

## NEW METHODS

### Development of a moored radium in situ sampler to measure annual time series

Lauren Kipp <sup>1\*</sup>, Matthew A. Charette <sup>2</sup>, Paul Henderson,<sup>2</sup> Joshua Benedict,<sup>1</sup> Igor Polyakov <sup>3</sup>,  
Andrey Pnyushkov <sup>3</sup>

<sup>1</sup>Department of Environmental Science, Rowan University, Glassboro, New Jersey, USA; <sup>2</sup>Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA; <sup>3</sup>International Arctic Research Center, University of Alaska Fairbanks, Fairbanks, Alaska, USA

#### Abstract

Radium is a useful tracer of sediment-derived materials, improving our understanding of the geochemical cycling of elements at ocean boundaries. We have developed an autonomous in situ sampler to collect time series samples of radium isotopes on mooring deployments. Samplers were deployed for 2 yr in the Arctic Ocean, a region particularly hard to access outside of the summer season, and collected monthly samples to create the first annual time series of radium-228 and radium-226 in the Arctic. Results from the Laptev Slope show increased radium-228 and radium-228/radium-226 ratios in spring/summer, concomitant with increased meteoric water and brine influence. Together, these tracers indicate seasonal periods of increased influence of shelf- and river-derived materials, findings which would not be possible to discern from summertime shipboard surveys alone. The development of this in situ sampler has therefore expanded our capability to use radium as a tracer to discern temporal changes in the geochemistry of remote areas of the ocean.

Radium isotopes have become well-established tracers of a range of oceanic processes that involve input of materials from ocean boundaries such as coastal aquifers (e.g., Moore 1996; Garcia-Orellana et al. 2021), continental shelf sediments (e.g., Rutgers van der Loeff et al. 1995; Charette et al. 2016; Sanial et al. 2018), and hydrothermal vents (e.g., Kadko and Moore 1988; Kipp et al. 2018b). This has been enabled by their continual production via the decay of thorium isotopes in marine sediments, where they are soluble and available for release into the ocean water column. Thus, ocean sediments from coastal embayments to the deep ocean are major sources of Ra to the marine environment. Because of their mostly conservative behavior in seawater, Ra isotopes can serve as proxies

for other, more reactive sediment-derived inputs, in particular those with biogeochemical significance such as inorganic nutrients (Cai et al. 2015; Tamborski et al. 2018), carbon (Burt et al. 2016), and trace metals such as iron (Fe) (Charette et al. 2007; Hong et al. 2018; Hsieh et al. 2021).

In the Arctic Ocean, radium has been established as a particularly valuable tracer of changing ocean conditions (e.g., Li et al. 2017; Vieira et al. 2018; Kipp et al. 2023). This is due to this ocean basin's high proportion of shelf area and river discharge, combined with warming conditions that have led to reduced sea ice cover that can increase sediment-water interactions over shallow shelves due to wind and waves (Kipp et al. 2018a). Despite this, the Arctic is still largely ice-covered for half of the year (Roach and Meier 2024), making it difficult to access via oceanographic sampling platforms. This highlights the need for remote sample collection technologies necessary to separate interannual (climate-driven) changes from potential seasonal variability in biogeochemical tracers such as radium.

Motivated by this need, we developed the moored radium in situ sampler (MoRIS)—a mooring-deployable system designed to autonomously collect radium isotopes in remote environments.

\*Correspondence: [kipp@rowan.edu](mailto:kipp@rowan.edu)

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial](https://creativecommons.org/licenses/by-nc/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Associate editor: Isaac Santos

The system was created to enable year-round collection of Ra isotopes—bridging the gap between research cruises, including during seasons that are largely inaccessible to research vessels. Here, we describe the development of MoRIS and the collection of the first seasonal radium time series in the Arctic Ocean.

## Materials and procedures

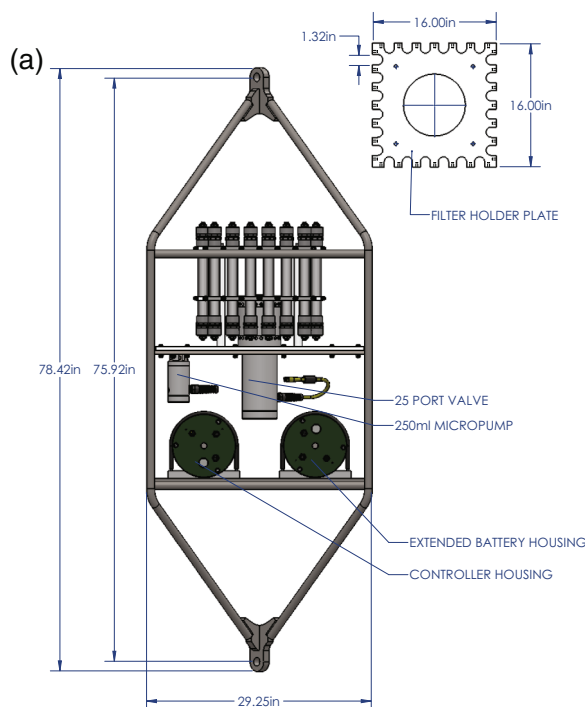
### Sampler design

Moored radium in situ sampler was designed through a partnership with McLane Research Laboratories, Inc., and is a modified version of their particle and phytoplankton sampler (PPS) (Fig. 1). The PPS is designed to collect 24 individual samples on a user-defined time interval, using a pump that pulls water through a multi-port valve. The original PPS filters water over a 47 mm GF/F filter at rates of 50–125 mL min<sup>-1</sup>, and has a maximum deployment time of 14 months (volume and flow rate dependent) based on a power supply of 24 D cell alkaline batteries. Our modifications to this design included (1) swapping the 24 GF/F filter holders for 24 1" PVC housings containing 15 g of manganese oxide (MnO<sub>2</sub>)-coated acrylic fiber, (2) adding quick disconnect tubing preceding the Ra sample housings to collect a ~ 20 mL water sample, (3) adding another 24 D cell battery pack (48 batteries total) to extend the deployment lifetime to 2 yr and allow for higher flow rates, and (4) placing the system on a larger frame to accommodate the added battery pack and new filter housings.

Radium is a dissolved cation that is scavenged by MnO<sub>2</sub>, thus pumping seawater through the housing packed with

MnO<sub>2</sub>-coated acrylic fiber quantitatively removes Ra from the water and collects it on the fiber (Moore and Reid 1973). MoRIS was programmed to run at a flow rate of 250 mL min<sup>-1</sup> to minimize backpressure on the pump and to ensure quantitative removal of Ra from the seawater. To remove any suspended particles that may be pumped through the housing, a small amount (~ 2.5–5 cm ball) of uncoated acrylic fiber preceded the MnO<sub>2</sub>-coated fiber in the housing, such that particles would be filtered out onto the uncoated fiber before reaching the MnO<sub>2</sub> fiber and thus would not be processed with the dissolved radium sample. As an additional measure to ensure no particles were trapped in the fiber, samples were rinsed three times with Ra-free MilliQ water after recovery. The offload files from each of the systems contains a record of the flow rate averaged over 5 min intervals, permitting an evaluation of whether flow rates were significantly reduced (e.g., due to particles clogging the fibers). Additionally, if flow rates drop below 100 mL min<sup>-1</sup>, the pump was programmed to stop automatically and the sample collection was aborted.

