

## Persistence and Decontamination of Radioactive Cesium-137 in a Model Drinking Water System



# **Persistence and Decontamination of Radioactive Cesium-137 in a Model Drinking Water System**

by

Jeffrey Szabo  
U.S. Environmental Protection Agency  
Office of Research and Development  
Homeland Security Research Program  
Cincinnati, OH 45268

Ryan James  
Battelle  
Columbus, OH 43201

## **DISCLAIMER**

The U.S. Environmental Protection Agency (EPA) through its Office of Research and Development funded and managed the research described herein under contract EP-C-15-010 with Battelle. Reene Watt served as the U.S. Environmental Protection Agency Contracting Officer's Representative. It has been subjected to the Agency's review and has been approved for publication. Note that approval does not signify that the contents necessarily reflect the views of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the U.S. Government or EPA. The EPA does not endorse any commercial products, services, or enterprises.

The contractor role did not include establishing Agency policy.

# TABLE OF CONTENTS

<b>DISCLAIMER</b> .....	ii
<b>EXECUTIVE SUMMARY</b> .....	vi
1.0 INTRODUCTION .....	1
2.0 SUMMARY OF PIPE DECONTAMINATION EXPERIMENTAL DESIGN.....	1
2.1 Experimental Reactor System.....	2
2.2 Persistence Evaluation Approach .....	3
2.3 Decontamination Approaches.....	5
2.3.1 Ammonium Chloride Chemical Cleaning Agent Evaluation.....	6
2.3.2 Potassium Chloride Chemical Cleaning Agent Evaluation.....	6
3.0 QUALITY ASSURANCE/QUALITY CONTROL .....	7
3.1 Experimental Controls .....	7
3.2 Measurement Methods.....	8
3.2.1 Liquid Scintillation Counting.....	8
3.2.2 Sodium Iodide Spectroscopy .....	8
3.2.3 Enumeration of Biofilm Growth .....	8
3.3 Quality Control .....	9
3.4 Audits.....	10
3.4.1 Technical Systems Audit.....	10
3.4.2 Data Quality Audit .....	10
4.0 RESULTS .....	11
4.1 Evaluation of Contaminant Persistence .....	11
4.2 Chemical Cleaning Agent Evaluations .....	14
4.2.1 Ammonium Chloride.....	14
4.2.2 Potassium Chloride.....	17
4.3 Biofilm Measurements.....	20
4.4 Water Quality Measurements .....	21
4.5 Summary and Conclusions .....	22
REFERENCES .....	24

**LIST OF FIGURES**

Figure 1. Annular reactor..... 2

Figure 2. Persistence evaluation for clean water exposure – average percent persistence (%P) of Cs-137 by coupon type (Cu, PVC, concrete-lined [Con]); Sodium iodide spectroscopy (NaI) method..... 12

Figure 3. Persistence evaluation for clean water exposure – percent persistence (%P) of Cs-137 of liquid scintillation counting (LSC) and sodium iodide spectroscopy (NaI) results on copper, PVC, and concrete-lined (Con) coupons individually. .... 13

Figure 4. NH<sub>4</sub>Cl chemical cleaning agent evaluation – average (Ave) percent persistence (%P) of Cs-137 by coupon type (Cu, PVC, concrete-lined [Con]); sodium iodide spectroscopy (NaI) method..... 15

Figure 5. Copper coupons with green and blue precipitate from the reaction of NH<sub>4</sub>Cl with the copper coupons. Left photo: One day of exposure to NH<sub>4</sub>Cl. Right photo: Four days of exposure to NH<sub>4</sub>Cl..... 15

Figure 6. Ammonium chloride chemical cleaning agent evaluation - percent persistence (%P) on of Cs-137 on copper, PVC, and concrete-lined (Con) coupons; sodium iodide spectroscopy (NaI) and liquid scintillation counting (LSC) methods. .... 16

Figure 7. KCl chemical cleaning agent evaluation – average (Ave) percent persistence (%P) of Cs-137 by coupon type (Cu, PVC, and concrete-lined [Con]); sodium iodide spectroscopy (NaI) method..... 18

Figure 8. Potassium chloride chemical cleaning agent evaluation – percent persistence (%P) on of Cs-137 on copper, PVC, and concrete-lined (Con) coupons; sodium iodide spectroscopy (NaI) and liquid scintillation counting (LSC) methods. .... 20

Figure 9. Testing coupons with biofilm growth: concrete-lined (left), PVC (middle), and copper (right). .... 21

**LIST OF TABLES**

Table 1. Experimental Steps of Persistence Evaluation..... 4

Table 2. Evaluation of Chemical Cleaning Agent as Decontamination Approach..... 6

Table 3. Experimental Controls ..... 8

Table 4. Data Quality Objectives for Sodium Iodide and Liquid Scintillation Analyses ..... 10

Table 5. Initial Cs-137 Activity Levels for the Persistence Evaluation..... 12

Table 6. Initial Cs-137 Activity Levels for the NH<sub>4</sub>Cl Cleaning ..... 14

Table 7. Initial Cs-137 Activity Levels before Tap Water Introduction..... 17

Table 8. Initial Cs-137 Levels for the KCl Cleaning ..... 18

Table 9. Colony Forming Units Grown on Coupon Surfaces..... 21

## LIST OF ABBREVIATIONS/ACRONYMS

AR	annular reactor
ASTM	ASTM International
AWWA	American Water Works Association
BSTC	BioSurface Technologies Corporation
cm	centimeter
CFU	colony forming units
CCA	chemical cleaning agent
Cs-137	cesium-137
DI	deionized water
DPM	disintegrations per minute
°C	degrees Celsius
EPA	U.S. Environmental Protection Agency
ft/s	foot/second
HPC	heterotrophic plate counts
in.	inch
KCl	Potassium chloride
L	liter
LSC	liquid scintillation counting
μCi	microcuries
μL	microliter
mg	milligram
min	minute
mm	millimeter
mL	milliliter
molar	M
NaISS	sodium iodide spectroscopy
NH <sub>4</sub> Cl	Ammonium chloride
NHSRC	National Homeland Security Research Center
%P	percent persistence
PE	persistence evaluation
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
rpm	revolutions per minute
s	second
S	Siemen
TTEP	Testing and Evaluation Program
UL	Underwriters Laboratories

## EXECUTIVE SUMMARY

The objective of this study was to evaluate the persistence of radioactive cesium-137 (Cs-137), on concrete-lined, copper, and polyvinyl chloride (PVC) pipe, and possible decontamination approaches. During this study, conditions within operational drinking water pipes were simulated using annular reactors (ARs) (i.e., ring-shaped reactors). The ARs consist of a glass outer cylinder and a rotating polycarbonate inner cylinder with 20 flush mounted rectangular slides (referred to as coupons) that are made of the aforementioned pipe materials with biofilm. Shear was applied to the coupon surfaces by setting the reactors' inner cylinder rotation to 100 revolutions per minute, which produces shear forces similar to those produced from 1 ft/sec flow in a 6-inch pipe.

The study was initiated with an evaluation of Cs-137 persistence. Pipe material coupons with biofilm were contaminated with Cs-137 for 24 hours and then exposed to fresh tap water in annular reactors operating at 100 rpm for up to five days. Exposure to fresh tap water was meant to simulate flushing of water pipes in a real distribution system. The results of the persistence evaluation showed that exposure to clean drinking water reduced the adhered Cs-137 levels by 75% for the copper pipe coupons, and 91% and 93% for the PVC and concrete pipe coupons, respectively.

After exposure to fresh tap water, a decontamination evaluation with two separate chemical cleaning agents was performed to remove the remaining Cs-137 adhered to the coupons. The pipe materials were exposed to either a solution containing 1 molar (M) ammonium chloride ( $\text{NH}_4\text{Cl}$ ) or a 1 M potassium chloride (KCl) solution, as cleaning agents. The reactors were operated at 100 rpm for up to six days after application of the cleaning agent. Decontamination with  $\text{NH}_4\text{Cl}$  removed 89% of the remaining Cs-137 activity from the copper coupons. However, there was variability in the decontamination results on the copper coupons, possibly due to a precipitate that formed during decontamination. The precipitate was likely corrosion of the copper piping material that resulted from exposure to  $\text{NH}_4\text{Cl}$ . The  $\text{NH}_4\text{Cl}$  cleaning treatment on PVC and concrete piping materials removed 91% and 85% of the remaining adhered Cs-137, respectively. Decontamination with the KCl solution removed 50% of the Cs-137 activity remaining on the copper coupons, and 90% of the Cs-137 activity remaining on both the PVC and concrete coupons.

