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New applications of KNiFC-PAN resin for broad scale monitoring of radiocesium following the Fukushima Dai-ichi nuclear disaster

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Abstract The absorber KNiFC-PAN, potassium-nickel hexacyanoferrate (II) (KNiFC) bound into modified poly-acrylonitrile (PAN) is capable of absorbing radiocesium with up to 99 % recovery. KNiFC-PAN was used to collect cesium during several cruises near Fukushima, Japan, and the U.S. and Canadian west coasts by passing seawater through 5 ml of KNiFC absorber followed by counting on a germanium well detector. Other applications of this resin include in situ collection via the use of the *Clio* SUPR sampler during a cruise in the Marshall Islands, and development of a wearable device containing the resin.

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Introduction

In 2011 the Japan coastline was hit by a category 9 earthquake and tsunami that caused major destruction to the Fukushima Dai-ichi Nuclear Power Plants (FDNPP) and the largest ever accidental release of radiocesium to the ocean. Since the accident, there has been mounting concern along the U.S. and Canadian west coasts about human exposure to the irradiated waters coming from Japan. These concerns lead to an increased need for monitoring of cesium along Pacific coastlines.

Following the Fukushima accident there was a need for faster and more reliable methods of extracting and measuring cesium in the ocean. In June, 2011, an international team of researchers set out to measure the initial activities of radiocesium following the accident [3]. During this cruise, an absorber made from ammonium molybdophosphate (AMP) bound to modified polyacrylonitrile (PAN) beads [7, 8], created by researchers at the Czech Technical University in Prague [7] was used to extract radiocesium from the ocean around coastal Japan [3, 6]. This method involved collection of a 20 L seawater sample filtered and processed through a column containing AMP-PAN. The AMP-PAN method involved 8 h of process time and proved to be both more reliable and much quicker than previous cartridge methods [6]. One drawback to the method was the need to acidify samples prior to processing. In 2012 we began using a new absorber, potassium nickel hexcyanoferrate bound onto modified polyacrylonitrile beads [4, 8]. KNiFC-PAN is in bead form and behaves similar to a resin that extracts a desired isotope from a

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sample. The primary advantage of this resin is the lack of acidification of samples prior to processing. This method has been used to extract radiocesium from 20 L samples collected from the central North Pacific [5], on several cruises off the Japan coast and for our crowd-funded project along the U.S. and Canadian Pacific coasts.

Our Radioactive Ocean (www.ourradioactiveocean.org), a crowd-funded campaign, was developed in 2013 in response to increasing public concerns about Fukushima derived radiocesium arriving with the Kuroshio current to the US and Canadian west coasts. Kits containing 20 L cubitainers were sent out to citizen scientists to collect and ship back to the laboratory for processing. Samples were processed via our 20 L KNiFC-PAN method, counted via gamma spectroscopy, and results were quickly posted to reassure public that the ocean and local beaches were safe for recreational activities and fish consumption.

To increase public involvement and decrease sample process time, we began development and testing of a RadBand, a mesh bracelet containing KNiFC-PAN absorber that can be worn around the ankle. The Rad-Band eliminated shipping and processing of the 20 L sample, but required digestion of the resin. Cesium was collected passively onto the resin via swimming or towed behind a surfboard or boat. Another version of the RadBand, placed inside a cutout in a surfboard fin is under development.

Most recently, an instrument capable of capturing cesium samples in situ, a Rad verison of a *Clio* SUPR Sampler was developed by John Breier and others at the Woods Hole Oceanographic Institute [1]. The Rad *Clio* SUPR sampler was deployed on an autonomous vehicle called a JetYak, (a vehicle resembling a kayak that can be propelled remotely). The JetYak carried the Rad version of *Clio* along transects in the Marshall Islands. The location was chosen for its above average radiocesium activities remaining from nuclear weapons testing in the 1950s–1960s. The sampler was programed to pump water through a designated cesium column. When the transect was complete, the instrument was programmed to switch to a new column so that a new sample could be collected, allowing for several discrete samples to be collected before the instrument was reloaded. In the future this could permit remote monitoring of radionuclides in the ocean.

