

RADIOACTIVITY IN THE MARINE ENVIRONMENT: URANIUM-THORIUM DECAY SERIES

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ABSTRACT

Natural and anthropogenic radionuclides are used to study a suite of environmental processes. Yet their applications in aquatic systems are hindered by a general lack of knowledge regarding the underlying concepts of radioactivity, the occurrence of radionuclides in ecosystems, and the equations used to describe their decay mechanisms in environmentally applicable ways. The goal of this lecture is to provide upper level undergraduate and graduate students with a basic understanding of how the naturally occurring uranium-thorium radioactive decay series can be used to address a range of environmentally relevant questions in marine systems. The lecture begins with a brief introduction to uranium-thorium series decay patterns and their distribution in the marine environment. The remaining lecture focuses on four case studies that cover a range of applications where uranium-thorium series radionuclides are used and includes: scavenging, air-sea gas exchange, tracing groundwater, and sedimentation/age dating. This lecture is the second of a four-part lecture series on radionuclides in the marine environment.

SLIDES

- 1) The overarching goal of this lecture is to provide a basic understanding of how naturally occurring uranium-thorium series radionuclides can be used in the marine environment to investigate a variety of processes. The lecture begins with a brief introduction to uranium-thorium series decay patterns and their distribution in the marine environment. The remaining lecture focuses on four case studies that cover a range of applications where uranium-thorium series radionuclides are used and includes: scavenging, air-sea gas exchange, tracing groundwater, and sedimentation/age dating.
- 2) Why study marine radionuclides? Radionuclides can be used as clocks to study key processes and rates in the ocean. They are ubiquitous, relatively easy to measure, and have a wide range of half lives spanning seconds to billions of years. One of the classic introductory texts on this topic is *Tracers in the Sea* by Broecker and Peng (1982) (Also available online at: http://www.ldeo.columbia.edu/~broecker/Home_files/TracersInTheSea_searchable.pdf). This text describes a general introduction to marine radioactivity and a suite of basic applications. While dated, the underlying approach remains the same.
- 3) There are three main sources of radionuclides to the environment and they are loosely classified as the naturally occurring U-Th series radionuclides, naturally occurring cosmogenic radionuclides, and radionuclides produced by anthropogenic processes. Some radionuclides have both cosmogenic and artificial sources (e.g., ^3H and ^{14}C). Note that other primordial radionuclides exist as well, such as ^{40}K , but are less commonly used in marine applications. Radionuclides enter the ocean via both point and non-point sources and their distributions are controlled by their biological and chemical reactivity and half lives. The goal of this lecture is to introduce students to using naturally occurring radioisotopes, specifically the U-Th decay series, to gauge marine processes.
- 4) For U-Th series radionuclides, the parent radionuclides (^{238}U , ^{235}U and ^{232}Th) are very long lived and are essentially considered “stable” for most environmental applications. The colors depict the “reactivity” of each radionuclide (both chemical and biological) in marine systems. Note that Astatine and Bismuth are depicted in white as it is unclear what their reactivity is in seawater. Downward arrows represent alpha (α) decay and diagonal arrows represent beta (β) decay.