Using traditional counting techniques, open ocean <sup>226</sup>Ra activities (~ 8–10 dpm/100 L) can typically be measured on sample volumes in the range of tens of liters: analysis via radon emanation and alpha spectrometry can be done on ~ 10–25 L samples (Ku and Lin 1976; Charette et al. 2015), gamma spectrometry requires volumes of 25–50 L (Gonneea et al. 2008), and analysis via Radium Delayed Coincidence Counter (RaDeCC) requires volumes ≥ 100–200 L (Geibert et al. 2013). Several labs have also developed techniques for



**Fig. 1.** (a) Schematic of MoRIS design from McLane Research Laboratories, Inc., and (b) photo of MoRIS during deployment in 2021.

measuring  $^{226}\text{Ra}$  via ICP-MS, which requires only  $\sim 100\text{--}1000\text{ mL}$  (Foster et al. 2004; Vieira et al. 2021).  $^{228}\text{Ra}$ , however, requires sample volumes that are larger and more variable based on location: activities in surface waters near the coast may be measurable on tens of liters, while deeper open ocean activities may only be measurable on hundreds of liters. MoRIS was designed to be deployed on continental slopes in the Arctic Ocean, where our previous work has shown relatively high  $^{228}\text{Ra}$  activities (Kipp et al. 2019, 2023). We therefore determined that activities would be measurable on 50 L samples. The filtration of each 50 L sample at a rate of  $250\text{ mL min}^{-1}$  therefore took approximately 200 min.

In addition to collecting Ra samples, it was also important to isolate a small water sample ( $\sim 20\text{ mL}$ ) that could be used for the analysis of water isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ). Along with the salinity measurements from a MicroCat CTD on the same mooring, this data permits a deconvolution of the Arctic water masses present at the time of sampling using a 3-endmember model and a system of linear equations (Kipp et al. 2023). To accomplish this, quick-disconnect tubing (Kent Systems Quick Couplings Shut-off Valves, Collection 1) was used to connect the PVC housings to the multi-port pump. Fittings were used that remain closed when the tubing is disconnected. Upon recovery, this tubing can thus be disconnected and the water can be drained into sample vials for water isotope analysis on shore.

To extend the deployment lifetime to 2 yr, an additional battery pack of 24 D cell alkaline batteries was added in line with the first battery pack (48 batteries total). The sampler was programmed to collect a sample every 30.5 d over the course of the 24-month deployment. The addition of the second battery pack increased the weight of the sampler such that a larger frame was used, constructed of 316 stainless steel with a single attachment point on top and bottom. This brought the total weight of the system to approximately 450 lbs in air ( $\sim 300\text{ lbs}$  in water).

## Testing

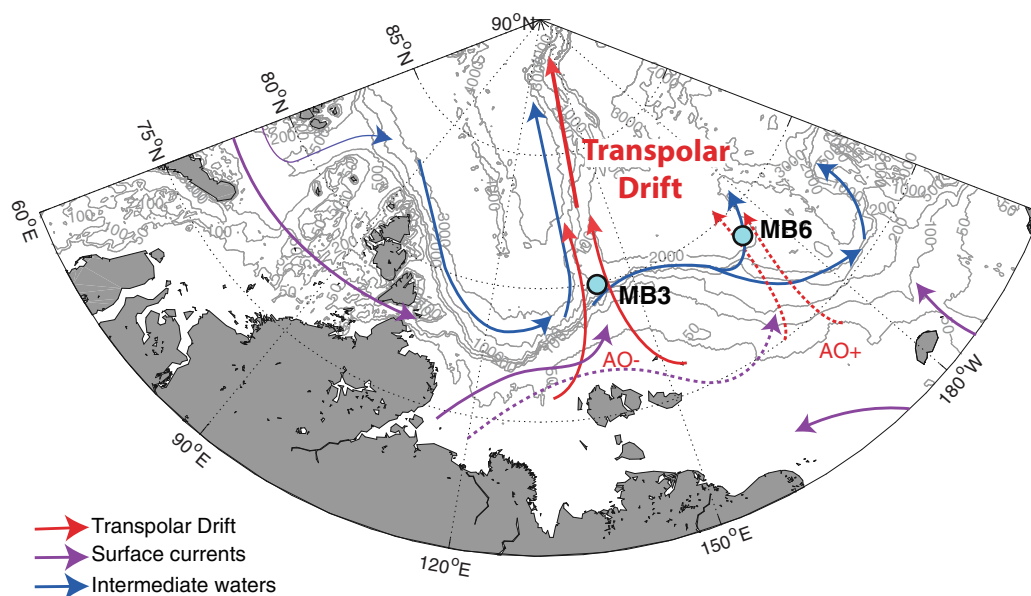
When the MoRIS samplers were received, the battery packs were connected and the empty filter holders (24) were filled with  $\text{MnO}_2$ -coated acrylic fibers. The sampling system was primed with filtered local seawater (Vineyard Sound, Woods Hole, Massachusetts). The sampler was programmed to pump the same flow rate and volume as the planned deployment in the Arctic. The exhaust water from the MoRIS sampler was captured and the volume measured to compare against the logged filter volumes stored within the sampler; the resulting volumes agreed within 5%. The next test included programming and deploying the McLane sampler autonomously in a seawater test tank located in the Coastal Research Laboratory building on the Quissett campus of the Woods Hole Oceanographic Institution (WHOI). The MoRIS instrument was hoisted and suspended into the tank overnight, filtering the same volume/flow rate as the planned deployment. Once

the deployment was complete, the logged file was downloaded from the instrument to ensure the total volume programmed was achieved. The instrument was then flushed with Ultrapure MilliQ water and the lines were emptied so that there was no residual water located in the tubing/filter holders. The outside of the instrument was also washed down with freshwater to remove any saltwater. The  $\text{MnO}_2$ -coated fibers were removed from their holders, rinsed with radium-free freshwater, and measured on a Radium Delayed Coincidence Counter (RaDeCC; Moore and Arnold 1996). Radium, naturally present in seawater, was measured on the fiber and it was deemed that the instrument functioned properly and was ready for deployment.

## Deployment

The two MoRIS samplers were deployed on the September–October 2021 Nansen and Amundsen Basin Observational System (NABOS) cruise on the RV *Akademik Tryoshnikov*, which facilitated water sampling and mooring deployments and recoveries along the Laptev and East Siberian Slopes. Samplers were primed with brine (salinity  $> 40$ ) made with table salt to avoid freezing while sitting on deck during mooring assembly. The samplers were deployed at moorings MB3 ( $79.93^\circ\text{N}$ ,  $142.25^\circ\text{E}$ ; Laptev Slope on the Lomonosov Ridge) and MB6 ( $78.99^\circ\text{N}$ ,  $173.78^\circ\text{E}$ ; East Siberian Slope) (Fig. 2). The moorings were designed to place MoRIS as close to the surface as possible, with the aim of capturing seasonal changes in the Transpolar Drift and Polar Surface Water, though this was limited by depth restrictions on the moorings (i.e., major flotation must not be shallower than 30 m to avoid ice). The target depth for each sampler was 40 m, and the final estimated MoRIS deployment depths were 44 and 54.5 m on MB3 and MB6, respectively. Samplers were recovered on the September–October 2023 NABOS cruise on the USCGC *Healy*, which re-occupied the same locations. These expeditions and MoRIS deployments were part of the Arctic Radium Isotope Observing Network (ARION), which aims to utilize radium as a tracer of climate-driven changes in Arctic Ocean chemistry (Kipp and Charette 2022).

