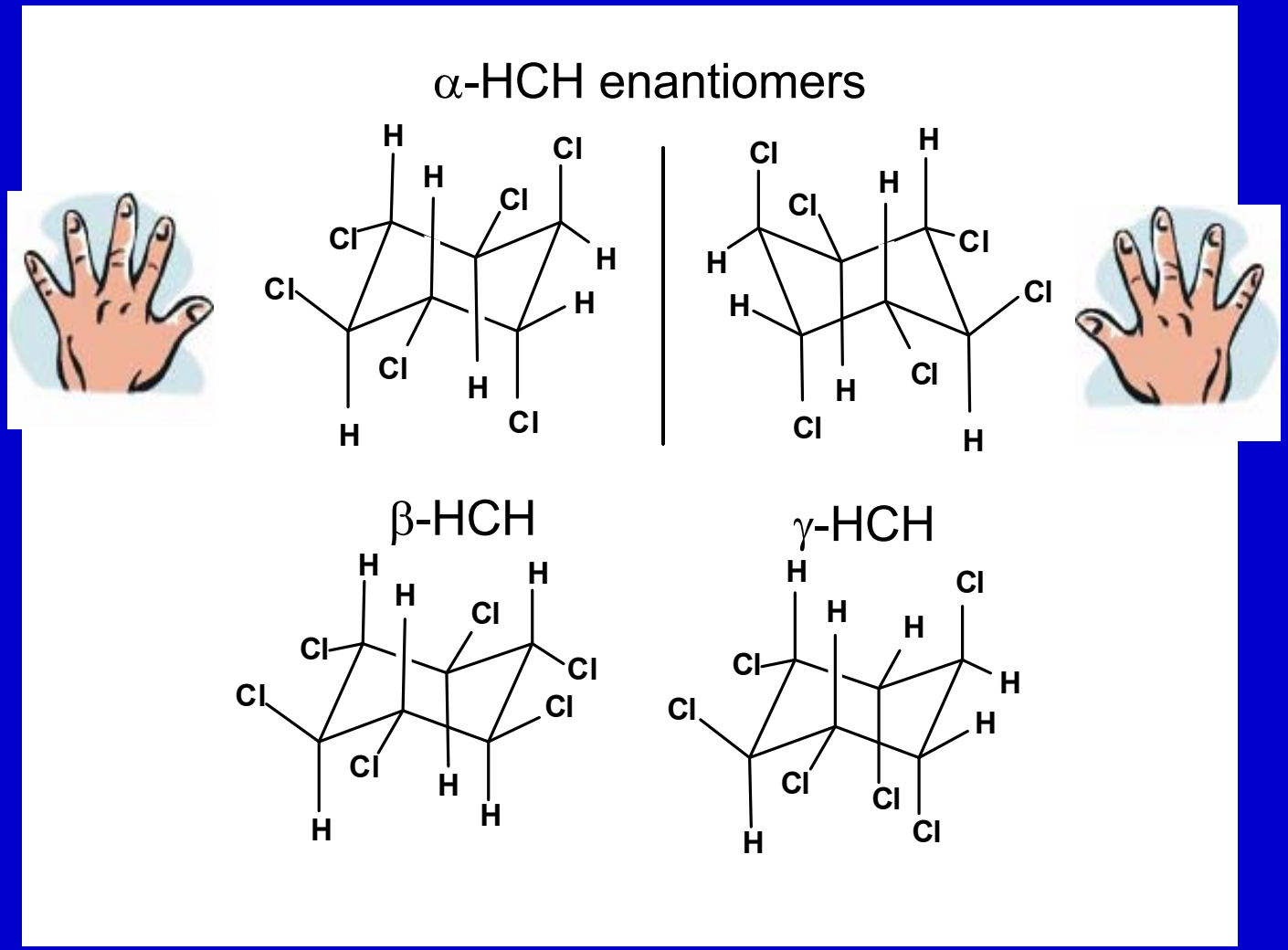
What are HCHs?

- two predominant products: technical HCH & lindane
  - technical HCH: α (60-70%), β (5-12%), γ **(10-12%)**, δ (6-10%), ε (3-4%)
  - **lindane: γ (90-100%)**
- use of technical HCH banned in North America in 1970s
- **lindane still used in many countries including North America**

Structures of HCH isomers including the optically active α-HCH isomer



Marine Mammals

Sum HCH (α+β+γ, ng/g wet wt.)
Preliminary Data NWFSC (Krahn et al.)

Beluga whale blubber:

Barrow (n=3)	398 ± 102
Bristol Bay (n=3)	158 ± 10
Cook Inlet (n=24)	138 ± 147
Norton Sound (n=4)	410 ± 99

Polar bear fat:

Barrow (n=2)	434 ± 99
Gambell (n=2)	1164 ± 558
Savoonga (n=3)	702 ± 132

Sum HCH (α+β+γ, ng/g wet wt.)
Preliminary Data NWFSC (Krahn et al.)

Ringed seal blubber:

Barrow (n=13)	217 ± 86
Norton Sound (n=5)	266 ± 99

Northern fur seal blubber :

Pribilofs (n=15)	241 ± 104

Arctic fox fat:

Pribilofs (n=37)	452 ± 398

Lindane (γ, ng/g wet wt.)
Preliminary Data NWFSC (Krahn et al.)

- Lindane mostly **< reporting limits** (i.e. polar bears, some belugas from Cook Inlet, and other biota).

- Lindane was the **smallest component**, often near or below detection limits for the arctic mammal samples evaluated at the NWFSC.

Lindane Only (ng/g wet wt., Krahn et al.)

