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# Determination of Plutonium Activity Concentrations and $^{240}Pu/^{239}Pu$ Atom Ratios in Brown Algae (*Fucus distichus*) Collected from Amchitka Island, Alaska.

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## Final Report

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**Summary**

Plutonium-239 ($^{239}Pu$) and plutonium-240 ($^{240}Pu$) activity concentrations and $^{240}Pu/^{239}Pu$ atom ratios are reported for Brown Algae (*Fucus distichus*) collected from the littoral zone of Amchitka Island (Alaska) and at a control site on the Alaskan peninsula. Plutonium isotope measurements were performed in replicate using Accelerator Mass Spectrometry (AMS). The average $^{240}Pu/^{239}Pu$ atom ratio observed in dried *Fucus d.* collected from Amchitka Island was 0.227 ± 0.007 (n=5) and compares with the expected $^{240}Pu/^{239}Pu$ atom ratio in integrated worldwide fallout deposition in the Northern Hemisphere of 0.1805 ± 0.0057 (Cooper et al., 2000). In general, the characteristically high $^{240}Pu/^{239}Pu$ content of *Fucus d.* analyzed in this study appear to indicate the presence of a discernible basin-wide secondary source of plutonium entering the marine environment. Of interest to the study of plutonium source terms within the Pacific basin are reports of elevated $^{240}Pu/^{239}Pu$ atom ratios in fallout debris from high-yield atmospheric nuclear tests conducted in the Marshall Islands during the 1950s (Diamond et al., 1960), the wide range of $^{240}Pu/^{239}Pu$ atom ratio values (0.19 to 0.34) observed in sea water, sediments, coral and other environmental media from the North Pacific Ocean (Hirose et al., 1992; Buesseler, 1997) and updated estimates of the relative contributions of close-in and intermediate fallout deposition on oceanic inventories of radionuclidies, especially in the Northern Pacific Ocean (Hamilton, 2004).

## 1.0 Introduction

The United States Atomic Energy Commission created a nuclear weapons testing facility on Amchitka Island, Alaska, in the early 1960s. Amchitka Island forms part of the Aleutian island chain that divides the Bering Sea from the northern Pacific Ocean, and is situated on a submarine ridge that extends from the Alaskan Peninsula to the Russian Far East. Three underground nuclear tests were conducted on Amchitka Island between 1965 and 1971; Long Shot, Milrow, and Cannikin with explosive yields of approximately 0.08 Mt, 1.0 Mt and 5.0 Mt, respectively (USDOE, 2000). The Cannikin test was the largest underground nuclear test ever conducted by the United States and produced a subsistence crater about 1.5 km wide and 16 m deep. The crater has since filled with water and is now known as Cannikin Lake. The nuclear test facilities on Amchitka Island were closed down in 1994 but scientists, the State of Alaska, and indigenous population groups continue to express concern about the long-term health and ecological consequences of the test program on the region. Moreover, the potential exists for seismic activity in the region to generate new underground fissures and rock fractures along the coastline of Amchitka Island, which could open up new pathways for release of residual radioactivity contained in nuclear blast cavities into the near-surface environment.

Numerous radiological studies took place at Amchitka from the late 1960 into the 1970's in order to evaluate the levels and origin of artificial radioactivity around the island. More recently, independent surveys conducted by environmental groups have reportedly detected the presence of americium-241 ($^{241}$Am) (and plutonium isotopes) in biological samples taken from surface- or groundwater flows (Greenpeace, 1996). Subsequent to the 1996 report, Greenpeace speculated that $^{241}$Am was a primary indicator of leakage from underground test cavities (Greenpeace, 1998) which raised concerns about the possible migration of radioactive contaminants into the marine environment. Aleut Natives living in the Aleutian Islands harvest fish, marine mammals and other subsistence foods from around the Amchitka Island. Consequently, there has been a renewed interest in assessing the radiological situation at Amchitka and the surrounding marine environment.

Scientists from the Lawrence Livermore National Laboratory (LLNL) in California were contracted by the State of Alaska to provide plutonium isotope data on dried *Fucus d.* samples as part of the first marine survey for radionuclides at Amchitka since the late 1970s. Radiological survey data for technicum-99 ($^{99}$Tc) and tritium ($^{3}$H) in *Fucus d.* and marine waters were developed by other groups and is to be reported separately.