Before each MoRIS deployment and recovery, a depth profile of  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  was collected using water from Niskin bottles mounted on the CTD rosette to calibrate the time series. This process is described in detail in Kipp et al. (2023). Briefly, six Niskin bottles were tripped at four depths (20 m, 40 m, 100 m, 250 m) and combined into  $\sim 60\text{--}72\text{ L}$  samples depending on bottle volume (10-L bottles on RV *Akademik Tryoshnikov*; 12-L on USCGC *Healy*). These were filtered through a PVC housing containing a small amount of untreated acrylic fiber followed by  $\text{MnO}_2$ -coated fiber (15–20 g) to extract Ra. Surface water (120–130 L) was collected using a submersible pump and filtered through 20 g of  $\text{MnO}_2$ -coated fiber. After collection, fiber samples were rinsed with Ra-free MilliQ water and stored at room temperature for the duration of the cruise.



**Fig. 2.** Locations of MoRIS samplers on 2021–2023 deployment (light blue circles). General circulation patterns are indicated on the map, including the location of the Transpolar Drift during positive Arctic Oscillation periods (AO+; dashed lines) and negative Arctic Oscillation periods (AO−; solid lines).

When the MoRIS samplers were recovered, the water isotope sample tubing from each sample port was disconnected and water was drained into 20 mL acid-cleaned polyethylene sample vials. A disposable pipette was used to transfer 2 mL of each sample into glass vials for water isotope analysis, which were stored refrigerated with no headspace. Water isotope samples were analyzed by cavity ring-down spectroscopy at the University of Wyoming Stable Isotope Facility.

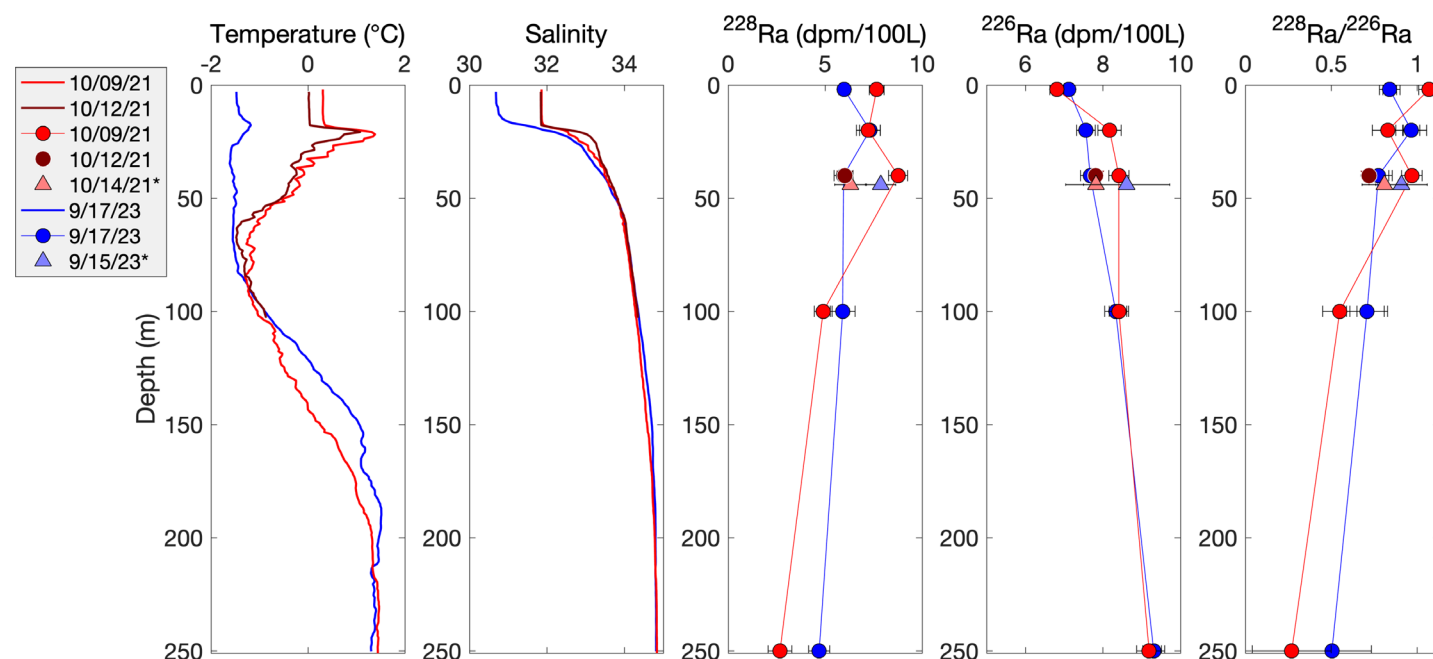
The PVC housings containing the  $\text{MnO}_2$ -coated fiber samples were disconnected from the outlet tubing, placed in individual plastic bags, and stored at room temperature until transport back to WHOI. On shore, the  $\text{MnO}_2$ -coated fibers were removed from the housings and squeezed dry over disposable beakers to catch the excess water. Any additional water from the housings was also added to these beakers. The amount of seawater retained was 71 g on average from 48 samples. To test whether all of the radium was captured on the  $\text{MnO}_2$  fiber, a new bundle of  $\text{MnO}_2$  fiber (2 g) was placed in each of the beakers and allowed to soak for 24 h, then processed in the same way as the samples. A random subset of these fibers was analyzed via gamma spectrometry; because activities were below background for Ra isotopes, we concluded that radium had been retained on the original  $\text{MnO}_2$  fiber.

Methods for quantifying  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  on  $\text{MnO}_2$  fiber are described in detail in Kipp et al. (2023). Briefly, fibers were ashed (820°C, 12 h) and sealed in polystyrene tubes with epoxy to prevent Rn loss. After 3 weeks, activities were measured by well-type germanium gamma-spectrometry at Rowan University or WHOI with intercalibration using duplicate samples and reference materials. Radium-228 was quantified from the average of  $^{228}\text{Ac}$  338 and 911 keV peaks, and  $^{226}\text{Ra}$  from

the  $^{214}\text{Pb}$  352 keV peak. Detector efficiencies were derived from ashed Mn-fiber spiked with  $^{226}\text{Ra}$  (NIST SRM 4967A) and  $^{232}\text{Th}$  (thorium nitrate) with daughters in equilibrium prepared identically to samples. Blanks associated with unused ashed fiber were analyzed and subtracted where applicable.

## Assessment

The offload data files from both MoRIS samplers indicated successful collection of all samples on the 2021–2023 deployment. The depth profiles measured before and after each MoRIS deployment provide confidence that the samplers are accurately measuring  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  activities (Figs. 3, 4). The  $^{226}\text{Ra}$  activities and  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios measured at MB3 were similar to the 40 m CTD sample in both 2021 and 2023 (Fig. 3). The  $^{228}\text{Ra}$  depth profiles showed more variability between the years, particularly around 40 m, near the depth of the sampler. When MB3 was deployed in 2021, the CTD cast down to 250 m was conducted approximately 3 d before the mooring was deployed; the mooring deployment was delayed due to weather, and the ship moved off station to sample elsewhere in the interim. When the ship returned to station to complete the deployment, an additional 40 m Ra sample was collected using the CTD rosette (dark red circle on Fig. 3). This sample provides the best comparison with the sample measured by MoRIS, which was collected ~34 h later (light red triangle in Fig. 3), and indeed shows good agreement between the two sample collection methods. The 2023 CTD cast was conducted ~2 d after the final MoRIS sample was collected (light blue triangle), and  $^{228}\text{Ra}$  activities differ by ~2 dpm/100 L. However, the repeat sampling in 2021 shows



**Fig. 3.** Depth profiles at MB3 (lines and circles) and corresponding MoRIS samples (triangles) from 2021 (red) to 2023 (blue). Dark red lines and symbols indicate data collected during a re-occupation of the station ~3 d after the initial CTD cast in 2021 (initial cast in bright red). Although straight line fits are used to connect samples on the depth profiles, the gradient in Ra activities may not be linear. Samples collected from MoRIS are indicated with an asterisk in the legend.

that the activities of  $^{228}\text{Ra}$  at this depth changed by  $\sim 2.7$  dpm/100 L over the course of 3 d, so this change is within the expected natural variability.

