# Lecture 15.   Chemical Tracers – Radionuclides

In this lecture we discuss the application of radioisotopes to oceanographic problems
- Radioisotopes provide the clocks that are used to measure rates of ocean processes
- They are valuable to marine science because they are
    - (a) Present in a variety of elements with different chemistry
    - (b) Have a variety of half lives, and a variety of sources
    - (c) Can be measured at very low concentration and extremely accurately
- Radioisotope tracers are both natural (^{10}Be, ^{14}C, ^{238}U, ^{230}Th) and anthropogenic (^{14}C, ^{90}Sr, ^{240}Pu), so they are "steady state" and "transient" tracers.

The application of a radiotracer to ocean processes is determined by the effective lifetime of the tracer. The effective lifetime is related to the isotope half-life or when it was introduced to the environment, in the case of anthropogenic tracers. In marine chemistry, radioactive elements have been used to study the rates of mixing of water and sediment, to calculate the age of water and sediment, to estimate rates of scavenging and production, gas exchange, and more.
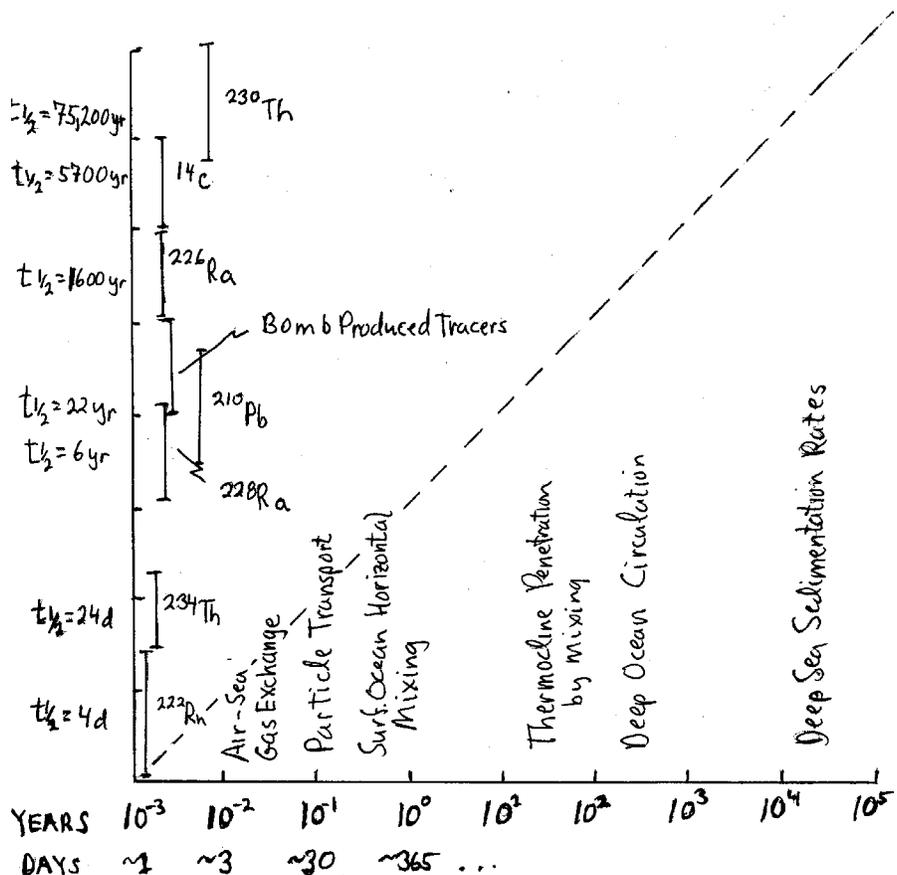
RADIOISOTOPES AND RADIOACTIVE DECAY (a brief reminder)

Units of Radioactivity

Activity = A = λ N λ = decay constant (0.693 / $t_{1/2}$); $t_{1/2}$ = half life
     N = isotope concentration (atoms / kg (liter))
Activity units are disintegrations per minute (dpm) / kg (liter) = dpm / kg
     λ N = min^{-1} x (atoms / kg)
Radioisotope activity is often presented in units of *Curies*
1 Curie (Ci) = activity of 1 gram of ^{226}Ra
1 Ci = λN dpm = [.693 / (1600 yr X 5.2 x 10^5 min yr^{-1})] [(1 g ^{226}Ra / 226 g mol^{-1})
     (6.1 x 10^{23} atoms / mole)] = **2.22 x 10^{12} dpm = 3.70 x 10^{10} dps**

The Radioactive Isotope Half- life
Radioactivity is the emission of energy (in the form of electromagnetic radiation or a particle) from an atom, sometimes with an accompanied elemental conversion. Radioactive decay is a purely random process unaffected by surroundings, not a function of temperature, pressure, or other environmental variables. It is a pure first order reaction:
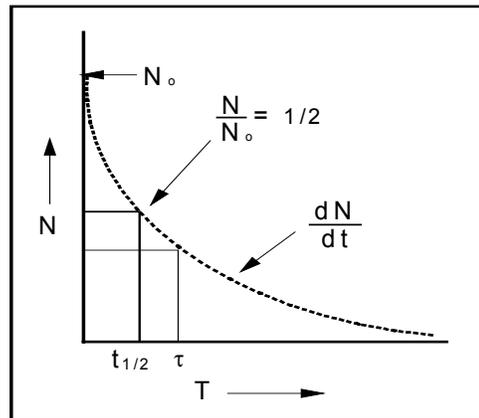
$$-\frac{dN}{dt} = \lambda N \tag{1}$$

Where, $-\dfrac{dN}{dt}$ = decay rate,

   N = concentration of radioactive atoms,
   λ = first-order decay constant (time^{-1})

The integral form of **(1)** is: $\displaystyle\int_{No}^{N}\frac{dN}{N} = -\lambda\int_{o}^{t}dt$,   or, $N = N_o e^{-\lambda}$ **(2)**

