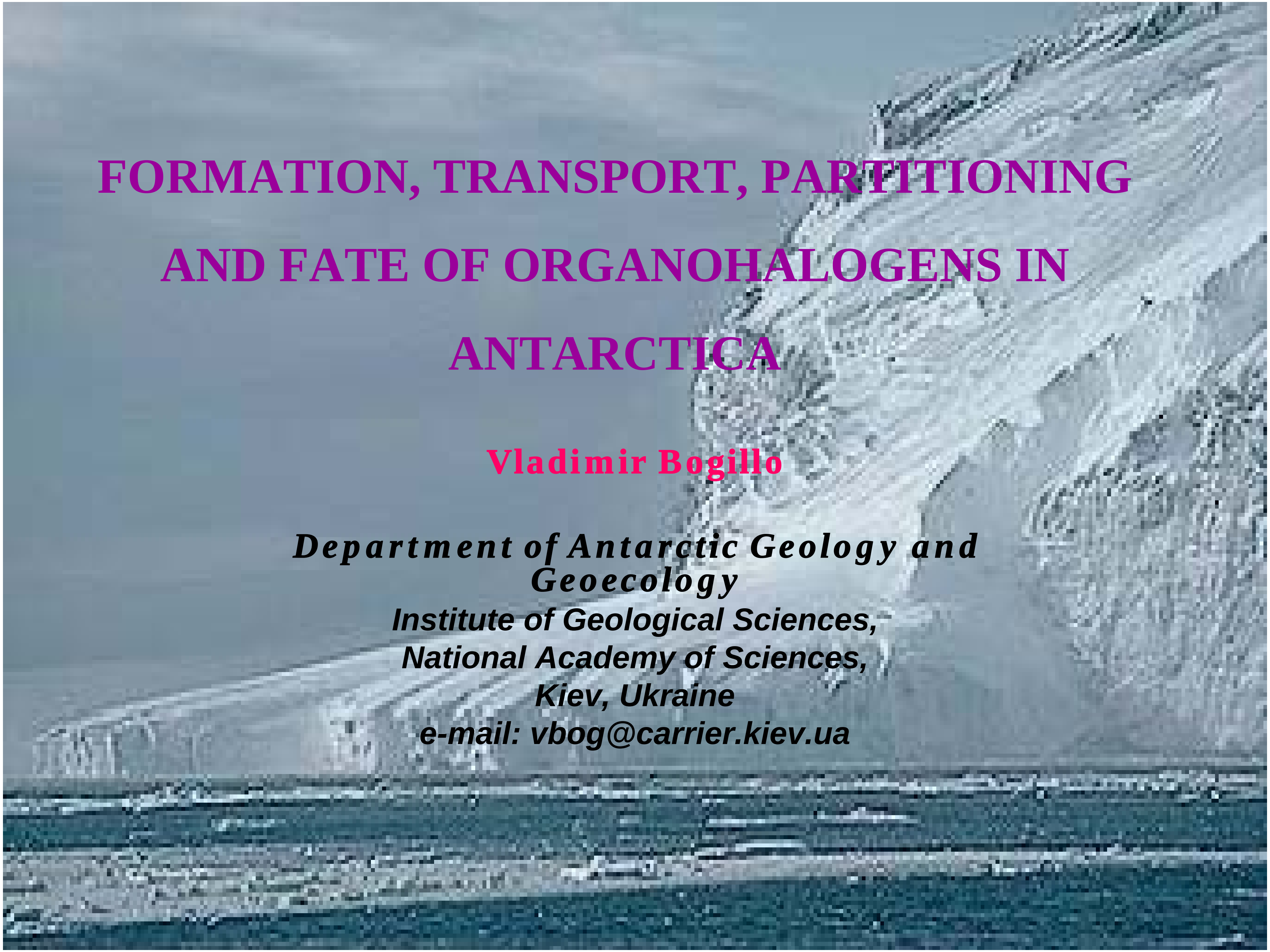

FORMATION, TRANSPORT, PARTITIONING AND FATE OF ORGANOHALOGENS IN ANTARCTICA

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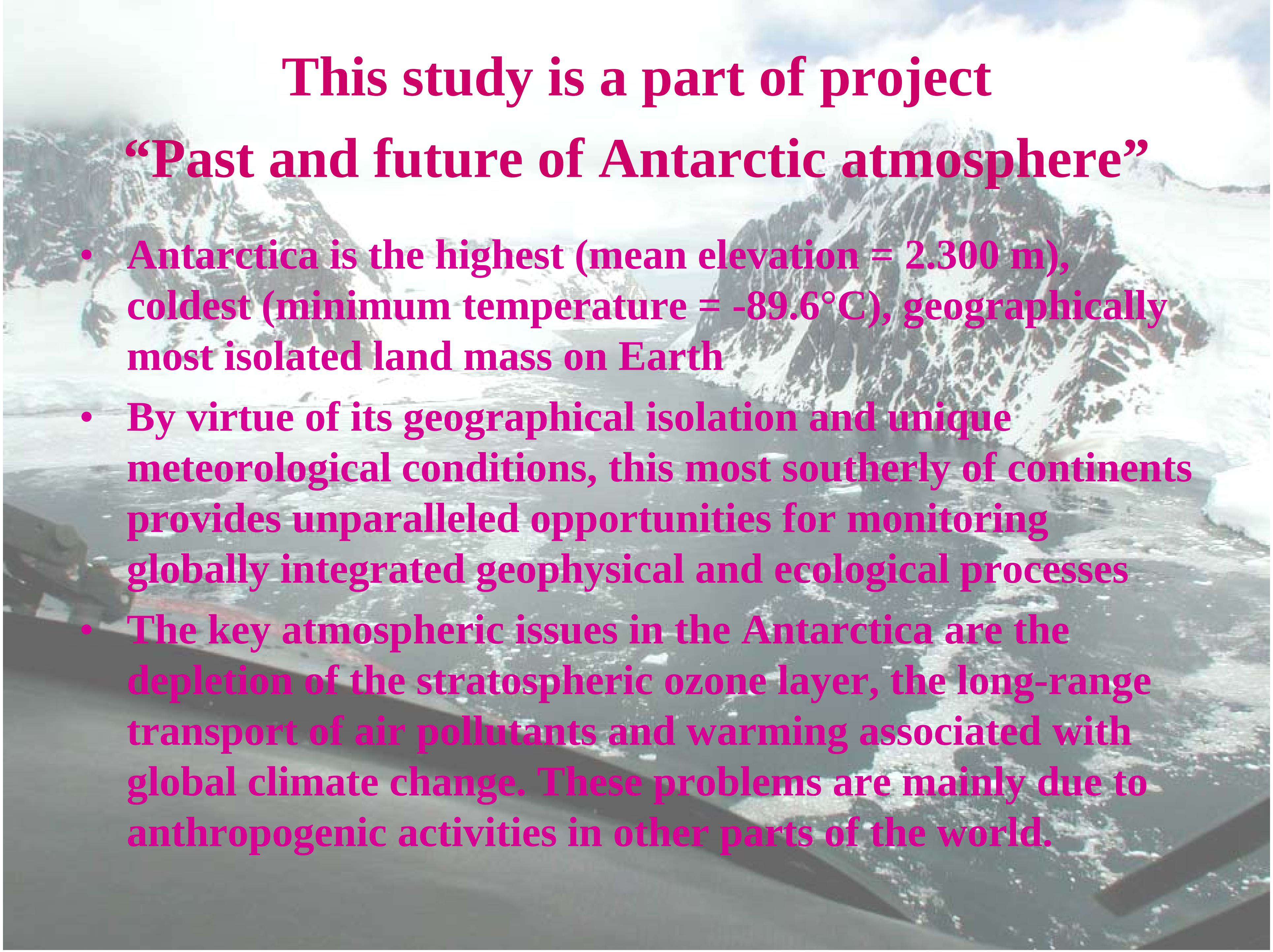
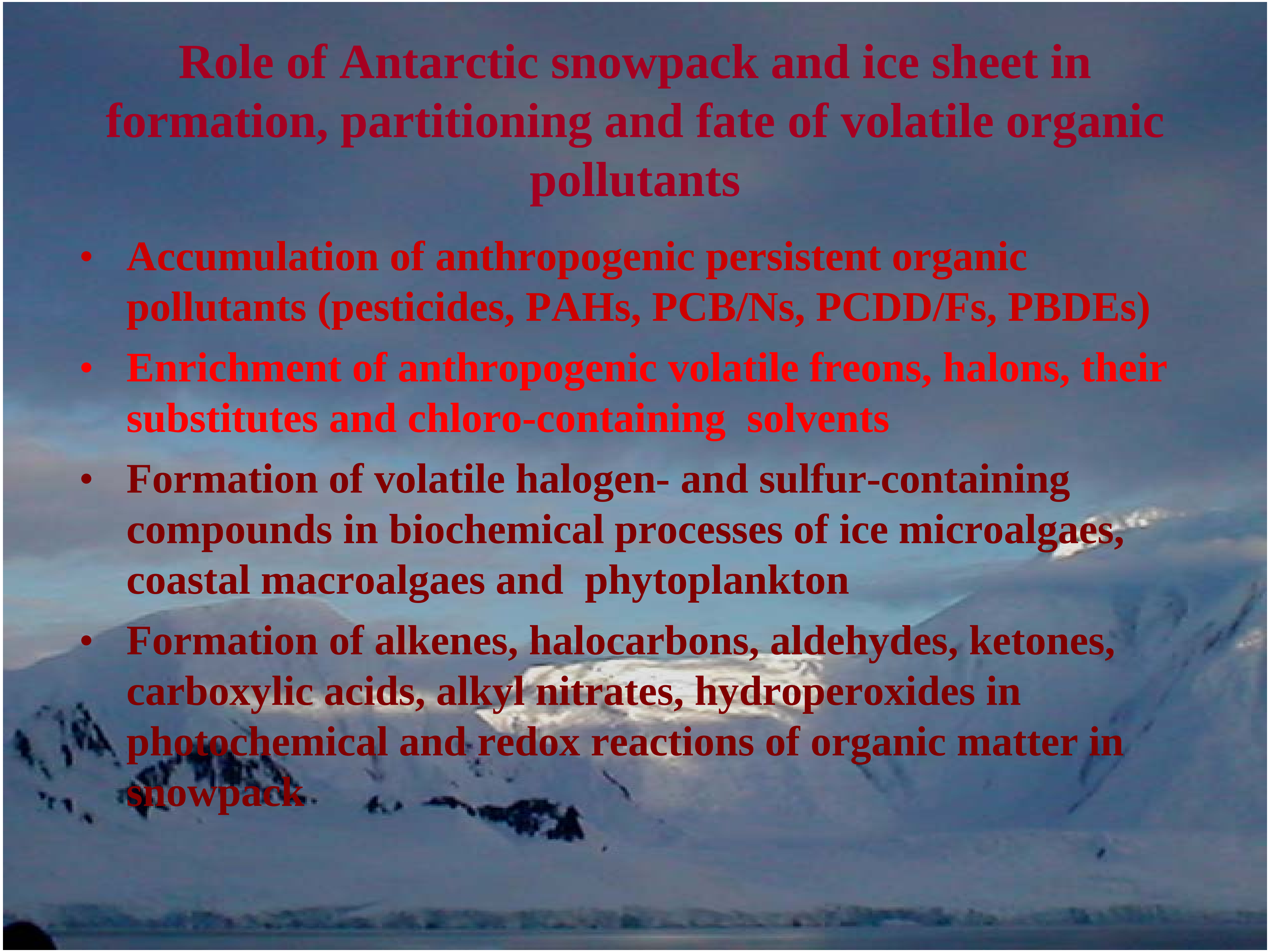


This study is a part of project “Past and future of Antarctic atmosphere”

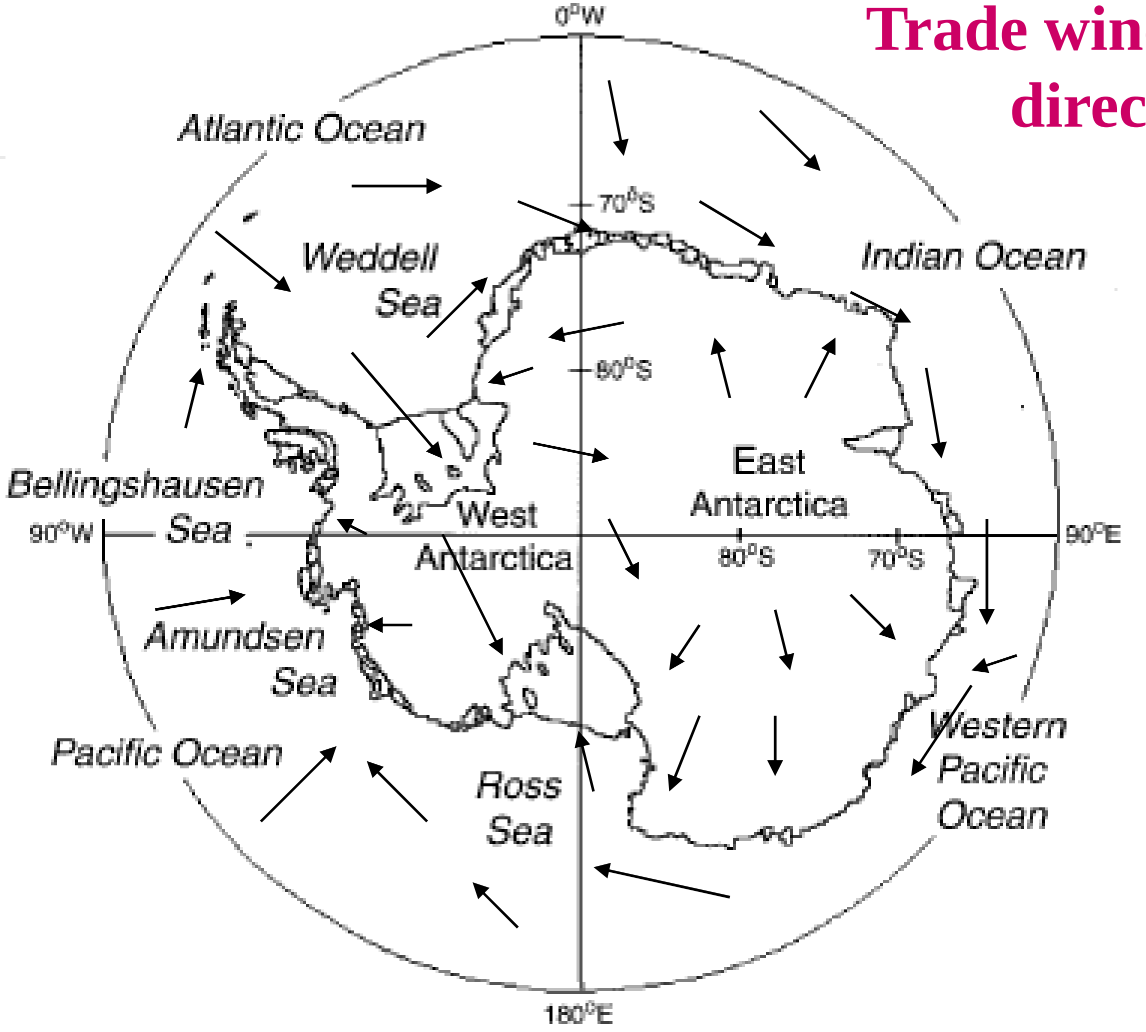
- Antarctica is the highest (mean elevation = 2.300 m), coldest (minimum temperature = -89.6°C), geographically most isolated land mass on Earth
- By virtue of its geographical isolation and unique meteorological conditions, this most southerly of continents provides unparalleled opportunities for monitoring globally integrated geophysical and ecological processes
- The key atmospheric issues in the Antarctica are the depletion of the stratospheric ozone layer, the long-range transport of air pollutants and warming associated with global climate change. These problems are mainly due to anthropogenic activities in other parts of the world.



Role of Antarctic snowpack and ice sheet in formation, partitioning and fate of volatile organic pollutants

- Accumulation of anthropogenic persistent organic pollutants (pesticides, PAHs, PCB/Ns, PCDD/Fs, PBDEs)
- Enrichment of anthropogenic volatile freons, halons, their substitutes and chloro-containing solvents
- Formation of volatile halogen- and sulfur-containing compounds in biochemical processes of ice microalgaes, coastal macroalgaes and phytoplankton
- Formation of alkenes, halocarbons, aldehydes, ketones, carboxylic acids, alkyl nitrates, hydroperoxides in photochemical and redox reactions of organic matter in snowpack

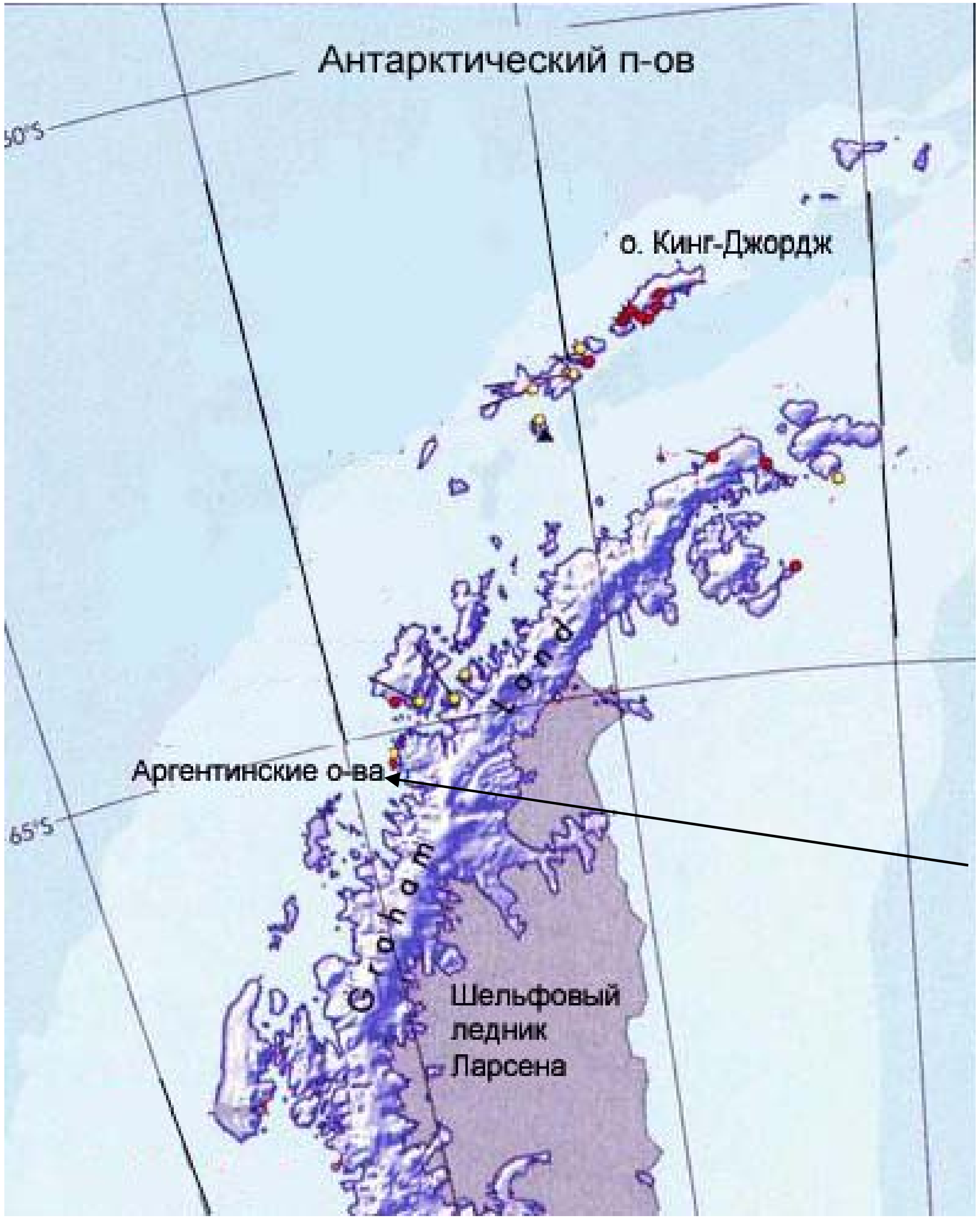
Transport of OCs to Antarctica

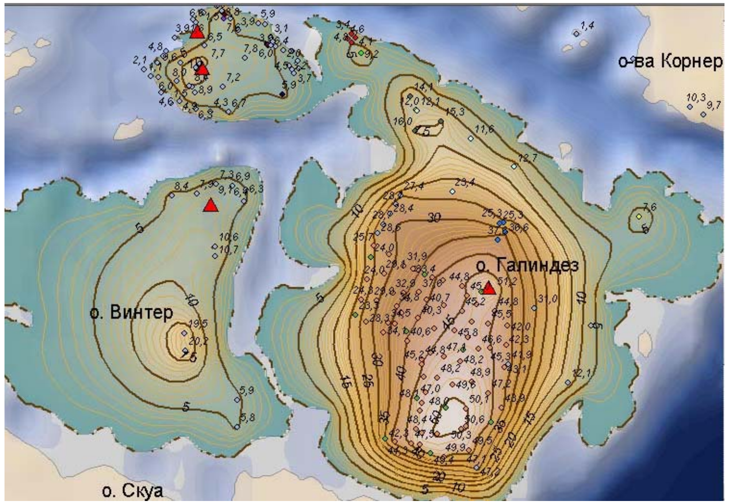


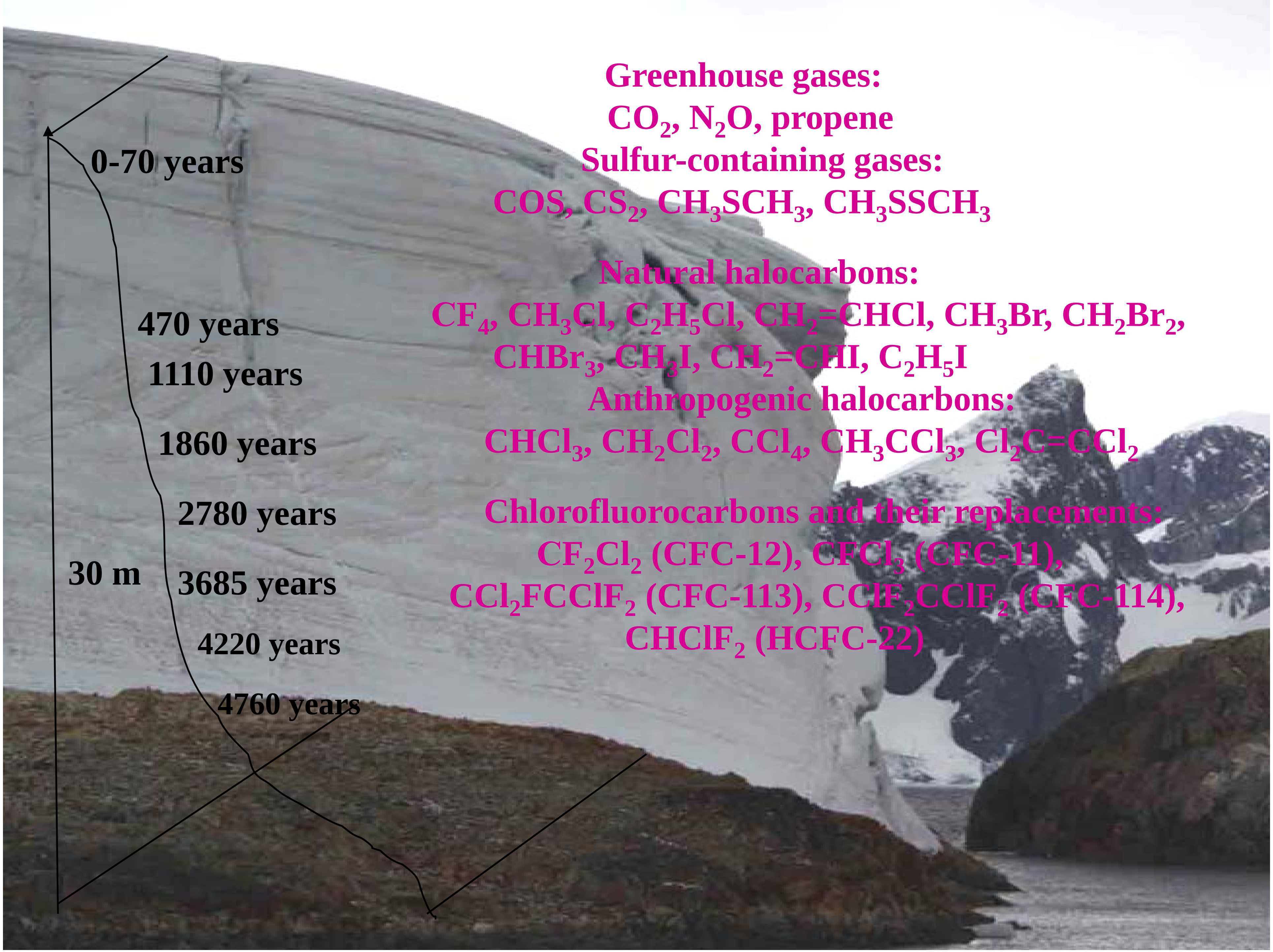
Trade winds and cyclones directions

Galindez island

65º 15’ S, 64º 16’ W



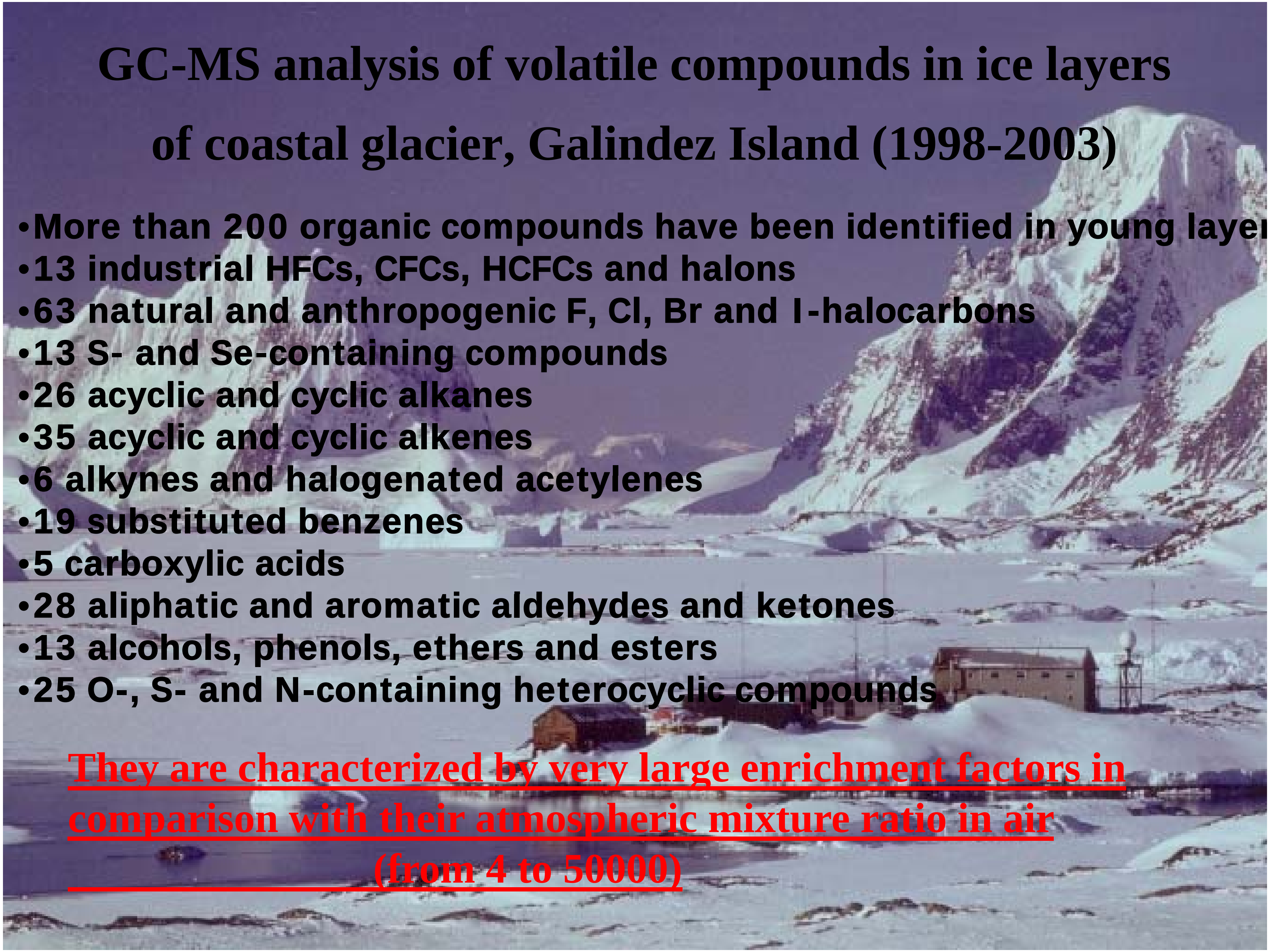




Greenhouse gases:
CO_2, N_2O, propene
Sulfur-containing gases:
COS, CS_2, CH_3SCH_3, CH_3SSCH_3

Natural halocarbons:
CF_4, CH_3Cl, C_2H_5Cl, $CH_2{=}CHCl$, CH_3Br, CH_2Br_2, $CHBr_3$, CH_3I, $CH_2{=}CHI$, C_2H_5I
Anthropogenic halocarbons:
$CHCl_3$, CH_2Cl_2, CCl_4, CH_3CCl_3, $Cl_2C{=}CCl_2$

Chlorofluorocarbons and their replacements:
CF_2Cl_2 (CFC-12), $CFCl_3$ (CFC-11), CCl_2FCClF_2 (CFC-113), $CClF_2CClF_2$ (CFC-114), $CHClF_2$ (HCFC-22)