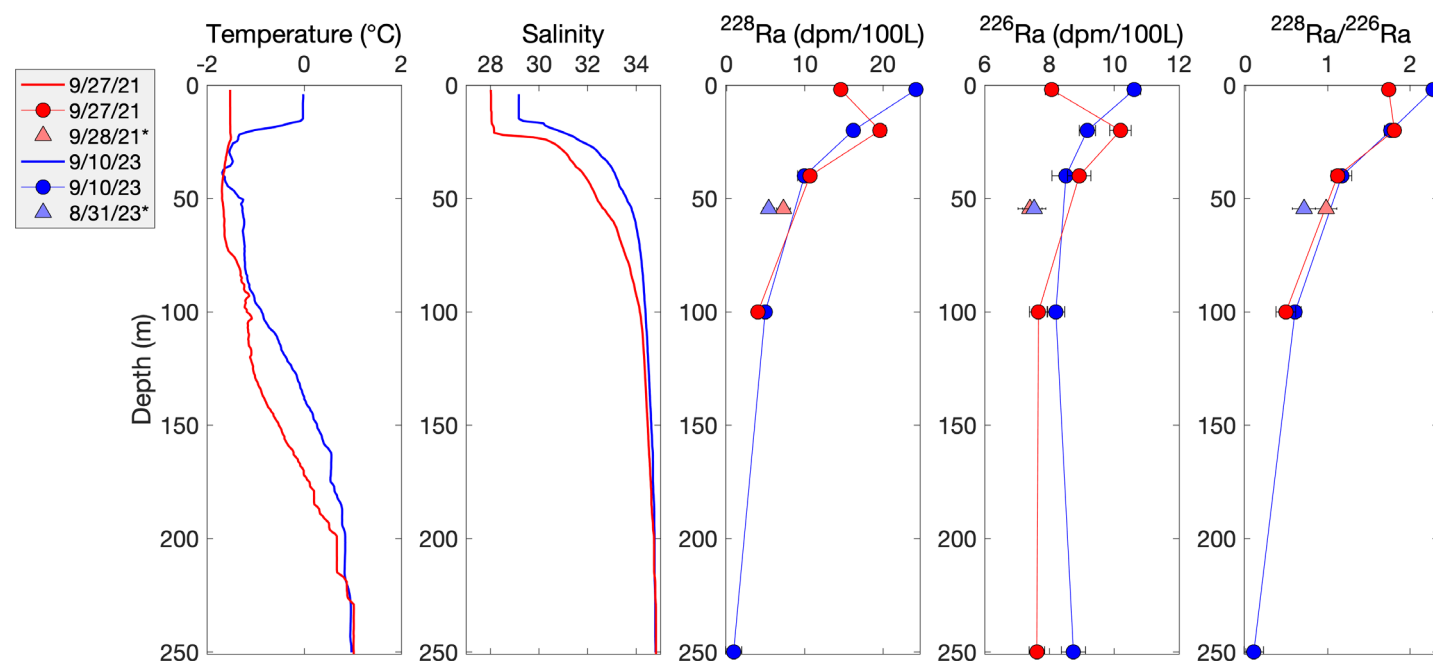
The MoRIS deployed at MB6 was moored at a slightly deeper depth than expected (54 m), so the closest CTD sample for intercomparison was  $\sim 14$  m shallower. Nonetheless, samples collected from MoRIS at MB6 had activities that fall between the samples measured above and below via the CTD rosette (Fig. 4). In general, the profiles at this station were very similar in 2021 and 2023, aside from lower Ra activities and a lower  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio at the surface in 2021. This may be related to the presence of water masses with different origins and/or pathways over the shelf at the surface in each year.

Here we will present the results of the full time series collected at mooring MB3; the results from MB6 will be the subject of another forthcoming paper. MB3 was located on the Lomonosov Ridge, where surface and intermediate waters are generally steered by bathymetry such that water moves along the Kara and Laptev Slopes (Coachman and Barnes 1963; Rudels 2009, 2012). The ADCP mounted on this mooring provides evidence of eastward-flowing currents (Polyakov et al. 2025) (Fig. 5). The CTD data from MB3 indicate that MoRIS (at 44 m) was located within the halocline, rather than capturing the PSL (Fig. 6).

Radium-226 activities were relatively constant throughout the 2-yr deployment period, varying between  $\sim 6$  and 8 dpm/100 L (Fig. 7). The highest activities were observed in

the last sample collected, reaching  $8.6 \pm 1.1$  dpm/100 L. Radium-228 was more variable, ranging from  $\sim 4.5$  to 9 dpm/100 L. This is consistent with the shorter half-life of  $^{228}\text{Ra}$  compared to  $^{226}\text{Ra}$ ; this isotope is regenerated more quickly in shelf sediments and can therefore respond to changes occurring on shorter timescales. Because of this faster regeneration rate following removal from sediments, higher ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$  tend to indicate a shelf sediment source (as opposed to a riverine- or fresh groundwater-derived signal, which is expected to have an activity ratio closer to  $\sim 1$ ; Bullcock et al. 2022; Charette 2007; Michael et al. 2011). The observed  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios varied between  $\sim 0.6$  and 1.2, with the highest ratios observed in November–December 2021, February–May 2022, and May–September 2023.

The  $\delta^{18}\text{O}$  measurements from each sample were matched with salinity measured on a SBE 37-IM MicroCAT (Seabird Scientific) located directly above MoRIS at 33–34 m, and used in a 3-endmember mixing model to deconvolve the contributions of (Atlantic-derived) seawater, meteoric water, and sea ice melt (for more information on the mixing model, see Kipp et al. 2023). As expected, the majority of the water at this depth is derived from Atlantic inflow (Fig. 7). Meteoric water fractions were typically around 4%, but increased to 5.8% in May 2022 and reached a maximum of 7.6% in July 2023. The fraction of sea ice melt was between  $-2.9\%$  and  $3.3\%$ , with positive values indicating sea ice melt and negative values indicating ice (and brine) formation. Negative values of sea ice



**Fig. 4.** Depth profiles at MB6 (lines and circles) and corresponding MoRIS samples (triangles) from 2021 (red) to 2023 (blue). The 250 m sample collected in 2021 was below detection limits for  $^{228}\text{Ra}$ . Although straight line fits are used to connect samples on the depth profiles, the gradient in Ra activities may not be linear. Samples collected from MoRIS are indicated with an asterisk in the legend.

melt were observed in spring 2022 and summer 2023, coincident with increased meteoric water values.

## Discussion

### Observed trends in Arctic Ocean chemistry

The time series data from MB3 shows increased  $^{228}\text{Ra}$  activities and  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios at times when fractions of sea ice melt were negative and fractions of meteoric water were highest (gray bars on Fig. 7). Together, these changes suggest an increased influence of shelf-derived water at MB3 during these time periods: higher  $^{228}\text{Ra}$  activities and  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios are indicative of a shelf sediment source (e.g., van der Rutgers Loeff et al. 2003; Vieira et al. 2018), negative fractions of sea ice melt indicate brine formation, which occurs over the shelf during freeze-up, and meteoric water influences are strongest over the shelf where river discharge is the most concentrated. These changes begin around February in both years and gradually increase to a peak in mid-summer. In 2023 these changes were shifted later in the summer (beginning to decrease in ~July) compared to 2022, when  $^{228}\text{Ra}$ ,  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios, and meteoric water fractions had decreased by July.

