Radioisotope Tracers

OCN 623 – Chemical Oceanography
23 March 2017

Reading: Emerson and Hedges, Chapter 5, p.153-169

Student Learning Outcomes

At the completion of this class, students should be able to:

1. Explain and use the concepts and equations governing *radioactive decay*

2. Explain the concept of "*secular equilibrium*", and how it relates to oceanographic applications

3. Describe the *common uses* of radioisotopes as oceanic tracers

Outline

- Background info
  - Radioactive decay - concepts and equations
  - Secular equilibrium
  - Matching decay rates with removal rates

- Case studies
  - Ra-226 → Rn-222
    - Air-sea gas exchange
  - U-238 → Th-234
    - Carbon export from the mixed layer via sinking particles

Radioactive Decay

Definitions

Parent – Original radioactive atom

Daughter – The product of a radioactive decay

Decay Chain – A series of radioactive decays:

Parent → Daughter-1 → Daughter-2 → Daughter-3.....

$$N_1 \rightarrow N_2 \rightarrow N_3 \rightarrow N_4....$$

Radioactive decay is a property of the nucleus, and is independent of chemistry, temperature, and pressure

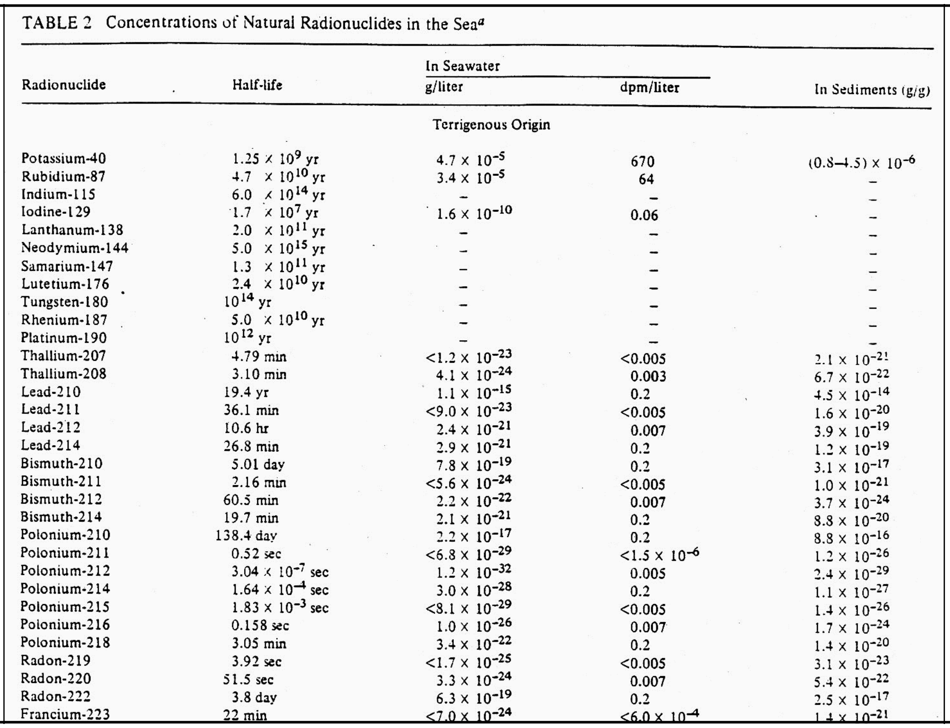
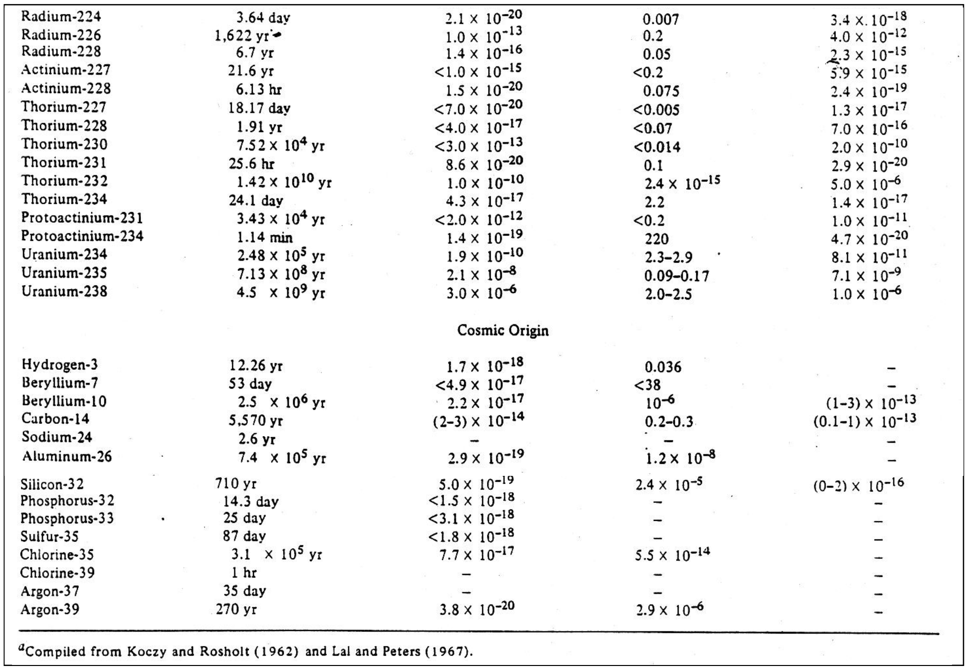


TABLE 2 Concentrations of Natural Radionuclides in the Sea[a]

