12-15-2019

The Retrospective Analysis of Radionuclides in Banded Coral from the Bikini Atoll

Athena Marie Gallardo

Follow this and additional works at: <https://digitalscholarship.unlv.edu/thesesdissertations>

Part of the [Environmental Sciences Commons](#), and the [Radiochemistry Commons](#)

Repository Citation

Gallardo, Athena Marie, "The Retrospective Analysis of Radionuclides in Banded Coral from the Bikini Atoll" (2019). *UNLV Theses, Dissertations, Professional Papers, and Capstones*. 3801.
<http://dx.doi.org/10.34917/18608646>

This Dissertation is protected by copyright and/or related rights. It has been brought to you by Digital Scholarship@UNLV with permission from the rights-holder(s). You are free to use this Dissertation in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Dissertation has been accepted for inclusion in UNLV Theses, Dissertations, Professional Papers, and Capstones by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

THE RETROSPECTIVE ANALYSIS OF RADIONUCLIDES IN BANDED CORAL FROM THE BIKINI ATOLL

By

Athena Marie Gallardo

Bachelor of Science – Health Physics
University of Nevada, Las Vegas
2011

Master of Science – Health Physics
University of Nevada, Las Vegas
2013

A dissertation submitted in partial fulfillment
of the requirements for the

Doctor of Philosophy – Radiochemistry

Department of Chemistry and Biochemistry
College of Sciences
The Graduate College

University of Nevada, Las Vegas
December 2019

Dissertation Approval

The Graduate College
The University of Nevada, Las Vegas

November 2, 2019

This dissertation prepared by

Athena Marie Gallardo

entitled

The Retrospective Analysis of Radionuclides in Banded Coral from the Bikini Atoll

is approved in partial fulfillment of the requirements for the degree of

Doctor of Philosophy – Radiochemistry
Department of Chemistry and Biochemistry

Frederic Poineau, Ph.D.
Examination Committee Chair

Kathryn Hausbeck Korgan, Ph.D.
Graduate College Dean

Kenneth Czerwinski, Ph.D.
Examination Committee Member

Terry Hamilton, Ph.D.
Examination Committee Member

Brenda Buck, Ph.D.
Graduate College Faculty Representative

Abstract

Nuclear weapons testing conducted within the Bikini Atoll in the Marshall Islands resulted in local fallout contamination, including long lived isotopes of plutonium (Pu) and uranium (U), within the surrounding environment. The Bikini lagoon provides a continuous source of Pu ($^{239+240}\text{Pu}$) and U (^{236}U) to the Pacific Basin. The rate at which these isotopes are flushed from the lagoon to the ocean is balanced by inputs from remobilization of lagoon sediments. This research will provide a basis for predicting future change in the solubility and export potential of Pu and U in lagoon sediments. This is important to better understand long-term consequences of these isotopes transferred to the marine environment and/or local food chains. A chronological record of $^{239+240}\text{Pu}$ and ^{236}U concentrations and isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$ and $^{236}\text{U}/^{239}\text{Pu}$) within the lagoon was developed by analyzing two banded corals retrieved from the Bikini Atoll in 2016. Chronology was determined using x-ray imaging and stable isotope analysis using isotope-ratio mass spectrometry (IRMS). Samples were removed along the growth axis of the slabbed corals. Extraction chromatography and anion exchange columns were utilized to separate and purify Pu and U from the coral matrix. $^{239+240}\text{Pu}$ and ^{236}U concentrations and isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$ and $^{236}\text{U}/^{239}\text{Pu}$) were calculated from measurements of Pu isotopes and ^{236}U using accelerator mass spectrometry (AMS). ^{235}U and ^{238}U concentrations and $^{235}\text{U}/^{238}\text{U}$ ratios were assessed using inductively coupled plasma mass spectrometry (ICP-MS). This information was used to construct a model of the loss rate of $^{239+240}\text{Pu}$ and ^{236}U inside Bikini Atoll Lagoon. Isotopic ratio measurements suggest that the source-term of Pu and U inside the lagoon is slowly changing overtime.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

This material is based upon work supported by the Department of Energy National Security Administration Award Number DE-NA0000979 through the Nuclear Science and Security Consortium.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or limited, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect the United States Government or any agency thereof.

LLNL-TH-797799

Table of Contents

Abstract.....	iii
Acknowledgments.....	iv
List of Tables	ix
List of Figures.....	x
List of Equations.....	xiii
Chapter 1- Introduction	1
1.1 Research goal	1
1.2 Background	2
1.2.1 Nuclear testing at the Marshall Islands	2
1.2.2 Bikini Atoll	2
1.2.3 Factors affecting fate and transport	4
1.2.4 Radionuclides analyzed in this study.....	5
1.2.4.1 Plutonium.....	6
1.2.4.2 Uranium	8
1.2.5 Corals as an archival tool for radionuclides within the Bikini Atoll.....	9
1.2.5.1 Coral skeletal formation	10
1.2.5.2 Chronology by x-rays and stable isotope analysis of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$	10
1.3 Research overview.....	12
Chapter 2- Instrumentation and Materials	14
2.1 Overview.....	14
2.2 Instrumentation and techniques	14
2.2.1 Isotope ratio mass spectrometry (IRMS)	14
2.2.2 Inductively coupled plasma- mass spectrometry (ICP-MS)	16
2.2.3 Isotope dilution mass spectrometry (IDMS)	17
2.2.4 Accelerator mass spectrometry (AMS)	18
2.2.5 Autoradiography	22

2.3	Radioanalytical separations	23
2.3.1	Extraction chromatography	23
2.3.1.1	TEVA	23
2.3.1.2	UTEVA	24
2.3.2	Ion-exchange chromatography	25
2.3.2.1	Anion exchange	25
2.4	Materials.....	26
2.4.1	Coral retrieval.....	26
2.4.2	Coral x-rays.....	27
2.4.3	Coral radiation spatial distribution.....	29
2.4.4	Coral chronologies	30
Chapter 3-	Plutonium Analysis.....	33
3.1	Overview.....	33
3.2	Pu method development.....	33
3.2.1	Enewetak coral.....	33
3.2.2	Analytical procedure.....	34
3.2.3	Results	35
3.2.4	Method optimization.....	35
3.2.4.1	Results	36
3.3	Bikini coral plutonium analysis	36
3.3.1	Coral sampling.....	36
3.3.2	Pu analytical procedure.....	38
3.3.2.1	Coral digestion.....	38
3.3.2.2	Pu separation and purification.....	38
3.3.2.3	Iron hydroxide precipitation	39
3.3.2.4	Cathode production	39
3.3.2.5	AMS measurements	40

3.4	Results and discussion	41
3.4.1	Plutonium analysis	41
3.5	Pu export model.....	52
3.6	Plutonium coral concentration factor	57
3.6.1	Lagoon filtrate processing.....	57
3.6.2	Results	58
3.6.2.1	Comparison of concentration factor.....	58
3.7	Conclusions.....	59
Chapter 4- Uranium Analysis		61
4.1	Overview.....	61
4.2	AMS analysis.....	61
4.2.1	AMS analysis of ^{233}U and ^{236}U using a NU tracer	61
4.2.1.1	Analytical procedure.....	62
4.2.1.2	U separations	62
4.2.1.3	AMS measurements	62
4.2.1.4	Results	63
4.2.2	AMS analysis of ^{236}U using ^{233}U spike	65
4.2.2.1	Analytical procedure.....	65
4.2.2.2	AMS measurements	66
4.2.2.3	Results	66
4.2.3	Bikini coral uranium analysis.....	68
4.3	Uranium export model	71
4.4	$^{236}\text{U}/^{239}\text{Pu}$ Atom Ratios	74
4.5	$^{235}\text{U}/^{238}\text{U}$ Ratios	76
4.5.1	ICPMS method.....	76
4.5.2	Results	79
4.6	^{236}U in bottom piece of Bravo Coral	81

4.7	Conclusions.....	83
	Chapter 5- Conclusions.....	85
5.1	Summary of work preformed.....	85
5.2	Conclusions.....	86
	Appendix – Tables	90
	References.....	95
	Curriculum Vitae.....	99

List of Tables

Table 1. Isotope half-life and decay constants.	22
Table 2. Location of coral samples.....	27
Table 3. Enewetak coral AMS results.....	35
Table 4. Enewetak coral AMS results from optimization of method.....	36
Table 5. Location of coral samples.....	37
Table 6. Storm data impacting Marshall Islands (Wright , Spennemann and Marschner 1994).....	51
Table 7. Bikini lagoon filtrate AMS results.	58
Table 8. ²³⁶ U atoms in the NU tracer and in the blanks.	63
Table 9. ²³⁶ U results for IAEA 368.....	67
Table 10. Method Parameters for ICP-MS.	78
Table 11. Instrumental and method check samples.	78
Table 12. Isotopics for ²³³ U standard.	78
Table 13 ²³⁸ U concentrations and ²³⁵ U/ ²³⁸ U ratios at 2σ error.	80
Table 14. ²³⁸ U concentrations calculated by isotope dilution and standard addition.	81
Table 15. ²³⁶ U concentrations in Bravo coral bottom piece.	82
Table 16. Activity concentrations and atom ratios for Bravo coral, Eneu coral and surrounding lagoon water calculated using the Noshkin concentration factor with 1σ error.	90
Table 17. Pu annual exported from Bikini Atoll.	91
Table 18. ²³⁶ U annual exported from the Bikini Atoll.	93

List of Figures

Figure 1. Image of the Bikini Atoll.....	3
Figure 2. The Marshall Islands. The dotted lines represent a distance of 500 km and the dashed lines represent a distance of 1000 km from the Bikini Atoll (UNSCEAR 2000).	4
Figure 3. Schematic of the Accelerator Mass Spectrometer at the Center for Accelerator Mass Spectrometry (Brown et al. 2004).	21
Figure 4. Image of two divers drilling a coral head in the Bikini Atoll Lagoon.....	26
Figure 5. A coral being slabbed using a brick saw.....	27
Figure 6. Coral slabs in place about to be analyzed at CSU.	28
Figure 7. X-ray image of the Eneu coral.	29
Figure 8. X-ray image of the Bravo coral.....	29
Figure 9. Autoradiograph of bottom piece of the Bravo coral.	29
Figure 10. $\delta^{18}\text{O}$ for Bravo coral and associated years.	30
Figure 11. $\delta^{18}\text{O}$ for Eneu coral and associated years.	31
Figure 12. $\delta^{13}\text{C}$ values for Bravo corals and associated years.....	31
Figure 13. $\delta^{13}\text{C}$ values for Eneu corals and associated years.	32
Figure 14. $\delta^{18}\text{O}$ per composite distance from the top of the coral and coral images. The part of the graph that is boxed represents the piece of Eneu coral shown in the bottom two images. The bottom left image is the x-ray of the piece of coral with the associated $\delta^{18}\text{O}$ pattern. The bottom right image shows the sample locations of the black highlighted portion of the graph.	37
Figure 15. Comparison of Bravo and Eneu annual coral concentrations in Bq/kg.	41
Figure 16. Bravo coral specific activity (x-axis) and atom ratios (secondary x-axis) with 1σ error versus year.	43

Figure 17. Enewetak coral specific activities (x-axis) and atom ratios (secondary x-axis) with 1σ error versus year.	44
Figure 18. Annual $^{240}\text{Pu}/^{239}\text{Pu}$ ratios from the Eneu and Bravo corals with 2σ error. Bravo $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in the top graph and Eneu $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in the bottom graph.	46
Figure 19. Modified image showing the locations of tests in relation to the Bravo and Eneu corals denoted by the red stars (Hamilton 2019).	47
Figure 20. Pu specific activity in Bikini coral from Noshkin study (Noshkin et al. 1975).	49
Figure 21. Annual rainfall data at Bikini from 1985 through 2000 (Gouveia et al. 2002).	52
Figure 22. Bravo coral observations and GP interpolations of $^{239+240}\text{Pu}$ in Bq/kg of coral.	55
Figure 23. Eneu coral observations and GP interpolations of $^{239+240}\text{Pu}$ in Bq/kg of coral.	55
Figure 24. Bravo Coral annual concentration model.	56
Figure 25. Eneu coral annual concentration model.	56
Figure 26. ^{236}U concentrations in mBq/kg of coral.	64
Figure 27. ^{233}U concentrations in Eneu and Bravo Corals at 1σ error.	65
Figure 28. ^{236}U concentrations in Bq/kg of coral in the Bravo corals at 2σ error.	67
Figure 29. Gaussian model of Bravo data set.	72
Figure 30. Export model for Bravo coral.	72
Figure 31. Gaussian model for Eneu Coral.	73
Figure 32. Export model for Eneu coral.	73
Figure 33. Annual Eneu ^{239}Pu and ^{236}U atoms/g of coral at 1σ error. X-axis shows the ^{239}Pu in atoms/g and secondary axis shows the ^{236}U in atoms/g.	74
Figure 34. Annual Bravo ^{239}Pu and ^{236}U atoms/g of coral. X-axis shows the ^{239}Pu in atoms/g and secondary axis shows the ^{236}U in atoms/g.	75
Figure 35. $^{236}\text{U}/^{239}\text{Pu}$ atom ratios in Bravo and Eneu corals at 2σ error.	76

Figure 36. $^{235}\text{U}/^{238}\text{U}$ atom ratios in KED mode at 2σ error.	79
Figure 37. Locations of samples removed from bottom of Bravo coral.	82

List of Equations

Equation 1	11
Equation 2	14
Equation 3	15
Equation 4	17
Equation 5	18
Equation 6	18
Equation 7	20
Equation 8	21
Equation 9	24
Equation 10	24
Equation 11	52
Equation 12	53
Equation 13	53
Equation 14	54

Chapter 1- Introduction

1.1 Research goal

The Bikini Atoll is a former atmospheric nuclear weapons test site and one of the most contaminated sites in the world due to the high contribution of local fallout deposited from nuclear weapons detonations. This is due to the atoll's history with atmospheric nuclear weapons testing and the behavior of plutonium (Pu) and uranium (U) within the atoll. The positioning of these tests resulted in local, "close-in" fallout injected within the lagoon and surrounding North Pacific. The Pu and U in the lagoon are mainly associated with lagoon sediments. However, these radionuclides from the sediments are continuously remobilizing into lagoon water and transported to the Pacific Ocean. The purpose of this research is to understand the behavior of Pu and U isotopes produced from nuclear weapons testing within the Bikini Atoll lagoon. This research will examine the solubility and export potential of the investigated radionuclides retained in the bottom lagoon sediments have changed over time. This research will assess changes in the levels and the origin of contamination for Pu and U isotopes within the Bikini Atoll. A chronological record of the long-lived isotopes of Pu and U within the lagoon will be constructed through the chemical analysis of coral. This research will provide a basis for understanding and predicting future change in the solubility and export potential of Pu and U contained in bottom sediments of highly contaminated areas which will help predict the long-term consequences of these radionuclides transferred to the surrounding marine organisms and/or local inhabitants of the atolls.

1.2 Background

1.2.1 Nuclear testing at the Marshall Islands

The Marshall Islands are comprised of 29 atolls and 5 islands which are located 4000 km west of Hawaii.

An atoll is a ring-shaped coral reef that encircles a lagoon. This site was used by the United States for nuclear weapons testing. This location was picked for nuclear testing because of the stable weather conditions, low number of inhabitants, and remoteness (Hamilton et al. 2002). The United States conducted 67 nuclear tests within the Marshall Islands at the Bikini and Enewetak Atolls between the years of 1946 - 1958 (Energy 2015). The combined explosive yield from both Enewetak and Bikini Atolls within the Marshall Islands was 1.08×10^5 kiloton (kt) TNT. A total of 76.8 megaton (Mt) yield was contributed from the Bikini Atoll testing (Simon and Robison 1997, Energy 2015).

1.2.2 Bikini Atoll

The Bikini Atoll is in the northwestern region of the Marshall Islands centered at 11° 35'N 165° 23'E and consists of 23 islands surrounding a 630 km² lagoon with a mean depth of 46 m. The United States conducted 23 nuclear weapons tests with various yields at the Bikini Atoll between 1946 and 1958. Two tests were detonated in 1946, five tests in 1954, six tests in 1956 and ten tests in 1958. Of the 23 nuclear detonations, one was considered low yield (< 20 kt), five were in the intermediate range (20 kt – 200 kt), five in the subMt range (greater than 20 kt and less than 1 Mt), and 11 were in the Mt range. These tests were detonated at or close to the ocean surface (0 – 10 ft) either as an airdrop, barge, surface or underwater test (Energy 2015).

Figure 1. Image of the Bikini Atoll.

The positioning of the tests resulted in local, “close-in” fallout within the lagoon and surrounding North Pacific Ocean. Close-in fallout can constitute as much as 50% of the total produced by surface tests and includes large radioactive aerosol particles that are deposited within about 100 km of the test site (UNSCEAR 2010). Locally deposited radionuclides provided a wide range of fission products, activation products, and refractory particles (unfissioned nuclear fuel containing isotopes of U and Pu). For near surface detonations, it is assumed that 50% of refractory fallout debris is deposited within the immediate vicinity of the test and an additional 25% is deposited regionally, within a few thousand kilometers (Hicks 1982, Hamilton 2004, UNSCEAR 2000). Nuclear testing at the Marshall Islands contributed to 97% of the world’s total close-in fallout with 70% (20 Mt yield) deposited by nuclear testing from the Bikini Atoll (Lindahl et al. 2012, UNSCEAR 2000).

Figure 2. The Marshall Islands. The dotted lines represent a distance of 500 km and the dashed lines represent a distance of 1000 km from the Bikini Atoll (UNSCEAR 2000).

1.2.3 Factors affecting fate and transport

The close-in fallout remained as either dissolved or particulate debris within the lagoon and was eventually emitted into the open ocean or settled to the bottom sediments within the lagoon. The injected radioactive species (atoms, ions, molecular fragments...etc) are heterogeneously distributed within the local environment. Fate and transport of the radioactive fallout within the surrounding environment depends on particle size, distribution, structure, oxidation state and release scenario (Salbu et al. 2018). Radionuclide species are defined in water by their diameters. Species with diameters less than $0.001 \mu\text{m}$ are low molecular mass species (LMM) and are considered mobile and bioavailable. Radioactive colloids, nanoparticles or pseudo-colloids are radioactive species containing diameters within the size range of $0.001 \mu\text{m}$ - $0.45 \mu\text{m}$. Radioactive species with diameters greater than $0.45 \mu\text{m}$

are defined as hot particles and species with a diameter greater than 2 mm are known as fragments. Colloids present in sea water are typically carbonates or oxide mineral systems and can be coated with humic acid (Choppin 2006). The elemental composition of the radioactive debris depends on the conditions surrounding the formation of the particle. This includes pressure and temperature conditions, construction materials, surrounding infrastructure, local geology, and altitude of the detonation (Salbu et al. 2018). Particles can carry substantial amounts of refractory material and settle heterogeneous throughout the bottom of the lagoon. The refractory material within the particles are considered inert and highly insoluble. Refractory U and Pu oxides are formed in the very high temperature nuclear weapon detonations and do not interact with the surrounding environment and remain in the forms in which they were injected into the environment for long periods of time (Choppin 2006). The behavior of refractory particles is dominated by conditions of the surrounding ecosystem (Choppin 2006). With the effect of weathering and remobilization, particles can solubilize, increasing the bioavailable activity within the surrounding environment. These factors delay the ecosystem transfer of particle associated radionuclides compared to the initially injected mobile species.

1.2.4 Radionuclides analyzed in this study

Long-lived isotopes of U (^{233}U $T_{1/2}$ 159.2 ky; ^{235}U $T_{1/2}$ 704 My; ^{236}U $T_{1/2}$ 23.42 My;) and Pu (^{239}Pu $T_{1/2}$ 24.11ky; ^{240}Pu $T_{1/2}$ 6.561ky) retained in coral will be analyzed in this study. These radionuclides have long half-lives and will remain in the environment for a long time. The selected Pu and U isotopes are alpha emitters with energies between 4 - 5 MeV. When transferred to local food chains and ingested, they can have significant dose contributions. The isotopes of U and Pu were chosen because the determination of ratios (the concentrations relative to one another) will provide information on the source contribution. The main contribution of these isotopes are produced from high energy devices but this ratio can become diluted if insoluble refractory particles are solubilizing and becoming mobile within the lagoon. The ^{234}U , ^{235}U and ^{238}U are found in nature with abundance of 0.0054% 0.7204% and 99.2742%

respectively (Baum et al. 2010). The natural U signal in the coral may overpower the anthropogenic signal, in this context ^{233}U and ^{236}U will also be analyzed. Concentrations for both ^{233}U and ^{236}U will be used as an indication of change in contamination source because they are produced in higher concentrations in high yield detonations vs low yield detonations.

1.2.4.1 Plutonium

The long-lived Pu isotopes (^{239}Pu $T_{1/2}$ 24.11 ky; ^{240}Pu $T_{1/2}$ 6.561 ky) are the two most abundant Pu isotopes within the marine environment. About 10 PBq of Pu was released into the atmosphere during nuclear weapons testing. Other sources of Pu in the Pacific Ocean have stemmed from discharges from the nuclear industry, nuclear waste dumping, uncontrolled releases from nuclear installations and accidents involving nuclear weapons/nuclear powered vessels/space vehicles (Muramatsu et al. 2001). These releases have contributed to the global $^{240}\text{Pu}/^{239}\text{Pu}$ fallout ratio of ~ 0.18 (Kelley, Bond and Beasley 1999). Each release condition has specific $^{240}\text{Pu}/^{239}\text{Pu}$ ratios associated with aspects of the release type and this information can be used to describe aspects and conditions of the source term. Refractory material from low yield nuclear devices contain Pu ratios similar to bomb-grade Pu ratios (0.03-0.08) because more of the fissionable material did not undergo fission (Muramatsu et al. 2001). Higher yield devices, like thermonuclear detonations, exhibit higher ratios due the significant change in the proportion of heavy Pu isotopes because more of the bomb grade material undergoes fission and there are more neutron capture and (n, 2n) reactions (Muramatsu et al. 2001). Higher ratios are also produced during long burn up time of nuclear fuel. The Bikini Atoll has a higher $^{240}\text{Pu}/^{239}\text{Pu}$ ratio than the global fallout ratio due to the higher yield tests within the lagoon that deposited a large amount of close-in Pu contamination to the atoll.