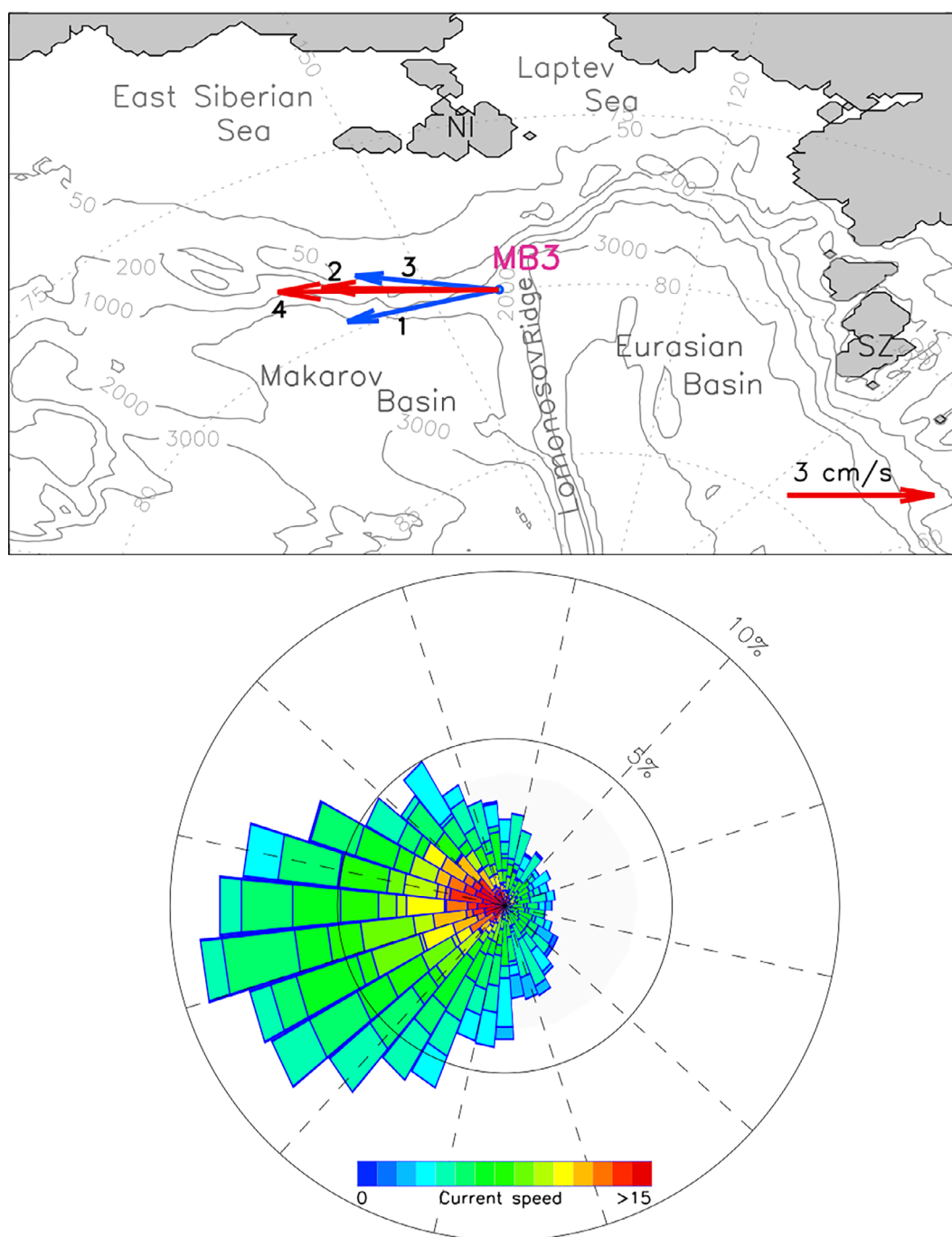
The Ob, Yenisey, and Lena River freshets typically occur in the last week of May and the first week of June (The Arctic Great Rivers Observatory 2025; <https://arcticgreatrivers.org/data>), thus increased river discharge cannot explain the observed increases of meteoric water, which occurred in April–May 2022 (preceding the freshet) and increased over the

course of the spring in 2023. A change in current direction could potentially transport more shelf-influenced water across the slope adjacent to MB3. Alternatively, these changes could be driven by a change upstream of the mooring. In the case of an upstream change, we suggest that these periods of increased shelf influence reflect periods of ice freeze-up and brine formation over the Kara and Barents Shelves, creating dense shelf water outflows that can ventilate the upper halocline (e.g., Cavalieri and Martin 1994; Schauer 1995; Janout et al. 2015). If freeze-up typically begins in October–November (Fetterer et al. 2017), this requires a transit time of ~6–10 months along the slope to reach MB3.

The concurrent changes in radium levels and water mass fractions captured by MoRIS provide evidence of a seasonal signal in shelf- and river-derived water masses that could not be captured by summertime shipboard surveys alone. The development of this in situ sampler has thus improved our ability to use radium as a tracer of climate-driven changes in the Arctic. Specifically, this time series has shown that comparisons between different years and/or seasons may be complicated by the timing of intermediate water formation and shelf outflows, and that it is important to have additional tracers—such as meteoric water and sea ice melt percentages—to help identify when these influences are present.

### Utility of radium time series sampling

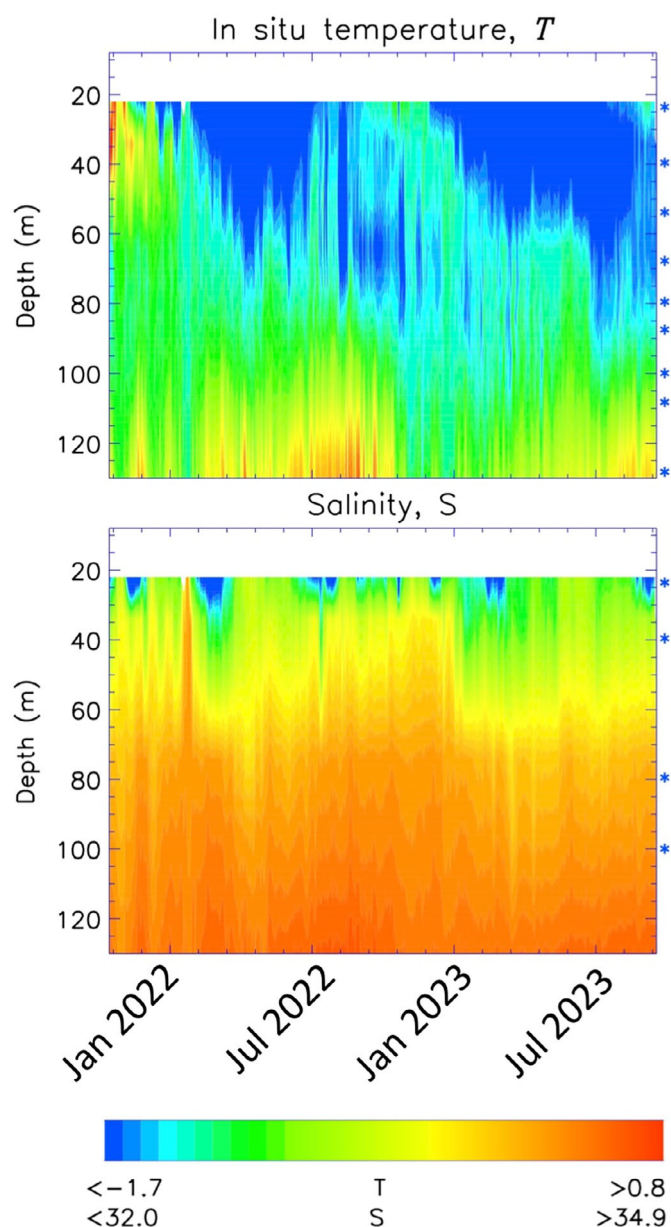
The successful collection of a 2-yr time series from the MoRIS platform expands our ability to investigate temporal changes in ocean chemistry, providing a useful complement