Radionuclide	Half-life	In Seawater g/liter	In Seawater dpm/liter	In Sediments (g/g)
		Terrigenous Origin		
Potassium-40	1.25×10^{9} yr	4.7×10^{-5}	670	$(0.8\text{–}4.5) \times 10^{-6}$
Rubidium-87	4.7×10^{10} yr	3.4×10^{-5}	64	–
Indium-115	6.0×10^{14} yr	–	–	–
Iodine-129	1.7×10^{7} yr	1.6×10^{-10}	0.06	–
Lanthanum-138	2.0×10^{11} yr	–	–	–
Neodymium-144	5.0×10^{15} yr	–	–	–
Samarium-147	1.3×10^{11} yr	–	–	–
Lutetium-176	2.4×10^{10} yr	–	–	–
Tungsten-180	10^{14} yr	–	–	–
Rhenium-187	5.0×10^{10} yr	–	–	–
Platinum-190	10^{12} yr	–	–	–
Thallium-207	4.79 min	$<1.2 \times 10^{-23}$	<0.005	2.1×10^{-21}
Thallium-208	3.10 min	4.1×10^{-24}	0.003	6.7×10^{-22}
Lead-210	19.4 yr	1.1×10^{-15}	0.2	4.5×10^{-14}
Lead-211	36.1 min	$<9.0 \times 10^{-23}$	<0.005	1.6×10^{-20}
Lead-212	10.6 hr	2.4×10^{-21}	0.007	3.9×10^{-19}
Lead-214	26.8 min	2.9×10^{-21}	0.2	1.2×10^{-19}
Bismuth-210	5.01 day	7.8×10^{-19}	0.2	3.1×10^{-17}
Bismuth-211	2.16 min	$<5.6 \times 10^{-24}$	<0.005	1.0×10^{-21}
Bismuth-212	60.5 min	2.2×10^{-22}	0.007	3.7×10^{-24}
Bismuth-214	19.7 min	2.1×10^{-21}	0.2	8.8×10^{-20}
Polonium-210	138.4 day	2.2×10^{-17}	0.2	8.8×10^{-16}
Polonium-211	0.52 sec	$<6.8 \times 10^{-29}$	$<1.5 \times 10^{-6}$	1.2×10^{-26}
Polonium-212	3.04×10^{-7} sec	1.2×10^{-32}	0.005	2.4×10^{-29}
Polonium-214	1.64×10^{-4} sec	3.0×10^{-28}	0.2	1.1×10^{-27}
Polonium-215	1.83×10^{-3} sec	$<8.1 \times 10^{-29}$	<0.005	1.4×10^{-26}
Polonium-216	0.158 sec	1.0×10^{-26}	0.007	1.7×10^{-24}
Polonium-218	3.05 min	3.4×10^{-22}	0.2	1.4×10^{-20}
Radon-219	3.92 sec	$<1.7 \times 10^{-25}$	<0.005	3.1×10^{-23}
Radon-220	51.5 sec	3.3×10^{-24}	0.007	5.4×10^{-22}
Radon-222	3.8 day	6.3×10^{-19}	0.2	2.5×10^{-17}
Francium-223	22 min	$<7.0 \times 10^{-24}$	$<6.0 \times 10^{-4}$	1.4×10^{-21}



Radium-224	3.64 day	2.1×10^{-20}	0.007	3.4×10^{-18}
Radium-226	1,622 yr	1.0×10^{-13}	0.2	4.0×10^{-12}
Radium-228	6.7 yr	1.4×10^{-16}	0.05	2.3×10^{-15}
Actinium-227	21.6 yr	$<1.0 \times 10^{-15}$	<0.2	5.9×10^{-15}
Actinium-228	6.13 hr	1.5×10^{-20}	0.075	2.4×10^{-19}
Thorium-227	18.17 day	$<7.0 \times 10^{-20}$	<0.005	1.3×10^{-17}
Thorium-228	1.91 yr	$<4.0 \times 10^{-17}$	<0.07	7.0×10^{-16}
Thorium-230	7.52×10^{4} yr	$<3.0 \times 10^{-13}$	<0.014	2.0×10^{-10}
Thorium-231	25.6 hr	8.6×10^{-20}	0.1	2.9×10^{-20}
Thorium-232	1.42×10^{10} yr	1.0×10^{-10}	2.4×10^{-15}	5.0×10^{-6}
Thorium-234	24.1 day	4.3×10^{-17}	2.2	1.4×10^{-17}
Protoactinium-231	3.43×10^{4} yr	$<2.0 \times 10^{-12}$	<0.2	1.0×10^{-11}
Protoactinium-234	1.14 min	1.4×10^{-19}	220	4.7×10^{-20}
Uranium-234	2.48×10^{5} yr	1.9×10^{-10}	2.3–2.9	8.1×10^{-11}
Uranium-235	7.13×10^{8} yr	2.1×10^{-8}	0.09–0.17	7.1×10^{-9}
Uranium-238	4.5×10^{9} yr	3.0×10^{-6}	2.0–2.5	1.0×10^{-6}
		Cosmic Origin		
Hydrogen-3	12.26 yr	1.7×10^{-18}	0.036	–
Beryllium-7	53 day	$<4.9 \times 10^{-17}$	<38	–
Beryllium-10	2.5×10^{6} yr	2.2×10^{-17}	10^{-6}	$(1\text{–}3) \times 10^{-13}$
Carbon-14	5,570 yr	$(2\text{–}3) \times 10^{-14}$	0.2–0.3	$(0.1\text{–}1) \times 10^{-13}$
Sodium-24	2.6 yr	–	–	–
Aluminum-26	7.4×10^{5} yr	2.9×10^{-19}	1.2×10^{-8}	–
Silicon-32	710 yr	5.0×10^{-19}	2.4×10^{-5}	$(0\text{–}2) \times 10^{-16}$
Phosphorus-32	14.3 day	$<1.5 \times 10^{-18}$	–	–
Phosphorus-33	25 day	$<3.1 \times 10^{-18}$	–	–
Sulfur-35	87 day	$<1.8 \times 10^{-18}$	–	–
Chlorine-35	3.1×10^{5} yr	7.7×10^{-17}	5.5×10^{-14}	–
Chlorine-39	1 hr	–	–	–
Argon-37	35 day	–	–	–
Argon-39	270 yr	3.8×10^{-20}	2.9×10^{-6}	–

