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Measurement of ^{224}Ra and ^{226}Ra Activities in Natural Waters Using a Radon-in-Air Monitor

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We report a simple new technique for measuring low-level radium isotopes (^{224}Ra and ^{226}Ra) in natural waters. The radium present in natural waters is first preconcentrated onto MnO_2-coated acrylic fiber (Mn fiber) in a column mode. The radon produced from the adsorbed radium is then circulated through a closed air-loop connected to a commercial radon-in-air monitor. The monitor counts alpha decays of radon daughters (polonium isotopes) which are electrostatically collected onto a silicon semiconductor detector. Count data are collected in energy-specific windows, which eliminate interference and maintain very low backgrounds. Radium-224 is measured immediately after sampling via ^{220}Rn (^{216}Po), and ^{226}Ra is measured via ^{222}Rn (^{218}Po) after a few days of ingrowth of ^{222}Rn. This technique is rapid, simple, and accurate for measurements of low-level ^{224}Ra and ^{226}Ra activities without requiring any wet chemistry. Rapid measurements of short-lived ^{222}Rn and ^{224}Ra, along with long-lived ^{226}Ra, may thus be made in natural waters using a single portable system for environmental monitoring of radioactivity as well as tracing of various geochemical and geophysical processes. The technique could be especially useful for the on-site rapid determination of ^{224}Ra which has recently been found to occur at elevated activities in some groundwater wells.

Introduction

The naturally occurring isotopes of radium (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra) as well as ^{222}Rn have been measured in natural waters for monitoring environmental radioactivity (*1, 2*) and for various geophysical studies including mixing and transport of different water masses and assessing submarine groundwater discharge (*3*−*5*). Recently, very high activities of ^{224}Ra have been discovered in some groundwater wells in New Jersey and elsewhere (*6, 7*). This discovery has raised the concern that moderate-to-high levels of alpha-particle activity may exist in many drinking water supplies but have gone undetected because of the time delays which are typical between sampling and analysis. Because drinking water analysis protocols typically do not specify any holding period for gross alpha or beta activity determinations, there is a high likelihood that high alpha activity from ^{224}Ra ($t_{1/2} = 3.66$ d) would be missed by routine monitoring protocols. Proper assessment requires a rapid and simple approach for analysis. Ideally, since time is of the essence, a field-based simple approach would be preferred. Unfortunately, the traditional techniques for measuring Ra isotopes, especially for short-lived ^{224}Ra, are time-consuming and cumbersome (*8*−*11*).

Traditionally, Ra isotopes have been measured by counting alphas (for ^{226}Ra, ^{223}Ra, and ^{224}Ra) and betas (for ^{228}Ra) following tedious chemical separations and source preparations (*8*−*10*). Alternatively, Ra isotopes have been measured by gamma counting of appropriate daughter nuclides (*11*). However, energy discrimination of Ra isotopes by alpha and gamma spectrometry is not always straightforward due to interfering peaks generated by Ra isotopes and their short-lived daughters. Furthermore, gamma spectrometry is not very sensitive because of relatively low efficiencies and high backgrounds.

Another, much simpler, approach has been achieved by measuring Rn and its daughters by alpha scintillation counting following adsorption of Ra onto Mn fiber and transfer/circulation of Rn into a detection chamber. Rama et al. (*12*) developed this approach for ^{224}Ra measurements, but the determination of low-level ^{220}Rn was significantly interfered by ^{218}Po generated from ^{222}Rn during long counting periods. More recently, Moore and Arnold (*13*) developed a technique which provides simultaneous measurement of ^{223}Ra and ^{224}Ra using a delayed coincidence counter designed originally by Griffin et al. (*14*) for detection of radon isotopes. In this approach, signals from a detector are sent to a delayed coincidence circuit which discriminates decays of the ^{224}Ra daughters, ^{220}Rn and ^{216}Po, from decays of the ^{223}Ra daughters, ^{219}Rn and ^{215}Po. The detection efficiency (two alpha decays per Ra decay) is very high with this system, but one disadvantage is increased chance coincidence between ^{223}Ra and ^{224}Ra when the activity of one radium isotope is much higher than the other. In this study we have developed a technique for alpha counting of radon daughters using a commercial radon-in-air monitor which uses electrostatic attraction of positively charged radon daughters to a silicon semiconductor detector. Once precipitated onto the surface of the detector, Po^+ ions produce well-resolved alpha spectra allowing excellent energy resolution.