The chemical processes (ex. solubility, hydrolysis, and complexation) of Pu in the lagoon water is affected by its oxidation state (Hirose 2009). Plutonium exists in the lagoon as reduced (+3 and +4) and oxidized (+5 and +6) species. The most significant states are Pu(+4) and Pu(+5) in natural water systems

(Hirose 2009, Choppin 2006). The bulk (90%) of the total Pu within in the lagoon is associated with sedimentary or particulate material in the reduced state (Noshkin et al. 1987). Humic acid in sea water has been shown to reduce Pu(+5) to Pu(+4). The reduced Pu is highly adsorbed onto calcium carbonate particles as surface complexes (Lindahl et al. 2011). The Pu in the lagoon is mainly associated with the lagoon sediments and is continuously remobilizing into solution (Noshkin et al. 1987, Buesseler et al. 2018). In the reduced oxidation state, Pu desorbs from sedimentary or particulate material, the Pu either adsorbs onto a new surface or oxidizes to a higher state. 78% of the total Pu exists in solution in the oxidized state Pu(+5) but can also exist in Pu(+4) which is present in colloidal form (Choppin 2006). The higher oxidation states are more stable in alkaline solutions and are less reactive than the reduced states (Hirose 2009, Choppin 2006). The reduced Pu in solution is located close to the bottom of the lagoon. The Bikini lagoon annually exports 0.12 - 0.2 TBq $^{239+240}\text{Pu}$ to the open Pacific (Lindahl et al. 2011, Hamilton, Millies-Lacroix and Hong 1996). The rate of the dissolved Pu within the lagoon water that is flushed from the lagoon to the ocean is balanced by input of Pu from the remobilization of Pu from the bottom sediments. The total average soluble Pu concentration in the Bikini Lagoon water has been estimated at $100 - 200 \pm 250 \text{ mBq/m}^3$ which is much larger than the average surface sea water value of $^{239+240}\text{Pu}$ in the northwest Pacific of $2.5 \pm 0.2 \text{ mBq/m}^3$ (Lindahl et al. 2011, Buesseler et al. 2018).

Plutonium is incorporated into the coral skeleton during growth with a constant relationship between Pu in the coral and the surrounding water with a concentration factor of 2.7×10^3 (Lindahl et al. 2011, Noshkin et al. 1975). This is driven by mechanisms of substitution, non-lattice inclusion and adsorption (Meece and Benninger 1993). The exact speciation, oxidation state and mechanism of incorporation of Pu in coral is unknown (Benninger and Dodge 1986). The Pu in the surrounding sea water can be reconstructed by analyzing natural archives such as dated coral cores. Concentrations of ^{239}Pu within coral from the Enewetak atoll range between $(8 - 39) \times 10^8 \text{ at/g}$, $(1.1 - 4.9) \times 10^3 \text{ mBq/kg}$,

post nuclear and from $(25 - 1189) \times 10^8$ at/g , $(4 - 140) \times 10^3$ mBq/kg, during the testing era (Froehlich et al. 2017) . Similar values are expected to be seen from the Bikini Coral. Due to the low concentration, accelerator mass spectrometry will be used for Pu analysis.

1.2.4.2 Uranium

Corals in shallow waters have heterogenous distribution of U with concentrations of 2 - 3.5 ppm (Robinson et al. 2006). Uranium has a negative correlation to the temperature of the surrounding water during growth. Uranium is present in ocean water as U(+6) and forms uranyl carbonate ions $\text{UO}_2(\text{CO}_3)_3^{4-}$ under aerobic conditions within the ocean which is driven by salinity (Owens, Buesseler and Sims 2011). Uranium becomes incorporated in the aragonite skeleton of the coral by substituting tetravalent uranyl carbonate for Ca within the coral lattice. U/Ca ratios in coral are assumed to reflect the concentrations within the surrounding sea water of 7.5×10^{-6} (Flor and Moore 1977). The U concentration within the surrounding lagoon waters during the lifetime of the coral can be constructed. Isotopes of U that are of interest include ^{233}U , ^{235}U , ^{236}U and ^{238}U . Ratios of $^{235}\text{U}/^{238}\text{U}$ and analysis of concentrations of ^{233}U and ^{236}U will provide information regarding change in source term.

The ^{236}U is produced by $^{235}\text{U}(\text{n},\gamma)$ and $^{238}\text{U}(\text{n},3\text{n})$ reactions and by the alpha decay of ^{240}Pu . In nature, ^{236}U is produced by (n,γ) reaction from (α,n) reactions on light elements such as Na and Mg. This reaction is also induced by thermal neutrons from cosmic radiation that interact with ^{235}U on the surface layer of the Earth. The ^{236}U deposited in the Marshall Islands was produced during nuclear weapons testing mainly through the $(\text{n},3\text{n})$ reaction on ^{238}U by fast neutrons in a thermonuclear device (Winkler, Steier and Carilli 2012). Fast neutrons (14 MeV) are created during fusion $^3\text{H}(\text{d},\text{n})^4\text{He}$ reaction and interact with ^{238}U ($\sigma = 0.4$ b) within the device. The ^{238}U has a fast neutron cross section of ~ 0.4 barns. The total estimated deposition of ^{236}U from global fallout is 900 kg. The $^{236}\text{U}/^{239}\text{Pu}$ ratio produced from global fallout has been estimated to be 0.22 - 0.30 (Sakaguchi et al. 2009). Ratios of $^{236}\text{U}/^{238}\text{U}$ were found to range from $10^{-7} - 10^{-8}$ atoms/g of dry soil from fall out which is significantly larger than the

natural ^{236}U from cosmogenic and nucleogenic production (Sakaguchi et al. 2009). The ^{236}U have been limited due to the long half-life of 2.342×10^7 years and low abundance. This will aid in oceanic tracer studies using ^{236}U which is of interest due to ocean residence time for U of 0.3 - 0.5 million years and its conservative behavior in the ocean (Winkler et al. 2012). The ^{236}U concentrations within coral from the Enewetak Atoll range between $(0.9 - 8.0) \times 10^8$ at/g post nuclear and a maximum concentration of 174 at/g during the testing era (Froehlich et al. 2017). Similar values are expected to be seen from the Bikini coral. Accelerator mass spectrometry will be used to analyze for ^{236}U due to its low concentrations.

1.2.5 Corals as an archival tool for radionuclides within the Bikini Atoll

The contamination from the nuclear weapons testing is continuously assimilating into the biota within the atolls and the biota can be analyzed to understand the radionuclides present within the atoll lagoon. Chemical analysis of immobile living organisms, like coral, can provide information regarding chronology, growth rates, source attribution as well as concentrations of radionuclides within the atoll. Coral incorporates both stable and unstable elements from the surrounding environment into its skeleton as it grows. Once the element becomes incorporated within the skeleton, it becomes fixed and there is no migration of the element within the skeleton (Moore, Krishnaswami and Bhat 1973). Concentrations of certain elements, including radionuclides, within the coral reflect the concentration of that element in the surrounding lagoon water during the time of uptake. Chemical analysis of corals can also provide chronological isotope information relating to environmental conditions within the surrounding lagoon at the time of incorporation and is commonly used as proxies for analysis in ocean chemistry, circulation and climate change (Quinn and Sampson 2002). The main advantage of using coral to retrieve the historical record of a certain element or isotope is the absence of mixing processes between the annual growth bands that occurs in ocean sediments. Corals analyzed in this research are reef building corals identified as *Porites australiensis* Vaughan, 1918.

1.2.5.1 Coral skeletal formation

Hermatypic corals are also known as reef building corals. The coral polyps that make up these corals have a symbiotic relationship with algae, zooxanthellae, living within their tissues. Due to this relationship, these corals are restricted to warm waters and depths where the sun can reach the corals. Organic carbon produced by the algae from photosynthesis is utilized as a food source by the coral. When there is more sunlight, more organic carbon is produced, and the corals deposit their limestone skeletons at a much faster rate than in times of less light. The skeletons are created mainly through precipitation of CaCO_3 that the coral polyps secrete. 98% of corals nutritional requirements are from the algae. The remaining nutrients are from prey such as zooplankton. Corals also absorb dissolved nutrients from surrounding waters (phosphates, nitrates, iron, etc). Corals fractionate calcium and carbonate from sodium, magnesium, chloride and other major ions in sea water (Moore et al. 1973). Elements which have chemistries similar to calcium will also become incorporated within the coral skeleton depending on the ratio of the element to calcium within the water and the fractionation factor.

1.2.5.2 Chronology by x-rays and stable isotope analysis of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$

Corals from the genus *Porites* will be analyzed in this research. Corals belonging to the genus *Porites* have a growth rate less than a cm per year. For this genus of coral, rapid growth is sacrificed due to long-term endurance and stability (Veron 1998). *Porites* can reach 8 meters in height and can be almost 1000 years old. *Porites* deposit layers or bands of skeleton in seasonal cycles. These bands vary in width and densities and are affected by environmental variables such as temperature, salinity, nutrients and food, light, wave action and sedimentation. A pair of light and dark density bands are produced annually. These different density bands can be observed normal to the axis of growth by taking an x-radiograph image of a slab of coral. The differences in density represents cyclic changes in environmental variables (Moore and Krishnaswami 1974, Buddemeier 1974, Weber, White and Weber 1975). The number of coupled density bands per cm can be used to determine the growth rate of the coral if no hiatus in growth is assumed. Studies analyzing coral within the Marshall Islands have shown that seasonal and

annual cycles in density are approximately synchronous for most corals growing in the same area. Higher density skeletal deposition in hermatypic coral colonies from the Marshall Islands have been found to coincide with the season of higher rainfall and warmer surface water at the atoll. Annual density banding can be counted and used to determine chronology (Buddemeier and Maragos 1974). The equation for a homogenous beam of x-rays transmitted through an object is shown in Equation 1.

Equation 1

$$I = I_0 e^{-\mu t}$$

Where I is the transmitted intensity beam at a given point when the object has an initial beam of intensity I_0 imparted at the same point. The linear absorption coefficient is denoted by μ and the thickness of the object is t . The differences in x-rays from the varying densities in the coral is due to the linear absorption coefficient which is dependent on the density of the object under investigation.

Combining density band counting with elemental analysis such as $\delta^{18}\text{O}$ ($^{18}\text{O}/^{16}\text{O}$) and $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$) allows for the construction of a more precise chronology. This isotope varies within the coral skeleton and is directly related to surface temperature (SST), salinity (SSS), precipitation, and isotopic composition of water during the time of skeletal formation (Asami et al. 2004). The $\delta^{18}\text{O}$ content in the coral genus *Porites* is temperature dependent and $\delta^{18}\text{O}$ increases as the ambient water temperature increases (Weber and Woodhead 1972, Weber et al. 1975). Ocean water is enriched in ^{16}O and as the temperature increases, ^{16}O is evaporated more readily from the ocean which causes $\delta^{18}\text{O}$ to be higher. During dry seasons $\delta^{18}\text{O}$ is higher due to evaporation of ^{16}O . During times of high precipitation, the $\delta^{18}\text{O}$ will be a more negative value due to the ^{18}O depleted meteoric rain water (Pereira et al. 2017). In areas like the Marshall Islands where the SST remains consistent, the variability in $\delta^{18}\text{O}$ will be dominated by the change in precipitation. The variability of $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$) in coral also corresponds to seasonal

variations of solar radiation. During photosynthesis the algae use ^{12}C to produce organic matter. This leaves ^{13}C behind to be utilized by the coral to construct its skeleton (Guilderson and Schrag 1999). Rainfall in the Bikini lagoon is lowest in February and highest in September on average. Values are expected for $\delta^{18}\text{O}$ to be smallest in September and the highest in February. This should be similar for $\delta^{13}\text{C}$ because less solar radiation will reach the corals during the raining season. The synchronous seasonal patterns will assist in the reconstruction of chronology. The analysis for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ will be performed simultaneously on microgram samples with a high resolution of 0.5 mm to 1mm using Isotope Ratio Mass Spectrometry (IRMS).

1.3 Research overview

This dissertation provides a chronological record of ^{236}U , ^{233}U and $^{239+240}\text{Pu}$ in the Bikini Atoll Lagoon. Prior to this study, there has been no chronological information of ^{236}U and ^{233}U within the lagoon. There has been one study that developed chronological $^{239+240}\text{Pu}$ concentrations by analyzing coral from 1953 to 1972 within the Bikini Lagoon (Noshkin et al. 1975). This research is different from the previous study because the chronology extends from 1956 to 2015 and shows how the concentration trends within the lagoon changes in 1970 to 2015 and decreases at a much slower rate than the older portions of the coral. New information in this study also shows different increasing and decreasing trends in $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios over time which indicates the source of Pu contamination is changing within the two coral sites. The $^{239+240}\text{Pu}$ and ^{236}U concentrations measured were used to develop export models and total and annual export was calculated throughout the lifetime of the corals. This work provides reassurance that concentrations of Pu and U have decreased and will continue to decrease over time. Measured and projected concentrations and export shows there is no impact from these isotopes on the wider Pacific. This data can be used to produce better estimates of Pu dose contributions in the aquatic food chain within the Bikini Atoll. This information will allow more informed decisions about resettlement and what

the conditions will look like in the future. Chapter 1 describes the site background, contamination and the behavior of Pu and U within the atoll. Chapter 2 provides information about the materials, analytical methods and instrumentation used in this research. Chapter 3 describes the Pu analysis which includes radioanalytical separations and analysis by accelerator mass spectrometry. Chapter 4 describes the U analysis which includes radioanalytical separations, analysis by accelerator mass spectrometry and induced coupled plasma mass spectrometry. Chapter 5 provides the conclusions of this work.

Chapter 2- Instrumentation and Materials

2.1 Overview

This chapter describes instrumentation, techniques and the corals analyzed in this research. Originally six corals were retrieved from the Bikini Atoll in February 2016. They were slabbed down the center axis into 0.25-inch-thick slabs using a brick saw. Chronologies of the corals were determined by x-ray imaging. Two corals with well-defined banding were chosen to perform a thorough radionuclide analysis. The chronologies of the two best suited corals were corrected based on the seasonal cycles of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analysis analyzed by IRMS. Extraction chromatography and ion exchange columns were used to separate and purify Pu and U isotopes from the coral matrix. ICP-MS was used to quantify $^{235}\text{U}/^{238}\text{U}$ ratios and concentrations within the coral. Accelerator mass spectroscopy was used to quantify ^{239}Pu , ^{240}Pu , ^{233}U and ^{236}U .

2.2 Instrumentation and techniques

2.2.1 Isotope ratio mass spectrometry (IRMS)

Isotope ratio mass spectrometry (IRMS) was used to measure $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonates. Microgram samples of carbonates are placed in glass vials within a carbonate device. Two to three drops per sample of phosphoric acid (ortho H_3PO_4) is added into sample vial under vacuum. Carbon dioxide (CO_2), water (H_2O) and calcium phosphate (Ca_2PO_4) are produced from this reaction as donated in Equation 2. The calcium phosphate stays within the vial.

Equation 2

The gaseous products (CO₂ and H₂O) are transferred to a cryogenic trapping system consisting of two liquid nitrogen (LN₂) traps under high vacuum. The first trap removes the water and non-condensable gasses from the CO₂ through fractional freezing. The CO₂ and H₂O are frozen within the first trap at -196°C. The non-condensable gasses are pumped away, and the trap temperature is increased to -115°C. The H₂O remains frozen in the first trap and the CO₂ will evolve into a gas and travel to the second trap set at -196°C. After 120 seconds, a valve between the two traps is closed and the temperature of the second trap is increased to 30°C. The CO₂ travels through a capillary to the spectrometer inlet system valve. The spectrometer inlet system is composed of two capillaries, one for reference gas (CO₂) and one for sample, connected to a set of changeover valves. These valves control the inlet of the gases allowing either the sample or the reference gas to enter the inlet probe to the ionization chamber. The reference gas is adjusted to the same volume and pressure as the sample gas and is used for comparison with the unknown sample as in Equation 3. The ion source is a tungsten filament under a small magnetic field which emits electrons that collide with the CO₂ gas molecules producing CO₂⁺ ions. An accelerating voltage (10 kV) is applied to the CO₂⁺ ions directing the ions out of the ionization chamber and into the flight tube. The flight tube has a 90° deflection path and a permanent magnet which can be adjusted up to a maximum field strength of 0.77 Tesla at full accelerating voltage. The accelerated ions traveling through the flight tube are deflected due to the force of the magnetic field. The difference in the deflection angle depends on the mass of the ion. The separated beams are collected onto faraday cups and an ion current is measured. The data is expressed in delta (δ) notation. The isotopic ratios of ¹⁸O/¹⁶O and ¹³C/¹²C are relative to the carbonate standard NBS-19 which has a given fixed isotope value for δ¹³C of 1.95‰ and δ¹⁸O of -2.2‰.

Equation 3

$$\delta\text{‰} = \left[\frac{Ratio_{sample} - Ratio_{standard}}{Ratio_{standard}} \right] \times 100$$

Samples were removed along the entirety of the growth axis of the coral using a Dremel with a 0.5mm burr at a 0.5-1 mm resolution. 50-90 μg of the powdered carbonate samples were analyzed using a Finnigan Mat252 isotope ratio mass spectrometer, equipped with an automated carbonate reaction device (Kiel III). Measurements were reported relative to NIST reference material NBS 19 with a PDB conversion and analyzed using ISODAT instrument software. PDB is an international standard *Belemnite* from the Peedee formation in South Carolina. This analysis was performed at the Stable Isotope Laboratory at Stanford University.

2.2.2 Inductively coupled plasma- mass spectrometry (ICP-MS)

Inductively coupled plasma- mass spectrometry (ICP-MS) is used for performing trace element analysis with detection limits at or below the ppt range. Samples are transferred to the nebulizer via a peristaltic pump. The liquid sample turns into fine droplets in the nebulizer and are transferred to a spray chamber. The finer sample droplets are filtered out from the larger droplets and are then introduced to the argon plasma. The sample enters the argon plasma ($\sim 6000^\circ\text{C}$) and dries to a solid and then heated to a gas. The sample gas dissociates, the atoms absorb energy, eventually releasing electrons and forming singly charged ions. The argon plasma is created from an argon ICP torch wrapped at one end by a radio frequency (RF) coil. The ions are focused by the sample and skimmer cones, under vacuum, and the beam is directed to and filtered in the quadrupole mass spectrometer. The quadrupole mass spectrometer which creates a magnetic field that only allows one mass-to-charge ratio (m/z) to pass through at a time. The quadrupole mass spectrometer is composed of four rods placed equal distance from each other where two rods in the horizontal x-plane are supplied with a voltage $+V_0$ and the other two rods are in the y-plane supplied with voltage $-V_0$. Ions travel in the z direction which is parallel to the rods and are guided through the mass spectrometer by the magnetic field. The ions filtered through the quadrupole mass spectrometer hit the detector which is an electron multiplier. The ion hits the first dynode of the electron multiplier which releases a cascade of electrons which are amplified until they

become a measurable pulse. The measured pulses are then compared to the intensities of a calibration curve or known spiked isotope to determine the concentration of that element using instrument software. Polyatomic interferences can be suppressed using the collision/reaction cell technology (CCT).

The Qcell collision cell removes polyatomic interferences based on the difference in the cross-sectional size between the analyte and the polyatomic using pure He as a collision gas with Kinetic Energy Discrimination (KED). In the CCT KED mode, the Qcell is pressurized with a He reaction gas. All analytes and polyatomic ions enter the cell from the plasma with uniform kinetic energies. The larger polyatomic ions will undergo more collisions and will exit the cell with much lower kinetic energy than the smaller ions. An energy barrier will only allow the target ions to pass to the mass analyzer while the larger polyatomic ions will be blocked from entering.

2.2.3 Isotope dilution mass spectrometry (IDMS)

Isotope dilution mass spectrometry is a common method used to determine concentration of an element in a sample by diluting the sample with a precisely known amount of a rare isotope of the element of interest, also known as a spike. The spike is equilibrated within the sample and alters the isotopic ratios within the sample. The measured sample will contain a combined isotopic ratio of the unknown sample and the spike as calculated in Equation 4. The ^{233}U was used as the spike for measuring ^{238}U and ^{235}U in the coral samples.

Equation 4

$$R_{\left(\frac{^{233}\text{U}}{^{238}\text{U}}\right)_{\text{measured}}} = \frac{^{233}\text{U}_{\text{spike}} + ^{233}\text{U}_{\text{sample}}}{^{238}\text{U}_{\text{spike}} + ^{238}\text{U}_{\text{sample}}}$$

An advantage of IDMS is that molecular interferences within the sample, or matrix effects, will not affect the measured ratios. $^{235}\text{U}/^{238}\text{U}$ ratios for each sample will be calculated by the ICPMS software and

corrected using certified reference material (New Brunswick Laboratory CRM 112-A, Uranium Metal Isotopic Standard). Bias on the ratios are due to instrumental discrimination/fraction effects or from differential transmission/detection by the mass spectrometry. This can lead to a negative or positive bias. A mass bias correction will be applied.

Equation 5

$$\text{mass bias factor} = R_t/R_m$$

Where R_t is the $^{235}\text{U}/^{238}\text{U}$ ratio of the certified value and R_m is the $^{235}\text{U}/^{238}\text{U}$ ratio of the measured value.

ThermoFisher ICAP Q ICPMS and Qtegra Software were used to measure and analyze the coral samples.

One coral sample in each ICPMS run was used to verify concentrations calculated by IDMS.

Equivalent amounts of sample used for IDMS were transferred to standard addition samples. CRM 112A spikes of increasing concentrations (0 ppb, 1 ppb, 3 ppb, 5 ppb and 10 ppb) were added to the samples.

Samples were graphed, a linear regression was applied. The unknown concentration was calculated using Equation 6.

Equation 6

$$C = \frac{b}{m}$$

Where C is the concentration of the unknown isotope in ppb, b is the y intercept from the linear regression equation and m is the slope from the linear regression equation.

2.2.4 Accelerator mass spectrometry (AMS)

Samples are prepared as oxides within an aluminum cathode and loaded within the sample holder of the detector. Cesium (Cs) vapor is sprayed onto a heated ionizer that thermally ionizes the Cs and forms Cs^+ .

These ions are focused into the cathode, sputter the sample within the cathode creating negative sample ions. The sample ions are accelerated by an electric field and exit the ion source and directed to an electrostatic deflector that bends the ions and filters the ions with a certain energy through the mass selection slits. The ion beam travels through a magnetic field which filters the mass of interests sending it to the accelerator. The sample ion is accelerated at approximately 1% of the speed of light which breaks up interfering molecular ions into atomic ions. The negative ions interact with argon (stripper gas) causing those ions to lose electrons with interactions with the argon gas and the sample ion becomes a positive ion and leaves the accelerator. The positive ion passes through a magnet and is bent at 30° which filters based due to mass rigidity and then the ion enters the electrostatic analyzer which filters ions with a specific energy. The ions fly through a thin mylar window and are implanted into a gas chamber detector. A schematic of the AMS instrument is shown in Figure 3.

Accelerator mass spectrometry was used for this research because of the low concentrations of Pu and U isotopes expected in the coral samples. The low detection sensitivities of AMS is 1×10^6 atoms per sample for several actinides including isotopes of Pu and AMS can resolve ^{239}Pu from ^{240}Pu unlike traditional alpha spectrometry methods (Brown et al. 2004). Expected concentrations are 10^8 atoms/g of coral for ^{239}Pu and ^{236}U . Using AMS allows for the quantification of small samples containing extremely low levels of radionuclides of interest for this study. Small samples are important to maintain an annual temporal resolution.

Reference isotopes of 3×10^9 atoms ^{242}Pu and 1 mg of NU (natural uranium) were added to samples at different steps of the chemical procedure. Measurements were taken by cycling between the isotope of interest and the reference isotope. Cycling is accomplished by alternating the injected ion mass. The isotope of interest (ex. $^{239}\text{Pu}^{5+}$) is measured for 0.4 s followed by the reference ion (ex. $^{242}\text{Pu}^{5+}$) and repeated for 10s. Settings for the ESA are adjusted and the next isotope of interest ($^{240}\text{Pu}^{5+}$) is measured. Performance of the measurements were analyzed for ^{239}Pu by measuring replicate samples

derived from a calibrated ^{239}Pu solution (IPL 630-22-3) covering a range from 10^6 to 10^{11} atoms.

