Pacific Northwest
NATIONAL LABORATORY

PNNL- 29672

Survey of Technologies to Meet PAG limits for Detection of Cesium-137 in Water

February 2020

Amoret L Bunn
Brett C Simpson
Eric M Becker
William C. Weaver
Rama Devagupta

U.S. DEPARTMENT OF ENERGY

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

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from
the Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: http://www.ntis.gov

PNNL- 29672

Survey of Technologies to Meet PAG limits for Detection of Cesium-137 in Water

February 2020

Amoret L Bunn
Brett C Simpson
Eric M Becker
William C. Weaver
Rama Devagupta

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

Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

The survey of technologies to meet (or be below) the Protective Action Guides (PAG) established by the U.S. Environmental Protection Agency (EPA) for the detection of radioactive, cesium-137 (Cs-137) in water. PAGs were established by EPA to help public officials during a radiological incident "select protective actions under emergency conditions during which exposures would occur for relatively short time periods" and are defined as the "projected dose to an individual from a release of radioactive material at which a specific protective action to reduce or avoid that dose is recommended". After a radiological event, incident response teams would collect water samples to determine if there was a release into drinking water supplies and provide the results to decision makers to determine what actions need to be taken to protect the public. The type of events considered in this evaluation include a Cs-137 Radiological Dispersion Device (RDD) and a release from a commercial Nuclear Power Plant (NPP). Currently, water samples would be analyzed by incident response teams with the assistance of EPA's Mobile Environmental Radiation Laboratory (MERL) or U.S. Department of Energy's Fly Away Laboratory (FAL). A 1-liter (1 L) water sample would be analyzed in the MERL using a BE6530 or in the FAL using a Falcon 5000 high purity germanium counters. With these assumptions for an NPP release, the counting time required by these instruments would take longer than results from sending the water sample to a contract or government laboratory for analysis by approved EPA methodologies.

The goal of this report is to evaluate the process of adding a sorbent to the sampling process to preconcentrate Cs-137 and then analyze the sorbent to provide a rapid assessment of results to guide decisions on drinking water sources and the protection of the public. Multiple unit design variables were considered: sample configuration/geometry, sorbent efficiency, sample volume. Model simulations demonstrated through these unit design efficiencies that 10 L of sample volume processed through a sorbent provides nearly two orders of magnitude improvement in sample counting time to provide results to a decision maker than the current process.

Over 60 publications and reports concerning Cs-137 and sorbents were evaluated. The key attributes were readiness of sorbent to be deployed in a mobile laboratory environment, and minimum sample preparation and conditioning. Examples of sorbents not considered further included nanomaterials, which have not been evaluated at a commercial scale and are limited in availability. The recommended sorbents for further consideration include: ferrocyanide salts, zeolite, and chemically modified granular activated carbon.

The following highlights the findings in this report and follow on recommendations.

- Align MERL and FAL capabilities with EPA PAG guidance.
- Evaluate an ion exchange flow-through system for sample concentration.
- Evaluate in-line separation and measurement with ICP-MS for rapid analysis and minimizing analytical interferences.
- Develop incident specific technical responses for Nuclear Power Plant emergency release and Radiological Dispersion Devices.

Acknowledgments

The authors would like to thank our colleagues on this project:

- Sandia National Laboratory: Sean Fournier
- Environmental Protection Agency, National Analytical Radiation Environmental Laboratory: John Griggs
- Environmental Management Support, Inc.: Robert Litman, and Robert Shannon

We would also like to thank the Murdock Trust, Partners in Science Program for funding our colleague, Dr. Rama Devagupta, and the support for her grant with the Kennewick School District.

Acronyms and Abbreviations

AAL	Analytical Action Level
Cs-137	Cesium-137
CFR	Code of Federal Regulations
CMRT	Consequence Management Response Team
d	day
DOE	U. S. Department of Energy
EPA	U. S. Environmental Protection Agency
FAL	DOE Fly Away Laboratory
fg/mL	femtograms/milliliter
GAC	granulated activated carbon
GADRAS	Gamma Detector Response and Analysis Software
h	hour
HPGe	high-performance germanium detector
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
keV	kiloelectron volt
L	liter
MCL	Maximum Contaminant Level
MCNP	Monte Carlo N-Particle model
MDC	Minimum Detectable Concentration
MERL	Mobile Environmental Radiation Laboratory
mL	milliliter
NaI	sodium iodide detector
NESHAP	National Emission Standards for Hazardous Air Pollutants
NPP	Nuclear Power Plant
PAG	Protective Action Guides
pCi/L	picocuries/liter
Pu-IND	Plutonium-based Improvised Nuclear Device
RDD	Radiological Dispersion Device
RTG	Radiothermal Generator

Contents

Figures

1.0 Introduction

After a radiological incident, the current methods for collecting and analyzing radionuclides in water by the Consequence Management Response Team (CMRT) involves laboratory assay of whole water samples, a process that inherently limits sensitivity to key radionuclides due to the typical small water volumes obtained and self-shielding of the sample. CMRT needs rapid, confident quantification of key radionuclides at concentrations corresponding to 1/10th (or better) of analytical action levels (AALs) derived from Protective Action Guides (PAG) established by the U.S. Environmental Protection Agency (EPA)[1] for drinking water and other resources. The analytical results are needed to provide clear communication and directed actions to responding federal, State, and local authorities for efforts such as turning off the intakes at municipal water treatment plants, providing evacuation notices and setting surveillance boundaries.

This report considers:

- Radioactive cesium-137 (Cs-137) in water
- Two types of radiological scenarios that result in the release of Cs-137 into water that would be used for public consumption
- Evaluation of the current approach for analyzing water by incident response teams, and the time for analysis of Cs-137
- Evaluation of a proposed approach using standard technologies for a sorbent to concentrate Cs-137 on a media that would then be analyzed, including:
    - Sorbent configuration for analysis
    - Volume of water to process for analysis
    - Time for processing water sample and for analysis of Cs-137
    - Sorbent characteristics/attributes
- Review of sorbents to concentrate Cs-137, considering attributes of the sorbent for use in incident response
- Conclusions and recommendations.

The goal of this report is to evaluate the process of adding a sorbent to the sampling process to preconcentrate Cs-137 and then analyze the sorbent to provide a rapid assessment of results to guide decisions on drinking water sources and the protection of the public. This report is a review, using available publications and reports. No experimental analyses were conducted. The conclusions include the next steps for the evaluation of the recommended sorbents and unit design for processing water sample for analysis.

1.1 Survey Parameters

Cs-137 was selected as the initial agent for study for several reasons [2]. Analysis and detection of Cs-137 in water has a long history [3-5]. Cs-137 is accessible through commercial channels in sealed sources, this feature makes it attractive for diversion by terrorists for use in dirty bombs. Cs-137 is also of interest because of its legitimate industrial uses and generation, thus there is the potential for an accident involving its release [6].

As part of developing improvements in nuclear incident response, several scenarios involving release of radioactive materials to the environment that result in contaminated water were identified [7-11]:

- A compromised radiothermal generator (RTG)

- A plutonium-based improvised nuclear device (Pu-IND)
- Emergency response and release from a damaged nuclear power plant (NPP; e.g., Chernobyl- or Fukushima Daiichi-type event)
- Radiological dispersion, either deliberately through a dirty bomb (radiological dispersion device, RDD [12, 13]); or as an inadvertent release through the mishandling of a sealed source [14, 15].

On review of the scenarios considered, Cs-137 does not provide a sufficient source term to be considered for further analysis for a Pu-IND or a compromised RTG. Thus, the remainder of this report will focus on measuring Cs-137 from NPP and RDD events.

The concept of protective actions started with the Federal Radiation Council in the 1960s where they established limiting guides for ingestion of a few radionuclides, including Cs-137 [1]. Cesium [16-19] can be assimilated by humans through its uptake by aquatic organisms as part of the food chain, or directly through ingestion of contaminated water, because of its biochemical similarity to the essential element potassium. Cs-137 as a gamma emitter is of concern for human health. EPA further refined these Federal Radiation Council guides as PAGs, considering the following principles in establishing exposure levels:

- Protect acute effects:
- Balance protection with other important factors and ensure that actions result in more benefit than harm.
- Reduce risk of chronic effects.

During the intermediate phase of activities for emergency planners, when the radiological source and releases have been brought under control, protective actions turn towards measurements of the environment and evaluations to determine if relocation of the public is needed, if the food supply and drinking water has become unacceptably contaminated, as well as other evaluations. Measurements of radioactive levels in the environment are taken for dose projections used to support decisions about protective measures. For drinking water, the protective action guidelines are [1]:

- 100 mrem (1 mSv or 0.1 rem) projected dose, for one year, to the most sensitive populations (e.g., infants, children, pregnant women and nursing women; most vulnerable populations to radioactivity);
- 500 mrem (5 mSv or 0.5 rem) projected dose, for one year, to the general population.

The guidelines are based on the “projected dose to an individual from a release of radioactive material at which a specific protective action to reduce or avoid that dose is recommended [1]. Dose includes contributions from all the radiological isotopes and background. They are not meant to be applied as strict numeric criteria, but rather as guidelines to be considered in the context of incident specific factors.

While the PAG is the notional guideline for the upper limit on intake for the public, in units of activity per liter, before action needs to be taken, the PAG only considers the isotope it corresponds to in the absence of any others. That is, the PAG of 6,200 pCi/L for Cs-137 [1] is only valid when no other isotopes are taken in by the public (above background). When other nuclides are present, Cs-137 represents only a part of the contribution to the dose received by the population. The dose limit and corresponding activity limit for Cs-137 then decrease when other nuclides are present. This adjusted limit is represented by the AAL, which is arrived at by generating a nuclide mixture and running the TurboFRMAC software. The significance of 10%

of the AAL is that is the decision limit concentration below which no action need be taken for drinking water.

For the purposes of this survey, the AAL will be evaluated for Cs-137 in water from a release due to an NPP or RDD scenario, comparing the time for analysis using current methods analyze water to methods that add a step to concentrate the Cs-137 onto an a sorbent and analyze the sorbent.

Sandia National Laboratories generated the AALs for each isotope for the NPP and Cs-137 based RDD scenarios using TurboFRMAC and provided the relative importance of each isotope in the overall mixture. This information was provided for the purposes of this report and in conjunction with the evaluation by EPA's National Analytical Radiation Environmental Laboratory and their preparation of "Use of Drinking Water Methods for Analysis of Radionuclides in Water Following a Radiological Event".

1.2 Outline of the Report

A base case is presented using current processes and procedures for the MERL and FAL mobile laboratories to analyze a water sample. This is compared to a case adding sorbents to the processes for preparing a water sample and then analyzing the sorbent. For the latter case, the configuration or geometry of the sorbent and the detector is further discussed. The time for processing a sample in the sorbent and the analysis time for various volumes of water are compared.

