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Comparison of techniques for pre-concentrating radium from seawater

M. Bourquin [a,*], P. van Beek [a], J.-L. Reyss [b], M. Souhaut [a], M.A. Charette [c], C. Jeandel [a]

[a] *LEGOS, Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (CNRS/CNES/IRD/UPS), Observatoire Midi Pyrénées, 14 avenue Edouard Belin, 31400 Toulouse, France*

[b] *LSCE, Laboratoire des Sciences du Climat et de l'Environnement (CNRS/CEA/UVSQ), avenue de la Terasse, 91198 Gif-sur-Yvette, France*

[c] *Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA*

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Abstract

In the framework of the KEOPS project (KErguelen: compared study of the Ocean and the Plateau in Surface water), we aimed to provide information on the water mass pathways and vertical mixing on the Kerguelen Plateau, Southern Ocean, based on ^{228}Ra profiles. Because ^{228}Ra activities are extremely low in this area (~0.1 dpm/100 kg or ~2.10^{-18} g kg^{-1}), the filtration of large volumes of seawater was required in order to be able to detect it with minimal uncertainty. This challenging study was an opportunity for us to test and compare methods aimed at removing efficiently radium isotopes from seawater. We used Mn-fiber that retains radium and that allows the measurement of all four radium isotopes (^{226}Ra, ^{228}Ra, ^{223}Ra, ^{224}Ra). First, we used Niskin bottles or the ship's seawater intake to collect large volumes of seawater that were passed onto Mn-fiber in the laboratory. Second, we filled cartridges with Mn-fiber that we placed in tandem on *in situ* pumps. Finally, we fixed nylon nets filled with Mn-fiber on the frame of *in situ* pumps to allow the passive filtration of seawater during the pump deployment.

Yields of radium fixation on the cartridges filled with Mn-fiber and placed on *in situ* pumps are ca. 30% when combining the two cartridges. Because large volumes of seawater can be filtered with these pumps, this yields to effective volumes of 177–280 kg (that is, higher than that recovered from fourteen 12-l Niskin bottles). Finally, the effective volume of seawater that passed through Mn-fiber placed in nylon nets and deployed during 4 h ranged between 125 and 364 kg. Consequently, the two techniques that separate Ra isotopes *in situ* are good alternatives for pre-concentrating radium from seawater. They can save ship-time by avoiding repeated CTD casts to obtain the large volumes of seawater. This is especially true when *in situ* pumps are deployed to collect suspended particles. However, both methods only provide ^{228}Ra/^{226}Ra ratios. The determination of the ^{228}Ra specific activity is obtained by multiplying this ratio by the ^{226}Ra activity measured in a discrete sample collected at the same water depth.

Keywords: Radium isotopes; Extraction techniques; Mn-fiber; KEOPS; Southern Ocean

1. Introduction

The study of radium isotopes (^{226}Ra, $T_{1/2}=1602$ a; ^{228}Ra, $T_{1/2}=5.75$ a; ^{223}Ra, $T_{1/2}=11.4$ d; ^{224}Ra, $T_{1/2}=3.66$ d) in seawater is of great interest in marine geochemistry. The global distribution of ^{226}Ra and ^{228}Ra has been widely documented during the GEOSECS

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[*] Corresponding author. Tel.: +33 0 5 61 33 29 30; fax: +33 0 5 61 25 32 05.
E-mail address: michael.bourquin@legos.obs-mip.fr (M. Bourquin).

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program (Broecker et al., 1967, 1976; Chung and Craig, 1980; Ku and Lin, 1976; Ku et al., 1980). Radium isotopes have been used to study the water mass pathways or to provide information on horizontal and vertical ocean mixing i) on a large scale using ^{226}Ra (Broecker et al., 1976; Chung, 1976, 1987; Chung and Craig, 1980; Ku et al., 1970, 1980; Ku and Lin, 1976; Ku and Luo, 1994) and ii) at mesoscale using ^{228}Ra (Charette et al., 2007; Kaufman et al., 1973; Key et al., 1985; Moore, 1969, 2000; Moore and Santschi, 1986; Moore et al., 1980; Rutgers van der Loeff, 1994; Rutgers van der Loeff et al., 1995; van Beek et al., in press). Residence time of water masses could be estimated using ^{228}Ra (Rutgers van der Loeff, 1994). Ra isotopes – including short lived ^{223}Ra and ^{224}Ra – have also been widely used to trace submarine groundwater discharge (SGD) (Charette et al., 2001; Krest et al., 2000; Moore, 1996, 2000). In particular, they are used to assess groundwater discharge rates in coastal environments (Charette et al., 2001; Krest et al., 2000; Windom et al., 2006). Measurement of ^{223}Ra and ^{224}Ra isotopes away from the shore can provide estimates of horizontal mixing rates (Moore, 2000).

The specific activity of radium isotopes in seawater, however, is particularly low (ie. usually ca. 0.1 to several tens of disintegrations per minute – dpm – per 100 kg of seawater). The radiometric measurement of radium isotopes thus requires the collection of large volumes of seawater. While the measurement of ^{226}Ra can be performed using relatively small volumes of seawater (ca. 5 l using gamma counting; 150 ml using MC-ICP/MS, Foster et al., 2004; 40 ml using TIMS; Staubwasser et al., 2004), larger volumes are required for the analysis of ^{228}Ra (ie. 30–150 l; Moore et al., 1985; Schmidt and Reyss, 1996; van Beek et al., 2007, in press) and especially for both ^{223}Ra and ^{224}Ra (several hundreds litres; Moore, 2000). Ship-time consuming collection of large volumes of seawater from a research vessel, however, is often problematic, especially when deep waters are concerned. Various techniques have been tested to collect such large volumes of seawater.