Measurement of IPL calibration samples verify little to no scattering in the AMS measurements due to counting statistics based uncertainties (Brown et al. 2004). Blank samples containing 10^{14} atoms of ^{238}U were analyzed to verify ^{238}U interferences are insignificant for ^{239}Pu measurements. National Institute of Standards and Technology (NIST) traceable standards CRM 128 ($^{239}\text{Pu}/^{242}\text{Pu} = 0.993 \pm 0.0003$) and CRM 138 ($^{240}\text{Pu}/^{239}\text{Pu} = 0.0863 \pm 0.0001$) were routinely measured throughout the Pu AMS measurement runs to monitor mass dependent normalization factors for ^{239}Pu , ^{240}Pu and ^{242}Pu isotope measurements (Brown et al. 2004). Tuning samples containing ^{242}Pu spike in addition to 10^9 atoms of ^{239}Pu and 10^9 atoms of ^{240}Pu are used tune the instrument for the appropriate masses. FeNb samples containing the ^{242}Pu spike are run to analyze the instrument background.

For the U that was spiked with natural uranium, tuning samples consist of 1 mg ($\sim 2.5 \times 10^{18}$ atoms) of ^{238}U and 3×10^9 atoms of both ^{233}U and ^{236}U . Natural U for the tunes, CRMs and IPL samples were prepared from a LLNL legacy sample Q metal. Natural U used for coral samples and process blanks was CRM 112A. Q metal blanks and CRM 112A blanks were analyzed for each run. IPL standards were prepared with 1 mg of NU and 10^5 to 10^{10} atoms of ^{233}U and ^{236}U .

For the U run that was spiked with ^{233}U , tuning samples consist of 2.0×10^{10} atoms of ^{233}U and ^{236}U legacy IPL standards. 3×10^9 atoms of ^{233}U of the IPL legacy standard was used as the ^{233}U tracer in all samples.

The AMS measurements raw data were obtained in atoms per sample and converted into specific activity using the following equation.

Equation 7

$$SA = \frac{N\lambda}{m_{processed}} \cdot \frac{10^3 g}{1 kg}$$

Where SA is specific activity in Bq/kg, N is the measured number of atoms of the isotope under investigation, λ is the decay constant of the isotope in s^{-1} which is calculated in Equation 8, $m_{\text{processed}}$ is the dry weight of the coral processed in the cathode in g.

Equation 8

$$\lambda = \frac{\ln 2}{T_{1/2}}$$

Where $T_{1/2}$ is the decay constant of the specified isotope. Table 1 lists the isotope and associated half-life and decay constants.

Figure 3. Schematic of the Accelerator Mass Spectrometer at the Center for Accelerator Mass Spectrometry (Brown et al. 2004).

Table 1. Isotope half-life and decay constants.

Isotope	Half-life $T_{1/2}$ (y)	Decay constant λ (s^{-1})
^{239}Pu	2.411×10^4	9.110×10^{-13}
^{240}Pu	6.563×10^3	3.347×10^{-12}
^{233}U	1.592×10^5	1.380×10^{-13}
^{236}U	2.342×10^7	9.379×10^{-16}

2.2.5 Autoradiography

Autoradiography is an imaging technique that allows for the visualization of the spatial distribution of radionuclides within a sample. Commercially available imaging plates containing europium-doped barium fluorobromide (BaFBr:Eu^{2+}) crystals. When the films are in contact with radiation, the phosphor crystal will absorb the incoming radiation, Eu^{2+} ion will oxidize to Eu^{3+} ions, the newly released electrons travel to the conduction bands of the phosphor crystals and become temporarily trapped in bromine vacancies. Exposure of the films to visible light from a helium-neon laser at 633 nm releases the trapped electrons from the bromine vacancies. The electrons travel back to the conduction band of the crystal reducing the Eu^{3+} ions to an excited Eu^{2+*} which returns to ground state by releasing a 390 nm photon. The 390 nm photon is collected by a photomultiplier tube, logarithmically amplified and converted to a digital image. Super resolution (SR) storage phosphor films from were used in this research. SR films have a pixel resolution of 50 μm . Coral slabs were placed between two SR films in an autoradiography cassette and exposed for one week. Films were scanned by the General Electric Typhoon FLA 7000. Images were analyzed using imageJ software. Images were erased from the image plates using the General Electric FLA Image Eraser prior to use.

2.3 Radioanalytical separations

Radionuclide separations from environmental matrices can be accomplished using precipitation, ion-exchange resins, extraction chromatography and liquid-liquid solvent extraction. The Pu and U isotopes will be extracted and purified from the coral matrix using extraction chromatography and ion exchange. After coral samples were digested, TEVA resin was used to separate Pu from the coral matrix. The Pu was further purified with AG 1- X8 resin. The U was initially separated from the Pu fraction with TEVA resin and further purified using UTEVA resin.

2.3.1 Extraction chromatography

Extraction chromatography (EXC) is a radionuclide separation technique which utilizes liquid-liquid extraction and column chromatography. EXC involves chemical changes and forming specific complexes which facilitate in the transfer of the ionic solute into the organic phase. The EXC columns are composed of a stationary phase, an inert support and a mobile phase. The inert support consists of porous silica or an organic polymer ranging from 50 to 150 μm in diameter (Horwitz). The stationary phase is an organic liquid containing extractants which are bound to the resin bead. The mobile phase is an aqueous solute typically a mineral acid. Varying the acid concentrations and adjusting oxidation states of constituents allows for the selective stripping of metal ions from the column. Adjusting oxidation states of constituents allows for the change in retention to the resins. The efficiency of the column depends on the specific chemical system, the particle size and porosity of the support, the extractant loading, mobile phase velocity and the operating temperature (Horwitz et al. 1995).

2.3.1.1 TEVA

The stationary phase of the TEVA resin contains a trialkylmethylammonium nitrate (or chloride) which allows the resin to selectively sorb all tetravalent ions as nitrate complexes. This allows for uptake of actinides (IV) over a wide range of nitric acid concentrations where the maximum uptake is at 3 M nitric acid (Horwitz). The active component is an aliphatic quaternary amine which has equivalent properties

of a strong base anion exchange resin. A difference in the EXC resin is that the functional groups are in a liquid form unlike anion exchange resins that are fixed to a polymer backbone. The functional group of the TEVA resin has greater flexibility to coordinate around the target anions and results in a higher uptake of these ions at lower acid concentrations. At higher acid concentrations > 4 M HNO₃ the retention of the tetravalent actinides decrease due to competition from nitrate anions for complexation sites on the resin (Horwitz). The Pu in the sample is oxidized to Pu(+4) with NaNO₂ and loaded onto the column in 3M HNO₃ - 0.5 M Al and retained as shown in the following equation.

Equation 9

Where An(4+) is a tetravalent actinide and E is the resin extractant. The Pu is eluted from the column with 0.1 M HCl- 0.05 M HF and 1.5% by volume NH₄I. NH₄I reduces Pu from Pu(+4) to Pu(+3) and is no longer retained on the column. HF assists in eluting Pu(+3) into solution.

2.3.1.2 UTEVA

The stationary phase of the UTEVA resin contains diamyl-amyolphosphonate (DAAP) which forms nitrate complexes with actinides. The uptake of actinides on this resin is driven by the concentration of nitrate within the sample and increases with nitric acid concentration. The resin has a high affinity for tetravalent and hexavalent actinides. The U(+6) is loaded onto the column in 3 M HNO₃ and eluted with 0.02 M H₂SO₄. Equation 10 shows the interaction of AnO₂²⁺ with the UTEVA column where E is the resin extractant.

Equation 10

2.3.2 Ion-exchange chromatography

The ion exchange chromatography (IXC) principle is due to the reversible interchange of metal ions between the solid phase and ions within the mobile liquid phase. The solid phase, resin, contains an ionic phase of opposing charge from the mobile liquid phase. The solid phase consists of a permeable insoluble polymeric matrix with an exchange site of a fixed charged group, opposite charge of the mobile counter ions. The ions within the mobile phase penetrate the pores of the resin beads to interact with the exchange sites. The ion least tightly bound to the resin at the exchange site will spend more time within the mobile phase and will elute from the column first. Retention to the exchange sites of the resin depends on the size and charge of the ion, the exchange group, the pH and the ionic strength of the liquid phase. Ion exchange resins can either be anion or cation exchangers. This work will utilize anion exchange columns BIO RAD AG 1-X8.

2.3.2.1 Anion exchange

The AG 1-X8 resin is a strongly basic anion exchange resin with a high crosslinkage of 8% divinylbenzene. This resin is composed of a styrene divinylbenzene copolymer lattice containing a quaternary ammonium functional group (Bio-Rad Laboratories 2017). Higher crosslinked resin has a reduction in pore size, permeability and swelling as opposed to lower crosslinked resins. However, the higher crosslinked resin has an increase in sensitivity due to the proximity of the ionic groups. The Pu is separated from nitric solutions as Pu(+4) anionic nitrate complexes. The complexation strength tendency of Pu decreases in the following order: $\text{Pu}(+4) > \text{Pu}(+6)\text{O}_2^{+2} > \text{Pu}(+3) > \text{Pu}(+5)\text{O}_2^+$. Pu(+4) is loaded onto the column in 8 M HNO_3 and adsorbs to the anion resin as the hexanitrate. The Pu(+4) is eluted from the column with NH_4I in concentrated HCl. NH_4I reduces Pu(+4) to Pu(+3) and is no longer adsorbed to the column.

2.4 Materials

2.4.1 Coral retrieval

Six coral cores were removed from the Bikini Atoll lagoon in February of 2016. Cores were removed from living *Porites australienus* using a Tech 2000 underwater core drill. Corals were drilled perpendicular to the growth axis. The drilling process is shown in Figure 4. A cement plug was placed in the coral where the core had been removed. Coral polyps will eventually grow over the cement plug. Epoxy was used to seal the plug and prevent further injury to the coral. Coral locations are presented in Table 2. Cores are 85-137 cm in length and 7 cm in diameter.

Figure 4. Image of two divers drilling a coral head in the Bikini Atoll Lagoon.

Cores were sectioned into 0.25" thick slabs along the growth axis of the coral using a double-bladed diamond brick saw shown in Figure 5. Coral residue from the brick saw slabbing process was immediately cleaned off with water. Slabs and coral half rounds were left to dry in the sun and put away for x-ray analysis.

Figure 5. A coral being slabbed using a brick saw.

Table 2. Location of coral samples

Site	Coral Length cm	Coordinates	
Eneu	85	N 11°37.379±30 ft	E 165°33.679±30 ft
Bravo Crater 1	99	N 11°41.704±36 ft	E 165°17.224±36 ft
Bravo Crater 2	93	N 11°42.026±36ft	E 165°16.893±36 ft
Eneman	130	N 11°30.363±30 ft	E 165°23.015±30 ft
Aoemen	105	N 11°41.747±30 ft	E 165°25.054±30 ft
Bikini	137	N 11°37.533±27 ft	E 165°32.545±27 ft

2.4.2 Coral x-rays

Coral slabs were analyzed by x-ray imaging at Colorado State University and at the Health Center at Lawrence Livermore National Laboratory to identify density bands. Images were analyzed using ImageJ software. Figure 6 shows the coral slab on the X-ray. Roughly counting the coral bands and identifying the coral patterns allowed for age estimates of the corals to be around 1960. Since all the corals appear

to be of similar age, patterns within the corals were assessed. To develop chronology and a sampling plan for radiochemical analysis, a coral with well-defined polyps and banding is preferred.

Figure 6. Coral slabs in place about to be analyzed at CSU.

Two corals with the best banding that were picked to be further analyzed are the corals retrieved from Bravo Coral 2 and Eneu. Bravo Coral 2 was collected from the outer southeast rim of Bravo crater and the second coral was located near the opening of the atoll by Eneu island. Bravo crater is a large crater formed in the atoll after Castle-Bravo, the largest thermonuclear device (15Mt) was detonated by the US and is located in the NW area of the lagoon (Energy 2015). These corals will be referred to as either Bravo or Eneu, based off the sampling locations, throughout the rest of this research. X-rays of the Eneu and Bravo Corals are shown in Figure 7 and Figure 8.

Figure 7. X-ray image of the Eneu coral.

Figure 8. X-ray image of the Bravo coral.

2.4.3 Coral radiation spatial distribution

Digital images of the corals were taken using autoradiography as described earlier in this chapter. The only image that contained resolvable radiation was the bottom piece of the Bravo coral. An image of the autoradiograph is shown in Figure 9. The remainder of the Bravo coral and the Eneu coral were unresolvable using the SR films.

Figure 9. Autoradiograph of bottom piece of the Bravo coral.

2.4.4 Coral chronologies

Chronologies were refined using $\delta^{18}\text{O}$ data from IRMS. Results of the IRMS measurements for Bravo and Eneu corals are shown in Figures 10-14. The peak minimums were assigned the month of September because it is the month that has the most rainfall and the most depleted in ^{18}O . Maximums were assigned to the month of February because this is the driest month of the year and $\delta^{18}\text{O}$ values should be the highest. Each peak was assigned a calendar year assuming the top of the core is 2016 (removal from the ocean). The Eneu coral dates extend to 1956 and the Bravo coral dates extend to 1960 based on the $\delta^{18}\text{O}$ values and the x-ray imaging. The corresponding patterns are in agreement with the $\delta^{13}\text{C}$ patterns.

Figure 10. $\delta^{18}\text{O}$ for Bravo coral and associated years.

Figure 11. $\delta^{18}\text{O}$ for Eneu coral and associated years.

Figure 12. $\delta^{13}\text{C}$ values for Bravo corals and associated years.

Figure 13. $\delta^{13}\text{C}$ values for Eneu corals and associated years.

Chapter 3- Plutonium Analysis

3.1 Overview

This chapter describes the sample analysis plan and method for radioanalytical separations of ^{239}Pu and ^{240}Pu from the coral matrix. This chapter will also discuss experiments for method development using coral from the Enewetak Atoll. The developed method was applied to corals from the Bikini lagoon. Temporal specific activities were calculated. A model of the annual combined activity of $^{239+240}\text{Pu}$ in Bq per kg of coral for each coral was produced. This was used to calculate the $^{239+240}\text{Pu}$ concentration in the lagoon water as well the annual $^{239+240}\text{Pu}$ exported from the lagoon to the Pacific Ocean.

Modifications are discussed in Section 3.2 and were applied to the original analytical procedure to increase Pu recoveries. Modifications include adding an HF digest and applying an additional round of post digest nitrification. Increasing the amount of time the sample was in column loading matrix before loading onto TEVA columns and increasing the time samples were rehydrated in 3 M HNO_3 before the analytical transfer to the iron precipitation centrifuge tube.

3.2 Pu method development

3.2.1 Enewetak coral

The coral from the Enewetak Atoll is approximately 15 cm in length and 4.5 cm wide. This coral was not slabbed, x-ray images and $\delta^{18}\text{O}$ measurements were not taken. The purpose of this coral was solely for AMS method development. The coordinates of this coral are 11°33.25 N and 162°20.45 E.

3.2.2 Analytical procedure

Coral material was removed 1.7 – 1.2 cm downwards from the top of the coral with a hand saw. 3 mm of the outer layer of coral was removed using the saw. 5 g of coral was removed for analysis, placed in a 60 mL neoprene bottle and manually homogenized using a scoopula. 0.3 g, 1 g and 3 g samples were removed from the bulk coral sample and transferred to glass beakers. The beakers were covered with perforated foil and dried in the oven at 40°C for 24 hours. 3.0×10^9 atoms of a ^{242}Pu tracer was gravimetrically added to each beaker. Samples were digested with 10 mL of concentrated ultra-pure HNO_3 on a hot plate set at 150°C topped with a ribbed watch glass. Samples were refluxed for about 45 min. H_2O_2 was slowly added to the hot samples in 1 mL increments three times in 15-minute intervals. This was added to break down organics within the sample. Beakers were evaporated to dryness. 5 mL of concentrated HNO_3 was added to each beaker and evaporate to dryness. 10 mL of 3 M HNO_3 -0.5 M Al was added to each beaker and parafilm was placed on top of beakers and the samples sat in this matrix overnight. Samples were filtered into 50 mL centrifuge tubes using a 30 mL Luer lock syringe attached to a 0.45 μm filter. Beakers were rinsed three times with ~2 mL 3 M HNO_3 . The aluminum had been previously scrubbed of U using UTEVA columns (Maxwell III and Culligan 2009). The Pu oxidation states was adjusted from Pu(+3) to Pu (+4) by adding 0.75 mL of freshly prepared 4 M NaNO_2 to each sample. Pu was isolated and purified using extraction chromatography (TEVA, Eichrom Industries Inc.) followed by ion-exchange chromatography (AG 1-X8, BioRad Industries) (Martinelli et al. 2009).

Samples were evaporated to near dryness and reconstituted in 3 mL of 3 M HNO_3 . Samples underwent an iron hydroxide coprecipitation. The precipitate was rinsed, transferred to a quartz crucible, dried and calcined at 800°C. 3 mg of Nb metal was added to each sample. Each sample was homogenized and pressed into an aluminum cathode for analysis by AMS (Hamilton et al. 2009). Separation procedure and iron hydroxide coprecipitation are in later sections of this chapter.

3.2.3 Results

Recoveries were determined by comparing the number of counts of ^{242}Pu from samples to spiked ^{242}Pu FeNb cathodes that have not undergone any chemistry. Results are shown in Table 3. Recoveries were low for all three samples, ranging from 12 - 14%. The Enewetak coral $^{240}\text{Pu}/^{239}\text{Pu}$ ratios ranged from 0.069(16) - 0.096(7). The largest error was associated with the sample of the smallest mass. These ratios are consistent with ratios from Enewetak Atoll soils of 0.062 - 0.260 (Lachner et al. 2010).

Table 3. Enewetak coral AMS results.

Sample #	Dry Weight	Recovery	Effective weight	^{239}Pu atoms	$\pm$	^{240}Pu atoms	$\pm$	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	$\pm$
1	0.294	14%	0.040	4.05E+08	2.76E+07	2.77E+07	6.40E+06	0.074	0.016
2	0.976	13%	0.130	1.36E+09	7.17E+07	1.29E+08	1.51E+07	0.096	0.012
3	2.31	12%	0.267	4.06E+09	2.00E+08	2.78E+08	2.55E+07	0.069	0.007

3.2.4 Method optimization

Three 0.5 g samples from the Enewetak bulk sample were analyzed using the same method as in the previous section. Modifications were made throughout the procedure to increase recoveries. An additional round of post digest nitrification was applied. This involves adding 5 mL of concentrated HNO_3 to the beaker and allowing sample to evaporate twice and ensuring samples are dry before proceeding to next step. Samples were rehydrated in TEVA column matrix (3 M HNO_3 – 0.5 M Al), allowed to sit overnight covered with parafilm, and filtered the following day. After the samples were run through both columns and dried, they were rehydrated in 3 M HNO_3 for a couple of hours prior to the analytical transfer to the iron precipitation centrifuge tube.

3.2.4.1 Results

Results are shown in Table 4. Recoveries improved and ranged from 62 - 80%. Ratios were consistent with the results from previous AMS measurements. Based off these results, the additional steps were applied to all coral samples in the following runs and 1-gram samples will be processed in order to improve counting statistics.

Table 4. Enewetak coral AMS results from optimization of method.

Sample #	Dry Weight	Recovery	Effective Weight	^{239}Pu atoms $\pm$	^{240}Pu atoms $\pm$	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio $\pm$
1	0.509	62%	0.316	$6.33\text{E}+08 \pm 1.53\text{E}+07$	$4.09\text{E}+07 \pm 3.02\text{E}+06$	0.0646 ± 0.005
2	0.505	71%	0.359	$6.17\text{E}+08 \pm 1.44\text{E}+07$	$4.64\text{E}+07 \pm 3.11\text{E}+06$	0.0751 ± 0.005
3	0.502	80%	0.402	$6.30\text{E}+08 \pm 1.39\text{E}+07$	$4.22\text{E}+07 \pm 2.76\text{E}+06$	0.0669 ± 0.004

3.3 Bikini coral plutonium analysis

3.3.1 Coral sampling

Samples were removed from September to February of biannually in the younger portion of the corals and annually in the older portion of the corals. Biannual samples are highlighted in black in Figure 14. This side of the peak is the least steep and provides a larger sampling area. Peaks were matched to the location the sample was taken from on the coral slab and the x-ray image. 1-gram samples were removed using a Dremel. The Dremel was cleaned in between uses with pressurized air. Samples were transferred to 150 mL glass beakers. Beakers were covered with perforated foil and dried in the oven at 40°C for 24 hours.

Figure 14. $\delta^{18}\text{O}$ per composite distance from the top of the coral and coral images. The part of the graph that is boxed represents the piece of Eneu coral shown in the bottom two images. The bottom left image is the x-ray of the piece of coral with the associated $\delta^{18}\text{O}$ pattern. The bottom right image shows the sample locations of the black highlighted portion of the graph.

Table 5. Location of coral samples.

Site	Coral Length	Coordinates
Eneu	85 cm	N 11°37.379 ± 30ft
		E 165°33.679±30 ft
Bravo Crater	99 cm	N 11°41.704±36ft
		E 165°17.224±36 ft

3.3.2 Pu analytical procedure

3.3.2.1 Coral digestion

Samples were spiked gravimetrically with 3.15×10^9 atoms of ^{242}Pu . Samples were digested with 10 mL of concentrated HNO_3 and 3 mL of H_2O_2 and evaporated to near dryness. Samples were rehydrated with 15 mL of concentrated ultrapure HNO_3 and allowed to heat. An HF digest was applied in order to digest refractory material that may be present in samples. 0.25 mL of HF was added, the samples were refluxed for 45 minutes and then saturated boric acid (BH_3O_3) was added to expel the fluorides. Samples were evaporated to near dryness and reconstituted in 3M HNO_3 - 0.5 M Al. The Al had been previously scrubbed of U using UTEVA columns (Maxwell III and Culligan 2009). Samples were filtered with a 0.45 μm filter into 50 mL centrifuge tubes. 5% (by weight) of each sample was removed and placed aside for U measurements which will be discussed in Chapter 4. Oxidation states of Pu were adjusted to Pu (+4) by adding 0.75 mL of freshly prepared 4 M NaNO_2 to each sample.