Radiochemical and traditional analytical chemical methods were explored, prospective trade-offs compared, and proposed efforts towards optimization identified for deployment in a forward operating scenario, such as a mobile laboratory [20-23]. Much of the recent research in Cs-137 separations and measurement is devoted to features associated high-level waste processing, with a substantial burst of research activity in monitoring and effluent remediation at scale following Fukushima [24-28], rather than rapid, confident detection of Cs-137 in an immediate post-release water incident environment [13, 28].

EPA approved analytical methods for Cs-137 are gamma spectroscopy are listed in 40 CFR 141.25 a., under "Gamma Emitters" (see Appendix II). However, 40 CFR 141.27 permits alternative techniques to be employed with the written permission of the State and concurrence by the Administrator of the EPA, "…only if it is substantially equivalent to the prescribed test in both precision and accuracy as it relates to the determination of compliance with any MCL [22, 23]."

After reviewing the contemporary regulatory literature, technical advances in Cs-137 sorbents and measurement methods, and post-incident exercise lessons learned there are opportunities to improve analytical performance and provide decision makers essential information for public water supplies [29-32].

The report concludes with recommendations for improvements to existing radiological response teams and their mobile laboratories as well as other considerations from the review of technologies for evaluating radionuclides in water.

2.0 Comparison of Methods for Cs-137 Lab Analysis for Radiological Response

This section discusses the base case for analyzing Cs-137 in water using current methodologies and systems, and options for improvement. The addition of a step for sample preparation and processing to include a sorbent that is analyzed (rather than the water) is presented. Configuration/geometry of the sorbent with analytical instruments is discussed (further evaluation is provided in Appendix A). Finally, a review of the most relevant literature for sorbents and Cs-137 is discussed, with further details in Appendix B.

2.1 Base Case: Consequence Management Scenarios

The base case analysis for this report assumes current procedures and methods are followed for collection and analysis of public drinking water. By the intermediate phase of a radiological incident, CMRT would set up mobile support systems such as EPA's Mobile Environmental Radiation Laboratory (MERL) or U.S. Department of Energy's Fly Away Laboratory (FAL). One of their tasks would be to determine if public drinking water has been affected by the radiological incident. Their methodology to analyze water is shown in Figure 1: (a) locations for water sampling would be identified; (b) 1 L samples of water would be collected; and (c) the water would be analyzed using gamma analyzers. For the purposes of this analysis, two field-deployable radiation detector systems were considered: the BE6530 (60% HPGe) detector available with the MERL; and the Canberra Falcon 5000 available with the FAL.

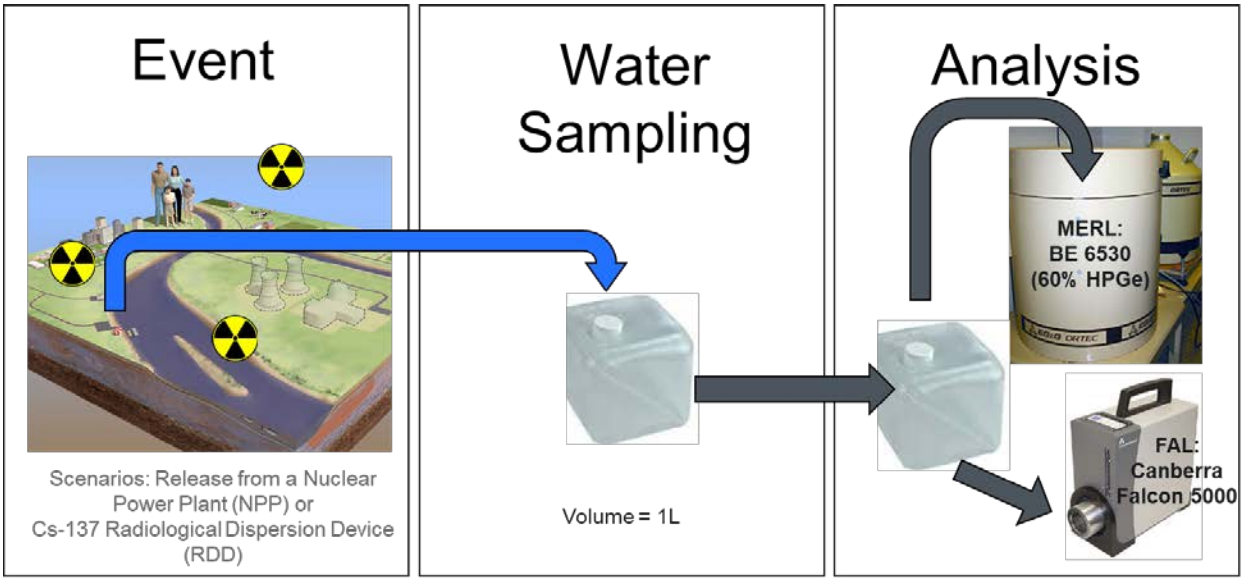

Figure 1. Base case for analysis of Cs-137 in water after a radiological release scenario by the MERL or FAL HPGe detectors.

CMRT prepare for several different radiological incidents. The [7-11] principal scenarios in which there is a significant Cs-137 contamination component include:

- RDD (a dirty bomb or the spread of contamination from a compromised [14, 15] sealed source): Simulated release assumes the entire composition is a single isotope, Cs-137, present in quantities higher than EPA's PAG for vulnerable populations [1]. This is a straightforward detection setting. However, this scenario is complicated by how

contamination is spread and transported by wastewater or stormwater flows to the receptors and selecting appropriate sampling points. Air dispersion models would likely be needed to augment understanding of Cs-137 contamination distribution and its relationship to drinking water sources, especially in an urban environment.

- NPP (e.g. Chernobyl or Fukushima-type events): Simulated releases are at pCi/L concentrations. For an NPP event, Cs-137 is one of the major remaining radioisotopes as a percentage of activity, however the contaminated effluent represents a complicated mixture. Cs-137 in a mixture of other radionuclides is more difficult to quantify and a sample treatment step before counting may be needed to achieve satisfactory signal fidelity (discussed further in Section 2.5.1).

For the base case, two HPGe detectors were modeled based on manufacturer-specified dimensions for the HPGe crystals. Detailed models including the complete mechanical design and surroundings were not included for this preliminary scoping study. MCNP[1] was used to model the detector efficiency for various sample media counting geometries, and GADRAS[2] was used to model typical detector backgrounds. Albuquerque, New Mexico was chosen as the location for background generation.

The base case modeling effort comprised a 10x10x10 cm^3 1 L container (simulating a Cubitainer [33]) positioned 0.5 cm from the detector face, with the Cs-137 source particles distributed evenly throughout. More detail on the MCNP model used can be found in Appendix A4.0Appendix A. The gamma ray energies were then tallied, and the absolute efficiency of the 661.657 keV peak from Cs-137 peak extracted. The efficiency and counts from the background spectra around the Cs-137 peak location were then used to calculate the minimum detectable concentration (MDC) for the measurement geometry based on the Currie method for determining the critical level found in the FRMAC Gamma Spectroscopist Knowledge Guide [34], modified to account for the number of liters of water and extraction efficiency. The MDC is calculated as in Equation 1:

$$MDC = \frac{4.65 \cdot \sqrt{N_B} + 2.71}{Y \cdot \varepsilon \cdot T \cdot V \cdot w}, \quad (1)$$

where *MDC* is the minimum detectable concentration in pCi/L; N_B is the number of counts in the background under the 661.657 keV Cs-137 peak; *Y* is the number of 661.657 keV gamma rays emitted per Cs-137 disintegration, ε is the absolute detector efficiency for a specific counting geometry; *T* is the sample count time; *V* is the volume of water in liters flowed through the sorbent; and *w* is the extraction efficiency of the process.

Figure 2 shows the results of the base case modeling effort for the MDC based on the time for counting a sample, which is proportional to the square root of the background counts. Also shown in Figure 2 are lines corresponding to the required critical level for laboratory analysis, which is 10% of the computed AAL [35], for the NPP and RDD scenarios. The solid black line denotes 10% of the AAL for the NPP and the dashed black line denotes 10% of the AAL for the RDD scenarios. The significance of 10% of the AAL is that is the decision limit concentration

[1] MCNP® is a registered trademark of Los Alamos National Laboratory
[2] GADRAS is a product of Sandia National Laboratory

below which no action need be taken for drinking water. Again, for the Cs-137 RDD, 10% of the AAL is 10% of the derived response level for the most vulnerable population (set at 100 mrem dose), which is 620 pCi/L Cs-137. The value for 10% of the AAL for the NPP is based on dose from all radioisotopes released (data provided by Sandia National Laboratory). The MDC allows for comparison of the sample count times by the BE6530 and the Falcon 5000 for both release scenarios.

Figure 2 shows that while an MDC exceeding the AAL for the RDD scenario is easily achieved with less than an hour of counting time by both HPGe detectors, an MDC meeting 10% of the AAL for the NPP scenario is not achieved by either detector even after 90 days of sample counting time. Though AALs can be modified based on established data quality and measurement quality objectives for a given response (resulting in reduced counting times), the modeled results represent a challenge to established methods even in the late phases of a response. Achieving such levels of detection for the intermediate phases of a response is an even more significant challenge. This modeling effort considered Cs-137 in the absence of other nuclides in water, a simplified case, which would be a highly, unlikely situation for an NPP scenario.

