Extraction of cesium in seawater off Japan using AMP-PAN resin and quantification via gamma spectroscopy and inductively coupled mass spectrometry

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Abstract The March 2011 earthquake off the Japanese coast and subsequent tsunami that devastated the Fukushima Dai-Ichi nuclear power plant resulted in the largest accidental release of cesium 137 and 134 to the oceans. Seawater samples were collected in June 2011 from 30 to 600 km off the coast of Japan as part of initial mapping of the spread of contamination in the ocean. Cesium was extracted from unfiltered and filtered (<1.0 μm) seawater using an absorber based upon an organic polymer polyacrylonitrile (PAN) containing ammonium molybdophosphate (AMP) Sebesta and Stefula (J Radioanal Nucl Chem 140:15–21, 1990). The AMP-PAN resin can be counted directly using gamma spectroscopy for ^{134}Cs and ^{137}Cs. Stable ^{133}Cs was added to evaluate extraction efficiency and quantified by ICP-MS. Our 5 mL AMP-PAN resin column was on average 95 % efficient in the removal of cesium from 20 L samples at an average flow rate of 35 mL min^{-1}. Measured activities of ^{134}Cs and ^{137}Cs ranged from a few Bq m^{-3} to >300 Bq m^{-3}. The extraction column can be adapted to different sample volumes and easily used in the field.

Keywords Cesium · Fukushima · AMP-PAN · Gamma spectroscopy

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Introduction

The Earthquake and following Tsunami off the east coast of Japan on March 11, 2011 severely damaged three nuclear reactors at the Fukushima Dai-Ichi nuclear power plant (NPP). The total direct release of ^{137}Cs to the marine environment by the damaged reactors was estimated to be between 12 and 41 PBq by mid-July 2011[1] and represents the largest accidental release of radiation to the ocean in history. In June 2011 scientists completed the first international research expedition off the coast of Japan to measure and map the fate of radiation released to Pacific Ocean by the damaged Fukushima NPP. Analysis of ^{134}Cs and ^{137}Cs reported in this paper are from water samples collected on board the R/V *Ka'imikai-o-Kanaloa* during June 5–12, 2011 and were used to assess sources, inventories and dispersion of these contaminants in the western Pacific Ocean [2].

The large number of samples proposed for collection off Japan and the need to extract and analyze samples quickly to provide near real time contamination levels were obstacles for collection methods previously used in oceanographic studies [3–5]. Presented is a simplified direct extraction and counting technique for cesium isotopes that requires no specialized laboratory equipment and

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allows for increased sample throughput and on-board analysis when necessary. Some prior methods for quantitative removal of cesium from seawater have used ammonium molybdophosphate (AMP) and potassium ferrocyanide (KCFC) as an extraction medium [3–6]. These methods used volumes of 10–100 L and samples could be easily collected using standard oceanographic water collection techniques. Extraction of cesium using KCFC in paired columns has been shown to be >95 % efficient in the first column [6] on sample sizes of 100 L. The AMP method was also >95 % efficient in extraction cesium, however a limiting factor is the considerable preparation prior to purification resulting in long processing times and reduced through put. After radiochemical purification, eluted cesium was co-precipitated as cesium-chloroplatinate, filtered, dried and beta counted which could not discriminate between ^{134}Cs and ^{137}Cs energies and provided only total cesium activities. Separation of the combined isotope activities could be accomplished by direct gamma counting but only if activities of the chloroplatinate were sufficient to be detected.

Alternatively, isotopic ratios from gamma counting of large volume samples collected at the same location can be applied to separate combined ^{134}Cs and ^{137}Cs identified by beta-counting the precipitate [4, 5]. The large volume method makes use of cupric ferrocyanide impregnated cartridges for extraction of cesium from seawater. This method was useful for large volume samples collected in situ or through deck pumping. An advantage to this method are filters can be gamma counted directly without further processing and separation of cesium isotopes is possible from spectrometry data. A disadvantage is cartridge collection efficiencies can be problematic because of batch to batch variability during cartridge preparation. To correct for collection efficiency, samples are pumped through paired cartridges which requires two measurements for each sample.