Moore (1969) attempted to raise great volumes of deep waters to the surface using a 700 l sampler consisting of a large canvas bag. However, handling the bag once on board the ship was not easy and sometimes more hazardous than efficient. During the GEOSECS program, seawater was brought on deck using 280 l-Gerard barrels (no longer in use) or 30 l-Niskin bottles (Broecker et al., 1976; Chung, 1987; Chung and Craig, 1980; Ku and Lin, 1976; Ku et al., 1980). 12 l-Niskin bottles can also be used but many bottles are required for a single sample. Approximately four 12 l-bottles are needed for waters from the Atlantic Ocean (van Beek et al., 2007) and twelve 12 l-bottles for samples from the Southern Ocean (van Beek et al., in press) in order to measure significant amount of ^{228}Ra, but only when using gamma detectors located in an underground laboratory (Reyss et al., 1995). These volumes thus represent the minimal volumes required to determine oceanic ^{228}Ra activities.

Upon collection, multiple methods can be used to pre-concentrate Ra isotopes for analysis. Early studies used co-precipitation with $BaSO_4$ (Kaufman et al., 1973; Moore, 1969). This method provides good yields of radium separation (60–90%; Moore, 1969). However, because large volumes of seawater are needed, this technique is not always easy to apply on a ship. Co-precipitation with Pb has also been used (Yamada and Nozaki, 1986). More commonly, radium isotopes can be removed from seawater using filtration techniques. Krishnaswami et al. (1972) found that several elements, including radium, could be extracted from seawater using acrylic fibers impregnated with iron hydroxide. Moore and Reid (1973) later showed that radium recovery was more efficient when acrylic fibers were impregnated with manganese oxides (so called "Mn-fibers"). Thus they proposed to pass seawater through PVC columns filled with Mn-fiber at low flow rate (<1 l min^{-1}) to maximize radium fixation on the Mn-fiber. At such a flow-rate, the yield of radium fixation is 100% (Moore et al., 1985; van Beek and Reyss, unpublished data).

^{223}Ra and ^{224}Ra activities can be measured directly on the Mn-fiber using a Radium Delayed Coincidence Counter (RaDeCC; Moore and Arnold, 1996). For further ^{226}Ra and ^{228}Ra analysis, the Mn-fiber can either i) be leached with HCl or HNO_3 to extract the Mn and Ra from the fiber, Ra being then recovered by $BaSO_4$ precipitation (Knauss et al., 1978; Moore, 1976, 1987; Moore et al., 1985; Moore and Reid, 1973; Moore and Santschi, 1986; Reid et al., 1979; Yamada and Nozaki, 1986) or ii) be ashed for gamma counting (Charette et al., 2001, 2007; van Beek et al., 2007, in press). Gamma counting of the ash thus provides ^{226}Ra and ^{228}Ra specific activities. Note that other techniques aimed at separating Ra from environmental samples are available in the literature, involving extraction chromatographic resins (Burnett et al., 1995; Maxwell, 2006), MnO_2-coated polyamide discs (Eikenberg et al., 2001; Surbeck, 1995) and 3M EMPORE™ Radium Rad disks (Joannon and Pin, 2001; Purkl and Eisenhauer, 2004; Rihs and Condomines, 2002), though none are currently practical for processing large volumes (>several litres) of seawater.

Alternatively, methods based on *in situ* filtration of seawater were developed, allowing the filtration of much larger volumes of seawater. *In situ* extraction of radium thus prevented collection of large volumes of seawater and the subsequent handling on the deck. The first method being used *in situ* relied on a system using Mn-fiber placed in a sampler that was deployed together with a Niskin bottle (Moore and Reid, 1973). This sampler was designed to limit interaction between seawater and Mn-fiber during sampler's descent or ascent. This method was improved using adapted Niskin bottles that contained Mn-fiber placed in nylon nets (Moore, 1976). Alternatively, a PVC-sampler (Knauss et al., 1978) or nylon nets filled with Mn-fiber and fixed directly onto the mooring cable, CTD wire or onto the frame of *in situ* pumps have also been used (Charette et al., 2007; Kim et al., 2003; van Beek et al., in press, respectively). These nylon nets were suspended at a given depth to passively filter large volumes of seawater. Finally, polypropylene cartridges coated with MnO_2 and placed in tandem on *in situ* pumps are also often used to remove radionuclides – including radium – from seawater (Bacon and Anderson, 1982; Baskaran et al., 1993; Hanfland, 2002; Rutgers van der Loeff and Berger, 1993; Rutgers van der Loeff, 1994; Rutgers van der Loeff et al., 1995). Cartridges can then either i) be leached using HCl or HNO_3, radium being recovered following $BaSO_4$ precipitation (Rutgers van der Loeff, 1994; Rutgers van der Loeff and Berger, 1993; Rutgers van der Loeff et al., 1995) or ii) ashed prior to gamma counting (Hanfland, 2002). With these *in situ* techniques, only the $^{228}Ra/^{226}Ra$ ratio can be determined. The ^{226}Ra and ^{228}Ra specific activities can be determined by analyzing the ^{226}Ra activity of a discrete sample collected at the same water depth. Combining the known ^{226}Ra activity and the $^{228}Ra/^{226}Ra$ ratio measured in the Mn-fiber thus provides the ^{228}Ra activities (as well as ^{224}Ra and ^{223}Ra activities if desired).