Blubber/fat

Ringed seal

Barrow	6.9 ± 5.6
Norton Sound	10.0 ± 4.6

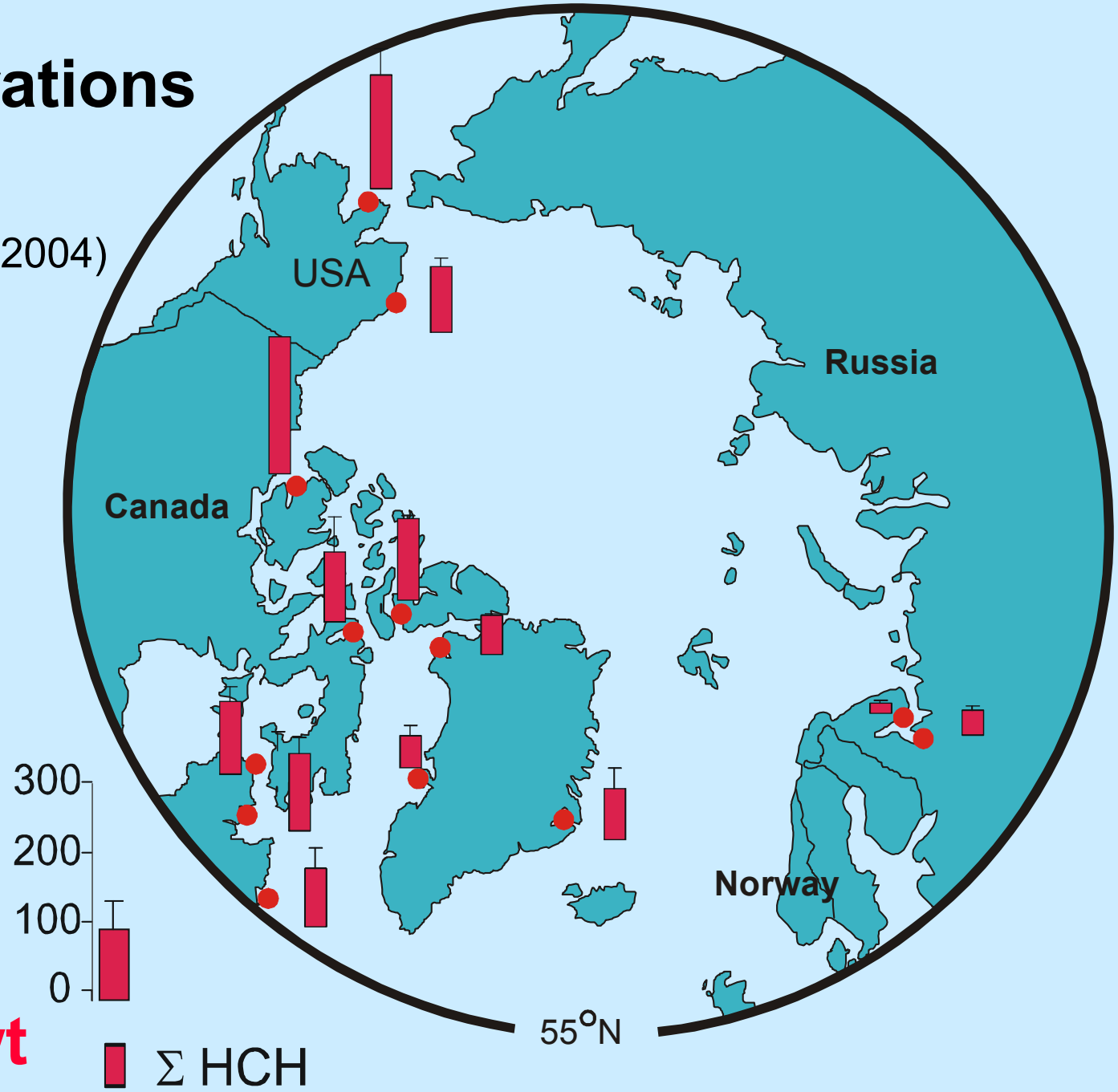
N fur seal	9.0 ± 6.2
Beluga averages	9.9 to 63.8 by location
Polar bear fat	about 50% < reporting limits

Polar Bears

- ~10-19% is α-HCH
- ~80-90% is β -HCH
- lindane is typically **less than 0.5%**

Σ HCH concentrations in ringed seals

(AMAP POPs Assessment 2004)

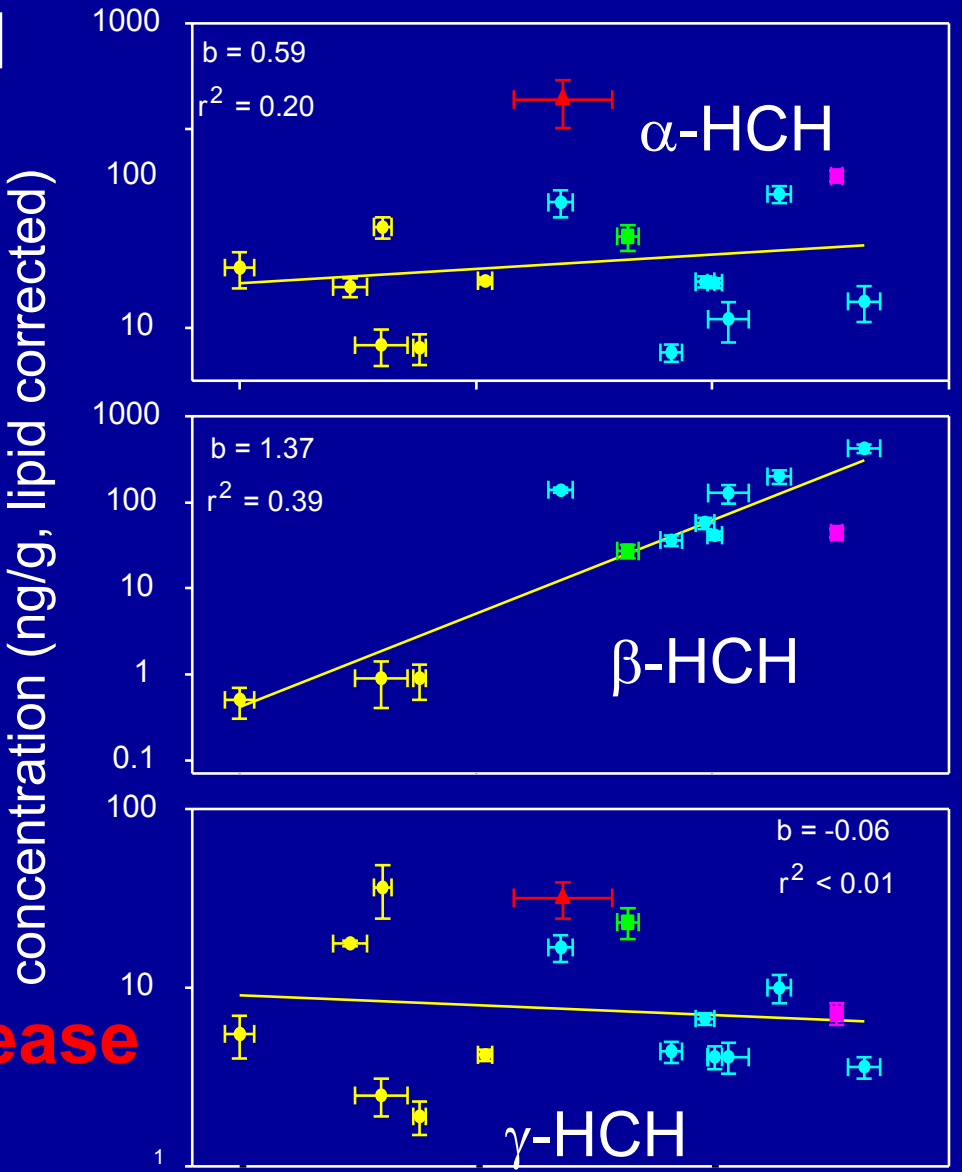


ng/g lipid wt

Relationship between HCH isomer concentrations and trophic level in a pelagic marine food web

