



U.S. DEPARTMENT OF
ENERGY

PNNL-20912

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Analysis of a Nuclear Accident: Fission and Activation Product Release from the Fukushima Daiichi Nuclear Facility as Remote Indicators of Source Identification, Extent of Release, and State of Damaged Spent Nuclear Fuel

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January 2012



Pacific Northwest
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Printed in the United States of America

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(9/2003)

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January 17, 2012

Abstract

Measurements of radionuclides within environmental samples taken from the Fukushima Daiichi nuclear facility and reported on the Tokyo Electric Power Company website following the recent tsunami-initiated catastrophe were evaluated. From this effort, Units 1 and 3 were identified as the major source of radioactive contamination to the surface soil close to the facility. This release was likely dictated primarily by chemical volatility driven by temperature and reduction potential within the primary containment vessels of the vented reactors. All coolant had likely evaporated by the time of venting and damage to fuel bundles was likely extensive, minimizing any containment due to physical migration of these species through the fuel matrix and across the cladding wall. Isotopic ratios of Pu with distance from the source indicated that the damaged reactors were the major contributor of plutonium to surface soil at the source but that this contribution likely decreased rapidly with distance from the facility. The fraction of the total plutonium inventory released to the environment from venting Units 1 and 3 relative to cesium was estimated to be ~0.003% based upon two independent evaluations. Significant volatile radionuclides within the spent fuel at the time of venting but not as yet observed and reported within environmental samples are suggested as potential analytes of concern for future environmental surveys around the site.

Introduction

One of the most severe nuclear accidents occurred at the Tokyo Electric Power Company (TEPCO) Fukushima Daiichi Nuclear Power Station on March 11, 2011, following the largest earthquake in recorded Japanese history (magnitude 9.0 on the Richter scale). The epicenter of the earthquake was located 112 miles offshore northwest of the facility. This event triggered a total of seven tsunamis that impacted the site, with a maximum height of 14 to 15 m. Water and debris from the tsunamis overtook a 6-meter-high seawall protecting the site, destroyed off-site power and most backup generators on-

site, blocked seawater intakes, and flooded most of the facilities under 4 m of water. An extensive summary of the events surrounding this accident has been provided by the Institute of Nuclear Power Operations (1).

The TEPCO Fukushima Daiichi Facility consisted of six boiling water reactors (BWRs), with a combined generating power capability of 5480 MWe. At the time of the accident, three of the six reactor units were in operation (Units 1, 2, and 3). The reactor at Unit 4 had been shut down since November 30, 2010, and all of its fuel had been offloaded to the shared spent fuel pool nearby. This pool was the largest spent fuel storage on site, containing 1,331 spent nuclear fuel assemblies or 1.4 times the amount of fuel contained within reactor Units 1 and 3 at the time of the earthquake (1). Units 5 and 6 were also in a planned shutdown, but still had their fuel loaded, reactor pressure vessels installed, and cooling water at normal levels. Units 5 and 6 were successfully shut down without any significant release of radionuclides to the environment (1).

The earthquake initiated automatic scrams for Units 1, 2 and 3, beginning a sequence designed to shut down these reactors safely. This sequence, which is designed to cool reactor cores to a safe temperature, was interrupted, however, upon the arrival of the tsunamis and loss of primary and backup power. With the loss of any heat removal capability, temperatures within the primary containment vessels of Units 1, 2, and 3 quickly rose to >900° C. Pressures in Units 1 and 3 also increased beyond the design specifications for these vessels due to a chemical reaction (2-3) between water and the zirconium cladding of the fuel. This reaction occurs at high temperatures and produces H_{2(g)} (Eq. 1).



This exothermic reaction initiates at ~900° C, but becomes autocatalytic at ~1300° C. Once the pressures within the primary containment vessels of Units 1 and 3 exceeded design specifications, the decision was made to vent the H_{2(g)} and any other volatile gases that had built up within the primary vessels to the atmosphere in an attempt to protect the structural integrity of the primary containment vessels (1). The first of a series of venting operations occurred roughly one day after units 1, 2, and 3 were scrammed (March 12, 1440 JST). Hydrogen gas released from the primary vessels of Units 1 and 3 subsequently accumulated within the superstructures above the core and eventually lead to a series of explosions. One of the explosions occurred at the spent-fuel pool at Unit 4, and is thought to be a result of H_{2(g)} that backed up and accumulated there from common piping connecting units 3 and 4 (1).

There is some debate over the source and extent of radionuclide contamination to the environment from the Fukushima Daiichi nuclear facility. It has been suggested, for instance, that the explosion at the Unit 4 cooling pool, which is not contained within any primary containment system, may have damaged fuel and contributed to or even composed the major source of the release of radionuclides to the environment (4-5). This was based upon a correlation in time observed between the application of water over the spent fuel pool and a decrease in the atmospheric plume measured over Europe.

However, large amounts of radioactive contamination detected across the site (6), as well as trace levels of radiation detected across the Northern hemisphere (7) were also correlated in time with the venting of Units 1 and 3.

Here, we evaluate the earliest reported measurements (within 20 days after the earthquake) of several radionuclides found within environmental samples taken from the Fukushima Daiichi nuclear facility (8). The purpose of this effort was to attempt to identify the source term, reconstruct the release mechanisms, estimate the extent of the release, and generally demonstrate the power of rapid evaluations based upon basic chemical and nuclear engineering concepts for purposes of consequence management.

Methods

Data Quality

Evaluations provided here were based upon analytical results reported on the TEPCO website (8) posted roughly 20 days after the earthquake. Some of the data we have used were subsequently removed from the website for reasons we assume were related to quality concerns stemming from the rather unique and short-lived nature of these isotopes. However, it is precisely the short-lived nature of these isotopes that make them powerful signatures of the state and identity of their source. As such, we have reviewed the retracted measurements of ^{136}Cs , ^{132}Te , $^{110\text{m}}\text{Ag}$, ^{140}Ba , ^{140}La , ^{106}Ru , ^{99}Mo , $^{99\text{m}}\text{Tc}$ and ^{95}Nb and have concluded that their reported measured activities in soil samples were consistent with both burnup model predictions of potential source terms and the published measurements of more commonly reported and longer-lived isotopes (^{131}I and ^{137}Cs). Based upon this review we cautiously defend our use of these data for qualitative assessments regarding the source. We assert no assurances with regards to the quality of these data or the evaluations we have generated beyond their use in assessments of a qualitative nature. Certainly, more thorough assessments of this accident will eventually be available from which to compare the results of this rough-but-rapid evaluation.

Conceptual Model for the Release of Radionuclides from the Primary Containments of Units 1 and 3 and cooling pool from Unit 4

Two possible sources of radionuclides released to the environment from the Fukushima Daiichi nuclear facility have been suggested; these include venting of scrammed Units 1, 2 and 3, and uncontrolled releases from damaged fuel located within the central cooling pool at Unit 4.

Figure 1 provides a graphical overview of the assumed mechanism for radionuclide release from the vented Fukushima Daiichi Units 1 and 3. The mechanism involves five steps: 1) volatilization of radionuclides within the fuel matrix, 2) migration of those volatile species through the interstices of the fuel to the cladding wall, 3) escape of the volatile radionuclides through damaged portions of the cladding, 4) bubbling of those volatile contaminants through the confined coolant during venting, and 5)

migration of these radionuclides to the environment. In our evaluation of the reported data, we make the following conservative, simplifying, assumptions:

1. The volatility of all radionuclides of interest is adequately described by assuming thermodynamic equilibrium (9). Kinetic limitations associated with phase transformation are assumed unimportant.
2. Any gaseous radionuclides that have evaporated within the fuel completely migrate to the cladding walls. Kinetic limitations associated with migration through the fuel matrix are assumed to be insignificant.
3. Any volatile radionuclides that have migrated to the cladding wall will escape across the damaged cladding wall. In other words, the cladding is assumed to be sufficiently damaged as to pose no significant barrier to escape.
4. All coolant within Units 1 and 3 has evaporated prior to venting, such that volatile radionuclides are released directly into the atmosphere without fractionation due to partitioning into a retained aqueous phase.
5. All volatile radionuclides released during venting immediately condense upon cooling and mixing with the atmosphere, and precipitate without significant fractionation to the surface soil at close distances from the source. The assumption that no fractionation had occurred between differing elements from the point of release to the point of measurement is likely only valid at short distances from the source.