High biological productivity takes place each year on the Kerguelen Plateau in the Indian sector of the Southern Ocean although it is known to be the largest High Nutrient-Low Chlorophyll (HLNC) region in the world (Blain et al., 2001). This high biological activity has been related to natural iron fertilization (Blain et al., 2007). In the framework of the KEOPS project (KErguelen: compared study of the Ocean and the Plateau in Surface water; P.I.: Stéphane Blain) that took place between 19 January and 13 February 2005, we analyzed Ra isotopes i) to provide information on water mass pathways and on vertical mixing and ii) to trace the input of sedimentary iron and its fate on the Kerguelen Plateau (van Beek et al., in press). This expedition provided the opportunity to compare different techniques aimed at efficiently separating and pre-concentrating radium isotopes from seawater. In particular, because ^{228}Ra activities are very low in the Southern Ocean (ca. 0.1 dpm/100 kg; ~2 ag kg^{-1}; *a* for *atto*, 10^{-18}; Charette et al., 2007; Hanfland, 2002; Kaufman et al., 1973; Li et al., 1980; van Beek et al., in press), analysis of this isotope was particularly challenging. Therefore, it was important to define a method that i) allowed collection or filtration of large volumes of seawater from surface to bottom waters, ii) removed efficiently radium from seawater, iii) was relatively easy to apply on a research vessel and iv) minimized ship-time. More generally, it is important to define which method is potentially the best method to use in future cruises and in particular in those that will take place in the framework of the emerging GEOTRACES program sponsored by SCOR (Scientific Committee on Oceanic Research) and aimed at studying the global marine biogeochemical cycles of trace elements and their isotopes. During the KEOPS expedition, we tested and compared methods aimed at filtering *in situ* large volumes of seawater to pre-concentrate Ra isotopes. We chose to employ Mn-fibers, which we find relatively easy to use to extract radium isotopes from seawater and that allow the measurement of the four radium isotopes (^{223}Ra and ^{224}Ra using RaDeCC, Moore and Arnold, 1996; ^{226}Ra and ^{228}Ra using gamma counting). In this work, Mn-fiber was either placed i) in nylon nets that were attached to the frame of *in situ* pumps or ii) within uncoated polypropylene cartridges mounted in tandem on Challenger Oceanics Systems™ large volume *in situ* pumps. Comparison of the amount of ^{226}Ra and ^{228}Ra retained using these *in situ* techniques with that retained when filtering a known volume of seawater through Mn-fiber in the laboratory (reference method) allows us to make comparisons about the relative benefits and drawbacks of these *in situ* techniques.

2. Material and methods

2.1. Stations investigated during KEOPS

During KEOPS, stations were investigated on and outside the Kerguelen Plateau to study biologically contrasting environments (low chlorophyll areas *versus* bloom areas; for details, see Blain et al., 2007; van Beek et al., in press). Two deep stations, considered as HNLC-type stations, were investigated east and west of the Kerguelen Plateau: station Kerfix located southwest of the Kerguelen Island (50°40′ S, 68°25′ E; 1700 m depth) and station C11 located east of the Kerguelen Plateau (51°38′ S, 77° 59′ E; 3500 m depth). In contrast, station A3, a shallow station above the Kerguelen Plateau was located in the middle of the phytoplankton bloom (50°39′ S, 72°04′ E; 520 m depth).

2.2. Methods used to extract radium from seawater

2.2.1. Extraction of radium in the laboratory

Radium was extracted from seawater using Mn-fiber made from standard techniques (Moore and Reid, 1973; Moore et al., 1985). On board the ship, water samples were passed through a PVC column filled with Mn-fiber at a flow rate lower than 200 ml min^{-1}, thus providing 100% extraction of radium (Moore et al., 1985; van Beek and Reyss, unpublished data).

Surface samples were collected using either i) the "OISO" seawater supply (used for the continuous $p\mathrm{CO}_2$ analysis as part of the OISO program, Océan Indien Service d'Observation; P.I.: Nicolas Metzl) that collects seawater at approximately 6 m depth (referred to as "OISO" samples further and in the Tables) and ii) an *in situ* pump that brought up seawater to the deck via a hose with a flow rate of 50 l min^{-1} (Trull and Armand, 2001), allowing us to collect samples down to 120 m depth (referred to as "HP" samples further and in the Tables). Below this depth, large volumes of seawater were collected using 12-l Niskin bottles. Up to twelve Niskin bottles were closed for a single depth. This provided up to 138 kg of seawater for one sample (referred to as "Niskin" samples further and in the Tables). For the three stations, vertical profiles of $^{228}\mathrm{Ra}$ and $^{226}\mathrm{Ra}$ were thus built using several successive CTD casts. For stations Kerfix and C11, a column filled with Mn-fiber was also directly connected to a second ship's seawater intake (referred to as "UW" samples further and in the Tables). A flow-meter connected to the bottom of the column allowed us to record the volume of seawater that passed through the Mn-fiber. The flow-rate was adjusted to <1 l min^{-1} to assure 100% yield of radium recovery.

2.2.2. In situ extraction of radium

Challenger Oceanics Systems™ large volume *in situ* pumps (Haslemere, UK) were deployed during four hours at stations Kerfix and C11 in order to filter large volumes of seawater (up to 1000 l) and to collect suspended particles. We used this opportunity to test a new method aimed at removing radium from seawater using Mn-fiber. Polypropylene cartridges impregnated with manganese oxide and placed in tandem on *in situ* pumps after the particle filter have often been used to remove radionuclides – including radium – from seawater (Bacon and Anderson, 1982; Hanfland, 2002; Rutgers van der Loeff, 1994; Rutgers van der Loeff and Berger, 1993). Here, we proposed to "fill" Hytrex™ cartridges (9–3/4 in.) with 17–20 g of dry Mn-fiber, rather than using cartridges impregnated with MnO_2 (Figs. 1 and 2). The cartridges placed in tandem were thus used as holders for Mn-fiber (referred to as "Cart.1" and "Cart.2" in the Tables). Following filtration through 0.8 μm Versapor™ filters, seawater is directly injected through the cartridges. First, this method has an advantage in that it avoids the lengthy chemical treatment required for the cartridges impregnated with MnO_2. Second, Mn-fibers are currently used to analyze $^{223}\mathrm{Ra}$ and $^{224}\mathrm{Ra}$ using a Radium Delayed Coincidence Counter (RaDeCC) (Charette et al., 2001; Moore, 2000; Moore and Arnold, 1996). The use of Mn-fiber, therefore, allows the measurement of both $^{223}\mathrm{Ra}$ and $^{224}\mathrm{Ra}$, in addition to $^{228}\mathrm{Ra}$ and $^{226}\mathrm{Ra}$. These short-lived isotopes can indeed not be easily measured using cartridges impregnated with MnO_2. The use of Mn-fiber for this analysis is more appropriate because it provides a better efficiency of radon (Rn) emanation, $^{219}\mathrm{Rn}$ and $^{220}\mathrm{Rn}$ being the daughters of $^{223}\mathrm{Ra}$ and $^{224}\mathrm{Ra}$ that are measured using the RaDeCC. Note that the flow-meters connected to the *in situ* pumps provide volumes in litres. By using the density of seawater at the depths where *in situ* pumps were deployed (based on CTD data), we converted these volumes (l) into mass (kg). This allows the comparison to the values of the other samples reported in kg.