[a] Compiled from Koczy and Rosholt (1962) and Lal and Peters (1967).

Types of Radioactive Decay

For this discussion we are really only going to concern ourselves with three types of radioactive decay:

Alpha (α) decay: Emission of a helium nucleus, which contains two protons and two neutrons (but no electrons!!!).

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He + \text{neutrinos } (\nu)$$

Beta (β) decay: Emission of a high energy electron

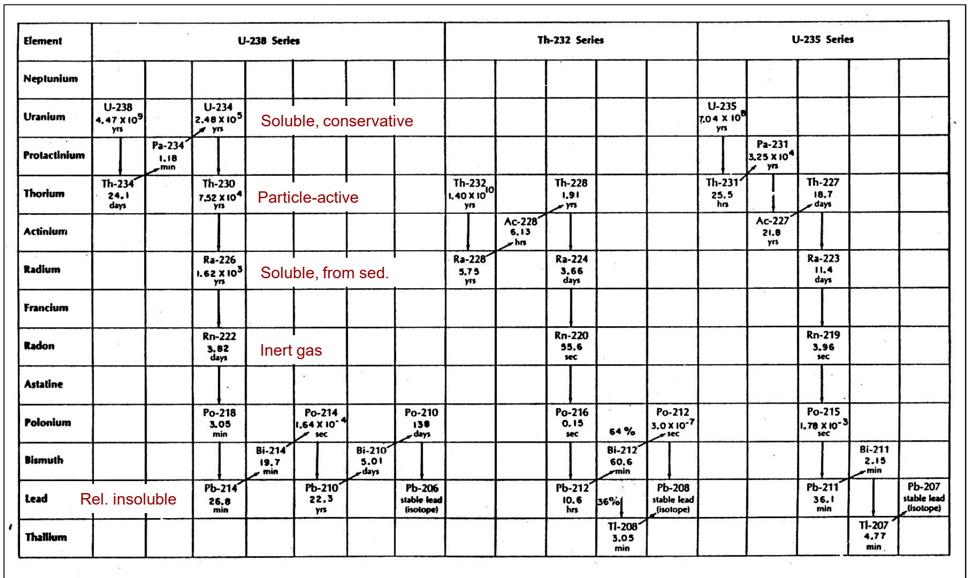
$$^{14}_{7}N + \text{neutron} \rightarrow {}^{14}_{6}C + \beta + \nu$$

Gamma (γ) Decay: Conversion of nuclear energy to electromagnetic energy, note that the atomic number *does not change*.

$$^{7}_{4}Be \rightarrow {}^{7}_{4}Be + \gamma$$

Excited state

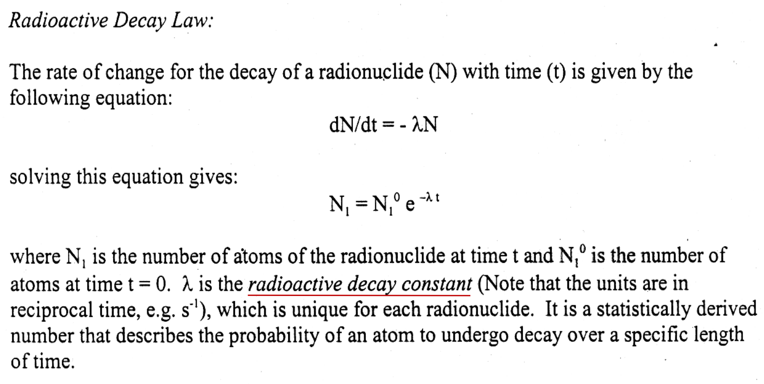
Ground state



Element	U-238 Series							Th-232 Series					U-235 Series				
Neptunium																	
Uranium	U-238 4.47×10^{9} yrs		U-234 2.48×10^{5} yrs	Soluble, conservative									U-235 7.04×10^{8} yrs				
Protactinium		Pa-234 1.18 min												Pa-231 3.25×10^{4} yrs			
Thorium	Th-234 24.1 days		Th-230 7.52×10^{4} yrs	Particle-active				Th-232 1.40×10^{10} yrs		Th-228 1.91 yrs			Th-231 25.5 hrs		Th-227 18.7 days		
Actinium									Ac-228 6.13 hrs					Ac-227 21.8 yrs			
Radium			Ra-226 1.62×10^{3} yrs	Soluble, from sed.				Ra-228 5.75 yrs		Ra-224 3.66 days					Ra-223 11.4 days		
Francium																	
Radon			Rn-222 3.82 days	Inert gas						Rn-220 55.6 sec					Rn-219 3.96 sec		
Astatine																	
Polonium			Po-218 3.05 min		Po-214 1.64×10^{-4} sec		Po-210 138 days			Po-216 0.15 sec	64 %	Po-212 3.0×10^{-7} sec			Po-215 1.78×10^{-3} sec		
Bismuth				Bi-214 19.7 min		Bi-210 5.01 days					Bi-212 60.6 min					Bi-211 2.15 min	
Lead	Rel. insoluble		Pb-214 26.8 min		Pb-210 22.3 yrs		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	

Figure 4-1. Chart showing the decay chain of the uranium and thorium series isotopes and the half-lives of each isotope. Alpha decays are shown by the vertical arrows and beta decays by the diagonal arrows.