It should be noted that when Cs-137 activity removal from both exposure to clean water (simulated flushing) and decontamination with the cleaning agents are added together, 99% of the activity was removed from PVC and concrete, regardless of which agent was applied or the duration of clean water exposure after contamination. Total Cs-137 activity removal from copper ranged from 97% removal with 5 days of clean water exposure and NH<sub>4</sub>Cl treatment, to 89% removal with one day of clean water exposure and KCl treatment. These results suggest that KCl may be a better decontamination chemical compared to NH<sub>4</sub>Cl since the decontamination performance is comparable, and KCl does not corrode the copper pipe. However, as noted earlier, exposure to clean water (simulated flushing) alone reduced Cs-137 levels by 75% for the copper pipe coupons, and 91% and 93% for the PVC and concrete pipe coupons. Since most of the adhered Cs-137 was removed via clean water exposure, flushing alone may be a sufficient decontamination method.



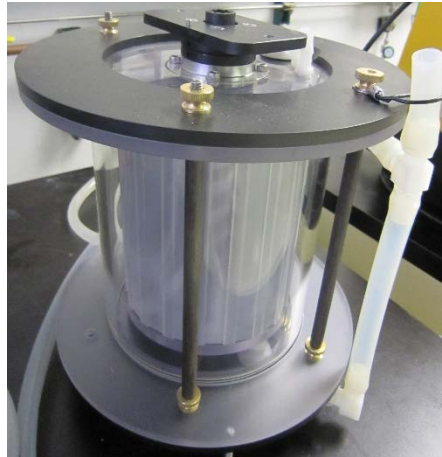
## **1.0 INTRODUCTION**

Contamination of drinking water distribution systems can occur following an intentional contamination incident, an industrial accident, a massive main break or a natural disaster. Natural and man-made incidents are further exacerbated by the declining integrity of the aging water infrastructure in the United States. Decontamination of drinking water distribution systems is critical for the effective and rapid return of the system to operation, and for restoring the safety of the water for drinking and other applications. The ability to reliably and cost effectively decontaminate miles of distribution system pipes and premise plumbing will be a critical capability that utilities will need to ensure public safety following a contamination incident.

Research is needed to better understand the adherence and persistence of selected contaminants on pipe walls, and to identify effective decontamination methods. In recent years, research studies have been conducted to determine the adsorption of chemical, biological, and surrogate (non-radioactive) radiological contaminants to various drinking water pipe materials, and to test various methods to destroy, reduce or remove adsorbed contaminants<sup>1-2</sup>. However, data on the persistence of radioactive species on common distribution system and premise plumbing pipe material are lacking. The following report attempts to address this data gap by examining the persistence of radioactive Cs-137 on copper, polyvinyl chloride (PVC) and cement-mortar, which are materials commonly used in home plumbing (copper and PVC) and drinking water distribution pipes (cement-mortar lined iron). Decontamination of Cs-137 is also examined using flushing with clean water, followed by pipe cleaning with 1 M ammonium chloride (NH<sub>4</sub>Cl) or 1 M potassium chloride (KCl).

## **2.0 SUMMARY OF PIPE DECONTAMINATION EXPERIMENTAL DESIGN**

One of the most important features in the experimental protocol is the use of an annular reactor (AR) (i.e., ring-shaped reactor) as the device that simulates flow through drinking water pipe, which is represented by coupons (excised samples) of various materials. Shown in Figure 1, the AR simulates pipe flow with a variable speed motor that drives an inner rotating cylinder. The rotation of this cylinder provides surface shear between pipe surface coupons and water within the AR.



**Figure 1. Annular reactor.**

ARs are commercially available, providing ease of repeatability across laboratories, as opposed to requiring the fabrication of a specialized setup.

The contaminant used during testing was radioactive Cs-137 (Cs-137), applied in separate experiments on three simulated pipe surfaces (concrete-lined, polyvinyl chloride [PVC], and copper).

## **2.1 Experimental Reactor System**

For the persistence and decontamination experiments, the conditions within operational drinking water pipes were simulated in ARs (Model 1320 LS Standard Laboratory AR, BioSurface Technologies Corporation, Bozeman, MT). The ARs consist of a glass outer cylinder and a rotating polycarbonate inner cylinder with 20 flush mounted rectangular coupons that can be manufactured from materials such as concrete, PVC, and copper and obtained from BioSurface Technologies Corporation (BSTC). For the concrete-lined pipe, the specifications of the concrete used for the coupons meet the requirements of the C150-07 ASTM Standard Specification for Portland Cement<sup>3</sup>. The thickness of the concrete was approximately 1.3 millimeters (mm), which is slightly less than 1.6 mm as specified in American Water Works Association (AWWA) C104-03 Standard for Cement-Mortar Lining for Ductile-Iron Pipe and Fittings for Water<sup>4</sup>. For the PVC pipe, the coupons carry an Underwriters Laboratories (UL) 94

V-0 rating and conform to the D-1784 ASTM standard specification for Rigid PVC Compounds and Chlorinated PVC Compounds<sup>5</sup>. The copper coupons are made of solid copper.

These coupons, which have surfaces that are 14 mm × 148 mm, simulated the inner surface of drinking water pipes. Shear stress was applied to the coupon surfaces by setting the inner cylinder rotation to 100 revolutions per minute (rpm), which produces shear similar to 30.5 centimeter (cm)/second (s) (1 foot [ft]/s) flow in a 15.2 cm (6 inch [in.]) pipe<sup>6</sup>.

Prior to any persistence or decontamination experiments, a biofilm was grown on the surface of the coupons. Biofilm was formed by submerging 21 coupons (for each AR used) of the applicable surface material in a 20 L reservoir containing recirculating dechlorinated tap water (at approximately 200-300 milliliter [mL]/ minute [min]) and 1 gram of yeast extract for seven days. Biofilm was formed from the native microorganisms in the dechlorinated tap water. The coupons were kept in the dark during the biofilm formation period. Following the 7-day biofilm formation period, growth was measured (procedure described in Section 3.2.3) using heterotrophic plate counts (HPC) to obtain the concentration of colony forming units (CFU)/mL from one of the coupons.

## **2.2 Persistence Evaluation Approach**

The persistence evaluation (PE) approach for concrete-lined, PVC, and copper surface coupons is summarized in Table 1. For each of the three experiments (one for each pipe material), biofilm was grown on 21 coupons. One coupon of each surface type was used for HPC analysis to confirm biofilm growth. At the conclusion of the biofilm formation period, background measurements were taken. Two coupons with biofilm growth were measured (non-destructively) directly using an EG&G Ortec Maestro Sodium Iodide Spectroscopy System (NaISS), and one coupon was measured (destructively) using liquid scintillation counting (LSC). Once counting was complete, the two coupons measured by NaISS and the remaining coupons were placed in the ARs. The reactors were contaminated with a bulk solution of Cs-137 at a concentration of 100 microcuries per liter ( $\mu\text{Ci/L}$ ) for the ARs containing PVC and copper, and 10  $\mu\text{Ci/L}$  in the AR containing the concrete-lined coupons. The ARs were set to continuously rotate at 100 rpm for 24 hours in contact with the Cs-137.

The initial level of Cs-137 used in the ARs was determined from small scale beaker experiments with pipe material coupons prior to testing. This was to ensure there would be

enough Cs-137 signal for the analytical measurements on all three pipe materials, but also to minimize Cs-137 dose. The results of these initial experiments showed that the concrete-lined coupons absorbed the Cs-137 contamination much more readily than PVC and copper, as evidenced by gamma counts that were several orders of magnitude higher than the other two surface types. Therefore, during the experiments, the concrete contamination solution was prepared and used at a concentration 10 times lower than the contamination solution used for the PVC and copper pipe materials.