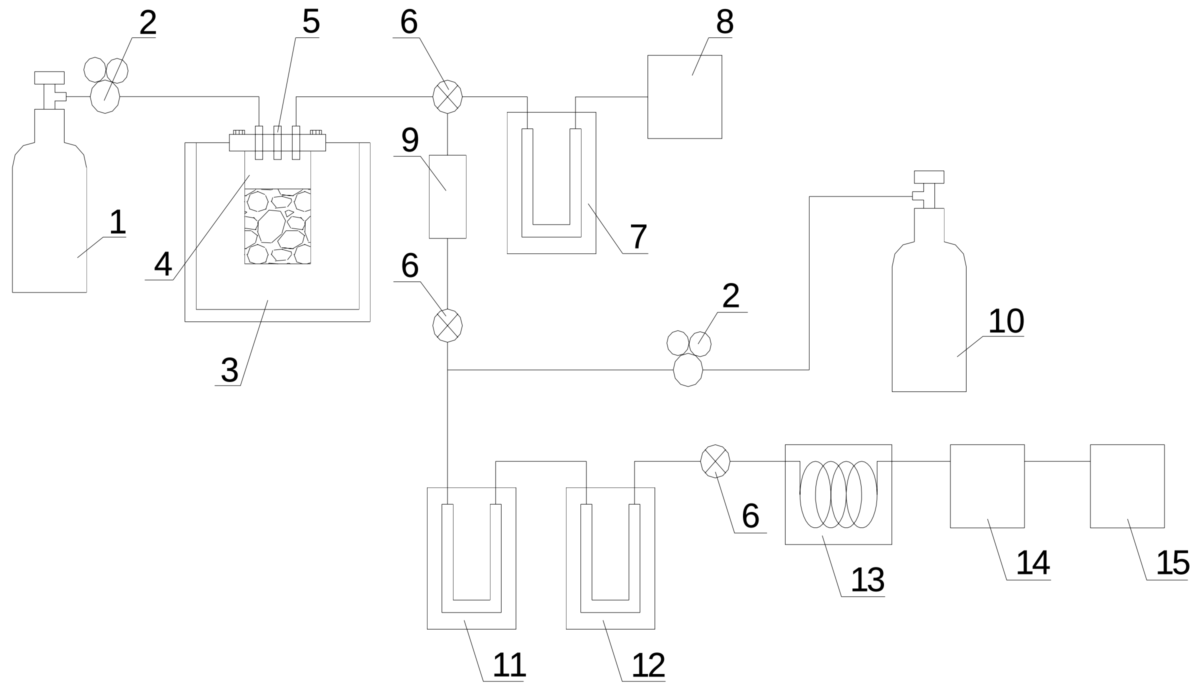
GC-MS analysis of volatile compounds in ice layers of coastal glacier, Galindez Island (1998-2003)

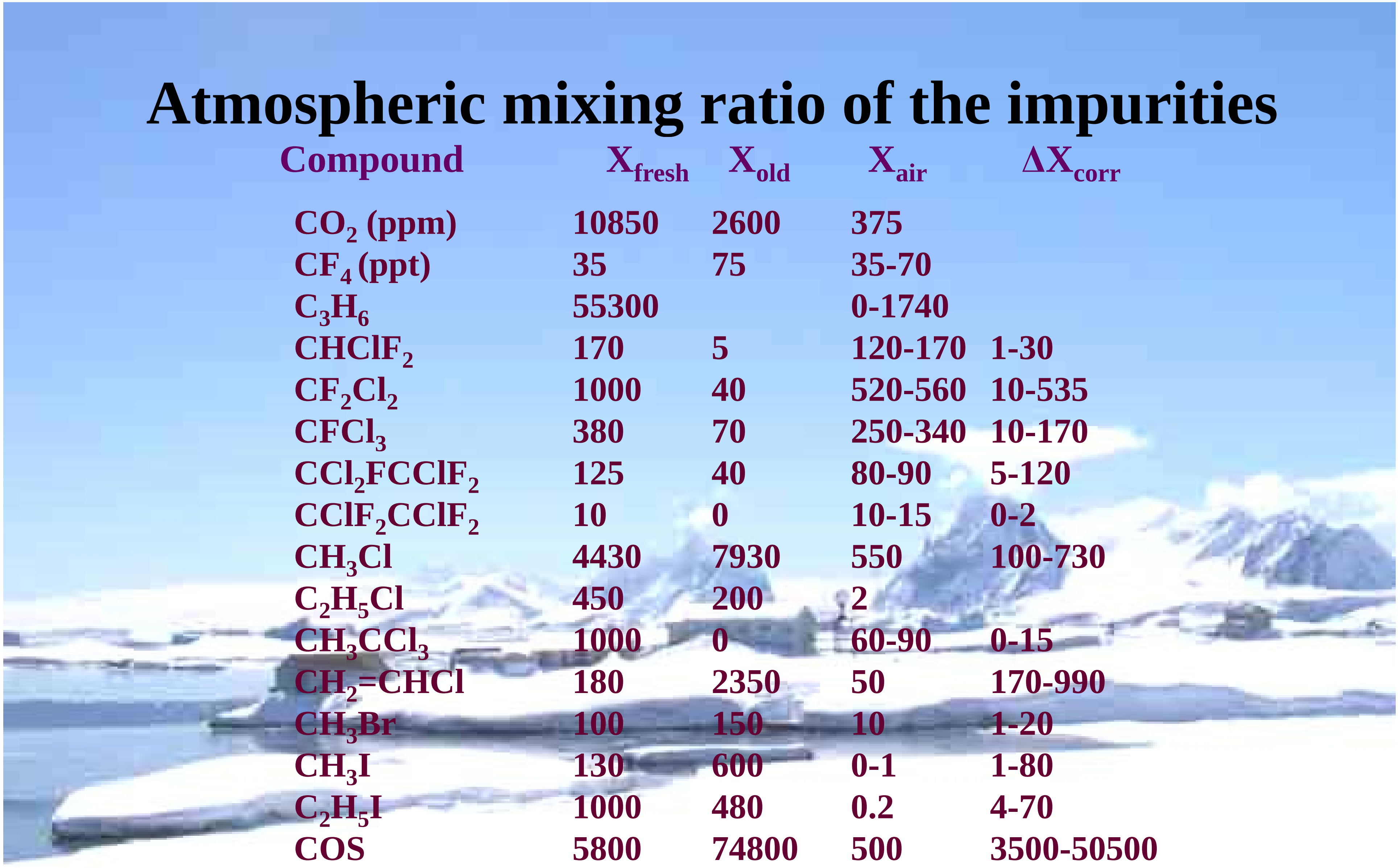
- More than 200 organic compounds have been identified in young layer
- 13 industrial HFCs, CFCs, HCFCs and halons
- 63 natural and anthropogenic F, Cl, Br and I-halocarbons
- 13 S- and Se-containing compounds
- 26 acyclic and cyclic alkanes
- 35 acyclic and cyclic alkenes
- 6 alkynes and halogenated acetylenes
- 19 substituted benzenes
- 5 carboxylic acids
- 28 aliphatic and aromatic aldehydes and ketones
- 13 alcohols, phenols, ethers and esters
- 25 O-, S- and N-containing heterocyclic compounds

They are characterized by very large enrichment factors in comparison with their atmospheric mixture ratio in air (from 4 to 50000)

Wet extraction, cryofocusing, thermal desorption and GC-MS analysis

of the volatile impurities in the ice blocks

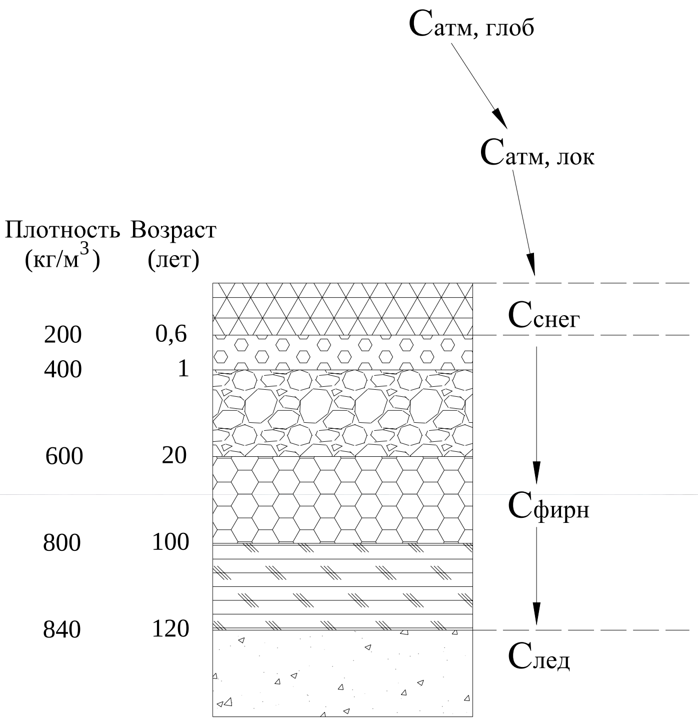




Atmospheric mixing ratio of the impurities

Compound	X_{fresh}	X_{old}	X_{air}	ΔX_{corr}
CO_2 (ppm)	10850	2600	375	
CF_4 (ppt)	35	75	35-70	
C_3H_6	55300		0-1740	
$CHClF_2$	170	5	120-170	1-30
CF_2Cl_2	1000	40	520-560	10-535
$CFCl_3$	380	70	250-340	10-170
CCl_2FCClF_2	125	40	80-90	5-120
$CClF_2CClF_2$	10	0	10-15	0-2
CH_3Cl	4430	7930	550	100-730
C_2H_5Cl	450	200	2	
CH_3CCl_3	1000	0	60-90	0-15
$CH_2{=}CHCl$	180	2350	50	170-990
CH_3Br	100	150	10	1-20
CH_3I	130	600	0-1	1-80
C_2H_5I	1000	480	0.2	4-70
COS	5800	74800	500	3500-50500
CS_2	16800	6700	2-20	140-1900
CH_3SCH_3	12000		10-600	
CH_3SSCH_3	44000		2-300	

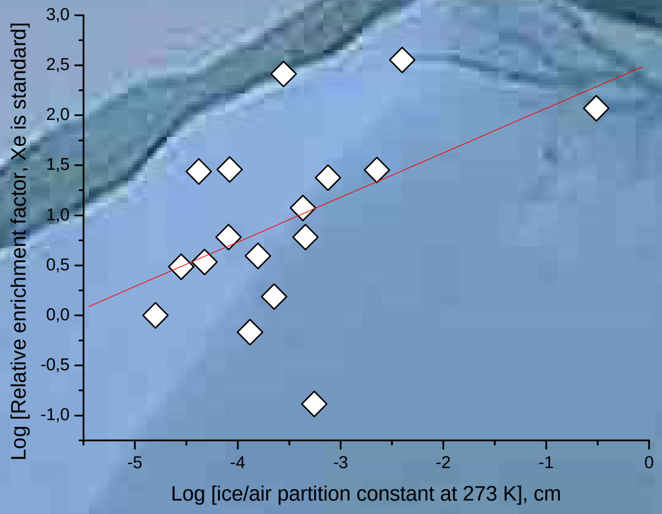
Change of concentrations for volatile atmospheric impurities after their deposition on snow surface and during snow metamorphism



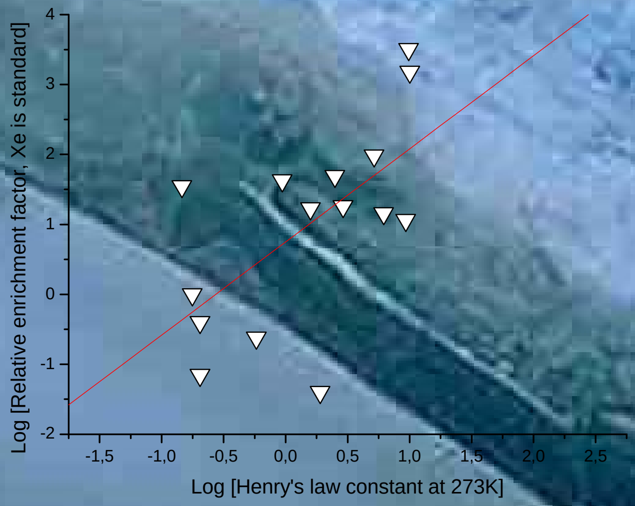
- Snowpack includes three phases: solid ice, water and airs
- Three main parameters determine behavior of chemical in snowpack: vapor pressure, water/air partition coefficient (Henry law constant) and ice surface/air partition coefficient
- One of possible reason of the enrichment in the warm glacier may be dissolution of the gases in meltwater percolating through the underlying firn layers, subsequent refreezing of the enriched solution during cold season and repeating of the melt-freeze cycles
- The dependence of CO_2 enrichment factor on age of the ice reflects the number and intensity of repetitive melt-freeze cycles, the enrichment has maximum in young ice and this correlates well with climatic history of coastal Western Antarctica
- However, the enrichment for most other species decreases as this value grows for CO_2. Even corrected on the solubility in meltwater, the content of the species is in large excess in comparison with their atmospheric level

Influence of the solubility in water and adsorption on ice/air interface in ice samples on enrichment coefficients of the impurities

70 years



4000 years



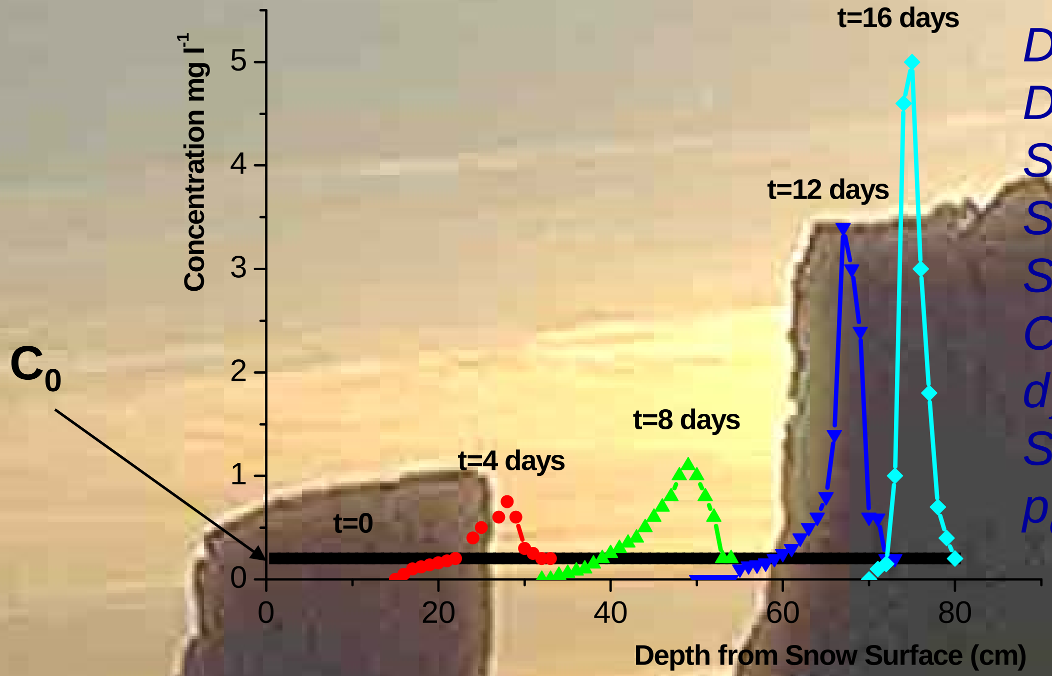
$\ln F = 0.5\times\ln H + 0.3\times\ln K_{IA} + 4.2$

(R = 0.639)

$\ln F = 0.9\times\ln H + 0.4\times\ln K_{IA} + 4.9$

(R = 0.699)

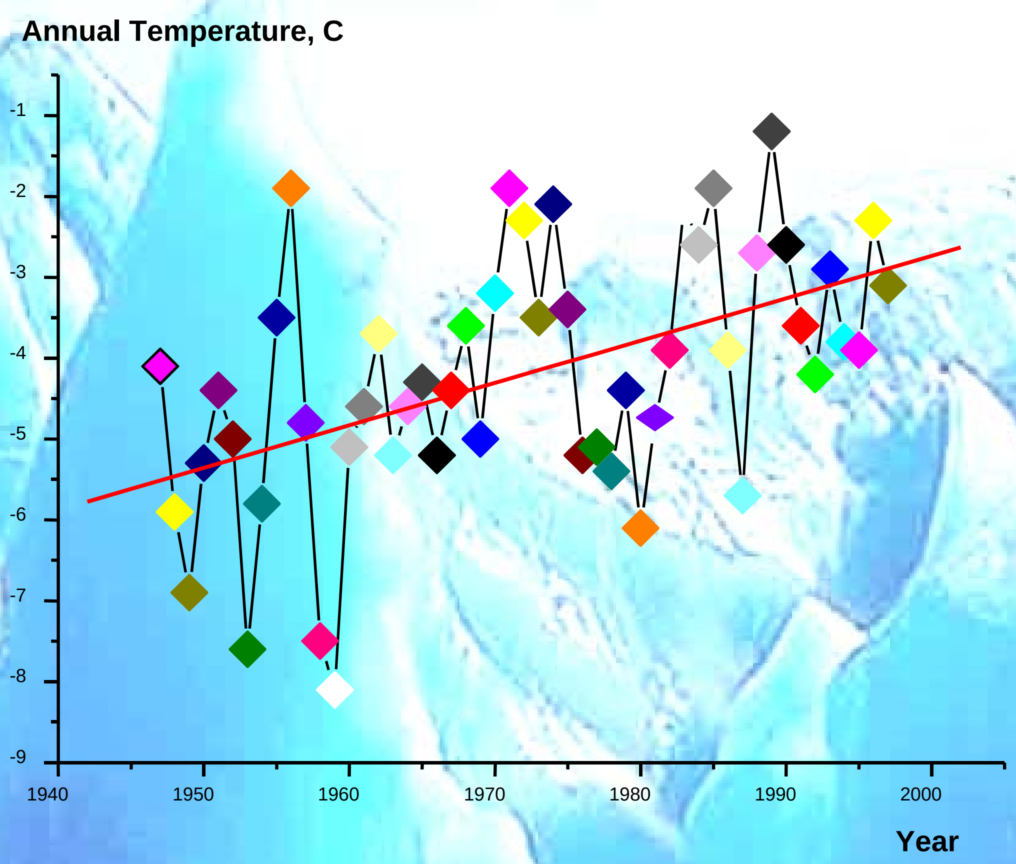
Simulation of enrichment for soluble impurities in snowpack



Depth: 80 cm
Diameter of grains: 5 mm
Snow density: 0.275 g/cm^3
Snow porosity: 0.70
Snow temperature: 272 K
$C_o = 0.2$ mg/l
$d_л = 0.917\ g/cm^3$
$S_0 = 0$
$p_c = -400\ N/m^2$
$g = 10\ m/s^2$, $d = 1.0\ g/cm^3$
$\sigma_0 = 0.0075$ N/m

Calculation of enrichment for water-soluble impurity in snowpack due to repetitive melting-freezing cycles during 20 days of warm season

TREND OF ANNUAL AIR TEMPERATURE (GALINDEZ, 1947 – 1997)



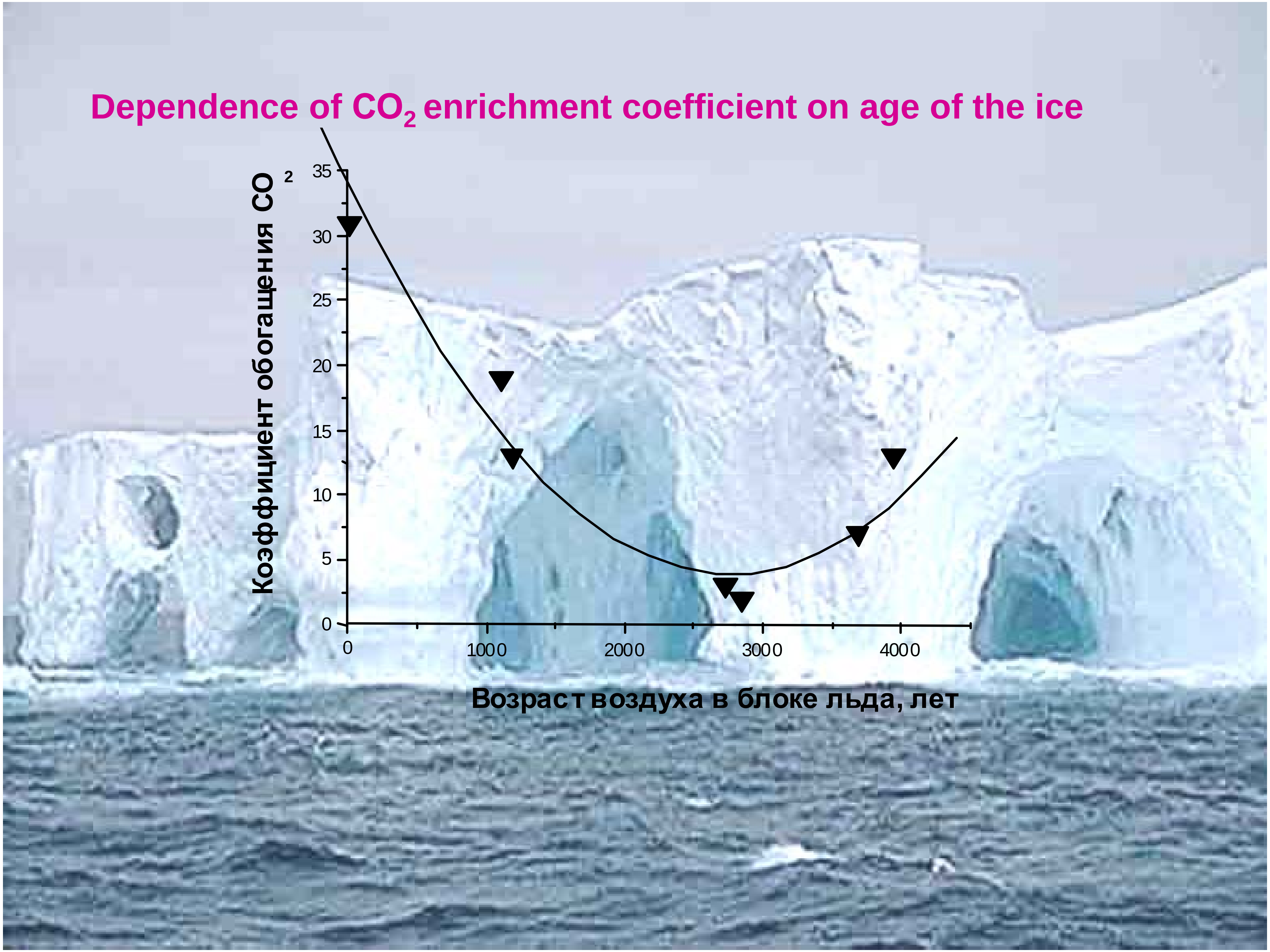
$$[Temperature, {}^{o}C] = (0.052 \pm 0.013) \times [Years] - (107.6 \pm 25.6)$$

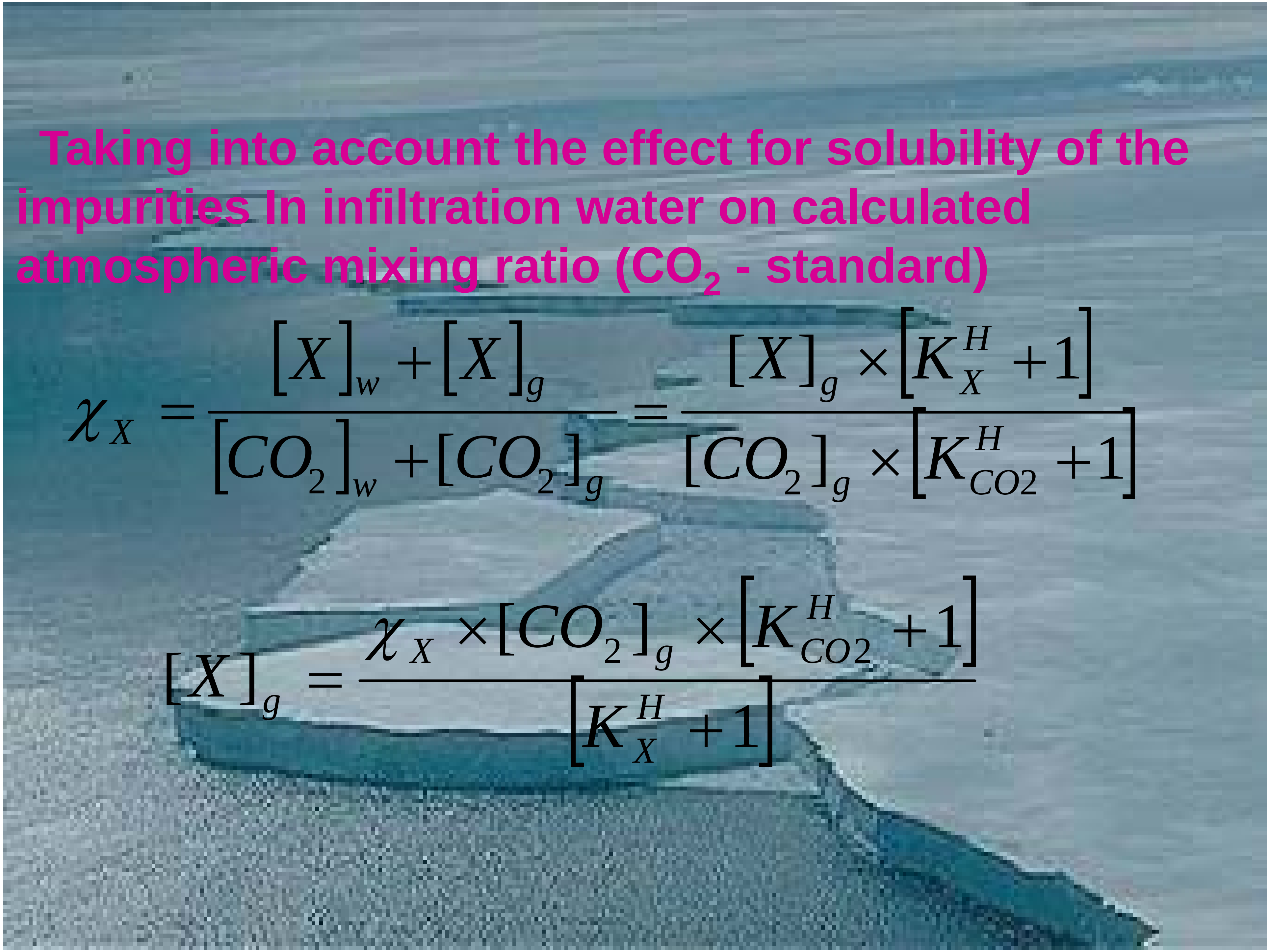
$$R = 0.4993; sd = 1.36651; N = 51; P = 0.000191$$

$$[RAIN] = (85.8 \pm 6.3) + (6.01 \pm 1.25) \times [TEMP]$$

$$R = 0.50047; sd = 39.74125; N = 71$$

Dependence of CO_2 enrichment coefficient on age of the ice





Taking into account the effect for solubility of the impurities In infiltration water on calculated atmospheric mixing ratio (CO_2 - standard)

$$\chi_X = \frac{[X]_w + [X]_g}{[CO_2]_w + [CO_2]_g} = \frac{[X]_g \times \left[K_X^H + 1\right]}{[CO_2]_g \times \left[K_{CO2}^H + 1\right]}$$

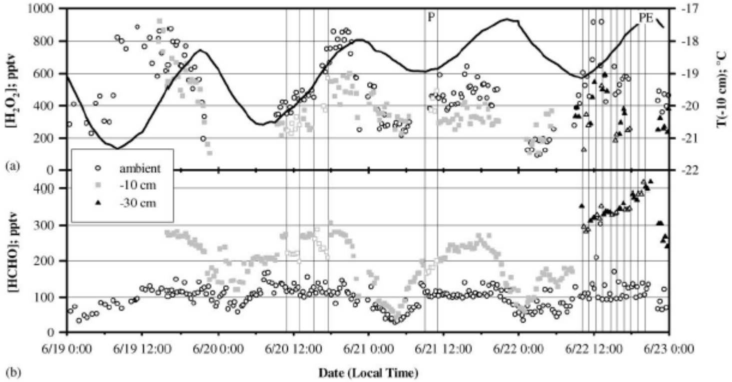
$$[X]_g = \frac{\chi_X \times [CO_2]_g \times \left[K_{CO2}^H + 1\right]}{\left[K_X^H + 1\right]}$$

High enrichment in firn and snowpack interstitial air was discovered during 1998-2008 years for many inorganic and organic compounds

- **NO, NO_2, $HONO$, (C1-C4)-$RONO_2$, $CH_3C(O)OONO_2$**
- **O_3, OH, HO_2, H_2O_2**
- **CO, $HCHO$, CH_3CHO, $(CH_3)_2C{=}O$, $C_2H_5C(O)CH_3$, $HCOOH$, CH_3COOH**
- **$CH_2{=}CH_2$, $CH_3CH{=}CH_2$, $CH_3CH_2CH{=}CH_2$**
- **BrO, CH_3Br, C_2H_5Br, CH_2Br_2, $CHBr_3$, $CHBrCl_2$, $CHBr_2Cl$, CH_3I, C_2H_5I, CH_2ClI**