Radioactive Decay Equations



Radioactive Decay Law:

The rate of change for the decay of a radionuclide (N) with time (t) is given by the following equation:

$$dN/dt = -\lambda N$$

solving this equation gives:

$$N_1 = N_1^0 e^{-\lambda t}$$

where N_1 is the number of atoms of the radionuclide at time t and N_1^0 is the number of atoms at time t = 0. λ is the *radioactive decay constant* (Note that the units are in reciprocal time, e.g. s^{-1}), which is unique for each radionuclide. It is a statistically derived number that describes the probability of an atom to undergo decay over a specific length of time.

Half Life

The half life is defined as the time required for half of the atoms initially present to decay.

After one half life: $N/N_o = ½$

Since $N = N_o e^{-\lambda t}$:

$$\lambda t_{1/2} = -\ln(1/2) = 0.693$$

or….

$$\boxed{t_{1/2} = \frac{0.693}{\lambda}}$$

Radioactive Activity

In oceanography, researchers rarely discuss radionuclides in terms of atoms. Rather, due to the measurement methods that we employ, we discuss radionuclides in terms of activities or disintegration rates. The activity, A, of a radionuclide is simply:

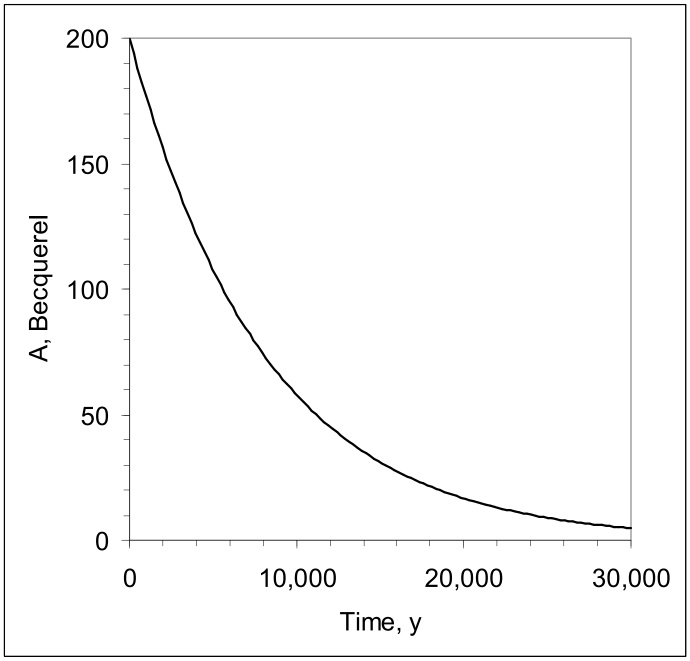
$$A = N\lambda$$

Units of activity in oceanography are typically given in disintegrations per minute, dpm, and disintegrations per second, dps (1 dps = 1 Becquerel or 2.7 x 10^{-10} Curies).

Group Calculation

The figure shows the change in activity of a radioisotope.

What is the decay constant for this radioisotope?



Group Calculation

The figure shows the change in activity of a radioisotope.

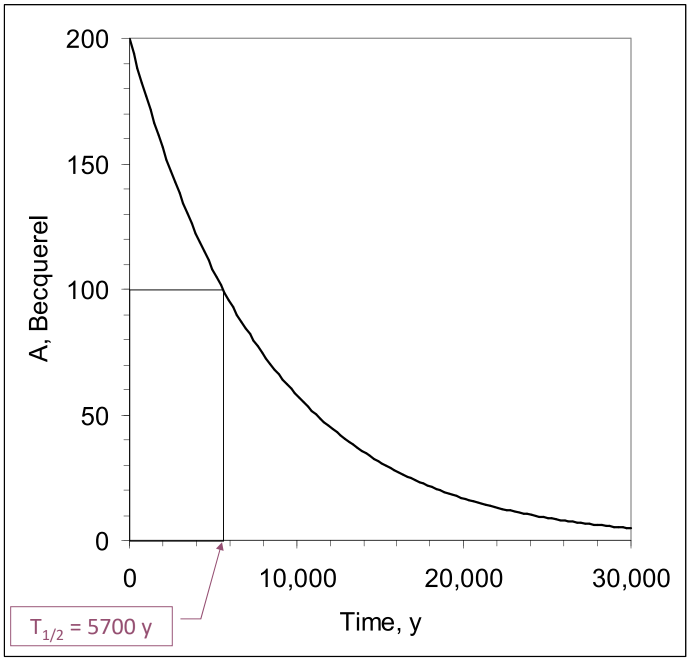
What is the decay constant for this radioisotope?