The incorporation of AMP with the organic polymer polyacrylonitrile (PAN) was proven to be a stable and very selective absorber of cesium [7]. This composite ion absorber was primarily proposed for radiocesium concentration and its monitoring in surface waters in the vicinity of nuclear power plants [8]. Later it was tested for cesium remediation of highly salted and acidic waste streams at nuclear production facilities [9–11] and was predicted to perform very well with acidified seawater samples. Extraction of cesium by pumping samples directly through chromatography columns with AMP-PAN as the absorber reduced chemicals and equipment needed for extraction, cut processing times from days to hours and made possible the rapid determination of cesium in a sample by gamma counting the resin directly without further preparation or purification [8]. During research efforts off Japan, the ability to complete on board processing of seawater using AMP-PAN allowed for immediate analysis of samples using a sodium iodide detector for ^{134}Cs and ^{137}Cs which provided critical evaluation of exposure levels to personnel and the ship. Presented in this study are results from laboratory tests and the first large scale environmental application of AMP-PAN to produce spatial and vertical distributions of ^{134}Cs and ^{137}Cs released by the damaged reactors at the Fukushima NPP.

Experimental

Initial extraction tests on AMP-PAN (Czech Technical University, Prague, Czech Republic) were conducted to evaluate appropriate column size, absorber volumes and pumping rates using North Atlantic water collected in May 2011 at Woods Hole, MA. Surface seawater samples used in these tests had high particle content, which significantly slowed flow rates of the sample through the column over the extraction period. As a result, surface water used for further extraction tests and during the June 2011 cruise were pre-filtered through a 1 μm, 10 inch HYTREX cartridge filter then pumped directly into a 20 L cubitainer and weighed. Measured activities of ^{134}Cs and ^{137}Cs on the 1 μm filters averaged <0.1 % of the total during laboratory tests and this cruise, consistent with the soluble nature of Cs in seawater [2]. Following collection, samples were acidified to pH 1–2 with JT Baker ultrapure nitric acid at 6 mL L^{-1} and shaken well. A stable ^{133}Cs carrier (25 mg mL^{-1} standard) was added to each sample, shaken and allowed to equilibrate for at least 1 h. Before processing the sample an initial aliquot of 1 mL was collected for stable cesium recovery measurement.

Prior to processing, glass chromatography columns (1.0 × 10 cm) (Bio-Rad Laboratories, Hercules, CA) were cleaned with 0.1 N nitric acid and stopcocks were positioned on the inlet and outlet of the column for flow regulation. Columns were calibrated with de-ionized H_2O to 5 mL, marked, and wetted AMP-PAN absorber in 0.1 N nitric acid was added to the mark. The 5 mL of wetted AMP-PAN used for each sample is equivalent to 1.10 g of dry absorbent which was calculated to have a loading capacity of 33 mg total cesium for expected sample volumes processed at a flow rate of 35–40 mL per minute. [7, 9, 11]. This volume of resin also ensures a consistent and maximum geometry for the well detectors used for gamma counting. The resin was allowed to settle and excess liquid was drawn off with a transfer pipette. Using a glass rod, a 70 μm frit (Bel-Art Products, Pequannock, New Jersey) was placed above the resin to prevent re-suspension of the resin during processing.

Flow of the sample was started carefully using a peristaltic pump and air was allowed to bleed out of the tubing. Care was taken to bleed all the air before closing the

stopcocks to avoid air locks or potential channeling of the sample by pumping air through the column. A column was then capped which was secured by a clamp to prevent leakage due to pressure build up from pumping. Samples were passed through the column at a flow rate of 35–40 mL per minute which was regulated by adjusting the peristaltic controller and stopcocks on the column. It was observed in laboratory tests that when flow rates were in excess of 50 mL per minute compression of the resin occurred and the resulting compaction in the column reduced the flow rate over time. After passing through the column the processed samples were collected into clean cubitainers and a final 1 mL aliquot was taken for recovery analysis. The AMP-PAN resin was then rinsed from the columns using 0.1 N nitric acid and transferred to polycarbonate counting vials for direct counting of Cs isotopes.