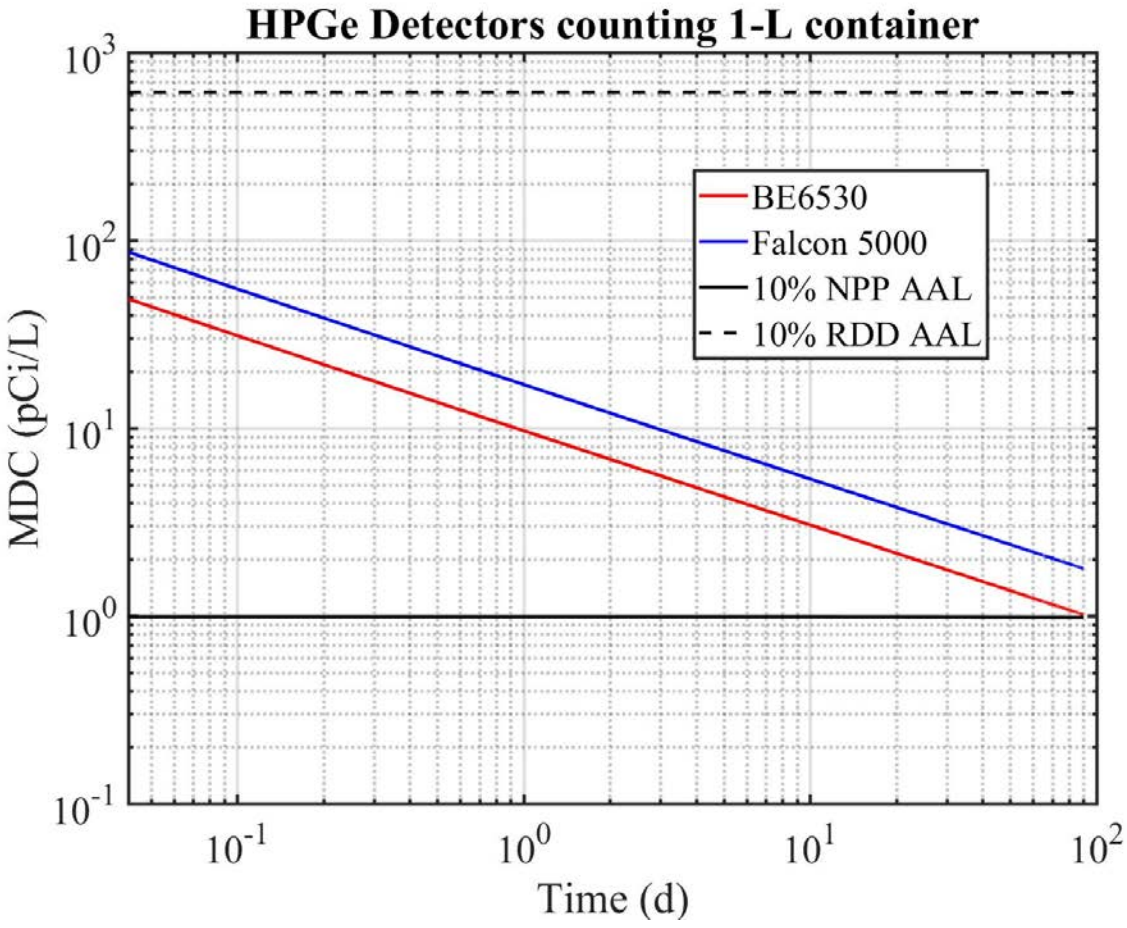

Figure 2. Minimum Detectable Concentration (MDC) curves vs. sample count time for a 1-liter container set adjacent to two different HPGe detectors.

Based on the information provided by Sandia National Laboratory for the release scenarios, there are no conditions as part of these scenarios where Cs-137 activity increases after the release event, though its activity relative to other isotopes increases dramatically in the NPP scenario between 30-90 days (from 0.14% at 0 hours to 2.1% at 2160 hours) due to the decay of shorter-lived isotopes. Because the potential for continuing, long-term losses to the environment in the NPP scenario and the elevation of its relative dose contribution, Cs-137 is of interest for decision makers. Additionally, in this case, if the concentration of Cs-137 remains relatively constant, inference regarding the presence and concentration of other radionuclides (e.g., strontium-90) can be made, simplifying subsequent data collection tasks.

2.2 Adding Sorbents to the Base Case: Sample Preparation and Processing

For comparison, Figure 3 shows the base case with the addition of a sample preparation and processing step. A greater volume of water would be collected and brought to the mobile laboratory for sample preparation and processing. Sorbent would be added to a sorbent filter housing, supporting the material for a single pass of the sample water volume, retaining the Cs-137 on the sorbent, and the discharge water collected for disposal. The sorbent would then be transferred to another container and analyzed for Cs-137. Figure 3 depicts the container as a disk, which is the configuration that produced the highest absolute efficiencies for counting Cs-137 on the two detectors.

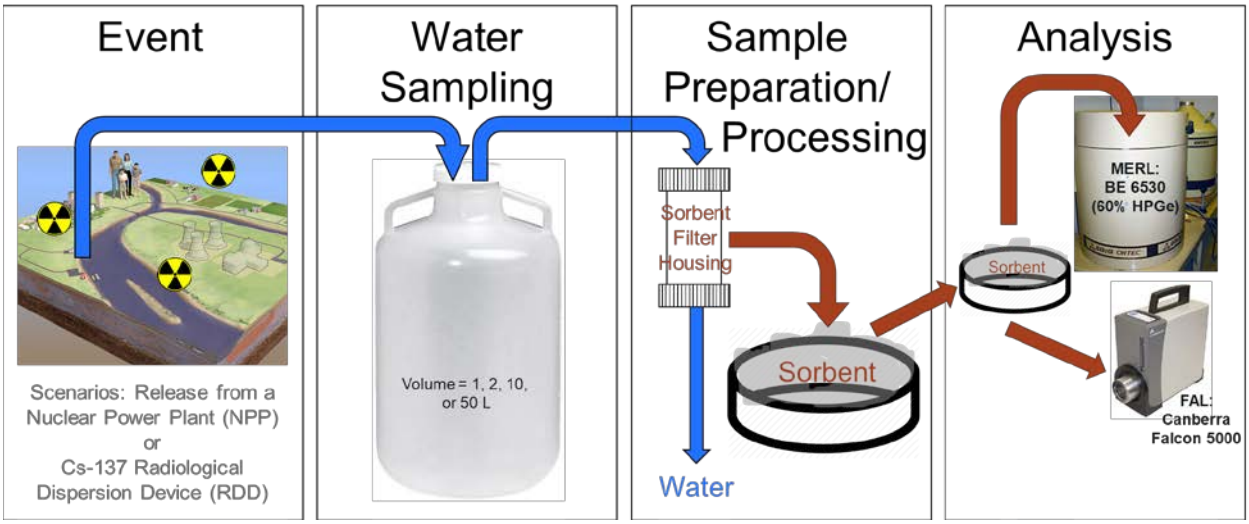

Figure 3. Addition of sample preparation/processing into the base case for analysis of Cs-137 in water after a radiological release scenario by the MERL or FAL HPGe detectors.

First, an evaluation of the sample geometry was conducted to identify the best configuration for analysis of the container holding the Cs-137 sample for analysis. For this analysis, the Cs-137 activity was constant for all the geometries. Appendix A describes additional model simulations performed to evaluate the effectiveness of alternate counting geometries that could be employed to measure a 1 L water sample, including a Marinelli beaker, a long vertical column (imitating a conventional ion exchange separations column), and a disc (similar to a petri dish), that could be an alternative exchange column geometry or the cake from a co-precipitation step. The column and disc geometries assume that the Cs-137 source term in the original 1 L water

sample can be retained on the media or precipitate through a chemical process to the smaller (target) volume.

The results for the most promising of these geometries, the disc, are shown in Figure 4. The results for a 1 L container are included in Figure 4 for comparison purposes. The disc geometry achieves the Cs-137 10% AAL level for the NPP scenario at 114 h (4.75 d) for the BE6530 and at 239 h (10 d) for the Falcon 5000. The disc geometry is presented for the remainder of these analyses.

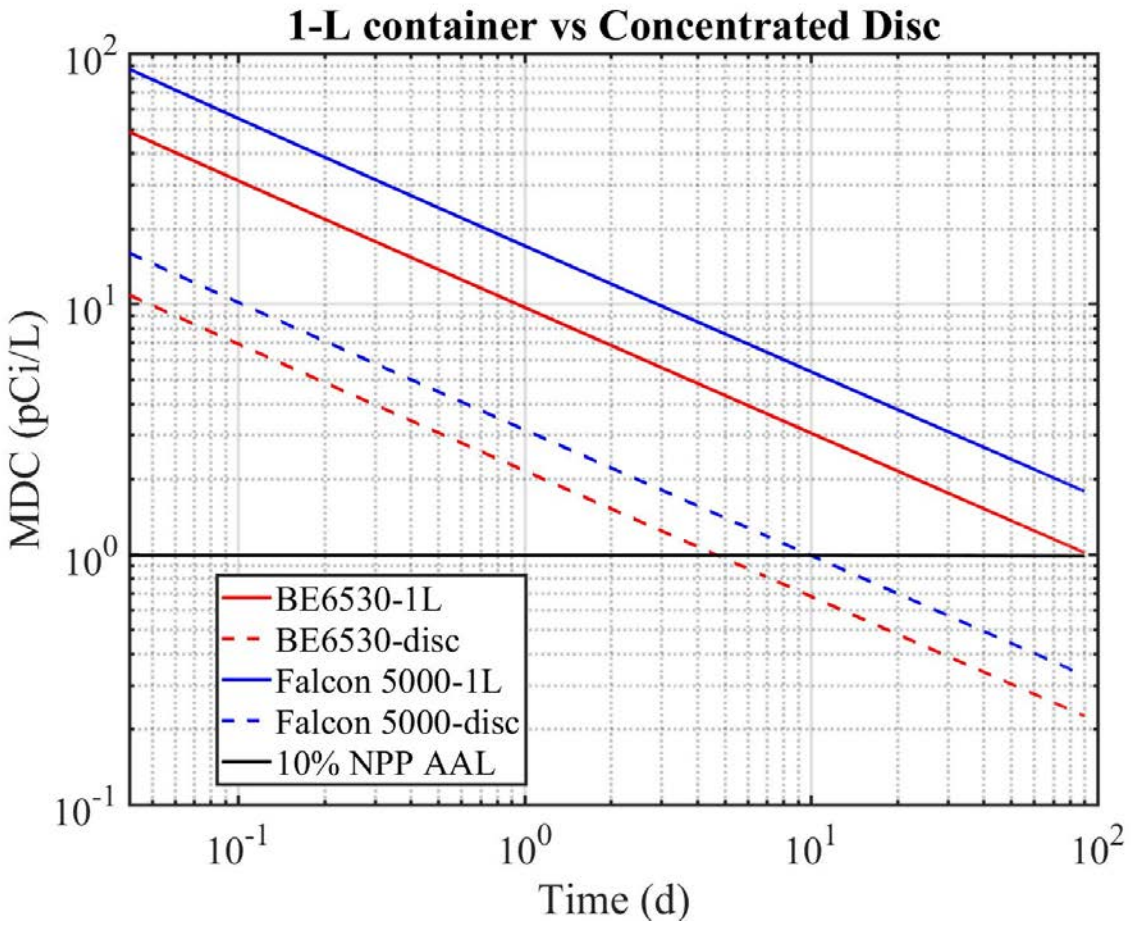

Figure 4. Minimum Detectable Concentration (MDC) curves for a sample containing the same Cs-137 activity in a 1 L container and a disc, counted by two different HPGe detectors.