Explosions at Unit 4 suggest the possibility of the dispersal of radionuclides from the irradiated fuel stored within the cooling pool of Unit 4. In order to assess radionuclide release to the local environment from this source, we assume that no fractionation of isotopes has occurred from the point of release to the point of measurement. When evaluating measurements of cesium within water from the cooling pool or sub-drains in close proximity to the pool, we assume a significant fraction of the inventory of the highly soluble cesium isotopes within the damaged fuel ends up dissolved in the water, whether these isotopes were explosively released as part of a fuel fragment or evolved during extreme overheating.

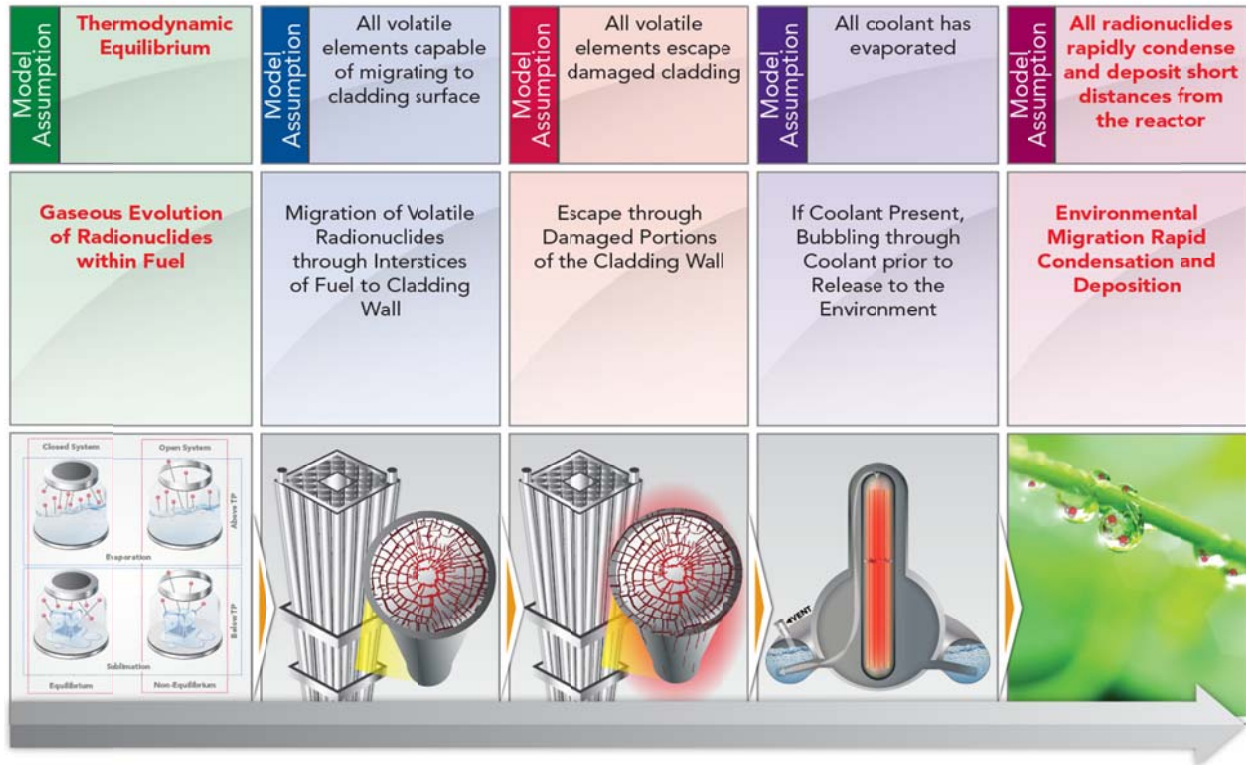


Figure 1. Major mechanisms to gaseous release of radioactive effluents during the venting of primary containment vessels of Units 1 and 3. Conservative, worst-case-scenario assumptions for each of the mechanisms made here for evaluation purposes are described within the “Methods” section.

Modeled Spent Fuel Inventories

Radionuclide inventories within spent nuclear reactor fuel was simulated using ORIGEN-ARP, part of the SCALE 5.1 simulation package (10). Assumptions were made to simulate the generic conditions expected at a Fukushima-style reactor (i.e., boiling-water reactor, Gen2, BWR4, Marc I containment). Reactors similar in design to those running at the time of the earthquake at the Fukushima Daiichi nuclear plant have been modeled by the authors previously. Modeled inventories in those cases agreed well with optical and mass spectrometric measurements of actual samples of the fuel (11). The Express function was used within ORIGEN-ARP. The fuel was assumed to be General Electric 8x8 fuel with 4% initial ²³⁵U enrichment. A one-metric-ton uranium basis was used. The power density was assumed to be 25 MW days per metric ton of uranium (MTU) and the moderator density was 0.7332 g/cm³ (grams per cubic centimeter). The burnup was simulated up to a cumulative of 30,000 MW/MTU over 3 cycles (400 days per cycle) using a single library per cycle. Nuclide lists were generated for the simulated fuel after cooling for several time points post-irradiation, including 1, 2, 3, 30, 100 and 365 days.

We utilize ORIGEN-ARP model predictions after 1 d of cooling to represent the radionuclide inventories within spent fuel from the scrammed reactors just before venting efforts commenced. The same model was used to predict radionuclide inventories contained within the spent fuel in the cooling pool at Unit 4, with the exception of using output from predictions after 100 d of cooling. This cooling time is consistent with the fuel most recently added to the pool from the reactor at Unit 4. Taking this most

recent fuel to represent the entirety of fuel assemblies contained within the spent fuel pool has the effect of dramatically overestimating the potential contribution of radionuclides coming from this source.

Results

Analytical results of environmental surveys taken from across the Fukushima Daiichi facility grounds and published on the TEPCO website within the first 20 days after the earthquake are provided in Tables 1 through 3. Table 4 provides model output from ORIGEN ARP computations designed to replicate the average radionuclide inventories within Units 1 and 3 just before venting and that of the most recently off-loaded fuel stored in the spent-fuel cooling pool at Unit #4.

Table 1. Analytical results of surface soil measurements taken from across the Fukushima Daiichi facility grounds published on the TEPCO website within the first 20 days after the earthquake (8).

