# Radioactivity in the Marine Environment: Uranium-Thorium Decay Series

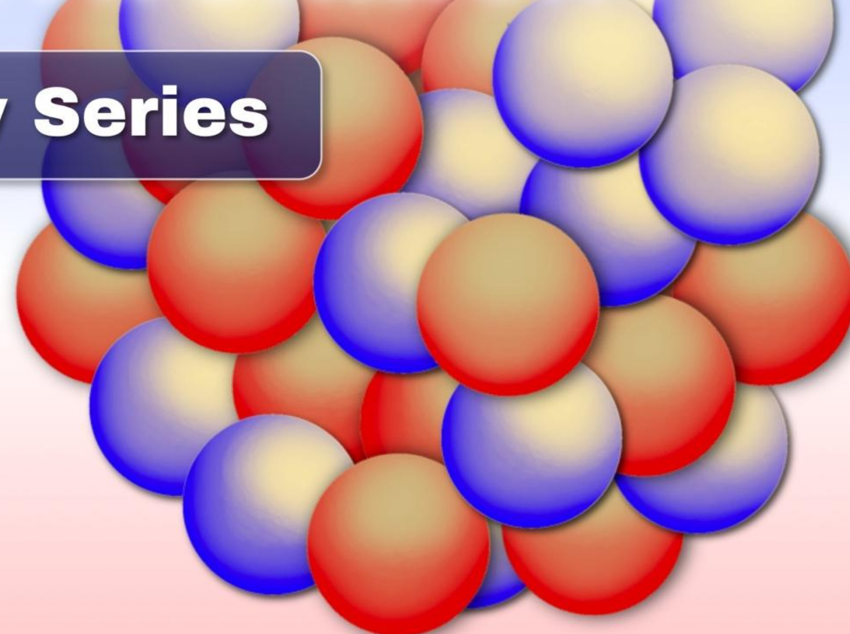
Claudia Benitez-Nelson, Ken Buesseler, Minhan Dai, Michio Aoyama, Núria Casacuberta, Sabine Charmasson, Andy Johnson, José Marcus Godoy, Vladimir Maderich, Pere Masqué, et al.

LIMNOLOGY AND OCEANOGRAPHY

ASLO e-Lectures

# Radioactivity in the Marine Environment

## Uranium-Thorium Decay Series



**Claudia R. Benitez-Nelson**

Ken Buesseler, Minhan Dai,
Michio Aoyama, Núria Casacuberta,
Sabine Charmasson, Andy Johnson,
José Marcus Godoy, Vladimir Maderich,
Pere Masqué, Willard Moore, Paul J. Morris,
Michiel Rutgers van der Loeff, John N. Smith

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# Radionuclides in the Marine Environment

Radionuclides, of both natural and anthropogenic 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)

*Tracers in the Sea*
Broecker and Peng, 1982



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# Three main sources of radionuclides to the Marine Environment:

1. **U-Th series radionuclides** – of primordial origin, occur naturally on land and in ocean, and produce a series of "daughter" radionuclides via radioactive decay.

   *Examples*: $^{238}U$, $^{234}Th$, $^{232}Th$, $^{210}Pb$, $^{223, 224, 226, 228}Ra$ and $^{222}Rn$.

2. **Cosmogenic Radionuclides** – continuously being created by cosmogenic rays that interact with materials in the atmosphere and on Earth.

   *Examples*: $^{3}H$, $^{14}C$, $^{7}Be$

3. **Anthropogenic radionuclides** – continuously being produced by humans since the 1940s.

   *Examples*: $^{3}H$, $^{14}C$, $^{90}Sr$, $^{137}Cs$, $^{129}I$, $^{238, 239, 240}Pu$

Note: *Some radionuclides have both cosmogenic and anthropogenic sources (e.g., $^{3}H$ and $^{14}C$).*

# The case of the Radioactive Daughter

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

| Element | U-238 Series | | | | | | | Th-232 Series | | | U-235 Series | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Uranium | U-238 4.5*10$^9$ y | | U-234 245500 y | | | | | | | | U-235 7.0*10$^8$ y | | |
| Protactinium | | Pa-234 1.2 m | | | | | | | | | | Pa-231 32800 y | |
| Thorium | Th-234 24.1 d | | Th-230 75400 y | | | | | Th-232 1.4*10$^{10}$ | | Th-228 1.91 y | Th-231 25.5 h | | Th-227 18.7 d |
| Actinium | | | | | | | | | Ac-228 6.1 h | | | Ac-227 21.8 y | |
| Radium | | | Ra-226 1600 y | | | | | Ra-228 5.75 y | | Ra-224 3.7 d | | | Ra-223 11.4 d |
| Francium | | | | | | | | | | | | | |
| Radon | | | Rn-222 3.8 d | | | | | | | | | | |
| Astatine | | | | | | | | | | | | | |
| Polonium | | | Po-218 3.1 m | | Po-214 0.00014 s | | Po -210 138 d | | | | | | |
| Bismuth | | | | Bi-214 19.9 m | | Bi-210 5.0 d | | | | | | | |
| Lead | | | Pb-214 26.8 m | | Pb-210 22.3 y | | Pb-206 stable | | | Pb-208 stable | | | Pb-207 stable |

α Decay
Z: - 2
N: - 4

β Decay
Z: + 1
N: ± 0

Decay Series of Short-lived radionuclides

Element Symbol — Mass Number
U-238
4.5 x 10$^9$ y
Half life

| Particle Reactivity in Seawater | |
|---|---|
| (blue) | Low |
| (pink) | Medium |
| (red) | High |

Rutgers van der Loeff (2014a)


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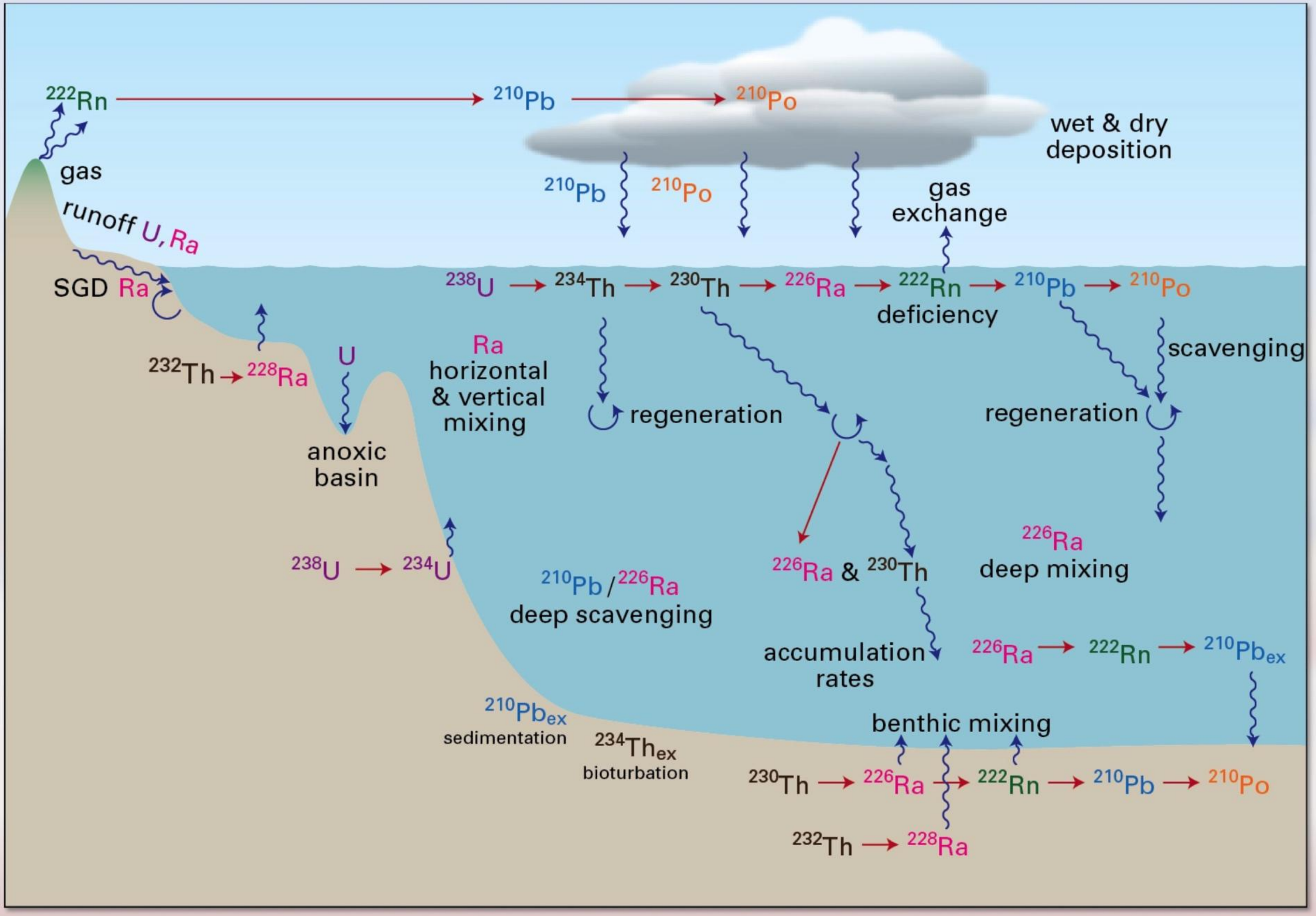
# U-Th series decay chains



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# Radionuclide distributions in the ocean are controlled by:

| Reservoir | Process | Parameter (examples) | Tracer nuclides | Reference |
|---|---|---|---|---|
| Atmosphere | Aerosol Scavenging | Residence time | $^{7}Be/^{10}Be$ $^{222}Rn/^{210}Pb/^{210}Po$ | Raisbeck *et al.*, (1981), Bleichrodt, (1978) Martell and Moore (1974), Robbins (1978) |
| | Dry and wet dep. | Rates | $^{131}I$, $^{137}Cs$, . . . | Wiffen (1958), Stewart and Crooks (1958) Santschi *et al.* (1988a) |
| | Atmospheric circulation | Rates | $^{14}C$, $^{37}Ar$, | Loosli *et al.* (1973), Feely *et al.* (1966) |
| Soil | Mechanical and chemical erosion | Residence time in top soil | $^{210}Pb$, $^{239,240}Pu$ $^{137}Cs$, $^{134}Cs$ $^{10}Be$ | Lewis (1979), Simpson *et al.* (1976) Dominik *et al.* (1987) Monaghan *et al.* (1983) |
| | Water movement | Rates | $^{3}H$ | Höhn and Santschi (1987), Santschi *et al.* (1987b) |
| Ocean and lake water | Horizontal | Diffusion | $^{228}Ra$, $^{222}Rn$, | Sarmiento and Roth (1980), Sarmiento *et al.* (1982), Moore and Santschi (1986), Broecker and Peng (1982) |
| | or vertical | coefficient | $^{3}He$, $^{3}H$ | Imboden and Emerson (1978), Roether *et al.* (1970), Imboden and Joller (1984), Li *et al.* (1984), Broecker and Peng (1982) |
| | diffusion | | $^{39}Ar$, $^{85}Kr$ | Loosli (1983), Schlitzer *et al.* (1985) |
| | Horizontal | Rates | $^{231}pa$, $^{230}Th$, | Anderson *et al.* (1983), Bacon and Rosholt (1982), Broecker and Peng (1982) |
| | or vertical | Mechanisms | $^{210}Pb$, $^{239,240}Pu$ | Carpenter and Beasley (1981), Beasley *et al.* (1982), Moore *et al.* (1981), Santschi *et al.* (1980b), Scott *et al.* (1983), Nyffeler *et al.* (1986, 1984) |
| | scavenging | | $^{10}Be$ $^{234}Th$, $^{228}Th$ | Mangini (1984) Santschi *et al.* (1979, 1980a, 1983a), Honeyman and Santschi (1989) |
| | Sediment | Rates | $^{234}Th$, $^{228}Th$ | Aller and Cochran (1976), Broecker and Peng (1982) |
| | resuspension | Mechanisms | $^{134,137}Cs$, $^{7}Be$, $^{210}Pb$ | Robbins and Eadie (1982), Santschi (1987a), Santschi *et al.* (1987c) |
| | Gas exchange | Rates | $^{222}Rn$, $^{14}C$, $^{3}H/^{3}He$ | Broecker and Peng (1982), Torgerson *et al.* (1977, 1982) |
| | Evaporation | Rates | $^{3}H$ | Herczeg and Imboden (1988) |
| Sediments | Bioturbation | Rates | $^{234}Th$, $^{210}Pb$, $^{14}C$ | Aller and Cochran (1976), Broecker and Peng (1982), Krishnaswami *et al.* (1984) |
| | | | $^{239,240}Pu$, $^{137}Cs$ | Santschi *et al.* (1980b, 1983b) |
| | Sedimentation | Rates | $^{230}Th$, $^{231}Pa$, $^{10}Be$ | Armi *et al.* (1975), Broecker and Peng (1982) |
| | | | $^{137}Cs$, $^{134}Cs$, $^{210}Pb$ | Wan *et al.* (1987), Robbin and Edington (1975), Robbins (1978) |
| | Diagenetic remobilization | Rates | $^{234}U$, $^{238}U$, $^{230}Th$, $^{234}Th$ | Osmond and Cowart (1982). Cochran *et al.* (1986), Cochran and Krishnaswami (1980), Colley *et al.* (1984), Colley and Thompson (1985) |
| | or fixation | | $^{239,240}Pu$ | Santschi *et al.* (1983b) |
| Groundwater | Sorption | Residence times | $^{334}Th$, $^{224}Ra$, $^{226}Ra$, $^{222}Rn$, $^{280}Pb$ | Krishnaswami *et al* (1982) Hussain and Krishnaswami (1980) Rama and Moore (1984) |
| | Rock–water interaction | Rates | $^{14}C$ | Mazor *et al.* (1986) |
| | Mixing | Rates | $^{36}Cl$, $^{81}Kr$ | Fabryka-Martin *et al.* (1987), Lehmann *et al.* (1986) |

Santschi and Honeyman (1989)

**Table of radionuclides used to quantify geochemical processes, with more applications waiting to be discovered!**


doi:10.1002/loe2.10008

# 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:** For example:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) - v\frac{\partial c}{\partial x} - \lambda c$$

- **Analytical Techniques**


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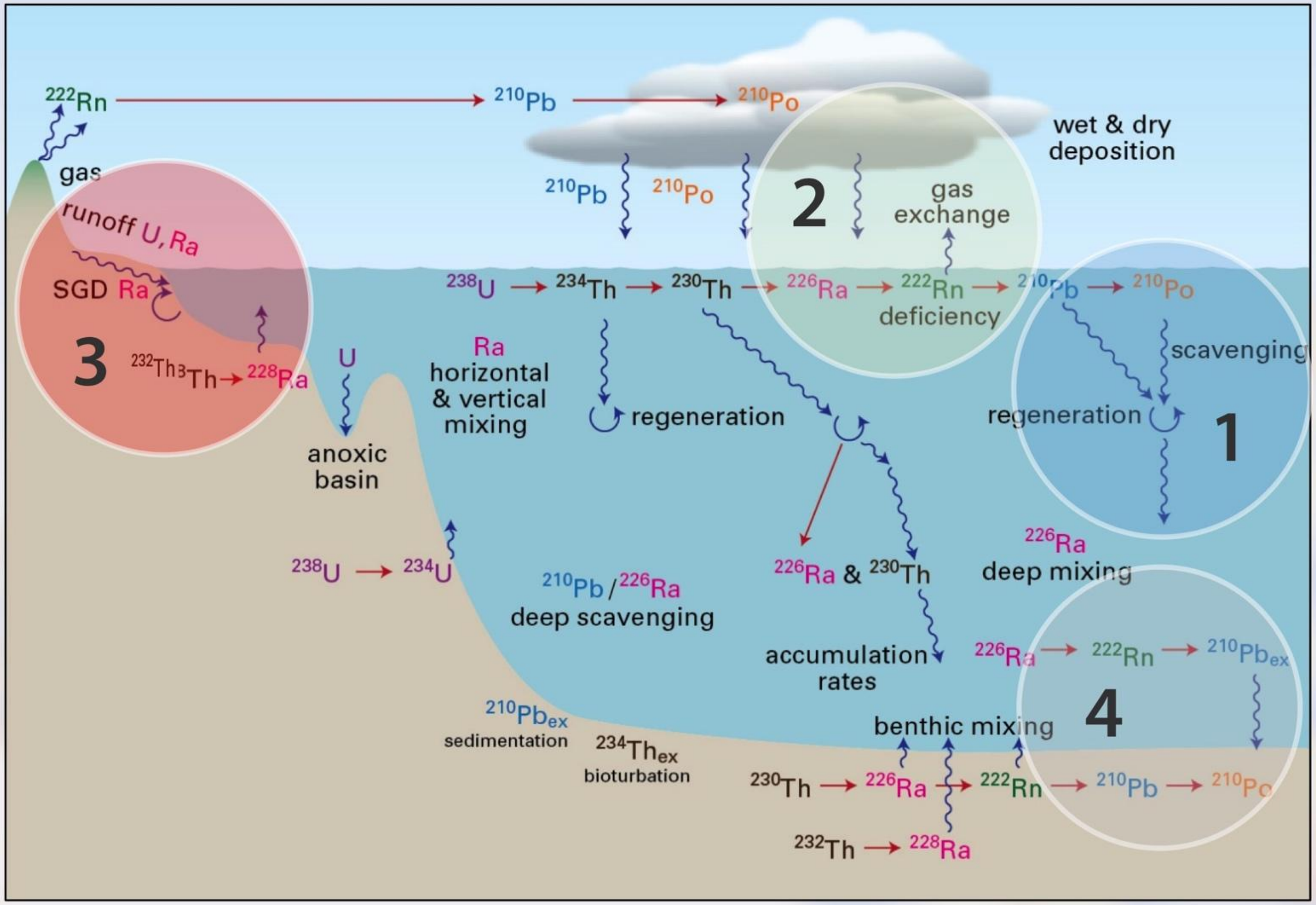
# Case Study Applications




1. Scavenging
2. Air-Sea gas exchange
3. Tracing groundwater discharge
4. Sedimentation/Age Dating

Claudia Benitez-Nelson

doi:10.1002/loe2.10008

# 1. Scavenging

- **Many elements have much lower dissolved sea water concentrations 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 scavenging sites for reactive elements (Fe, Cu, Pb, Th, Pa, etc.)**