$T_{1/2} = 0.693/\lambda$

$\lambda = 0.693/T_{1/2}$

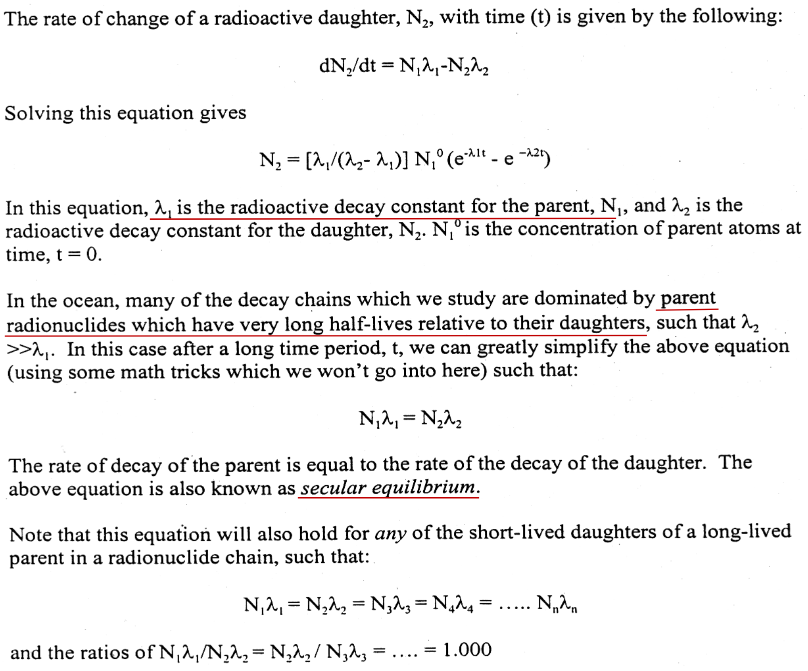
$\lambda = 0.693 / 5700\ y = 1.22 \times 10^{-4}\ y^{-1}$

The radioisotope is C-14



$T_{1/2}$ = 5700 y

Secular Equilibrium



The rate of change of a radioactive daughter, N_2, with time (t) is given by the following:

$$dN_2/dt = N_1\lambda_1 - N_2\lambda_2$$

Solving this equation gives

$$N_2 = [\lambda_1/(\lambda_2 - \lambda_1)]\, N_1^0\, (e^{-\lambda 1t} - e^{-\lambda 2t})$$

In this equation, λ_1 is the radioactive decay constant for the parent, N_1, and λ_2 is the radioactive decay constant for the daughter, N_2. N_1^0 is the concentration of parent atoms at time, t = 0.

In the ocean, many of the decay chains which we study are dominated by parent radionuclides which have very long half-lives relative to their daughters, such that $\lambda_2 >> \lambda_1$. In this case after a long time period, t, we can greatly simplify the above equation (using some math tricks which we won't go into here) such that:

$$N_1\lambda_1 = N_2\lambda_2$$

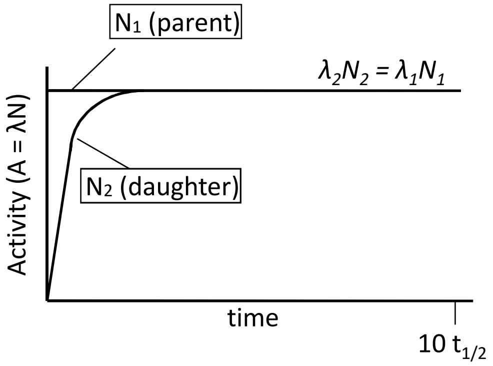
The rate of decay of the parent is equal to the rate of the decay of the daughter. The above equation is also known as *secular equilibrium*.

Note that this equation will also hold for *any* of the short-lived daughters of a long-lived parent in a radionuclide chain, such that:

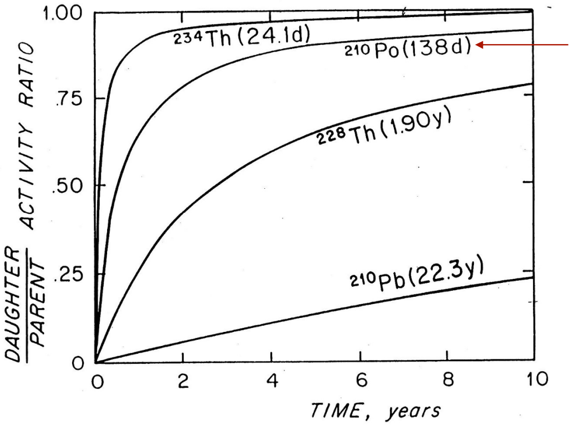
$$N_1\lambda_1 = N_2\lambda_2 = N_3\lambda_3 = N_4\lambda_4 = \ldots\ldots N_n\lambda_n$$

and the ratios of $N_1\lambda_1/N_2\lambda_2 = N_2\lambda_2 / N_3\lambda_3 = \ldots. = 1.000$

Secular Equilibrium

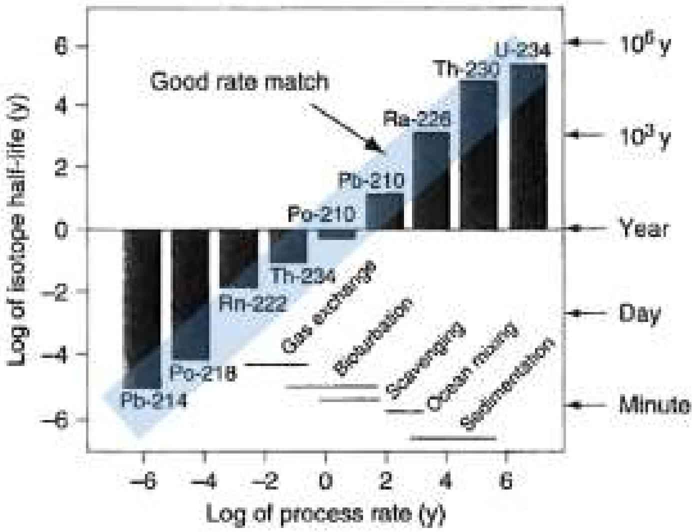


The longer the half-life, the longer it takes to achieve a daughter/parent ratio of 1