| Location* | FP1 | | | FP2 | | FP3 | | SP4 | SP5 | SP6 | SP7 | SP8 | |
|--------------------|------------------------|---------|--------|--------|--------|---------|--------|---------|--------|--------|--------|---------|----|
| Date of Sampling | 21 Mar | 25 Mar | 28 Mar | 25 Mar | 28 Mar | 25 Mar | 28 Mar | 25 Mar | 22 Mar | 22 Mar | 22 Mar | 22 Mar | |
| Date of Analysis | 24 Mar | 28 Mar | 30 Mar | 28 Mar | 30 Mar | 28 Mar | 30 Mar | 28 Mar | 25 Mar | 25 Mar | 24 Mar | 25 Mar | |
| Days After | 11 Mar | 13 | 17 | 19 | 17 | 19 | 17 | 19 | 17 | 14 | 14 | 13 | 14 |
| Isotope | Bq/kg dry soil | | | | | | | | | | | | |
| I-131 | 5.8E+6 | 5.7E+6 | 3.8E+6 | 3.0E+6 | 3.9E+4 | 1.2E+7 | 2.6E+6 | 4.6E+5 | 3.1E+6 | 7.9E+5 | 2.2E+6 | 5.4E+6 | |
| I-132 | - | - | 2.3E+5 | - | 1.3E+2 | - | 1.5E+5 | - | - | - | - | - | |
| Cs-134 | 3.4E+5 | 4.9E+5 | 5.3E+5 | 7.7E+4 | 3.2E+2 | 3.5E+6 | 9.7E+5 | 6.8E+4 | 9.5E+5 | 8.7E+3 | 1.7E+4 | 1.6E+5 | |
| Cs-136 | 7.2E+4 | 6.1E+4 | 3.3E+4 | 1.0E+4 | 2.8E+1 | 4.6E+5 | 6.9E+4 | 8.6E+3 | 1.1E+5 | 1.9E+3 | 2.2E+3 | 2.5E+4 | |
| Cs-137 | 3.4E+5 | 4.8E+5 | 5.1E+5 | 7.6E+4 | 3.2E+2 | 3.5E+6 | 9.3E+5 | 6.7E+4 | 1.0E+6 | 2.0E+6 | 1.6E+4 | 1.6E+5 | |
| Te-129m | 2.5E+5 | 2.9E+5 | 8.5E+5 | 5.3E+4 | - | 2.7E+6 | 6.0E+5 | 2.8E+4 | 8.9E+5 | 9.5E+3 | 1.9E+4 | 1.7E+5 | |
| Te-132 | 6.1E+5 | 3.4E+5 | 3.0E+5 | 6.5E+4 | 1.4E+2 | 3.1E+6 | 2.0E+5 | 3.2E+4 | 1.9E+6 | 2.1E+4 | 3.9E+4 | 3.8E+5 | |
| Ba-140 | 1.3E+4 | 1.5E+4 | - | 2.5E+3 | - | - | - | - | 8.0E+4 | - | - | - | |
| Nb-95 | 1.7E+3 | 2.4E+3 | - | - | - | 5.3E+3 | - | - | 8.1E+3 | - | - | 7.9E+2 | |
| Ru-106 | 5.3E+4 | - | - | 6.4E+3 | - | 2.7E+5 | - | - | 6.8E+4 | 1.9E+3 | - | 3.2E+4 | |
| Mo-99 | 2.1E+4 | - | - | - | - | 6.6E+4 | - | - | - | - | - | - | |
| Tc-99m | 2.3E+4 | 2.0E+4 | - | - | - | 4.5E+4 | - | 1.8E+3 | 2.3E+4 | - | - | 8.3E+3 | |
| La-140 | 3.3E+4 | 3.7E+4 | - | 2.3E+3 | - | 9.7E+4 | - | 2.5E+3 | 2.1E+5 | 4.2E+2 | 6.2E+2 | 7.8E+3 | |
| Be-7 | - | - | - | - | - | - | - | - | 3.2E+4 | - | - | - | |
| Ag-110m | 1.1E+3 | 2.6E+3 | - | - | - | - | - | 1.7E+2 | 1.8E+4 | - | - | - | |
| Isotope Ratio | Corrected To Time Zero | | | | | | | | | | | | |
| Soil Cs-134/Cs-137 | 1.01 | 1.04 | 1.06 | 1.03 | 1.02 | 1.01 | 1.06 | 1.03 | 0.961 | 0.440 | 1.07 | 1.01 | |
| Soil Cs-136/Cs-137 | 0.420 | 0.311 | 0.176 | 0.322 | 0.238 | 0.321 | 0.202 | 0.314 | 0.229 | 0.198 | 0.272 | 0.326 | |
| I-131/Cs-137 | 52.4 | 51.5 | 38.4 | 171 | 629 | 14.9 | 14.4 | 29.8 | 10.4 | 132 | 422 | 113 | |
| Te-132/Cs-137 | 29.9 | 28.1 | 36.0 | 34.0 | 26.8 | 35.1 | 13.2 | 19.0 | 39.4 | 21.8 | 40.7 | 49.2 | |
| Ba-140/Cs-137 | 0.0774 | 0.0786 | - | 0.0828 | - | - | - | - | 0.171 | - | - | - | |
| Nb-95/Cs-137 | 0.00646 | 0.00670 | - | - | - | 0.00212 | - | - | 0.0107 | - | - | 0.00651 | |
| Ru-106/Cs-137 | 0.160 | - | - | 0.0868 | - | 0.0795 | - | - | 0.0697 | 0.0974 | - | 0.205 | |
| Mo-99/Cs-137 | 1.64 | - | - | - | - | 1.37 | - | - | - | - | - | - | |
| Tc-99m/Cs-137 | 1.79 | 3.03 | - | - | - | 0.935 | - | 1.95 | 0.785 | - | - | 1.77 | |
| La-140/Cs-137 | 0.197 | 0.194 | - | 0.0762 | - | 0.0697 | - | 0.0939 | 0.449 | 0.0449 | 0.0785 | 0.104 | |
| Ag-110m/Cs-137 | 0.00335 | 0.00567 | - | - | - | - | - | 0.00266 | 0.0187 | - | - | - | |
| Te-129m/Cs-137 | 0.961 | 0.857 | 2.46 | 0.989 | - | 1.09 | 0.954 | 0.593 | 1.19 | 0.633 | 1.55 | 1.42 | |

*Fixed Point (FP) 1 – Playground, ~500 m west-northwest of stacks from Units 1 and 2. FP-2 – Forest of wild birds~500 m west of stacks from Units 1 and 2. FP-3 – Adjacent to industrial waste disposal facility, ~500 m south-southwest of stacks from Units 1 and 2. Sampling Point(SP) -4 – Front of administration building for Units 5 and 6, ~1000 m north of stacks from Units 1 and 2. SP-5 – Adjacent to solid waste storage near Units 1 and 2, ~500 m north of stacks from Units 1 and 2. SP-6 – ~500 m south-southwest from stacks of Units 1 and 2. SP-7 – ~750 m south-southwest from stacks of Units 1 and 2.. SP-8 – ~1000 m south-southwest from stacks of Units 1 and 2..

Table 2. Analytical results of water samples taken from sub drains and turbine water from units 1 through 6 of the Fukushima Daiichi nuclear facility published on the TEPCO website within the first 20 days after the earthquake (8).

| Location | Unit 1 | | | Unit 2 | | Unit 3 | | Unit 4 | Unit 5 | Unit 6 |
|----------------------|--------------------------|----------|---------------|-----------|----------|-------------------------|----------|-----------|-----------|-----------|
| | Sub Drain | | Turbine Water | Sub Drain | | Sub drain Turbine Water | | Sub Drain | Sub Drain | Sub Drain |
| Date of Analysis | 26 Mar | 30 Mar | 30 Mar | 26 Mar | 30 Mar | 26 Mar | 30 Mar | 24 Mar | 30 Mar | 30 Mar |
| Days After 11 Mar | 15 | 19 | 19 | 15 | 19 | 15 | 19 | 13 | 19 | 19 |
| Isotope | <i>Bq/cm³</i> | | | | | | | | | |
| Cs-134 | - | 8.81E-01 | 8.86E-01 | - | 7.00E-01 | - | 1.00E+01 | - | 2.50E-01 | 4.70E+00 |
| Cs-136 | 8.46E-02 | 6.61E-02 | 6.46E-02 | 2.50E+01 | 6.50E-02 | 6.50E+00 | 9.40E-01 | 3.70E+00 | 2.70E-02 | 3.90E-01 |
| Cs-137 | - | 8.81E-01 | 8.86E-01 | 2.30E+02 | 6.30E-01 | 5.60E+01 | 1.00E+01 | 3.20E+01 | 2.70E-01 | 4.90E+00 |
| Isotope Ratio | | | | | | | | | | |
| Cs-134/Cs-137 | - | 8.81E-01 | 8.86E-01 | - | 1.11E+00 | - | 1.00E+00 | - | 9.26E-01 | 9.59E-01 |
| Cs-136/Cs-137 | 8.46E-02 | 6.61E-02 | 6.46E-02 | 1.09E-01 | 1.03E-01 | 1.16E-01 | 9.40E-02 | 1.16E-01 | 1.00E-01 | 7.96E-02 |