Half life definition:

$\ln (N / N_o) = -\lambda t$
when ½ of the original number of atoms decayed
$\ln (1/2) \quad = -\lambda t_{1/2}$
$t_{1/2} = 0.693 / \lambda$ = isotope half life

The *Mean life (τ)* = the average time that a radioisotope exists before decay. Or the integral of all lifetimes divided by the total number of atoms

$$\tau = \frac{1}{N_0}\int_0^\infty t\,dN = \frac{1}{N_0}\int_0^\infty t\lambda N\,dt = \lambda\int_0^\infty t e^{-\lambda t}\,dt = \left[\frac{\lambda t + 1}{\lambda}e^{-\lambda t}\right]_0^\infty = \frac{1}{\lambda}$$

Origin of Isotopes Used in Marine Chemistry
Naturally occurring radioactive isotopes used in marine chemistry applications are typically from the Uranium and Thorium Decay Chains, and those produced by Cosmic Rays in the upper atmosphere. Anthropogenically introduced radioisotopes that come primarily from weapons testing and energy generation are also used.

Naturally Occurring Radioisotopes from the Uranium Decay Series

Element	U-238 series							Th-232 series					U-235 series				
Neptunium																	
Uranium	U-238 4.47×10^9 y		U-234 2.48×10^5 y										U-235 7.04×10^8 y				
Protactinium		Pa-234 1.18 min												Pa-231 3.25×10^4 y			
Thorium	Th-234 24.1 d		Th-230 7.52×10^4 y					Th-232 1.40×10^{10} y		Th-228 1.91 y			Th-231 25.5 hrs		Th-227 18.7 d		
Actinium									Ac-228 6.13 hrs					Ac-227 21.8 y			
Radium			Ra-226 1.62×10^3 y					Ra-228 5.75 y		Ra-224 3.66 d					Ra-223 11.4 d		
Francium																	
Radon			Rn-222 3.82 d							Rn-220 55.6 s					Rn-219 3.96 s		
Astatine																	
Polonium			Po-218 3.05 min		Po-214 1.64×10^{-4} s		Po-210 138 d			Po-216 0.15 s	64%	Po-212 3.0×10^{-7} s			Po-215 1.78×10^{-3} s		
Bismuth				Bi-214 19.7 min		Bi-210 5.01 d				Bi-212 60.6 min						Bi-211 2.15 min	
Lead			Pb-214 26.8 min		Pb-210 22.3 y		Pb-206 Stable lead isotope			Pb-212 10.6 hrs	36%	Pb-208 Stable lead isotope			Pb-211 36.1 min		Pb-207 Stable lead isotope
Thallium											Tl-208 3.05 min					Tl-207 4.77 min	

- Three long-lived elements (^{238}U, ^{232}Th and ^{235}U) are the origin of 12 different elements, 36 radioactive isotopes and three stable daughters (^{206}Pb, ^{208}Pb and ^{207}Pb)
- α decay on the above chart involves a release of a He nucleus (↓ 2 steps down)
- β decay involves the release of an electron (β⁻ particle) and is one step up and to the right;

The utility of the naturally occurring Decay Series for applications other than straightforward radioactive decay chronology originates when the daughter isotopes are separated from the parent because the chemistry of the two is different (e.g they are different element with different chemical characteristics).

Secular Equilibrium
In a closed system (equivalent to the absence of chemical separation in the environment), all activities in a given decay chain would be the same as that of the parent (the longest half life). This is called **secular equilibrium** which occurs, in a closed system, when the half live of the daughter radioisotope is ≪ than that of the parent.
  For the decay series $N_1 \rightarrow N_2 \rightarrow$

$$dN_2/dt = \text{production} - \text{decay} = \lambda_1 N_1 - \lambda_2 N_2 = -\lambda_2 N_2 + \lambda_1 N_1^0 \exp(-\lambda_1 t)$$

The solution for $N = N^o$
at t=0 is:

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

if: $t_{1/2,1} \gg t_{1/2,2}$; then $\lambda_1 \ll \lambda_2$;

$$N_2(t) = \left(\frac{\lambda_1}{\lambda_2}\right) N_1 \left(1 - e^{-\lambda_2 t}\right)$$

assuming $N_2{}^o = 0$;
since $N_1(t) = N_1{}^o \exp(-\lambda_1 t)$

or $A_2(t) = A_1(t) \{1-\exp(-\lambda_2 t)\}$
as $t\rightarrow$ gets large $A_2(t) = A_1(t)$

at $t = 1/\lambda$, $A_2/A_1 = (1- 1/e) = 0.63$

The system approaches *secular equilibrium* with the characteristic half-life of the daughter (the shorter the daughter's half-life, the faster secular equilibrium is achieved).

Chemical separation of parent and daughter elements, such as the separation of ^{238}U from its more particle-reactive daughters of ^{234}Th or $^{230\text{Th}}$, creates a situation where the daughter isotope activity can be different than the parent activity; *It is no longer in a closed system or in secular equilibrium.*