Preliminary gamma counting for pre-screening of samples aboard the ship was performed using a $3'' \times 3''$ NaI(Tl) (Ametek) shielded with 2 mm lead foil (Atnuke.com). For laboratory tests and samples returning from sea, a more precise gamma-spectrometric analysis was performed using two High Purity Germanium (HPGe) well detectors. The ORTEC MN# GWL 190210-S (Perkin-Elmer) is a closed-ended germanium coaxial well detector with an end cap diameter of 23.2 mm, depth of 53.5 mm and active crystal volume of 182 cm^3. The Princeton Gamma-Tech P-type intrinsic germanium coaxial well detector is also a closed-ended detector with an end cap diameter of 25 mm, depth of 45 mm and active crystal volume of 183.6 cm^3. Both detectors have an energy range from 10 to 1500 keV and detection limit of 0.001 cps. Captured events were analyzed using Aptec MCA V6.31 software. Gamma spectrometers were efficiency calibrated for a 5 mL AMP-PAN matrix using certified standards from Eckert and Ziegler Isotope Products (Valencia, California) of ^{134}Cs and ^{137}Cs activities ranging from 0.01 to 300 Bq.

Chemical recoveries were determined from initial and final aliquots of each sample diluted with 10 % ultrapure nitric acid and analyzed for stable ^{133}Cs. Measurements were made using a magnetic sector inductively coupled mass spectrometer (Element II, Thermo Finnigan MAT GmbH, Bremen, Germany) at low resolution (LR: R = 300 where $R = M/\Delta M$ at 10 % peak height). A free-aspirating PFA MicroFlow nebulizer quartz spray chamber (Cetac Technologies) using standard cones was used for sample introduction and sample flow rates through this nebulizer were approximately 120 µl min^{-1}. To ensure that there was no blank carry over, the method included a 4 min washing with 10 % HNO_3 between samples.

The experimental results discussed in this paper are from samples collected from 30 to 600 km offshore of the Fukushima Dai-Ichi NPP. Sampling onboard the R/V *Ka'imikai-o-Kanaloa* took place over a 2 week period in June 2011 from more than 50 stations [2]. Twenty liter samples taken by surface pumps were pre-filtered as describe earlier. Deep profile samples from 20 to 1,000 m were collected by Niskin bottles deployed on an oceanographic rosette and were not filtered before processing.

Results/discussion

Gamma efficiencies were determined for both detectors using a matrix of 5 mL wetted AMP-PAN over a range of activities of mixed ^{134}Cs and ^{137}Cs calibration standards from 0.01 to 300 Bq followed by direct counting of the resin. HPGe detector efficiencies on two detectors ranged from 5.5 to 6.2 % for ^{134}Cs at 604 keV, 4.1–4.6 % at 795 keV and 10.5–11.7 % for ^{137}Cs peak at 661 keV These efficiencies were obtained from calibration with known ^{134}Cs and ^{137}Cs standards, which allows for correction of coincidence-summing effects which significantly lower the effective ^{134}Cs efficiencies using these well type HPGe detectors [12, 13]. Initial extraction tests conducted on seawater samples ($n = 10$) from Woods Hole, MA measured ^{137}Cs values at 1.6–2.2 ± 0.2 Bq m^{-3} and fell within the range of North Atlantic activities [14]. The concentration of cesium isotopes in water is reported in units of Bq (1 Becquerel = one disintegration per second) per unit volume (Bq m^{-3}). Further evaluation of the AMP-PAN method for ^{137}Cs extraction and recovery method using stable ^{133}Cs was conducted on replicate analysis of calibration standards of seawater with results shown in Fig. 1. Good agreement was found between archived water from the Sargasso Sea collected in