Table 3. Analytical results of Pu activity in surface soil with distance from the Fukushima Daiichi nuclear facility measured after the earthquake on March 11, 2012 (6, 8).

| Distance From Source | Pu-238 (Bq/kg dry soil) | Pu-239,240 (Bq/kg dry soil) | Pu-238/Pu-239,240 |
|----------------------|----------------------------|--------------------------------|-------------------|
| 45.4 | 0.82 | 2.5 | 0.328 |
| 38.6 | 0.77 | 0.6 | 1.283 |
| 31.2 | 4 | 1.8 | 2.222 |
| 23.9 | 2.3 | 1.8 | 1.278 |
| 5.25 | 0.55 | 0.66 | 0.833 |
| 0.17 | 0.051 | 0.026 | 1.96 |
| 0.17 | 0.14 | 0.087 | 1.61 |
| 0.17 | 0.26 | 0.12 | 2.17 |

Table 4. ORIGEN ARP output of simulations of the average inventories contained within Fukushima Daiichi Units 1 and 3 one day after scrambling, just prior to venting.

| Isotope | Cooling Time (days) | | Isotope | Cooling Time (days) | |
|---------|---------------------|----------|---------|---------------------|----------|
| | 1 Day | 100 Days | | 1 Day | 100 Days |
| | Bequerels | | | Bequerels | |
| Np-239 | 3.09E+17 | 2.66E+11 | Sr-90 | 2.87E+15 | 2.85E+15 |
| Xe-133 | 4.83E+16 | 1.17E+15 | Te-127 | 1.97E+15 | 2.05E+14 |
| La-140 | 4.55E+16 | 1.01E+16 | Te-129m | 1.18E+15 | 6.49E+14 |
| Nb-95 | 4.40E+16 | 2.75E+16 | Cs-136 | 1.02E+15 | 2.21E+14 |
| Zr-95 | 4.32E+16 | 1.65E+16 | Te-129 | 9.27E+14 | 4.16E+14 |
| Ba-140 | 4.23E+16 | 8.75E+15 | Pm-148m | 8.82E+14 | 5.42E+14 |
| Ce-141 | 4.15E+16 | 2.24E+16 | Cm-242 | 7.64E+14 | 5.24E+14 |
| Pr-143 | 3.83E+16 | 9.32E+15 | Am-242 | 5.09E+14 | 1.80E+11 |
| Ru-103 | 3.63E+16 | 2.18E+16 | Pr-144m | 5.00E+14 | 4.03E+14 |
| Rh-103m | 3.62E+16 | 2.17E+16 | Nb-95m | 5.00E+14 | 3.71E+14 |
| Mo-99 | 3.62E+16 | 2.41E+13 | Kr-85 | 3.64E+14 | 3.58E+14 |
| Pr-144 | 3.57E+16 | 2.88E+16 | Te-127m | 3.58E+14 | 2.10E+14 |
| Ce-144 | 3.57E+16 | 2.88E+16 | Sb-125 | 2.31E+14 | 2.19E+14 |
| Tc-99m | 3.48E+16 | 2.33E+13 | Eu-154 | 1.24E+14 | 1.21E+14 |
| Y-91 | 3.32E+16 | 1.16E+16 | Sn-121 | 9.26E+13 | 2.91E+11 |
| I-132 | 2.94E+16 | 6.15E+13 | Eu-155 | 7.10E+13 | 6.84E+13 |
| Te-132 | 2.86E+16 | 5.97E+13 | Te-125m | 5.02E+13 | 5.12E+13 |
| Sr-89 | 2.55E+16 | 1.71E+16 | Pu-238 | 4.51E+13 | 4.65E+13 |
| I-131 | 2.30E+16 | 1.93E+15 | Ag-110m | 4.14E+13 | 3.23E+13 |
| Nd-147 | 1.57E+16 | 2.51E+15 | Sn-123 | 3.31E+13 | 2.05E+13 |
| U-237 | 1.44E+16 | 7.33E+14 | H-3 | 1.81E+13 | 1.78E+13 |
| Ru-106 | 1.22E+16 | 1.04E+16 | Cm-244 | 1.80E+13 | 1.79E+13 |
| Rh-106 | 1.22E+16 | 1.04E+16 | Pu-240 | 1.46E+13 | 1.46E+13 |
| Pm-147 | 6.60E+15 | 6.35E+15 | Sm-151 | 1.08E+13 | 1.09E+13 |
| Eu-156 | 3.60E+15 | 9.58E+14 | Pu-239 | 8.93E+12 | 9.01E+12 |
| Cs-137 | 3.57E+15 | 3.55E+15 | Am-241 | 3.59E+12 | 4.71E+12 |
| Pm-148 | 3.54E+15 | 1.11E+14 | Tc-99 | 4.78E+11 | 4.80E+11 |
| Ba-137m | 3.37E+15 | 3.35E+15 | Sn-121m | 3.76E+11 | 3.75E+11 |
| Cs-134 | 3.16E+15 | 2.92E+15 | Eu-152 | 2.85E+11 | 2.82E+11 |
| Y-90 | 2.93E+15 | 2.85E+15 | Am-243 | 2.66E+11 | 2.66E+11 |
| Pu-241 | 2.91E+15 | 2.87E+15 | Cm-243 | 2.00E+11 | 1.99E+11 |

Discussion

Source Identification

Besides global fallout, there are two main possible sources of radionuclides in the surface soil surrounding the Fukushima Daiichi nuclear facility, including (1) potential releases as a result of the

emergency venting of scrammed reactor Units 1 and 3, and/or (2) releases from damaged spent nuclear fuel located in the cooling pool at Unit 4. The dominant of these potential sources to the local environment may be identified using activity ratios of $^{136}\text{Cs}/^{137}\text{Cs}$ and $^{134}\text{Cs}/^{137}\text{Cs}$. Figure 2 shows the $^{136}\text{Cs}/^{137}\text{Cs}$ and $^{134}\text{Cs}/^{137}\text{Cs}$ activity ratios reported in the topsoil and within the water of the sub-drains across the Fukushima Daiichi facility taken between 13 and 19 d after Units 1, 2, and 3 were scrammed. These ratios are compared with model output from burnup calculations of the expected spent fuel inventories of the reactors operating at the time of the tsunami. Estimates of the cesium ratios of the freshest of the spent fuel assemblies within the cooling pool of Unit 4 (which was approximately 100 days old) provide a conservatively high ratio representing this source for comparison against measured values from across the site. A comparison of the modeled and measured Cs ratios within sub-drains close to the pool and surface soil from across the site indicate that essentially all of the cesium released to the local environment came from the venting of Units 1 and 3, suggesting that fuel within the cooling pool at Unit 4 remained intact. Similar conclusions can be drawn (not shown herein) based upon $^{129\text{m}}\text{Te}/^{132}\text{Te}$ and (assuming no significant fractionation) $^{131}\text{I}/^{137}\text{Cs}$ (see Figure A-1 in supporting documentation).