**Table 1. Experimental Steps of Persistence Evaluation (PE)**

<b>PE Step</b>	<b>Description</b>	<b>Net Coupons Consumed</b>
PE 1	Develop a biofilm on 21 coupons. Confirm the biofilm with heterotrophic plate count (HPC) on one coupon, leaving 20 for use in experiments.	1
PE 2	Remove two coupons from the AR to serve as uncontaminated blanks (NaISS) and one coupon for LSC analysis. Measure the background activity on these coupons and return the NAISS coupons to the AR.	1
PE 3	Add Cs-137 contamination solution to AR, sample the bulk contamination solution; wait 24 hrs with AR rotation at 100 rpm.	0
PE 4	Following the 24 hr exposure to the Cs-137 solution, sample the solution and remove 4 coupons. Measure two coupon using LSC and the other two using NaISS. Return the NAISS coupons to the AR (these two coupons were measured by NaISS each day and returned to AR).	2
PE 5	Replace the contamination solution with fresh drinking water and allow coupons to reside in 100 rpm AR for 24 hrs; sample the water and remove one or two coupons and measure the activity with a LSC. Remove NaISS coupons, measure activity and return to AR. This step was repeated four additional times.	10
PE 6	Calculate percent persistence (%P) for PE coupons by comparing to contaminated control coupons.	0

Following 24 hrs of exposure to Cs-137, the contamination solution was sampled and drained. The same two coupons from each AR previously measured by NaISS were measured again to establish the contamination activity remaining on the coupons. Being a nondestructive method, the same two coupons were measured by NaISS each day and returned to the ARs. Two contamination coupons were also removed from the ARs and their activity measured by LSC. The ARs were then filled with deionized (DI) water and drained to ensure the contamination solution was removed from the ARs. Then they were filled with fresh drinking water and

rotation of the AR at 100 rpm was restarted (Day 1). After 24 hrs of exposure to drinking water, the two NaISS-designated coupons were removed from the AR and their activity measured by NaISS. Again, two coupons were removed for LSC analysis. This procedure was repeated daily for five days; however, because of the limited number of coupons available for duplicate samples, only one coupon was removed for LSC analysis during Days 3 to 5. The activity of the water was also measured at every daily exchange. These measurements were accomplished by transferring 1 mL aliquots of water from the AR into a vial and measuring the activity using the LSC.

Following the activity measurements of the coupons removed from the AR, activity from the surface was compared with the activity from the contaminated coupons measured after contamination with Cs-137. This comparison was made by calculating the percent persistence (%P) of the contaminant on the coupons as described by the following equation.

$$\%P = \frac{A_{PE}}{A_C} \times 100$$

Where  $A_{PE}$  is the activity of the contaminant recovered from the PE coupon surface and  $A_C$  is the average activity of the contaminant originally measured from the surfaces of the contaminated control coupons. Note that any background activity was subtracted from  $A_{PE}$  and  $A_C$ .

### **2.3 Decontamination Approaches**

With Cs-137 persisting on the surface of the pipe materials after drinking water exposure, decontamination experiments were conducted. The ARs were spiked with either ammonium or potassium chloride to remove the residual Cs-137. The chemical cleaning agent evaluation was performed as shown in Table 2, and used the coupons remaining in the AR following the PE.

**Table 2. Evaluation of Chemical Cleaning Agent (CCA) as Decontamination Approach**

<b>Step</b>	<b>Description</b>	<b>Net Coupons Consumed</b>
CCA 1	Drain the AR and add the CCA solution. Wait 24 hrs with AR rotation at 100 rpm.	0
CCA 2	Following 24 hrs of exposure to the CCA solution, sample the CCA solution, remove one or two coupons and measure their activity with the LSC. Remove two NaISS coupons, measure, and return them to the AR. Replace the CCA solution with fresh CCA solution and continue AR rotation at 100 rpm.	1
CCA 3	Repeat the step above until no Cs-137 is detected on the surface of the coupon, or until no coupons remain. Collect a CCA solution sample from the AR with each coupon.	6

### ***2.3.1 Ammonium Chloride Chemical Cleaning Agent Evaluation***

At the start of the experiment, the drinking water in the AR was replaced with a chemical cleaning agent consisting of 1 molar (M) ammonium chloride (NH<sub>4</sub>Cl), and the inner cylinder of the AR was set to rotate at 100 rpm. The chemical solution remained in contact with the surface of the coupons for 24 hrs, after which point the AR was drained and one coupon was removed and its activity counted using a LSC. Additionally, the same two coupons were removed from the AR and counted using the NaISS, then returned to the AR. The AR rotated at 100 rpm for the duration of the experiment and was only stopped to remove coupons and exchange the chemical. The process of draining the AR, removing three coupons (one measured via LSC and two measured via NaISS), and then refilling every 24 hrs was repeated for four days for the NH<sub>4</sub>Cl solution. Each time a coupon was removed from the AR, a sample of the NH<sub>4</sub>Cl solution in the AR was also collected. The NaISS coupons were returned the AR after measurement. The %P was calculated using these results in the same manner as for the PE.

### ***2.3.2 Potassium Chloride Chemical Cleaning Agent Evaluation***

As during the NH<sub>4</sub>Cl experiment, the coupons in the ARs had biofilms cultivated and the CFU/coupon was calculated for each pipe material. Background measurements were taken and then the coupons were contaminated with a DI water solution of Cs-137 at a concentration of 100 microcuries per liter (μCi/L) for the ARs containing PVC and copper, and 10 μCi/L in the AR containing the concrete-lined coupons. The rotation was set for 100 rpms and started for 24 hours. The contamination solution was sampled and drained. The same two coupons from each

AR previously measured by NaISS were measured again to establish the contamination activity on the coupons. Being a nondestructive method, the same two coupons were measured by NaISS each day and returned to the ARs. Two contamination coupons were also removed from the ARs and their activity measured by LSC. The ARs were filled with deionized (DI) water and drained to ensure the contamination solution was removed from the ARs. Then they were filled with fresh drinking water and rotation of the AR at 100 rpm was restarted (Day 1 Tap Water). After 24 hrs of exposure to drinking water, the two NaISS-designated coupons were removed from the AR and their activity measured by NaISS. Again, two coupons were removed for LSC analysis.

The drinking water in the AR was then replaced with a chemical solution consisting of 1 M KCl and the AR was set to rotate at 100 rpm. This chemical solution remained in contact with the surface of the coupons for 24 hrs. After 24 hours, the AR was drained, two coupons were removed, and their activity counted using a LSC (Day 1 KCl). Additionally, the original two coupons were removed from the AR and counted using the NaISS, then returned to the AR. The AR rotated at 100 rpm for the duration of the test and was only stopped to remove coupons and exchange the chemicals. The process of draining the AR, removing four coupons (two measured via LSC and two measured via NaISS), and then refilling every 24 hrs was repeated for five days for the copper and PVC pipe materials and six days for the concrete-lined coupons. Each time a coupon was removed from the AR, a sample of the KCl solution in the AR was collected. The %P was calculated using these results in the same manner as for the PE.

### **3.0 QUALITY ASSURANCE/QUALITY CONTROL**

#### **3.1 Experimental Controls**

Table 3 summarizes the controls included in the experiments. The controls are important because the results of the persistence and decontamination experiments are dependent on the original concentration of contaminant on the surface of the control coupons. In addition, the AR has more available surface area that could become contaminated, thus becoming a source of secondary contamination.

**Table 3. Experimental Controls**

Type of Control	Description
Non-contaminated control coupons blanks	Taken from set of coupons following biofilm growth; allows comparison of coupons that have been contaminated from the bulk solution and those that have not
Contaminated control coupons	Removed from AR after contamination of coupons, but before PE testing in clean water; allows comparison of coupons containing a “diminished” amount of contaminant (due to the shear from rotating within drinking water) with coupons containing “total” amount of contaminant (not influenced by the shear from rotating within drinking water)

### 3.2 Measurement Methods

#### 3.2.1 *Liquid Scintillation Counting*

The analytical method used for the Tri-Carb 3110TR Low Activity (Perkin-Elmer, Waltham, MA) liquid scintillation analyzer is based on EPA Method 900.0 “Gross Alpha and Gross Beta Radioactivity in Drinking Water”<sup>7</sup>. Cs-137 was used as calibration standards and calibration followed the manufacturers guidelines. The method for liquid analysis was very straight forward as 1 mL of each sample was added to a LSC vial containing 9 mL of Bio-Safe LSC II cocktail (Research Products International, Mount Prospect, IL), placed in the auto sampler and programmed for analysis. The method for the coupon analysis was similar; however, the coupons were cut into thirds, placed into the LSC vial with 18 mL of the Bio-Safe II LSC cocktail, and programmed for analysis. The analysis took 1 minute per sample and the results were presented in disintegrations per minute (DPM).