**Fig. 5.** Current rose from MB3 for Oct 2021–Sep 2023. Current direction is shown with the orientation of each bar (orientation of rose matches the map, so north is at the bottom of each rose and east is to the left). The length of the bar indicates the percentage of time that the current was moving in that direction; solid circles indicate 5% and 10%. Color indicates current speed. Arrows on the map indicate the average current speed and direction for four different time periods: (1) Jan–May 2022, (2) Sep–Dec 2022, (3) Feb–Jul 2023, and (4) Jul–Sep 2023.

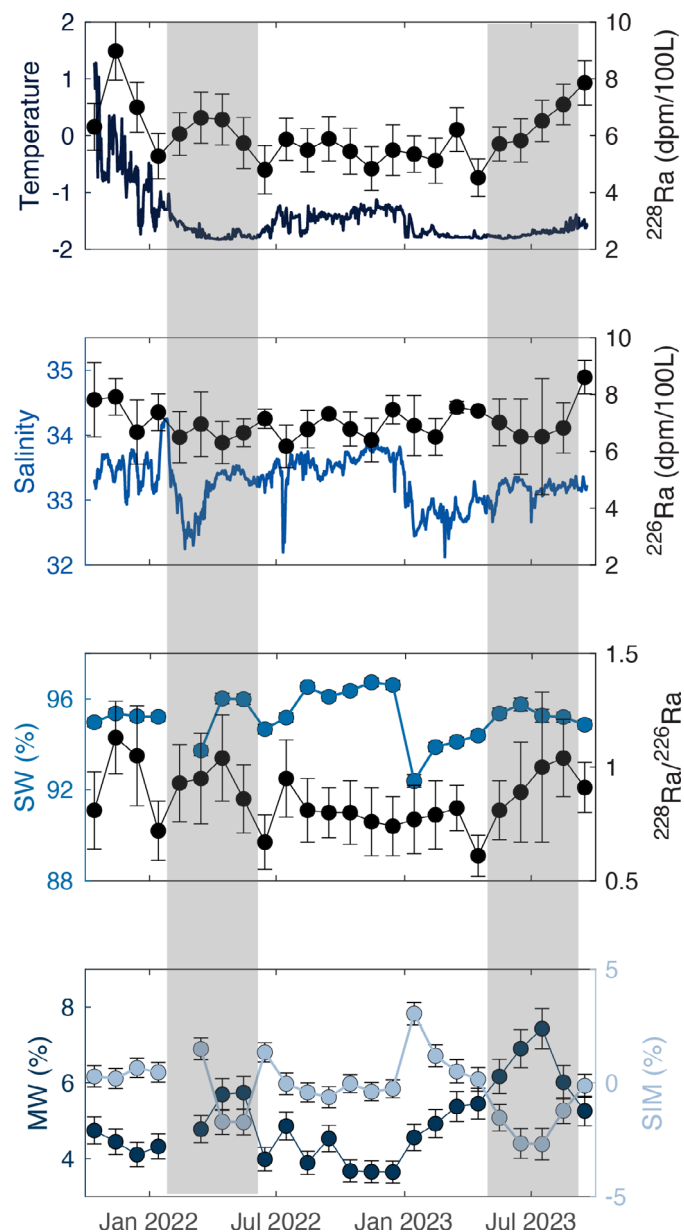
to the physical oceanographic data traditionally collected from moored instruments. Radium isotopes are an excellent proxy for other sediment-derived elements such as carbon, nutrients, and trace metals, but unlike these other constituents, radium samples do not require preservation. Our results

show that the radium activities measured on samples collected at the beginning of the time series agreed well with activities measured from CTD casts taken within days of sampler deployment, illustrating that fiber samples yielded reliable results despite hold times of up to 2 yr. The radium time series



**Fig. 6.** Salinity and temperature measured in the top 22–130 m at MB3 mooring location for Oct 2021–Sep 2023. Blue stars on the right vertical axes indicate the positions of temperature and salinity sensors.

can thus be used to infer changes in other shelf-derived materials that would be difficult to directly measure with moored samplers. This pairing of physical and chemical monitoring is particularly useful in the Arctic Ocean, where it is important to separate seasonal changes from longer-term ongoing climate-driven changes, and year-round sampling is prohibited by ice coverage. However, there are many potential applications in the temperate oceans as well; for example coincident measurements of radium with velocity or temperature could be used to monitor how increased turbulence or periods of upwelling influence the levels of sediment-derived



**Fig. 7.** Time series measurements (Oct 2021–Sep 2023) of  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ , the  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio, temperature, salinity, and percentages of meteoric water (MW), seawater (SW), and sea ice melt (SIM) at MB3. Gray bars indicate periods where  $^{228}\text{Ra}$  activities,  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios, and meteoric water percentages increased, and sea ice melt percentages decreased. Temperature and salinity are 1-d moving means.

elements. While our research interests motivated a long (2-yr) deployment, the sample collection timeframe can easily be modified to take samples on a more frequent basis over a shorter deployment period (e.g., weekly for 6 months).

Moored radium in situ sampler deployment requires dedicated ship time and a team experienced in mooring operations, adding research costs beyond those typical for standard sampling efforts. Compared to traditional sampling methods,

wherein  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  radium samples can be collected relatively quickly using a submersible pump deployed over the side or via Niskin bottles on the CTD rosette, sampling with MoRIS therefore represents a larger investment of time and resources. However, the effort involved (including sampler procurement and programming and deployment of instrumentation) is somewhat similar to the collection of radium samples via the McLane Large Volume Water Transfer System (WTS-LV), which has become a common method for measuring all four radium isotopes in the open ocean (Charette et al. 2015; Henderson et al. 2013). The key distinction is that MoRIS provides a continuous time series, so any cost-benefit analysis should consider the expense of multiple cruises that would otherwise be needed to achieve similar temporal coverage.

### Comments and recommendations

When both MoRIS samplers were inspected after deployment, there were several locations that were compromised by corrosion, including a majority of the waterproof bulkhead connectors and the coated aluminum end caps of the battery housings. This impairment caused a leak within the housing in a subsequent short-term deployment. For future deployments, we have designed a plastic o-ring adapter for the bulkhead connectors to isolate the dissimilar metals and prevent areas already affected by corrosion from contacting seawater. We recommend that future iterations of MoRIS also use high-quality sacrificial anodes to prevent similar corrosion issues.