- 5) Here is a schematic diagram of radioactive decay (horizontal arrows) and typical transport processes in the ocean and atmosphere (Adapted from Rutgers van der Loeff (2014a)). Particle reactive radionuclides (thorium, lead, and polonium) are tracers of “scavenging” processes (Goldberg, 1954) and include particle flux and export from surface to depth, and mixing in bottom sediments. Conservative tracers (uranium and radium) are tracers of physical processes and include horizontal and vertical mixing as well as dilution. Other tracers are used as point sources, such as radium for groundwater and radon for gas exchange. The half life for radioactive decay gauges processes that can be traced and range from days (^{224}Ra) and weeks (^{234}Th) to decades (^{210}Pb) and millennia (^{234}U) according to their mean life.
- 6) Radionuclides have a long history of being used to trace processes in the marine environment.
- 7) In order to address oceanographic questions using radionuclides, one must first understand three basic components of the radioisotope to be used: Source, biogeochemistry, and half life. The behavior of the radionuclide must then be described using a model and there must be an appropriate analytical technique to measure the radionuclide of interest within reasonable errors (dependent on the question).
- 8) The remaining lecture focuses on four case studies where U-Th decay series radionuclides are used: Scavenging, air-sea gas exchange, tracing groundwater, and sedimentation/age dating. We focus in more detail on scavenging so that one can have a better appreciation of how the radionuclide pairs are developed and used with various models to investigate major oceanographic research questions.
- 9) Many elements in seawater are particle reactive and scavenge onto particles that subsequently sink through the water column. Here, scavenging includes both biological uptake and accumulation and surface adsorption. Particle size and shape are key factors as they influence surface area and, in the open ocean, biological productivity is the major source of particles to the water column.
- 10) Why do we care about scavenging? The biological pump is responsible for the uptake of atmospheric CO_2 and the conversion of carbon from a gaseous phase into particulate form. These particles not only transfer carbon and nutrients to depth, but other particle reactive compounds, such as trace metals (iron and mercury) and organic compounds, such as polychlorinated biphenyls (PCBs).
- 11) A compilation of particle reactive elements in seawater is depicted. Concentrations that increase with depth are diagnostic of particle scavenging and biological uptake and remineralization/regeneration with increasing depth.
- 12) Uranium is soluble in seawater and repeated measurements demonstrate that in oxic systems, uranium is conservative and varies linearly with salinity in the open ocean. As such, measurements of salinity provide quick and easy accurate estimates of the parent radionuclide, U, in marine systems.
- 13) ^{238}U - ^{234}Th disequilibria is a common method used to investigate scavenging. Unlike U (green circles), Th (red circles) is very particle (yellow circles) reactive. ^{234}Th has a half life that is on the same time scale as biologically mediated particle formation (e.g., days to months). Once ^{234}Th is produced via alpha decay from ^{238}U , ^{234}Th rapidly scavenges onto particles. When those particles sink, they carry ^{234}Th with it.
- 14) We can model U-Th disequilibria using the case of the radioactive daughter (see Lecture 1, Radioactivity in the Marine Environment: Understanding the Basics of Marine Radioactivity). In

the simplest sense, the solution to the differential equation is solved using the Bateman Equations.