Most of processes for the products formation are photochemically driven

F. Domine, P. Shepson,
Nature, 2002, v. 297, p. 1506



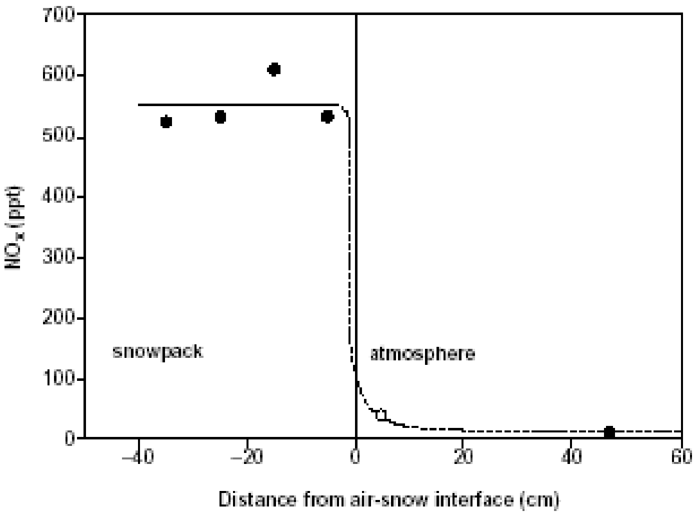
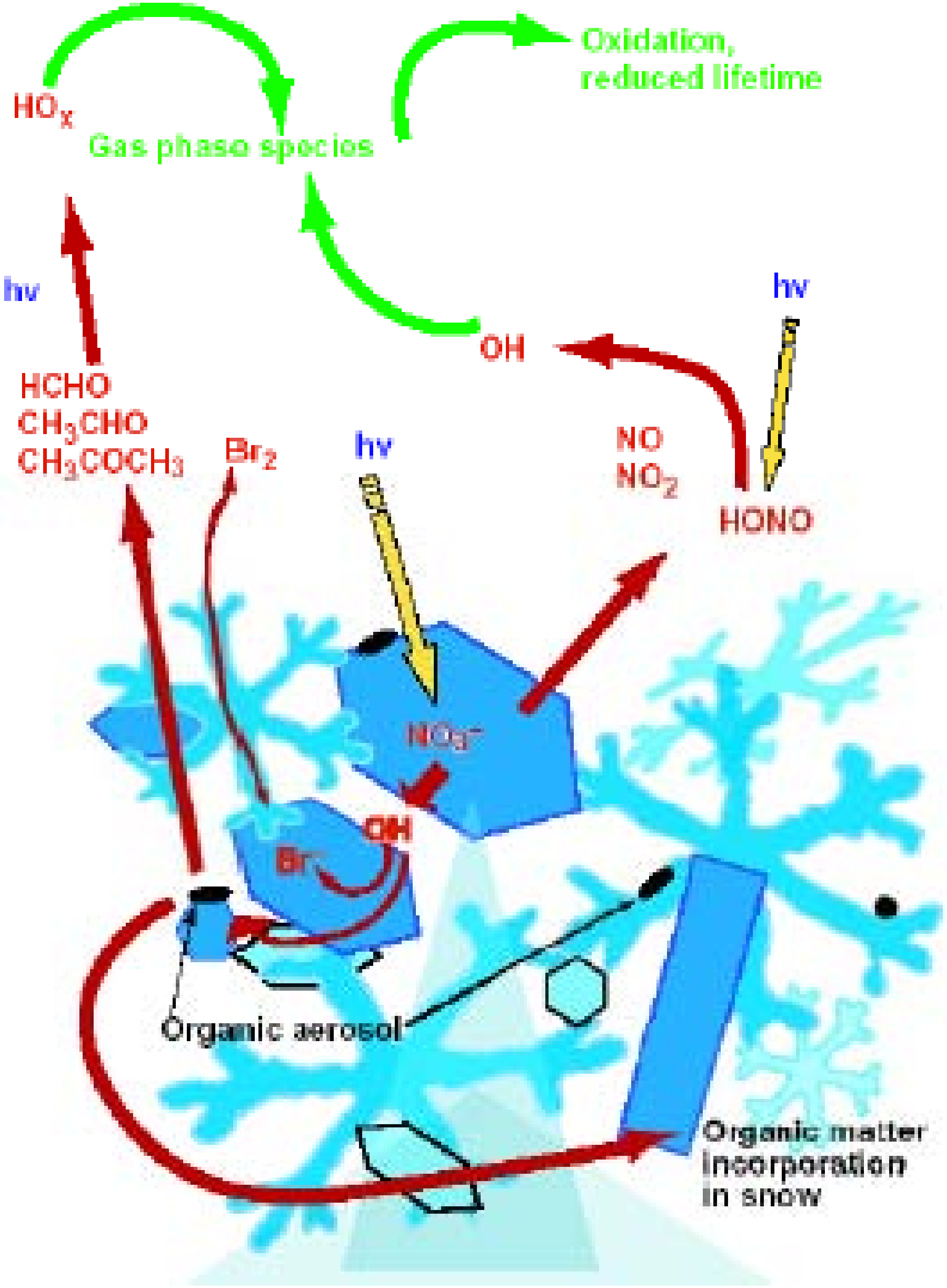


Fig. 2. Vertical profile of NO_x measured at Summit on 23 June 2000, showing that concentrations are much larger in the sunlit snowpack interstitial air than in the overlying atmosphere. The observed gradients result in fluxes of NO_x from the snow to the atmosphere. [Data from R. Honrath *et al.*, Michigan Tech Univ.]



Reactants in firn and snowpack

- **Inorganic aerosols (terrigenous, sea salts)→ NO_3^-, S^{2-}, Cl^-, Br^-, I^-; Fe^{n+}, Mn^{n+}, Cu^{n+}, Co^{n+}**
- **Organic aerosols from surface oceanic layer → phenols, hydroxyacetophenones, hydroxybenzaldehydes, carbohydrates, C8 – C18 – monoacids, C5 – C11 – diacids, amino acids, proteins**
- **Phytoplancton, ice microalgae, microbes**
- **O_2, O_3, OH, HO_2, HOCl, HOBr, HOI, ClO, BrO, IO, Cl, Br, I**

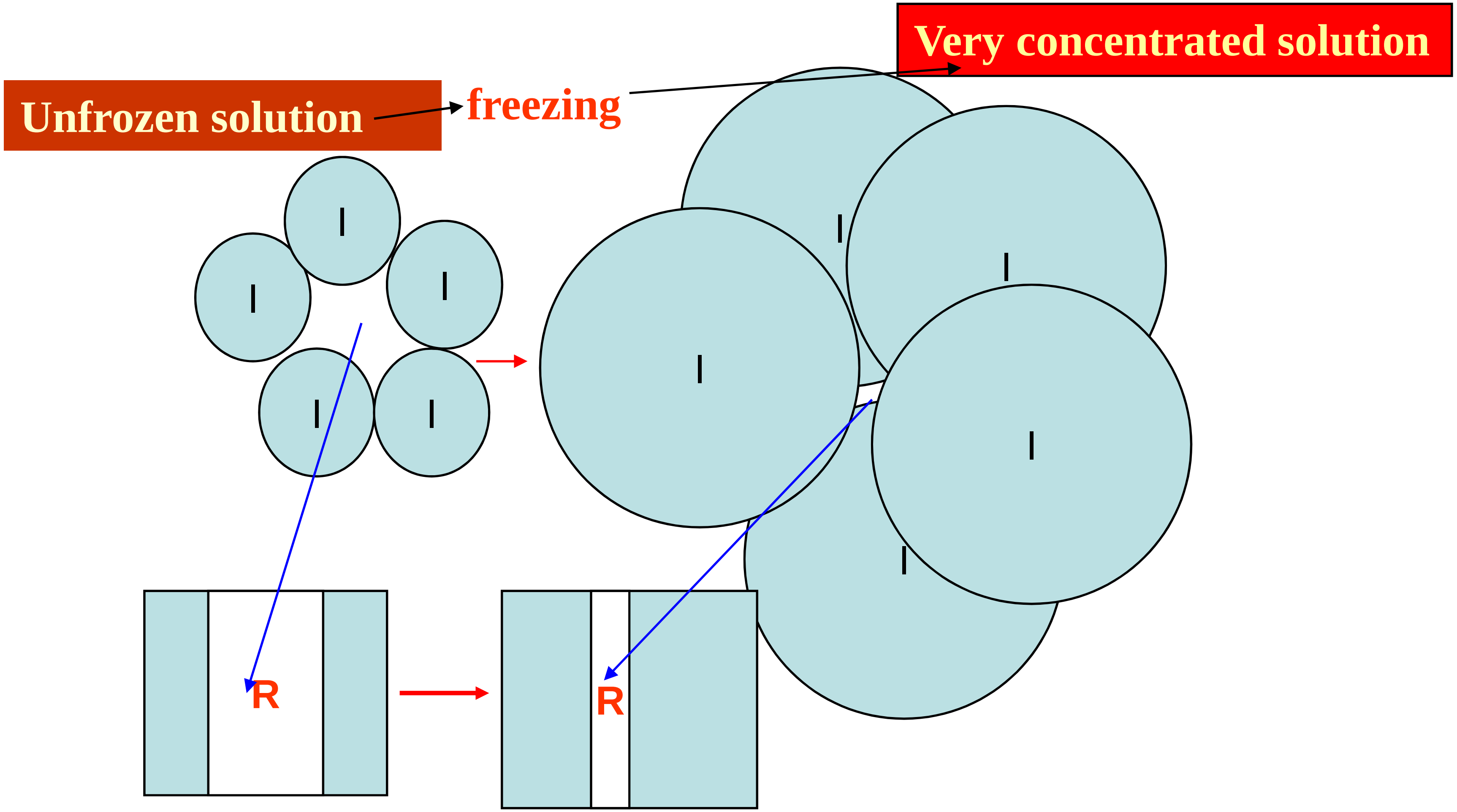
Pathways for the products formation:

- **Direct and indirect photolysis**
- **Radical reactions**
- **Ionic reactions**
- **Biochemical reactions**
- **Redox-reactions**

Phenomena occur in freezing of aqueous solutions and in snowpack:

- **freeze – concentration (segregation of reactants)**
- **freezing potential (up to 100 V)**
- **pH change (up to 4 pH units)**
- **concentration diffusion**
- **cage effect in recombination of ions and radicals**
- **formation of H-bonds, solvation and formation of ion pairs**
- **temperature and matrix effects (restricted diffusion and conformational mobility)**
- **high photochemically active medium → low activation barriers for photochemical formation of reactive species**
- **dispersion kinetics**

Acceleration of chemical reaction by freeze-concentration in polycrystalline ice



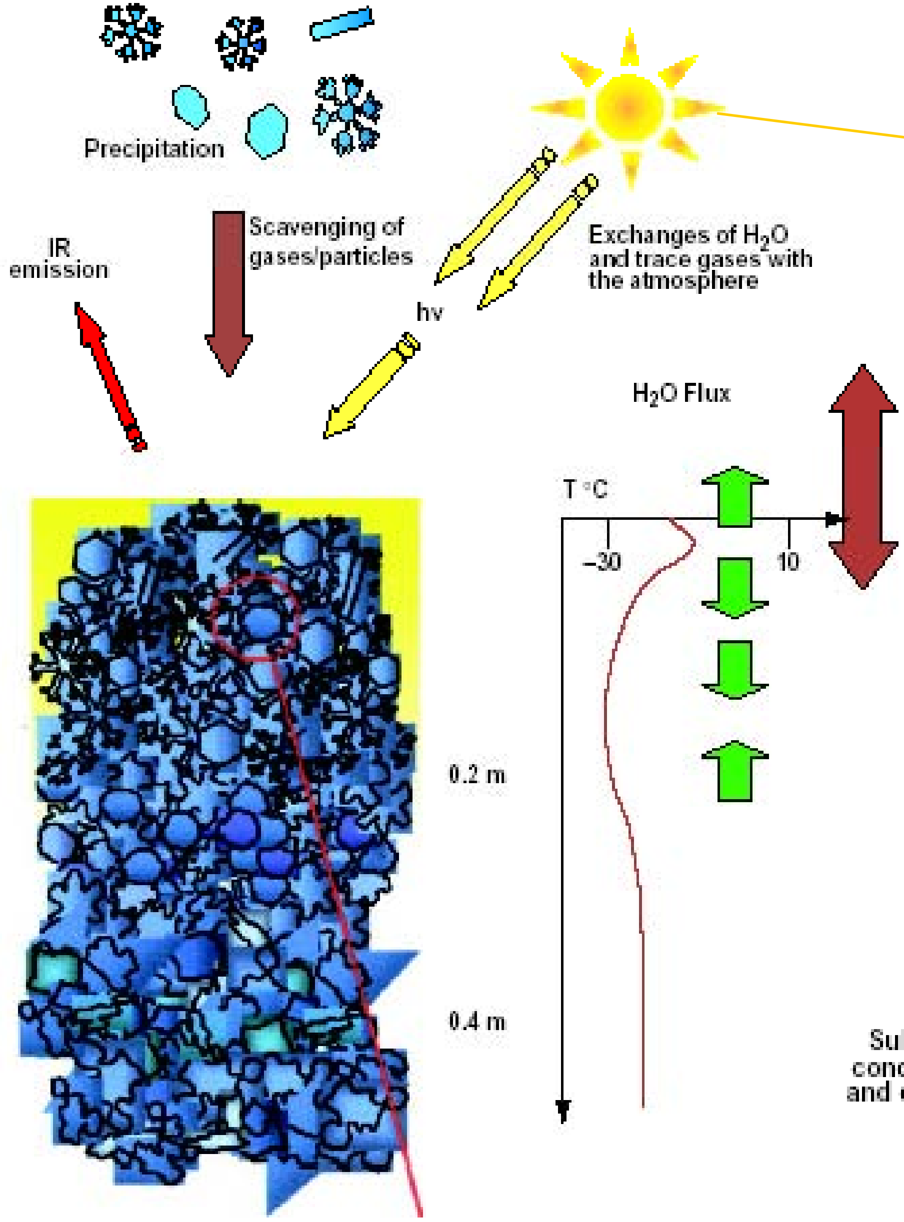
Unfrozen solution

freezing

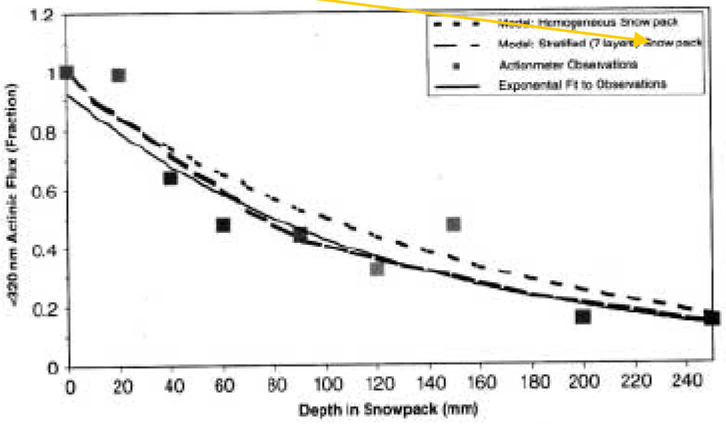
Very concentrated solution

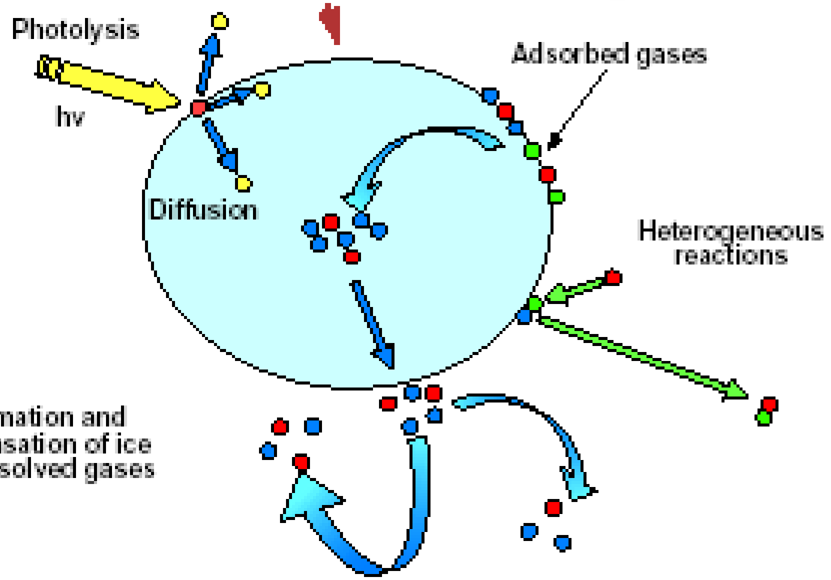
Processes in snowpack

Actinic Flux into Snowpack



M. Peterson et al. / Atmospheric Environment 36 (2002) 2545–2551





Direct and indirect photolysis, radical reactions

- $R(C{=}O)CH_2CH_2CH_3 + \lambda\nu \rightarrow RC{=}O\cdot + \cdot CH_2CH_2CH_3$
- $RC{=}O\cdot + \cdot CH_2CH_2CH_3 \rightarrow R(C{=}O)H + CH_2{=}CHCH_3$
- $R(C{=}O)R' + \lambda\nu \rightarrow [RC{=}O\cdot + \cdot R']$
- $[RC{=}O\cdot + \cdot R'] + R''SH \rightarrow R''S\cdot + RC{=}O\cdot + \cdot R'H$
- $R''S\cdot + RC{=}O\cdot \rightarrow RC{=}O\text{-}SR''$
- $RC{=}O\text{-}SR'' + \lambda\nu \rightarrow R\text{-}R'' + COS$
- $CH_3SCH_2CH_2CH(NH_2)COOH + \lambda\nu \rightarrow CH_3SCH_2CH_2CHO + NH_3 + CO_2$
- $CH_3SCH_2CH_2CHO + OH \rightarrow CH_2{=}CH_2 + CH_3S\cdot + HCOOH$
- $CH_3S\cdot + CH_3S\cdot + M \rightarrow CH_3SH + CH_2S + M$
- $CH_2S + \lambda\nu \rightarrow HCS\cdot + H$
- $CH_2S + OH\cdot \rightarrow HCS\cdot + H_2O$
- $HCS\cdot + O2 \rightarrow COS + OH\cdot$
- $HSCH_2CH(NH_2)C({=}O)OH + O_2 + h\nu \rightarrow HSCH_2CHO + NH_3 + CO_2$
- $HSCH_2CHO + OH \rightarrow HCS + CO_2$
- $2HCS \rightarrow CS_2 + CH2{:}$
- $HCS + O_2 \rightarrow COS + OH$

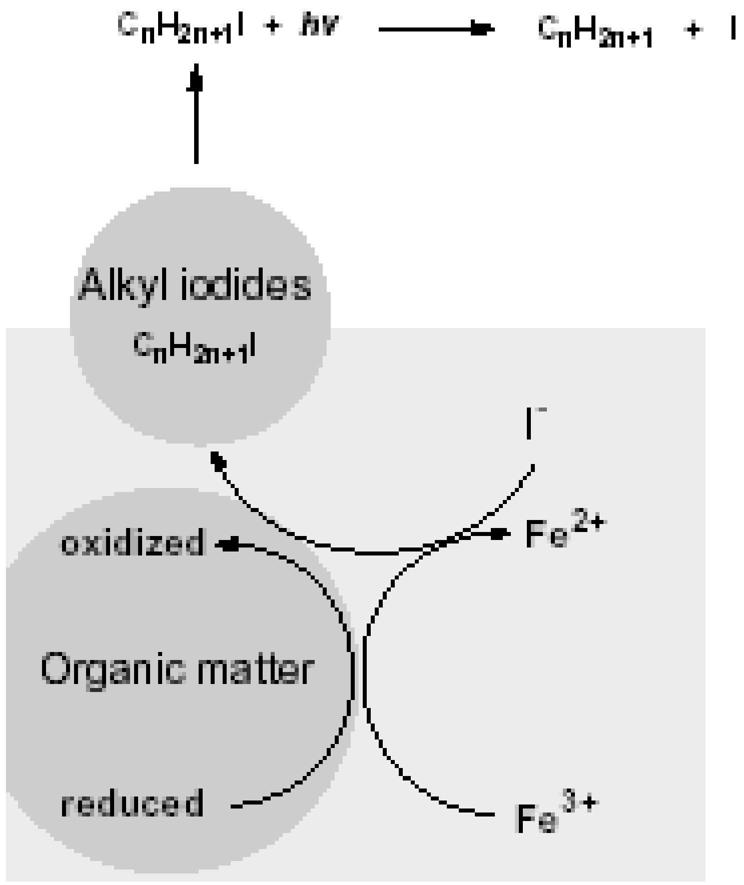
Direct and indirect photolysis, radical reactions

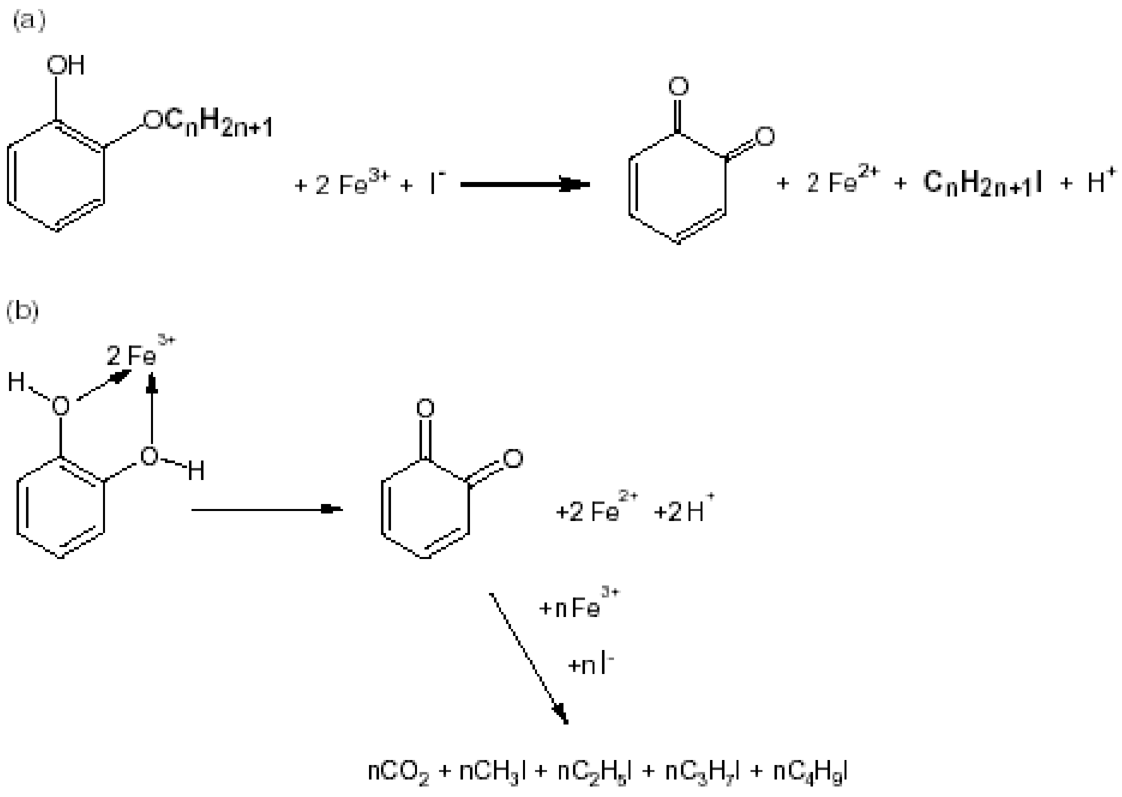
- $CH_3SCH_3 + OH\cdot \rightarrow CH_3SCH_2\cdot + H_2O$
- $CH_3SCH_2\cdot + O_2 + M \rightarrow CH_3SCH_2O_2\cdot + M$
- $CH_3SCH_2O_2\cdot + NO \rightarrow CH_3SCH_2O\cdot + NO_2$
- $CH_3SCH_2O\cdot \rightarrow CH_3S\cdot + CH_2O$
- $CH_3S\cdot + CH_3S\cdot \rightarrow CH_3SSCH_3$
- $CH_3SCH_2O\cdot + O_2 \rightarrow CH_3SCHO + HO_2$
- $CH_3SCHO + OH\cdot \rightarrow COS + CH3\cdot + H_2O$
- $CS_2 + OH\cdot \rightarrow COS + HS\cdot$
- $N_2O_5 + NaCl \rightarrow NaNO_3 + ClNO_2$
- $ClNO_2 + NaCl \rightarrow NaNO_2 + Cl_2$
- $NO_3 + NaCl \rightarrow NaNO_3 + Cl\cdot$
- $ClNO_2 + hv \rightarrow Cl + NO_2$
- $Cl_2 + hv \rightarrow 2Cl\cdot$
- $R\cdot + Cl\cdot \rightarrow RCl\ (R = CH_3, C_2H_5, CH{=}CH_2)$
- $R'(C{=}O)CH_3 + \lambda\nu \rightarrow R'C{=}O\cdot + CH3\cdot$
- $OH\cdot\ (RO\cdot, ROO\cdot) + Br^- \rightarrow OH^-\ (RO^-, ROO^-) + Br\cdot$
- $CH_3\cdot + Br\cdot \rightarrow CH_3Br$
- $CH_3SCHO + OH\cdot \rightarrow CH_3S(OH)CHO\cdot$
- $CH_3S(OH)CHO\cdot + Br\cdot \rightarrow COS + CH_3Br + H_2O$

Ionic and biochemical reactions

- $(CH_3)_2S^+CH_2CH_2COO^-$ + enzyme → $(CH_3)_2S$ + $CH_2{=}CH\text{-}CHO$
- $(CH3)2S+CH_2CH_2COO-$ + OH^-→ $CH_3SCH_2CH_2COO-$ + CH_3OH
- $CH_3SCH_2CH_2COO^-$ + H^+ → CH_3SH + CH_3CH_2COOH
- $(CH_3)_2S$ + (H^+,OH^-) → CH_3SH + CH_3OH
- 2 CH_3SH + OH^- → CH_3SSCH_3 + H_2O
- $(CH_3)_2S^+CH_2CH_2COO^-$ + Cl^- → CH_3Cl + $CH_3SCH_2CH_2COO^-$
- $HOOCCH(NH_2)CH_2CH_2S^+(CH_3)$ -adenosine + Cl^- → CH_3Cl + $HOOCCH(NH_2)CH_2CH_2S$-adenosine
- $NH_2C(COOH)CH_2CH_2S^+(CH_3)_2$ + Cl^- → CH_3Cl + $NH2C(COOH)CH_2CH_2SCH_3$
- H_2O_2 + Cl^- + chloroperoxidase → H_2O + OCl^-
- OCl^- + H^+→ HOCl → HO^- + (Cl^+)
- R'(CO)RH + (Cl^+) → RCl + R'(CO)H + (R = CH_3, C_2H_5, CH_2=CH)
- R-C(=O) + enzyme + Br^- + H_2O_2 → R-COOH + $CHBr_3$
- $R\text{-}S(O_2)CH_3$ + $Br^{(\delta+)}$ → $R\text{-}S(O_2)CBr_3$
- $R\text{-}S(O_2)CBr_3$ + OH^- → RS(=O)OOH + $CHBr_3$

Redox reactions





Organic matter + $Me^{n+} + X^- \rightarrow R\text{-}X + M^{(n-1)+}$

(Me = Fe, Co, Mn, Cu; X = Cl, Br, I; R = CH_3, C_2H_5, $CH_2{=}CH$)

Sources of the impurities in ice samples of coastal glacier

- **Chlorofluorocarbons and their replacements, chloro-containing solvents**

  Anthropogenic origin
- **Tetrafluorocarbon: anthropogenic (50%) + emission from granites (50%)**
- **Propene: photochemical decomposition of dissolved organic matter from micro/macroalgaes**

  $R(C{=}O)CH_2CH_2CH_3 + \lambda\nu \rightarrow RC{=}O^{\cdot} + {}^{\cdot}CH_2CH_2CH_3$

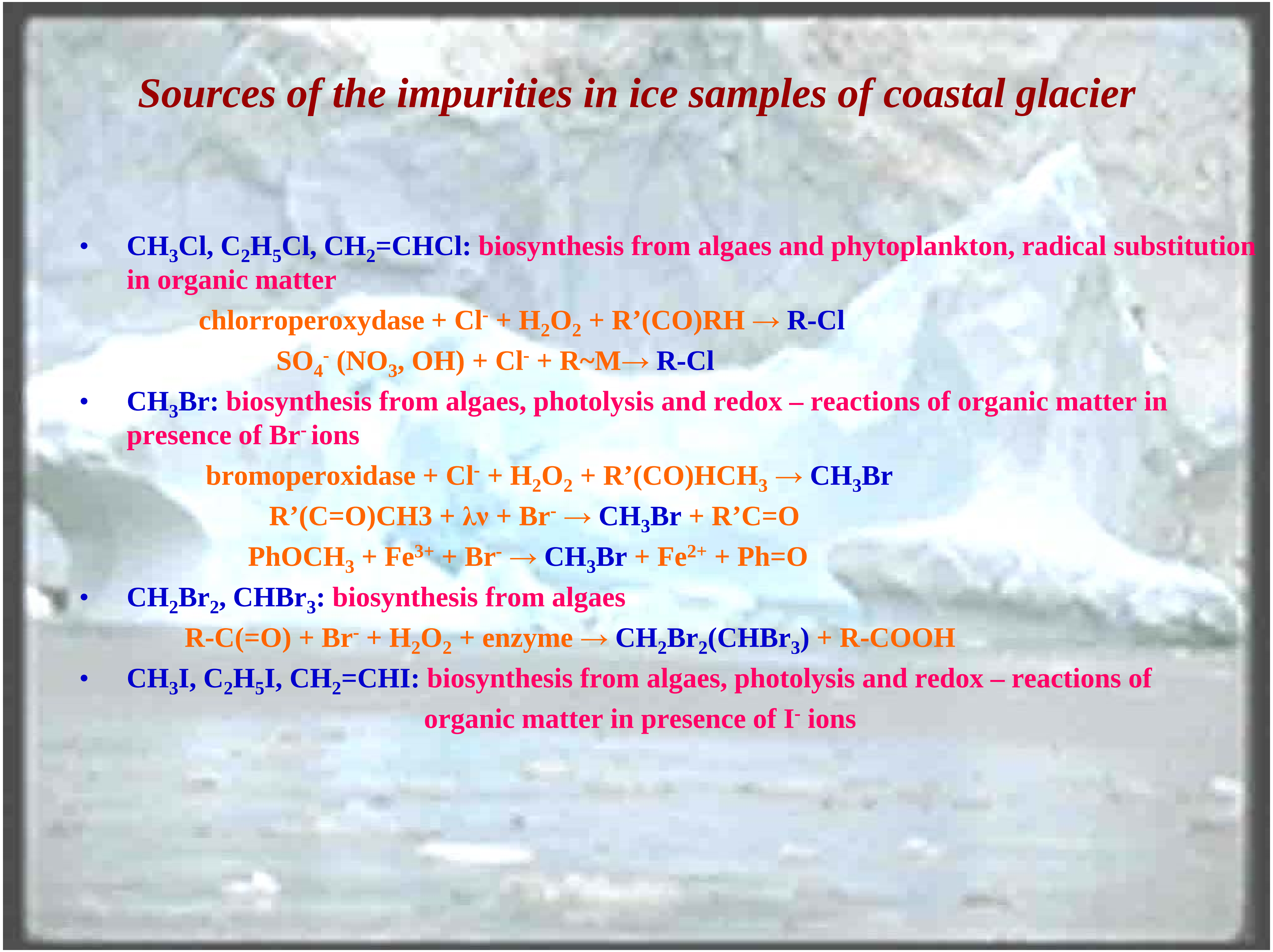
  $RC{=}O^{\cdot} + .CH_2CH_2CH_3 \rightarrow R(C{=}O)H + CH_2{=}CHCH_3$
- **Dimethyl sulfide and dimethyl disulfide: biosynthesis from algaes**