By the end of the deployment period, the battery voltage on both samplers had decreased by approximately 5 V (from ~37 to 31–32 V). This suggests a loss of 0.004 V per liter of water pumped. The pump will operate down to 28 V before returning an error message; thus we estimate that an additional 32 L could be pumped per sampling event. Our initial approach of pumping 50 L per sample resulted in activities that were close to the detection limits of the gamma detector, producing relatively large error bars. We therefore recommend that larger sample volumes (60–80 L) be pumped on future deployments in this area. However, if MoRIS is deployed over a shallower region of the shelf, 50 L may remain an appropriate volume due to the higher expected activities and possible concerns about resuspended sediment clogging the fibers.

### Author Contributions

Lauren Kipp: Conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, visualization, writing – original draft preparation. Joshua Benedict: Investigation, visualization. Matthew A. Charette: Conceptualization, funding acquisition, investigation, methodology, validation, writing – original draft preparation. Paul Henderson: Investigation, methodology, validation, writing – original draft preparation. Andrey Pnyushkov: Data

curation, formal analysis, funding acquisition, investigation, methodology. Igor Polyakov: Data curation, formal analysis, funding acquisition, investigation, methodology, visualization.

### Acknowledgments

We are thankful for the assistance of Adele Anderson during the deployment of MoRIS in 2021, and for the help of Laura Whitmore in the recovery of radium and water isotope samples in 2023. We thank the captains and crews of the RV *Akademic Tryoshnikov* and the USCGC *Healy*, as well as the WHOI Mooring Team, for the successful deployment and recovery of both instruments. The staff at McLane Research Laboratories, Inc. helped with the development of the MoRIS design, and Emily Coleman assisted with the water mass deconvolution modeling. This work was financially supported by the National Science Foundation Office of Polar Programs, with awards OPP-2031853 to Lauren Kipp, OPP-2031854 to Matthew A. Charette, and OPP-1724523 to Igor Polyakov and Andrey Pnyushkov.

### Conflicts of Interest

None declared.

### Data Availability Statement

The data used in this manuscript are available through the Arctic Data Center at <https://doi.org/10.18739/A28C9R60N>.

### References

- Bullock, E. J., L. Kipp, W. Moore, et al. 2022. "Radium Inputs Into the Arctic Ocean From Rivers: A Basin-Wide Estimate." *Journal of Geophysical Research: Oceans* 127: e2022JC018964. <https://doi.org/10.1029/2022JC018964>.
- Burt, W. J., H. Thomas, M. Hagens, et al. 2016. "Carbon Sources in the North Sea Evaluated by Means of Radium and Stable Carbon Isotope Tracers: Tracing Carbon With Ra and  $\delta^{13}\text{C}_{\text{DIC}}$ ." *Limnology and Oceanography* 61: 666–683. <https://doi.org/10.1002/lno.10243>.
- Cai, P., X. Shi, Q. Hong, et al. 2015. "Using  $^{224}\text{Ra}/^{228}\text{Th}$  Disequilibrium to Quantify Benthic Fluxes of Dissolved Inorganic Carbon and Nutrients Into the Pearl River Estuary." *Geochimica et Cosmochimica Acta* 170: 188–203. <https://doi.org/10.1016/j.gca.2015.08.015>.
- Cavaliere, D. J., and S. Martin. 1994. "The Contribution of Alaskan, Siberian, and Canadian Coastal Polynyas to the Cold Halocline Layer of the Arctic Ocean." *Journal of Geophysical Research: Oceans* 99: 18343–18362. <https://doi.org/10.1029/94JC01169>.
- Charette, M. A. 2007. "Hydrologic Forcing of Submarine Groundwater Discharge: Insight From a Seasonal Study of Radium Isotopes in a Groundwater-Dominated Salt Marsh Estuary." *Limnology and Oceanography* 52: 230–239. <https://doi.org/10.4319/lno.2007.52.1.0230>.

- Charette, M. a., M. E. Gonneea, P. J. Morris, et al. 2007. "Radium Isotopes as Tracers of Iron Sources Fueling a Southern Ocean Phytoplankton Bloom." *Deep Sea Research Part II: Topical Studies in Oceanography* 54: 1989–1998. <https://doi.org/10.1016/j.dsr2.2007.06.003>.
- Charette, M. A., P. J. Lam, M. C. Lohan, et al. 2016. "Coastal Ocean and Shelf-Sea Biogeochemical Cycling of Trace Elements and Isotopes: Lessons Learned From GEOTRACES." *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 374: 20160076. <https://doi.org/10.1098/rsta.2016.0076>.
- Charette, M. A., P. J. Morris, P. B. Henderson, and W. S. Moore. 2015. "Radium Isotope Distributions during the US GEOTRACES North Atlantic Cruises." *Marine Chemistry* 177: 184–195. <https://doi.org/10.1016/j.marchem.2015.01.001>.
- Coachman, L. K., and C. A. Barnes. 1963. "The Movement of Atlantic Water in the Arctic Ocean." *Arctic* 16: 8. <https://doi.org/10.14430/arctic3517>.
- Fetterer, F., K. Knowles, W. N. Meier, M. Savoie, and A. K. Windnagel. 2017. Sea Ice Index. <https://doi.org/10.7265/N5K072F8>.
- Foster, D. A., M. Staubwasser, and G. M. Henderson. 2004. "<sup>226</sup>Ra and Ba Concentrations in the Ross Sea Measured With Multicollector ICP Mass Spectrometry." *Marine Chemistry* 87: 59–71. <https://doi.org/10.1016/j.marchem.2004.02.003>.
- Garcia-Orellana, J., V. Rodellas, J. Tamborski, et al. 2021. "Radium Isotopes as Submarine Groundwater Discharge (SGD) Tracers: Review and Recommendations." *Earth-Science Reviews* 220: 103681. <https://doi.org/10.1016/j.earscirev.2021.103681>.
- Geibert, W., V. Rodellas, A. Annett, et al. 2013. "<sup>226</sup>Ra Determination Via the Rate of <sup>222</sup>Rn Ingrowth With the Radium Delayed Coincidence Counter (RaDeCC)." *Limnology and Oceanography: Methods* 11: 594–603. <https://doi.org/10.4319/lom.2013.11.594>.
- Gonneea, M. E., P. J. Morris, H. Dulaiova, and M. A. Charette. 2008. "New Perspectives on Radium Behavior Within a Subterranean Estuary." *Marine Chemistry* 109: 250–267. <https://doi.org/10.1016/j.marchem.2007.12.002>.
- Henderson, P. B., P. J. Morris, W. S. Moore, and M. A. Charette. 2013. "Methodological Advances for Measuring Low-Level Radium Isotopes in Seawater." *Journal of Radioanalytical and Nuclear Chemistry* 296: 357–362. <https://doi.org/10.1007/s10967-012-2047-9>.
- Hong, Q., P. Cai, W. Geibert, et al. 2018. "Benthic Fluxes of Metals Into the Pearl River Estuary Based on <sup>224</sup>Ra/<sup>228</sup>Th Disequilibrium: From Alkaline Earth (Ba) to Redox Sensitive Elements (U, Mn, Fe)." *Geochimica et Cosmochimica Acta* 237: 223–239. <https://doi.org/10.1016/j.gca.2018.06.036>.
- Hsieh, Y.-T., W. Geibert, E. M. S. Woodward, et al. 2021. "Radium-228-Derived Ocean Mixing and Trace Element Inputs in the South Atlantic." *Biogeosciences* 18: 1645–1671. <https://doi.org/10.5194/bg-18-1645-2021>.
- Janout, M. A., Y. Aksenov, J. A. Hölemann, et al. 2015. "Kara Sea Freshwater Transport through Vilkitsky Strait: Variability, Forcing, and Further Pathways Toward the Western Arctic Ocean From a Model and Observations." *Journal of Geophysical Research: Oceans* 120: 4925–4944. <https://doi.org/10.1002/2014JC010635>.
- Kadko, D., and W. S. Moore. 1988. "Radiochemical Constraints on the Crustal Residence Time of Submarine Hydrothermal Fluids: Endeavour Ridge." *Geochimica et Cosmochimica Acta* 52: 659–668. [https://doi.org/10.1016/0016-7037\(88\)90328-6](https://doi.org/10.1016/0016-7037(88)90328-6).
- Kipp, L., and M. Charette. 2022. "The Arctic Radium Isotope Observing Network (ARION): Tracking Climate-Driven Changes in Arctic Ocean Chemistry." *Oceanography* 35: 28–37. <https://doi.org/10.5670/oceanog.2022.105>.
- Kipp, L., M. Charette, A. Robbins, A. Pnyushkov, I. Polyakov, and L. Whitmore. 2023. "Radium Isotopes as Tracers of Shelf-Basin Exchange Processes in the Eastern Arctic Ocean." *Journal of Geophysical Research: Oceans* 128: e2023JC020303. <https://doi.org/10.1029/2023JC020303>.
- Kipp, L. E., M. A. Charette, W. S. Moore, P. B. Henderson, and I. G. Rigor. 2018a. "Increased Fluxes of Shelf-Derived Materials to the Central Arctic Ocean." *Science Advances* 4: eaao1302. <https://doi.org/10.1126/sciadv.aao1302>.
- Kipp, L. E., D. C. Kadko, R. S. Pickart, P. B. Henderson, W. S. Moore, and M. A. Charette. 2019. "Shelf-Basin Interactions and Water Mass Residence Times in the Western Arctic Ocean: Insights Provided by Radium Isotopes." *Journal of Geophysical Research: Oceans* 124: 3279–3297. <https://doi.org/10.1029/2019JC014988>.
- Kipp, L. E., V. Sanial, P. B. Henderson, et al. 2018b. "Radium Isotopes as Tracers of Hydrothermal Inputs and Neutrally Buoyant Plume Dynamics in the Deep Ocean." *Marine Chemistry* 201: 51–65. <https://doi.org/10.1016/j.marchem.2017.06.011>.
- Ku, T.-L., and M.-C. Lin. 1976. "<sup>226</sup>Ra Distribution in the Antarctic Ocean." *Earth and Planetary Science Letters* 32: 236–248. [https://doi.org/10.1016/0012-821X\(76\)90064-9](https://doi.org/10.1016/0012-821X(76)90064-9).
- Li, Q., M. Chen, R. Jia, et al. 2017. "Transit Time of River Water in the Bering and Chukchi Seas Estimated From <sup>δ</sup><sup>18</sup>O and Radium Isotopes." *Progress in Oceanography* 159: 115–129. <https://doi.org/10.1016/j.pocean.2017.08.004>.
- Michael, H. A., M. A. Charette, and C. F. Harvey. 2011. "Patterns and Variability of Groundwater Flow and Radium Activity at the Coast: A Case Study From Waquoit Bay, Massachusetts." *Marine Chemistry* 127: 100–114. <https://doi.org/10.1016/j.marchem.2011.08.001>.
- Moore, W. S. 1996. "Large Groundwater Inputs to Coastal Waters Revealed by <sup>226</sup>Ra Enrichments." *Nature* 380: 612–614. <https://doi.org/10.1038/380612a0>.
- Moore, W. S., and R. Arnold. 1996. "Measurement of <sup>223</sup>Ra and <sup>224</sup>Ra in Coastal Waters Using a Delayed Coincidence Counter." *Journal of Geophysical Research* 101: 1321–1329. <https://doi.org/10.1029/95JC03139>.

