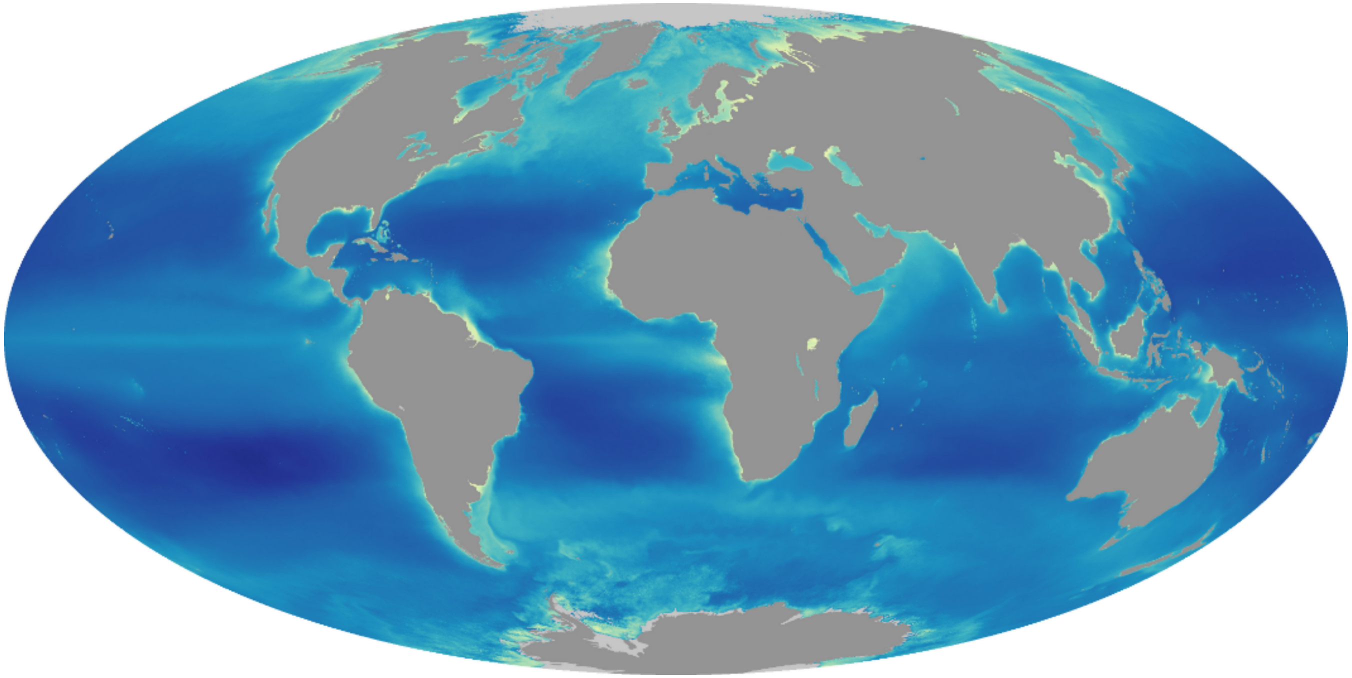
Radionuclides as Tracers in the Ocean



- **Radionuclides**, of both natural and artificial origins, can be used as **CLOCKS of key processes** (age and/or rates) in the oceans, mainly because they:
    - Are **ubiquitous** in all compartments of the oceans
    - Have a large **range of half-lives** (from seconds to billions of years)

- Here we provide you with some examples of how radionuclides are used, such as:

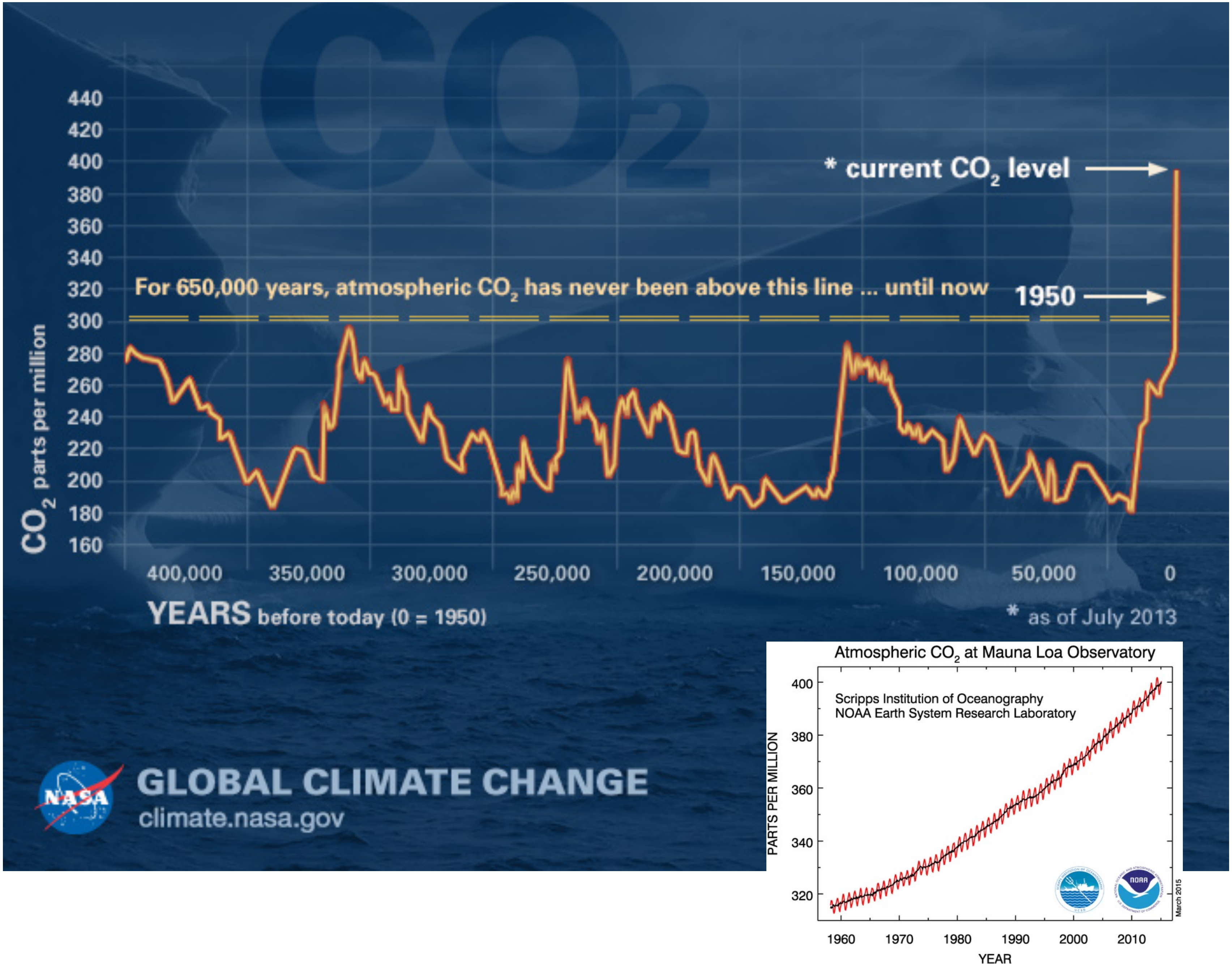
1) What are the **sources, rates and pathways** of substances to and from the ocean (both natural and anthropogenic)?

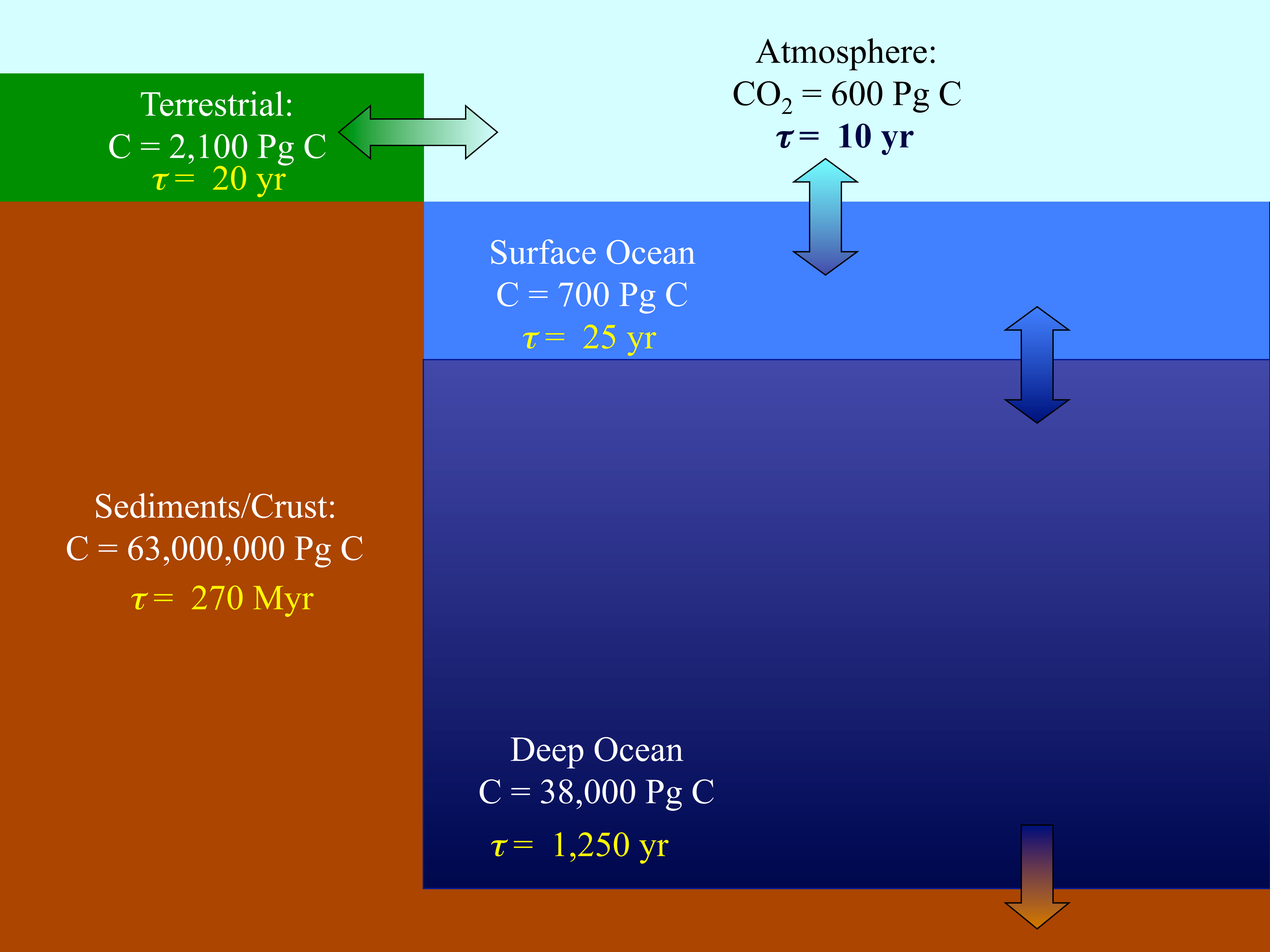
2) How do water masses move in the ocean? Present and Past **circulation**

3) How are substances **transported** from the surface ocean to the deep ocean?

4) How do we study the **past** (climate, anthropogenic impacts, ...)? The sedimentary record

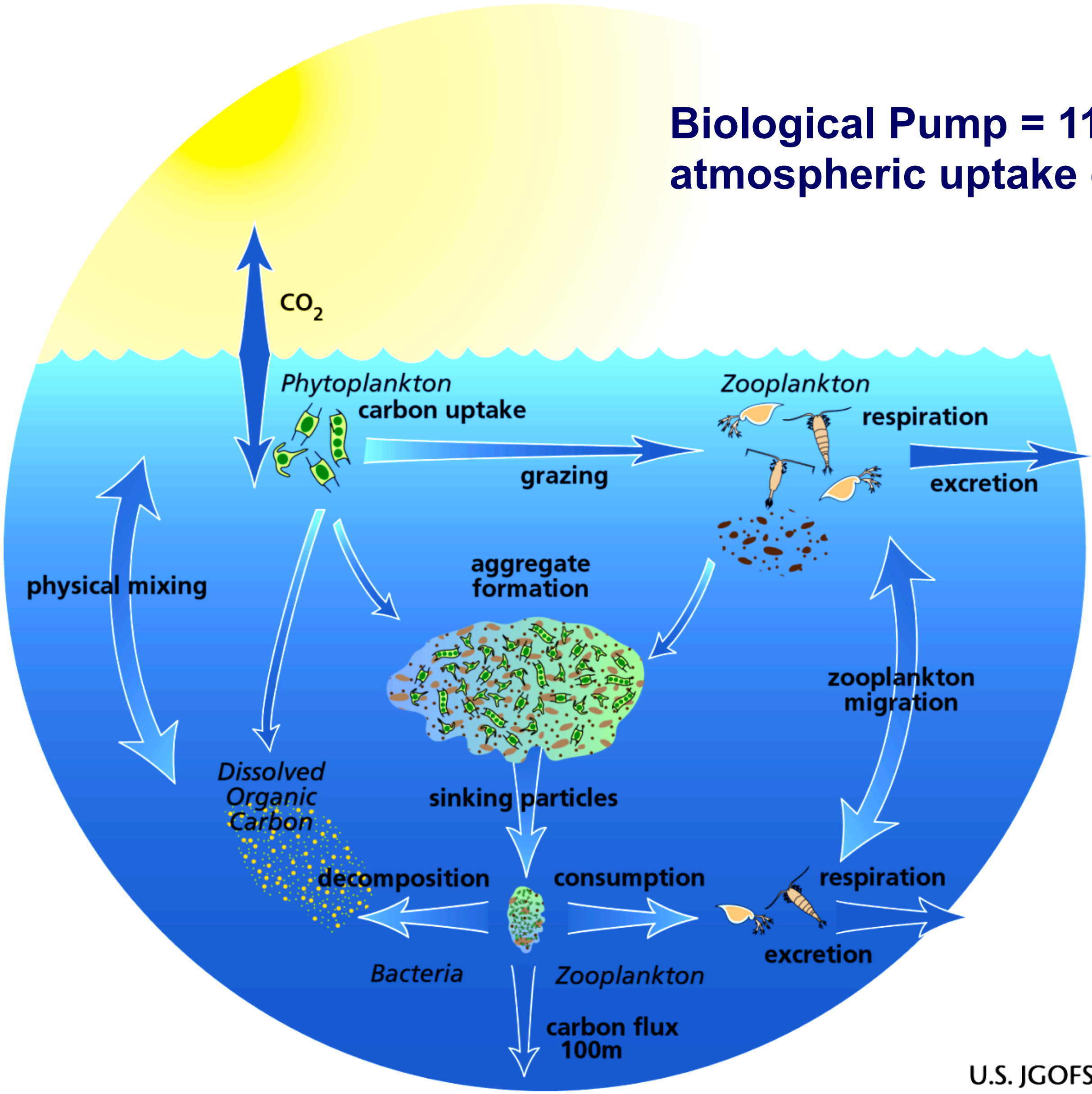
Climate Change




Atmosphere:
CO_2 = 600 Pg C
τ = 10 yr
Terrestrial:
C = 2,100 Pg C
τ = 20 yr
Surface Ocean
C = 700 Pg C
τ = 25 yr
Sediments/Crust:
C = 63,000,000 Pg C
τ = 270 Myr
Deep Ocean
C = 38,000 Pg C
τ = 1,250 yr

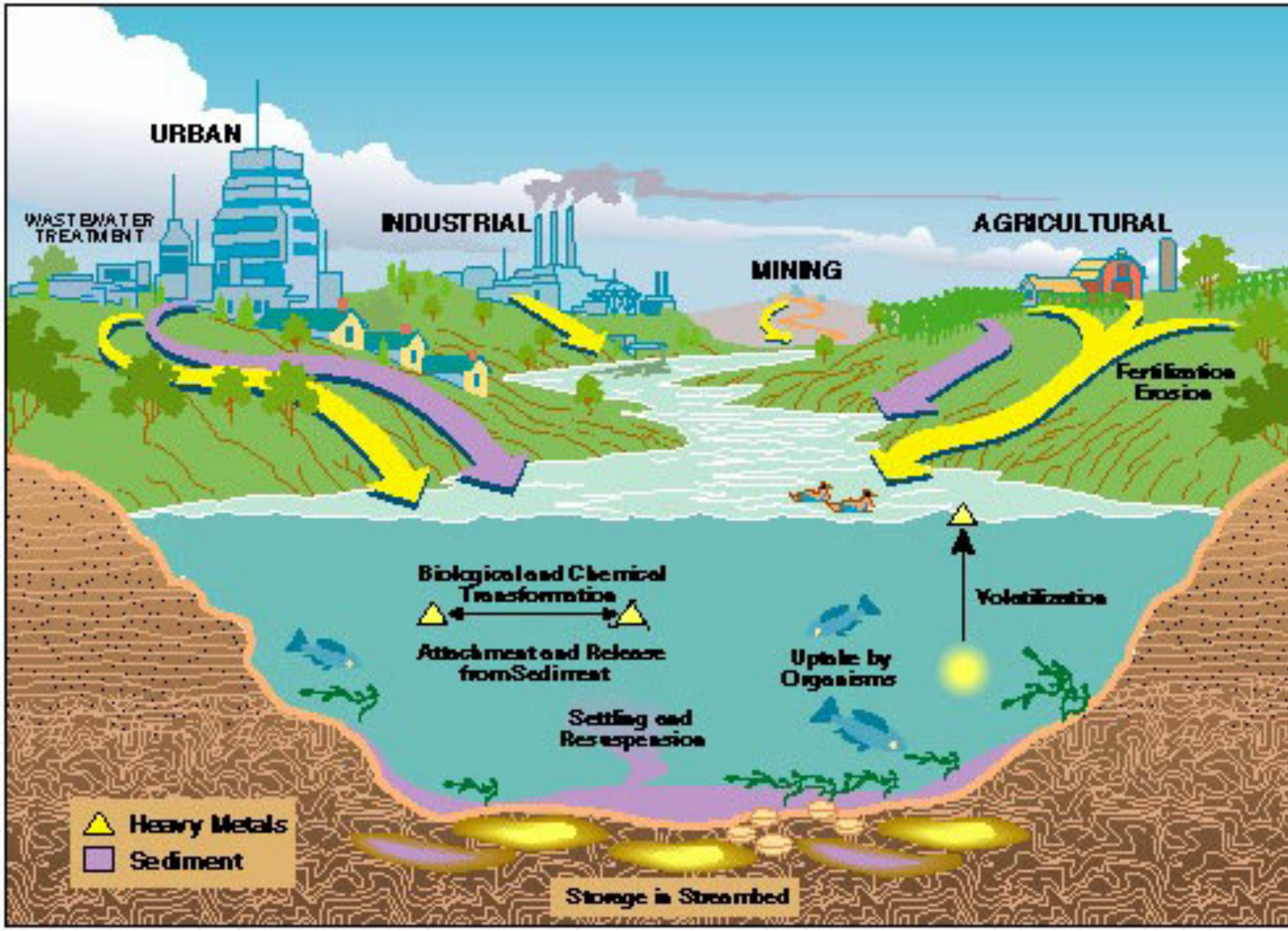
The "Biological Pump"

Biological Pump = 11-16 Gt C/year = an atmospheric uptake of CO_2 ~ 200 ppm.

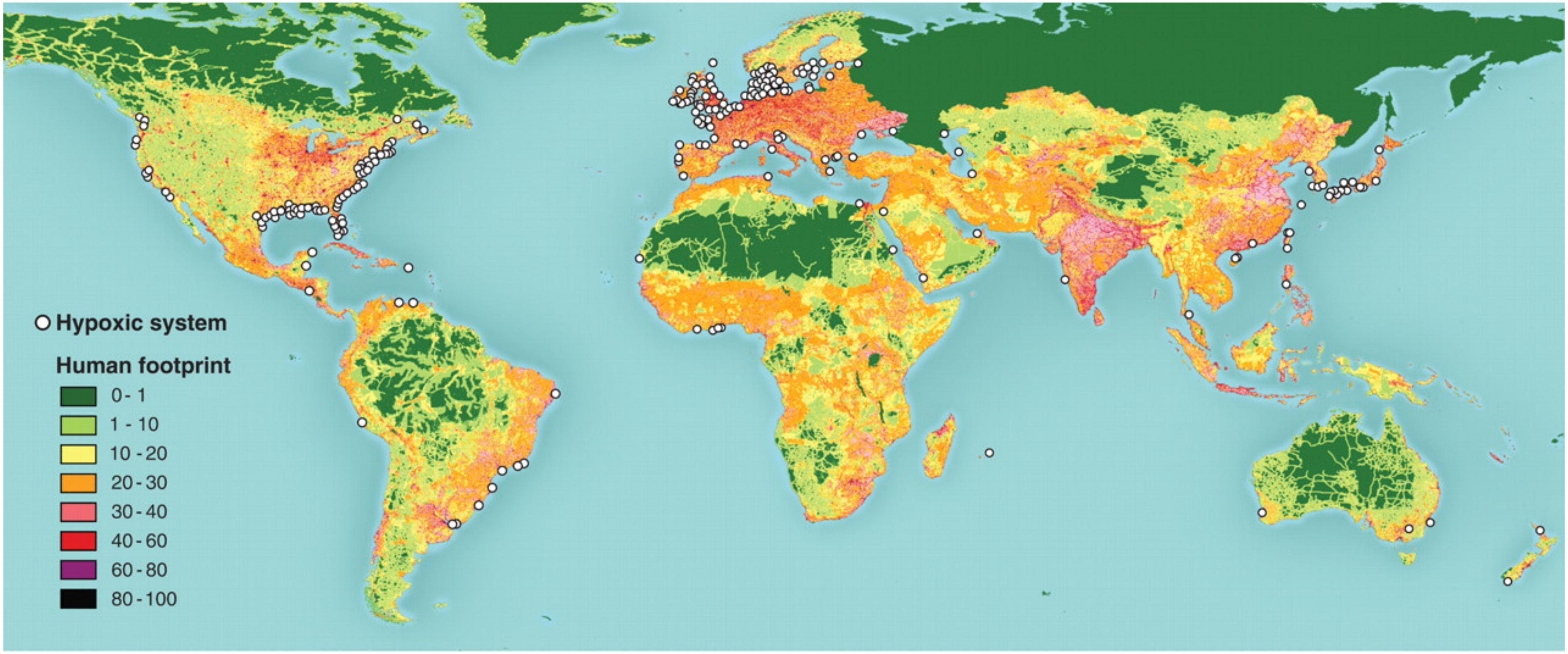


These biological processes not only transfer organic matter to depth, but other particle reactive elements and compounds, such as heavy metals and organic compounds like PCB's.

Contaminants



Global distribution of 400-plus systems that have scientifically reported accounts of being eutrophication-associated dead zones



Robert J. Diaz, and Rutger Rosenberg Science
2008;321:926-929

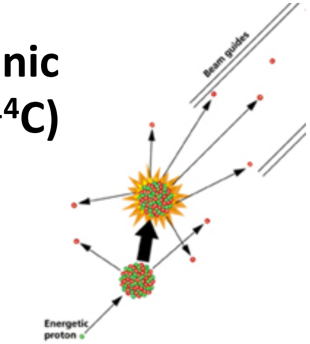
Published by AAAS

How do we address these oceanographic questions?