Relative Activities of U Series Isotopes in Seawater

^{234}U = 1.14 ^{238}U
^{230}Th < 0.01 ^{234}U
^{226}Ra > 30 (^{230}Th)
^{222}Rn < ^{226}Ra (in the surface ocean)
^{222}Rn > ^{226}Ra (near ocean sediments)
^{210}Pb < ^{226}Ra
The differences in activity rise from the different reactivity (chemical behavior) of the elements involved. These "disequilibria" are utilized for many applications.
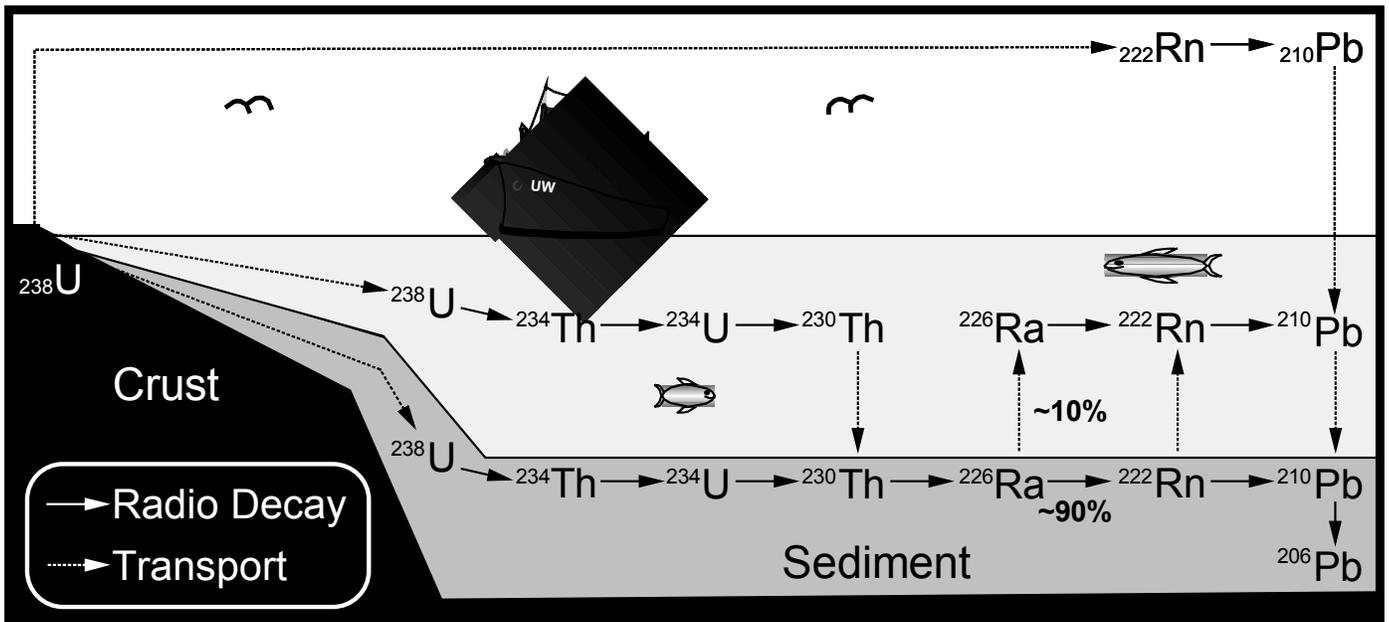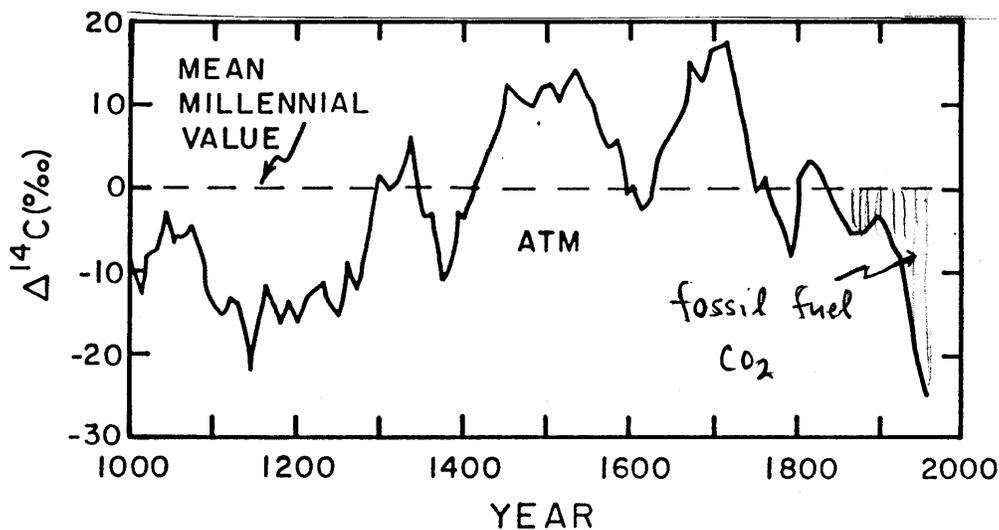
Cosmic Ray Produced Nuclides

^{3}He; ^{7}Be; ^{10}Be; ^{14}C; ^{32}Si; ^{32}P; ^{33}P are produced in the upper atmosphere by cosmic-ray "spallation" reactions. Of these, carbon-14 is the best known because of its utility as a dating tool. High-energy cosmic-ray protons from beyond our solar system enter and collide with a nitrogen atom in the atmosphere. The sequence of events to the right follows these collisions.
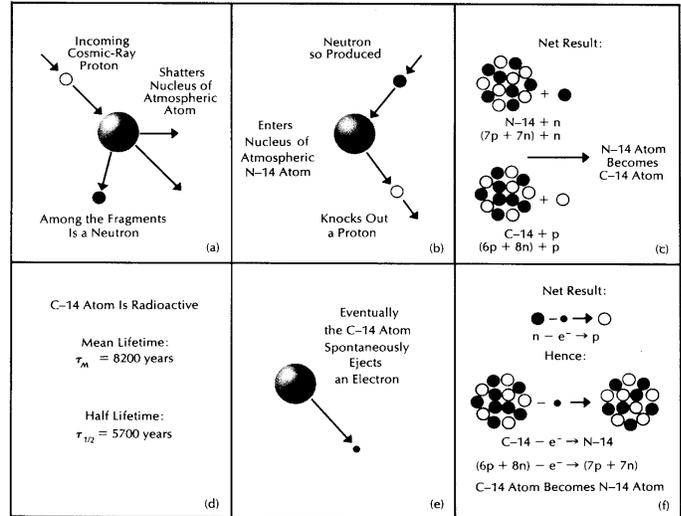
The ^{14}C-formation reaction is written as:
$$^{14}N \ (n,p) \ ^{14}C$$

Figure 3-1   The "life cycle" of a carbon-14 atom. Created in the atmosphere by the collision of a neutron (produced by primary cosmic-ray protons) with a nitrogen atom, the average C-14 atom "lives" for 8200 years. Its life is terminated by the ejection of an electron which returns the atom to its original form, N-14.