Experimental Section

General Strategy. This method is based on the principle of radioactive equilibria of Ra isotopes and their short-lived daughters and the different chemical characteristics of each daughter species (Figure 1). The Ra isotopes are first adsorbed onto Mn-fiber by pumping water through a cartridge packed with the Mn-impregnated fiber. This process is quantitative for radium in natural waters at flow rates below about 2 L/min (*15, 16*). The water content of the Mn fiber is then adjusted to obtain constant recoil efficiency for Rn. The Ra daughters (^{222}Rn, ^{220}Rn, and ^{219}Rn) are circulated through an air-loop connected to (1) a desiccant column to remove any moisture that immobilizes the charged Po species; (2) an air filter to keep out particles and attached radon daughters; and (3) a radon-in-air monitor where Rn daughter isotopes (^{218}Po, ^{216}Po, and ^{215}Po) are electrostatically precipitated onto a semiconductor detector which produces alpha spectra thus allowing isotopic separation by energy discrimination (Figure 2). We use a RAD-7 (Durridge Co. Inc., 7 Railroad Ave., Suite

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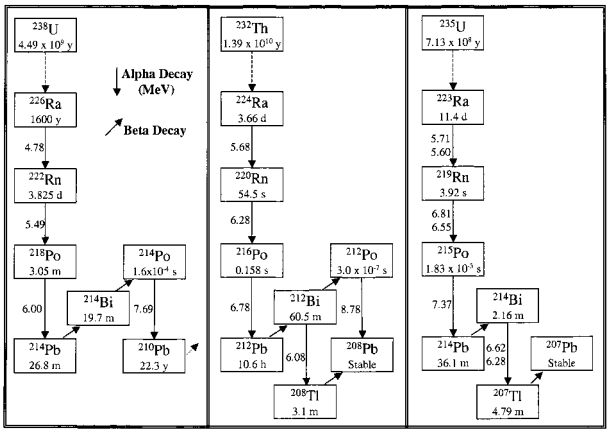

FIGURE 1. Chart showing partial decay chain of the uranium and thorium series isotopes (Ra isotopes and their daughters) and the half-lives of each isotope.

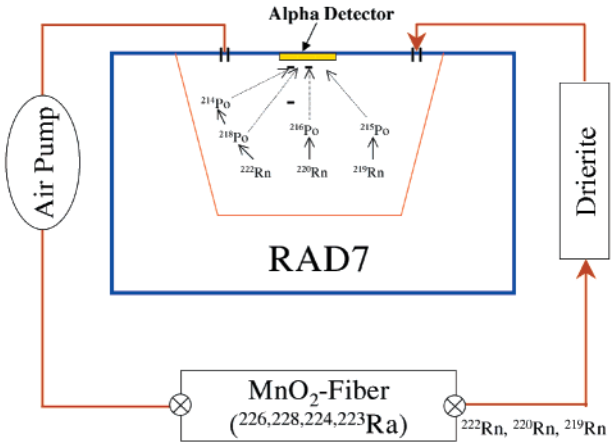

FIGURE 2. Schematic diagram of the Rn circulation and Po isotope measurement system. The Ra isotopes in natural waters are first quantitatively extracted onto MnO_2 fiber in a column mode, and then the Mn-fiber column is connected to a desiccant column and radon-in-air monitor (RAD-7). Since all radium isotopes are adsorbed onto MnO_2 fiber, ^{228}Ra (via ^{228}Ac) may be measured later by gamma spectrometry if desired.