Name of parent

Need to match the parent half-life with the time-scale of the process being studied



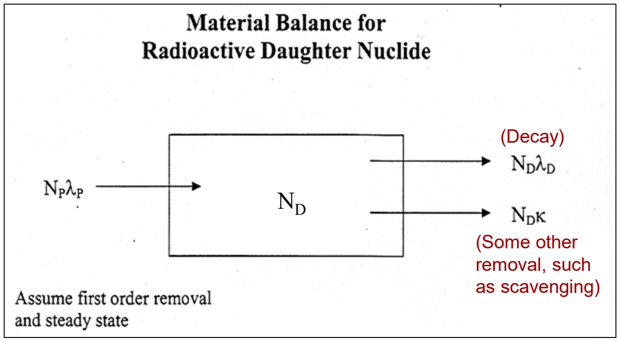
The relation between the half-life of a radioisotope and the characteristic time-scale for marine processes.

The shaded area indicates the range where the two life-times are a good match.

Emerson & Hedges (2008)

$$\boxed{\lambda_2 N_2 = \lambda_1 N_1}$$

- This equation for secular equilibrium assume no other source and no other removal mechanism. Nevertheless, we know that this is generally not the case in the ocean.
- However, this is what makes radionuclides so useful!
- For example, what if the daughter nuclide is removed by processes other than decay (*e.g.*, scavenging)?



$$\overset{A_P}{\cancel{\lambda_P N_P}} = \overset{A_D}{\cancel{\lambda_D N_D}} + \kappa N_D$$

κ = removal constant

Multiply by λ_D: $\lambda_D A_P = \lambda_D A_D + \kappa A_D$

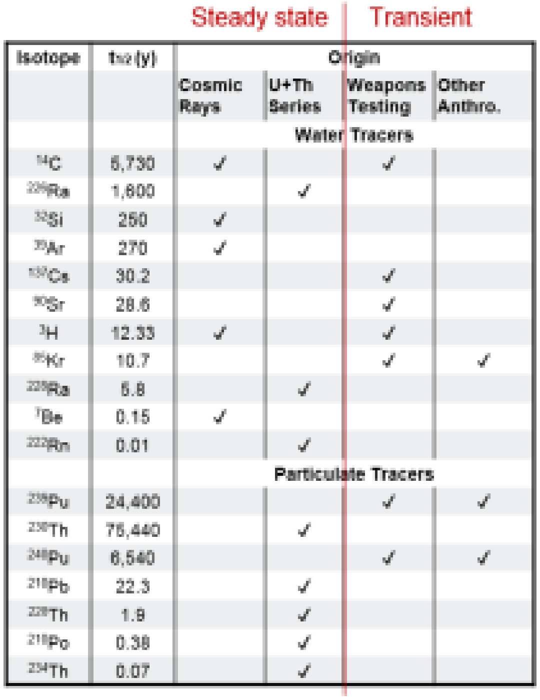
$$\kappa = \lambda_D\left[\underline{(A_P / A_D)} - 1\right]$$

Scavenging residence (turnover) *time* = $1/\kappa$

Case Studies

Radio-isotopes that have been used in Oceanography:

These tracers have a range of origins, chemistries and half lives



Isotope	$t_{1/2}$ (y)	Origin			
		Cosmic Rays	U+Th Series	Weapons Testing	Other Anthro.
		Water Tracers			
^{14}C	5,730	✓		✓	
^{226}Ra	1,600		✓		
^{32}Si	250	✓			
^{39}Ar	270	✓			
^{137}Cs	30.2			✓	
^{90}Sr	28.6			✓	
^{3}H	12.33	✓		✓	
^{85}Kr	10.7			✓	✓
^{228}Ra	5.8		✓		
^{7}Be	0.15	✓			
^{222}Rn	0.01		✓		
		Particulate Tracers			
^{239}Pu	24,400			✓	✓
^{230}Th	75,440		✓		
^{240}Pu	6,540			✓	✓
^{210}Pb	22.3		✓		
^{228}Th	1.9		✓		
^{210}Po	0.38		✓		
^{234}Th	0.07		✓		