#### 3.2.2 *Sodium Iodide Spectroscopy*

The analytical method used for the NaISS (Maestro, EG&G Ortec, Oak Ridge, TN) was based on EPA Method 901.1 “Gamma emitting Radionuclides in Drinking Water”<sup>8</sup>. Cs-137 was used as calibration standards and calibration followed the manufacturers guidelines. Non-destructive analysis was performed by placing the surface coupons within the detection chamber in a common geometry. Counting took place for 15 minutes.

#### 3.2.3 *Enumeration of Biofilm Growth*

This method was used to determine the extent of biofilm growth on the coupons. A sterile 0.05% solution (by volume) of Triton X-100 (Fisher # BP151-500, Fisher BioReagents,



Waltham, MA) in phosphate buffered saline was prepared. The coupons were placed in sterile centrifuge tubes (VWR # 89004-364, VWR, West Chester, PA) containing 30 mL of the 0.05% Triton X solution, mixed using a vortex mixer, and then decanted. Thereafter, two tenfold dilutions of that decanted solution were prepared using the 0.05% Triton X solution as the diluent. Each of those solutions were plated in triplicate by dispensing 100 microliter ( $\mu\text{L}$ ) onto agar plates (Teknova #T0134, Teknova, Hollister, CA). Using a spreader, the aliquot was evenly distributed on the plate and placed in an incubator for 48 hours at 35-37 degrees Celsius ( $^{\circ}\text{C}$ ).

After incubation, the distinguishable colonies on each plate were counted. In order to be considered a viable plate count, the number of colonies on a given plate should be between 30 and 300. If the number of colonies was below 30, a more concentrated dilution was re-plated in triplicate. If the number of colonies was more than 300, a less concentrated dilution was re-plated in triplicate. The CFU/coupon was obtained by dividing the average number of colonies by the plated volume and then adjusting for the dilution factor.

### **3.3 Quality Control**

Quality control samples for the contaminant reference method included continuing calibration checks and laboratory blanks. The data quality objectives for each of these quality control (QC) samples are provided in Table 4. The acceptable ranges limit the error introduced into the experimental work. Both instruments operated within the QC requirements for continuing calibration checks and laboratory reagent blanks during this evaluation.

**Table 4. Data Quality Objectives for Sodium Iodide and Liquid Scintillation Analyses**

Method	Sample Type	QC Requirement	Corrective Action
Liquid Scintillation Counter (LSC)	Continuing calibration/efficiency check	90-110% of known; daily	Repeat sample analysis; if still outside of range repeat calibration
	Laboratory reagent blank	<Detection limit for analyte; include with each batch of 10 samples	Determine and correct cause of contamination
Sodium Iodide Spectroscopy (NaISS)	Continuing calibration/efficiency check	80-120% of known concentration; 10% of all samples	Repeat sample analysis; if still outside of range repeat calibration
	Laboratory reagent blank	<Detection limit for analyte; include with each batch of 10 samples	Determine and correct cause of contamination

### 3.4 Audits

#### 3.4.1 Technical Systems Audit

The Battelle Quality Assurance (QA) Manager conducted a technical systems audit at the Columbus, OH testing location to ensure that the evaluation was performed in accordance with the quality assurance and quality control procedures for this study. As part of the audit, the Battelle QA manager reviewed the reference sampling and analysis methods used, compared actual evaluation procedures with those specified in the quality assurance and quality control procedures for this study, and reviewed data acquisition and handling procedures.

Two deviations from the quality assurance and quality control procedures for this study were noted during the audit. The biofilm could not be grown according to the originally planned procedure. Instead of using drinking water and allowing the biofilm to grow over a 30-day period, the growth was enhanced using yeast extract and dechlorinated drinking water over a 7-day period. The second deviation changed the coupon sampling regimen. Instead of removing three coupons for analysis by the NaISS, two coupons were removed. In addition, instead of one coupon for LSC analysis, two were used. These changes were made with acceptance from EPA to ensure there were enough coupons to complete the experiments using duplicate coupons for both analysis methods.

#### 3.4.2 Data Quality Audit

At least 10% of the data acquired during the evaluation were audited. These data include the biofilm measurements, water quality measurements, LSC and NaISS measurements. The Battelle QA manager traced the data from the initial acquisition, through analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked. No significant adverse findings were noted in this audit.

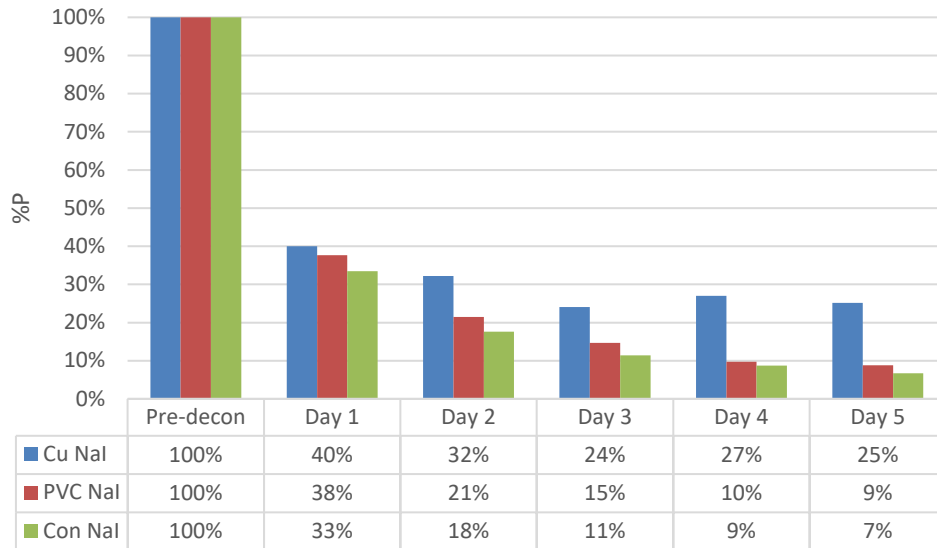
## **4.0 RESULTS**

Note that data for both the NaISS and LSC measurement techniques are presented in this section. However, for simplicity, percent persistence and discussion of decontamination effectiveness of the NaISS data is presented herein. Note that any background activity was subtracted from all samples presented in this section.

### **4.1 Evaluation of Contaminant Persistence**

The persistence evaluation results are presented in Figure 2 for each coupon surface type. This graph presents the average result of the two NaISS measurements for the same two coupons on each testing day. The vertical axis (%P) show the percent of the Cs-137 remaining on the coupon after each experimental day (shown on the horizontal axis). The columns at the far-left side of the graphs (pre-decontamination) represent the initial contamination level (as measured on the contaminated control coupons) and each successive column represents the number of days of exposure to clean water.

The persistence evaluation results show a similar initial decrease in Cs-137 of approximately 60-70% for all coupon types. The residual Cs-137 on the copper coupons continued to decrease through Day 3, but ceased decreasing thereafter, remaining at approximately 25 %P. The PVC and concrete coupons continued to decrease each day, culminating at a %P of just less than 10% on the last two days of testing. These calculations were based on the initial activity levels on each coupon. The starting activity levels (in counts for the NaISS and DPM for the LSC) for each type of coupon are shown in Table 5.



**Figure 2. Persistence evaluation for clean water exposure – average percent persistence (%P) of Cs-137 by coupon type (Cu, PVC, concrete-lined [Con]); Sodium iodide spectroscopy (NaI) method.**