  $(CH3)_2S^+CH_2CH_2COO^- \rightarrow (CH_3)_2S + CH_2{=}CH\text{-}CHO$

  $2\ CH_3SH + OH^- \rightarrow CH_3SSCH_3 + H_2O$
- **Carbonyl sulfide and carbon disulfide: photolysis of organic matter**

  $R(C{=}O)R' + \lambda\nu \rightarrow RC{=}O\text{-}SR'' + \lambda\nu \rightarrow R\text{-}R'' + COS$

  $HSCH_2CH(NH_2)C({=}O)OH\ '' + \lambda\nu \rightarrow CS_2 + CH_2{:}$



Sources of the impurities in ice samples of coastal glacier

- **CH_3Cl, C_2H_5Cl, CH_2=CHCl:** **biosynthesis from algaes and phytoplankton, radical substitution in organic matter**

  chlorroperoxydase + Cl^- + H_2O_2 + R'(CO)RH → R-Cl

  SO_4^- (NO_3, OH) + Cl^- + R~M→ R-Cl

- **CH_3Br:** **biosynthesis from algaes, photolysis and redox – reactions of organic matter in presence of Br^- ions**

  bromoperoxidase + Cl^- + H_2O_2 + R'(CO)HCH_3 → CH_3Br

  R'(C=O)CH3 + $\lambda\nu$ + Br^- → CH_3Br + R'C=O

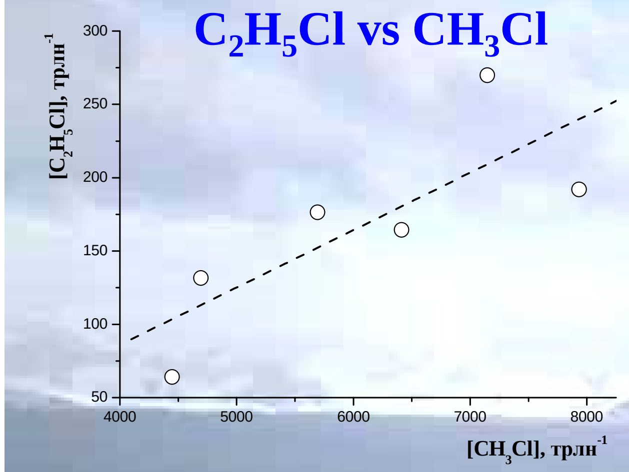
  $PhOCH_3$ + Fe^{3+} + Br^- → CH_3Br + Fe^{2+} + Ph=O

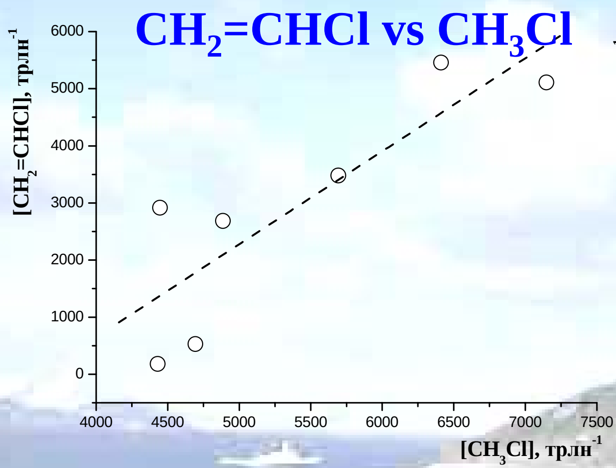
- **CH_2Br_2, $CHBr_3$:** **biosynthesis from algaes**

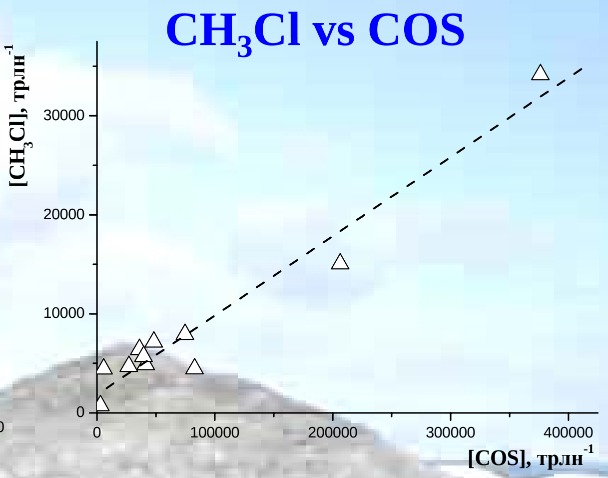
  R-C(=O) + Br^- + H_2O_2 + enzyme → CH_2Br_2($CHBr_3$) + R-COOH

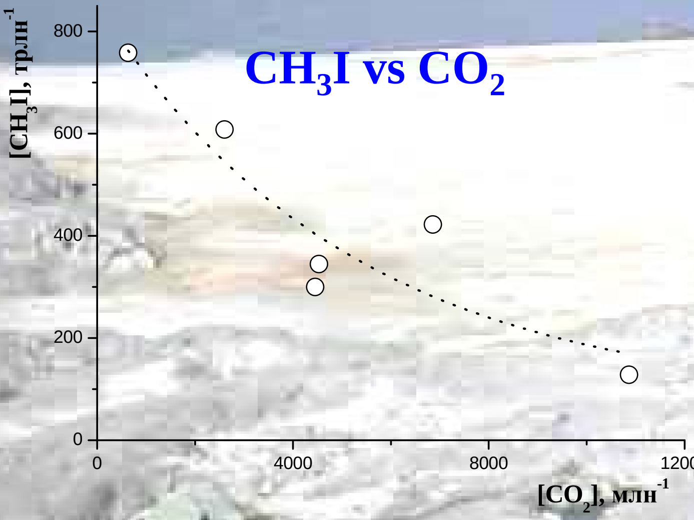
- **CH_3I, C_2H_5I, CH_2=CHI:** **biosynthesis from algaes, photolysis and redox – reactions of organic matter in presence of I^- ions**

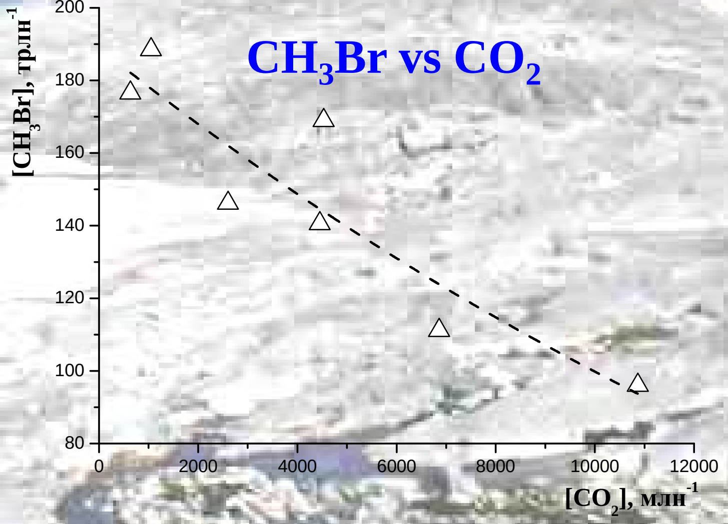
Relationships between impurity concentrations in the glacier and their temporal dependencies

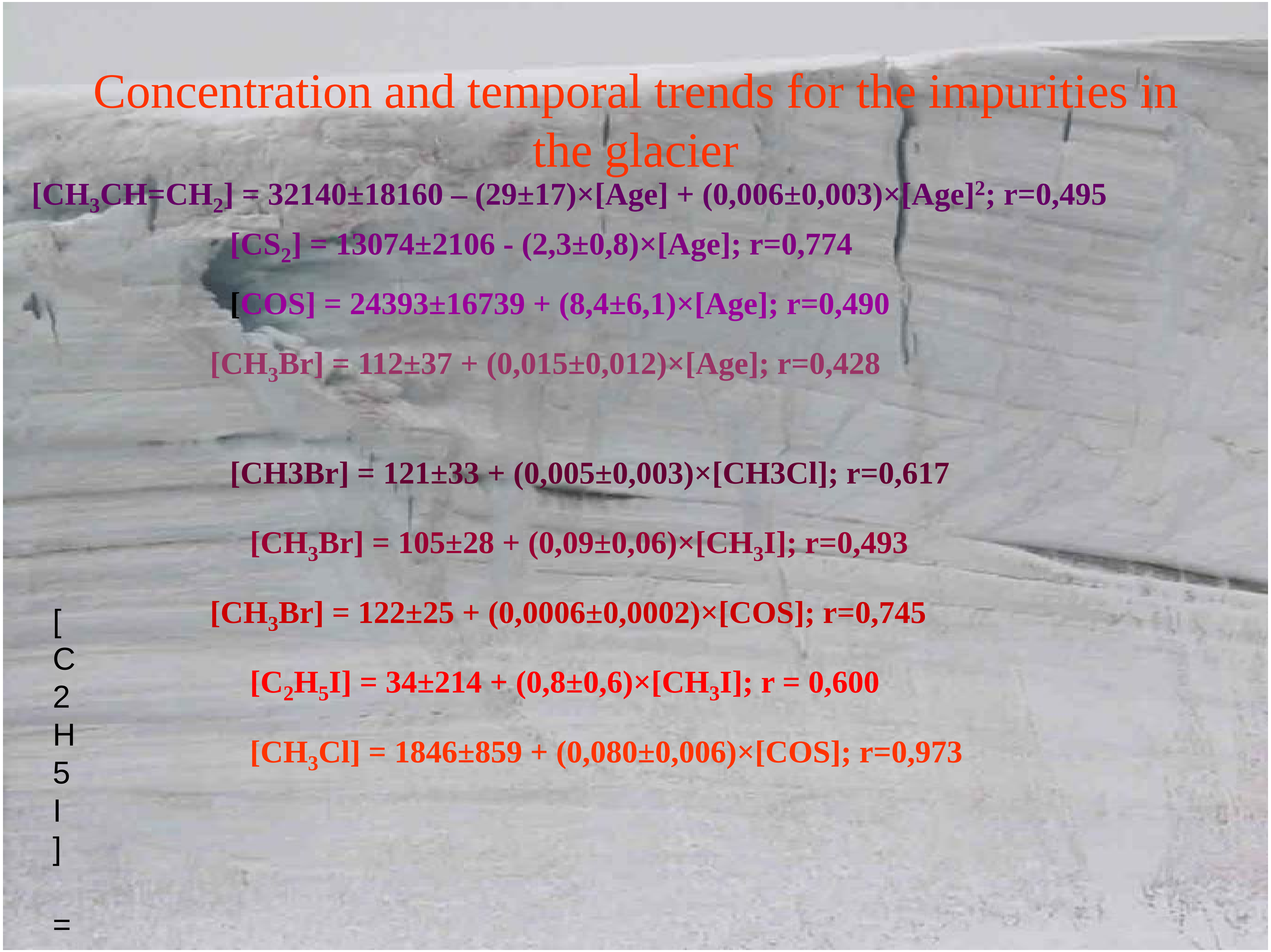

C_2H_5Cl vs CH_3Cl


CH_2=$CHCl$ vs CH_3Cl


CH_3Cl vs COS


CH_3I vs CO_2


CH_3Br vs CO_2



Concentration and temporal trends for the impurities in the glacier

[$CH_3CH=CH_2$] = 32140±18160 – (29±17)×[Age] + (0,006±0,003)×[Age]^2; r=0,495

[CS_2] = 13074±2106 - (2,3±0,8)×[Age]; r=0,774

[COS] = 24393±16739 + (8,4±6,1)×[Age]; r=0,490

[CH_3Br] = 112±37 + (0,015±0,012)×[Age]; r=0,428

[CH3Br] = 121±33 + (0,005±0,003)×[CH3Cl]; r=0,617

[CH_3Br] = 105±28 + (0,09±0,06)×[CH_3I]; r=0,493

[CH_3Br] = 122±25 + (0,0006±0,0002)×[COS]; r=0,745

[C_2H_5I] = 34±214 + (0,8±0,6)×[CH_3I]; r = 0,600

[CH_3Cl] = 1846±859 + (0,080±0,006)×[COS]; r=0,973

[
C
2
H
5
I
]

=

Sources and fate of volatile impurities in Antarctic

oxidation, radical reactions
(OH, NO_3, RO, O_3), photolysis

emission from rocks

Biosynthesis by ice microalgae and microbes,
Photolysis and redox-reactions of organic matter in presence of halide ions in snowpack and firn

dry and wet deposition

advective transport with aerosols

photolysis,
hydrolysis,
nucleophylic substitution,
oxidation

biosynthesis from macroalgaes and phytoplankton
photolysis and redox-reactions of organic matter in surface layers of the ocean

microbial decomposition, hydrolysis, oxidation

Interface Processes between the Ocean, Atmosphere, Sea Ice, and Snow in Antarctica

- **In the near future climate change is predicted to be at a significantly faster rate in Western coastal Antarctic than for the planet as a whole, due to the influence of feedbacks related to the changing surfaces of glaciers and Southern Ocean**
- **Numerous recent observations indicate that the exchange of atmospherically important chemical species with this surface is driven by physical and photochemical processes occurring on the surface of the snowpack and sea ice, and that this exchange significantly impacts the concentrations of chemical species such as ozone and mercury**
- **Biologically-mediated processes have also been observed to impact the interactions between ocean, ice, and/or snow and the atmosphere**
- **Both dynamic (movement) and thermodynamic (temperature) processes in the marine cryosphere affect the exchange process of mass and energy, and the latter are being affected by global scale climate variability and change**

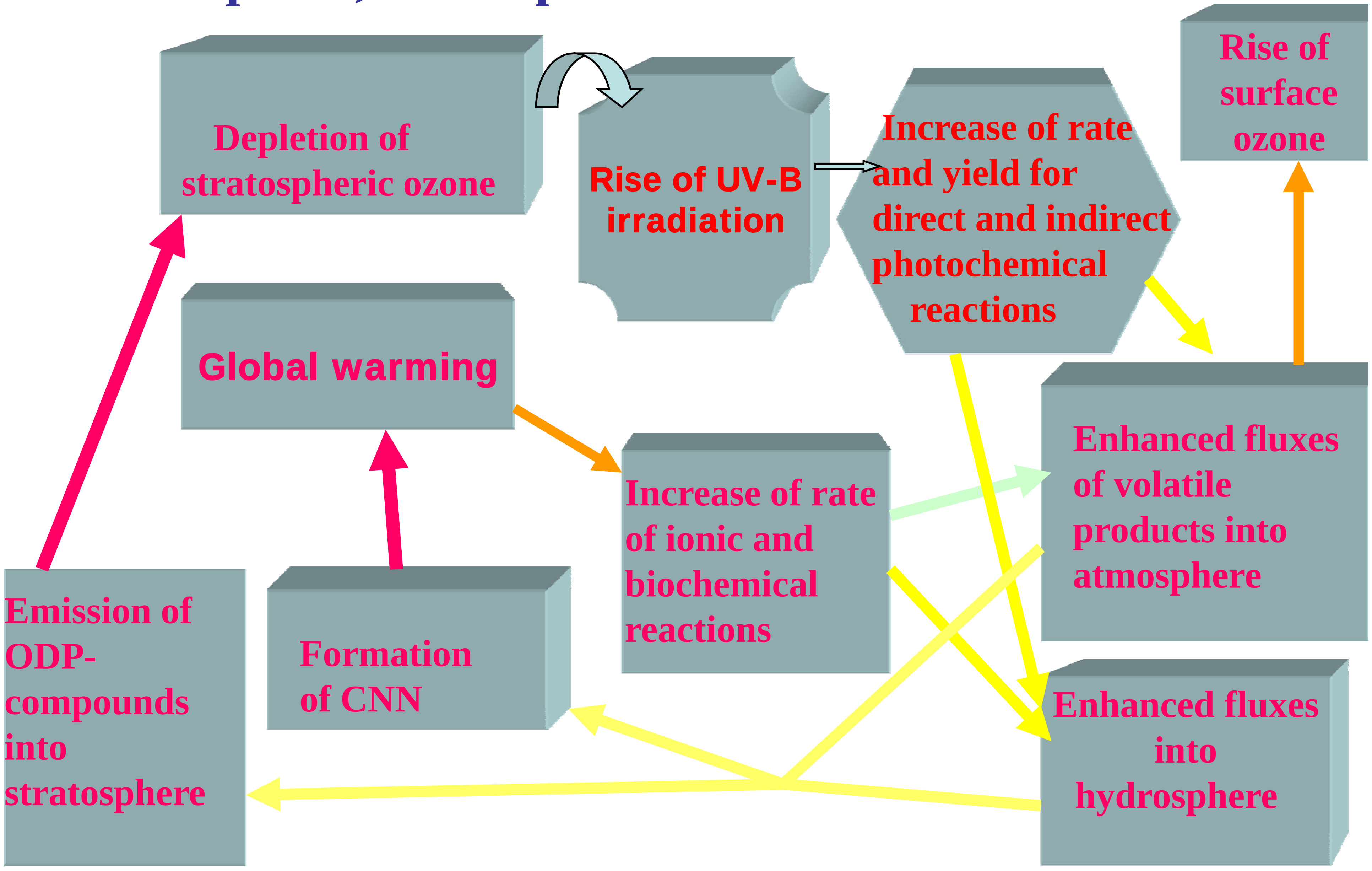
Interface processes between the Ocean, Atmosphere, Sea Ice, and Snow in Polar Regions

How the lower atmosphere in the Polar regions will change as climate and the nature of the ice volume change?

International programs (IPY2007-2008)

- OASIS (Ocean-Atmosphere-Sea Ice and Snow exchange processes)
- AICI (Atmosphere-Ice Chemical Interactions),
- ASCOS (Arctic Summer Cloud Ocean Study)
- POLARCAT (Polar Study using Aircraft, Remote Sensing, Surface Measurements and Models, of Climate, Chemistry, Aerosols, and Transport)

Future effects of snowpack reactions on lower atmosphere, stratosphere and climate over Antarctic



Depletion of stratospheric ozone

Rise of UV-B irradiation

Increase of rate and yield for direct and indirect photochemical reactions

Rise of surface ozone

Global warming

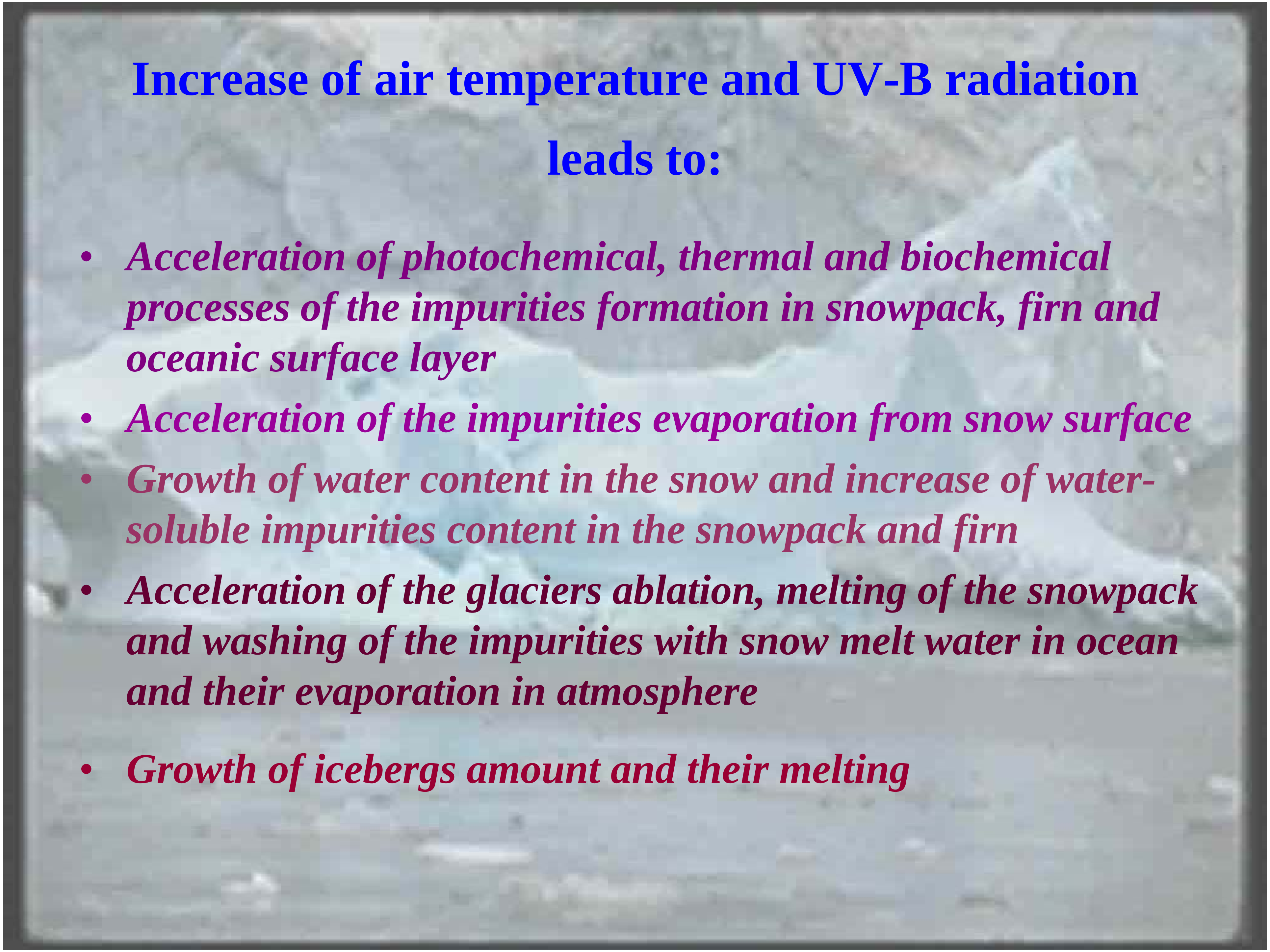
Increase of rate of ionic and biochemical reactions

Enhanced fluxes of volatile products into atmosphere

Emission of ODP-compounds into stratosphere

Formation of CNN

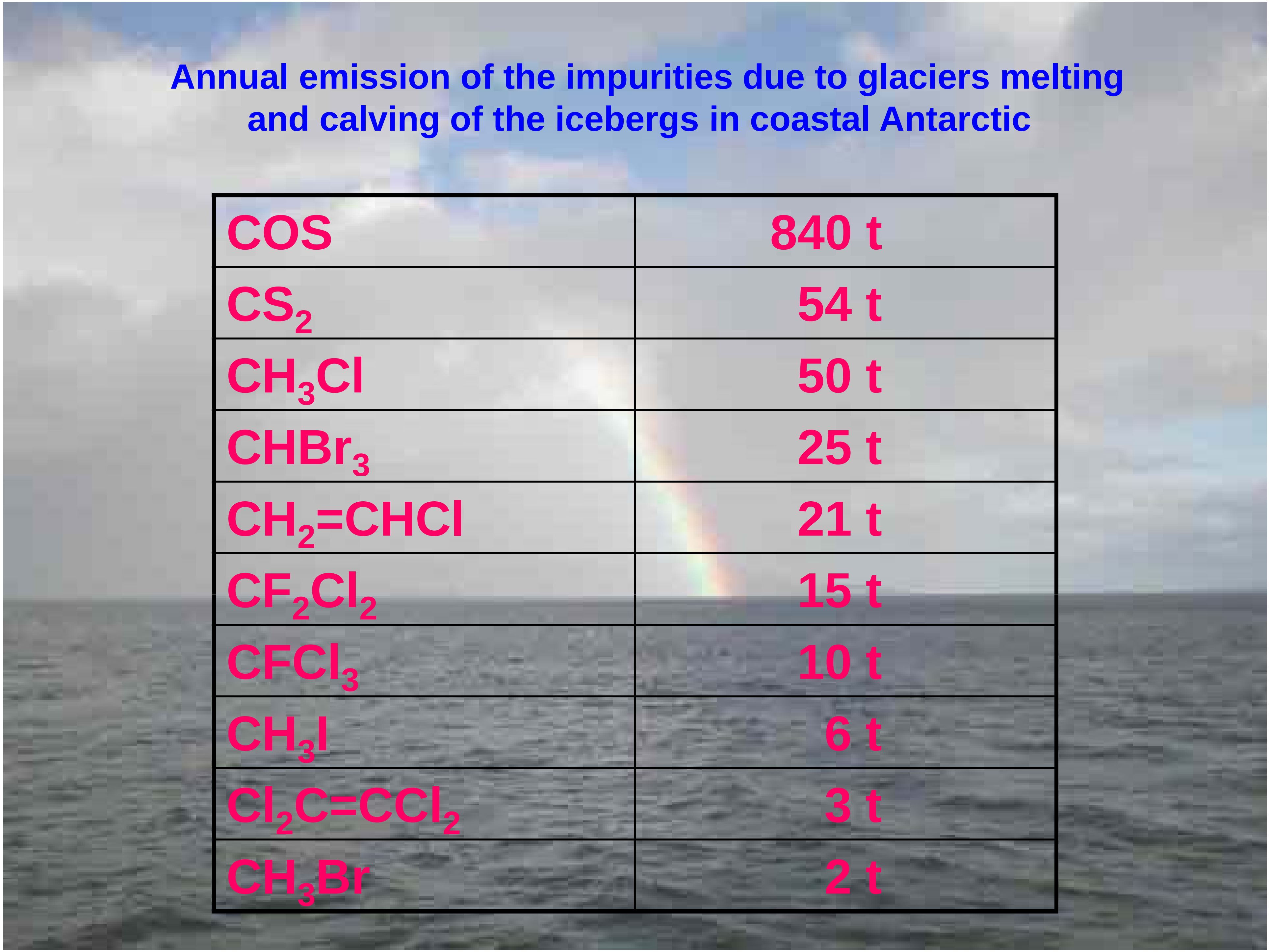
Enhanced fluxes into hydrosphere



Increase of air temperature and UV-B radiation leads to:

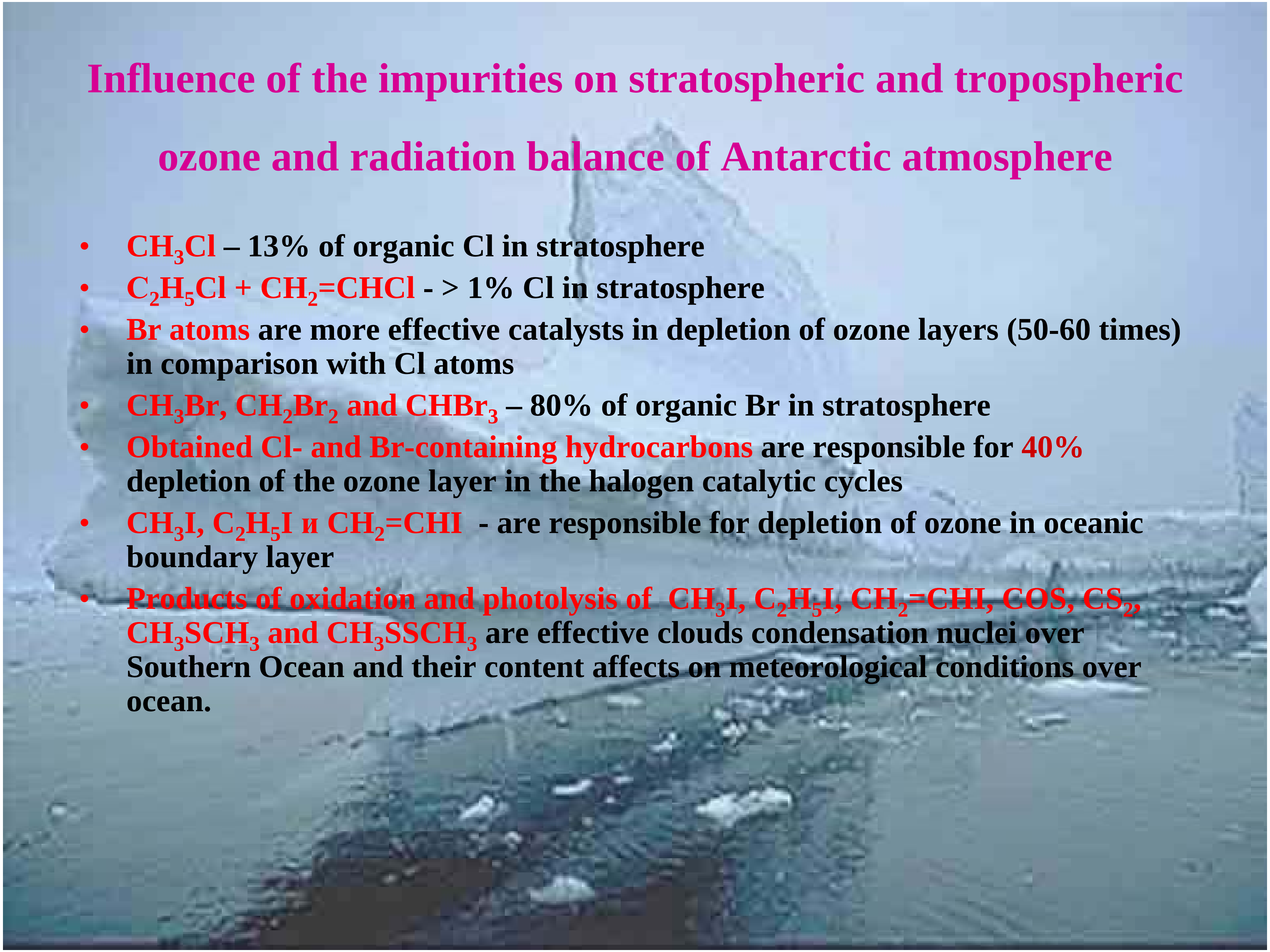
- *Acceleration of photochemical, thermal and biochemical processes of the impurities formation in snowpack, firn and oceanic surface layer*
- *Acceleration of the impurities evaporation from snow surface*
- *Growth of water content in the snow and increase of water-soluble impurities content in the snowpack and firn*
- *Acceleration of the glaciers ablation, melting of the snowpack and washing of the impurities with snow melt water in ocean and their evaporation in atmosphere*