The production rate of ^{14}C as determined in tree rings seems to be correlated with the activity of the Sun. When the solar wind is high, ^{14}C production is low and vice versa. Neutrons created by the sun must interfere with the reactions caused by high-energy cosmic rays. A decrease in activity since 1800 is observed, but this is due to the dilution effect caused by "dead" CO_2 from fossil fuel burning and not by change in the production on ^{14}C (The **Suess Effect**). The graph below is the deviation of ^{14}C activity in the atmosphere relative to the millennial mean; this figure is pre-1960s, so it does not show the effect of nuclear weapons testing.

Anthropogenically Produced Radioisotopes

^{14}C, ^{3}H, ^{137}Cs, ^{90}Sr, ^{85}Kr, ^{239}Pu, ^{240}Pu are among the radioactive elements that entered the atmosphere during nuclear weapons testing. These isotopes are tracers not because of their half-lives, but because they were added to the environment in a pulse (mid 1960s). The ones that have been used the most as transient tracers are ^{14}C and ^{3}H.

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Following are several examples for applications of radionuclides as tracers in marine chemistry research:

Thorium Isotopes as Tracers of Particle Transport
There are four isotopes of Thorium.
  Two in the ^{238}U decay series (^{234}Th and ^{230}Th) and
 Two in the Thorium decay series (^{232}Th and ^{228}Th)

^{234}Th and ^{230}Th are the most useful as tracers because of their half-lives match time scales of interest for different oceanic processes.

^{238}U and ^{234}U are almost uniformly distributed in the ocean because U mostly occurs as the soluble ion $UO_2(CO_3)_3^{4-}$ and is a conservative element in the ocean.

A_{238U} = 2.5 dpm/kg
A_{234U} = 2.8 dpm/kg

Thorium isotope concentrations are very low because they are particle reactive; they readily "stick" to the solid phase, like many trace metals that are scavenged in the ocean. This chemical property makes thorium isotopes ideal tracers of particle fluxes in the ocean.
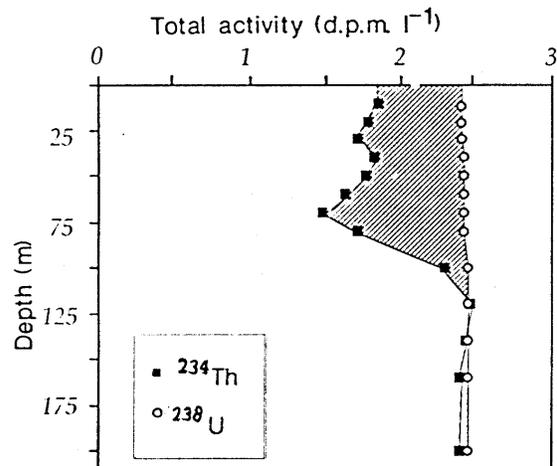
U-238
4.47×10^9 y

U-234
2.48×10^5 y

Pa-234
1.18 m

Th-234
24.1 d

Th-230
7.52×10^4 y
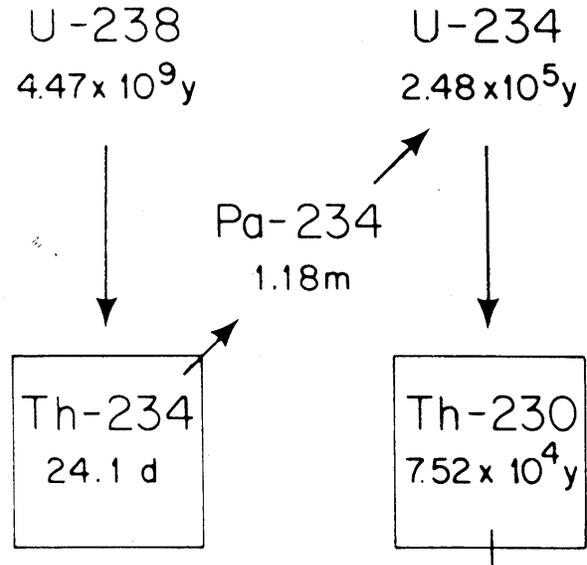
Because of the very different half-lives of ^{234}Th and ^{230}Th, they are useful for tracing particle fluxes in very different locations of the ocean.

- ^{234}Th is depleted form its parent ^{238}U by processes that occur on time scales of months. It turns out this is nearly ideal for particle transport out of the upper ocean
- ^{230}Th is useful as a tracer of deep ocean process and as a tracer of sedimentation rates.

Surface Ocean Particle Flux

^{234}Th is depleted in the upper ocean when compared to the activity expected from secular equilibrium. This is where most particles are created.

