Massachusetts Department of Environmental Protection
Results of Non-Radiological Oil and Hazardous Material Split Sampling and Analysis
Conducted at the
Decommissioned Pilgrim Nuclear Power Plant
Plymouth, Massachusetts
May 19, 2023

This summary documents the procedures and results for the non-radiological oil and hazardous material (OHM) sampling and analysis of water samples from the reactor building at the Pilgrim Nuclear Power Plant coordinated by the Massachusetts Department of Environmental Protection (MassDEP). At the same time MassDEP collected their samples, the Massachusetts Department of Public Health (DPH) collected samples for the analysis of radionuclides at the Massachusetts Environmental Radiation Laboratory (MERL). The results of the radionuclide analysis will be prepared separately by DPH.

BACKGROUND

In Massachusetts, the bulk of environmental samples are collected and analyzed by contractors working for entities that are regulated by MassDEP. MassDEP receives analytical results with thousands of permit applications, monitoring reports and environmental assessment reports every year to support all the programs implemented by MassDEP.

Environmental Professionals

Because MassDEP does not have the staff resources or the money to conduct the environmental sampling necessary to support submittals made to MassDEP, the environmental sampling is conducted by environmental professionals (such as Professional Engineers (PEs), Licensed Site Professionals (LSPs) and other qualified environmental professionals). The samples collected by these environmental professionals are analyzed by certified laboratories.

Certified Laboratories

The Massachusetts State Laboratory, the William X. Wall Experiment Station (WES), Division of Environmental Laboratory Sciences certifies commercial and municipal laboratories to perform routine compliance analyses. The MassDEP Laboratory Certification Program is the largest program among the New England states. Over 160 laboratories in Massachusetts and neighboring states are certified by WES for chemical and/or microbiological analyses of potable and/or non-potable water. Through the Laboratory Certification Program, educational outreach, and other activities, WES plays an important role in ensuring that contractors collecting and analyzing environmental samples are producing high-quality monitoring data.

Standard Analytical Methods and QA/QC

The analysis conducted by certified laboratories follows analytical methods developed by the United States Environmental Protection Agency (EPA) and, in some cases, the MassDEP. The analytical data reports also contain information of Quality Assurance (QA) and Quality Control (QC) procedures conducted as part of the sample analysis.

Split Sampling

Split samples typically consist of a single field sample taken by a single entity that is divided into two separate sub-samples for subsequent laboratory analysis. Typically, split samples are submitted to different laboratories, or analyzed by different analysts to determine the precision of laboratory results. Alternatively, split samples can be analyzed at a single laboratory without knowledge of the sample origin (referred to as a "blind sample"). Any discrepancy between the two sub-samples suggests a lack of precision or repeatability introduced during sample collection or lab analysis.

Split samples can also be samples that are divided between two entities for comparison purposes. Usually each entity (for example, the regulated entity and the regulators) collects the samples for independent shipping and analyses. At times, MassDEP has collected environmental samples at the same time a regulated entity has collected a sample (split sample) to confirm the sampling and analysis conducted by the regulated entity.

REASON FOR SPLIT SAMPLES AT PILGRIM NUCLEAR POWER PLANT

Many of the members of the Nuclear Decommissioning Citizens Advisory Panel (NDCAP) and the public requested analytical data for the water in the reactor building and raised concerns about the fact that samples used to make decisions relative to the decommissioning of the plant were collected by Holtec. Specifically, those in the public asked how it can be confirmed that the samples collected by Holtec were from the locations identified by Holtec. To address this, MassDEP and DPH agreed to collect split samples and ship them independently to a laboratory.

The sampling and analysis conducted by MassDEP was for comparison purposes and was not conducted for compliance purposes, for instance, as a regulatory requirement or to support a permit application. The sampling and analysis were conducted solely to determine if the analytical results for the samples collected by Holtec could be duplicated by MassDEP and to share information requested by the public and the NDCAP about the quality of the water in the reactor systems at Pilgrim Nuclear Power Plant. Holtec has conducted, and may conduct, additional separate sampling and analysis to support its federal NPDES and Massachusetts Surface Water Discharge Permit Modification Applications submitted to U.S. EPA and MassDEP requesting to discharge decommissioning-related wastewater to Cape Cod Bay.

As explained at the March 27, 2023 NDCAP meeting, MassDEP has contracted with GEL Laboratories to analyze the non-radiological parameters in the split samples collected by MassDEP. Due to the fact that there are not many laboratories that can handle water containing radioactive material, MassDEP was not able to contract with a different laboratory to conduct these analyses. GEL Laboratories is certified by the Commonwealth of Massachusetts William X. Wall Experiment Station and holds a license issued which authorizes the lab to receive, acquire, possess, and transfer radioactive material. DPH utilized the Massachusetts Environmental Radiation Laboratory (MERL) located at the Massachusetts State Public Health Laboratory to conduct analysis of radiological parameters.