D, Bedford, MA) model radon-in-air monitor because it is portable, durable, very sensitive (low background, high efficiency), and can operate in a continuous mode. The short-lived ^{224}Ra and ^{223}Ra are measured very soon after sampling, and then the Mn fiber cartridge is sealed for several days to allow ingrowth of ^{222}Rn from ^{226}Ra. The initial ^{222}Rn in the column may be eliminated by blowing radon-free air through the column to set the exact ingrowth time. Although the determination of ^{223}Ra via ^{219}Rn is possible using this system, we have found that the detection efficiency is not high enough for the extremely low-level ^{223}Ra found in the natural waters we have tested (using sample volumes up to ~500 L). We thus discuss here application of the Mn-fiber/RAD-7 system for determination of ^{224}Ra and ^{226}Ra activities in natural waters.

Preconcentration of Radium. The Ra isotopes are extracted by passing 20−200 L (more or less may be used depending upon the expected activities) of water through a plastic column (5 cm diameter, and 20 cm length) filled with Mn fiber (~60 g-wet). This can be done conveniently in the field by pumping the water directly through the cartridge—no "sample" needs to be collected but a volume measurement is necessary. The Mn fiber is prepared by impregnating acrylic fiber with MnO_2 following the method described by Moore (*17*) and Reid et al. (*15*). We used two different approaches

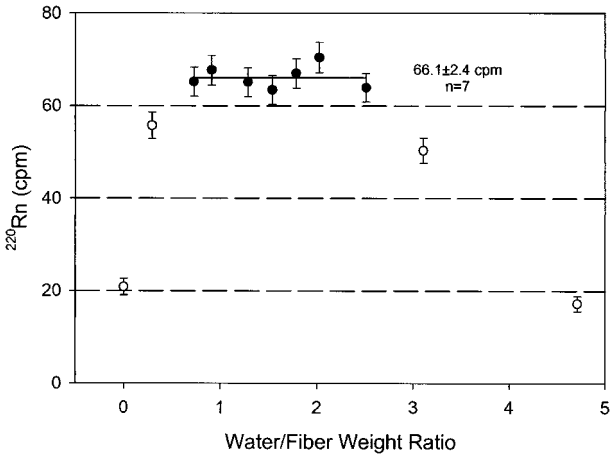

FIGURE 3. Variation in ^{220}Rn emanation efficiencies (counts per minute) plotted against the water content of the Mn fiber for a standard prepared with known amounts of ^{228}Th-^{224}Ra. The water/fiber weight ratio = $(x_i - x_o)/x_o$, where x_i = mass of fiber at each stage of drying, and x_o = mass of fiber when completely dry.

for extraction of Ra isotopes in natural waters. In the first approach, the flow rate of water through a Mn-fiber column is controlled to be lower than ~1.2 L/min which ensures quantitative adsorption of Ra (*15*). We have checked for complete radium uptake by pumping a large-volume sample through two-columns connected in series. No radium was found on the downstream column, while significant radium was on the initial column confirming quantitative adsorption on the first cartridge. In the alternative approach, water samples are passed through a Mn-fiber column using a high flow-rate to yield only the ratios of ^{224}Ra to ^{226}Ra, then the ^{224}Ra was quantified by a separate measurement of ^{226}Ra using a standard radon-emanation method (*18*). The later approach is preferred if the sampling time needs to be as short as possible and would also be more effective for anoxic waters when MnO_2 is partially reduced during preconcentration, causing loss of some Ra.