The ^{234}Th deficiency is a measure of the thorium removal from the upper ocean by particulate matter. If we assume that the only processes removing Th from the upper ocean are decay and export in the solid phase then:

Total activity (d.p.m l^{-1})

Depth (m)

- ^{234}Th
○ ^{238}U

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At any depth:
^{234}Th change with time = Production - Decay - Removal by particles

$$d[^{234}Th] / dt = [^{238}U]\lambda_{238} - [^{234}Th]\, \lambda_{234} - F^P_{234} \qquad (atoms\ m^{-3}\ d^{-1})$$
$$where,\ F\ is\ particle\ flux$$

multiply by λ_{234} to change concentrations into activities

$$dA^{234} / dt = A^{238}\, \lambda_{234} - A^{234}\, \lambda_{234} - F^{P*}_{234} \qquad (dpm\ m^{-3}\ d^{-1})$$

integrate over the depth of the euphotic zone (h), z=h

$$\frac{d}{dt}\int_{z=0}^{z=h} A_{234}\,dz = \lambda_{234}\int_{z=0}^{z=h}(A_{238} - A_{234})\,dz - \int_{z=o}^{z=h}F^{P*}_{234}\,dz \quad (dpm\ m^{-2}\ d^{-1})$$

The last term in the right side is $F^{P*}_{234}(h) - 0$, which is equal to the particle flux at the base of the euphotic zone

Buessler (1991) compared Particle fluxes calculated by this method with particulate thorium fluxes actually measured by sediment traps deployed in the upper ocean.

The comparison shows a lot of scatter. Either the traps are not reliable to about a factor of three, or the equations do not adequately represent the ^{234}Th dynamics, or some of both.
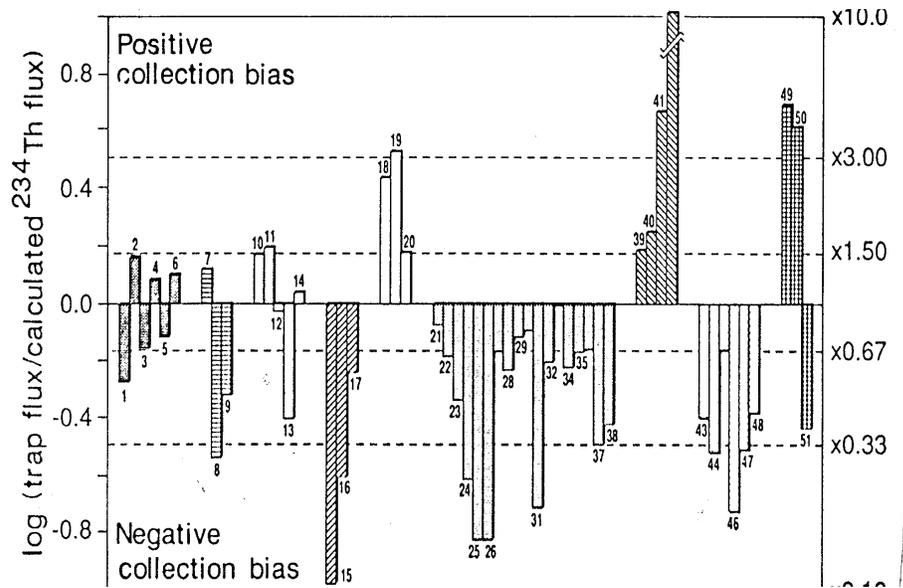
The main possibilities for the discrepancies are:
   (1) Usually there is not enough data to determine the time rate of change so a steady state is assumed. This is probably not true.
   (2) Trap deployments rarely are long enough to cover the mean life of ^{234}Th
   (3) The model assumes all fluxes are vertical
   (4) It is known that particles do not fall directly into the traps if there are currents across the top of the traps
   (5) Particle specific scavenging may effect the scavenging efficiency.

Deep Ocean Particle Fluxes Using ^{230}Th

Sediment Traps
The same method can be used with the isotope pair ^{234}U and ^{230}Th to calibrate sediment trap efficiency in the deep ocean.

Rewriting the integration over the depth equation (above) using ^{234}U and ^{230}Th:

$$\frac{d}{dt}\int_0^h A_{230}dz = \lambda_{230}\int_o^h (A_{234U} - A_{230})dz - \int_0^h F_{230}^{P*}dz$$

At steady state and since the activity of $^{234}U >> ^{230}Th$

$$F_{230}^{P*}(z = h) = \lambda_{230}\int_0^h A_{234U}dz = \lambda_{230}A_{234U}H$$

Where:
H is the height of the water column
$A_{234} = 2800$ dpm m^{-3}
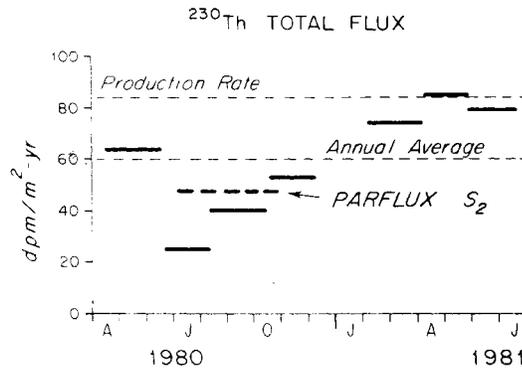$H = 3200$ m
$\lambda_{230} = .693 / (7.5 \times 10^4 yr)$

$A_{234} H \lambda_{230} = 82$ dpm m^{-2} yr^{-1}

Bacon (1984) measured the ^{230}Th in particles of a deep sediment trap (at 3200 m) and compared the result with the calculated flux.

^{230}Th TOTAL FLUX

Total flux of $^{230}Th_{ex}$ measured at 3200 m in the Sargasso Sea from April 1980 to July The PARFLUX S value, shown for comparison, was taken from the 3694-m data of ANDERSON et al. (1983a), corrected by the factor 0.87 for the difference in depth.

 The annual average Th flux measured in traps is about 70 % of the calculated ^{230}Th production rate. Deep sediment traps behave better than those in the energetic surface ocean because of less horizontal currents, but they tend to under trap.