Additional model runs were conducted to show the effect of various levels of extraction inefficiency for a single liter (1 L) of sample water processed (Figure 5). At 90% retention rate, the BE6530 detector achieves the Cs-137 10% AAL at 5.8 d (compared to 4.75 d at 100% retention), and the Falcon 5000 achieves the Cs-137 10% AAL at 12.5 d (compared to 10 d at 100% retention). In both cases, decreasing the extraction retention factor by 10% increases the amount of time to achieve the Cs-137 10% AAL by a factor of 1.25. Since the extraction efficiency is inversely proportional to the MDC, it has a greater effect on the MDC than the counting time.

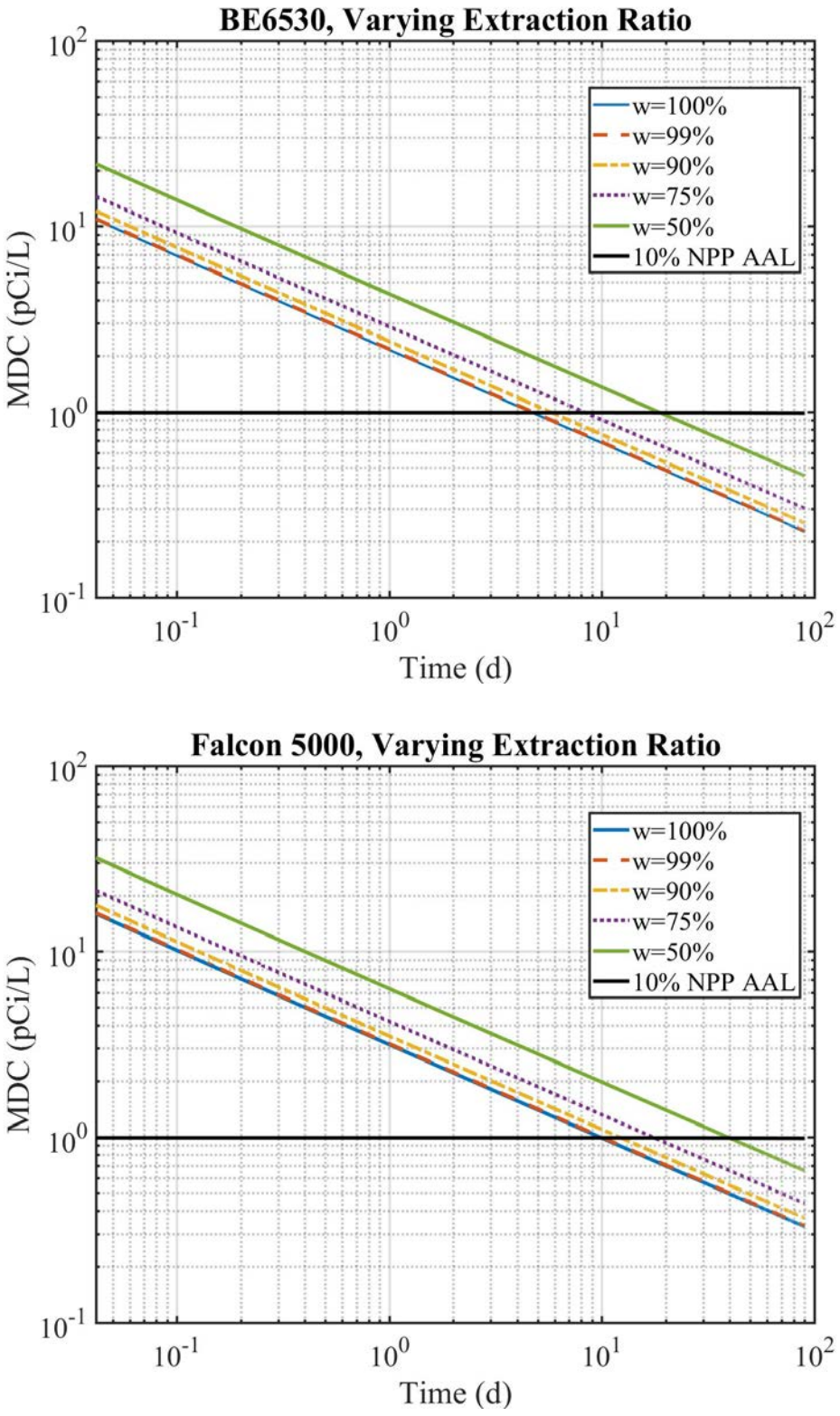

Figure 5. Minimum Detectable Concentration (MDC) curves for different HPGe detectors for a concentrated disc with various retention rates of concentrated contamination.

There are two important takeaways concerning sorbent efficiencies. One, as Cs-137 removal efficiency of the sorbent decreases, the length of time for a result is still better than the time to receive results from samples away to offsite laboratories for alternative analyses. Two, the efficiency of the sorbents should be further evaluated in laboratory studies (outside the scope of this report) and documented because the efficiency of the sorbent should be included in the calculations for the results and decisions by CMTR.

The volume of the water sample to be processed with the sorbent was considered next. The MDC curves in Figure 2 only consider 1 L of water volume processed through the sorbent filter housing. If more water is processed and a proportional amount of Cs-137 removed onto the sorbent, more radioactivity will be present in the same disc of material and improve the counting time for the HPGe detectors.

The sample water passes through the sorbent held in a filter housing. Water could be pumped or gravity-feed through the sorbent filter housing. Sorbent filter housings were not evaluated specifically. Filter housings are readily constructed out of plumbing supplies or prepared filter systems for water analyses are available through dealers that offer analyses for agricultural purposes.

Figure 6 shows several MDC curves illustrating the sample counting time of sorbent with different volumes of water: 1, 2, 10 and 50 L. Note, the x-axis on Figure 6 is different from the x-axis on Figure 2, Figure 4 and Figure 5. The MDC curves show that if 2 L of sample water were processed, the counting time to get to the Cs-137 10% AAL would be 30.5 h (1.3 d) for the BE6530 and 61.7 h (2.6 d) for the Falcon 5000. And if 10 L of sample water were processed, the counting time to get to the Cs-137 10% AAL would be 3.46 h (<1 d) for the BE6530 and 11.9 h (<1 d) for the Falcon 5000.

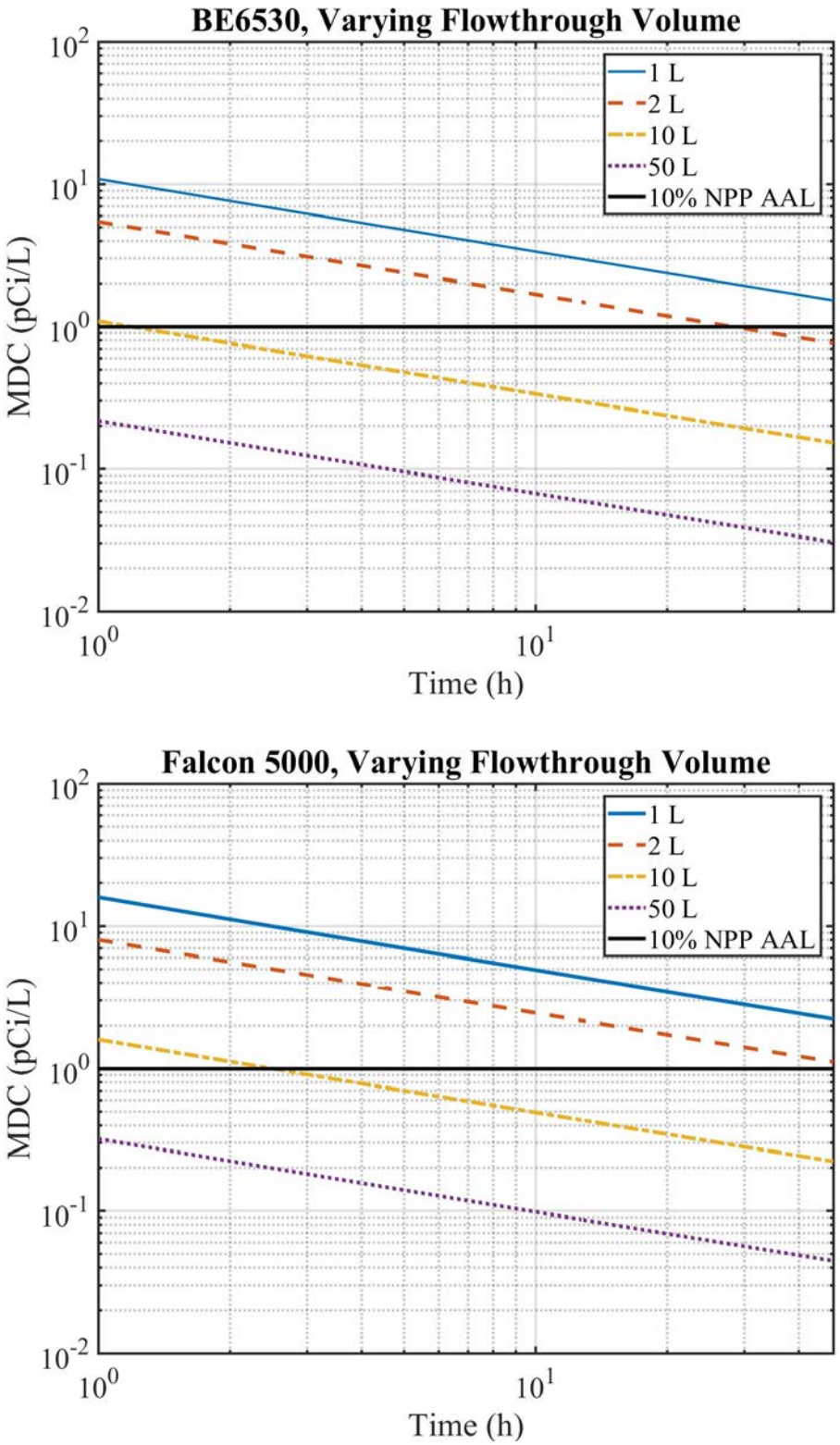

Figure 6. Minimum Detectable Concentration (MDC) curves for various HPGe detectors counting a disc of sorbent processed with various volumes of sample water, with the X-axis scale shown in hours (not days).

These counting times present a much more viable picture for intermediate phase response, improving significantly as more water flows through the extraction process. The effective volume of water counted is inversely proportional to the MDC, unlike the counting time which is tied to the number of background counts in the numerator, and so only decreases the MDC proportional to $1/T^{1/2}$. Thus, the water volume flowed through the extraction process has a much greater effect on MDC than counting time.