Water Content of Mn Fiber. The efficiency of Rn escape from Mn fiber to the air depends on the water content of Mn fiber (*19*). This is apparently due to a balance in the stopping effect of water on recoiling radon atoms. Too much moisture will significantly inhibit radon escape, while very dry conditions result in recoiling radon atoms becoming embedded in adjacent Mn fiber particles. We have tested the variation in the escape efficiency of Rn against the water content of Mn fiber by repetitive counting of one standard after several moisture adjustments (Figure 3). We prepared the ^{224}Ra standard fiber for this experiment by repetitive rinsing of a 2-L, pH ≅ 6 solution containing 1020 dpm ^{228}Th (direct parent of ^{224}Ra) through a single Mn fiber cartridge. Since thorium adsorbs to Mn fiber as well as radium, this standard will decay at the longer (1.91 y) half-life of ^{228}Th. After six rinses of the standard solution, the fiber cartridge was drained until excess solution stopped flowing. We then gently squeezed the Mn fiber by hand to reduce the water content further, and the first RAD-7 measurement was taken. Each counting interval consisted of a 5-min cycle to allow equilibration between ^{220}Rn and ^{216}Po, followed by a 30-min counting period. The drying-counting cycle was repeated once more, and then we used compressed air as a drying technique for the rest of the experiment. The initial wet weight of the fiber was ~130 g, and the final dry weight was ~23 g. Most water loss occurred during the first few steps when the fiber was still very saturated. The loss during the RAD-7 counting intervals were evaluated as well and found to be very slight, on the order of 1% or less.

We observed that the highest efficiency of Rn loss from the fiber occurred for weight ratios of water-to-fiber between 0.7 and 2.5, similar to that reported by Sun and Torgersen (*19*). They claimed that even at optimal moisture conditions ^{220}Rn is not completely released from the Mn-fiber although the very high efficiencies observed on delayed coincidence counters (*13*) suggest that the removal must be very high. We find that we can maintain nearly the same water content (wt. ratio ~2) for all standards and samples by firmly hand-squeezing the Mn fiber. This ensures that we are near the high (wet) end of the counting plateau so any additional drying will be of little consequence. The firm hand-squeezing approach also eliminates the need for bulky equipment in the field. Our observations thus suggest that as long as the weight ratio is between about 0.7−2.5, the escape efficiency of Rn from Mn fiber is reproducible.

Determination of ^{224}Ra. Since radioactive equilibrium is achieved between ^{220}Rn and ^{224}Ra in about 5 min, the measurement of ^{224}Ra via ^{220}Rn can be done immediately after sampling. After the moisture on the Mn-fiber is reduced to the proper range, the column is connected to the system (Figure 2), and ^{220}Rn is circulated via an air loop, and ^{216}Po events are monitored using the RAD-7. To test the effect of airflow rate on the detection efficiency of ^{220}Rn, we set the flow rate to 1, 3, and 5 L/min using an external air pump (the internal pump of the RAD-7 may be set to generate a fixed flow rate of 1 L/min). We observed no significant difference in the count rates using the same source at these various flow rates. Thus, one may conveniently use the internal air pump of the RAD-7 for determination of ^{224}Ra. As mentioned earlier, it is important to remove any moisture which comes off the Mn fiber before the air circulates into the RAD-7 chamber. To minimize ^{220}Rn decay in air before it reaches the radon chamber (volume ~700 mL) of the RAD-7, we used a small Drierite column (2 cm diameter, 20 cm length). To allow equilibration of ^{220}Rn and ^{224}Ra, we run the system for 5 min before initiating counting. In general, we program the RAD-7 to integrate ^{220}Rn count data every hour to check the influence of any external factors (i.e., moisture effects) during the total count time. Total counts are integrated when the full time cycle is completed (in general, 4−5 h).