- 15) When the parent, ^{238}U ($t_{1/2} = 4.5 \times 10^9$ y) is much longer lived relative to the daughter, ^{234}Th ($t_{1/2} = 24.1$ d), the number of parent atoms is essentially constant and the activities, $A (= N\lambda)$, are the same in a closed system.
- 16) Evidence for ^{234}Th scavenging was first described by Bhat et al. (1969), but was not really applied as a tracer of scavenging processes until the work of Coale and Bruland (1985). In a closed system the $^{234}\text{Th}:$ ^{238}U activity ratio should be 1. In this case, the $^{234}\text{Th}:$ ^{238}U ratio is significantly less than 1 in the upper 100 m, corresponding to a peak in pigment concentrations (used here as an analog for biomass/particles). ^{234}Th is preferentially scavenged onto particles and removed when particles sink to deeper depths. Note that the $^{234}\text{Th}:$ ^{238}U ratio increases above 1 between 100-150 m. Here, ^{234}Th carried to depth by sinking particles is remineralized (released to the dissolved phase with particle breakdown). This results in ^{234}Th being in excess of its parent, ^{238}U , at depth.
- 17) Indeed, the magnitude of disequilibrium is easily observed between high and low particle fluxes to depth in two very different biological regimes in the Pacific Ocean.
- 18) We can model ^{238}U - ^{234}Th radioactive disequilibria using a simple box model, where the arrows depict production (from ^{238}U decay) and removal via ^{234}Th radioactive decay and scavenging onto particles. In this case, scavenging is parameterized as a first order removal process with a scavenging coefficient, k .
- 19) Assuming steady state on time scales of the mean life of the radionuclide and minimal physical processes (e.g., advection and diffusion), we can calculate the vertical flux of ^{234}Th through a specific depth horizon. Remember that ^{238}U can be calculated from salinity (see slide 12) or determined more precisely using other analytical methods. The activity of ^{234}Th is directly measured at specific depths in the water column. In many instances, the vertical flux at a specific depth horizon (typically 100 m, 150 m, or depth of the euphotic zone) is calculated using trapezoidal integration.
- 20) The application of $^{234}\text{Th}:$ ^{238}U disequilibria to scavenging processes can be expanded to multiple boxes by measuring ^{234}Th in discrete size classes (e.g., dissolved versus small versus large particles) within a given depth interval of interest. Net movement between boxes can only be determined with one isotope. By measuring multiple isotopes of the same element (e.g., ^{228}Th and ^{230}Th) within various compartments, forward (k_1) and reverse (k_{-1}) rates can also be determined.
- 21) Once the vertical ^{234}Th flux is determined, we can convert vertical ^{234}Th fluxes into vertical element/compound fluxes to the depth of interest using the element (or compound) to ^{234}Th ratio on sinking particles across that same depth horizon.
- 22) It is critical, however, to use the element (or compound) to ^{234}Th ratio measured at the *depth horizon of interest* for the conversion of ^{234}Th vertical fluxes into other chemical or compound fluxes as differences in biogeochemical reactivity may differ between ^{234}Th and the element (or compound) of interest. Major issues include how to define “sinking” particles and their collection mechanisms.
- 23) This is a transect of total ^{234}Th measurements across the Atlantic Ocean from the Antarctic to the Arctic Oceans. In this figure the average activity of ^{238}U is ~ 2.5 dpm L^{-1} or ~ 43 mBq Kg^{-1} . ^{234}Th measurements have become routine and allow for high temporal and spatial resolution of

particle scavenging (low ^{234}Th , colder colors, blue circles) and remineralization (high ^{234}Th , warm colors, red circles). This figure demonstrates that scavenging can occur in both surface waters, due to biological activity, and bottom waters, due to resuspension or plumes near hydrothermal vents. Remineralization typically occurs in deeper waters underlying high productivity regions, but this is not always apparent in single transects as waters may be advected from elsewhere. This data was collected as part of the GEOTRACES Program (<http://www.egeotraces.org/>).