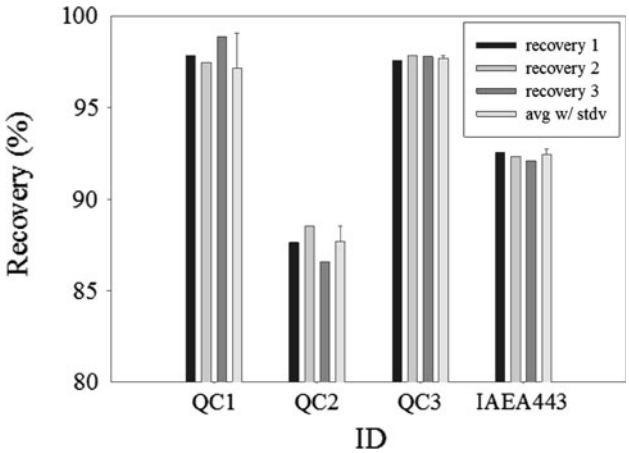

Fig. 1 Recovery results for internal WHOI lab standard analyzed in triplicate (QC1–3) and IAEA Irish Sea water reference material (IAEA-443). Results are presented for triplicate recovery measurement of stable ^{133}Cs by ICP-MS with average and standard deviation as error. Average value in this study for the internal WHOI QC standard for $^{137}Cs = 3.7 \pm 0.2$ Bq m^{-3} and for IAEA-443 $^{137}Cs = 369 \pm 8$ Bq m^{-3}

1978 considered an internal WHOI lab standard with an activity of ^{137}Cs: 3.4 ± 0.4 Bq m^{-3} and results of triplicate analysis in this study (3.7 ± 0.2 Bq m^{-3}). Also measured was the ^{137}Cs activity in a single 5 L sample of an IAEA Irish Sea water reference material SRM IAEA-443. Our result of ^{137}Cs activity of 369 ± 8 Bq m^{-3} was in good agreement with the certified 95 % confidence limit value of 340–370 Bq m^{-3} [15]. While there was no obvious reason for the lower recovery in QC2, it is clear that the ability to correct for column efficiency is an important advancement in the method.

For recovery of stable cesium using ICP-MS, tests were first conducted on standard sea water samples used for quality control. To evaluate potential sea water matrix interferences with the instrument, initial and final elution aliquots were analyzed over a range of serial dilutions (100,300,500:1) using 10 % HNO_3 analyte solution. The results in Fig. 1 show consistent recovery values over the range of dilutions for these standards with minor sample to sample differences. High count rates on the order of 10^6–10^7 cps measured in initial aliquots at 500:1 dilutions suggest that the amount of stable cesium added for recoveries could be significantly reduced ($\sim$1 mg mL^{-1}) based on the sensitivity of ICP-MS. Count rates from ICP-MS analysis were corrected for blanks and dilution factors and converted to recovery values determined from initial and final ratios: where CPSF is final aliquot count rate; CPSI is initial aliquot count rate; DFF is final aliquot dilution factor; DFI is initial aliquot dilution factor; Blnk is a mean blank count rate for the run

$$\frac{(CPSF - Blnk)x\ DFF}{(CPSI - Blnk)x\ DFI} = \%recovery$$

Chemical recoveries were very consistent for all Pacific Ocean samples (93.5 ± 5 %, $n = 55$). Using dilutions of initial and final aliquots, combined with the high sample through put of the ICP-MS, the quantification of stable ^{133}Cs as a yield monitor has been greatly simplified compared with filtration and weighing of precipitates [3–5]. If stable cesium is to be analyzed by less sensitive methods, such as flame or furnaces atomic absorption spectrometry, the spike level of 25 mg mL^{-1} would be sufficient and not exceed the capacity of the absorber [7, 8].