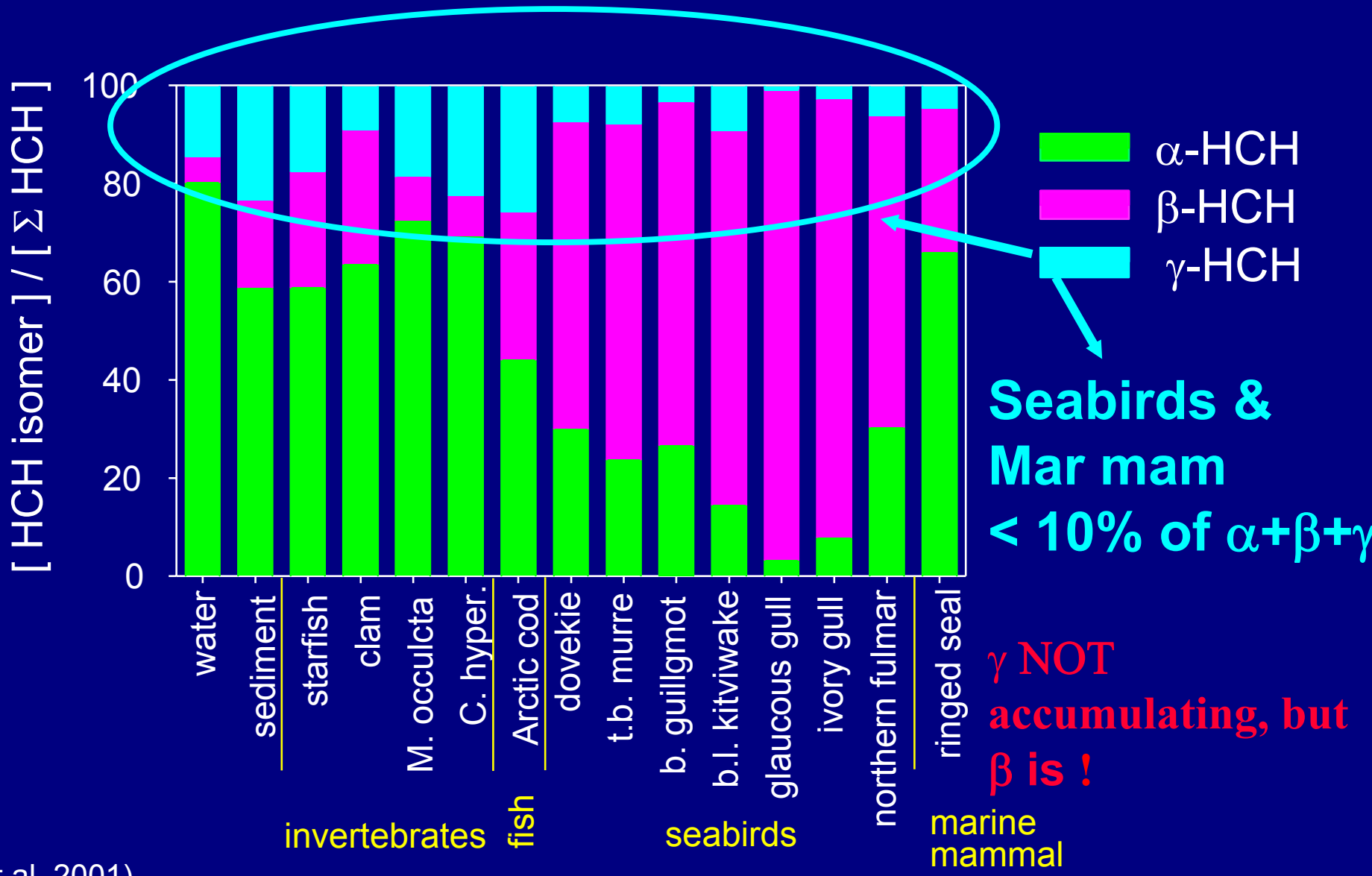
(Moisey et al. 2001)