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

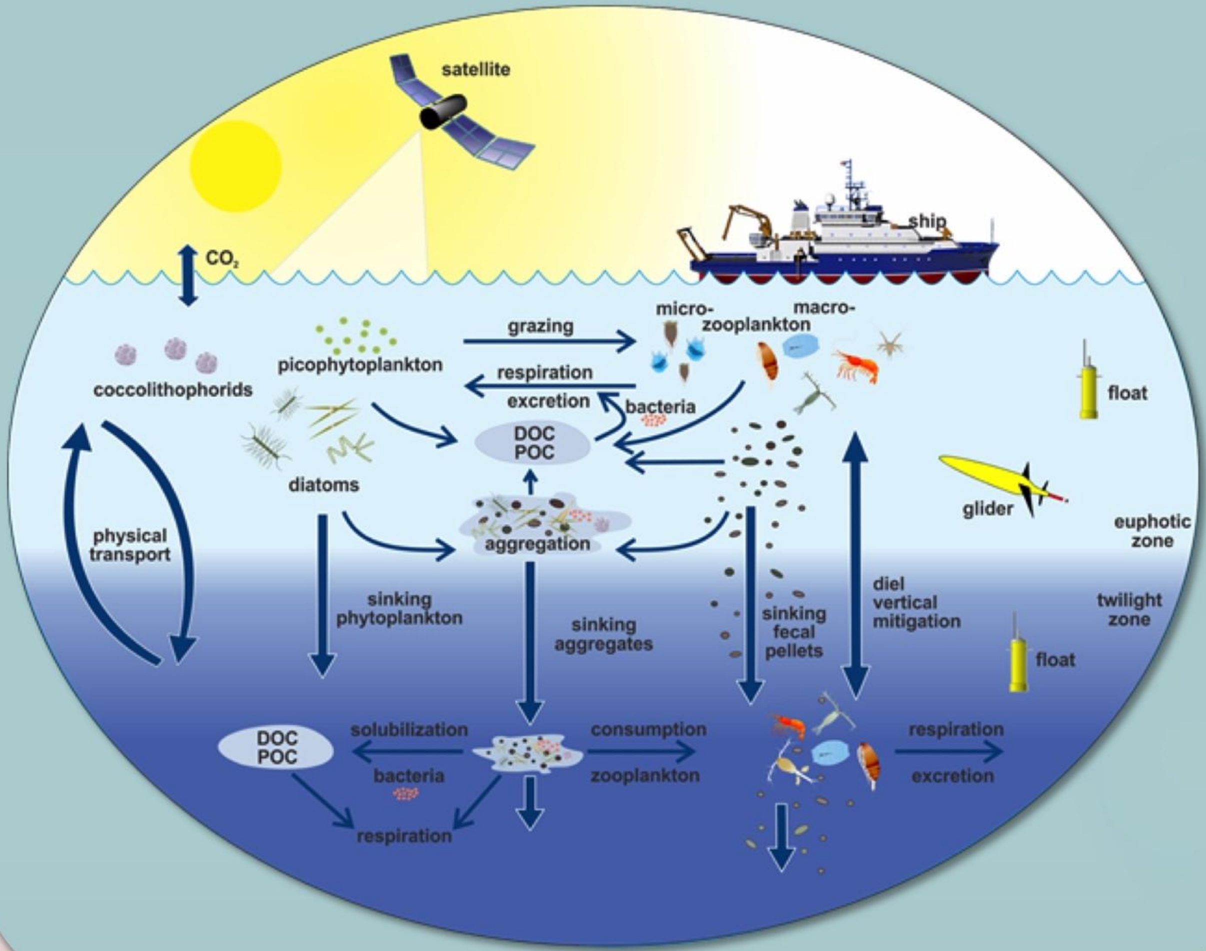
**In the open ocean, particle production is primarily a result of biological processes.**


doi:10.1002/loe2.10008

# Scavenging and the "Biological Pump"

**Biological Pump = 5 to >12 Gt C $y^{-1}$**

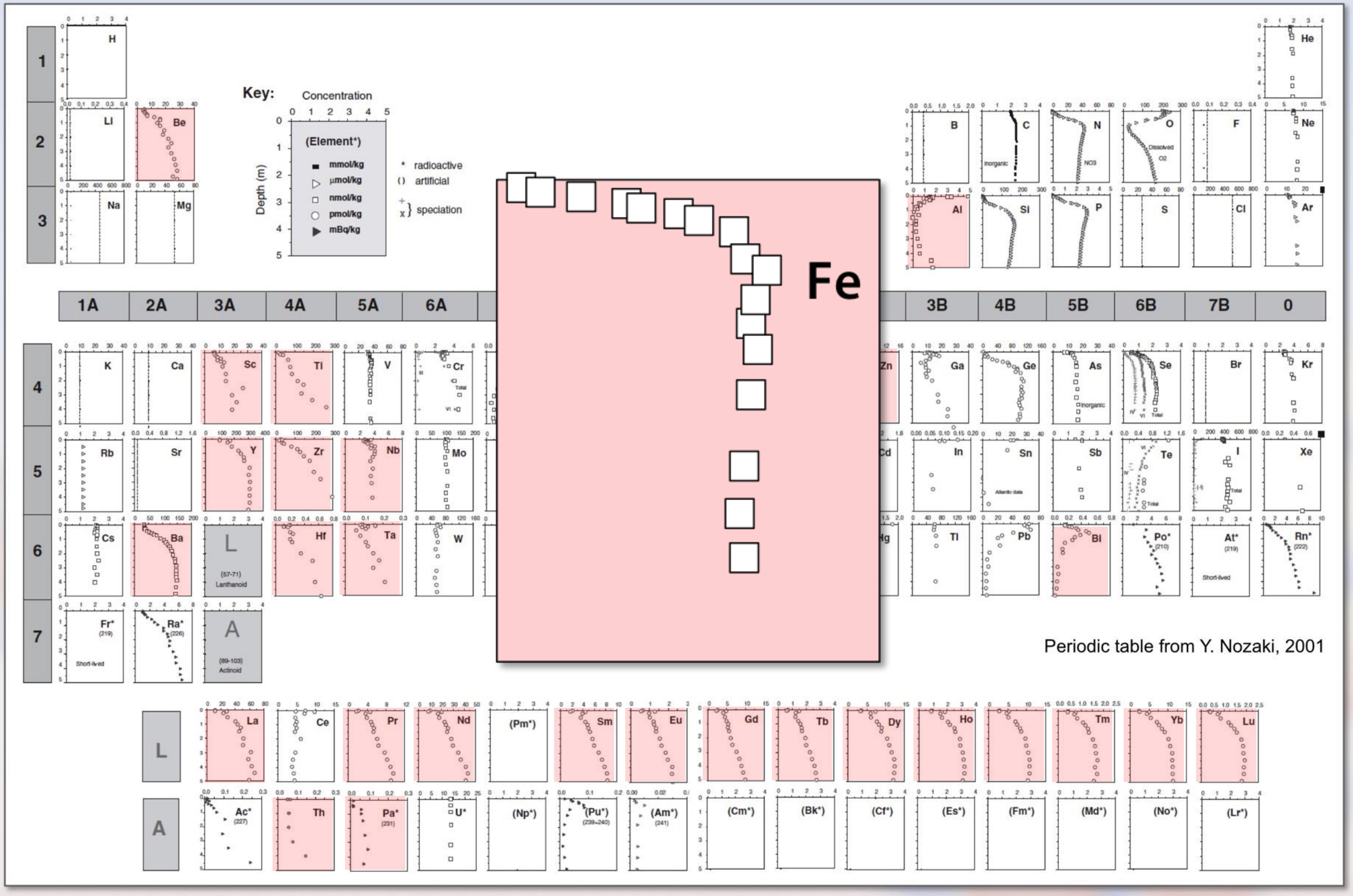
**Turning off biological pump would increase atmospheric $CO_2$ by ~ 200 ppm.**




These biological processes not only transfer organic matter to depth, but other particle reactive elements and compounds as well, such as trace metals (e.g., Hg, Zn, and Pb) and organic compounds like polychlorinated biphenyls (PCBs).


doi:10.1002/loe2.10008

# Geochemical Implications



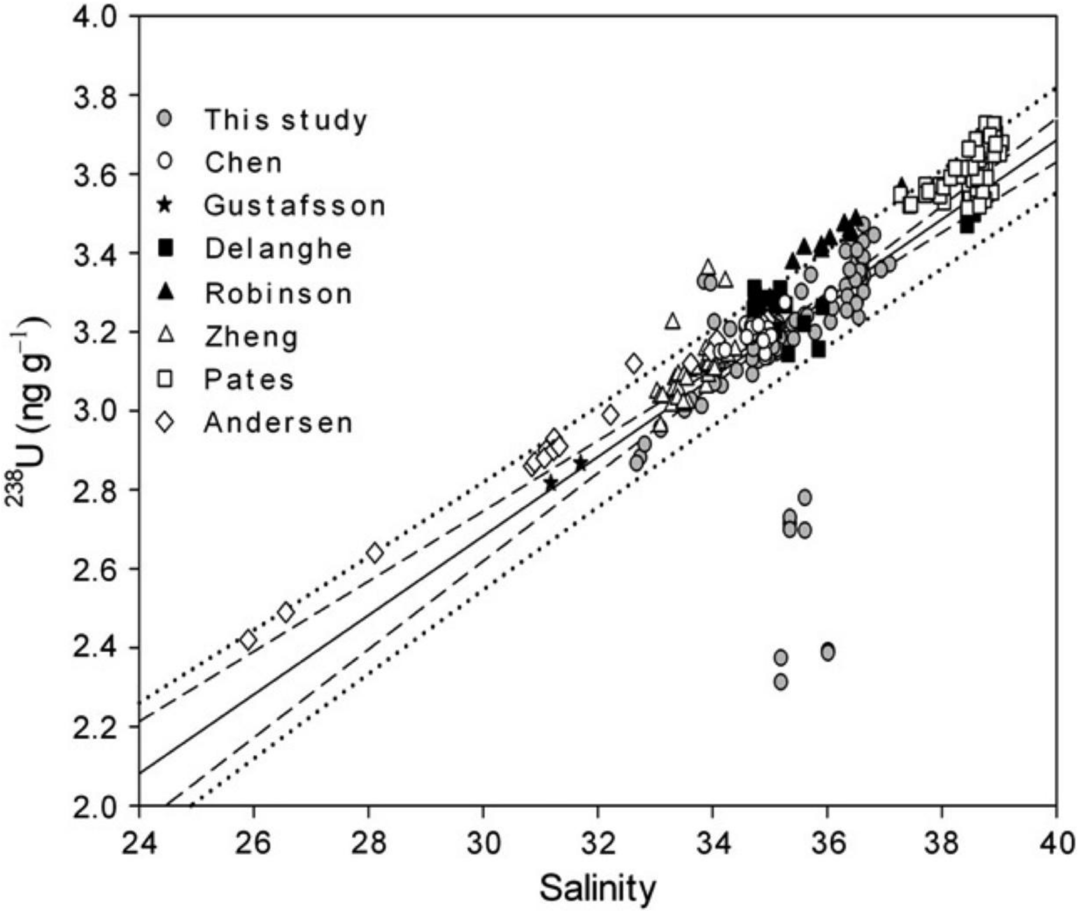

Many elements in the ocean are influenced by scavenging. Concentrations increasing with depth are diagnostic of scavenging and regeneration at depth (red boxes are not exhaustive).


doi:10.1002/loe2.10008

# U-Th series disequilibria

**Uranium is soluble and therefore conservative in seawater.**

**Its distribution can be described by measuring salinity.**




ng g$^{-1}$: $^{238}U\ (\pm 0.061) = 0.100 \times S - 0.326$

dpm L$^{-1}$: $^{238}U\ (\pm 0.047) = 0.0786 \times S - 0.315$

Owens *et al.*, 2011


doi:10.1002/loe2.10008

# How does it work?

## $^{234}$Th as a tracer for particle export

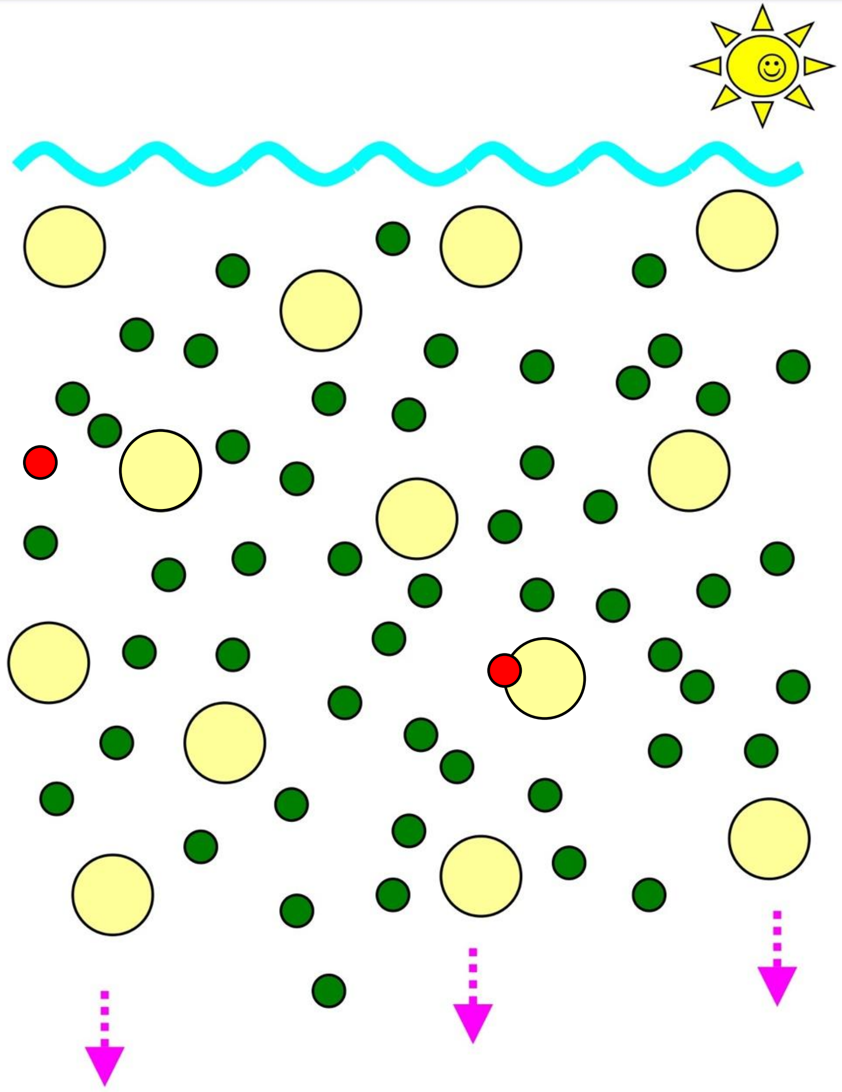
$^{238}U \xrightarrow{\alpha} {}^{234}Th$ ($t_{1/2}$ = 24.1 d)

○ = marine particle

- ● $^{238}$U is conservative in seawater
- ● $^{234}$Th is highly particle-reactive

Secular equilibrium is expected in an ocean without particles (Activities should be the same…)

○ Particulate matter
● $^{238}$U
● $^{234}$Th




doi:10.1002/loe2.10008

# $^{238}$U Decays to $^{234}$Th: The Case of the Radioactive Daughter

## The Bateman Equations

$$
\begin{array}{ccccccc}
A & \rightarrow & B & \rightarrow & C & \rightarrow & D \\
N_1, \lambda_1 & & & & N_2, \lambda_2 & & N_3, \lambda_3
\end{array}
$$

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

$$N_1 \xrightarrow{\lambda_1} N_2 \xrightarrow{\lambda_2} N_3$$

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

Bateman, 1910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# Secular Equilibrium

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \Rightarrow N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \left[e^{-\lambda_1 t} - e^{-\lambda_2 t}\right] + N_2^0 e^{-\lambda_2 t}$$

**When $\lambda_1 << \lambda_2 \Rightarrow \lambda_1 N_1 = \lambda_2 N_2$**

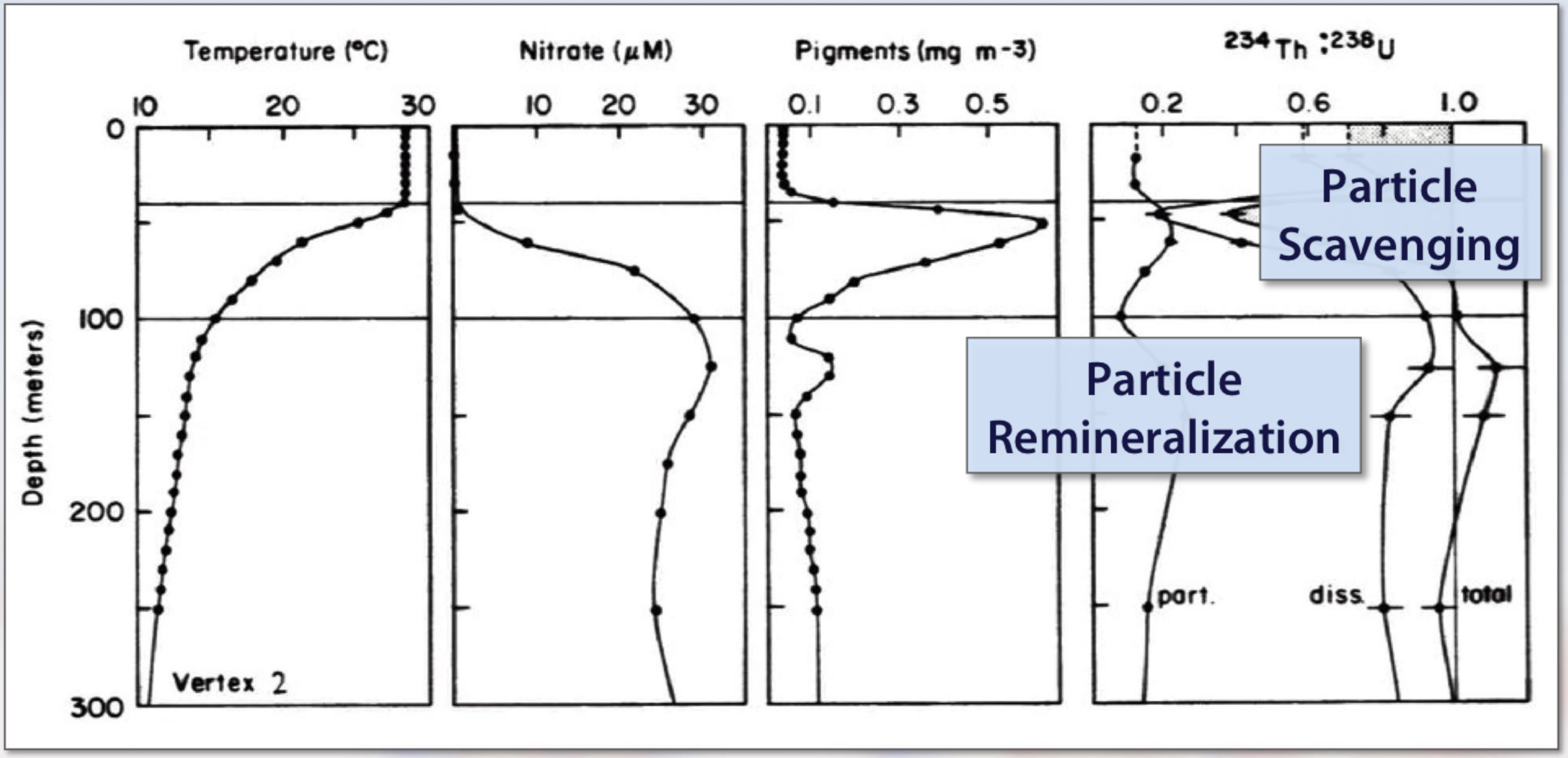
**For the naturally occurring radionuclides $^{238}U$, $^{235}U$, and $^{232}Th$, the half-lives of the parent nuclides are much longer than their daughter products:**

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

- **The number of parent ($N_1$) atoms therefore remains ~ constant**
- **$^{238}U$ and $^{234}Th$ in equilibrium = same activity, A, where $A = N\lambda$**


doi:10.1002/loe2.10008

# Radionuclide distributions in the ocean are controlled by:




Coale and Bruland (1987)