Ra-226 → Rn-222 Air-Sea Gas Exchange

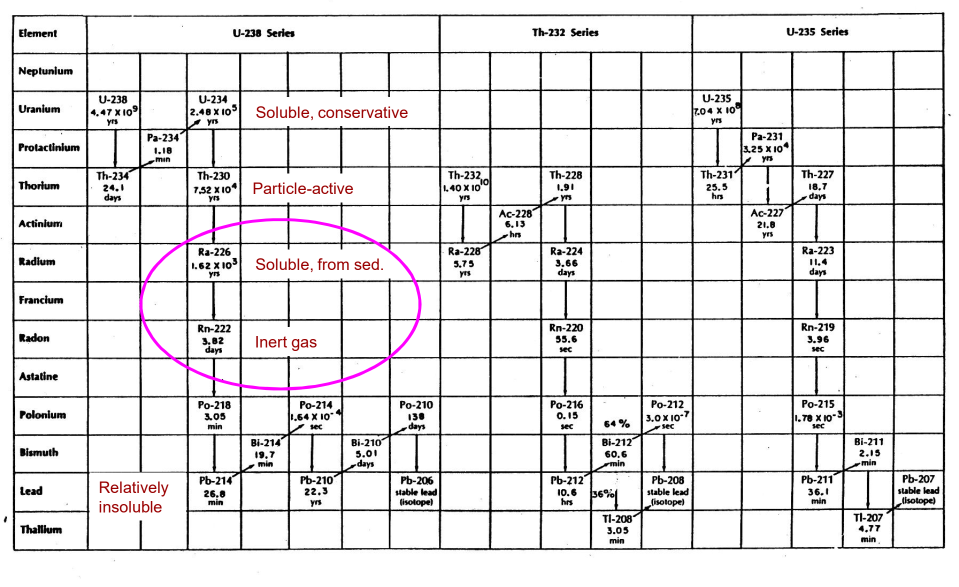
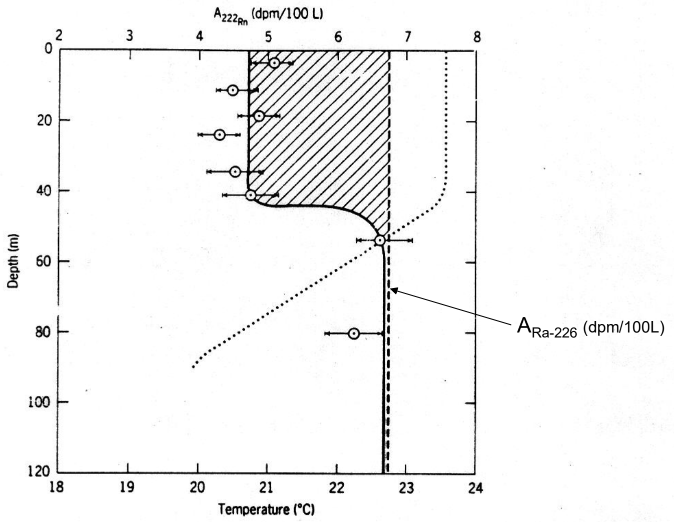


Figure 4-1. Chart showing the decay chain of the uranium and thorium series isotopes and the half-lives of each isotope. Alpha decays are shown by the vertical arrows and beta decays by the diagonal arrows.



A_{Ra-226} (dpm/100L)

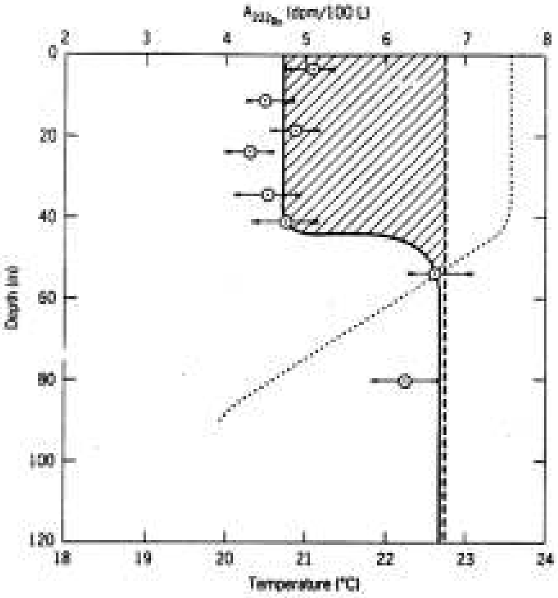
FIGURE 28.16. A_{222Rn} as a function of depth in the Atlantic Ocean at 24°S 35°W. The activity expected if no radon were escaping to the atmosphere is shown by the dashed line. The difference between this equilibrium value and the observed value is a measure of the amount of radon lost to the atmosphere and is shown by the shaded area. The dotted line is the temperature profile at this station which defines the depth of the mixed layer. *Source*: From W. S. Broecker and T.-H. Peng, reprinted with permission from *Tellus*, vol. 26, p. 30, copyright © 1974 by Munksgaard International Publishers, Ltd., Copenhagen, Denmark.

Group Discussion

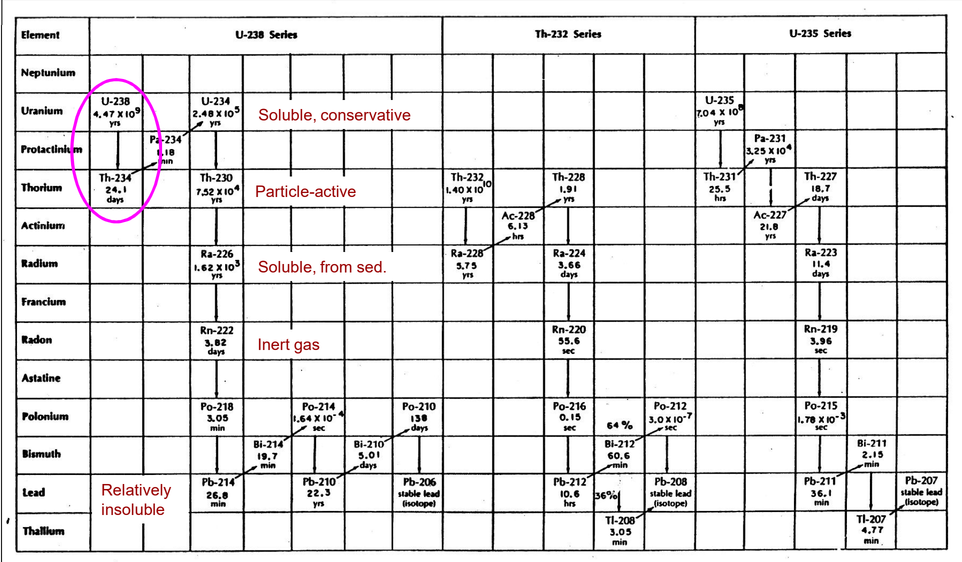
The half-life of Rn-222 is 3.8 days.