- *Growth of icebergs amount and their melting*



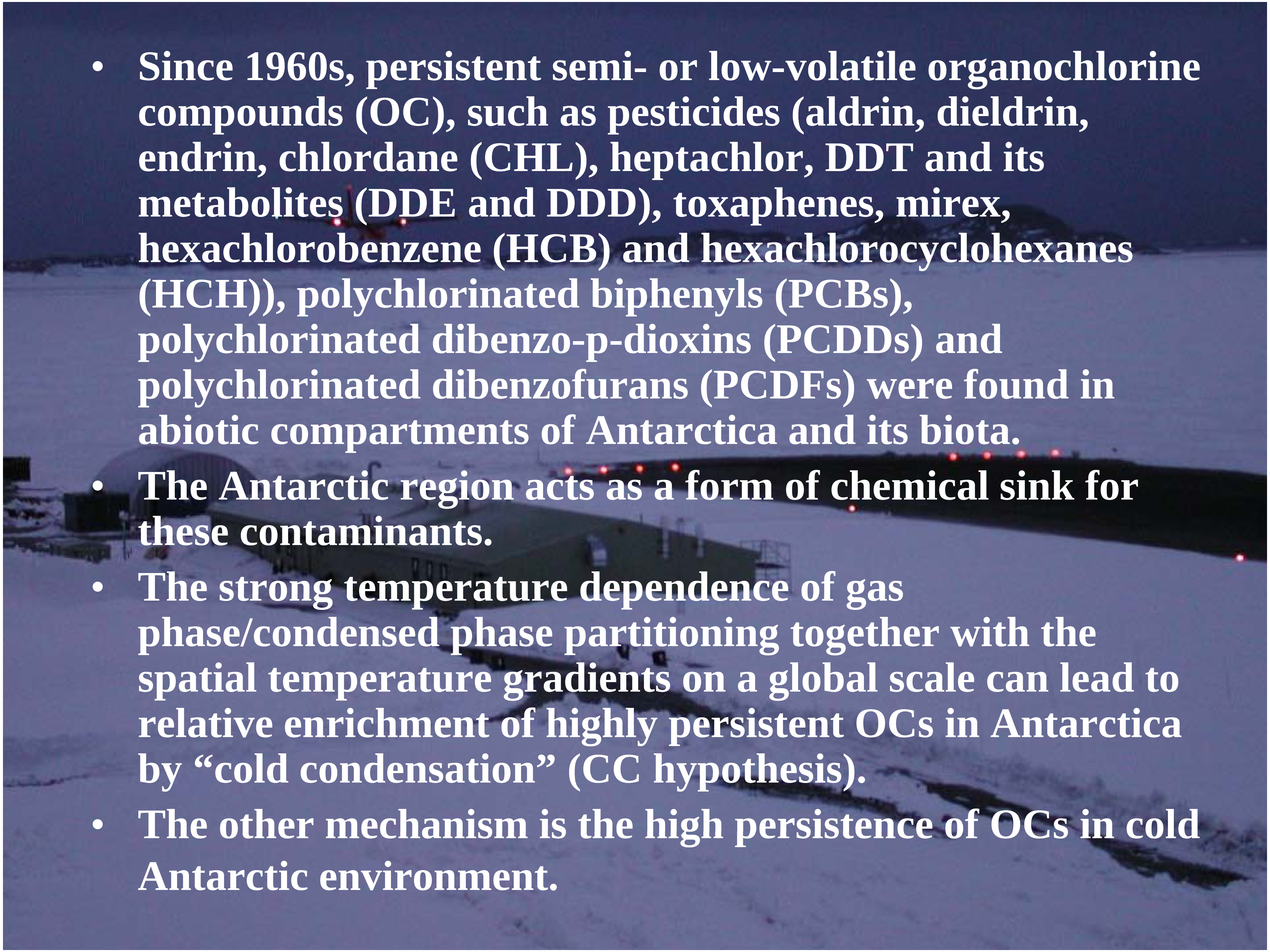
Annual emission of the impurities due to glaciers melting and calving of the icebergs in coastal Antarctic

COS	840 t
CS_2	54 t
CH_3Cl	50 t
$CHBr_3$	25 t
$CH_2{=}CHCl$	21 t
CF_2Cl_2	15 t
$CFCl_3$	10 t
CH_3I	6 t
$Cl_2C{=}CCl_2$	3 t
CH_3Br	2 t

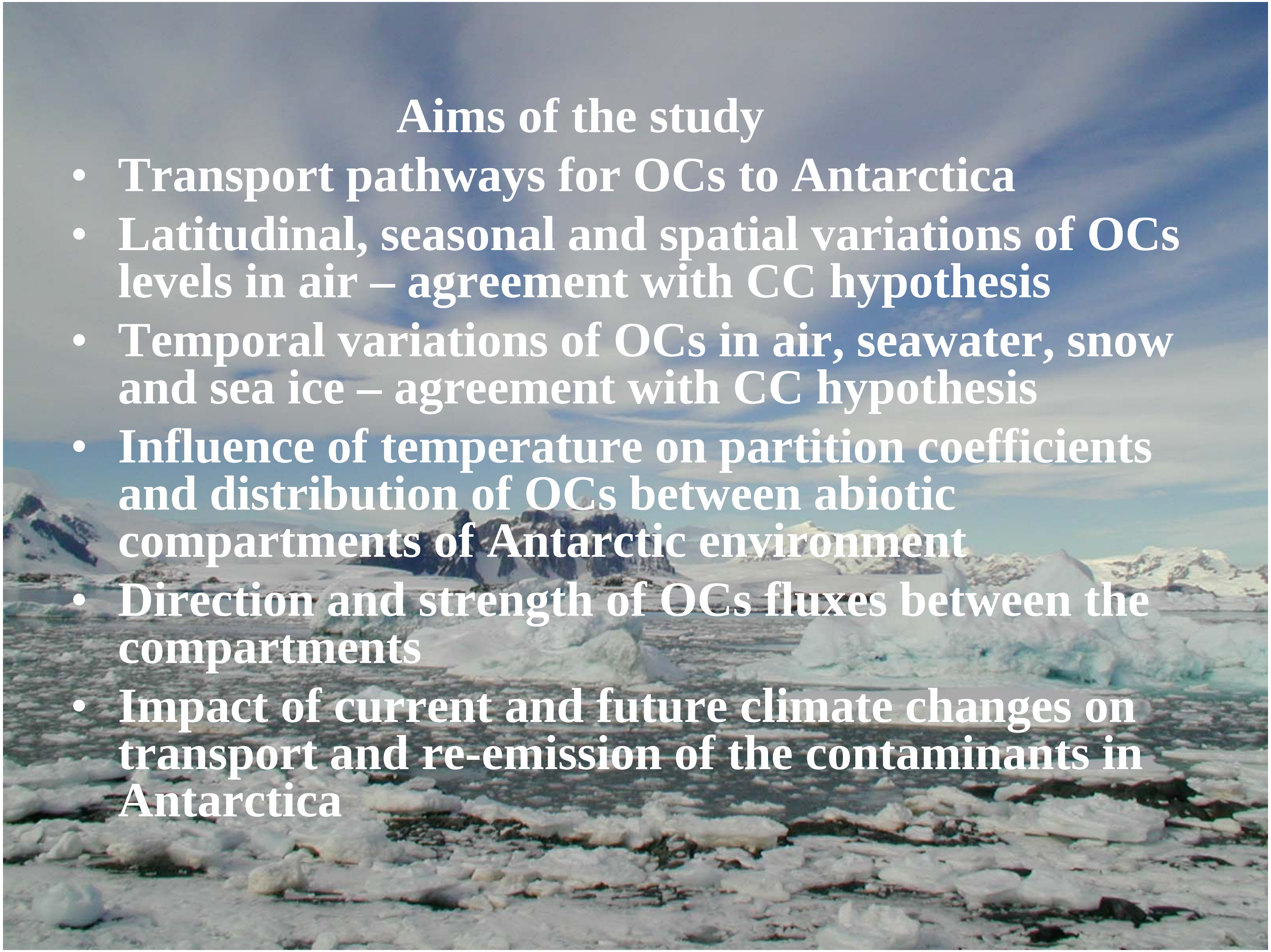


Influence of the impurities on stratospheric and tropospheric ozone and radiation balance of Antarctic atmosphere

- **CH_3Cl** – 13% of organic Cl in stratosphere
- **C_2H_5Cl + CH_2=CHCl** - > 1% Cl in stratosphere
- **Br atoms** are more effective catalysts in depletion of ozone layers (50-60 times) in comparison with Cl atoms
- **CH_3Br, CH_2Br_2 and $CHBr_3$** – 80% of organic Br in stratosphere
- **Obtained Cl- and Br-containing hydrocarbons** are responsible for **40%** depletion of the ozone layer in the halogen catalytic cycles
- **CH_3I, C_2H_5I и CH_2=CHI** - are responsible for depletion of ozone in oceanic boundary layer
- **Products of oxidation and photolysis of CH_3I, C_2H_5I, CH_2=CHI, COS, CS_2, CH_3SCH_3 and CH_3SSCH_3** are effective clouds condensation nuclei over Southern Ocean and their content affects on meteorological conditions over ocean.



- Since 1960s, persistent semi- or low-volatile organochlorine compounds (OC), such as pesticides (aldrin, dieldrin, endrin, chlordane (CHL), heptachlor, DDT and its metabolites (DDE and DDD), toxaphenes, mirex, hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCH)), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were found in abiotic compartments of Antarctica and its biota.
- The Antarctic region acts as a form of chemical sink for these contaminants.
- The strong temperature dependence of gas phase/condensed phase partitioning together with the spatial temperature gradients on a global scale can lead to relative enrichment of highly persistent OCs in Antarctica by “cold condensation” (CC hypothesis).
- The other mechanism is the high persistence of OCs in cold Antarctic environment.

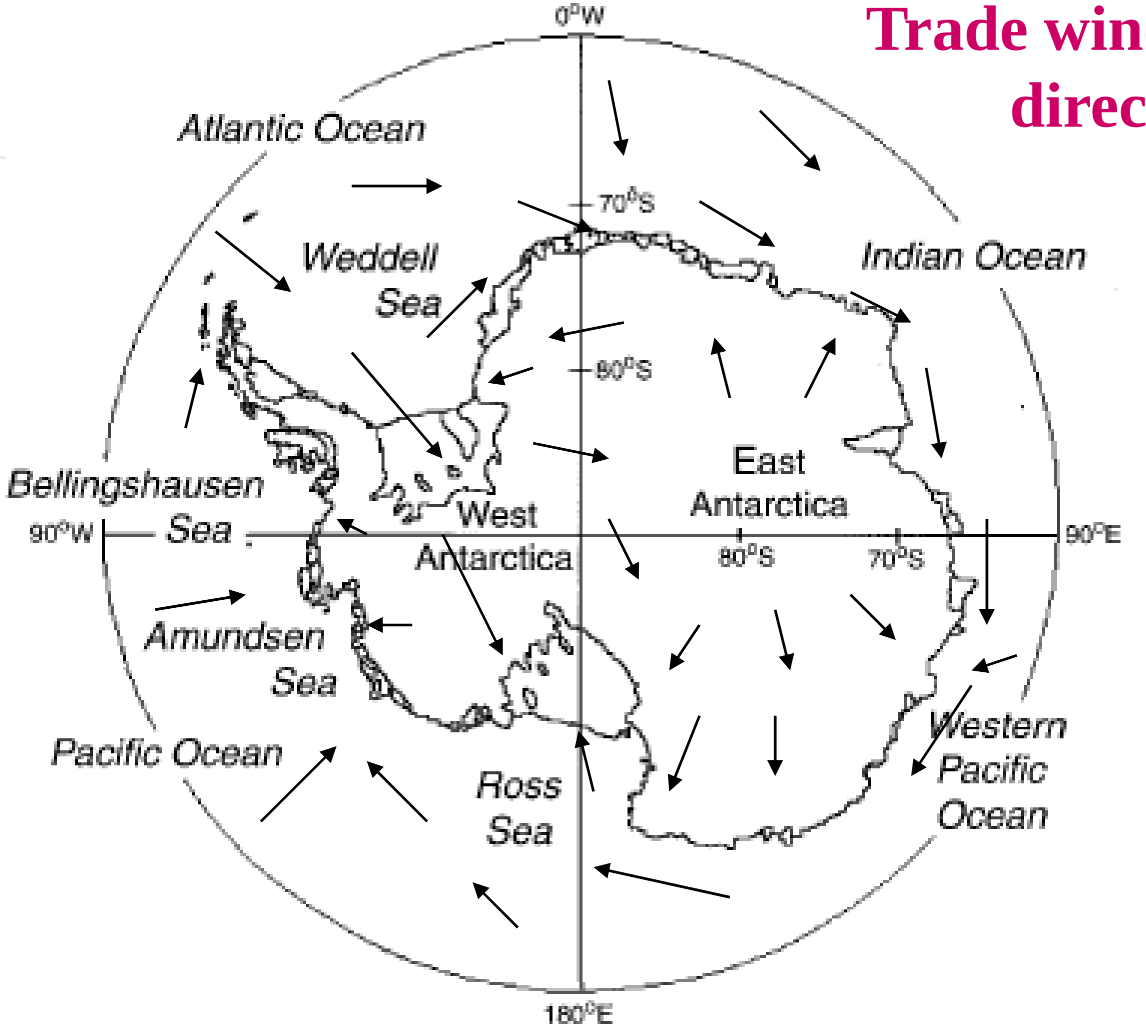


Aims of the study

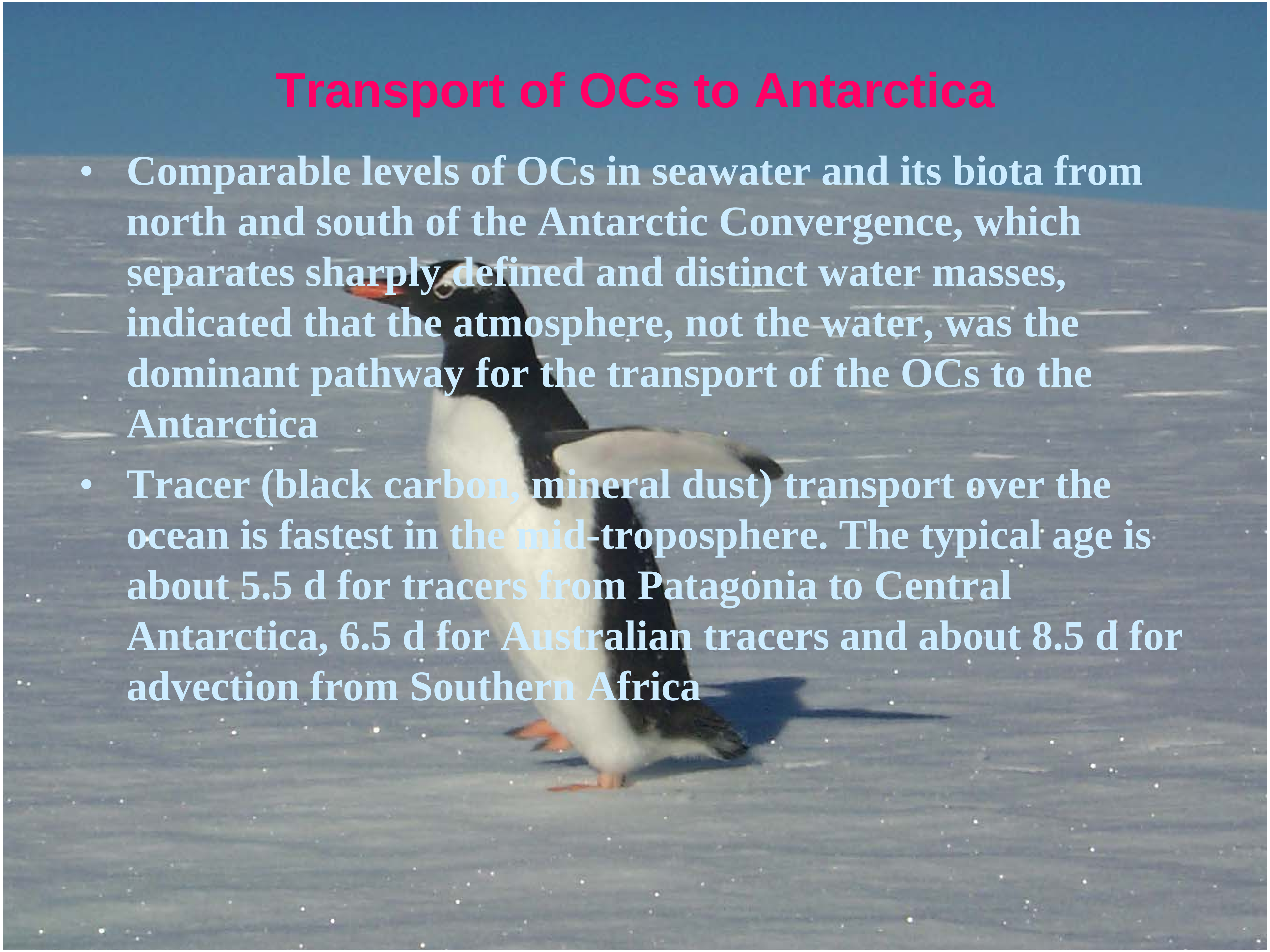
- Transport pathways for OCs to Antarctica
- Latitudinal, seasonal and spatial variations of OCs levels in air – agreement with CC hypothesis
- Temporal variations of OCs in air, seawater, snow and sea ice – agreement with CC hypothesis
- Influence of temperature on partition coefficients and distribution of OCs between abiotic compartments of Antarctic environment
- Direction and strength of OCs fluxes between the compartments
- Impact of current and future climate changes on transport and re-emission of the contaminants in Antarctica

Transport of OCs to Antarctica

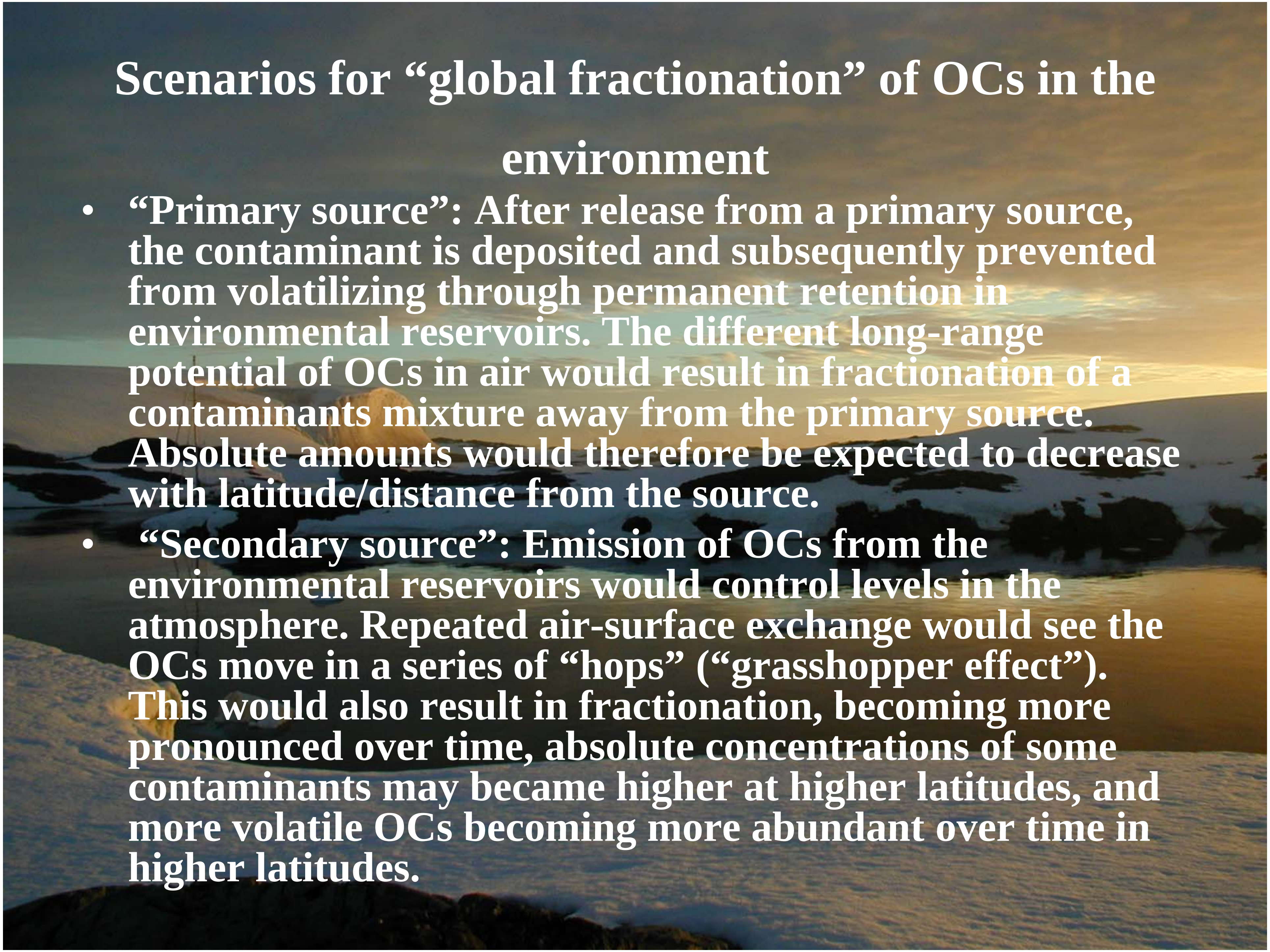
Trade winds and cyclones directions



Transport of OCs to Antarctica



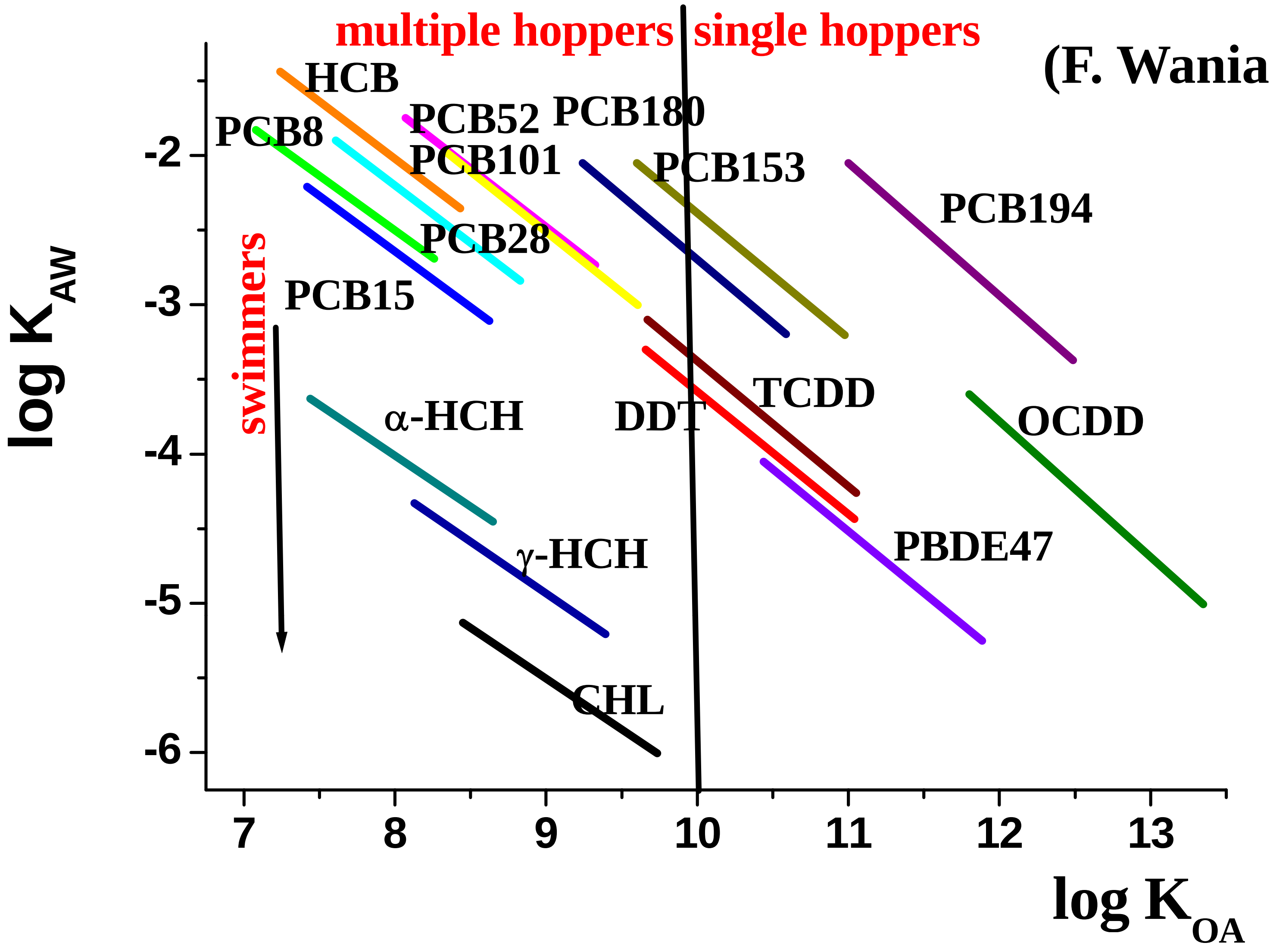
- Comparable levels of OCs in seawater and its biota from north and south of the Antarctic Convergence, which separates sharply defined and distinct water masses, indicated that the atmosphere, not the water, was the dominant pathway for the transport of the OCs to the Antarctica
- Tracer (black carbon, mineral dust) transport over the ocean is fastest in the mid-troposphere. The typical age is about 5.5 d for tracers from Patagonia to Central Antarctica, 6.5 d for Australian tracers and about 8.5 d for advection from Southern Africa



Scenarios for “global fractionation” of OCs in the environment

- “Primary source”: After release from a primary source, the contaminant is deposited and subsequently prevented from volatilizing through permanent retention in environmental reservoirs. The different long-range potential of OCs in air would result in fractionation of a contaminants mixture away from the primary source. Absolute amounts would therefore be expected to decrease with latitude/distance from the source.
- “Secondary source”: Emission of OCs from the environmental reservoirs would control levels in the atmosphere. Repeated air-surface exchange would see the OCs move in a series of “hops” (“grasshopper effect”). This would also result in fractionation, becoming more pronounced over time, absolute concentrations of some contaminants may became higher at higher latitudes, and more volatile OCs becoming more abundant over time in higher latitudes.