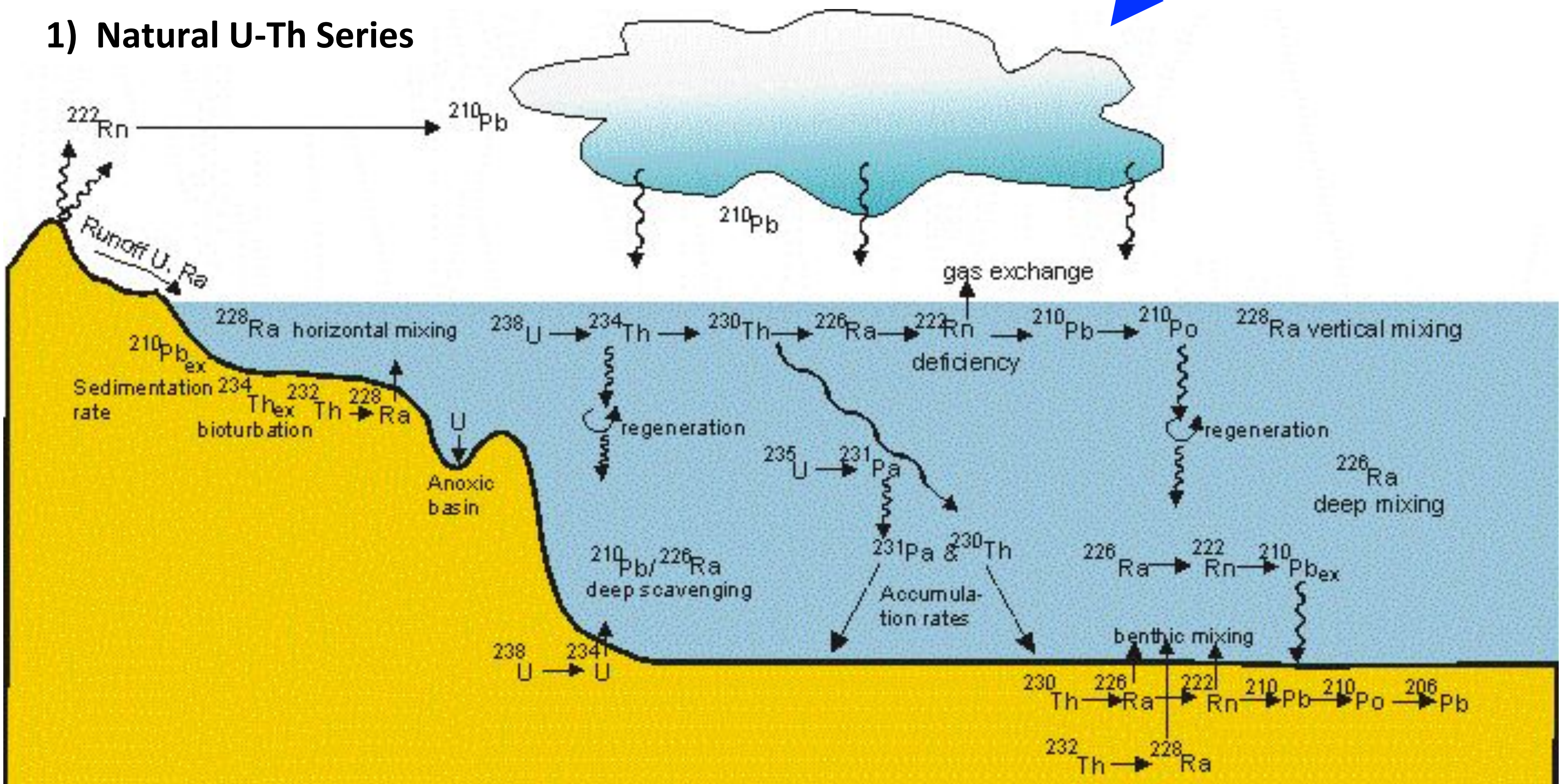
- Choose the **appropriate tracer**(s), with 3 major constraints:
  - **Source** term: is the source function well resolved?
  - **Biogeochemistry**: is it relevant? known?
  - **Timescale**: is the half-life ($T_{1/2}$) of the radionuclide appropriate?
- We need
  - A **model**: $$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) - v\frac{\partial c}{\partial x} - \lambda c$$
  - Analytical **techniques**

3) Artificial Radionuclides
(^{3}H, ^{14}C, ^{90}Sr, ^{129}I, ^{137}Cs, …)

2) Cosmogenic
(^{7}Be, 10Be, ^{14}C)



1) Natural U-Th Series



http://www.awi.de/en/research/research_divisions/geosciences/marine_geochemistry/research_themes/natural_radionuclides_and_geotraces/tracers_for_transport_processes/

Case studies

1. Submarine groundwater discharge (SGD)

   – Radium quartet (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) and ^{222}Rn

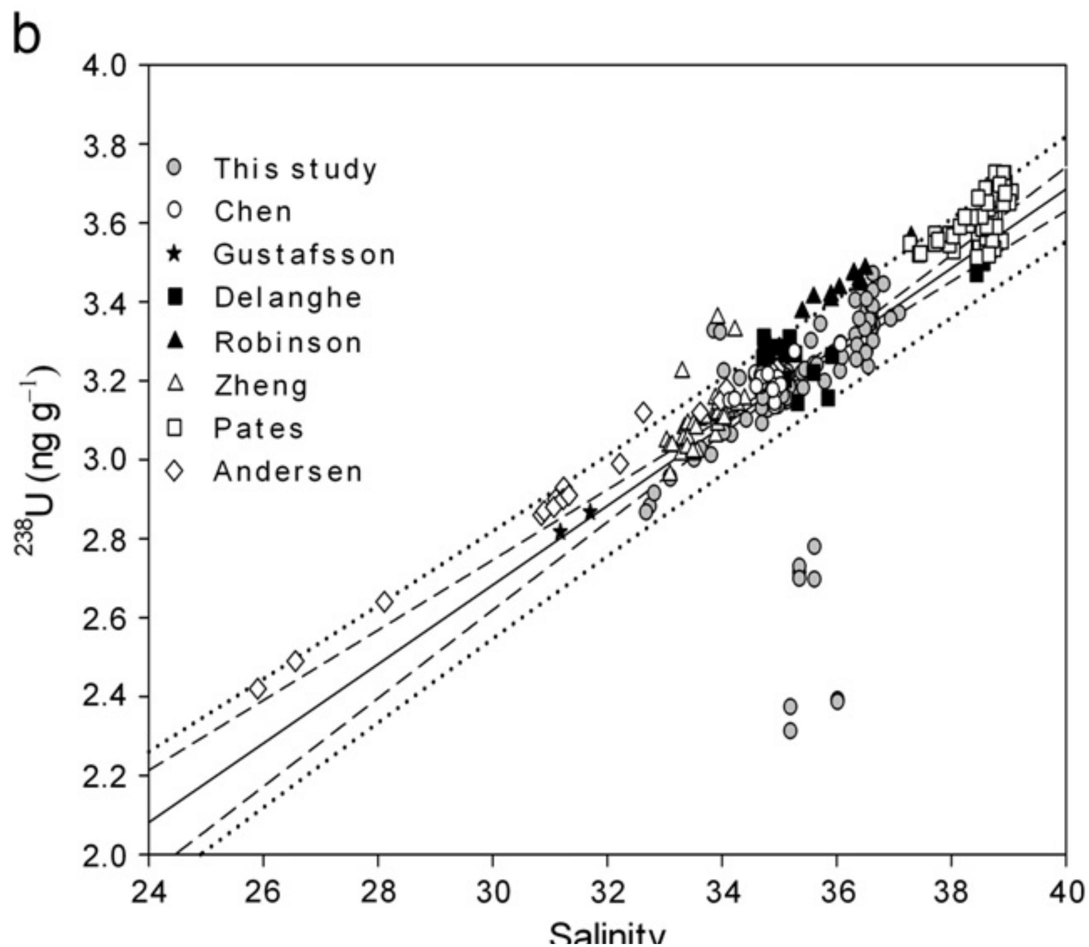
     → Specific Lecture 4 (Billy Moore)

Case studies

1. Export of particles and particulated-substances from the surface to the deep ocean

   – $^{234}Th/^{238}U$

U is conservative in seawater



ng g^{-1}: ^{238}U (± 0:061) = 0.100 × S − 0.326

dpm L^{-1}: ^{238}U (± 0:047) = 0.0786 × S − 0.315

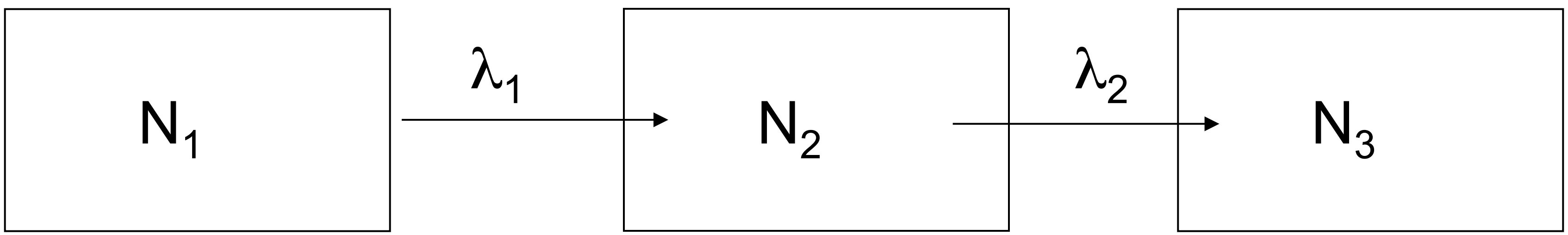
Owens *et al*., 2011

^{238}U decays in ^{234}Th: **The Case of the Radioactive Daughter**

A	$\rightarrow$	B	$\rightarrow$	C	$\rightarrow$	…
N_1,λ_1		N_2,λ_2		N_3,λ_3		

The Bateman Equations

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$



$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 [e^{-\lambda_1 t} - e^{-\lambda_2 t}] + N_2^0 e^{-\lambda_2 t}$$

If $^{N1}t_{½}$ >> $^{N2}t_{½}$ → $\lambda_1 << \lambda_2$ → Secular Equilibrium

For the naturally occurring radionuclides: ^{238}U, ^{235}U, and ^{232}Th the half-lives of the parent nuclides are much longer than their daughter products:

$$^{238}U\ (t_{1/2} = 4.5 \cdot 10^9\ yr) \xrightarrow{\alpha} {}^{234}Th\ (t_{1/2} = 24.1\ d)$$

→ The number of parents atoms essentially remains constant

→ **^{238}U and ^{234}Th in equilibrium: same activity**

Scavenging

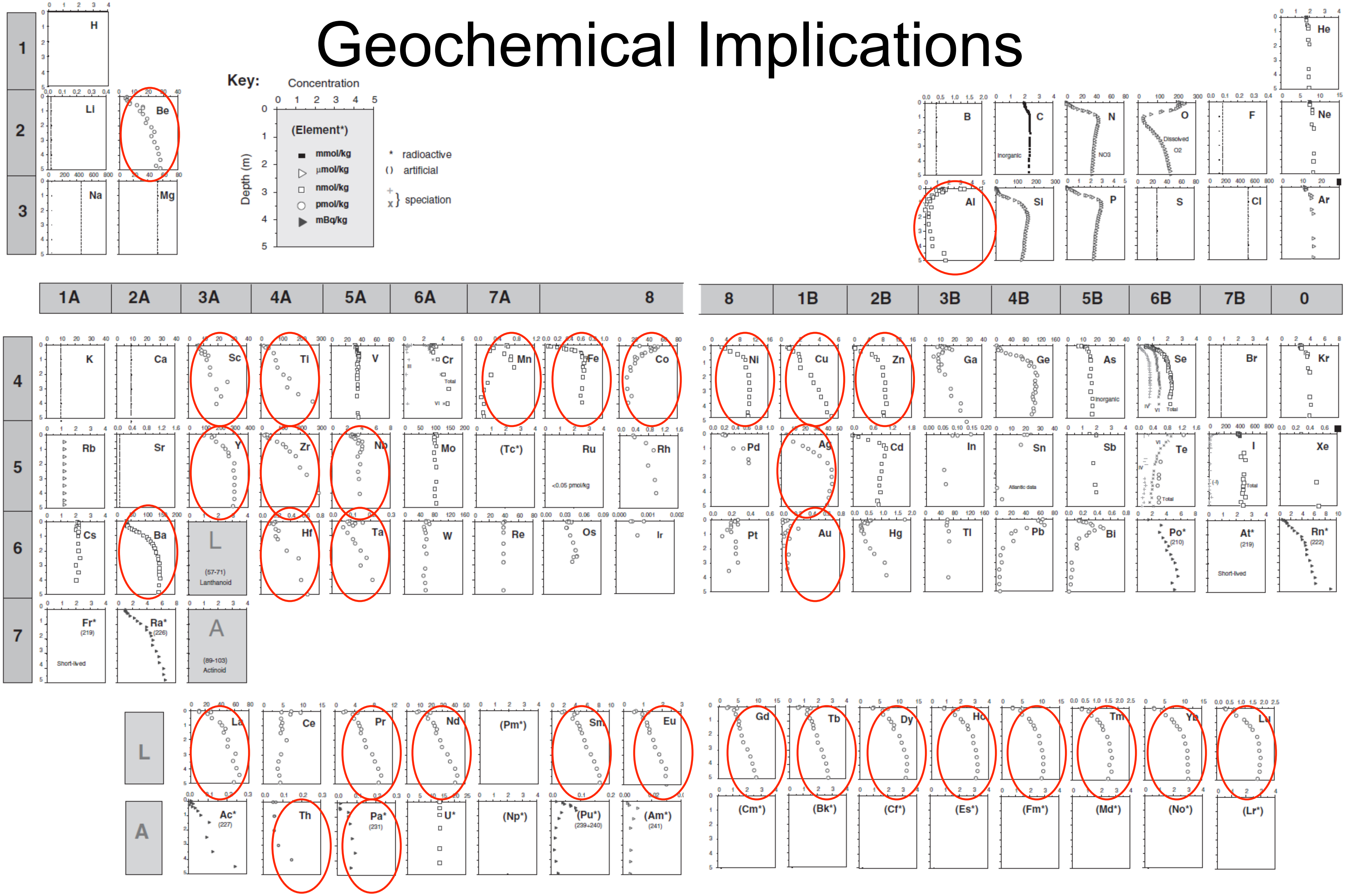
- Many trace metals have much lower dissolved sea water concentration than they should have based on continental weathering supply -- *Fritz Haber (Nobel Prize in 1918)*

- "Sorption" onto suspended and sinking phases leads to removal of inorganic and organic compounds *(Goldberg- 1954) **Note that here we are not differentiating between biological uptake and surface sorption*

- Particles therefore act as sequestering agents for reactive elements (Fe, Cu, Pb, Th, Pa, etc.)

- Small particles (0.01 – 100 µm) provide increased surface area for adsorption of dissolved chemicals

Geochemical Implications



Many elements in the ocean are influenced by scavenging (adsorption onto sinking particles) Concentrations increasing with depth are diagnostic of scavenging and regeneration (circles are not exhaustive)

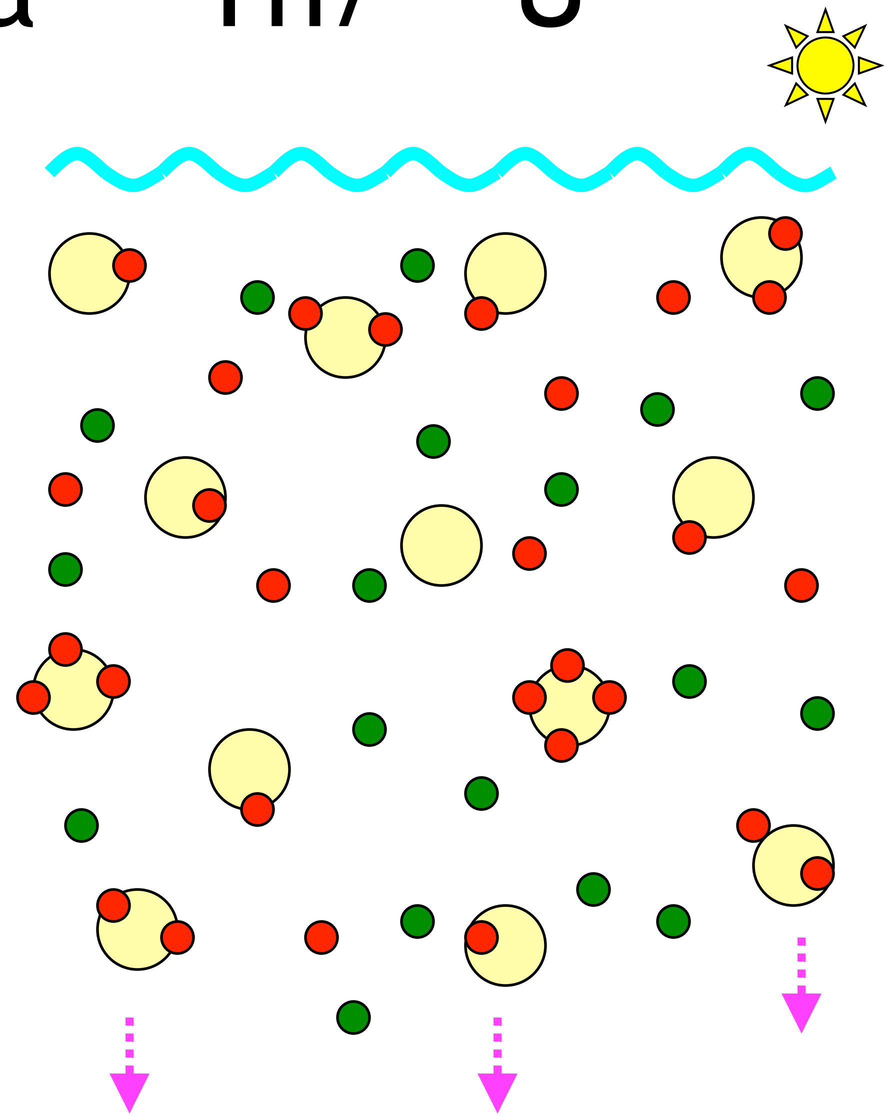
Periodic table from Y. Nozaki

Disequilibria $^{234}Th/^{238}U$

$^{238}U \xrightarrow{\alpha} {}^{234}Th$ ($t_{1/2} = 24.1$ d)

^{238}U: dissolved

^{234}Th: particle-reactive



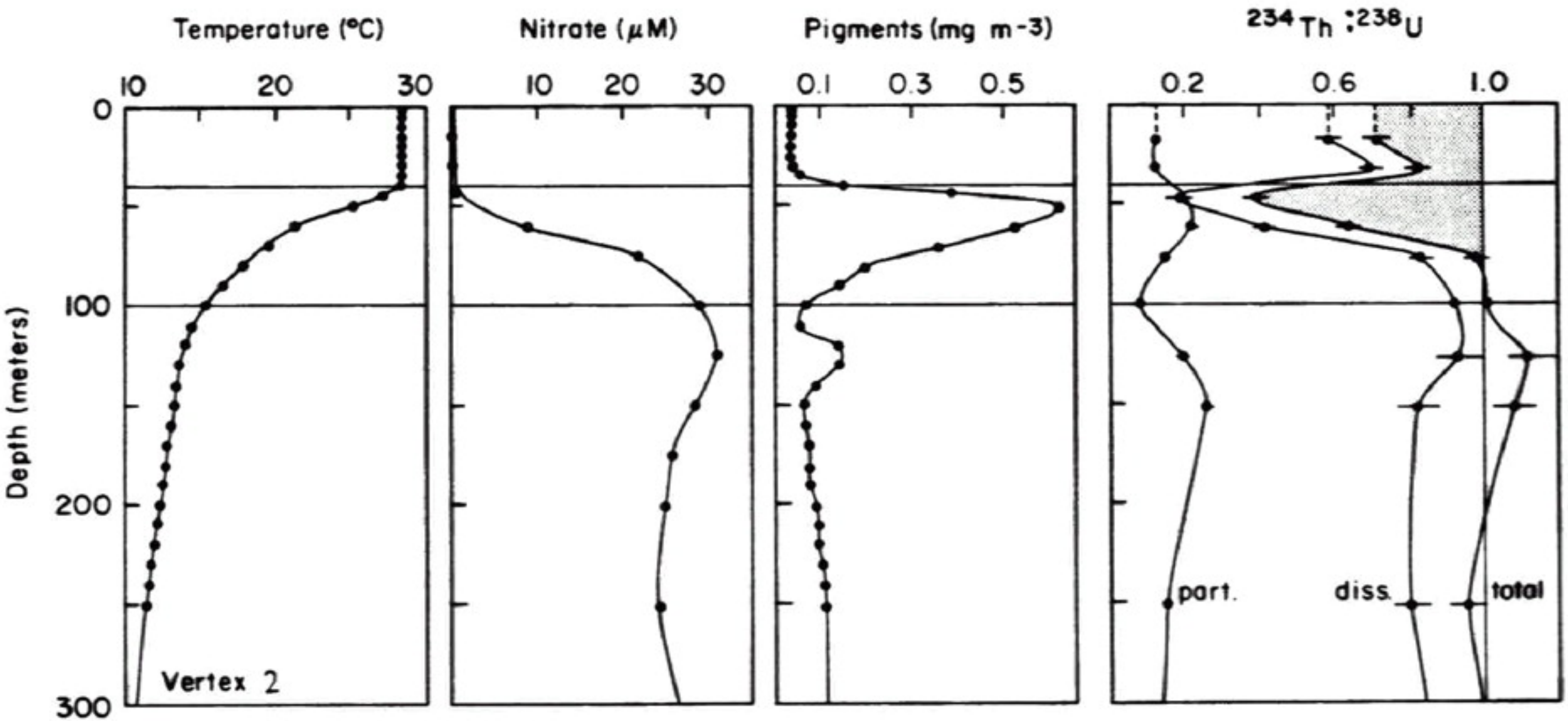
particles

^{238}U

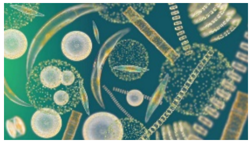
^{234}Th

^{234}Th as a tracer for particle export

See decrease in ^{234}Th activity correlated with biological activity!!



Indicator of biomass

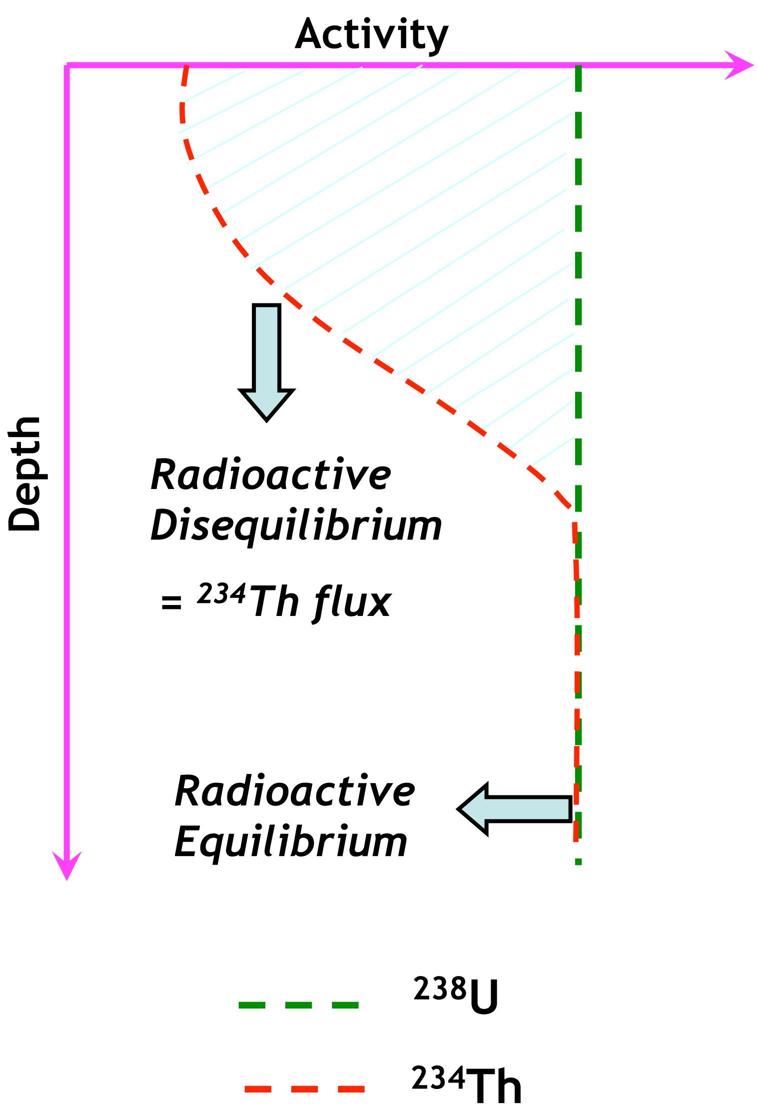


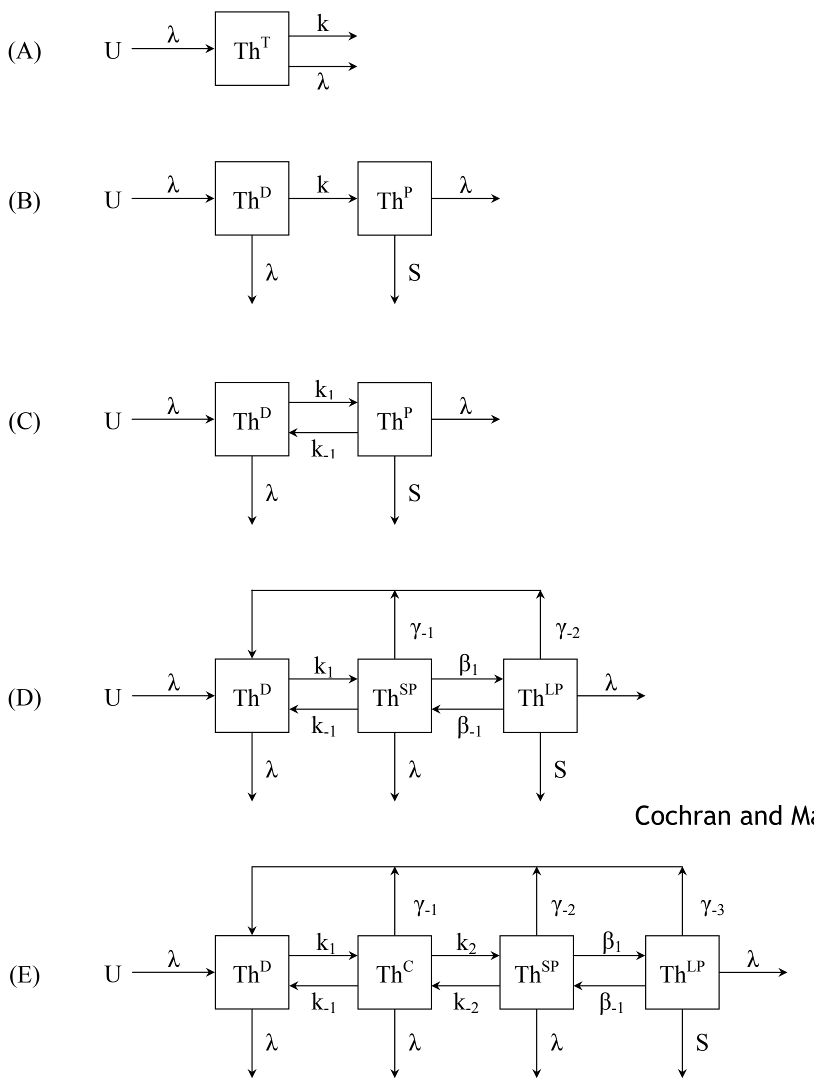
Coale and Bruland (1987)

Export of Th

$$^{234}\text{Th flux} = \lambda_{Th}\int(A_U - A_{Th})dz$$

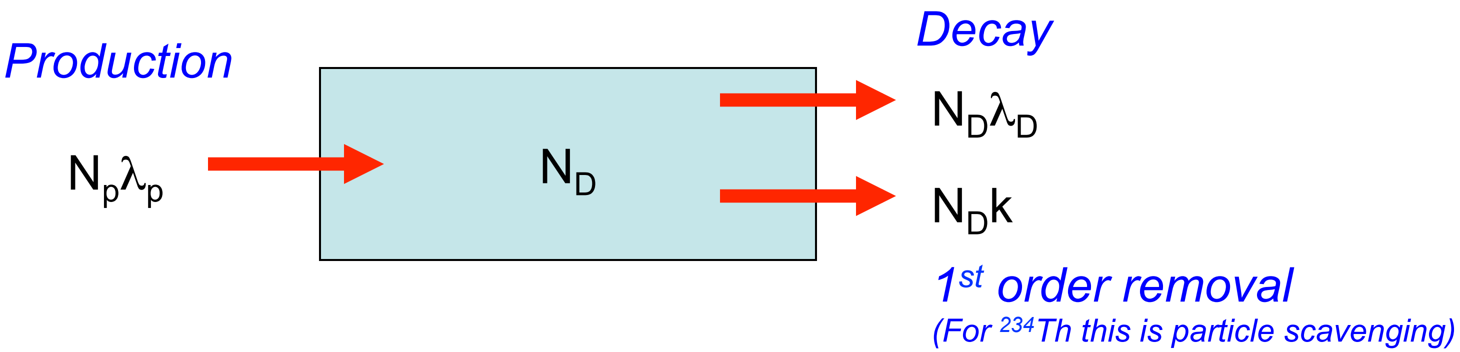
$$\text{Carbon flux} = {}^{234}\text{Th flux} \bullet [C/{}^{234}\text{Th}]_{part}$$





Cochran and Masqué, 2003

^{234}Th Source from ^{238}U decay in seawater (conservative), loss due to radioactive decay AND due to particle attachment and sinking.