**See decrease in $^{234}$Th activity correlated with increasing biomass as evidenced by pigment concentrations.**


doi:10.1002/loe2.10008

# Large scale differences are well-captured

Hawaii $^{234}Th/^{238}U$ ~1
Low Particle Flux to Depth

NW Pacific $^{234}Th/^{238}U$ <1
High Particle Flux to Depth

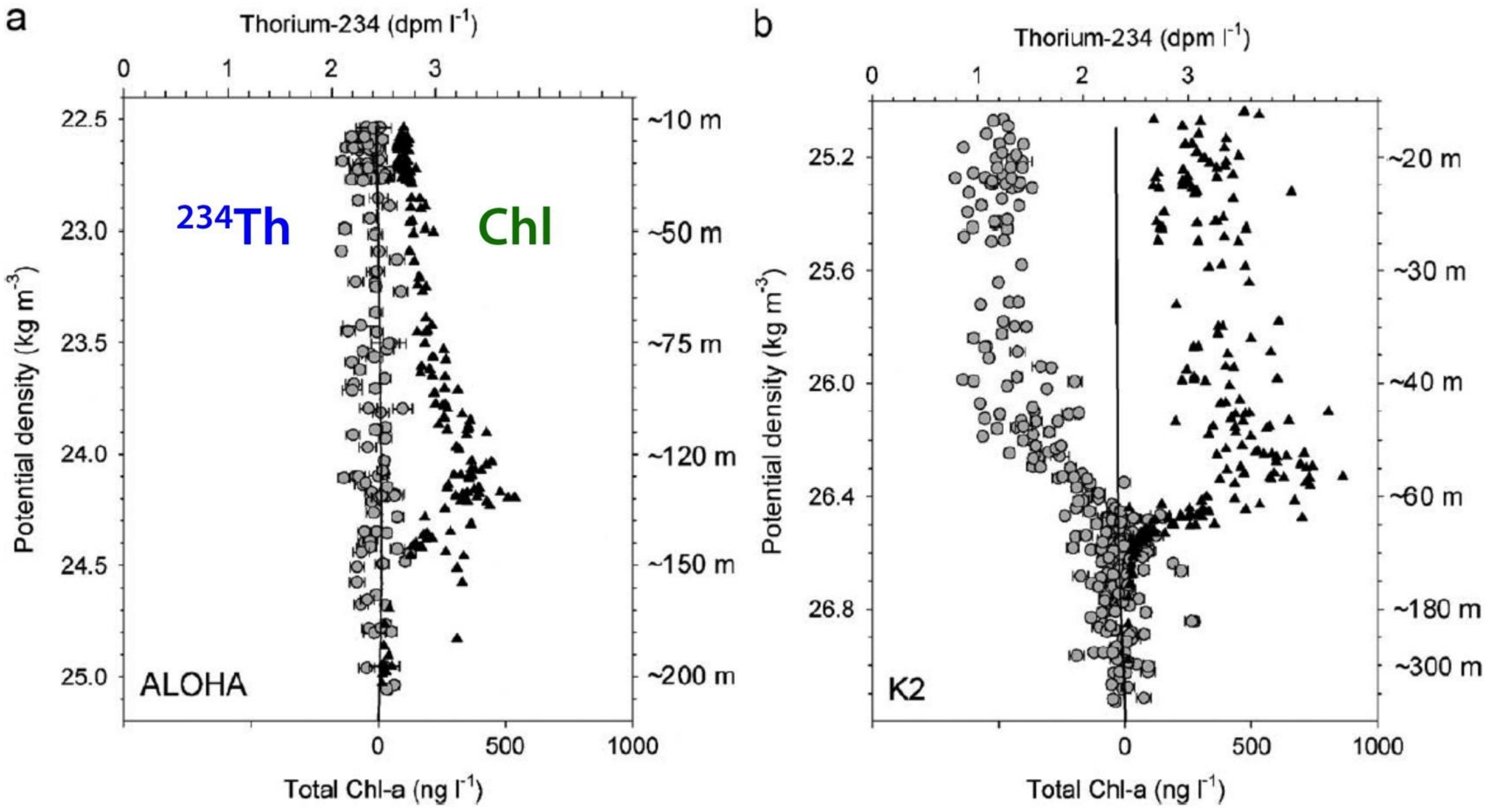
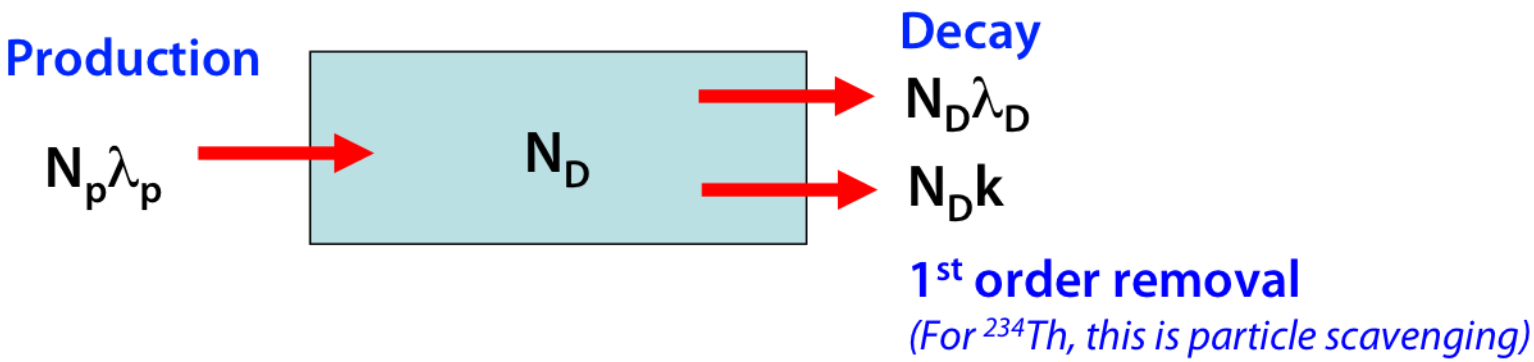



**Fig. 1.** Total $^{234}$Th activities (dpm l$^{-1}$) and total chlorophyll-*a* (ng l$^{-1}$) vs. potential density (kg m$^{-3}$) for (a) ALOHA and (b) K2. Thorium-234 data are plotted as gray circles with error bars shown if greater than the symbol size, using the upper *X*-axis and plotted relative to $^{238}$U (black line) near 2.3 dpm l$^{-1}$. Total chl-*a* data are offset to run from 0 to 1000 ng l$^{-1}$ starting at the point along the lower *X*-axis, where $^{234}Th = ^{238}U$, to emphasize $^{234}$Th removal associated with the euphotic zone. Density scales (*Y*-axis—left) differ at the two sites, and for convenience, approximate water depths are shown along the right *Y*-axis specific to each site.

Buesseler et al. (2009)

# The Basic Model

**Particle reactive $^{234}$Th is sourced from conservative $^{238}$U in seawater, and $^{234}$Th is lost via radioactive decay AND particle attachment (scavenging) 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 $A_D$ "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

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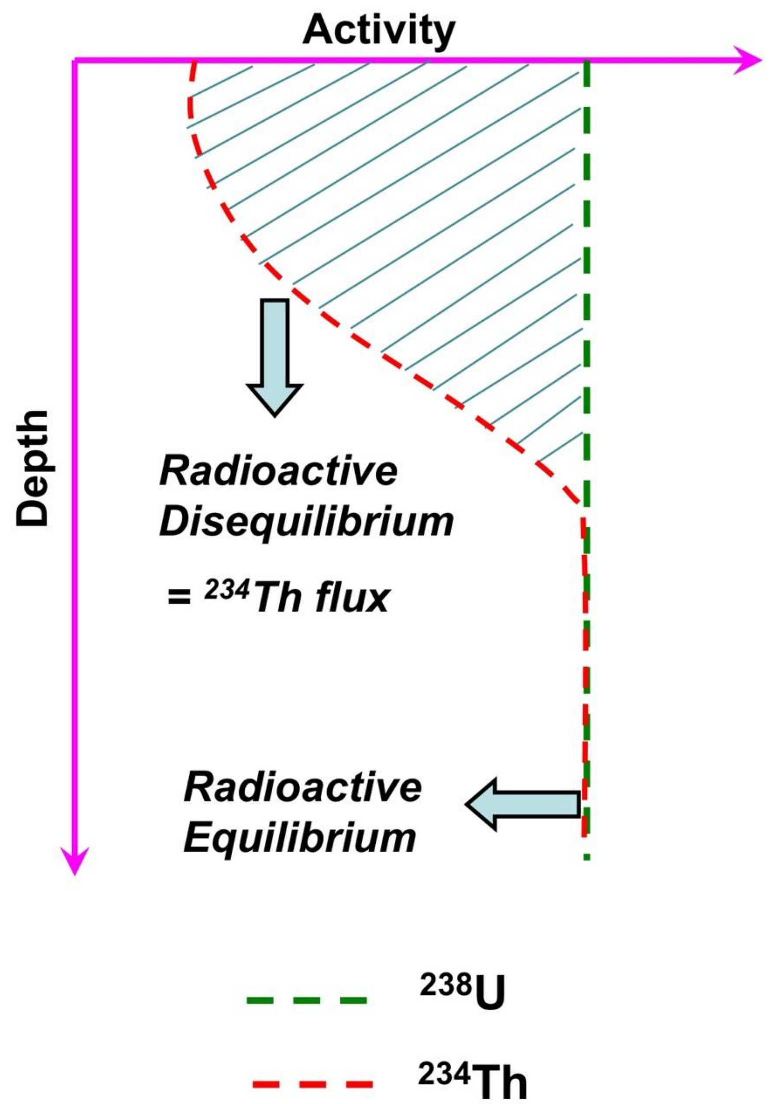
# Particle Export using $^{238}U$ : $^{234}Th$




**Assumes Steady State and minimal physical processes:**

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

$$(dpm\ m^{-2}\ d^{-1})$$

**Where:**

$\lambda$ = Radioactive Decay Constant for $^{234}Th$ ($d^{-1}$)

$A_U$ = Activity of $^{238}U$ (dpm $L^{-1}$)

$A_{Th}$ = Activity of $^{234}Th$ (dpm $L^{-1}$)

z = Depth interval in water column.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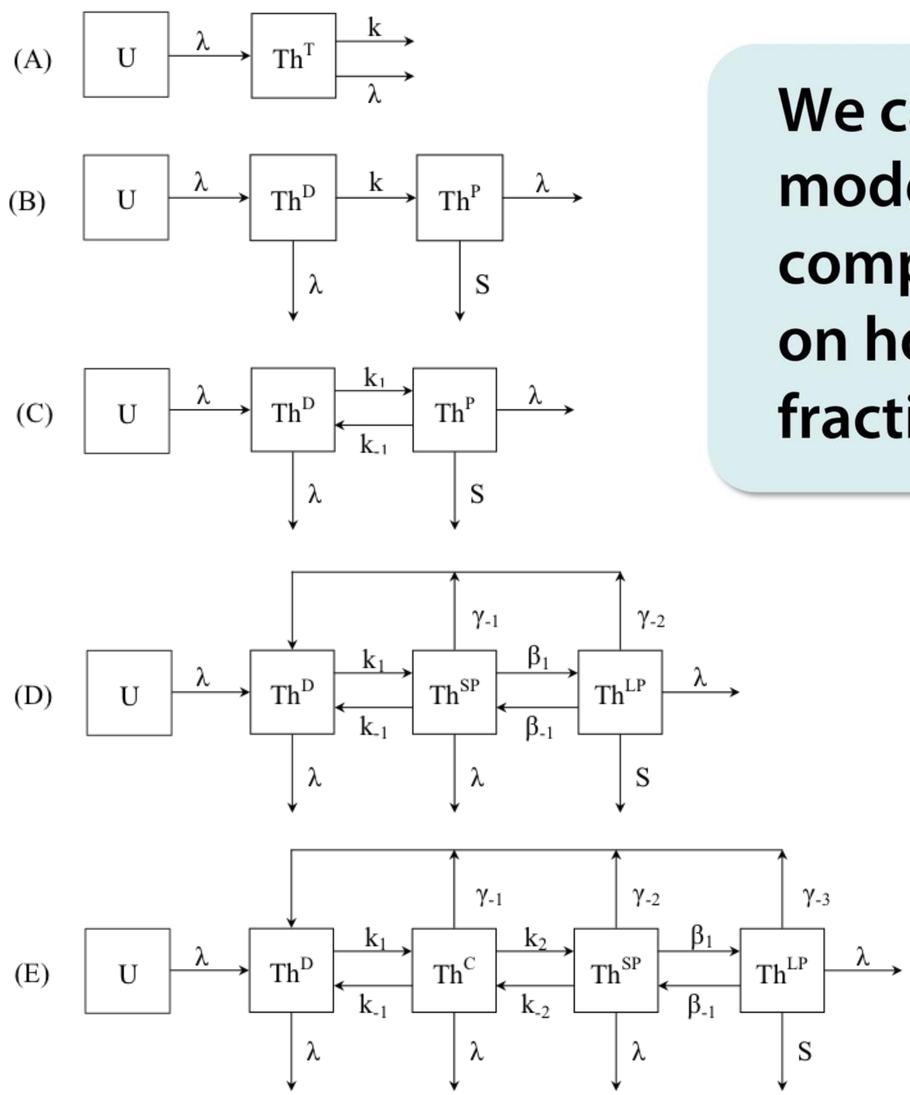
# Particle Export using $^{238}U : ^{234}Th$




Cochran and Masqué (2003)

**We can make these box models even more complicated depending on how many particle size fractions are measured.**

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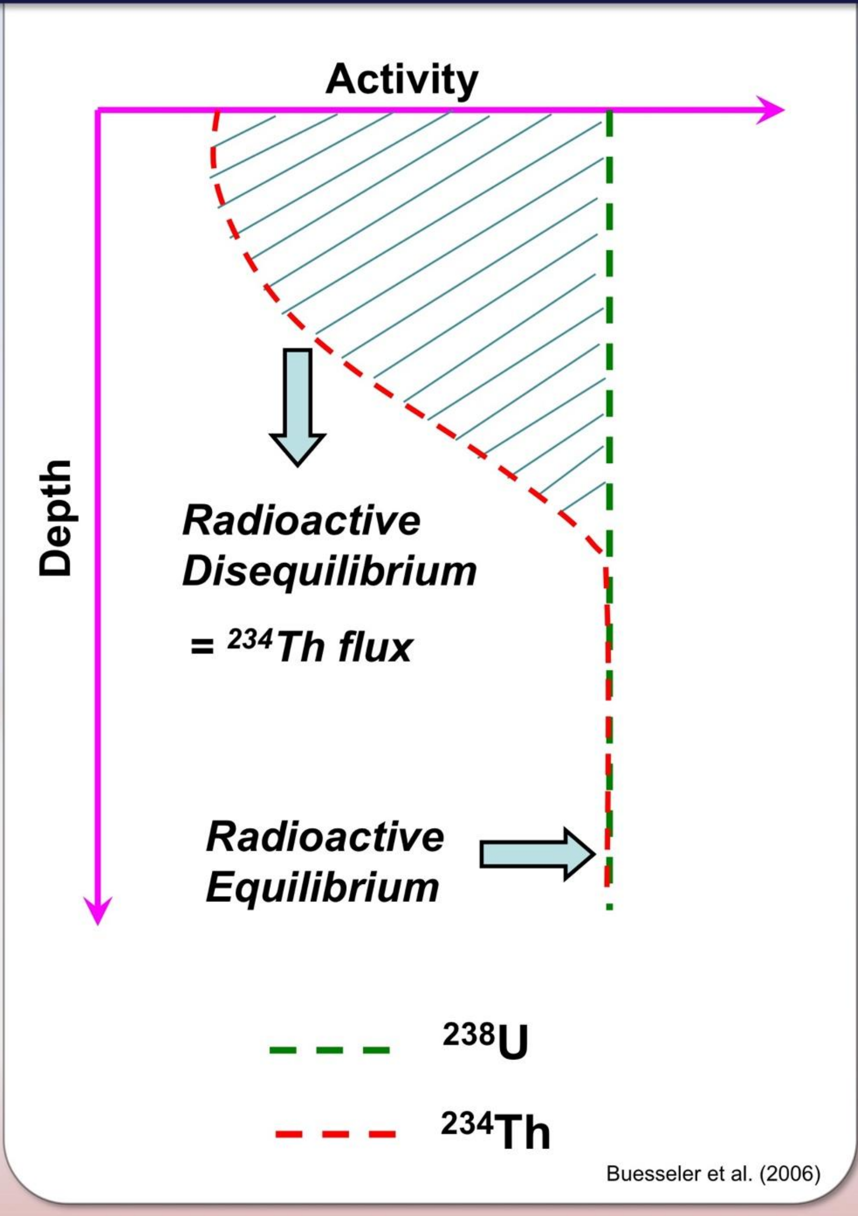
# Particle Export using $^{238}U : ^{234}Th$