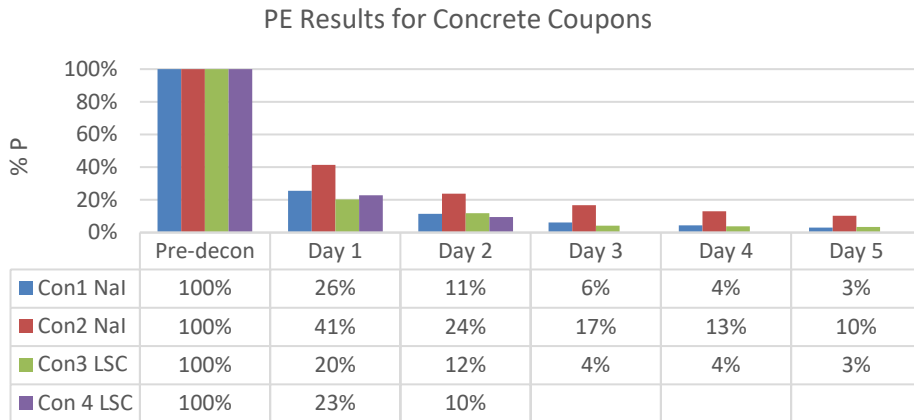
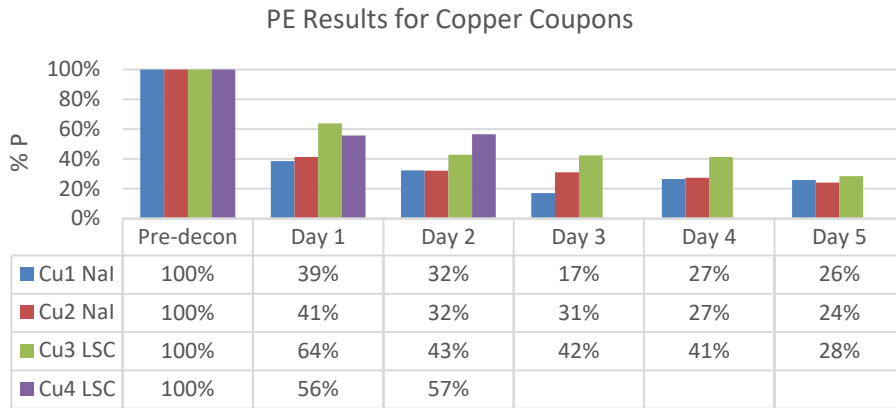
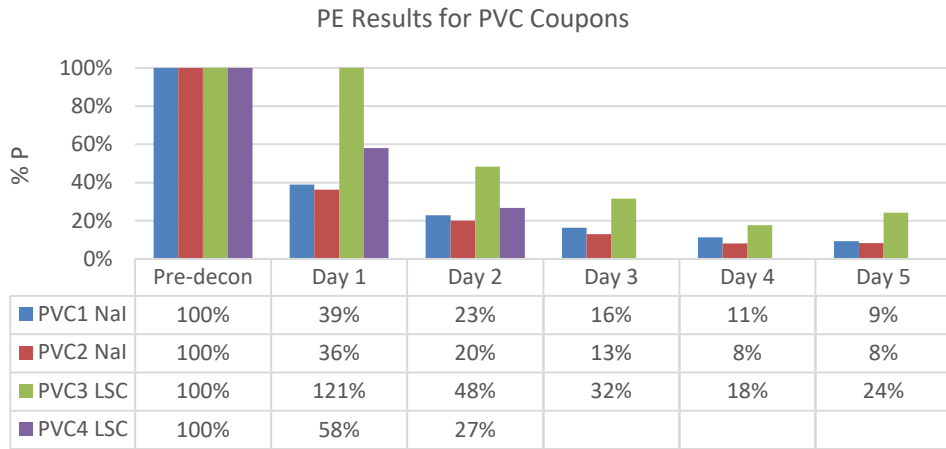
**Table 5. Initial Cs-137 Activity Levels for the Persistence Evaluation**

Analysis Method	Coupons					
	Copper		PVC		Concrete	
NaISS (counts)	1,870	Cu1	15,364	PVC1	58,233	Con1
	1,793	Cu2	8,838	PVC2	57,057	Con2
LSC (DPM)	5,441	Cu3	36,901	PVC3	221,694	Con3
	4,638	Cu4	46,148	PVC4	180,811	Con4

Con, concrete-lined; DPM, disintegrations per minute; LSC, liquid scintillation counting; NaISS, sodium iodide spectroscopy

These trends are shown in more detail in the graphs in Figure 3. The individual NaISS and LSC results are presented for the different coupon types separately. Note that the NaISS results are from daily measurements of the same two coupons and the LSC results are measurements of different coupons exposed to the same contamination and decontamination conditions. Because of the limited space for replicate coupons in the AR and to ensure enough coupons were available for the decontamination evaluation, only one coupon was removed for LSC analysis on some days (no purple bar is present on days 3 to 5 in Figure 3). Overall, the NaISS and LSC show similar trends. Based on the NaISS data in Figure 2, flushing with clean water during the persistence evaluation reduced the contamination level by approximately 75%

for the copper pipe material, and 91% and 93% for the PVC and concrete pipe materials, respectively.



**Figure 3. Persistence evaluation for clean water exposure – percent persistence (%P) of Cs-137 of liquid scintillation counting (LSC) and sodium iodide spectroscopy (NaI) results on copper, PVC, and concrete-lined (Con) coupons individually.**

## 4.2 Chemical Cleaning Agent Evaluations

### 4.2.1 Ammonium Chloride

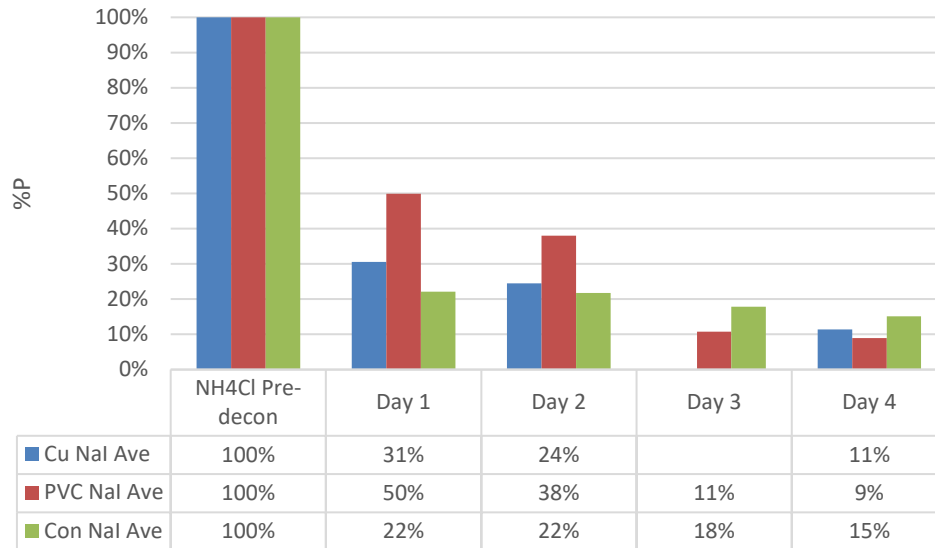
Directly after the persistence evaluation, the NH<sub>4</sub>Cl chemical cleaning experiment was conducted. Results are presented in Figure 4 for each coupon surface type. This graph presents the average result of the two NaISS measurements for the same two coupons on each testing day. The bars to the far-left side of the graphs present the initial contamination level for this portion of the testing, which began one day after the final day (Day 5) of the PE experiment. The ARs were not re-spiked with Cs-137 before this portion of the testing, and the coupons sat overnight between the PE and cleaning phases of the experiment. Therefore, the amount of activity on the coupons at the beginning of this experiment (Table 6) was less than what remained on Day 5 of the persistence evaluation. The remaining bars represent the %P of Cs-137 after exposure to the NH<sub>4</sub>Cl chemical solution noted along the horizontal axis.

The NH<sub>4</sub>Cl cleaning results for copper and concrete coupons had a similar initial Cs-137 activity decrease of approximately 75%. The Cs-137 was more persistent on the PVC coupons in the NH<sub>4</sub>Cl solution, decreasing by 50%; however, after four days, the PVC coupons had the least amount of contamination. Percent P was calculated from the initial activity levels presented in Table 6 (the activity present at Day 5 of the PE experiment).