$N_p\lambda_p = N_D\lambda_D + kN_D$ Remember that $A = \lambda N$

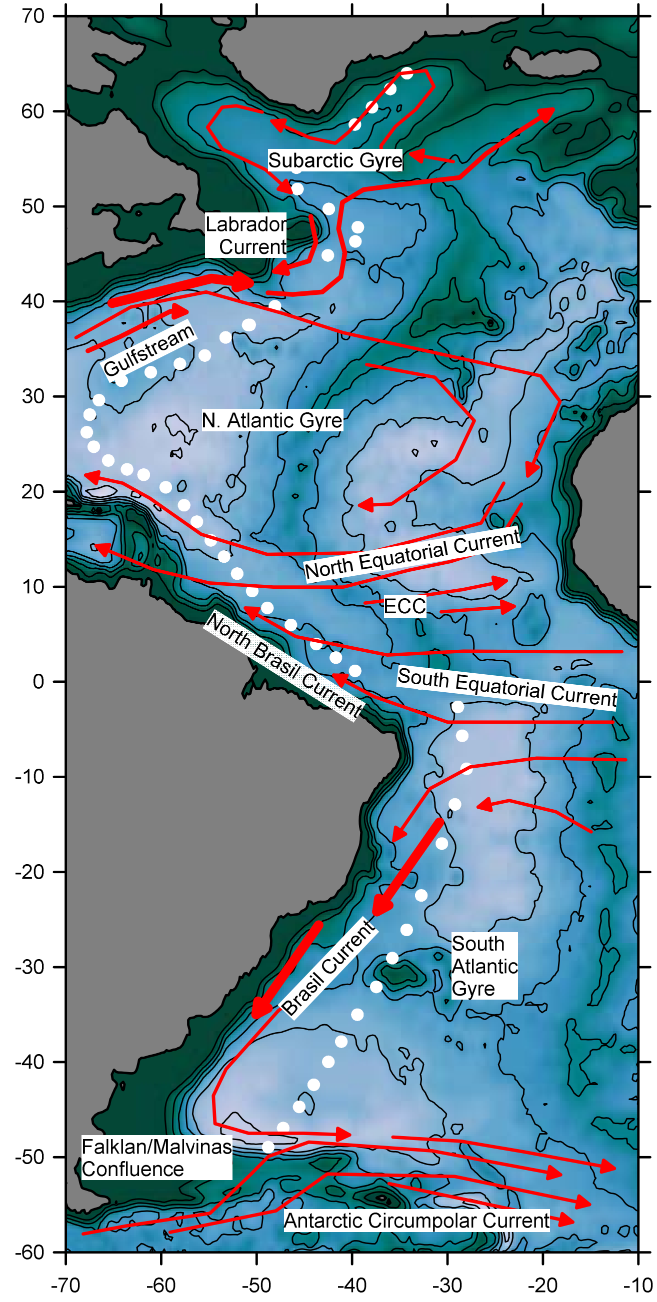
$A_p\lambda_D = A_D\lambda_D + kA_D$ where kA_D is the "Flux"

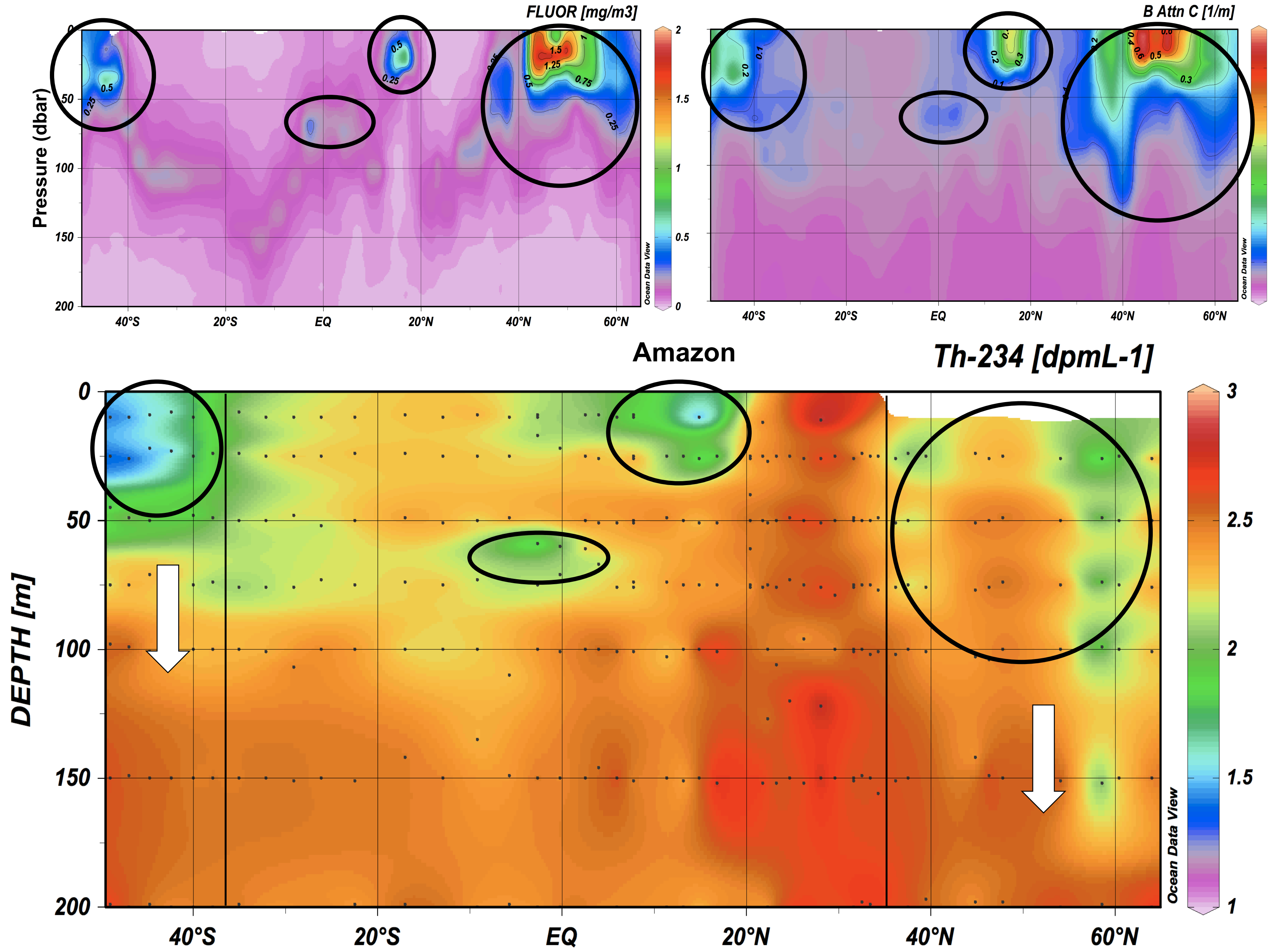
$k = \lambda_D\,(A_p/A_D - 1)$ where k is the scavenging coefficient

$\tau_D = 1/k$ = Residence time of N_D with respect to scavenging!!

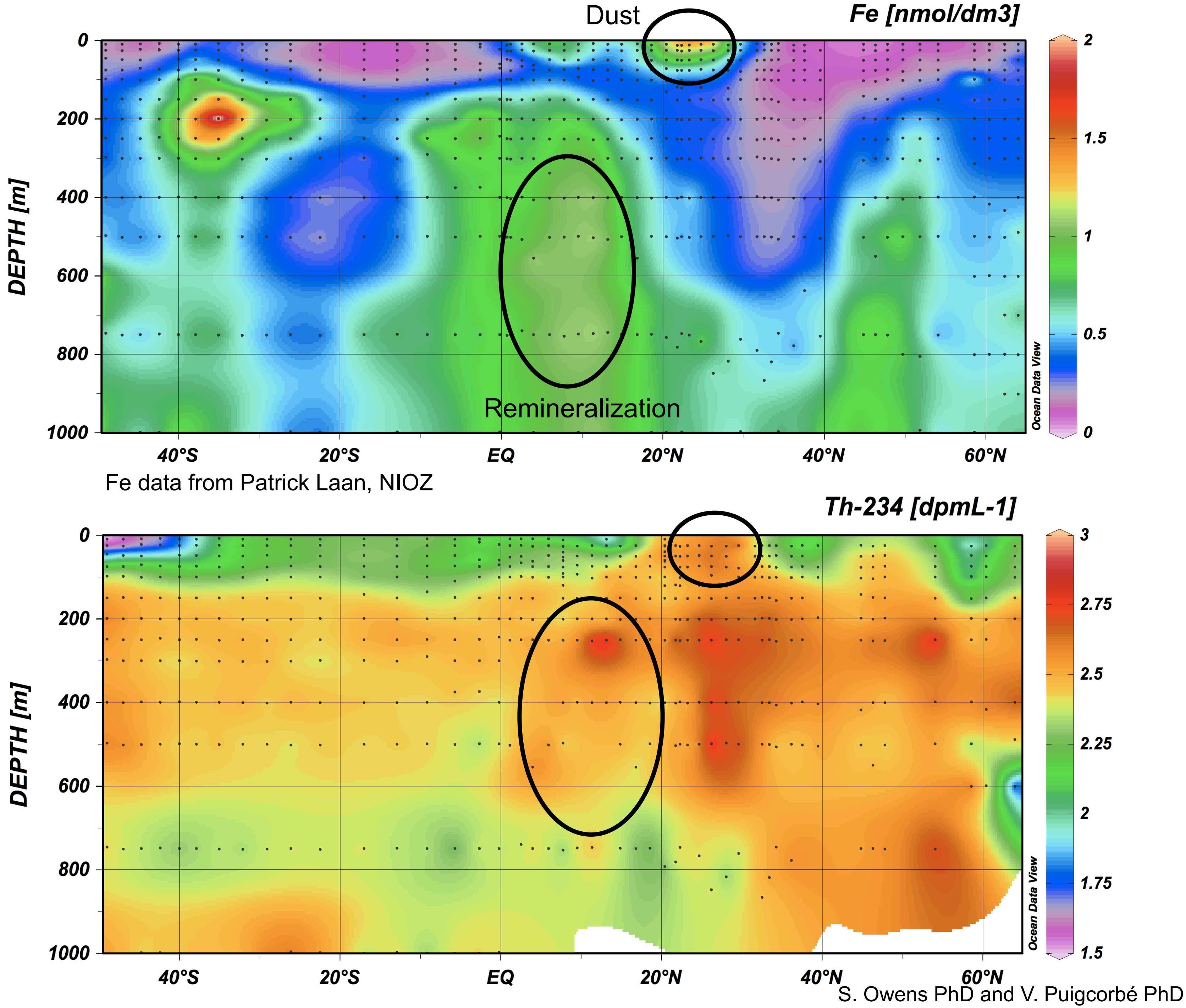
An example in the Atlantic Ocean

GEOTRACES GA02,2010-11



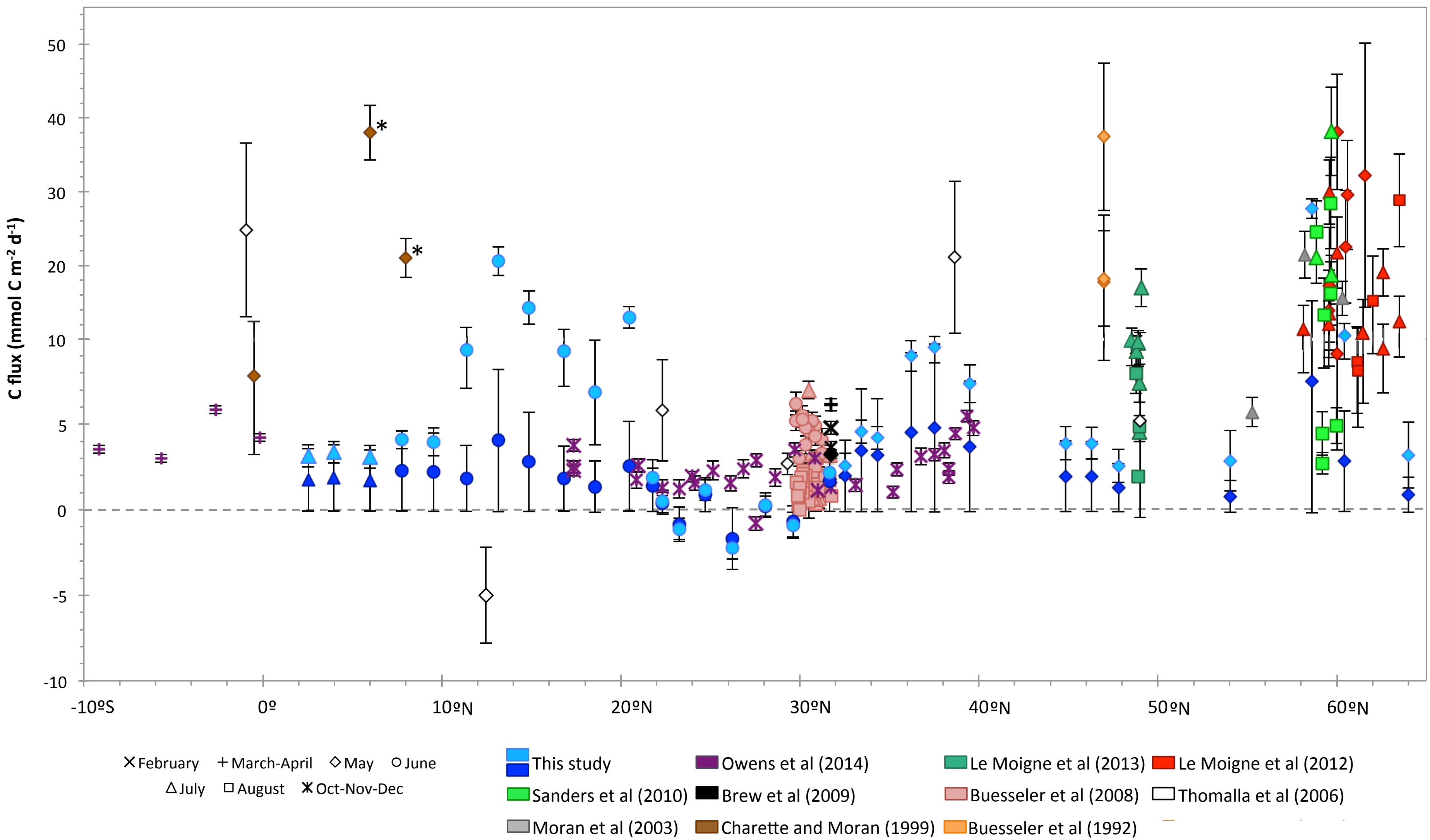


S. Owens PhD and V. Puigcorbé PhD



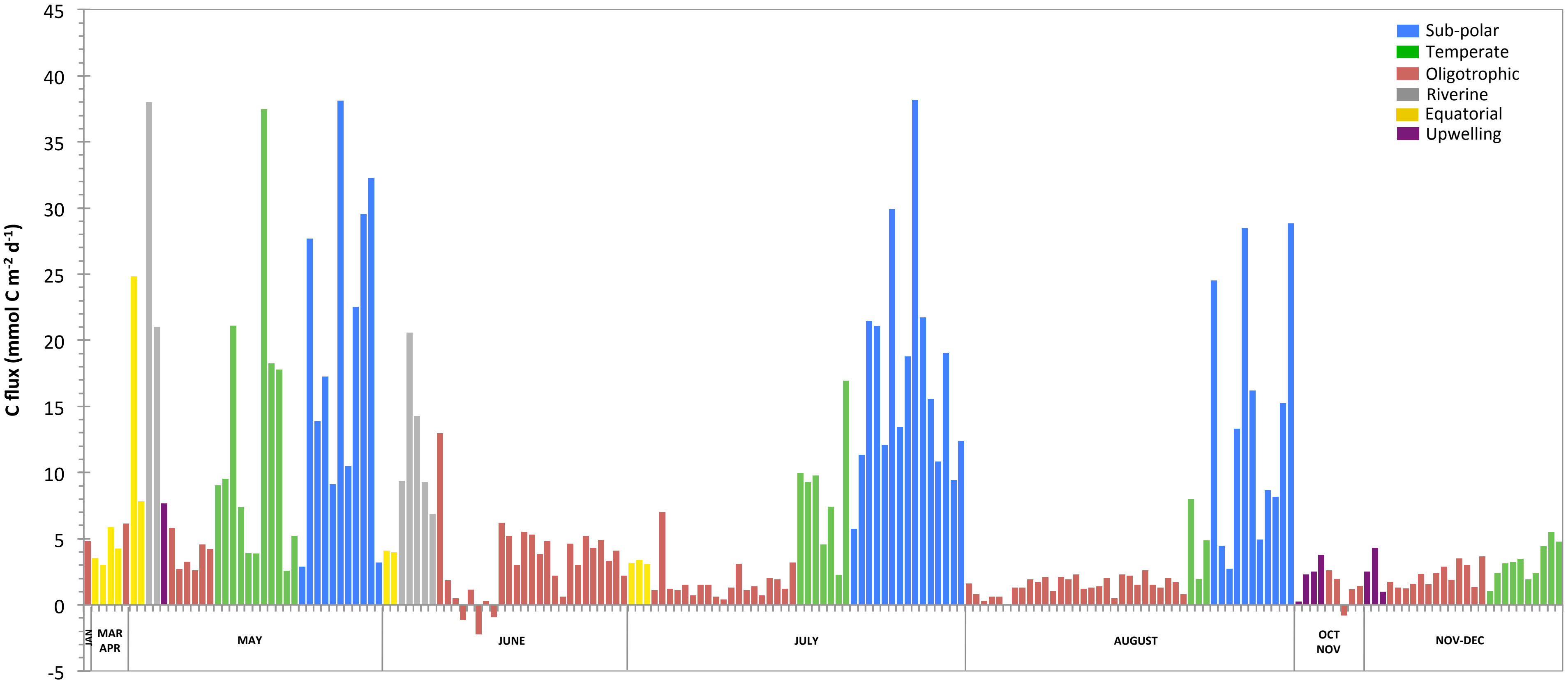
Dust
Fe [nmol/dm3]
DEPTH [m]
0
200
400
600
800
1000
Remineralization
40°S
20°S
EQ
20°N
40°N
60°N
Ocean Data View
2
1.5
1
0.5
0
Fe data from Patrick Laan, NIOZ
Th-234 [dpmL-1]
DEPTH [m]
0
200
400
600
800
1000
40°S
20°S
EQ
20°N
40°N
60°N
Ocean Data View
3
2.75
2.5
2.25
2
1.75
1.5
S. Owens PhD and V. Puigcorbé PhD

Carbon export fluxes at 100 m



Puigcorbé et al. In prep.

Carbon export fluxes at 100 m



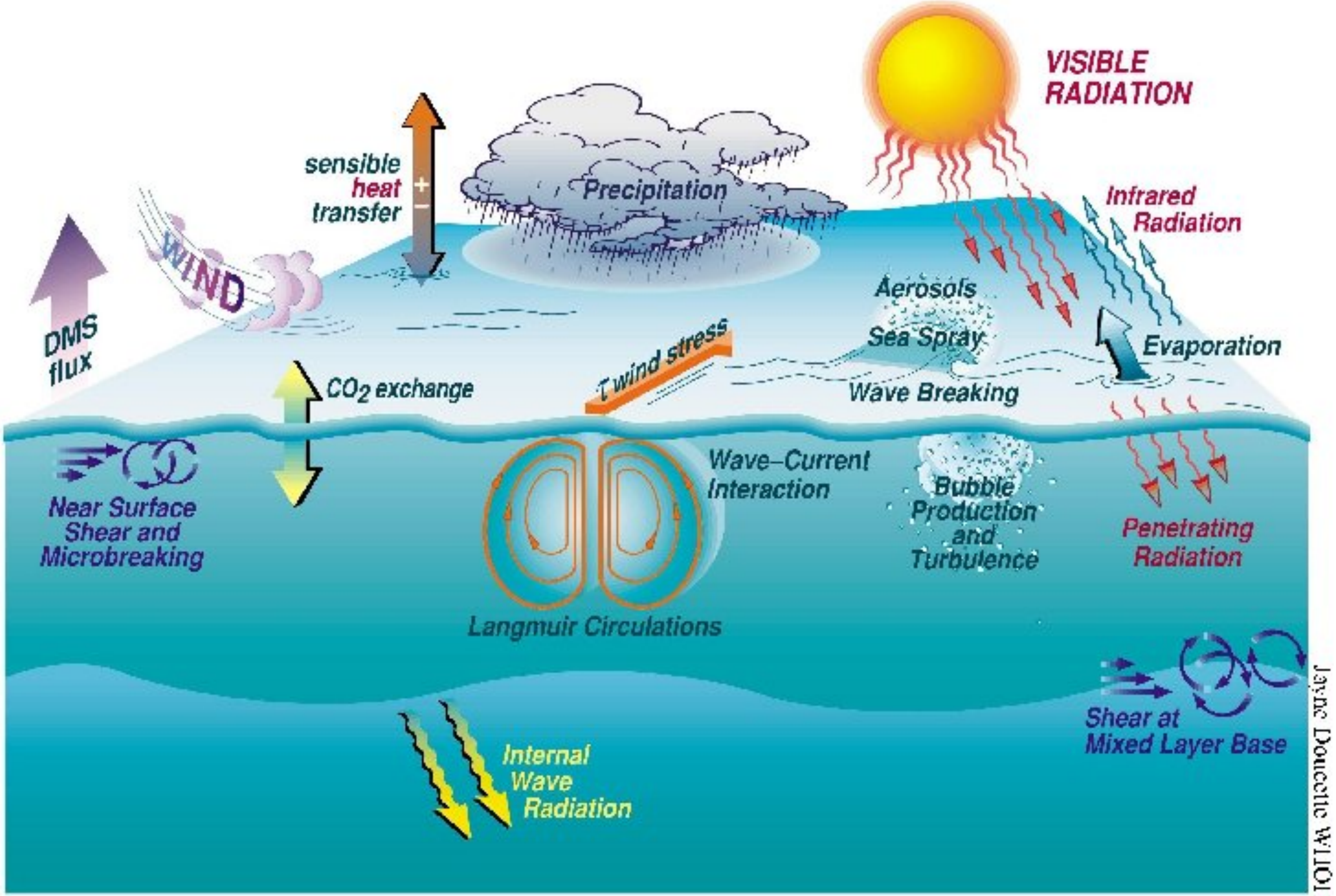
Puigcorbé et al. In prep.

Case studies

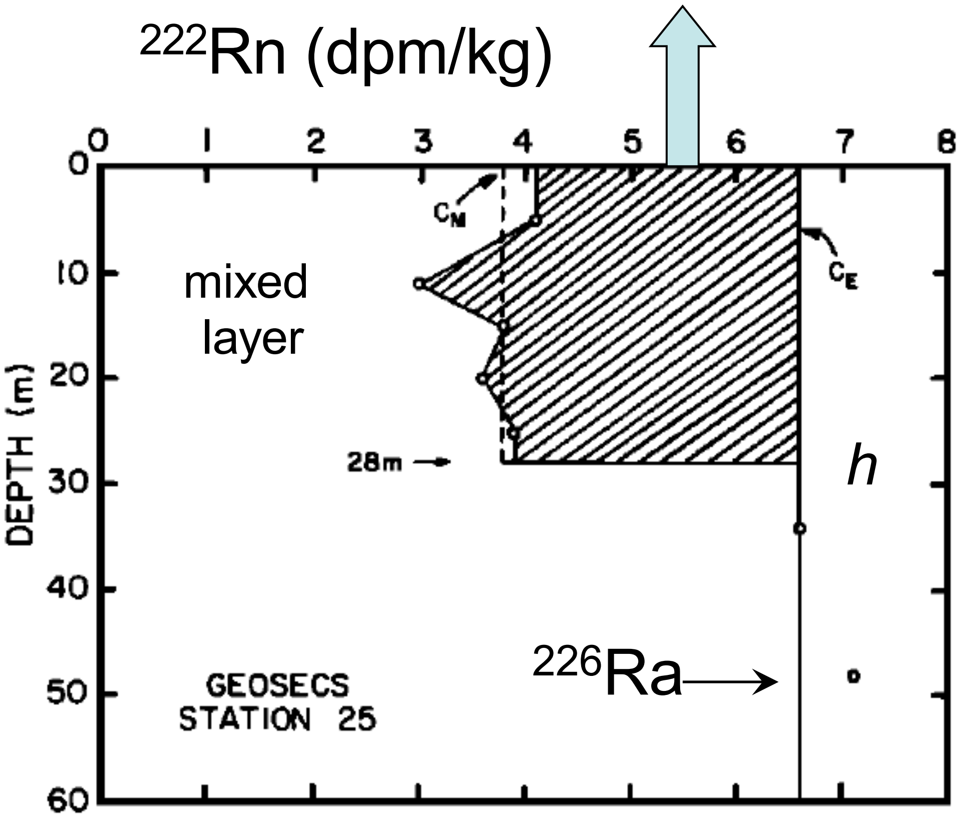
2. Gas exchange

- ^{222}Rn

Processes influencing gas exchange (CO_2, Methane,…)