- zooplankton
- benthic amphipod
- arctic cod
- seabirds
- ringed seal



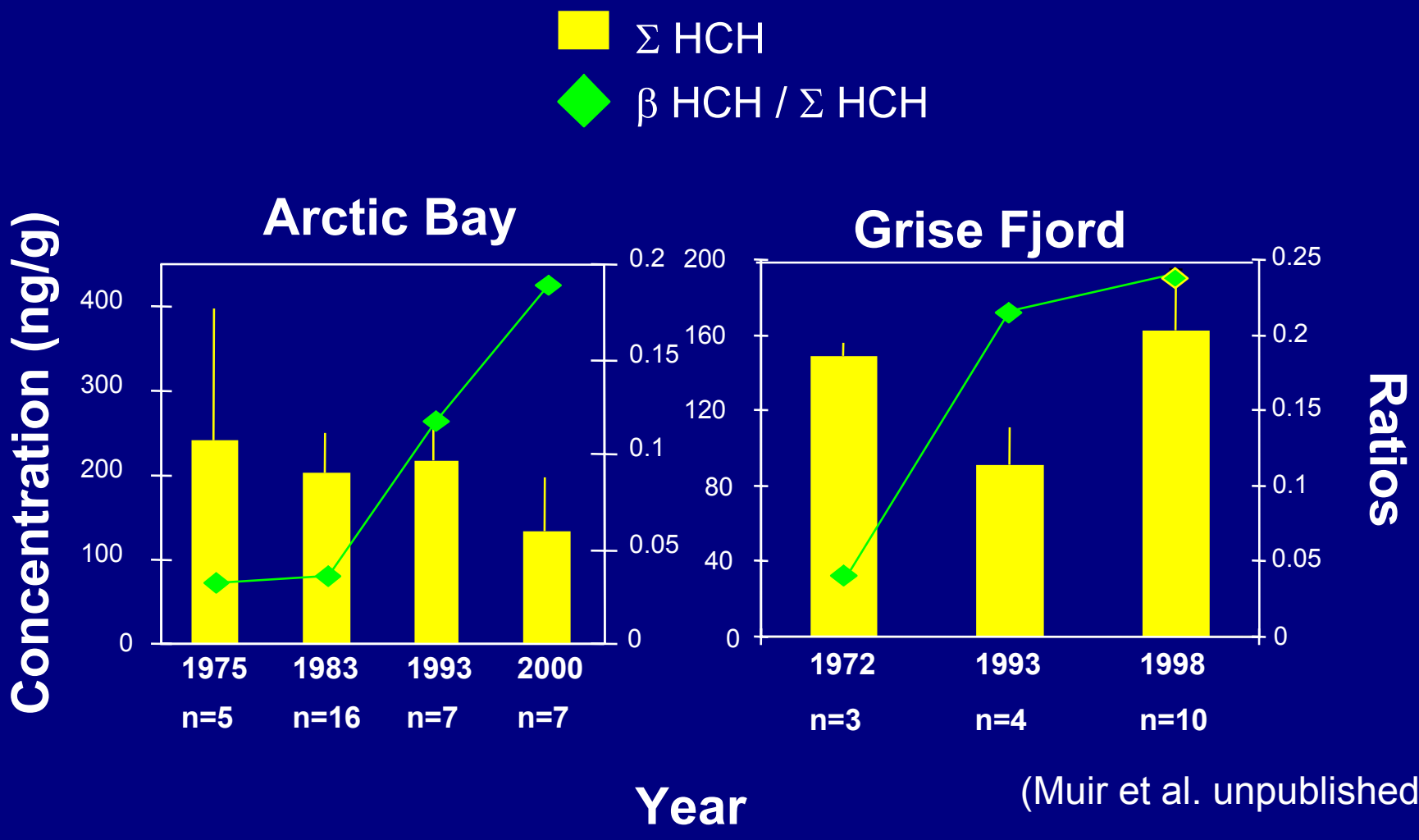
Lindane and α do not increase with TL while β does.

Proportions HCH isomers: pelagic food web



(Moisey et al. 2001)

Temporal trends of HCHs in ringed seals



(Muir et al. unpublished data)

Proportionately β accumulating over time!

Bowhead Whale Data (Hoekstra et al. & O'Hara et al.)

- ΣHCH (9.5 ng/g ww) most abundant POP in liver.
- α-HCH a dominant analyte in liver & blubber, & in both water and zooplankton (Hoekstra *et al.*, 2001b)
- Some HCH isomers (i.e., γ -) regarded as easily metabolized by marine mammals & potentially by lower trophic organisms (Hoekstra *et al.*, 2001b; Moisey *et al.*, 2001; Willett *et al.*, 1998)

Bowhead Whale Data con'd (Hoekstra et al. & O'Hara et al.)

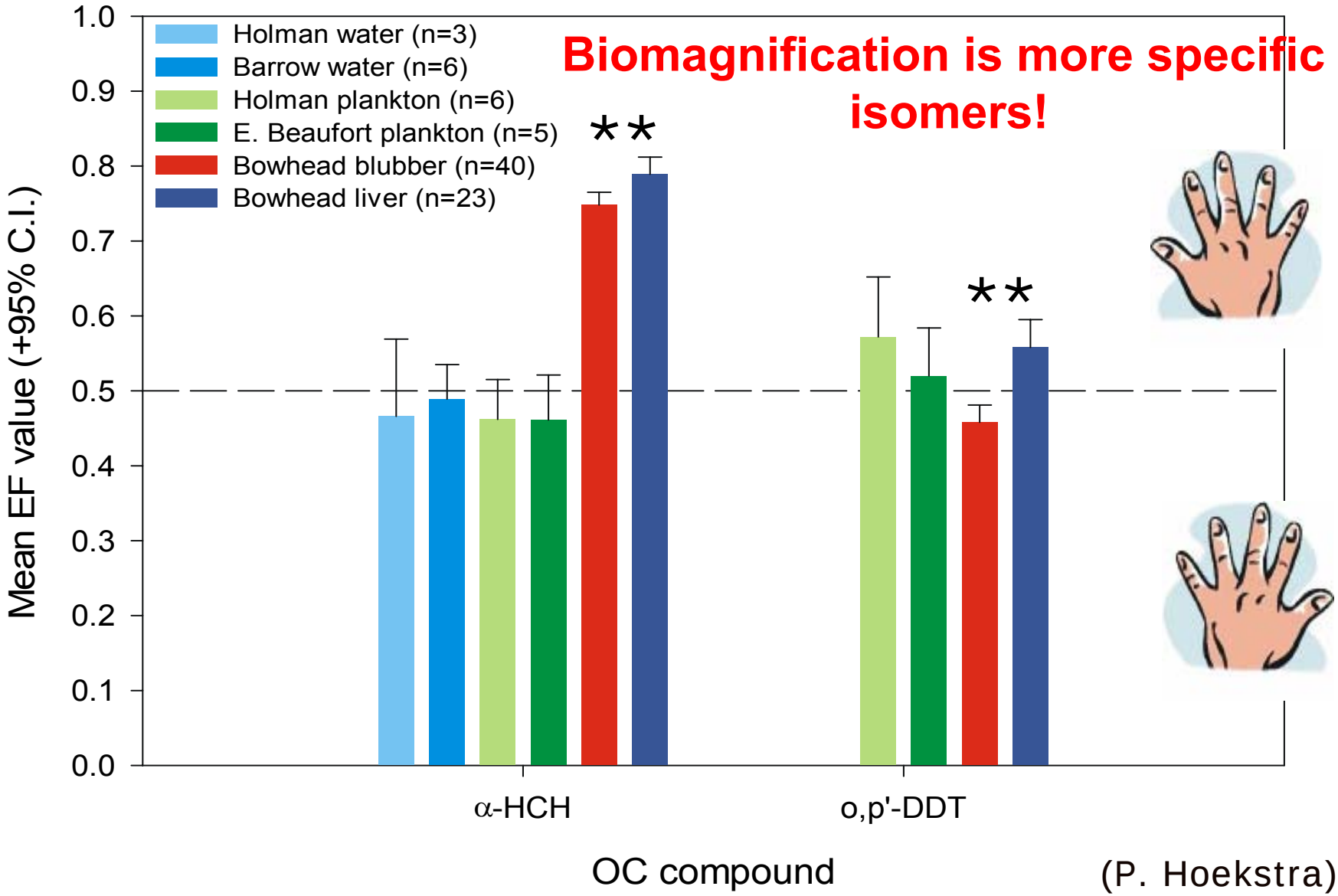
- Relatively higher β-HCH (blubber BMFs: 8.4) suggests biomagnification &/or biotransformation to this compound by bowhead whale.