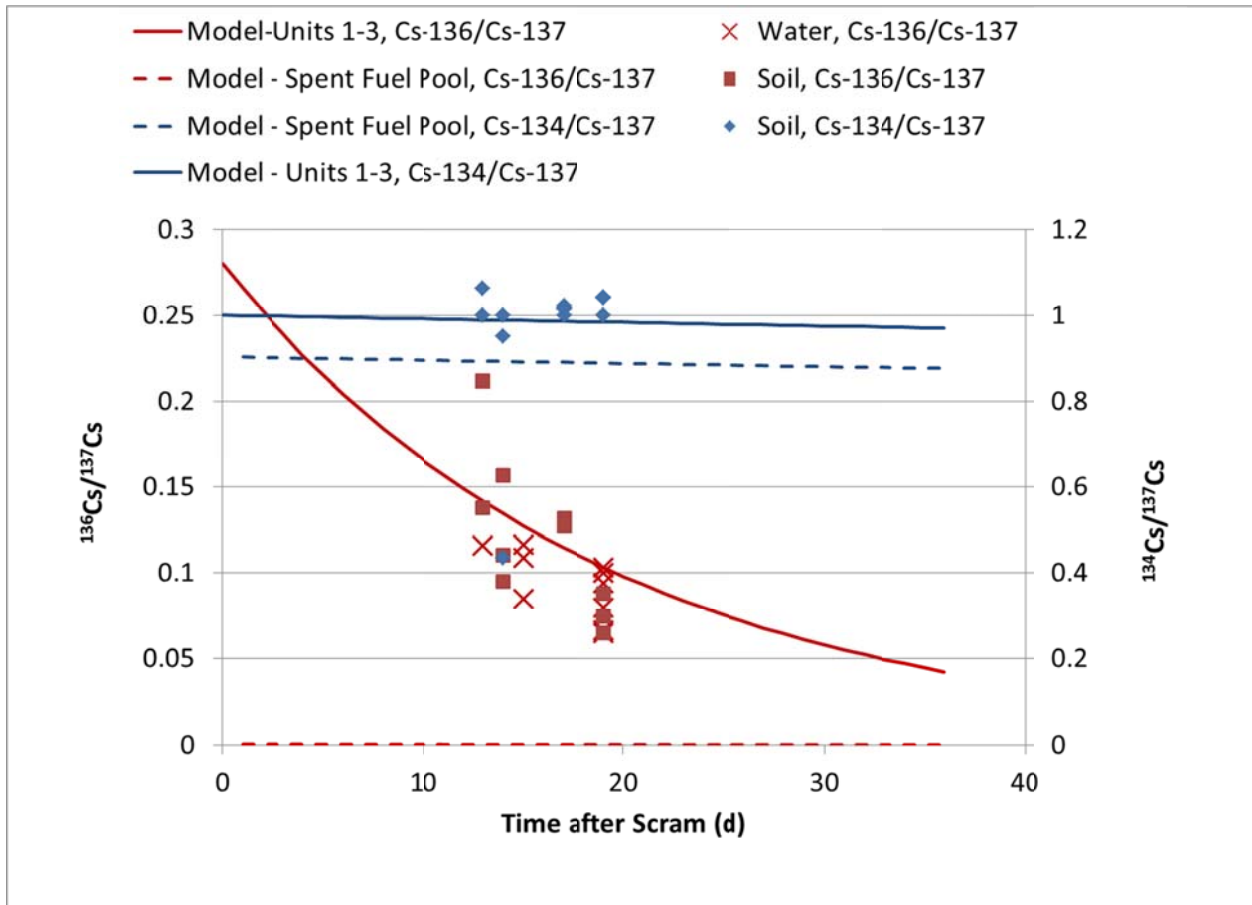


Figure 2. $^{134}\text{Cs}/^{137}\text{Cs}$ and $^{136}\text{Cs}/^{137}\text{Cs}$ ratios from water and soil samples taken at the Fukushima Daiichi Facility 13 to 19 days after scrambling Units 1, 2, and 3. Average model inventory ratios from operating Units 1-3 are shown in solid lines, while the dashed line represent the highest possible ratios representing those predicted from spent nuclear fuel within the cooling pool at Unit 4. The ratios used

to represent the fuel within the cooling pool were based upon the same generic Origen model developed for BWRs at Units 1, 2, and 3, with the exception of utilizing predicted inventories for fuel cooled for 100 d, consistent with the cooling time of the most recently added fuel to the cooling pool at Unit 4.

Evidence of Minor Amounts of Plutonium Released to the Environment

Reports have suggested that plutonium was released from these reactors based upon total plutonium activity measurements in surface soil (8). However, Hirose et al. (12) has shown that global fallout deposition rates can vary by 50% or more at the same location of measurement. As such, the use of absolute activity or deposition rates to soil is of qualitative value at best as an indicator of source identity.

An excerpt from T. Sekiguchi (13), quoting Japan's Science Ministry analysis, reports, "...²³⁸Pu believed to have been emitted from the damaged Fukushima Reactors, was found in soil samples from six separate locations, ranging from 0.55 to 4.0 becquerels per square meter."

Sekiguchi goes on to report that "Samples from Litate, a village located 28 miles from the power plant, registered 0.82 becquerels of ²³⁸Pu and 2.5 becquerels of ^{239,240}Pu. Litate was evacuated earlier this year."

Sekiguchi quotes measured values that equate to a ²³⁸Pu/^{239,240}Pu activity ratio of 0.328 within Litate's surface soil. Employing a simple two-term mixing model represented by global fallout (6) (²³⁸Pu/^{239,240}Pu activity ratio = 0.026) and plutonium emanating from the damaged reactors (predicted ²³⁸Pu/^{239,240}Pu activity ratio = 1.92), the contribution from the damaged reactors to surface soil 28 miles (45 km) from the source was estimated to be roughly 16%.

Figure 3 shows published (14) measurements of the ²³⁸Pu/^{239,240}Pu activity ratios in surface soil with distance from the Fukushima Daiichi Nuclear Power Station taken soon after venting Units 1 and 3. These values are compared with those indicative of global fallout for the region (12). The predicted ²³⁸Pu/^{239,240}Pu activity ratio within the spent fuel at Units 1 and 3 just prior to venting is also shown. The average of the measured ratios in surface soils at the source correlates well with the model estimates of the spent-fuel inventory from Units 1 and 3, and is significantly different from the ratio measured from global fallout for the region. This indicates that plutonium was released to the local environment during the venting of Units 1 and 3. Additionally, the ²³⁸Pu/^{239,240}Pu activity ratio decreases with distance from the source, indicating the majority of the plutonium contamination from venting the reactors appears to be localized within a few tens of kilometers from the site. A simple model shown in Equation 2 was developed and fit to the experimental data to describe the deposition of plutonium with distance from the site:

$$\frac{^{238}}{^{239,240}P} = d^2 \cdot r_d, \quad \text{Eq. 2}$$

where $\frac{^{238}\text{Pu}}{^{239,240}\text{Pu}}$ is the predicted $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio within the spent fuel in the damaged reactor prior to venting (taken to be 1.92), d is the distance from the source in kilometers, and r_d is the deposition parameter. A value of $5.97\text{E-}4$ was used for r_d , generated by a least squares fit to the experimental data as a function of distance from the source. Using this model (dashed line in Figure 3), vented plutonium from Units 1 and 3 account for roughly 100% of the plutonium in surface soil at the site, but only ~20% of the total plutonium in surface soil 50 km from the source.