The $^{222}Rn/^{226}Ra$ method



Peng et al., 1979

$^{226}Ra \rightarrow {}^{222}Rn$

$T_{½}$ = 3.8 days

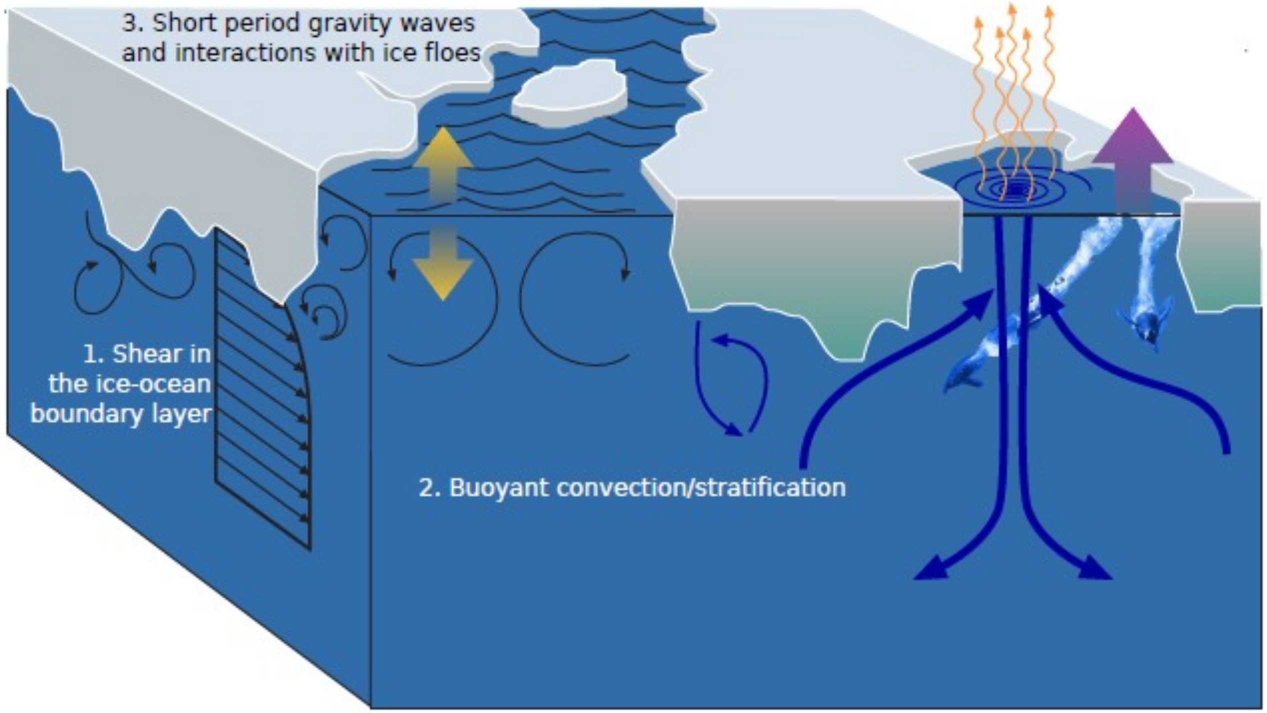
$$k \cdot (C_{Rn222} - C_{air}) = (C_{Ra226} - C_{Rn222}) \cdot h \cdot \lambda$$

k: gas transfer velocity (m/d)

$$k = \left(\frac{C_{Ra226}}{C_{Rn222}} - 1 \right) \lambda h$$

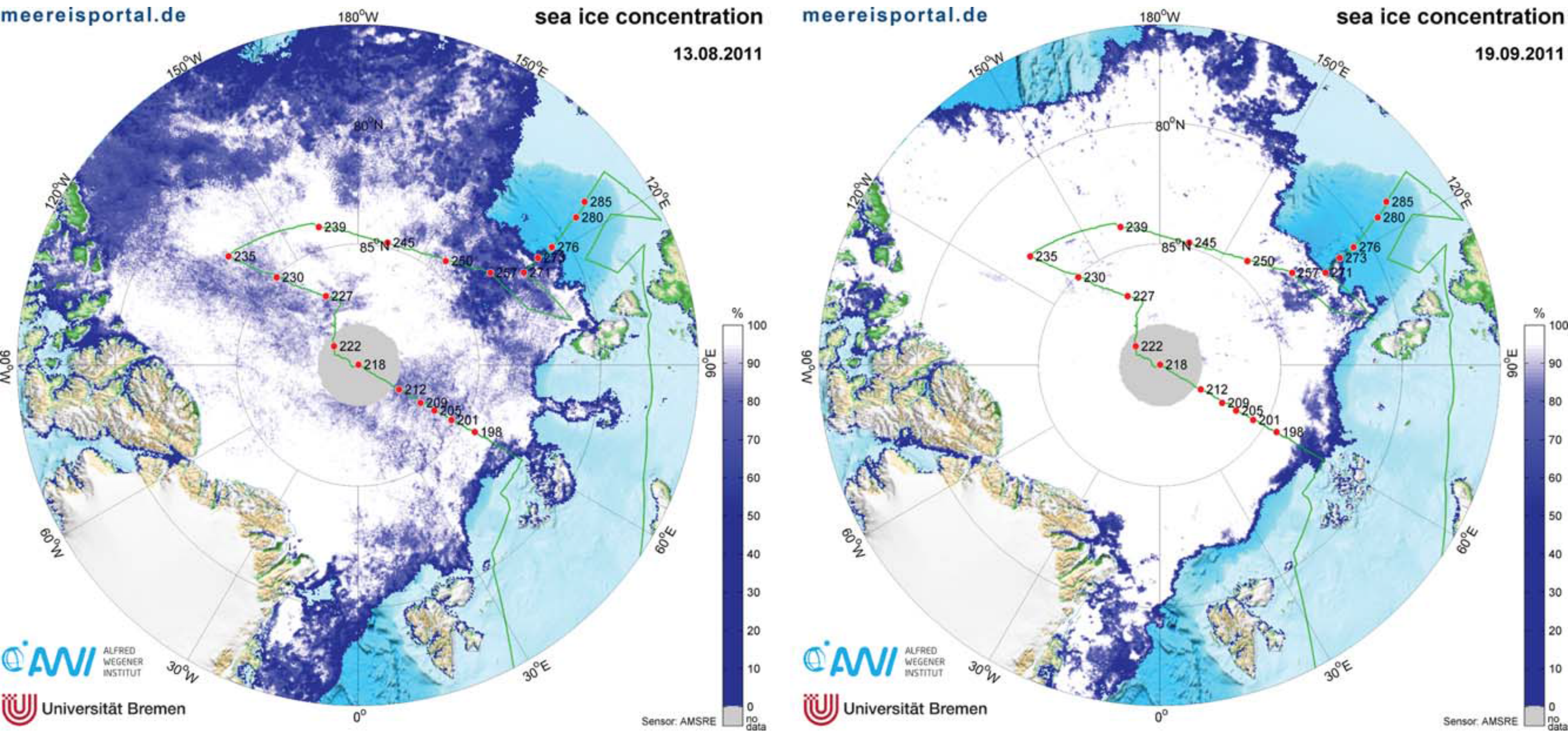
Courtesy of Michiel Rutgers van der Loeff

Application in the Arctic Ocean – Sea Ice



Loose et al., 2013

ARK XXIV/3 TransArc 2011



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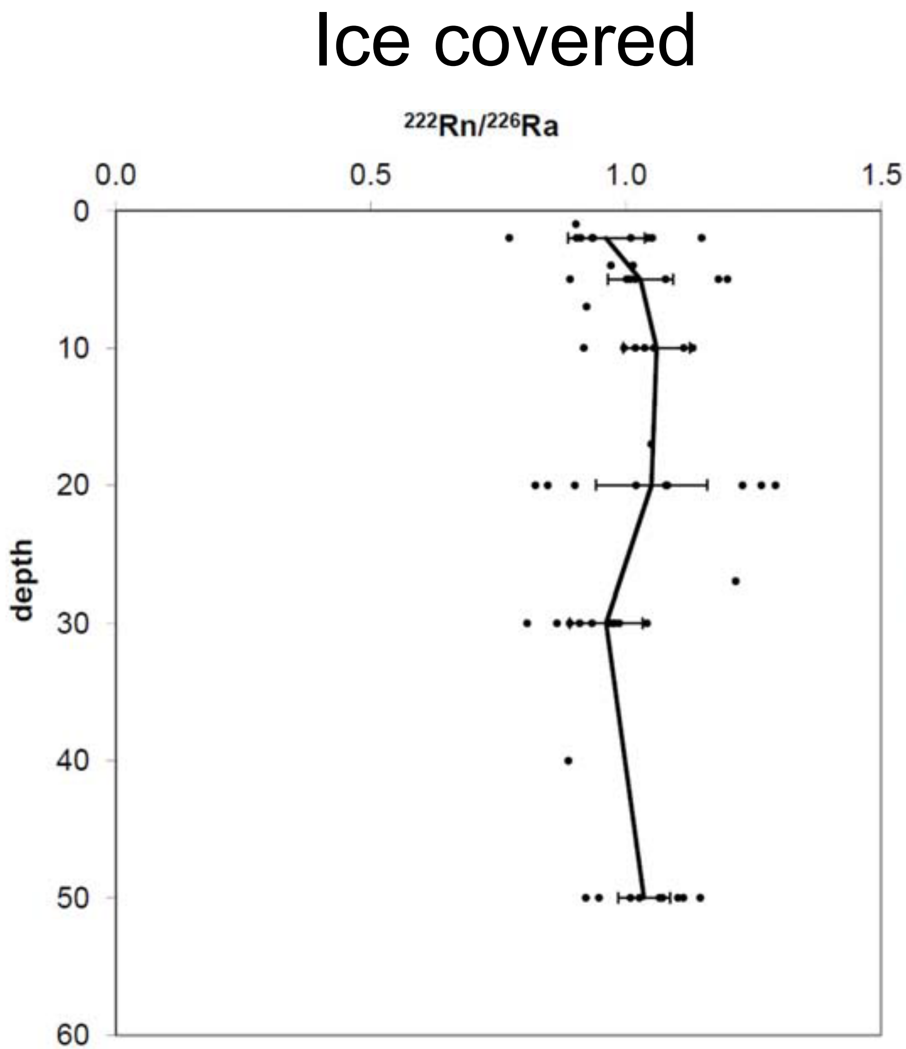
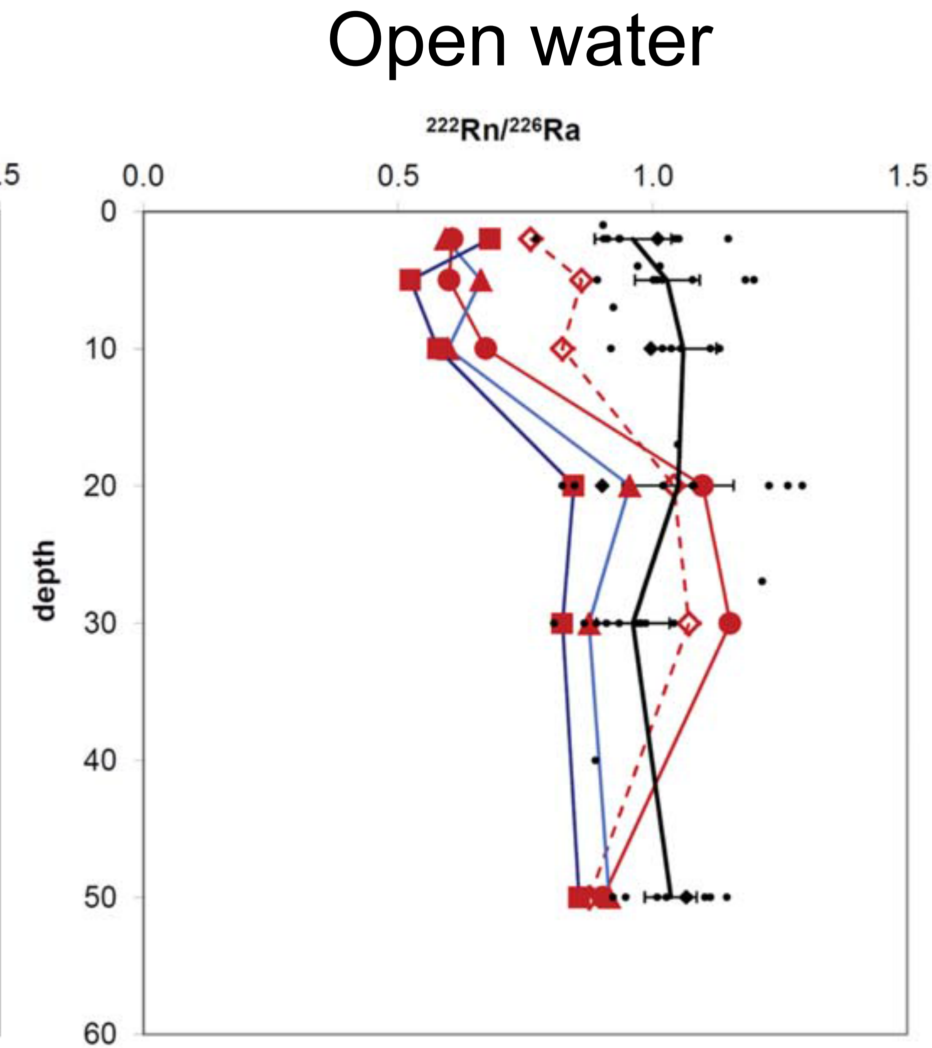
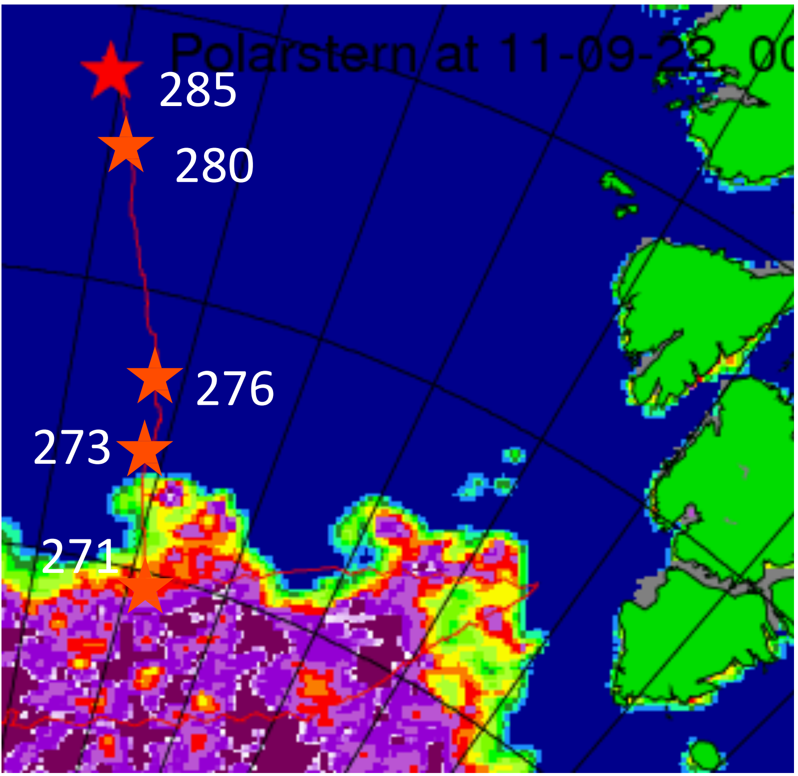
Rutgers van der Loeff et al., 2014

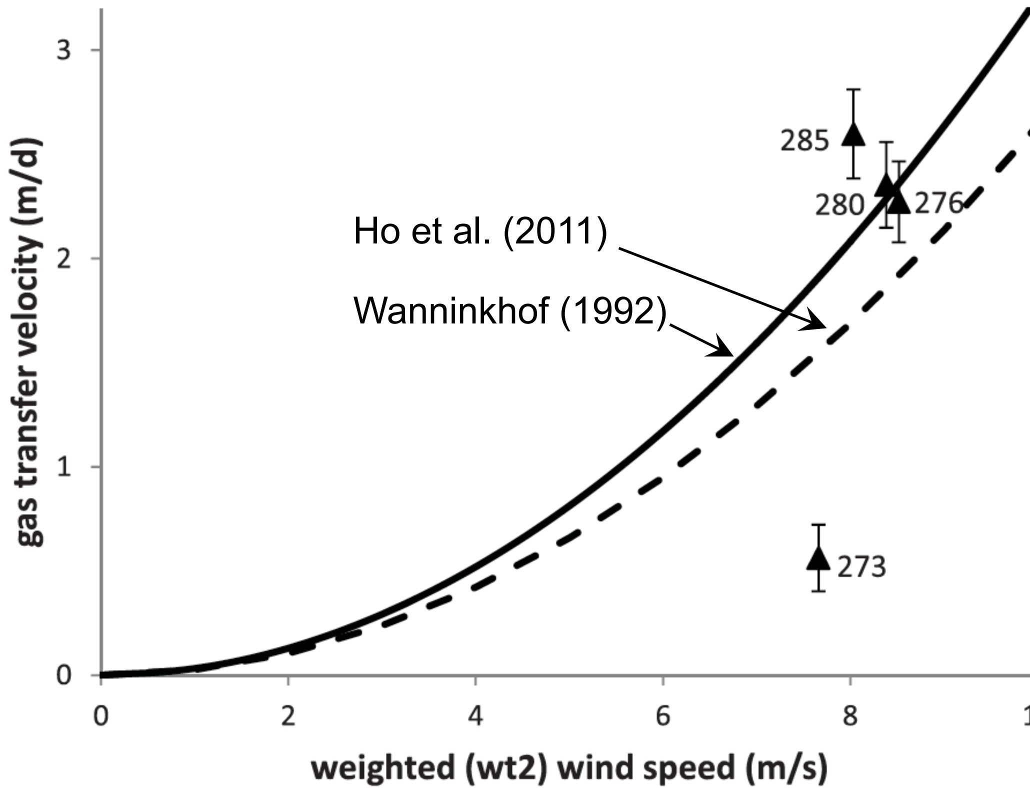




Rutgers van der Loeff et al., 2014

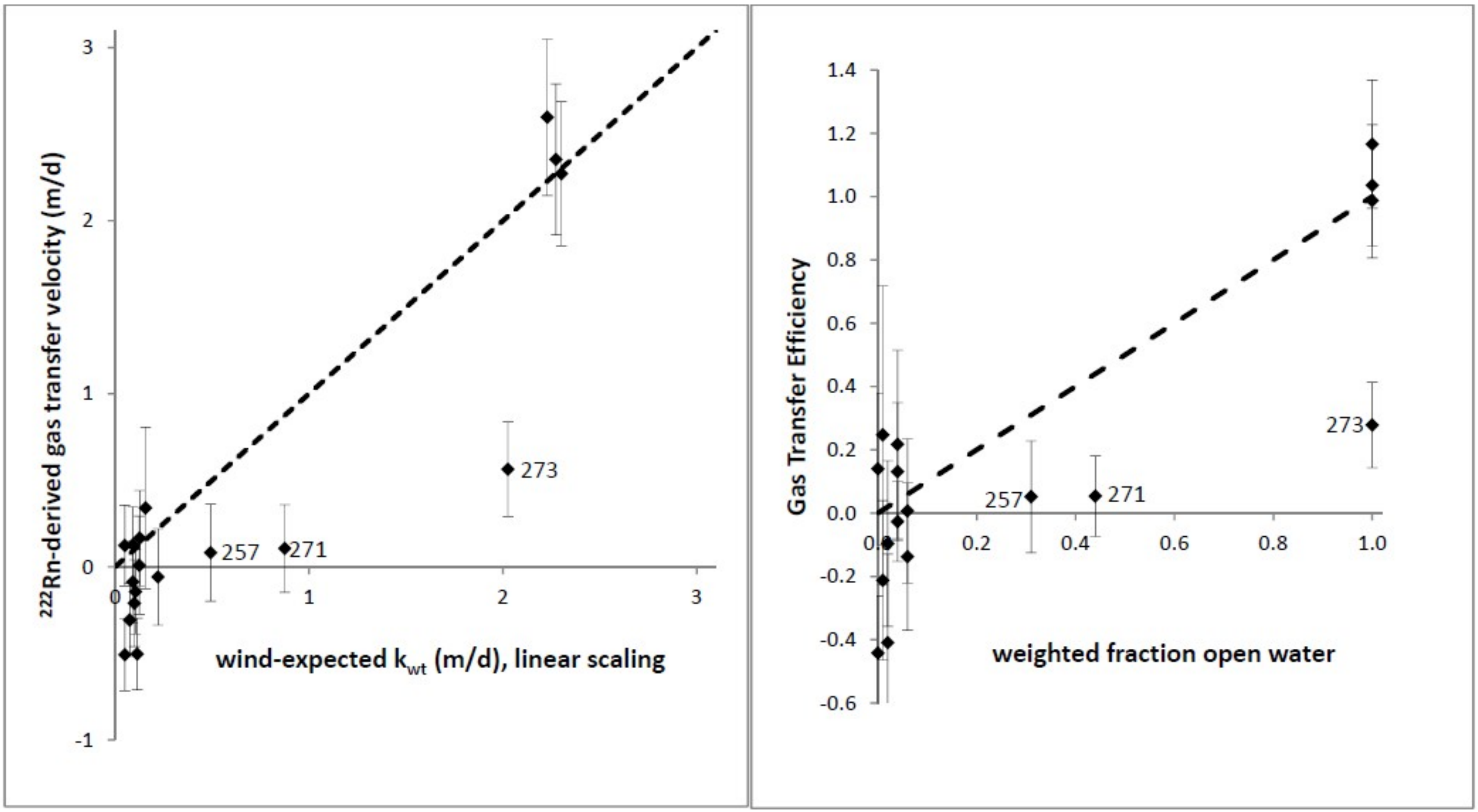
Open water stations





Rutgers van der Loeff et al., 2014

- Ice covered: Average gas transfer velocity < 0.1 m/d
- Open water: expected 0.5-2.2 m/d
- Partially ice-covered regions: gas exchange is lower than expected



Rutgers van der Loeff et al., 2014

Case studies

3. Artificial radionuclides

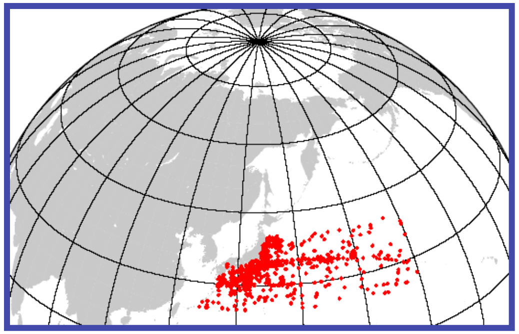
1. Ocean Circulation

Artificial radionuclides derived from (1) atmospheric fallout (weapons tests), (2) point sources from nuclear facilities (Sellafield, La Hague) and (3) nuclear accidents (Chernobyl, Fukushima) used to trace currents and deep water formation.

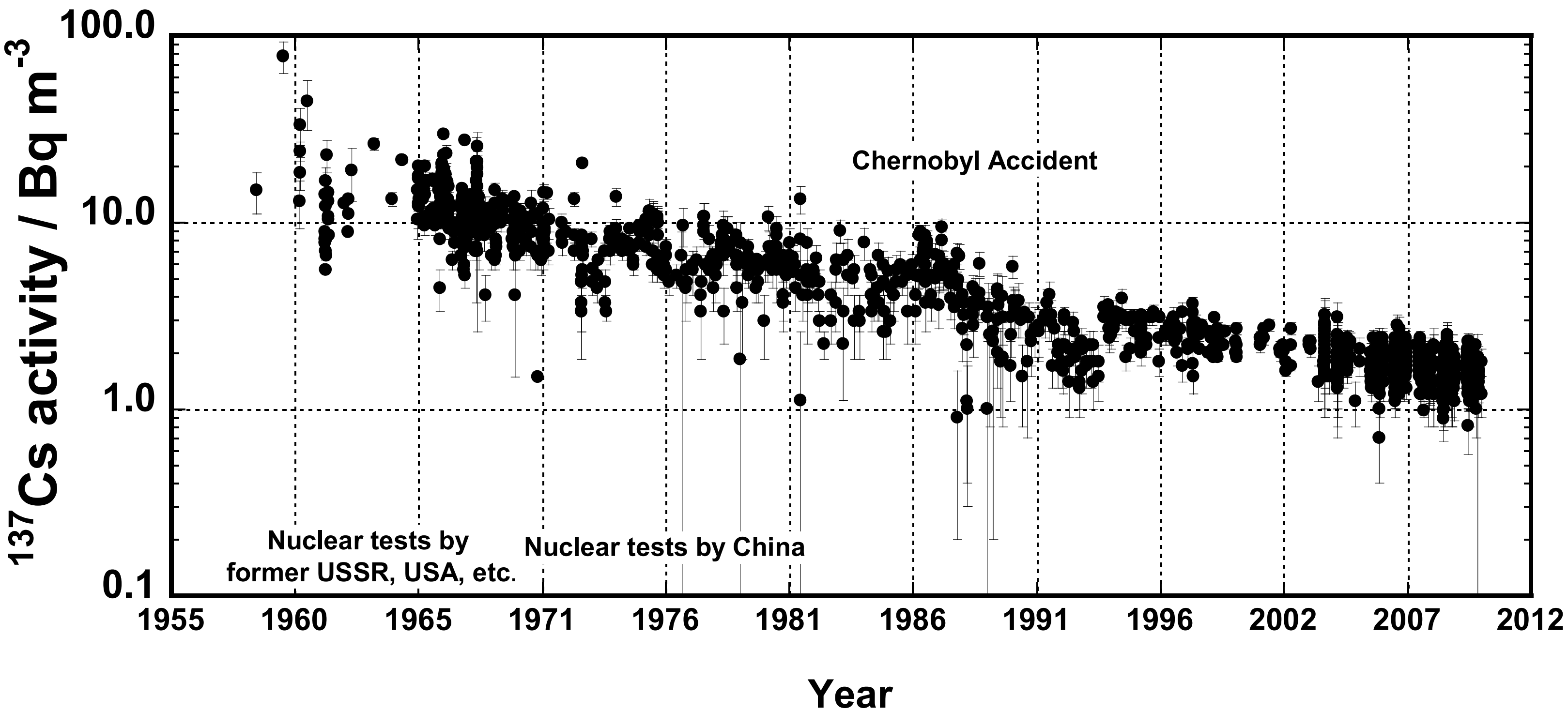
2. Particle Transport

Artificial radionuclides that are particle reactive used to determine particle transport pathways, sediment geochronologies.

1.Fallout Inputs

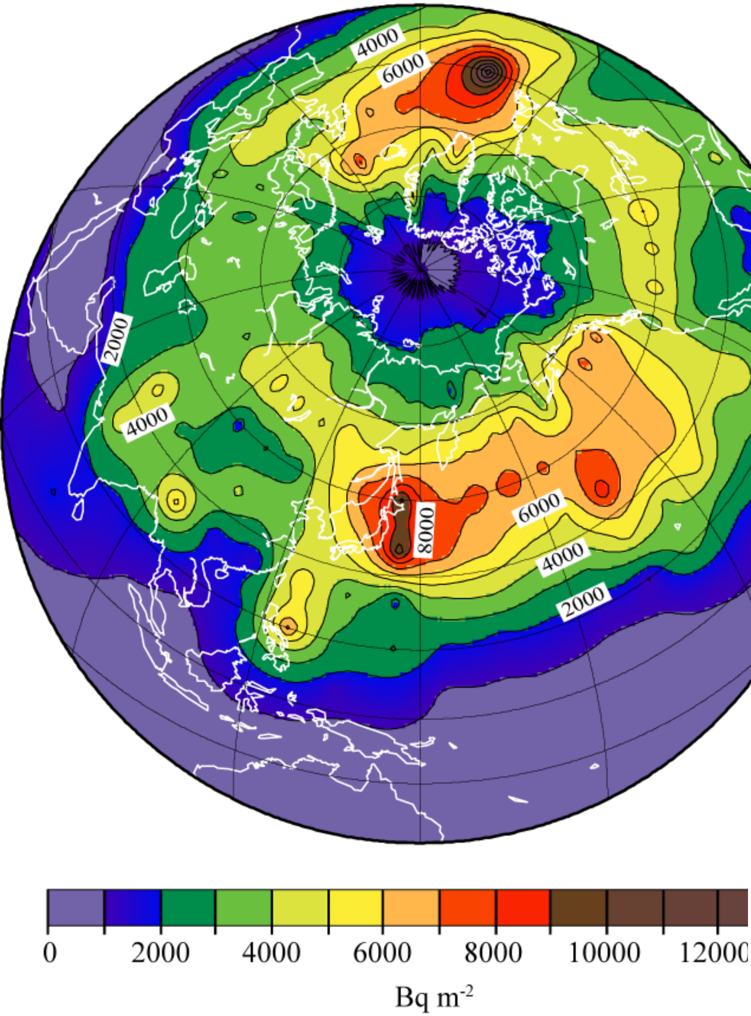


Long-term trend of ^{137}Cs in surface water in the western North Pacific Ocean: past



Updated after Aoyama and Hirose, 2004

Decay corrected accumulative fallout: ^{137}Cs



Aoyama et al., 2006.