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

Carbon (other element or compound) Flux =

$$^{234}\text{Th flux} \times [C/^{234}\text{Th}]_{part}$$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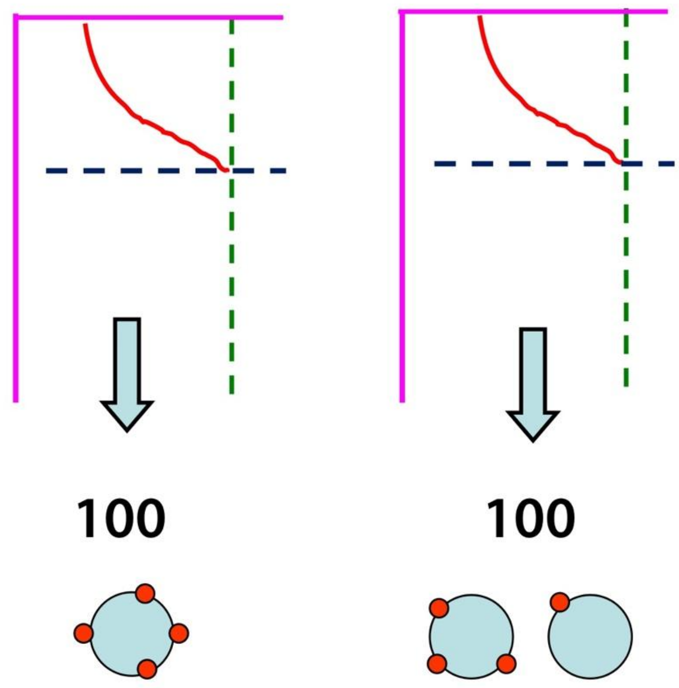
# Estimate of particulate organic carbon (POC) or other element/compound flux from $^{234}Th$ flux

$$Flux = {}^{234}Th\ flux \bullet [POC/{}^{234}Th]_{sinking\ particles}$$



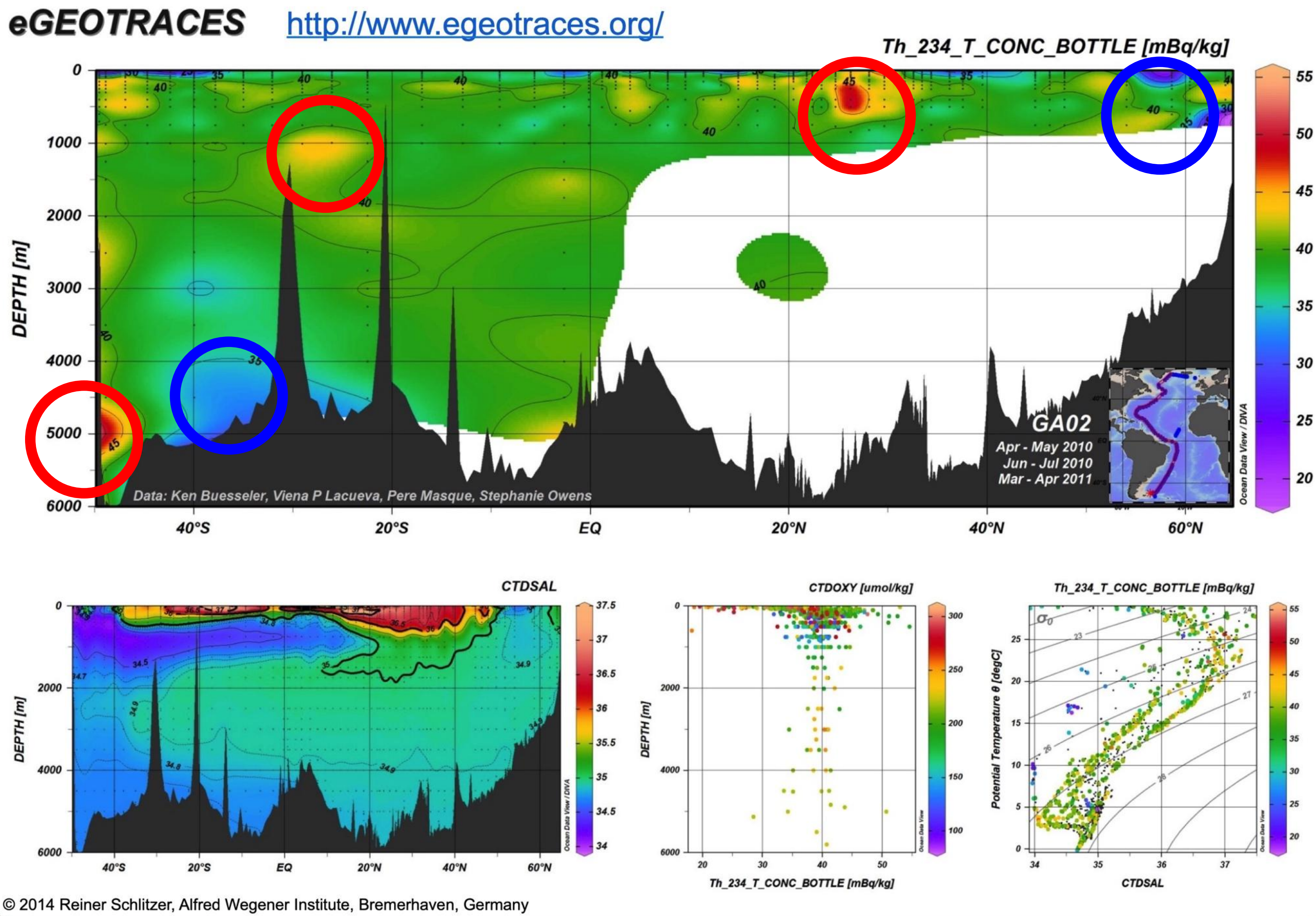
*Depth depends on question of interest (e.g., the Euphotic Zone)*

| | | | |
|---|---|---|---|
| $^{234}Th$ flux | 100 | 100 | @ 100m |
| $POC/^{234}Th$ | 1:4 | 2:4 | @ 100m |
| POC flux | 100 * 1/4 | 100 * 2/4 | @ 100m |

Buesseler et al. (2006)



doi:10.1002/loe2.10008





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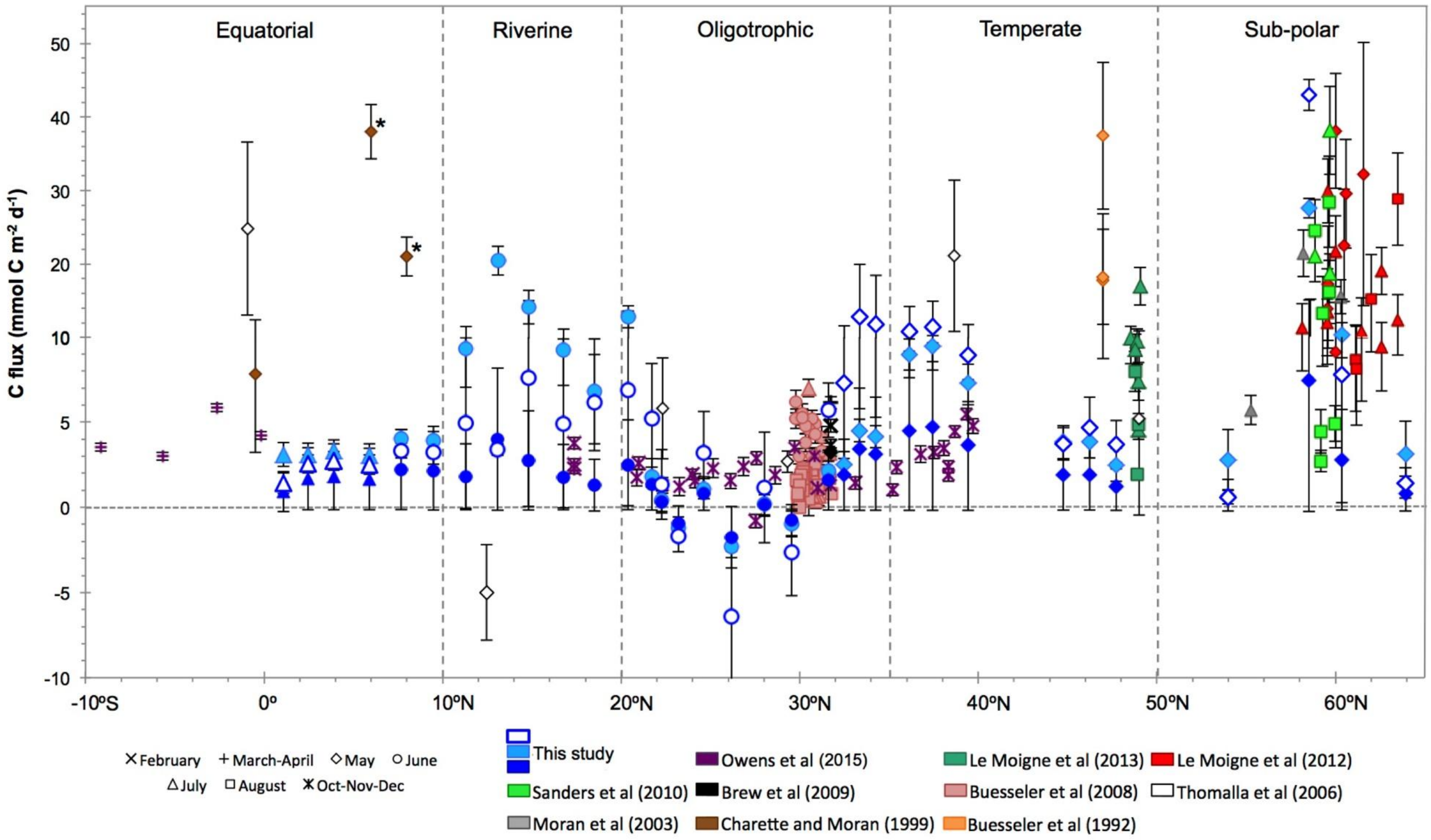
# Compilation of Carbon Export fluxes at 100m in the Atlantic Ocean

*From the Equator to the Arctic…*

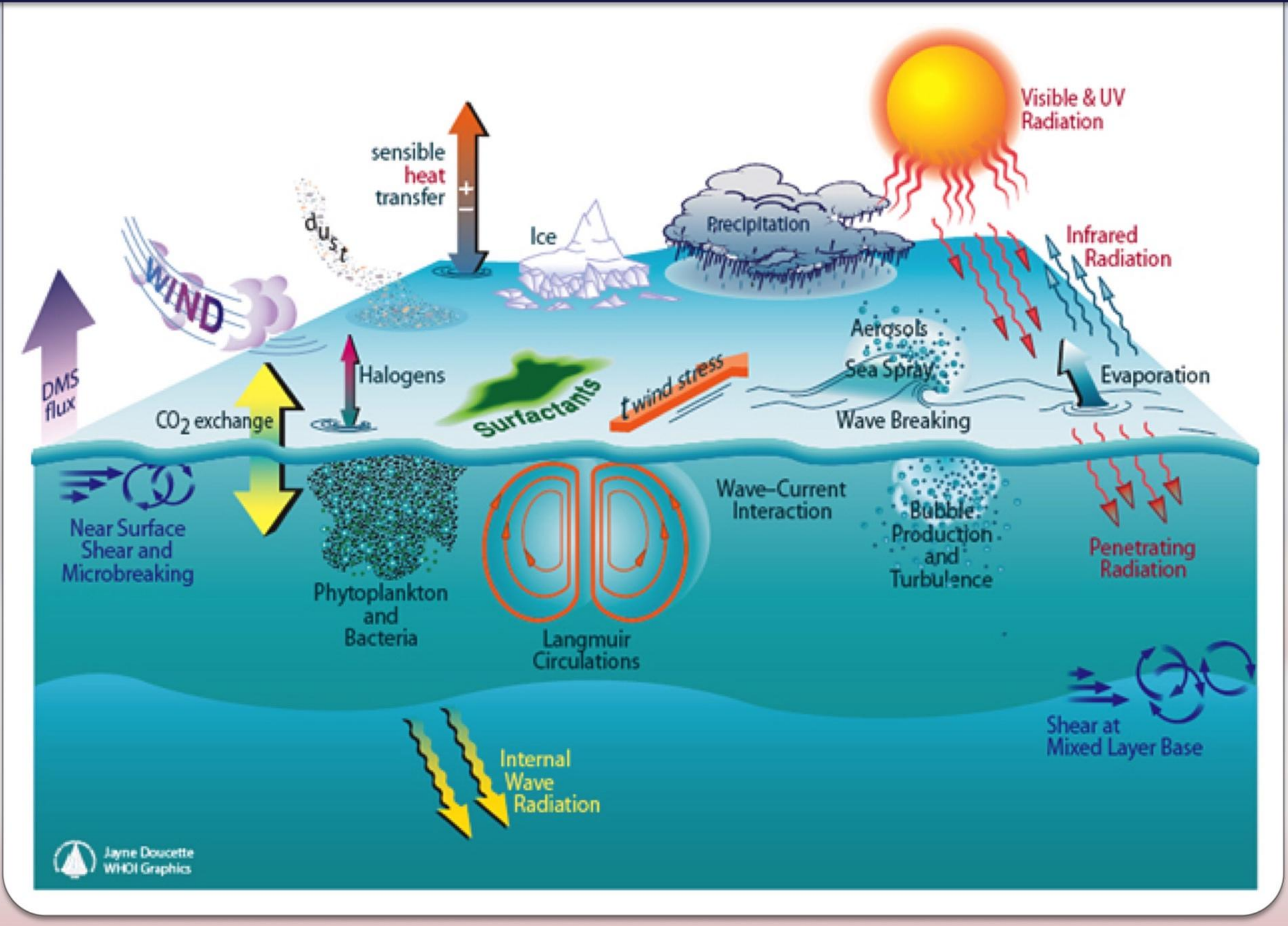



Puigcorbé et al. (2017)



doi:10.1002/loe2.10008

# 2. Air-Sea Gas Exchange

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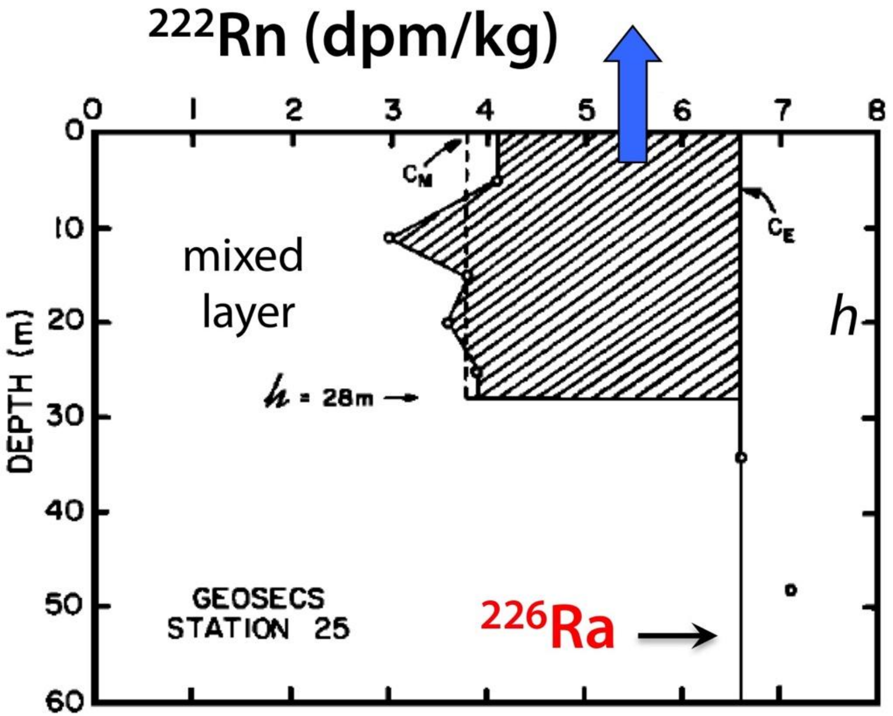
doi:10.1002/loe2.10008

# Air-Sea Gas Exchange Using $^{226}Ra$ : $^{222}Rn$




Peng et al.,1979

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

$^{226}t_{1/2} = 1600$ y $\quad$ $^{222}t_{1/2} = 3.8$ days

$$k^*({}^{222}Rn_{water} - {}^{222}Rn_{air}) = \quad ({}^{222}Rn_{air} = 0)$$

$$^{222}\lambda\int({}^{226}Ra_{water} - {}^{222}Rn_{water})dh$$

***Where:***

**k = Gas transfer velocity (m/d)**

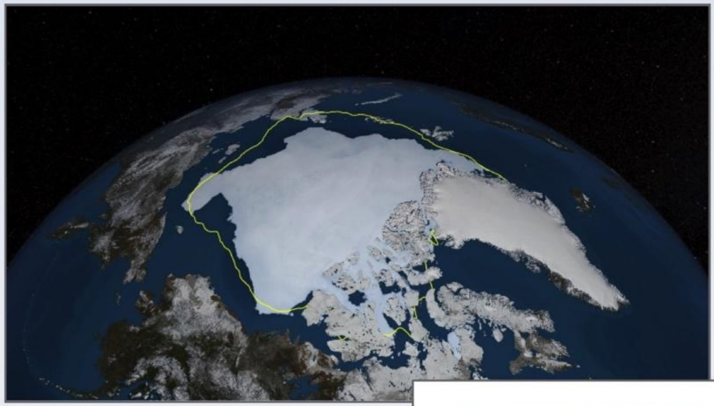
**$^{226}Ra$ and $^{222}Rn$ = Activity measured in seawater or air**

**h = Depth of disequilibrium**

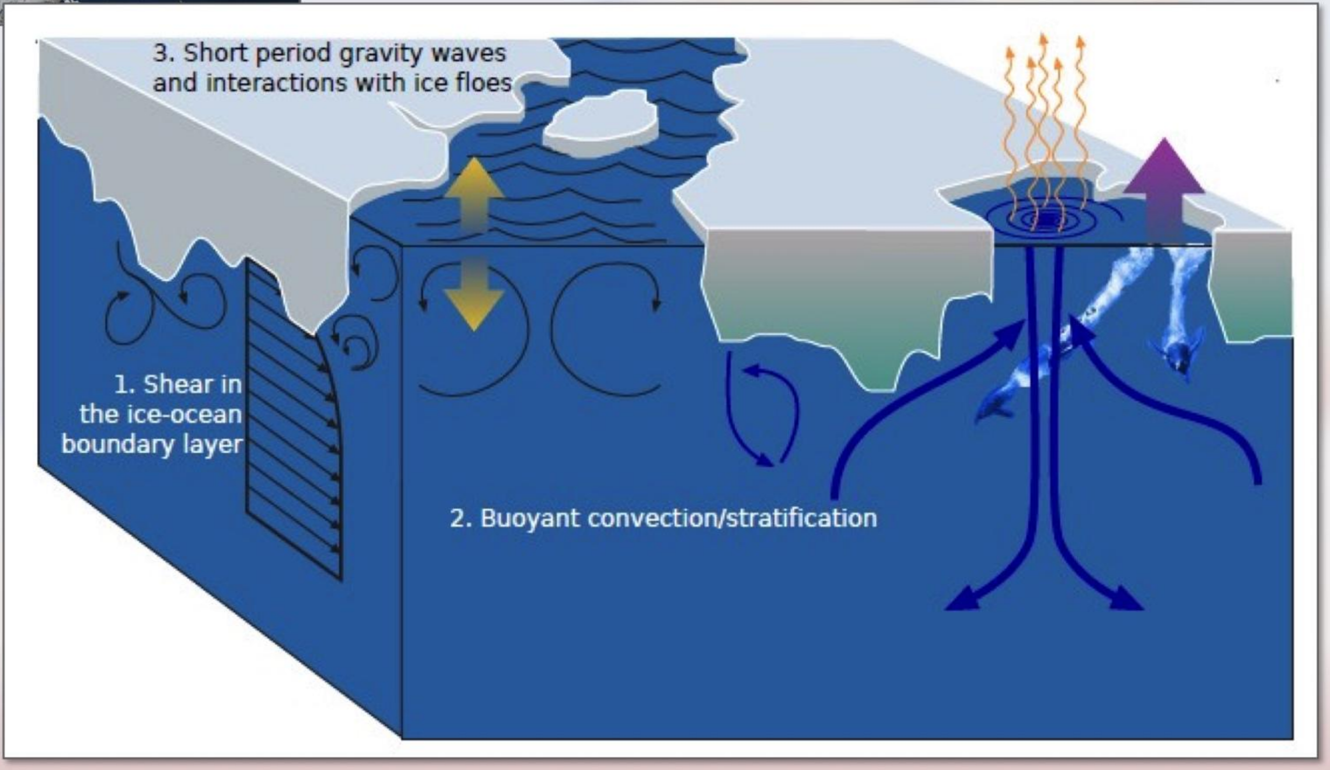
$$k = \left(\frac{^{226}Ra_{water}}{^{222}Rn_{water}} - 1\right)^{222}\lambda h$$


doi:10.1002/loe2.10008

# Application in the Arctic Ocean – Sea Ice



**The relationship between ice cover and gas exchange in partially ice-covered regions can have a large effect on calculated annual $CO_2$ fluxes to and from the atmosphere.**