**Table 6. Initial Cs-137 Activity Levels for the NH<sub>4</sub>Cl Cleaning**

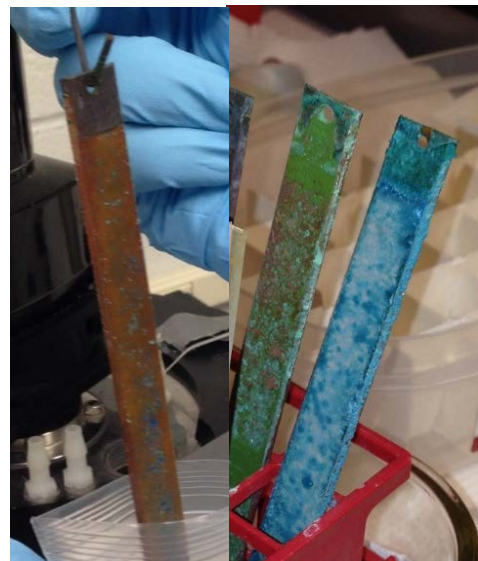
Analysis Method	Coupons					
	Copper		PVC		Concrete	
NaISS (counts)	502	Cu1	1,031	PVC1	1,515	Con1
	444	Cu2	575	PVC2	4,771	Con2
LSC (DPM)	1,725	Cu3	6,446	PVC3	4,103	Con3

DPM, disintegrations per minute; LSC, liquid scintillation counting; NaISS, sodium iodide spectroscopy



**Figure 4. NH<sub>4</sub>Cl chemical cleaning agent evaluation – average (Ave) percent persistence (%P) of Cs-137 by coupon type (Cu, PVC, concrete-lined [Con]); sodium iodide spectroscopy (NaI) method.**

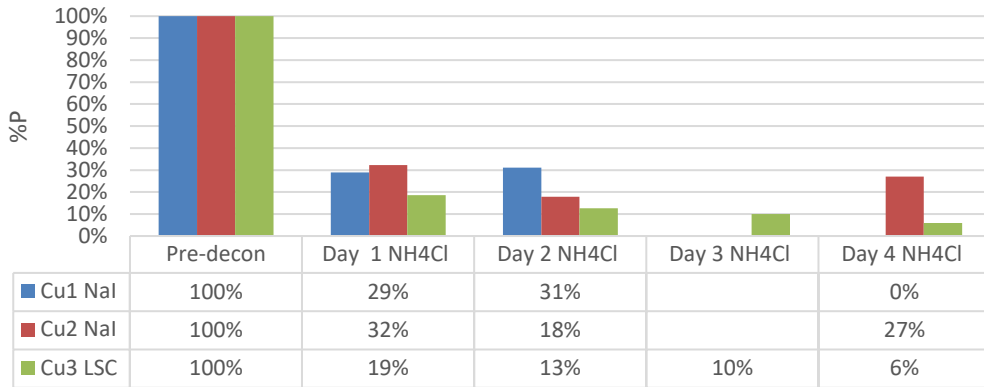
After the first day of exposure to the NH<sub>4</sub>Cl chemical cleaning solution, the bulk solution in the AR with the copper coupons was a brilliant blue. After draining the AR, it became clear that the NH<sub>4</sub>Cl was reacting with the copper to form a blue/green precipitate throughout the AR, and especially on the copper coupons. Because of this precipitate, the copper coupons were extremely difficult to remove from the AR slots and, therefore, the NaISS coupons were unable to be removed and measured on Day 3. Figure 5 shows two pictures of the copper coupons with the precipitate at Day 1 and Day 4 respectively. The wet precipitate looked blue, as did the bulk solution. Once the coupons were removed from the AR and placed into the drying rack, the precipitate appeared green.



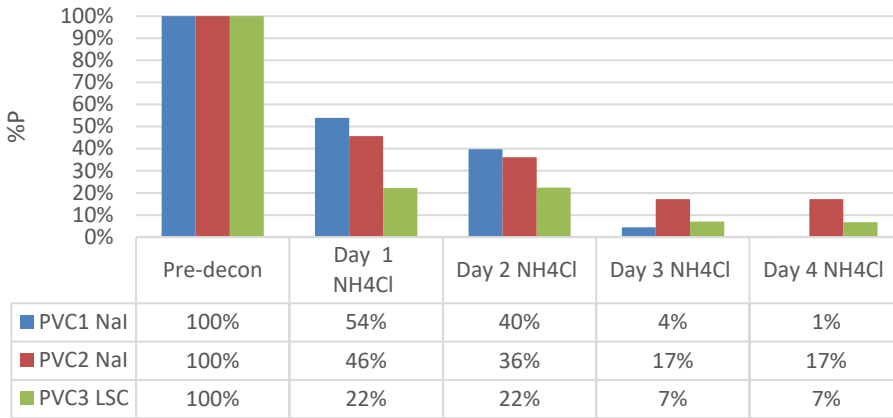
**Figure 5. Copper coupons with green and blue precipitate from the reaction of NH<sub>4</sub>Cl with the copper coupons. Left photo: One day of exposure to NH<sub>4</sub>Cl. Right photo: Four days of exposure to NH<sub>4</sub>Cl.**

The results of the NH<sub>4</sub>Cl chemical cleaning are shown in more detail in the graphs in Figure 6. The individual NaISS and LSC results are presented for the different coupon types separately.

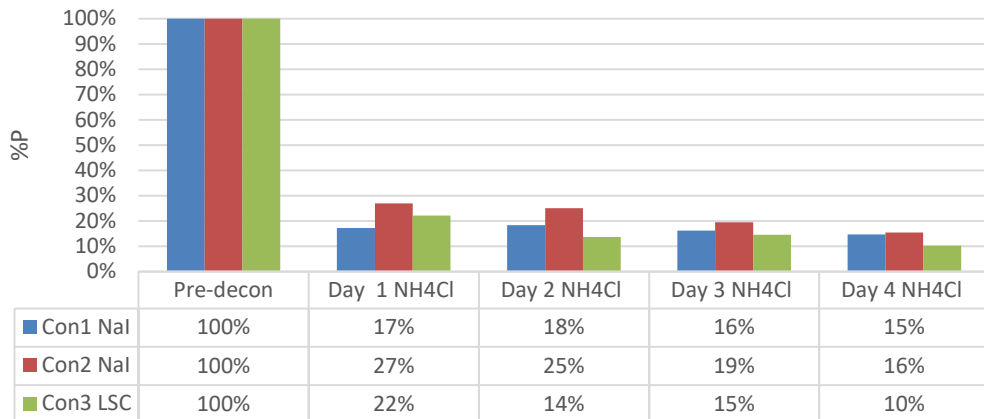
NH<sub>4</sub>Cl Cleaning Results for Copper Coupons



NH<sub>4</sub>Cl Cleaning Results for PVC Coupons



NH<sub>4</sub>Cl Cleaning Results for Concrete Coupons



**Figure 6. Ammonium chloride chemical cleaning agent evaluation - percent persistence (%P) on of Cs-137 on copper, PVC, and concrete-lined (Con) coupons; sodium iodide spectroscopy (NaI) and liquid scintillation counting (LSC) methods.**



In general, the NaISS and LSC results agree and show similar trends; however there appears to be more variability in the results compared to the PE results, possible due to the precipitate. The precipitate or corrosion could cause physical damage to a home plumbing system with copper piping. The %P following 4 days of NH<sub>4</sub>Cl treatment on the copper, PVC and concrete piping materials was 11%, 9% and 15% (89%, 91% and 85% removal), respectively, based on the NaI measurements in Figure 4. However, when adding together the Cs-137 activity removal (measured by NaISS) achieved during exposure to clean water for 5 days (persistence evaluation) and the NH<sub>4</sub>Cl cleaning experiment, total removals of 97%, 99% and 99% for copper, PVC and concrete were observed. This demonstrates that flushing with clean water will remove 75-93% of the Cs-137 activity (depending on pipe material), but chemical cleaning is needed to obtain more removal.

#### 4.2.2 Potassium Chloride

As described in section 2.3.2, the coupons were exposed to clean tap water for 24 hours after spiking with Cs-137 before the cleaning with KCl began. Table 7 presents the initial NaISS and LSC activity measurements for each coupon type immediately after spiking. After exposure to clean water for 24 hrs, the average %P on the copper coupons was 20% for the NaISS (12% for LSC) results. For the PVC coupons, the average %P with the tap water exposure was 11 % for the NaISS (9% for LSC) results. Finally, the average %P for the concrete coupons with tap water exposure was 19% for the NaISS (11% for LSC) results.