In this paper we present three new methods and applications of KNiFC for improved collection and monitoring of radiocesium in the ocean. Some of these methods are already being used extensively for research programs (20 L methods), while others (RadBand and autonomous sampling) are still in conceptual and developmental stages.

Experimental

20 L cubitainer method

Samples collected by this lab since 2012 have been processed using the KNiFC 20 L cubitainer method (Fig. 1). This method is similar to the AMP-PAN method [6], except in this case no acid is added prior to processing, a different column is used, and samples are pumped at a faster flow rate (Table 1). Samples were weighed then filtered through a 1 u Hytrex pre-filter to reduce particle load that slows processing. A stable ^{133}Cs salt (25 mg/ml) was added to each sample to determine recovery of Cs on the column by taking an initial and final aliquot from the sample and eluent, respectively. Samples were allowed to equilibrate for at least 1 h prior to processing. Columns (Supelco brand- 5 ml empty rezorian tube kit) were filled with 5 ml of KNiFC-PAN absorber. A polyethylene frit (Sigma Aldrich) was placed at the bottom and top of the column. Samples were pumped directly from a cubitainer through columns at 60 ml per minute. Processing takes approximately 5.5 h. KNiFC absorber was transferred to 30 ml clear plastic gamma vials and dried at 60 deg C prior to counting on 3 different high purity germanium well detectors (HPGe). These detectors have an energy range of 10–2800 keV and detection limits of 0.001 cps. Gamma efficiencies were determined from standards made from a matrix of KNiFC-PAN spiked with certified Eckert and Ziegler Isotope Products ^{134}Cs and ^{137}Cs standards. Recovery on the column was determined via ICP-MS. To determine recovery, initial and final aliquots were diluted $30\times$ in a 10 % JT Baker ultrapure nitric acid solution and stable ^{133}Cs concentrations in the aliquots were measured on an Element II ICP-MS (Thermo-Finnigan MAT GmbH, Bremen, Germany) at low resolution [6].

RadBands and KNiFC digestions

To increase public involvement in cesium monitoring and decrease process time, we designed the RadBand (Fig. 1), a mesh bag that contains KNiFC resin that can be worn or towed through the water. The concept of the RadBand relies upon the conservative behavior of stable ^{133}Cs in the ocean, which at salinities near 33 ppt is 0.5 ppb. Because this concentration is known we can determine the effective volume that has been seen by the absorber in the passive mode by extracting and measuring stable ^{133}Cs in the sample via ICP-MS.

