Transport of Lindane and other HCHs through Air and Water

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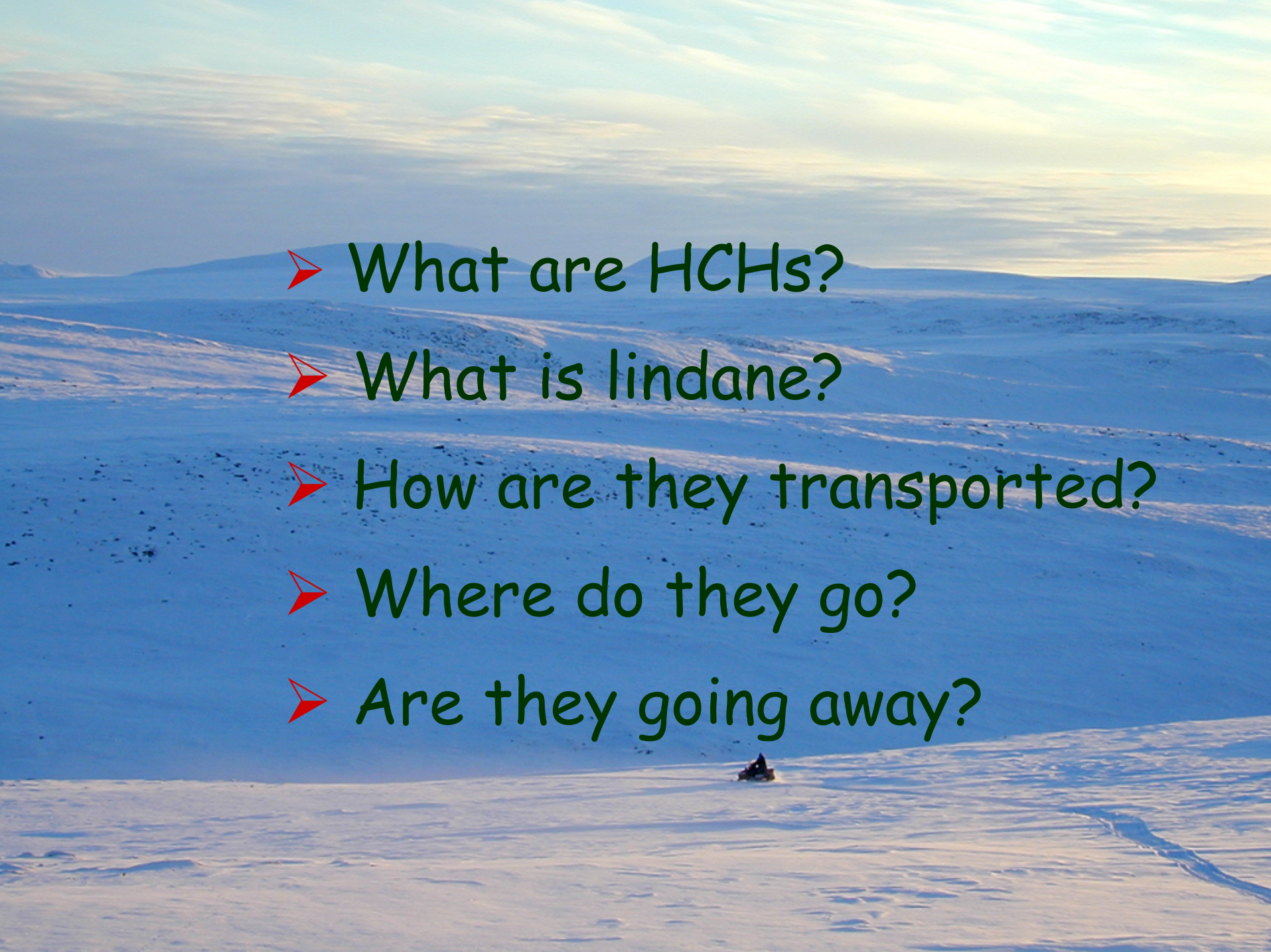
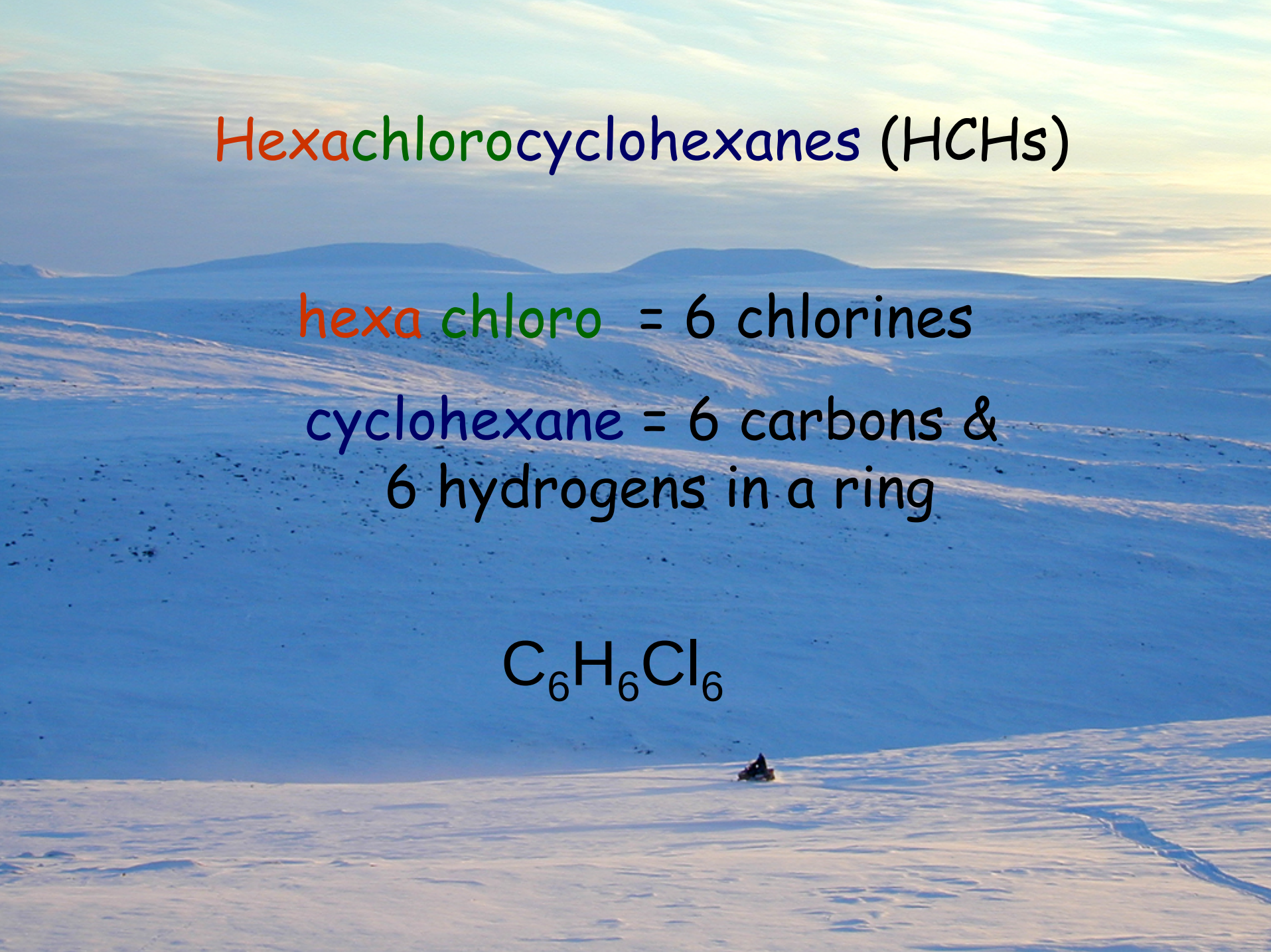
Work supported in part by the Northern Contaminants Program of Indian & Northern Affairs Canada

Photo: Jim Milne, DRDC, Canada


What are HCHs?
What is lindane?
How are they transported?
Where do they go?
Are they going away?



Hexachlorocyclohexanes (HCHs)

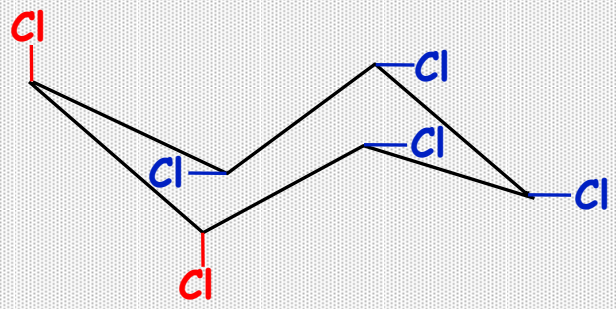
hexa chloro = 6 chlorines

cyclohexane = 6 carbons &
6 hydrogens in a ring

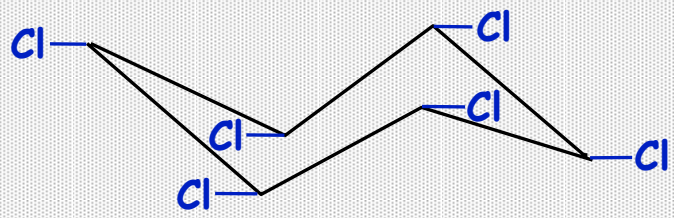
$C_6H_6Cl_6$

"Technical" HCH

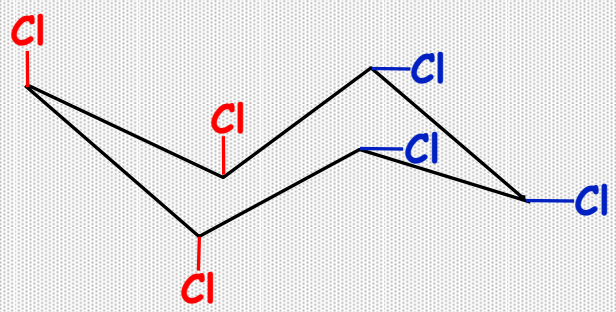
A cheap mixture of different HCHs



Alpha-HCH: 60 - 70%



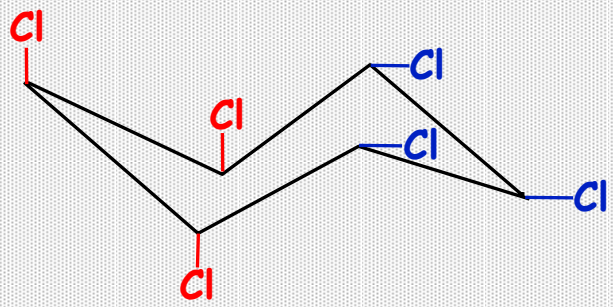
Beta-HCH: 5 - 12%



Gamma-HCH: 10 - 15%

What is lindane?

Only one form of HCH is effective for killing insects



Gamma-HCH

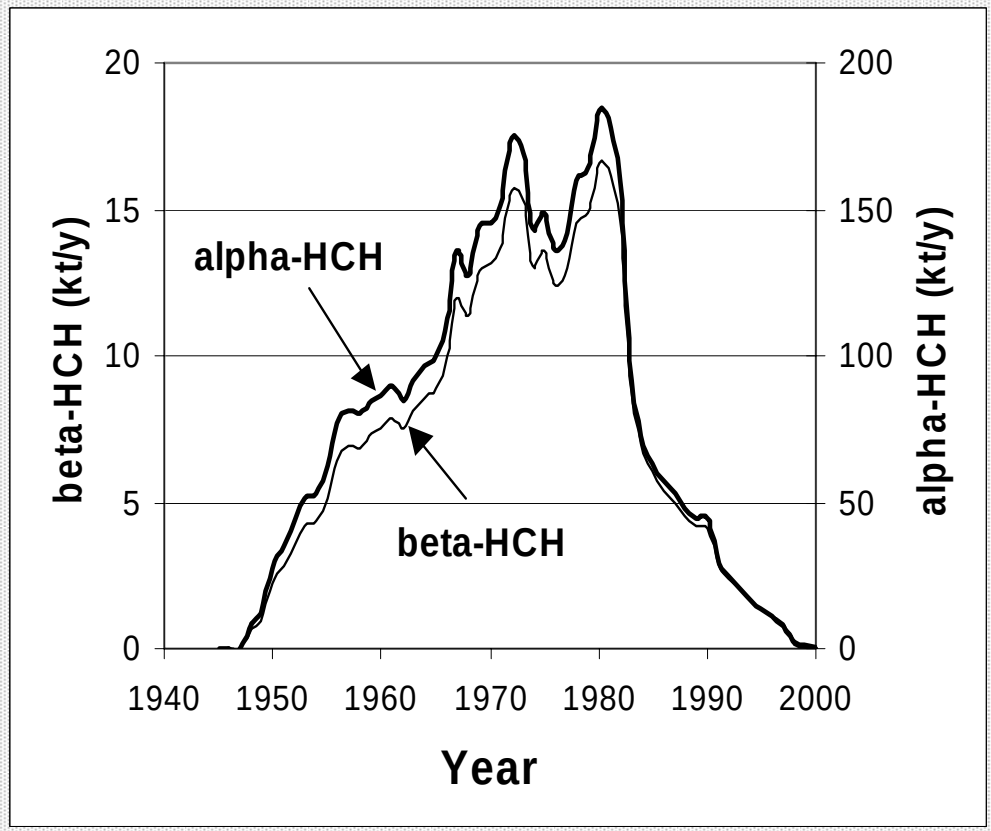
- Gamma-HCH is 10-15% of technical HCH
- The rest of technical HCH is junk!
- Most countries now use only 99+% pure gamma-HCH, not technical HCH

Lindane is the common name for pure gamma-HCH

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

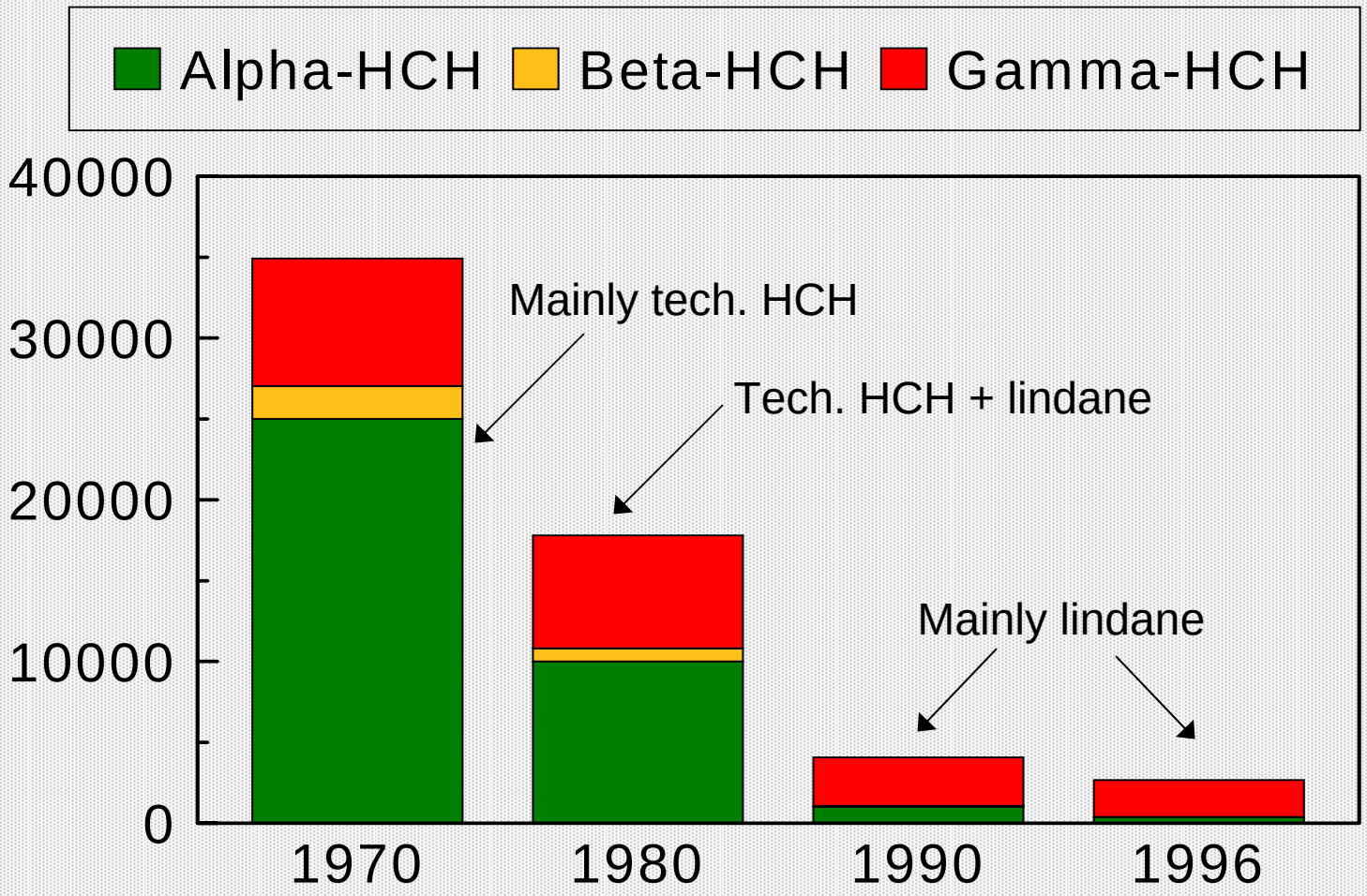
- Manufactured since 1945.
- Used in Canada and U.S.A. until the 1970s, replaced by lindane.
- Over 6 million tonnes used in Asia between 1948 - 1997.
- Main usage in China, India, former Soviet Union.
- Now banned in most countries.

Global emissions of HCHs



Li & Macdonald, Science of the Total Environment, 2004
Li et al., Environmental Science & Technology, 2003

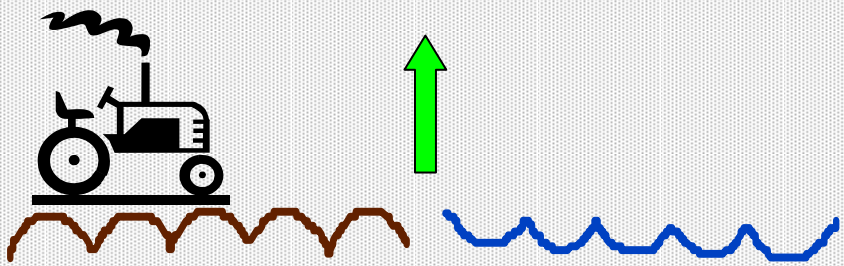
Use of HCHs in Europe, tonnes/year
as technical HCH + lindane



Breivik et al., Science of the Total Environment, 1999

HCHs get around!

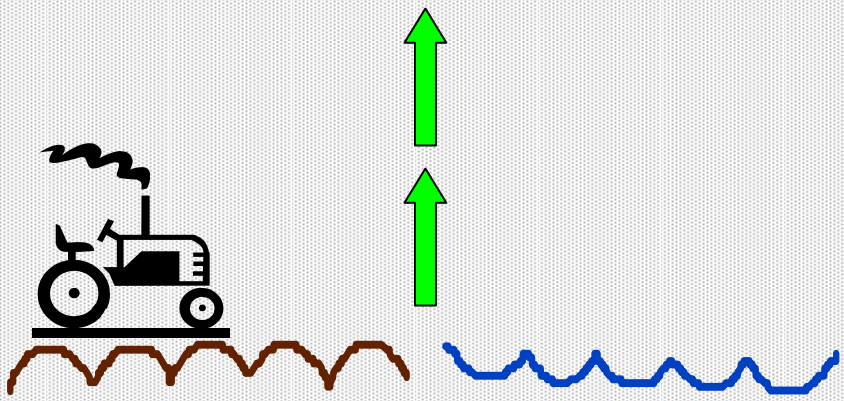
evaporation



contaminated soil & water

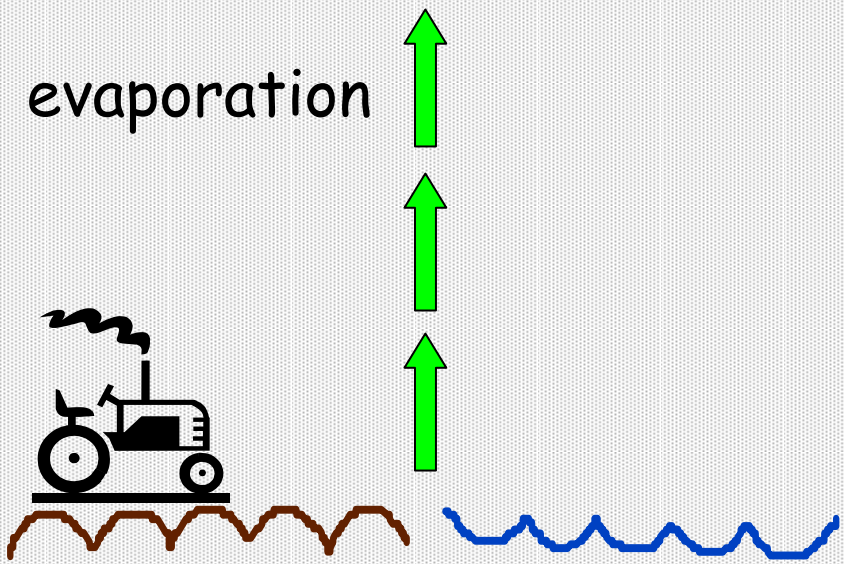
HCHs get around!

evaporation

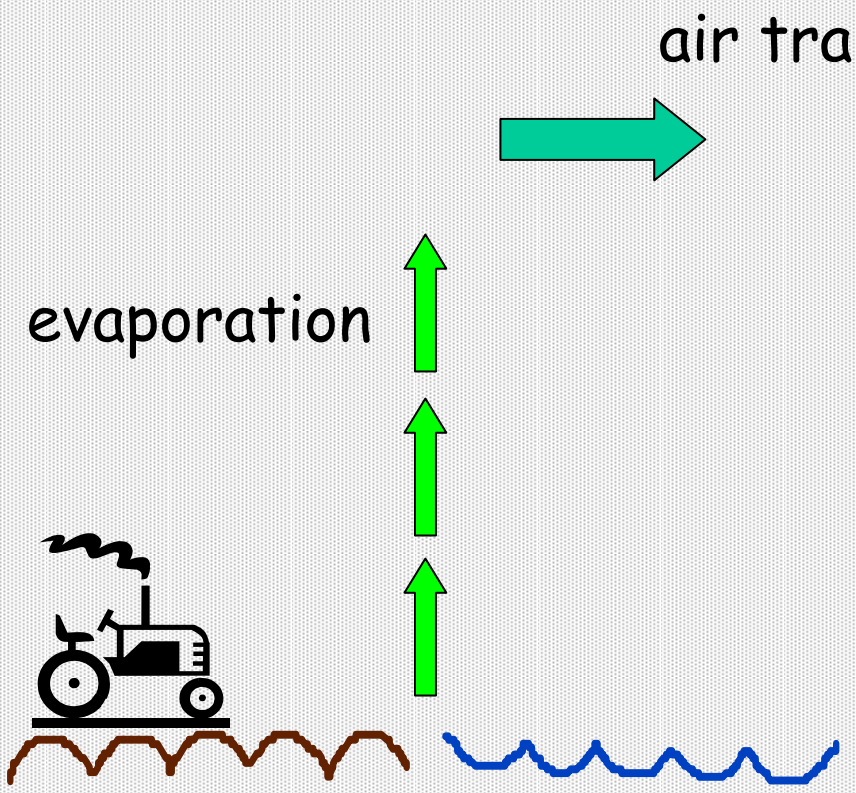


contaminated soil & water

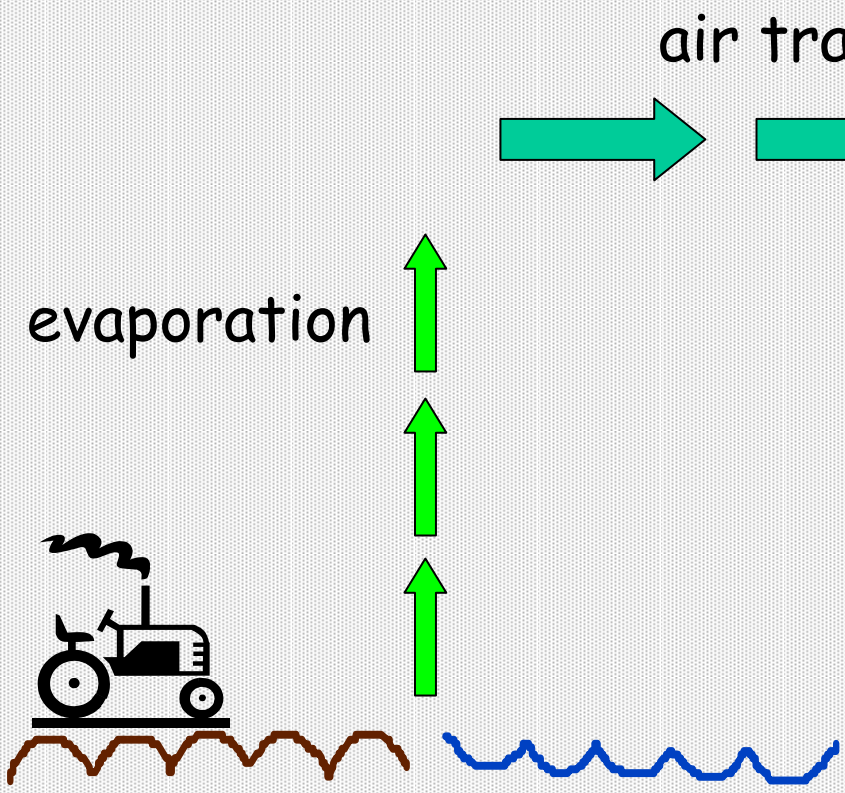
HCHs get around!