**Table 7. Initial Cs-137 Activity Levels before Tap Water Introduction**

Analysis Method	Coupons					
	Copper		PVC		Concrete	
NaISS (counts)	2,806	Cu1	2,573	PVC1	39,242	Con1
	2,930	Cu2	2,390	PVC2	71,847	Con2
LSC (DPM)	8,458	Cu3	14,984	PVC3	307,417	Con3
	8,947	Cu4	9,149	PVC4	238,010	Con4

Con, concrete; DPM, disintegrations per minute; LSC, liquid scintillation counting; NaISS, sodium iodide spectroscopy

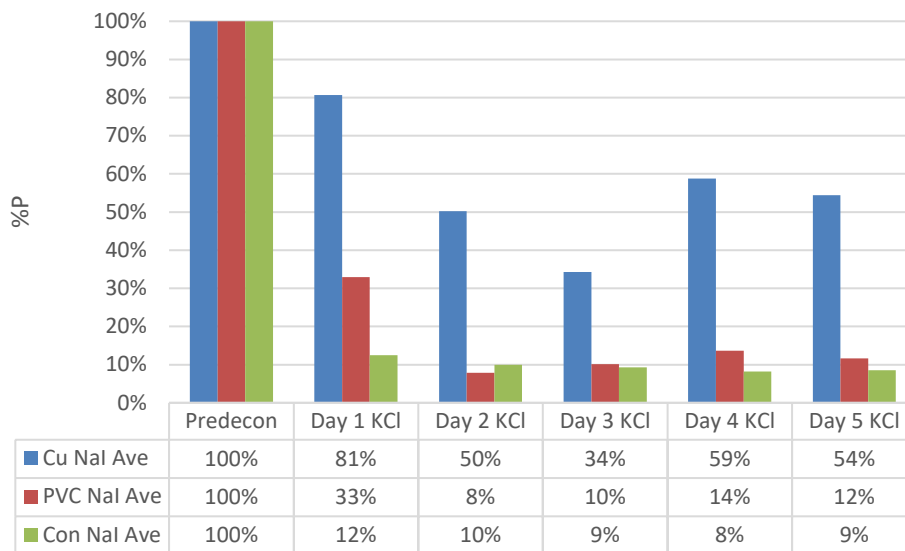
After exposure to clean water for 24 hrs, the KCl solution was added for the following 5 days (6 days for the concrete coupons). Cs-137 activities on the coupons at the beginning of the

KCl cleaning experiment are presented in Table 8. These activity levels are what remained on the coupons after exposure to clean water for 24 hrs. Figures 7 and 8 shows the %P (vertical axis) results for Cs-137 decontamination using the 1 M KCl solution on the three coupon surface types. The bars to the far-left side of the graph present the residual activity after 24 hours of exposure to clean tap water. The remaining bars along the horizontal axis represent the %P of Cs-137 after exposure to the KCl.

**Table 8. Initial Cs-137 Levels for the KCl Cleaning**

Analysis Method	Coupons					
	Copper		PVC		Concrete	
NaISS (counts)	598	Cu1	271	PVC1	9,085	Con1
	562	Cu2	267	PVC2	10,775	Con2
LSC (DPM)	1,171	Cu3	794	PVC3	13,731	Con3
	865	Cu4	1,189	PVC4	39,975	Con4

DPM, disintegrations per minute; LSC, liquid scintillation counting; NaISS, sodium iodide spectroscopy



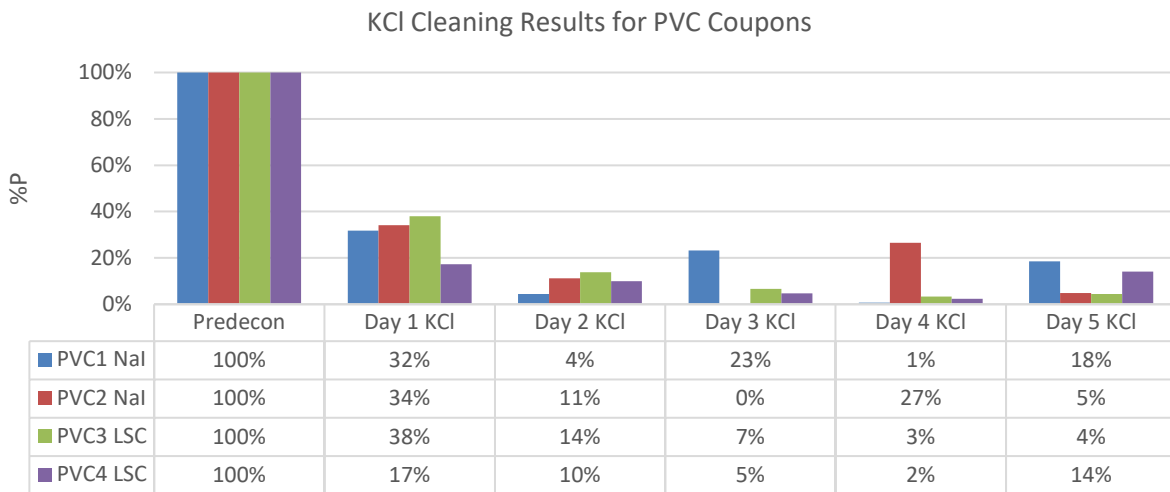
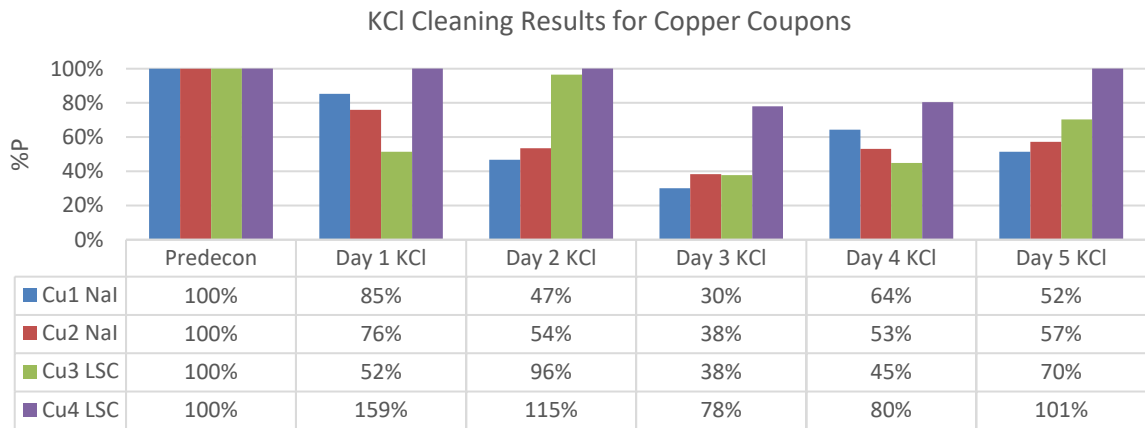
Results after Day 2 are at or below the detection limits for the PVC coupons.

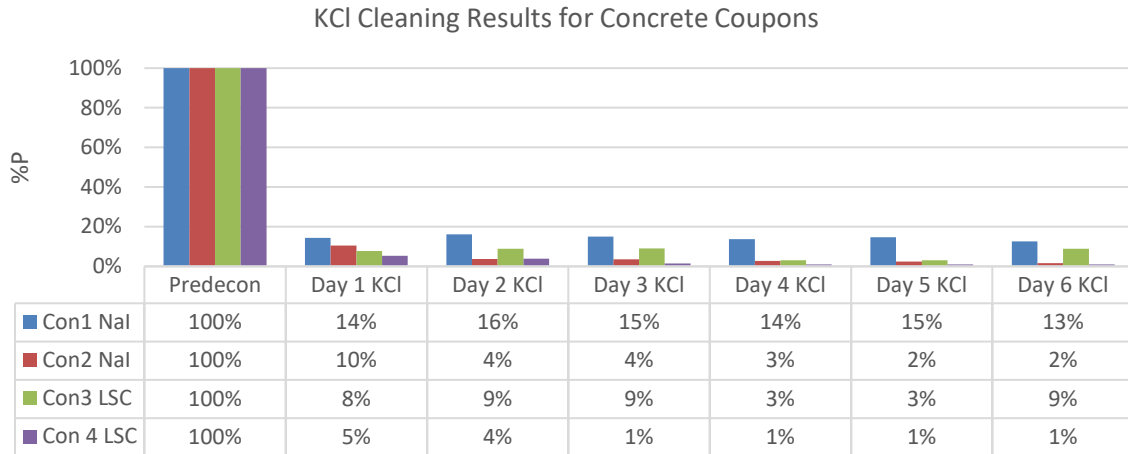
**Figure 7. KCl chemical cleaning agent evaluation – average (Ave) percent persistence (%P) of Cs-137 by coupon type (Cu, PVC, and concrete-lined [Con]); sodium iodide spectroscopy (NaI) method.**

The KCl cleaning results show initial decreases in Cs-137 activity of approximately 19% for copper, 67% for PVC, and 88% for concrete coupons with the first 24 hours of KCl exposure

(%P of 81%, 33% and 12% respectively). The Cs-137 persisted on the copper coupons at approximately 50% P for the remainder of the experiment. The PVC and concrete coupons decreased to roughly 10 %P at 2 days after introduction of the KCl solution, and remained at that level for the duration of the experiment.