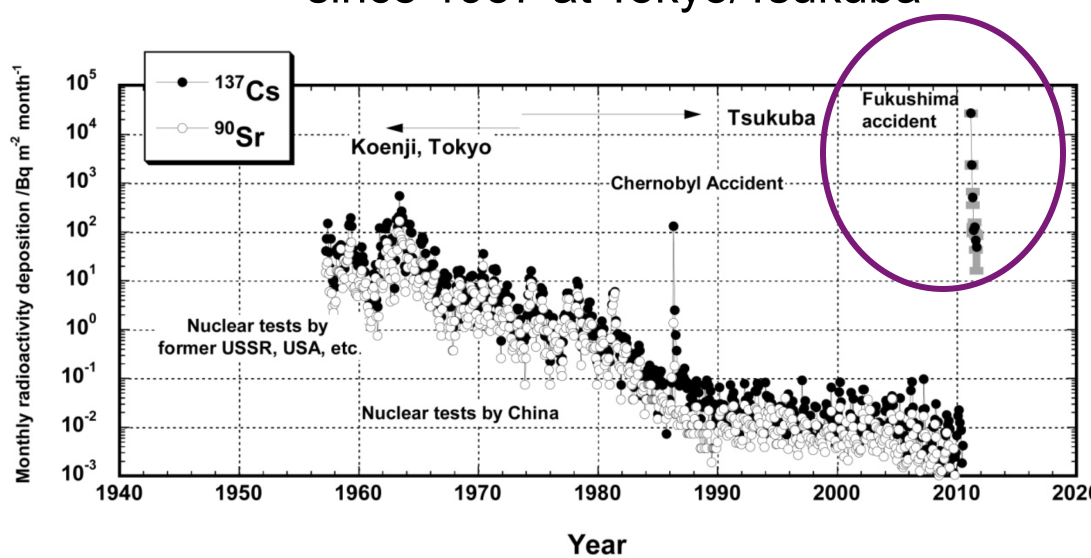
Globally (1970): 765 ± 79 PBq

North Pacific Ocean (1970): 290 ± 30 PBq

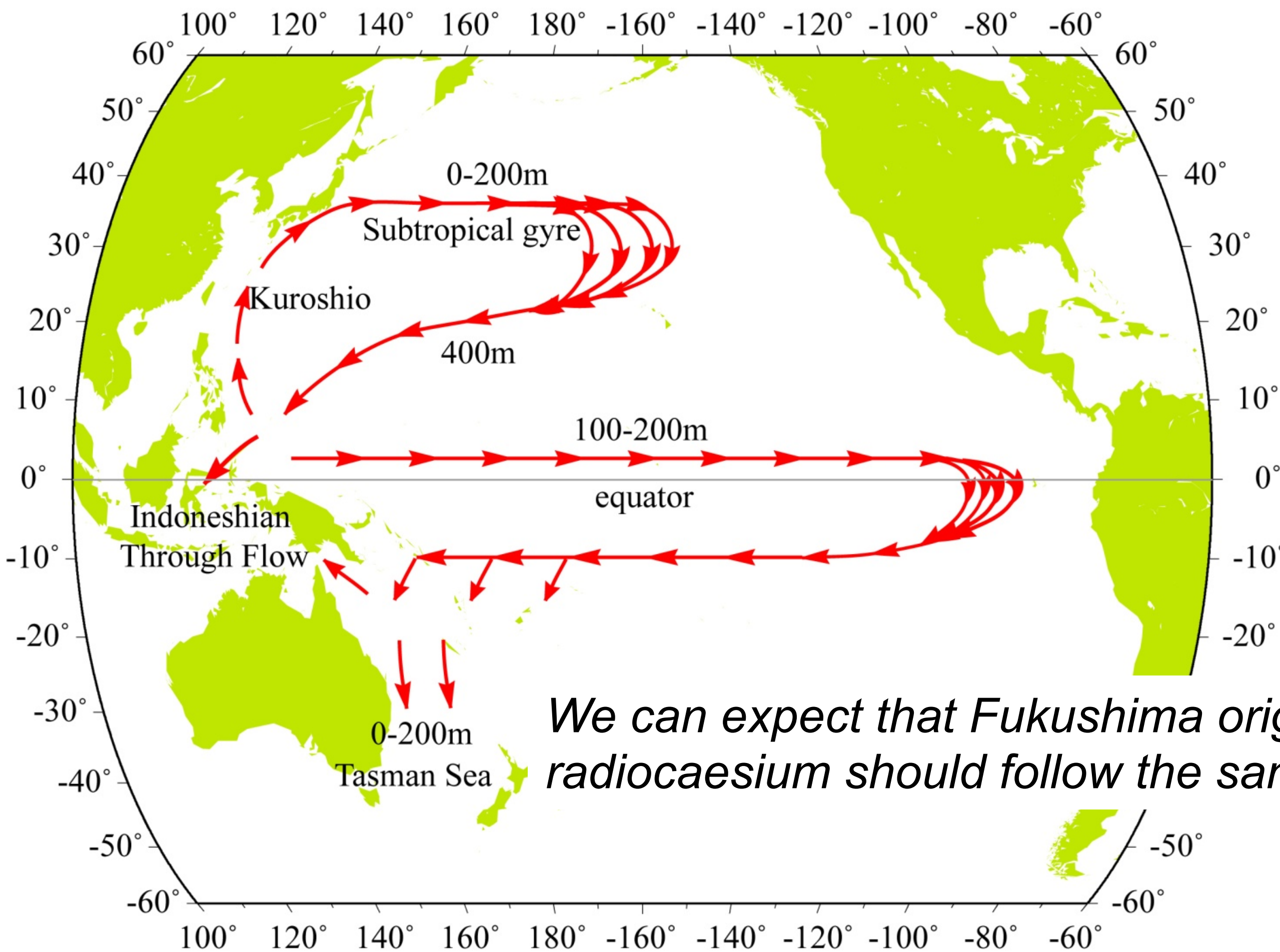
(2011): 69 ± 7 PBq

Chernobyl accident 1986: 85 PBq released

Monthly fallout of ^{137}Cs and ^{90}Sr since 1957 at Tokyo/Tsukuba



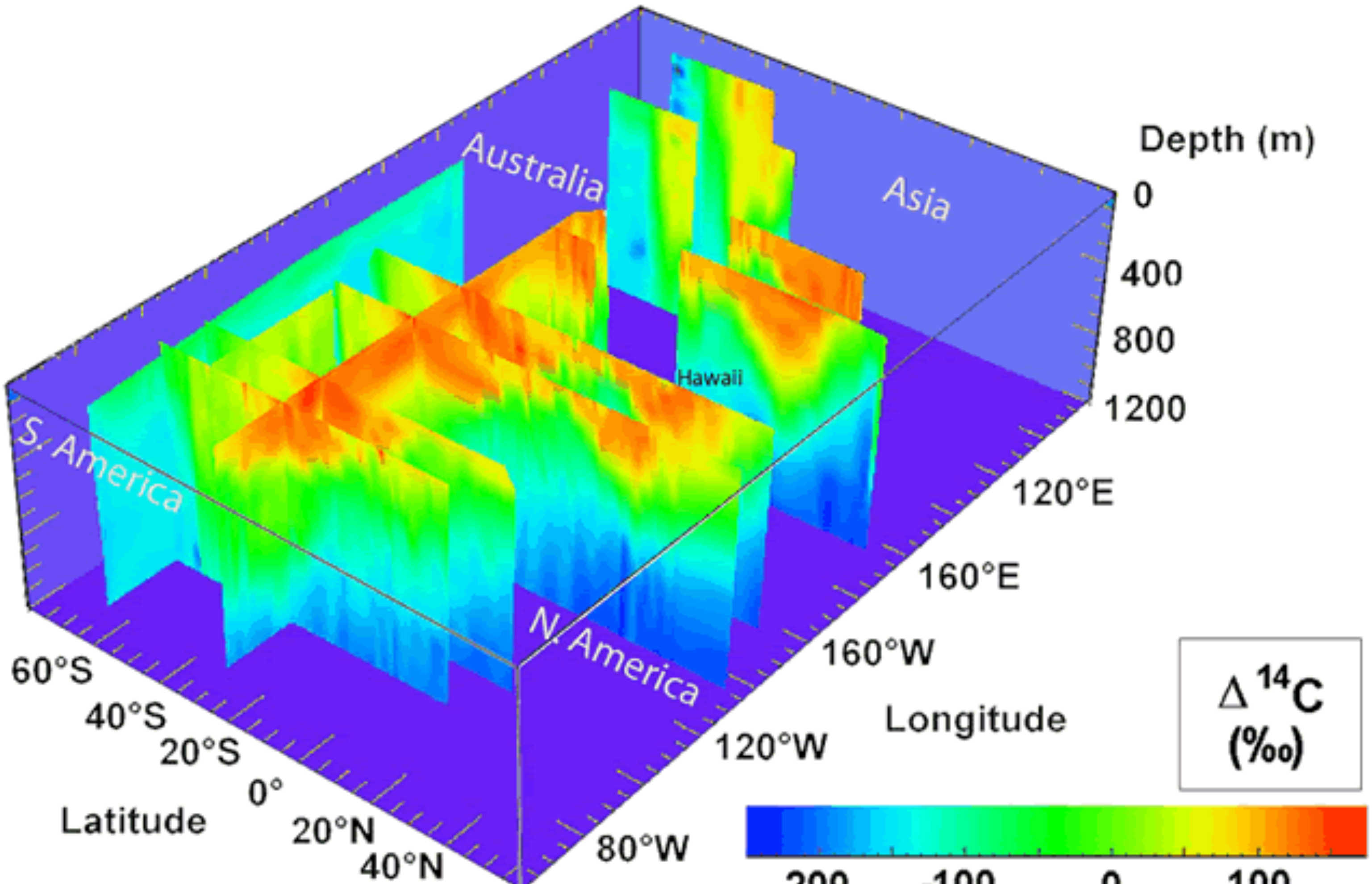
Pathway of weapons tests derived ^{137}Cs in the Pacific Ocean: tracer of sea water movement



We can expect that Fukushima origin radiocaesium should follow the same pathway

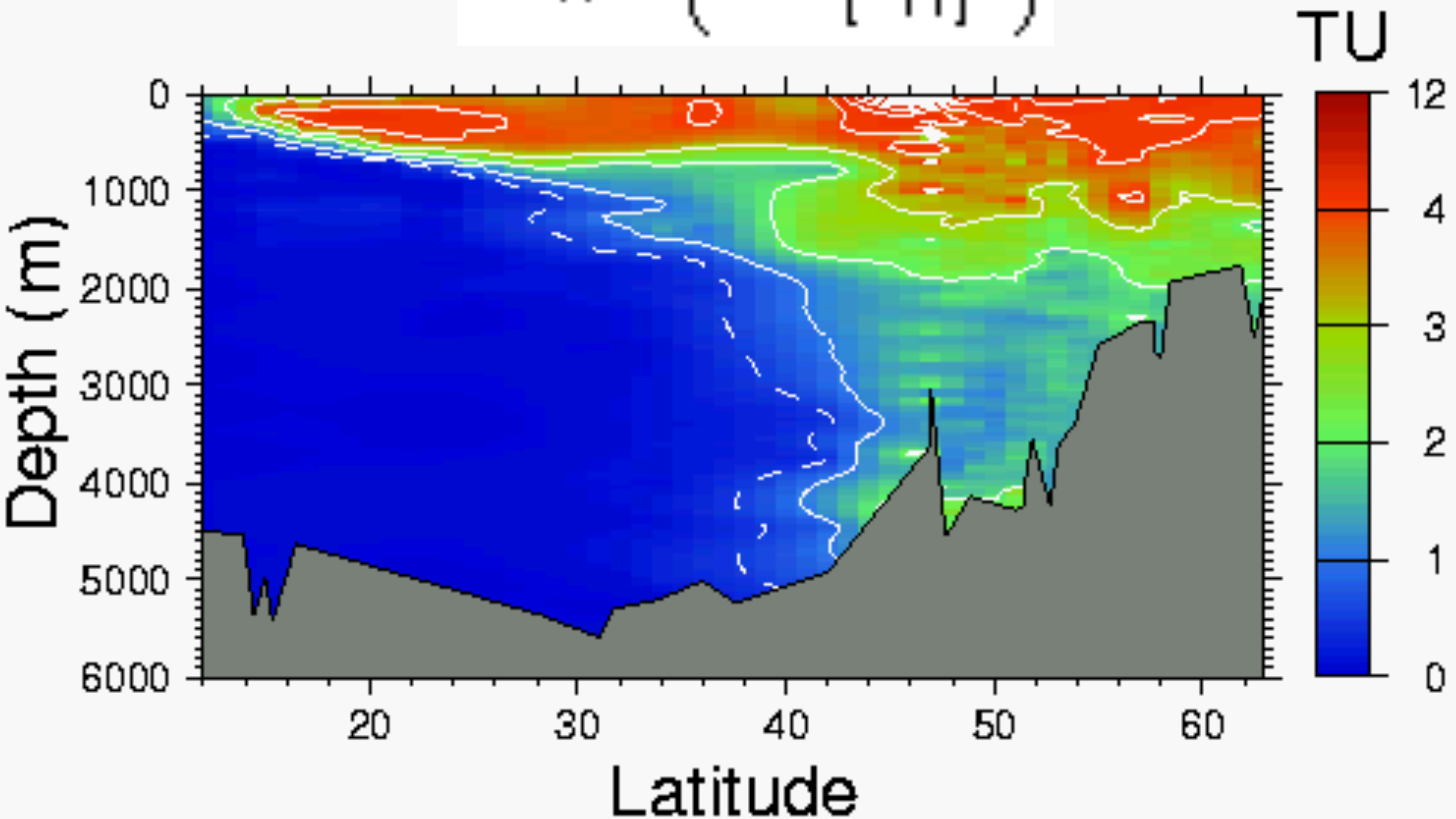
Aoyama et al., 2013

Bomb ^{14}C and Gas Exchange: Measuring how much ^{14}C has penetrated the ocean since nuclear weapon's testing.



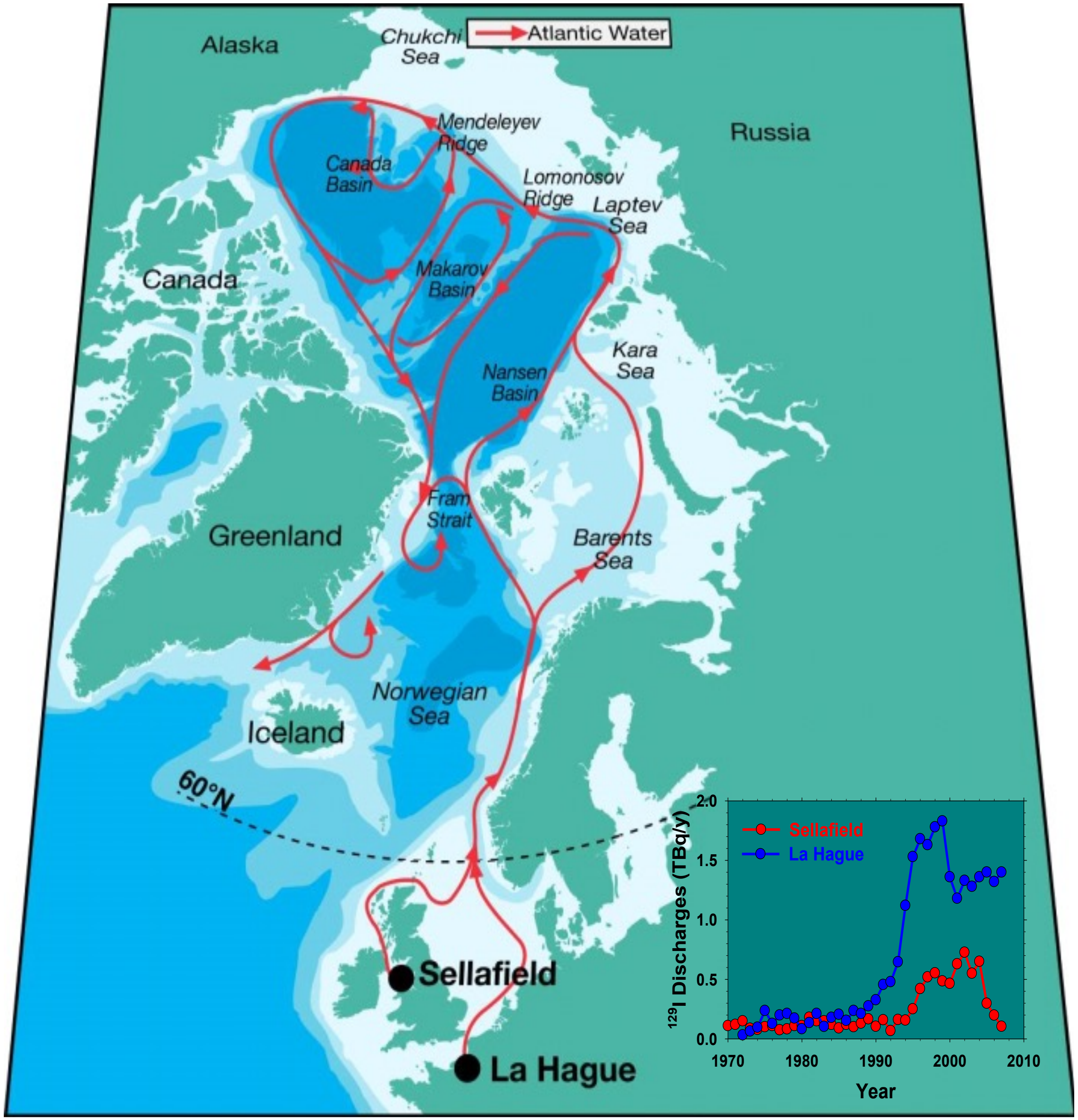
Age of water masses: ^3H-^3He (1981)

$$\tau = \frac{1}{\lambda} \cdot \ln\left(1 + \frac{[^3He_{tri}]}{[^3H]}\right)$$



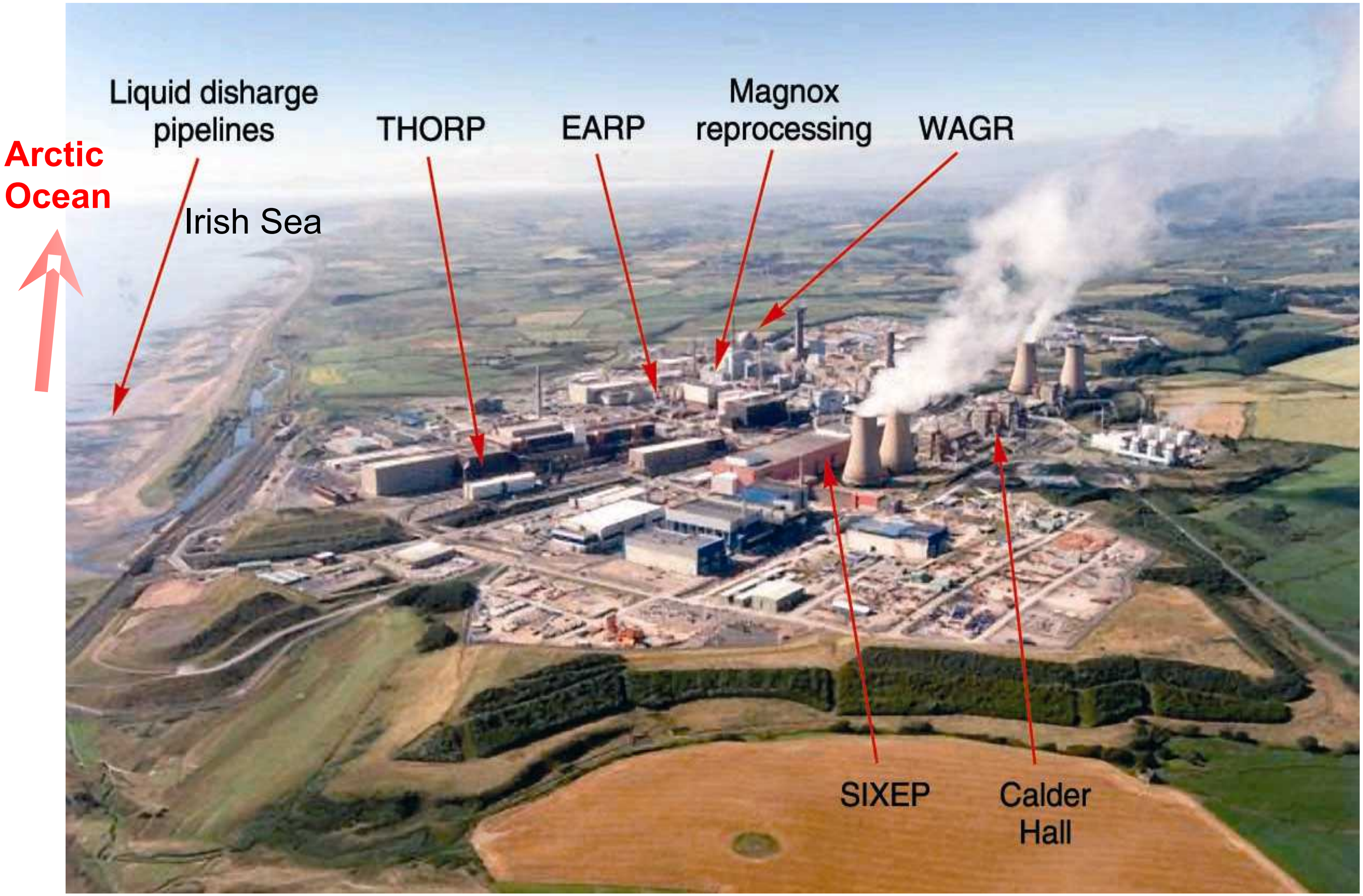
Courtesy of Bill Jenkins

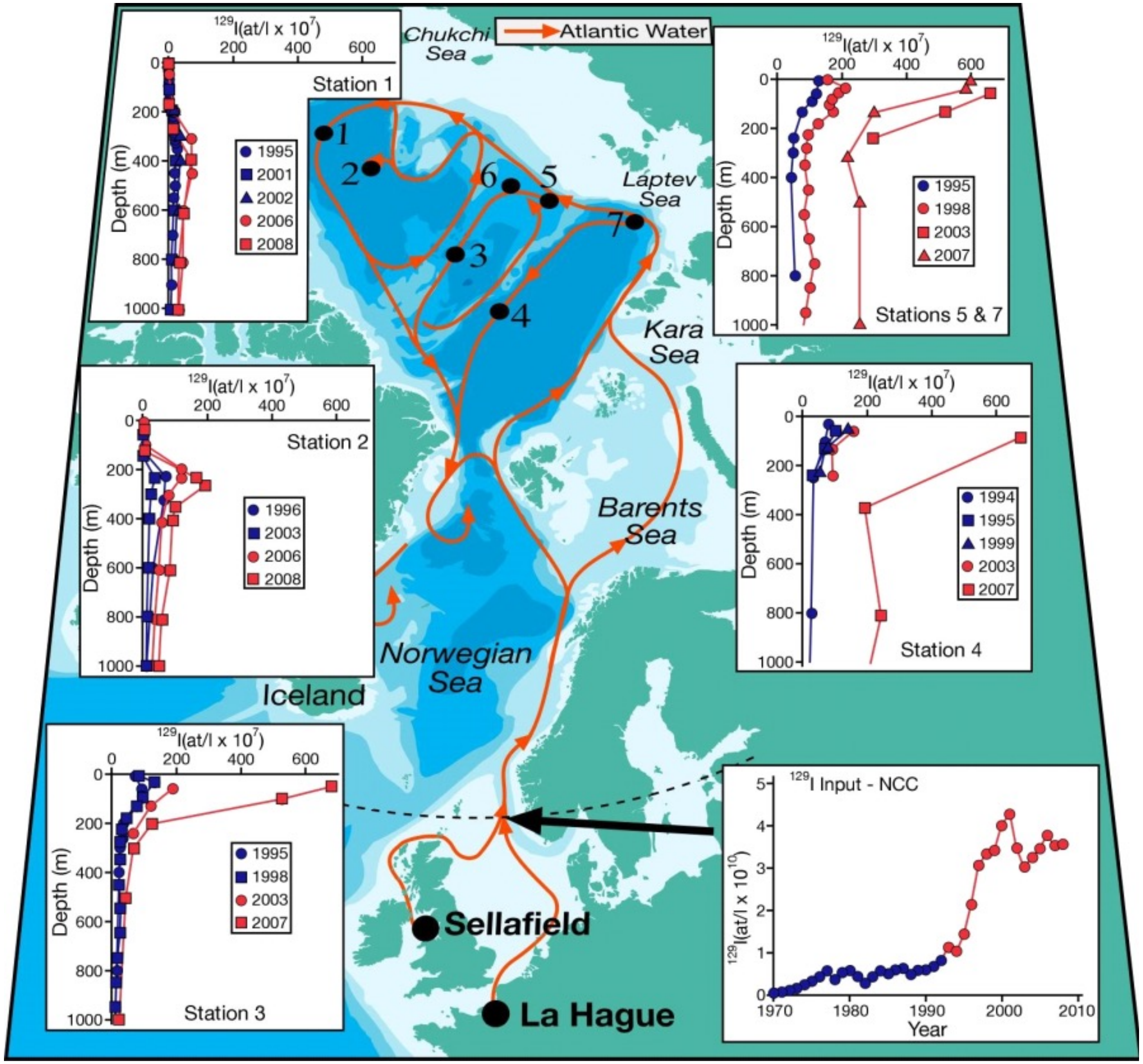
2. Point source inputs: Arctic Ocean



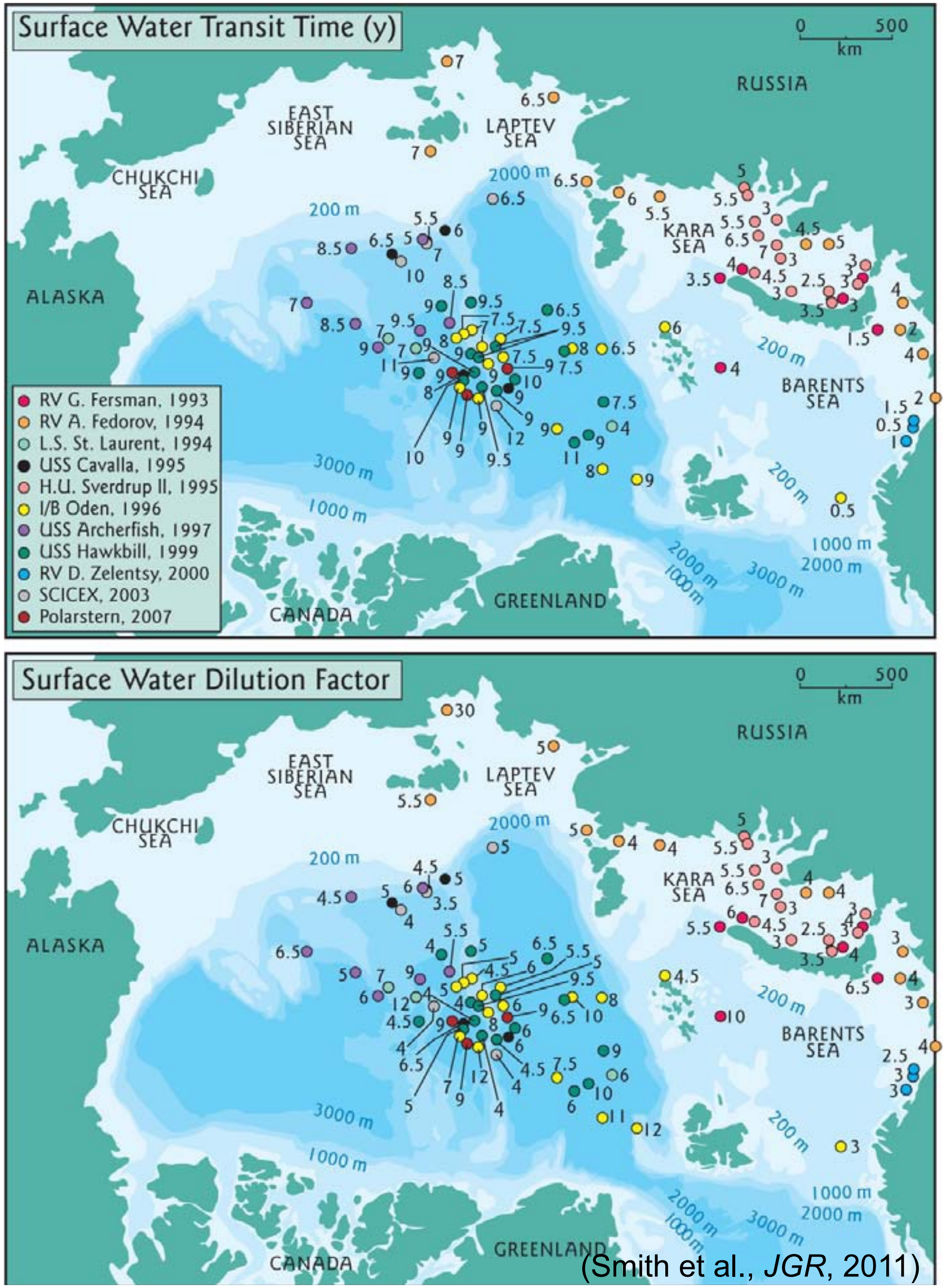
Pathways (red arrows) for the transport of tracers from Sellafield and La Hague through Arctic Ocean. Inset shows ^{129}I input functions from the nuclear fuel reprocessing plants.