^{230}Th in Marine Sediments

Marine sediments accumulate at rates of $0.1 - 10$ cm kyr^{-1}, thus sediment cores provide a chronology for changes in the ocean over time. ^{230}Th has an ideal half life for determining the age of these sediments for the past 350,000 years:
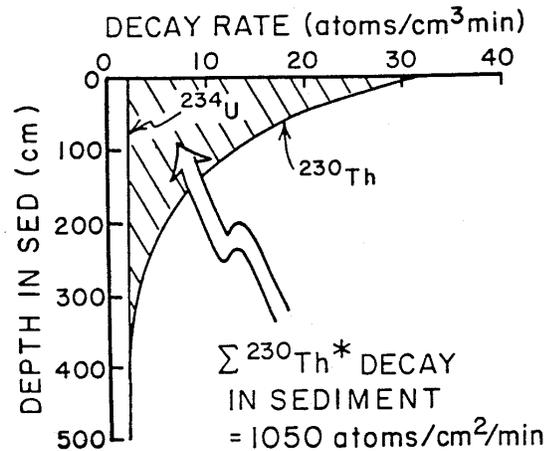
First, the total integrated ^{230}Th activity in the sediments must equal that produced in the water column. Thus, the total flux of ^{230}Th to the sediment is that produced in the water column by ^{238}U decay.

$F^P_{230} = A_{234U} H \lambda_{230}$

where H is the water depth

At steady state, the flux at H is also equal to the integrated decay rate in the sediments at that site:

$$F_{230}^{P} = \lambda_{230}\int_0^\infty A_{230}dz$$

DECAY RATE (atoms/cm^{3}min)

$\Sigma\ ^{230}Th^*$ DECAY IN SEDIMENT = 1050 atoms/cm^2/min

$\eth$

Therefore,

$$A_{234U} H = \int_0^\infty A_{230} dz$$

To determine the Sediment accumulation rate using ^{230}Th depth profiles, one must assume:

A constant sediment accumulation rate
A constant input of Th from above

e.g at a water depth of 3200 meters 82 dpm ^{230}Th accumulates per m^{-2} yr^{-1}.

The total activity must be corrected for the activity of ^{234}U in the sediments. It is only the "unsupported" ^{230}Th that will decrease with time and depth.
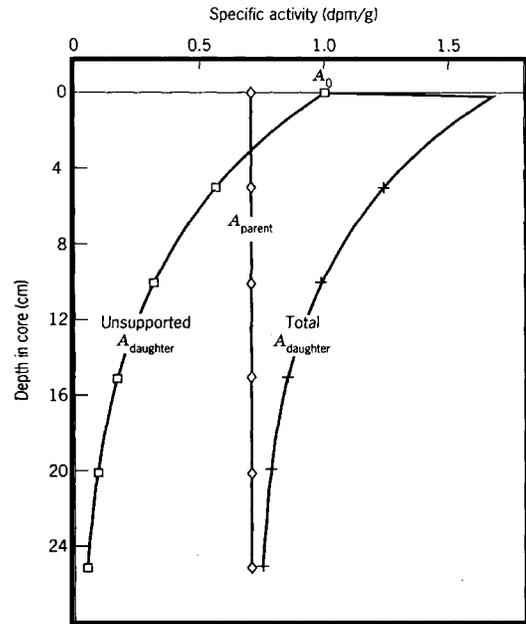
At steady state, the relationship between thorium concentration and depth, z, is related to the sedimentation rate, s (cm yr^{-1}) by:

$$0 = \frac{d\left[^{230}Th\right]}{dt} = s \frac{\left[^{230}Th\right]}{dz} - \lambda_{230}\left[^{230}Th\right]$$
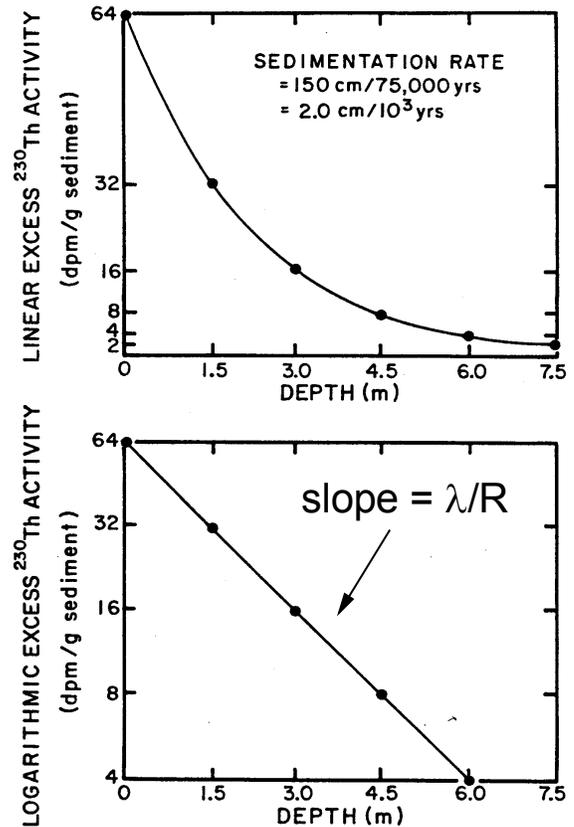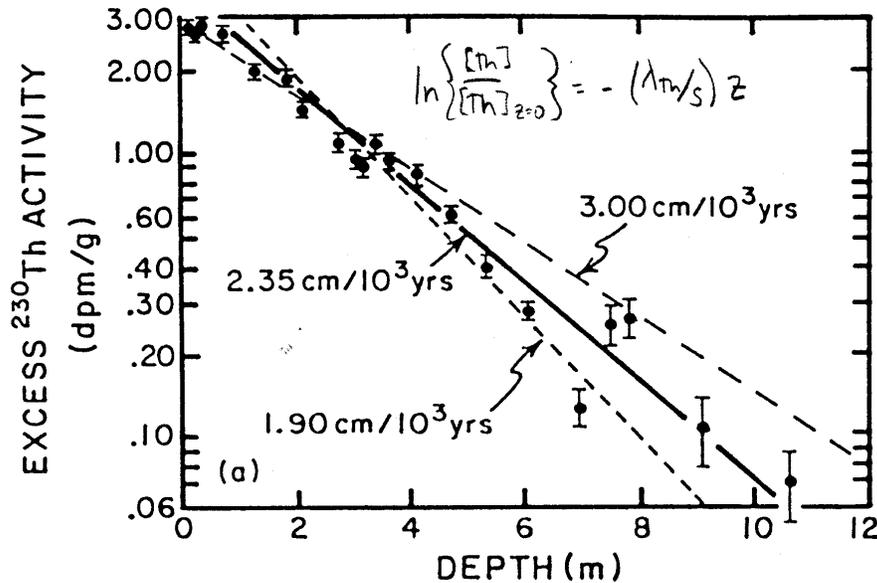
which has the solution

