Alpha-HCH Enantiomers Trace Sea-to-Air Exchange During Ice Breakup in the Canadian Archipelago

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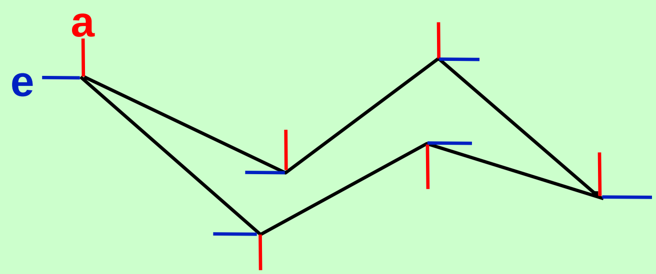
Hexachlorocyclohexane (HCH)



Technical HCH

aaeeee	α-HCH	60-70%
eeeeee	β-HCH	5-12%
aaaeee	γ-HCH	10-15%

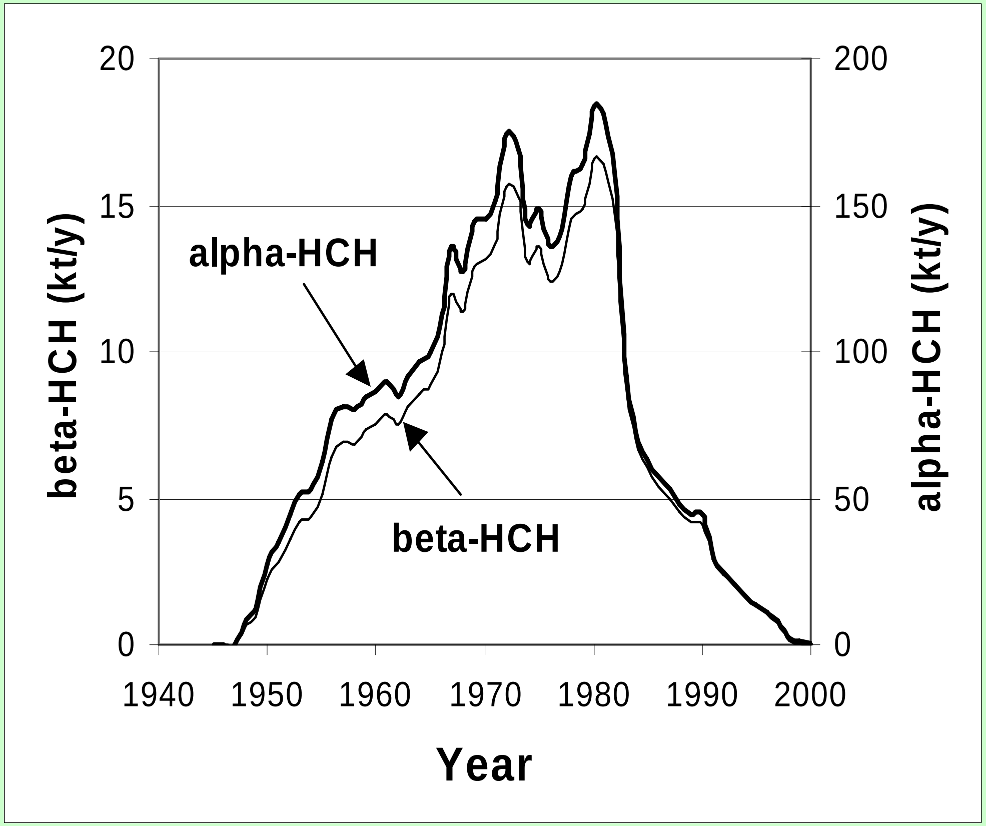
+ other isomers

Most abundant pesticide in arctic air & water.

"Technical" HCH
was the most heavily used insecticide in the world!

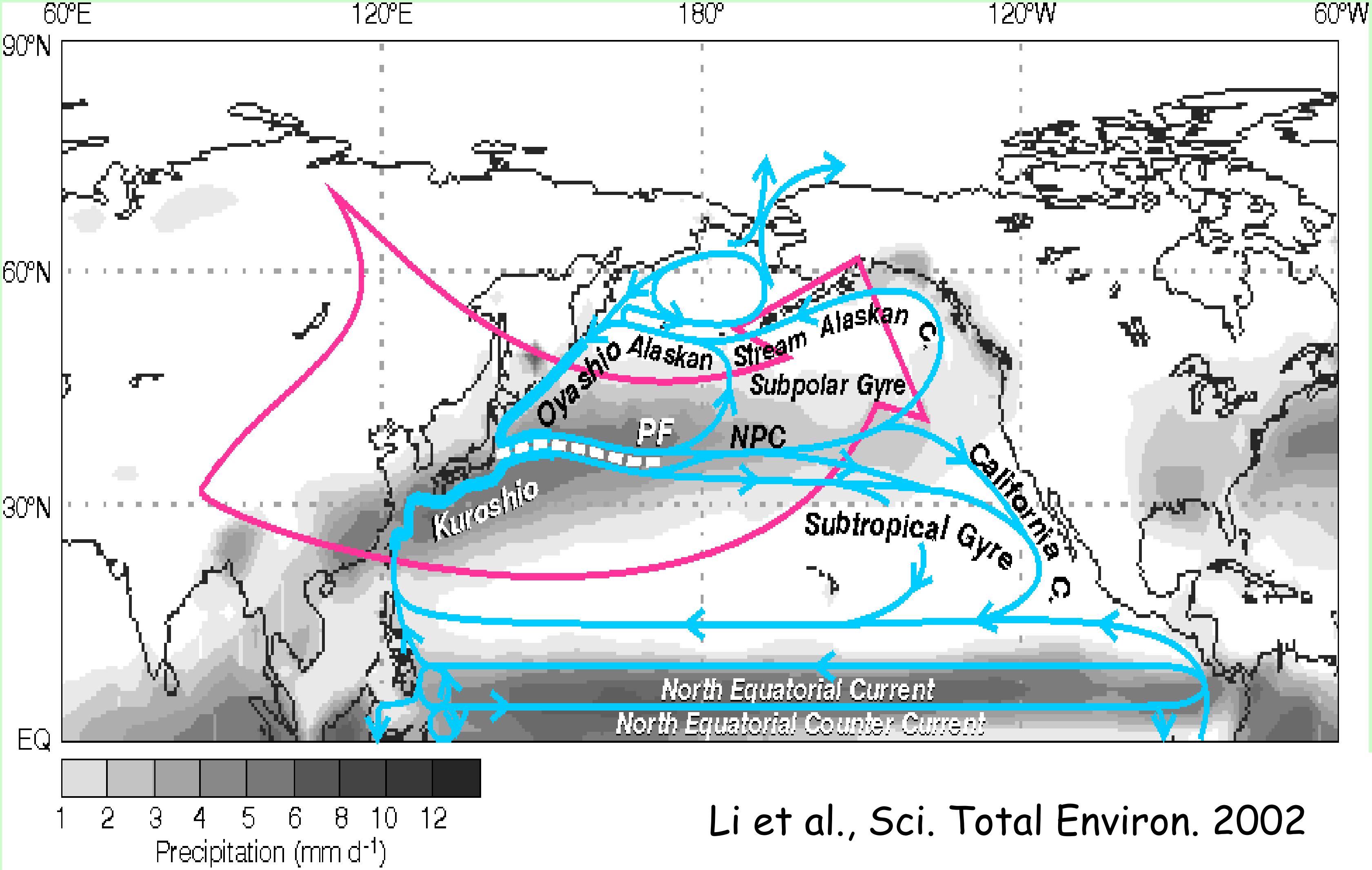
- Manufactured since 1945.
- Used in Canada and U.S.A. until the 1970s, phased out in Europe in the 1980s, replaced by lindane.
- Over 6 million tonnes used in Asia, 1948 - 1997.
- Main usage in China, India, former Soviet Union.
- Now banned in most countries.