RadBands were made by cutting rectangles of 90 um Nitex® mesh (based on PAN bead diameter) then filling
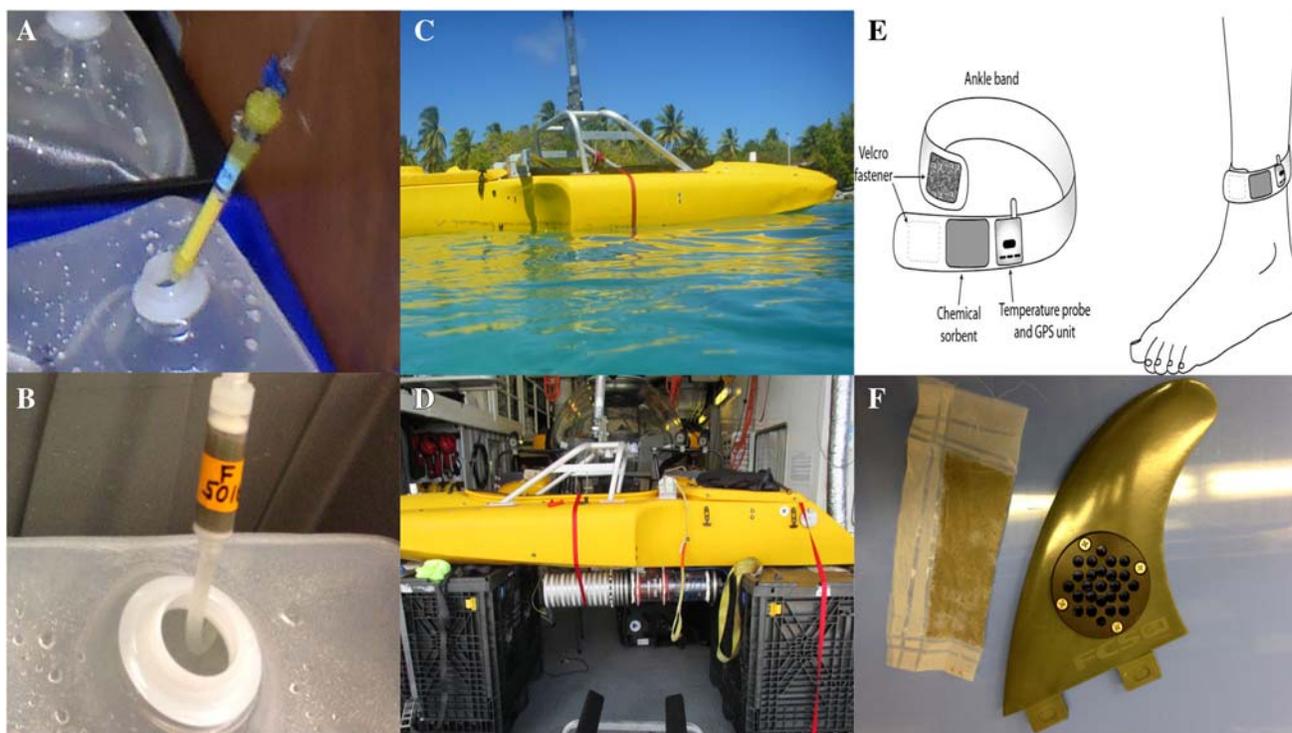
Fig. 1 Sampling methods. **a** AMP-PAN column; **b** KNiFC-PAN column; **c** JetYak; **d** Rad *Clio* on JetYak; **e** RadBand design; **f** Radband mesh bag & surf fin designed to hold RadBand

with 5 ml of wet KNiFC-PAN and sealing edges. Resin sat loosely in a 10×5 cm rectangle and was kept wet prior to use. Multiple bag and mesh sizes and configurations were tested in the lab. Mesh sizes smaller than 90 um had lower efficiencies due to reduced flow. The size of the bag also proved important. RadBands that had resin more tightly packed had lower efficiencies, therefore having the bag large enough is important for maximizing water flow.

RadBands were tested in May and October of 2014 on two separate cruises off the coast of the Fukushima, Japan. RadBands were deployed at station NP0, approximately 2 km from the Fukushima NPP, at a depth of 0.5 M. During the May cruise, samples were towed alongside the ship at a 2 knots for 2–5 h. During the October cruise, samples were collected while stationary at NP0. At the same station and during the 5 h, multiple 20 L cubitainer samples were collected and later compared to the RadBand samples. All samples were counted via gamma spectroscopy and exposure volumes for the bands were estimated based upon measured ^{134}Cs and ^{137}Cs values from co-located 20 L samples collected at the same time (Table 2).

RadBands were also tested on the ankle of a surfer and towed behind a surfboard. Recently we designed a prototype of a removable surfboard fin with a cutout that holds a mesh bag filled with KNiFC, allowing cesium to be collected as the surfboard moves through the water (Fig. 1). Upon return to the lab, absorbent in the RadBands was transferred to vials and gamma counted wet. Wet standards (5 ml) of KNiFC were made to determine detector efficiencies. Samples were kept wet in this case as it improves recovery of the cesium during the digestion process that is used to recover and calculate the volume of water the sample was exposed to.