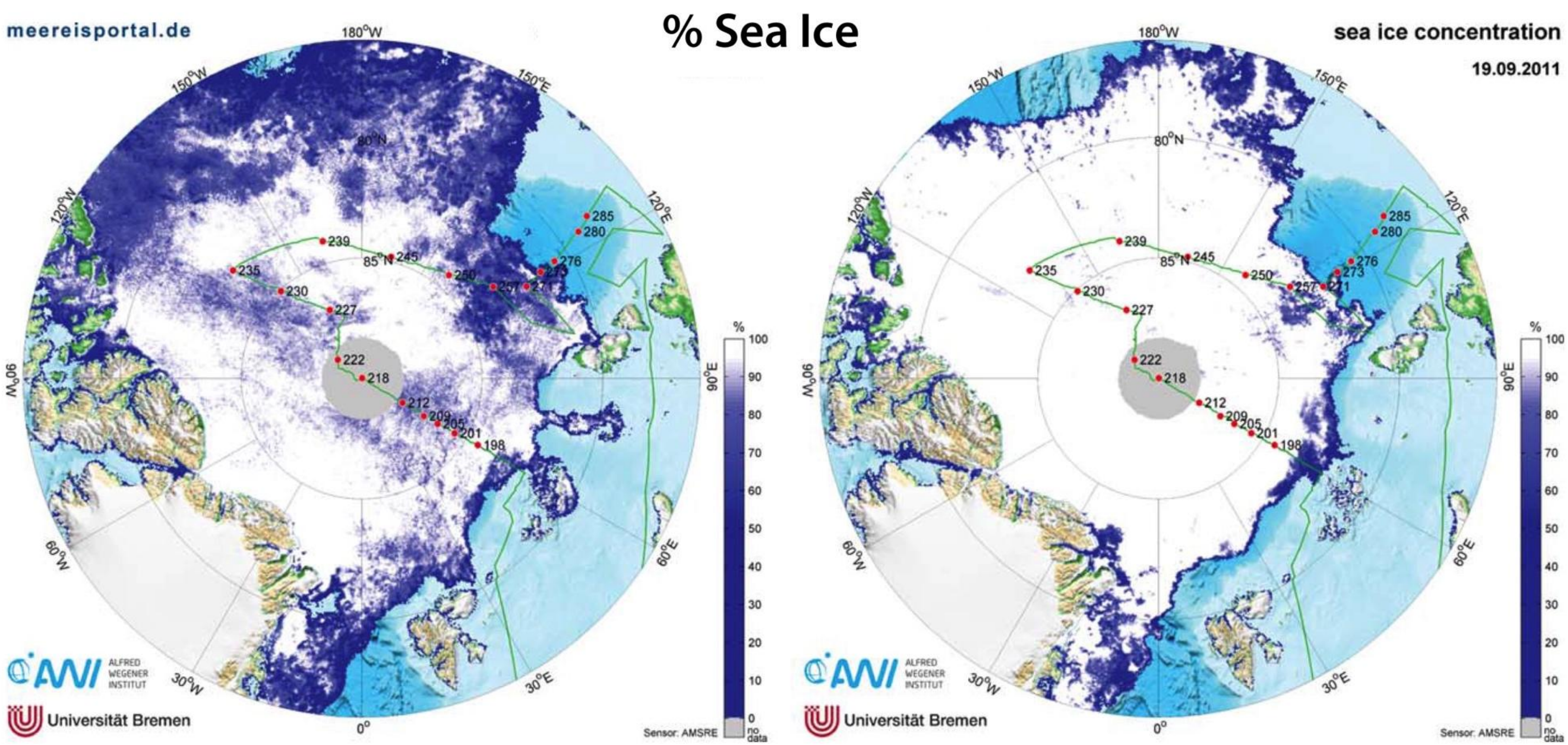



Loose et al., 2014


doi:10.1002/loe2.10008

# ARK XXIV/3 TransArc 2011

## This map depicts station locations of $^{222}Rn$ and $^{226}Ra$ samples collected during varying ice conditions in the Arctic Ocean.




August 13, 2011

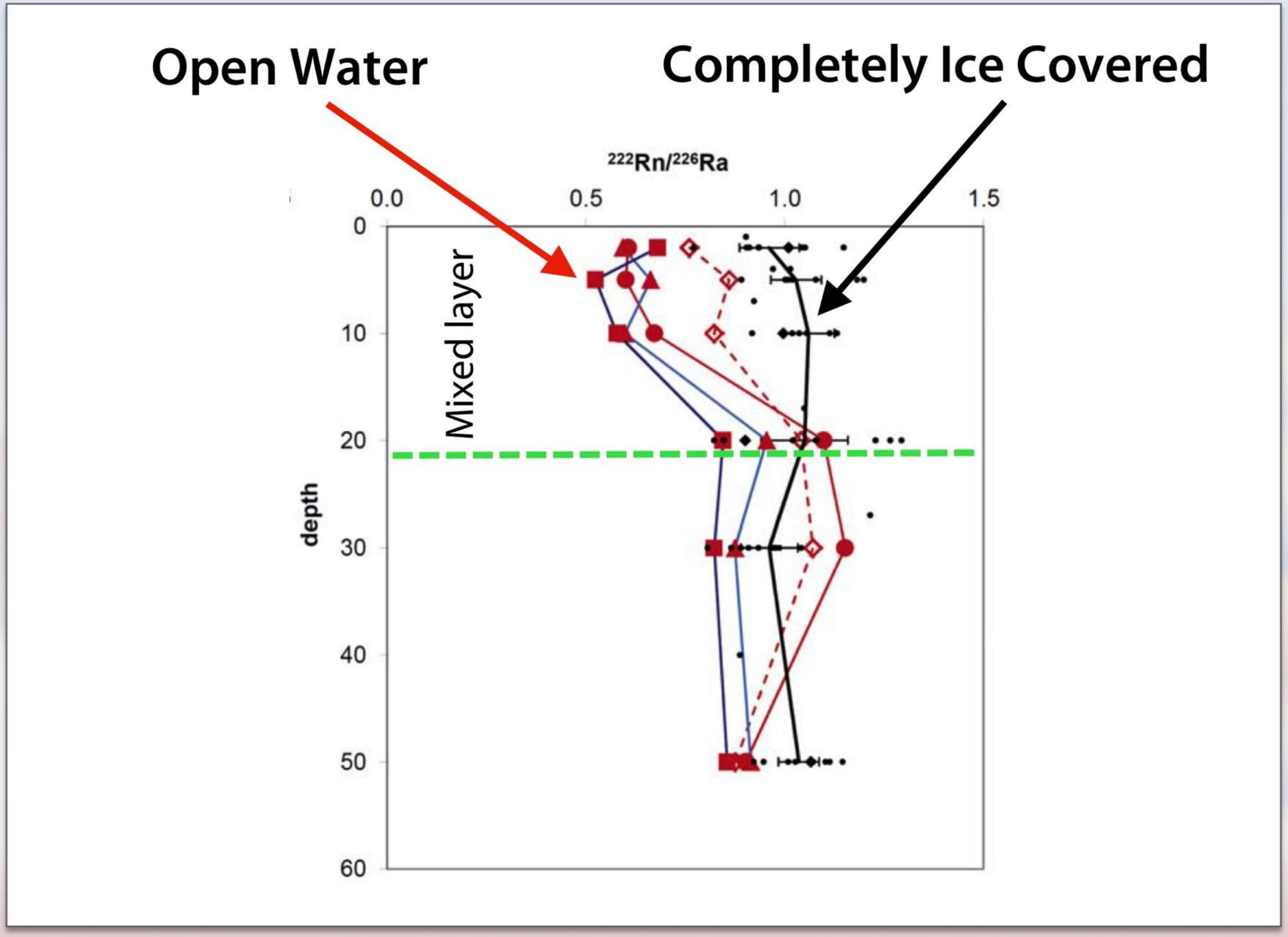
September 19, 2011

Rutgers van der Loeff et al. (2014b)



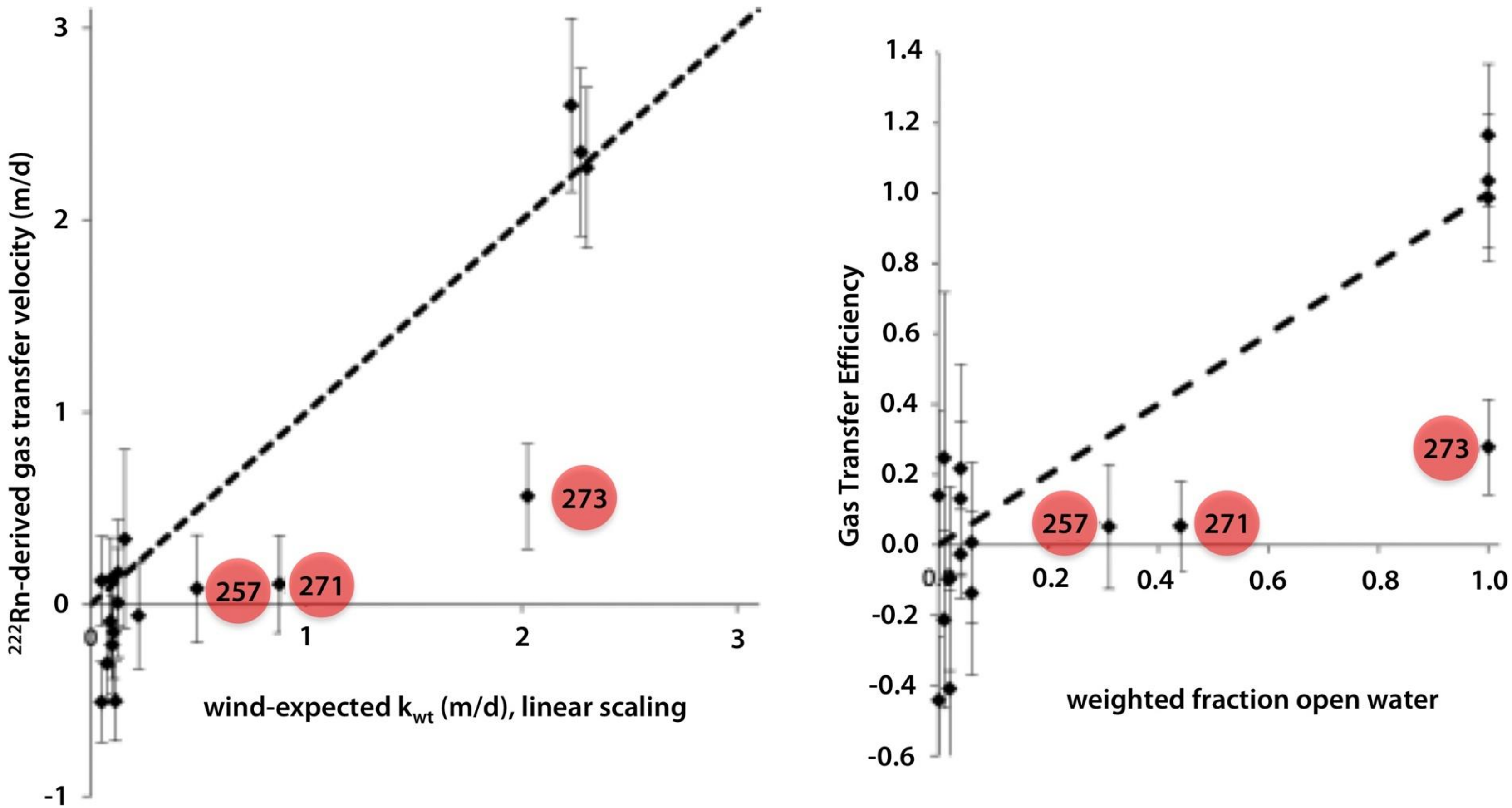
doi:10.1002/loe2.10008

# ARK XXIV/3 TransArc 2011




Rutgers van der Loeff et al. (2014b)

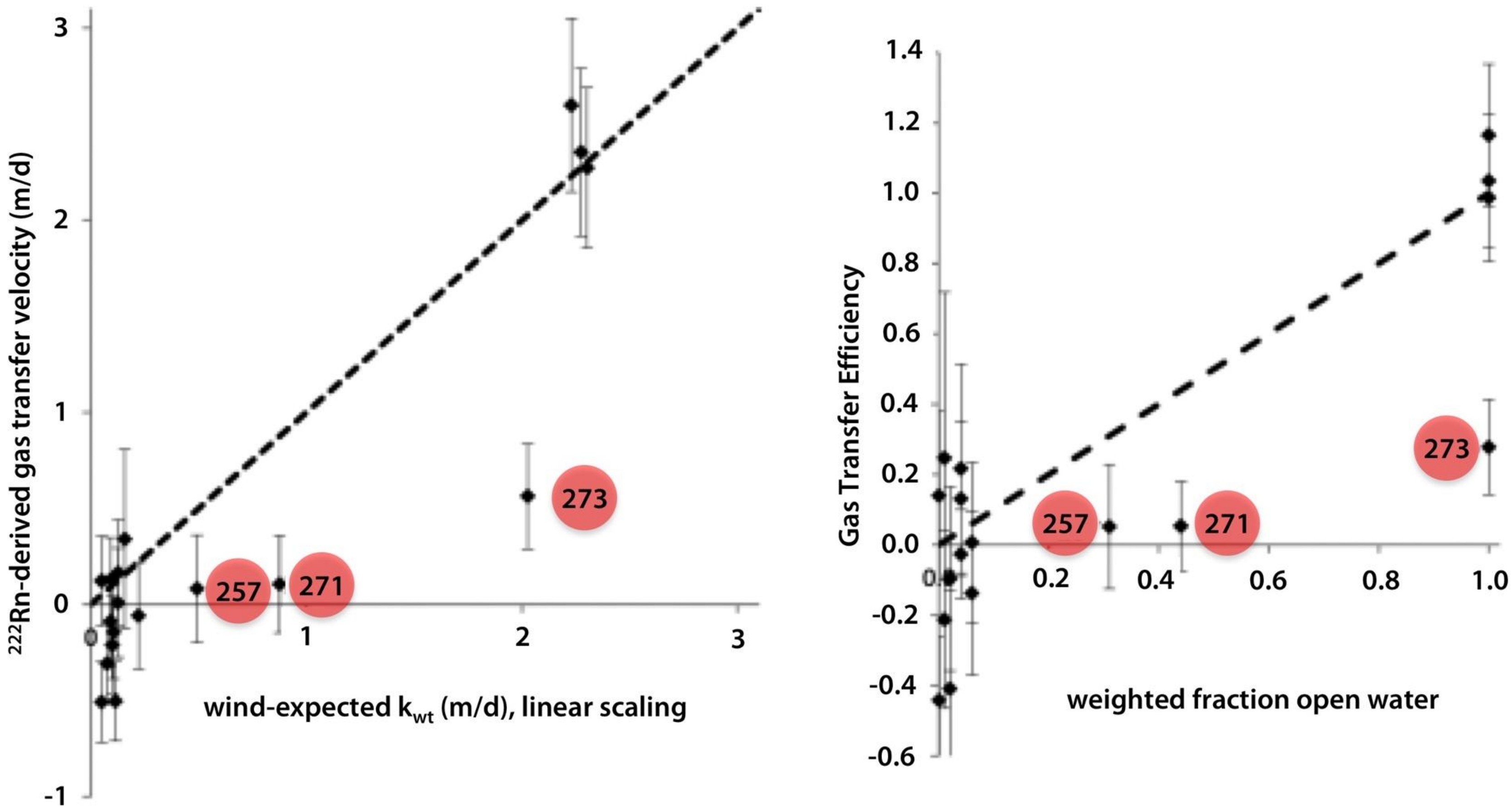
# Ice covered regions had average gas transfer velocities < 0.1 m d$^{-1}$. Open water gas transfer velocities were as expected and ranged from 0.6 - 2.6 m d$^{-1}$.




Rutgers van der Loeff et al. (2014b)


doi:10.1002/loe2.10008

# Partially ice-covered stations (red circles) exposed to wind had gas exchange rates significantly lower than expected.

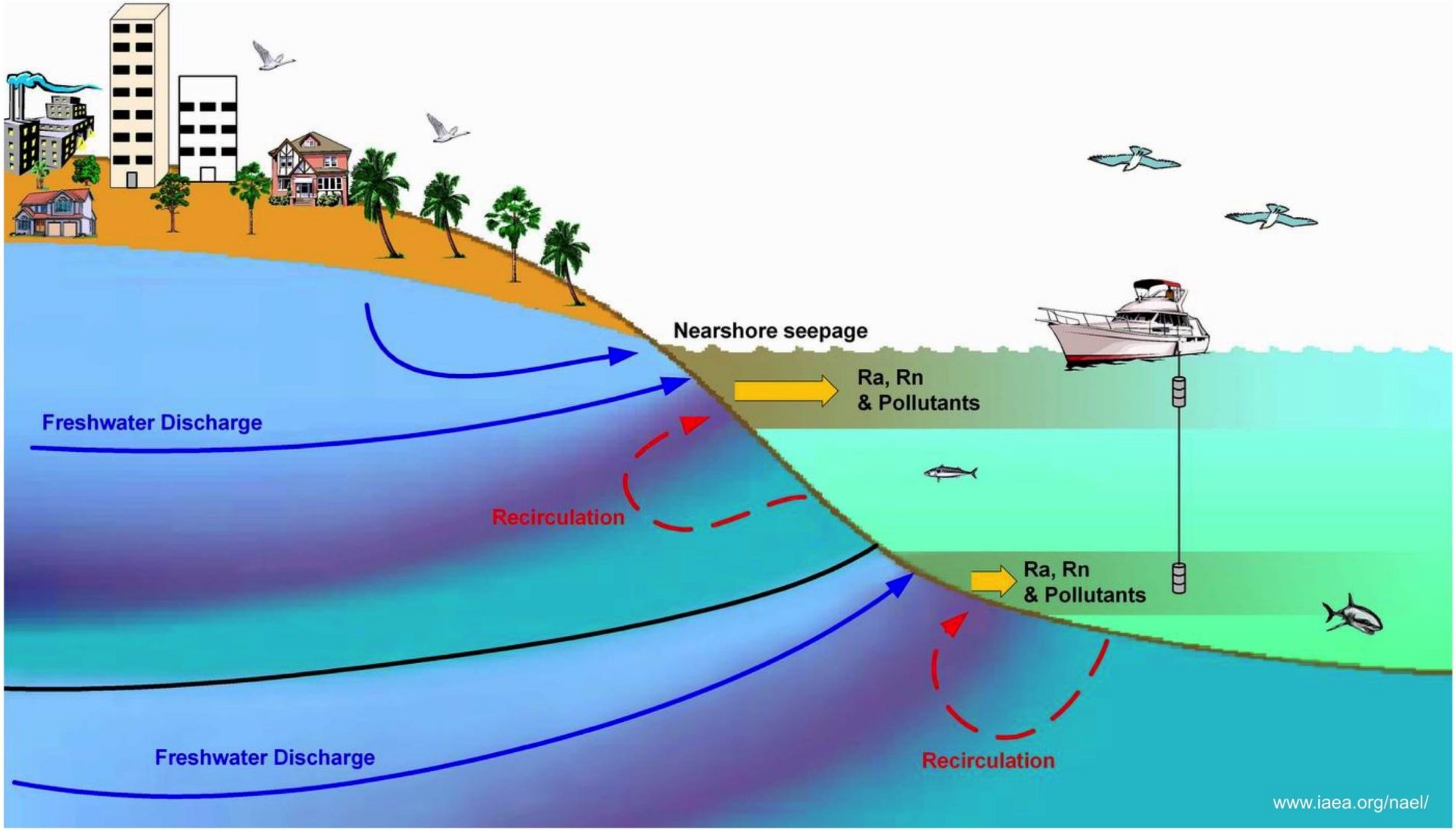



Rutgers van der Loeff et al. (2014b)