3.3.2.2 Pu separation and purification

TEVA columns were prepared by attaching a funnel to the top of the column, pushing the frit in place with a pipette tip column and placing on a rotating stand. 50 mL centrifuge tubes were placed underneath the columns. Columns were preconditioned with 6 mL of 3 M HNO_3 . After all conditioning solution had passed through the columns, the centrifuge tubes under the columns were removed and replaced with U labeled 50 mL centrifuge tubes. The sample load was poured directly into the column. Pu(+4) is retained on the TEVA resin. The $\text{Al}(\text{NO}_3)_3$ in the load solution acts as a salting agent by increasing the nitrate concentration without increasing the acidity which aids in Pu retention to the column. Uranium in the load solution is in the +6 state and is not retained on the column. 20 mL of 3 M HNO_3 was added to the columns. After HNO_3 had passed through the columns, the U centrifuge tube was removed, capped and placed in storage. A waste tube was placed under columns. 9 M HCL was added to columns to assist the change in the chloride form. 20 mL of 8 M HCL was added to the columns

which removed any Th(+4) that had been retained to the column. Centrifuge tubes were removed, and 50 mL labeled beakers were placed under columns. The Pu was eluted with 20 mL 0.01 M HCl, 0.05 M HF and 1.5% NH₄I. Iodine reduces the Pu(+4) to Pu(+3) which is not retained on the TEVA resin. 3 - 5 mL of concentrated HNO₃ was added to beakers and samples were evaporated to dryness.

Anion exchange columns (AG1-X8, BioRad Industries) were prepared by placing a wool frit in the column and setting them up on the rotating sample holder. Samples were reconstituted with 4 mL of 8 M HNO₃. The Pu was oxidized from +3 to +4 by adding 0.75 mL of 4 M NaNO₂. Columns were conditioned with 20 mL of 8 M HNO₃. Samples were loaded onto columns and columns were washed with 20 mL of 8 M HNO₃ followed by 20 mL of concentrated HCl. The elution tubes were removed. Analyte beakers were placed under each column and the Pu was stripped using NH₄I and concentrated HCl. 3 – 5 mL of HNO₃ was added to each analyte beaker after elution. Beakers were placed on a hot plate and covered with plastic ribbed watch glass and evaporated to dryness (Martinelli et al. 2009).

3.3.2.3 Iron hydroxide precipitation

Samples were reconstituted in 3 mL of 3 M HNO₃ and transferred to 15 mL centrifuge tubes. Sample beakers were rinsed multiple times using 2 mL of HNO₃. 300 µg of Fe solution was added to each sample. The Pu was coprecipitated with Fe by adding 4 mL of ammonium hydroxide. Samples were capped and left overnight to precipitate. The following day, the samples were centrifuged for 15 min at 3000 rpm. Supernatant was discarded from each sample and milliQ water (~3 mL) was added to each sample. The sample was sonicated and then centrifuged for 15 min at 3000 rpm. The supernatant was discarded.

3.3.2.4 Cathode production

A drop of milliQ water was added to the centrifuge tube and the solution was mixed with the precipitate with a disposable pipette tip. The pipette was used to transfer the sample solution to a clean quartz crucible. This was repeated until the entire sample was transferred. Crucibles were placed under a heat lamp to dry for an hour. Crucibles were placed in a quartz holder with etched identifying markers.

Crucibles were capped and placed on a hot plate set at 250°C for an hour. Samples were calcined at 800°C in a furnace. After samples were cool, 3 mg of Nb metal was added to each sample. Samples were homogenized by scrapping the walls and bottom of the crucible and mixing the sample with a #60-gauge drill stem. The mixture was carefully decanted into a pretreated aluminum AMS sample holder (cathode) which had been drilled 0.006" deep with a #60-gauge drill bit. The drill bit was pounded into the cathode using a hammer until the material was compacted. The cathode was placed into a clean labeled cathode holder for measurement by AMS.

3.3.2.5 AMS measurements

Accelerator mass spectrometry measurements of Pu were performed at the Center for Accelerator Mass Spectrometry (CAMS) at LLNL. Process blanks were prepared and analyzed as well as quality assurance (QA) samples. The QAs were prepared with certified reference material IAEA 368 (ocean sediment from the Mururoa Atoll) using the same separation procedure and AMS target prep as above so that the QAs contain 10^9 atoms of ^{239}Pu . National Institute of Standards and Technology (NIST) traceable standards CRM 128 ($^{239}\text{Pu}/^{242}\text{Pu} = 0.993 \pm 0.0003$) and CRM 138 ($^{240}\text{Pu}/^{239}\text{Pu} = 0.0863 \pm 0.0001$) were routinely measured throughout the AMS measurement run to monitor mass dependent normalization factors for ^{239}Pu , ^{240}Pu and ^{242}Pu isotope measurements (Brown et al. 2004). Background from FeNb blanks as well as process blanks were subtracted from sample measurements. Coral sample measurements were converted from atoms per sample of ^{239}Pu and ^{240}Pu to specific activity in Bq/kg.

3.4 Results and discussion

Figure 15. Comparison of Bravo and Eneu annual coral concentrations in Bq/kg.

3.4.1 Plutonium analysis

The measured values and associated time periods for the two cores are presented in Table 16 and Figures 2-4. Concentrations for the Eneu core range from 0.46 ± 0.01 to 7.38 ± 0.27 Bq/kg and Bravo range from 0.49 ± 0.02 to 15.29 ± 0.38 Bq/kg. The oldest region of both corals contains the highest $^{239+240}\text{Pu}$ concentrations. The rate of change of the Pu concentrations throughout the corals lifespans are not constant. Concentrations in both corals decrease more rapidly from the oldest section (1960 or 1956) to 1964. Both corals have an increase of concentration in 1965. Concentrations for the Eneu coral in 1965 is 2.4 times higher than in 1964. In Bravo the concentration is 1.4 times higher than 1964.

Concentrations following 1965 continue to decrease rapidly until 1970 where the concentrations start to level off, but still slowly decreasing, until 2015. Concentrations are five times higher in 1960 in the Bravo coral than in Eneu in the same year. Concentrations of $^{239+240}\text{Pu}$ in the Bravo coral are about three to four times higher than the Eneu coral between 1961 - 1964 and Bravo concentrations are slightly higher than Eneu concentrations until 1970. Concentrations from 1970 - 2015 are relatively similar for both corals.

Lagoon $^{239+240}\text{Pu}$ concentrations were calculated by applying a concentration factor of 2.7×10^3 for the uptake of Pu into coral from surrounding lagoon water and assuming a density of 1027 kg/m^3 (Noshkin et al. 1975). Present day lagoon concentrations are reported to be $100 - 200 \text{ mBq/m}^3$ which agree with the current values measured from the Eneu and Bravo corals (Buesseler et al. 2018). The average $^{240+239}\text{Pu}$ measured value of the QA samples (IAEA 368 Mururoa Atoll sediment) is $32.81 \pm 2.33 \text{ Bq/kg}$ with an atom ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ 0.03 ± 0.006 . The recommended $^{240+239}\text{Pu}$ concentration value reported by IAEA is 31 Bq/kg with a confidence interval of $29 - 34 \text{ Bq/kg}$. $^{240}\text{Pu}/^{239}\text{Pu}$ ratio is comparable to literature values (Liao et al. 2008, Donard et al. 2007).

Bravo Coral Specific Activity and Atom Ratio

Figure 16. Bravo coral specific activity (x-axis) and atom ratios (secondary x-axis) with 1σ error versus year.

Eneu Coral Specific Activity and Atom Ratio

Figure 17. Enewetak coral specific activities (x-axis) and atom ratios (secondary x-axis) with 1σ error versus year.

Eneu $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios exhibit a maximum value of 0.208 ± 0.01 in 1964 and a minimum value of 0.152 ± 0.01 in 2015. The average value throughout the entire lifespan of the Eneu coral is 0.179 ± 0.06 . The maximum value in the Bravo coral is 0.214 ± 0.02 in 2005 and the minimum value is $0.162 \pm$

0.01 in 2015. The average $^{240/239}\text{Pu}$ atom ratio throughout the Bravo coral lifespan is 0.190 ± 0.07 . Bravo ratios in the oldest section of the coral are close to the minimum value and increase over time.

There is a decreasing trend with the ratios within the Eneu coral over time. Eneu coral has a lower average than the Bravo coral. The average Eneu coral ratios are more consistent with the global background of 0.18 (Kelley et al. 1999). Comparing ratios of the two corals, the ratios from 1956 - 1966 in the Eneu coral are slightly higher than the Bravo coral. Ratios in both corals have similar values in 1967 - 1989. The Bravo ratio is slightly higher than Eneu in 1991 - 2015 as the Eneu ratios begin to decrease.

Figure 18. Annual $^{240}\text{Pu}/^{239}\text{Pu}$ ratios from the Eneu and Bravo corals with 2σ error. Bravo $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in the top graph and Eneu $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in the bottom graph.

The available Pu within the lagoon water surrounding the corals depends on the location. Bravo concentrations are higher than Eneu due to the higher number of tests near the location where the coral was growing in the lagoon as seen in Figure 19. There were seven tests within Bravo crater and four of these tests had yields within the megaton (Mt) range. There were an additional 8 tests (three in the Mt range) to the East of the Bravo coral and one just north of the atoll. The Eneu coral was retrieved

from the south eastern part of the lagoon near the opening of the atoll where the ocean flows in and out of the lagoon. The closest tests to this coral were the first two tests detonating within the atoll in 1946 which were in the kt range and one of these tests was conducted underwater. The next closest tests were detonated on land west of the Eneu coral. Testing within the Bikini Atoll took place in 1946, 1956 and 1958. The concentrations within the Bravo coral extend to 1960, two years after the last test.

Figure 19. Modified image showing the locations of tests in relation to the Bravo and Eneu corals denoted by the red stars (Hamilton 2019).

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio differences within the corals are also location specific. The ratios within the Eneu coral slowly decrease over time. The two highest ratios in the Eneu coral are 0.2 and 0.208 in 1956 and 1965. Pu concentration decreases in 1965 which also has the highest $^{240}\text{Pu}/^{239}\text{Pu}$ ratio showing

that this area is more concentrated with Pu from higher yield devices during this time period and throughout the years the ratios have slightly decreased showing that either the signal is being diluted from the global ratio from the ocean water mixing with lagoon water or it is being diluted with Pu with lower ratios from lower yield tests. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratio within the Bravo coral displays an opposing trend to the Eneu coral. It shows a slow increase in ratio throughout the lifetime of the coral. This indicates that the higher Pu contamination within this area is from higher yield tests. This agrees with Pu ratios in sediment that have been analyzed in locations close to these corals. Ratios from Bravo crater sediment have ratios of 0.263 ± 0.003 and sediment analyzed around the Baker site, which is the test that was the closest to the Eneu coral, have lower ratios of 0.063 ± 0.005 (Lachner et al. 2010).

Noshkin et al. analyzed a banded coral from the Bikini Atoll. The coral was retrieved in 1972 from the western region of the lagoon about 10 km south west of the Bravo crater coral, located between Bokoneijin and Bokaetokutoku. Chronology was determined through x-radiographs. This coral lived from 1953 - 1972. Samples were chemically processed for Pu and assayed via alpha spectrometry and mass spectrometry. Concentrations are shown in Figure 20. The highest Pu concentrations within this coral were in 1954 - 1955 with concentrations of 1441.89 Bq/kg and continually decreased and leveled off around 3.7 Bq/kg in 1967. This coral exhibited higher concentrations in 1958 and 1964. The concentration in this coral is about an order magnitude higher than Eneu from 1957 - 1961. The values from 1962 to 1972 are similar to the Bravo coral except for 1964 where the Noshkin coral is higher with a value of 17.76 Bq/kg while Bravo coral has a value of 4.25 Bq/kg. The Bravo and Eneu corals both have an increase in concentration in 1965. The $^{240}/^{239}\text{Pu}$ atom ratios in the Noshkin coral were higher than the Eneu and Bravo corals and were between 0.186 - 0.230. The differences in the Pu values between this coral and the Eneu and Bravo coral show that values are different due to differences in location, type of Pu (high vs low yield) contamination at the site, and the uptake may also be species dependent. The coral from the Noshkin study is *Favites virens* and the coral from this study is *Porites australiensis*.

Noshkin Coral (1956-1972)

Figure 20. Pu specific activity in Bikini coral from Noshkin study (Noshkin et al. 1975).

The rate of change and the mechanisms that drive the Pu concentration changes within the atoll and coral are not well understood. Strong weather events that impact the Marshall Islands include typhoons, droughts and storm waves. These weather events are normally weak when passing through this region but are stronger during intense El Nino years and are followed by an extended dry season (Program 2011). There is no correlation between strong storms and typhoons in the area with the changes in concentrations and ratios in the coral. A list of weather events that impacted the Marshall Islands and possibly the Bikini Atoll are listed in Table 6. Precipitation data for the Bikini Atoll is shown in Figure 21. This can be further studied by analyzing samples with a more detailed temporal resolution to fully understand how small seasonal weather changes within the atoll impacts the Pu concentrations. Pu concentrations within *Porites Lutea* coral from Enewetak Atoll covering a lifespan from 1952 - 1964 was analyzed with a bi-monthly temporal resolution by Froelich et al. This study was able to show an

oscillatory pattern which corresponds to seasonal patterns associated with the months of strongest wind stress and lagoon surface currents. The authors suggest that there is more disturbance of the lagoon sediment which enhances the remobilization of Pu from sediment into the lagoon (Froehlich et al. 2017). A seasonal dependence of Pu remobilization was not observed in the Bravo and Eneu coral due to the larger annual temporal resolution samples analyzed.

The small change in concentration in the Eneu coral from 1961 to 1962 is not a result of global fallout from atmospheric testing. Nuclear testing within the Marshall Islands ceased in 1958. Between 1958 and 1961 testing between the US and former Soviet Union temporarily ended. Atmospheric nuclear testing continued in the Pacific Ocean northeast of the Marshall Islands at Johnston Island and Christmas Island in 1962. A total of 36 nuclear weapons were detonated at these locations and these were mainly high-altitude tests which would contribute to global fallout (Energy 2015). The former Soviet Union also conducted a series of atmospheric tests in 1961 - 1962. The limited Test Ban Treaty came into effect in 1963 which halted all atmospheric testing by the US and Soviet Union. This small change in concentration is insignificant and not observed in the Bravo coral. This change is not a result of global fallout because it is not observed in other corals within the Pacific (Lindahl et al. 2010, Froehlich et al. 2017).

The change in concentration in 1964 is observed in corals from other locations outside of the Marshall Islands. Lindahl et al. analyzed Pu in a coral, covering a time period of 1943 - 1999, outside of Guam about 1900 km west of the Marshall Islands along the North Equatorial Current (NEC) pathway. The Pu concentration within this coral is attributed to the nuclear testing at the Marshall Islands until 1960. The concentrations from 1961 - 1980 have been attributed to global fallout with small increases (~ 40 mBq/kg) in concentration in 1963 and 1964 (Lindahl et al. 2011). Noshkin and Froehlich determined that the fallout from the northern hemisphere was insignificant compared to the observed change in Pu concentrations (Noshkin et al. 1975, Froehlich et al. 2017). The Pu increase from Noshkin in

1964 and the increase from this study in 1965 are likely from the same year. Error in this study and previous studies can be assumed to have an error of ± 1 to 3 years. The Pu concentration in the Enewetak coral in the 1960s is 100 times less than in the Bikini corals. The increase in Pu in the corals from the Bikini Atoll is most likely from an isolated event or disturbance within this Atoll that increased the remobilization of Pu and requires further investigation.

Table 6. Storm data impacting Marshall Islands (Wright , Spennemann and Marschner 1994).

Year	Month	Storm Name
1955	March	Unnamed
1957	November	Kit
		Lola
		Mamie
1958	January	Ophelia
1977	December	Mary
1978	October	Rita
1979	January	Alice
1981	March	Freda
1982	December	Pamela
1986	December	Norris
1988	January	Roy
1990	November	Page
1991	November	Zelda
1992	January	Axel
	November	Gay
1997	December	Paka
2004	December	Talas

Figure 21. Annual rainfall data at Bikini from 1985 through 2000 (Gouveia et al. 2002).

3.5 Pu export model

A Gaussian Process (GP) model was produced using the observed data. The GP model was used to generate interpolation data points as seen in Figure 22 and Figure 23. The GP regression is a nonparametric Bayesian approach that computes a posterior distribution over random functions and is useful to quantify uncertainty in model estimates. The GP approach works well on small datasets and has the ability to provide uncertainty measurements on the interpolations of the data. This data was fit to an exponential function as shown Figure 24 and Figure 25. Fitting interpolation and observed data points to the function reduces the uncertainty in the curve fitting.

Equation 11

$$f(x) = a \cdot e^{-bx} + c$$

The standard deviation ($\pm\sigma$) of the Pu concentration is plotted as a vertical for each data point within Figure 24 and Figure 25.

Chi-squared (χ^2) and R-squared metrics were used to evaluate the fit of the function to the observed Pu concentrations (y_i). The figures also show the residuals of the fitted curve which is the difference between the actual Pu concentration (y_i) and the fitted value $f(x_i)$. The chi-squared value (χ^2) is defined as the sum of the weighted squared residuals. The chi-squared value was employed in order to weight the data points that have smaller uncertainty more heavily than those with greater uncertainty.

Equation 12

$$\chi^2 = \sum_i \left(\frac{y_i - f(x_i)}{\sigma_i} \right)^2$$

Equation 13

$$\chi_r^2 = \frac{\chi^2}{n - m}$$

The overall quality of the fit is the reduced chi-squared value (χ_r^2). Where n is the number of data points and m is the number of parameters in the fitting function. A chi-squared value larger than one indicates the error variance (σ_i^2) of the data points is possibly underestimated.

The coefficient of determination (R^2) measures how well observations are replicated by the fitting curve based on the proportion of the total variation of the observed data.

Equation 14

$$R^2(y, f(x)) = 1 - \frac{\sum_{i=1}^n (y_i - f(x_i))^2}{\sum_{i=1}^n (y_i - \frac{1}{n} \sum_{i=1}^n f(x_i))^2}$$

The R-squared values of the fitted curves have values above 0.9, indicating that they are a suitable fit to the observations.

A Pu export model of the combined ^{239}Pu and ^{240}Pu was produced using the coral data. The curve fitting equations that were fit to the Pu data and residuals are shown in Figure 8 and Figure 9. The model shows $^{239+240}\text{Pu}$ in Bq/kg in coral per year. Pu export in the lagoon was calculated using the conservative uptake value of 2.7×10^3 from Noshkin et al. A flushing rate of seven years was assumed. The lagoon area is estimated to be 629 km^2 with an average depth of 45 m. The estimated volume used for the model is $2.83 \times 10^{10} \text{ m}^3$ (Noshkin et al. 1987). Table 17 shows the amount of Pu in Bq/kg in coral calculated using the fitted equations for each coral. The table also shows the Pu activity in the lagoon water calculated using the concentration factor. The total lagoon activity of Pu in Bq in the estimated lagoon volume and the amount of Pu exported annually from the lagoon to the open ocean are also shown in Table 6. The total export for the combined Pu using the Bikini coral data is 8.35 TBq and using the Eneu coral data (1960 - 2015) is 5.30 TBq. The total export activity of Pu from the entire life span (1957-2015) of the Eneu coral is 6.90 TBq. The total export of Pu from the Bikini and Enewetak Atolls over the past 35 - 40 years have been reported to be 8 - 9 TBq (Hamilton et al. 1996). The total export calculated from the corals is less than 0.25% of the global Pu activity of 4 PBq (Hamilton 2004). The annual export of Pu from the Bikini Atoll has been reported to be 0.12 - 0.20 TBq (Hamilton et al. 1996, Lindahl et al. 2011). The annual export from this study ranges from 0.036 - 1 TBq. The amount of $^{239+240}\text{Pu}$ in the lagoon water accounts for only 0.08 - 0.09% of the sediment inventories to a depth of 16

cm (Noshkin et al. 1987). Under this assumption, the sediment inventories to a depth of 16 cm would be estimated as 6.5 - 196 TBq.

Figure 22. Bravo coral observations and GP interpolations of $^{239+240}\text{Pu}$ in Bq/kg of coral.

Figure 23. Eneu coral observations and GP interpolations of $^{239+240}\text{Pu}$ in Bq/kg of coral.

Figure 24. Bravo Coral annual concentration model.

Figure 25. Eneu coral annual concentration model.

3.6 Plutonium coral concentration factor

A concentration factor is a term that describes the uptake of an element such as Pu in a living organism. It is the concentration of the element in the tissue of a marine organism divided by its concentration on an equivalent weight basis in the surrounding lagoon water (Noshkin, Eagle and Wong 1976). The Pu concentration factor was calculated by Noshkin et al. using the average activities from the four most recent growth sections (1969 - 1972) of coral and the average concentrations of $^{239+240}\text{Pu}$ in the lagoon (Noshkin et al. 1975). Pu activities were determined by alpha spectroscopy and ranged from 0.1 ± 0.04 to 0.13 ± 0.09 pCi/g and the average activity in the lagoon water in 1972 was 49 fCi/liter (Noshkin et al. 1974). The concentration factor calculated by Noshkin was 2.7×10^3 using a density of 1027 kg/m^3 . Filtered bikini lagoon samples retrieved from the same locations the Eneu and Bravo corals were taken (Table 2). Two samples were retrieved at each location, one at the surface of the lagoon (within 1 meter of the surface) and another at the bottom of the lagoon (51-meter depth for Eneu and 12-meter depth at the Bravo coral location). Average coral Pu concentrations were calculated using the four most recent AMS measurements from 2009, 2011, 2013 and 2015 from Table 16.

3.6.1 Lagoon filtrate processing

Lagoon samples were acidified to approximately 5% HCl (v/v), and periodically agitated for at least 48 hours. Samples were spiked with 3.0×10^9 atoms of ^{242}Pu tracer and periodically agitated for 24 hours. 0.3 g of Fe 500 ug of Fe standard solution was added. 2 g of sodium sulfite was added to samples and samples were agitated until salt dissolution, and periodically agitated over another 24-hour period. Plutonium and Fe were coprecipitated with NH_4OH by raising the pH to 8.5 or 9. The precipitate was recovered by pumping the sample through a 0.45 micrometer capsule filters (pressure filtration using a peristaltic pump). The precipitate was dissolved in 1 M HCl solution and transferred to a beaker. The capsule filter was washed three times with 1M HCl and the wash was added to the sample beaker. 10 mL of concentrated HNO_3 was added to the sample beakers to ensure dissolution of solids in sample and

ensure a nitrate salt conversion. Samples were taken to dryness and rehydrated in TEVA column loading matrix and filtered using a 0.45 µm syringe filter. The separations procedures for AMS measurements were identical to the Pu coral procedures. The QA samples used for the lagoon water AMS run was IAEA-443, Irish Sea Water with $^{239+240}\text{Pu}$ value of 0.0147 Bq/kg. The average lagoon sample from each location in Bq/kg was used to calculate the coral uptake value.

3.6.2 Results

Table 7 shows the aqueous sample mass for each sample and QA and the associated Pu specific activity in Bq/kg. The average Eneu value is $2.42 \times 10^{-4} \pm 8.71 \times 10^{-5}$ Bq/kg and for Bravo is $5.37 \times 10^{-4} \pm 1.69 \times 10^{-4}$ Bq/kg. The uptake value is $1.16 \times 10^3 - 2.18 \times 10^3$ for soluble Pu. The QA value is in good agreement with the certified value of 0.0147 Bq/kg. Concentrations were also calculated in mBq/m³ using a density of 1027 kg/m³.

Table 7. Bikini lagoon filtrate AMS results.