BNFL Sellafield





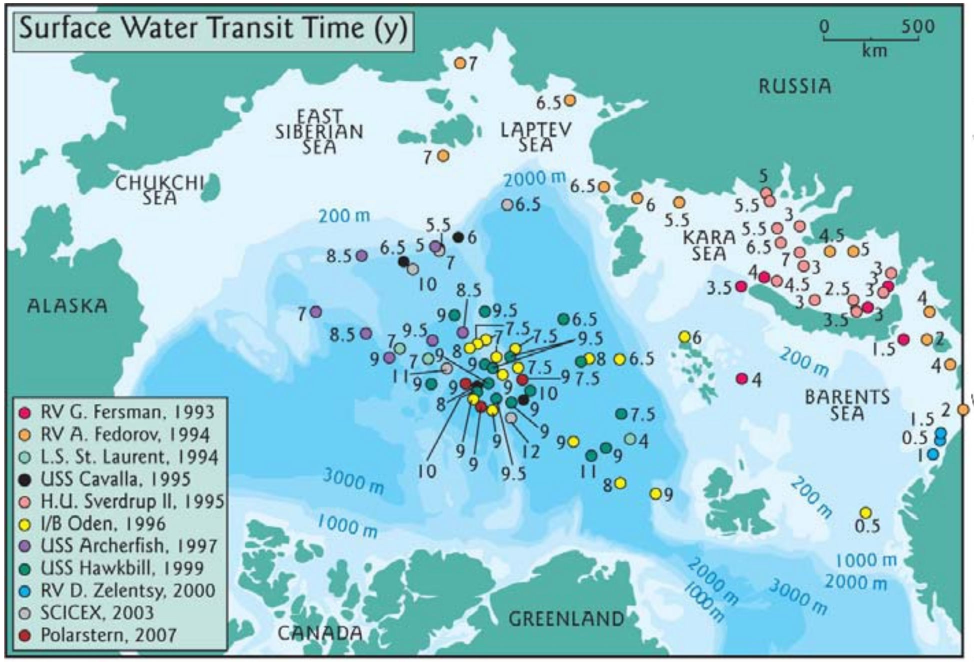
^{129}I water-depth profiles in Arctic Ocean show the arrival of the large pulse produced in the 1990s from Sellafield and La Hague. Inset (lower right) shows ^{129}I input function at 60°N. The arrival of the lower, pre-1993 signal (blue color) is indicated at each station by blue ^{129}I profiles. The arrival of the higher, post-1993 signal is indicated by red profiles. For example, the ^{129}I level at Sta. 4 (North Pole) is constant (blue color) between 1994-1999, but begins to increase (red color) in 2000 and then further increases by 2007. This shows that the 1990s pulse in ^{129}I takes about 10 years to get to Station 4.

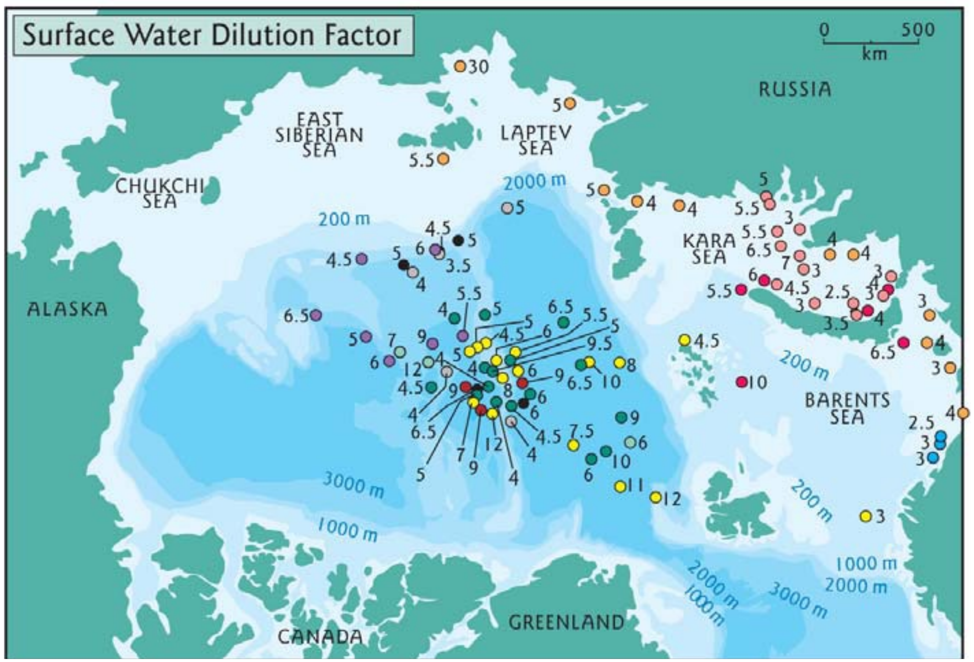


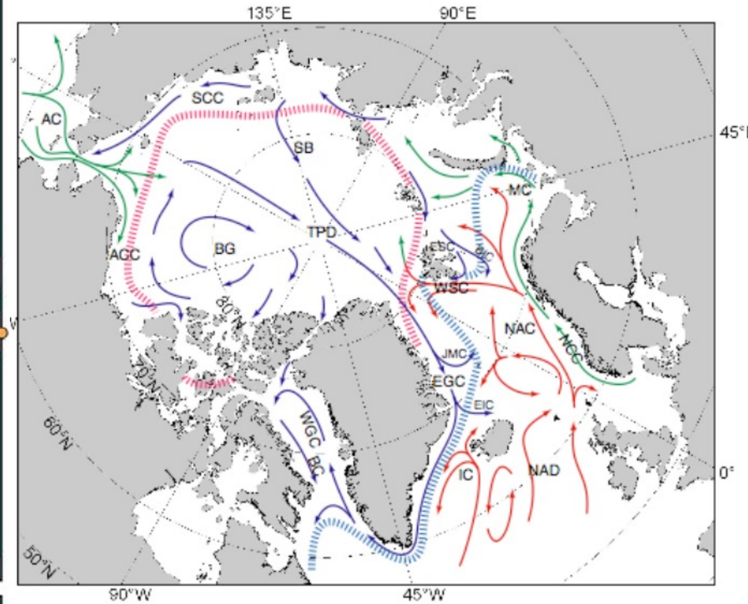
(Smith et al., *JGR*, 2011)

The comparison of ^{129}I and ^{137}Cs levels measured in surface water on a wide range of oceanographic cruises (noted in legend) gives transit times and dilution factors referenced to 60ºN in the North Sea. It takes Atlantic Water 1 year to flow to the Barents Sea, 3-5 y to the Kara Sea, 6-7 y to the Laptev Sea, 9-10 y to the North Pole. The tracer signal is diluted by a factor of 5 by the time it reaches the North Pole; most of this dilution occurs in the marginal Russian seas. The surface flow is advective with very little mixing: it almost flows like a river (not true of underlying intermediate water).

Schematic of surface arctic circulation

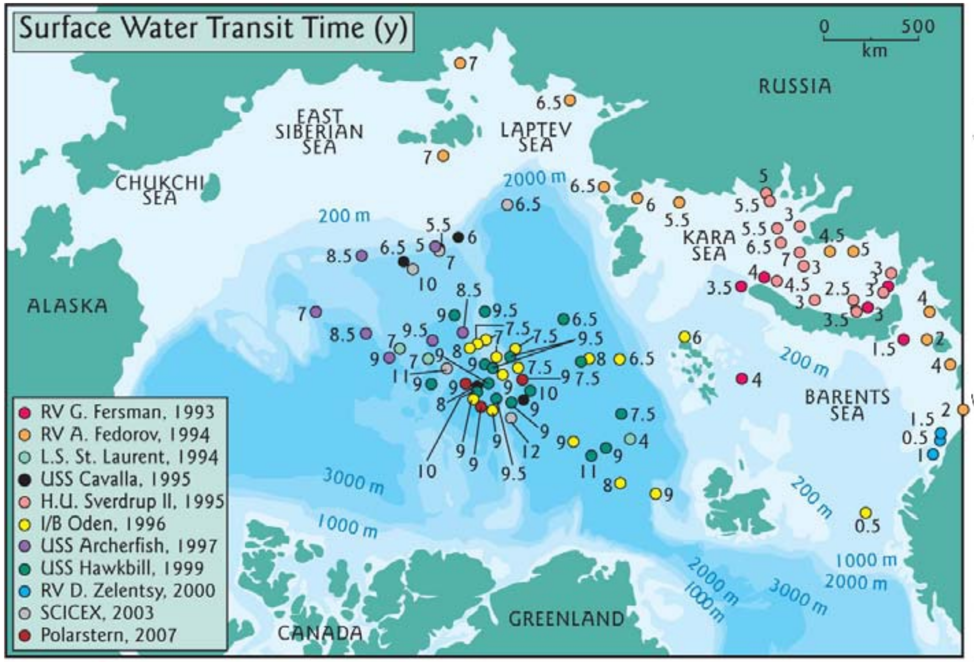




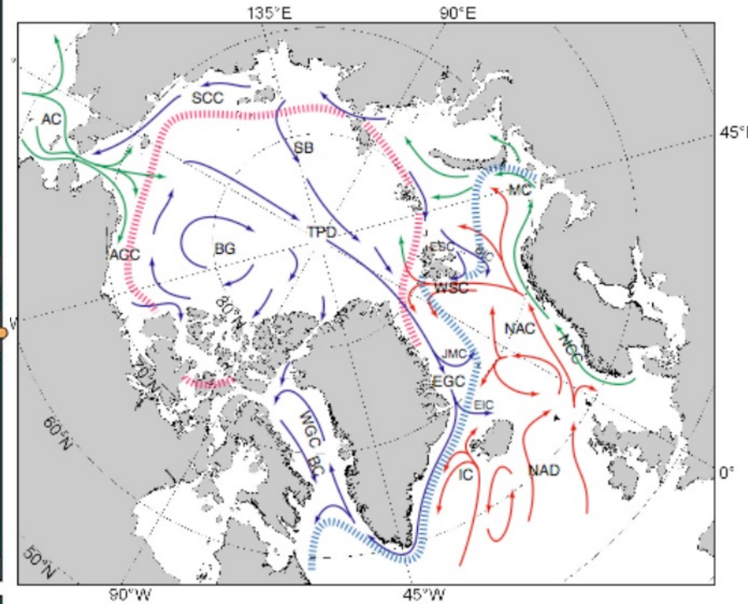


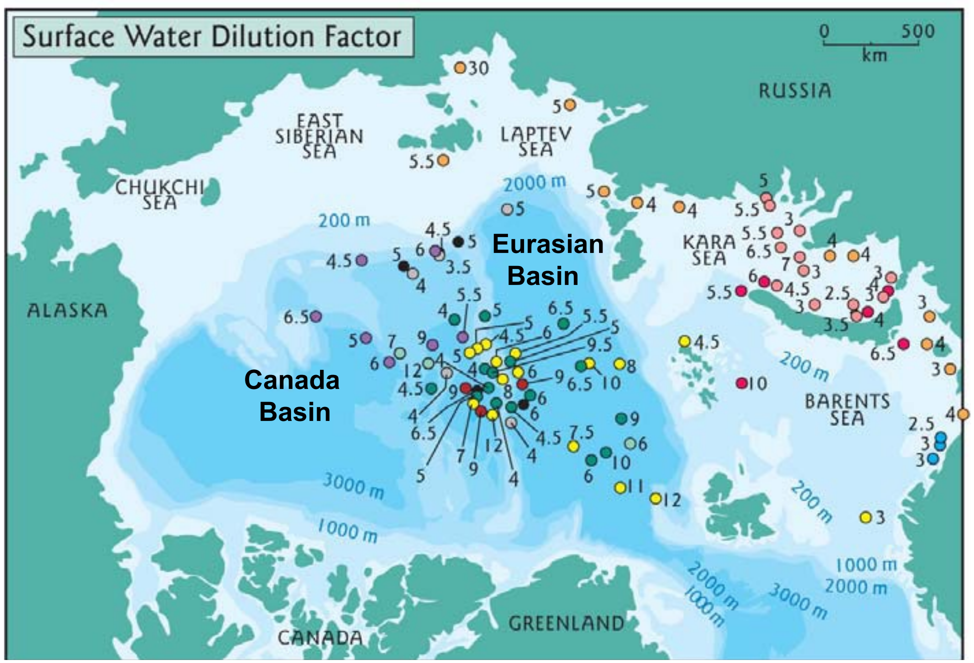
Surface flow (0-200 m).

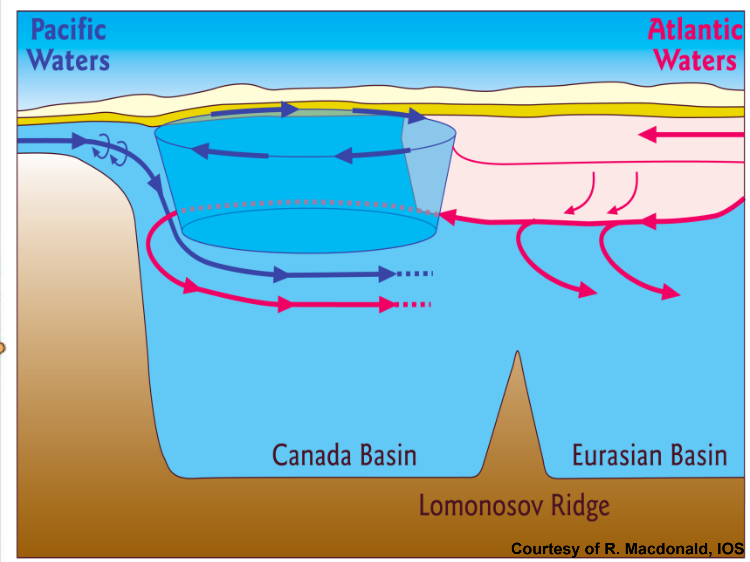
(Figure from Rudels, 2006)



Schematic of surface arctic circulation



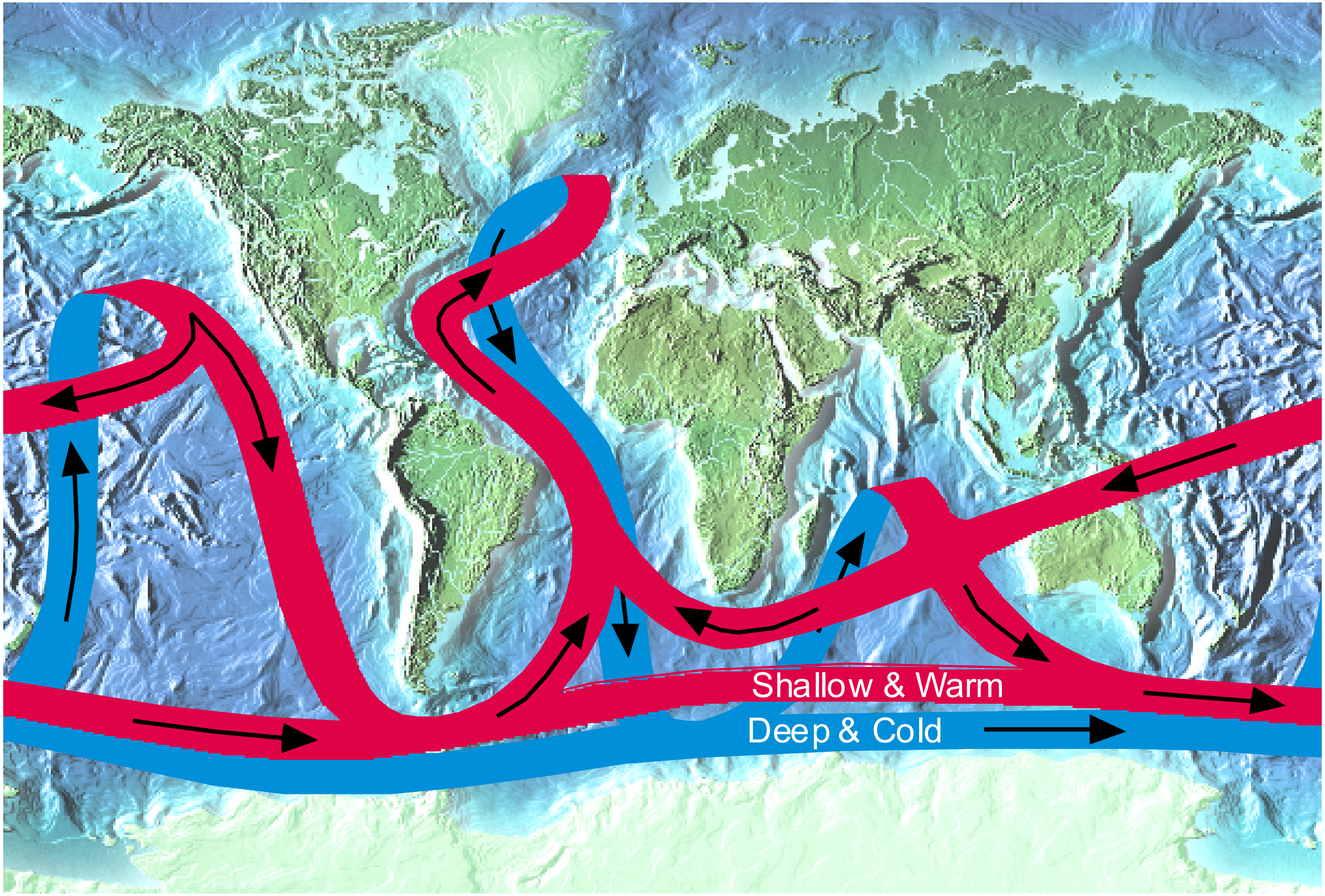


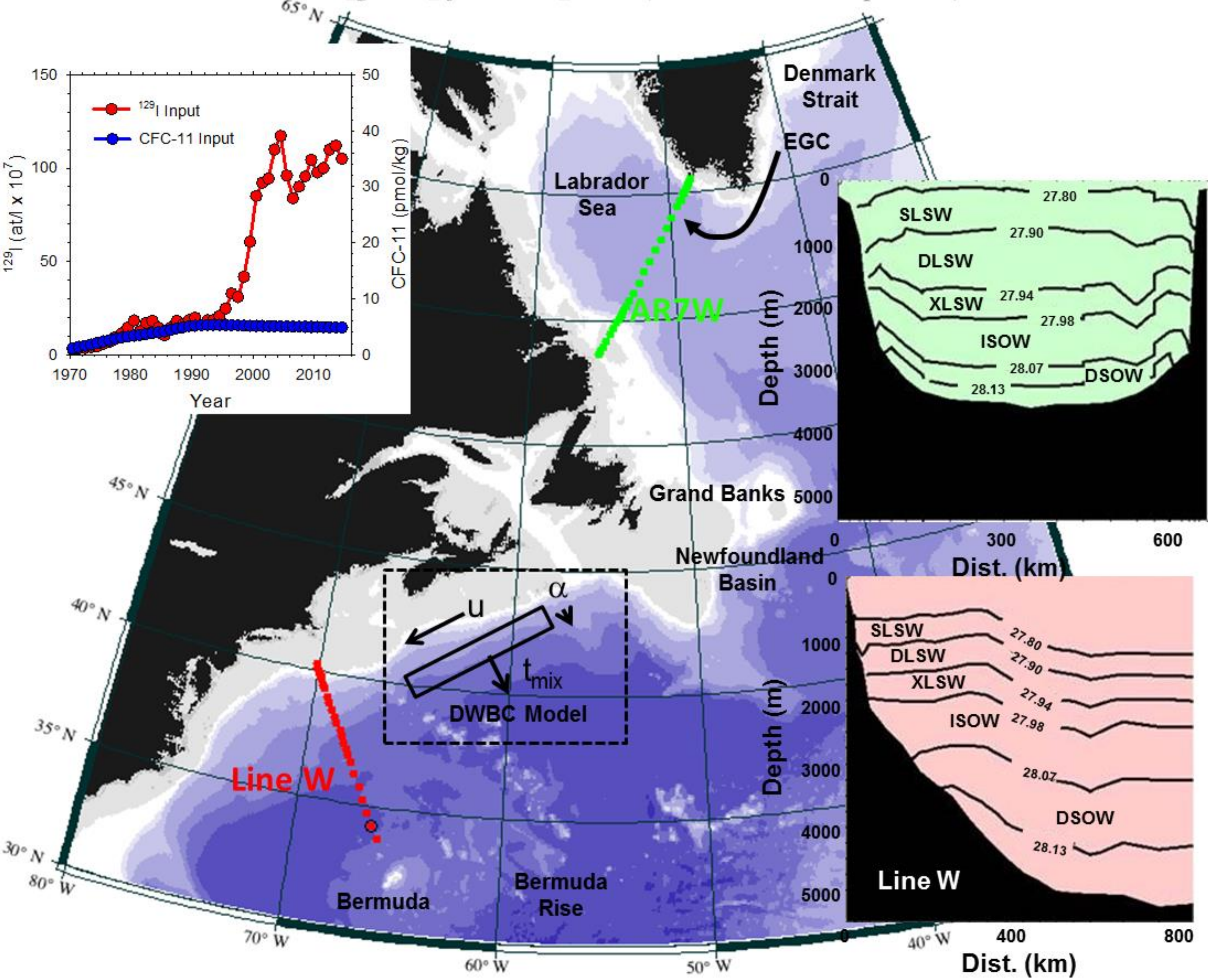


Note that there are no tracer data from Canada Basin: surface water is from Pacific with no $^{129}I/^{137}Cs$ source.