Initial digest tests to extract radiocesium from KNiFC-PAN were performed at the Czech Technical University in Prague. Digesting of the absorber in the surplus of a 10 % solution of $AgNO_3$ in DI water, followed by a rinse with DI water was able to remove 99 % of the cesium from the absorber. Lab tests at WHOI began in 2014 on seawater samples on both spiked (^{137}Cs standard, Eckert & Ziegler) and un-spiked, natural samples. The digestion process takes only 20 min. Samples were counted wet prior to digestion by gamma spectroscopy to obtain initial values. To digest samples, 5 ml of wet KNiFC-PAN sample was placed in a 40 ml centrifuge vial with overlying water removed and 20 ml of $AgNO_3$ solution was added. Samples were stirred vigorously, shaken intermittently for 20 min and allowed to settle. Supernatant was removed and placed in a tared vial. A further rinse of KNiFC with 5 ml of DI water was done to ensure complete removal, added to the tared vial and total weight was recorded. The liquid sample was then

Table 1 Comparison of methods using AMP-PAN and KNiFC absorbers

Method	Collection time (h)	Process time (h)	Absorbent vol. (ml)	Column Dimensions	Sample vol. (L)	Pump speed ml min^{-1}	Avg. % Chem. Recovery	Advantages	Disadvantages
20L cubitainer AMP-PAN	0.1	8	5	1.0 × 10 cm	20	40	93.5	Consistently reliable. High chemical recovery.	Requires use of acid at sea. 8 h process time. Shipping cost.
20L cubitainer KNiFC-PAN	0.1	6	5	1.3 × 5 cm	20	60	95	No acid. Consistently reliable. High chemical recovery.	6 h process time. Shipping cost.
Autonomous Sampling (KNiFC-PAN)	1	0.1	14	2.1 × 4.7 cm	12–25	200–350	Est. 95	Autonomous sampling. Captures spatial variability.	Cost of instrument. Requires personnel to run equipment.
Radband Towed (KNiFC-PAN)	2–5	0.2	5	Mesh bag 5 × 10 cm	Est. 14–36	Towed	75–90	In situ collection. Involves citizen scientists. Minimal processing. Higher extraction eff.	Longer collection time. Requires stable Cs analysis.
Radband Passive (KNiFC-PAN)	2–5	0.2	5	Mesh bag 5 × 10 cm	Est. 5–12	Passive	75–90	In situ collection. Involves citizen scientists. Minimal processing.	Longer collection time. Need to optimize to increase sample volume. Requires stable Cs analysis. Lower extract. eff due to passive collection.

measured via gamma spectrometry. A liquid standard was used to calculate detector efficiencies.

To measure recovery of stable cesium via mass spectrometry, an aliquot was removed from the supernatant and diluted in a 10 % solution of JT Baker ultrapure nitric acid. A Finnegan Element II ICP-MS was used to measure stable Cs in low resolution mode. The concentration of ^{133}Cs was determined using a standard curve made in the same matrix as the samples. Standard curves were run at the beginning, middle and end of the run to account for instrument drift over the run. Effective sample volume was calculated by dividing the measured concentration of stable ^{133}Cs by the known ocean concentration of 0.5 ppb at salinities of 33. If salinities were not 33, the expected concentration of stable ^{133}Cs was calculated by using a linear fit for expected conservative behavior. Radiocesium in samples was then calculated using effective volumes determined via ICP-MS.

Table 2 Cesium activities in samples collected in coastal Japan, N. American west coast & Marshall Islands using three methods; 20 L cubitainer, Radband and Autonomous Rad version of the *Clio* SUPR sampler