Global emissions of HCHs



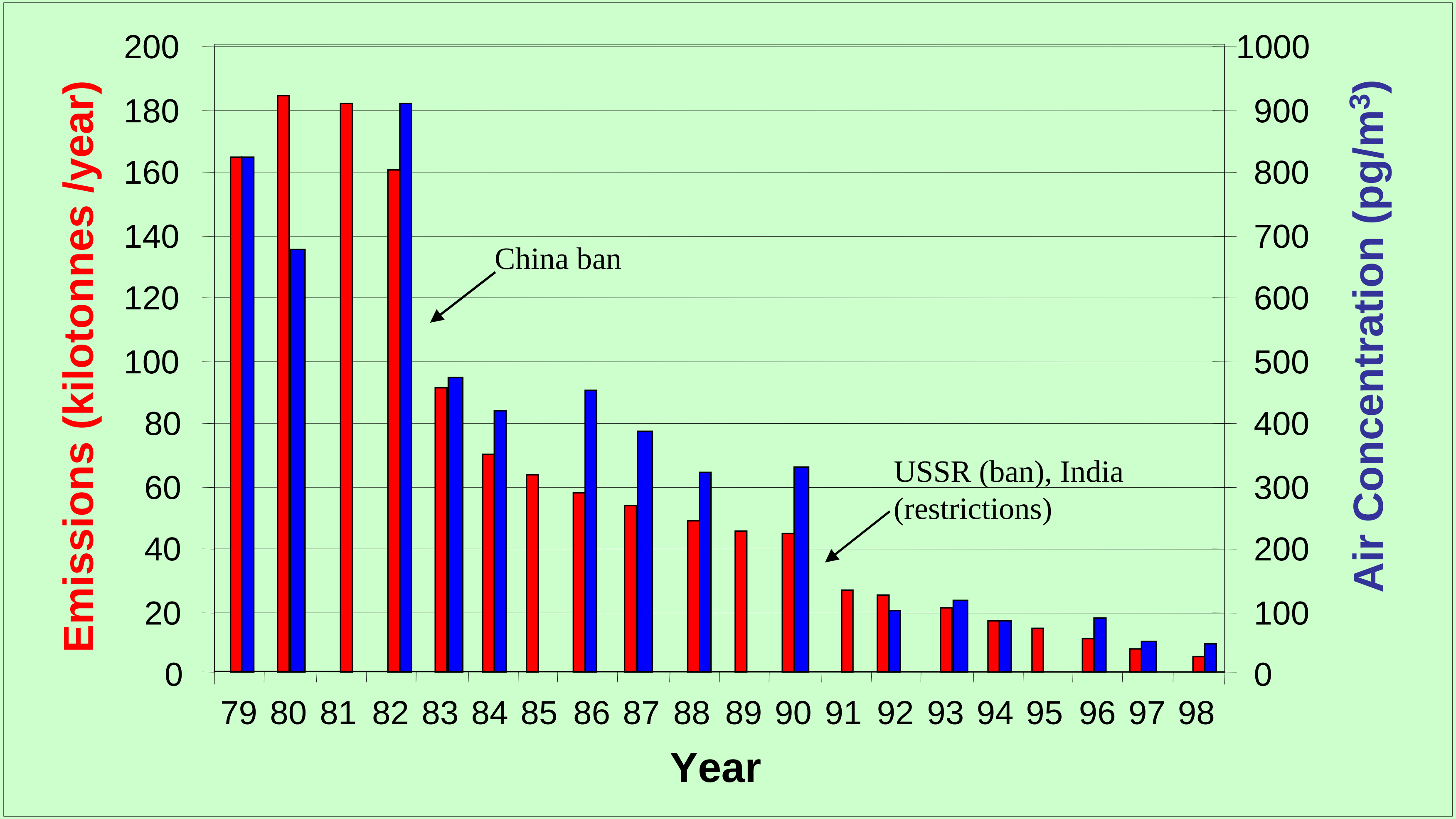
Li & Macdonald, Sci. Total Environ., 2005; Li et al., Environ. Sci. Technol., 2003

Air and ocean pathways brought HCHs to the western Arctic



Li et al., Sci. Total Environ. 2002

Controls on technical HCH emissions have reduced levels of alpha-HCH in arctic air

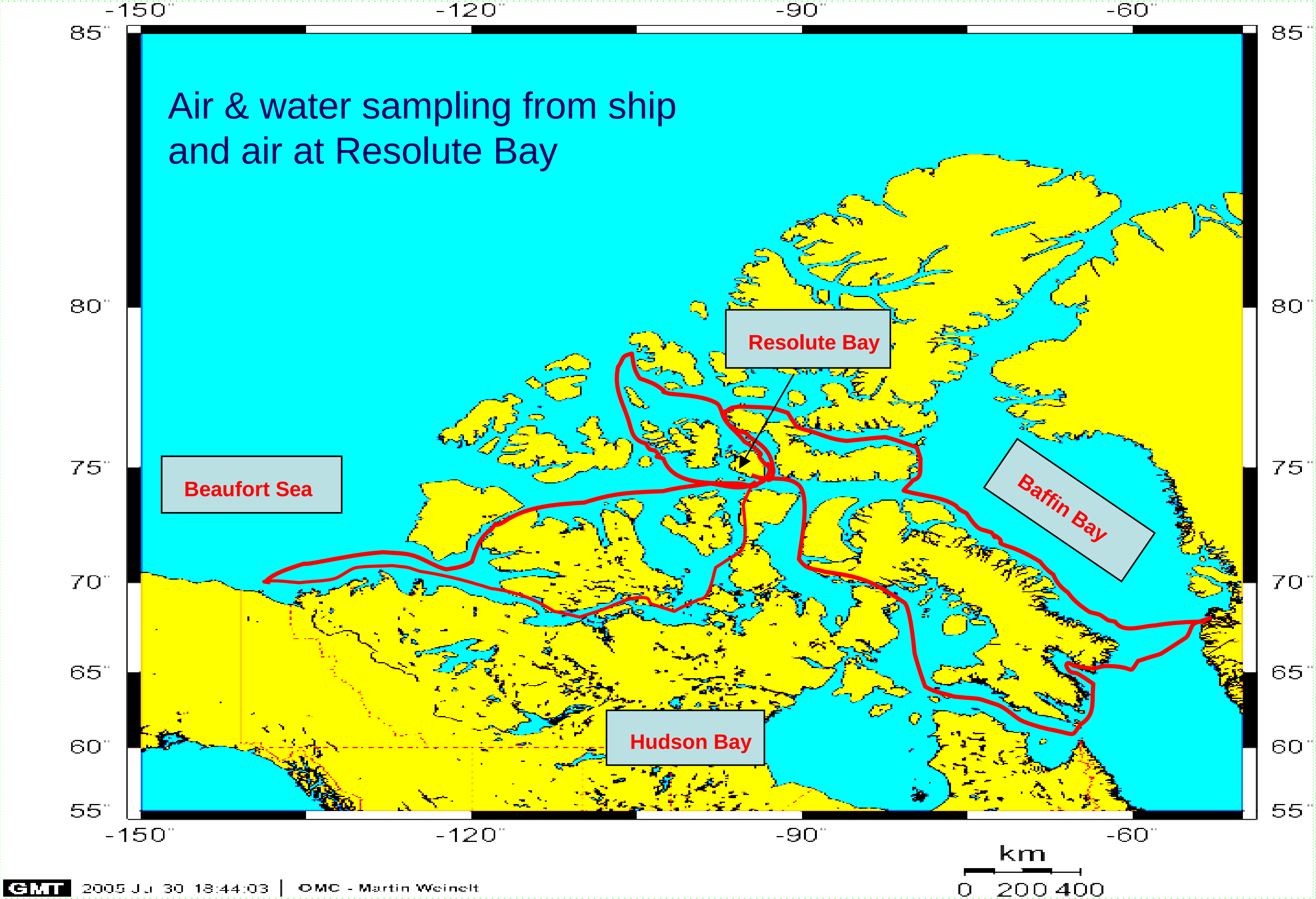


Li and Bidleman, J. Environ. Informatics, 2003 inflow

circulation & outflow

Figure 3·29. Surface currents in the Arctic region. Square boxes indicate that the denser inflowing (Atlantic and Pacific) waters are submerging under the Polar Surface Water. The continuation of these flows can be seen in Figure 3·27.