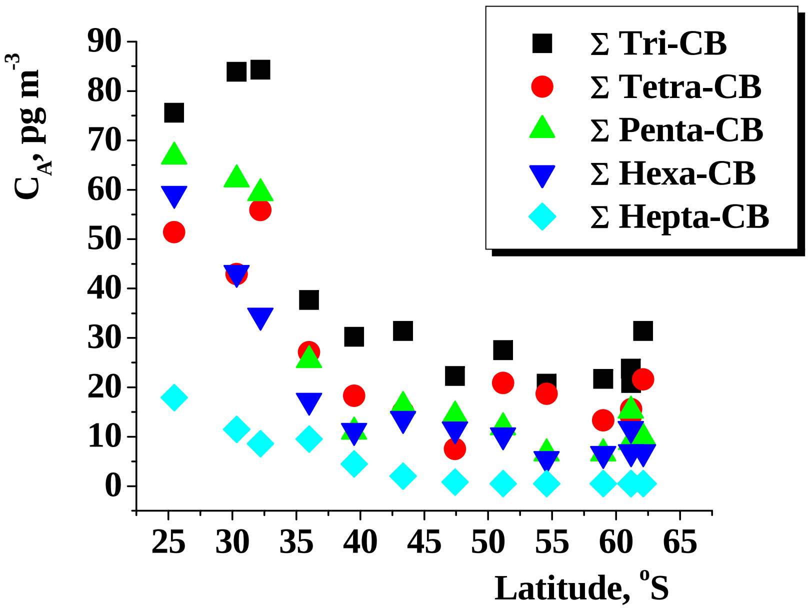
Major modes of OCs transport in range 25 - 0 °C

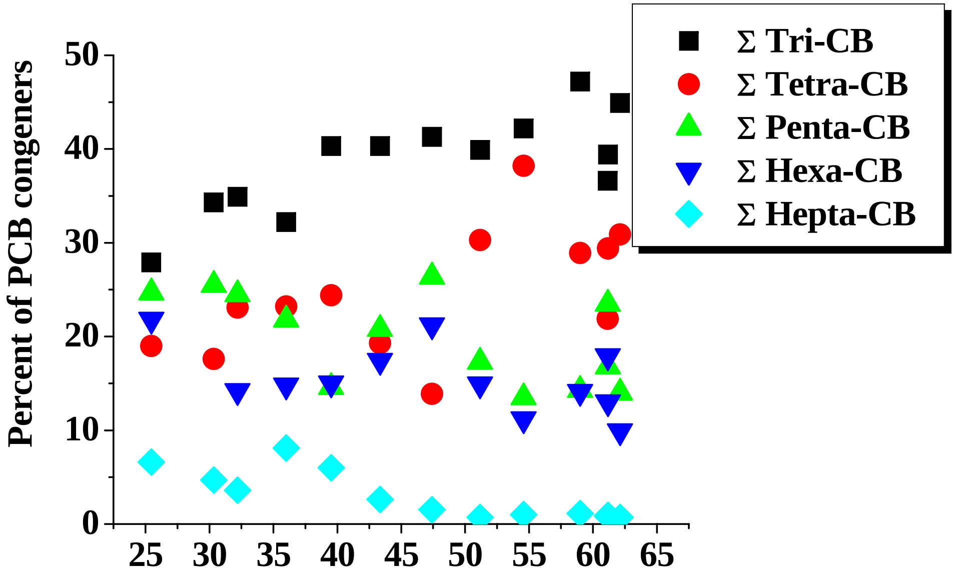


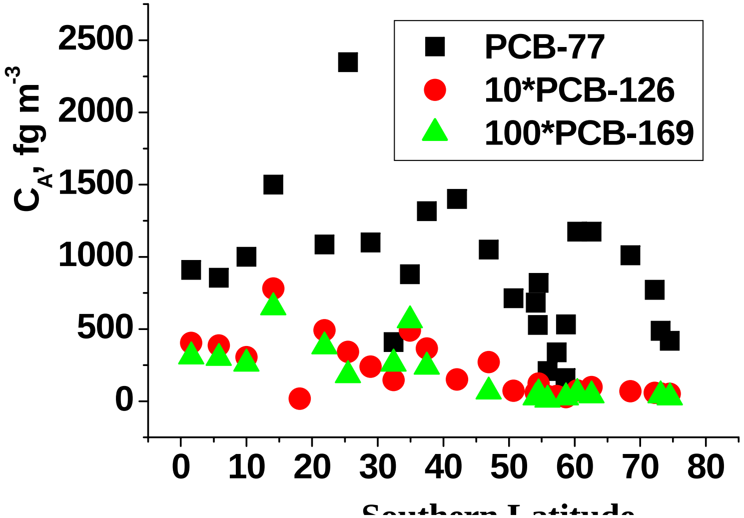
(F. Wania, 2006)

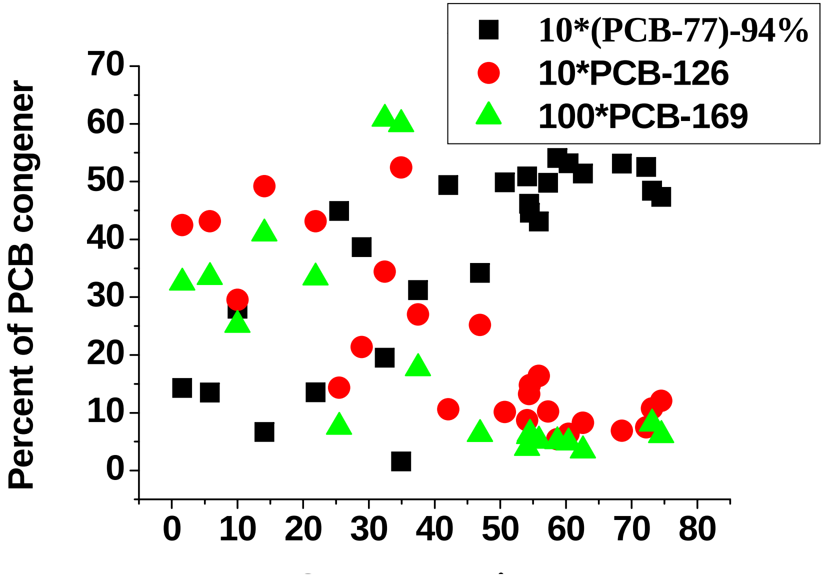
Latitudinal variations

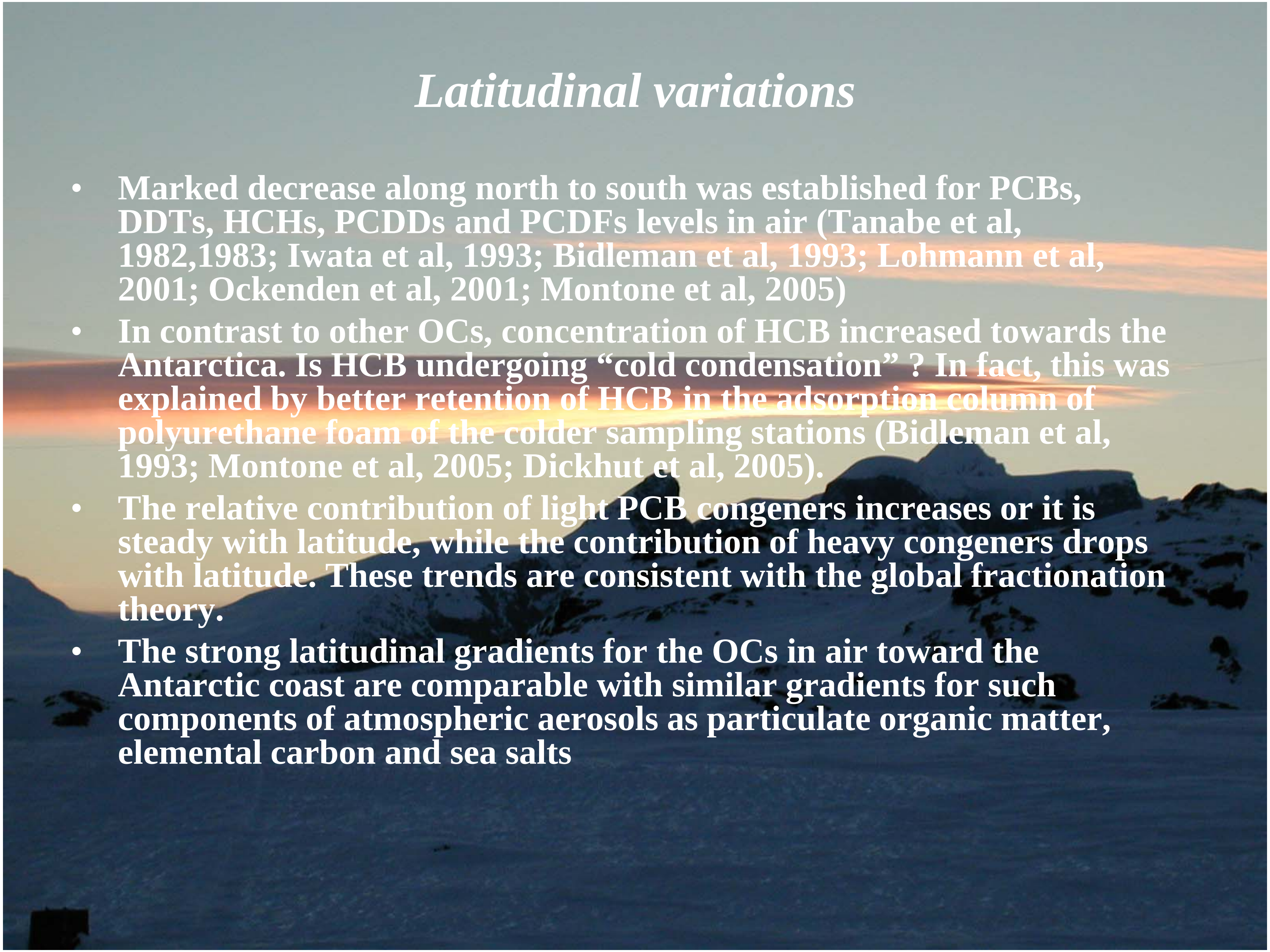
(Data from Montone et al, 2005 and Lohmann et al, 2001)







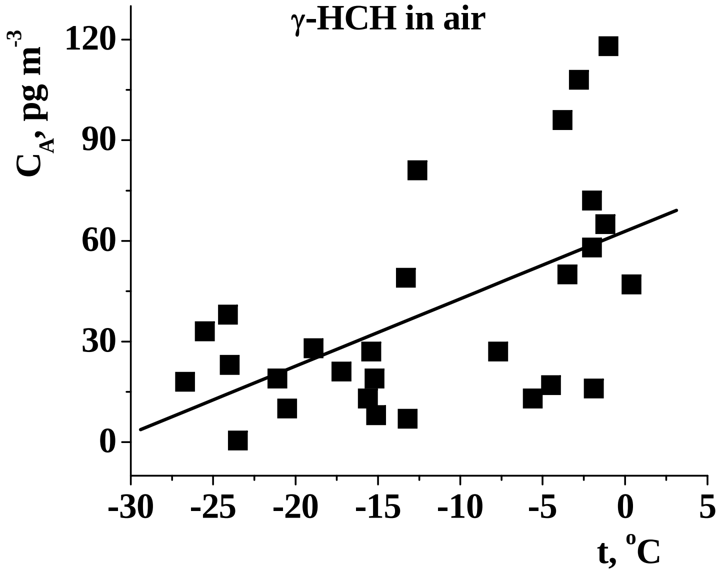




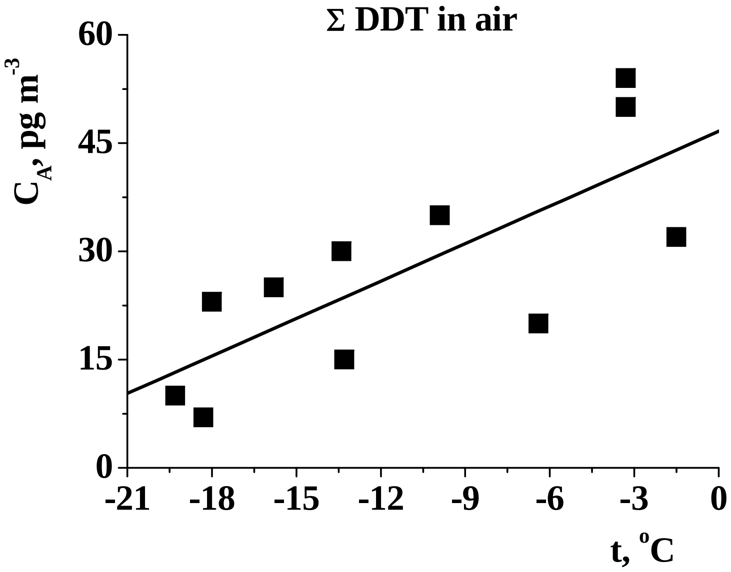
Latitudinal variations

- **Marked decrease along north to south was established for PCBs, DDTs, HCHs, PCDDs and PCDFs levels in air (Tanabe et al, 1982,1983; Iwata et al, 1993; Bidleman et al, 1993; Lohmann et al, 2001; Ockenden et al, 2001; Montone et al, 2005)**
- **In contrast to other OCs, concentration of HCB increased towards the Antarctica. Is HCB undergoing “cold condensation” ? In fact, this was explained by better retention of HCB in the adsorption column of polyurethane foam of the colder sampling stations (Bidleman et al, 1993; Montone et al, 2005; Dickhut et al, 2005).**
- **The relative contribution of light PCB congeners increases or it is steady with latitude, while the contribution of heavy congeners drops with latitude. These trends are consistent with the global fractionation theory.**
- **The strong latitudinal gradients for the OCs in air toward the Antarctic coast are comparable with similar gradients for such components of atmospheric aerosols as particulate organic matter, elemental carbon and sea salts**

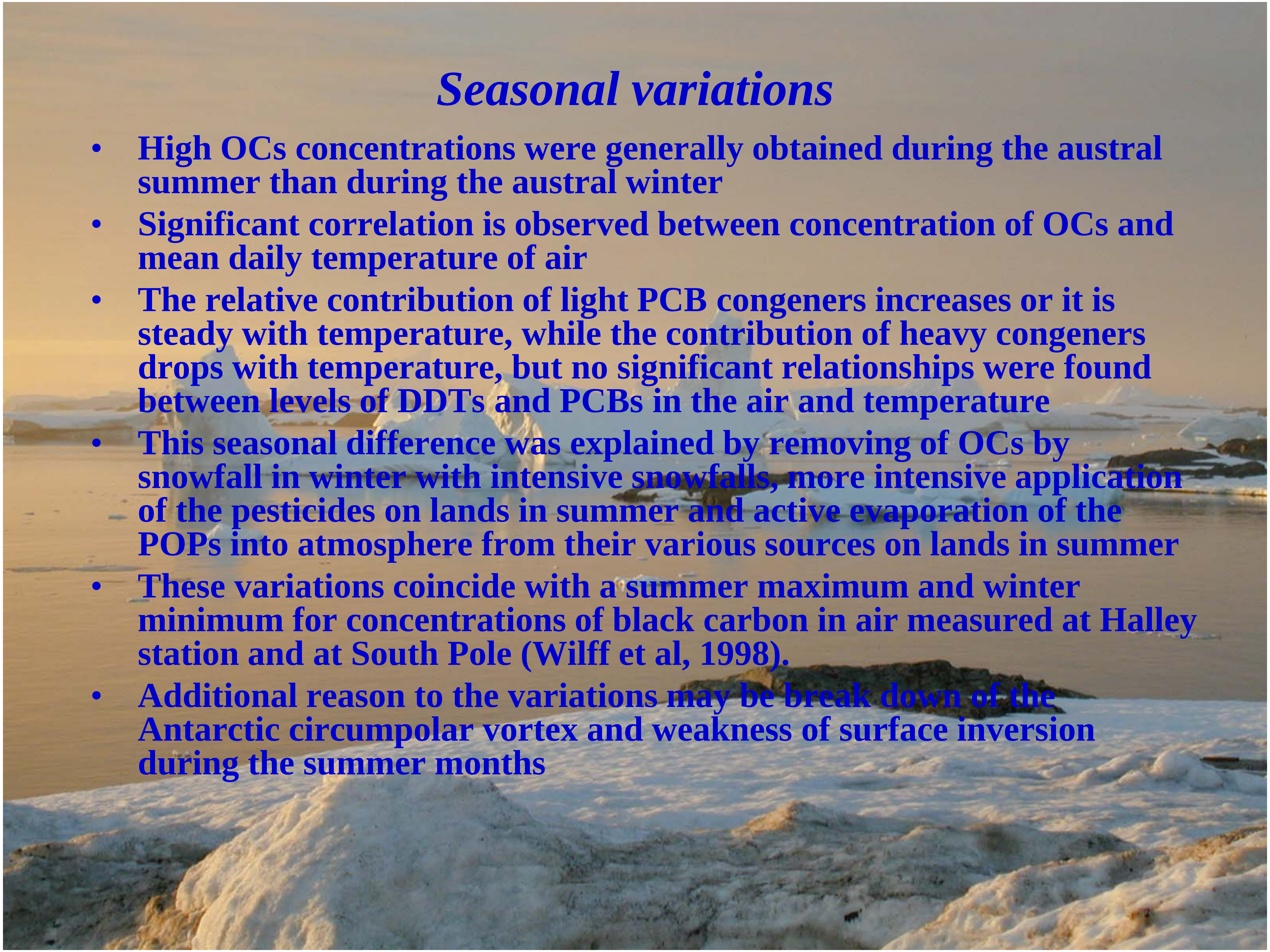
Seasonal variations



Data from Larsson et al, 1992

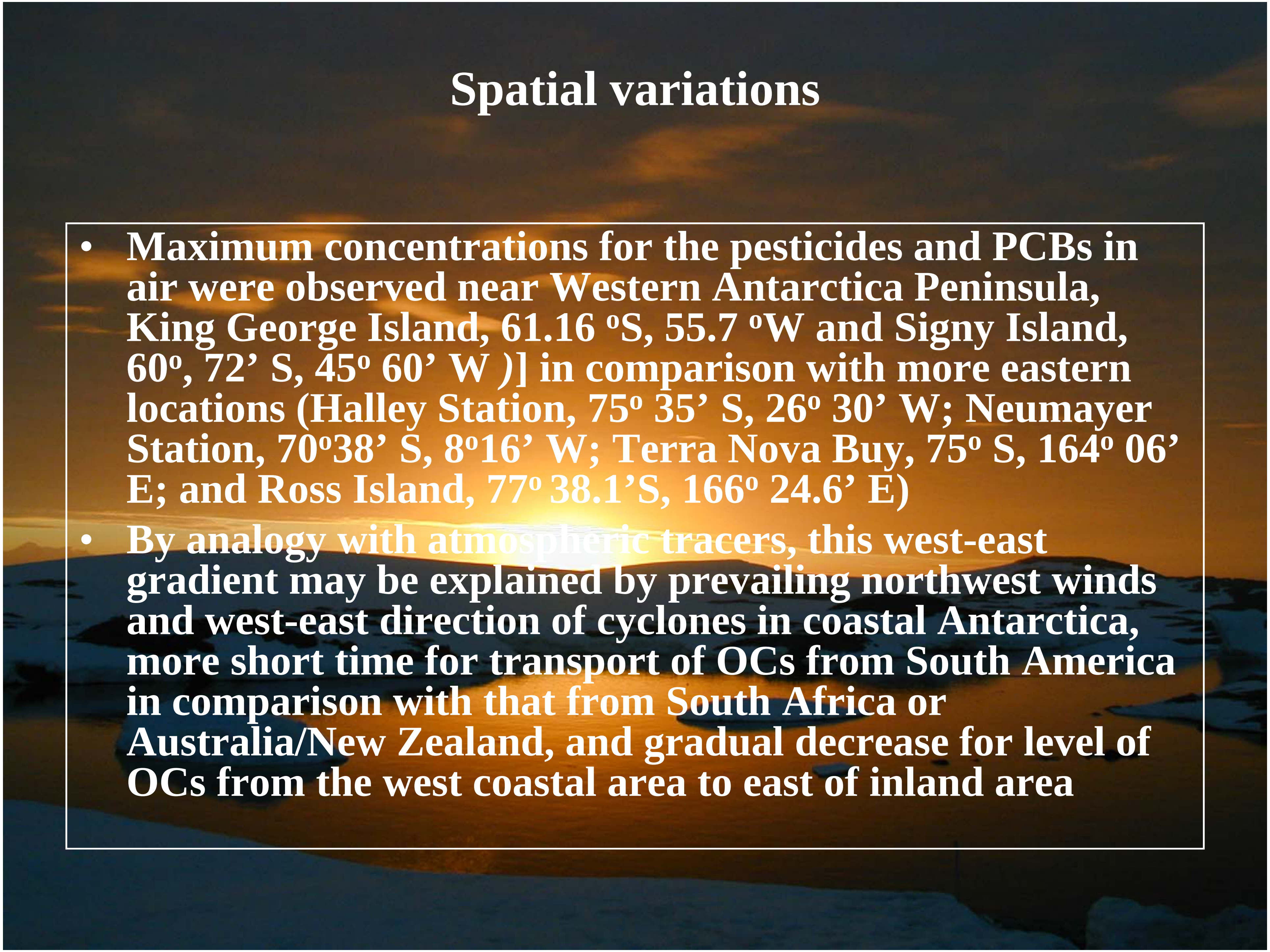


Data from Tanabe et al, 1983



Seasonal variations

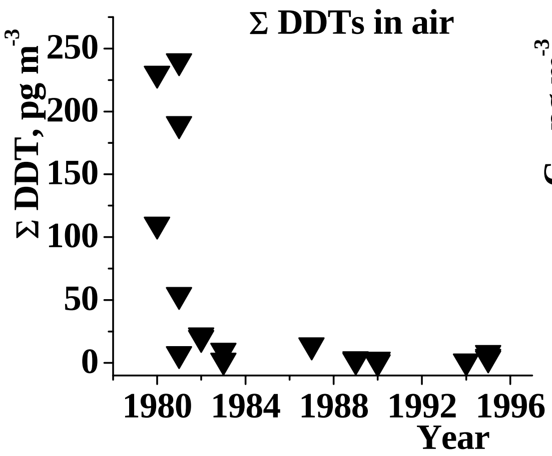
- **High OCs concentrations were generally obtained during the austral summer than during the austral winter**
- **Significant correlation is observed between concentration of OCs and mean daily temperature of air**
- **The relative contribution of light PCB congeners increases or it is steady with temperature, while the contribution of heavy congeners drops with temperature, but no significant relationships were found between levels of DDTs and PCBs in the air and temperature**
- **This seasonal difference was explained by removing of OCs by snowfall in winter with intensive snowfalls, more intensive application of the pesticides on lands in summer and active evaporation of the POPs into atmosphere from their various sources on lands in summer**
- **These variations coincide with a summer maximum and winter minimum for concentrations of black carbon in air measured at Halley station and at South Pole (Wilff et al, 1998).**
- **Additional reason to the variations may be break down of the Antarctic circumpolar vortex and weakness of surface inversion during the summer months**

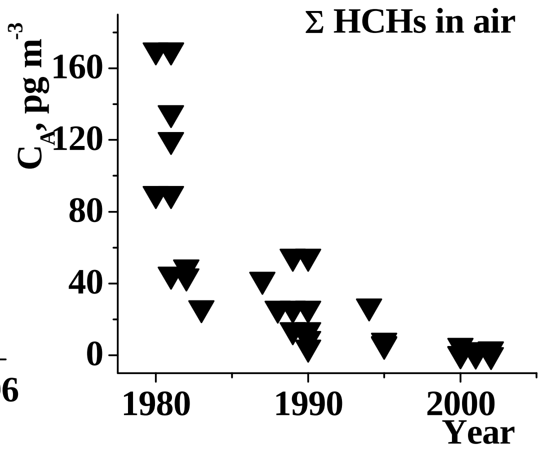


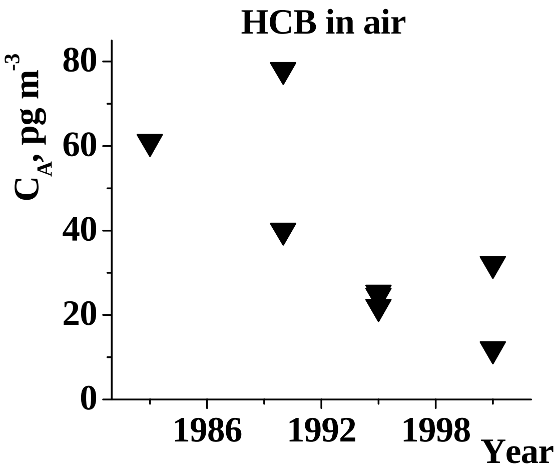
Spatial variations

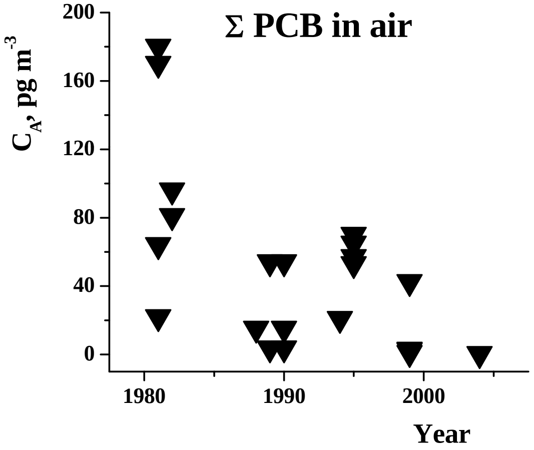
- Maximum concentrations for the pesticides and PCBs in air were observed near Western Antarctica Peninsula, King George Island, 61.16 ^{o}S, 55.7 ^{o}W and Signy Island, 60^{o}, 72’ S, 45^{o} 60’ W *)*] in comparison with more eastern locations (Halley Station, 75^{o} 35’ S, 26^{o} 30’ W; Neumayer Station, 70^{o}38’ S, 8^{o}16’ W; Terra Nova Buy, 75^{o} S, 164^{o} 06’ E; and Ross Island, 77^{o} 38.1’S, 166^{o} 24.6’ E)
- By analogy with atmospheric tracers, this west-east gradient may be explained by prevailing northwest winds and west-east direction of cyclones in coastal Antarctica, more short time for transport of OCs from South America in comparison with that from South Africa or Australia/New Zealand, and gradual decrease for level of OCs from the west coastal area to east of inland area