Determination of ^{226}Ra. To measure ^{226}Ra using this system, we placed Mn fiber in a column which was then sealed to allow ingrowth of ^{222}Rn for several days in a manner similar to the approach used by Butts et al. (*20*). Before the column is sealed, any Rn in the Mn fiber is expelled to reset the ingrowth time. We maintained a slightly negative pressure inside a thick plastic or glass column (by pumping air out) to minimize any escape of Rn from the column during the ingrowth period. For measurements of ^{226}Ra via ^{222}Rn, the circulation rate of air is not an important factor due to the long half-life of ^{222}Rn. To allow equilibration of ^{222}Rn and ^{218}Po, the system is allowed to run for 15 min before data are collected. In general, about 1−2 h count times are used for each sample, but this is highly dependent upon the ^{226}Ra activities and the sample volume passed through the fiber. The alpha spectrum clearly discriminates ^{218}Po (6.00 MeV) from the other radon daughters, and if there is any interference from ^{212}Bi (6.08 MeV), the RAD-7 corrects for this by simultaneously counting ^{212}Po (8.78 MeV), the direct daughter of ^{212}Bi.

Applications to ^{223}Ra and ^{228}Th Measurements. In principle, measurements of ^{223}Ra can be made simultaneously with ^{224}Ra by counting ^{215}Po as shown in Figure 4. However, we have found that natural activities of ^{223}Ra are typically too low to be detected easily with this system. We were able to obtain a clear ^{215}Po peak for a 1000-L groundwater sample, but such large samples are not often practical. However, if one should encounter higher levels of ^{223}Ra, it can be measured easily with this system in a manner similar to the ^{224}Ra measurement. Our testing for the large-volume sample shows that it is helpful if any Rn in the column is first eliminated, and ^{214}Po peaks in the detector are allowed to decay away before ^{223}Ra measurements are initiated. Since the half-life of ^{219}Rn (daughter of ^{223}Ra) is very short (3.9 s), the air circulation rate is an important factor (we estimate that approximately 7 L air / min with an external pump would be sufficient). In addition, one should open the air loop for ^{219}Rn counting in order to minimize ingrowth of ^{214}Po in the chamber from ^{222}Rn.

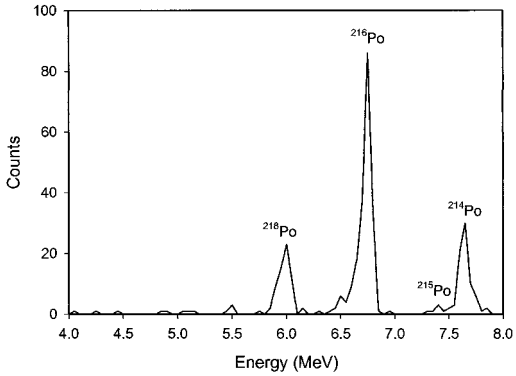

FIGURE 4. A spectrum showing Po peaks produced by the alpha detector located in the RAD-7. If any ^{220}Rn alphas happen by chance to reach the detector, they will have passed through an indeterminate air thickness en route. The pulses will thus be distributed across the spectrum at lower apparent energies than its theoretical value (<6.2 MeV). Very few such events occur, and any effect on the lower energy ^{218}Po peak is further lessened because of the rapid decay of ^{224}Ra during ^{222}Rn ingrowth.

Although thorium isotopes tend to be very low in natural waters, thorium, as well as radium, will be adsorbed onto Mn fibers. If the measurement of ^{228}Th (parent of ^{224}Ra) is desired using this system, it can be measured via the same ^{224}Ra method described here after they reach radioactive equilibrium (~20 days) and any excess ^{224}Ra has decayed away.

Results and Discussion

To obtain the detection efficiency of ^{226}Ra, ^{224}Ra, and ^{223}Ra, we prepared a mixed standard solution containing known activities of ^{226}Ra, ^{232}U/^{228}Th/^{224}Ra, and ^{227}Ac/^{223}Ra. The solution was added to 1 L of deionized water, and a few drops of NH_4OH were added to adjust the pH to ~8, close to that of seawater. The solution was passed through a Mn-fiber column by gravity flow and repeated three times to avoid any loss of Th, Ac, and Ra isotopes. After the water content was adjusted in a manner similar to that used for the samples (firmly hand-squeezed), the detection efficiencies of the system were determined for each isotope.