- 24) Such high resolution ^{234}Th : ^{238}U disequilibria data can now be used to determine particulate carbon export across space and time. In this example, data from the preceding figure was used to separate the Atlantic Ocean into latitudinal regimes and compared to sinking carbon fluxes from previous studies across different seasons. Note that error bars reflect the variety of methods used to determine carbon flux in each study (e.g., multiple stations, particle sizes, models used, etc.). Higher carbon fluxes at 10-20°N are associated with Amazon River discharge and higher carbon fluxes at 50-60°N in the sup-polar region are associated with greater biological activity. Seasonality in carbon fluxes are most readily apparent in the temperate region and are associated with enhanced biological production that occurs during the North Atlantic bloom.
- 25) Now that we understand how to develop and apply a radionuclide pair to answer specific questions, we can use similar constructs to investigate other processes, such as air-sea gas exchange. Air-sea gas exchange is a complicated process controlled by a variety of physical mixing processes that vary in timescale from seconds to years. Yet, gas exchange plays a critical role in our understanding of processes ranging from greenhouse gas related climate change (CO_2 , dimethyl sulfide (DMS)) to ocean oxygenation.
- 26) Here we use another radionuclide pair in the U-Th series decay chain, ^{222}Rn ($t_{1/2} = 3.8$ days) and ^{226}Ra ($t_{1/2} = 1600$ y). Given the differences in half lives, activities of ^{226}Ra and ^{222}Rn should be in secular equilibrium. However, ^{226}Ra is mostly conservative in seawater, while ^{222}Rn is a gas. As such, there is ^{226}Ra : ^{222}Rn disequilibria caused by ^{222}Rn degassing to the atmosphere in the surface ocean. We can therefore develop a very similar model to the one used for ^{234}Th : ^{238}U , where the rate of ^{222}Rn degassing is a function of the integrated difference between ^{226}Ra and ^{222}Rn activities measured in the mixed layer of the water column. While this provides us with a gas effusion rate for radon, this is not necessarily useful for other, more reactive gases. As such, we can define gas exchange as driven by a gas transfer velocity coefficient, k , and the difference in ^{222}Rn measured in water versus that measured in the atmosphere. There is little to no ^{222}Rn in the atmosphere given its very short half life. We can therefore solve the equation and determine, k , simply by measuring ^{222}Rn and ^{226}Ra activities in the ocean mixed layer. The resulting gas transfer coefficient can be subsequently used to understand the physical processes that influence gas exchange of other gases of interest.
- 27) In the following example, gas exchange was determined using ^{226}Ra - ^{222}Rn disequilibrium in the Arctic Ocean. 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. This is a graphic illustration of three mechanisms that can lead to turbulence production and gas exchange in the ice-ocean boundary layer.
- 28) In 2011, ^{222}Rn and ^{226}Ra samples were collected during varying ice conditions in the Arctic Ocean (<http://www.meereisportal.de/en/>). The cruise tracks of expedition ARK XXVI/3 are

superimposed on AMRSR-2 sea ice concentrations at the time of the (left) first and (right) last ice station.

- 29) Very different $^{222}\text{Rn}:$ ^{226}Ra disequilibria profiles were measured depending on location, with activities being close to secular equilibrium (~ 1) in completely ice-covered regions (black circles) and in disequilibrium (< 1) in open water conditions (red symbols).
- 30) These figures depict gas transfer velocities (with standard deviation) at all stations determined from $^{222}\text{Rn}:$ ^{226}Ra disequilibria versus the velocity expected from previously derived and reanalyzed wind relationships (Left) and as a function of the weighted fraction of open water, compared with the relationship expected if gas transfer scaled linearly with ice cover (dashed lines represent 1:1 slope, negative values have no physical meaning) (Right). One might expect that gas transfer velocities would scale with %open water. Open water and completely ice covered regions had gas transfer velocities that were expected.
- 31) Partially ice covered stations (red shaded circles), however, were significantly lower than calculated and lower than that determined using wind velocity versus gas transfer relationships. Rutgers van der Loeff et al. (2014) hypothesized that this difference may be due to a reduction in wind fetch for these stations. Regardless of the mechanism, %ice cover does not scale with atmospheric gas exchange. This has large implications for parametrizing how these polar ecosystems, which are experiencing large changes in ice cover, serve as atmospheric sinks for gases such as CO_2 .
- 32) Groundwater plays a critical role in the flow of material from terrestrial to oceanic regimes. Groundwater is typically separated into direct freshwater flow and into recirculating flow, i.e., seawater that is recirculated through coastal sediments and results in the release of material (due to changing ionic strength) to the dissolved phase. This has been called the subterranean estuary.
- 33) One of the most useful tracers of recirculating salty groundwater flow, or submarine groundwater discharge (SGD) is the radium quartet. Radium is produced from Th in the U-Th decay series, and spans a range of half-lives, from 3.7 d to 1660 y. In freshwater systems, both Th and Ra are particle reactive. However, in salt water, radium is released to the dissolved phase and is conservative, i.e., not biologically or chemically reactive. As a result, Ra activities tend to be higher in SGD relative to open ocean waters. This difference in Ra activity has been used to examine processes ranging from horizontal advection to the residence time of water in an estuary, to the magnitude of SGD to the open-ocean.
- 34) This figure shows the distribution of ^{228}Ra activities (dpm m^{-3}) in surface waters of the Mediterranean Sea. Dots indicate sampled stations. The sub-basin division and the weighted average ^{228}Ra concentration in each sub-basin for surface (SW) and *intermediate (LIW)* waters are also provided (a range is reported to include the activities derived from different approaches). Note that the highest ^{228}Ra activities occurred in the northern basins and are associated with high SGD.
- 35) This is a general box model for describing Ra distributions. Each of these processes is typically described as linear rates and depending on the isotope, various input and loss rates may be considered negligible.
- 36) A classic example of a Ra application is the use of ^{226}Ra to examine the magnitude of SGD. Off the southeastern coast of the Atlantic Ocean, surface ocean ^{226}Ra activities are elevated nearshore versus offshore due to SGD.