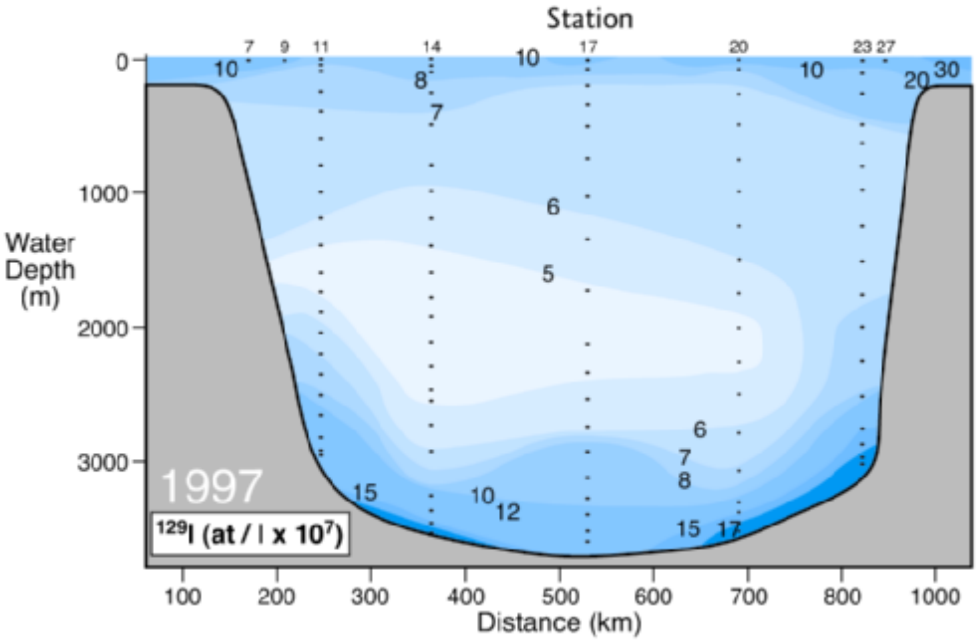
2. Point Source Inputs: North Atlantic

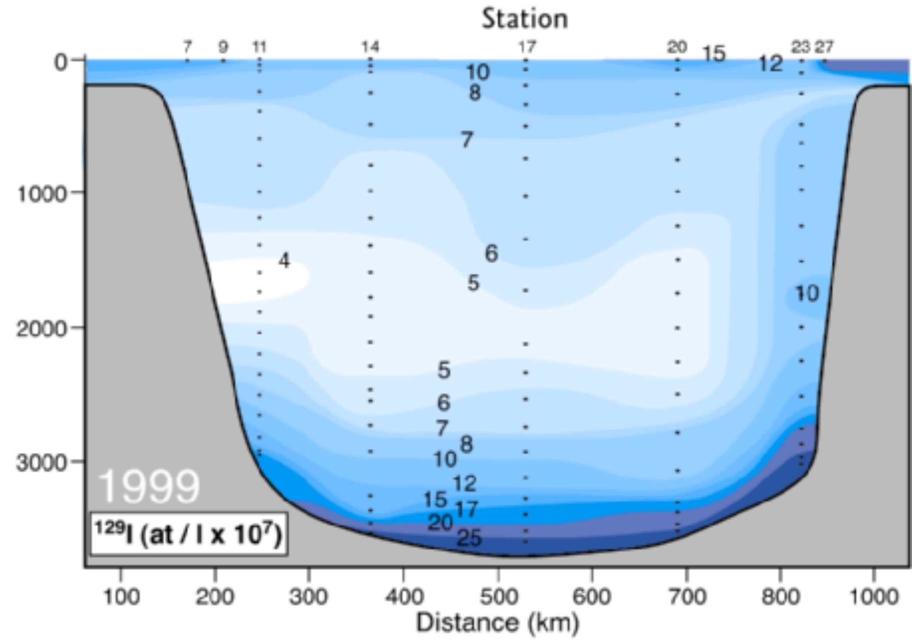
The Global Ocean Conveyor Belt



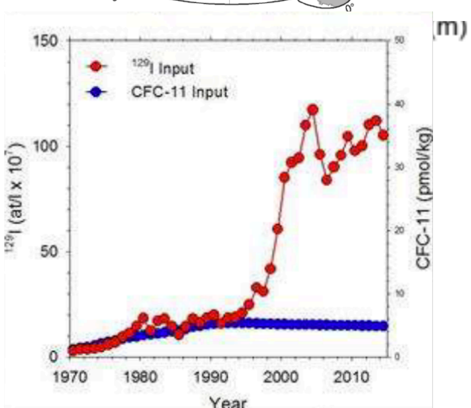


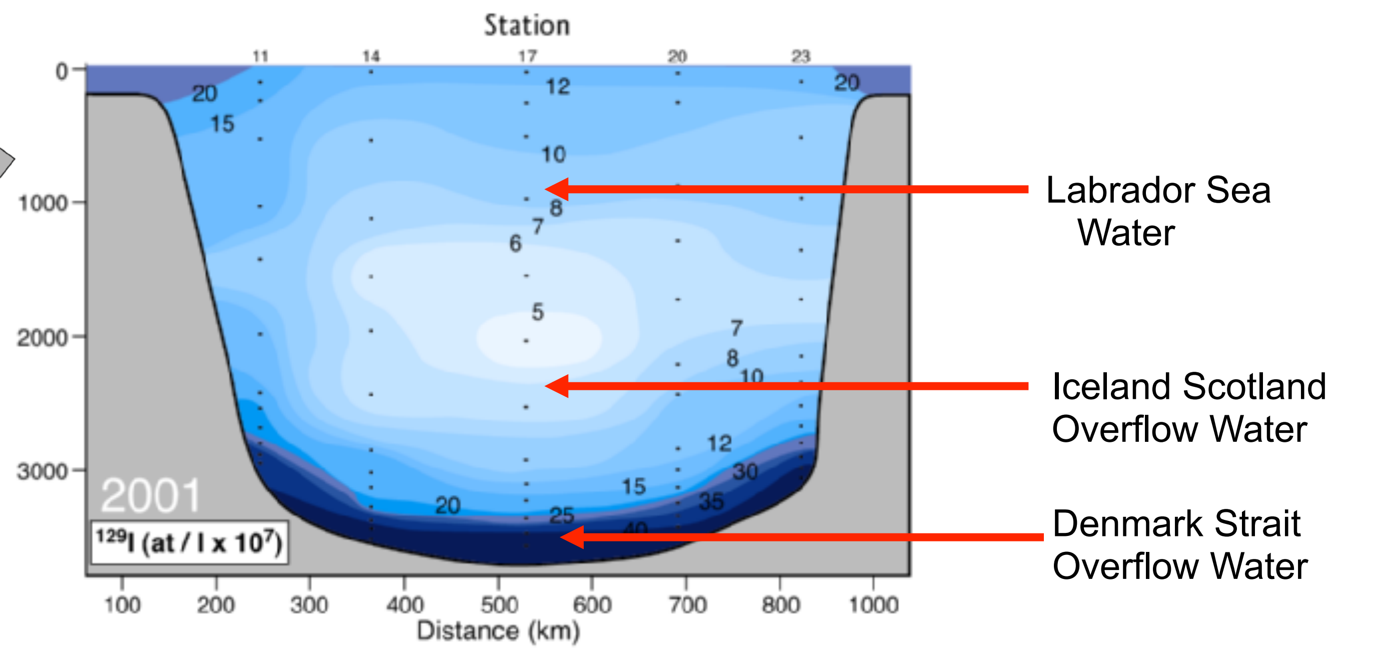
150
100
50
0
50
40
30
20
10
0
^{129}I Input
CFC-11 Input
^{129}I (at/l x 10^{7})
CFC-11 (pmol/kg)
1970
1980
1990
2000
2010
Year
65° N
45° N
40° N
35° N
30° N
80° W
70° W
60° W
50° W
40° W
Denmark Strait
EGC
Labrador Sea
AR7W
Grand Banks
Newfoundland Basin
u
α
t_{mix}
DWBC Model
Line W
Bermuda
Bermuda Rise
0
1000
2000
3000
4000
5000
Depth (m)
27.80
SLSW
27.90
DLSW
XLSW
27.94
27.98
ISOW
28.07
DSOW
28.13
0
300
600
Dist. (km)
0
1000
2000
3000
4000
5000
Depth (m)
SLSW
DLSW
XLSW
ISOW
27.80
27.90
27.94
27.98
28.07
DSOW
28.13
Line W
0
400
800
Dist. (km)


Station
Water Depth (m)
1997
^{129}I (at / l x 10^7)
Distance (km)

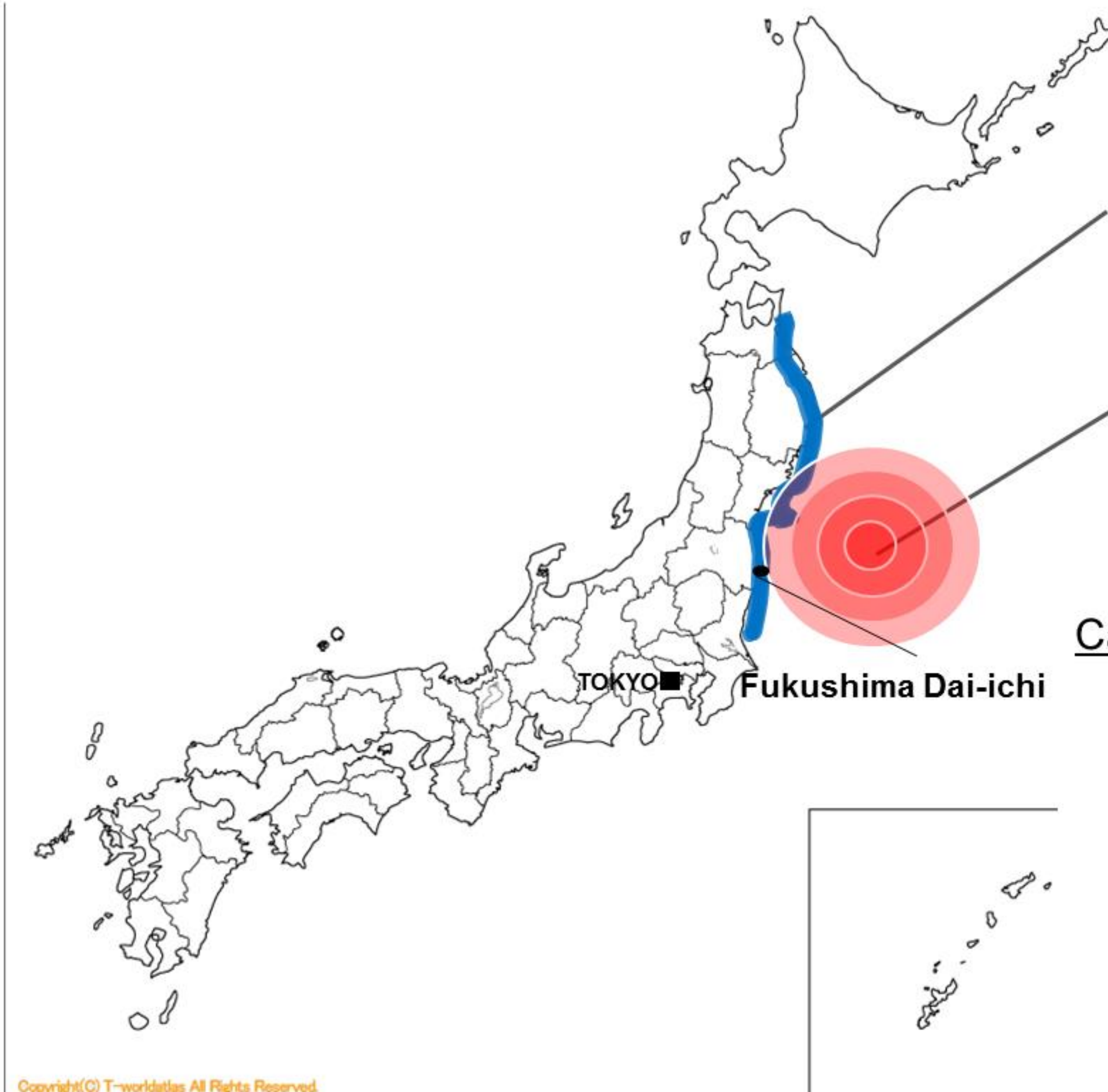

Station
1999
^{129}I (at / l x 10^7)
Distance (km)


Greenland Sea
Norwegian Sea
Labrador Sea
Irminger Sea
North Sea
ISOW
Sellafield
La Hague


^{129}I Input
CFC-11 Input
^{129}I (at/l x 10^7)
CFC-11 (pmol/kg)
Year

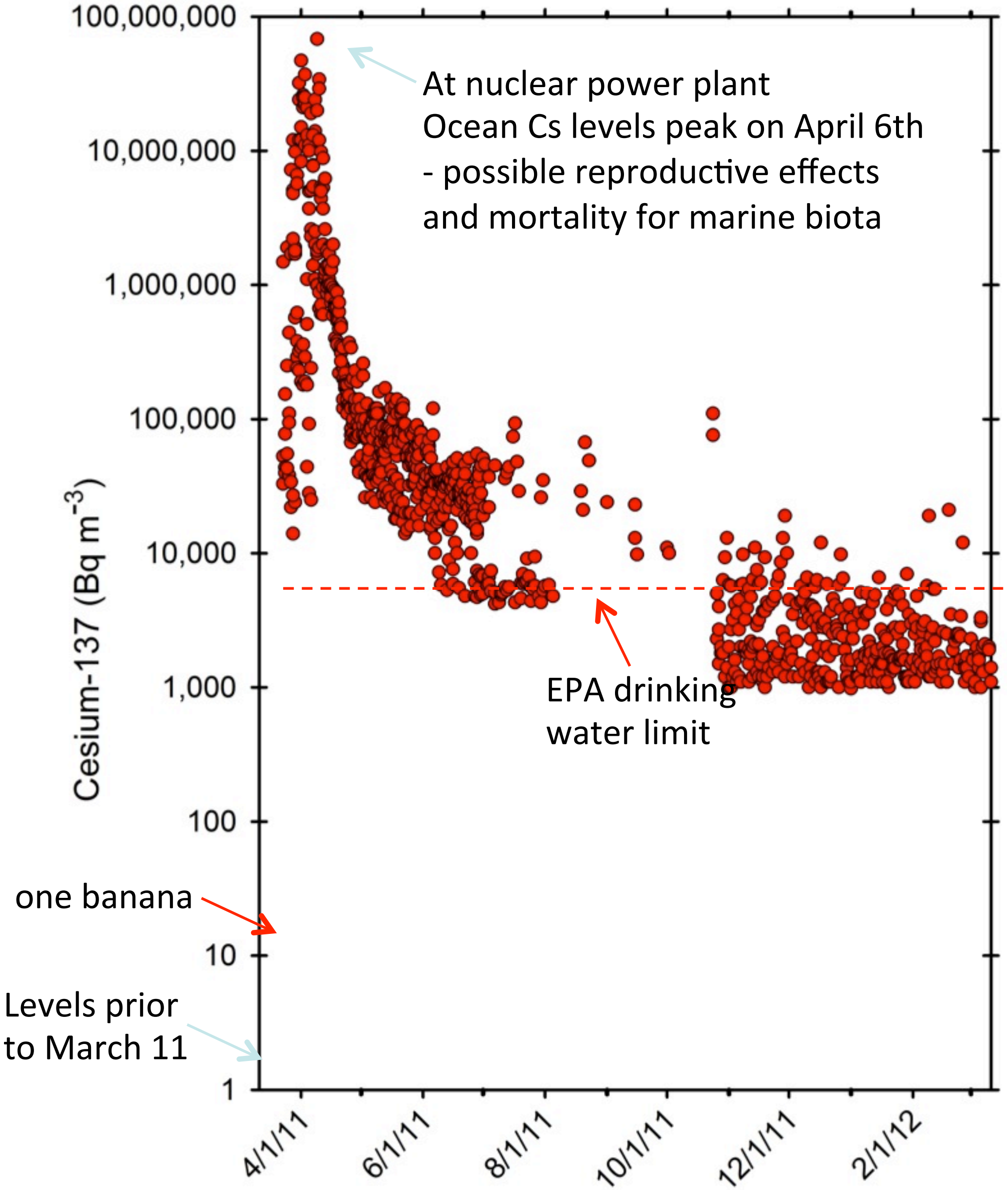

Station
2001
^{129}I (at / l x 10^7)
Distance (km)
Labrador Sea Water
Iceland Scotland Overflow Water
Denmark Strait Overflow Water

3. Nuclear Accidents-Fukushima



Casualties - Tsunami: 18,500
Chernobyl: 40
Fukushima: 0

One year history of ^{137}Cs in ocean immediately off Fukushima



Levels of concern for seafood

Highest ocean levels post Chernobyl

Buesseler, 2012

- Fukushima NPP represents unprecedented release of radionuclides to the ocean

- levels decreased rapidly, then leveled off

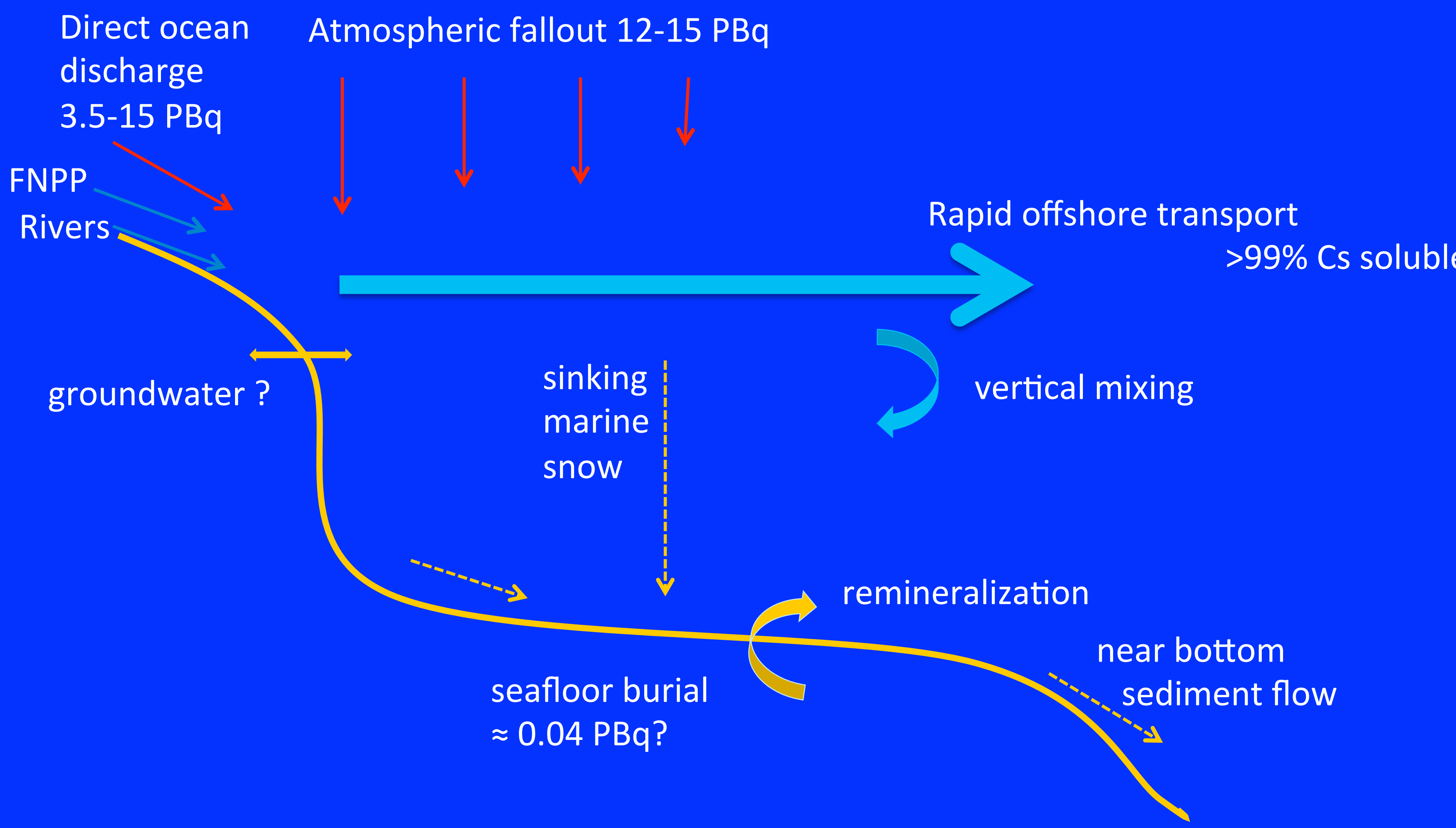
- so reactors were still a source (through Sept.'12)

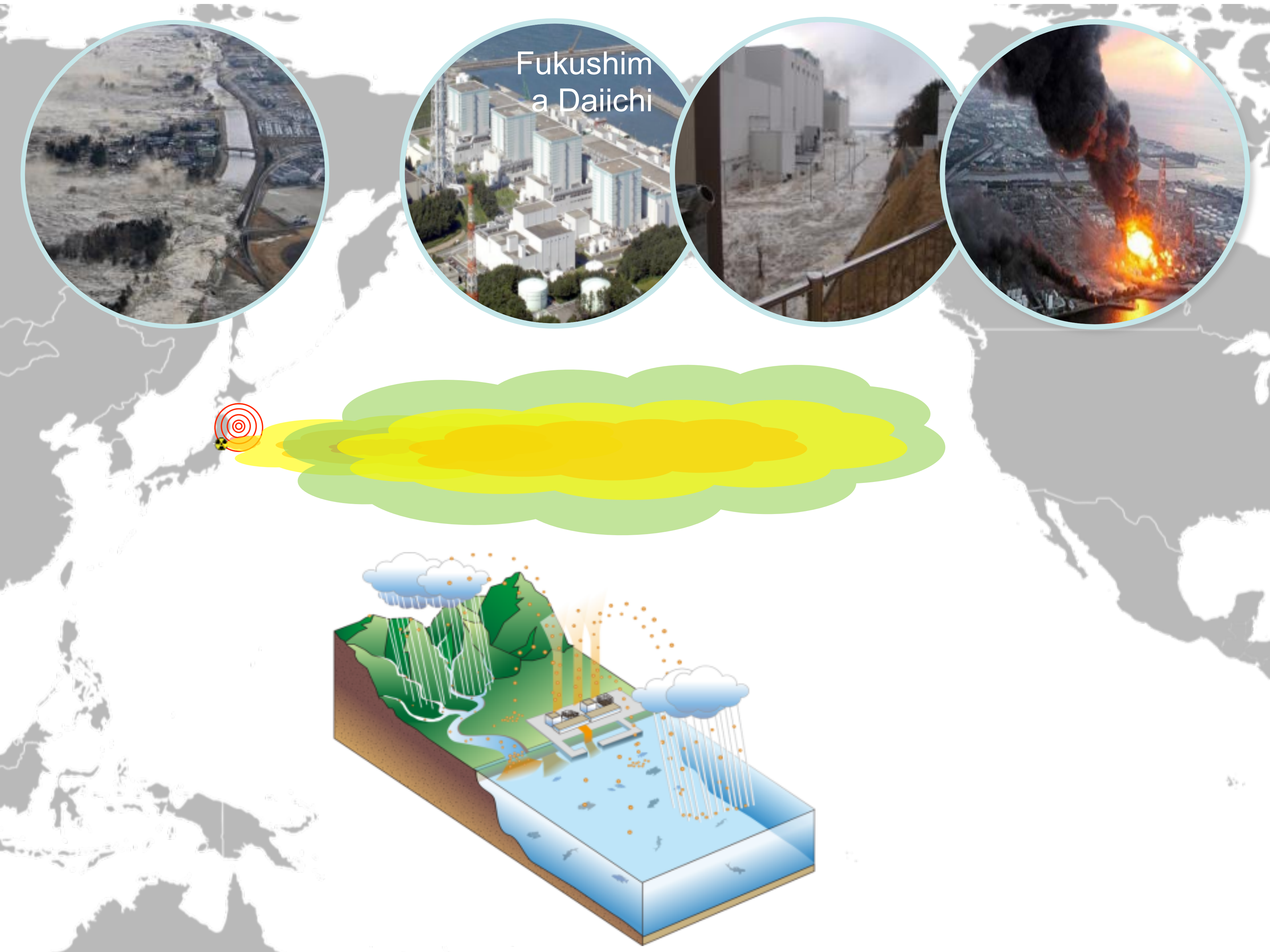
-but levels now safe for marine biota & human exposure

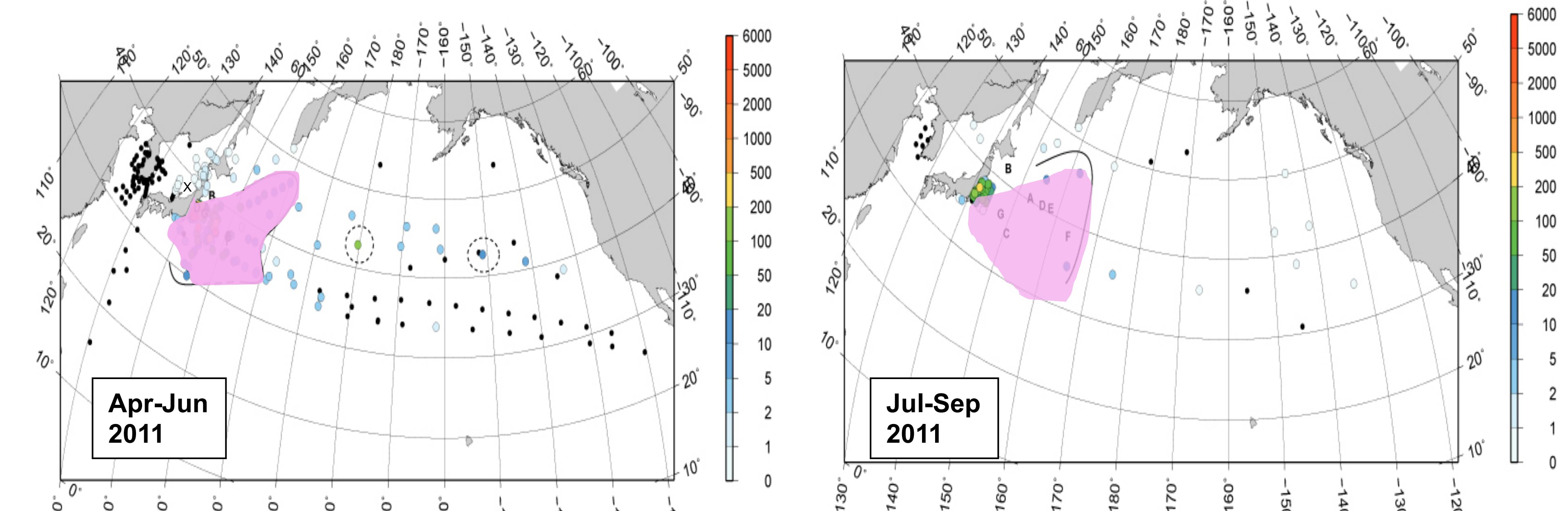
-^{137}Cs levels in Irish Sea from Sellafield were 40,000 Bq/m^3 for 5 years....Fukushima not totally unprecedented

-Radiation dose in oganisms from natural rdionuclides, ^{40}K and ^{210}Po is much greater than from ^{137}Cs away from Fukushima.