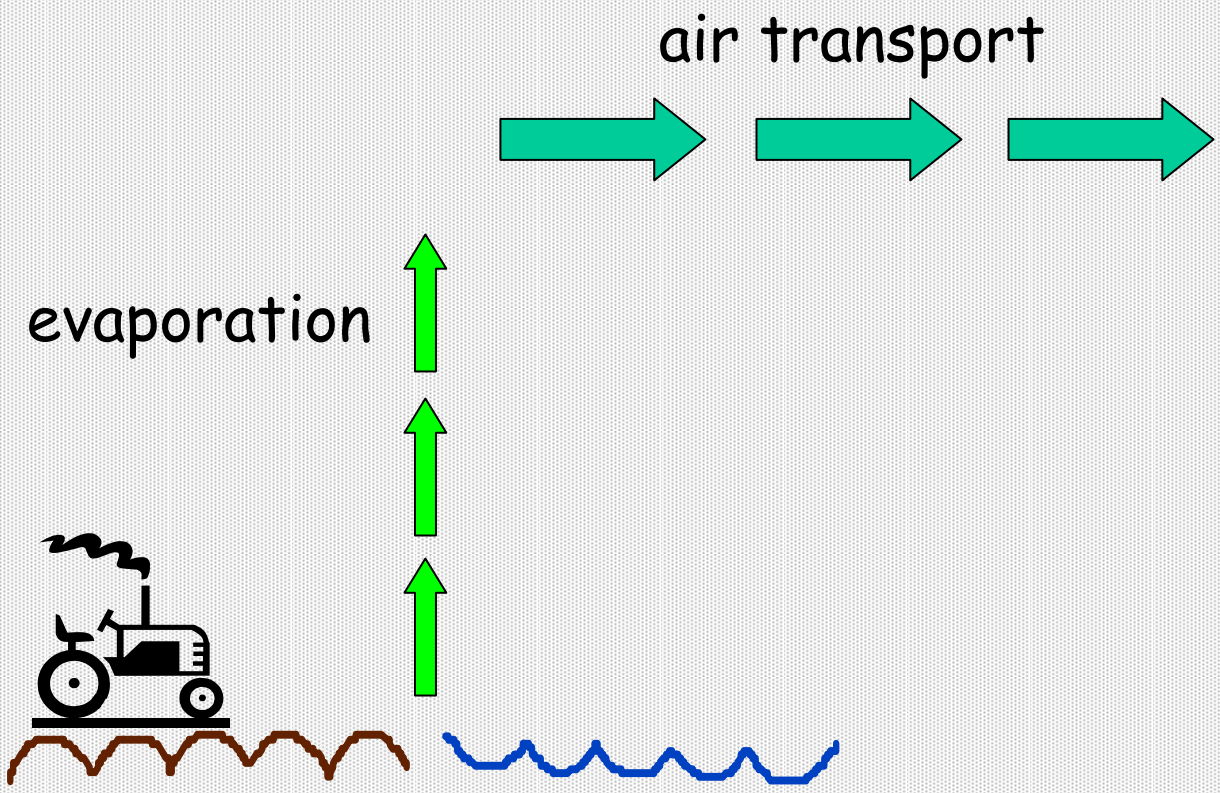
HCHs get around!



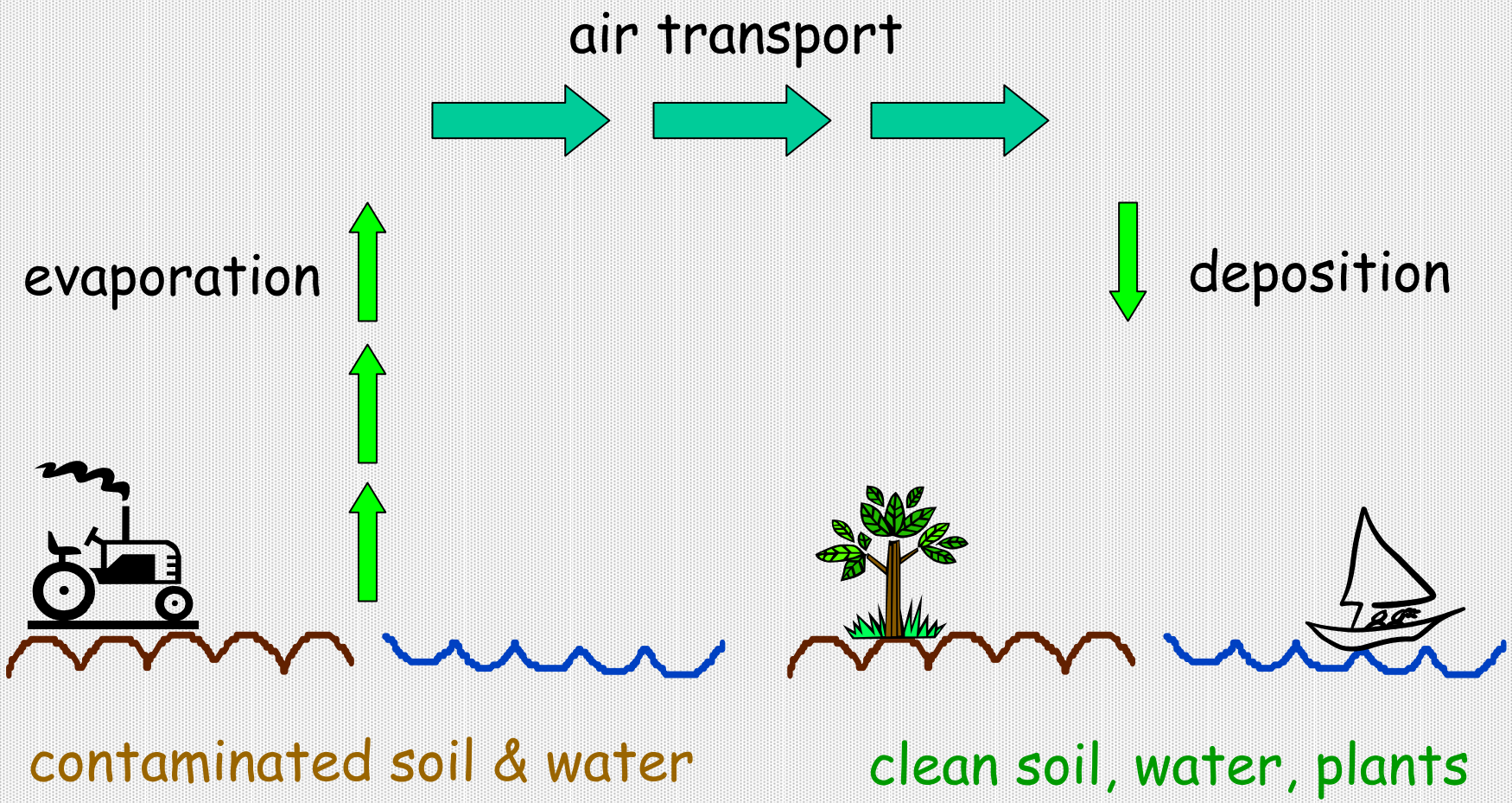
HCHs get around!



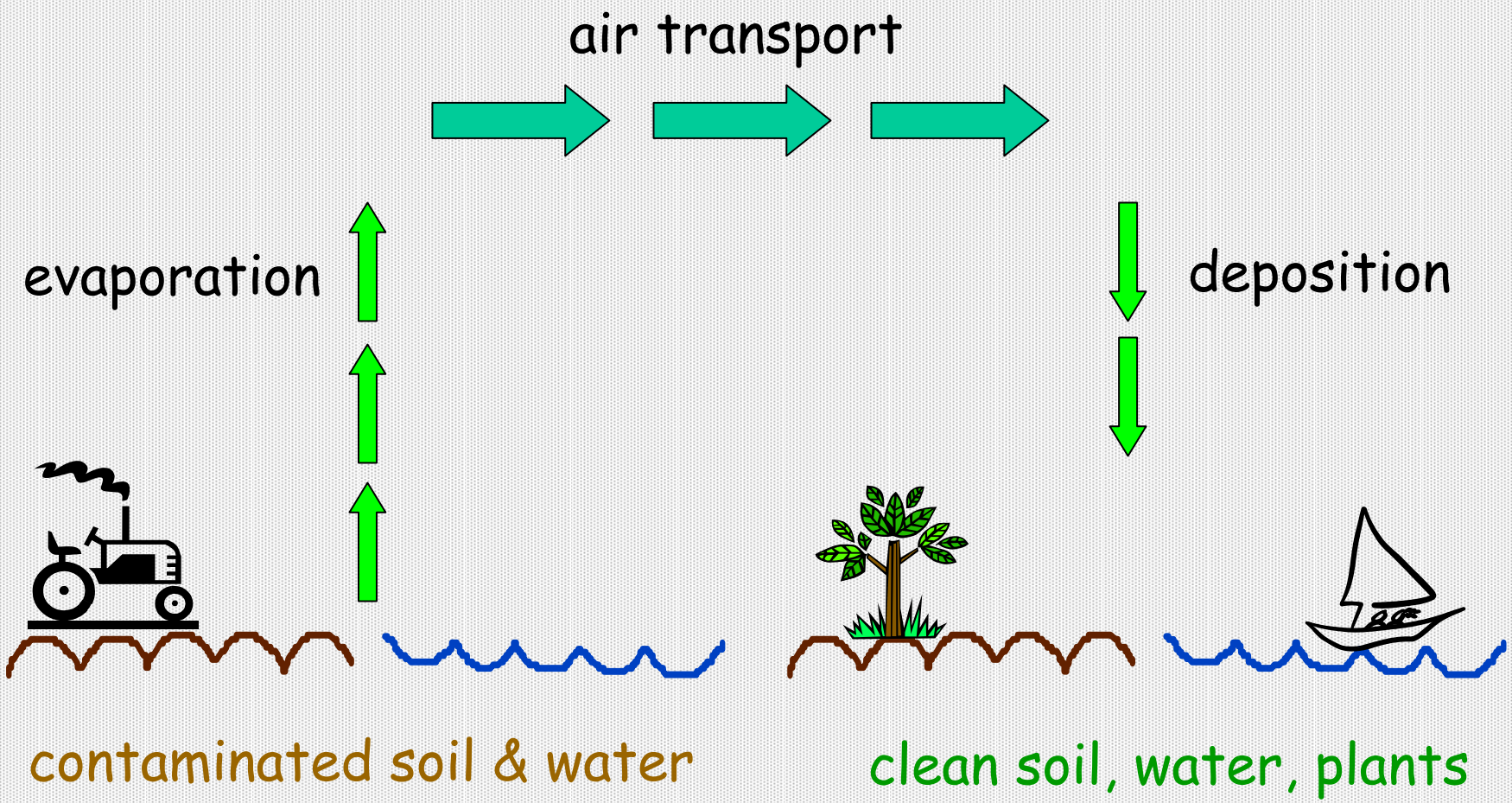
HCHs get around!



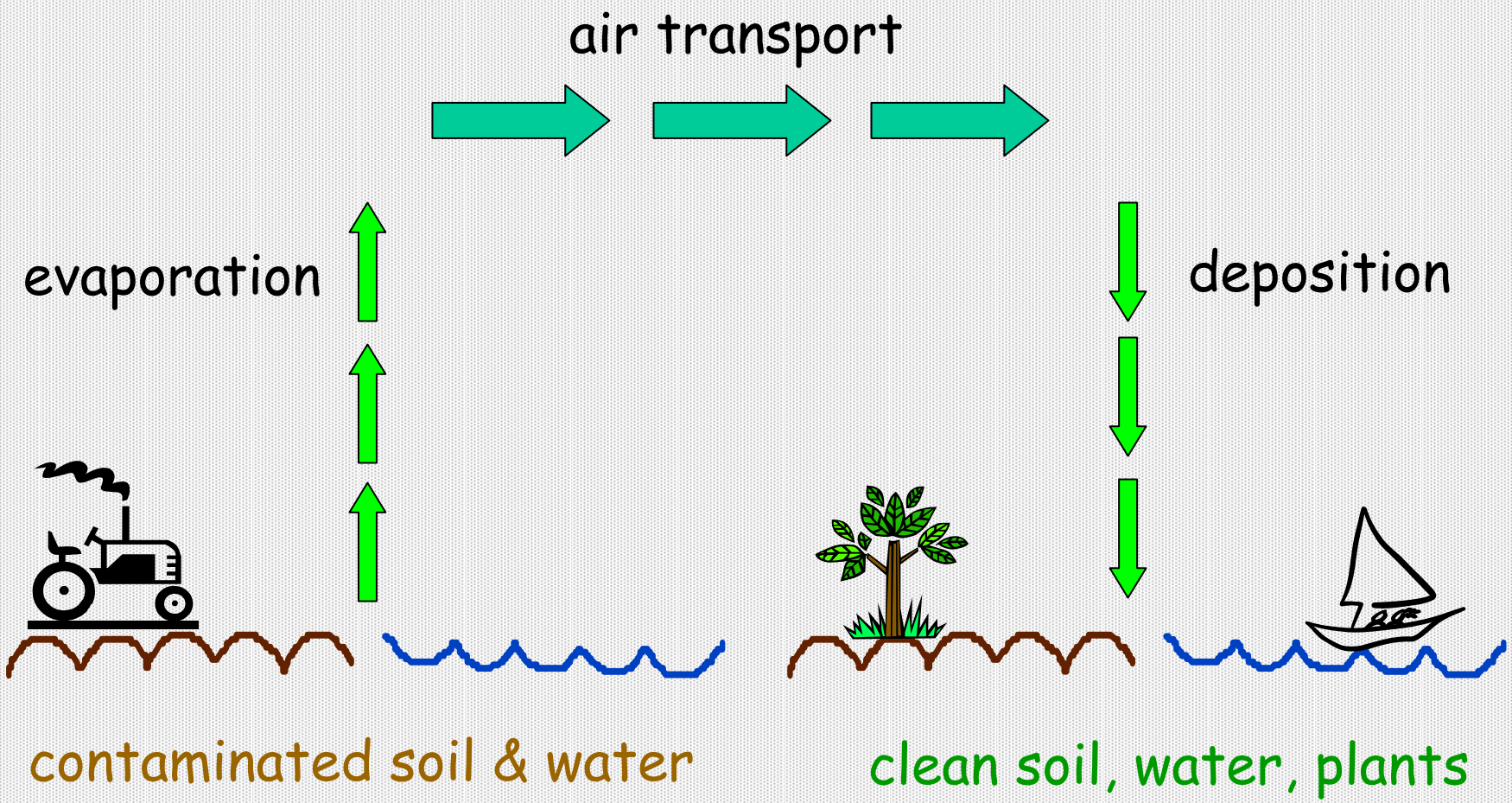
HCHs get around!



HCHs get around!

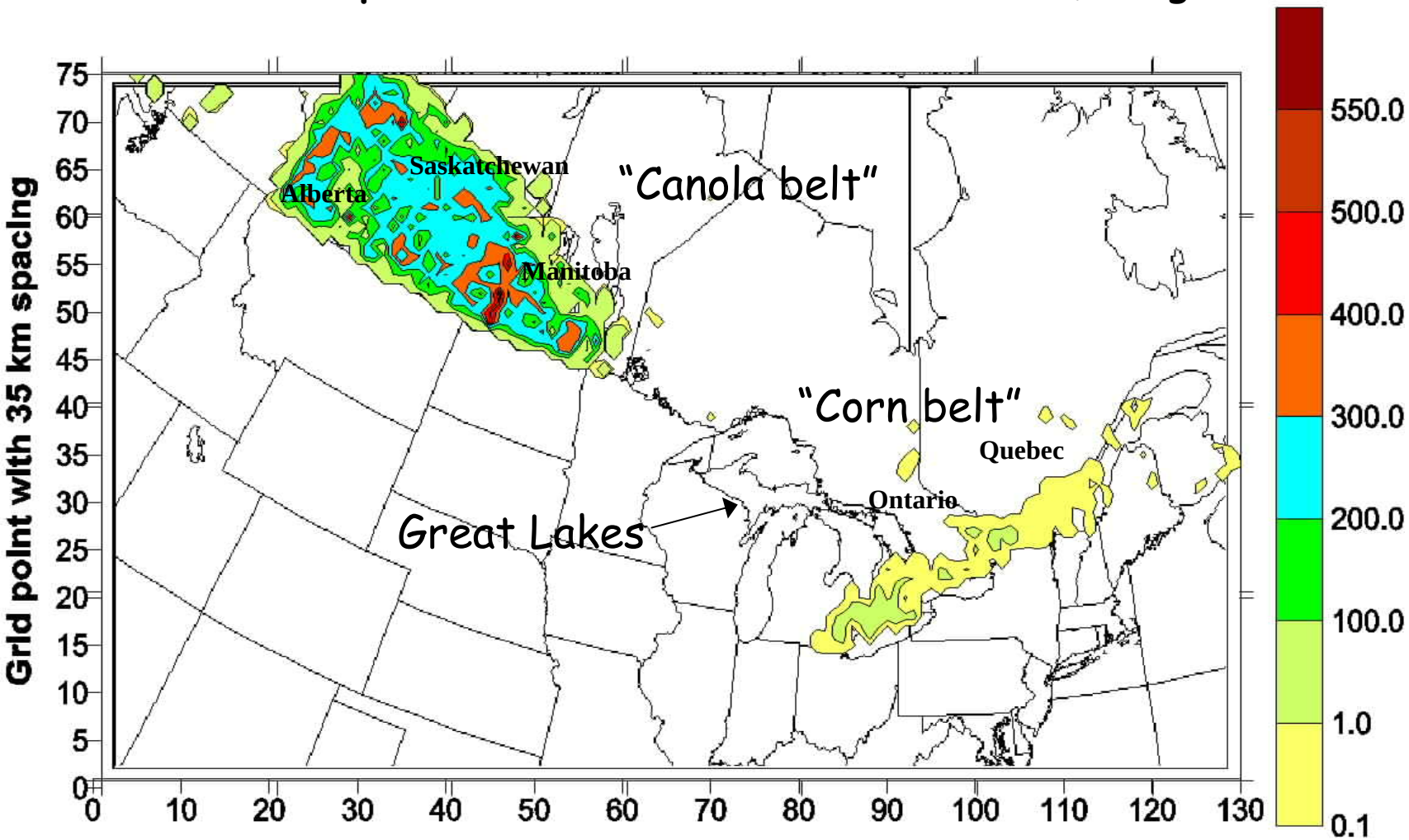


HCHs get around!



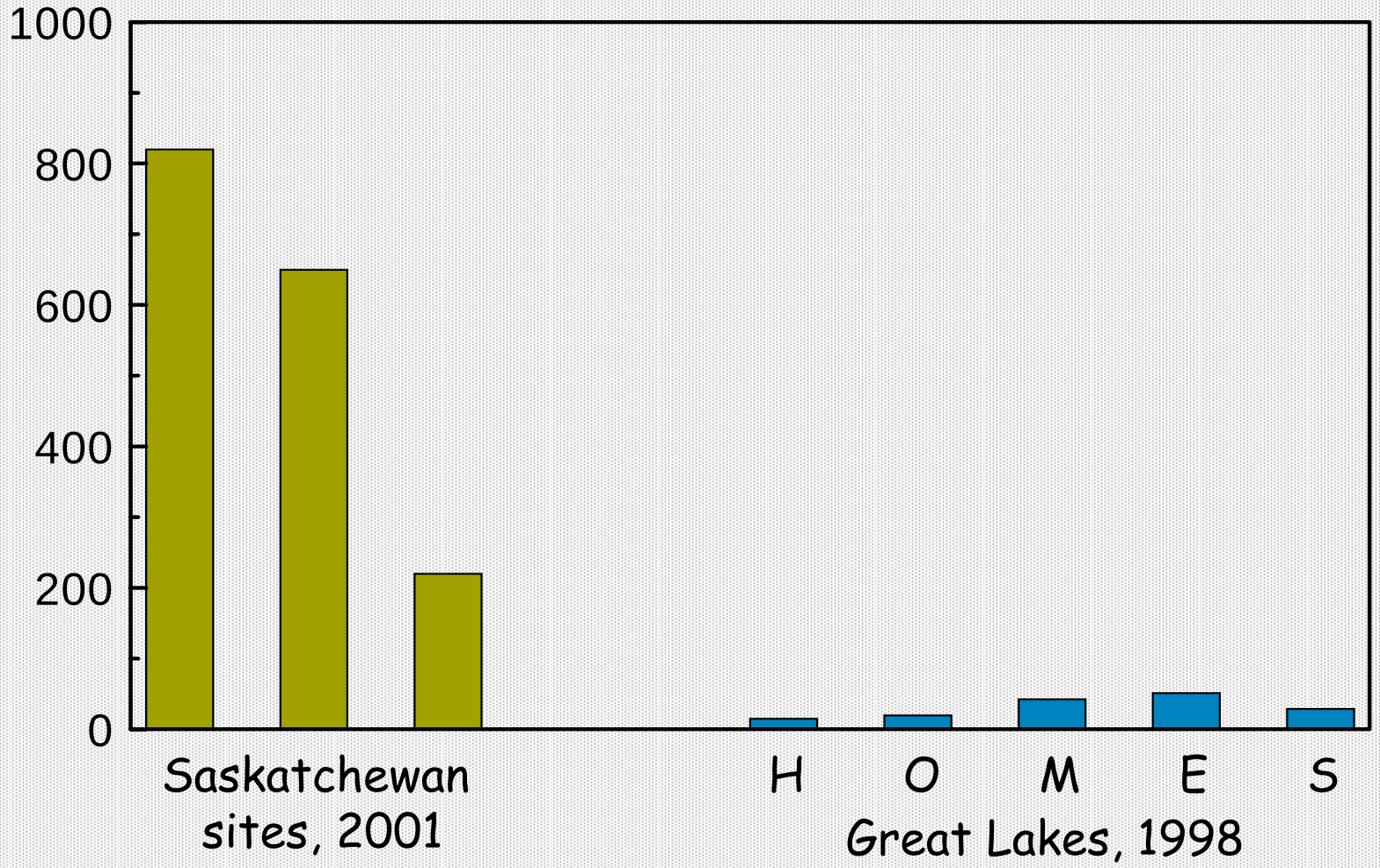
Model of lindane emissions in Canada, 1998

Annual lindane evaporation within a 35 km × 35 km cell, kilograms



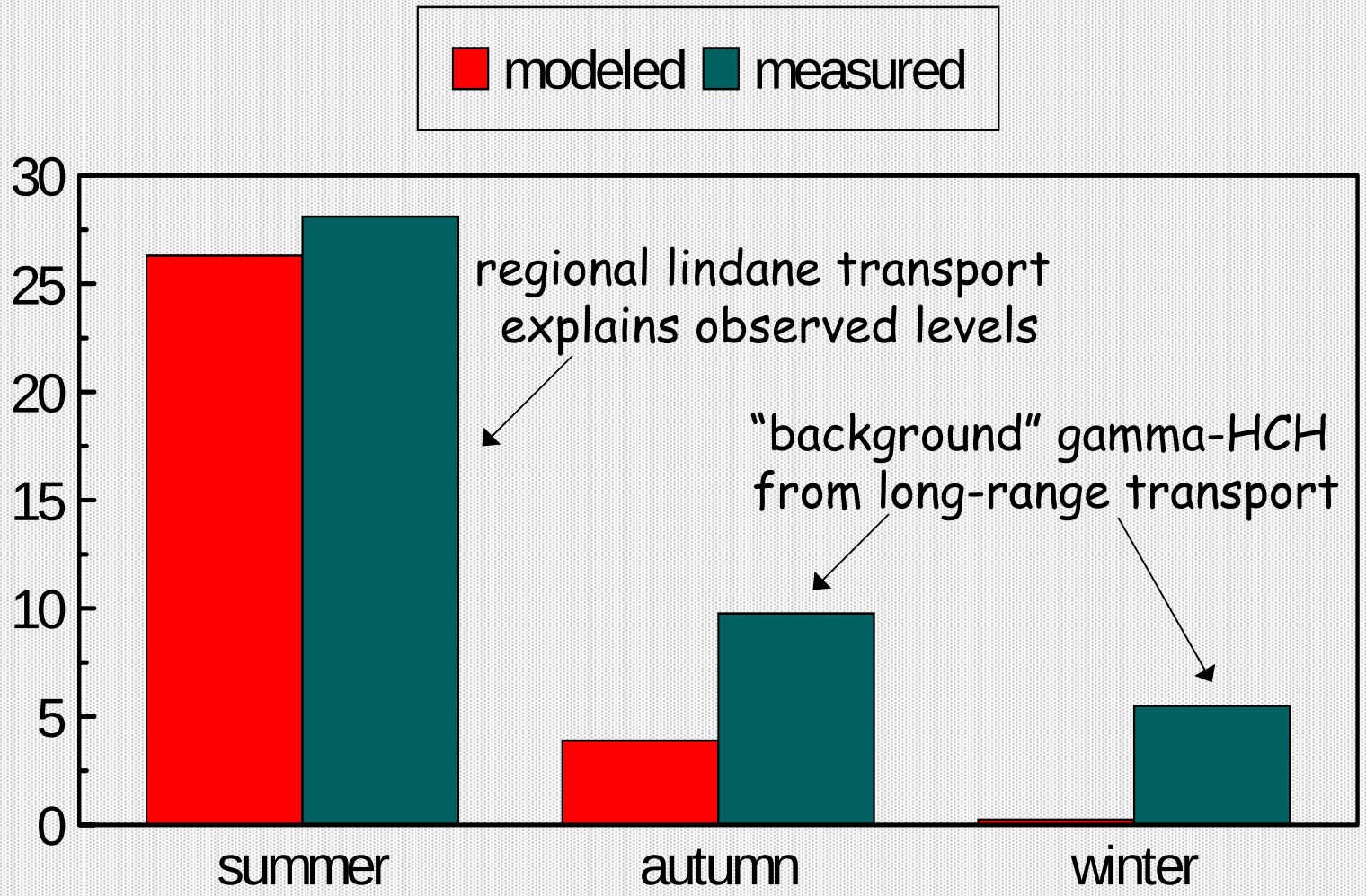
J. Ma et al., Environmental Science & Technology, 2003