Sample Description	Mass of Aqueous Sample (kg)	$^{239+240}\text{Pu}$ (Bq/kg)	$^{239+240}\text{Pu}$ (mBq/m ³)
IAEA-443 #1; Irish Sea Water	0.5	1.42E-02 ± 8.65E-05	
Eneu surface	19.317	2.59E-04 ± 6.64E-05	266 ± 68
Eneu 51-meter depth	18.535	2.24E-04 ± 5.67E-05	230 ± 58
Bravo surface	18.626	4.69E-04 ± 1.08E-04	481 ± 111
Bravo 12-meter depth	18.78	6.04E-04 ± 1.30E-04	620 ± 134

3.6.2.1 Comparison of concentration factor

Noshkin used 49 fCi/kg to calculate the 2.7×10^3 coral uptake value for $^{239+240}\text{Pu}$ in the Bikini Atoll. This value includes the average of ten filtered lagoon surface water samples and six filtered bottom water

samples. This factor also accounts for Pu associated with particulate material in the lagoon water which is $30 \pm 25\%$ of the total $^{239+240}\text{Pu}$ in the lagoon water (Noshkin et al. 1974). The lagoon samples in the Noshkin study were retrieved from various locations throughout the entire Bikini lagoon. The uptake value from this study is derived from four filtered lagoon water measurements from the locations where the corals were retrieved. This study only accounts for soluble $^{239+240}\text{Pu}$ and does not include $^{239+240}\text{Pu}$ associated with particles. Pu associated with particles can account for up to 3 - 90% of total $^{239+240}\text{Pu}$ in the lagoon (Noshkin et al. 1974). The uptake factor in this study underestimates the total amount of $^{239+240}\text{Pu}$ in the lagoon. Differences between samples may also be attributed to concentration changes with time where tide-controlled currents can influence the concentrations at any location in the lagoon over a period of time (Noshkin et al. 1974).

3.7 Conclusions

Two corals from the Bikini Atoll were analyzed for ^{239}Pu , ^{240}Pu and $^{240}\text{Pu}/^{239}\text{Pu}$ ratios. 1-gram samples of coral were removed throughout the lifetime of the coral. The samples were chemically processed for Pu and analyzed by AMS. A Pu export model was produced using the coral results. The annual export and total export of Pu was calculated during the lifetime of the coral. Coral concentration factors were determined for each coral and compared to the Noshkin coral concentration value. This study provides new $^{239+240}\text{Pu}$ concentration and export information ranging from 1956 to 2015 in addition to new trends associated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios within the Bikini lagoon. This study showed the concentration of Pu in the lagoon has decreased over time and has reached a steady-state and is still continuing to slowly decrease. $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios were used to determine if the source of contamination has changed over time. The concentrations and ratios within the corals were location specific. The ratios within the Eneu coral slowly decrease over time, indicating that this area is more concentrated with Pu from higher yield devices during the oldest portion of the coral. Throughout the years the ratios have slightly

decreased indicating that the signal is being diluted from the global ratio from ocean water mixing with lagoon water or being diluted with Pu with lower ratios from lower yield tests. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratio within the Bravo coral displays an opposing trend to the Eneu coral. The Bravo coral shows a slow increase in ratio throughout the lifetime of the coral. This indicates that the Pu contamination within this area from the older portions of the coral were from lower yield devices and slowly through time, higher yield devices are contributing more to the Pu within this area.

Chapter 4- Uranium Analysis

4.1 Overview

This chapter describes the method and results for the analysis of ^{236}U and ^{233}U by AMS. The ^{238}U concentrations and $^{235}\text{U}/^{238}\text{U}$ ratios throughout the lifetime of the corals was determined using ICP-MS. The first AMS analysis method discussed was applied to the U fraction set aside from the Pu separations. ICP-MS measurements were applied to the 5% sample digest that was removed from the Pu samples after digestion and filtration. The second AMS method was applied to samples that were removed from the corresponding coral half-rounds. This chapter will assess the U isotopes in the coral. An export model was developed using the ^{236}U data and the model was used to calculate the total ^{236}U exported from the Bikini lagoon to the Pacific Ocean during the lifetime of the corals. Modifications were made to the original U analytical method which include, processing samples in Teflon vials instead of glass and removing the anion exchange column.

4.2 AMS analysis

4.2.1 AMS analysis of ^{233}U and ^{236}U using a NU tracer

A method using UTEVA and AG1-X8 columns have been previously used in CAMS for U analysis. As a starting point, this procedure was applied to four experimental coral samples and analyzed using AMS. Regions of interest (ROIs) were selected in the detector software system to analyze for ^{236}U and ^{233}U signals. There was a signal interference overlapping into the ^{233}U ROI. Experiments were done to optimize the method and suppress ^{233}U signal interferences. Samples were compared that were run through UTEVA and AG1-X8 columns to samples only run through the UTEVA column. Processing samples using glass beakers were compared to processing samples using Teflon vials throughout the procedure. Addition of the AG1-X8 column did not add or take away from the signal strength in the AMS

detector and it was determined that AG1-X8 column is not necessary for this work. The ^{233}U interference stemmed from the glass beakers and was mitigated using Teflon vials throughout the U procedure. The U method was optimized by removing the AG1-X8 column from the procedure and removing the use of glass beakers and replacing with Teflon vials. The final method involves spiking 1 mg of natural uranium to U fractions from Pu, separating U from matrix using UTEVA columns, preparing cathodes as in the Pu procedure, by precipitating U with Fe and homogenizing with Nb.

4.2.1.1 Analytical procedure

Uranium sample fraction, from the Pu separation procedure, volumes were ~45 mL in 3 M HNO_3 0.5 M Al. Samples were transferred to 30 mL Teflon vials and taken to dryness using a hotblock, reconstituted in 10 mL 3 M HNO_3 0.5 M Al, and filtered with a 0.45 μm syringe filter into a 50 mL centrifuge tube. 1 mg of natural U (CRM 112A) was added by weight to samples and process blanks.

4.2.1.2 U separations

2 mL prepacked UTEVA columns were prepared by properly seating the frit onto the resin bead. The UTEVA column was conditioned with 6 mL of 3 M HNO_3 . Samples were loaded onto the UTEVA column. Sample containers were rinsed three times with 1 mL 3 M HNO_3 and transferred to column. Columns were rinsed with 20 mL 3 M HNO_3 , followed by 20 mL of 5 M HCL - 0.05 M oxalic acid. U was eluted with 20 mL of 0.02M H_2SO_4 into a 30 mL Teflon vial. 3 mL of concentrated HNO_3 was added to each vial. A ribbed watch glass was placed on top of the vial, and the sample refluxed slowly in a hotblock and evaporated to complete dryness. Samples were rehydrated with 3 M HNO_3 , transferred to 15 mL centrifuge tubes, precipitated and pressed into a cathode, following the same procedure as applied to Pu AMS samples.

4.2.1.3 AMS measurements

Measurements of ^{236}U and ^{233}U were performed by AMS at CAMS at LLNL. Process blanks, CRM 112A and Q metal blanks were also analyzed. QAs were spaced seven samples apart and analyzed throughout the entire sample run. QAs contained 1 mg ($\sim 2.5 \times 10^{18}$ atoms of ^{238}U) Q metal and 3×10^9 atoms of both

^{233}U and ^{236}U . Measurements were taken by cycling between the isotope of interest ($^{236}\text{U}^{5+}$ or $^{233}\text{U}^{5+}$) and the reference isotope ($^{238}\text{U}^{5+}$) as described in Chapter 2. Measurements for coral samples were converted from atoms per sample to specific activity in mBq/kg of coral.

4.2.1.4 Results

Results are shown in Figure 26 at 1σ error. After background subtraction, the specific activity for ^{236}U in the coral samples ranged from 0 - 0.26 mBq/kg. The Bravo coral has higher concentrations than the Eneu coral. There appears to be no ^{236}U in the Eneu coral from 1973 to present. There is a decreasing trend in activity from the oldest portion of the corals to about 1970. The process blanks and CRM 112A for wheel 1 are shown in Table 8. This shows the background was limited by the CRM 112A spike. The CRM 112A spike #1-3 in the table is the spike that had been coprecipitated with $\text{Fe}(\text{OH})_3$ and produced into a cathode. The process blank, includes the CRM 112A, and is also known as the reagent blank for the chemical process. The weighted average process blank for each wheel were used as the background correction. The background was too high to resolve ^{236}U in this coral. Samples were re-drilled and remeasured from both corals and a different tracer was employed in order to improve background levels for ^{236}U .

Table 8. ^{236}U atoms in the NU tracer and in the blanks.

Sample name	^{236}U atoms	Error $\pm\sigma$ atoms
Blank CRM 112A #1	1.97E+09	$\pm 1.81\text{E}+07$
Blank CRM 112A #2	1.96E+09	$\pm 1.63\text{E}+07$
Blank CRM 112A #3	1.99E+09	$\pm 1.93\text{E}+07$
Process Blank #1	1.92E+09	$\pm 1.75\text{E}+07$
Process Blank #2	1.92E+09	$\pm 1.62\text{E}+07$
Process Blank #3	1.95E+09	$\pm 2.06\text{E}+07$

Figure 26. ^{236}U concentrations in mBq/kg of coral.

Figure 27. ^{233}U concentrations in Eneu and Bravo Corals at 1σ error.

The ^{233}U in the corals were measured at 2.0×10^7 atoms to 8.0×10^3 atoms per gram of coral.

Figure 27 shows the ^{233}U specific activity in mBq/kg of coral. The highest concentration of 2.8 mBq/g is observed in 1957 in the Eneu coral. From 1960 to 1973 concentrations in the Bravo coral are slightly elevated than the Eneu coral. From 1975 to present, the concentrations are similar for both corals.

4.2.2 AMS analysis of ^{236}U using ^{233}U spike

4.2.2.1 Analytical procedure

1-gram samples were removed along the length of the coral rounds. Samples were transferred to Teflon vials and dried in an oven for 24 hours at 40°C . Samples were spiked with 3.0×10^9 atoms of ^{233}U legacy IPL standard. Samples were digested using the same method for Pu analysis. U was separated, coprecipitated and packed into a cathode following the same procedure.

4.2.2.2 AMS measurements

Measurements of ^{236}U were performed by AMS at CAMS at LLNL. Process blanks, IAEA 368, CRM 129A and three 1-gram samples from the bottom piece of the Bravo coral around areas that appeared to be higher in activity based off autoradiography imaging were also analyzed. Measurements were taken by cycling between the isotope of interest ($^{236}\text{U}^{5+}$) and the reference isotope ($^{233}\text{U}^{5+}$) as described in Chapter 2. Measurements for coral samples were converted from atoms per gram sample to specific activity in Bq/kg of coral.

4.2.2.3 Results

1-gram coral samples contain $1.5 \times 10^7 - 4.35 \times 10^8$ ^{236}U atoms for the Bravo coral and $1.38 \times 10^7 - 2.0 \times 10^8$ ^{236}U atoms for the Eneu coral. The background for spiking with ^{233}U method is in the 10^5 -atom range, with a weighted average background of $3.13 \times 10^5 \pm 9.14 \times 10^4$ of ^{236}U atoms, which is much lower than spiking with NU which had a background in the 10^9 -atom range. The 10^9 -atom background is too high to resolve ^{236}U within the coral samples. There is no reported ^{236}U concentration for the IAEA 368 standard. The background subtracted values are in Table 9 and are at or around background levels with high errors. Figure 28 shows the ^{236}U concentration in Bq/kg of coral measured in both corals. Concentrations in the Bravo coral are higher than the Eneu coral from 1960 to 1975. After 1975, concentrations are slightly higher than the Eneu coral until 2015. Both corals decrease at a higher rate and have larger fluctuations in concentrations in the older portion of the coral. From 1975 to present, the concentrations are decreasing but at a much slower rate. The Eneu coral has increases in ^{236}U concentrations in 1957, 1960, 1962 and 1969 while there are increases at 1963, 1965, 1971 and 1975 in the Bravo coral.

Table 9. ^{236}U results for IAEA 368.

IAEA-368 Sample	^{236}U atoms $\pm$ error at 1σ	
IAEA 368 #1	$8.61\text{E}+05$	$3.84\text{E}+05$
IAEA 368 #2	$1.44\text{E}+06$	$4.78\text{E}+05$
IAEA 368 #3	$5.58\text{E}+05$	$3.53\text{E}+05$
IAEA 368 #4	$1.93\text{E}+06$	$4.83\text{E}+05$
IAEA 368 #5	$8.21\text{E}+05$	$4.35\text{E}+05$
IAEA 368 #6	$1.37\text{E}+06$	$4.97\text{E}+05$

Figure 28. ^{236}U concentrations in Bq/kg of coral in the Bravo corals at 2σ error.

4.2.3 Bikini coral uranium analysis

The ^{236}U and ^{233}U in the corals at the Bikini Atoll derived from thermonuclear weapons detonations with high yields. The ^{236}U is produced from $^{235}\text{U}(n,\gamma)^{236}\text{U}$ and $^{238}\text{U}(n,3n)^{236}\text{U}$ reactions with either the uranium material in the weapons core (enriched U or Pu) or uranium in the tamper (depleted or enriched U or Pb). ^{233}U is produced by $^{234}\text{U}(n,2n)^{233}\text{U}$ in thermonuclear weapons. The ^{233}U is produced more efficiently in higher yield thermonuclear weapons detonations like ^{236}U but in much smaller quantities.

Concentrations of ^{233}U should follow a similar pattern as the ^{236}U in the Bikini Atoll and the corals.

The ^{236}U and ^{233}U concentrations in the lagoon water are due to the remobilization from the sediments on the lagoon floor from the continuing dissolution of material deposited from nuclear weapons testing. The main input of ^{236}U in the Northwest Pacific Ocean is from nuclear testing in the Marshall Islands. Rapid increases in ^{236}U concentrations have been linked to years associated with thermonuclear testing within the Marshall Islands (Froehlich et al. 2017, Sakaguchi et al. 2016, Nomura et al. 2017). ^{236}U concentrations are much higher in the older portions of the corals. Concentrations in both corals decrease more rapidly from 1957 - 1970 and continue to decrease at a slower rate after 1970 to 2015 with small fluctuations. Environmental research associated with ^{233}U and ^{236}U is limited due to low levels that are difficult to detect and because of this there are few articles analyzing ^{236}U in coral in the Northwest Pacific and there are no articles analyzing ^{233}U in corals.

Sakaguchi et al. analyzed a coral core for ^{236}U from Iki island in the Tsushima Strait, Japan. The purpose of this research was to reconstruct the input history of ^{236}U to the surface seawater of the Japan Sea (Sakaguchi et al. 2016). The coral was slabbed and chronology was developed using laser ablation ICP-MS (LA ICP-MS) and measuring $^{87}\text{Sr}/^{43}\text{Ca}$ at 0.5 mm resolution. Samples were taken from the low-density portions of the banding, during the optimum time of growth in the summer. Corals were chemically digested and purified with Dowex anion exchange resin. Uranium was coprecipitated with

Fe(OH)₃, calcined and ²³⁶U/²³⁸U ratios were analyzed by AMS. ²³⁸U was measured using ICP-MS. ²³⁶U/²³⁸U ratios were used to calculate the concentration of ²³⁶U in surface seawater assuming the ²³⁸U concentration of 3.0 ppb. This coral has pre nuclear ratios at $\sim 0.1 \times 10^{-9}$ with sharp increases in 1955, 1959 and 1963. The author associates the high ratio peaks from the high yield tests conducted in the Marshall Islands in 1954 and 1958 and estimated that it would take 1 year for the surface current from the Marshall Islands to travel to the Iki Island coral site ($\sim 7,000$ km) (Sakaguchi et al. 2016). The sharp increases in the Iki coral would reflect testing from both Enewetak and Bikini Atolls. Increases are shown in the Bikini corals in 1957, 1960, 1962 and 1963. The increase in ²³⁶U signatures in the Iki coral in 1958, 1959 and 1963 could be associated with the increases reflected in the Bikini corals.

Nomura et al. analyzed a coral core for ²³⁶U/²³⁸U atom ratios from Kume Island in the Kuroshio current. This coral is south of the Iki coral and Northwest of the Marshall Islands. The chronology and ratios were determined similarly to the Sakaguchi coral. Chronology was developed using LA-ICPM of Sr/Ca ratios and ²³⁶U/²³⁸U atom ratios were determined using AMS. This coral covered a time period from 1940 to 2014. This research showed consistent ²³⁶U/²³⁸U ratios within the coral in 2014 and measured surface water samples from the coral location. The author concludes that the ratios in sea water around the sampling site are recorded without fractionation in the coral core (Nomura et al. 2017). The highest peak ratios were 100 times higher than the pre nuclear background levels ($0.09-11 \times 10^{-9}$). Increases in ratios began in 1952 with the detonation of the first hydrogen bomb at the Marshall Islands and steep increases occurred in 1954 and 1958. The ratios in 1954 and 1958 also derived from thermonuclear testing from the Marshall Islands traveling via the North Equatorial Current to the Kuroshio Current. A small increase in ratios was seen in 1963 and the author attributes this increase to the period where the most global nuclear fallout was released to the environment in 1963-1964 which resulted in the contamination of surface sea water worldwide. The ratios gradually decreased after 1964 to the most recent part of the coral. The decrease corresponds to the dilution of the ²³⁶U/²³⁸U signal

with the inflow of less contaminated water through the North Equatorial Current. The Eneu and Bravo corals do exhibit a decreasing trend similar to the Kume and Iki coral ratios. The sharp increases in the Kume and Iki corals are shown in different years and the difference between these studies may be attributed to low time resolution, variations in the coral core, sampling techniques and different coral species. The Nomura and the Sakaguchi studies both analyzed the $^{236}\text{U}/^{238}\text{U}$ ratios in 0.5 - 0.2 g of coral which was not measured in this research.

Froelich et al. analyzed ^{236}U in a coral from the Enewetak Atoll. Chronology was developed using ICP-AES of Sr/Ca ratios. Samples were spiked with ^{242}Pu and ^{233}U and Pu and U were separated from the coral matrix with anion exchange resins and analyzed using AMS. Coral samples ranged from $(0.9 - 149) \times 10^8$ atoms of ^{236}U per gram of coral. Highest levels of ^{236}U were found in samples for the following years 1952, 1954, 1956 and 1958. The highest in Jan-April 1958 sample with $149 \pm 14 \times 10^8$ atoms/g. Samples following the last nuclear test at the Enewetak from 1959 - 1965 contain $(0.9 - 8) \times 10^8$ ^{236}U atoms/g. The concentration decreased significantly from 1958 to 1959 at $(149 - 8) \times 10^8$ atoms/g. The Bravo and Eneu corals range from $(0.13 - 2.74) \times 10^8$ of ^{236}U atoms/g with the higher values associated with the older portion of the corals. The resolution of the Enewetak coral was bimonthly. This resolution showed a seasonal dependence of uptake with the beginning of each year containing the lowest amount of U and increasing towards the end of the year to a maximum increasing by a factor of ~ 3 . The values are higher in the Enewetak coral than in the Bikini coral and this stems from the characteristics of the different tests detonated within each site.

Nuclear tests were conducted in 1946, 1954, 1956 and 1958 in the Bikini Atoll and in 1948, 1951, 1952, 1954, 1956 and 1958 in the Enewetak Atoll. Corals from the above studies have shown a consistency with the increasing concentrations associated to the years of nuclear testing within the Marshall Islands. These corals have shown a slow decrease in concentrations after nuclear testing ceased in 1958 within the Marshall Islands. Differences in ratios and concentrations vary when

comparing the corals directly due to distance from the detonations, characteristics and sources of device contamination (combined Marshall Island Signal or specific to Atoll) and dilution of signals from uncontaminated water.

4.3 Uranium export model

A ^{236}U export model was produced using the coral data. The curve fitting equations that were fit to the ^{236}U data and residuals are shown in Figure 8 and Figure 9. U export in the lagoon was calculated using a coral uptake value of 1.0×10^3 relative to seawater (Nomura et al. 2017, Sakaguchi et al. 2016). A flushing rate of seven years was assumed. The lagoon area is estimated to be 629 km^2 with an average depth of 45 m. The estimated volume used for the model is $2.83 \times 10^{10} \text{ m}^3$ (Noshkin et al. 1987). Table 17 shows the concentration of ^{236}U in Bq/kg in coral calculated using the fitted equations for each coral. The table also shows the ^{236}U concentration in the lagoon water calculated using the concentration factor. The total lagoon activity of ^{236}U in Bq in the estimated lagoon volume and the amount of ^{236}U exported annually from the lagoon to the open ocean are also shown in Table 6. The total export for the combined ^{236}U using the Bravo coral data is $7.45 \times 10^{-4} \text{ TBq}$ and using the Eneu coral data (1960 - 2015) is $3.8 \times 10^{-4} \text{ TBq}$. The total export of ^{236}U from the entire life span (1956 - 2015) of the Eneu coral is $4.9 \times 10^{-4} \text{ TBq}$. The annual export ranges from $(0.4 - 6.4) \times 10^{-5} \text{ TBq}$. Total global fallout of ^{236}U has been reported at 900 - 1500 kg (Winkler et al. 2012, Nomura et al. 2017, Sakaguchi et al. 2009). It is estimated that the U.S. contributed 240 kg of ^{236}U to the equatorial Pacific from nuclear testing (Winkler et al. 2012). The total export from this study is 0.21 - 0.31 kg which represents 0.09-0.13% of the total ^{236}U deposited into the Pacific.

Figure 29. Gaussian model of Bravo data set.

Figure 30. Export model for Bravo coral.

Figure 31. Gaussian model for Eneu Coral.

Figure 32. Export model for Eneu coral.

4.4 $^{236}\text{U}/^{239}\text{Pu}$ Atom Ratios

Atom ratios of $^{236}\text{U}/^{239}\text{Pu}$ were calculated from the AMS data. The atoms for each isotope per gram of coral for each coral are shown in Figure 33 and Figure 34. ^{239}Pu in atoms/g of coral is shown on the left x-axis while ^{236}U is on the secondary x-axis. The fluctuations in concentration throughout the lifetime of the corals for both isotopes have similar patterns. Ratios of $^{236}\text{U}/^{239}\text{Pu}$ are shown in Figure 35. The ratios fluctuate around mean values of 0.06 ± 0.02 and 0.04 ± 0.007 for the Bravo and Eneu corals respectively. The ratios range from 0.03-0.08 in the Eneu coral and 0.03-0.09 in the Bravo coral. The averages from this study are lower than the average value of 0.144 ± 0.014 , spanning a period of 1959-1664, from the coral analyzed by Froehlich from the Enewetak Atoll. These values are similar to the sediment also analyzed by Froehlich from the Enewetak Atoll with a ratio of 0.04 ± 0.003 (Froehlich et al. 2017).

Figure 33. Annual Eneu ^{239}Pu and ^{236}U atoms/g of coral at 1σ error. X-axis shows the ^{239}Pu in atoms/g and secondary axis shows the ^{236}U in atoms/g.

Figure 34. Annual Bravo ^{239}Pu and ^{236}U atoms/g of coral. X-axis shows the ^{239}Pu in atoms/g and secondary axis shows the ^{236}U in atoms/g.