Date (month/year)	Station	^{0}N	^{0}E	Type	V_Ab	Kg_Sm	^{134}Cs Bq/m^3	± error	^{137}Cs Bq/m^3	± error
Japan coastline 2014 Cruises—20 L cubi vs. Radband 20 L cubi vs. Radband										
5/14	NP0 (coast)	37.42	141.05	20 L cubi	5	23	24.0	0.6	63.5	1.3
5/14	NP0 (coast)	37.42	141.05	Radband	5	17	20.9	0.6	61.5	1.3
5/14	NP2 (coast)	37.42	141.10	Radband	5	20	5.8	0.2	15.0	0.4
5/14	NP2 (coast)	37.42	141.10	20 L cubi	5	24	6.0	0.2	18.5	0.4
5/14	NP1 (offshore)	37.42	141.18	20 L cubi	5	23	0.9	0.1	4.5	0.1
5/14	NP1 (offshore)	37.42	141.18	Radband	5	24	1.2	0.1	4.7	0.1
5/14	NPE1 (coast)	37.33	141.08	20 L cubi	5	24	6.7	0.2	20.8	0.5
5/14	NPE1 (coast)	37.33	141.08	Radband	5	12	5.3	0.2	15.9	0.4
5/14	NPE2 (coast)	37.33	141.08	20 L cubi	5	22	4.2	0.2	14.0	0.3
10/14	NP0 (coast)	37.42	141.05	20 L cubi	5	23	5.3	0.3	16.5	0.4
10/14	NP0 (coast)	37.42	141.05	Radband	5	32	3.8	0.1	13	0.3
10/14	NP0 (coast)	37.42	141.05	Radband	5	1	bd		8.1	0.8
Crowd Source—West Coast of N. America & Pacific islands										
11/13	Grayland, WA	46.81	124.09	20 L cubi	5	22	bd	–	1.3	0.1
7/14	Pt. Reyes, CA	38.24	123.01	20 L cubi	5	23	bd	–	1.5	0.1
12/13	San Diego, CA	32.87	117.25	20 L cubi	4	19	bd	–	1.7	0.1
5/14	Haida Gwaii	53.16	132.62	20 L cubi	5	20	bd	–	1.4	0.1
5/14	Kaneohe Bay, HI	21.42	157.8	20 L cubi	5	27	bd	–	1.5	0.1
2/14	Bamfield, BC	48.85	125.16	20 L cubi	6	20	bd	–	1.3	0.1
2/15	Ucluelet, BC	48.94	125.55	20 L cubi	5	25	1.4	0.1	6.1	0.1
Marshall Islands—autonomous sampling autonomous sampling										
1/15	T1	11.35	162.34	*Clio* SUPR	14	12	bd	–	2.0	0.4
1/15	C1	11.39	162.36	20 L cubi	5	18	bd	–	2.0	0.2
1/15	T2	11.35	162.34	*Clio* SUPR	14	20	bd	–	1.3	0.2
1/15	C2	11.35	162.34	20 L cubi	5	19	bd	–	1.3	0.1
1/15	C2	11.56	162.33	20 L cubi	5	21	bd	–	1.4	0.2
1/15	T3	11.55	162.34	*Clio* SUPR	14	21	bd	–	1.4	0.2
1/15	C3	11.53	162.36	20 L cubi	5	19	bd	–	1.4	0.2
1/15	T4	11.55	162.34	*Clio* SUPR	14	25	bd	–	3.3	0.2
1/15	C4-1	11.34	162.32	20 L cubi	5	19	bd	–	1.3	0.2
1/15	C4-2	11.55	162.35	20 L cubi	5	19	bd	–	3.3	0.4
1/15	St 5	11.55	162.35	*Clio* SUPR	14	23	bd	–	2.8	0.2
1/15	T6	11.55	162.34	*Clio* SUPR	14	14	bd	–	2.0	0.5

V_Ab stands for volume of adsorbent KNiFC used in extraction. Kg_Sm stands for kg of sample collected. Kg_Sm is kilograms of sample

In situ autonomous sampling method

In an effort to improve broad scale monitoring of cesium, the Rad *Clio* SUPR Sampler was designed to capture samples in situ (Fig. 1). In January of 2015, the instrument was tested on a cruise around the Marshall Islands. This location was chosen as it has above background cesium levels leftover from bomb testing in the 1950s. The Rad version of *Clio* SUPR holds up to 17 smaller and narrower column (2.1 × 4.7 cm) that can be automatically switched during deployment. The instrument was deployed on a JetYak which can be programmed with GPS co-ordinates to follow a transect. Samples were collected along transects by automated pumping at 200–350 ml min^{-1} through the columns. Transects were completed in 1–2 h, and covered a distance of 1–3 km. Upon recovery, columns were emptied into vials and immediately ready for analysis via gamma spectroscopy. Detector efficiencies were determined using a 14 ml KNiFC standard spiked with ^{134}Cs and ^{137}Cs reference standards (Eckert and Ziegler).