Measured ambient air concentrations of lindane, spring-summer (pg/m^3)



J. Ma et al., Environmental Science & Technology, 2003
D. Waite, Environment Canada, pers. Commun.

Air concentrations of lindane at Eagle Harbor, Lake Superior in 1998, pg/m^3

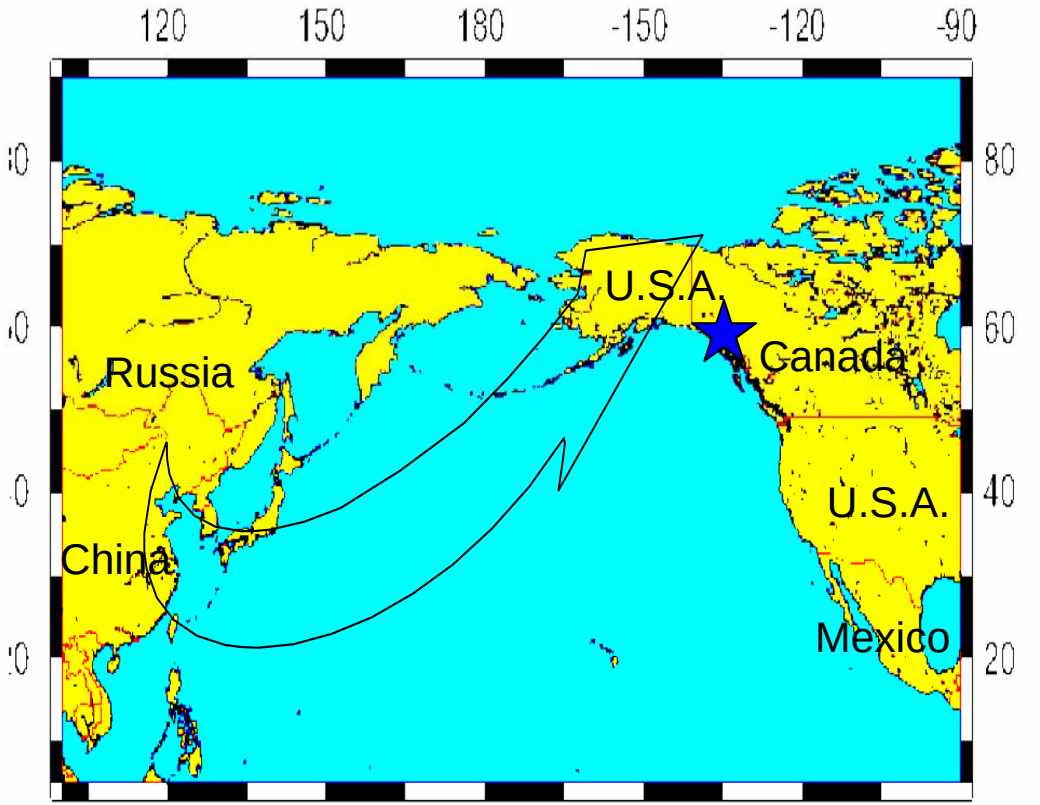


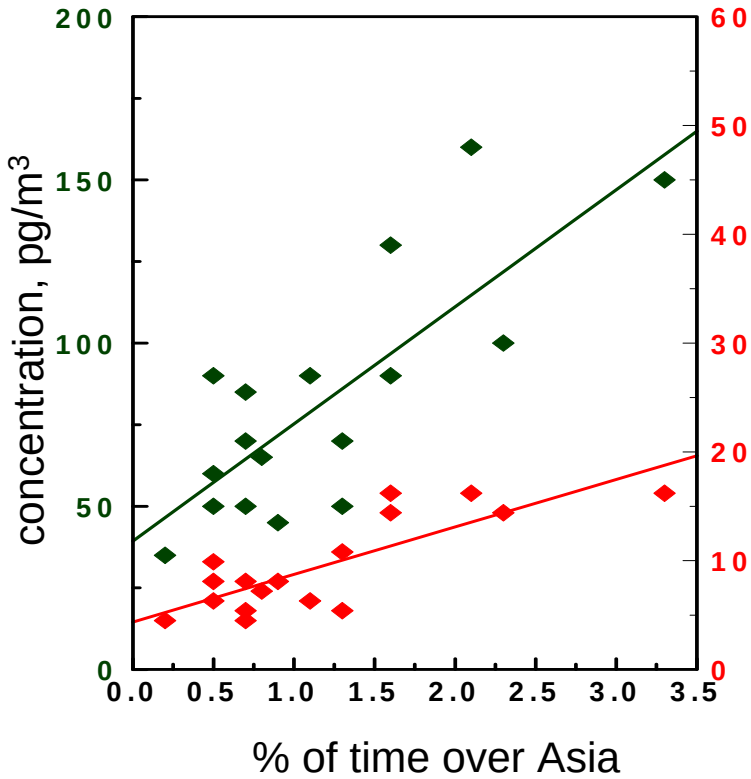
J. Ma et al., Environmental Science & Technology, 2003
D. Waite, Environment Canada, personal communication

Air transport of HCHs from Asian source regions

Air sampled at Tagish, Yukon (1994-95) ★

Alpha- and gamma-HCHs are higher when air spends a greater % of time over Asia.



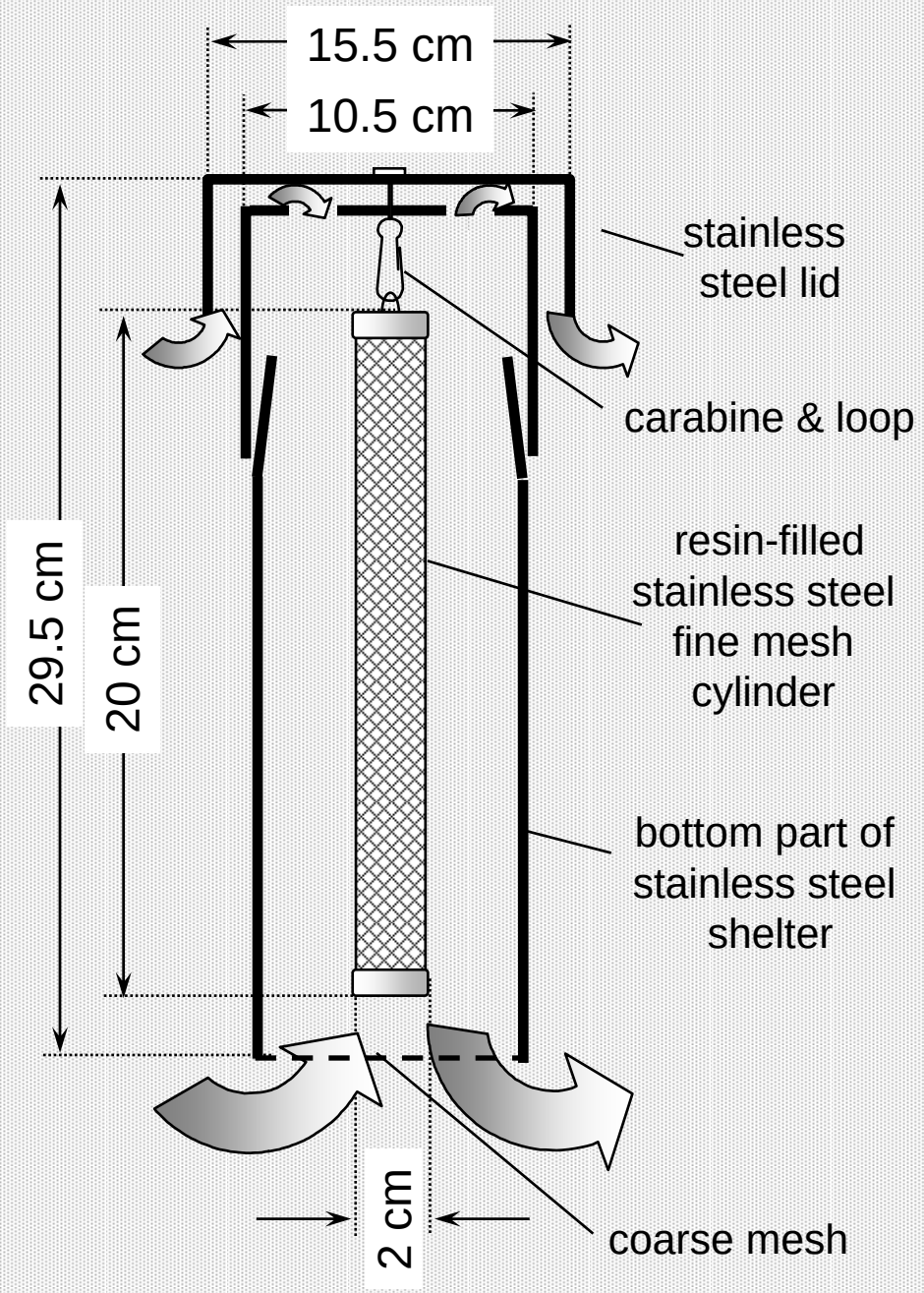


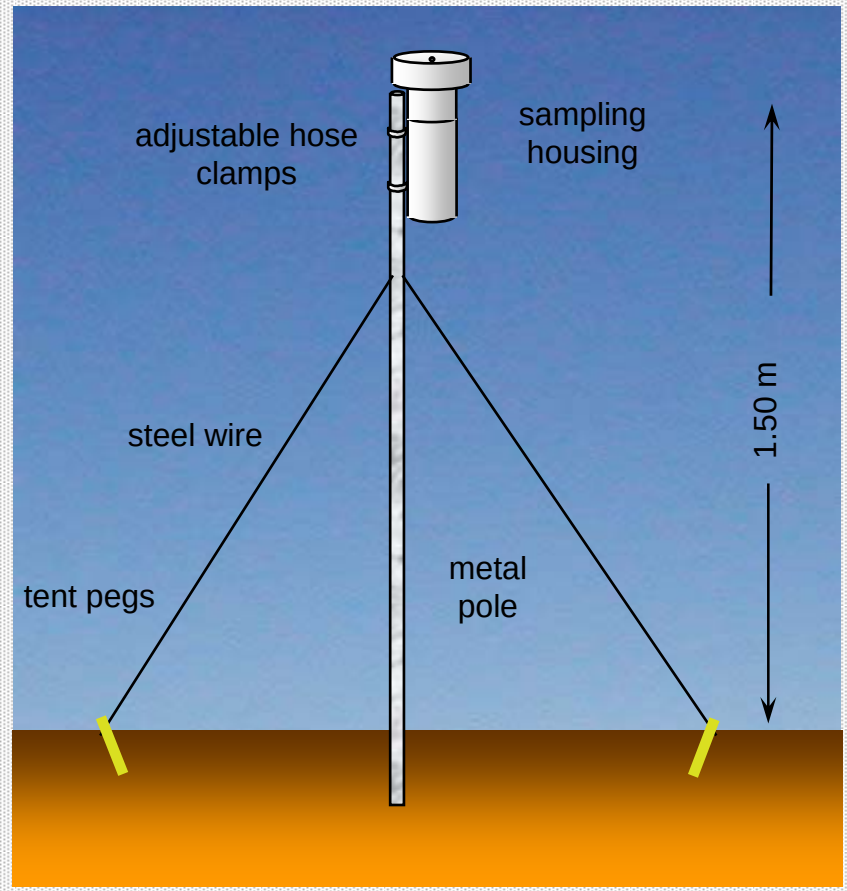
R. Bailey et al., Journal of Geophysical Research, 2000

How do HCH concentrations in air vary?

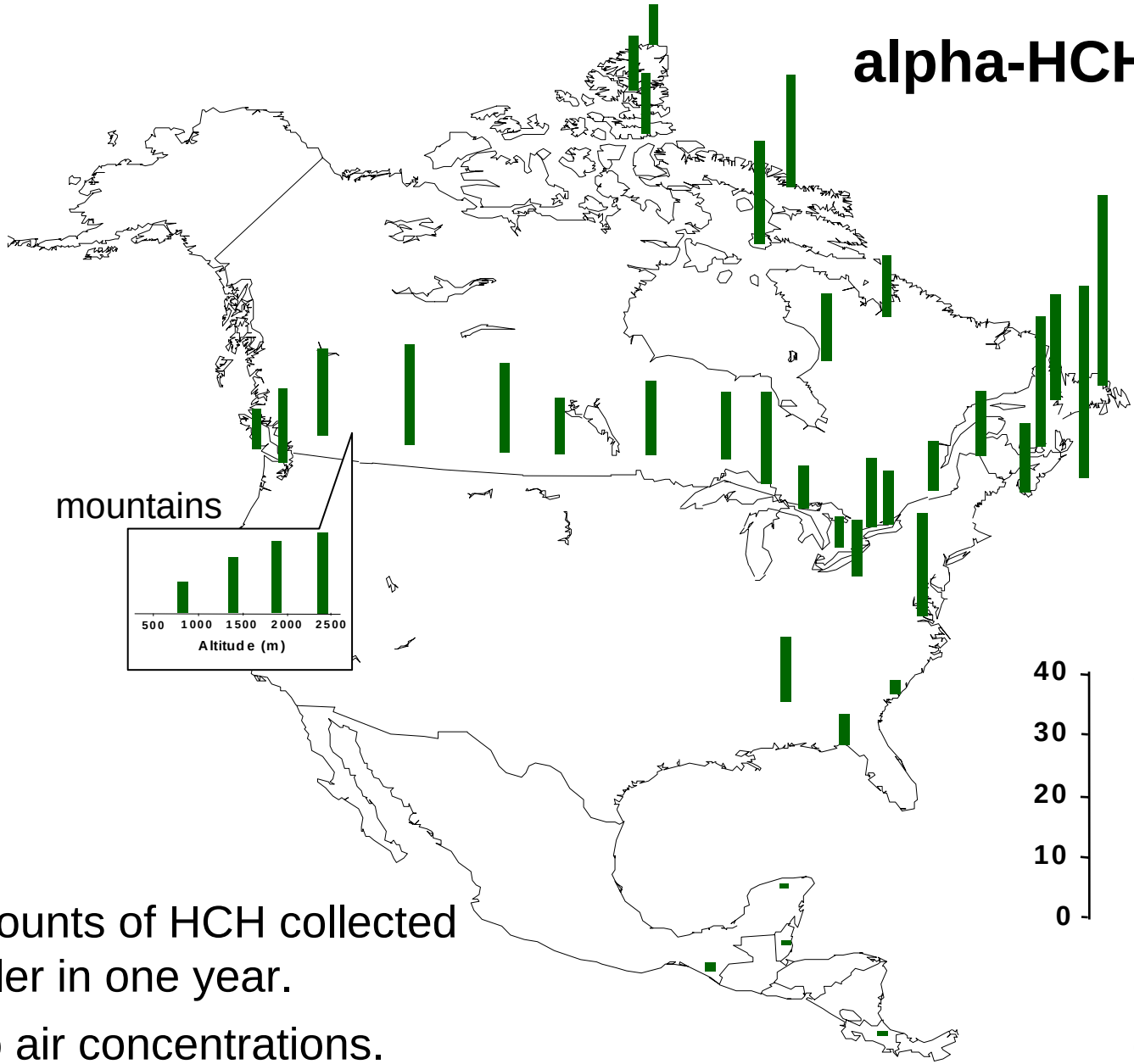
- University of Toronto scientists set up "passive"samplers across North America
- The samplers were small tubes of resin that absorbed the HCHs from the air
- Samplers were exposed for one year (2000-01)

Li Shen et al., Environmental Science & Technology, 2004

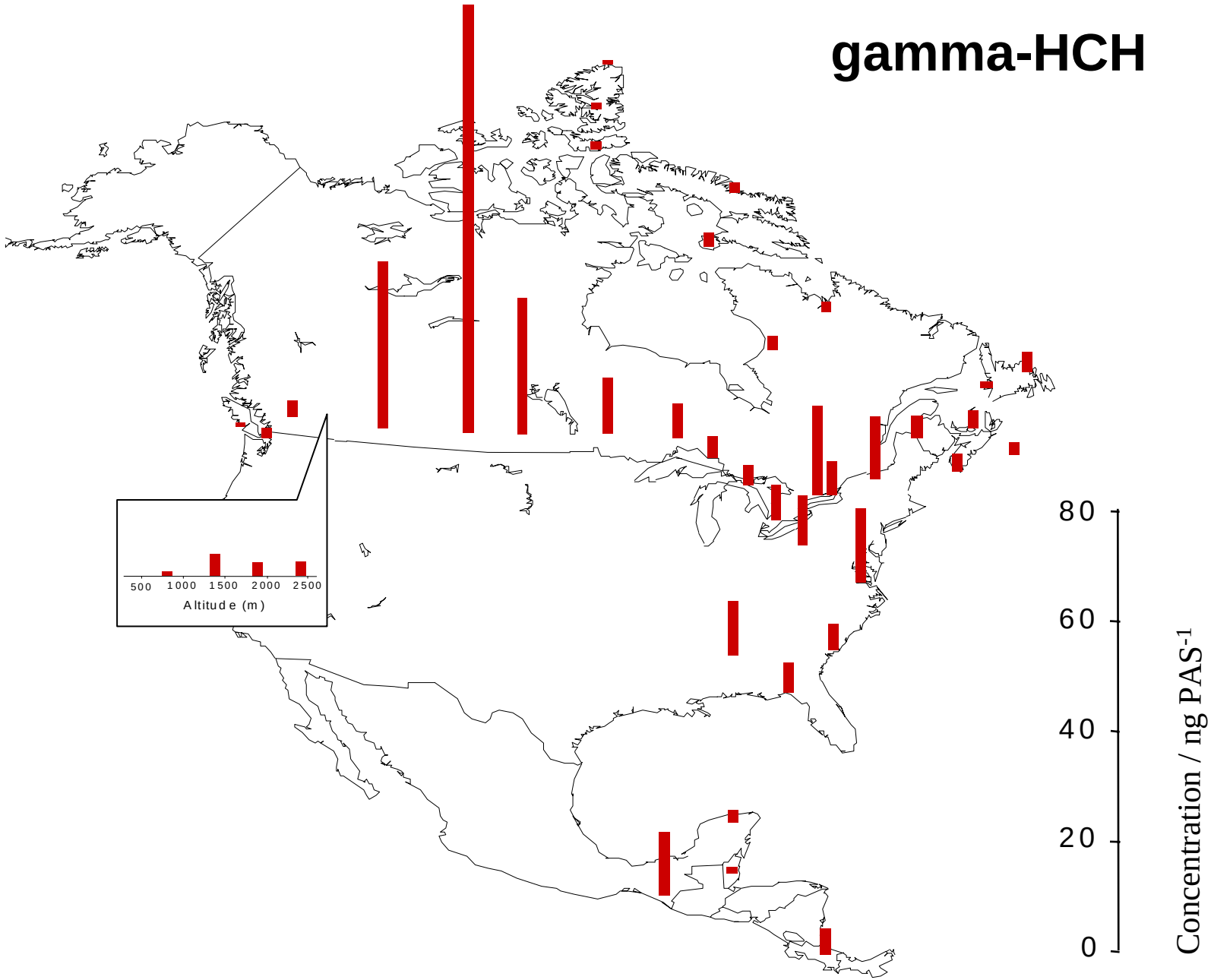

15.5 cm
10.5 cm
stainless steel lid
carabine & loop
resin-filled stainless steel fine mesh cylinder
bottom part of stainless steel shelter
coarse mesh
29.5 cm
20 cm
2 cm


adjustable hose clamps
sampling housing
steel wire
tent pegs
metal pole
1.50 m

alpha-HCH



- Bars show amounts of HCH collected by each sampler in one year.
- Proportional to air concentrations.


gamma-HCH
500 1000 1500 2000 2500
Altitude (m)
80
60
40
20
0
Concentration / ng PAS-1

Distinguishing the two sources of gamma-HCH

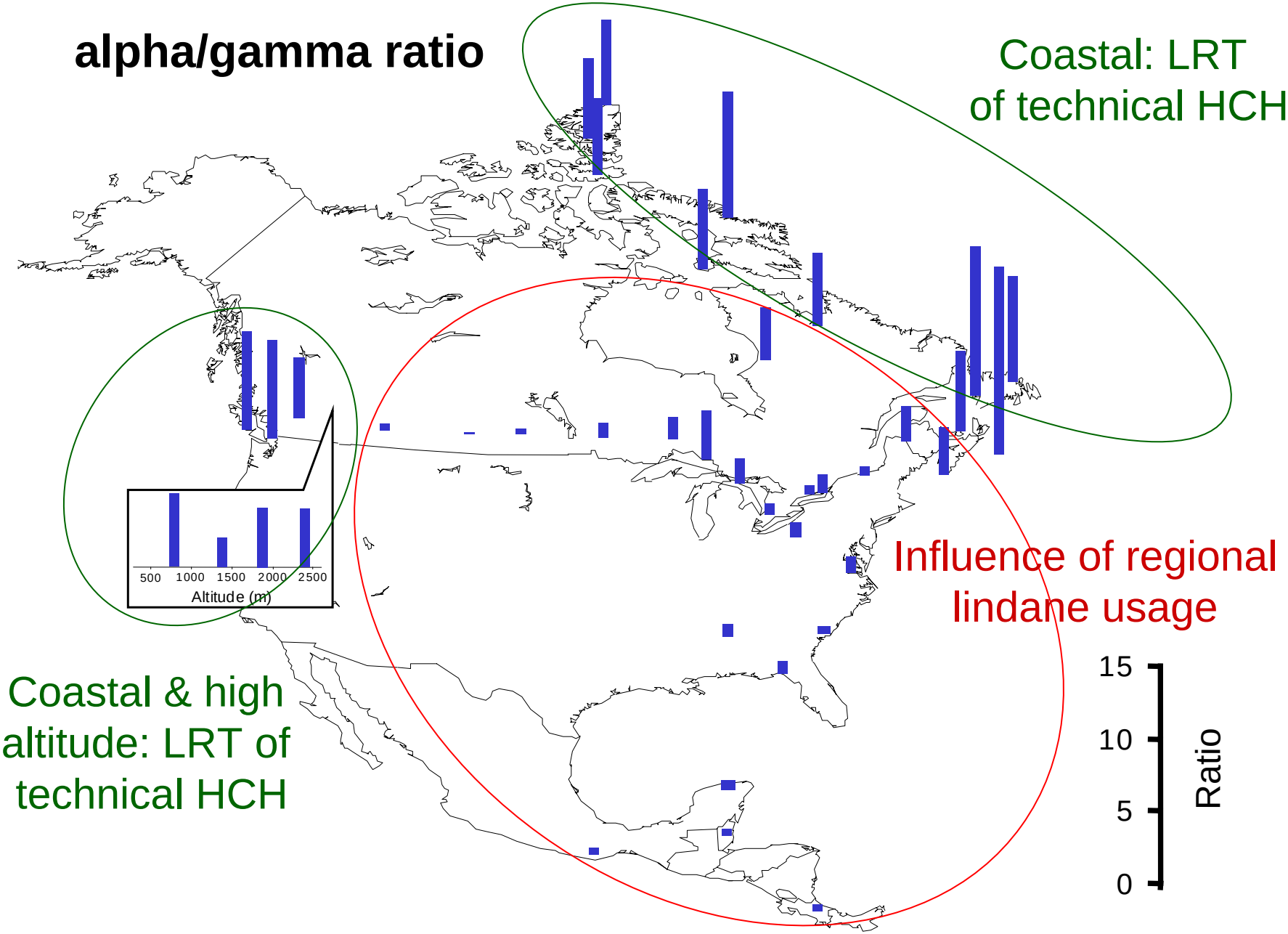
- Lindane: only gamma-HCH
- Technical HCH: alpha, beta and gamma-HCHs