- 37) The change in ^{226}Ra activity can be described as a function of the distance offshore. In this example, advection (w) is strongest parallel to shore (e.g., the Gulf Stream current). As such, dispersion (K_h) dominates the offshore radium flux. Solving this equation can provide an estimate of the dispersion coefficient. Using the suite of radium isotopes, Moore (2000) determined an eddy diffusion coefficient that ranged from $360 - 420 \text{ m}^2 \text{ s}^{-1}$.
- 38) Once the dispersive coefficient, K_h , is known, we can then determine the flux of SGD offshore in this area. For more information on these types of calculations, see Moore (2000) and Moore (2010).
- 39) We can determine the overall flux of SGD to the Southeastern North Atlantic Ocean by measuring the concentration of ^{226}Ra in SGD at the source (e.g., in nearshore wells). Results argue that SGD (the recycling of water from the ocean) is the same order of magnitude as fresh water input from local rivers. We can further determine the flux of nutrients, trace metals, and other elements and compounds via SGD by measuring those components in the well and using the element or compound to Ra ratio (similar to that done for ^{234}Th : ^{238}U particle export case study). Given that SGD is often significantly higher in nutrients and trace elements, SGD to the Southeastern North Atlantic Ocean is a substantial source of constituents to the coastal zone (Moore, 2010).
- 40) Sedimentation and 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.
- 41) ^{210}Pb ($t_{1/2} = 22.3 \text{ y}$) is a particle reactive radionuclide produced from the radioactive decay of ^{226}Ra via ^{222}Rn . Atmospheric ^{210}Pb is produced from the decay of ^{222}Rn that has emanated from terrestrial rocks and soils. In marine systems, both atmospherically derived ^{210}Pb and ^{210}Pb produced from ^{226}Ra decay are scavenged in the water column and enter sediments, where it can be used to examine both mixing and accumulation processes on 100 y timescales.
- 42) ^{210}Pb in sediments is a combination of supported (produced *in situ* from ^{226}Ra decay in sediments) and "excess" ^{210}Pb , that which reaches the sediments from the overlying water column. Excess ^{210}Pb can then be described using the classic radioactive decay equation. It is important to remember that this formulation only allows for relative age dates to be determined. Absolute ages require additional confirmation using other stratigraphic tools (see Lecture 3, Radioactivity in the Marine Environment: Cosmogenic and Anthropogenic Radionuclides).
- 43) There are several models used to determine sedimentation and mass accumulation rates: The Constant Flux-Constant Sedimentation rate (CF:CS) Model, the Constant Initial Concentration (CIC) model, and the Constant Rate of Supply (CRS) model. In the simplest sense, sediment accumulation rates are assumed to be constant in all sediment layers and are therefore determined from the slope of the semi-logarithmic excess ^{210}Pb against depth (m) or cumulative dry mass (g cm^{-2}). When ^{210}Pb activities are plotted on a logarithmic scale the resulting ^{210}Pb activity versus depth profile will appear linear and the mean sedimentation rate, S , can then be determined using a least squares fit. This model works best in anoxic, quiescent settings. Note that porosity/compaction corrections are NOT included in this formulation for clarity.