## 2.0 Materials and Methods

All samples of *Fucus d.* were collected within the littoral zone of the marine environment. Eighteen samples of dried *Fucus d.* from 6 different sampling transects were received from the University of Alaska, Fairbanks (UAF) analyzed for plutonium isotopes at the Center for Accelerator Mass Spectrometry (CAMS). The sample collection included 5 sites located around Amchitka Island and 1 control site, near Unalaska, about 1300 km

in distance, northeast of Amchitka Island, on the Alaskan Peninsula. No additional sample treatment or homogenization was performed other than to pool sample aliquots collected from each transect. Each composite sample contained about 60 g of dried material. All samples were analyzed as replicate splits (N=3) from a single bulk digest and the results reported as the mean and standard deviation of these measurements. Reagent blanks and a mixed seaweed reference material, supplied by the International Atomic Energy Agency (IAEA) (IAEA-308) were prepared and analyzed with the test samples. Plutonium isotope activity concentrations and $^{240}Pu/^{239}Pu$ atom ratios for each sample site are reported as the arithmetic mean and standard deviation of the replicate measurements.

#### $^{239}Pu/^{240}Pu$ activity concentrations and $^{240}Pu/^{239}Pu$ atom ratios

Plutonium isotope concentration and atom ratio measurements were performed at the LLNL using Accelerator Mass Spectrometry (AMS) (Brown et al., 2004). Samples of dried Fucus d. were first weighed into glass beakers and ashed at 400°C for 64 hours. The ash residue was then spiked with $1.8\times10^{10}$ atoms of plutonium-242 ($^{242}Pu$) and digested in concentrated nitric acid with periodic additions of hydrogen peroxide. Plutonium isotopes were separated from the bulk-sample matrix by ion-exchange chromatography (AG1-X8, BioRad Industries) and eluted into 10 M $HCl/NH_4I$ solution. The elutant was evaporated to near-dryness and plutonium recovered by coprecipitation on a small amount of iron (Fe) hydroxide. The Fe hydroxide precipitate was recovered by centrifugation, transferred to a quartz vial and ignited at 800°C. The residue was then mixed with 3 mg of niobium metal powder and packed into aluminum AMS sample target ready for analysis. Isotope dilution measurements based on the reference isotope spike ($^{242}Pu$) were normalized to Certified Reference Materials, (CRM) 128 ($^{239}Pu/^{242}Pu$ = 0.9993 ± 0.0003) and CRM 138 ($^{240}Pu/^{239}Pu$ = 0.0863 ± 0.0001), traceable to the U.S. National Institute of Standards and Technology (NIST).

The AMS system used for low-level plutonium isotope measurements at the Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratory is shown in Figure 1.

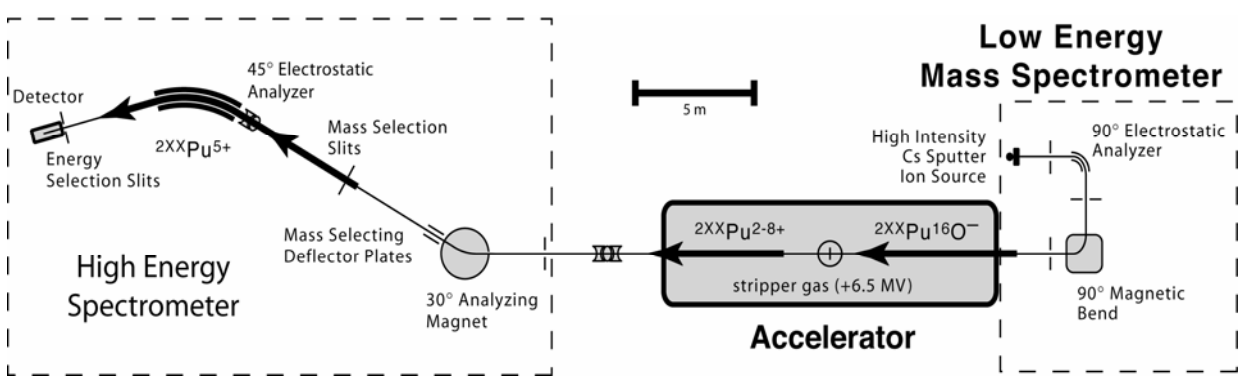


Figure 1. Heavy isotope accelerator mass spectrometry system at LLNL

Negative plutonium ions (e.g., $^{239\text{-}244}Pu^{16}O^{-}$) are produced from sample targets using a cesium sputter source and injected into the accelerator through a 90° electrostatic analyzer. Negative ions entering the accelerator are stripped, converted to positive ions and accelerated into the high-energy spectrometer of the AMS system. The high-energy spectrometer was designed to selectively transport 5+ ions to the detector using electrostatic deflection of desired ions through image slits coupled with fast mass switching of the low-energy spectrometer and quasi-continuous normalization to the reference isotope (e.g., $^{242}Pu^{5+}$). Ions are counted on a two-anode, longitudinal field gas-ionization detector with sufficient resolution to allow clean rejection of interfering ions at 4+ and lower charge states. The total measurement efficiency is about ~$5\times10^{-5}$ with observed background levels routinely falling below ~$5\times10^{5}$ atoms (equivalent to about 0.5 μBq and 2 μBq of $^{239}Pu$ and $^{240}Pu$, respectively).