Clues from the proportion of HCHs in air

- Low alpha/gamma: mainly lindane
- High alpha/gamma: mainly technical HCH

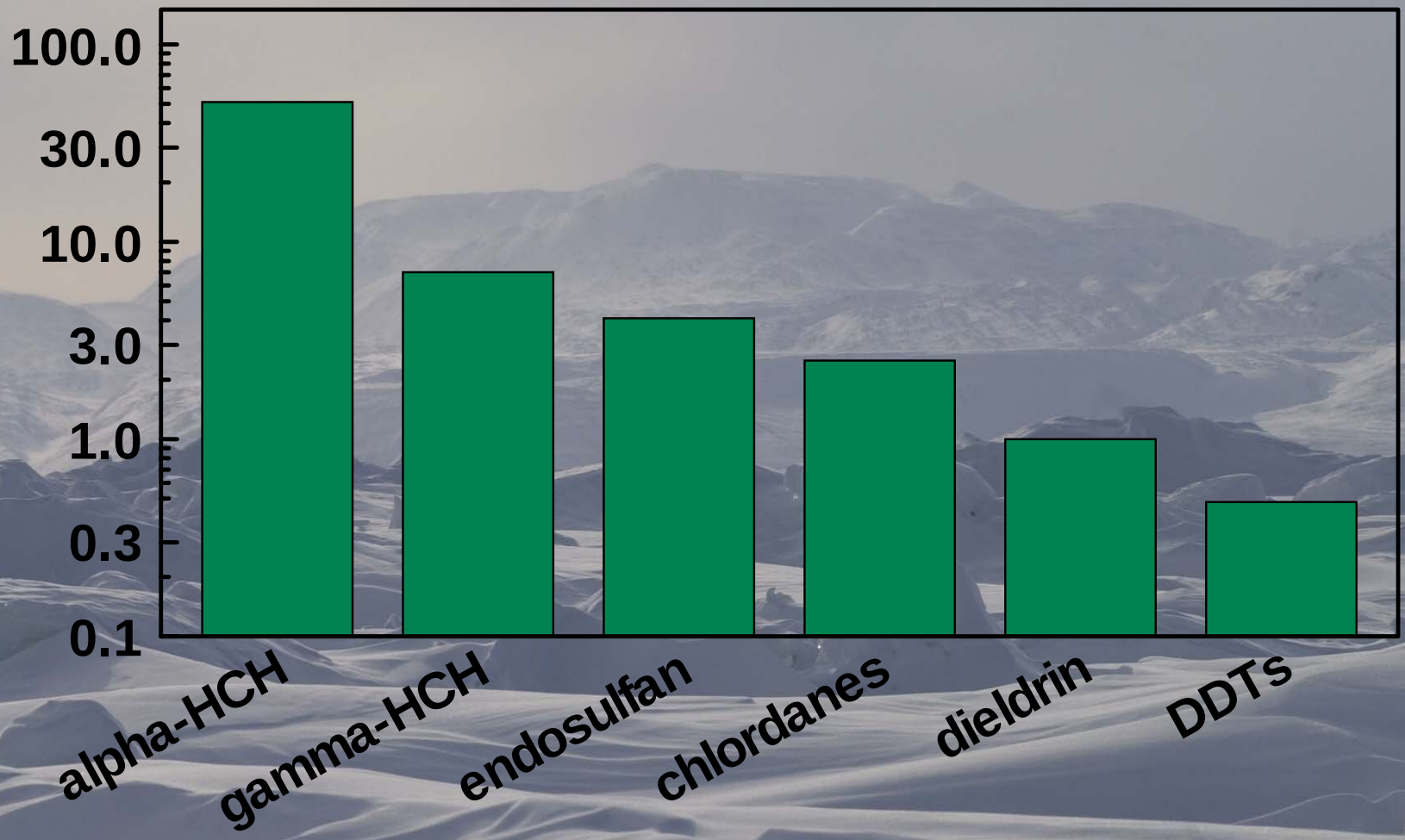
Does this work?

alpha/gamma ratio



Li Shen et al., Environmental Science & Technology, 2004

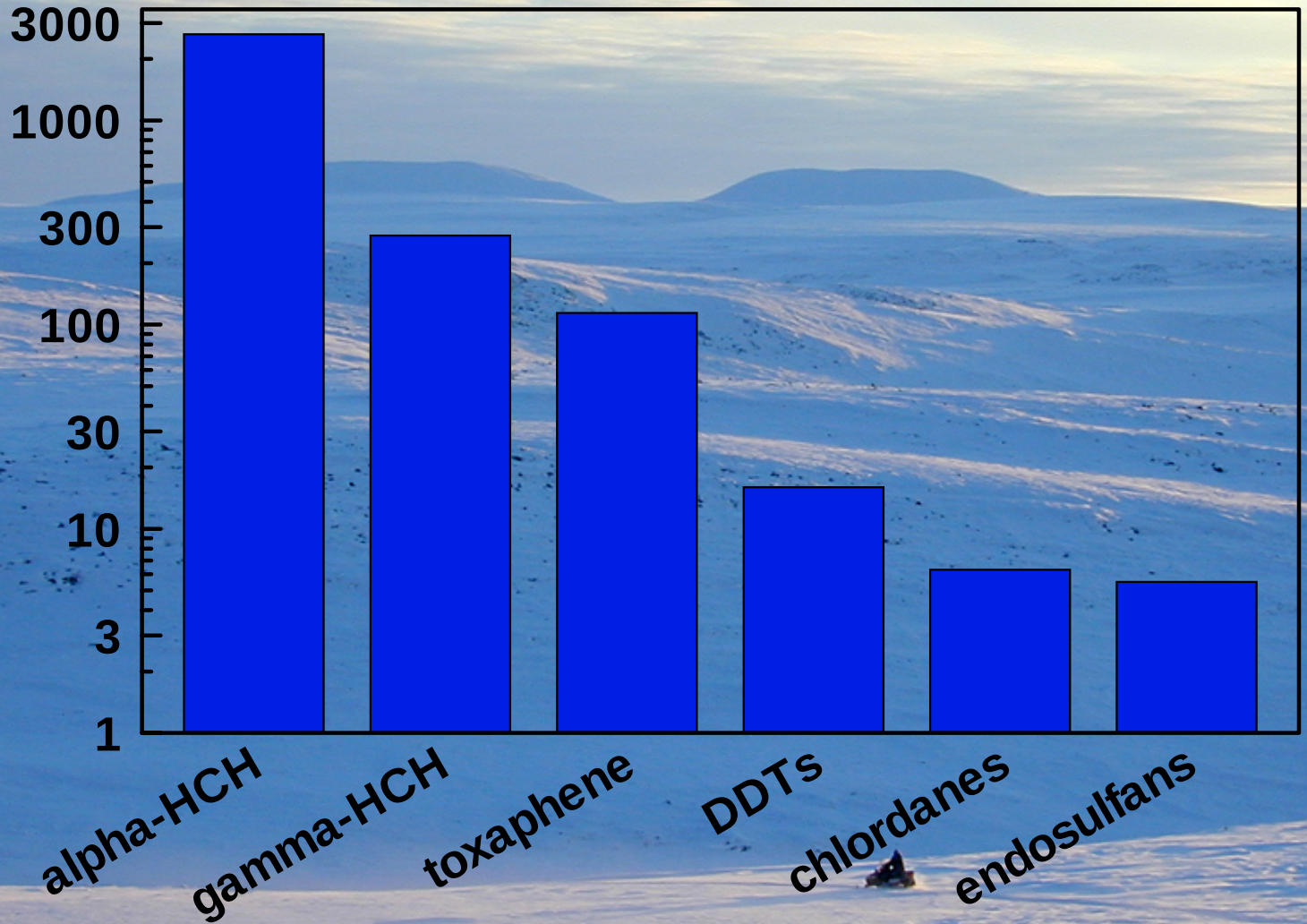
Pesticides in Canadian arctic air, pg/m^3



Hung et al., Environmental Science & Technology, 2002;
Hung et al., Science of the Total Environment, 2004 (submitted)

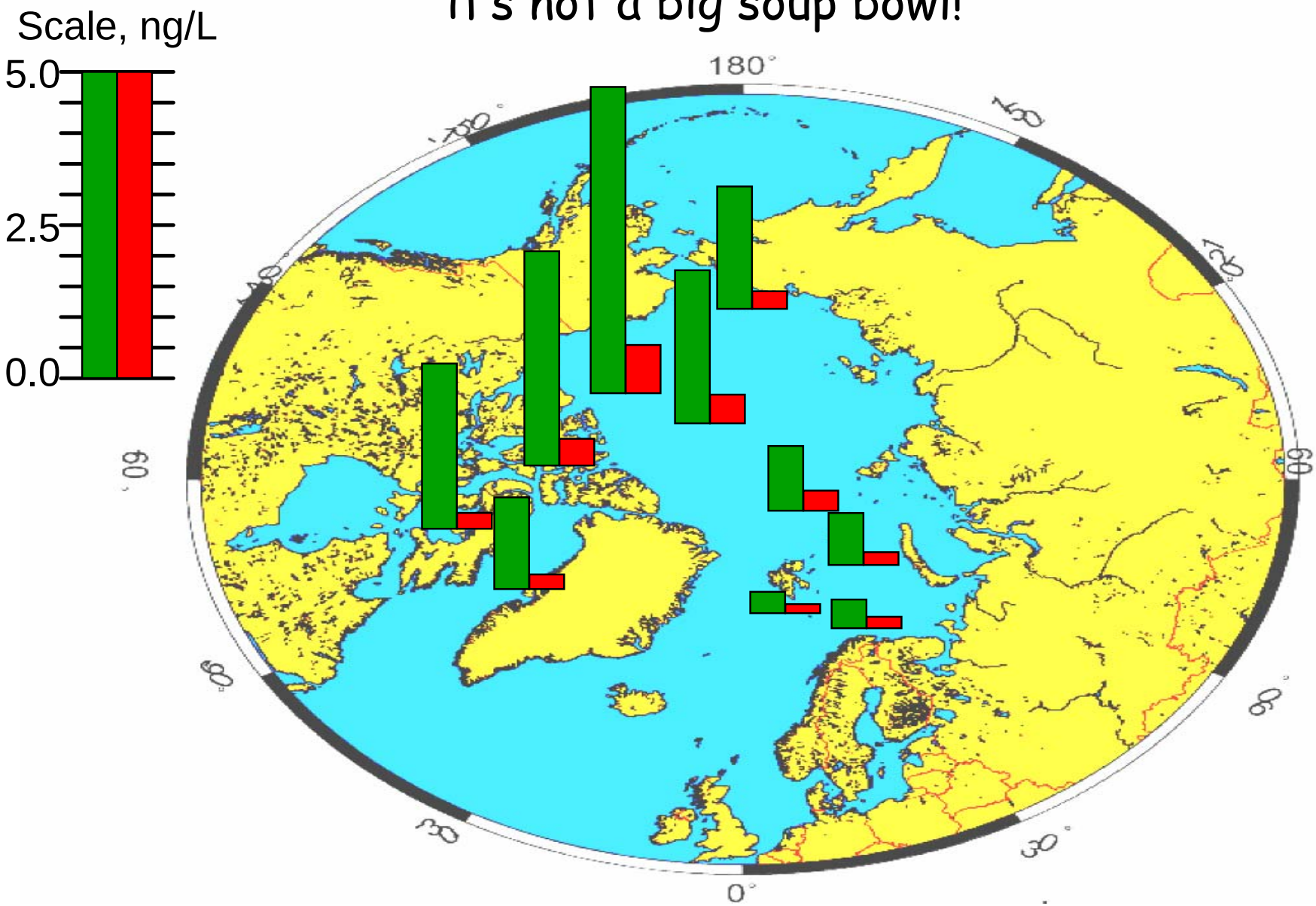
Photo: Janice Lang, DRDC, Canada

Pesticides in western Arctic Ocean water, pg/L

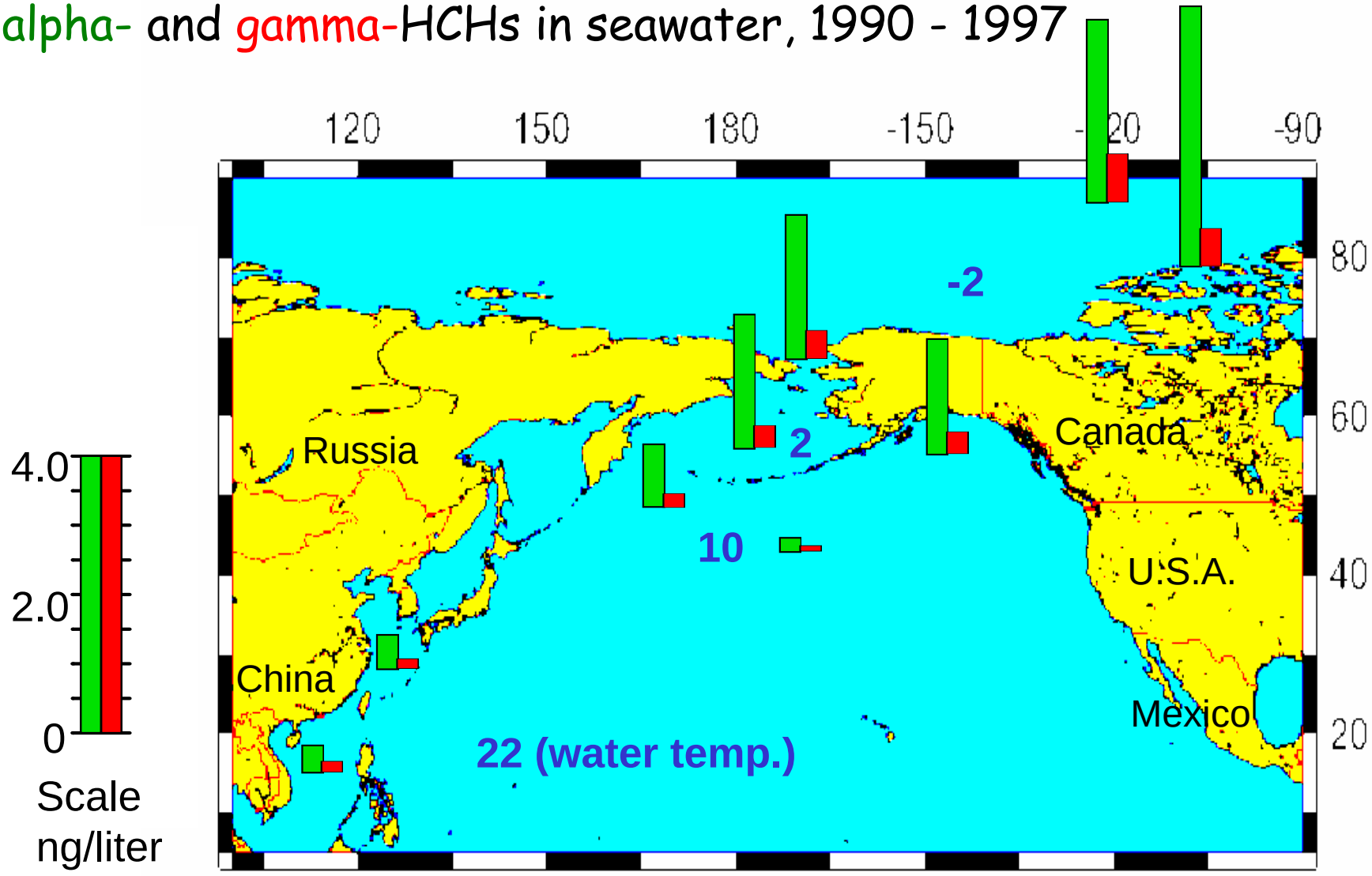


Jantunen & Bidleman, Arch. Environ. Contam. Tox., 1998
Canadian Arctic Contaminants Assessment Report, 2003

Alpha- and gamma-HCHs in Arctic Ocean water
it's not a big soup bowl!

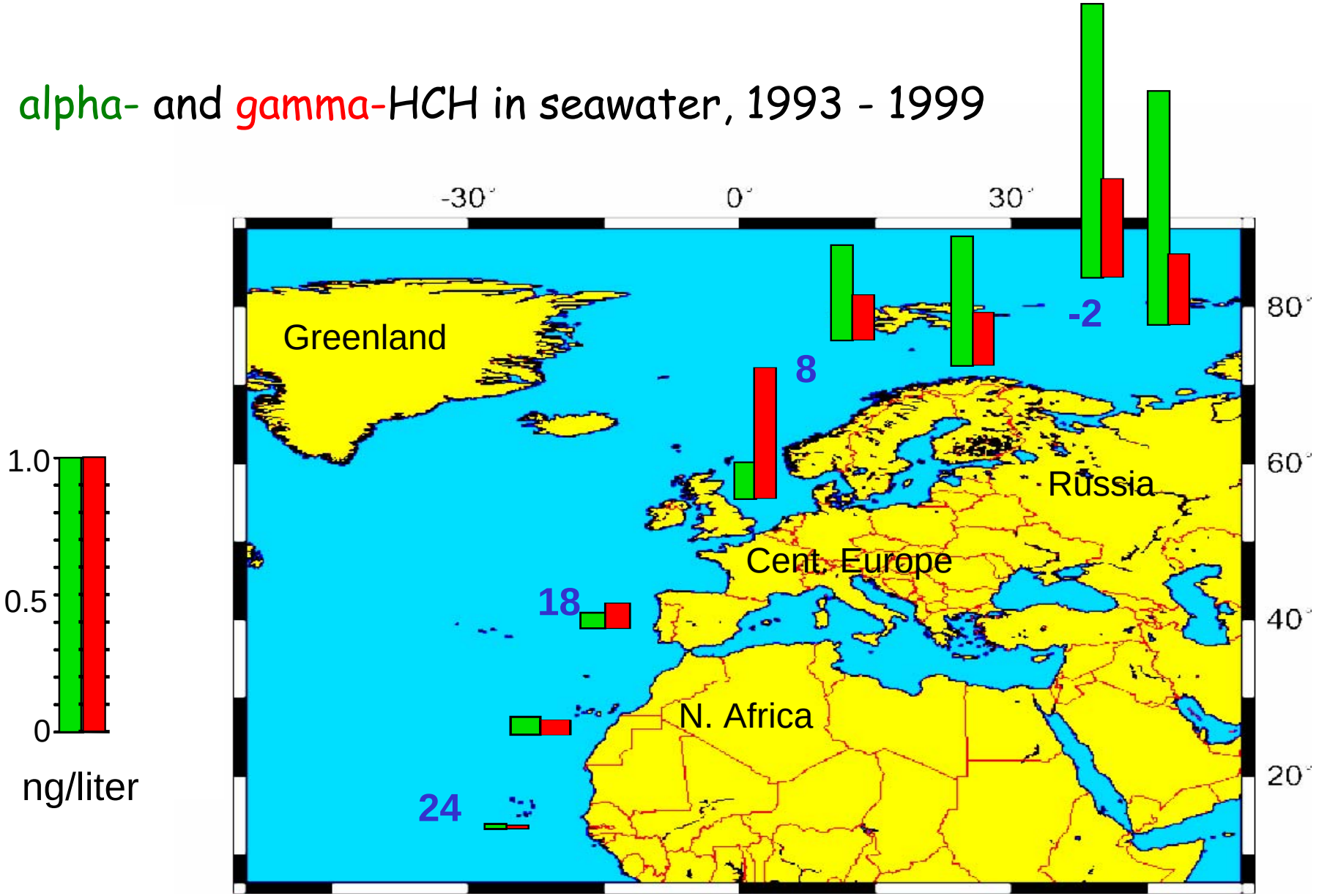


alpha- and gamma-HCHs in seawater, 1990 - 1997



Iwata et al., Environmental Science & Technology, 1993
Jantunen & Bidleman, Arch. Environ. Contam. Tox., 1998
Li et al., Canadian Arctic Contaminants Assessment Report II, 2003.

alpha- and gamma-HCH in seawater, 1993 - 1999

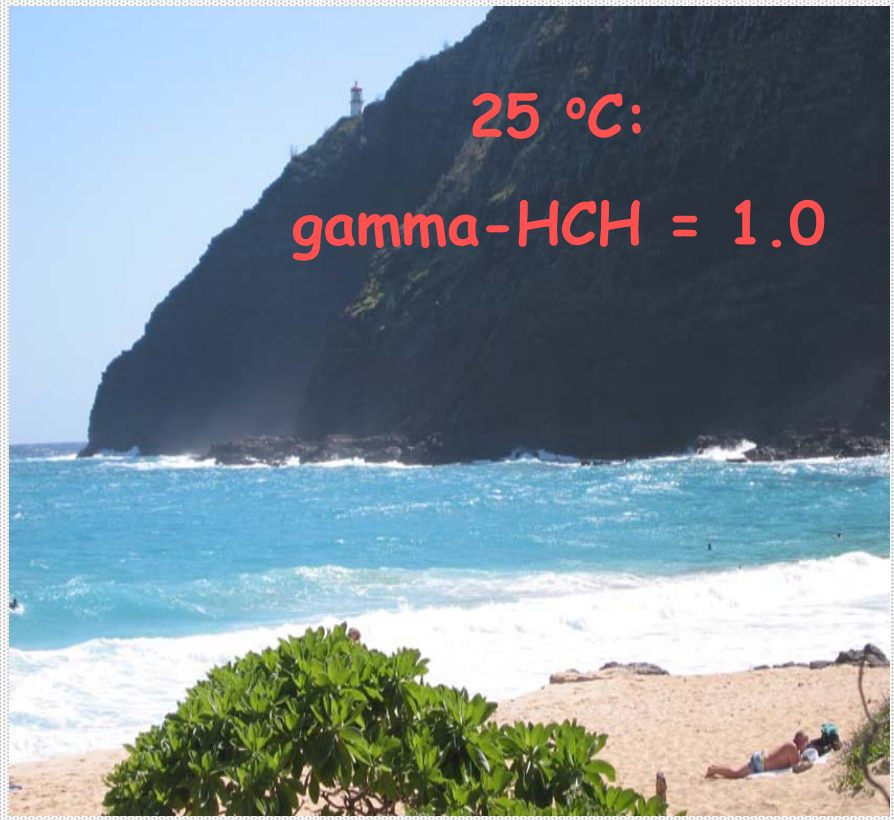


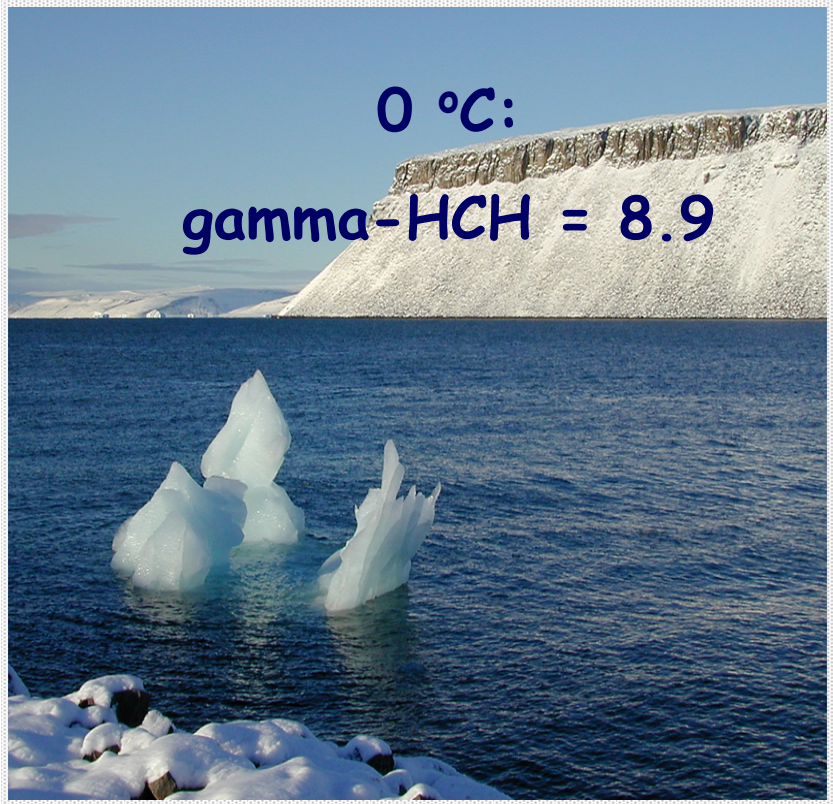
Lakaschus et al., Environmental Science & Technology, 2002;
Harner et al., Environmental Science & Technology, 1999.

Why are HCHs higher in northern waters?

Cold water holds more dissolved gas!