Results/discussion

A comparison of the 6 different applications of KNiFC absorbents used is shown in Table 1. In Fig. 1 a photo of each method is shown for reference. Here we will review results and compare the use of the various methods.

KNiFC 20 L method cubitainer method

The KNiFC 20 L cubitainer method proved very successful when employed during four cruises along the Japan coastline and offshore Japan in 2013–2014. Radiocesium data for samples collected during these cruises is shown in Table 2. Samples at these coastal Japan stations ranged from 0.9 to 24 Bq/m^3 ^{134}Cs in May 2013 and 3.8–6.7 Bq/m^3 ^{134}Cs in October 2014. Although these samples are elevated, compared to background, they are over 100 orders of magnitude lower than the first cruise that took place in June 2011 [3]. The 20 L cubitainer method was effectively used in our crowd-funded campaign for samples collected along the N. American west coast, Pacific islands such as Hawaii and along a transect between Dutch Harbor, Alaska and Eureka, CA. The majority of samples taken from beaches along the N. American west coast and Pacific islands were at background levels with an average ^{137}Cs activity of 1.5 ± 0.1 Bq/m^3 and a range of ^{137}Cs = 0.6–1.9 Bq/m^3. ^{134}Cs in these very coastal samples was below detection for all but one sample ($N = 77$). ^{134}Cs, the signature of waters coming from Fukushima, was detected offshore (150 km) California, and along the line between AK and CA, and in one beach sample from Ucluelet, British Columbia (Crowd Source, Table 2). The Ucluelet, British Columbia beach sample collected in February, 2015 was the first in which our group found above background ^{137}Cs (5.8 Bq/m^3) and detectable ^{134}Cs (1.4 Bq/m^3), indicating arrival of waters from Fukushima to the Canadian coast. Samples with detectable ^{134}Cs along the AK-CA transect had similar values (^{134}Cs, max = 1.7 Bq/m^3, ^{137}Cs max = 6.4 Bq/m^3). These levels although above background are still well below the U.S. and Japanese drinking water standards (7400 Bq/m3) and are safe for recreational activities as well as fish consumption.

The KNiFC adsorber proved very comparable in chemical extraction efficiency (average 95 %, with many recoveries at 99 %) to the AMP-PAN absorber (average 93 %) using the 20 L cubitainer method. Both KNiFC-PAN and AMP-PAN absorbers have similarly high extraction efficiency compared to two cartridge methods employed several years ago [2]. The method is very reliable, with similar chemical extraction efficiencies seen in hundreds of samples. The ability to process samples at sea was improved with the KNiFC-PAN as no acid was required. Process times between AMP and KNiFC were comparable, requiring between 6 and 8 h. Although the process time for the 20 L cubitainer method is considerably shorter than previous methods, an in situ method that eliminates virtually all processing time would be ideal.

Surfer bag/crowd source application

Our surfer bag tests showed a range of success in recovering Cs from seawater in both natural and artificially spiked sample conditions. The most important factor proved to be the flow of water over the Radband as those that were towed from a moving boat or surfboard had much better results. In our first tests, a Radband was towed behind a surfboard in coastal New England for 2–3 h. After counting on the gamma spectrometer for 2 days, we were able to measure 1.2 ± 0.2 Bq/m^3 of ^{137}Cs. Other samples were tested in a flume at a very slow flow rate of 1–2 L min^{-1}. These samples were still below detection after 12 h of exposure. Greater success was obtained in Japan by towing RadBands from the ship at 2 knots for 3–4 h. Results comparing our 20 L cubitainer method to the RadBands from two cruises can be seen in Table 2. In this case we did not digest samples but estimated volumes based upon co-located cubitainer samples collected in similar time and space. Using the co-located cubitainer values, we were able to estimate that the effective volume seen by the RadBands during the two cruises was 16–36 L. Once transferred to a vial, these Fuksuhima RadBand samples required only 1 day of counting, partly due to the higher levels of ^{134}Cs and ^{137}Cs seen in these waters and partly because the larger effective volume of the sample.