Finally, by adding a sample processing step to the base case, time is needed to run the water through the sorbent filter housing and configure the sorbent into the disc configuration for analyzing with the HPGe detector. Appendix A includes more information on the assumptions used in this evaluation. The disc geometry was assumed. The volume of the disc represents a media bed volume for the purposes of estimating how long to process liquid through a sorbent, e.g., ion exchange, for sample processing. Time to process through the sorbent was considered to be bounded by the time to process a 2 L volume through a typical ion exchange media (~4 h). Figure 7 shows the relative time to process sample volumes of 1, 2, 10 and 50 L. This is the time needed by the staff of the MERL or FAL to work with the water sample and sorbents prior to starting the count time with a detector.

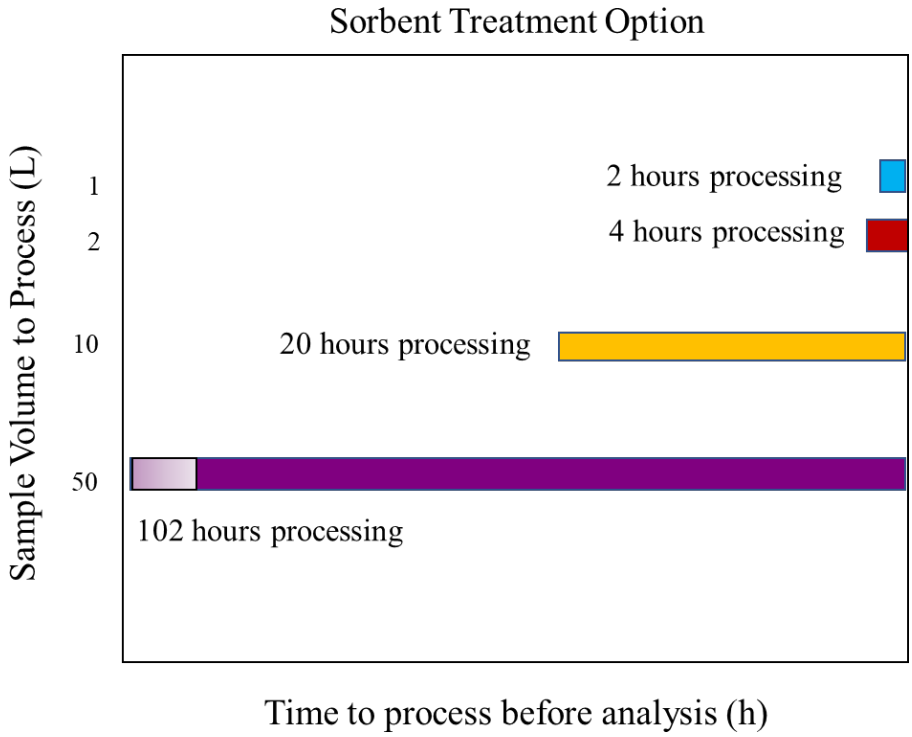

Figure 7 Time to process volumes of 1, 2, 10 and 50 L prior to analyses with an HPGe detector

A caveat must be added to the promising results in Figure 6 and Figure 7 because concentrating Cs-137 on sorbents is not 100% efficient or instantaneous. Figure 5 demonstrates that the counting time does not change significantly if the sorbent is 90% efficient [29, 36]. However, the analyst must consider sorbent efficiencies and the keep track of the sample water volume processed as part of providing the result of Cs-137 in pCi/L of sample water.

These modeled results indicate that efficiencies in counting time varies based on:

- Configuration/geometry of water sample for analysis with HPGe detectors (disc has highest absolute efficiency)
- Sorbent removal efficiency is inversely proportional to the MDC, which has a greater effect on the MDC than the counting time
- Sample volume processed onto the sorbent is also inversely proportional to the MDC.

Considering the time to process a sample with the improvements in counting time through the concentration of Cs-137 on a sorbent, rapid analyses are possible, and the results can get to the decision makers reliably and with less time than offsite analyses of public drinking water. Processing 10 L of sample onto a disc of sorbent provides nearly two orders of magnitude improvement in counting time to provide results for a decision maker compared to the current practice (base case).

2.3 EPA Methods for Analysis

EPA Method 901.1 [37] provides specific guidance regarding the sampling and analysis of Cs-137 contaminated water samples. There are currently 11 qualified methods from the mid-1970s to the early 1990s for Cs-137 measurement with well-documented steps to obtain high-quality data. With respect to maintaining compliance, this prescriptive regulatory framework provides highly accurate and reliable results for maintaining a safe water supply.

However, the reliance on a prescriptive regulatory framework aimed at compliance presents several drawbacks, regardless of radiochemical analytical method, for application in an incident response for the CMRT:

- Time consuming (preparation and analysis)
- Infrastructure needs
- Requires tailored processes and procedures that deliver qualified results

The same characteristics that provide robust and consistent results from these methods developed to protect the water supply present drawbacks for application as part of rapid incident response. Three of them require a specific radiochemical separation step, prior to testing and one of them involves an ion exchange step prior to measurement [22, 38]. The methods using separation and concentration require up to date test instructions to be available to the laboratory team, regardless of the laboratory used for analysis. There is a process available to qualify new test methods, but it has not been applied with respect to meeting the PAG limits for detection as part of incident response (http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100MESN.txt).

Additionally, these methods have not been updated to reflect advances in the state of the art to qualify new materials and techniques. Although, seven of them can use a homogenous liquid sample, similar to the separation techniques used in [21], the detector technologies in the methods have been specifically identified; thus newer, more robust detection technologies have not been qualified. There is a process for qualifying new analytical methods, but it has not been applied with respect to meeting the PAG limits for detection as part of incident response (https://www.epa.gov/dwanalyticalmethods/drinking-water-alternate-test-procedure-program).

Once the preparation and handling methods for the sample are qualified and the new instrumentation is qualified, procedures and instructions can be prepared for the CMRT mobile laboratories and other facilities that may be considered as part of a wider response effort (e.g., analytical laboratories at commercial nuclear plants or U.S. Government facilities such as the DOE National Laboratories).

2.4 Technologies to Meet PAG Limits in Forward Operating Laboratories and as Prospective First-Responder Use

A broad technology review was undertaken to identify detection methods and separation techniques that satisfied an envelope of technical sensitivity, maturity, availability, cost, and scalability. NaI detectors, liquid scintillation counters (LSC), and HPGe detectors were reviewed for sample quantities, throughput, and counting times [39-46]. Through a literature review, NaI detectors and LSC were discarded as possibilities due to their more limited performance compared to HPGe. Especially in the NPP case, where an abundance of other fission-product nuclides would create a crowded gamma ray spectrum, an HPGe detector provides the resolution needed to sufficiently differentiate the Cs-137 peak from other nuclides in order to accurately estimate the Cs-137 activity present in a sample.

2.5 Desired Features of a Forward-Based System

This section summarizes additional considerations for the complexity of evaluating drinking water sources after a radiological incident. Drinking water sources may contain more radionuclides than Cs-137, and present additional analytical challenges. The process for evaluating the most promising sorbents is discussed, with particular emphasis on the constraints for operations during incidence response with the MERL or FAL

2.5.1 Improve Signal to Noise Ratio

Although contaminated liquid samples can be taken and processed as individual batches, this method of sequencing introduces several constraints. Measuring 1-L samples using radiochemical methods without a concentration step takes a long time to provide analytical results (Figure 2) and occupies the subject HPGe detectors for the duration of the counting time.

Unlike in the RDD scenario, in the NPP scenario, there are several potential interferences with Cs-137 gamma lines (662 keV). Interference would be considered a signal within ~3 keV either lower or higher from 661.657 keV to interfere with HPGe (~2 keV FWHM at 662 keV, thus ~4 keV rounded up for 5 sigma fidelity was assumed). The “interference range” for the detector is then 657.657 keV – 665.657 keV.

- La-141 has a 662.06 keV gamma, Y = 0.0259%
- Ba-142 has a 660.9 keV gamma, Y = 0.227%
- I-135 has a 656.09 keV gamma, Y = 0.075%
- Mo-101 has a 660.64 keV gamma, Y = 0.224%
- Pu-239 has a 658.86 keV gamma, Y = 9.7E-6%; 664.58 keV gamma, Y = 1.66E-6%
- Fr-223 has a 663.7 keV gamma, Y = 0.0012%
- Th-227 has a 662.8 keV gamma, Y = 5.9E-5%
- Te-131m has a 665.05 keV gamma, Y = 4.18%
- Nb-97 has a 657.94 keV gamma, Y = 98.23%

Using a batch reactor system or in-line flow configuration to process multiple volumes of contaminated water and specifically concentrate the Cs-137 with a favorable media and geometry can address speed and scalability issues while maintaining analytical precision.

It should be noted for completeness that signal-to-noise can also be improved by reducing the amount of background radiation flux that reaches the detector. However, because the background counts term is proportional to the square root of the MDC, it is not as effective as concentrating the amount of material placed in front of the detector which has a directly proportional effect. Additionally, the most effective gamma shielding takes the form of dense, high atomic number materials, and such materials are thus heavy. Effective gamma ray shielding is accordingly non-ideal for long-distance transport, which is often a requirement for CMRT response.

2.5.2 Complexity in Operations with the Addition of Sorbents

Appendix B summarizes the review of publications and reports for sorbents of Cs-137. Around 60 publications and reports were collected and reviewed. Many of these papers provided additional insight on unit operations, and other considerations included in this report. However, only 10 of the papers are applicable to the intermediate phase for a radiological response. Those papers are included in Appendix B, with summaries of the sorbent material, type of adsorption, targeted radionuclide (some sorbents are not Cs-137 specific), sample water type (e.g., fresh- or saltwater), and complexing ions (possible interferences). This section highlights the conclusions of the review of publications.

For the purpose of this study, sample preparation and conditioning requirements were kept to a minimum. Direct measurement of the liquid or using single-stage, solid-liquid separations were assumed. Technologies using reverse osmosis [47] or nanofiltration as pretreatment steps before ion exchange to enhance equilibrium performance or co-precipitation could be worth considering because they can be done relatively quickly but were not considered further in this stage. Accounting for the mass (volume) of the permeate and reject fractions as part of this system during processing becomes a required, high precision exercise for quantitation and introduces an added level of complexity that may not be warranted. In other cases where the lag time introduced by a potential conditioning step took too long, that sorbent option was removed from consideration. Furthermore, liquid-liquid extraction technologies, or applications involving eluting ion exchange media, although promising in some instances, were not considered at this stage. Many of these options would be ideal for contract laboratories, improving existing EPA approved methodologies for Cs-137 and other radionuclide analyses.