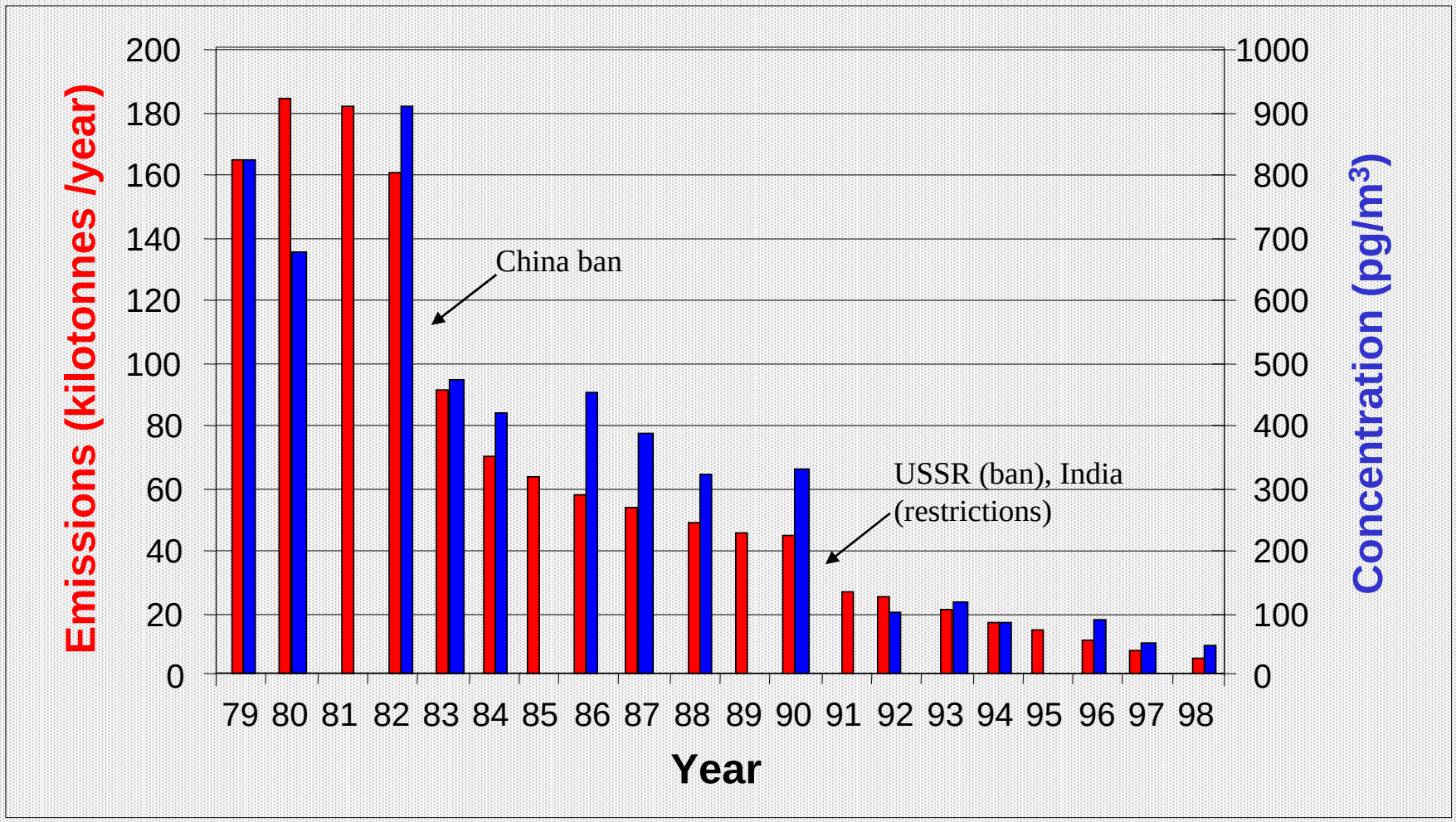
Relative solubility of gamma-HCH





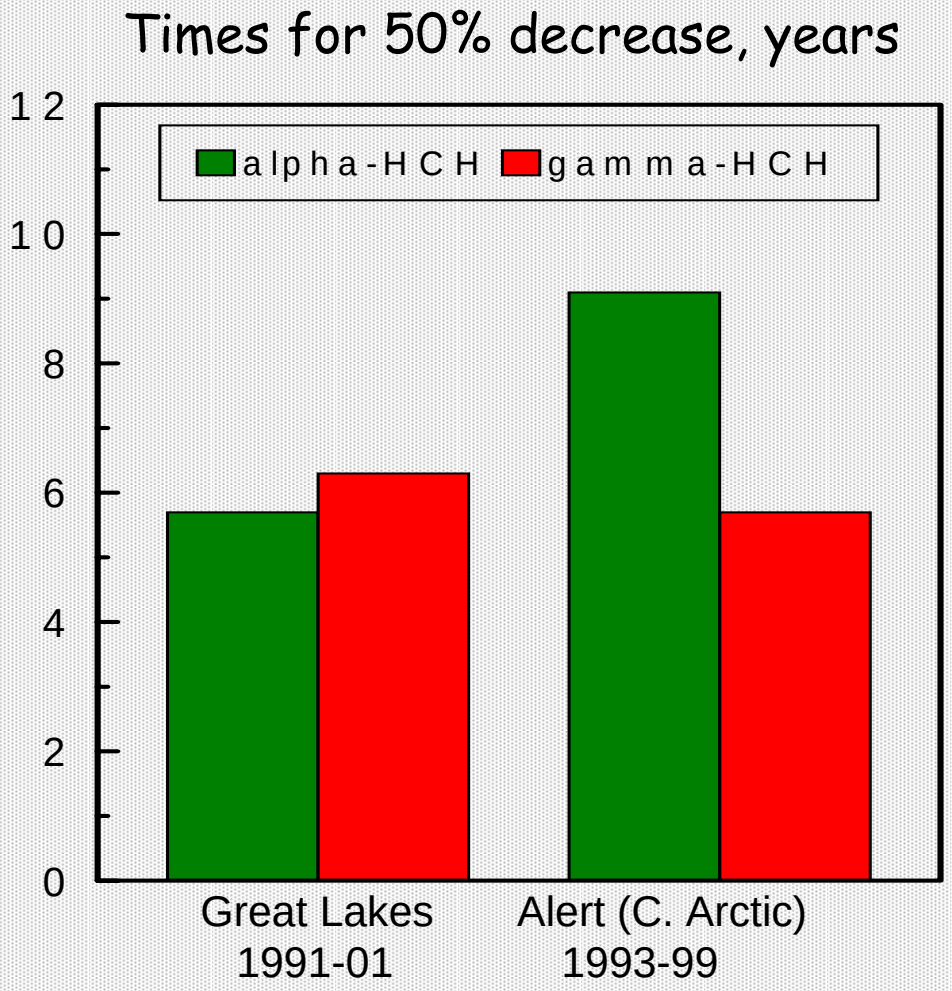
1. HCHs show the "Cold Condensation" Effect
2. HCHs break down more slowly in cold water

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



Li and Bidleman, J. Environ. Informatics, 2003

HCHs in air continue to decline slowly
Would they decline faster if we stopped lindane use?



Buehler et al., Environmental Science & Technology, 2004
Hung et al., Science of the Total Environment, 2004 (submitted)

Consequence of lower air levels: direct atmospheric deposition to the Arctic Ocean is becoming less significant

inflow →

circulation & outflow →

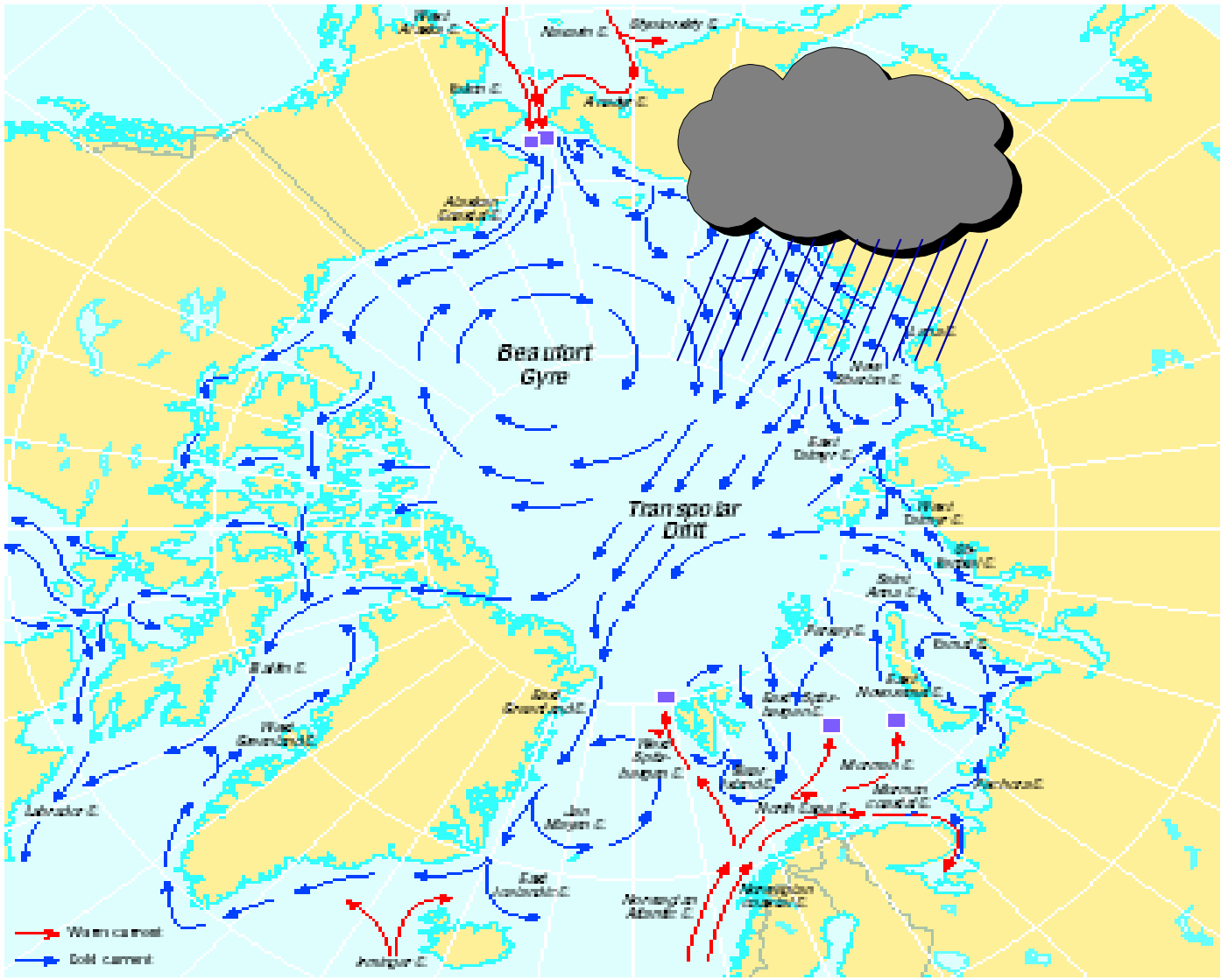
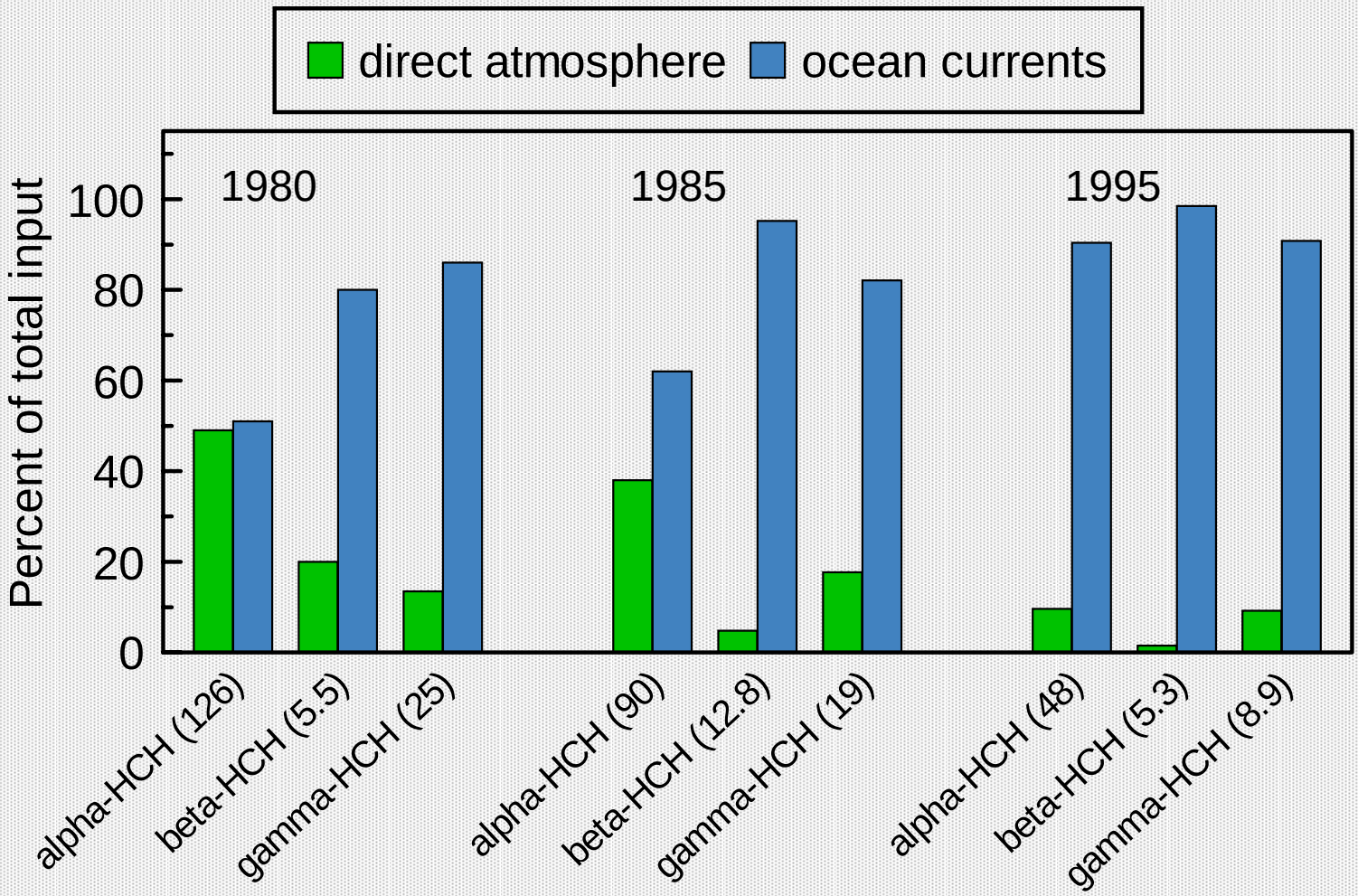


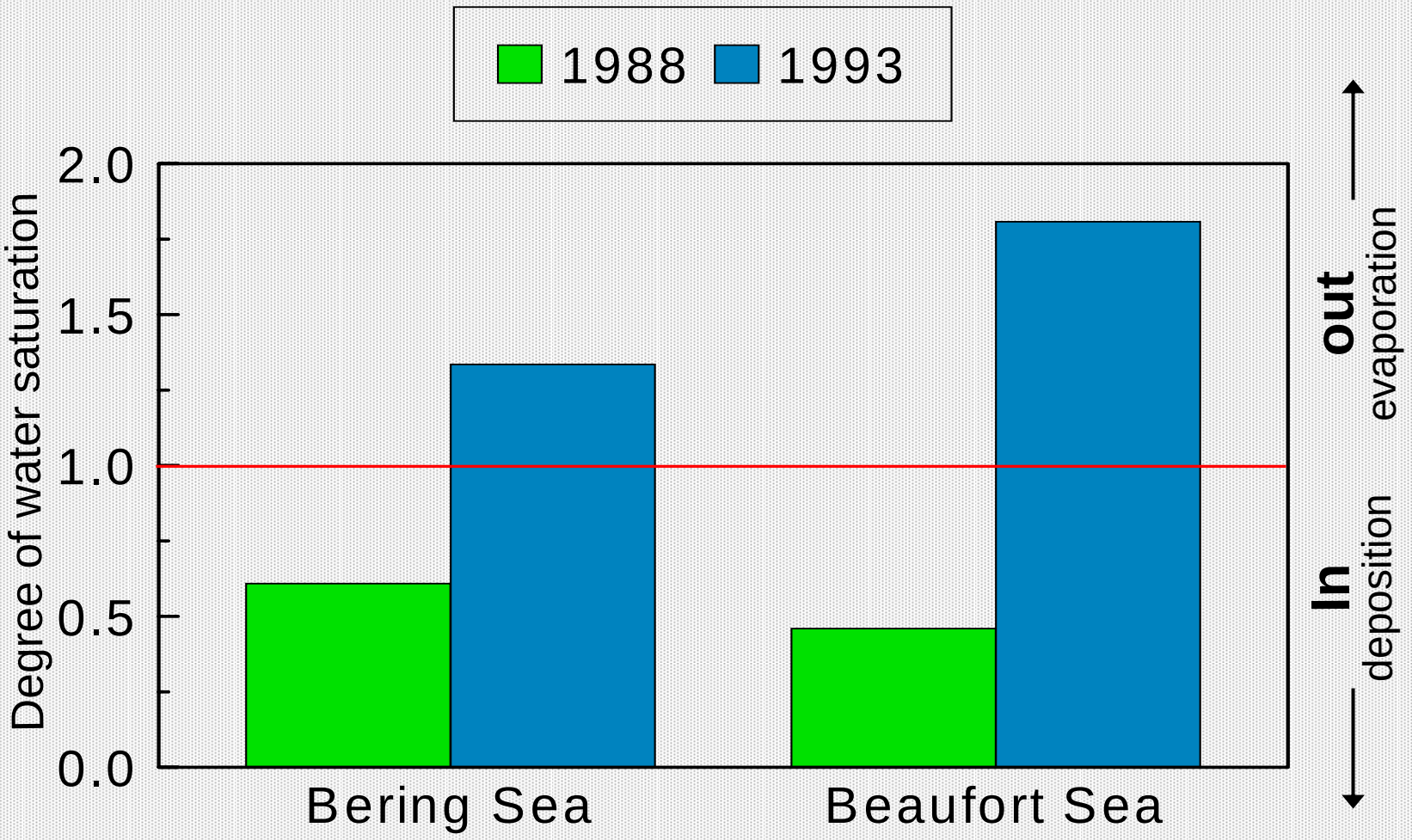
Figure 3-28. Surface currents in the Arctic region. Square boxes indicate that the denser inflowing (Atlantic and Pacific) waters are submerging under the Polar Surface Water. The continuation of these flows can be seen in Figure 3-27.

Input of HCHs to the western Arctic Ocean has become increasingly dominated by ocean currents (tonnes/year)



Li et al., Science of the Total Environment, 2002;
Li et al., Canadian Arctic Contaminants Assessment Report II, 2003

Another consequence: re-emission of alpha-HCH from water to the atmosphere. Exchange is a two-way street!



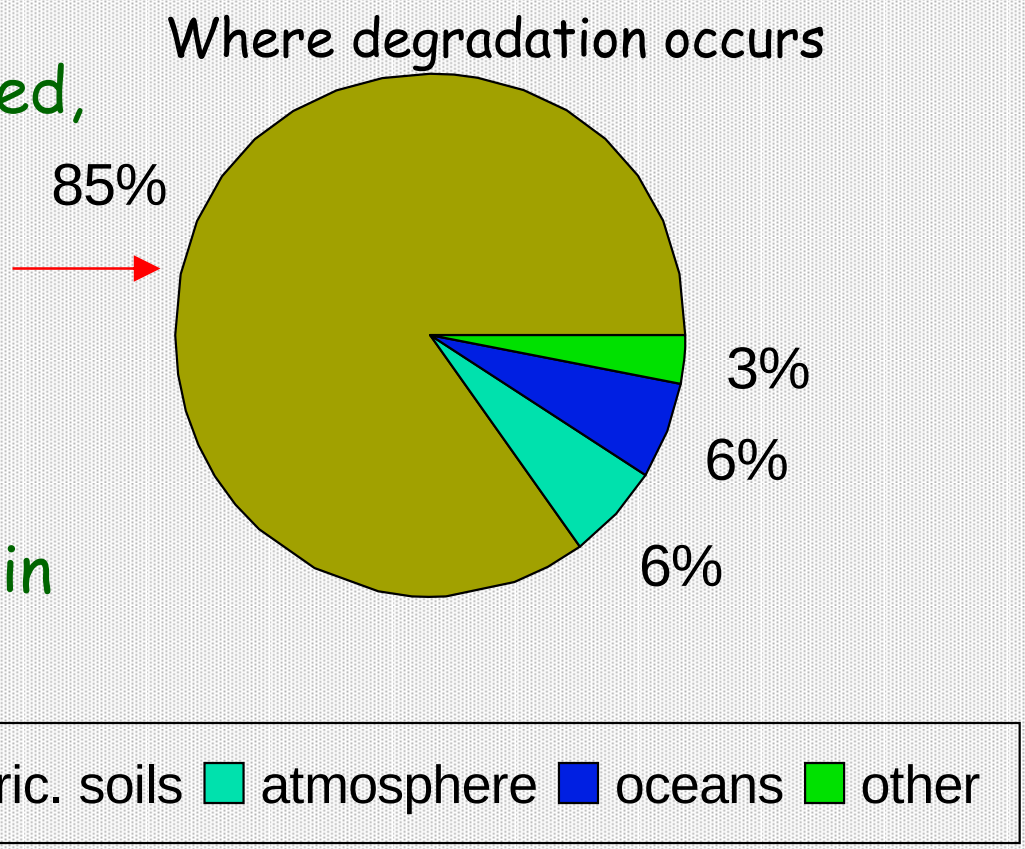
Sahsuvar et al., Atmospheric Environment, 2003; Jantunen & Bidleman, Environmental Science & Technology, 1995; Li et al., Canadian Arctic Contaminants Assessment Report, 2003

Where have all the HCHs gone? (long time passin'…)

Global mass balance model of alpha-HCH

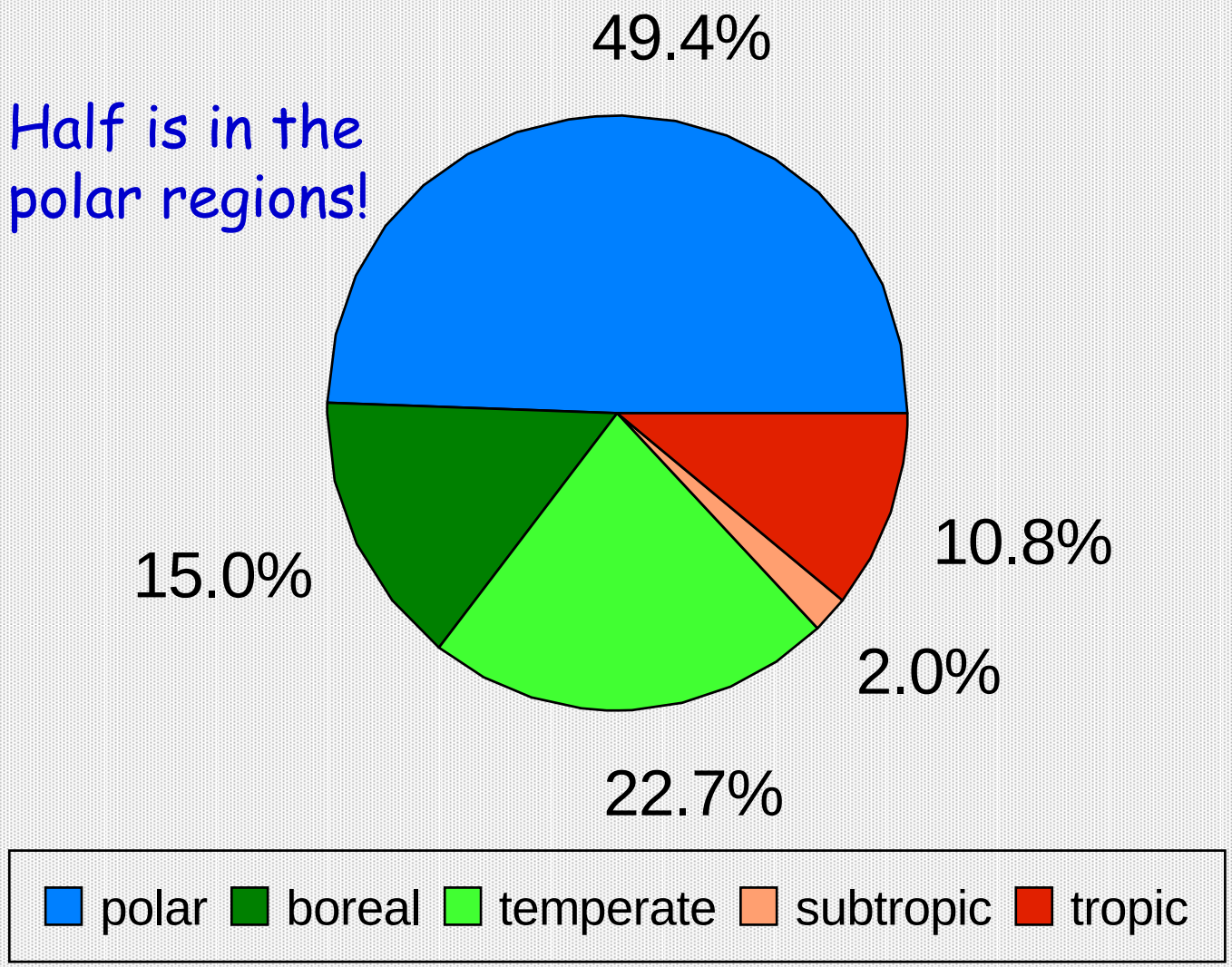
(Wania & Mackay, Environmental Toxicology & Chemistry, 1999)

- 6.8 million tonnes released, 1947 to 1997
- 99% has been degraded
- 0.6% in sediments
- 0.2% in the deep sea
- 0.2% remains dispersed in the global environment



0.2% in the global environment… that's 13,600 tonnes!
Where is it, as of 1995?

Half is in the polar regions!