Finally, we employed a method based on the passive filtration of seawater (Knauss et al., 1978). Following

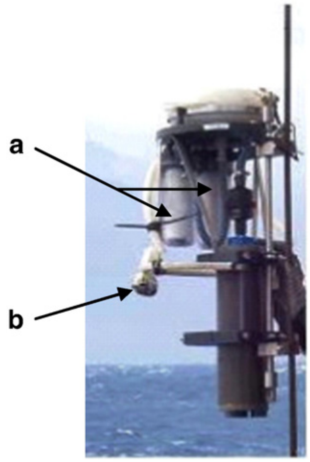

Fig. 1. *In situ* techniques of Ra extraction used in this work. a. Hytrex™ cartridges filled with Mn-fiber and placed in tandem on a Challenger *in situ* pump. Here, we use the polypropylene cartridges as holders for the Mn-fiber. b. Mn-fiber placed in a nylon net that is attached to the frame of the *in situ* pump.

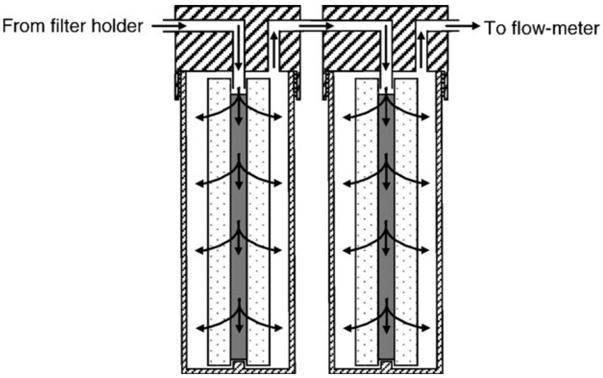

Fig. 2. Cross-section of the two cartridges placed in tandem on *in situ* pumps. The shaded zones represent the Mn-fiber placed in the middle of the cartridges. Arrows indicate the seawater flow passing through the cartridges.

Kim et al. (2003) and Charette et al. (2007), Mn-fibers packed in nylon bags were attached to the *in situ* pump's frame (Fig. 1). The Mn-fibers were thus left in seawater during the 4-hour pumping sessions. These samples are referred to as "Nylon" further and in the Tables.

2.2.3. MnO_2 co-precipitation

Rutgers van der Loeff and Moore (1999) used MnO_2 co-precipitation to remove ^{234}Th from seawater. During KEOPS, we used this technique to remove ^{231}Pa, ^{230}Th and Nd isotopes from 30-l samples (Venchiarutti et al., in revision). Because co-precipitation with MnO_2 also removes radium from seawater (Ghaleb et al., 2004; Ollivier, 2006), we measured the ^{226}Ra activities in the MnO_2 precipitate for samples collected at station A3. We used minimal amounts of reagents in order to reduce the blank levels for the quantification of ^{231}Pa, ^{230}Th and Nd isotopes. 30 litres of seawater were collected with Niskin bottles and filtered to remove particles. The pH was adjusted to 8–9 using NH_4OH; 375 µl of $KMnO_4$ solution (60 g l^{-1}) and 150 µl of $MnCl_2$ solution (400 g l^{-1}) were then added. The MnO_2-precipitate was recovered by filtering the water through 0.8 µm Versapor™ or 0.65 µm Durapore™ filters.

2.3. Analytical methods

Back in laboratory, the Mn-fibers recovered from the different techniques (laboratory *versus in situ*) were ashed at 820 °C for 16 hours (Charette et al., 2001; van Beek et al., 2007). The ash was transferred into sealed vials for gamma counting. Samples were counted at the underground laboratory of Modane (Laboratoire Souterrain de Modane, French Alps). High-efficiency, low-background, well-type germanium detectors (430 cm^3 and 980 cm^3, EURISYS Mesures and CANBERRA companies) were used (Reyss et al., 1995). These detectors are shielded from cosmic radiation by 1700 m of rocks; a very low background is thus achieved, allowing the measurement of very low activities. ^{226}Ra activities were determined using the ^{214}Pb (295 keV and 352 keV) and ^{214}Bi (609 keV) peaks. ^{228}Ra activities were determined using the 338 keV, 911 keV and 969 keV peaks of ^{228}Ac. Counting time for each sample ranges from 300 min to 5 days. We report ^{228}Ra activities only for samples that were counted for a long period of time (>3 days). Uncertainties reported for ^{226}Ra and ^{228}Ra activities are errors due to counting statistics (one standard deviation).

3. Results and discussion

3.1. Counting statistics

Net counts (bulk counts given by the detector and corrected for the continuum) are reported in Table 2 to provide information on the counting statistics of the samples that we measured by gamma counting. Net counts vary according to i) the length of the gamma counting sessions (315 to 5722 min), ii) the volume of seawater that passed through the Mn-fiber and iii) the amount of Ra that was retained by the Mn-fiber. Net counts are much higher for ^{226}Ra and are often close to detection limits for ^{228}Ra. The number of ^{226}Ra counts per minute (cpm) range from 3.7 to 134.3 cpm for samples processed in the laboratory (Niskin, HP, UW and OISO samples) and from 3.8 to 19.9 cpm for samples collected *in situ* (that is, 6.7–19.9 cpm for nylon samples and 3.8–7.2 cpm for cartridge samples). These values mainly reflect the volume of seawater that passed through Mn-fiber rather than the seawater activities.