Preferred sorbents had long successful histories of cesium removal, were safe and shelf stable, and immediately available at low cost. EPA methods allow for the use of ion exchange media (sorbents) and precipitation as potential techniques to enhance radiochemical assays. The sorbents identified for additional study and fast-track qualification included various ferrocyanide salts (Prussian blue), zeolites, and chemically modified granular activated carbon. These materials satisfy the principal design features identified at a high level. They are reliable, relatively quick-acting, and easily accessible. If any of these materials are used to concentrate cesium as part of a pre-process step, they can be dried safely and simply as part of sample preparation. They were also considered likely to be qualified quickly as part of a new or amended test method because of their long heritage in Cs-137 separations.

The literature [43] has identified several advanced materials, such as carbon nanotubes, titanate nanofiber, and graphene oxides that are very effective and appear amenable to miniaturization, implementation in a flow-based system, and developing a standard sample geometry for counting. However, many of these high-tech sorbents were still in early stages of technical maturity, costly (or unavailable in commercial quantities), and their shelf-stability was not certain.

Using Prussian blue (or a variant) as a co-precipitate or as an additive to an ion exchange bed appears to meet the initial requirements for improving the signal to noise ratio by concentrating Cs-137 into a smaller volume (fostering rapid, quantitative results for Cs-137). It is fast-acting, safe, robust across chemical environments, and selective for cesium. However, the collection, handling, and water processing of the media or precipitated cake demands a compact wet chemistry infrastructure platform for forward operations [18, 36, 48, 49].

Recently tested ion exchange media (e.g. zeolites) would need to be specifically qualified for use. Zeolites are inexpensive, well understood agents with high specificity, and are safe to handle. However, a significant drawback of ion exchange methods in general is that the method of action is equilibrium-based. At the low concentrations defined by the AALs (10% of the limit), this functional characteristic requires processing several unit volumes of liquid to achieve meaningful uptake of the target contaminant for eventual analysis. Similar to using Prussian blue, additional effort would be needed to identify and define proper media handling procedures before counting.

Prospective sorption techniques using chemically modified granulated activated carbon (GAC) have several of the same positive features of ion exchange. GAC is an inexpensive and mature technology [42] it can also be conditioned with additives to enhance its specificity [50]. However, with chemical treatment, some negative features are accentuated. It becomes more costly and its shelf stability is not well-known. Furthermore, GAC's principal method of action is adsorption is also slow and non-specific, therefore even with chemical treatment, there may be undesired sorption of interfering contaminants. On further examination, GAC is much more suited to large-scale industrial water treatment, than as a target for increasing the signal to noise ratio while maintaining analytical fidelity and precision for Cs-137 detection in an NPP scenario.

3.0 Recommendations

The following highlights the findings in this report and follow on recommendations.

1. Align MERL and FAL capabilities with EPA PAG guidance.
Methods and techniques regarding currently installed (HPGe) conform to NESHAP requirements, but other laboratories that may be called upon to perform analyses using this technology should use identified pathways to document and qualify incumbent processes for PAG/regulatory requirements.

HPGe detectors were found to provide the requisite performance and had been going through successive optimizations, allowing greater sensitivity and a more compact footprint, favoring installation on a mobile laboratory platform.

2. Evaluate an ion exchange flow-through system for sample concentration.
Using Prussian blue as a co-precipitate or as an additive to an ion exchange bed in a flow system processing 10 L of water appears to meet the requirements for improving the signal to noise ratio by concentrating Cs-137 into a smaller volume in a timely manner. The proposed configuration provides rapid, quantitative results for Cs-137 with equipment already installed on the FAL and MERL. The methods and techniques would take some time to qualify, and process engineering design for a mobile system would represent some challenges, but there do not appear to be significant technological advances needed to implement this solution.

As part of an engineered flow-based system that could be installed on a mobile platform instead of a time-consuming batch process, several novel engineered materials appear promising for Cs-137 detection and quantitation but are early in technical maturity. Additional research and development efforts are needed to assemble the individual technologies as part of a compact analytical solution in the future.

3. Evaluate in-line separation and measurement with ICP-MS.
Although radiochemical methods are the default selection for analysis, the target MDC range is attainable using ICP-MS technology with an in-line chromatographic separation from barium [51] with a high degree of specificity and fidelity (three sigma detection limit of 0.9 fg/mL). This performance practically achieves the target sensitivity of 10% of the AAL with turnaround times of ~30 minutes. Other ICP-MS techniques have promise for $^{Cs\text{-}137}$ and other radioisotopes of interest [52].

The sources that interfere with Cs-137 in mass spectroscopy have been found to be straightforward to control

- Ba-135, Ba-137
- Stable Cs-133 peak tailing on Cs-135
- Requires chemical separation including ion exchange chromatography or reaction cell to remove isobaric interference
- No direct interference from isotopes identified scenarios, but Ba-137 will interfere after the Cs-137 decays into it.

Therefore, pursue qualification (and ruggedization) of ICP-MS methods for Cs-137 and other species to address incident response needs. This option is where many researchers in radiochemical characterization are moving with respect to sensitivity, lifecycle cost, and scalability (equipment size and throughput) for analytical methods. Partner with experts in

nuclear waste processing analytical techniques to leverage their experience with respect to ICP-MS and expand to analyze other fission products as well.

4. Develop incident specific technical responses for Nuclear Power Plant emergency release and Radiological Dispersion Devices.

The NPP analytical requirements are far more complex than those anticipated for a dirty bomb or compromised source. However, the RDD response would benefit by having a variety of water models performed with respect to their drinking water and wastewater treatment networks [53] to identify relevant sampling points for a water-based contamination scenario.

4.0 References

1. EPA, U.S., *EPA-400/R-17/001, PAG Manual: Protective Action Guides and Planning Guidance for Radiological Incidents*. 2017.
2. DHHS, U.S., *Public Health Statement for Cesium.* 2004.
3. EPA, U.S., *EPA-600/4-80-032, Prescribed Procedures for Measurement of Radioactivity in Drinking Water*. 1980.
4. EPA, U.S., *EPA-600/4-75-008 (revised), Interim Radiochemical Methodology for Drinking Water*. 1976.
5. U.S.G.S., *Methods for determination of radioactive substances in water and fluvial sediments: Techniques of Water-Resources Investigations 05-A5*. 1977.
6. Initiative, N.T., *Radiological: Raising Awareness, Improving Security and Strengthening Global Standards to Prevent Dirty Bombs*. 2019: Washington, D.C.
7. DOE, U.S., *DOE-NV-25946--1554, Federal Radiological Monitoring and Assessment Center, Monitoring Manual Volume 1: Operations*. 2012.
8. DOE, U.S., *DOE-NV-25946--1558, Federal Radiological Monitoring and Assessment Center, Monitoring Manual Volume 2: Radiation Monitoring and Sampling*. 2012.
9. Laboratories, S.N., *SAND2015-2884R, Federal Radiological Monitoring and Assessment Center, Manual, Volume 1: Overview and Methods*. 2015.
10. Laboratories, S.N., *SAND2010-2575P, Federal Radiological Monitoring and Assessment Center, Manual, Volume 2: Pre-Assessed Default Scenarios*. 2010.
11. EPA, U.S., *Use of Drinking Water Methods for Analysis of Radionuclides in Water Following a Radiological Event*. 2019, National Analytical Radiation Environmental Laboratory.
12. DHHS, U.S., *Radiation Emergency Medical Management, Radiological Dispersion Devices* 2019.
13. DHS, U.S., *Radiological Dispersal Device Response Guidance: Planning for the First 100 Minutes*. 2017, National Urban Security Technology Laboratory.
14. NRC, U.S., *Event 54042 Notification Report for May 21, 2019, Unplanned contamination event due to breached Cs-137 Source*. 2019.
15. Rana, D., et al., *Radioactive decontamination of water by membrane processes — A review.* Desalination, 2013. **321**: p. 77-92.
16. Li, W., et al., *Measurement of stable and radioactive cesium in natural waters by the diffusive gradients in thin films technique with new selective binding phases.* Anal Chem, 2009. **81**(14): p. 5889-95.
17. Nakanishi, T.M., *Agricultural implications of the Fukushima nuclear accident.* J Radiat Res, 2016. **57 Suppl 1**: p. i47-i52.
18. Shizuma, K., et al., *Identification and temporal decrease of (137)Cs and (134)Cs in groundwater in Minami-Soma City following the accident at the Fukushima Dai-ichi nuclear power plant.* Environ Pollut, 2018. **234**: p. 1-8.
19. Steinhauser, G., A. Brandl, and T.E. Johnson, *Comparison of the Chernobyl and Fukushima nuclear accidents: a review of the environmental impacts.* Sci Total Environ, 2014. **470-471**: p. 800-17.
20. Mariet, C., et al., *Microfluidics devices applied to radionuclides separation in acidic media for the nuclear fuel cycle.* Micro and Nano Engineering, 2019. **3**: p. 7-14.
21. Castrillejo, M., et al., *Reassessment of (90)Sr, (137)Cs, and (134)Cs in the Coast off Japan Derived from the Fukushima Dai-ichi Nuclear Accident.* Environ Sci Technol, 2016. **50**(1): p. 173-80.
22. GPO, U.S., *40 CFR § 141.25 - Analytical methods for radioactivity*. 2019.
23. GPO, U.S., *40 CFR 141.27 - Alternate analytical techniques*. 2012.