The last step in processing the RadBands was to measure stable ^{133}Cs to determine the effective volume collected onto the KniFC resin. KNiFC was removed from the bag, placed into a 60 ml centriguge tube. A 10 % AgNO$_3$ solution was added to extract stable ^{133}Cs from the KNiFC adsorber. The method was also tested by adding radiotracers of known activity (Eckert & Ziegler) ^{134}Cs and ^{137}Cs. Average recovery of radiocesium measured by gamma spectroscopy was 83 % for both ^{134}Cs (in spiked seawater samples) and ^{137}Cs in both spiked and un-spiked, background level seawater samples (Table 1). The average recovery of ^{133}Cs measured via ICP-MS was 74 %. Recoveries measured via ICP-MS proved less reliable, and less consistent. Because this was an initial test, ICP-MS samples were simply diluted prior to running without further chemistry or cleaning, thus further cleaning of the sample to reduce interferences and possible matrix effects is likely necessary.

The greatest benefits of the RadBand include the ability for citizen scientists to collect directly onto a KNiFC absorber and elimination of shipping and processing the
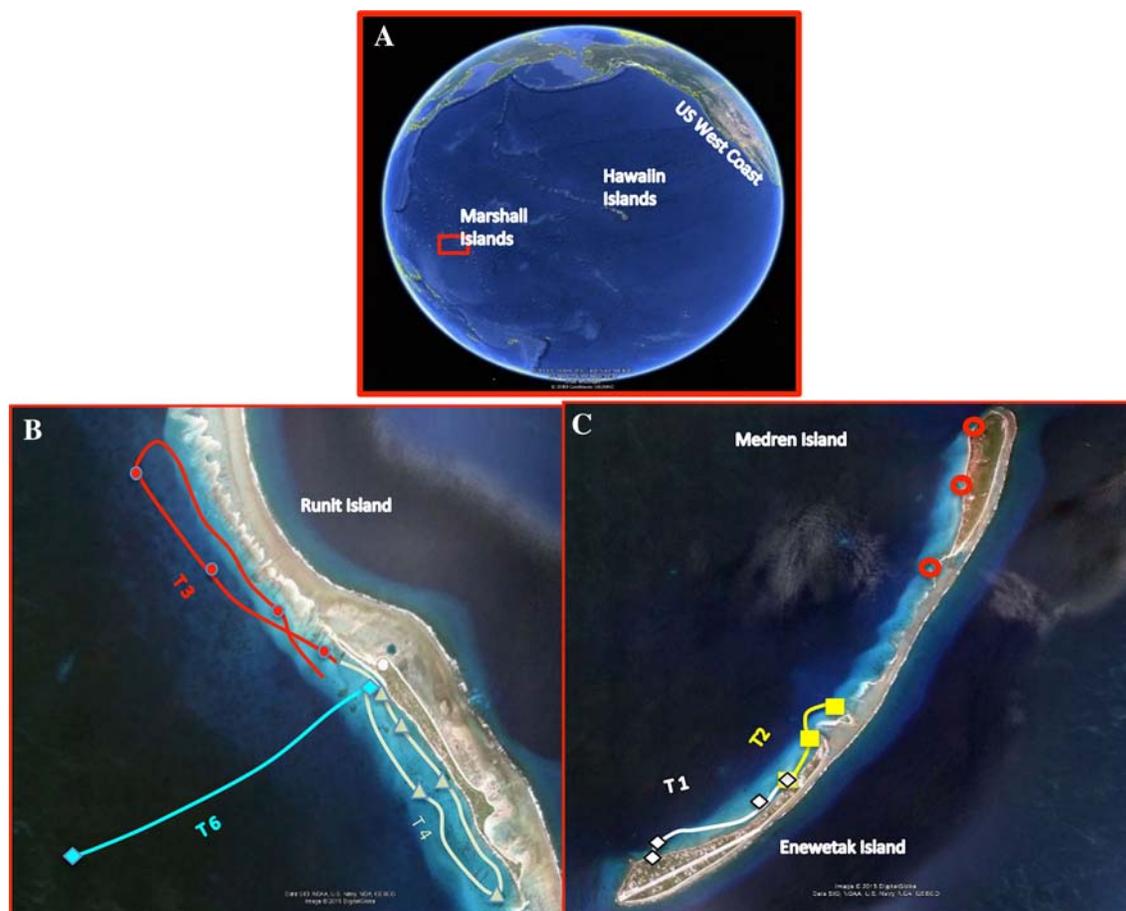
Fig. 2 Marshall Islands. **a** *Red square* represents Marshall Islands chain. **b** Runit Island with transects 3 (*red*), 4 (*white*), 6 (*aqua*) with co-located cubitainer samples and stationary sample 5 (*aqua circle* near coast). **c** Enewetak Isalnd (south) with transects 1 & 2 and co-located cubitainers (*white squares*); Mederen Island with cubitainer sample collections (*open red circles*)