3.2. Ra activities and ^{228}Ra/^{226}Ra ratios

^{226}Ra activities (expressed in dpm/100 kg) are reported in Table 2. ^{228}Ra activities (expressed in dpm/100 kg) and ^{228}Ra/^{226}Ra ratios are reported only for samples that were counted long enough (ca. 3 days counting minimum). ^{226}Ra and ^{228}Ra specific activities can be directly determined in samples that were filtered through Mn-fiber in the laboratory. In the latter case, the volume of seawater that passes through the Mn-fiber and the flow rate are known, therefore, the yield of Ra fixation is assumed to be 100% (Moore et al., 1985). In contrast, for nylon samples, because the volume of seawater is unknown, the analysis of these Mn-fibers only provides ^{228}Ra/^{226}Ra ratios. Similarly, for cartridge samples, filtration at high flow-rate (up to 10 l min^{-1} when using Challenger Oceanic Systems™ pumps) through Mn-fibers does not yield 100% radium fixation. Therefore, the analysis of the cartridge samples, like the nylon samples, only provides ^{228}Ra/^{226}Ra ratios. For these two methods, the determination of the ^{228}Ra activity is obtained when combining the ^{228}Ra/^{226}Ra ratios with the ^{226}Ra activity of a discrete sample collected at the same water depth.

The ^{228}Ra/^{226}Ra ratios found in samples filtered *in situ versus* those measured on samples filtered in the laboratory display a relatively good agreement (Table 2 and Fig. 3). The ^{228}Ra/^{226}Ra ratio at station C11, 200 m depth is 0.007 ± 0.004 for the Niskin sample filtered in the laboratory and is 0.008 ± 0.002 for the nylon sample. The ratio is 0.013 ± 0.002 for the Niskin sample collected at 3300 m depth and 0.010 ± 0.001 for the nylon sample (3200 m depth). Finally, the ^{228}Ra/^{226}Ra ratio of the nylon sample collected at 500 m depth at station Kerfix is 0.003 ± 0.001 and is 0.006 ± 0.003 for the Niskin sample collected at the same water depth and filtered in the laboratory. The ^{228}Ra/^{226}Ra ratios measured in nylon samples have lower counting uncertainties. This pattern can be related to the larger effective volume of seawater that passed through these Mn-fibers. Finally, we note that the ^{226}Ra activities found in surface samples at station Kerfix are very similar when comparing the OISO sample (15.3 ± 0.19 dpm/100 kg) and the UW sample (15.4 ± 0.10 dpm/100 kg; Table 2). In contrast, the ^{226}Ra and ^{228}Ra activities of the UW sample collected at station C11 (14.5 ± 0.03 dpm/100 kg and 0.036 ± 0.010 dpm/100 kg, respectively) are significantly lower than the OISO sample filtered in the laboratory (17.1 ± 0.05 dpm/100 kg and 0.062 ± 0.02 dpm/100 kg for the ^{226}Ra and ^{228}Ra activities, respectively); the ^{228}Ra/^{226}Ra ratios in both samples, however, are quite similar (0.002 ± 0.001 for the UW sample, 0.004 ± 0.001 for the OISO sample; Table 2 and Fig. 3). Because a very large volume of seawater was filtered through that UW sample (ie. 2926 kg), it cannot be excluded that the Mn-fiber was saturated with respect to radium adsorption. It that case, Ra isotopes might not be retained quantitatively anymore.

3.3. Comparison of the methods used to extract radium from seawater

We compare the efficiency of the different methods by taking into account the volume of seawater that could be filtered through Mn-fiber and the yield of Ra fixation associated with each method (Table 1). Ship-time required for the different methods is also an important aspect to consider.

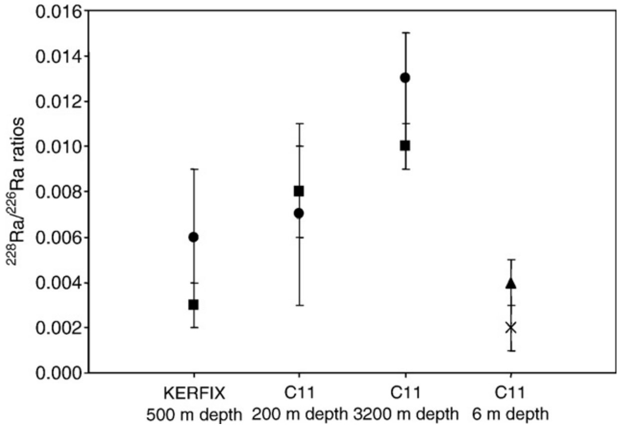

Fig. 3. Comparison of the ^{228}Ra/^{226}Ra ratios measured in samples collected at the same water depths: Niskin samples (circles); Nylon samples (squares); UW sample (cross); OISO sample (triangle).