Tundra Northwest Expedition (TNW-99)
July – September, 1999



Sample Collection and Processing

Air, 400-800 m^3
GFF + PUF

Water, 4L
pump into stainless steel cans, add deuterated HCH surrogates

GFF + SPE cartridge (ENV+)

solvent extraction & cleanup
(silicic acid, sulphuric acid

Analysis

Low-Res GC-ECNI-MS
Ions 255/257 (deuterated 261)

Quantitative:

60-m DB-5

Surrogate recoveries:

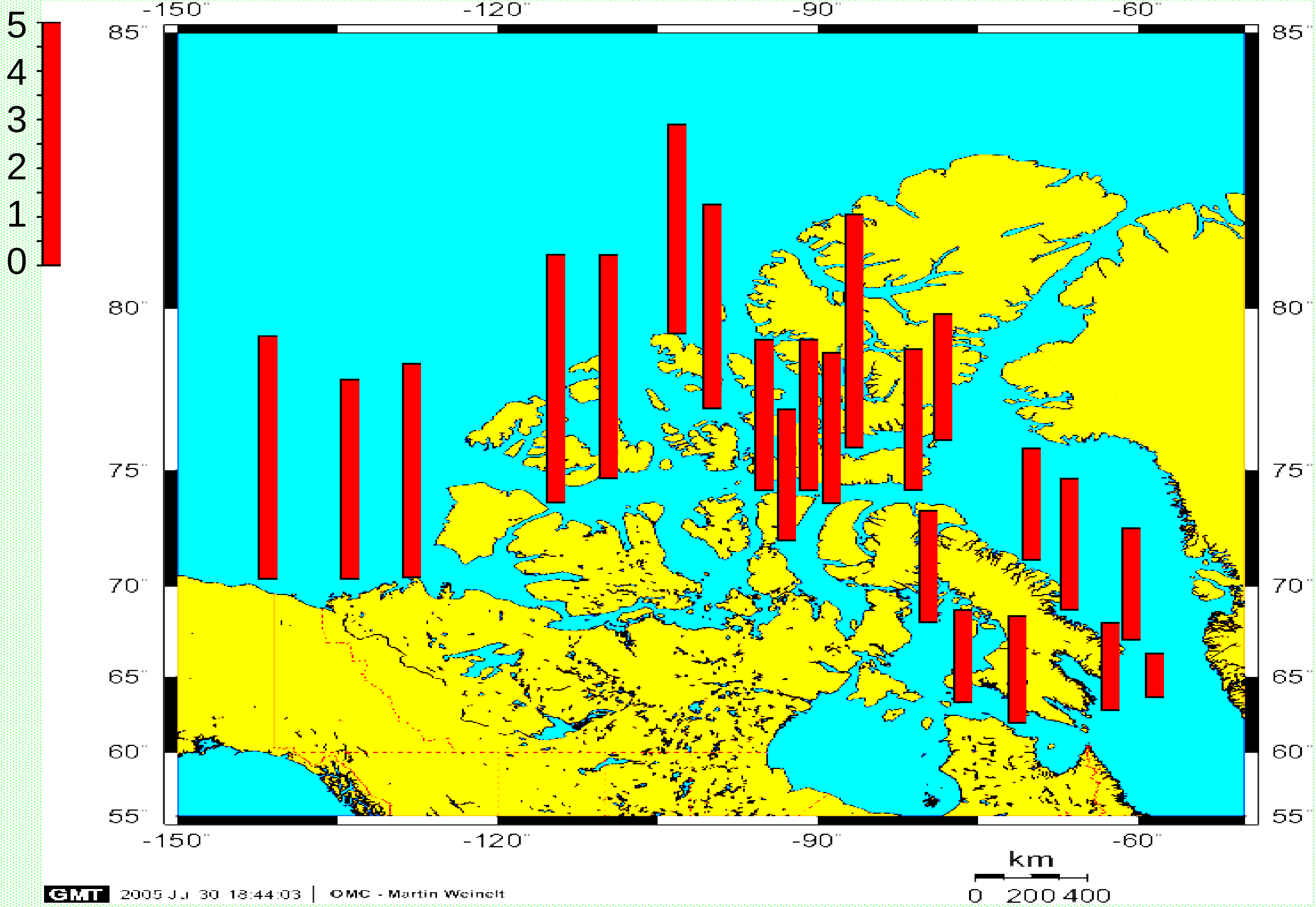
α-HCH 83 ± 13%

γ-HCH 79 ± 20%

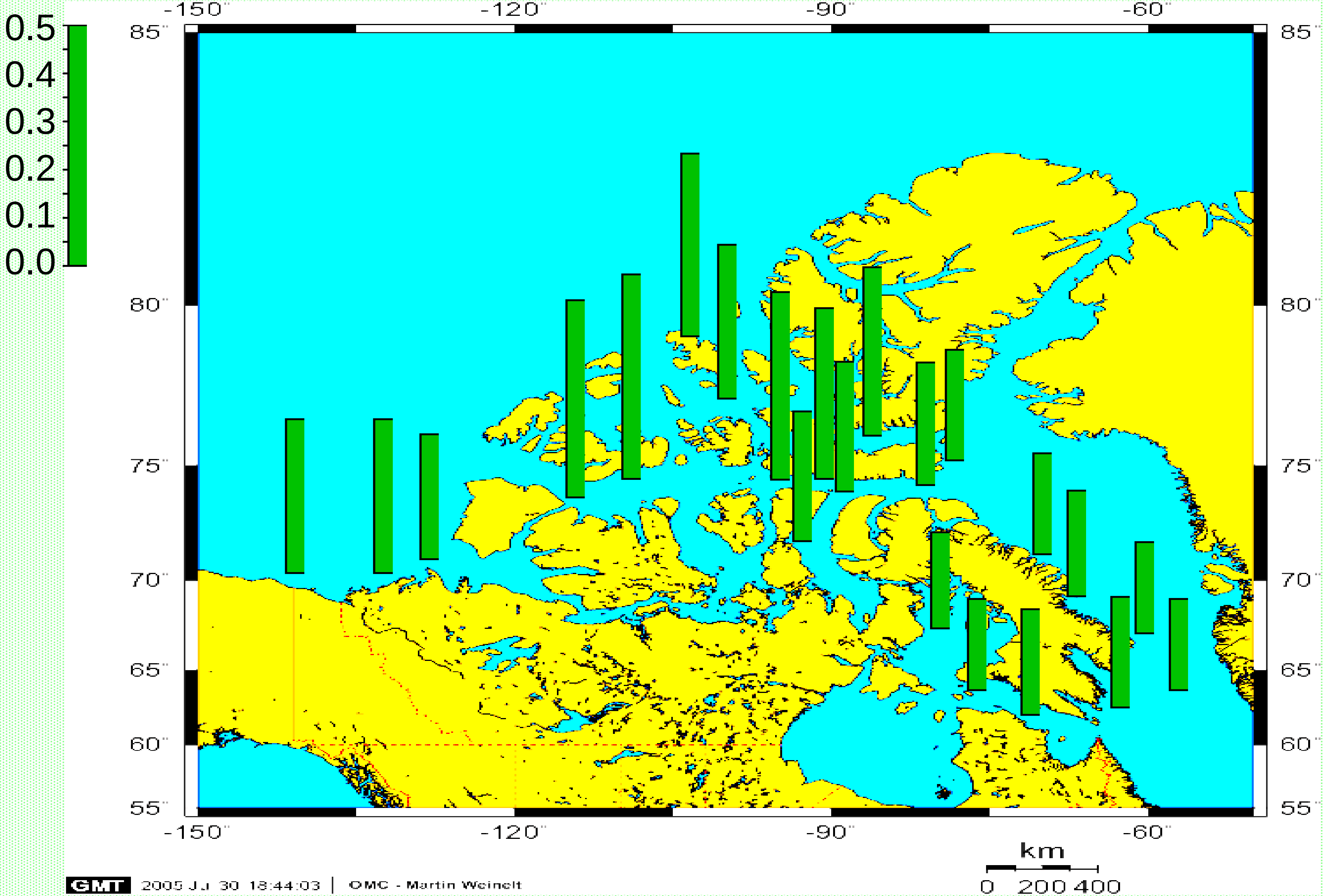
Chiral (α-HCH enantiomers):