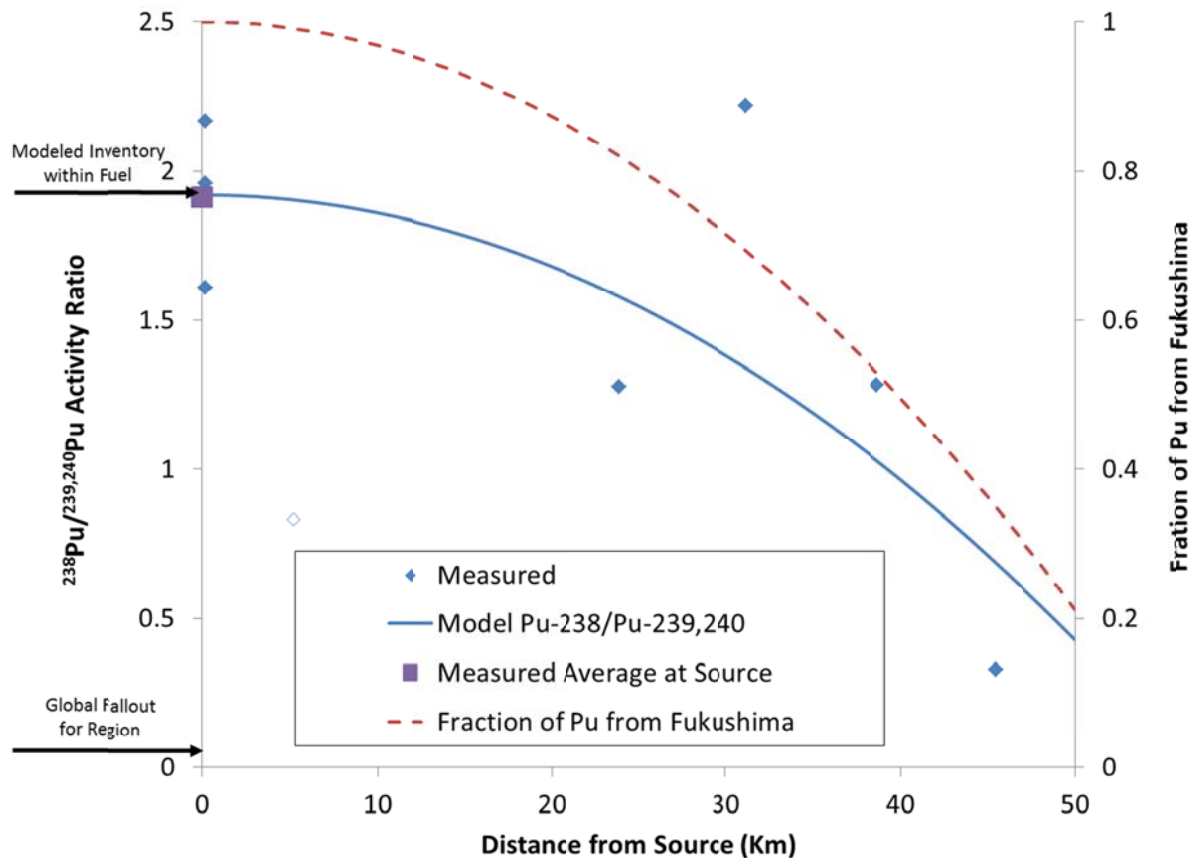


Figure 3. Measured (δ) $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratios as a function of distance from the Fukushima Daiichi Power station. The average of the three measured values at the source is also shown. For comparison, the average measured (1986) ratio from global fallout (corrected to 2011) in the region (14) and the average modeled inventory within the fuel prior to venting is also shown. A single data point shown with the open symbol “ \diamond ” was defined as an outlier and excluded during the development of the deposition model.

Estimated Fraction of the Total plutonium Inventory from Units #1 and 3 Vented to the Environment

The activity ratio of $^{239,240}\text{Pu}/^{137}\text{Cs}$ within Units 1 and 3 prior to venting was estimated from burnup calculations to be ~150 (see Table 4), whereas the measured activity ratio in surface soil at the site reported by TEPCO ranged from about 2×10^5 to 1×10^6 . If we assume that the majority of the plutonium and cesium that escaped from the reactors followed the same general fate within the environment (namely, rapid condensation and deposition close-in from the location of venting) and that 100% of the

total inventory of cesium within Units 1 and 3 was released to the environment, the discrepancy between the $^{239,240}\text{Pu}/^{137}\text{Cs}$ activity ratio within the spent fuel and that found in the close-in fallout within the soil provides a measure of the fraction of the total plutonium inventory that escaped from the damaged reactors relative to that of cesium. Based upon a comparison of modeled and measured $^{239,240}\text{Pu}/^{137}\text{Cs}$ activity ratios it is estimated that less than 0.002% of the total plutonium inventory from Units 1 and 3 was released to the environment as a result of the Fukushima disaster.

Relative Release Fractions of Fission and Activation Products Trends with Volatility

Radionuclides other than cesium and plutonium were also detected within the soil at the Fukushima Daiichi Power Station soon after the disaster and provide some independent confirmation of the estimated fraction of the total plutonium inventory released from Units 1 and 3. Cubicciotti and Sehgal (9) **Error! Bookmark not defined.** have suggested that under nuclear-accident conditions the chemistry within a primary containment vessel is adequately described assuming thermodynamic equilibrium. At these high temperatures under a normal atmosphere, often the most stable form of an element will be its oxide form. However, the environment within the primary containment vessel will also become strongly reducing as $\text{H}_{2(\text{g})}$ builds up from the high-temperature reaction between the fuel cladding and water (15). This means volatilization can occur directly from the oxide form within a damaged primary containment vessel if temperatures within the vessel exceed the boiling point of the oxide, or indirectly if the buildup of $\text{H}_{2(\text{g})}$ is sufficient to reduce the oxide into a more volatile form. The metallic form of barium, for instance, is more volatile than its oxide form (10). Hobbins et al. (16) has used the Gibbs Free Energy of Formation (ΔG_f^0) for the oxide form of a metal (a.k.a., the oxygen potential) as a rough measure of that element's volatility under extreme nuclear accident conditions. Assuming chemical thermodynamics alone dictated the overall release mechanisms of radionuclides from the primary containment vessels to the close-in environment (see Figure 1 and earlier discussion), one might expect a correlation between the relative fraction of an isotope released from the vented reactors and the ΔG_f^0 for the oxide form of the element it represents. Table 5 provides a summary of the applicable ΔG_f^0 values from the literature. Figure 4 plots these values against the fraction of the isotope released, which was defined as the ratio of the measured activity of an isotope within surface soil relative to ^{137}Cs over its predicted activity inventory relative to ^{137}Cs from Origen calculations within Units 1 and 3 prior to venting. The measured activities of daughters ^{140}La and $^{99\text{m}}\text{Tc}$ were assumed to be in metastable equilibrium with their parent.

From Figure 4, $^{140}\text{Ba}(\text{La})$ is an obvious outlier from a relatively good trend observed for most other vented radionuclides and indicates a larger fraction of this isotope was released than would be predicted assuming the oxide form dictated volatility. Enhanced volatility of ^{140}Ba has been observed during experiments designed to replicate extreme accident conditions when $\text{H}_2/\text{H}_2\text{O}$ ratios exceeded 100 (9, 15, 17-18), suggesting that little or no steam remained within the primary containment vessels prior to venting. These observations have been attributed to the fact that barium is one of the few elements whose metallic form is more volatile than its oxide form (10). These findings warrant the exclusion of ^{140}Ba data from the empirical model in Figure 4.

Table 5. Gibbs Free Energy of Formation (ΔG_f^0) for select oxides at 1000K (16, 19-20).

| Oxide | $\Delta G_f^0 \left(\frac{kJ}{mol} \right)$ |
|--------------------------------|--|
| CsO ₂ | -297 |
| BaO ₂ | -915 |
| NbO ₂ | -649 |
| IO ₂ | 0* |
| TeO ₂ | -126 |
| PuO ₂ | -879 |
| ZrO ₂ | -900 |
| La ₂ O ₃ | -915** |
| AgO ₂ | 62 |
| MoO ₂ | -335 |
| TeO ₂ | -126 |
| RuO ₄ | -50 |
| Pr ₂ O ₃ | -1026 |
| CeO ₂ | -875 |
| Pm ₂ O ₃ | -794 |
| Y ₂ O ₃ | -1076 |
| SrO | -984 |
| Rh ₂ O ₃ | -50** |
| Sb ₂ O ₃ | -293 |
| EuO ₂ | -247 |
| Cm | -896*** |
| Am | -896*** |
| Tc | -335** |
| SnO ₂ | -368 |
| Nd ₂ O ₃ | -794 |
| UO ₂ | -913 |

* ΔG_f^0 taken to be zero, since 1000K is above the boiling point of this species.