Table 1
Methods used in this work to extract Ra from seawater (laboratory *versus in situ* techniques)

Method used	Way to collect or filter seawater	Way to use Mn-fiber	What do we measure?	Volume of seawater filtered through Mn-fiber
OISO	Ship's seawater supply	Filtration in laboratory	^{226}Ra and ^{228}Ra activities	Known
Niskin	12 l-Niskin bottles	Filtration in laboratory	^{226}Ra and ^{228}Ra activities	Known
HP	*in situ* pump that brings up seawater to the deck via a hose	Filtration in laboratory	^{226}Ra and ^{228}Ra activities	Known
UW	Ship's seawater supply (Mn-fiber directly connected to the intake)	Filtration in laboratory	^{226}Ra and ^{228}Ra activities	Known
Nylon	Mn-fiber in nylon nets attached to the *in situ* pump's frame	Filtration *in situ*	Only ^{226}Ra/^{228}Ra ratios[a]	Unknown
Cart.1 Cart.2	Cartridges filled with Mn-fiber and placed in tandem on *in situ* pumps	Filtration *in situ*	Only ^{226}Ra/^{228}Ra ratios[a]	Known[b]

[a] The ^{228}Ra activities can be determined when combining the ^{228}Ra/^{226}Ra ratios of these samples with the ^{226}Ra activity of a discrete sample collected at the same water depth.

[b] The volume of seawater that passed through the flow-meter of the *in situ* pump is known. However, the yields of Ra extraction are unknown. Therefore, the effective volume is unknown. See text for further details.

3.3.1. Filtration of seawater in the laboratory

The use of six to twelve 12 l-Niskin bottles allowed us to collect between 68 kg and 138 kg of seawater for a single sample (Table 2). Up to 103 kg of seawater were collected using HP at station C11 (100 m), up to 274 kg using the OISO seawater supply (surface samples) and up to 2926 kg using UW (surface samples). The major advantage of this latter method is that radium isotopes are retained with 100% yield on the fiber (Moore et al., 1985). Hence, the volume of seawater that passed through Mn-fiber is known. We have access, therefore, to specific Ra activities (expressed in dpm/100 kg;

Table 2
Results obtained with the different techniques designed to extract Ra isotopes from seawater (laboratory *versus in situ* techniques)

Station	Depth (m)	Method used to collect or filter seawater	Volume (kg)	Counting time (min.)	^{226}Ra (dpm/100 kg)	Net counts	Counts per minute	^{228}Ra (dpm/100 kg)	Net counts	^{228}Ra/^{226}Ra
KERFIX	6	OISO	141	974.7	15.3±0.19	6661±84	6.8±0.1	Short counting	Short counting	Short counting
	6	UW	557[c]	970.3	15.4±0.10	25681±164	26.5±0.2	Short counting	Short counting	Short counting
KERFIX	50	Niskin	85	4366.4	16.2±0.12	19160±142	4.4±0.03	0.069±0.037	57±30	0.004±0.002
	50	Cart.1	634[b]	315.1	Unknown	2277±49	7.2±0.2	Unknown	Short counting	Short counting
KERFIX	500	Niskin	97	3921.2	17.3±0.12	20764±148	5.3±0.04	0.107±0.046	75±32	0.006±0.003
	500	Nylon	Unknown	5589.8	Unknown[a]	111191±340	19.9±0.1	Unknown[a]	187±63	0.003±0.001
	500	Cart. 1	996[b]	–	Unknown	8147±93	–	Unknown	Short counting	Short counting
	500	Cart. 2	996[b]	–	Unknown	7651±91	–	Unknown	Short counting	Short counting
C11	6	OISO	274	7954.2	17.1±0.05	117679±350	14.8±0.04	0.062±0.020	203±66	0.004±0.001
	6	UW	2926[c]	2537.9	14.5±0.03	340766±594	134.3±0.2	0.036±0.010	351±102	0.002±0.001
C11	100	HP	103	2882.5	18.0±0.14	16940±134	5.9±0.05	0.143±0.063	66±29	0.008±0.003
	80	Cart.1	537[b]	307.3	Unknown	1579±42	5.1±0.1	Unknown	Short counting	Short counting
	80	Cart.2	537[b]	299.9	Unknown	1151±36	3.8±0.1	Unknown	Short counting	Short counting
C11	200	Niskin	68	4268.3	16.9±0.14	15637±130	3.7±0.03	0.119±0.062	64±33	0.007±0.004
	200	Nylon	Unknown	5722.2	Unknown[a]	38444±201	6.7±0.04	Unknown[a]	143±42	0.008±0.002
C11	3300	Niskin	138	4430.5	22.2±0.11	43020±212	9.7±0.05	0.278±0.049	240±42	0.013±0.002
	3200	Nylon	Unknown	5629.6	Unknown[a]	102590±326	18.2±0.1	Unknown[a]	436±63	0.010±0.001

Short counting: counting duration was too short (<17 h) to provide accurate ^{228}Ra activities. Errors given are based on counting statistics (one standard deviation).

See text for further details.

[a] Ra specific activities will be determined in the following tables.

[b] We report the volume of seawater that passed through the flow-meter of the *in situ* pump.

[c] We converted into mass (kg) the volume given by the flow-meter (in l) using the density of seawater at the sampling depth (based on CTD data).

Table 2). However, the ship-time needed to collect these samples (this is especially true for Niskin bottles) together with the difficulty in handling large volumes of seawater in the laboratory often limit the amount of seawater that is available.

3.3.2. Nylon nets

The volume of seawater that passed through Mn-fiber using nylon nets as well as the yield of Ra fixation onto Mn-fiber are unknown. The analysis of these samples, therefore, only provides $^{228}Ra/^{226}Ra$ ratios (Table 2). Note that the Ra specific activities can be determined when combining these ratios with the ^{226}Ra activity of a discrete sample collected at the same water depth. Comparison of the amount of ^{226}Ra activity (expressed in dpm) measured in the nylon sample with the ^{226}Ra activity measured in a sample collected at same depth and filtered in the laboratory allows us to estimate the volume of seawater from which Ra could be efficiently removed (Table 2). We call this latter volume the *effective volume*.