β-DEX-120 (Supelco)	(+) (-)
BGB-172 (BGB Analytik)	(-) (+)
Rtx βDEXcst (Restek)	(+) (-)

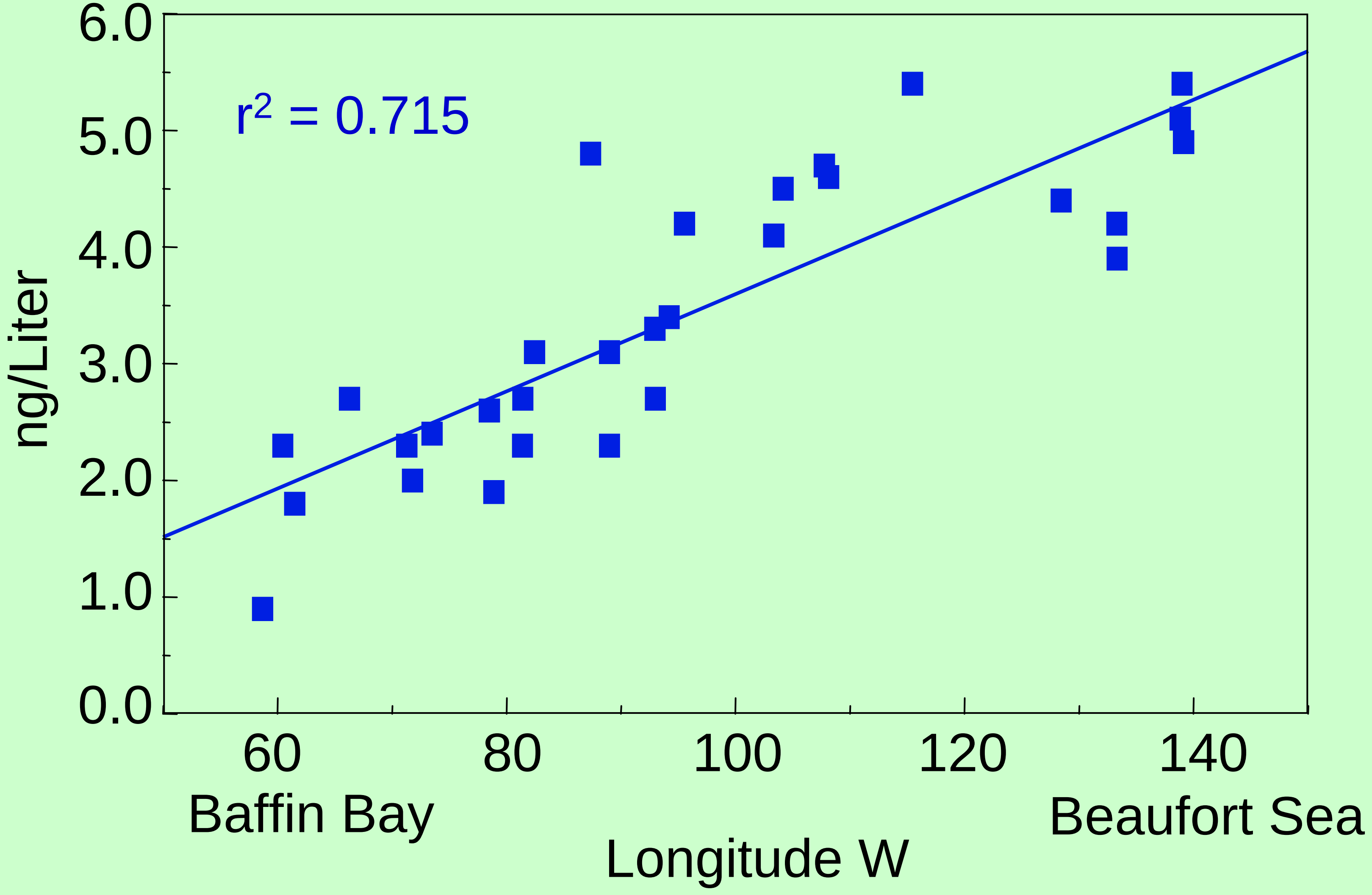
Alpha-HCH in Surface Water, ng/L



Gamma-HCH in Surface Water, ng/L



Alpha-HCH concentration in surface water



Air-Water Gas Exchange

$$\text{water/air fugacity ratio} = \frac{C_{water}H}{C_{air}RT}$$

$R = 8.314$ Pa m^3/mol K

T = air temperature: K

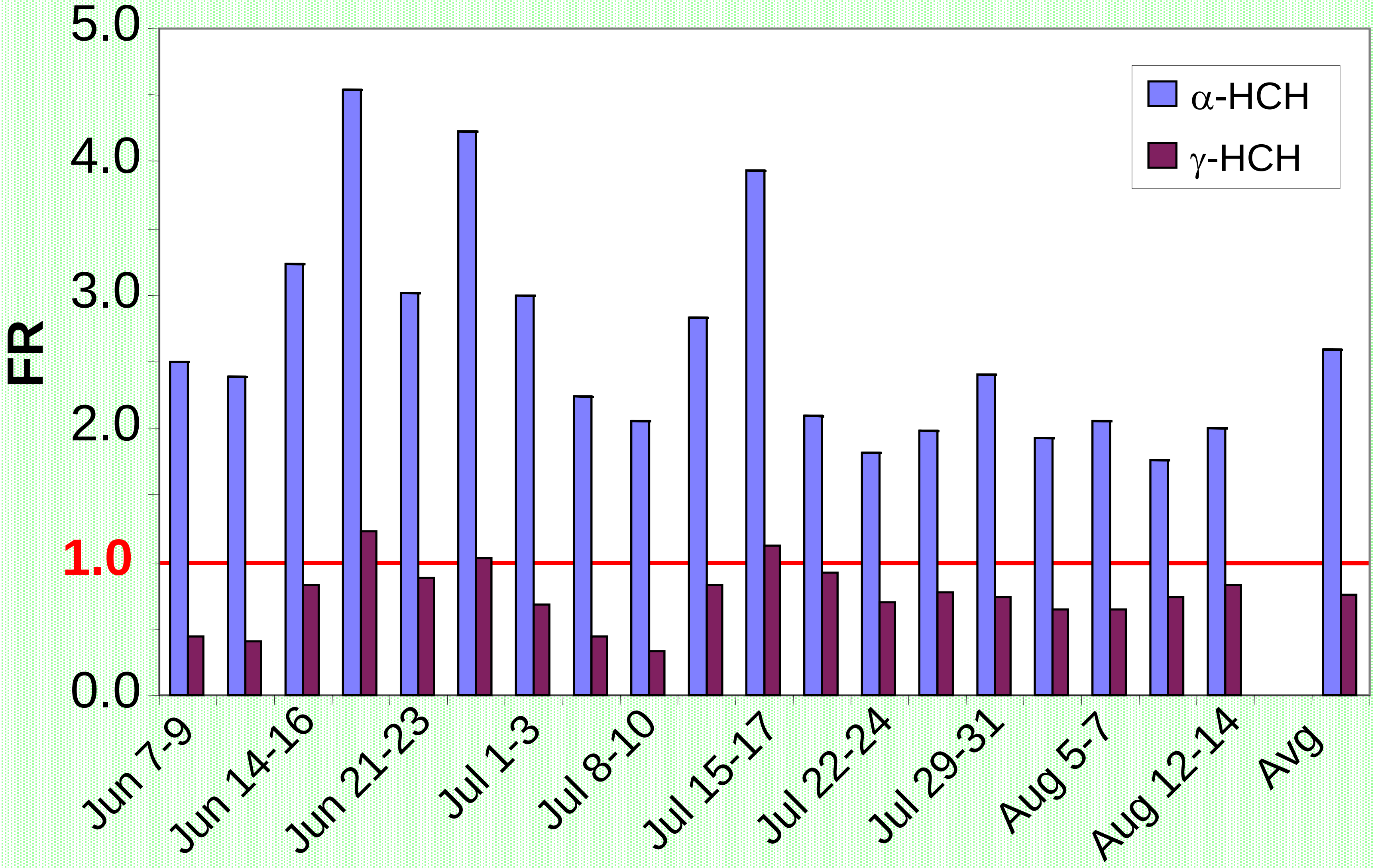
H = Henry's law constant, Pa m^3/mol
f(T), Sahsuvar et al., 2003