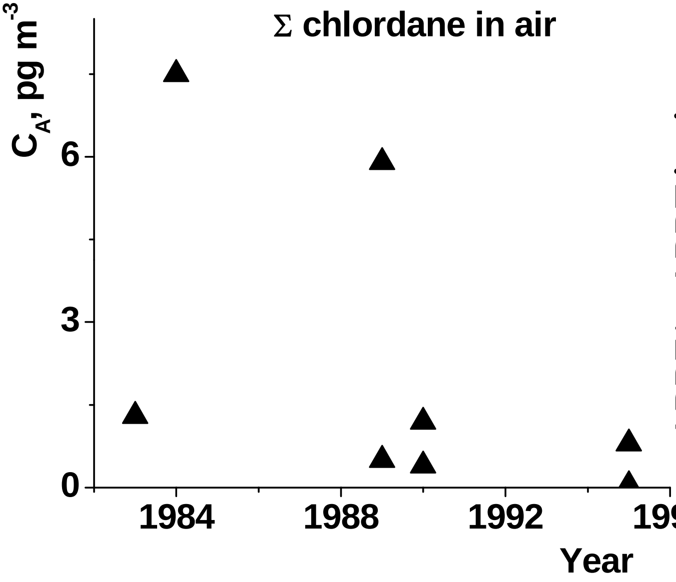
Temporal variations in air

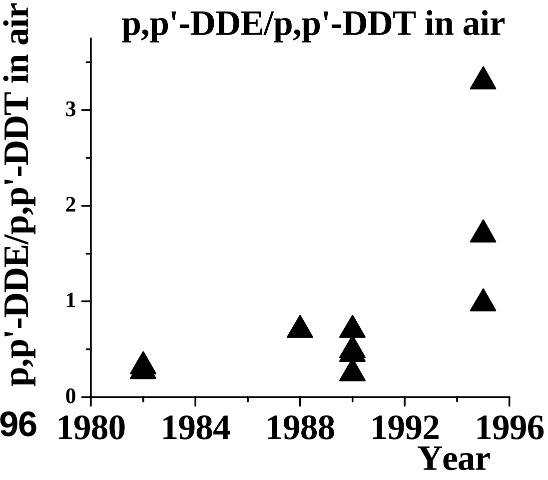




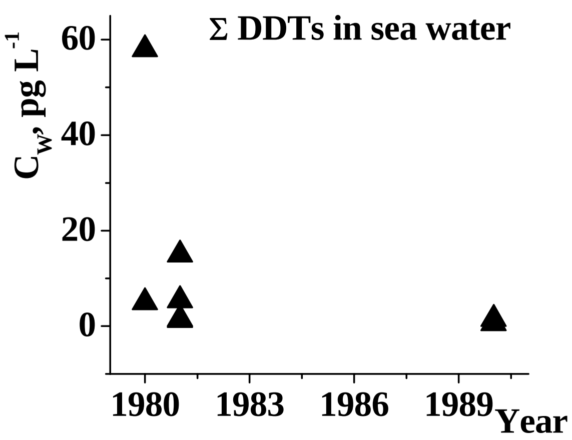


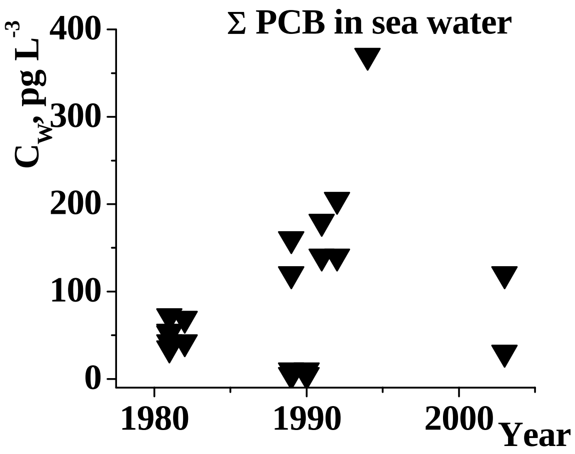


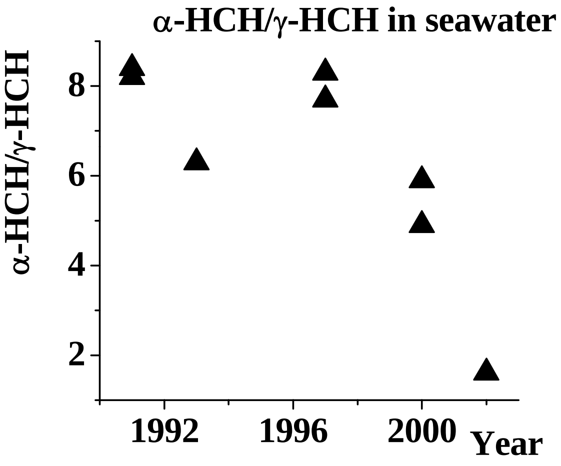


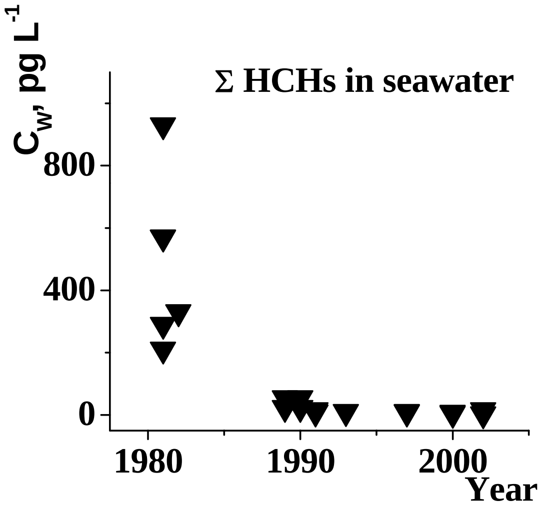


Temporal variations in seawater

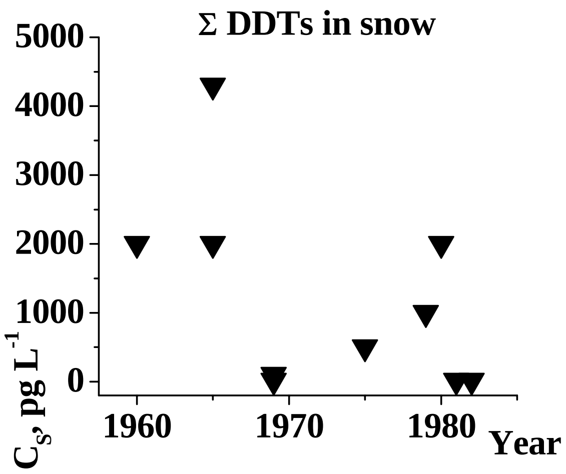


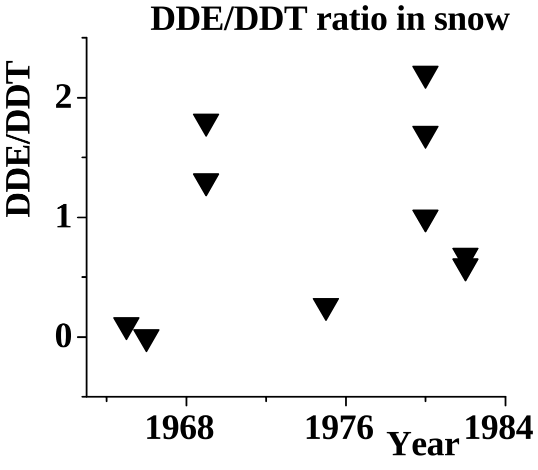


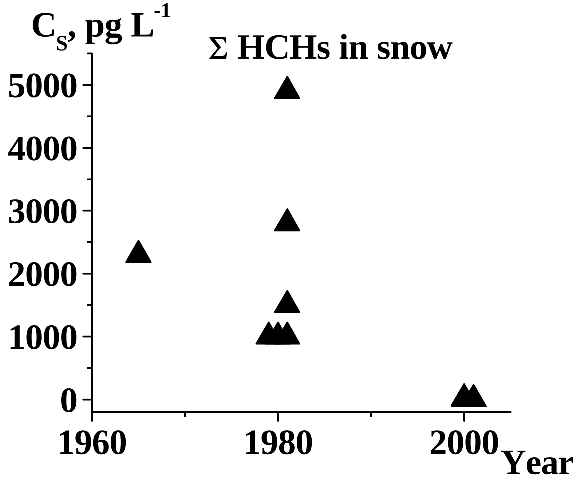


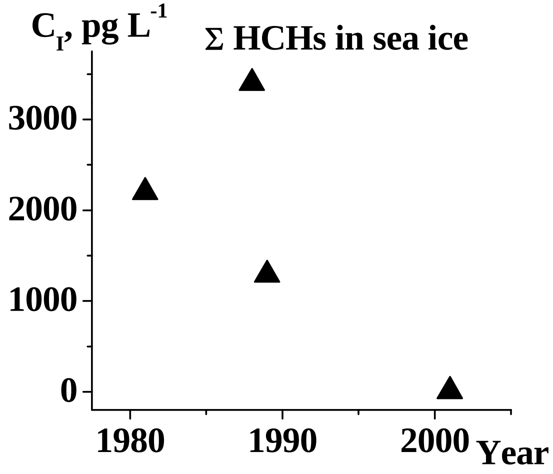


Temporal variations in snow and sea ice









Temporal variations

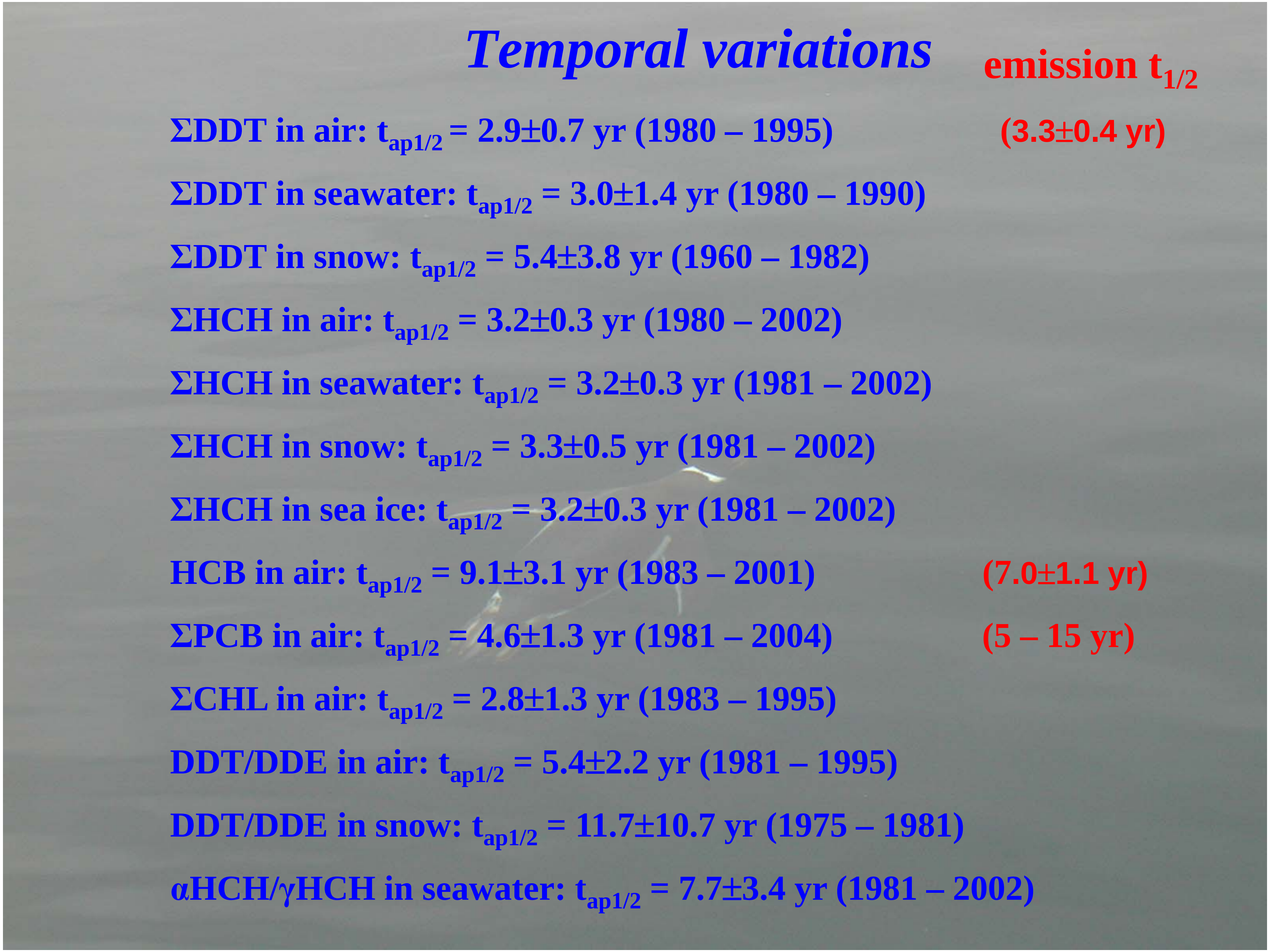
Distinct declines are observed for ΣDDT and ΣHCH in air, seawater and snow, HCB, ΣPCB and ΣCHL in air, ΣHCH in sea ice, DDT/DDE ratio in air and snow, and α-HCH/γ-HCH ratio in seawater.

These trends were treated assuming first-order kinetics:

$$\ln C_i = A - k_{ap} \times (\text{Year})$$

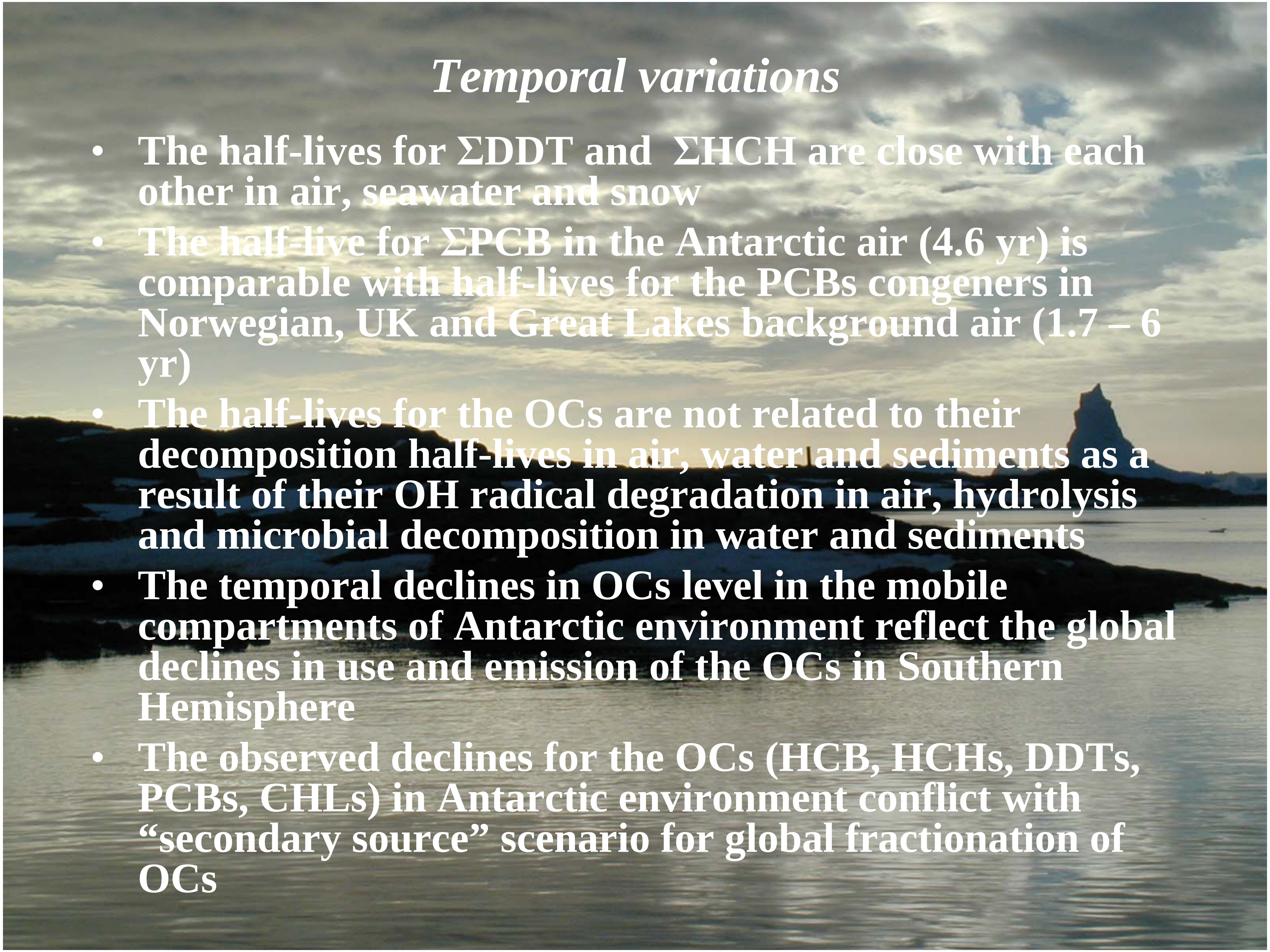
and first-order half-lives for OCs in different mobile mediums were estimated:

$$t_{ap1/2} = (\ln 2)/k_{ap}$$



Temporal variations

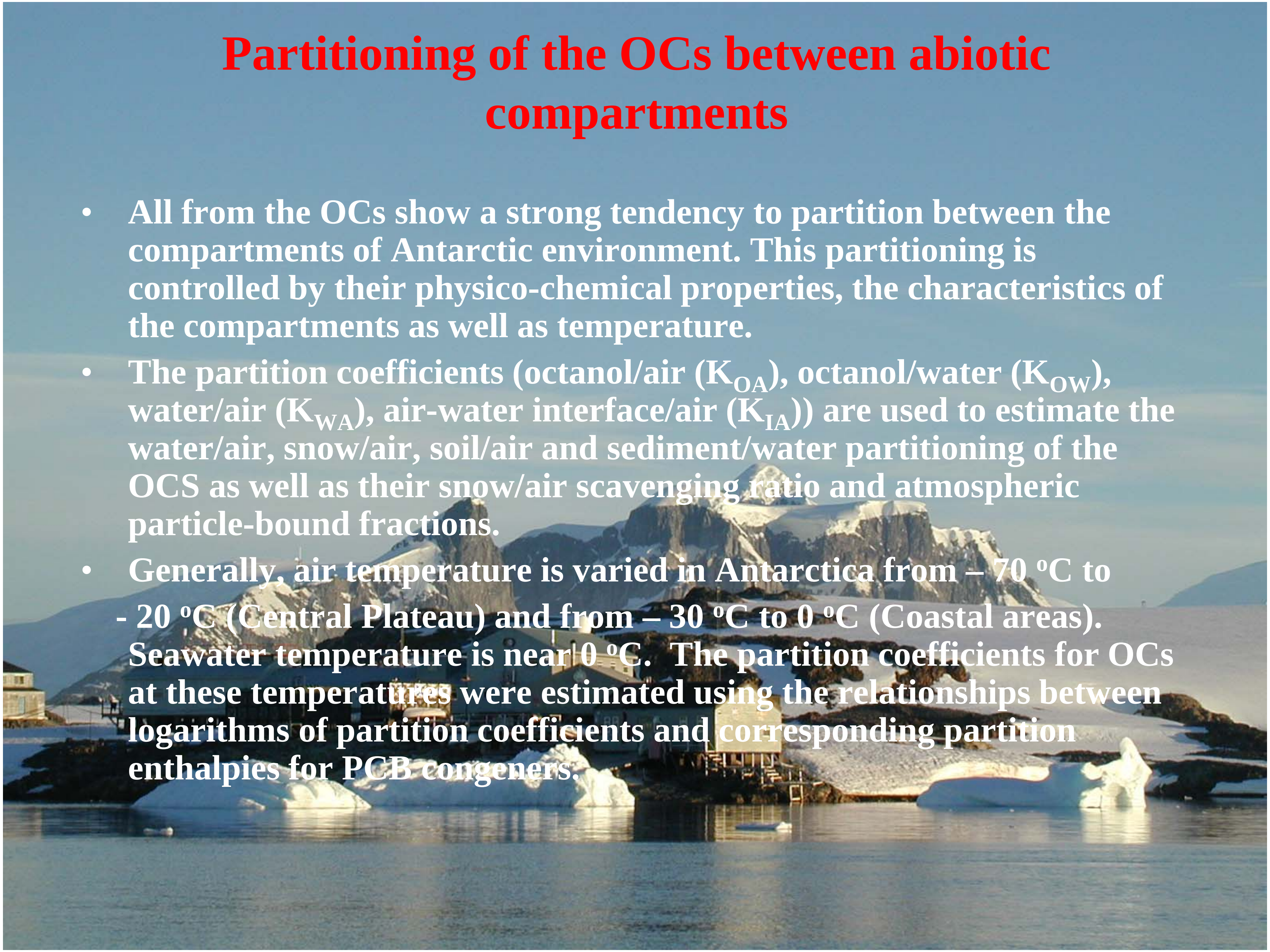
	emission $t_{1/2}$
ΣDDT in air: $t_{ap1/2}$ = 2.9±0.7 yr (1980 – 1995)	(3.3±0.4 yr)
ΣDDT in seawater: $t_{ap1/2}$ = 3.0±1.4 yr (1980 – 1990)	
ΣDDT in snow: $t_{ap1/2}$ = 5.4±3.8 yr (1960 – 1982)	
ΣHCH in air: $t_{ap1/2}$ = 3.2±0.3 yr (1980 – 2002)	
ΣHCH in seawater: $t_{ap1/2}$ = 3.2±0.3 yr (1981 – 2002)	
ΣHCH in snow: $t_{ap1/2}$ = 3.3±0.5 yr (1981 – 2002)	
ΣHCH in sea ice: $t_{ap1/2}$ = 3.2±0.3 yr (1981 – 2002)	
HCB in air: $t_{ap1/2}$ = 9.1±3.1 yr (1983 – 2001)	(7.0±1.1 yr)
ΣPCB in air: $t_{ap1/2}$ = 4.6±1.3 yr (1981 – 2004)	(5 – 15 yr)
ΣCHL in air: $t_{ap1/2}$ = 2.8±1.3 yr (1983 – 1995)	
DDT/DDE in air: $t_{ap1/2}$ = 5.4±2.2 yr (1981 – 1995)	
DDT/DDE in snow: $t_{ap1/2}$ = 11.7±10.7 yr (1975 – 1981)	
αHCH/γHCH in seawater: $t_{ap1/2}$ = 7.7±3.4 yr (1981 – 2002)	



Temporal variations

- **The half-lives for ΣDDT and ΣHCH are close with each other in air, seawater and snow**
- **The half-live for ΣPCB in the Antarctic air (4.6 yr) is comparable with half-lives for the PCBs congeners in Norwegian, UK and Great Lakes background air (1.7 – 6 yr)**
- **The half-lives for the OCs are not related to their decomposition half-lives in air, water and sediments as a result of their OH radical degradation in air, hydrolysis and microbial decomposition in water and sediments**
- **The temporal declines in OCs level in the mobile compartments of Antarctic environment reflect the global declines in use and emission of the OCs in Southern Hemisphere**
- **The observed declines for the OCs (HCB, HCHs, DDTs, PCBs, CHLs) in Antarctic environment conflict with “secondary source” scenario for global fractionation of OCs**

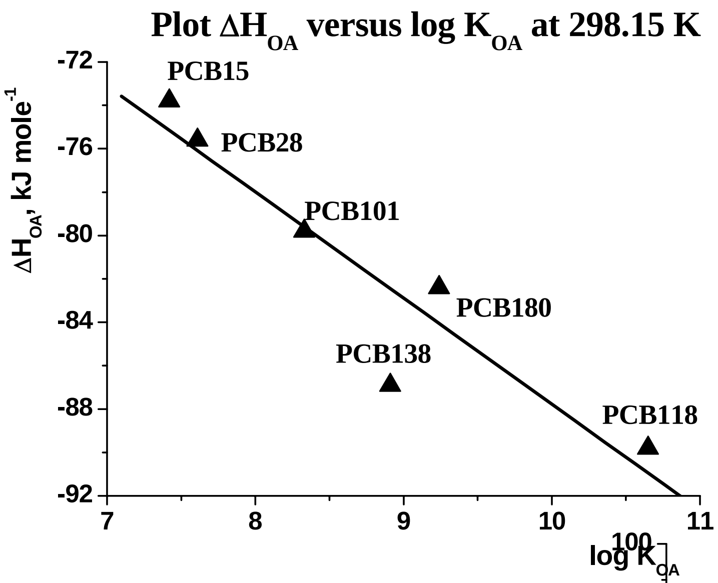
Partitioning of the OCs between abiotic compartments

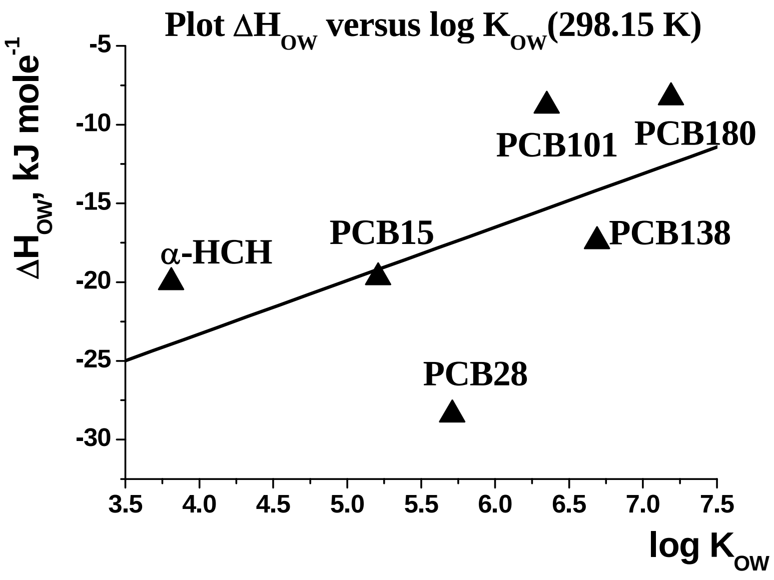


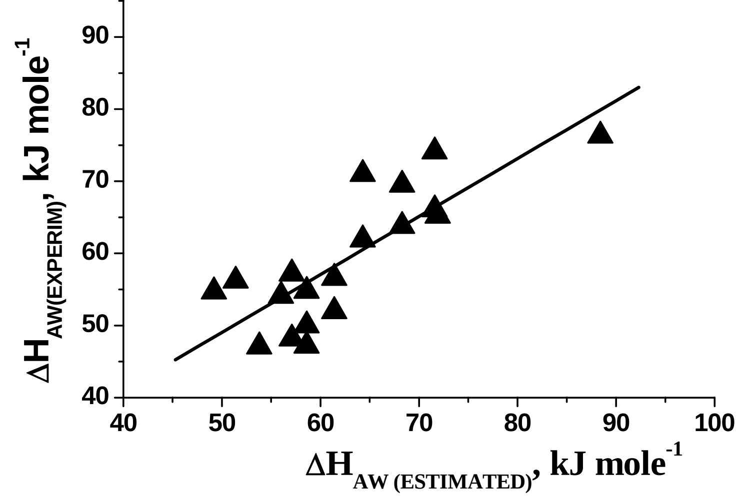
- All from the OCs show a strong tendency to partition between the compartments of Antarctic environment. This partitioning is controlled by their physico-chemical properties, the characteristics of the compartments as well as temperature.
- The partition coefficients (octanol/air (K_{OA}), octanol/water (K_{OW}), water/air (K_{WA}), air-water interface/air (K_{IA})) are used to estimate the water/air, snow/air, soil/air and sediment/water partitioning of the OCS as well as their snow/air scavenging ratio and atmospheric particle-bound fractions.
- Generally, air temperature is varied in Antarctica from – 70 ^{o}C to

- 20 ^{o}C (Central Plateau) and from – 30 ^{o}C to 0 ^{o}C (Coastal areas). Seawater temperature is near 0 ^{o}C. The partition coefficients for OCs at these temperatures were estimated using the relationships between logarithms of partition coefficients and corresponding partition enthalpies for PCB congeners.

Partitioning of the OCs between abiotic compartments

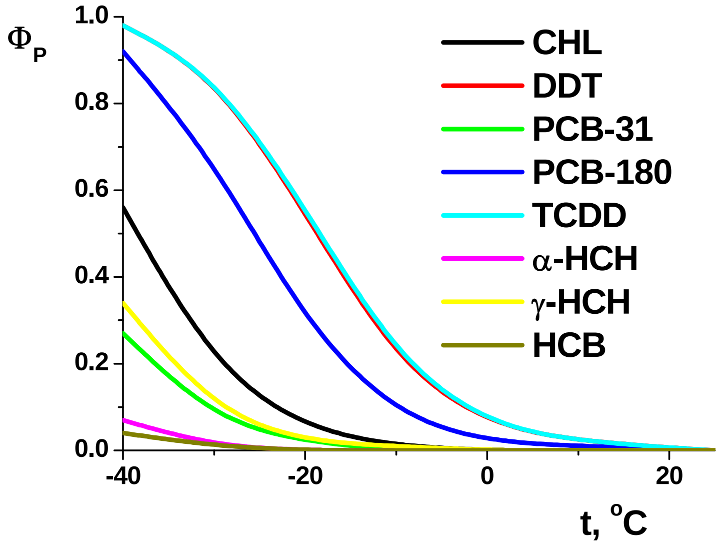




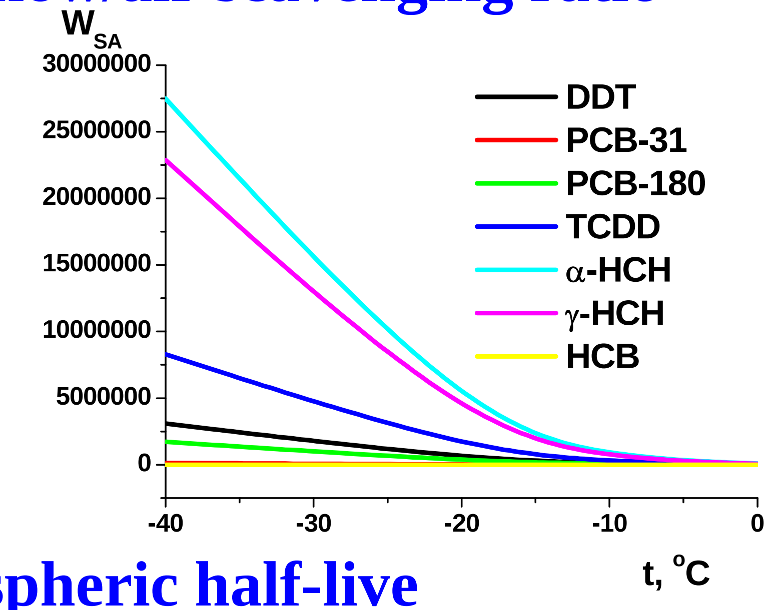


Influence of temperature

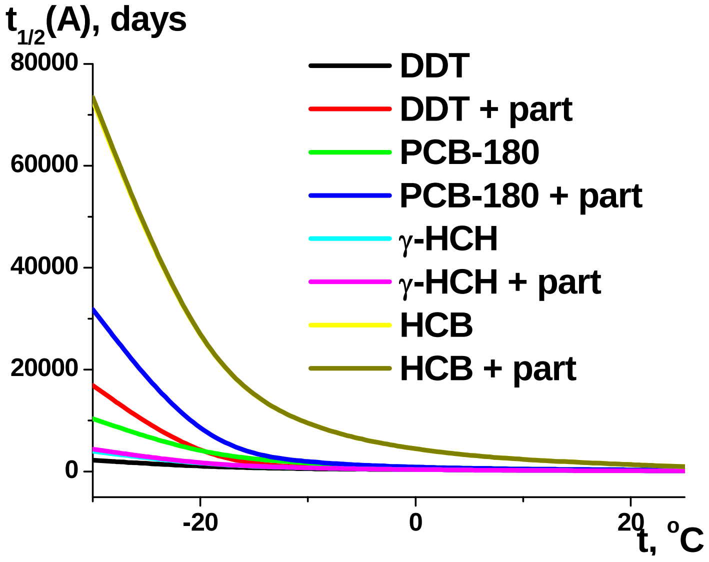
Particle-bound fraction



Snow/air scavenging ratio



Mean atmospheric half-live



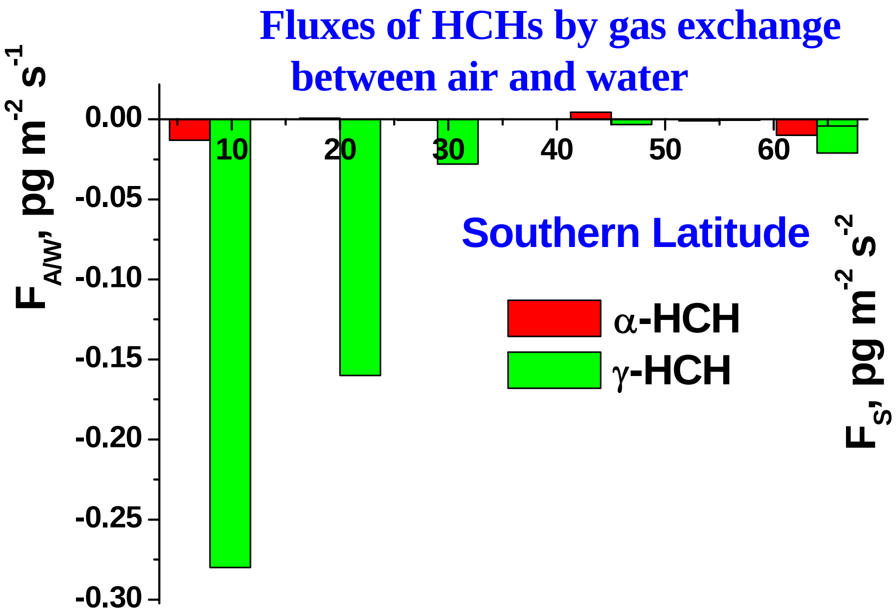
T ↓

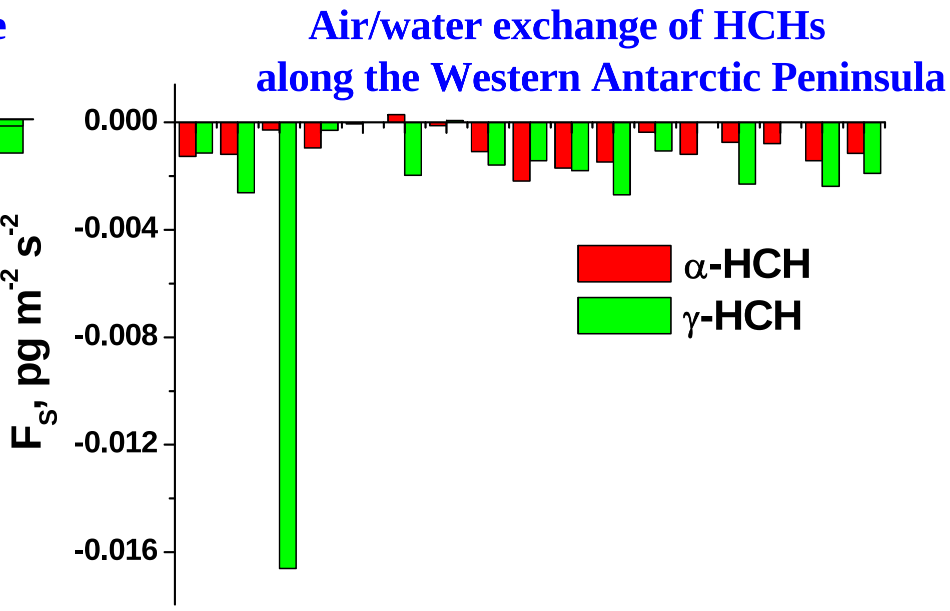
decrease of reactivity of OH radical

decrease of concentration of OH radical

Increase of inert particle-bound fraction

Air-seawater exchange





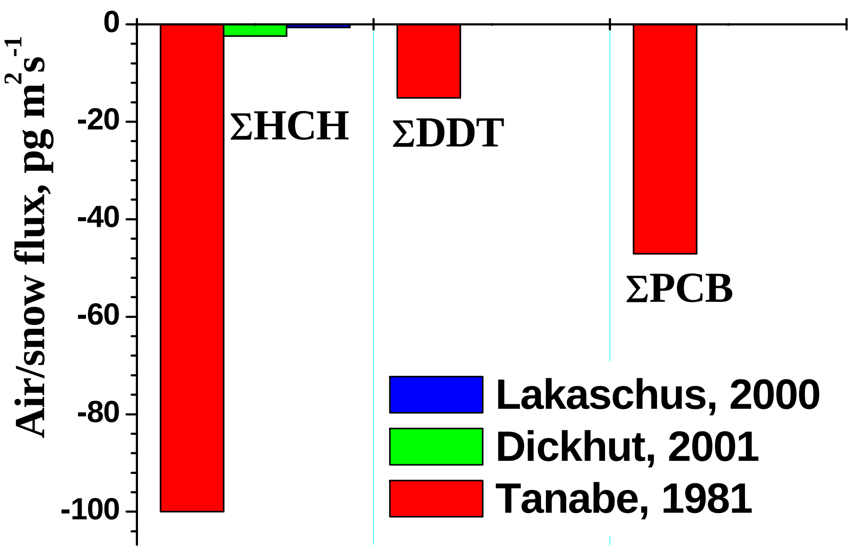
C_A and C_W values from
Lakaschus et al, 2002