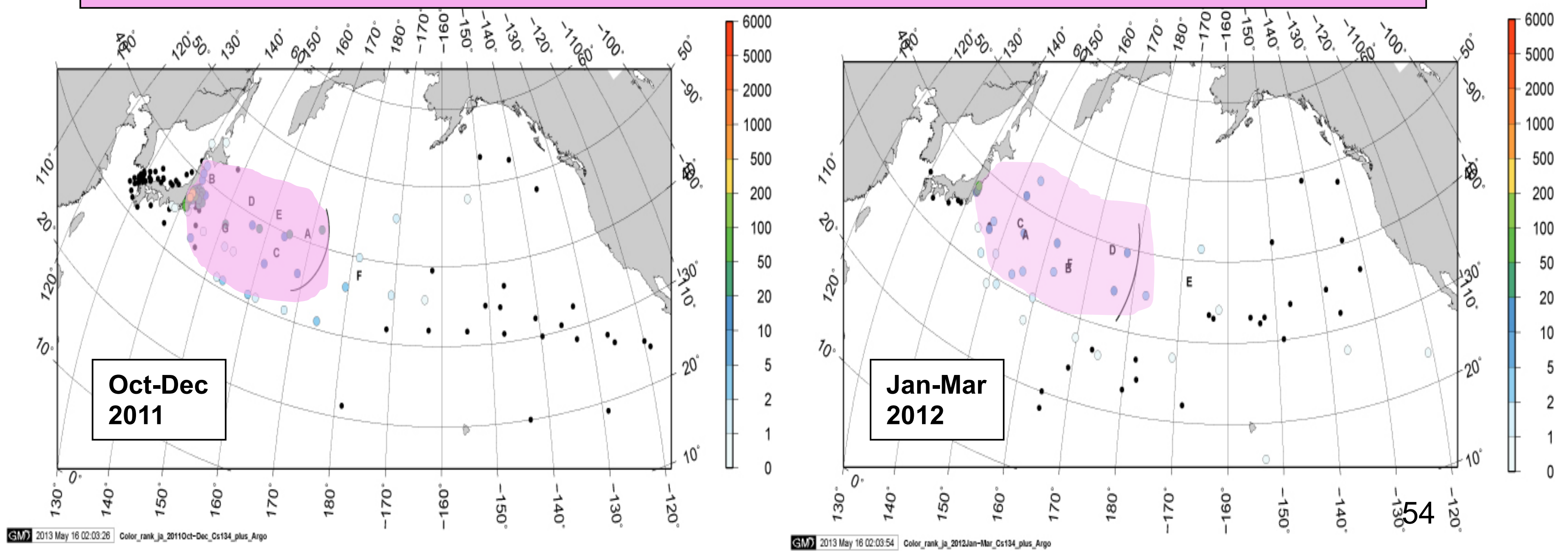
Summary of sources and fate of Fukushima Cs in the ocean




Fukushim
a Daiichi



Surface speed of contaminated water ca. 7 km day^{-1}



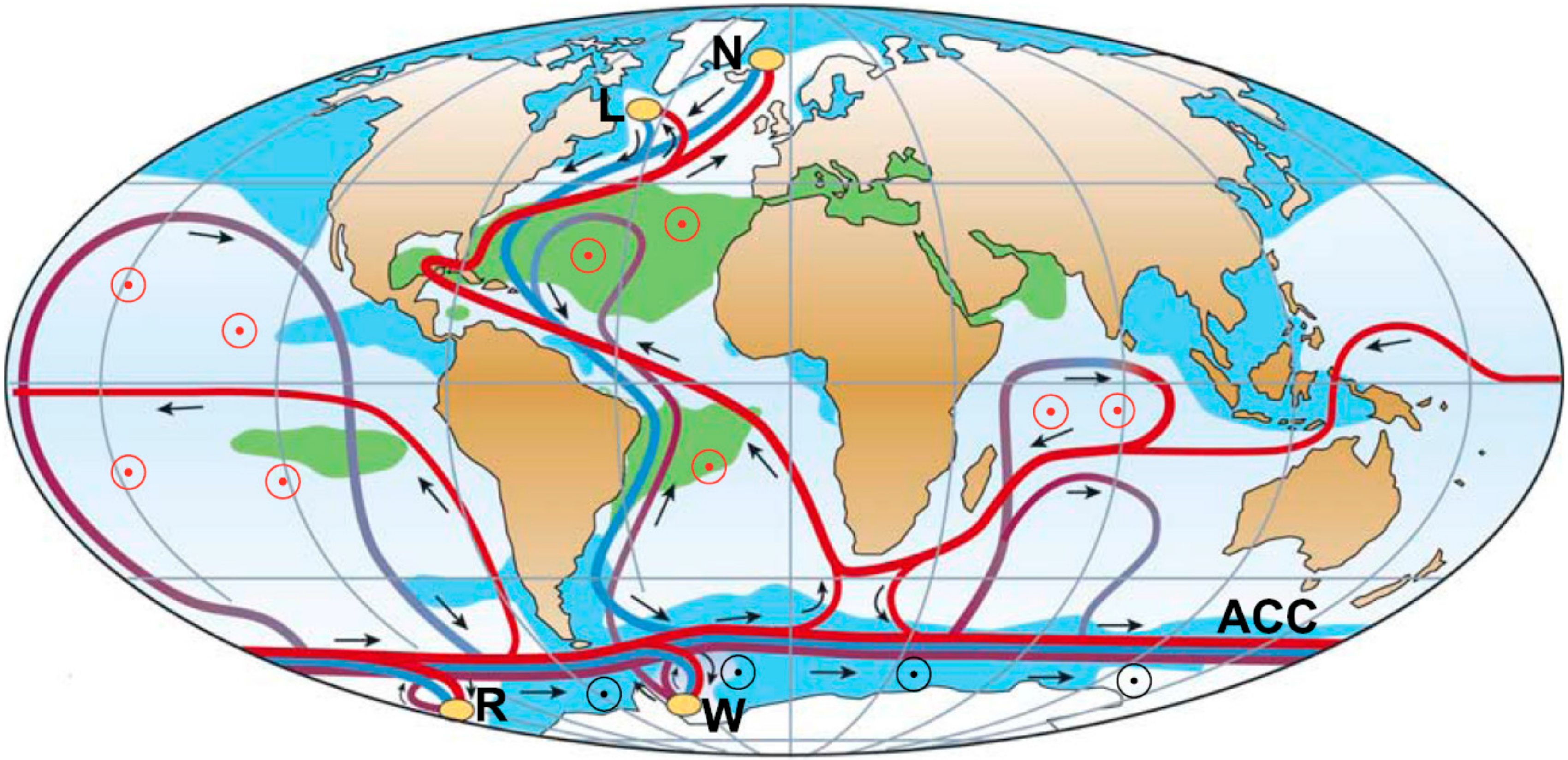
(Aoyama et al., BG 10 3067-3078, 2013)

Case studies

4. Deep ocean circulation, present & past

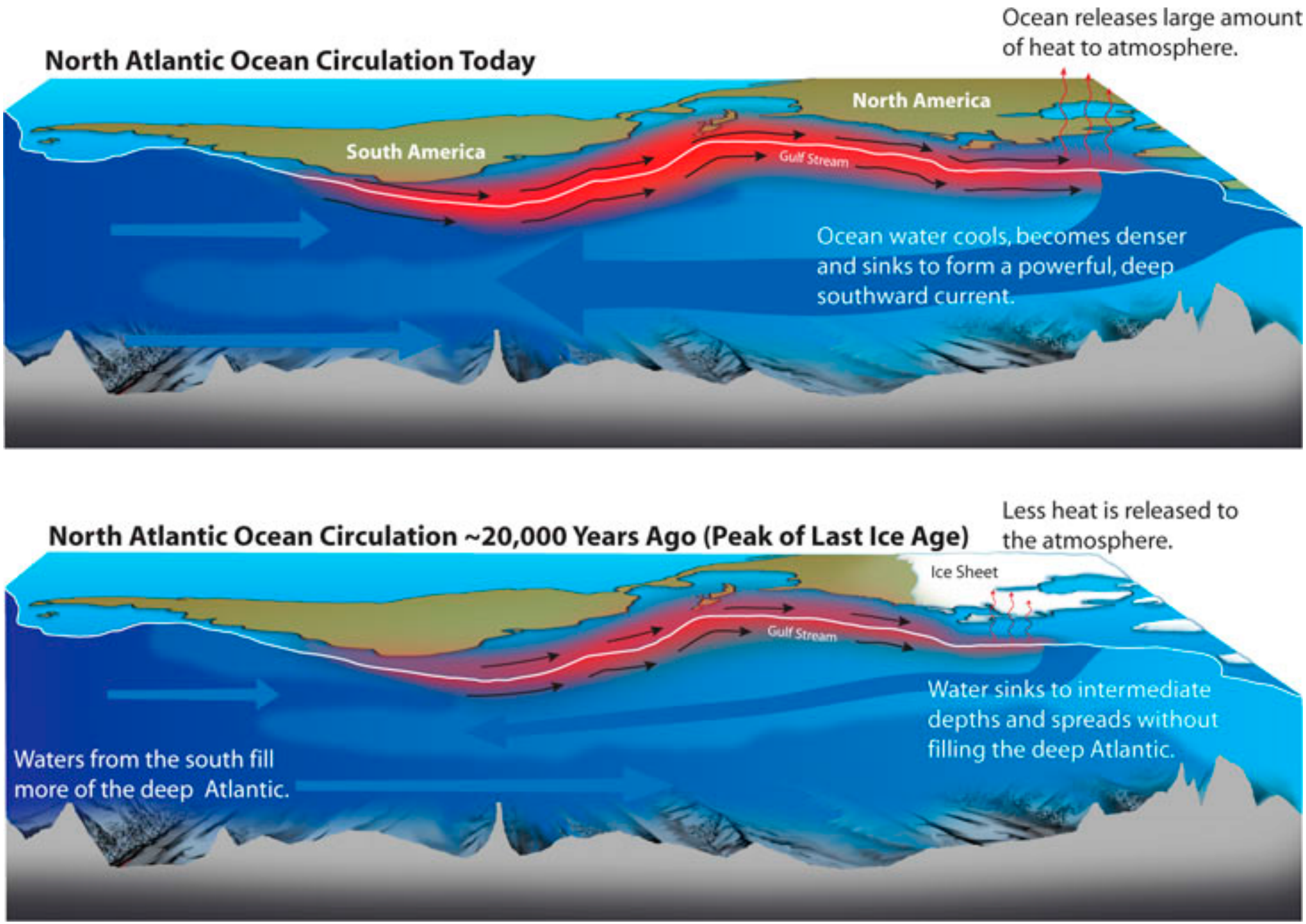
– $^{231}Pa/^{230}Th$

Ocean Conveyor Belt Circulation



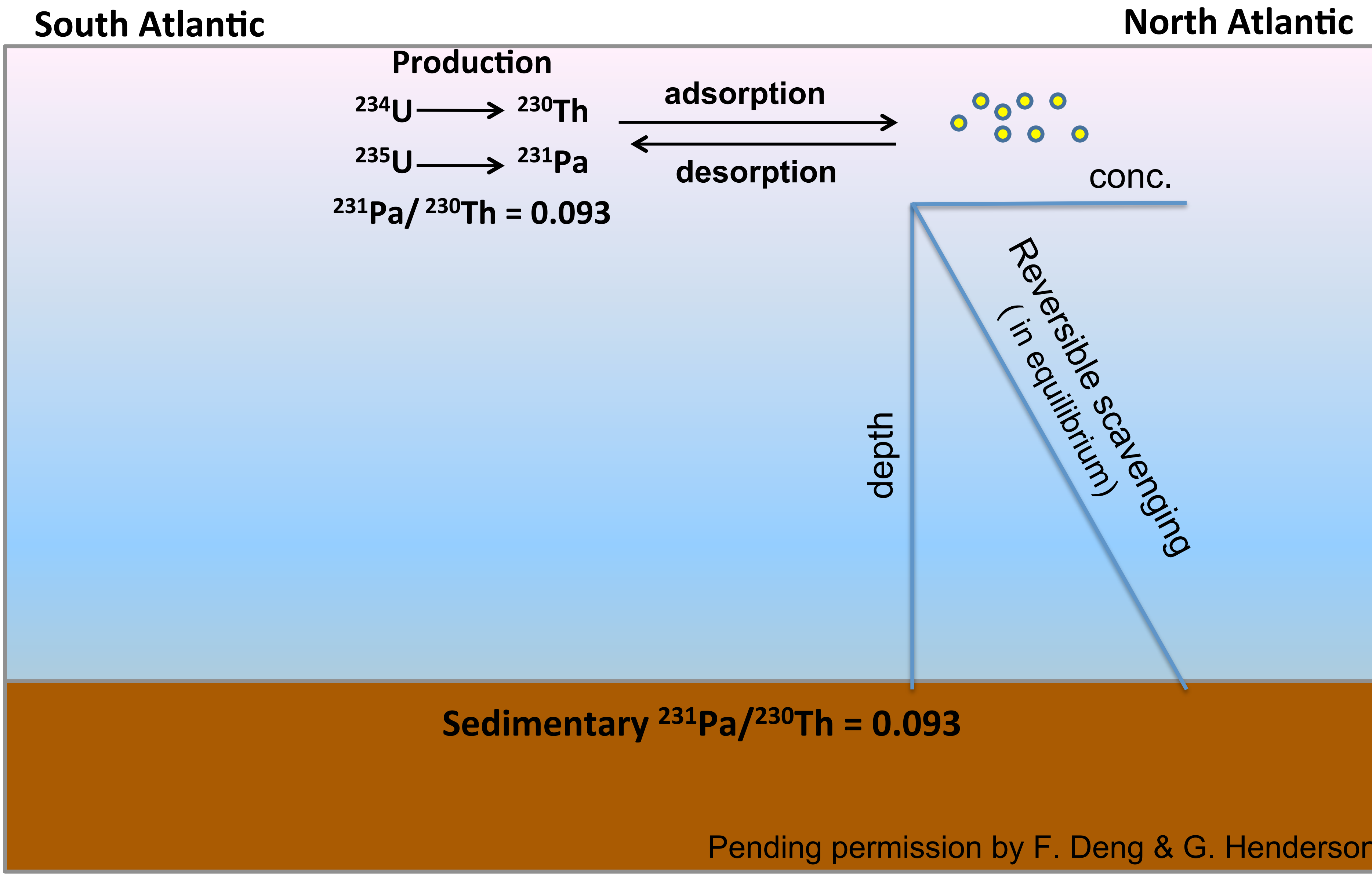
Surface flow		Wind-driven upwelling		L	Labrador Sea
Deep flow		Mixing-driven upwelling		N	Nordic Seas
Bottom flow		Salinity > 36 ‰		W	Weddell Sea
Deep Water Formation		Salinity < 34 ‰		R	Ross Sea

In Negre (2009), from Kuhlbrodt et al. (2007) after Rahmstorf (2002)

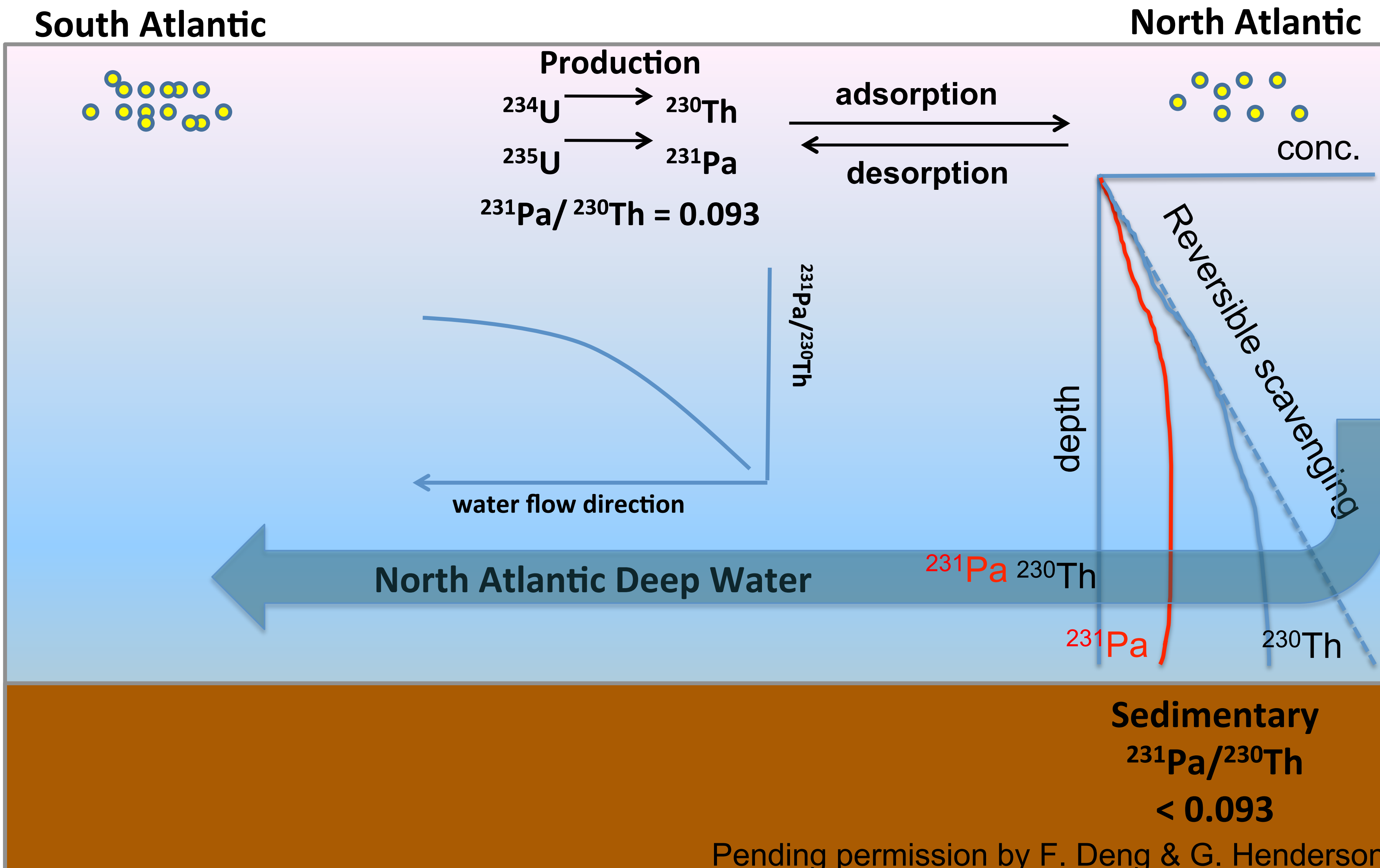


E. Paul Oberlander (http://www.whoi.edu/oceanus/)

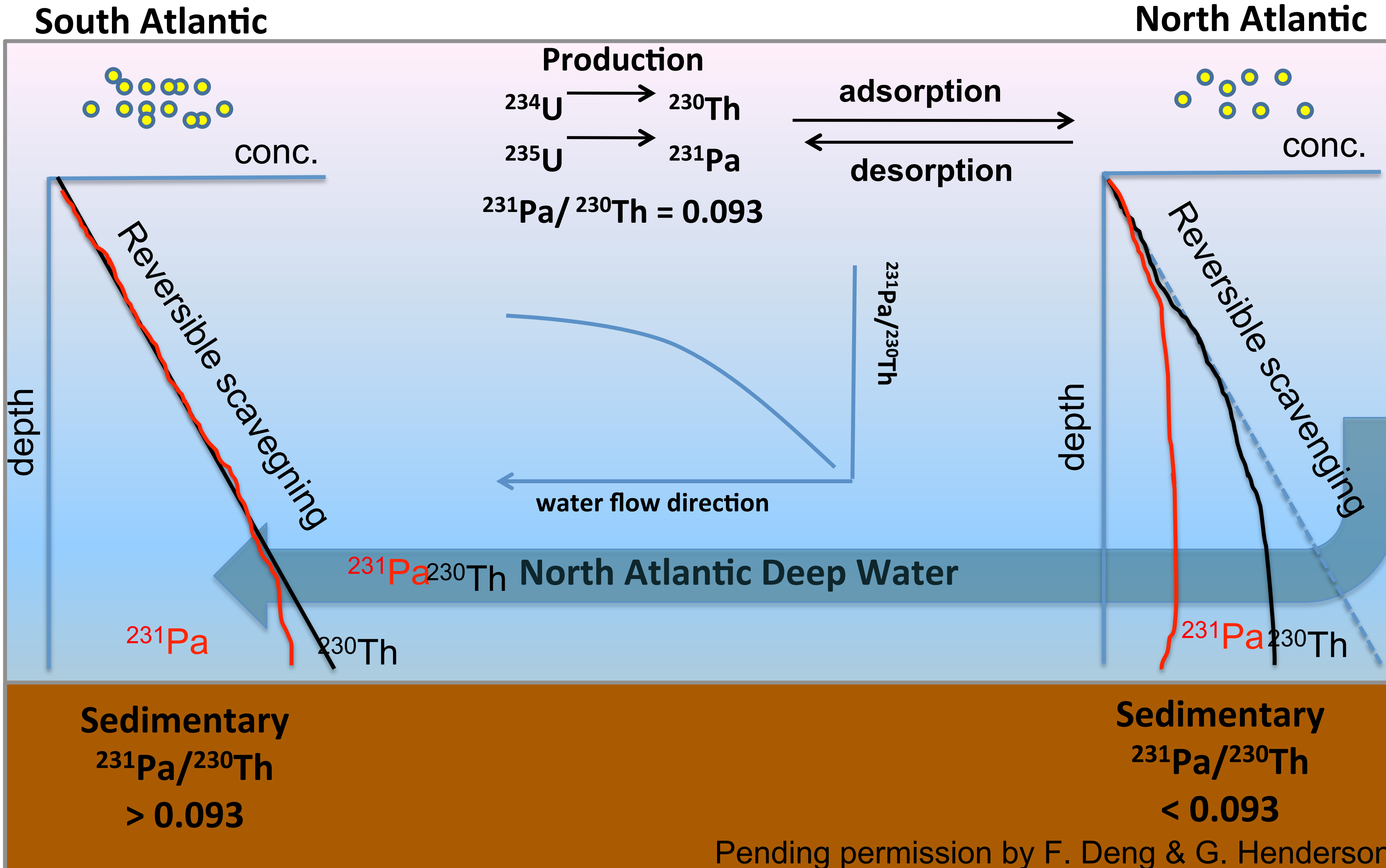
Traditional view of $^{231}Pa/^{230}Th$ to trace deep ocean circulation



Traditional view of $^{231}Pa/^{230}Th$ to trace deep ocean circulation

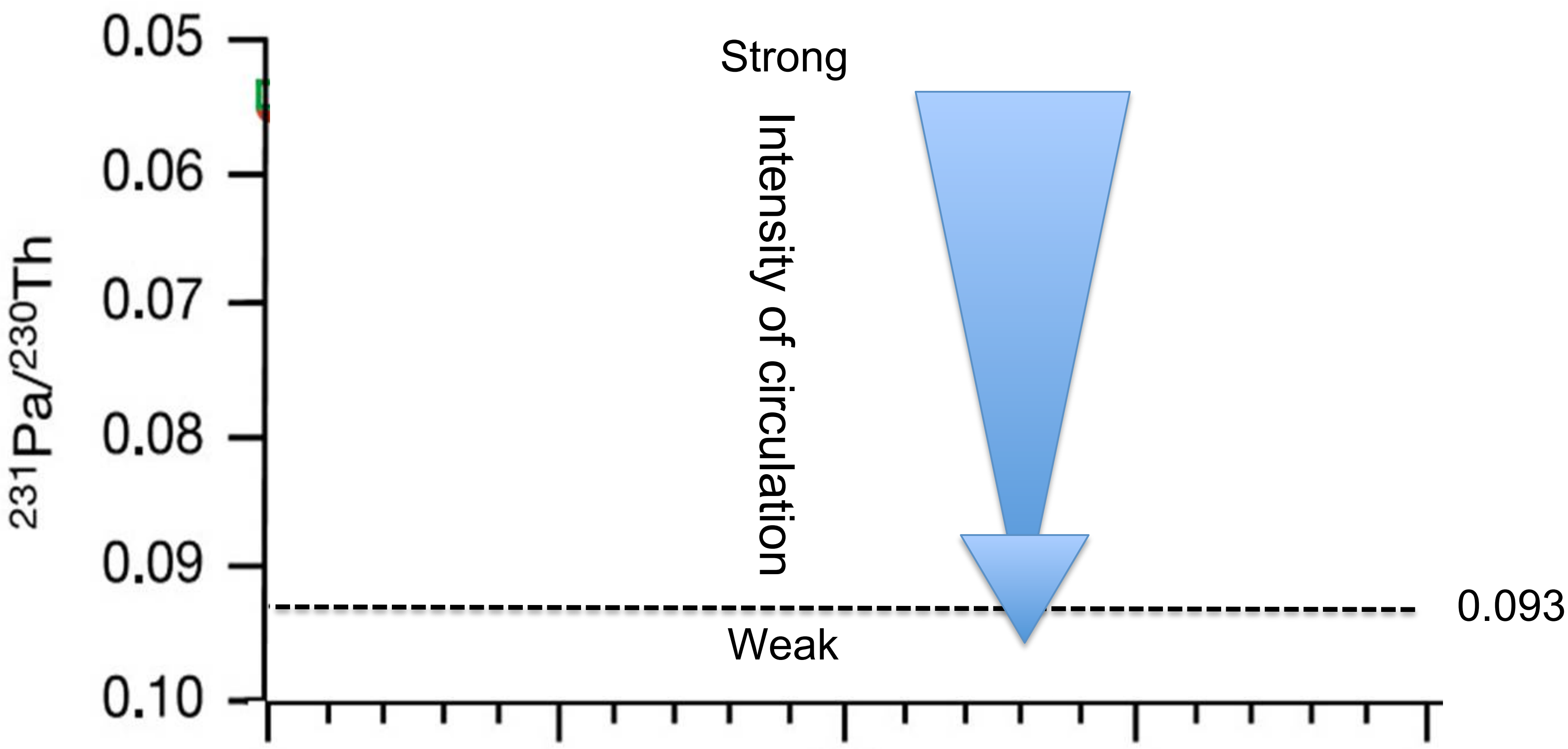


Traditional view of $^{231}Pa/^{230}Th$ to trace deep ocean circulation

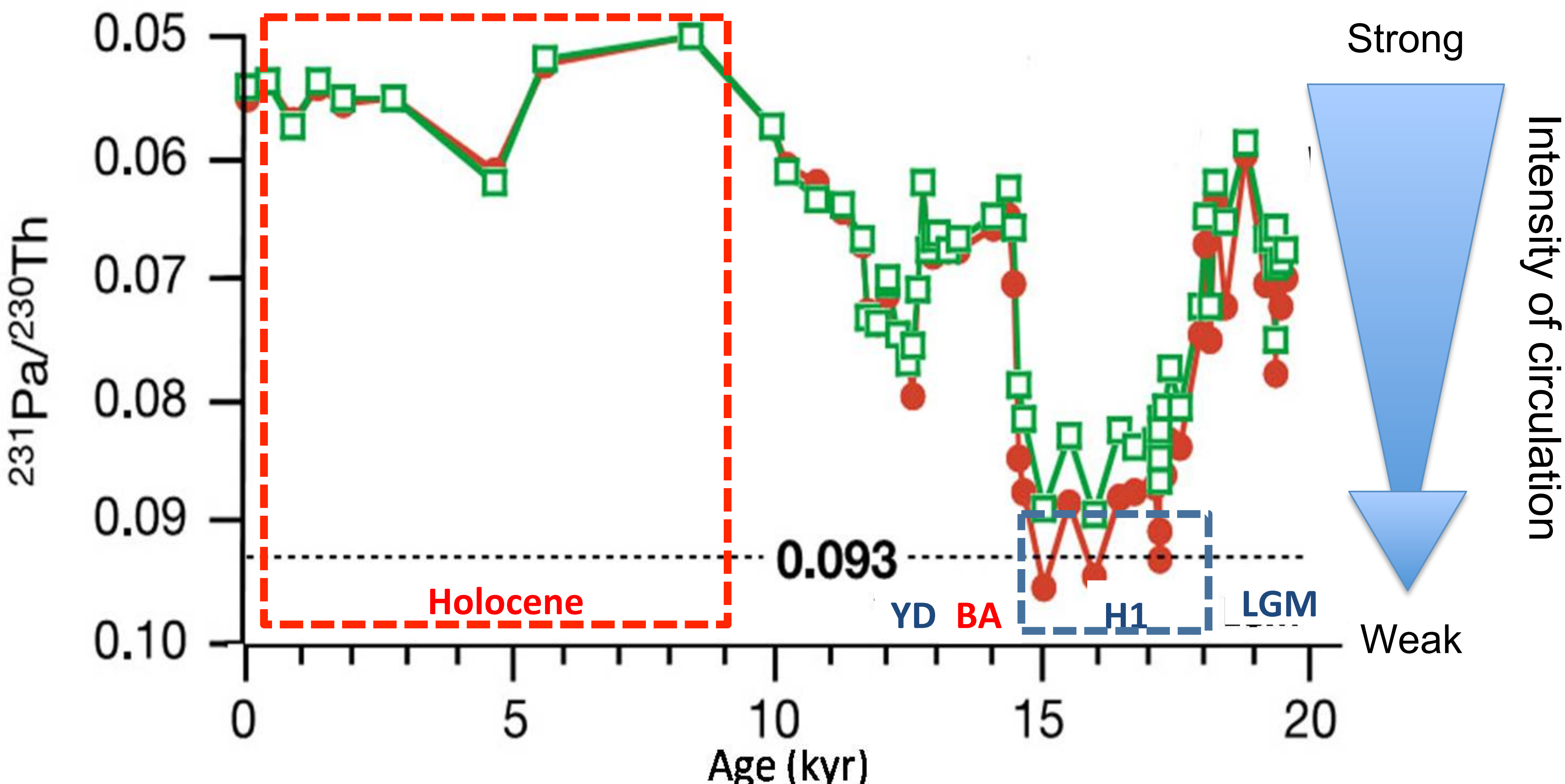


Pending permission by F. Deng & G. Henderson

Sediment $^{231}Pa/^{230}Th$ as a proxy of ocean circulation rate



Sediment records of abrupt climate changes in the past 20 kyr



McManus et al. (2004)

Blue: cold events

Red: warm events

Examples / Case studies

5. Sediment mixing and sedimentation

   – Pb-210 → Specific lecture 3

In summary

- **Radionuclides** are very useful tools as **tracers** to study a **large variety of processes** in the oceans at various **time scales** from days to milions of years, such as

  - Inputs and outputs
  - Circulation
  - Transfer of substances
  - Sedimentary record