The amount of ^{226}Ra recovered using nylon nets deployed during 4 hours corresponds to effective volumes of 364 kg (Kerfix, 500 m), 125 kg (C11, 200 m) and 259 kg (C11, 3200 m) (Table 3). The differences observed between the effective volumes could be mainly explained by the movement of the wire. The wind and waves induce a bouncing of the wire and the associated *in situ* pumps. The amplitude of this bouncing is expected to increase with increasing depth. Thus, for a given deployment (same wind and wave conditions), the deepest sample is likely to filter larger volumes of seawater than the shallowest ones. Despite the differences observed in the effective volumes filtered on nylon samples, the amount of Ra recovered using this technique is satisfying. However, note that nylon nets are not isolated from seawater during the deployment. The Mn-fiber thus extracts radium from surrounding waters during the descent and the ascent of the hydrowire. Deep samples are thus presumably more prone to Ra fixation during sample deployment in comparison to shallow samples. Such fixation and the differences in radium concentrations between shallow and deep waters may bias the estimate of the effective seawater volume that passed through the Mn-fiber placed in nylon nets as well as the $^{228}Ra/^{226}Ra$ ratios of these samples (Table 3). This is especially true for sample collected at 3200 m, because the transit time of that sample was especially long when considering deployment and recovery (ca. 2 h). We note, however, that the estimated effective volume that passed through that Mn-fiber is not the highest reported here (Table 3). For samples collected at 200 m and 500 m depth, we can consider that the transit time of the samples during deployment is short (7 and 17 min, respectively) in comparison to the time that the samples were moored at a given depth (4 h).

Table 3
Comparison of the amount of ^{226}Ra that is retained by Mn-fiber following filtration of seawater through Mn-fiber in the laboratory (referred to as “Niskin”) and using Mn-fiber placed in nylon nets (referred to as “Nylon”)

Station	Depth (m)	Method used	^{226}Ra (dpm)	Effective volume [a] (kg)	^{228}Ra (dpm/100 kg)
KERFIX	500	Niskin	16.7±0.12	97	0.107±0.046
	500	Nylon	62.9±0.19	364	0.056 [b]±0.019
C11	200	Niskin	11.6±0.10	68	0.119±0.062
	200	Nylon	21.2±0.11	125	0.131 [b]±0.038
C11	3300	Niskin	30.7±0.15	138	0.278±0.049
	3200	Nylon	57.6±0.18	259	0.217 [b]±0.031

Errors given are based on counting statistics (one standard deviation). See text for further details.

[a] Comparison of the amount of ^{226}Ra that is retained by Mn-fiber using the two techniques allows us to estimate the effective volume of seawater that passed through Mn-fiber placed in nylon nets. This effective volume corresponds to the volume of seawater needed to account for the amount of ^{226}Ra recovered on the Mn -fiber placed in nylon nets.

[b] We report also the ^{228}Ra specific activity deduced from the $^{226}Ra/^{228}Ra$ ratio measured in the nylon net sample and the ^{226}Ra total activity measured in sample collected at same water depth and filtered in the laboratory.

3.3.3. In situ pumps

The use of *in situ* pumps, deployed during 4 h at stations Kerfix and C11, allowed us to filter very large volumes of seawater: 634 kg (Kerfix, 50 m) and 996 kg (Kerfix, 500 m); 537 kg (C11, 80 m) (Table 2). Yield of Ra fixation, however, is not quantitative because the flow rate of seawater that passes through these pumps is up to 10 l min^{-1} (that is, much larger to the 1 l min^{-1} flow recommended to get a yield of 100%).

We estimated the yield of Ra fixation on the Mn-fiber placed in the cartridge by comparing the amount of ^{226}Ra (expressed in dpm) thus recovered by the Mn-fiber with that recovered following filtration in the laboratory of a sample collected at the same water depth (Table 4). Yields of Ra fixation range from 16.1% to 22.2% when considering the first cartridge only and are approximately 12% for the second cartridge. When combining the two cartridges, the yield of Ra fixation is thus 28.2–33% (Table 4). Using the ratio of cartridge 2 (“MnA”) to cartridge 1 (“MnB”) according to the relationship described by Livingston and Cochran

Table 4
Comparison of the amount of ^{226}Ra that is retained by Mn-fiber following filtration of seawater through Mn-fiber in the laboratory (referred to as “Niskin”) and using cartridges filled with Mn-fiber placed in tandem on *in situ* pumps (referred to as “Cart.1” and “Cart.2”)

Station	Depth (m)	Method used	Volume (kg)	^{226}Ra (dpm)	Efficiency of Ra fixation (%)	Efficient volume[b] (kg)
KERFIX	50	Niskin	85	13.9±0.10	100	85
	50	Cart.1	634[a]	22.8±0.50	22.2	141
KERFIX	500	Niskin	97	16.7±0.12	100	97
	500	Cart. 1	996[a]	27.6±0.32	16.0	159
	500	Cart. 2	996[a]	21.0±0.25	12.2	121
					(total 1+2:28.2%)	**(total 1+2:280 kg)**
C11	100	HP	103	18.6±0.15	100	103
	80	Cart.1	537[a]	19.4±0.51	20.1	108
	80	Cart.2	537[a]	12.4±0.39	12.9	69
					(total 1+2:33.0%)	**(total 1+2:177 kg)**

In situ pumps were deployed during 4 h.
Errors given are based on counting statistics (one standard deviation). See text for further details.

[a] Comparison of the amount of ^{226}Ra that is retained by Mn-fiber using the two techniques allows us to estimate the efficiency of Ra fixation by the two cartridges filled with Mn-fiber. The effective volume corresponds to the volume of seawater from which ^{226}Ra could be efficiently removed from seawater (i.e. total volume of seawater that passed through the flow-meter of the *in situ* pump corrected by the efficiency of Ra fixation).

[b] Total volume of seawater that passed through the flow-meter.

(1987) (eff=1−MnA/MnB) provides a very similar result (23.8–35.8%).