## RESULTS

Results of the analyses are shown in Table 1. Measurement data for AMS targets containing Certified Reference Material were all within stated uncertainties and, therefore, show no evidence of mass-dependent biases. The measured $^{239+240}Pu$ content of the quality control sample (IAEA-308, Mixed Seaweed) was also consistent with the recommended value (Table 1).

The activity concentration of $^{239}Pu$ and $^{240}Pu$ in dried *Fucus d.* (N=5) from Amchitka Island ranged from 0.043 ± 0.001 to 0.060 ± 0.002 Bq $kg^{-1}$, and 0.035 ± .004 to 0.048 ± 0.002 Bq $kg^{-1}$, respectively. The arithmetic mean $^{239+240}Pu$ activity concentration of these samples of 0.095 ± 0.011 Bq $kg^{-1}$ is statistically higher that the level of 0.044 ± 0.003 Bq $kg^{-1}$ measured in *Fucus d.* from the control site (Table 1).

The $^{240}Pu/^{239}Pu$ atom ratios of Amchitka samples (arithmetic mean = 0.227 ± 0.007) are also outside the expected range observed in integrated worldwide fallout deposition in the Northern Hemisphere, i.e., 0.1808 ± 0.0057 (Cooper et al., 2000). However, the range of plutonium isotope ratio values observed in *Fucus d.* from the Bering Sea are consistent previously reported results for sea water and sediments collected from the Bering Sea and Bristol Bay (Hameedi et al., 1999), and in seawater, surface sediment and coral from the central North Pacific (Buesseler, 1997). Samples of *Fucus d.* sampled near the Cannikin and Milrow test sites in 1997 also contained an elevated average $^{240}Pu/^{239}Pu$ atom ratio (Dasher et al., 2002) relative to integrated worldwide fallout deposition. In contrast, previous studies in the terrestrial environment at Amchitka have found no evidence of perturbations in the $^{240}Pu/^{239}Pu$ atom ratio relative to that contained in integrated fallout deposition (Dasher et al., 2002). We conclude from these data that any assessment of the radiological situation at Amchitka, especially in relation to uptake and transfer of plutonium through the marine foodchain, will require knowledge of other major *basin-wide* sources of plutonium in the Pacific Ocean, the largest contributor of which is close-in and tropospheric fallout from the Pacific Proving Ground in the Marshall Islands (Hamilton, 2004) and export of soluble forms of plutonium into the Bering Sea.

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Table 1. Measurement of plutonium activity concentrations and $^{240}$Pu/$^{239}$Pu isotope ratios in *Fucus* distichus from Amchitka Island, Alaska

| Location & Field ID# | $^{239}$Pu | $^{240}$Pu | $^{239+240}$Pu | $^{240}$Pu/$^{239}$Pu atom ratio |
|---|---|---|---|---|
| | Bq kg$^{-1}$, dry (arithmetic mean and standard deviation of replicate measurements) | | | |
| **Amchitka** | | | | |
| 2.17.01-2.17.03 | 0.060 ±0.002 | 0.048 ±0.002 | 0.108 ±0.003 | 0.220 ±0.004 |
| 3.17.01-3.17.03 | 0.043 ±0.001 | 0.035 ±0.004 | 0.077 ±0.004 | 0.220 ±0.02 |
| 4.17.01-4.17.03 | 0.050 ±0.001 | 0.042 ±0.004 | 0.092 ±0.004 | 0.228 ±0.02 |
| 23.17.01-23.17.03 | 0.055 ±0.001 | 0.048 ±0.006 | 0.103 ±0.006 | 0.236 ±0.02 |
| 22.1701-22.17.03 | 0.051 ±0.007 | 0.044 ±0.006 | 0.095 ±0.009 | 0.233 ±0.02 |
| arithmetic mean & standard deviation | 0.052 ±0.002 | 0.043 ±0.001 | 0.095 ±0.002 | 0.227 ±0.007 |
| **Control Site**[a] | | | | |
| 25.17.01-25.17.03 | 0.024 ±0.001 | 0.020 ±0.002 | 0.044 ±0.003 | 0.219 ±0.03 |
| **QC sample** (N=2)[b] | 0.312 ±0.013 | 0.199 ±0.008 | 0.511 ±0.015 | 0.173 ±0.0003 |

[a.] Single sample station located in the littoral zone off Unalaska, Alaska (mean and standard deviation of 3 replicate measurements)

[b.] IAEA 308 Seaweed Mix, Recommended value $^{239+240}$Pu = 0.5 Bq kg$^{-1}$, dry weight (95% confidence interval = 0.46 to 0.52 Bq kg$^{-1}$)