doi:10.1002/loe2.10008

# 3. Tracing Groundwater Discharge





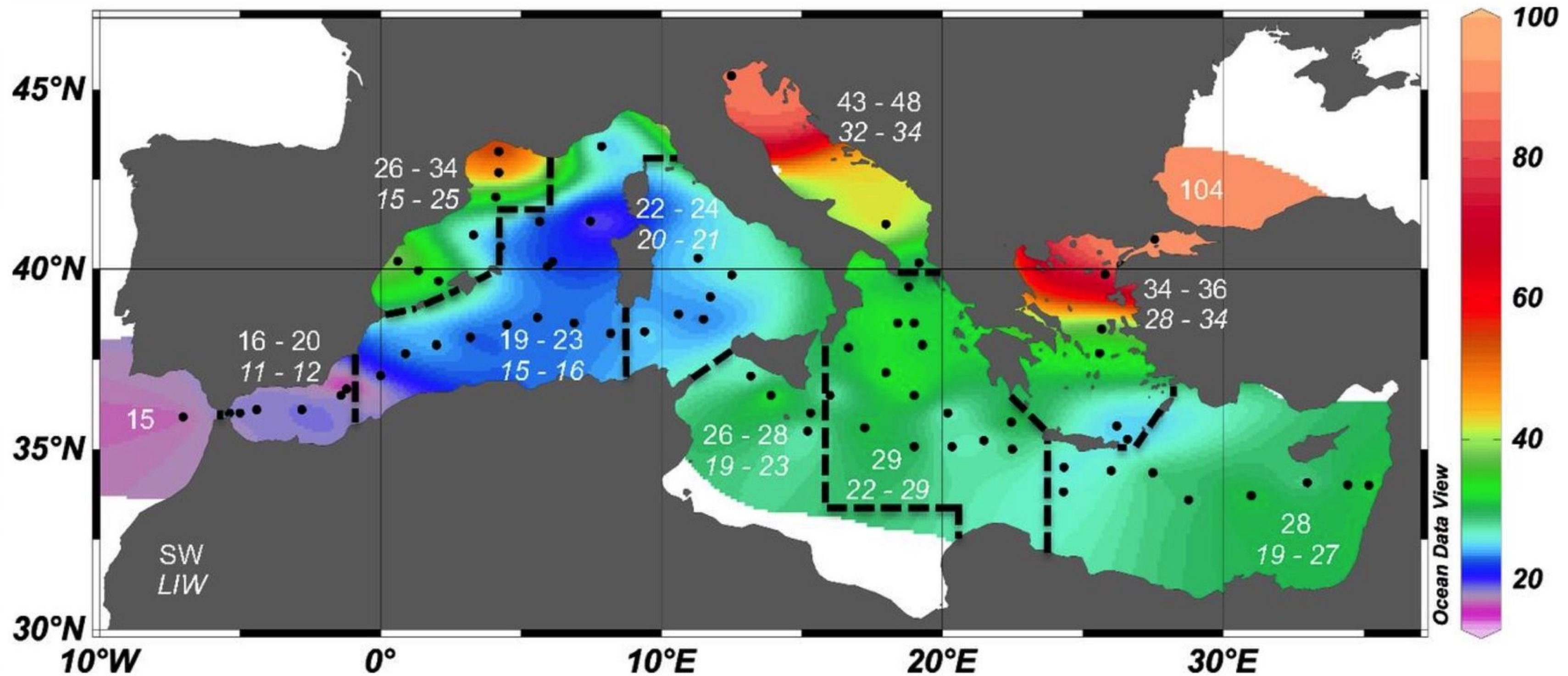
doi:10.1002/loe2.10008

# The Radium Quartet


- Radioactive radium is derived from the decay of thorium isotopes.
- Ra adsorbs to particles in fresh water, but is mobile in salt water.
- Ra is not reactive in coastal waters.
- Ra concentrations are usually high in salty submarine groundwater (SGD) and low in ocean water.


doi:10.1002/loe2.10008

# Distribution of $^{228}Ra$ concentrations (dpm $m^{-3}$) in surface waters of the Mediterranean Sea.

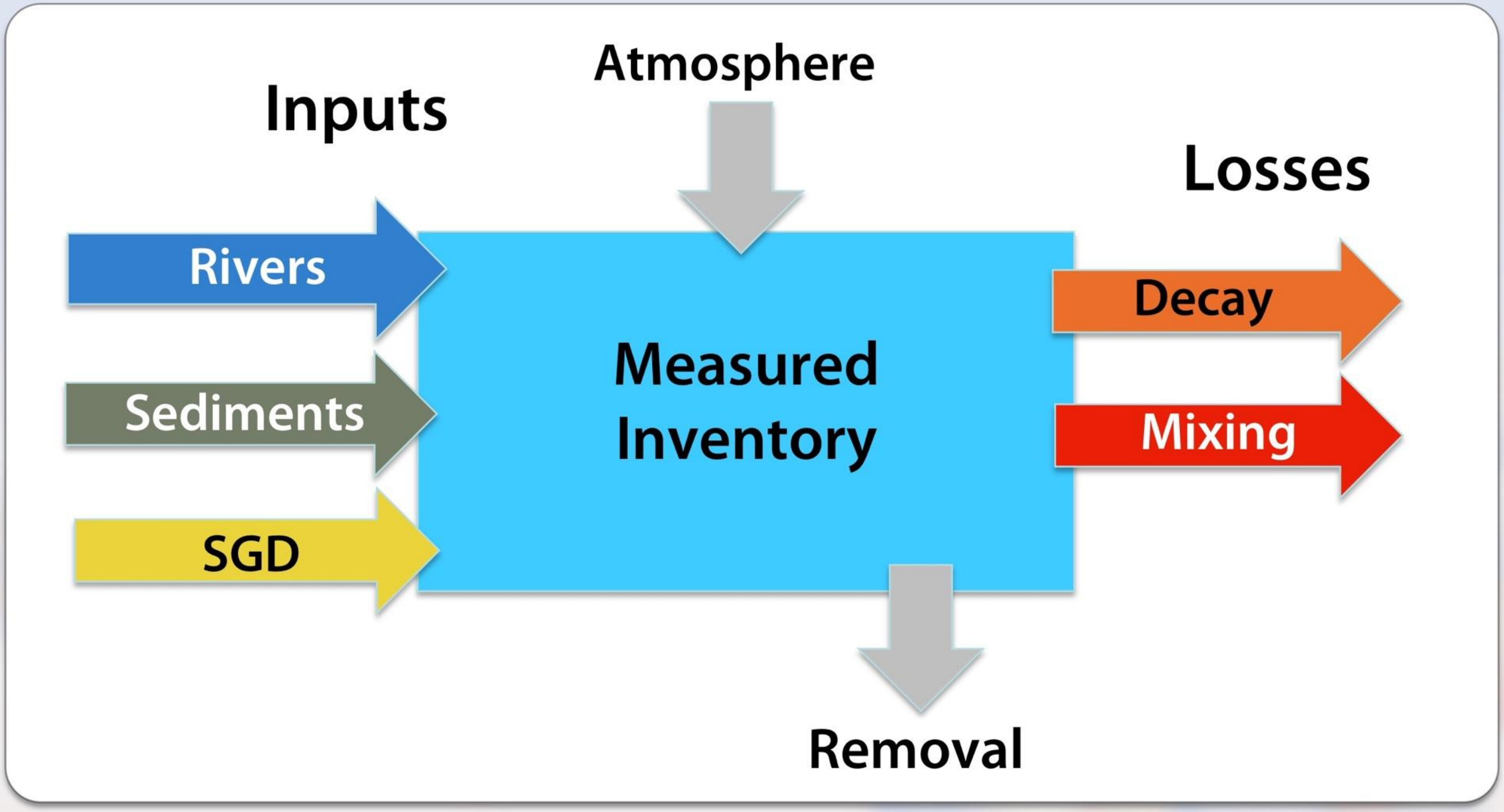



Rodellas et al. (2015)



doi:10.1002/loe2.10008

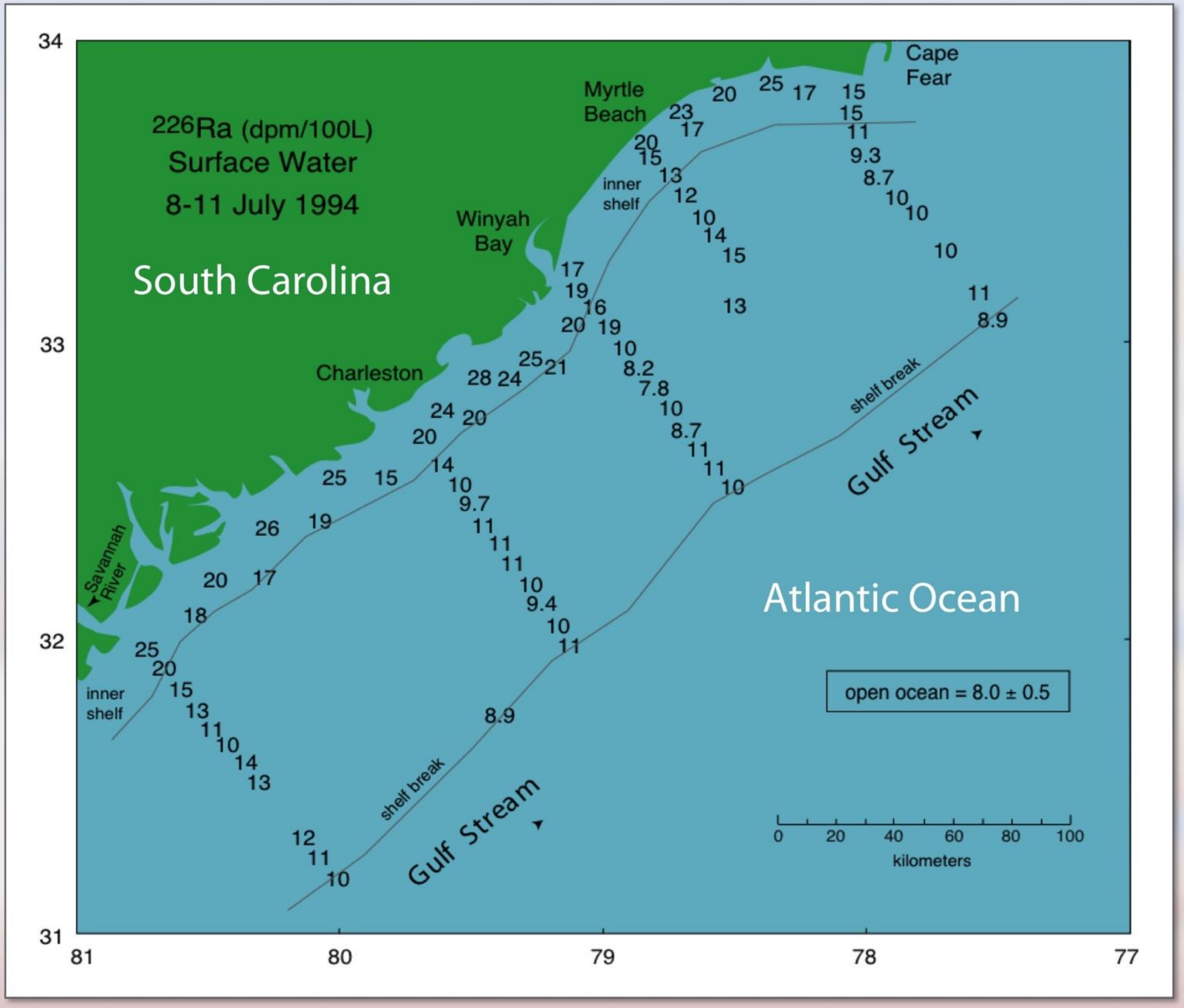
# General Model for Quantifying SGD Using Radium Isotopes




Depending on the radium isotope used, various aspects of this model (e.g., decay for $^{226}Ra$) can be assumed minimal.


doi:10.1002/loe2.10008

# Offshore Mixing and SGD using Radium isotopes




Moore (2000)


doi:10.1002/loe2.10008

# Offshore Mixing using $^{223}Ra$ & $^{224}Ra$ (short half-lives)

The change in concentration or activity (A) with time (t) as a function of distance offshore (x) for a radioactive tracer with decay constant (λ) may be expressed as a balance of advection (ω), dispersion ($K_h$), and radioactive decay.

$$\frac{dA}{dt} = K_h\left[\frac{d^2A}{dx^2}\right] - \omega\left[\frac{dA}{dx}\right] - \lambda A$$

**If ω = 0:**

$$\frac{dA}{dt} = K_h\left[\frac{d^2A}{dx^2}\right] - \lambda A$$

**If $K_h$ is constant and the system is in steady state**

$$A_x = A_0 \exp[-x\sqrt{\frac{\lambda}{K_h}}]$$

Moore (2000)

# SGD to the southeastern N. Atlantic Ocean using $^{226}Ra$

Flux of $^{226}Ra$ = $K_h$ x offshore gradient

Flux $^{226}Ra$ = 400 $m^2$ $s^{-1}$ x 2.2 dpm $m^{-3}$ $km^{-1}$

F = 7.6 x $10^7$ dpm $d^{-1}$ $m^{-1}$ $km^{-1}$ (convert seconds to days)

F = 7.6 x $10^{10}$ dpm $d^{-1}$ $km^{-2}$ (convert m to km)

The Ra is transported in a 10 m thick surface layer (0.01 km).

Therefore: F = 7.6 x $10^8$ dpm $d^{-1}$ $km^{-1}$

For a 320 km long coast, the flux is 2.43 x $10^{11}$ dpm $d^{-1}$

Moore (2010)


doi:10.1002/loe2.10008

# SGD to the southeastern N. Atlantic Ocean using $^{226}Ra$

To translate the $^{226}Ra$ flux to a flux of SGD, we must know the concentration of $^{226}Ra$ in SGD.

The average concentration of $^{226}Ra$ in 111 analyses of coastal groundwater from the region is 1.6 dpm $L^{-1}$.

$$SGD = \frac{2.43 \times 10^{11} \text{ dpm d}^{-1}}{1.6 \text{ dpm L}^{-1}} = 15 \times 10^{10} \text{ L d}^{-1}$$

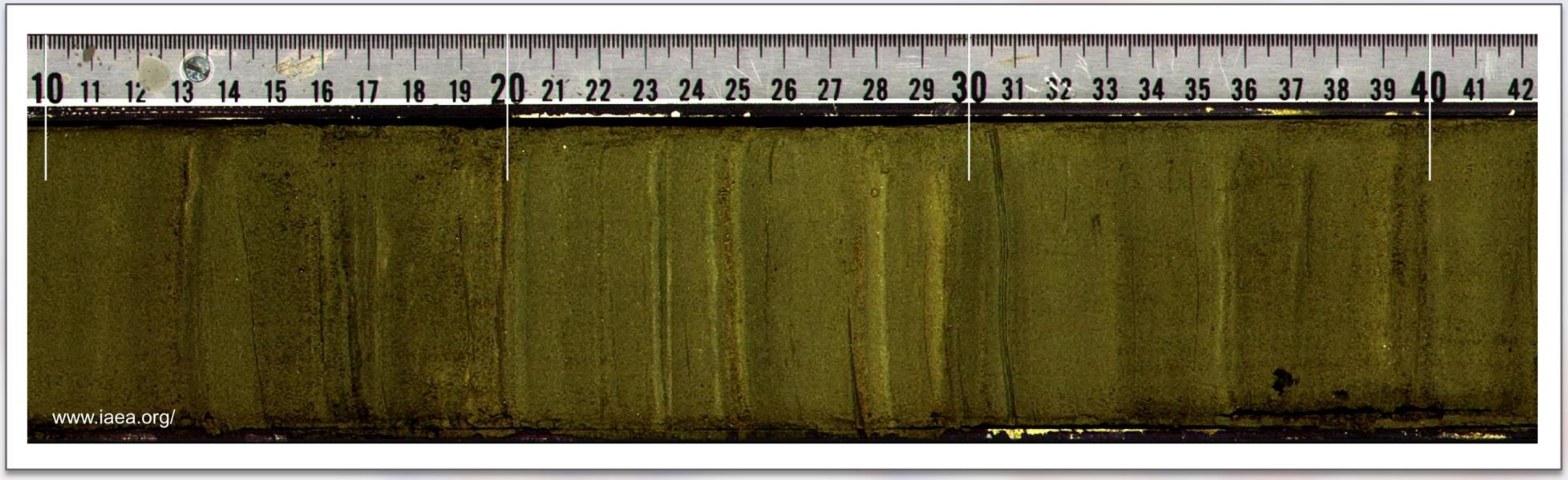
Moore (2010)

Average river flow is $7 \times 10^{10}$ L $d^{-1}$.


doi:10.1002/loe2.10008

# 4. Sedimentation/Age Dating

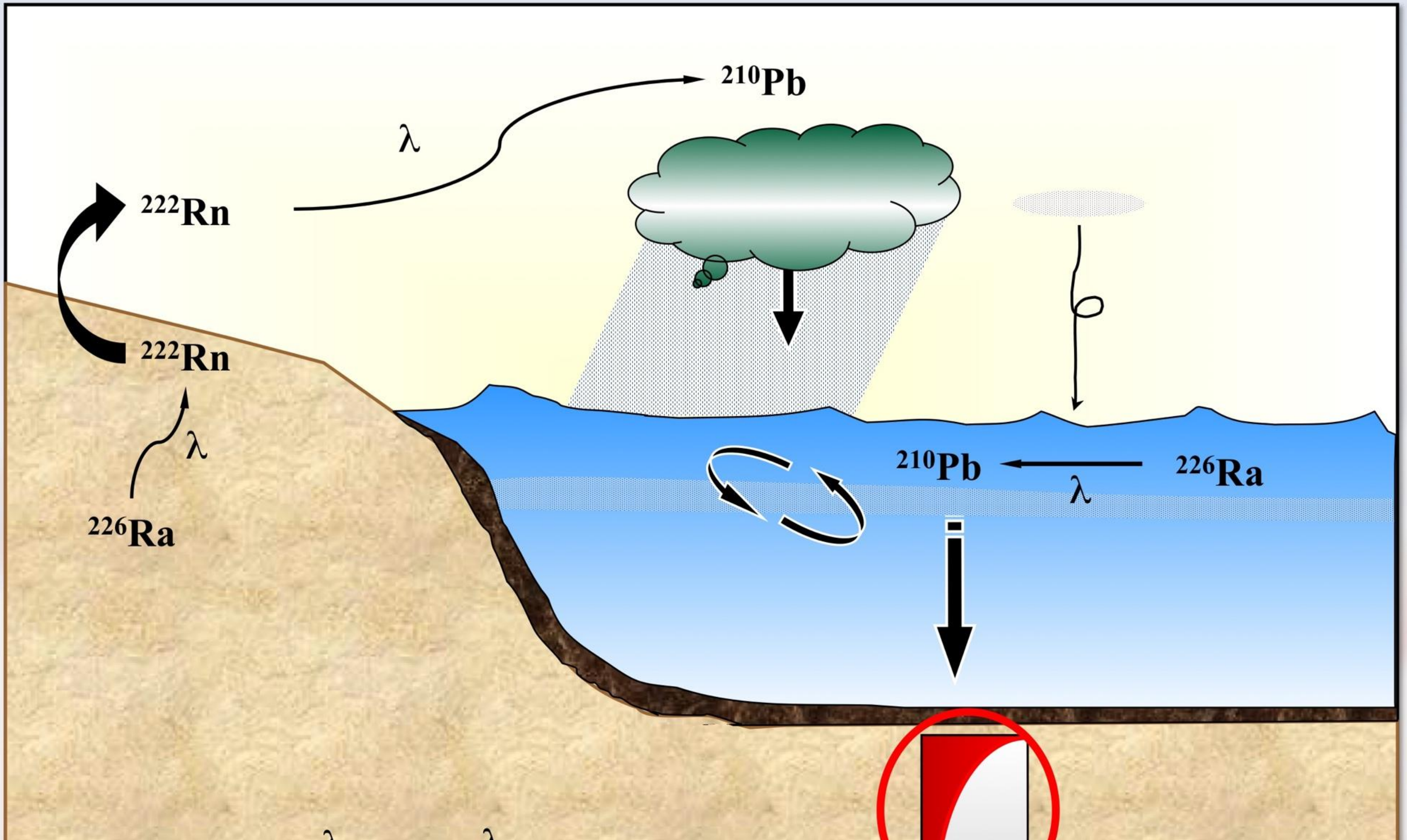
Sediments provide records of processes that have occurred in the past. Sediments further serve as a storage reservoir for chemically and biologically reactive elements, such as carbon and heavy metals.