24. Denton, M.S., M.J. Manos, and M.G. Kanatzidis, *Highly Selective Removal of Cesium and Strontium Utilizing a New Class of Inorganic Ion Specific Media (Paper Number 9267)*, in *Waste Management Symposia 2009, Waste Management for the Nuclear Renaissance*. 2009: Phoenix, AZ.
25. Denton, M.S. and M.G. Kanatzidis, *Innovative Highly Selective Removal of Cesium and Strontium Utilizing a Newly Developed Class of Inorganic Ion Specific Media (Paper Number 16221)*, in *12th International Conference on Environmental Remediation and Radioactive Waste Management*. 2009, ASME: Liverpool, UK. p. 249-262.
26. Denton, M.S., J.L. Mertz, and K. Morita, *Isotope Specific Remediation Media and Systems (Paper Number 13614)*, in *Waste Management Symposia 2013, International Collaboration and Continuous Improvement*. 2013: Phoenix, AZ.
27. Choi, W.N., U. Lee, and H.R. Kim, *Radiological assessment on spent resin treatment facility and transportation for radioactive waste disposal.* Progress in Nuclear Energy, 2020. **118**.
28. DHHS, U.S., *Population Monitoring in Radiation Emergencies: A Guide for State and Local Public Health Planners, second edition*. 2014.
29. Hamasaki, T., et al., *Removal efficiency of radioactive cesium and iodine ions by a flow-type apparatus designed for electrochemically reduced water production.* PLoS One, 2014. **9**(7): p. e102218.
30. Gilmour, S., et al., *Current Measures on Radioactive Contamination in Japan: A Policy Situation Analysis.* PLoS One, 2016. **11**(3): p. e0152040.
31. Hamada, N., H. Ogino, and Y. Fujimichi, *Safety regulations of food and water implemented in the first year following the Fukushima nuclear accident.* J Radiat Res, 2012. **53**(5): p. 641-71.
32. Ishikawa, T., *Radiation Doses and Associated Risk From the Fukushima Nuclear Accident.* Asia Pac J Public Health, 2017. **29**(2_suppl): p. 18S-28S.
33. America, H.D.o.Z., *CUBITAINER®*. 2020.
34. Laboratories, S.N., *SAND2019-9768R, Federal Radiological Monitoring and Assessment Center, Gamma Spectroscopist Knowledge Guide.* 2019.
35. Laboratories, S.N., *SAND2013-10382P, Federal Radiological Monitoring and Assessment Center, Laboratory Analysis Manual*. 2013.
36. Zhang, H., et al., *Removal of cesium from low-level radioactive wastewaters using magnetic potassium titanium hexacyanoferrate.* Chemical Engineering Journal, 2015. **275**: p. 262-270.
37. EPA, U.S., *EPA/600/4/80/032, Method 901.1: Gamma Emitting Radionuclides in Drinking Water." Prescribed Procedures for Measurement of Radioactivity in Drinking Water* 1980.
38. DOE, U.S., *Compendium of EPA-Approved Analytical Methods for Measuring Radionuclides in Drinking Water*. 1998.
39. Currie, L.A., *Limits for qualitative detection and quantitative determination. Application to radiochemistry.* Analytical Chemistry, 2002. **40**(3): p. 586-593.
40. Hou, X. and P. Roos, *Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples.* Anal Chim Acta, 2008. **608**(2): p. 105-39.
41. Hossain, I., N. Sharip, and K.K. Viswanathan, *Efficiency and resolution of HPGe and NaI(Tl) detectors using gamma-ray spectroscopy.* Scientific Research and Essays, 2012. **7**(1).
42. Higaki, S. and M. Hirota, *Decontamination efficiencies of pot-type water purifiers for (131)I, (134)Cs and (137)Cs in rainwater contaminated during Fukushima Daiichi nuclear disaster.* PLoS One, 2012. **7**(5): p. e37184.
43. Technologies, M., *Germanium Detectors*. 2020.

44. Mirion Technologies (Canberra), I., *Falcon 5000® Portable HPGe-Based Radionuclide Identifier*. 2017.
45. ORTEC, *High Purity Germanium (HPGe) Radiation Detectors*. 2020.
46. ORTEC, *The Best Choice of High Purity Germanium (HPGe) Detector*. 2003.
47. Combernoux, N., et al., *Treatment of radioactive liquid effluents by reverse osmosis membranes: From lab-scale to pilot-scale.* Water Res, 2017. **123**: p. 311-320.
48. Parajuli, D., et al., *Comparative study of the factors associated with the application of metal hexacyanoferrates for environmental Cs decontamination.* Chemical Engineering Journal, 2016. **283**: p. 1322-1328.
49. Michel, C., et al., *Breakthrough studies of the adsorption of Cs from freshwater using a mesoporous silica material containing ferrocyanide.* Chemical Engineering Journal, 2018. **339**: p. 288-295.
50. Kosaka, K., et al., *Removal of radioactive iodine and cesium in water purification processes after an explosion at a nuclear power plant due to the Great East Japan Earthquake.* Water Res, 2012. **46**(14): p. 4397-404.
51. Liezers, M., O.T. Farmer, and M.L. Thomas, *Low level detection of (135)Cs and (137)Cs in environmental samples by ICP-MS.* Journal of Radioanalytical and Nuclear Chemistry, 2009. **282**(1): p. 309-313.
52. Ohno, T. and Y. Muramatsu, *Determination of radioactive cesium isotope ratios by triple quadrupole ICP-MS and its application to rainwater following the Fukushima Daiichi Nuclear Power Plant accident.* Journal of Analytical Atomic Spectrometry, 2014. **29**(2).
53. Mikelonis, A., et al., *Urban Fate and Transport Modeling of Contaminants: The Unique Needs of Emergency Response and the Potential for Adapting Existing Models.* Journal of Water Management Modeling, 2018.
54. Simpson, B.C., et al., *Development of Ion Specific Media to Treat 90Sr-Contaminated Water at Fukushima Daiichi Nuclear Power Plant - (Paper Number 5029)*, in *GLOBAL 2015: Nuclear Fuel Cycle for a Low-Carbon Future*. 2015, Societe Francaise d'Energie Nucleaire - SFEN: Paris, France.

Appendix A – Additional Details on Analyses for Unit Design

Additional details are included here to support: the geometry of the sample to be counted on the HPGe detectors; and the basis for the time to process sample volume through the sorbent filter housing.

A.1 MCNP Model Geometry for Sample and HPGe Detectors

Figure A.1 shows the MCNP geometry used to model the BE6530 (60% HPGe) and Falcon 5000 detectors, as well as the 1-L container and concentrated disc source media. Not all geometries are depicted here, but the geometry parameters such as the size of the 1-L container (a 10x10x10 cm^3 cube) and the distance from detector face to the container face were preserved for all detector-container model variations (e.g., disc and BE6530 (60% HPGe) and 1-L container and Falcon 5000).

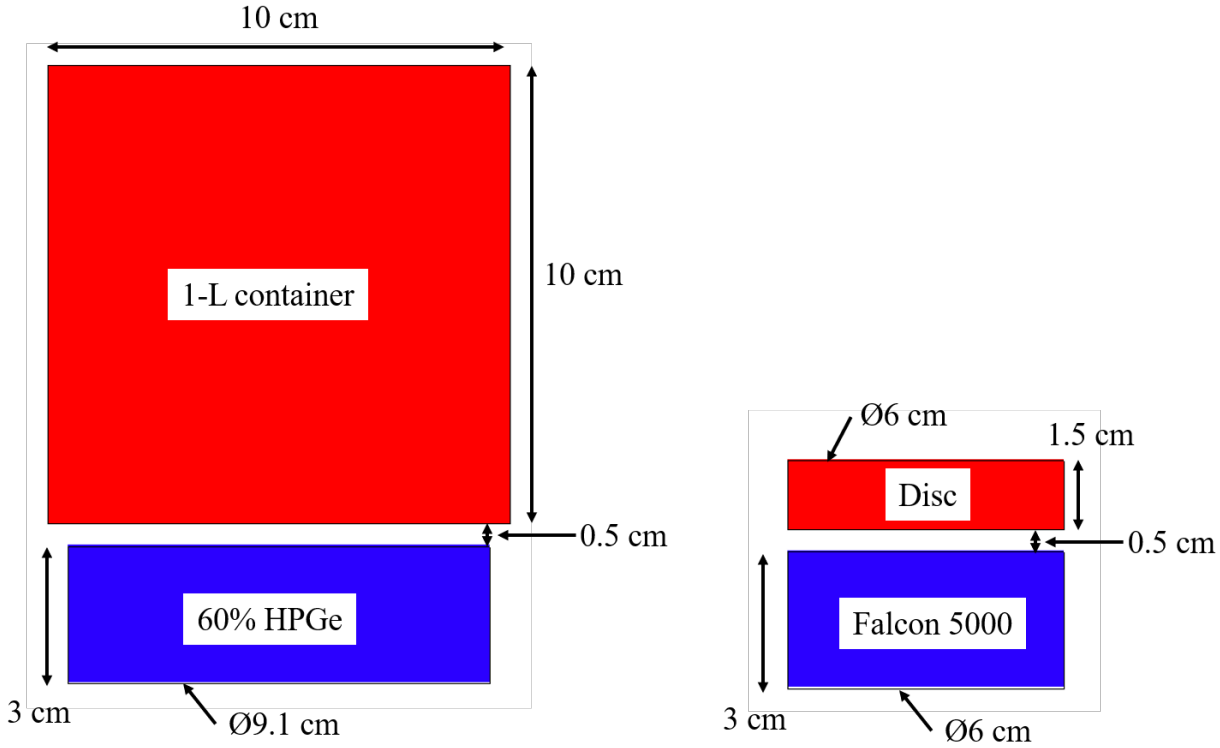

Figure A.1. MCNP geometry for the BE6530 (60% HPGe) and Falcon 5000 detectors counting a 1 L container and a concentrated disc.

The MCNP geometries for the 1-L Marinelli beaker and the separation column are show in Figure A.2.

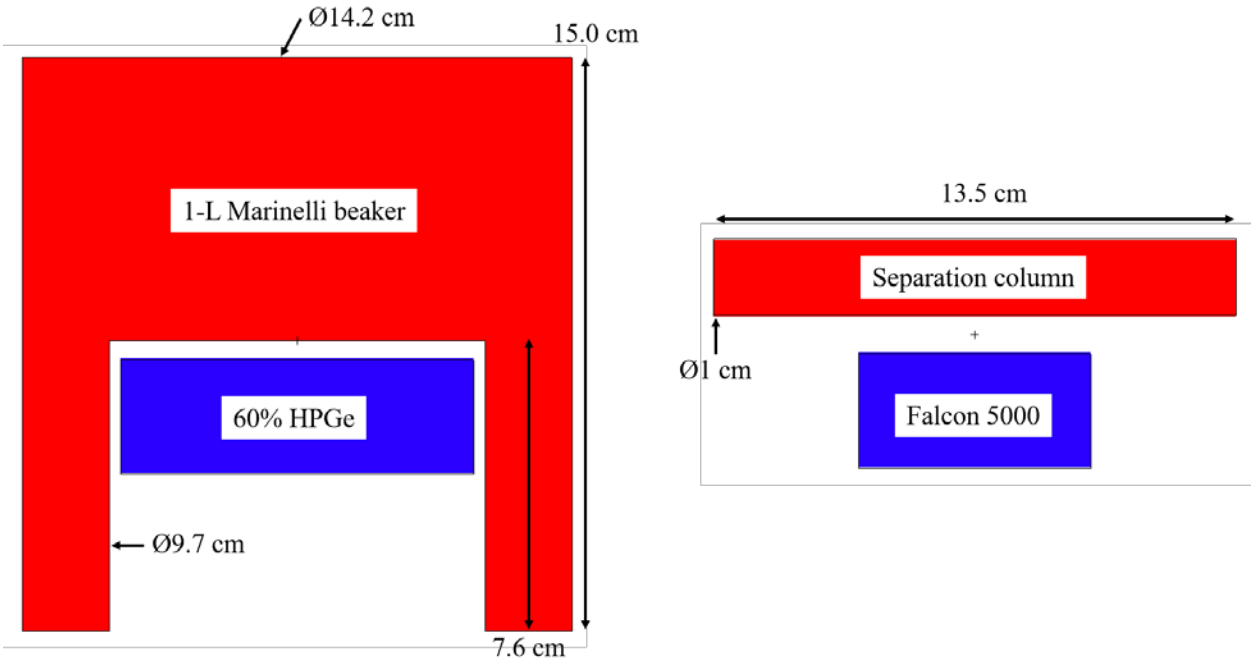

Figure A.2. MCNP geometry for the BE6530 (60% HPGe) and Falcon 5000 detectors counting a 1-L Marinelli beaker and a separation column.