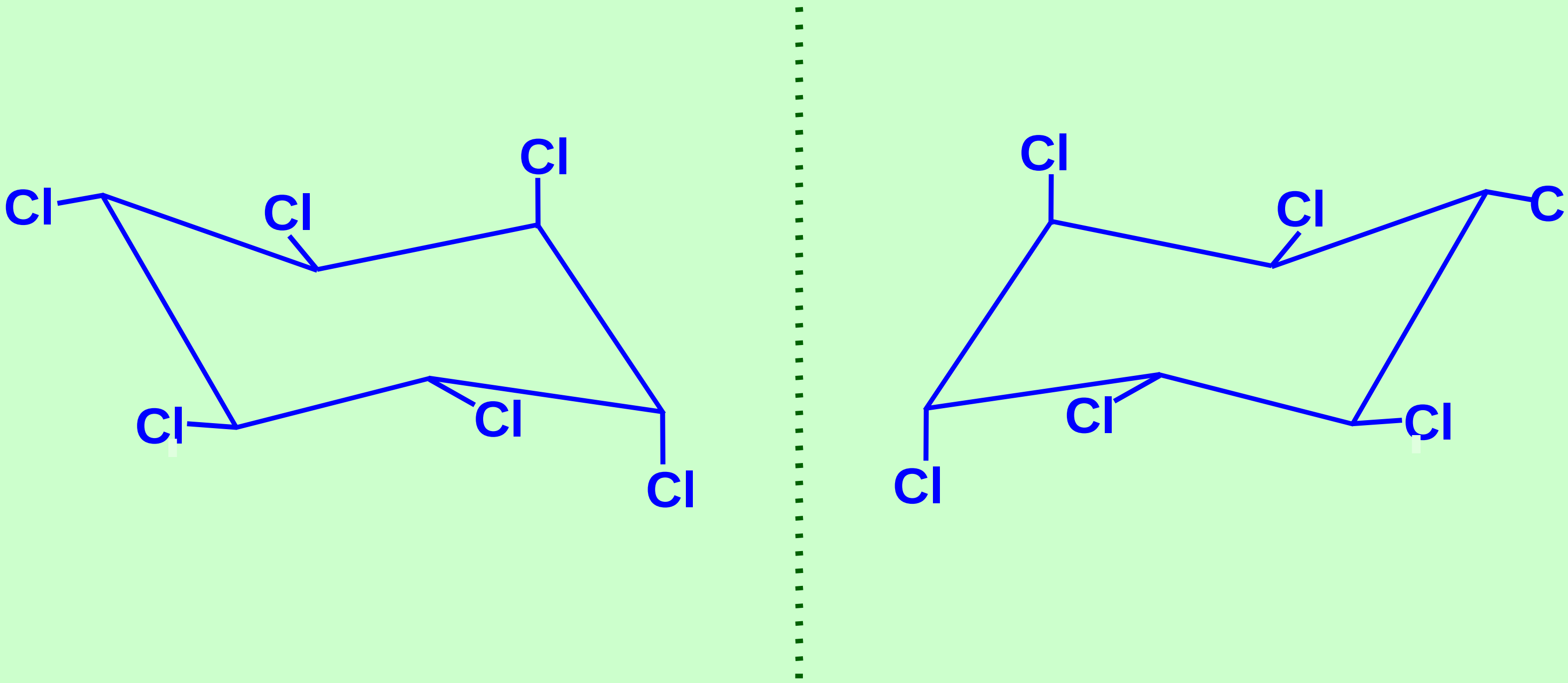
FR = 1 steady state, no net flux

FR > 1 potential for net volatilization

FR < 1 potential for net deposition