These trends are shown in more detail in the graphs in Figure 8. The individual NaISS and LSC results are presented for the different coupon types separately. Overall, the NaISS and LSC results show similar trends, although there is some variation in the copper coupon results.





**Figure 8. Potassium chloride chemical cleaning agent evaluation – percent persistence (%P) on of Cs-137 on copper, PVC, and concrete-lined (Con) coupons; sodium iodide spectroscopy (NaI) and liquid scintillation counting (LSC) methods.**

In conclusion, the KCl solution removed approximately 90% of the Cs-137 activity (10 %P) from the PVC and concrete pipe materials (based on the NaISS results in Figure 7). For PVC and concrete, the 90% decrease in Cs-137 activity occurred one day after introduction of the KCl, and the activity levels were stable thereafter. This contrasts with the NH<sub>4</sub>Cl cleaning solution results where Cs-137 activity decreased continuously over 4 days. The copper coupons retained approximately 50 % of the contamination after 5 days of being exposed to the KCl solution, although % P fluctuated between 34 and 60% (NaISS results, Figure 7) over the decontamination period. It should be noted that when adding together the Cs-137 activity removal achieved during exposure to clean water for 24 hrs (persistence evaluation) and the KCl cleaning, total removals of 89%, 99% and 99% for copper, PVC and concrete, respectively, were observed. This demonstrates that flushing with clean water will remove 80-89% of the Cs-137 activity (with one day of clean water exposure, depending on pipe material), but chemical cleaning is needed to obtain more removal.

### 4.3 Biofilm Measurements

Biofilm was grown and counted on the three types of coupons before the experiments began. Figure 9 is a photo of the coupons removed from the biofilm recirculating system after 7 days. Table 9 presents the HPC results for each coupon type. Biofilm grew on all three coupons types, with concrete and PVC returning similar results and copper holding the least biofilm on the coupon surface. The CFU per coupon ranged from  $6.3E+04$  to  $6.6E+07$ . There was a span of time between the biofilm measurement and the Cs-137 contamination that allowed for continued biofilm formation, which was not measured. The coupon CFU count for the persistence evaluation was measured on November 11, 2016 and testing began seven days later on November 18, 2016. Similarly, the CFU on the coupons were measured on February 17, 2017 for the KCl cleaning and testing began 10 days later on February 27, 2017. The coupons remained in the dark in the biofilm recirculating system until the first day of testing.



**Figure 9. Testing coupons with biofilm growth: concrete-lined (left), PVC (middle), and copper (right).**

**Table 9. Colony Forming Units Grown on Coupon Surfaces**

Coupon Type	CFU/Coupon	
	11/11/2016	2/17/2017
Copper	$5.1E+05$	$6.3E+04$
PVC	$3.3E+07$	$6.6E+07$
Concrete	$2.5E+07$	$1.7E+07$

#### 4.4 Water Quality Measurements

Throughout this evaluation the pH, conductivity, and free and total chlorine concentrations of the tap water were all measured on a batch basis. The pH of the tap water was on average  $7.5 \pm 0.26$  with an average conductivity of  $566 \pm 56$  Siemen (S)/cm. The average free chlorine concentration of the tap water was measured to be  $0.17 \pm 0.39$  milligram per liter (mg/L).

#### 4.5 Summary and Conclusions

The objective of this study was to evaluate the persistence of radioactive Cs-137 on concrete-lined, copper, and PVC pipe surfaces, and possible chemical decontamination approaches. During this study, conditions within operational drinking water pipes were simulated using ARs. Concrete-lined, copper, and PVC coupons (samples) with biofilm growth were used as representative pipe materials. Radioactive Cs-137 was used to contaminate the ARs, and its persistence was calculated after exposure to clean water and decontamination with two chemical solutions (in separate experiments).

Persistence results showed that continued exposure to clean tap water reduced the adhered Cs-137 activity level by 75% for the copper pipe material, and 91% and 93% for the PVC and concrete pipe materials, respectively. When 1 M  $\text{NH}_4\text{Cl}$  was used to decontaminate the coupons, there appeared to be more variability in the results on the copper coupons compared to the other pipe material tested, possibly due to a precipitate that formed. The precipitate, or corrosion on the copper piping material, may cause physical damage to a home plumbing water system. The %P following 4 days of  $\text{NH}_4\text{Cl}$  treatment on the copper, PVC and concrete piping materials was 11%, 9% and 15% (89%, 91% and 85% removal). However, when adding together the Cs-137 activity removal (measured by NaISS) achieved during exposure to clean water for 5 days (persistence evaluation) and the  $\text{NH}_4\text{Cl}$  solution, total removals of 97%, 99% and 99% for copper, PVC and concrete, respectively, were observed.

The 1 M  $\text{KCl}$  chemical cleaning results show that Cs-137 activity remained persistent on copper coupons at 50 %P after five days of  $\text{KCl}$  exposure, although % P fluctuated between 34 and 60%. There was no damage to the copper coupons from a precipitate or corrosion when using  $\text{KCl}$ . The  $\text{KCl}$  solution removed approximately 90% of the remaining Cs-137 activity (10 %P) from the PVC and concrete pipe materials. For PVC and concrete, the 90% decrease in Cs-137 activity occurred one day after introduction of the  $\text{KCl}$ , and the activity levels were stable thereafter. This contrasts with the  $\text{NH}_4\text{Cl}$  cleaning results where Cs-137 activity decreased continuously over 4 days. It should be noted that when adding together the Cs-137 activity removal achieved during exposure to clean water for 24 hrs (persistence evaluation) and the  $\text{KCl}$  solution, total removals of 89%, 99% and 99% for copper, PVC and concrete, respectively, were observed.

These results suggest that KCl would be a better decontamination agent compared to  $\text{NH}_4\text{Cl}$  since the decontamination performance is comparable across materials, KCl acts faster on PVC and concrete, and KCl does not corrode the copper pipe. However, it should also be considered that exposure to clean water alone removed 75% of the Cs-137 activity on copper pipe material, and 91% and 93% of the activity adhered to PVC and concrete pipe materials, respectively. When using a decontamination chemical, these removal totals increased to 97% ( $\text{NH}_4\text{Cl}$ ) and 89% (KCl) on copper, and 99% for all other pipe material and cleaning agent combination. Following a Cs-137 contamination event in a water system, responders and decision makers may want to consider whether flushing with clean water alone is an adequate decontamination measure.

## REFERENCES

1. Szabo, J. G., E. W. Rice, and P. L. Bishop. 2006. Persistence of *Klebsiella pneumoniae* on simulated biofilm in a model drinking water system. *Environ. Sci. Technol.* 40:4996–5002.
2. Szabo, J.G., Persistence and decontamination of surrogate radioisotopes in a model drinking water distribution system, *Water Research* (2009), doi:10.1016/j.watres.2009.08.012.
3. ASTM C 150-07 Standard, 2007, “Standard Specification for Portland Cement,” ASTM International, West Conshohocken, PA, [www.astm.org](http://www.astm.org).
4. American Water Works Association C104-03 Standard, 2004, “Standard for Cement-Mortar Lining for Ductile-Iron Pipe and Fittings for Water” Denver, CO, [www.awwa.org](http://www.awwa.org).
5. Welter, G., M. Lechevallier, S. Spangler, J. Cotruvo, R. Moser, Guidance for Decontamination of Water System Infrastructure. Denver, CO: AWWA Research Foundation, 2009.
6. ASTM Standard D1784, 2011, " Standard Specification for Rigid Poly(Vinyl Chloride) (PVC) Compounds and Chlorinated Poly (Vinyl Chloride) (CPVC) Compounds," ASTM International, West Conshohocken, PA, [www.astm.org](http://www.astm.org).
7. U.S. EPA, EMSL. “Method 900.0: Gross Alpha and Gross Beta Radioactivity in Drinking Water.” *Prescribed Procedures for Measurement of Radioactivity in Drinking Water*, EPA/600/4/80/032, 1980.
8. U.S. EPA, EMSL. “Method 901.1: Gamma Emitting Radionuclides in Drinking Water.” *Prescribed Procedures for Measurement of Radioactivity in Drinking Water*, EPA/600/4/80/032, 1980.





PRESORTED STANDARD  
POSTAGE & FEES PAID  
EPA  
PERMIT NO. G-35

Office of Research and Development (8101R)  
Washington, DC 20460

Official Business  
Penalty for Private Use  
\$300