Figure 35. $^{236}\text{U}/^{239}\text{Pu}$ atom ratios in Bravo and Eneu corals at 2σ error.

4.5 $^{235}\text{U}/^{238}\text{U}$ Ratios

4.5.1 ICPMS method

After coral samples were digested and had undergone filtration, 5% (wt/wt) of each sample was removed and transferred to a 15 mL centrifuge tube and diluted to 10 mL with milliQ water. 1 mL of the diluted sample was transferred to a 15 mL centrifuge tube containing 2 ppb of ^{233}U . The sample was diluted to 10 mL with 2% ultrapure HNO_3 and measured. One sample from each run was also analyzed by standard addition. 1 mL of the diluted sample was transferred to a 15 mL centrifuge tube containing 2 ppb ^{233}U and ^{238}U (0, 1, 3, 5 and 10 ppb) and diluted to 10 mL. A Thermo Fisher Scientific iCAP Q ICP-MS was used to analyze the samples. The ICP-MS was warmed up for an hour prior to running daily performance tests. Method parameters are listed in Table 10.

Samples and standards were run in the following order: two acid blanks, spike blank, process blank, QA- mass bias, IAEA 368 sample, half of samples in the sample set, acid blank, QA-mass bias, remaining half of samples in the sample set, spike blank, process blank, QA- mass bias, IAEA 368 sample, acid blank, Standard addition samples (0 ppb, 1 ppb, 3 ppb, 5 ppb, 10 ppb), two acid blanks. Acid blanks were run periodically to check for sample carryover and to provide an instrument background. Acid blanks contain 2% HNO₃ acid all other samples and descriptions are listed in Table 11. A known amount of ²³³U standard was added to samples and QAs and used to measure analytes using the isotope dilution method. The ²³³U standard was used to monitor instrumental drift. The ²³³U standard was diluted from Eckert and Ziegler Isotope Products Catalog No. 7233, source No. 1999-11 containing 0.2075 µCi/g reported with a total uncertainty of ±3% at the 99% confidence level. The uranium nuclides in the ²³³U standard are in Table 12. The CRM 112A standard was used as a mass bias correction for ²³⁵U/²³⁸U atom ratios. The standard addition samples were used as a secondary check to verify coral concentrations determined by isotope dilution. Spike blank was used to monitor measurement consistency over time and to analyze for analytes in the ²³³U standard. Measurements were made in both KED and STD mode. The KED mode pressurizes the collision cell with gas and applies an energy discrimination barrier while the STD mode is the standard mode of operation and does not pressurize the collision cell. The wash solution was 2% ultrapure HNO₃.

Table 10. Method Parameters for ICP-MS.

Method Parameters	
Sweeps	100
Time per sweep	0.7 s
Number of Replicates	3
Dwell time for U-233	0.1 s
Dwell time for U-235	0.5 s
Dwell time for U-238	0.1 s
Scan mode	Peak Hopping
Time per sweep	0.7 s
Spacing	0.1 u
Uptake time	100 s
Nebulizer flow	1 l/min
Wash time	100 s
Nebulizer type	PFA-ST MicroFlow Nebulizer
Spray chamber type	Glass cyclonic spray chamber

Table 11. Instrumental and method check samples.

Name	Radionuclides in sample
Spike blank	2ppb U-233
Process blank	2ppb U-233
QA- mass bias	2ppb U-233; 2ppb natural uranium (CRM 112A $^{235}\text{U}/^{238}\text{U}$ atom ratio 0.0072543 $\pm$ 0.0000040)
Standard addition samples	2ppb U-233 in addition to 0 ppb, 1 ppb, 3 ppb, 5 ppb and 10 ppb NU (CRM 112A) and coral sample

Table 12. Isotopics for ^{233}U standard.

Nuclide	Weight%
U-232	0.000310
U-233	99.764
U-234	0.01900
U-235	0.008000
U-236	0.00100
U-238	0.2080

4.5.2 Results

^{238}U was calculated in ppb in diluted coral samples using isotope dilution method. Concentrations were multiplied by the dilution factor (DF) for each sample and are reported in ppm. Concentrations calculated using the KED mode had better precision and smaller error than the STD mode. STD concentrations will not be included in this work. Concentrations and ratios in KED mode are shown in Figure 36 and Table 13. ^{238}U concentrations range from 1.98 ± 0.06 ppm to 3.74 ± 0.1 ppm. Ratios indicate that they were possibly higher during the oldest portion of the Eneu coral. The remainder of the coral is more representative of natural uranium. Changes during years where there was an increase in ^{236}U and ^{239}Pu does not correspond to any changes associated with the $^{235}\text{U}/^{238}\text{U}$. Uranium within the corals is diluted with natural U and does not provide information regarding the source term of contamination from anthropogenic U.

Figure 36. $^{235}\text{U}/^{238}\text{U}$ atom ratios in KED mode at 2σ error.

Table 13 ^{238}U concentrations and $^{235}\text{U}/^{238}\text{U}$ ratios at 2σ error.

Year	Eneu Coral				Bravo Coral			
	^{238}U ppm	$\pm$ Error	$^{235}\text{U}/^{238}\text{U}$ Atom Ratio	$\pm$ Error	^{238}U ppm	$\pm$ Error	$^{235}\text{U}/^{238}\text{U}$ Atom Ratio	$\pm$ Error
2015	2.01	0.07	7.33E-03	2.8E-05	2.10	0.07	7.32E-03	6.3E-05
2013	2.07	0.07	7.30E-03	5.3E-05	2.22	0.07	7.34E-03	4.8E-05
2011	2.11	0.07	7.27E-03	3.7E-05	2.19	0.08	7.30E-03	5.3E-05
2009	2.08	0.07	7.33E-03	3.1E-05	2.21	0.07	7.28E-03	6.5E-05
2007	1.98	0.06	7.35E-03	2.8E-05	2.29	0.08	7.33E-03	5.4E-05
2005	2.04	0.07	7.29E-03	2.6E-05	2.26	0.09	7.27E-03	5.3E-05
2003	2.05	0.07	7.29E-03	2.5E-05	2.34	0.09	7.27E-03	4.8E-05
2001	2.14	0.07	7.32E-03	5.2E-05	2.27	0.12	7.26E-03	5.1E-05
1999	2.49	0.08	7.30E-03	3.6E-05	2.23	0.08	7.32E-03	5.4E-05
1997	2.61	0.09	7.31E-03	2.3E-05	2.13	0.07	7.32E-03	6.9E-05
1995	2.54	0.08	7.29E-03	3.9E-05	2.20	0.08	7.28E-03	5.5E-05
1993	1.30	0.05	7.36E-03	4.3E-05	2.17	0.07	7.35E-03	5.1E-05
1991	2.53	0.09	7.29E-03	2.4E-05	3.74	0.13	7.27E-03	6.7E-05
1989	2.24	0.08	7.33E-03	3.7E-05	2.17	0.08	7.32E-03	4.9E-05
1987	2.20	0.08	7.30E-03	2.8E-05	2.23	0.07	7.30E-03	4.9E-05
1985	2.19	0.07	7.29E-03	2.9E-05	2.34	0.07	7.31E-03	5.4E-05
1983	2.35	0.07	7.33E-03	3.8E-05	2.27	0.09	7.28E-03	3.8E-05
1981	2.44	0.08	7.29E-03	2.3E-05	2.13	0.08	7.32E-03	3.8E-05
1979	2.09	0.07	7.34E-03	3.4E-05	2.19	0.07	7.34E-03	4.6E-05
1977	2.59	0.10	7.28E-03	5.7E-05	2.44	0.08	7.29E-03	3.5E-05
1975	2.39	0.08	7.29E-03	6.1E-05	2.18	0.08	7.29E-03	3.1E-05
1974	2.74	0.09	7.26E-03	4.9E-05	2.31	0.08	7.31E-03	5.0E-05
1973	2.65	0.09	7.32E-03	5.3E-05	2.32	0.07	7.28E-03	3.0E-05
1971	2.54	0.09	7.33E-03	4.9E-05	2.10	0.07	7.29E-03	2.5E-05
1969	2.26	0.08	7.32E-03	6.7E-05	2.21	0.08	7.32E-03	5.2E-05
1968	2.54	0.08	7.26E-03	5.3E-05	2.70	0.09	7.30E-03	3.6E-05
1967	2.55	0.09	7.25E-03	5.5E-05	2.66	0.09	7.31E-03	2.3E-05
1966	2.58	0.10	7.27E-03	4.9E-05	2.79	0.09	7.29E-03	3.9E-05
1965	2.56	0.09	7.26E-03	5.0E-05	1.96	0.07	7.36E-03	4.3E-05
1964	2.67	0.10	7.27E-03	6.1E-05	2.72	0.09	7.29E-03	2.4E-05
1963	2.68	0.09	7.27E-03	5.4E-05	2.21	0.08	7.33E-03	3.7E-05
1962	2.57	0.09	7.26E-03	5.4E-05	2.25	0.08	7.30E-03	2.8E-05
1961	2.59	0.09	7.24E-03	4.9E-05	2.34	0.08	7.29E-03	2.9E-05
1960	2.50	0.08	7.24E-03	7.1E-05	2.46	0.08	7.33E-03	3.8E-05
1959	2.54	0.08	7.25E-03	5.6E-05				
1958	2.60	0.08	7.29E-03	5.7E-05				
1957	2.93	0.10	7.34E-03	5.8E-05				
1956	2.74	0.09	7.39E-03	5.7E-05				

Table 14 shows the ^{238}U concentrations in ppb calculated using the isotope dilution method and the standard addition method. Both methods agree. The standard addition method validates the ^{238}U concentration calculated by the isotope dilution method. There was a total of five ICPMS KED runs with standard addition applied to one sample per run.

Table 14. ^{238}U concentrations calculated by isotope dilution and standard addition.

ICPMS Run	Sample	Conc. Isotope		Conc. Standard	
		Dilution ^{238}U ppb		Addition ^{238}U ppb	
1	Eneu 2009	1.08	± 0.04	1.09	± 0.04
2	Bravo 2009	1.30	± 0.03	1.29	± 0.02
3	Bravo 1969	1.19	± 0.04	1.18	± 0.04
4	Eneu 1968	1.45	± 0.05	1.46	± 0.04
5	Bravo 1971	1.29	± 0.04	1.21	± 0.06

4.6 ^{236}U in bottom piece of Bravo Coral

Three 1-gram samples were removed from the dead piece of the coral. They were analyzed the same way and included in the ^{236}U AMS run. These were areas that had produced images in the autoradiograph. Locations of the three samples are shown in Figure 37.

Figure 37. Locations of samples removed from bottom of Bravo coral.

The concentrations in the bottom bravo piece are shown in Table 15. The concentrations vary from 9.88×10^8 to 1.76×10^9 atoms/g. These samples were not taken from the same banding. These concentrations are higher than the oldest year in Bravo coral in 1960 which had 4.35×10^8 atoms/g. We were unable to date this coral and cannot associate the concentrations within this piece with a specific year.

Table 15. ^{236}U concentrations in Bravo coral bottom piece.

Sample Name	Atoms/g	Error at 1σ	Bq/kg	Error at 1σ
BB-01	1.76E+09	3.74E+07	1.65E-03	3.50E-05
BB-02	9.88E+08	1.64E+07	9.27E-04	1.54E-05
BB-03	1.18E+09	1.69E+07	1.11E-03	1.59E-05

The Bravo coral was further analyzed with a small anode germanium detector (SAGe). 1-gram samples were removed throughout the coral (2003, 1969, 1962) and digested in the same way as for AMS prep. Samples were rehydrated in column loading solution and transferred to a 20 mL scintillation vial with a volume of 10 mL. Samples were counted on the SAGe detector for 3 days. ^{207}Bi (0.016 ± 0.003

Bq) and ^{137}Cs (0.005 ± 0.002 Bq) were detected in only the BB-01 sample. ^{137}Cs has been detected only in the years of 1954-1958 in the Bikini coral studied from Noshkin and ^{207}Bi was also detected throughout the lifetime of this coral (Noshkin et al. 1975). ^{207}Bi was likely produced by the activation of stable bismuth or deuterium capture in lead. ^{207}Bi has been detected in Bravo crater sediments with activities up to 2500 Bq/kg (Buesseler et al. 2018). BB-01 may correspond to the years of 1954-1958 in which the fission product of ^{137}Cs was also detected.

4.7 Conclusions

Two corals from the Bikini Atoll were analyzed for ^{236}U and ^{233}U . Two methods were investigated and compared, one using a ^{238}U spike and the other method using a ^{233}U spike. The ^{236}U background in the ^{238}U spike was too high and did not produce measurable ^{236}U data but did provide ^{233}U data. ^{233}U in the coral samples ranged from 2.0×10^7 to 8.0×10^3 atoms/g with the Bravo coral containing higher concentrations than the Eneu coral in the older portions of the coral. Samples were redrilled and processed using a ^{233}U spike. The ^{236}U data from this method was used to calculate the annual export for ^{236}U from the Bikini Atoll. The corals contained 1.38×10^7 to 4.35×10^8 ^{236}U atoms/g. This study showed that the remobilization of ^{236}U follows a similar trend as $^{239+240}\text{Pu}$. The ^{236}U in both corals are higher in the older portions of the coral and decrease at a higher rate from the oldest portion of the corals to ~1980 and then decrease at a much slower rate to 2015. ^{236}U export in the lagoon was calculated assuming an uptake value of 1.0×10^3 relative to seawater (Nomura et al. 2017). The annual export ranges from $(0.43 - 6.40) \times 10^{-5}$ TBq and the total export from this study is between $(4.95 - 7.45) \times 10^{-4}$ TBq or 0.21 – 0.31 kg of ^{236}U which represents 0.09 - 0.31 % of the total ^{236}U deposited into the Pacific Ocean. New information this study has provided includes a chronological record of concentrations showing the trends of ^{236}U and ^{233}U in addition to $^{236}\text{U}/^{239}\text{Pu}$ atom ratios within the Bikini lagoon. This

new data was used to develop an export model for ^{236}U which shows the annual and total export of ^{236}U throughout the lifetime of the corals within the Bikini Atoll lagoon

Chapter 5- Conclusions

5.1 Summary of work preformed

The retrospective analysis of Pu and U isotopes in dated coral has provided a basis for predicting future change in the solubility and export potential of radionuclides contained in bottom sediments, and of possible long-term consequences of these changes on radiation doses delivered to marine organisms and/or local inhabitants of the Bikini Atoll. The Bikini lagoon sediments are one of the most contaminated sites in the world due to local fallout from past nuclear weapons testing. The fallout is mainly associated with sediments and is solubilized into the lagoon overtime, providing a continuous source of these isotopes to the Pacific Ocean. The solubility and export potential of $^{239+240}\text{Pu}$ and ^{236}U isotopes were analyzed using banded coral. U and Pu from the surrounding environment become incorporated and immobilized within the coral skeleton as it grows and were used to determine concentrations of these isotopes within the surrounding lagoon water during time of growth. Coral cores were removed in 2016 from the Bikini lagoon by drilling cores perpendicular to the growth axis. Corals were cut into 0.25" slabs and x-rayed to analyze growth patterns and banding. Subsamples were removed at a 0.5 - 1 mm resolution down the apex of the density bands and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ seasonal patterns were determined by IRMS. These seasonal patterns were used to develop a chronology. 1-gram samples were removed from the slabs during the lifetime of the coral. $^{239+240}\text{Pu}$ and ^{236}U were chemically extracted and purified using extraction chromatography and anion exchange resins and concentrations were determined by AMS. These concentrations were used to calculate lagoon concentrations and an export model was developed for Pu and U. A small fraction of each sample digest was analyzed for ^{238}U and $^{235/238}\text{U}$. Atom ratios were analyzed and used to asses source of contamination. Concentrations were used to analyze behavior of the isotope over time in this environment.

5.2 Conclusions

1. Chronologies were determined for each coral. The Eneu coral extends to 1956 and the Bravo coral extends to 1960. The most bottom piece of the Bravo coral was not able to be dated due to a growth hiatus between the most bottom piece and the 1960 portion. The lifetime of this piece was unable to be determined because there is a large area where the coral is growing in a different direction not perpendicular to where the core was cut.
2. $^{239+240}\text{Pu}$ concentrations have decreased over time in both corals. Concentrations in the Eneu coral range from $0.460.46 \pm 0.01$ to 7.38 ± 0.27 Bq/kg and Bravo range from 0.49 ± 0.02 to 15.29 ± 0.38 Bq/kg. The oldest region of both corals contains the highest concentrations. The rate of change of the Pu concentrations throughout the corals lifespans are not constant. Concentrations in both corals decrease more rapidly from the oldest section (1960 or 1956) to 1964. Both corals have an increase of concentration in 1965. Concentrations following 1965 continue to decrease rapidly until 1970 where the concentrations start to level off, but still slowly decreasing, until 2015.
3. Bravo concentrations are higher than Eneu concentrations due to location in the atoll relative to nuclear tests. Concentrations are five times higher in 1960 in the Bravo coral than in Eneu in the same year. Concentrations of $^{239+240}\text{Pu}$ in the Bravo coral are about three to four times higher than the Eneu coral between 1961-1964 and Bravo concentrations are slightly higher than Eneu concentrations until 1970. Concentrations from 1970-2015 are relatively similar for both corals.
4. The remobilization of ^{236}U follows a similar trend as $^{239+240}\text{Pu}$. The ^{236}U in both corals are higher in the older portions of the coral and decrease at a higher rate from the oldest portion of the corals to ~1980 and then decrease at a much slower rate to 2015.
5. $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios show the source of contamination has changed over time for both corals. The ratios within the Eneu coral slowly decrease over time, indicating that this area is

more concentrated with Pu from higher yield devices during the oldest portion of the coral.

Throughout the years the ratios have slightly decreased indicating that the signal is being diluted from the global ratio from ocean water mixing with lagoon water or being diluted with Pu with lower ratios from lower yield tests. The Bravo coral shows a slow increase in ratio throughout the lifetime of the coral. This indicates that the Pu contamination within this area from the older portions of the coral were from lower yield devices and slowly through time, higher yield devices are contributing more to the Pu within this area.

6. $^{236}\text{U}/^{239}\text{Pu}$ atom ratios fluctuate around mean values of 0.06 ± 0.02 and 0.04 ± 0.007 for the Bravo and Eneu corals respectively. The ratios range from 0.03 - 0.08 in the Eneu coral and 0.03 - 0.09 in the Bravo coral.
7. The total export for the combined Pu using the Bikini coral data is 8.35 TBq and using the Eneu coral data (1960 - 2015) is 5.30 TBq. The total export activity of Pu from the entire life span (1957 - 2015) of the Eneu coral is 6.90 TBq. The total export calculated from the corals is less than 0.25% of the global Pu activity of 4 PBq (Hamilton 2004). The annual export from this study ranges from 0.036 - 1 TBq. The amount of $^{239+240}\text{Pu}$ in the lagoon water accounts for only 0.08 - 0.09% of the sediment inventories to a depth of 16 cm (Noshkin et al. 1987). Under this assumption, the sediment inventories to a depth of 16 cm would be estimated as 6.5 - 196 TBq.
8. The total export for the combined ^{236}U using the Bikini coral data is 7.45×10^{-4} TBq and using the Eneu coral data (1960 - 2015) is 3.80×10^{-4} TBq. The total export of ^{236}U from the entire life span (1956 - 2015) of the Eneu coral is 4.95×10^{-4} TBq. The annual export ranges from $(0.43 - 6.40) \times 10^{-5}$ TBq. It is estimated that the U.S. contributed 240 kg of ^{236}U to the equatorial Pacific from nuclear testing (Winkler et al. 2012). The total export from this study is 0.21 - 0.31 kg which represents 0.09 - 0.13% of the total ^{236}U deposited into the Pacific.

9. ^{238}U concentrations range from 1.98 ± 0.06 ppm to 3.74 ± 0.1 ppm. Ratios indicate that they were possibly higher during the oldest portion of the Eneu coral. The remainder of the coral is more representative of natural uranium. Changes during years where there was an increase in ^{236}U and ^{239}Pu does not correspond to any changes associated with the $^{235}\text{U}/^{238}\text{U}$. Uranium within the corals is diluted with natural uranium and does not provide information regarding the source term of contamination from anthropogenic U.

New information acquired from this dissertation includes a chronological record of ^{236}U and ^{233}U concentrations from 1956 to 2015 and an extended chronological record of $^{239+240}\text{Pu}$ concentrations in the Bikini lagoon. Prior to this study, there has been no chronological information on concentrations of ^{236}U and ^{233}U within the Bikini lagoon or corals living in the Bikini lagoon. A study by Noshkin et al. developed a chronological record of $^{239+240}\text{Pu}$ concentrations and $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in the Bikini lagoon from 1953 to 1972 while this dissertation covers a period from 1956 to 2015 (Noshkin et al. 1975). This dissertation shows how the concentrations in the lagoon changes in 1970 to 2015. The $^{239+240}\text{Pu}$ and ^{236}U concentrations decrease at a much slower steady-state rate from 1970 to 2015 than the older portions of the coral. This dissertation also provides new information regarding the ratios within the Bikini lagoon. The two corals exhibit different increasing and decreasing trends in $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios over time which indicates the primary source of Pu contamination is changing within the two coral sites. The $^{239+240}\text{Pu}$ and ^{236}U concentrations measured were used to develop export models and total and annual export was calculated throughout the lifetime of the corals which is also new information.

This research verifies the concentrations and export for Pu and U have decreased over time and will continue to decrease, currently at slow steady state. This information provides reassurance to the local government that concentrations of these isotopes are decreasing and projected concentrations and export in the lagoon show no impact to the wider Pacific. Lagoon concentrations for Pu from this study can be used to improve the accuracy and reliability of predictive dose for Pu from ingestion of biota

through the aquatic food chain within the Bikini Atoll using known uptake values for aquatic organism. Understanding the past and current behavior of these isotopes in this study will provide for informed decisions for resettlement and allows for a better understanding of future conditions.

Appendix – Tables

Table 16. Activity concentrations and atom ratios for Bravo coral, Eneu coral and surrounding lagoon water calculated using the Noshkin concentration factor with 1 σ error.