The improvements this method afforded made possible the detection of high-resolution spatial and vertical distributions of ^{134}Cs and ^{137}Cs and more accurate calculations of inventories of cesium released to the ocean off Japan. In June of 2011, more than 150 samples were collected at sea and analyzed for ^{134}Cs and ^{137}Cs using this new technique. Surface samples collected at more than 50 stations from 30 to 600 km off the coast covering an area of 150,000 km^2 provided high resolution spatial mapping of cesium [2]. Surface activities of ^{134}Cs and ^{137}Cs ranged from background levels of 1–2 Bq m^{-3} to >3,000 Bq m^{-3} measured in an eddy south east of the accident site. Vertical profiles were collected at 22 stations with results from Station 27 and 29 presented in Table 1; Fig. 2. Maps, station data and complete Cs results are detailed in Buesseler et al. [2]. Recoveries via ^{133}Cs were applied to activities reported and a mean recovery value of 93.5 % was applied to samples

Table 1 Station information, activities (Bq m^{-3}) and isotope ratios of ^{134}Cs and ^{137}Cs measured in two water column profiles from coastal waters off Fukushima NPP

Station	Collection date	Depth (meter)	Lat-N	Lon-E	^{137}Cs (Bq m^{-3})	Error	^{134}Cs (Bq m^{-3})	Error	^{134}Cs/^{137}Cs (Bq/Bq)	Error
27	6/15/2011	2	36.50	141.40	729.9	40.0	766.7	31.8	1.05	0.07
27	6/15/2011	10	36.50	141.40	501.2	26.1	519.9	19.4	1.04	0.07
27	6/15/2011	20	36.50	141.40	428.0	23.2	417.8	17.1	0.98	0.07
27	6/15/2011	50	36.50	141.40	301.6	16.0	305.3	11.8	1.01	0.07
27	6/15/2011	100	36.50	141.40	37.0	2.2	35.1	1.7	0.95	0.07
27	6/16/2011	200	36.50	141.40	8.9	0.7	7.2	0.6	0.81	0.09
27	6/16/2011	500	36.50	141.40	2.3	0.3	1.7	0.3	0.76	0.14
27	6/16/2011	1,000	36.50	141.40	1.8	0.3	1.7	0.4	0.91	0.25
29	6/16/2011	2	36.50	142.01	3628.5	187.7	3631.1	132.9	1.03	0.06
29	6/16/2011	10	36.50	142.01	391.7	20.3	352.2	13.0	0.90	0.06
29	6/16/2011	20	36.50	142.01	331.2	17.5	351.4	13.5	1.06	0.07
29	6/16/2011	50	36.50	142.01	117.0	6.1	121.5	4.6	1.04	0.07
29	6/16/2011	100	36.50	142.01	32.4	2.0	30.6	1.6	0.95	0.08
29	6/17/2011	200	36.50	142.01	13.7	0.8	12.9	0.6	0.95	0.07
29	6/17/2011	500	36.50	142.01	1.2	0.1	bd	bd		
29	6/17/2011	1,000	36.50	142.01	bd	bd	bd	bd		

Samples were collected onboard R/V *Ka'imikai-o-Kanaloa* during June, 2011 (*bd* below detection)