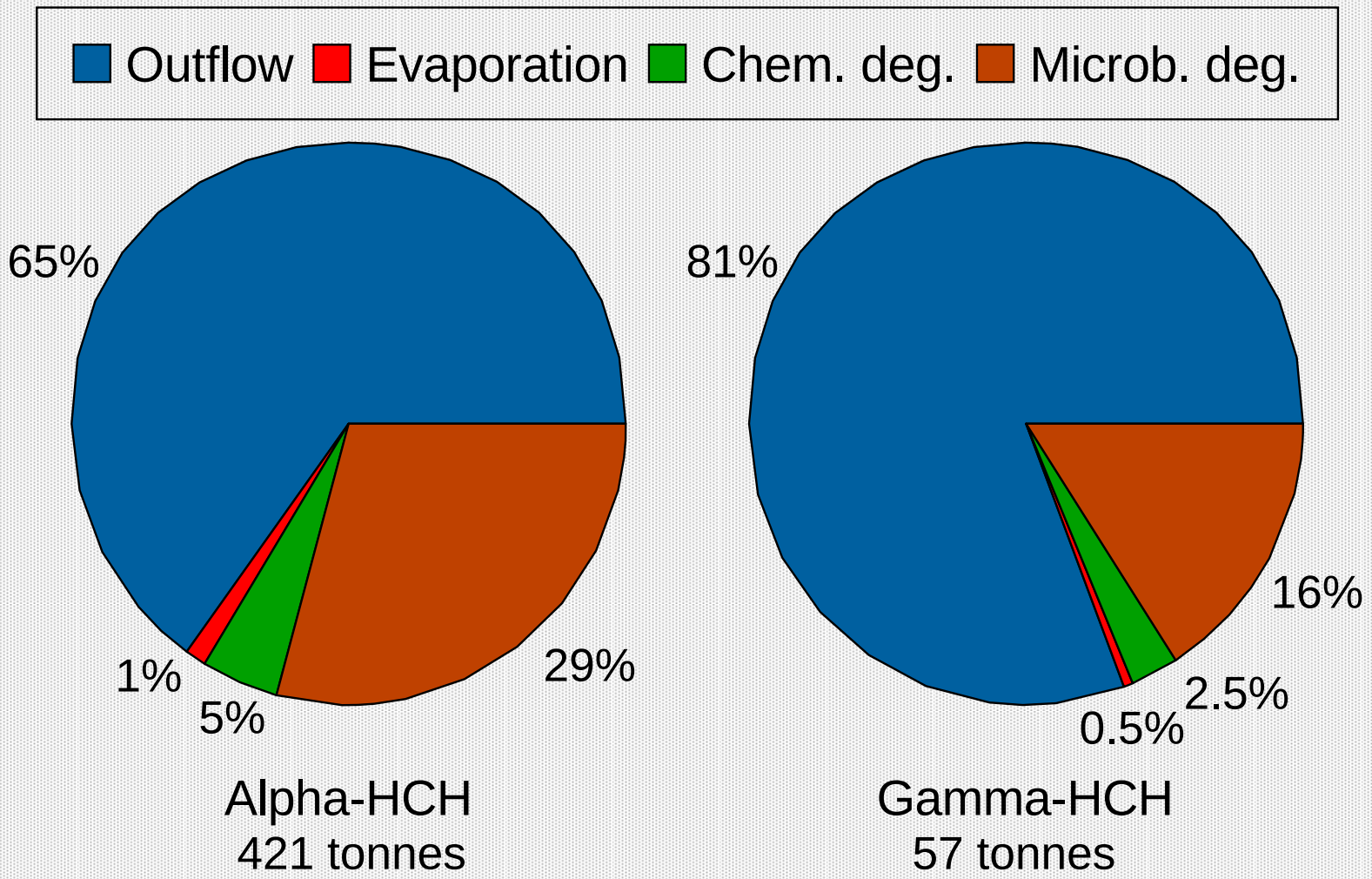
Good news: the Arctic Ocean is cleansing itself

Budget of HCHs in the western Arctic Ocean, tonnes/year (1995)

	Alpha-HCH	Gamma-HCH
In	48	8.9
Out	421	57

Li et al., Science of the Total Environment, 2002;
Li et al., Canadian Arctic Contaminants Assessment Report, 2003

Annual losses of HCHs from the western Arctic Ocean



Li et al., Canadian Arctic Contaminants Assessment Report, 2003
Harner et al., Geophysical Research Letters, 2000

Some critical issues

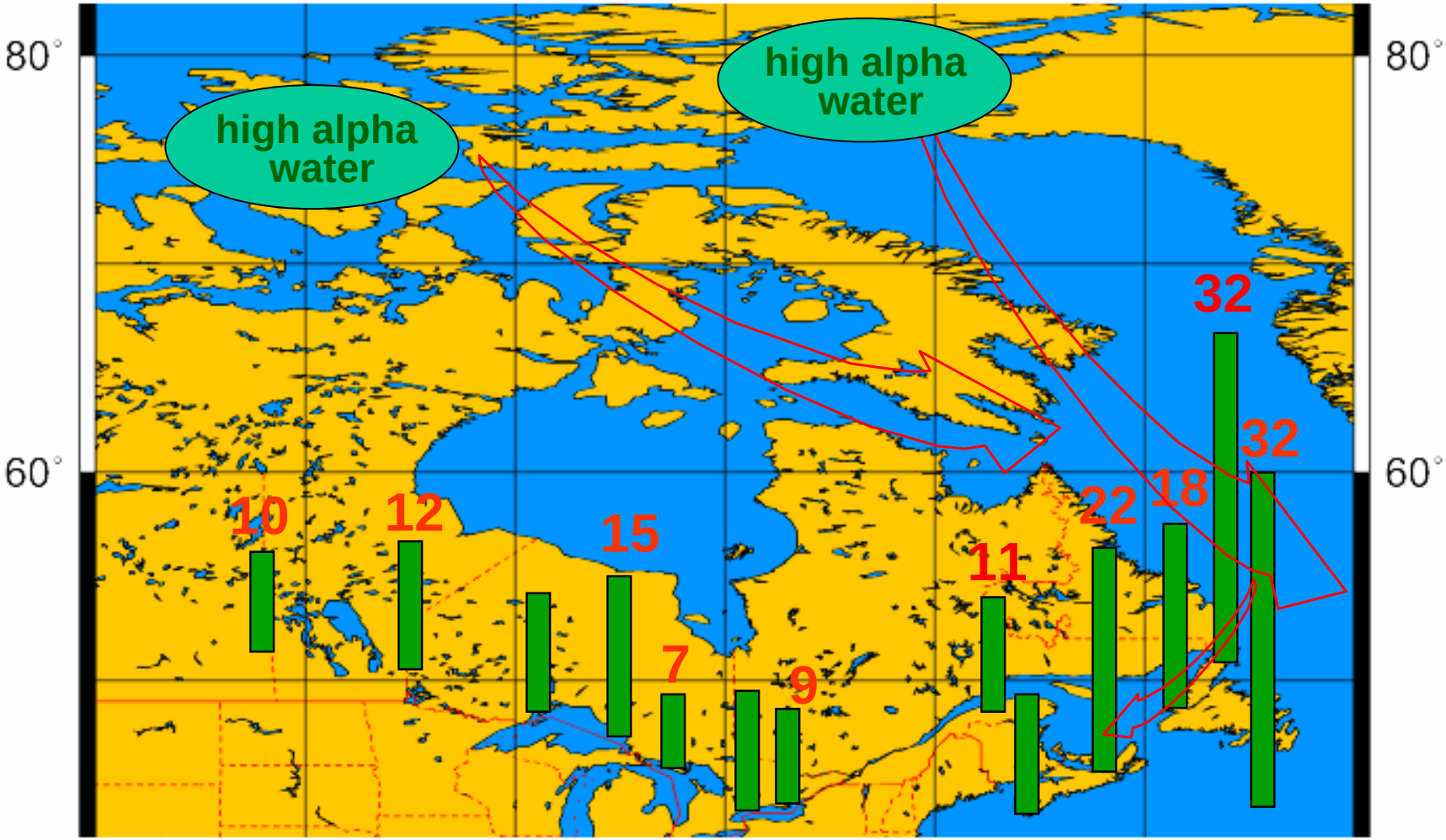
- How can gamma-HCH, from lindane vs. technical HCH use, be distinguished (especially in remote regions)?
- Would continued use of lindane impact non-target areas (arctic, Great Lakes, mountain ecosystems)?
- How to determine the relative contribution of new usage vs. "legacy" emissions from soil & water?
- Can the different HCHs be converted into one another?

Photo: Al Gallant, MSC, Canada

Extras

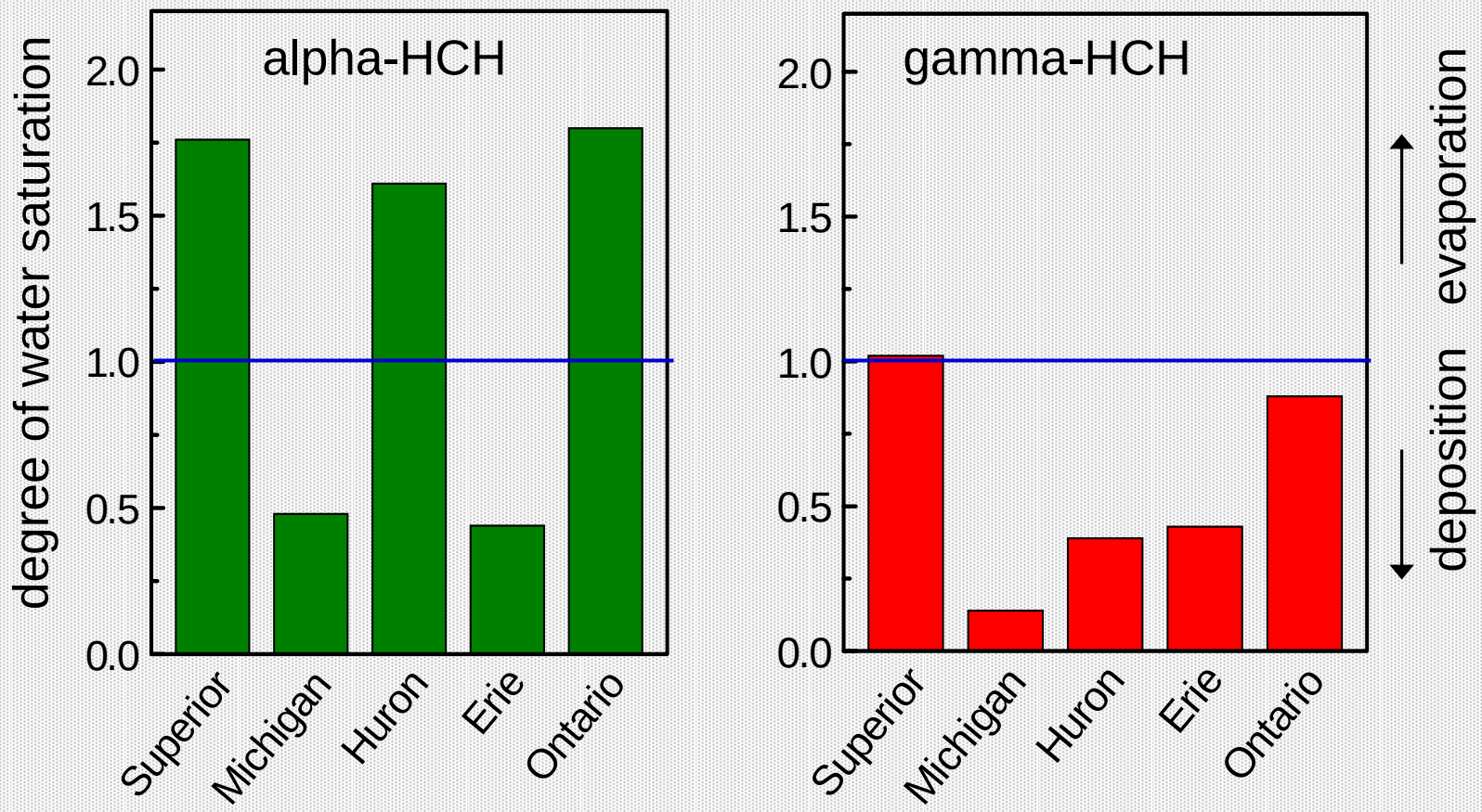
Does all the alpha-HCH in air come from LRT? No!!

Higher alpha-HCH in east coast passive samplers: Cold water from the Arctic flows south, warms and releases alpha back to the air.



Data from Li Shen et al., Environmental Science & Technology, 2004

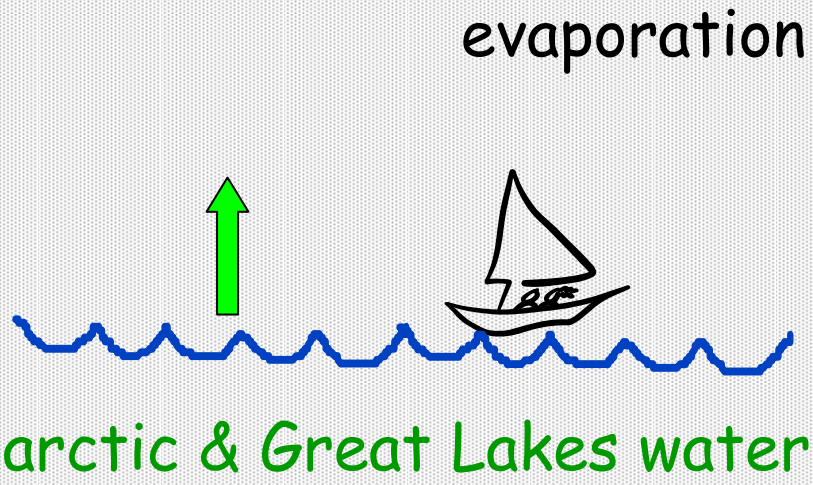
Air-water exchange of HCHs in the Great Lakes, 1998



Buehler et al., IADN Loadings Report, U.S. EPA and Environment Canada, 2001

What happens when HCHs in air are reduced?

Lakes and oceans give them up to the air again.
Gas exchange is a two-way street!



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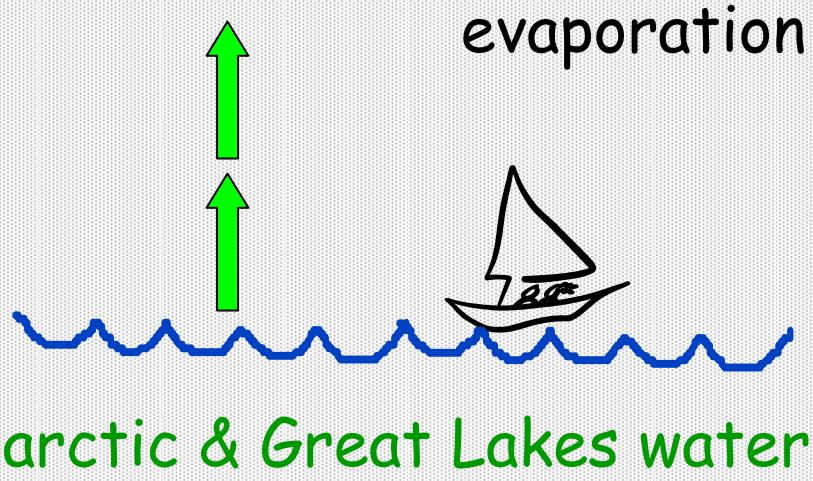

What happens when HCHs in air are reduced?

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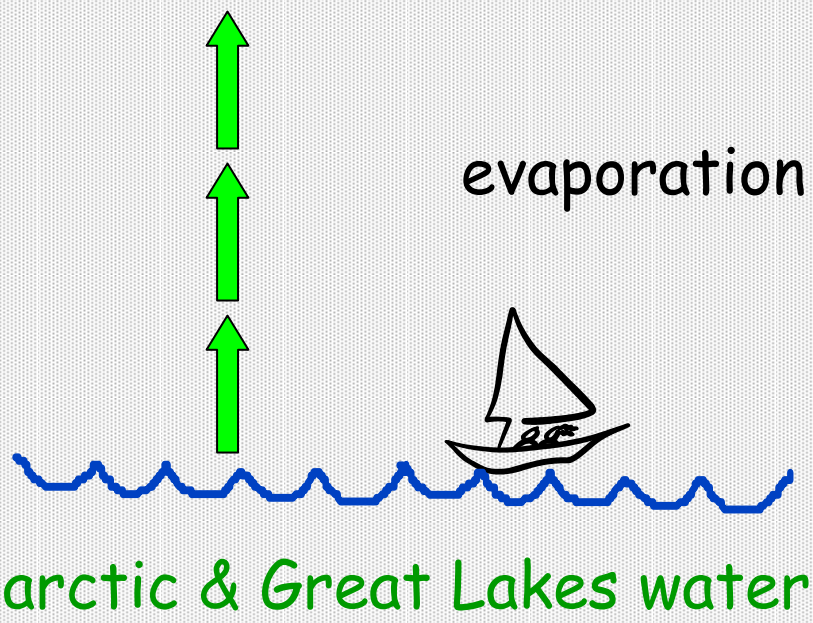

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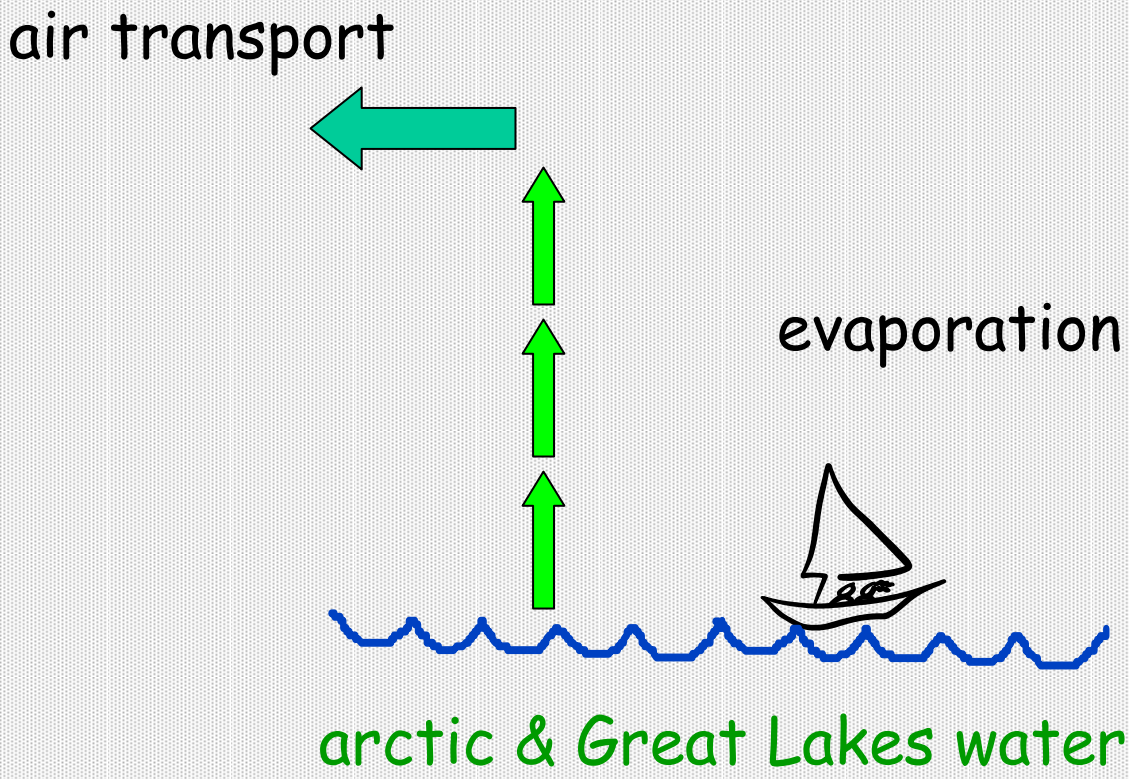

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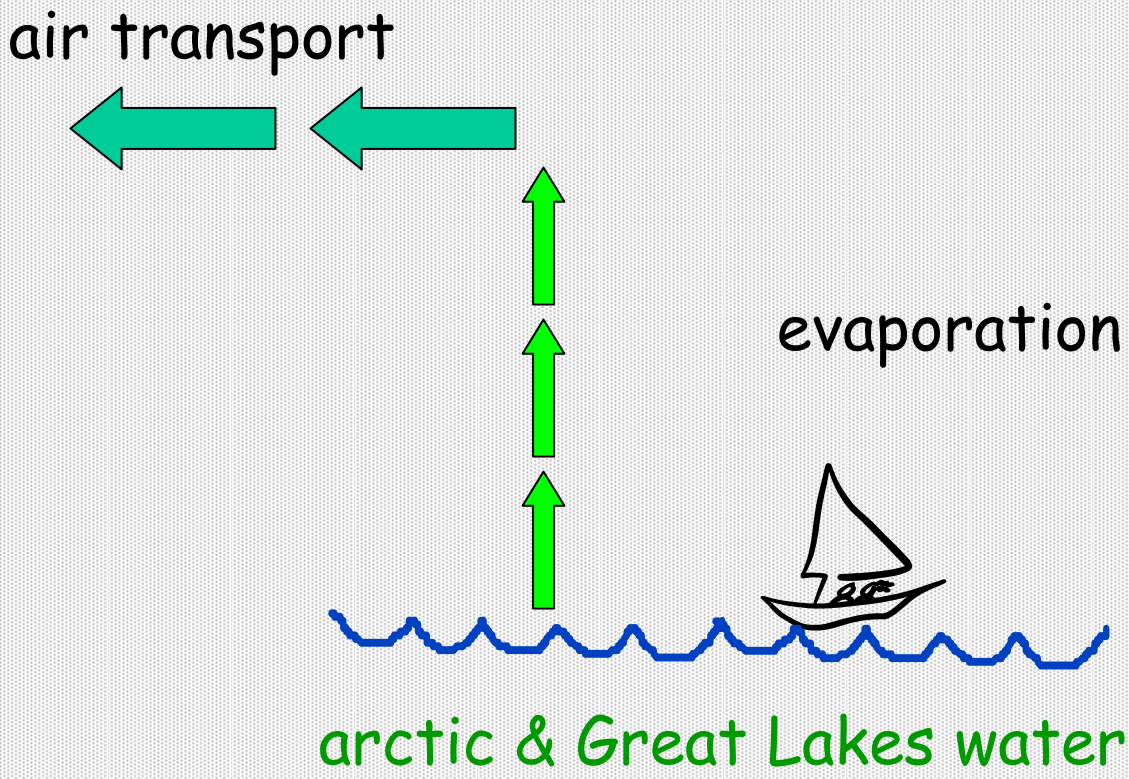

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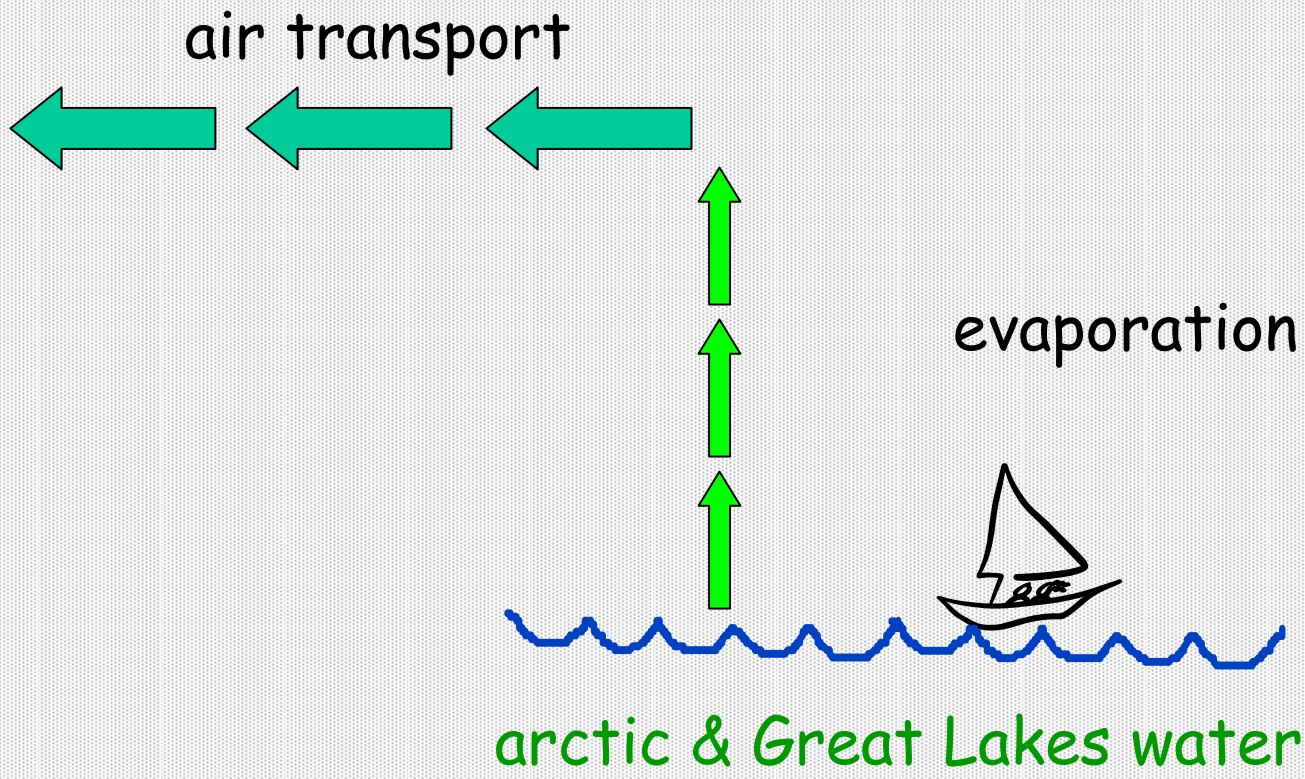
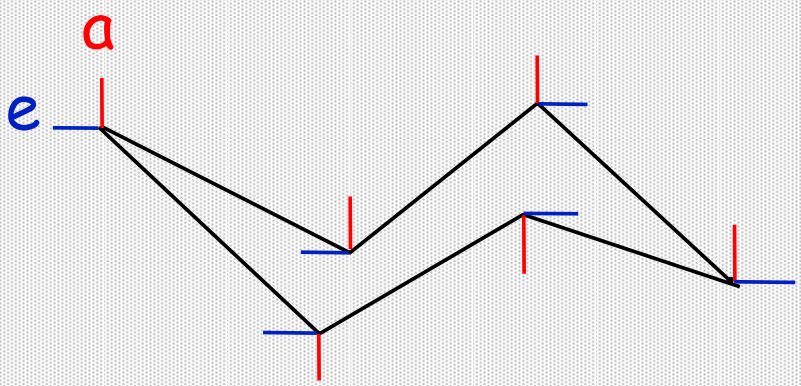