The absolute efficiencies resulting from the MCNP simulations for these counting geometries for each of the two HPGe detector models for 661.657 keV photons is provided in Table A.1.

Table A.1. Absolute efficiencies at 661.657 keV for each counting geometry for each of the two HPGe detectors.

	Absolute Efficiency at 661.657 keV	
Counting Geometry	**BE6530**	**Falcon 5000**
1-L Container (Cubitainer)	1.49E-02	6.20E-03
1-L Marinelli beaker	1.80E-02	7.10E-03
Separation column	3.86E-02	1.72E-02
Concentrated disc	6.68E-02	3.37E-02

A.2 Assumptions for Processing Times Varied by Sample Volume

The disc volume also represents a media bed volume for the purpose of estimating how long to process liquid through an ion exchange column for pre-concentration (Table A.2). A flow rate of 11.5 bed volumes/hour was assumed. The disc dimensions were also assumed for a nominal solids volume that results from co-precipitation in a potential batch process. Time to process for co-precipitation for co-precipitation was considered to be bounded by the time to process 2 L via ion exchange (~4 hours).

Table A.2. Estimated Processing Times for Various Sample Volumes.

Volume (L)	V (mL)	Bed Volumes (BV)	Time to process (h)
1	1000	23.58	2.05
2*	2000	47.16	4.10
10*	10000	235.8	20.5
50	50000	1179	103

*Co-precipitation contact time of 4 to 20 hours was considered satisfactory for comparison to ion exchange performance.

Nominal Disc Volume (Bed Volume)	42.41	Flow rate (BV/h)	11.5**

**The flow rate (BV/h) is considered conservative; testing is needed to understand media or co-precipitation processing time

Typical process engineering considerations such as optimizing media use, minimizing chemical addition, and/or understanding the length of the mass transfer zone were not high priorities for purpose of this analysis. The bed volume or co-precipitate amount needed is assumed to be far in excess of the amount of Cs-137 targeted for retention, a reasonable assumption considering conservatism to assist a decision maker when the Cs-137 is difficult to measure (close to 10% AAL).

Appendix B - Evaluation of Sorbents

The review of the top 10 publications and reports are included in Table B.1. References are included in Section 4.

Table B.1. Top 10 publications and reports reviewed for sorbents recommended for further evaluation.

Reference[1]	Separation Method / Type of Sorbent	Type of Adsorption Study	Targeted Radionuclide	Test Substrate	Competing Ions
Breakthrough studies of adsorption of Cesium from freshwater using a mesoporous silica material containing ferrocyanide [49]	Sorbmatech 202: mesoporous silica containing Cu or K ferrocyanide (hexacyanoferrate)	Continuous fixed-bed Column / flow through	Cs^{+}	Freshwater	Ca^{2+} Mg^{2+}
Identification and temporal decrease of ^{137}Cs and ^{134}Cs in groundwater in Minami-Soma City following the accident at the Fukushima Daiichi Nuclear Power Plant [18]	Concentrate of radiocesium in water on a ferrocyanide solid, slurry of $Ni_2[Fe(CN)_6]$ and collect on filter	Batch	Cs^{+}	Public tap water at 6 sites & 11 groundwater sites	--
Comparative study of factors associated with application of metal hexacyanoferrates for environmental Cesium decontamination [48]	Calcium alginate cohered beads of CuHCF-b (copper hexacyanoferrate) & FeHCF-b (iron hexacyanoferrate).	Flow experiments	Cs^{+}	Ash or soil extract	K^{+} Ca^{2+} Mg^{2+} Sr^{2+}
Development of Ion Specific Media and Modular Processing Systems to Treat Strontium-Contaminated Water at Fukushima Daiichi Nuclear Power Plant [54]	1. Kurion Ion Specific Media System - ISMS. (zeolite based - H and EH) 2. Kurion Mobile Processing System - KMPS (zeolite based - FAS-P, and titanosilicate TSG)	Dual treatment: 1. Powder batch contact with filtration 2. Ion exchange vessels	ISMS targeted Cs^{+} KMPS target Ca^{2+}, Sr^{2+}	Sea water Brackish water	Na^{+} Ca^{2+} Mg^{2+}
Removal of Cesium from low-level radioactive wastewaters using magnetic K Ti hexacyanoferrate [36]	Magnetic Potassium Titanium Hexaferrocyanate (M-PTH)	Batch equilibrium	Cs^{+}	Low-level radioactive wastewater	Na^{+} Ca^{2+} K^{+}

Decontamination Efficiencies of Pot-Type Water Purifiers for ^{131}I, ^{134}Cs and ^{137} Cs in Rainwater Contaminated during Fukushima Daiichi Nuclear Disaster [42]	Filtration: Purifier A: activated charcoal + ion exchanger Purifier B: activated charcoal, ceramics, & hollow fiber membrane	Batch	Cs^{+} I^{-}	Rainwater	Na^{+} Ca^{2+} Mg^{2+} K^{+}
Removal of Radioactive Iodine and Cesium in Water Purification Processes After an Explosion at a Nuclear Power Plant due to the Great East Japan Earthquake [50]	Slow Sand filtration Granulated Activated Charcoal Biologically Activated Carbon Powdered Activated Charcoal and Cation Exchange Resin	Batch	Cs^{+} I^{-}	Raw water Process water Finished water sample	--
Treatment of Radioactive Liquid Effluents by Reverse Osmosis Membranes: From Lab-Scale to Pilot-Scale [47]	Reverse Osmosis (RO) membranes for filtration: cross-flow filtration cell for pilot study and spiral wound pilot for semi-industrial scale	Feed flow	Cs^{+} Sr^{2+}	Ground water near nuclear site & sea water	Na^{+}

Appendix C – Questions and Responses on Project

During the course of this project, the authors received several questions or comments radionuclide detection in water related to U.S. Department of Energy Small Business Innovation Research. Below are the questions, followed by the authors answers.

Question 1: The Required Capability Description states "Insufficient detection sensitivity for key radionuclides 3 to 10 fold to address the new EPA Protective Action Guides (PAG) for drinking water to a level of 1/10th or better.". There are 3 parts of questions to follow.

Question 1a: Since the PAG identifies a radiation dose rather than a quantity of radioactive materials that can be measured in drinking water, it is necessary to determine Derived Response Levels (DRLs), which are dependent on the specific radioisotope and scenario, in order to specify the requirements for a measurement instrument. What are the key radionuclides referred to in this Required Capability Description for which the detection sensitivity is insufficient? We could make some assumptions but might identify radionuclides not identified by the required capability

Response: The original estimates made in the proposal for this work considered a specific scenario indicated in the PAG manual. As part of this year's project, Turbo FRMAC was used to generate scenario-based AAL sets based on some common assumptions for scenarios with C-137, including a cesium-137 RDD and a commercial NPP release. For the scenarios involving Cs-137, these AAL sets were shared with researchers to assess the need for pre-concentration techniques as opposed to direct water measurement. Section 1.1 discusses the use of AAL and Sections 2.1 demonstrates how the analytical measurements relate to the AAL for the RDD and NPP scenarios.

Question 1b: Detection sensitivity is a function of three primary factors: 1) the counting efficiency of the detection apparatus, 2) the volume of the sample, and 3) the counting time. For example, the detection sensitivity could be increased by increasing the counting time. But perhaps the deployed scenario has unspecified requirements on analysis time. Please clarify if there are any unstated limits on analysis time.

Response: Analysis time should be minimized in the emergency phase to allow for rapid assessment of results to guide decisions on drinking water embarkation and/or abandonment. Follow-up recovery sampling has the luxury of allowing for more careful radiochemical analysis and prolonged count times. This project aims to identify technologies that will assist in the rapid assessment of drinking water sources using current field-deployed laboratory capability, field measurement, or rapid analysis at offsite laboratories utilizing the FRMAC Laboratory Analysis process. Sections 2 addresses the detection sensitivity factors mentioned in the question and other factors.

It should be noted that there are scientific limits on achievable capabilities. For example, it may not be scientifically possible to measure a concentration 3.7 Bq/L of Sr-90 in a 100 mL sample in 10 minutes to 95% confidence even if the detection apparatus had a 100% counting efficiency. Therefore, any requirements on analysis time or sample size should be identified.

Response: Agreed, the pre-concentration techniques, while focusing on Cs-137 in this project could theoretically be used to increase the virtual sample volume a great deal, making previously unachievable limits possible through this pre-concentration. This is discussed in Sections 2.1 and 2.5.2. Specific requirements on sample size and count time are scenario-dependent but this research group has made an attempt at making realistic but conservative estimates of such (see Sections 1.1, 2.1, 2.2 and 2.5.2).

Question 1b: The term "to a level of 1/10th or better" is not a sufficient specification. What measurement confidence is required? i.e. 2 σ, 3 σ, 6 σ?

Response: More specifically, FRMAC Lab Analysis sets critical level requirements at the 95% confidence level to be at or below 1/10th the calculated analytical action level (AAL) which is derived from the emergency drinking water PAG. At the discretion of the event stakeholders, FRAMC Lab Analysis may increase or even decrease this requirement to meet the data quality objectives of the stakeholder. This project will apply this logic to the estimated scenario-based AAL sets. Section 2.1 demonstrates the AAL for a base case with the RDD and NPP scenarios, and Section 2.2 demonstrates similarly the AAL for the same scenarios and the use of a sorbent.

Question 2: The desired material solution requires "a means to measure the concentration of radionuclides in the water sample that is deployable and usable by trained personnel."

What is considered deployable? For example, does this mean man-portable, or transportable in a vehicle? Or could a mobile laboratory with self- contained power and utilities be considered deployable.

Response: The researchers at SNL, LLNL, and RSL involved in this project fill many of the roles within the FRMAC and represent these "trained personnel". PNNL researchers were given the details of what the field equipment and capabilities are in the current MERL, and FAL assets to help make decisions in their survey of technologies. The ideal technology will be able to be operated by trained CMRT and RERT field teams and analyzed by field assets in the MERL and FAL or even the nearby state department of health laboratories.

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

www.pnnl.gov