- β-HCH may accumulate in mammals due to its structure limiting biotransformation (Moisey *et al.*, 2001).

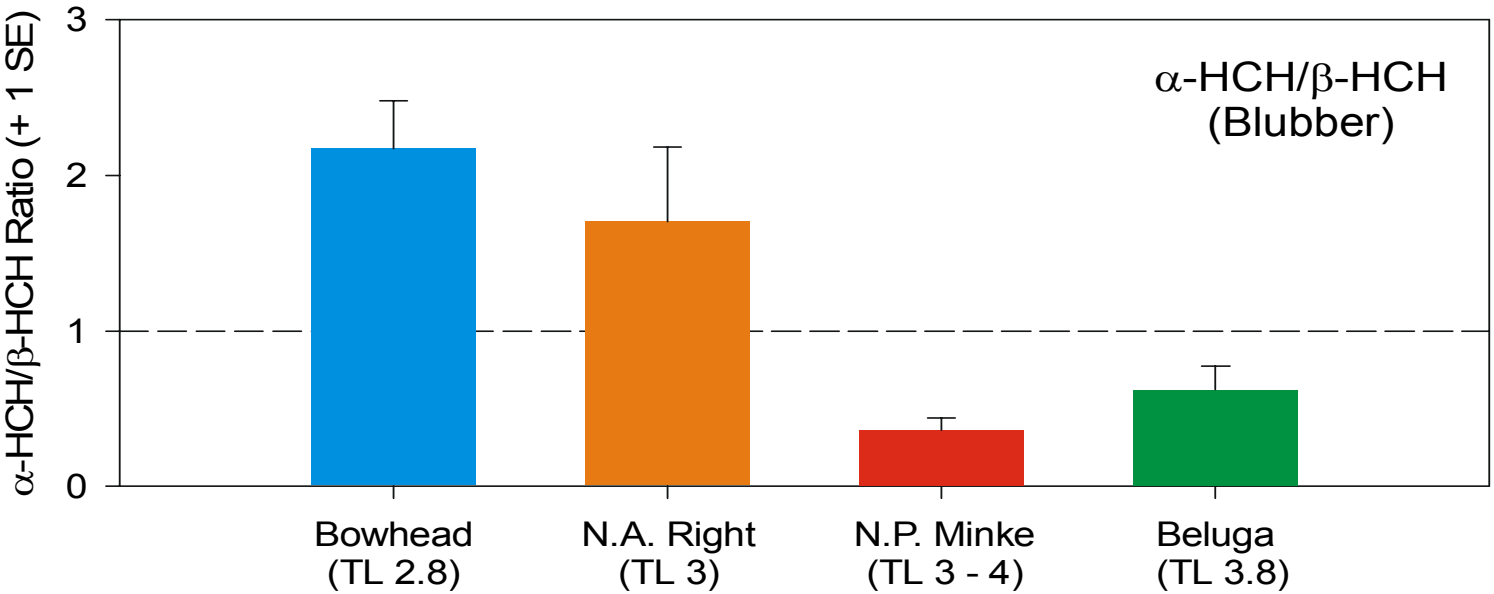
HCH Isomer Conc, BMF and % of ΣHCH for Bowhead Whales

	ng/g, wet weight		BMF (lipid weight basis)	
	Liver	Blub	Liver/ *Calanus*	Blub /*Calanus*
α-HCH	6.2 ± 0.4	114 ± 11	3.4	5.4
β-HCH	2.3 ± 0.2	57 ± 2.9	3.9	8.4
γ-HCH	0.8 ± 0.1 8.4% of Σ	29 ± 2.6 14.3% of Σ	2.1	6.7
ΣHCH	9.5 ± 0.5	203 ± 13	3.4	6.3

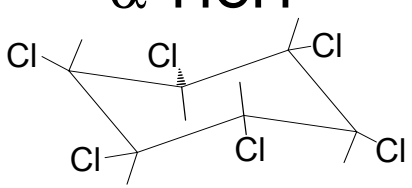
Enantiomer specific accumulation of an HCH isomer in bowheads

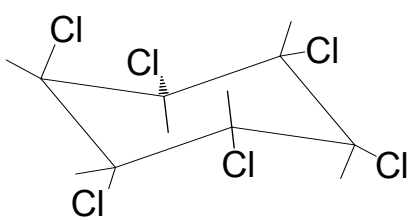


Comparison of cetaceans- Decrease alpha as TL increases!