Year	Bravo	Lagoon		Eneu	Lagoon	
	Coral	²⁴⁰⁺²³⁹ Pu	²⁴⁰⁺²³⁹ Pu	Coral	²⁴⁰⁺²³⁹ Pu	²⁴⁰⁺²³⁹ Pu
	²⁴⁰ Pu/ ²³⁹ Pu	Bq/kg	mBq/m ³	²⁴⁰ Pu/ ²³⁹ Pu	Bq/kg	mBq/m ³
2015	0.21 ± 0.02	0.53 ± 0.02	203.18 ± 7.03	0.15 ± 0.01	0.51 ± 0.02	195.60 ± 6.46
2013	0.21 ± 0.02	0.63 ± 0.03	237.82 ± 10.21	0.19 ± 0.01	0.46 ± 0.02	176.28 ± 6.10
2011	0.19 ± 0.01	0.65 ± 0.02	247.69 ± 7.99	0.18 ± 0.01	0.62 ± 0.02	235.60 ± 6.47
2009	0.20 ± 0.01	0.68 ± 0.02	258.22 ± 7.80	0.16 ± 0.01	0.51 ± 0.02	194.29 ± 5.76
2007	0.19 ± 0.01	0.59 ± 0.02	225.90 ± 6.14	0.18 ± 0.01	0.70 ± 0.02	266.34 ± 7.80
2005	0.21 ± 0.02	0.50 ± 0.02	188.45 ± 8.49	0.18 ± 0.01	0.55 ± 0.02	208.62 ± 6.02
2003	0.21 ± 0.02	0.53 ± 0.02	200.77 ± 6.86	0.18 ± 0.01	0.63 ± 0.02	238.01 ± 6.91
2001	0.20 ± 0.01	0.85 ± 0.02	322.64 ± 9.34	0.17 ± 0.01	0.65 ± 0.02	245.66 ± 6.43
2000	0.19 ± 0.01	0.72 ± 0.02	272.99 ± 6.37			
1999	0.19 ± 0.01	0.89 ± 0.03	337.20 ± 10.69	0.17 ± 0.01	0.64 ± 0.02	244.68 ± 6.72
1998	0.20 ± 0.01	0.70 ± 0.02	267.93 ± 6.17			
1997	0.19 ± 0.01	0.80 ± 0.02	303.45 ± 6.99	0.16 ± 0.01	0.90 ± 0.02	343.33 ± 8.97
1995	0.19 ± 0.01	0.69 ± 0.02	262.99 ± 8.07	0.17 ± 0.01	0.66 ± 0.02	250.76 ± 7.32
1994	0.20 ± 0.01	1.19 ± 0.02	453.40 ± 13.30			
1993	0.19 ± 0.01	0.93 ± 0.02	355.37 ± 6.70	0.17 ± 0.01	0.59 ± 0.02	225.87 ± 6.54
1992	0.21 ± 0.01	0.92 ± 0.02	349.95 ± 7.45			
1991	0.20 ± 0.01	1.06 ± 0.03	403.22 ± 8.58	0.18 ± 0.01	0.71 ± 0.02	271.39 ± 8.33
1989	0.19 ± 0.01	0.94 ± 0.03	355.85 ± 7.42	0.18 ± 0.01	0.92 ± 0.02	350.47 ± 9.16
1987	0.19 ± 0.01	1.23 ± 0.03	467.36 ± 13.30	0.19 ± 0.01	1.00 ± 0.03	381.24 ± 9.64
1985	0.20 ± 0.01	1.11 ± 0.03	423.28 ± 12.65	0.18 ± 0.01	1.01 ± 0.03	384.41 ± 10.81
1983	0.18 ± 0.01	1.73 ± 0.05	657.77 ± 16.77	0.19 ± 0.01	1.27 ± 0.03	483.14 ± 12.55
1981	0.19 ± 0.01	1.57 ± 0.04	595.97 ± 15.85	0.18 ± 0.01	1.42 ± 0.04	538.51 ± 13.72
1979	0.19 ± 0.01	1.72 ± 0.04	655.12 ± 19.00	0.19 ± 0.01	1.50 ± 0.04	570.53 ± 15.15
1977	0.18 ± 0.01	2.08 ± 0.05	793.06 ± 19.68	0.17 ± 0.01	1.78 ± 0.05	678.00 ± 18.53
1976				0.18 ± 0.01	1.87 ± 0.05	711.78 ± 20.46
1975	0.20 ± 0.01	1.86 ± 0.05	706.08 ± 17.41	0.18 ± 0.01	2.00 ± 0.05	762.07 ± 17.95
1974				0.17 ± 0.01	2.14 ± 0.06	813.20 ± 21.89
1973	0.18 ± 0.01	2.34 ± 0.06	890.42 ± 23.01	0.17 ± 0.01	2.60 ± 0.07	989.41 ± 26.36
1971	0.21 ± 0.01	2.49 ± 0.06	948.91 ± 24.59	0.18 ± 0.01	2.02 ± 0.05	769.46 ± 18.91
1970	0.19 ± 0.01	2.11 ± 0.05	804.00 ± 19.48			
1969	0.17 ± 0.01	3.43 ± 0.09	1306.15 ± 33.57	0.19 ± 0.01	2.12 ± 0.05	807.42 ± 20.25
1968	0.18 ± 0.01	3.52 ± 0.08	1337.99 ± 33.23	0.17 ± 0.01	1.94 ± 0.05	737.19 ± 20.47
1967	0.18 ± 0.01	4.16 ± 0.10	1583.66 ± 39.50	0.18 ± 0.01	2.29 ± 0.06	872.33 ± 24.18
1966	0.18 ± 0.01	4.92 ± 0.12	1871.72 ± 44.31	0.18 ± 0.01	2.38 ± 0.06	904.13 ± 24.11

1965	0.17 ± 0.01	5.91 ± 0.14	2247.35 ± 53.29	0.19 ± 0.01	3.37 ± 0.09	1281.50 ± 32.50
1964	0.18 ± 0.01	4.25 ± 0.10	1618.26 ± 39.87	0.21 ± 0.01	1.40 ± 0.04	533.44 ± 14.15
1963	0.17 ± 0.01	5.77 ± 0.13	2194.59 ± 51.31	0.20 ± 0.01	2.24 ± 0.06	853.40 ± 22.74
1962	0.17 ± 0.01	6.84 ± 0.16	2600.11 ± 59.55	0.19 ± 0.01	3.33 ± 0.08	1265.52 ± 31.43
1961	0.16 ± 0.01	9.24 ± 0.22	3514.99 ± 79.84	0.19 ± 0.01	2.95 ± 0.08	1120.52 ± 29.30
1960	0.17 ± 0.01	15.29 ± 0.38	5814.48 ± 136.73	0.17 ± 0.01	3.54 ± 0.09	1346.15 ± 32.51
1959				0.18 ± 0.01	4.70 ± 0.12	1788.53 ± 43.80
1958				0.19 ± 0.01	5.81 ± 0.14	2208.56 ± 54.30
1957				0.19 ± 0.01	5.51 ± 0.15	2094.61 ± 55.18
1956				0.20 ± 0.02	7.38 ± 0.27	2808.82 ± 103.40

Table 17. Pu annual exported from Bikini Atoll.

Year	ENEU				BRAVO			
	Calculated Pu Coral Activity	Surrounding Pu lagoon water	Total Pu lagoon Activity	Pu Exported Annually	Calculated Pu Coral Activity	Surrounding Pu lagoon water	Total Pu lagoon activity	Pu Exported Annually
	Bq/kg	Bq/kg	Bq	Bq	Bq/kg	Bq/kg	Bq	Bq
1956	7.015	2.60E-03	7.16E+10	5.01E+11				
1957	6.113	2.26E-03	6.24E+10	4.37E+11				
1958	5.297	1.96E-03	5.41E+10	3.78E+11				
1959	4.558	1.69E-03	4.65E+10	3.26E+11				
1960	3.889	1.44E-03	3.97E+10	2.78E+11	15.389	5.70E-03	1.57E+11	1.10E+12
1961	3.284	1.22E-03	3.35E+10	2.35E+11	9.662	3.58E-03	9.86E+10	6.90E+11
1962	2.737	1.01E-03	2.79E+10	1.96E+11	6.876	2.55E-03	7.02E+10	4.91E+11
1963	2.241	8.30E-04	2.29E+10	1.60E+11	5.521	2.04E-03	5.64E+10	3.95E+11
1964	1.793	6.64E-04	1.83E+10	1.28E+11	4.862	1.80E-03	4.96E+10	3.47E+11
1965	3.444	1.28E-03	3.52E+10	2.46E+11	5.992	2.22E-03	6.12E+10	4.28E+11
1966	2.488	9.21E-04	2.54E+10	1.78E+11	4.917	1.82E-03	5.02E+10	3.51E+11
1967	2.181	8.08E-04	2.23E+10	1.56E+11	4.114	1.52E-03	4.20E+10	2.94E+11
1968	2.083	7.72E-04	2.13E+10	1.49E+11	3.515	1.30E-03	3.59E+10	2.51E+11
1969	2.052	7.60E-04	2.09E+10	1.47E+11	3.068	1.14E-03	3.13E+10	2.19E+11
1970	2.042	7.56E-04	2.08E+10	1.46E+11	2.734	1.01E-03	2.79E+10	1.95E+11
1971	2.039	7.55E-04	2.08E+10	1.46E+11	2.484	9.20E-04	2.54E+10	1.78E+11
1972	2.315	8.57E-04	2.36E+10	1.65E+11	2.298	8.51E-04	2.35E+10	1.64E+11
1973	2.390	8.85E-04	2.44E+10	1.71E+11	2.159	8.00E-04	2.20E+10	1.54E+11
1974	2.208	8.18E-04	2.25E+10	1.58E+11	2.056	7.61E-04	2.10E+10	1.47E+11
1975	2.043	7.57E-04	2.09E+10	1.46E+11	1.978	7.33E-04	2.02E+10	1.41E+11
1976	1.894	7.02E-04	1.93E+10	1.35E+11	1.971	7.30E-04	2.01E+10	1.41E+11
1977	1.760	6.52E-04	1.80E+10	1.26E+11	1.919	7.11E-04	1.96E+10	1.37E+11
1978	1.639	6.07E-04	1.67E+10	1.17E+11	1.821	6.75E-04	1.86E+10	1.30E+11
1979	1.529	5.66E-04	1.56E+10	1.09E+11	1.730	6.41E-04	1.77E+10	1.24E+11
1980	1.431	5.30E-04	1.46E+10	1.02E+11	1.645	6.09E-04	1.68E+10	1.18E+11
1981	1.342	4.97E-04	1.37E+10	9.59E+10	1.565	5.80E-04	1.60E+10	1.12E+11

1982	1.261	4.67E-04	1.29E+10	9.01E+10	1.490	5.52E-04	1.52E+10	1.06E+11
1983	1.189	4.40E-04	1.21E+10	8.49E+10	1.420	5.26E-04	1.45E+10	1.01E+11
1984	1.123	4.16E-04	1.15E+10	8.03E+10	1.354	5.02E-04	1.38E+10	9.68E+10
1985	1.064	3.94E-04	1.09E+10	7.60E+10	1.293	4.79E-04	1.32E+10	9.24E+10
1986	1.011	3.74E-04	1.03E+10	7.22E+10	1.235	4.57E-04	1.26E+10	8.83E+10
1987	0.963	3.57E-04	9.83E+09	6.88E+10	1.181	4.37E-04	1.21E+10	8.44E+10
1988	0.919	3.40E-04	9.38E+09	6.57E+10	1.130	4.19E-04	1.15E+10	8.08E+10
1989	0.880	3.26E-04	8.98E+09	6.29E+10	1.083	4.01E-04	1.11E+10	7.74E+10
1990	0.845	3.13E-04	8.62E+09	6.04E+10	1.039	3.85E-04	1.06E+10	7.42E+10
1991	0.813	3.01E-04	8.30E+09	5.81E+10	0.997	3.69E-04	1.02E+10	7.12E+10
1992	0.784	2.90E-04	8.00E+09	5.60E+10	0.958	3.55E-04	9.78E+09	6.84E+10
1993	0.758	2.81E-04	7.74E+09	5.42E+10	0.921	3.41E-04	9.41E+09	6.58E+10
1994	0.734	2.72E-04	7.50E+09	5.25E+10	0.887	3.29E-04	9.06E+09	6.34E+10
1995	0.713	2.64E-04	7.28E+09	5.10E+10	0.855	3.17E-04	8.73E+09	6.11E+10
1996	0.694	2.57E-04	7.08E+09	4.96E+10	0.825	3.06E-04	8.42E+09	5.90E+10
1997	0.677	2.51E-04	6.91E+09	4.84E+10	0.797	2.95E-04	8.13E+09	5.69E+10
1998	0.661	2.45E-04	6.75E+09	4.72E+10	0.771	2.85E-04	7.87E+09	5.51E+10
1999	0.647	2.40E-04	6.61E+09	4.62E+10	0.746	2.76E-04	7.61E+09	5.33E+10
2000	0.634	2.35E-04	6.48E+09	4.53E+10	0.723	2.68E-04	7.38E+09	5.16E+10
2001	0.623	2.31E-04	6.36E+09	4.45E+10	0.701	2.60E-04	7.16E+09	5.01E+10
2002	0.613	2.27E-04	6.25E+09	4.38E+10	0.681	2.52E-04	6.95E+09	4.86E+10
2003	0.603	2.23E-04	6.16E+09	4.31E+10	0.662	2.45E-04	6.75E+09	4.73E+10
2004	0.595	2.20E-04	6.07E+09	4.25E+10	0.644	2.38E-04	6.57E+09	4.60E+10
2005	0.587	2.18E-04	6.00E+09	4.20E+10	0.627	2.32E-04	6.40E+09	4.48E+10
2006	0.580	2.15E-04	5.93E+09	4.15E+10	0.611	2.26E-04	6.24E+09	4.37E+10
2007	0.574	2.13E-04	5.86E+09	4.10E+10	0.597	2.21E-04	6.09E+09	4.26E+10
2008	0.569	2.11E-04	5.81E+09	4.06E+10	0.583	2.16E-04	5.95E+09	4.17E+10
2009	0.564	2.09E-04	5.75E+09	4.03E+10	0.570	2.11E-04	5.82E+09	4.07E+10
2010	0.559	2.07E-04	5.71E+09	4.00E+10	0.558	2.07E-04	5.70E+09	3.99E+10
2011	0.555	2.06E-04	5.67E+09	3.97E+10	0.547	2.02E-04	5.58E+09	3.91E+10
2012	0.551	2.04E-04	5.63E+09	3.94E+10	0.536	1.99E-04	5.47E+09	3.83E+10
2013	0.548	2.03E-04	5.59E+09	3.92E+10	0.526	1.95E-04	5.37E+09	3.76E+10
2014	0.545	2.02E-04	5.56E+09	3.89E+10	0.517	1.91E-04	5.28E+09	3.69E+10
2015	0.542	2.01E-04	5.53E+09	3.87E+10	0.508	1.88E-04	5.19E+09	3.63E+10

Table 18. ²³⁶U annual exported from the Bikini Atoll.

Year	ENEU				BRAVO			
	Calculated ²³⁶ U Coral Activity	Surrounding ²³⁶ U lagoon water	Total ²³⁶ U lagoon Activity	²³⁶ U Exported Annually	Calculated ²³⁶ U Coral Activity	Surrounding ²³⁶ U lagoon water	Total ²³⁶ U lagoon Activity	²³⁶ U Exported Annually
	Bq/kg	Bq/kg	Bq	Bq	Bq/kg	Bq/kg	Bq	Bq
1956	1.74E-04	1.74E-07	4.81E+06	3.37E+07				
1957	1.56E-04	1.56E-07	4.29E+06	3.00E+07				
1958	1.39E-04	1.39E-07	3.83E+06	2.68E+07				
1959	1.24E-04	1.24E-07	3.43E+06	2.40E+07				
1960	1.12E-04	1.12E-07	3.08E+06	2.16E+07	3.32E-04	9.14E+06	6.40E+07	6.40E-05
1961	1.01E-04	1.01E-07	2.77E+06	1.94E+07	2.90E-04	7.98E+06	5.59E+07	5.59E-05
1962	9.09E-05	9.09E-08	2.50E+06	1.75E+07	2.53E-04	6.99E+06	4.89E+07	4.89E-05
1963	8.23E-05	8.23E-08	2.27E+06	1.59E+07	2.22E-04	6.13E+06	4.29E+07	4.29E-05
1964	7.49E-05	7.49E-08	2.06E+06	1.44E+07	1.96E-04	5.39E+06	3.77E+07	3.77E-05
1965	6.83E-05	6.83E-08	1.88E+06	1.32E+07	1.72E-04	4.75E+06	3.33E+07	3.33E-05
1966	6.26E-05	6.26E-08	1.73E+06	1.21E+07	1.53E-04	4.21E+06	2.95E+07	2.95E-05
1967	5.76E-05	5.76E-08	1.59E+06	1.11E+07	1.36E-04	3.74E+06	2.62E+07	2.62E-05
1968	5.32E-05	5.32E-08	1.47E+06	1.03E+07	1.21E-04	3.33E+06	2.33E+07	2.33E-05
1969	4.94E-05	4.94E-08	1.36E+06	9.53E+06	1.08E-04	2.98E+06	2.09E+07	2.09E-05
1970	4.60E-05	4.60E-08	1.27E+06	8.88E+06	9.74E-05	2.68E+06	1.88E+07	1.88E-05
1971	4.31E-05	4.31E-08	1.19E+06	8.31E+06	8.81E-05	2.43E+06	1.70E+07	1.70E-05
1972	4.05E-05	4.05E-08	1.12E+06	7.81E+06	8.00E-05	2.21E+06	1.54E+07	1.54E-05
1973	3.82E-05	3.82E-08	1.05E+06	7.38E+06	7.31E-05	2.01E+06	1.41E+07	1.41E-05
1974	3.63E-05	3.63E-08	1.00E+06	7.00E+06	6.71E-05	1.85E+06	1.30E+07	1.30E-05
1975	3.45E-05	3.45E-08	9.52E+05	6.66E+06	6.20E-05	1.71E+06	1.20E+07	1.20E-05
1976	3.30E-05	3.30E-08	9.10E+05	6.37E+06	5.76E-05	1.59E+06	1.11E+07	1.11E-05
1977	3.17E-05	3.17E-08	8.74E+05	6.12E+06	5.38E-05	1.48E+06	1.04E+07	1.04E-05
1978	3.05E-05	3.05E-08	8.42E+05	5.89E+06	5.05E-05	1.39E+06	9.75E+06	9.75E-06
1979	2.95E-05	2.95E-08	8.14E+05	5.70E+06	4.77E-05	1.32E+06	9.21E+06	9.21E-06
1980	2.86E-05	2.86E-08	7.89E+05	5.52E+06	4.53E-05	1.25E+06	8.74E+06	8.74E-06
1981	2.79E-05	2.79E-08	7.68E+05	5.37E+06	4.32E-05	1.19E+06	8.34E+06	8.34E-06
1982	2.72E-05	2.72E-08	7.49E+05	5.24E+06	4.14E-05	1.14E+06	7.99E+06	7.99E-06
1983	2.66E-05	2.66E-08	7.33E+05	5.13E+06	3.99E-05	1.10E+06	7.70E+06	7.70E-06
1984	2.61E-05	2.61E-08	7.18E+05	5.03E+06	3.86E-05	1.06E+06	7.44E+06	7.44E-06
1985	2.56E-05	2.56E-08	7.06E+05	4.94E+06	3.74E-05	1.03E+06	7.22E+06	7.22E-06
1986	2.52E-05	2.52E-08	6.95E+05	4.86E+06	3.65E-05	1.00E+06	7.03E+06	7.03E-06
1987	2.49E-05	2.49E-08	6.85E+05	4.79E+06	3.56E-05	9.81E+05	6.87E+06	6.87E-06
1988	2.45E-05	2.45E-08	6.76E+05	4.74E+06	3.49E-05	9.61E+05	6.73E+06	6.73E-06
1989	2.43E-05	2.43E-08	6.69E+05	4.68E+06	3.43E-05	9.44E+05	6.61E+06	6.61E-06
1990	2.40E-05	2.40E-08	6.63E+05	4.64E+06	3.37E-05	9.29E+05	6.51E+06	6.51E-06
1991	2.38E-05	2.38E-08	6.57E+05	4.60E+06	3.33E-05	9.17E+05	6.42E+06	6.42E-06
1992	2.37E-05	2.37E-08	6.52E+05	4.56E+06	3.29E-05	9.06E+05	6.34E+06	6.34E-06
1993	2.35E-05	2.35E-08	6.48E+05	4.53E+06	3.25E-05	8.96E+05	6.27E+06	6.27E-06

1994	2.34E-05	2.34E-08	6.44E+05	4.51E+06	3.22E-05	8.88E+05	6.22E+06	6.22E-06
1995	2.32E-05	2.32E-08	6.41E+05	4.48E+06	3.20E-05	8.81E+05	6.17E+06	6.17E-06
1996	2.31E-05	2.31E-08	6.38E+05	4.46E+06	3.18E-05	8.75E+05	6.13E+06	6.13E-06
1997	2.30E-05	2.30E-08	6.35E+05	4.45E+06	3.16E-05	8.70E+05	6.09E+06	6.09E-06
1998	2.30E-05	2.30E-08	6.33E+05	4.43E+06	3.14E-05	8.66E+05	6.06E+06	6.06E-06
1999	2.29E-05	2.29E-08	6.31E+05	4.42E+06	3.13E-05	8.62E+05	6.03E+06	6.03E-06
2000	2.28E-05	2.28E-08	6.29E+05	4.40E+06	3.11E-05	8.58E+05	6.01E+06	6.01E-06
2001	2.28E-05	2.28E-08	6.28E+05	4.39E+06	3.10E-05	8.56E+05	5.99E+06	5.99E-06
2002	2.27E-05	2.27E-08	6.26E+05	4.38E+06	3.10E-05	8.53E+05	5.97E+06	5.97E-06
2003	2.27E-05	2.27E-08	6.25E+05	4.38E+06	3.09E-05	8.51E+05	5.96E+06	5.96E-06
2004	2.26E-05	2.26E-08	6.24E+05	4.37E+06	3.08E-05	8.49E+05	5.94E+06	5.94E-06
2005	2.26E-05	2.26E-08	6.23E+05	4.36E+06	3.08E-05	8.48E+05	5.93E+06	5.93E-06
2006	2.26E-05	2.26E-08	6.23E+05	4.36E+06	3.07E-05	8.46E+05	5.92E+06	5.92E-06
2007	2.26E-05	2.26E-08	6.22E+05	4.35E+06	3.07E-05	8.45E+05	5.92E+06	5.92E-06
2008	2.25E-05	2.25E-08	6.21E+05	4.35E+06	3.06E-05	8.44E+05	5.91E+06	5.91E-06
2009	2.25E-05	2.25E-08	6.21E+05	4.35E+06	3.06E-05	8.43E+05	5.90E+06	5.90E-06
2010	2.25E-05	2.25E-08	6.20E+05	4.34E+06	3.06E-05	8.43E+05	5.90E+06	5.90E-06
2011	2.25E-05	2.25E-08	6.20E+05	4.34E+06	3.06E-05	8.42E+05	5.89E+06	5.89E-06
2012	2.25E-05	2.25E-08	6.20E+05	4.34E+06	3.05E-05	8.41E+05	5.89E+06	5.89E-06
2013	2.25E-05	2.25E-08	6.19E+05	4.33E+06	3.05E-05	8.41E+05	5.89E+06	5.89E-06
2014	2.25E-05	2.25E-08	6.19E+05	4.33E+06	3.05E-05	8.41E+05	5.88E+06	5.88E-06
2015	2.24E-05	2.24E-08	6.19E+05	4.33E+06	3.05E-05	8.40E+05	5.88E+06	5.88E-06