$$A_{230}(z) = A_{230}{}^o \{\exp(- \lambda_{230}/s)\, z\}$$

or

$$\ln (A_{230}) = (- \lambda_{230}/ s)\, z + \ln (A_{230}{}^o)$$

An example of this method is dating of a core from the Caribbean Sea over the top ten meters and a time interval of about 300,000 yrs, (Ku, 1976) is shown below.


SEDIMENTATION RATE
= 150 cm/75,000 yrs
= 2.0 cm/10^3 yrs

slope = λ/R

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$$\ln \left\{ \frac{[Th]}{[Th]_{z=0}} \right\} = - \left(\lambda_{Th}/s \right) z$$

3.00 cm/10³yrs

2.35 cm/10³yrs

1.90 cm/10³yrs

(a)

The solid line is the best fit through the data. Dashed lines indicate the uncertainty in the sedimentation rate from the scatter of the data.

Application of ^{210}Pb for Several Oceanic Processes

In marine sediments, ^{210}Pb has a supported (decay chain of ^{230}Th) and excess component (excess over ^{226}Ra). The excess ^{210}Pb is present at the sediment surface it is scavenged from seawater and the depth to which it can penetrate depends on the sedimentation and the degree of sediment mixing. Mixing processes allow the short-lived excess ^{210}Pb associated with "newer" sediments to penetrate more deeply into the sediment column before it disappears by radioactive decay. Therefore, the ^{210}Pb activity profiles in marine sediments could be used to assess sedimentation rates in high accumulating sediments and bioturbation depths in open ocean sediments.
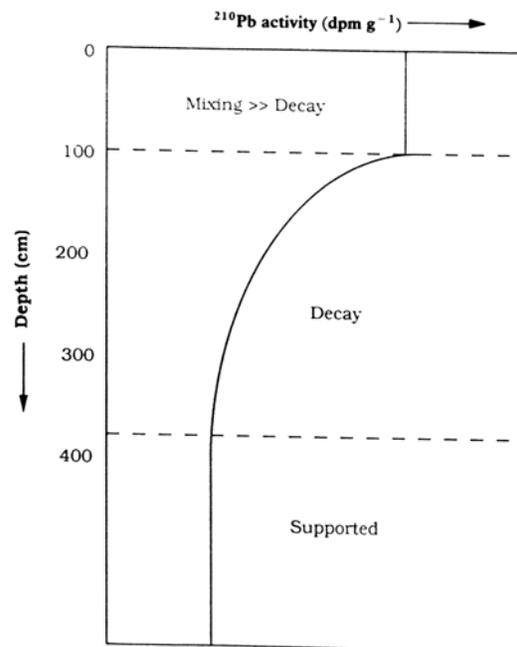
A significant source of ^{210}Pb to the surface oceans is the atmosphere, where it is produced from ^{222}Rn decay. ^{210}Pb is removed from the surface ocean by adsorption on to sinking particles and radioactive decay; it has been shown that concentrations of ^{210}Pb correlate well with particulate fluxes and thus it can be used to estimate export production from the photic zone.

^{14}C Distribution in the Ocean and Ocean Mixing Rates

The ^{14}C/C (or Δ^{14}C) distribution in the deep ocean (pre-bomb) indicates that surface water has more ^{14}C ($\sim$ -50‰) than deep water and that the deep Pacific (-250‰) has less ^{14}C compared to the deep Atlantic (-150‰). The distribution of ^{14}C is hence quite consistent with what we have learned about ocean circulation. The distribution of radiocarbon in the ocean has been used to estimate the ventilation time of the deep sea (how long would on average a parcel of water spend at depth before being up welled and seeing the surface). For this, one must know the ^{14}C/C ratio in the deepwater source when it just formed and the half-life of ^{14}C (5700 years). The Δ^{14}C value of pre-bomb NADW component has been estimate after correction for bomb-derived ^{14}C using tritium data to be -89‰. Similarly, the Δ^{14}C values of other source waters have been determined. From these data and the Δ^{14}C distribution in deep water the ventilation time for each oceanic basing was calculated and determined to be in the range of 500 years for the Atlantic and 1000 years for the Pacific.
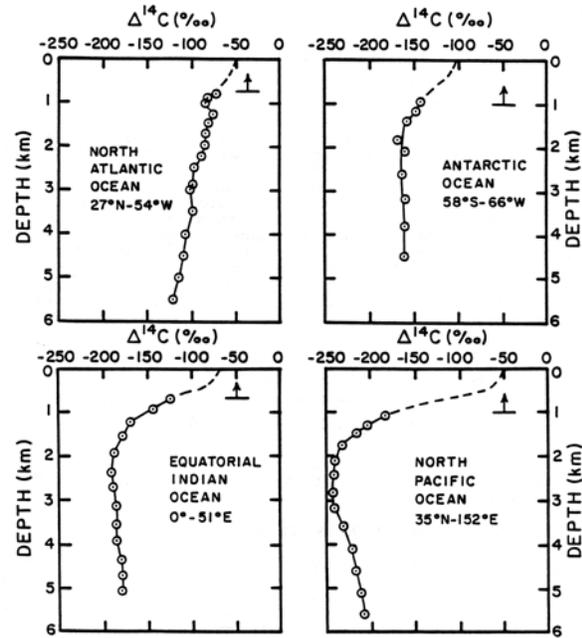
^{222}Radon Isotopes use for Determining Gas Exchange Rates