As such, knowledge of the age of sediments and rate at which sediments accumulate is critical information for answering a wide variety of questions.


doi:10.1002/loe2.10008

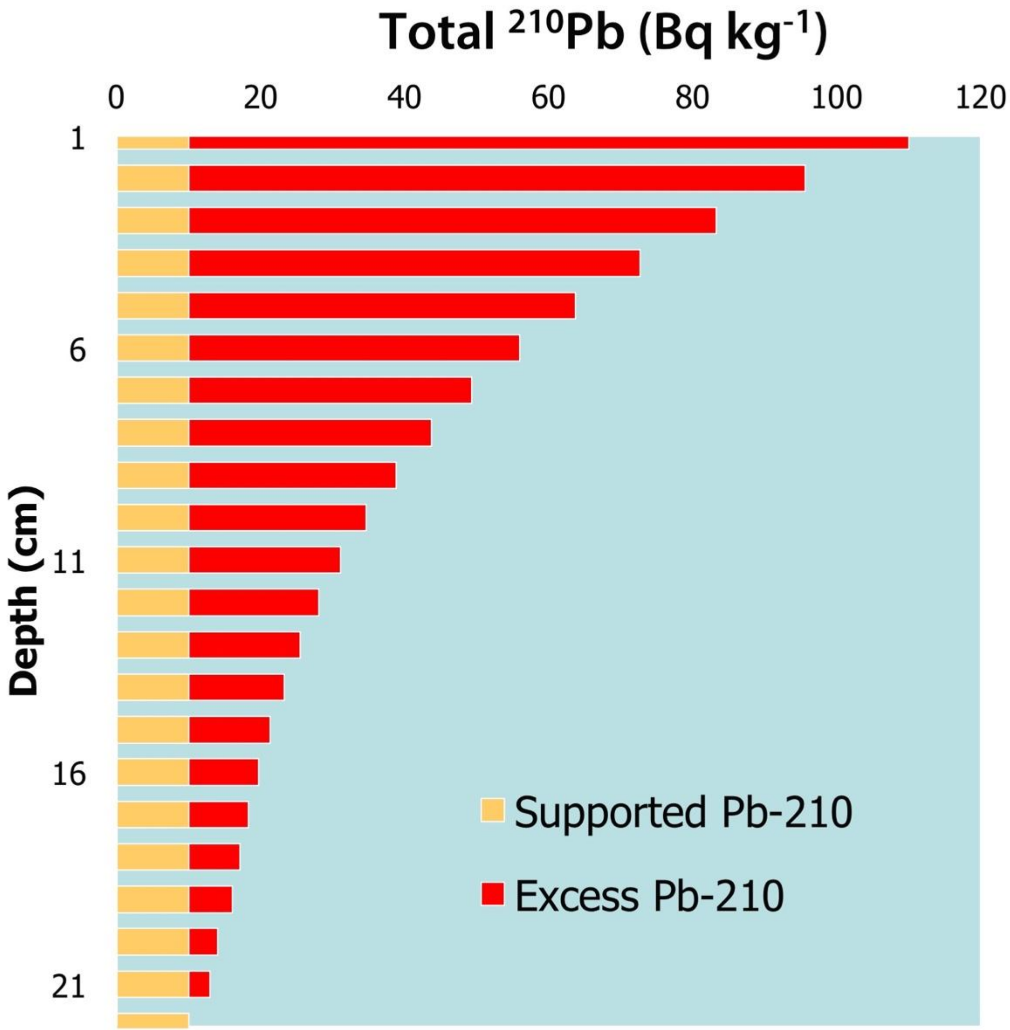
# The $^{210}$Pb cycle in the ocean




$^{226}$Ra $\xrightarrow{\lambda}$ $^{222}$Rn $\xrightarrow{\lambda}$ supported $^{210}$Pb


doi:10.1002/loe2.10008

# Age dating and sedimentation/mass accumulation rates using "excess" $^{210}Pb$: The Basics




The decay of excess $^{210}Pb$ can be described by the classic radioactive decay equation:

$$A = A_0 e^{-\lambda t}$$

**Supported $^{210}Pb$** is derived from in situ decay from $^{226}Ra$ via $^{222}Rn$

**Excess $^{210}Pb$** is from overlying water column

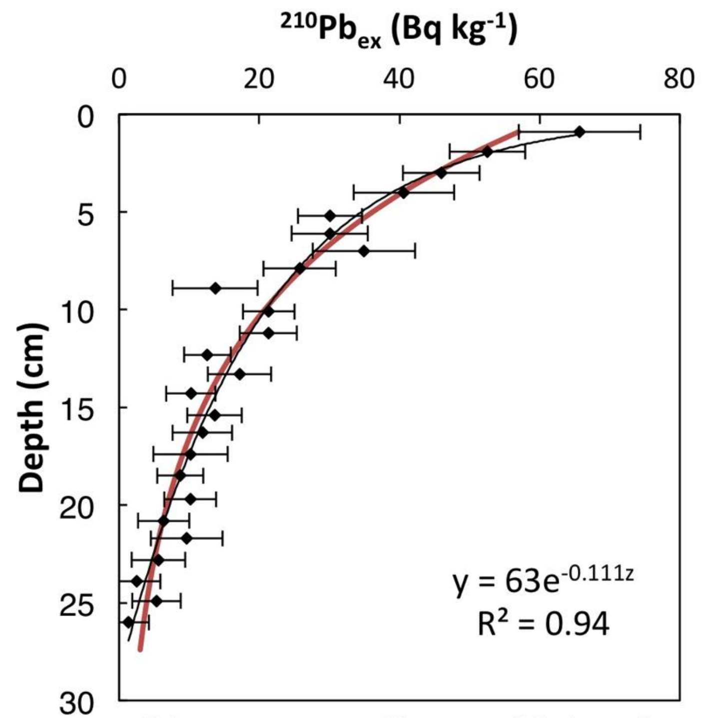

doi:10.1002/loe2.10008

# $^{210}$Pb: Constant flux-constant sedimentation rate (CF:CS) Model

$$A_Z = A_0 e^{-\lambda t} \rightarrow A_0 e^{-\left(\frac{\lambda}{S}\right)z} \rightarrow \ln A_Z = \ln A_0 - \left(\frac{\lambda}{S}\right)z$$

**Where:**

- **$\lambda$ is the radioactive decay constant for $^{210}$Pb (in $y^{-1}$)**
- **$A_o$ is the excess $^{210}$Pb activity at the initial depth**
- **$A_z$ is the excess $^{210}$Pb activity at depth, z**
- **S is the average sedimentation rate over the depth interval of interest.**




**Mangrove sediment, Malaysia**
Alongi et al. (2004)


doi:10.1002/loe2.10008

# $^{210}$Pb: Constant Initial Concentration (CIC) Model

$$A_Z = A_0 e^{-\lambda t} \longrightarrow t = \frac{1}{\lambda} * \ln \frac{A_0}{A_Z}$$

**Where:**

- $\lambda$ is the radioactive decay constant for $^{210}$Pb (in $y^{-1}$)
- $A_o$ is the excess $^{210}$Pb activity at the initial depth
- $A_z$ is the excess $^{210}$Pb activity at depth, z

# $^{210}$Pb: The constant rate of supply model (CRS)

$$I_x = \int_t^\infty e^{-\lambda t} dt = I_0 e^{-\lambda \cdot t} \rightarrow t_m = \frac{1}{\lambda}[\ln\left(\frac{I_0}{I_x}\right)]$$

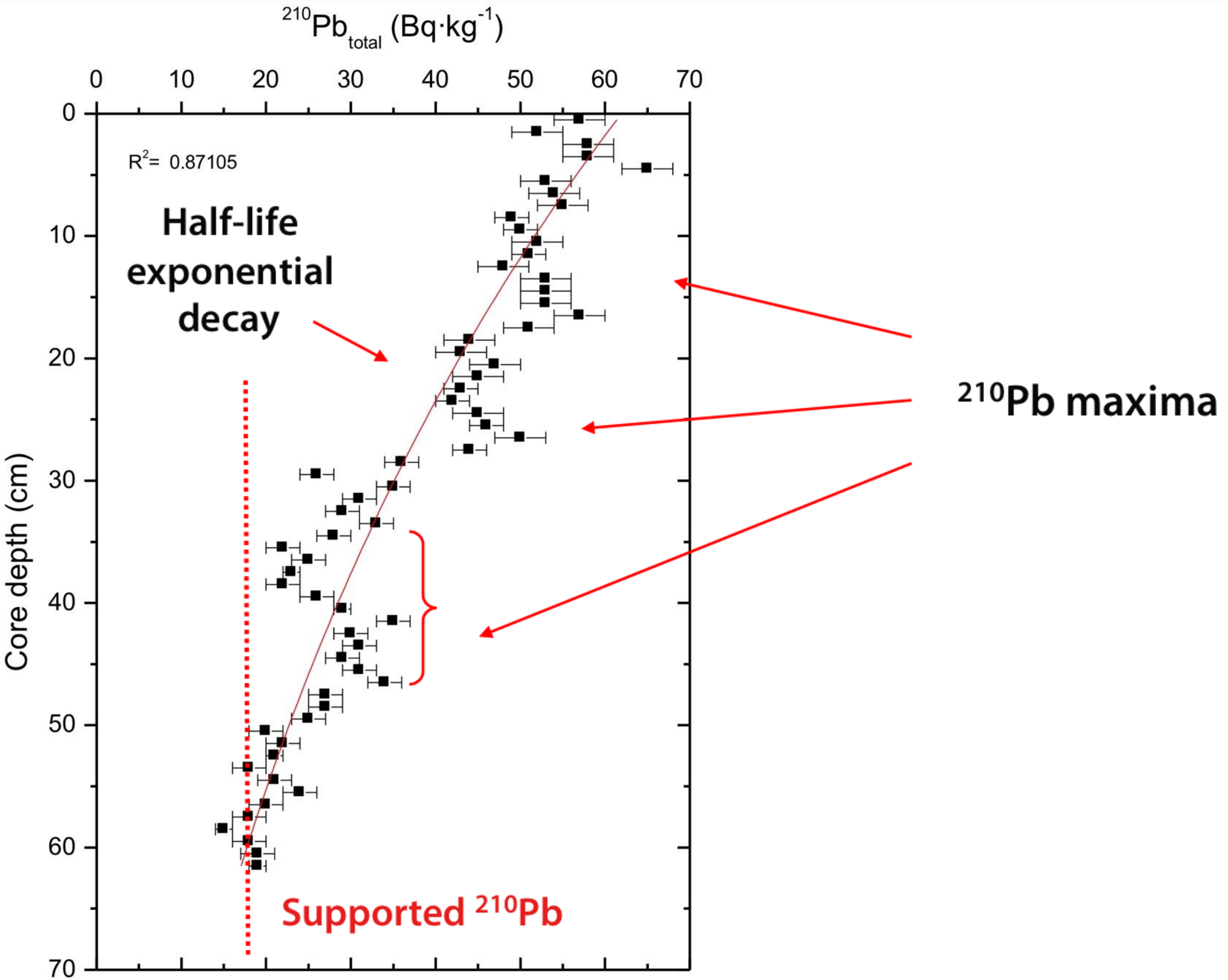
**Where:**

- $\lambda$ is the radioactive decay constant for $^{210}$Pb (in $y^{-1}$)
- $A_x$ is the excess $^{210}$Pb activity at depth, x (per $cm^{-3}$)
- $I_o$ is the excess $^{210}$Pb inventory of the entire core (per $cm^{-2}$)
- $I_x$ is the excess $^{210}$Pb inventory beneath depth, x, of sediments (per $cm^{-2}$)
- $t_m$ is the sediment age at depth x

$$\text{Sedimentation rate (cm y}^{-1}\text{)} = S = \frac{\lambda I_x}{A_x}$$


doi:10.1002/loe2.10008

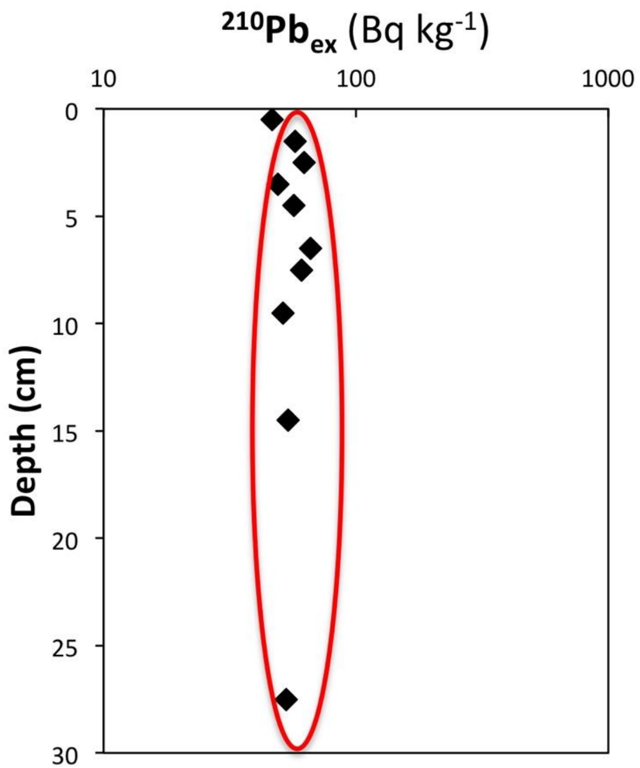
# $^{210}$Pb: Example of a more complicated core



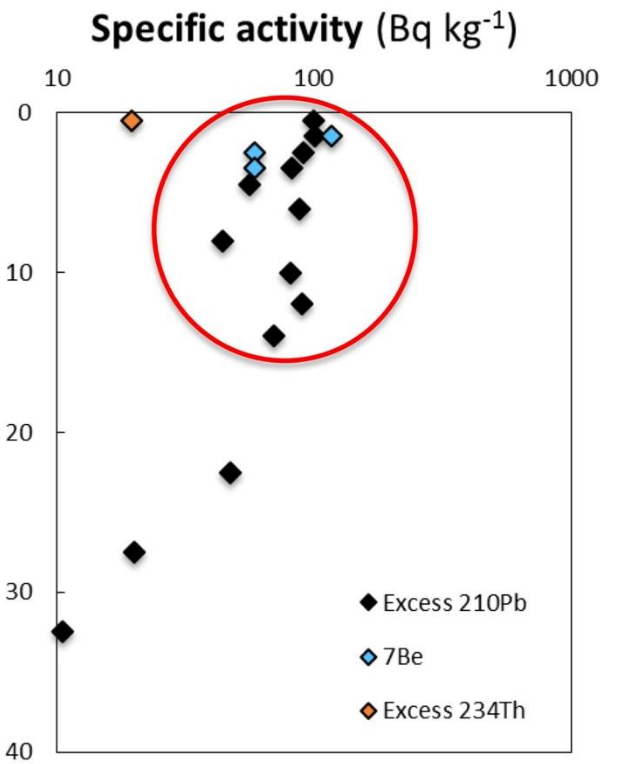


doi:10.1002/loe2.10008

# $^{210}Pb$: Example of a more complicated core




No benthic fauna
= Physical mixing

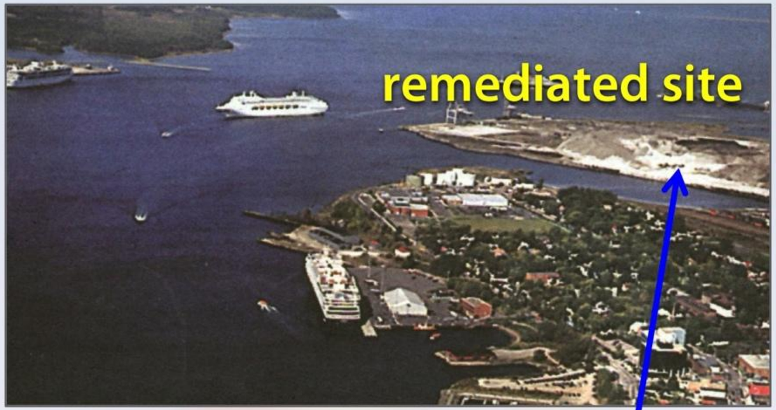


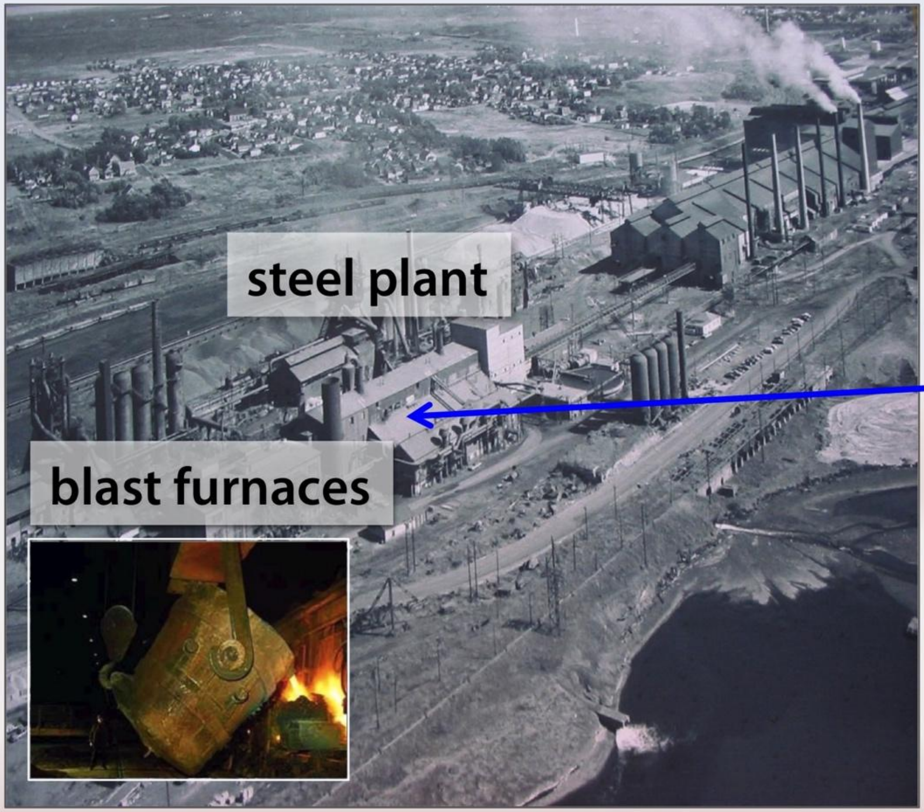

Many species of benthic fauna
$^{7}Be$ and $^{234}Th$ in subsurface layers suggest recent deposition
= Bioturbation

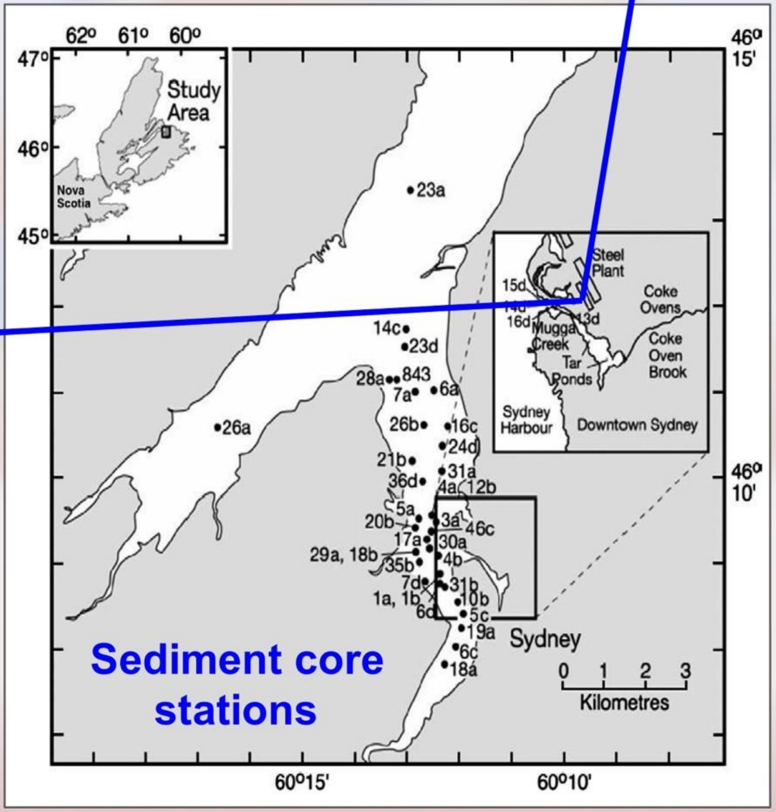
Smoak and Patchineelam (1999)


doi:10.1002/loe2.10008

# $^{210}Pb$ applied to history of PAH contamination from steel plant/coke ovens in sediment cores from Sydney Harbour, Nova Scotia, Canada.