- 44) In most marine systems, however, erosion and sedimentation rates vary over time. Thus we often use the CIC or CRS Models. In the CIC model it is assumed that any changes in flux are proportional to the scavenging and sinking of particles from the water column, which may or may not be the case depending on the regime. Note that porosity corrections are NOT included in this formulation for clarity.
- 45) In the CRS model, it is assumed that atmospheric deposition of ^{210}Pb is constant and results in a constant rate of supply to sediments, independent of sediment accumulation rate. In this formulation, knowledge of the total excess ^{210}Pb inventory (I_0) is critical as underestimation of I_0 will result in ^{210}Pb derived dates to be too old. Sedimentation rates can then be converted to mass accumulation rates using density. Note that porosity corrections are NOT included in this formulation for clarity.
- 46) In this example, the sediment core was deposited in oxic waters and the down core profile of ^{210}Pb is more complicated. Here, the CRS model would be most appropriate and other processes, such as bioturbation or physical mixing, would also need to be considered (unpublished data from P. Masqué)
- 47) Here are examples of even more complicated sediment cores. In the first core, ^{210}Pb is near constant with depth due to physical mixing, bioturbation, dilution from organic carbon, or episodic neutral erosional sources, such as sand. In the second core, benthic mixing has mixed high activity ^{210}Pb sediment consistently deeper into the core and indicates ~ 20 cm of potential bioturbation. Supporting evidence for mixing is derived from the short lived radionuclides ^{234}Th ($t_{1/2} = 24.1$ d) and ^7Be ($t_{1/2} = 53.3$ d).
- 48) How is ^{210}Pb applied to marine systems? A classic example is examining contaminants in Sydney Harbor, Nova Scotia, Canada. This region has one of the highest cancer rates in Canada. Sydney Harbor received significant discharges from coking and steel manufacturing, beginning in the 1890s and ending in the late 1980s. These discharges included metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). After the plants were closed, the city built a recreational park. A key question is understanding the magnitude of contaminants in the Harbor, when they were deposited, and if they are mobile in sediments.
- 49) ^{210}Pb activities were determined throughout the Harbor and sedimentation rates, ω , ranged between < 0.2 and 0.8 cm y^{-1} . Using these sedimentation rates, the sediments were dated and linked to historical records of manufacturing in the region with peaks in PAHs occurring in the 1980's, but with dramatic declines occurring once manufacturing related dumping ceased.
- 50) Data from these cores argued strongly that the majority of the PAHs produced in the 1980s are being buried over time. Studies such as these have been used to determine if contaminated sediments should be removed or allowed to continue to be buried over time. In this instance, it was decided to leave the sediments in place. For more information, see Smith et al. (2009).
- 51) In summary, U-Th series radionuclides can be used to examine a suite of processes. The examples provided above are only snapshots into their applications in marine systems. For example, just as ^{238}U : ^{234}Th disequilibria can be used to trace scavenging rates, so can ^{210}Pb : ^{210}Po disequilibria or ^{230}Th . See Slide 5 and the included reading lists for more details.
- 52) Acknowledgements
- 53) References

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Useful Websites

Online Nuclear and Radiochemistry teaching material:

<https://nucwik.wikispaces.com/Nuclear+and+Radiochemistry+Textbook+and+Compendia>

eGeotraces. An online Electronic Atlas of Artificial and Naturally Occurring Radionuclides measured during the GEOTRACES Program: <http://www.egeotraces.org/>

Rio5 Cookbook. For more information on how to measure specific radionuclides in seawater:

<https://cmer.whoi.edu/cookbook>

Acknowledgements

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. This work was supported by the Scientific Committee on Ocean Research, SCOR Working Group 146: Radioactivity in the Ocean, 5 Decades Later (RiO5) and the Woods Hole Oceanographic Institution's Center for Marine and Environmental Radioactivity.