^{226}Ra is the daughter of ^{230}Th in the ^{238}U decay chain: Ra is much more soluble than Th and exists in solution in the ocean in easily measure quantities. ^{226}Ra decays to a gaseous daughter product ^{222}Rn, which has a 3.85 day half life.

$$^{226}\text{Ra} \quad \rightarrow \quad ^{222}\text{Rn} \quad + \quad \alpha$$
$$(t_{1/2} = 1600 \text{ yr}) \qquad (t_{1/2} = 3.85 \text{ d})$$
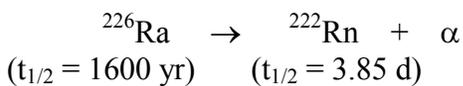
In the upper ocean, ^{222}Rn escapes to the atmosphere; so the activity of ^{222}Rn and ^{226}Ra are not in secular equilibrium – the activity of Rn is less. The change in integrated radon concentration with respect to time should equal the integrated activity (production rate - decay rate) - exchange to the atmosphere

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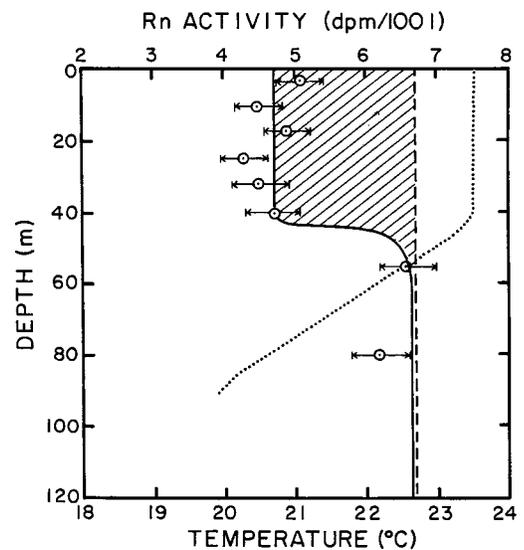
(1)
$$\frac{d\int_{z=0}^{z=\infty}\left[^{222}Rn\right]dz}{dt}=\int_{z=0}^{z=\infty}\lambda_{226}\left[^{226}Ra\right]dz-\int_{z=0}^{z=\infty}\lambda_{222}\left[^{222}Rn\right]dz-F_{z=0}^{Rn}\quad(\text{atoms m}^{-2}\,\text{d}^{-1})$$

(Here I use [ ] to indicate concentration instead of N.)

At steady state:

(2)
$$F_{Rn}=\int_{z=0}^{z=\infty}(A_{226}-A_{222})dz\quad(\text{atoms m}^{-2}\,\text{d}^{-1})$$

but also, form the boundary layer theory:

(3) $F_{Rn} = G_{Rn}\ \{[^{222}Rn]_{surf} - P_{Rn}\ H_{Rn}]\ (\text{atoms m}^{-2}\,\text{d}^{-1})$

Since there is very little Rn in the atmosphere
$[^{222}Rn]_{surf} \gg P_{Rn}\ H_{Rn}$

(4) $F_{Rn} = G_{Rn}\{[^{222}Rn]_{surf}\}$

multiplying eq. (2) and (4) by λ_{222} , to get dpm units, and combining:

(5)
$$G_{Rn}=\frac{\lambda_{222}\int_{0}^{\infty}(A_{226}-A_{222})dz}{A_{222}^{surf}}\quad(\text{m d}^{-1})$$

The mass transfer coefficient is related to the stagnant boundary layer thickness via:

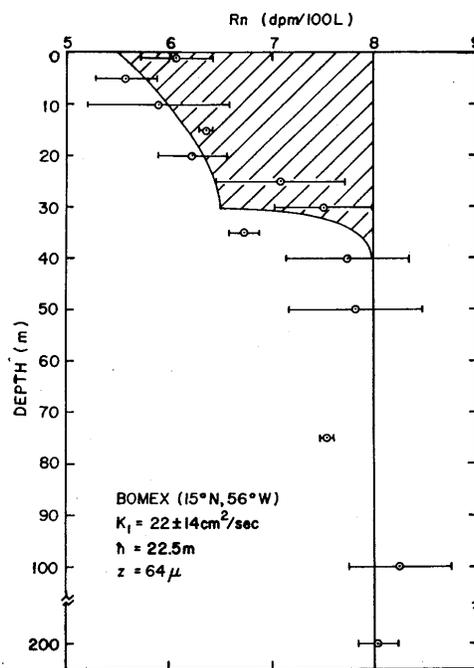$$z = D_{Rn} / G_{Rn}$$

A series of profiles from the Subtropical Atlantic in summer where the mixed layer depth is 30 m is shown on the right.

Wind speed $U_{10} = 7$ m s^{-1}, $G_{Rn} = 1.8$ m d^{-1}; $z = 64\ \mu m$

U_{10} is the wind speed at 10 meters above the ocean surface

Such measurments were used to calculate the gas exchange rate and/or the stagnant film layer thickness.

BOMEX (15°N, 56°W)
$K_1 = 22 \pm 14$ cm^2/sec
$h = 22.5$ m
$z = 64\ \mu$

References

Bacon, M. and R. Anderson (1982) Distribution of thorium isotopes between dissolved and particulate forms in the deep sea, Jour. Geoph. Res, 87, 2045 – 2056.

Bacon, M. et al. (1984) Seasonality in th eflux of natural radionuclides and plutohnium in the deep Sargasso Sea, Deep-Sea Res. , 32, 273 - 286.

Buessler, K.O. (1991) Do upper-ocean sediment traps provide and accurate record of particle flux?, Nature, 353, 420-423.