Despite the use of two cartridges in series that were designed to retain the maximum of radium isotopes, the yields of radium fixation on Mn-fiber are relatively low. However, because the total volume of seawater that passed through the pump is very high, the effective volume of seawater from which Ra could be efficiently extracted range from 176 to 282 kg when combining the two cartridges (Table 4). The advantage of employing *in situ* pumps is that the filtration of seawater begins only when the sampling depth is reached. The Mn-fiber is thus not in contact with seawater during the descent and ascent of the wire, as is the case for the Mn-fiber placed in nylon nets. The advantage of filling the cartridge holders with Mn-fiber rather than using cartridges coated with MnO_2 is that this technique allows the measurement of the four radium isotopes – ^{223}Ra and ^{224}Ra being firstly measured using a RaDeCC – which is not straightforward when using cartridges when these ones are impregnated with MnO_2. Finally, when *in situ* pumps are deployed to collect suspended particles, this technique can save significant ship-time.

3.3.4. MnO_2 co-precipitation

For several samples, we compared the ^{226}Ra activities measured in the MnO_2 precipitates with the ^{226}Ra activities found in Niskin samples filtered on Mn-fiber in the laboratory (Table 5). ^{226}Ra specific activities measured in the MnO_2 precipitate are lower than those measured in samples filtered through Mn-fiber. Because the yield of Ra fixation in the latter samples is considered to be 100%, this result indicates that the yield of Ra fixation is not 100% when using the MnO_2 co-precipitation technique. We can calculate the yields of Ra fixation associated with MnO_2 co-precipitation, which range from 23.9% to 39%. Only the sample collected at 20 m depth displays a higher yield (55.1%).

Table 5
Comparison of the amount of ^{226}Ra that is retained by Mn-fiber following filtration of seawater through Mn-fiber in the laboratory (reference method) and the amount of ^{226}Ra recovered following MnO_2 co-precipitation

Station	Depth (m)	Water passed through Mn-fiber in the laboratory				MnO_2 co-precipitation				Yield of Ra fixation (%)
		Volume (kg)	^{226}Ra (dpm)	net counts	^{226}Ra (dpm/100 kg)	Volume (kg)	^{226}Ra (dpm)	net counts	^{226}Ra (dpm/100 kg)	
A3-4	20	137	20.9±0.26	6847±85	15.3±0.19	34	2.9±0.19	265±18	8.4±0.57	55.1
	100	138	23.3±0.52	2072±47	16.9±0.38	34	1.9±0.09	639±29	5.6±0.25	33.4
	150	105	18.6±0.45	1809±44	17.7±0.43	34	1.7±0.18	113±12	5.1±0.54	29.0
	250	102	15.3±0.39	1588±41	15.1±0.39	35	2.1±0.21	126±13	5.9±0.60	39.0
	450	85	14.5±0.21	5121±74	17.1±0.25	35	1.4±0.09	378±23	4.1±0.25	23.9

This comparison allows us to estimate the yield of Ra fixation when using the co-precipitation technique.
Errors given are based on counting statistics (one standard deviation).

This result contrasts with that obtained by Ghaleb et al. (2004) who used the MnO_2 co-precipitation technique to remove ^{226}Ra from seawater and who found that Ra was removed with a yield of 100%. However, because we were worried by the blank levels that could be introduced with the reagents for the determination of ^{231}Pa, ^{230}Th and Nd isotopes, we reduced the amount of reagents. Thus, we used 53 times less $KMnO_4$ and 31 times less $MnCl_2$ than Ghaleb et al. (2004). This likely explains the relatively small radium recovery in our samples. Because the yields of Ra recovery vary from one sample to the other, spiking the samples with ^{228}Ra is obviously needed in order to use this method to determine ^{226}Ra activities.

4. Conclusion

In this work, we compared different methods to separate radium isotopes from seawater. We chose to use Mn-fibers that we find easier to use on a research vessel when compared to co-precipitation techniques and to cartridges impregnated with MnO_2. Mn-fiber also has the great advantage of permitting the measurement of the two short lived radium isotopes ^{223}Ra and ^{224}Ra (and ^{227}Ac) using a RaDeCC, in addition to ^{226}Ra and ^{228}Ra. However, the analysis of Ra isotopes often requires the collection of large volumes of seawater, which is not always an easy task, especially when deep waters are concerned. Large volumes of seawater are also difficult to handle on a ship. Collection of seawater followed by filtration through Mn-fiber in the laboratory is the only method that provides Ra specific activities. However, the ship-time required by this technique can be significant, especially when repeated CTD casts are needed to build Ra vertical profiles. We show that the techniques that consist of deploying Mn-fiber *in situ* (using nylon nets or cartridges mounted on *in situ* pumps) constitute good alternative methods that allow pre-concentration of Ra from large volumes of seawater. When *in situ* pumps are already deployed to collect suspended particles, these techniques allow one to conserve significant ship-time. However, contrary to nylon nets, Mn-fiber placed in cartridges does not separate Ra isotopes from seawater during the descent and the ascent of the *in situ* pumps. The use of this method, therefore, seems to be ideal when considering the differences in Ra concentrations between shallow and deep waters observed in most oceans. This technique could be further improved to increase the yield of Ra fixation by using new cartridges designed with Mn-fiber (R. Arnold, personal communication) and perhaps also by slightly reducing the flow rate of seawater passing through the *in situ* pumps. However, because the effective volume of seawater that passes through the Mn-fiber is unknown, only the $^{228}Ra/^{226}Ra$ ratios can be determined when using the two *in situ* techniques discussed here. The determination of the ^{228}Ra specific activities (and also ^{223}Ra, ^{224}Ra) in these samples thus requires the measurement of the ^{226}Ra specific activity in a discrete sample collected at the same water depth. With the development of the measurement of ^{226}Ra activity using MC-ICP/MS (Foster et al., 2004) or TIMS (Staubwasser et al., 2004), such analysis could be performed on a small-size sample using this technique. These methods could thus be used in the framework of the emerging GEOTRACES program.

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