20 L sample. The method uses direct counting of the adsorbent followed by only a quick 20 min digestion process for stable Cs, compared to the 6–8 h of processing required for a 20 L cubitainer, but it does require measuring recoveries and effective volumes via ICP-MS. The greatest disadvantage is that without enough volume flowing through the RadBand, the sample can be below detection. Some samples had low effective volumes, so there is a need to improve flow over the absorber. We found that increasing flow around the resin increased extraction of cesium from the water, for example by towing (such as behind a surfboard or kayak), or alongside a slow moving boat during collection. Significant work will be needed to optimize the design to improve flow conditions for different applications.

In situ autonomous sampling method

In situ sampling of radiocesium with the JetYak vehicle and Rad version of *Clio* SUPR sampler proved very

successful. Surface samples collected by vehicle and co-located cubitainers on Enewetak, Medren and Runit Islands in the Marshall Island chain (Fig. 2) ranged from 1.3 to 3.3 Bq/m^3, ^{137}Cs (Table 2). These levels are elevated compared to other parts of the Pacific (^{137}Cs background of 1.2 Bq/m^3), due to radiocesium leftover from nuclear weapons testing in the area in the 1950s–1960s. Co-located cubitainer samples were collected from a mixture of water along each transect. Seawater volumes used to calculate cesium activities were both measured from a flow meter on the instrument during pumping or, in cases were the flow meter was not functioning properly, volumes were estimated by comparing Cs collected by the instrument to co-located cubitainer samples that were processed via 20 L method above. An estimated 12–25 L of seawater was pumped through each column during six, 1–2 h transects along the islands.

The advantages of in situ sampling are great: collection is automated, the vehicle can be programmed to move along a path and collect samples at designated locations,

sample process time is essentially eliminated as it is done on board the vehicle, and samples can be immediately counted via gamma spectroscopy. Use of a vehicle can allow for monitoring on larger scales and would eliminate the need for cruise expenses. The disadvantages are that the cost of the vehicle and instrument are high, and a skilled person is required to set up and operate the vehicle and sampler. With continued work to improve operational efficiency and simplify the user interface this method will be very useful and could successfully be applied for studies of chemical tracers and radiological monitoring.

Conclusions

The absorber KNiFC-PAN has greatly improved our ability to efficiently collect and measure cesium both as a tracer in studies of ocean movement as well as in studies of radiological monitoring. We have provided here new applications of this resin that, with further work could make collection and measurement of cesium from the ocean even more efficient. Our 20 L cubitainer method is well established; hundreds of samples have been measured with good chemical recoveries that are consistency achieved. The Radband was developed to increase involvement of citizen scientists in radiological monitoring. With further development to improve flow over the band, this band could be more widely distributed. The Rad *Clio* SUPR sampler was successful in collecting cesium onto columns in situ. With further efforts to improve operation and user interface, the sampler could be used autonomously on a vehicle to

improve our understanding of movement of radionuclides such as cesium on broader spatial scales.

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