** ΔG_f^0 assumed equal to that of the radioactive parent due to metastable equilibrium.

*** ΔG_f^0 estimated from Pu^(III)₂O₃.

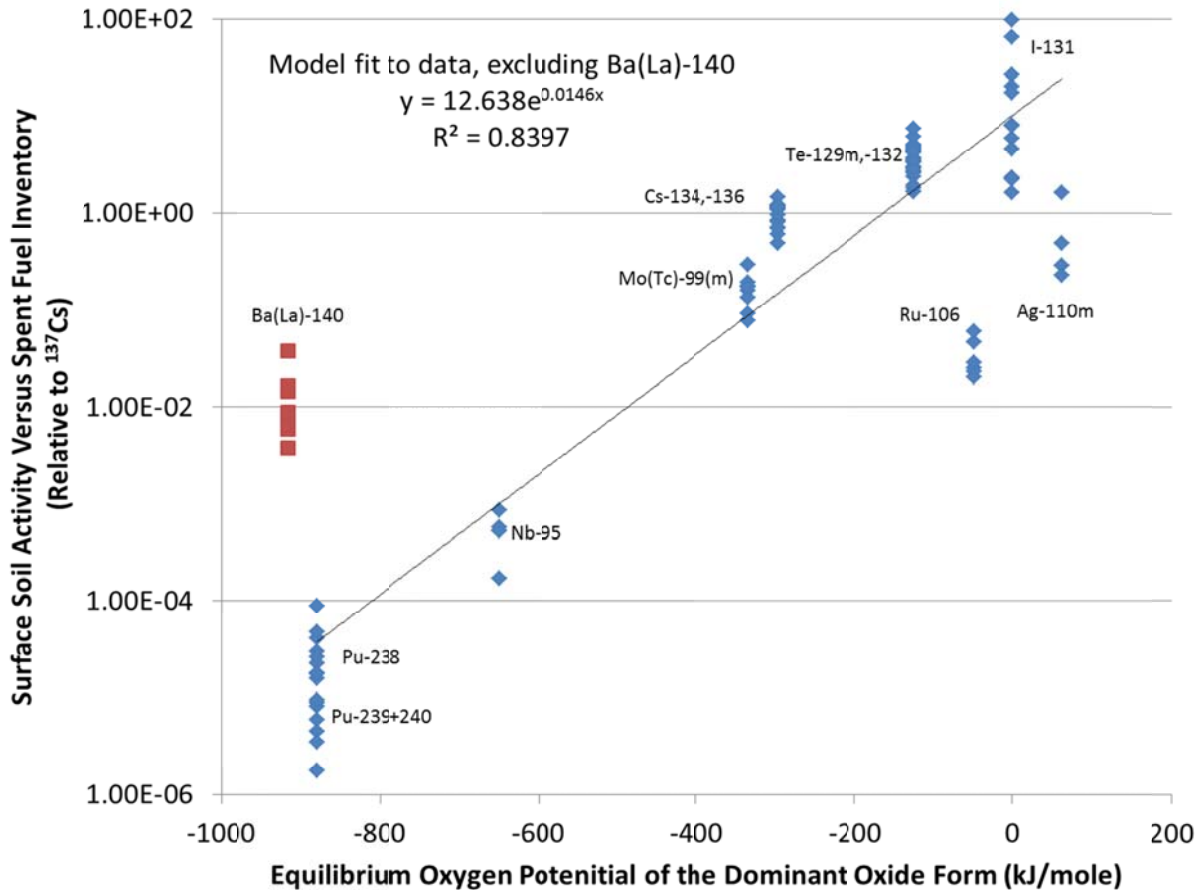


Figure 4. Estimated fraction of isotope released from Units 1 and 3 as a function of the equilibrium oxygen potential of their dominant oxide form.

The empirical fit shown in Figure 4 can be used to correct for fractionation due to volatility at the time (and temperature) that venting occurred. As discussed earlier, the fraction of plutonium released relative to ^{137}Cs was estimated to be $0.0016\% \pm 0.0031\%$ (expanded uncertainty) based upon the $^{239,240}\text{Pu}/^{137}\text{Cs}$ ratios in soil compared to the predicted inventories within the fuel prior to venting. A comparable result for the fraction of the plutonium released into the environment is obtained (0.0035%) when using the empirical model from Figure 4 and the ΔG_f^0 for $\text{PuO}_{2(s)}$ from the literature.

Other Radionuclides not Measured but of Potential Environmental Concern

It is possible that, considering the uniqueness of the radionuclides released into the environment during the venting of units 1, 2, and 3, hard-to-detect radionuclides released in significant quantities (more volatile radionuclides) could have escaped detection thus far by first responders. Figure 5 provides model predictions of the total activity of several isotopes relative to ^{137}Cs present within the fuel of the damaged reactor Units 1, 2, and 3 prior to venting (solid line). Relative activities of those isotopes present in the environment 1, 30, 300, and 3000 days after venting are also shown in Figure 5 (shaded areas), calculated using the empirical relationship provided in Figure 4. Seven of the twelve most radioactive isotopes predicted to be within the environment after 300 days have thus far eluded

measurement and reporting; these include ^{85}Kr , ^{103}Ru , ^{91}Y , $^{127\text{m}}\text{Te}$, ^{125}Sb , ^{151}Sm , and ^{129}Te . However, these seven isotopes represent less than 20% of the total predicted activity released from Fukushima. Assuming these model results are accurate, this suggests that while initial surveys of radionuclides emitted to the environment from Fukushima may be incomplete, the majority of the isotopes providing the most impact to human health and the environment have been identified.