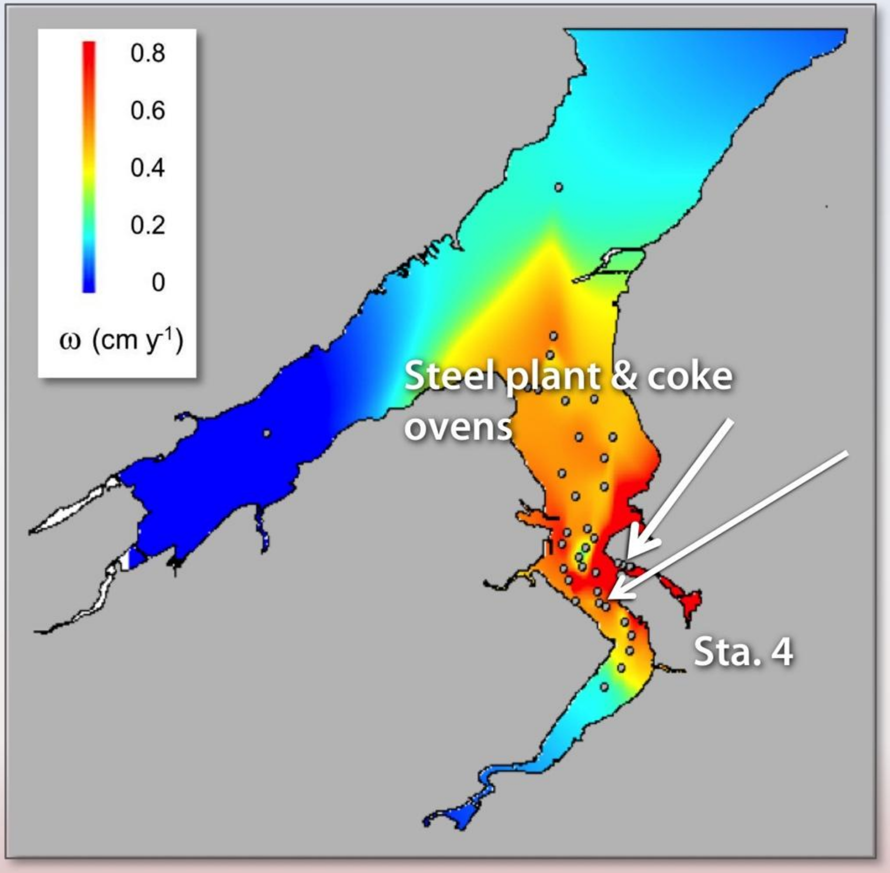



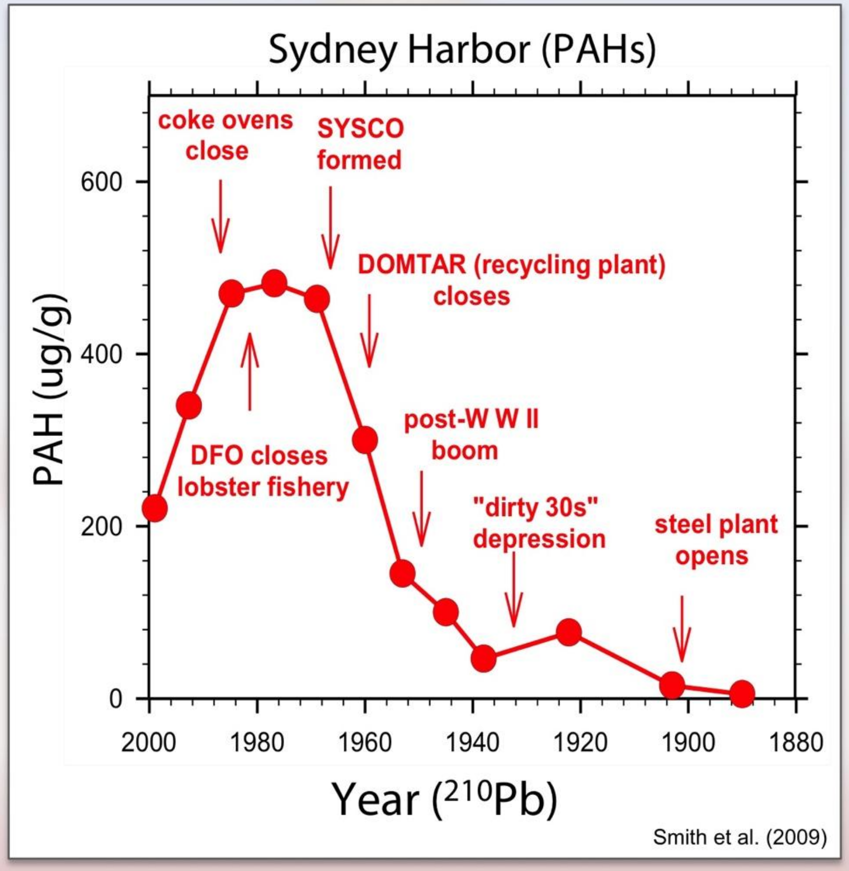

Smith et al. (2009)


doi:10.1002/loe2.10008

$^{210}$Pb derived sedimentation rates ω (cm $y^{-1}$) for 41 cores in Sydney Harbour. Below right is PAH history for Sta. 4. PAH decrease near core top reflects closure of steel mill and coke ovens in 1989.

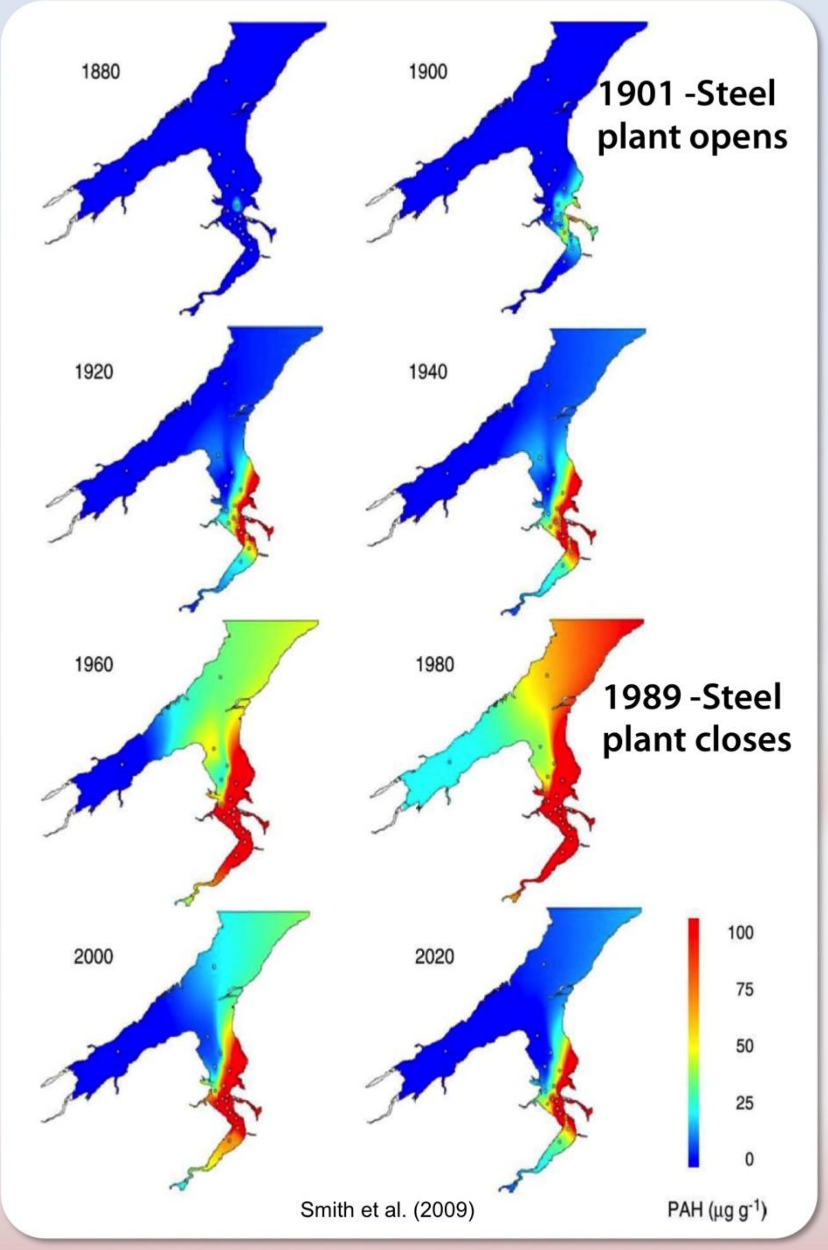
PAH (Sta 4) plotted vs. $^{210}$Pb date gives core PAH geochronology. Time slices through data set of 41 cores provide surface concentration maps for entire history of harbour.

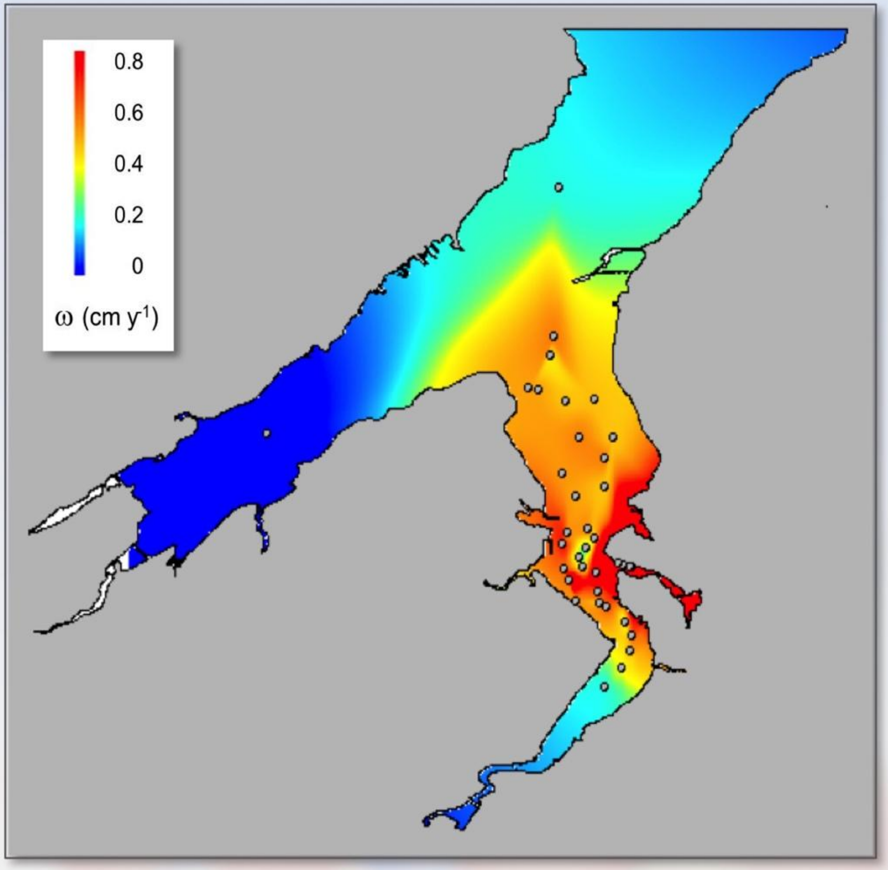




doi:10.1002/loe2.10008




**Historical PAH surface concentration maps based on $^{210}Pb$ core dates. Extrapolation to 2020 is based on transport model using watershed residence time for PAHs of 10 years.**

# In summary

U-Th series radionuclides are very useful tools as tracers to study a large variety of processes in the oceans at various time scales from days to millions of years.

Examples include:

- Scavenging
- Air-Sea exchange
- Tracing groundwater discharge
- Sedimentation rates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This work would not have been possible without the generous contributions and thoughtful comments of Drs. Robert Anderson, Kirk Cochran, Peter Santschi and Alan Shiller. We wish to thank two anonymous reviewers who provided constructive comments that improved the presentation. Lectures would not have been possible without the outstanding assistance of graphic designer Jason Emmett.

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# References


- Alongi, D.M., Sasekumar, A., Chong, V.C., Pfitzner, J., Trott, L.A., Tirendi, F., Dixon, P., Brunskill, G.J., (2004) Sediment accumulation and organic material flux in a managed mangrove ecosystem: estimates of land-ocean-atmosphere exchange in peninsular Malaysia. Mar. Geol. 208: 383–402.
- Bateman, H. (1910), The Transformation of the Electrodynamical Equations. Proceedings of the London Mathematical Society, s2-8: 223–264. doi:10.1112/plms/s2-8.1.223.
- Bhat, S. G., Krishnaswami, S., Lal, D., Rama, Moore, W.S. (1969) 234Th/238U ratios in the Ocean, Earth and Planetary Science Letters, 32: 277-296.
- Broecker, W.S. and Peng, T-H (1982) Tracers in the sea. New York: Lamont-Doherty Geological Observatory. Eldigio Press, Columbia University. Available online at: http://www.ldeo.columbia.edu/~broecker/Home_files/TracersInTheSea_searchable.pdf
- Buesseler, K. O., Benitez-Nelson, C.R., Moran, S.B., Burd, A., Charette, M., Cochran, J.K., Coppola, L., Fisher, N.S., Fowler, S.W., Gardner, W.D., Guo, L.D., Gustafsson, O., Lamborg, C., Masque, P., Miquel, J.C., Passow, U., Santschi, P.H., Savoye, N., Stewart, G., Trull, T. (2006) An assessment of particulate organic carbon to thorium-234 ratios in the ocean and their impact on the application of 234Th as a POC flux proxy. Marine Chemistry, 100: 213-233.
- Buesseler, K.O., Pike, S., Maiti, K., Lamborg, C.H., Siegel, D.A., Trull, T.W. (2009) Thorium-234 as a tracer of spatial, temporal and vertical variability in particle flux in the North Pacific. Deep Sea Research Part I: Oceanographic Research Papers 56: 1143-1167.
- Coale, K.H., Bruland, K.W. (1985) 234Th:238U disequilibria within the California Current. Limnology and Oceanography 30: 22-33.
- Coale, K.H., Bruland, K.W. (1987) Oceanic stratified euphotic zone as elucidated by 234Th:238U disequilibria. Limnology and Oceanography 32: 189-200.
- Cochran, J.K., Masqué, P. (2003) Short-lived U/Th Series Radionuclides in the Ocean: Tracers for Scavenging Rates, Export Fluxes and Particle Dynamics. Reviews in Mineralogy and Geochemistry 52: 461-492.
- Goldberg, E.D. (1954) Marine geochemistry 1. Chemical scavengers of the sea. J. Geol. 62: 249–265.
- Loose, B., McGillis, W.R., Perovich, D., Zappa, C.J., Schlosser, P. (2014) A parameter model of gas exchange for the seasonal sea ice zone, Ocean Sci., 10: 17–28.
- Moore, W.S. (2000) Determining coastal mixing rates using radium isotopes. Continental Shelf Research 20: 1993-2007.
- Moore, W.S. (2010) A reevaluation of submarine groundwater discharge along the southeastern coast of North America. Global Biogeochemical Cycles, 24: 10.1029/2009GB003747
- Nozaki, Y. (2001) Elemental distribution: Overview. In: Encyclopedia of Ocean Sciences, vol. 2. J.H. Steele, S.A. Thorpe, and K.K. Turekian, eds, Academic Press, London, Pp. 840–845 http://dx.doi.org/10.1006/rwos.2001.0402
- Owens S.A., Buesseler K.O., Sims K.W.W. (2011) Re-evaluating the 238U-salinity relationship in seawater: Implications for the 238U–234Th disequilibrium method. Marine Chemistry 127: 31-39.
- Peng, T.-H., Broecker, W.S., Mathieu, G.G., Li, Y.H., Bainbridge, A.E. (1979) Radon evasion rates in the Atlantic and Pacific oceans as determined during the GEOSECS program. Journal of Geophysical Research 84: 2,471–2,486

# References


- Puigcorbé, V., Roca-Martí, M., Masqué, P., Benitez-Nelson, C., Rutgers van der Loeff, M., Bracher, A., Moreau, S. (2017). Latitudinal distributions of particulate carbon export across the North Western Atlantic Ocean. Deep Sea Research Part I: Oceanographic Research Papers, 129: 116-130. https://doi.org/10.1016/j.dsr.2017.08.016.
- Rodellas, V., Garcia-Orellana, J., Masqué, P., Feldman, M., Weinstein, Y. (2015) Submarine groundwater discharge as a major source of nutrients to the Mediterranean Sea. Proceedings of the National Academy of Sciences 112: 3926-3930.
- Rutgers van der Loeff, M.M. (2014a) Uranium-Thorium Decay Series in the Oceans: Overview. In Elias S (ed.) Earth Systems and Environmental Sciences, (Reference Module in Earth Systems and Environmental Sciences). Amsterdam: Elsevier 1-16.
- Rutgers van der Loeff, M.M. et al. (2014b): The influence of sea ice cover on air-sea gas exchange estimated with radon-222 profiles. Journal of Geophysical Research-Oceans, 119(5): 2735-2751
- Santschi, P.H., Honeyman, B.D. (1989) Radionuclides in aquatic environments, Radiat. Phys. Chem., 34: 213–240
- Smith, J.N., Lee K., Gobeil, C., Macdonald, R.W. (2009) Natural rates of sediment containment of PAH, PCB and metal inventories in Sydney Harbour, Nova Scotia. Science of The Total Environment 407: 4858-4869.
- Smoak, J.M., Patchineelam, S.R. (1999) Sediment mixing and accumulation in a mangrove ecosystem: evidence from $^{210}Pb$, $^{234}Th$ and $^{7}Be$. Mangroves and Salt Marshes 3: 17-27.



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