α-HCH





β-HCH

α-HCH

- Predominant OC in water; zooplankton
- Excreted/metabolized

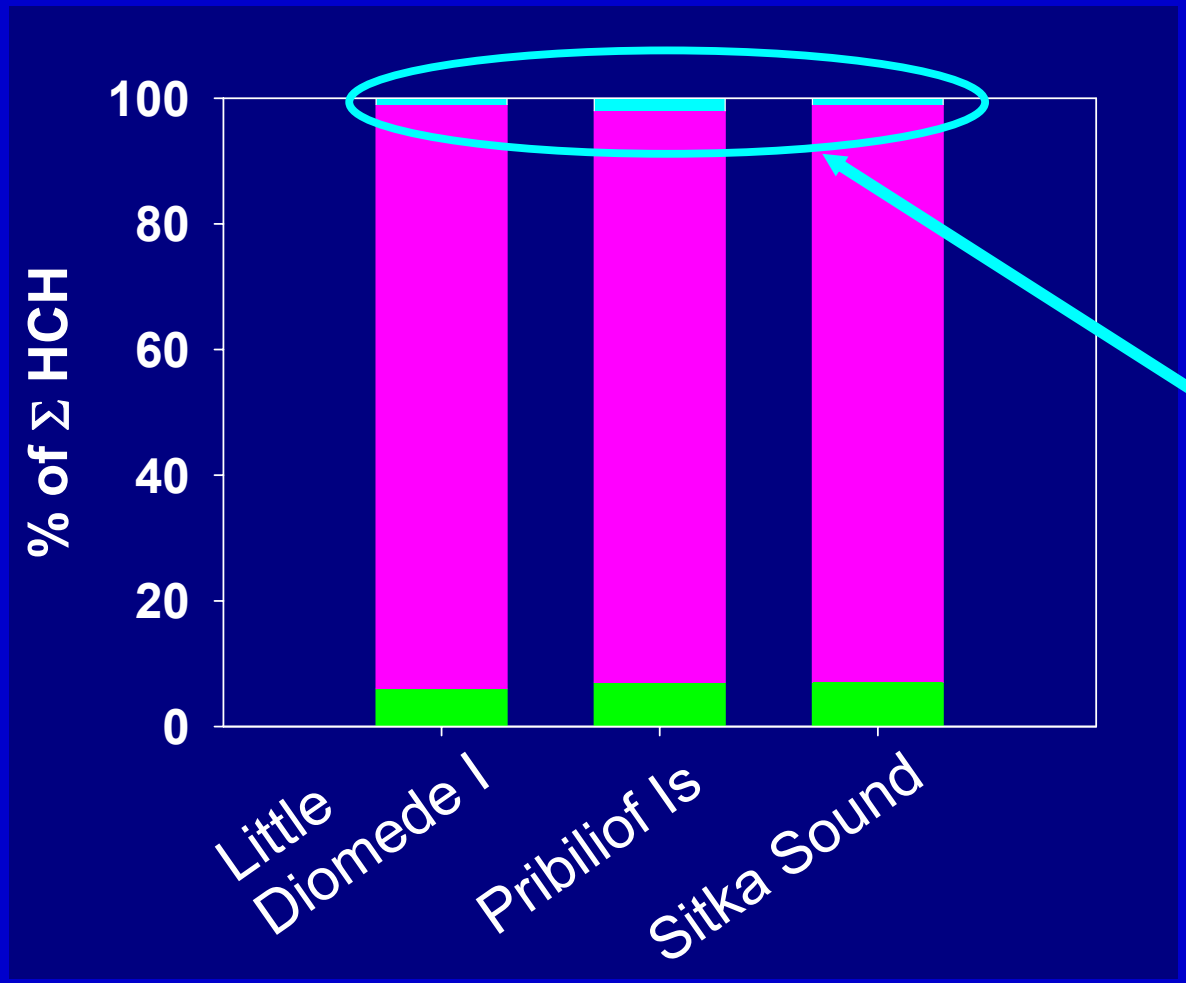
β-HCH

- Recalcitrant, bioaccumulates
- Lower vapor pressure

Derived from: Hoekstra et al., Environ. Pollut., 2003; Hoekstra et al., AEC&T, 2002; Weisbrod et al., ET&C, 2000; Aono et al., Environ. Pollut., 1997.

Seabirds

Relative proportions of HCH isomers in common murre eggs from Alaska 1999



Vander Pol et al. 2003

Lindane (γ–HCH) Only (ng/g wet wt.) from Vander Pol et al. 2003

Common murre eggs (collected 1999):

Little Diomede Island (n=10) 0.312 ± 0.260

1% of sum HCH

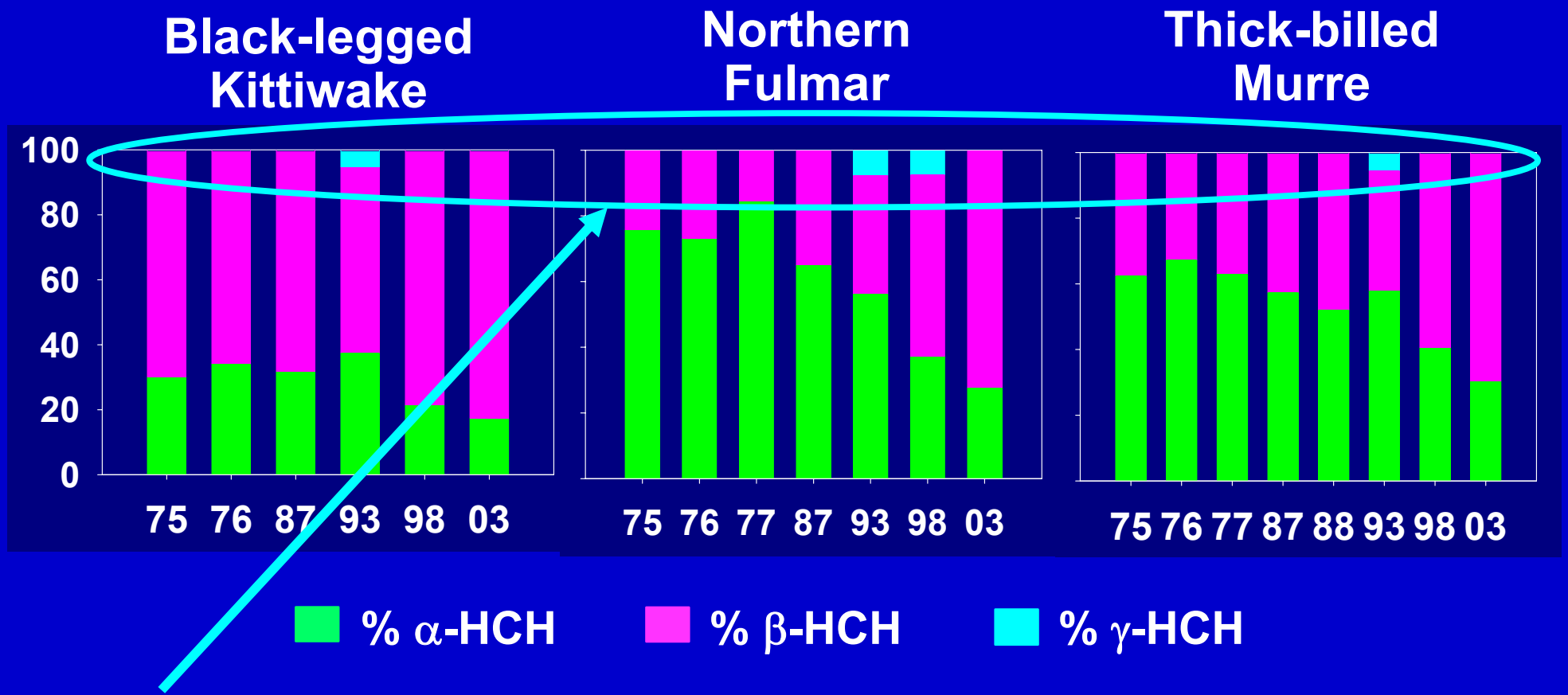
St. George I., Pribilof Is. (n=11) 0.338 ± 0.290