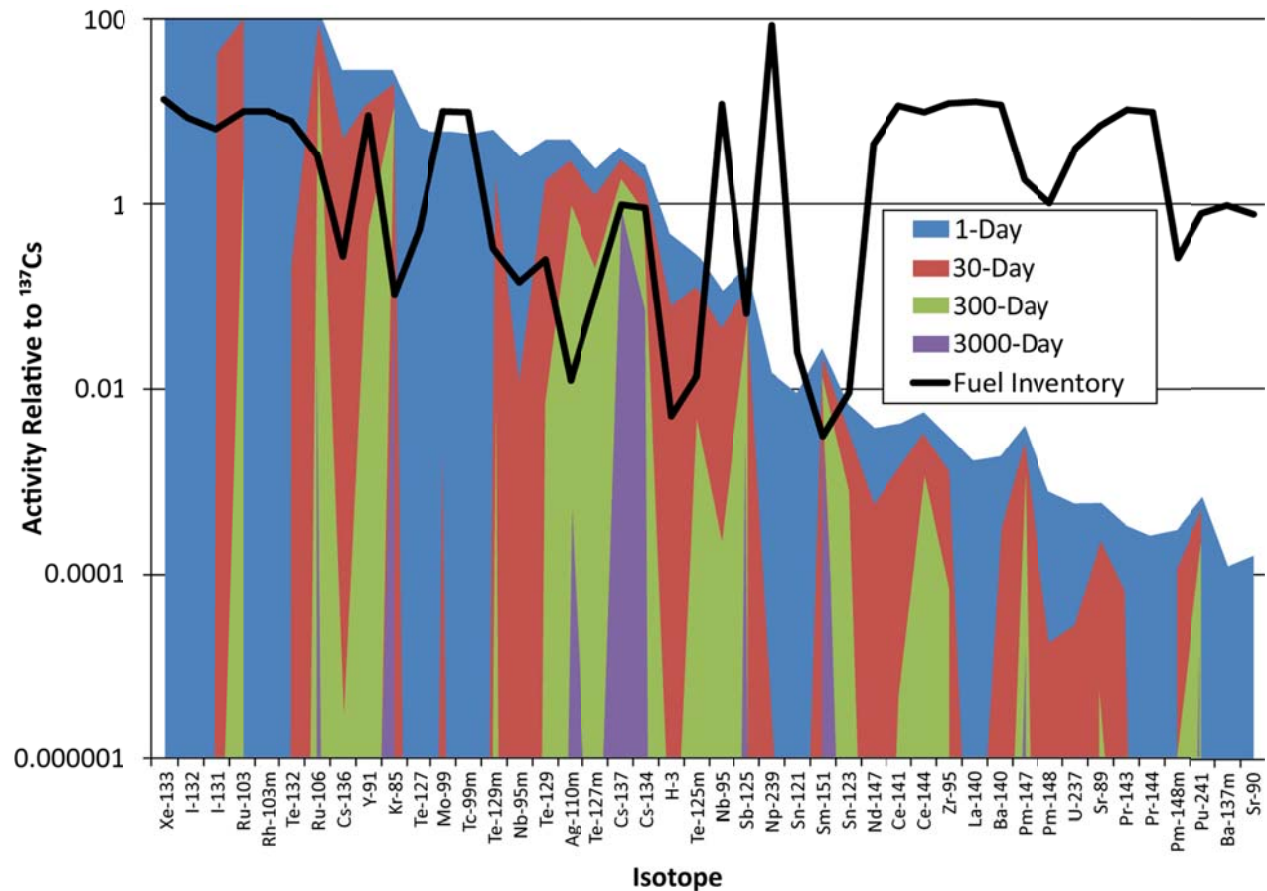


Figure 5. Predicted activity relative to ^{137}Cs within the fuel of damaged reactors prior to venting and within the environment 1, 30, 300, and 3000 days after scrambling Units 1,2 and 3. All of the predicted inventory of noble gas isotopes within scrambled units 1 and 3 were assumed to be released to the environment during venting of the primary containment vessels.

Conclusions

Measurements of several radionuclides within environmental samples taken days after the earthquake from the Fukushima Daiichi nuclear facility provided powerful evidence of their source, the physical and chemical mechanisms of their release, and the extent of the impact to the surrounding environment. $^{136}\text{Cs}/^{137}\text{Cs}$ ratios indicated the majority of the radioactivity found in the surface soil at the site was from the venting of Units 1 and 3. A trend was observed between the fraction of the total core inventory released for a number of fission product isotopes and their corresponding ΔG_f^0 for the primary oxide

form of the isotope, suggesting that release was dictated primarily by chemical volatility driven by temperature and reduction potential within the primary containment of the vented reactors. The absence of any major fractionation beyond volatilization and the anomalously high fraction of ^{140}Ba released suggested that all coolant from within the primary containment vessel had evaporated prior to venting. The estimated fraction of the total inventory released of the more volatile elements (tellurium, cesium, iodine) within the spent fuel from the vented reactors indicated the damage to fuel bundles was likely extensive, minimizing any potential containment by physical transport of these species through the fuel matrix and across the cladding wall. $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratios close-in and up to 45 km from the facility indicated that the damaged reactors were the major contributor of plutonium to surface soil at the source, but also that this contribution likely decreased rapidly with distance from the facility. The fraction of the total plutonium inventory released from Units 1, 2 and 3 was estimated to be $\sim 0.003\%$, relative to the assumed total release of ^{137}Cs , based upon plutonium/cesium isotope ratios relative to the within-reactor modeled inventory prior to venting. This was also consistent with an independent model evaluation that considered chemical volatility based upon measured fission product release trends. Volatile radionuclides with high activities within the spent fuel at the time of venting have been identified. Seven of the twelve most active isotopes predicted to be residing within the environment after 300 d (including ^{85}Kr , ^{103}Ru , ^{91}Y , $^{127\text{m}}\text{Te}$, ^{125}Sb , ^{151}Sm , and ^{129}Te) have gone undetected thus far, possibly due to difficulties in their measurement or potential inaccuracies with the model presented here. Until these inconsistencies are addressed, we offer these isotopes as potential analytes of concern for future environmental surveys around the site.

Acknowledgements

We would like to acknowledge Dr.'s Thomas Zemanian, Michaele Brady-Rapp and Gregg Lumetta for their thoughtful reviews and comments. We would also like to acknowledge Lisa Staudinger, Courtland Johnson and Duane Balvage for their help with technical editing and graphics. This research was conducted by Pacific Northwest National Laboratory under DOE contract number DE-AC06-76RLO-1830.

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Supporting Documentation

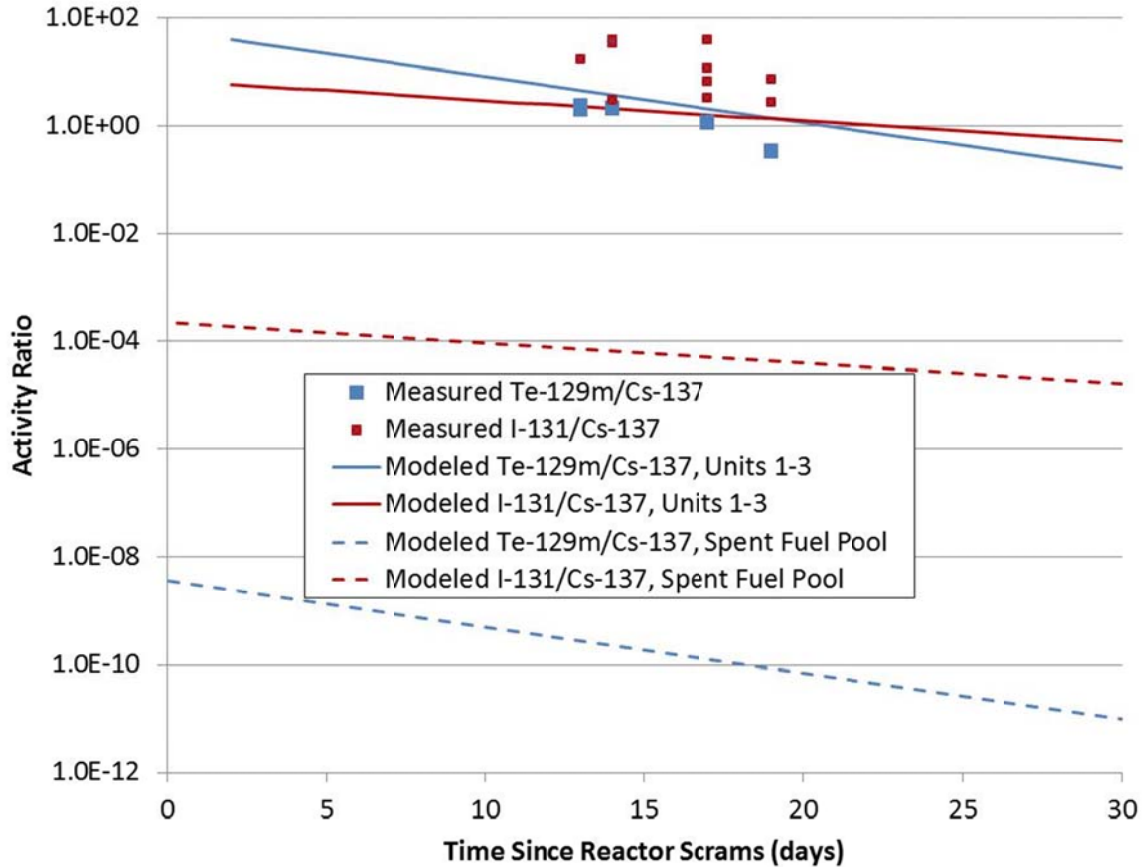


Figure A-1. Measured $^{129m}\text{Te}/^{137}\text{Cs}$ and $^{131}\text{I}/^{137}\text{Cs}$ ratios in the surface soil at the Fukushima Daiichi Nuclear Facility days after the earthquake. Average model inventory ratios from operating Units 1-3 are shown in solid lines, while the dashed lines represent the highest possible ratios representing those predicted from spent nuclear fuel within the cooling pool at Unit 4. The ratios used to represent the fuel within the cooling pool were based upon the same generic Origen model developed for BWRs at Units 1-3, with the exception of utilizing predicted inventories for fuel cooled for 100 d, consistent with the cooling time of the most recently added fuel to the cooling pool at Unit 4.