What would the $A_{Rn\text{-}222}$ distribution look like if the wind speed doubled for 1 day?

Why???



U-238 → Th-234 Carbon Export from the Mixed Layer



Element	U-238 Series							Th-232 Series					U-235 Series				
Neptunium																	
Uranium	U-238 4.47 X 10^9 yrs		U-234 2.48 X 10^5 yrs	Soluble, conservative									U-235 7.04 X 10^8 yrs				
Protactinium		Pa-234 1.18 min												Pa-231 3.25 X 10^4 yrs			
Thorium	Th-234 24.1 days		Th-230 7.52 X 10^4 yrs	Particle-active				Th-232 1.40 X 10^{10} yrs		Th-228 1.91 yrs			Th-231 25.5 hrs		Th-227 18.7 days		
Actinium									Ac-228 6.13 hrs					Ac-227 21.8 yrs			
Radium			Ra-226 1.62 X 10^3 yrs	Soluble, from sed.				Ra-228 5.75 yrs		Ra-224 3.66 days					Ra-223 11.4 days		
Francium																	
Radon			Rn-222 3.82 days	Inert gas						Rn-220 55.6 sec					Rn-219 3.96 sec		
Astatine																	
Polonium			Po-218 3.05 min		Po-214 1.64 X 10^{-4} sec		Po-210 138 days			Po-216 0.15 sec	64 %	Po-212 3.0 X 10^{-7} sec			Po-215 1.78 X 10^{-3} sec		
Bismuth				Bi-214 19.7 min		Bi-210 5.01 days					Bi-212 60.6 min					Bi-211 2.15 min	
Lead	Relatively insoluble		Pb-214 26.8 min		Pb-210 22.3 yrs		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	

Figure 4-1. Chart showing the decay chain of the uranium and thorium series isotopes and the half-lives of each isotope. Alpha decays are shown by the vertical arrows and beta decays by the diagonal arrows.

Th-234 in the Upper Ocean

U-238 → Th-234 → Pa-234

Particles that remove Th can also remove other particle-active materials (*e.g.*, POC)

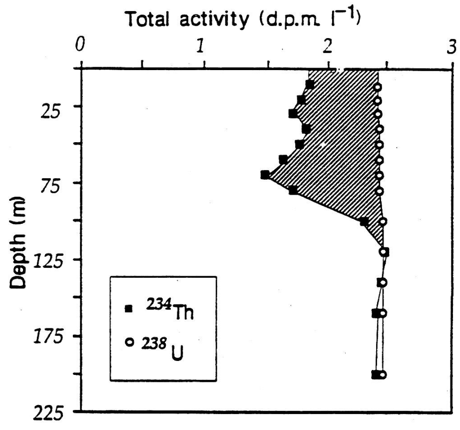


FIG. 1 Typical profile of ^{234}Th in the upper open ocean. Shaded area represents disequilibrium between total ^{234}Th and ^{238}U. Data taken from VERTEX 3 (ref. 11).

This profile integrates removal processes over a several-week period (a function of the decay rates)

How to Calculate ^{234}Th Export on Sinking Particles

U-238 → Th-234 → Pa-234

$$\frac{dN_{^{234}Th}}{dt} = \underset{\text{Production}}{N_{^{238}U}\lambda_{238}} - \underset{\text{Decay}}{N_{^{234}Th}\lambda_{234}} - \underset{\text{Removal}}{\kappa N_{^{234}Th}} \underset{\text{Physical processes}}{\pm \nu}$$

$$= A_{238} - A_{234} - \kappa N_{^{234}Th} \pm \nu$$

- Multiply by λ_{234} to convert to ^{234}Th activity
- Assume steady state: $dA_{234}/dt = 0$
- Assume negligible advection and diffusion ($v = 0$)

$$\frac{dA_{234}}{dt} = 0 = (A_{238} - A_{234})\lambda_{234} - \kappa A_{234}$$

$$\kappa A_{234} = (A_{238} - A_{234})\lambda_{234}$$

← Removal rate (dpm L^{-1} d^{-1})

How to calculate ^{234}Th flux:

$$\underset{\text{dpm m}^{-2}\text{ d}^{-1}}{\text{Flux}} = \underbrace{\kappa A_{234}}_{\text{Removal rate}}\underset{\text{Depth of mixed layer}}{z} = (A_{238} \underset{\text{dpm L}^{-1}}{-} A_{234})\ \underset{\text{d}^{-1}}{\lambda_{234}}\ \ \underset{\text{m}}{z}\ \ \underset{\text{L m}^{-3}}{10^{3}}$$

How to calculate flux of any element or compound in the particles:

Multiply ^{234}Th flux by the ratio (in the particles) of ^{234}Th to the species of interest

e.g.: C flux = ^{234}Th flux * $(\text{C} / {}^{234}\text{Th})_{\text{particle}}$

Buesseler, Benitez-Nelson et al. (2006) An assessment of particulate organic carbon to thorium-234 ratios in the ocean and their impact on the application of ^{234}Th as a POC flux proxy. *Marine Chemistry* 100: 213–233