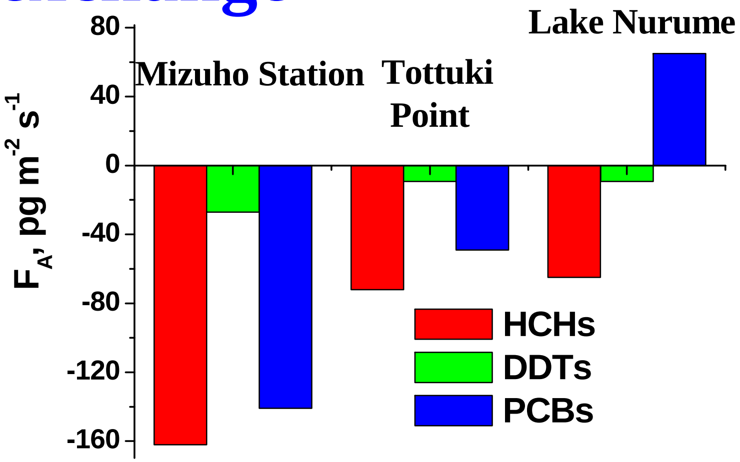
C_A and C_W values from
Dickhut et al, 2005

These fluxes indicate on net deposition of HCHs in seawater near to equilibrium

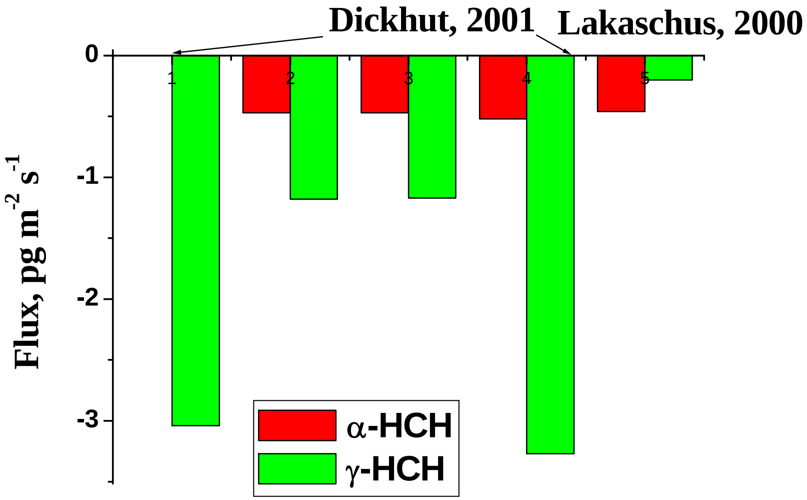
Air-snow exchange

Fluxes of OCs from air to snowpack





C_A and C_S values from Tanabe et al, 1981



These fluxes indicate on net deposition of OCs into snowpack in 1980s and they are close to equilibrium in 2000s

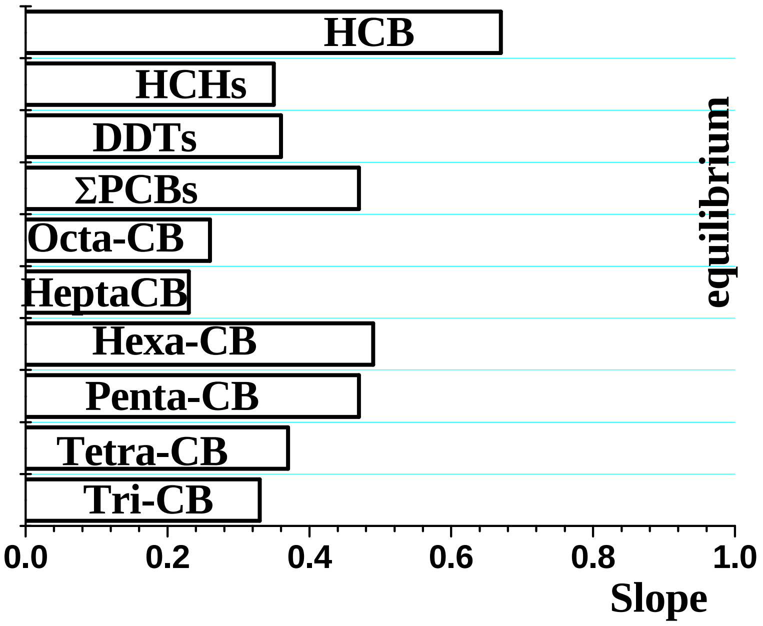
Air-soil exchange

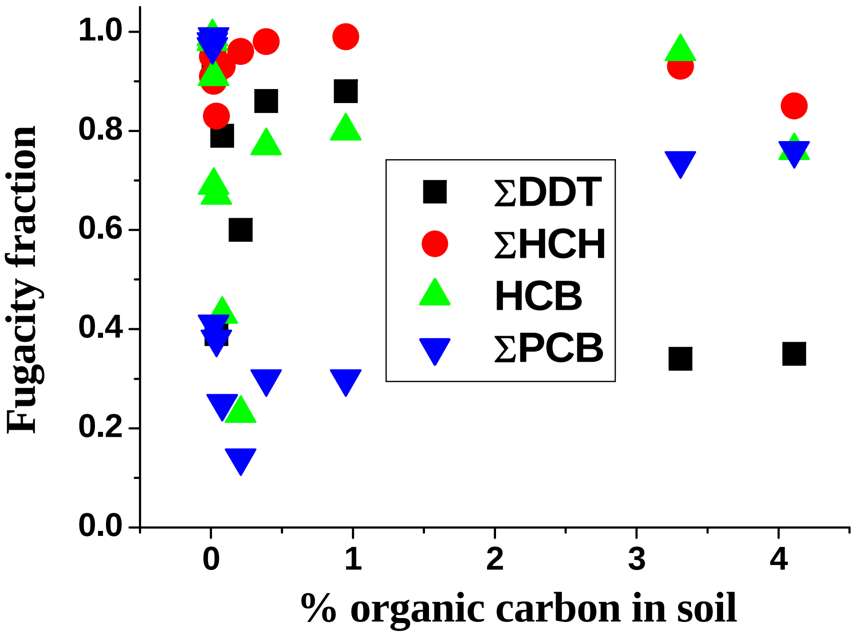
A plot of log C_S versus log [OM] will have a slope of 1 at equilibrium between soil and air (Gouin et al, 2004)

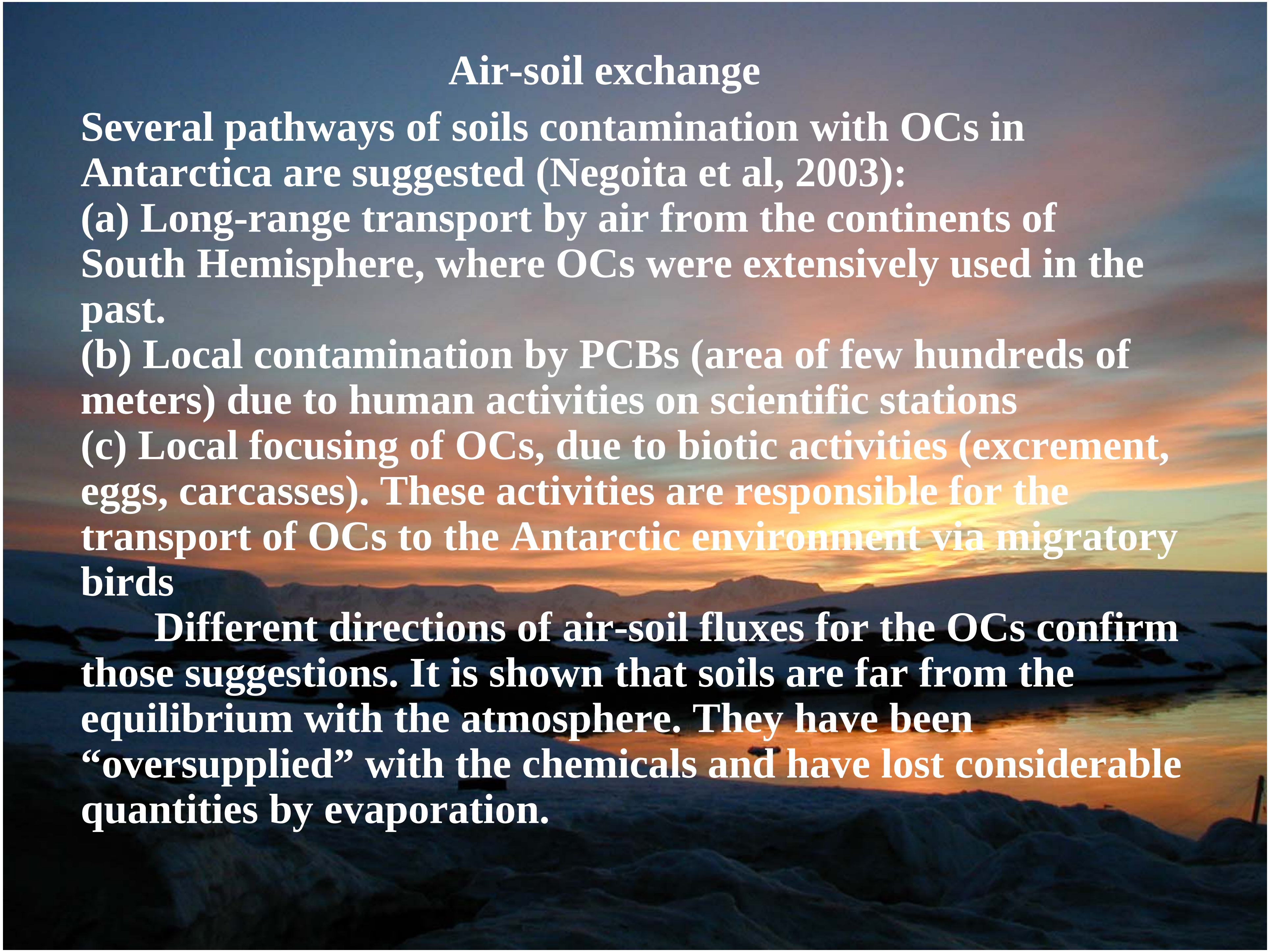
Soil-air equilibrium is indicated by fugacity fraction = 0.5.

Net volatilization and deposition of gas-phase OCs are indicated by fugacity fractions > 0.5 and <0.5 (Harner et al, 2001)

For 11 soils from East Antarctica (Negoita et al, 2003)







Air-soil exchange

Several pathways of soils contamination with OCs in Antarctica are suggested (Negoita et al, 2003):

(a) Long-range transport by air from the continents of South Hemisphere, where OCs were extensively used in the past.

(b) Local contamination by PCBs (area of few hundreds of meters) due to human activities on scientific stations

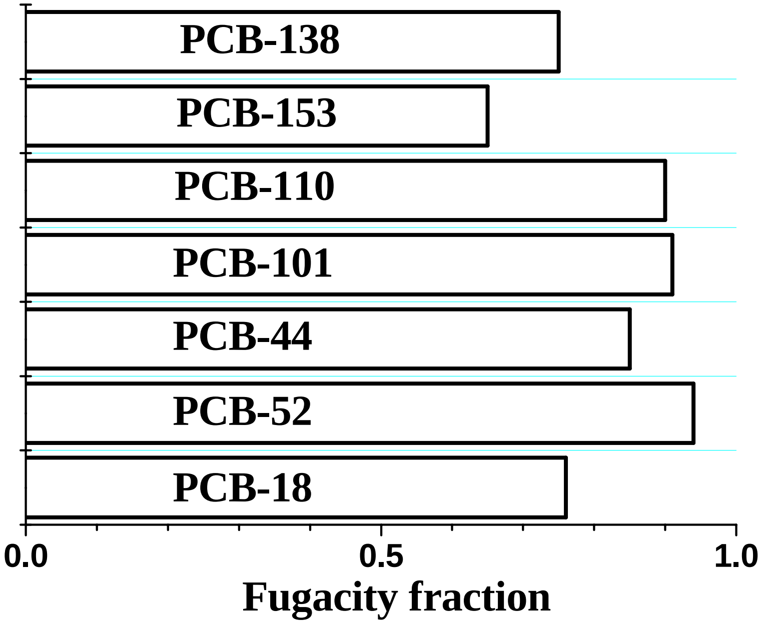
(c) Local focusing of OCs, due to biotic activities (excrement, eggs, carcasses). These activities are responsible for the transport of OCs to the Antarctic environment via migratory birds

Different directions of air-soil fluxes for the OCs confirm those suggestions. It is shown that soils are far from the equilibrium with the atmosphere. They have been “oversupplied” with the chemicals and have lost considerable quantities by evaporation.

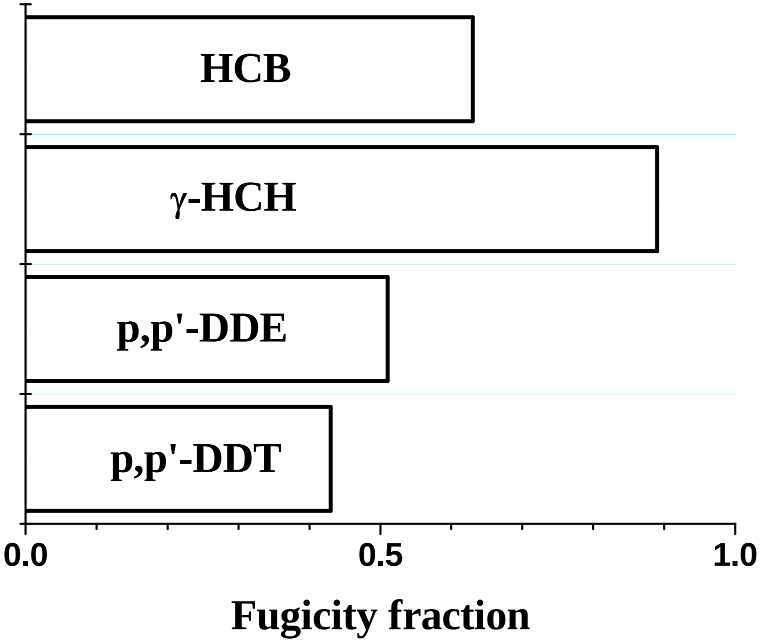
Seawater-sediment exchange

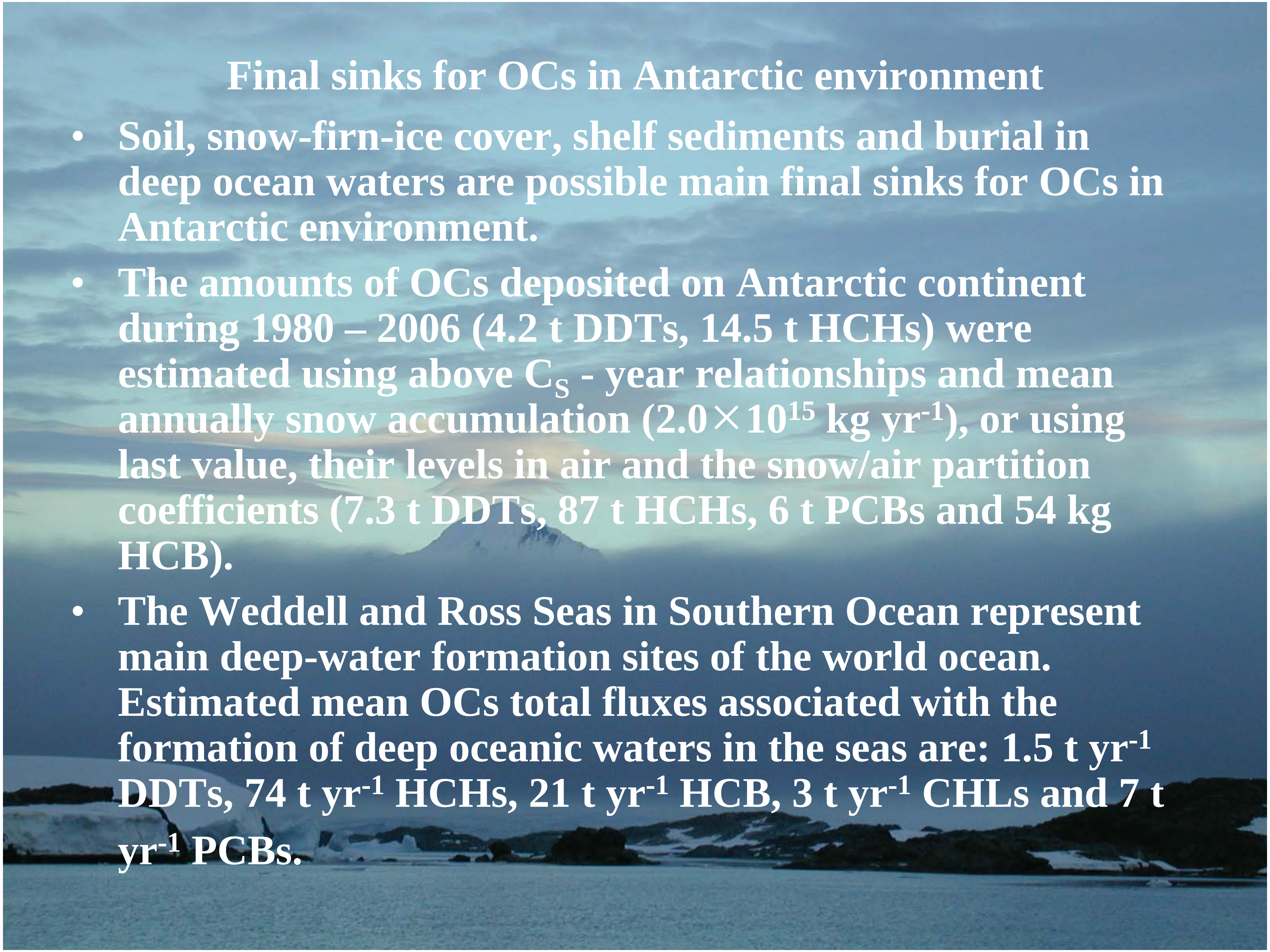
By analogy with soil-air equilibrium, seawater-sediment equilibrium is indicated by fugacity fraction = 0.5. Net desorption from sediments and deposition of dissolved OCs are indicated by fugacity fractions > 0.5 and <0.5

Data from Montone et al, 2001



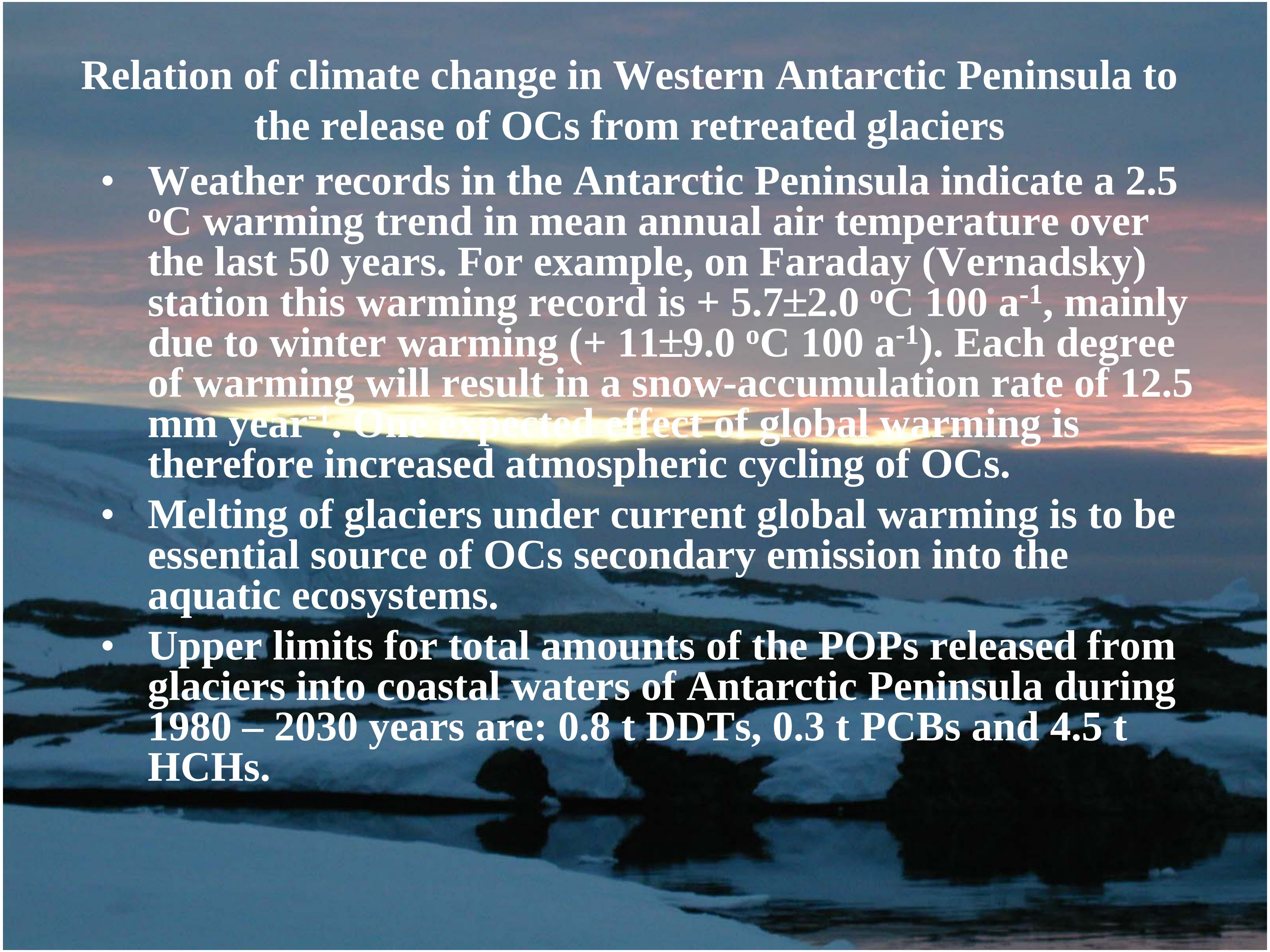
Data from Bondar et al, 2000





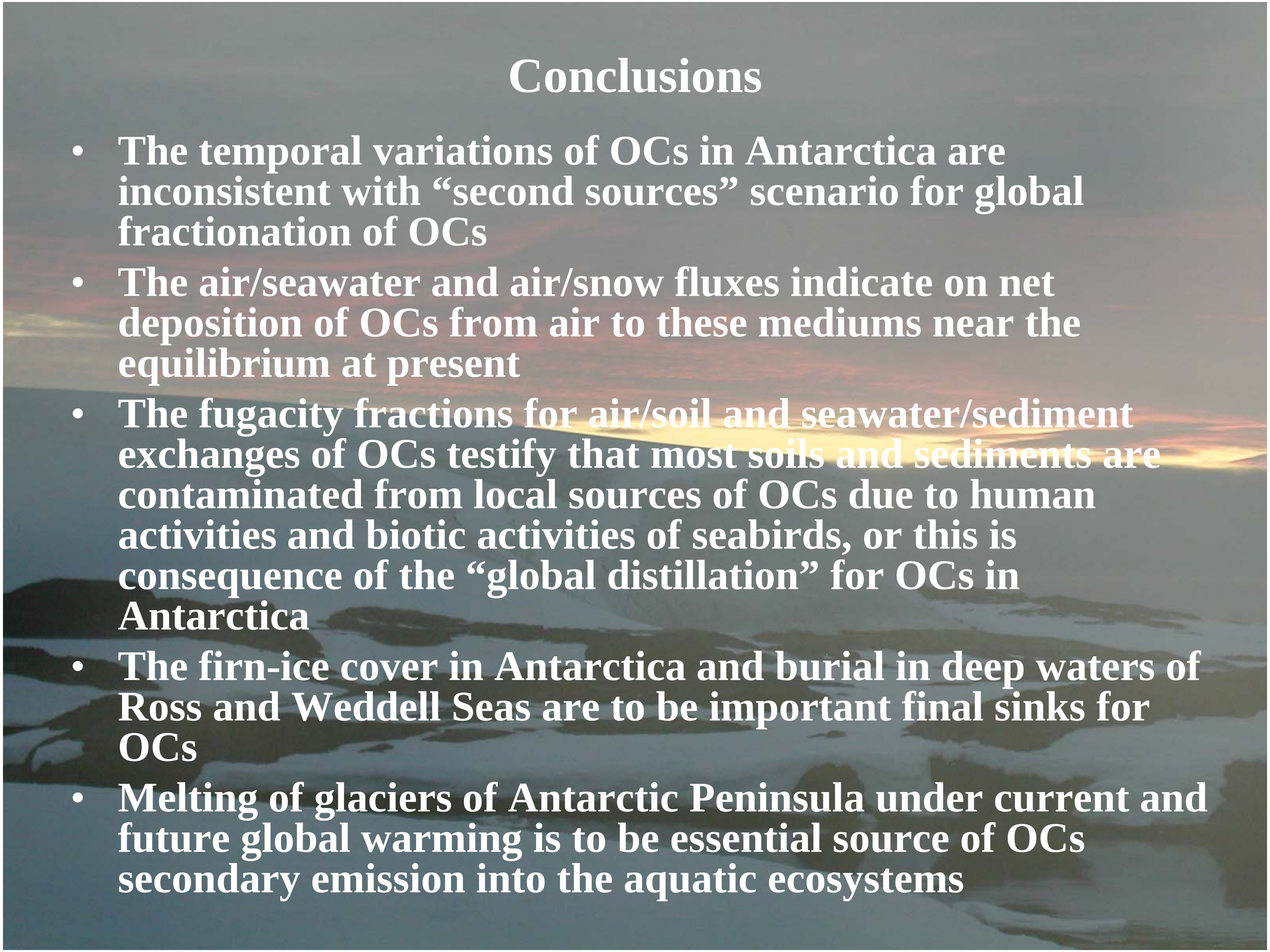
Final sinks for OCs in Antarctic environment

- Soil, snow-firn-ice cover, shelf sediments and burial in deep ocean waters are possible main final sinks for OCs in Antarctic environment.
- The amounts of OCs deposited on Antarctic continent during 1980 – 2006 (4.2 t DDTs, 14.5 t HCHs) were estimated using above C_S - year relationships and mean annually snow accumulation (2.0×10^{15} kg yr^{-1}), or using last value, their levels in air and the snow/air partition coefficients (7.3 t DDTs, 87 t HCHs, 6 t PCBs and 54 kg HCB).
- The Weddell and Ross Seas in Southern Ocean represent main deep-water formation sites of the world ocean. Estimated mean OCs total fluxes associated with the formation of deep oceanic waters in the seas are: 1.5 t yr^{-1} DDTs, 74 t yr^{-1} HCHs, 21 t yr^{-1} HCB, 3 t yr^{-1} CHLs and 7 t yr^{-1} PCBs.



Relation of climate change in Western Antarctic Peninsula to the release of OCs from retreated glaciers

- Weather records in the Antarctic Peninsula indicate a 2.5 °C warming trend in mean annual air temperature over the last 50 years. For example, on Faraday (Vernadsky) station this warming record is + 5.7±2.0 °C 100 a^{-1}, mainly due to winter warming (+ 11±9.0 °C 100 a^{-1}). Each degree of warming will result in a snow-accumulation rate of 12.5 mm year^{-1}. One expected effect of global warming is therefore increased atmospheric cycling of OCs.
- Melting of glaciers under current global warming is to be essential source of OCs secondary emission into the aquatic ecosystems.
- Upper limits for total amounts of the POPs released from glaciers into coastal waters of Antarctic Peninsula during 1980 – 2030 years are: 0.8 t DDTs, 0.3 t PCBs and 4.5 t HCHs.



Conclusions

- The temporal variations of OCs in Antarctica are inconsistent with “second sources” scenario for global fractionation of OCs
- The air/seawater and air/snow fluxes indicate on net deposition of OCs from air to these mediums near the equilibrium at present
- The fugacity fractions for air/soil and seawater/sediment exchanges of OCs testify that most soils and sediments are contaminated from local sources of OCs due to human activities and biotic activities of seabirds, or this is consequence of the “global distillation” for OCs in Antarctica
- The firn-ice cover in Antarctica and burial in deep waters of Ross and Weddell Seas are to be important final sinks for OCs
- Melting of glaciers of Antarctic Peninsula under current and future global warming is to be essential source of OCs secondary emission into the aquatic ecosystems

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