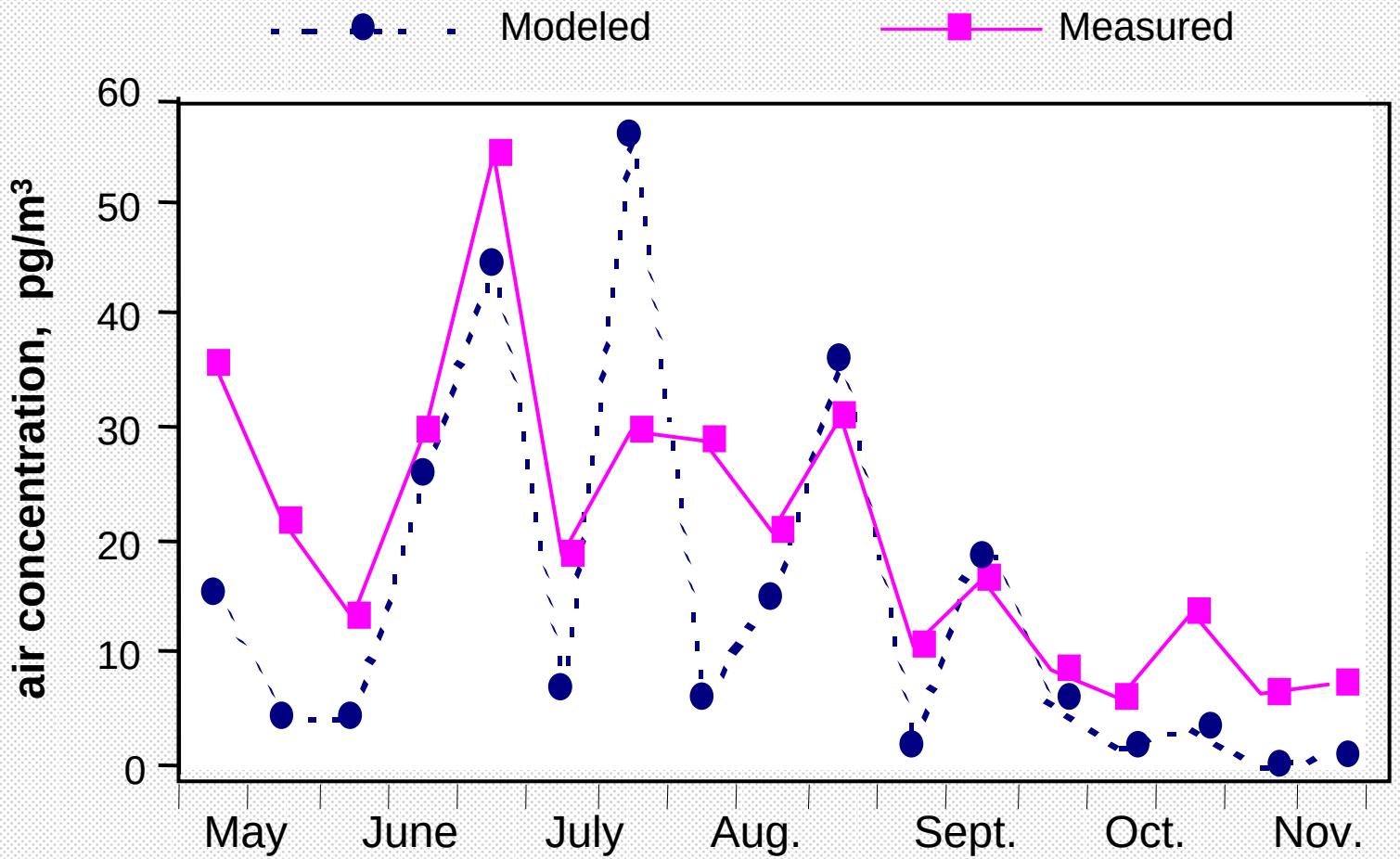
The 6-carbon ring isn't flat, it's puckered.
Viewed from the side:



Chlorines are placed:

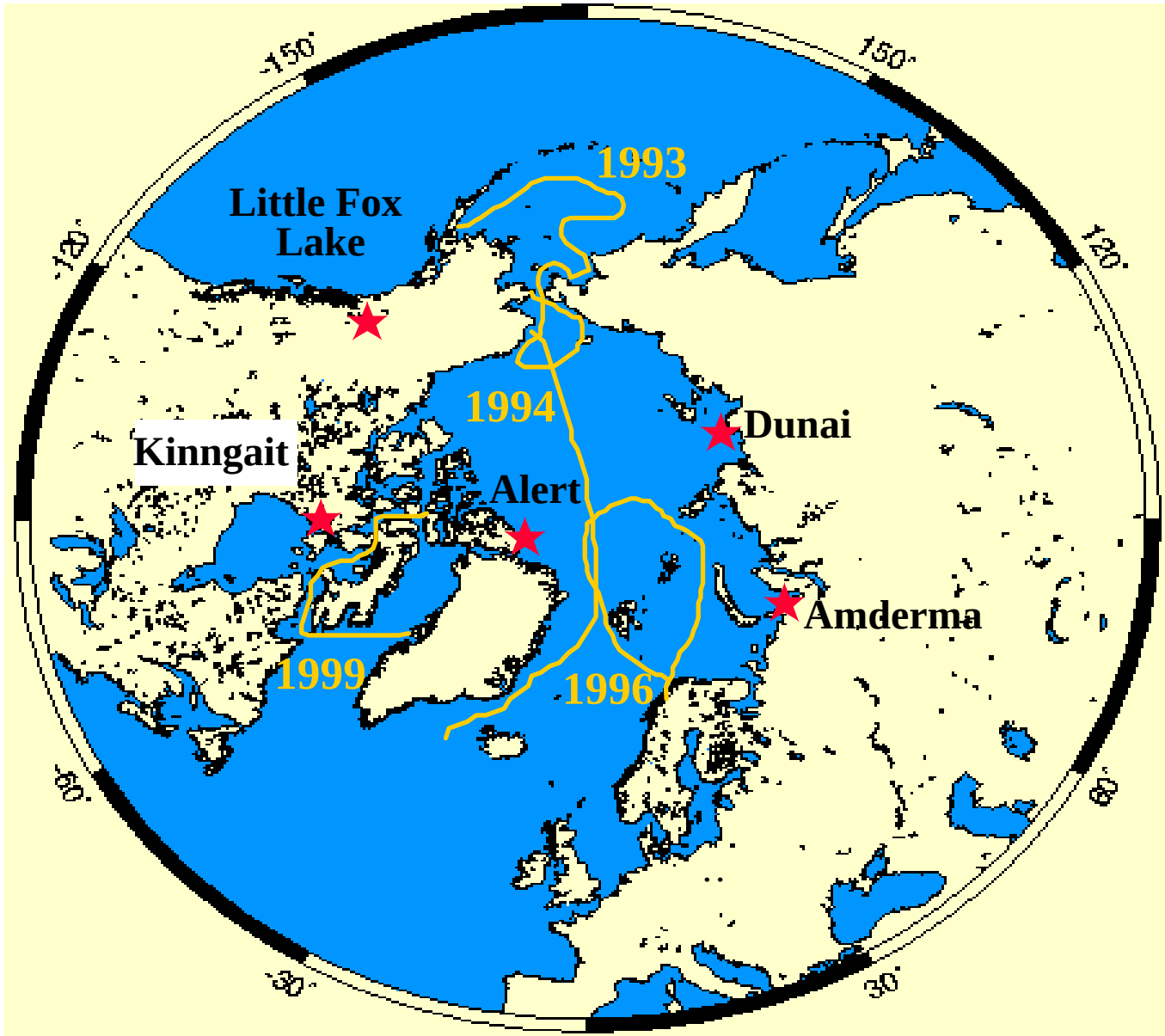
- either up and down (a = axial)
- or along the plane of the ring (e = equatorial).

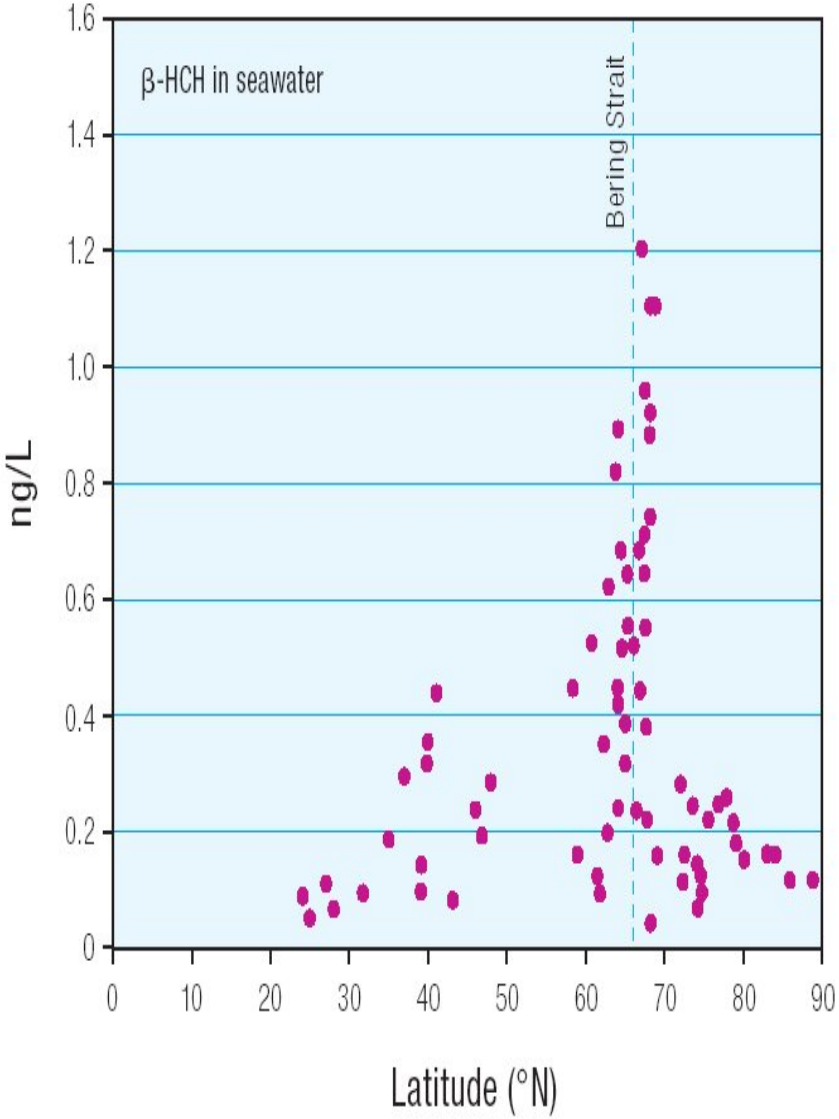
Lindane transport, Canadian prairies to the Great Lakes: modeled and measured air levels at Lake Superior, 1998

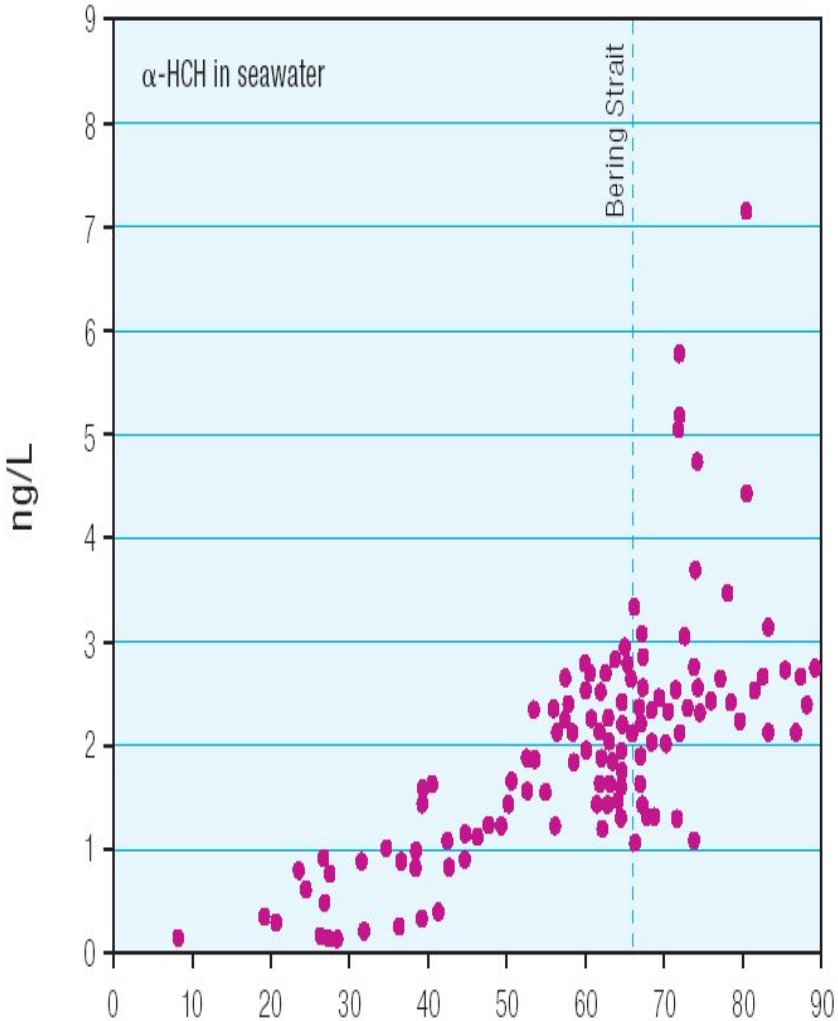


J. Ma et al., Environmental Science & Technology, 2003

Air ★ and water —— sampling in the Arctic

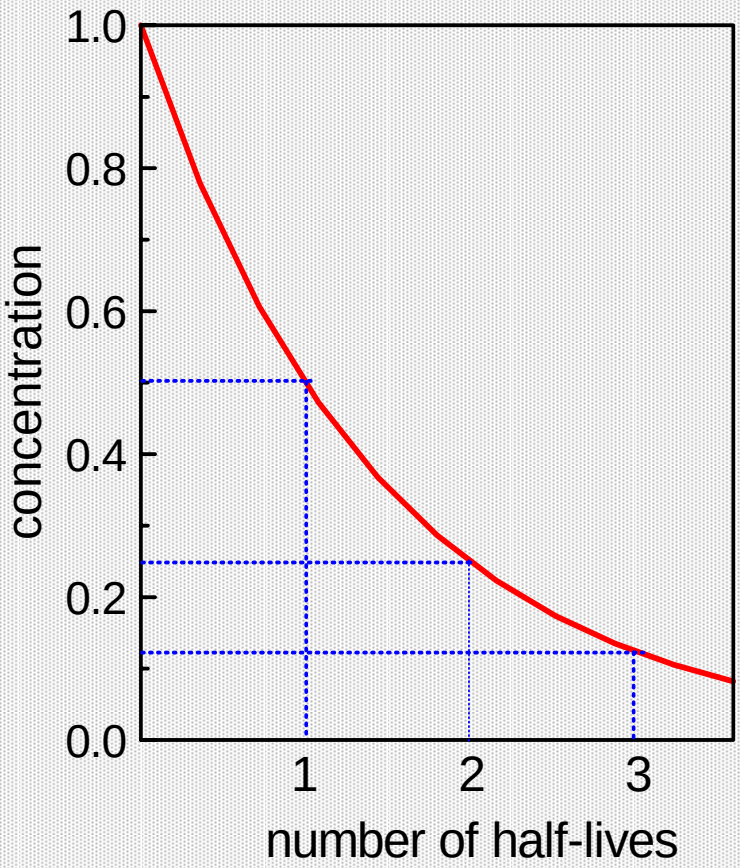


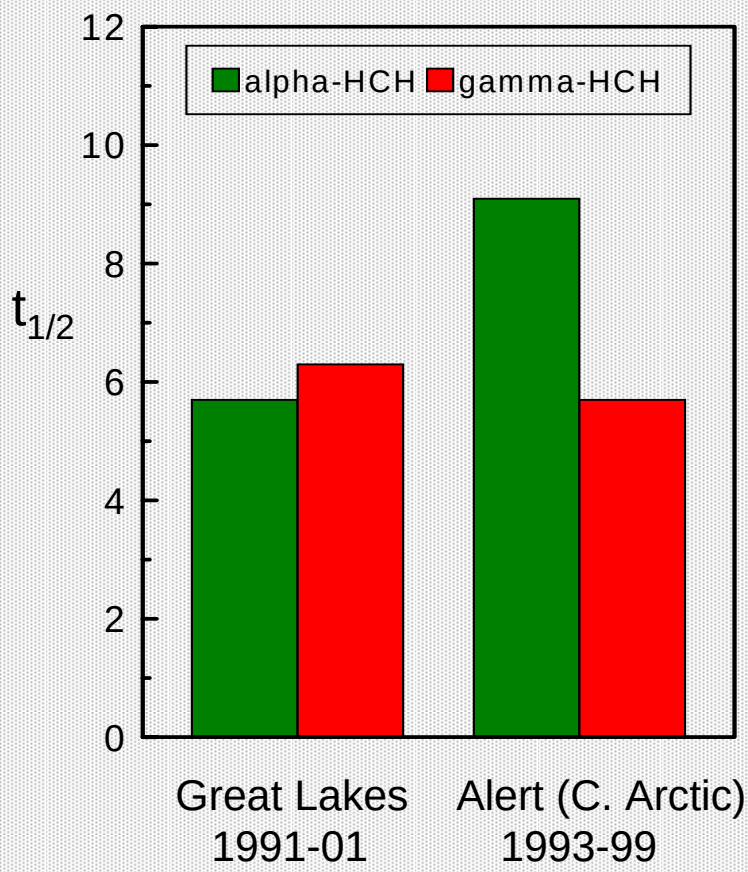

β-HCH in seawater
Bering Strait
ng/L
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
70
80
90
Latitude (°N)


α-HCH in seawater
Bering Strait
ng/L
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90

In recent years, HCHs in air continue to decline slowly

Times for 50% decrease ($t_{1/2}$, years)





Buehler et al., Environmental Science & Technology, 2004
Hung et al., Science of the Total Environment, 2004 (submitted)

Degradation in Water

Chemical degradation depends on temperature and pH

(B. Ngabe et al., Environmental Science & Technology, 1993)

Half lives (years) at pH = 8 (seawater, Great Lakes)

	25 °C	0 °C
alpha-HCH	0.5	80
gamma-HCH	0.7	135

In addition to "cold condensation", slower degradation also accounts for higher concentrations in the Arctic Ocean

Microbial Degradation is Faster!

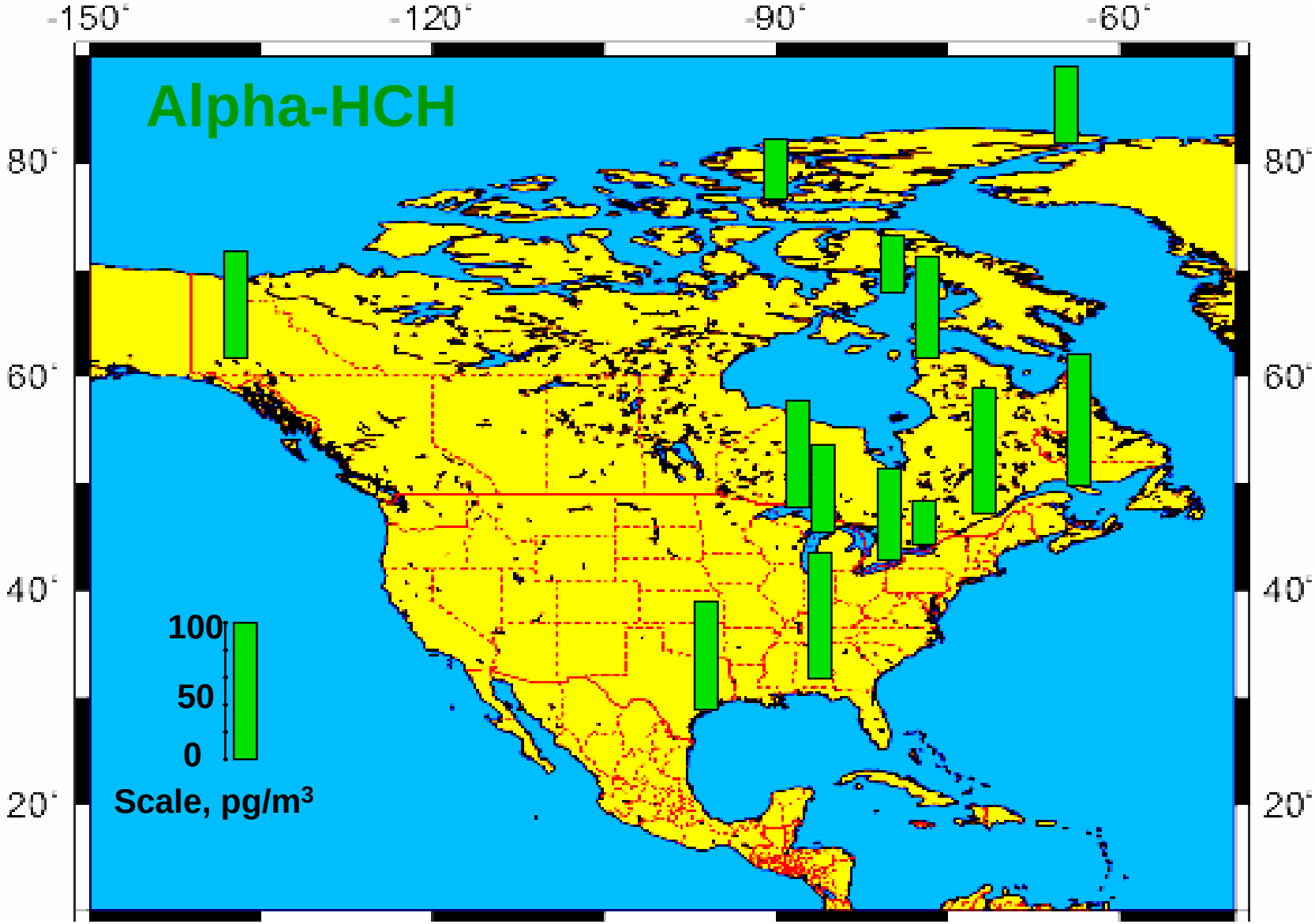
Microbial degradation rates the eastern Arctic Ocean

(T. Harner et al., Environmental Science & Technology, 1999; Geophysical Research Letters, 2000)

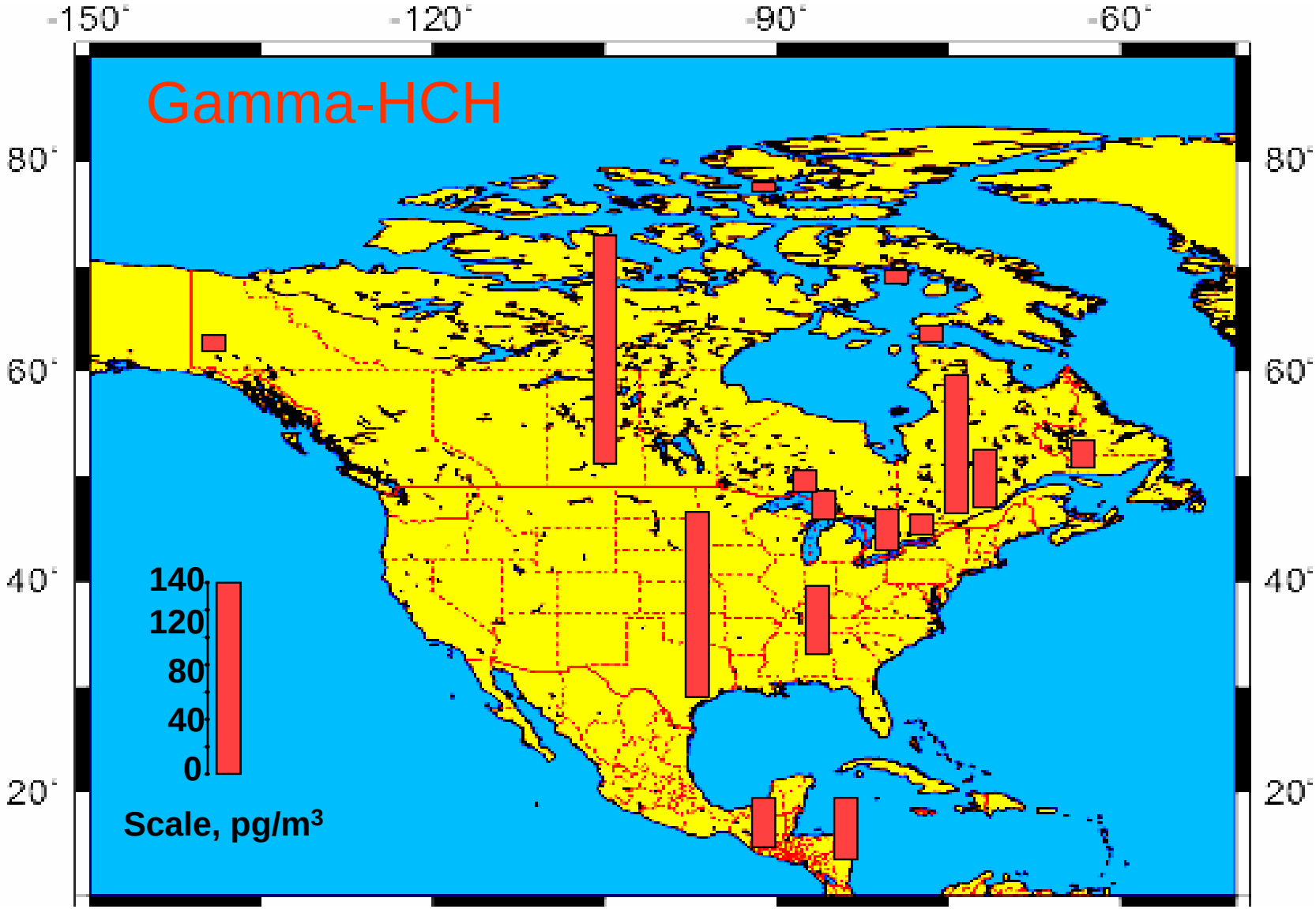
Half lives (years) in arctic water:

	Microbial	Chemical
alpha-HCH	6 - 23	80
gamma-HCH	19	135

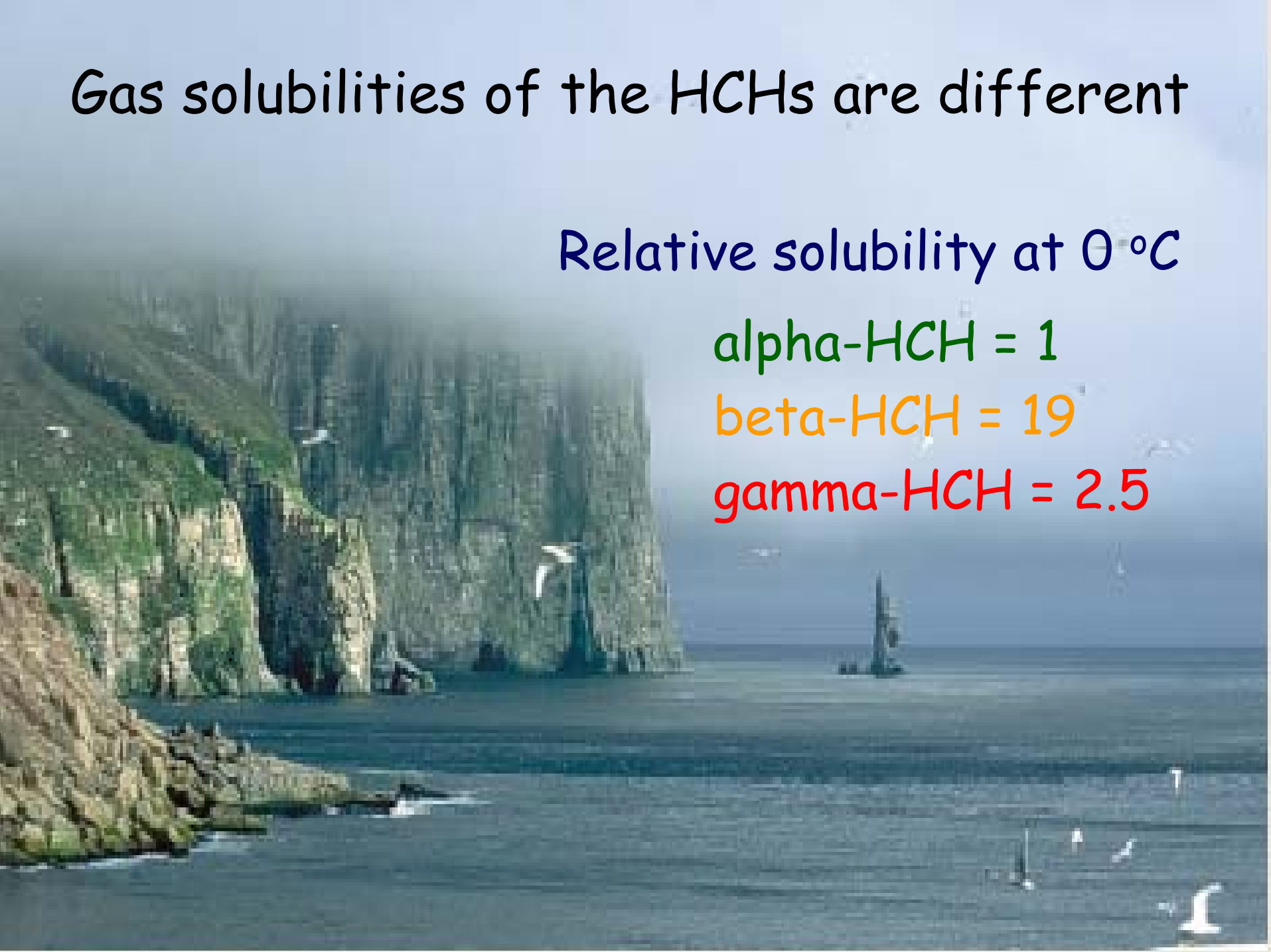
Measured concentrations in ambient air



Measured concentrations in ambient air



Gas solubilities of the HCHs are different



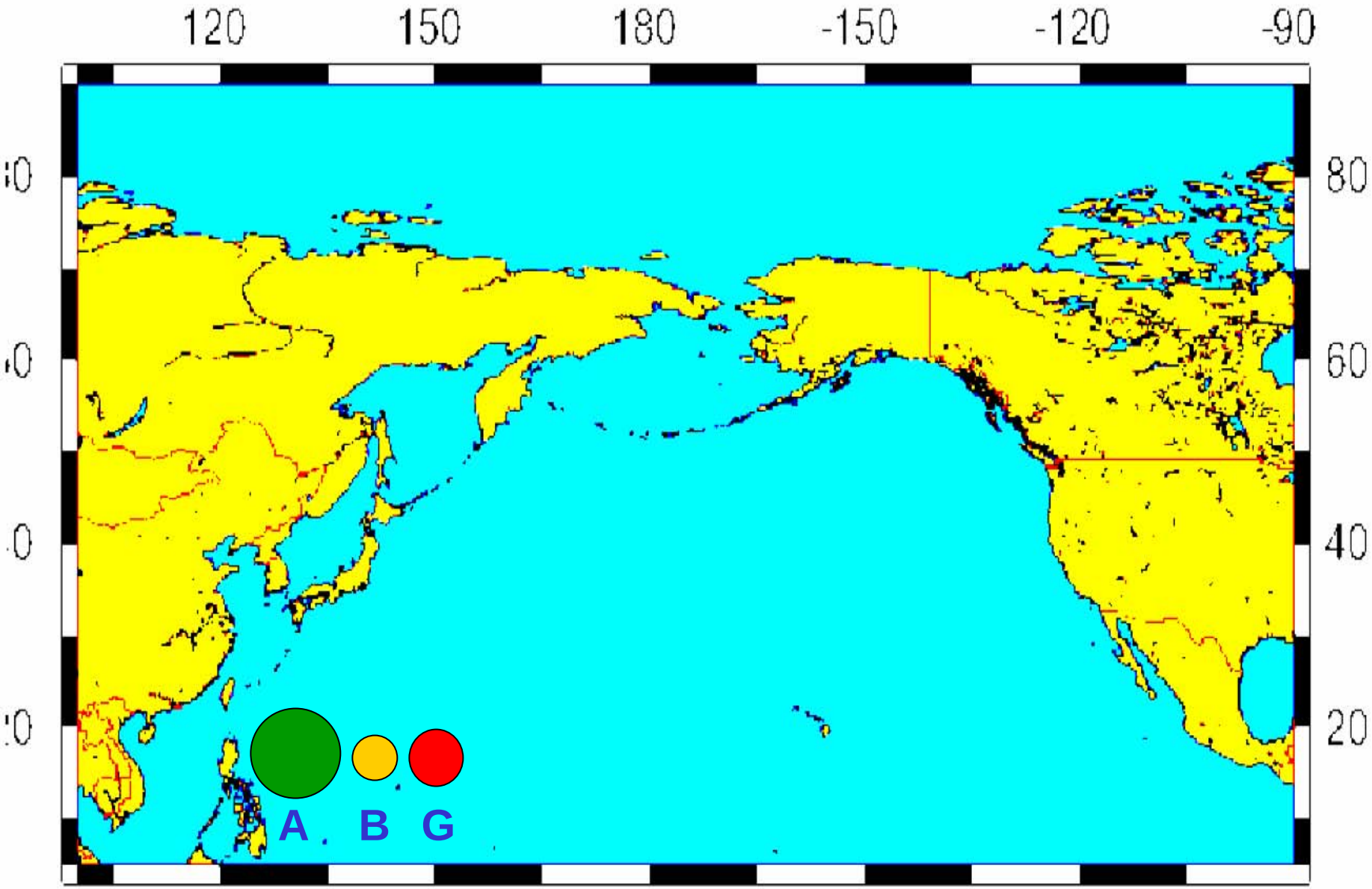
Relative solubility at 0 °C

alpha-HCH = 1

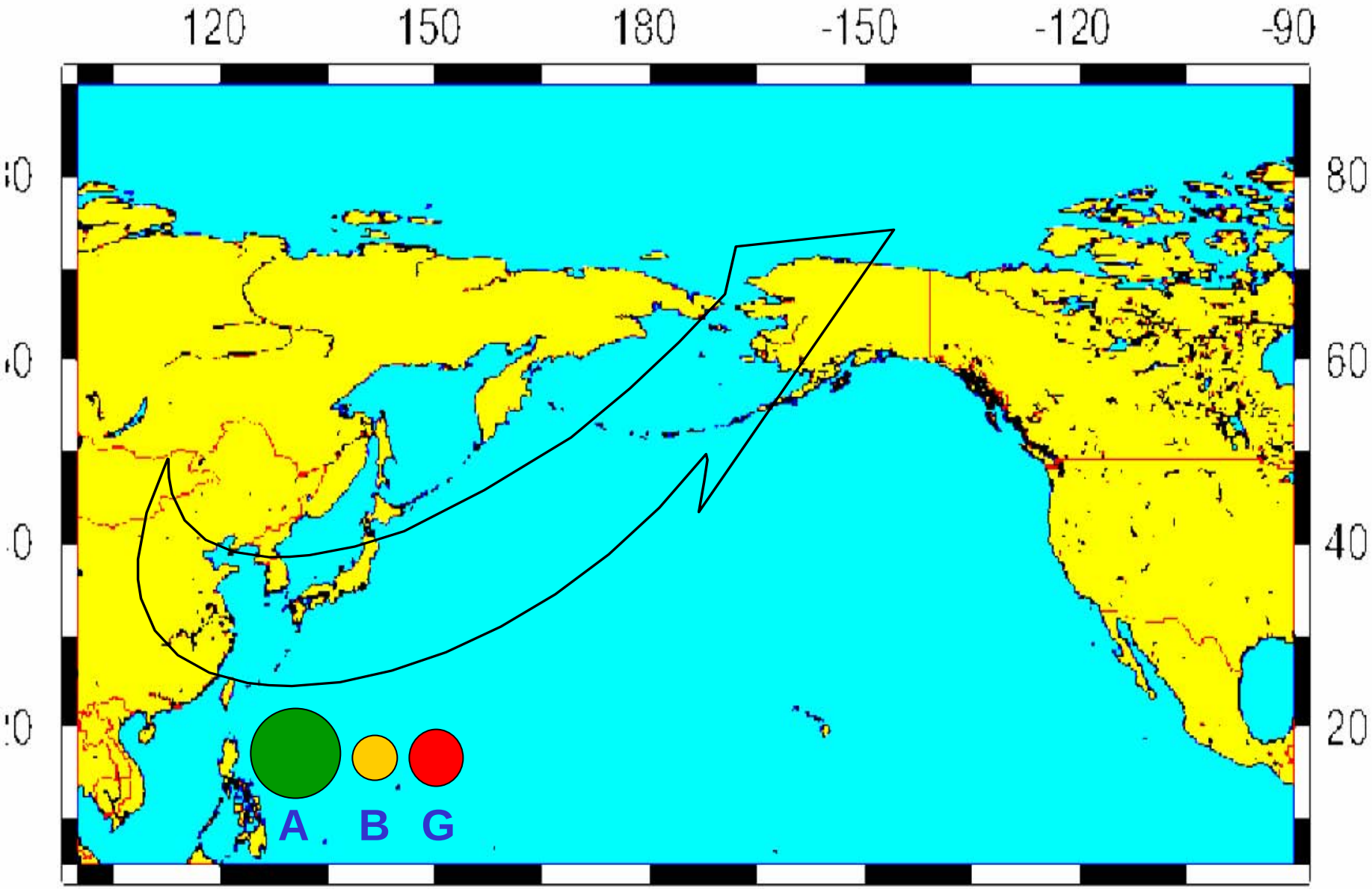
beta-HCH = 19

gamma-HCH = 2.5

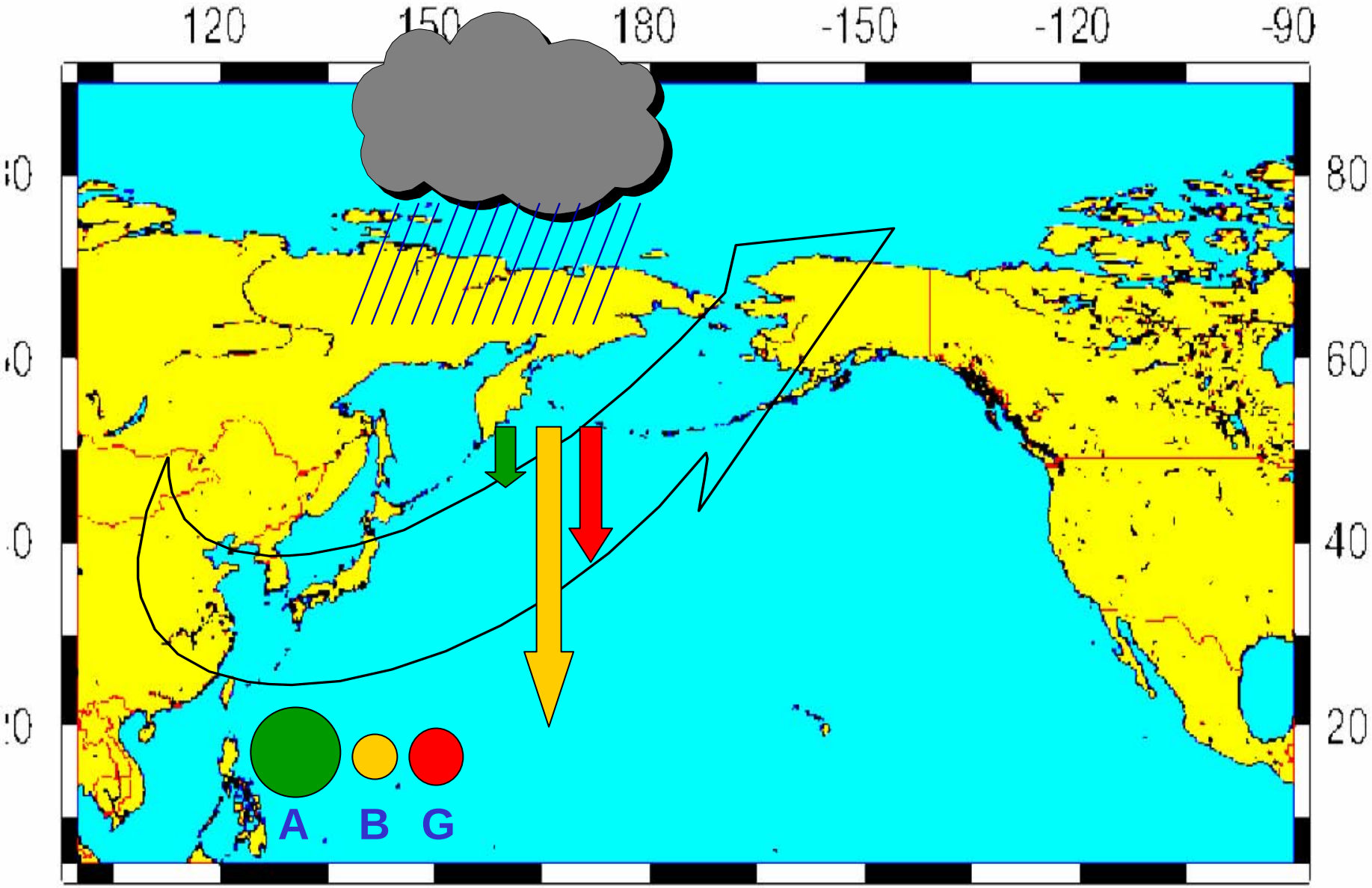
Air transport of technical HCH from Asian source regions



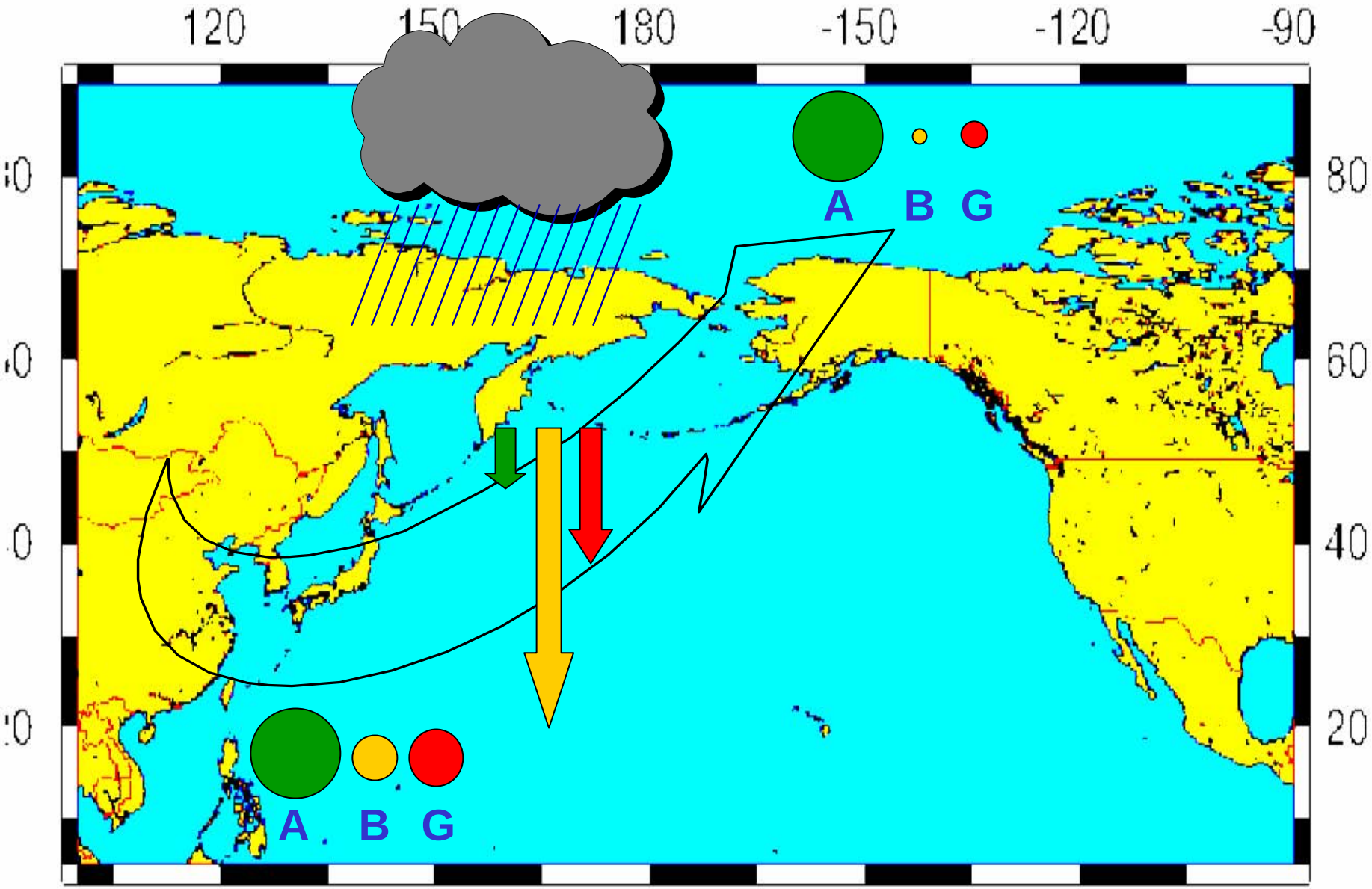
Air transport of technical HCH from Asian source regions



Fractionation of the HCHs
different solubilities in rain and seawater



Result: different proportions of HCHs in arctic air



Consequences

1. Screws up ability to distinguish lindane from technical HCH
2. HCHs deposited in northern seas flow into the Arctic Ocean

inflow →

circulation & outflow →

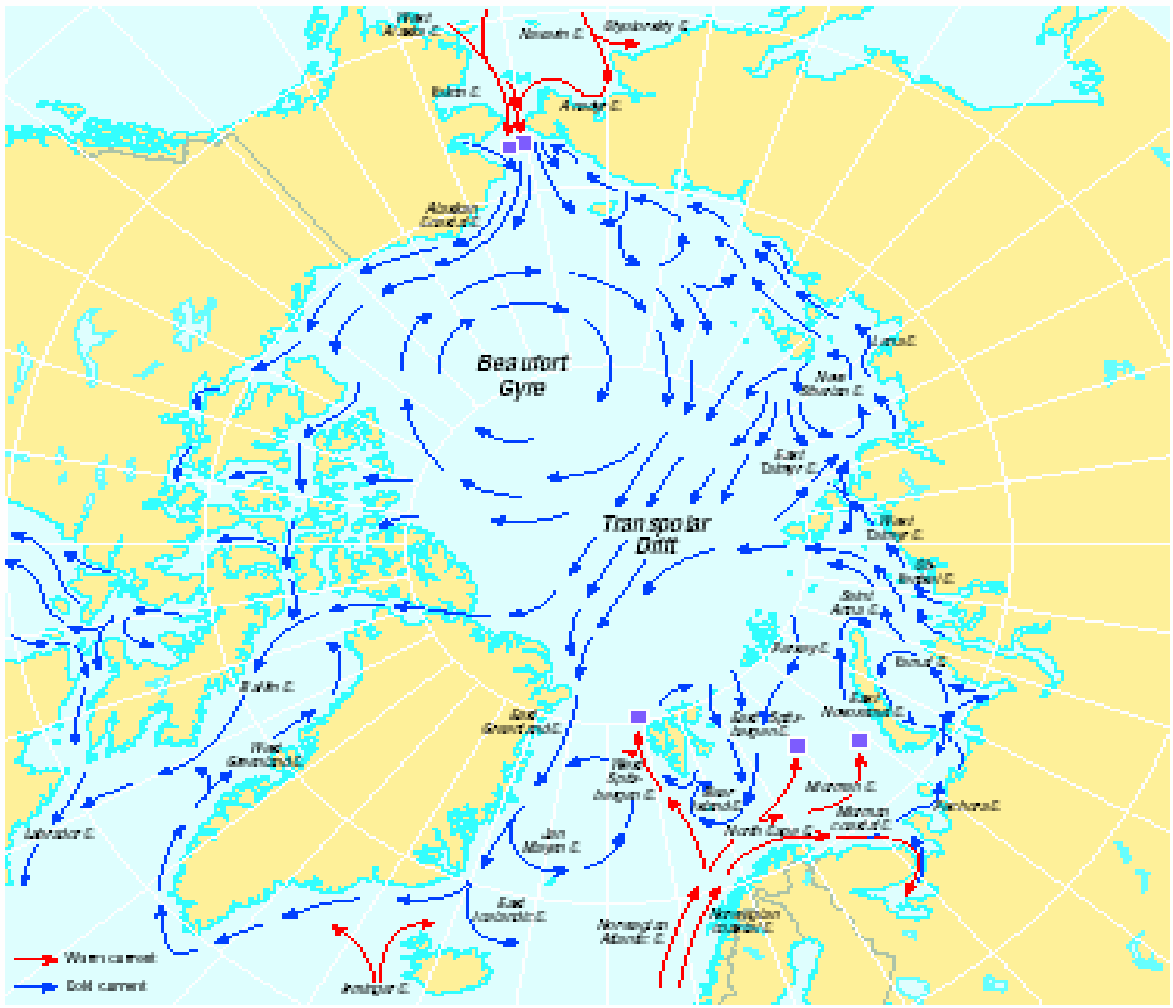


Figure 3-29. Surface currents in the Arctic region. Square boxes indicate that the denser inflowing (Atlantic and Pacific) waters are submerging under the Polar Surface Water. The continuation of these flows can be seen in Figure 3-27.