The purity of ^{224}Ra determined via ^{220}Rn-^{216}Po counting was confirmed using a counting-time series from a large-volume groundwater sample. As shown in Figure 5a, the slope of the excess ^{224}Ra decay curve matches precisely the theoretical decay constant of ^{224}Ra ($\lambda_{Ra-224} = 0.00793\ h^{-1}$). In addition, we monitored the ingrowth of ^{222}Rn-^{218}Po from ^{226}Ra in a column (Figure 5b). The slope of the ingrowth curve matches exactly the theoretical ^{222}Rn ingrowth curve ($\lambda_{Rn-222} = 0.00755\ h^{-1}$), confirming that no escape of ^{222}Rn occurred during ingrowth.

To validate our technique against a documented methodology, we processed several large volume groundwater and seawater samples through Mn fibers. These samples were measured by the RAD-7 system first, and the fibers from the groundwater and standard samples were then sent to the USGS (St. Petersburg, FL) and the seawater samples to the University of South Carolina (Columbia, SC) where delayed

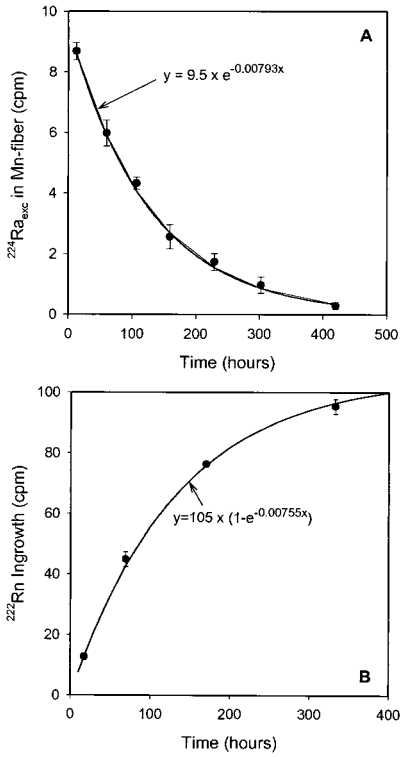

FIGURE 5. The decay curve of ^{224}Ra via ^{220}Rn (A) and the ingrowth curve of ^{222}Rn (B) in a column determined by using a radon monitor (RAD-7) for a large-volume groundwater sample.

TABLE 1. Intercomparison of ^{224}Ra (Disintegrations per Minutes) Results Measured by the Delayed Coincidence Counter (*13*) versus Radon-in-Air Monitor (This Study) for Deep-Well Waters and Offshore Seawaters

sample description	coincidence counter	radon monitor
FSU deep well A	19.52 ± 3.08[a]	17.26 ± 0.42[a]
FSU deep well B	7.80 ± 0.13	6.65 ± 0.37
FSU deep well C	6.44 ± 0.45	6.96 ± 0.33
seawater[b] (5 m)	4.94 ± 0.25	5.51 ± 0.41
seawater (10 m)	5.41 ± 0.27	5.24 ± 0.39
seawater (19 m	7.12 ± 0.36	6.73 ± 0.43
FSU standard	200.16 ± 0.06	200

[a] The uncertainties for the delayed coincidence counter are based on standard deviations of multiple measurements, and for the radon monitor the uncertainties are based on 1-σ counting statistics. [b] The seawater samples were collected around the K-tower, Gulf of Mexico, off FSU Marine Laboratory on August 15, 2000.

coincidence counters (*13*) were available. The results (Table 1) are reported based on each laboratory's calibration, and ^{224}Ra is decay-corrected to the time of sample collection. The activities of ^{224}Ra determined by the two different systems for six natural water samples agree with each other within counting uncertainties. In addition, the FSU standard (200 dpm ^{224}Ra) sent to the USGS was reproduced exactly by the delayed coincidence counter.