Fugacity Ratios of HCHs at Resolute Bay

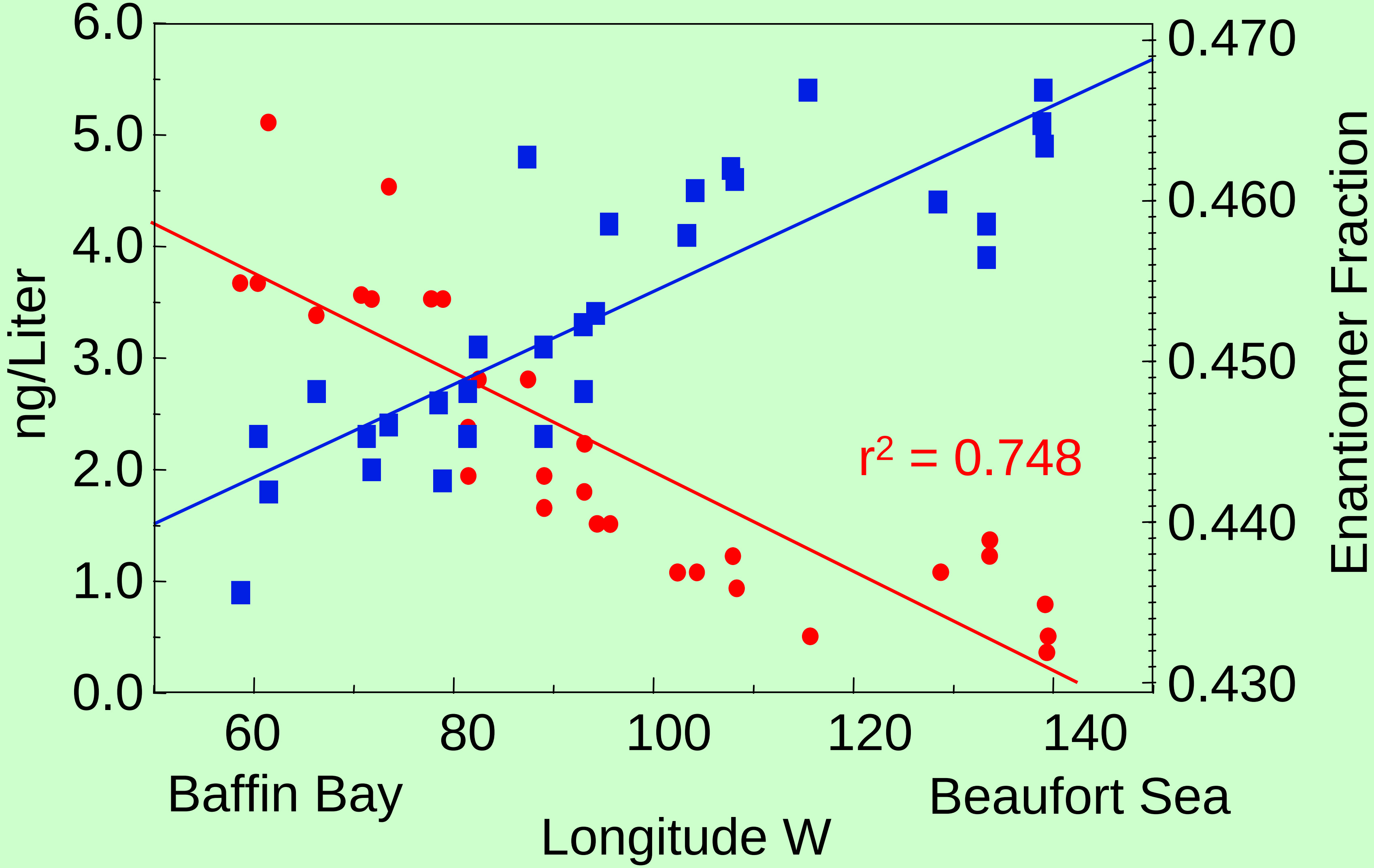


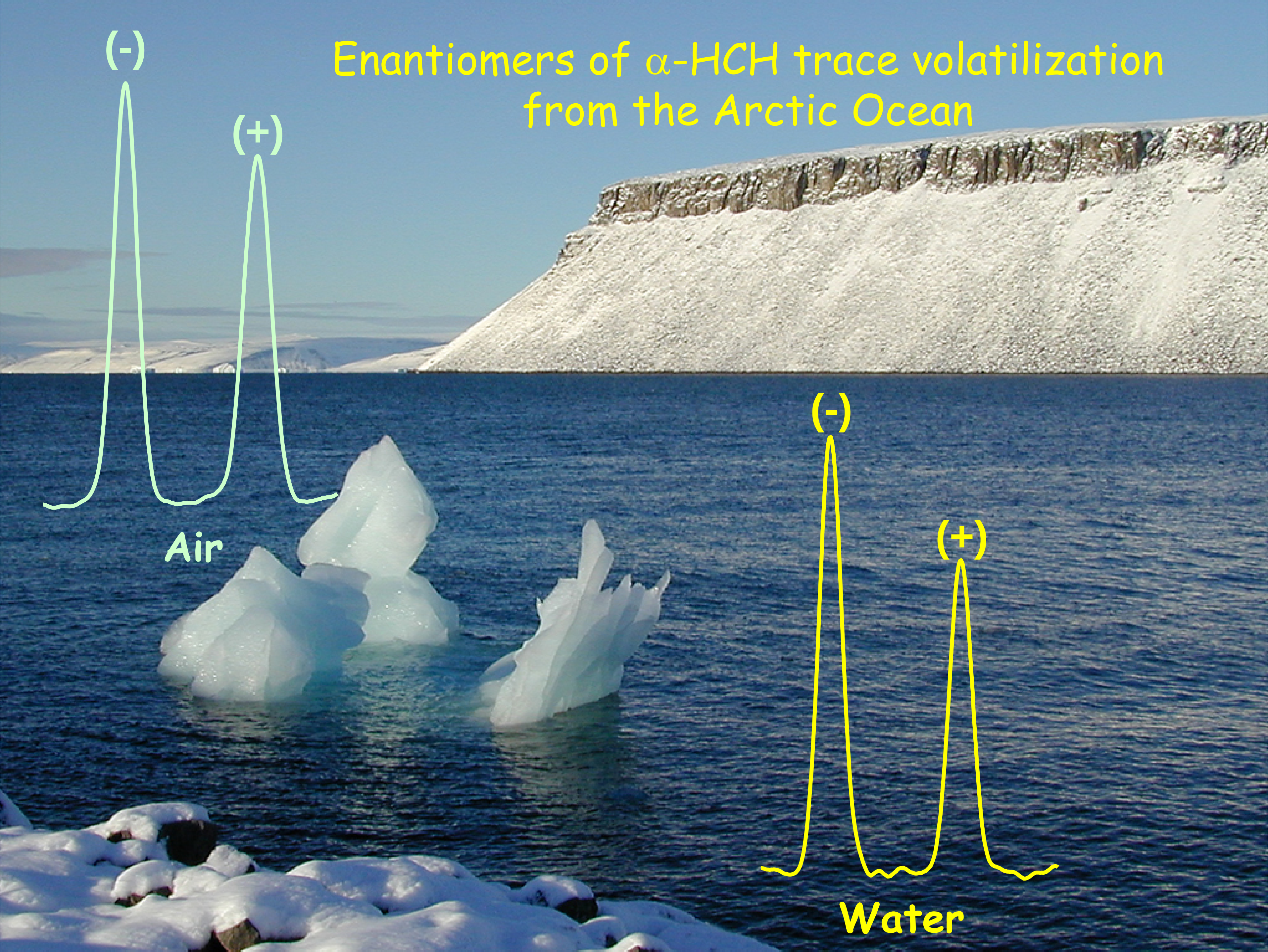


alpha-HCH, $C_6H_6Cl_6$
(hydrogens not shown)