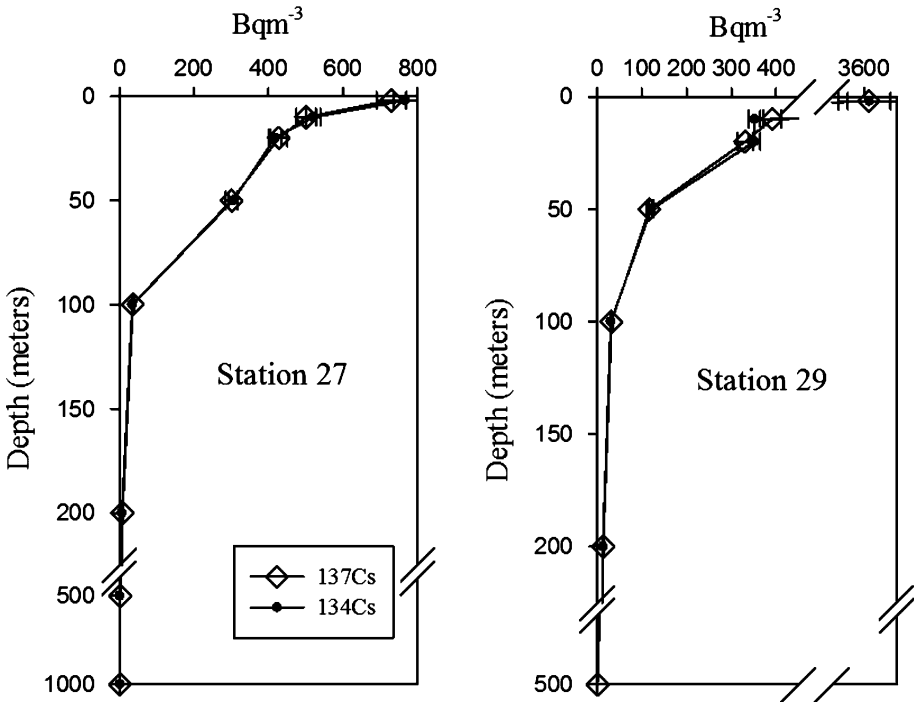

Fig. 2 Profiles of ^{134}Cs and ^{137}Cs activities collected in June 2011 from coastal waters off Fukushima NPP. Recoveries were quantified by ICP-MS on all samples. *Circles* represent ^{134}Cs and *diamonds* indicate ^{137}Cs with recovery correction applied and activities are given in Bq m^{-3}. *Note*: some *error bars* are $\leq$ symbol size

not processed and analyzed by ICP-MS. In both profiles the highest cesium activities are observed in the upper 50 m and return to near background levels by 200 m. These characteristics were observed in all profiles and demonstrate the degree of vertical mixing of the NPP contaminant plume by early June 2011. By integrating these depth profiles over the study area, calculated inventories of ^{137}Cs were 2.0 PBq in June 2011 [2].

Conclusions

As demonstrated by advancements introduced in this work, development of this extraction technique has significantly improved the sampling and processing protocols for extracting cesium from seawater. AMP fixed to PAN has proven to be an efficient absorber for the removal of cesium from seawater. Laboratory tests on SRM's found an average recovery rate of $>93 \pm 5$ %, at flow rates of 30–40 mL min^{-1}. Extraction columns with 5 mL bed volumes of AMP-PAN can be easily adapted to different sample volumes and allows for the rapid processing of large numbers of samples in the field compared with earlier methods. The AMP-PAN resin remains stable after processing and can be counted directly using gamma spectroscopy for ^{134}Cs and ^{137}Cs with isotope ratios determined on the same sample. While recoveries were reproducible and consistent, the use of stable cesium for recovery corrections increases the confidence placed in Cs activities obtained from single column extraction and gamma counting alone.

Seawater samples from this study had measured activities of ^{134}Cs and ^{137}Cs ranging from a few Bq m^{-3} to >3,000 Bq m^{-3}. These results have been integrated into the larger study of mapping and transport, risks to the biota and impacts of continued releases of cesium and other radionuclides from the Fukushima NPP. Results from this work were made possible by the great reduction in time from collection to counting allowing for large numbers of samples to be processed. It should be noted that the reduction in cost of laboratory and technical resources required using this method means that laboratories with limited resources could be involved with ocean monitoring with minimal investment in equipment assuming the use of NaI (Tl). Where counting facilities are not available, low level environmental samples collected on AMP-PAN are stable and can be easily shipped to a supporting facility for analysis.

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