References

- Asami, R., T. Yamada, Y. Iryu, C. P. Meyer, T. M. Quinn & G. Paulay (2004) Carbon and oxygen isotopic composition of a Guam coral and their relationships to environmental variables in the western Pacific. *Palaeogeography Palaeoclimatology Palaeoecology*, 212, 1-22.
- Baum, E. M., M. C. Ernesti, H. D. Knox, Miller, T. R. & A. M. Watson. 2010. *Nuclides and Isotopes Chart of the Nuclides* United States of America: Bechtel Marine Propulsion Corporation.
- Benninger, L. K. & R. E. Dodge (1986) Fallout plutonium and natural radionuclides in annual bands of the coral *Montastrea annularis*, St. Croix, U.S. Virgin Islands. *Geochim. Cosmochim. Acta*, 50, 2785-97.
- Bio-Rad Laboratories, I. 2017. 140-1454 Datasheet -- Bio-Rad Laboratories, Inc. -- AG 1-X8 Resin | Engineering360.
- Brown, T. A., A. A. Marchetti, R. E. Martinelli, C. C. Cox, J. P. Knezovich & T. F. Hamilton (2004) Actinide measurements by accelerator mass spectrometry at Lawrence Livermore National Laboratory. *Nuclear Instruments and Methods in Physics Research B: Beam Interactions*, 223-224, 788-795.
- Buddemeier, R. W. 1974. Environmental controls over annual and lunar monthly cycles in hermatypic coral calcification. : ReefBase :: ReefBase Pacific - Database. In *Second International Coral Reef Symposium*. Brisbane, Australia: The Great Barrier Reef Committee.
- Buddemeier, R. W. & J. E. Maragos (1974) Radiographic studies of reef coral exoskeletons: Rates and patterns of coral growth - ScienceDirect. *Journal of Experimental Marine Biology and Ecology*, 14, 179-199.
- Buesseler, K. O., M. A. Charette, S. M. Pike, P. B. Henderson & L. E. Kipp (2018) Lingering radioactivity at the Bikini and Enewetak Atolls. *Science of the Total Environment*, 621, 1185-1198.
- Choppin, G. R. (2006) Actinide speciation in aquatic systems. *Marine Chemistry*, 99, 83-92.
- Donard, O. F. X., F. Bruneau, M. Moldovan, H. Garraud, V. N. Epov & D. Boust (2007) Multi-isotopic determination of plutonium (²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu) in marine sediments using sector-field inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*, 587, 170-179.
- Energy, U. S. D. o. 2015. United States Nuclear Tests July 1945 through September 1992, DOE/NV--209 REV 16. ed. U. S. D. o. Energy. Las Vegas, NV: U.S. Department of Energy.
- Flor, T. H. & W. S. Moore. 1977. Radium/calcium and uranium/calcium determinations for western Atlantic reef corals. 556-561. Miami, Florida: 3rd International symposium on coral reefs.
- Froehlich, M. B., S. G. Tims, S. J. Fallon, A. Wallner & L. K. Fifield (2017) Nuclear weapons produced U-236, (PU)-P-239 and Pu-240 archived in a *Porites Lutea* coral from Enewetak Atoll. *Journal of Environmental Radioactivity*, 178, 349-353.
- Gouveia, F., R. Bradsher, J. Brunk, W. Robison & T. Hamilton. 2002. Meteorological Monitoring on Bikini Atoll: System Description and Data Summary (May 2000-April 2001). Livermore, CA: LLNL.
- Guilderson, T. P. & D. P. Schrag (1999) Reliability of coral isotope records from the western Pacific warm pool: A comparison using age-optimized records. *Paleoceanography*, 14, 457-464.
- Hamilton, T., D. Dasher, T. Brown, R. Martinelli, A. Marchetti & S. Kehl (2009) Determination of plutonium activity concentrations and Pu-240/Pu-239 atom ratios in Brown Algae (*Fucus distichus*) collected from Amchitka Island, Alaska. *Journal of Radioanalytical and Nuclear Chemistry*, 282, 477-482.
- Hamilton, T., D. Hickman, C. Conrado, T. Brown, J. Brunk, A. Marchetti, C. Cox, R. Martinelli, S. Kehl, K. Johannes, D. Henry, T. Bell & G. Petersen. 2002. Individual radiation protection monitoring in the Marshall Islands: Enewetak Island Resettlement support (May-December 2001). LLNL.

- Hamilton, T. F. 2004. Linking legacies of the Cold War to arrival of anthropogenic radionuclides in the oceans through the 20th century. In *Marine radioactivity*, ed. H. D. Livingston, 30-87. Amsterdam: Elsevier.
- . 2019. History of Plutonium Contamination Inside Bikini Lagoon: Retrospective Analysis of Coral Cores. DOE-RMI Annual Meeting. Majuro.
- Hamilton, T. F., J. C. Millies-Lacroix & G. H. Hong. 1996. ^{137}Cs (^{90}Sr) and Pu Isotopes in the Pacific Ocean: Sources & Trends. In *International Symposium of Radionuclides in the Ocean*. Cherbourg-Octeville, France.
- Hicks, H. G. (1982) Calculation of the Concentration of Any Radionuclide Deposited on the Ground by Offsite Fallout from a Nuclear Detonation. *Health Physics*, 42, 585-600.
- Hirose, K. (2009) Plutonium in the Ocean Environment: Its Distributions and Behavior. *Journal of Nuclear and Radiochemical Sciences*, 10.
- Horwitz, E. P. Extraction Chromatography of actinides and Selected Fission Products: Principles and Achievement of Selectivity. *Eichrom Inc.* <http://www.eichrom.com/products/extraction.aspx> (last accessed).
- Horwitz, E. P., M. L. Dietz, R. Chiarizia, H. Diamond, S. L. Maxwell III & M. R. Nelson (1995) Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions - ScienceDirect. *Analytica Chimica Acta*, 310, 63-78.
- Kelley, J. M., L. A. Bond & T. M. Beasley (1999) Global distribution of Pu isotopes and ^{237}Np . *Science of The Total Environment*, 237-238, 483-500.
- Lachner, J., M. Christl, T. Bisinger, R. Michel & H.-A. Synal (2010) Isotopic signature of plutonium at Bikini atoll. *Applied Radiation and Isotopes*, 68, 979-983.
- Liao, H., J. Zheng, F. Wu, M. Yamada, M. Tan & J. Chen (2008) Determination of plutonium isotopes in freshwater lake sediments by sector-field ICP-MS after separation using ion-exchange chromatography. *Applied Radiation and Isotopes*, 66, 1138-1145.
- Lindahl, P., M. B. Andersen, M. Keith-Roach, P. Worsfold, K. Hyeong, M. S. Choi & S. H. Lee (2012) Spatial and temporal distribution of Pu in the Northwest Pacific Ocean using modern coral archives. *Environment International*, 40, 196-201.
- Lindahl, P., R. Asami, Y. Iryu, P. Worsfold, M. Keith-Roach & M. S. Choi (2011) Sources of plutonium to the tropical Northwest Pacific Ocean (1943-1999) identified using a natural coral archive. *Geochimica Et Cosmochimica Acta*, 75, 1346-1356.
- Lindahl, P., M. Keith-Roach, P. Worsfold, M. S. Choi, H. S. Shin & S. H. Lee (2010) Ultra-trace determination of plutonium in marine samples using multi-collector inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*, 671, 61-69.
- Martinelli, R. E., T. F. Hamilton, R. W. Williams & S. R. Kehl (2009) Separation of uranium and plutonium isotopes for measurement by multi collector inductively coupled plasma mass spectroscopy. *Journal of Radioanalytical and Nuclear Chemistry*, 282, 343-347.
- Maxwell III, S. L. & B. K. Culligan (2009) Rapid separation method for emergency water and urine samples. *Journal of Radioanalytical and Nuclear Chemistry*, 279.
- Meece, D. E. & L. K. Benninger (1993) The coprecipitation of plutonium and other radionuclides with calcium carbonate. *Geochimica et Cosmochimica Acta*, 57, 1447-1458.
- Moore, W. S. & S. Krishnaswami. 1974. CORRELATION OF X RADIOGRAPHY REVEALED BANDING IN CORALS WITH RADIOMETRIC GROWTH RATES.
- Moore, W. S., S. Krishnaswami & S. G. Bhat (1973) Coral Reef Project—Papers in Memory of Dr. Thomas F. Goreau. 6. Radiometric Determinations of Coral Growth Rates. *Bulletin of Marine Science*, 23, 157-176.

- Muramatsu, Y., T. Hamilton, S. Uchida, K. Tagami, S. Yosida & W. Robison (2001) **Measurement of $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratios in soils from the Marshall Islands using ICP-MS.** *The Science of the Total Environment*, 278, 151-159.
- Nomura, T., A. Sakaguchi, P. Steier, R. Egl, A. Yamakawa, T. Watanabe, K. Sasaki, T. Watanabe, R. Golser, Y. Takahashi & H. Yamano (2017) Reconstruction of the temporal distribution of $^{236}\text{U}/^{238}\text{U}$ in the Northwest Pacific Ocean using a coral core sample from the Kuroshio Current area - ScienceDirect. *Marine Chemistry*, 190, 28-34.
- Noshkin, V. E., R. J. Eagle & K. M. Wong (1976) Plutonium levels in Kwajalein Lagoon. *Nature*, 262, 745-748.
- Noshkin, V. E., K. M. Wong, R. Eagle & C. Gatrouris. 1974. Transuranics at Pacific Atolls 1. Concentrations in the waters at Eniwetok and Bikini. Univ. of Calif. Lawrence Livermore Laboratory.
- Noshkin, V. E., K. M. Wong, R. J. Eagle & C. Gatrouris (1975) Transuranics and other radionuclides in Bikini Lagoon. Concentration data retrieved from aged coral sections. *Limnol. Oceanogr.*, 20, 729-42.
- Noshkin, V. E., K. M. Wong, T. A. Jokela, J. L. Brunk & R. J. Eagle. 1987. Plutonium and americium behavior in coral atoll environments. In *Oceanic Processes in Marine Pollution*, eds. T. P. Conner, W. V. Burt & I. A. Duedall, 159-174. Malabar, Florida: Robert E. Krieger Publishers.
- Owens, S. A., K. O. Buesseler & K. W. W. Sims (2011) Re-evaluating the ^{238}U -salinity relationship in seawater: Implications for the ^{238}U – ^{234}Th disequilibrium method. *Marine Chemistry*, 127, 31-39.
- Pereira, N. S., A. N. Sial, R. Frei, C. V. Ullmann, C. Korte, R. K. P. Kikuchi, V. P. Ferreira & K. H. Kilbourne (2017) The potential of the coral species *Porites astreoides* as a paleoclimate archive for the Tropical South Atlantic Ocean. *Journal of South American Earth Sciences*, 77, 276-285.
- Program, P. C. C. S. 2011. Current and Future Climate of the Marshall Islands.
- Quinn, T. M. & D. E. Sampson (2002) A multiproxy approach to reconstructing sea surface conditions using coral skeleton geochemistry. *Paleoceanography*, 17, 11.
- Robinson, L. F., J. F. Adkins, D. P. Fernandez, D. S. Burnett, S.-L. Wang & A. C. Gagnon, Krakauer, Nir (2006) Primary U distribution in scleractinian corals and its implications for U series dating. *Geochemistry Geophysics Geosystems*, 7.
- Sakaguchi, A., K. Kawai, P. Steier, F. Quinto, K. Mino, J. Tomita, M. Hoshi, N. Whitehead & M. Yamamoto (2009) First results on ^{236}U levels in global fallout. *Science of The Total Environment*, 407, 4238-4242.
- Sakaguchi, A., T. Nomura, P. Steier, R. Gloser, K. Sasaki, T. Watanabe, T. Nakakuki, Y. Takahashi & H. Yamano (2016) Temporal and vertical distributions of anthropogenic U-236 in the Japan Sea using a coral core and seawater samples. *Journal of Geophysical Research-Oceans*, 121, 4-13.
- Salbu, B., V. Kashparov, O. C. Lind, R. Garcia-Tenorio, M. P. Johansen, D. P. Child, P. Roos & C. Sancho (2018) Challenges associated with the behaviour of radioactive particles in the environment. *Journal of Environmental Radioactivity*, 186, 101-115.
- Simon, S. L. & W. L. Robison (1997) A compilation of nuclear weapons test detonation data for U.S. Pacific ocean tests (Journal Article) | SciTech Connect. *Health Physics*, 73, 258-264.
- Spennemann, D. H. R. & I. Marschner. 1994. Stormy Years. On the association between the El Nino Southern oscillation phenomenon and the occurrence of typhoons in the Marshall Islands. Report to the Federal Emergency Management Agency, Region IX, San Francisco. In *Johnston Centre for Parks, Recreation and Heritage Report*. Albury, NSW: Charles Sturt University.
- UNSCEAR. 2000. Sources and Effects of Ionizing Radiation: United Nations Scientific Committee on the Effects of Atomic Radiation. New York.
- . 2010. Sources and effects of ionizing radiation: United Nations Scientific Committee on the Effects of Atomic Radiation 2008 Report. New York.

- Veron, J. E. N. 1998. *Corals of Australia and the Indo-Pacific*. Honolulu: University of Hawaii Press.
- Weber, J. N., E. W. White & P. H. Weber (1975) CORRELATION OF DENSITY BANDING IN REEF CORAL SKELETONS WITH ENVIRONMENTAL PARAMETERS THE BASIS FOR INTERPRETATION OF CHRONOLOGICAL RECORDS PRESERVED IN THE CORALLA OF CORALS. *Paleobiology*, 1, 137-149.
- Weber, J. N. & P. M. Woodhead (1972) TEMPERATURE DEPENDENCE OF OXYGEN-18 CONCENTRATION IN REEF CORAL CARBONATES. *Journal of Geophysical Research*, 77, 463-&.
- Winkler, S. R., P. Steier & J. Carilli (2012) Bomb fall-out U-236 as a global oceanic tracer using an annually resolved coral core. *Earth and Planetary Science Letters*, 359, 124-130.
- Wright, T. Tropical storm Talas formation and impacts at Kwajalein Atoll. American Meteorological Society.

Curriculum Vitae

Athena M. Gallardo
a.m.gallardo85@gmail.com

Education

Doctor of Philosophy – Radiochemistry 2013-2019
University of Nevada, Las Vegas, GPA 4.0 Las Vegas, NV
Thesis: “The Retrospective Analysis of Radionuclides in Banded Coral from the Bikini Atoll”
Advisor: Dr. Frederic Poineau

Master of Science – Environmental Health Physics 2011- 2013
University of Nevada, Las Vegas, GPA 3.65 Las Vegas, NV
Thesis: “Investigation of Storage-phosphor Autoradiography for the Rapid Quantitative Screening of Air Filters for Emergency Response Purposes”
Advisor: Dr. Ralf Sudowe

Bachelor of Science – Health Physics 2006-2011
University of Nevada, Las Vegas, GPA 3.07 Las Vegas, NV

Research Experience

Lawrence Livermore National Lab– Ph.D. Research 2016-2019

Ph.D. research analyzed the change in solubility and export potential of Pu and U in bottom lagoon sediments at the Bikini Atoll which provides a continuous source of Pu ($^{239+240}\text{Pu}$) and U (^{236}U) to the Pacific Basin. The rate at which these isotopes are flushed from the lagoon to the ocean is balanced by inputs from remobilization of lagoon sediments. This is important to better understand long-term consequences of these isotopes transferred to the marine environment and/or local food chains. A chronological record of $^{239+240}\text{Pu}$ and ^{236}U concentrations and isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$ and $^{236}\text{U}/^{239}\text{Pu}$) within the lagoon was developed by analyzing two banded corals retrieved from the Bikini Atoll in 2016. Chronology was determined using x-ray imaging and stable isotope analysis using isotope-ratio mass spectrometry (IRMS). Extraction chromatography and anion exchange columns were utilized to separate and purify Pu and U from the coral matrix. $^{239+240}\text{Pu}$ and ^{236}U concentrations and isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$ and $^{236}\text{U}/^{239}\text{Pu}$) were calculated from measurements of Pu isotopes and ^{236}U using accelerator mass spectrometry (AMS). ^{235}U and ^{238}U concentrations and $^{235}\text{U}/^{238}\text{U}$ ratios were assessed using inductively coupled plasma mass spectrometry (ICP-MS). This information was used to construct a model of the loss rate of $^{239+240}\text{Pu}$ and ^{236}U inside Bikini Atoll Lagoon. Isotopic ratio measurements suggest that the source-term of Pu and U inside the lagoon is slowly changing overtime.

University of Nevada, Las Vegas 2013-2015
Conducted preliminary research which aims to investigate the mechanism that resulted in the migration of ^{241}Am away from the refractory matrix WGP contained in BOMARC soil cores. Segmented soil cores were analyzed for WGP and ^{241}Am was quantified using a broad energy germanium detector. This research will help to investigate the effect of weathering on special

nuclear materials and potentially provide access to new signatures from the local environment in which hot particles are present.

Lawrence Livermore National Lab- NSSC-MSI Summer Fellowship Research Summer 2015

Assisted the bioassay lab with developing a quick method to quantify low levels of ^{242}Pu in urine samples using extraction chromatography and ICP-MS.

University of Nevada, Las Vegas 2014

Assisted the Department of Energy Remote Sensing Laboratory and the UNLV Department of Geosciences with ground truth measurements at Lake Mojave. Soil samples, radon measurements, HPGE measurements and gamma dose measurements were taken. This data will be used to determine a radiological background dose which will be associated to geological formations.

University of Nevada, Las Vegas- M.S. Research 2011-2013

M.S. researched focused on the preliminary development of a quantitative and qualitative method using autoradiography for the rapid quantitative screening of air filters containing plutonium and americium. This method provides spatial distribution of the radioactivity within the filter debris which is important during emergency response situations. Samples containing varying activities of either ^{241}Am or ^{239}Pu tracers were produced through microprecipitation and assayed by alpha spectroscopy. Samples were subsequently imaged, using storage phosphor autoradiography, and an activity calibration curve was produced by comparing the digital light units recorded from the image to the known activity of the source. The usefulness of different phosphor screens was examined by exposing each type of film to the same standard nuclide for varying quantities of time. Unknown activity samples created through microprecipitation containing activities of either ^{241}Am or ^{239}Pu as well as air filters doped with beta and alpha emitting nuclides were imaged and activities were determined by comparing the image to the activity calibration curve.

University of Nevada, Las Vegas- Undergraduate Research 2011

Assisted a Radiochemistry PhD student with optimizing an extraction chromatography-based separation procedure for multiple actinide elements which was applied to NIST ocean sediment standard reference material. Analyses of all samples were performed by alpha spectroscopy.

Awards and Honors

- F. Ward Whicker Scholarship, HPS Environmental Section, Fall 2016-Spring 2017
- Nuclear Science and Security Consortium Graduate Fellowship, Fall 2013-2017
- Nuclear Science and Security Consortium MSI Summer Fellowship, Summer 2015
- Roy G Post Scholarship Recipient, 2015
- Longenecker & Associates Scholarship Recipient, 2015
- Health Physics Travel Grant, Summer 2010 and Summer 2011
- Dean's List- Fall 2003, Spring 2004, Fall 2005

Related Training

- NSSC Nuclear Analytical Techniques Summer School, UC Davis, July 13-19, 2016
- LANL-SNL Nuclear Security and Safeguards Summer School, August 3-12, 2015
- Basics of Nuclear Reactor Operations Summer School, UCI, July 21- August 1, 2014
- Public Policy and Nuclear Threats Boot Camp, UCSD IGCC, July 6-16, 2014
- Mass Spectroscopy Workshop, PNNL, June 17-18, 2014
- Ludlum Basic Radiation Instrumentation Calibration Course, Las Vegas 2013

Publications

1. **A. M. Gallardo**, C. Than, C. T. Wong, R. Sudowe. A rapid method for quantification of ^{242}Pu in urine samples using extraction chromatography and ICP-MS. *Health Physics Journal*, 112, 246-251, 2017.
2. S. A. Faye, J. M. Richards, **A. M. Gallardo**, K. R. Campbell, R. Sudowe. Development of a standardized sequential extraction protocol for simultaneous extraction of multiple actinide elements. *Journal of Radioanalytical and Nuclear Chemistry*, 311, 2017.

Presentations and Posters

1. **A. M. Gallardo**, R. Sudowe, "Investigation of Storage-phosphor Autoradiography for the Rapid Quantitative Screening of Air Filters for Emergency Response Purposes," American Nuclear Society Student Conference 2013, Boston, MA, April 2013, *Presentation*
2. **A. M. Gallardo**, R. Sudowe, "Investigation of Storage-phosphor Autoradiography for the Rapid Quantitative Screening of Air Filters for Emergency Response Purposes," 54th Radiobioassay and Radiochemical Measurements Conference, Rohnert Park, CA, October 2013, *Presentation*
3. **A. M. Gallardo**, R. Sudowe, "Quantification of Americium in Soil Cores from the Site of the BOMARC Accident," American Nuclear Society Student Conference 2014, State College, PA, April 2014, *Poster*
4. **A. M. Gallardo**, R. Sudowe, "Quantification of Americium in Soil Cores from the Site of the BOMARC Accident," 248th American Chemical Society National Meeting and Exposition, San Francisco, CA, August 2014, *Presentation*
5. **A. M. Gallardo**, R. Sudowe, "Quantification of Americium in Soil Cores from the Site of the BOMARC Accident," Conference of the National Society of Black Physicists, Baltimore, MD, February 2015, *Presentation*
6. **A. M. Gallardo**, R. Sudowe, "Investigation of the Release and Mobility of Americium from Refractory Plutonium at the Site of the BOMARC Accident," Methods & Applications of Radioanalytical Chemistry X, Kailua-Kona, HI, April 2015, *Poster*
7. **A.M. Gallardo**, T. Hamilton, R. Sudowe, "Quantification of Plutonium in Coral from a Former Nuclear Test Site," University & Industry Technical Interchange Program & Technical Review Meeting, Raleigh, NC, June 2016, *Presentation*
8. **A.M. Gallardo**, T. Hamilton, F. Poineau, "Retrospective Analysis of Plutonium in Banded Coral Cores from Bikini Atoll," University Program Review Meeting, Ann Arbor, MI, June 2018, *Presentation*

9. **A.M. Gallardo**, T. Hamilton, F. Poineau, "Retrospective Analysis of Plutonium in Banded Coral Cores from Bikini Atoll," Schubert Review Meeting-NSSC Radiochemistry and Forensics Focus Area, Las Vegas, NV, September 2018, *Presentation*
10. **A.M. Gallardo**, T. Hamilton, F. Poineau, "Retrospective Analysis of Plutonium in Banded Coral Cores from Bikini Atoll," 2018 NSSC Fall Workshop and Advisory Board Meeting, Livermore, CA, October 2018, *Poster*
11. **A.M. Gallardo**, T. Hamilton, F. Poineau, "Retrospective Analysis of Plutonium in Banded Coral Cores from Bikini Atoll," 2019 NSSC Fall Workshop and Advisory Board Meeting, Livermore, CA, October 2019, *Presentation*

Skills

- Chemistry of actinides and fission product elements- inorganic, trace and environmental chemistry
- Separation and chromatography techniques- extraction chromatography, solvent extraction, ion exchange
- Analytical- ICP-MS, α -spectroscopy, γ -spectroscopy, LSC, gas proportional counting, autoradiography