- Moore, W. S., and D. F. Reid. 1973. "Extraction of Radium From Natural Waters Using Manganese-Impregnated Acrylic Fibers." *Journal of Geophysical Research* 78: 8880–8886. <https://doi.org/10.1029/JC078i036p08880>.
- Polyakov, I. V., A. V. Pnyushkov, E. C. Carmack, et al. 2025. "Role of Sea Ice, Stratification, and Near-Inertial Oscillations in Shaping the Upper Siberian Arctic Ocean Currents." *Ocean Science* 21: 3105–3122. <https://doi.org/10.5194/egusphere-2025-2316>.
- Roach, L. A., and W. N. Meier. 2024. "Sea Ice in 2023." *Nature Reviews Earth & Environment* 5: 235–237. <https://doi.org/10.1038/s43017-024-00542-0>.
- Rudels, B. 2009. "Arctic Ocean Circulation." In *Encyclopedia of Ocean Sciences*, 211–225. Elsevier. <https://doi.org/10.1016/B978-012374473-9.00601-9>.
- Rudels, B. 2012. "Arctic Ocean Circulation and Variability—Advection and External Forcing Encounter Constraints and Local Processes." *Ocean Science* 8: 261–286. <https://doi.org/10.5194/os-8-261-2012>.
- Rutgers van der Loeff, M., R. M. Key, J. Scholten, D. Bauch, and A. Michel. 1995. " $^{228}\text{Ra}$  as a Tracer for Shelf Water in the Arctic Ocean." *Deep Sea Research Part II: Topical Studies in Oceanography* 42: 1533–1553. [https://doi.org/10.1016/0967-0645\(95\)00053-4](https://doi.org/10.1016/0967-0645(95)00053-4).
- Sanial, V., L. E. Kipp, P. B. Henderson, et al. 2018. "Radium-228 as a Tracer of Dissolved Trace Element Inputs From the Peruvian Continental Margin." *Marine Chemistry* 201: 20–34. <https://doi.org/10.1016/j.marchem.2017.05.008>.
- Schauer, U. 1995. "The Release of Brine-Enriched Shelf Water From Storfjord Into the Norwegian Sea." *Journal of Geophysical Research: Oceans* 100: 16015–16028. <https://doi.org/10.1029/95JC01184>.
- Tamborski, J., S. Bejannin, J. Garcia-Orellana, et al. 2018. "A Comparison Between Water Circulation and Terrestrially-Driven Dissolved Silica Fluxes to the Mediterranean Sea Traced Using Radium Isotopes." *Geochimica et Cosmochimica Acta* 238: 496–515. <https://doi.org/10.1016/j.gca.2018.07.022>.
- The Arctic Great Rivers Observatory. 2025. Discharge Dataset (Version 20250327). <https://arcticgreatrivers.org/data/>.
- van der Rutgers Loeff, M., S. Kuhne, M. Wahsner, et al. 2003. " $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  in the Kara and Laptev Seas." *Continental Shelf Research* 23: 113–124. [https://doi.org/10.1016/S0304-4203\(98\)00070-X](https://doi.org/10.1016/S0304-4203(98)00070-X).
- Vieira, L. H., E. P. Achterberg, J. Scholten, et al. 2018. "Benthic Fluxes of Trace Metals in the Chukchi Sea and Their Transport Into the Arctic Ocean." *Marine Chemistry* 208: 43–55. <https://doi.org/10.1016/j.marchem.2018.11.001>.
- Vieira, L. H., W. Geibert, I. Stimac, D. Koehler, and M. M. Rutgers Van Der Loeff. 2021. "The Analysis of  $^{226}\text{Ra}$  in 1-Liter Seawater by Isotope Dilution Via Single-Collector Sector-Field ICP-MS." *Limnology and Oceanography: Methods* 19: 356–367. <https://doi.org/10.1002/lom3.10428>.

Submitted 19 August 2025

Revised 24 November 2025

Accepted 25 November 2025