Our technique is characterized by a lower ^{224}Ra detection efficiency (cpm/dpm = 0.069) than the delayed coincidence counting (cpm/dpm = 0.45−0.55). This is due to 2-π geometry counting of the electrostatically precipitated Po onto the detector surface compared to the high-efficiency, large-volume scintillation counting in which two alphas per radium decay are measured by the delayed coincidence counter. The efficiency is especially low for ^{223}Ra due to rapid decay of ^{219}Rn in the air stream, which must pass through the Mn-fiber, a Drierite column, and an air filter. However, the technique described here has the advantage of energy discrimination of each Ra isotope using alpha spectrometry. In addition, the equipment is less expensive than a delayed coincidence system and is completely portable allowing field measurements. The system can also be used for precise measurements of ^{222}Rn in air and water. Since the RAD-7 can determine ^{222}Rn in water using a water−air gas equilibrator (*21*), our system allows one to determine Rn as well as Ra isotopes using a single portable radon-in-air monitor for environmental monitoring of radioactivity as well as for various geophysical studies.

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Literature Cited

(1) Baeza, A.; del Rio, L. M.; Jimenez, A. *Radiochim. Acta* **1998**, *83*, 53−60.
(2) Hopke, P. K. et al. *Environ. Sci. Technol.* **2000**, *34*, 921−926.
(3) Kasemsupaya, V.; Tsubota, H.; Nozaki, Y. *Estuarine, Coastal Shelf Sci.* **1993**, *36*, 31−45.
(4) Moore, W. S. *Geochim. Cosmochim. Acta* **1995**, *59*, 4285−4298.
(5) Moore, W. S. *Nature* **1996**, *380*, 612−614.
(6) Parsa, B. J. *Radioact., Radiochem.* **1998**, *9*, 41−50.
(7) Parsa, B.; Nemeth, W. K.; Obed, R. N. *Radioact., Radiochem.* **1999**, *11*, 11−22.
(8) Hamilton, T. F.; McRae, V. M.; Smith, J. D. *J. Radioanal. Nucl. Chem.* **1994**, *177*, 365−371.
(9) Alvarado, J. S.; Orlandini, K. A.; Erickson, M. D. *J. Radioanal. Nucl. Chem.* **1995**, *194*, 163−172.
(10) Eikenberg, J.; Tricca, A.; Vezzu, G.; Bajo, S.; Ruethi, M.; Surbeck, H. *J. Environ. Radioactivity* **2001**, *54*, 109−132.
(11) Moore, W. S. *Nucl. Inst. Methods* **1984**, *223*, 407−411.
(12) Rama; Todd, J. F.; Butts, J. L.; Moore, W. S. *Mar. Chem.* **1987**, *22*, 43−54.
(13) Moore, W. S.; Arnold, R. *J. Geophys. Res.* **1996**, *101*, 1321−1329.
(14) Griffin, C.; Kaufman, A.; Broecker, W. S. *J. Geophys. Res.* **1963**, *68*, 1749−1757.
(15) Reid, D. F.; Key, R. M.; Schink, D. R. *Earth Planet. Sci. Lett.* **1979**, *43*, 223−226.
(16) Moore, W. S.; Key, R. M.; Sarmiento, J. L. *J. Geophys. Res.* **1985**, *90*, 6983−6994.
(17) Moore, W. S. *Deep Sea Res.* **1976**, *23*, 647−651.
(18) Mathieu, G. G.; Biscaye, P. E.; Lupton, R. A.; Hammond, D. E. *Health Physics* **1988**, *55*, 989−992.
(19) Sun, Y.; Torgersen, T. *Mar. Chem.* **1998**, *62*, 299−306.
(20) Butts, J. L.; Todd, J. F.; Lerche, I.; Moore, W. S.; Moore, D. G. *Mar. Chem.* **1988**, *25*, 349−357.
(21) Burnett, W. C.; Kim, G.; Lane-Smith, D. *J. Radioanal. Nucl. Chem.* **2001**, *249*, 167−172.

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