2% of sum HCH

St. Lazaria I., Sitka Sound (n=10) 0.268 ± 0.190

1% of sum HCH

Relative proportions of HCH isomers in arctic seabird eggs 1975-2003



Braune et al. 2001,
Braune, unpubl. data

- Concentrations of sum HCH measured in the Alaskan murre eggs collected in 1999 (Vander Pol et al. 2003) were similar to concentrations reported in Canadian murres collected in 1993 and 1998 (Braune et al. 2001; Braune et al. 2002)

Biotransformation of HCHs

- Biodegradation of γ-HCH to
  - tetrachlorohexene;
  - tri-, tetra-, pentachlorinated benzenes;
  - penta- and tetra cyclohexanes;
  - other isomers of HCH;
  - tetrachloro -1,4-dimethoxybenzene & others
- Conjugates of mercapturic acid, glucuronide, and sulfate.
- Labs demonstrated **bioisomerization** of γ-HCH to α-, β-, and δ-HCH but importance in arctic is less certain (unlikely)

Biotransformation of HCHs

- α-HCH and β-HCH isomers (longer half-life) are metabolized, but γ-HCH is metabolized faster;
- Other environmental compounds, particularly chlorobenzene, produce the same metabolites.
- To discuss lindane biotransformation in arctic wildlife is likely VERY premature.
- Recent research has improved but proper studies of biotransformation and adverse effects eludes us in this remote region.

Summary

ΣHCH levels in ringed seals are associated with α-HCH

- seals may not metabolize α-HCH very well
- highest levels in seals from Beaufort and Bering Seas which parallels water patterns of HCH isomers
- reflect seasonal invertebrate diet

Although concentrations of β-HCH are much lower than α-HCH and γ-HCH in Canadian Arctic waters, β-HCH is found in increasing concentrations at higher trophic levels (biomagnifies) over time in ringed seals and seabirds.

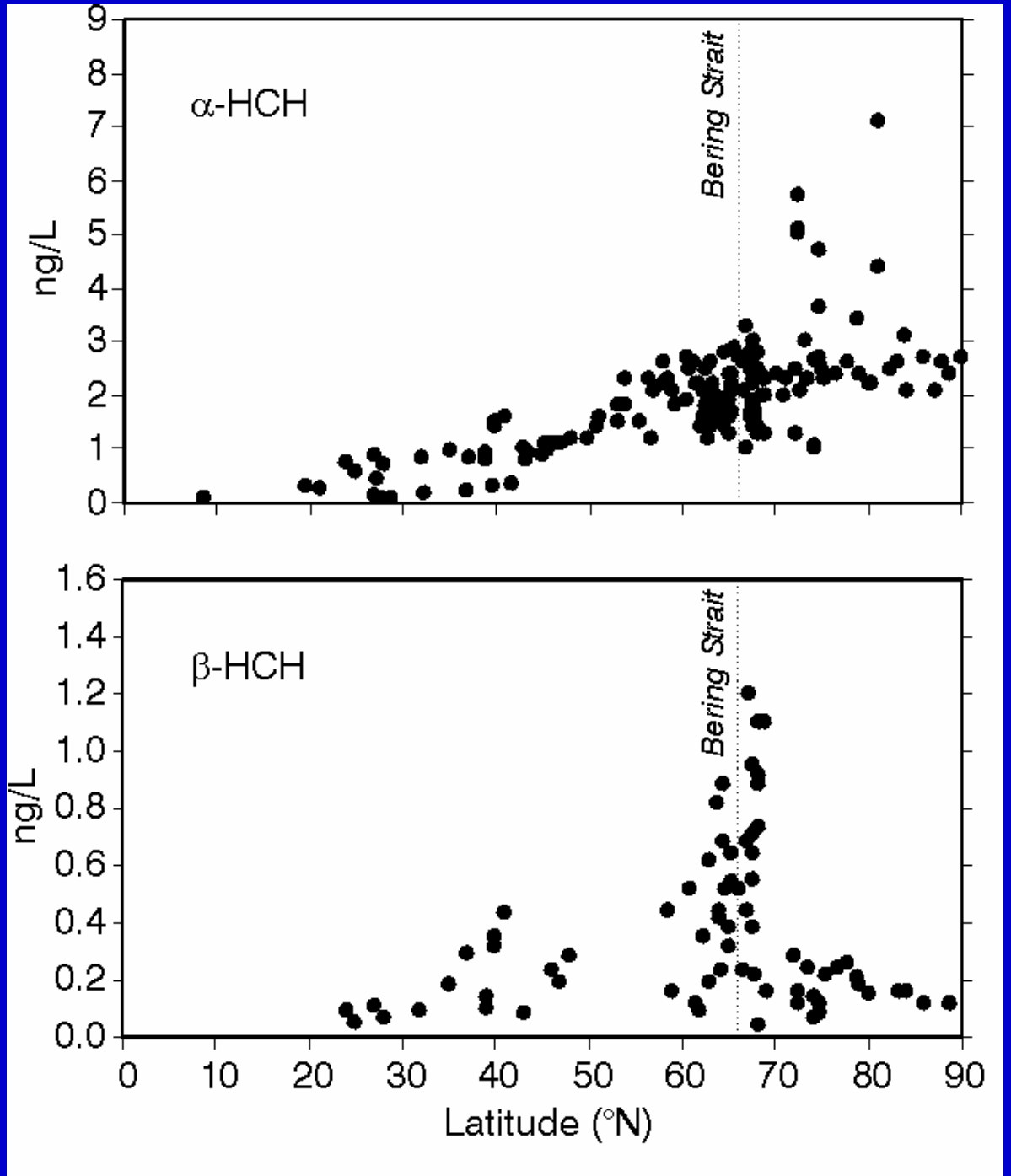
Summary - con'd

- β-HCH biomagnifies whereas γ-HCH is more readily metabolized by seabirds and some marine mammals.
- α-HCH is metabolized by seabirds and polar bears but not as readily by ringed seals and bowhead whales. (?)
- Lindane is particularly vulnerable to biotransformation and excretion and does not accumulate as readily.
- α & β are not produced from γ via bioisomerization in the Arctic to any appreciable amount based on weight of evidence.