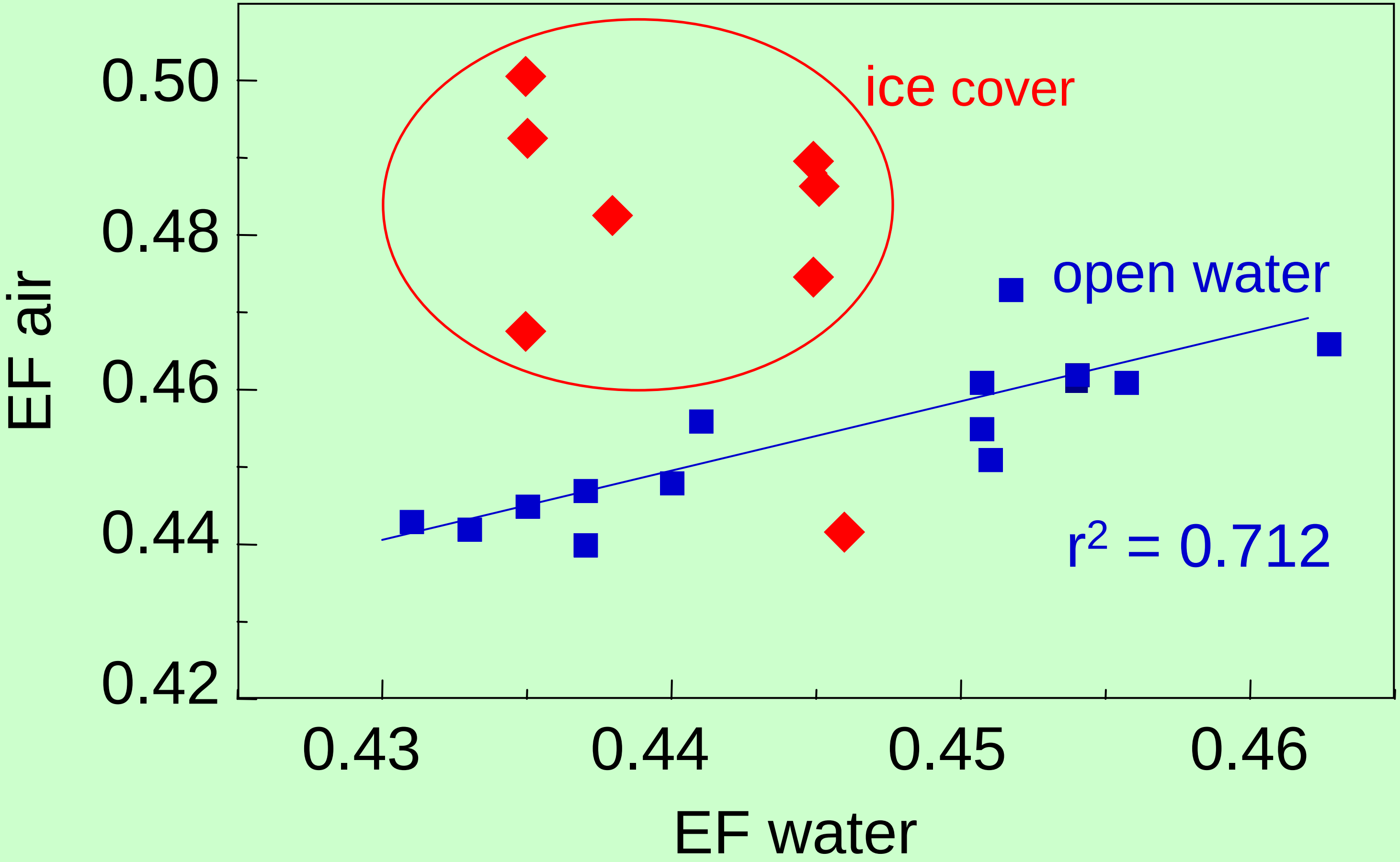
Microbes in water and soil
preferentially degrade one enantiomer

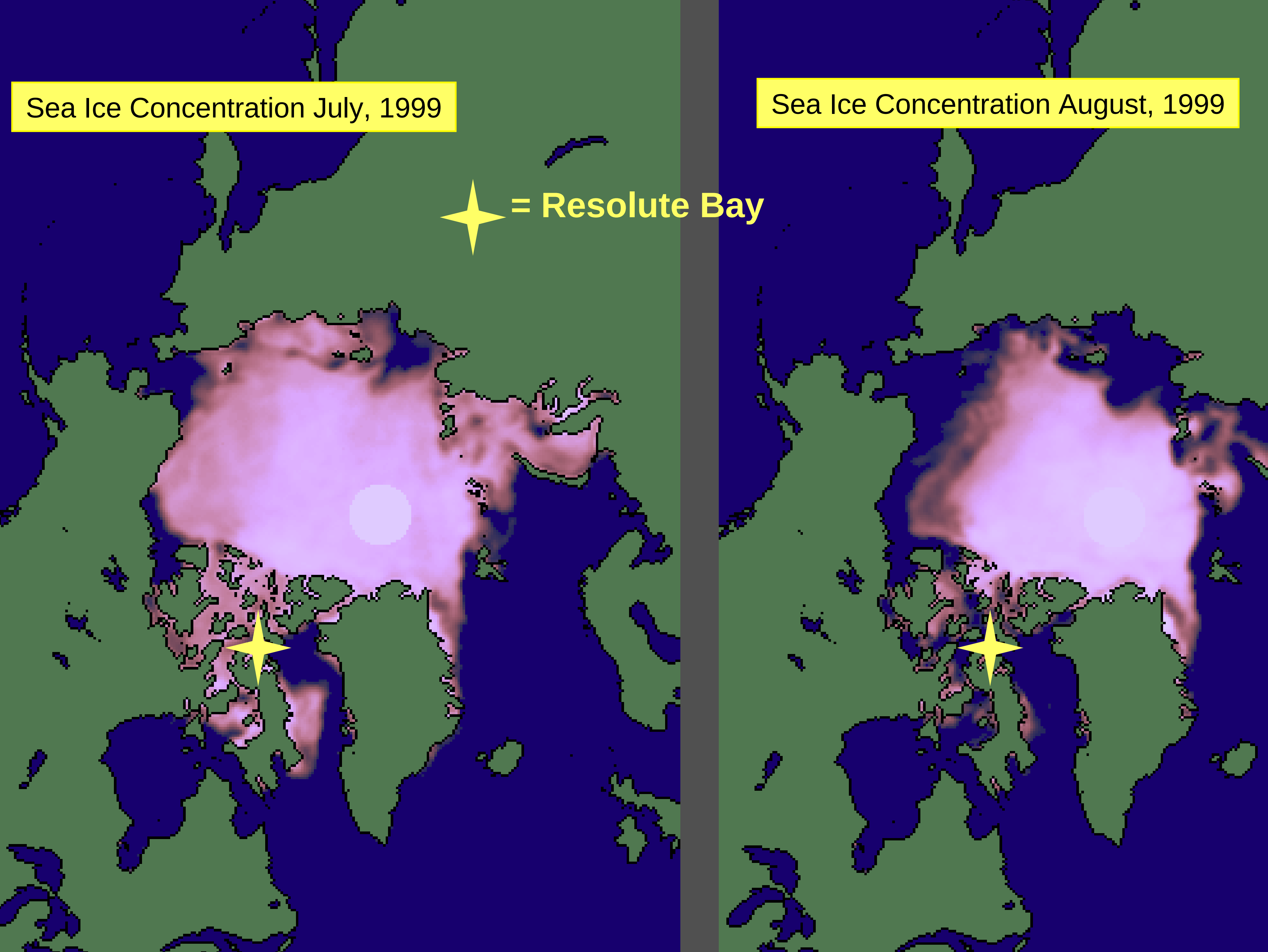
Alpha-HCH concentration and EF in surface water




Enantiomers of α-HCH trace volatilization
from the Arctic Ocean
(-)
(+)
Air
(-)
(+)
Water