Thank You!

Concentrations of α-HCH and β-HCH in surface waters of the North Pacific and western Arctic Ocean

(Li et al. 2002)



Biomagnification & temporal trends

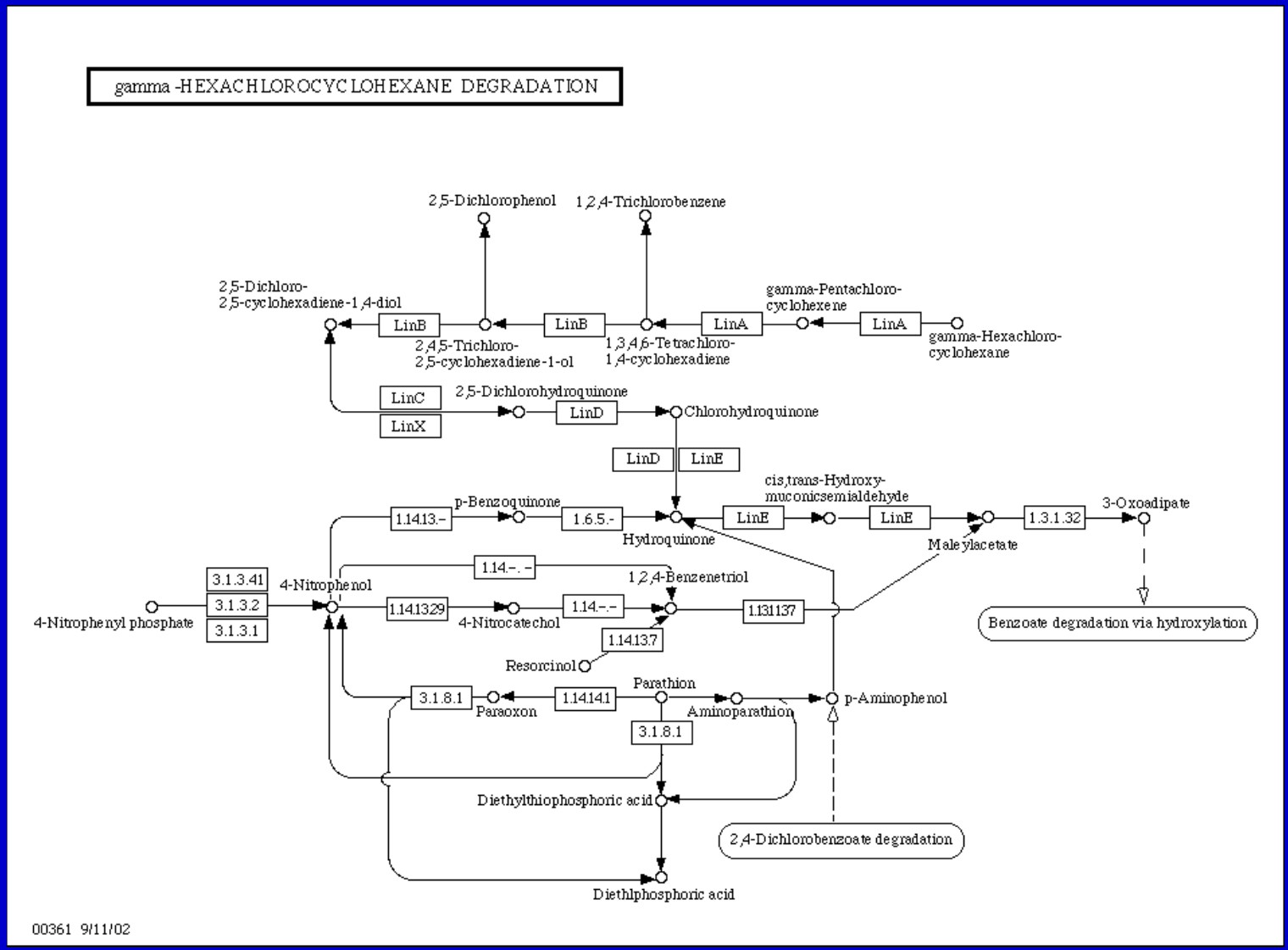
β -HCH biomagnifies, and this component drives the temporal trends for total HCHs in higher-trophic-level organisms.

In other words, the decline in total HCHs that would be expected based on

AMAP POPs Assessment, 1998 & 2004

- **Mueller et al. 1992** (Environ. Sci. Technol. 26:566)
- - g-HCH can be transformed to the more stable a-HCH by microorganisms
- - a-HCH is the only chiral HCH isomer
- **Engst et al. 1977** (Residue Rev. 68:59)
- - lindane (g-HCH) degraded to trichlorophenols & polychlorobenzenes
- **Wiemeyer 1996** (SETAC Spec. Public., Environmental Contaminants in Wildlife:interpreting tissue concentrations (Beyer, Heinz, Redmon-Norwood, eds)
- - lindane - three major uses: seed, hardwood lumber, livestock
- - lindane readily metabolized & excreted in birds - minimally accumulated in tissues
- - ~30 mg/kg ww in avian liver - dangerous exposure
- - hatchability doesn't seem to be affected (up to 10 mg/kg ww in egg)
- **Malaiyandi & Shah 1984** (J. Environ. Sci. Health A19(8):887)
- - a-HCH most stable isomer photochemically - conversion from both g-HCH and b-HCH in sunlight
- - b-HCH prevalent metabolic product in mammalian species
- - thermodynamic stability: b > d > a > g
- - photochemical stability: a > d > g > b

Do I blow them away with this- this gets very complicated! I only have 15-20 minutes?!



Relative proportions of HCH isomers in common murre eggs collected in 1999 (Vander Pol et al. 2003)

Murre Colonies - Alaska	α-HCH	β-HCH	γ-HCH
Little Diomede I.	0.06	0.93	0.01
St. George I., Pribilof Is.	0.07	0.91	0.02
St. Lazaria I., Sitka Sound	0.07	0.92	0.01

Again <10% α-HCH! β-HCH dominates in AK.