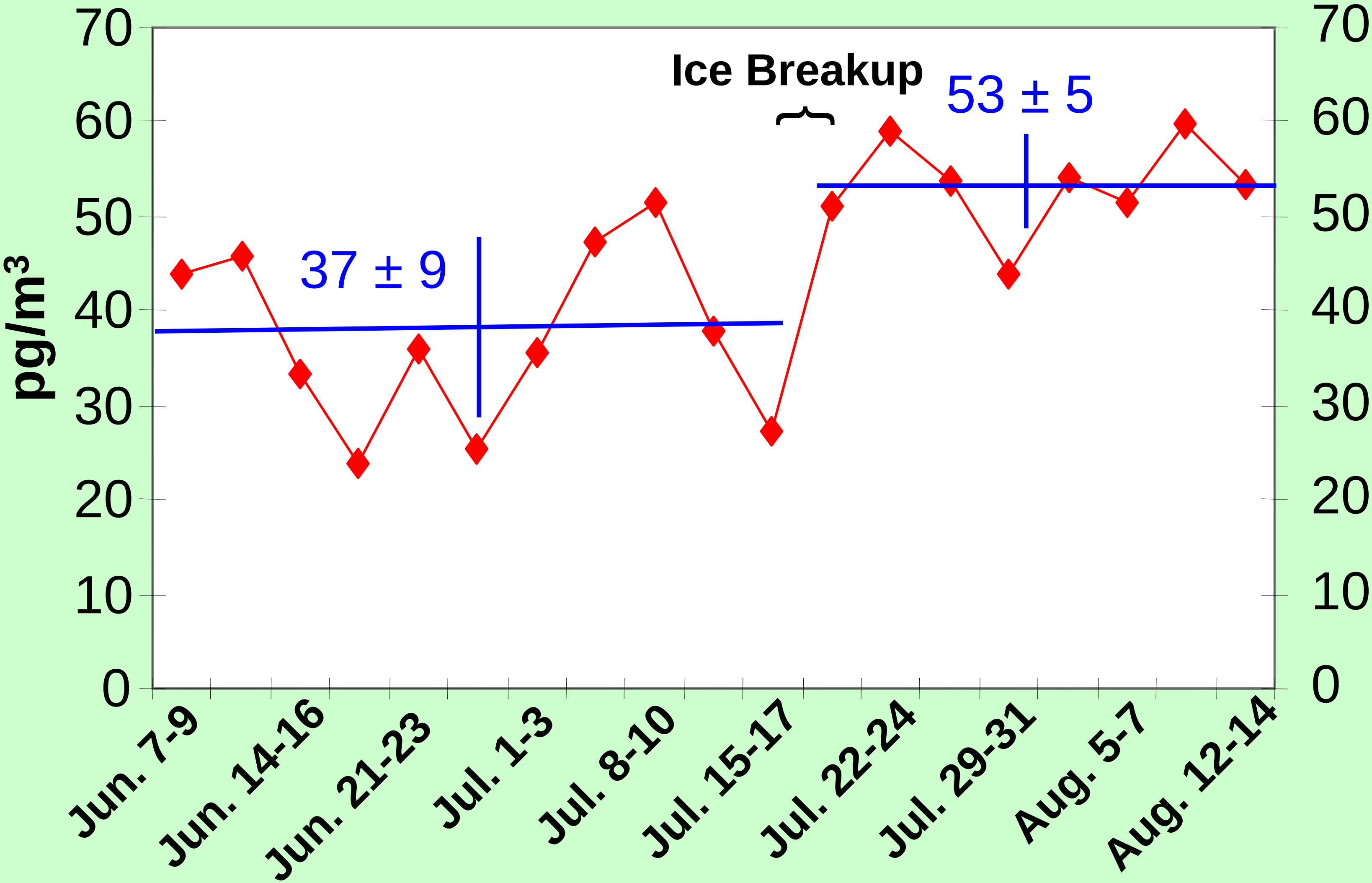
EFs in water and air on TNW-99



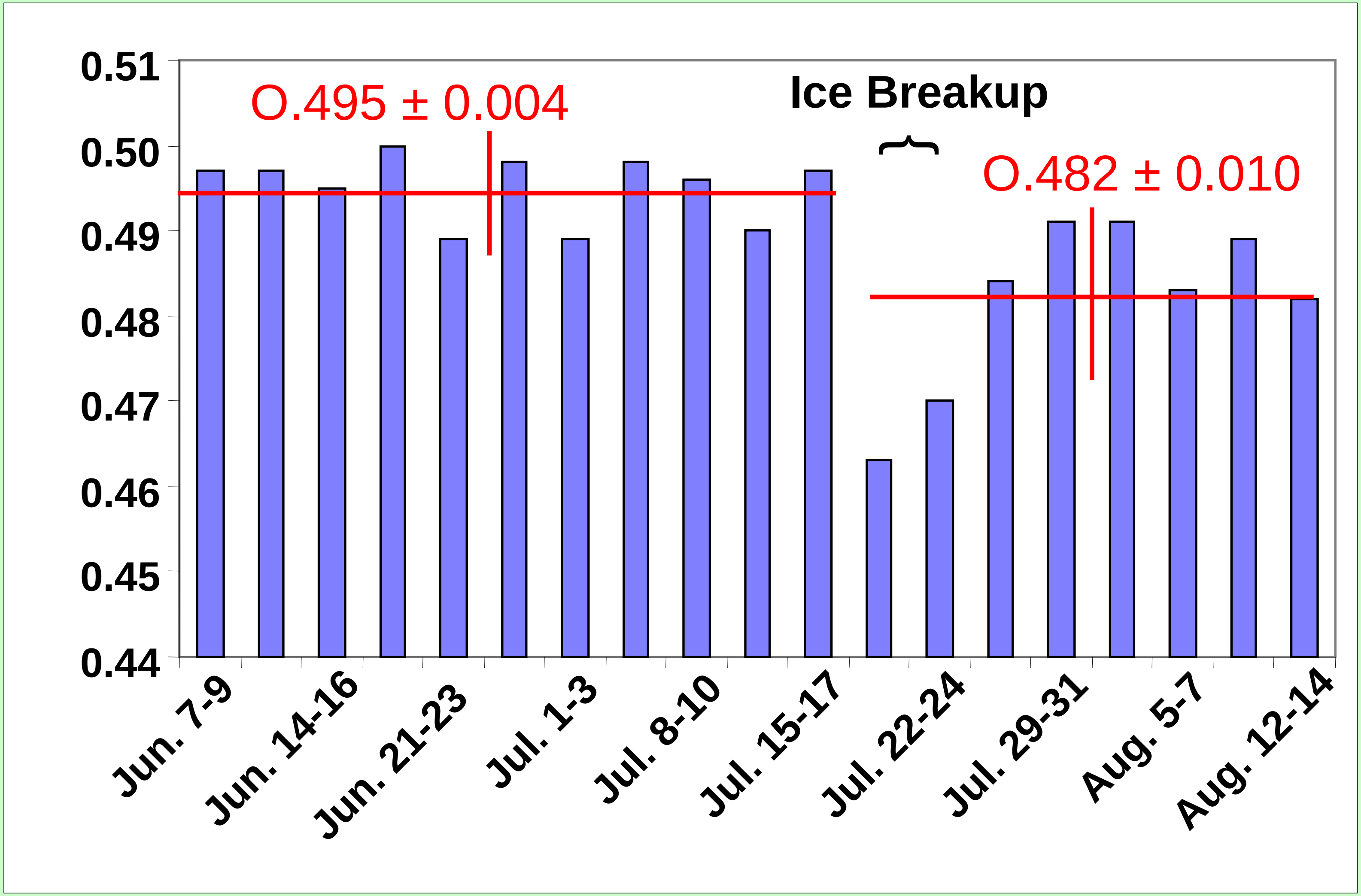


Sea Ice Concentration July, 1999
= Resolute Bay
Sea Ice Concentration August, 1999

Alpha-HCH in air at Resolute Bay <u>increases</u> by ~30% after ice breakup



EFs of alpha-HCH in air decrease after ice breakup
(surface water EF at Resolute Bay = 0.441)



Conclusions

- α-HCH in the W. Arctic Ocean is a "ghost of the past"
- Slowly dissipated by:*

• Outflow	65%
• Degradation	34%
• Volatilization	1%

* Li et al., Canadian Arctic Contaminants Assessment Report, 2003

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- Volatilization now minor because of extensive ice cover
- Global warming will result in ice cover loss

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• Outflow	65%
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- Volatilization now minor because of extensive ice cover
- Global warming will result in ice cover loss
- Increased role of air-water exchange for POPs
- α-HCH is an elegant tracer of this process

∗ Li et al., Canadian Arctic Contaminants Assessment Report, 2003

Acknowledgements

- TNW-99: Swedish Polar Secretariat, Canadian Coast Guard and Fisheries & Oceans Canada
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Photo: Mike Harwood, CARE