SAMPLE COLLECTION, SHIPMENT AND ANALYSIS

On March 22, 2023 two sealed coolers were delivered to MassDEP from GEL Laboratories, LLC, 2040 Savage Road, Charleston, South Carolina. The coolers contained the required sampling bottles and, in some cases, with the required preservatives. The coolers were stored in the lab at MassDEP's 20 Riverside Drive, Lakeville office building. The lab is not accessible to public.

On April 5, 2023, representatives from MassDEP and DPH met at the Pilgrim Nuclear Power Plant to collect the samples. Prior to sample collection the representatives from MassDEP took a 90-minute training program on handling radioactive liquids.

David Gould of the Town of Plymouth Department of Natural Resources attended the sampling event to observe sample collection.

Sampling was conducted at three locations, Spent Fuel Pool, Dryer Separator Pit, and the Torus. See figure below:

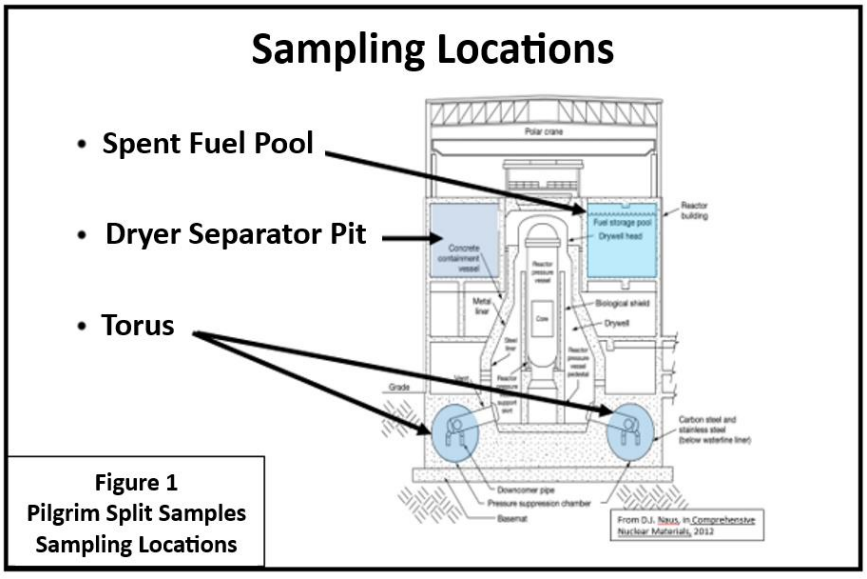

Figure 1
Pilgrim Split Samples
Sampling Locations

Sampling procedures

Given that the samples from the Dryer Separator Pit and Spent Fuel Pool were collected from above the respective tanks, and state personnel are not qualified radiation workers authorized to access areas where the samples were collected, the sample collection was conducted by Holtec personnel under direct observation of representatives from the Town of Plymouth, DPH and MassDEP. Samples were collected by lowering a hose connected to a pump approximately 20 feet below the surface of the water and circulating the water through the pump and back into the tank until a sufficient volume was circulated to adequately flush the pump. At this time the water was pumped into 1-gallon plastic jugs labeled #1 for the Dryer Separator Pit and #2 for the Spent Fuel Pool. The samples were collected this way to reduce the amount of time the sampling team had to spend in the vicinity of the Dryer Separator Pit and Spent Fuel Pool. The containers were wiped dry and checked for external radiation before being loaded on a cart for transport to the on-site lab at the Pilgrim Nuclear Power Plant. The samples never left the direct observation of MassDEP personnel.

On the way to the on-site lab the third sample was collected from the Torus. The sample was collected from a valve that was directly connected to the Torus and again the samples were collected in 1-gallon jugs (#3) by Holtec personnel under the direct observation by the Town of Plymouth, DPH and MassDEP.

All the samples were transported to the on-site lab. The samples to be shipped by MassDEP were decanted into the appropriate sample containers by MassDEP personnel and the samples to be shipped by Holtec were decanted into the sample containers by Holtec personnel. The sample containers were labeled, and chain-of-custody forms were completed at this time.

Shipping procedures

The samples to be transported by MassDEP were packed in ice and delivered on site and signed over to a representative of Atlantic Nuclear Corporation (a DPH contractor licensed to ship radioactive samples). The samples were transported to Atlantic Nuclear Corporation's office at 100 Weymouth Street Unit E, Rockland, Massachusetts, repacked and iced for shipping to GEL Laboratories and shipped on April 5, 2023.

Receipt of samples

As indicated on the analytical data report (attached), the samples were received by GEL Laboratories on April 6, 2023 and it was reported that the samples were "…delivered with the proper chain of custody documentation and signatures. All sample containers arrived without any visible signs of tampering or breakage."

Analytical parameters

As discussed at the November 28, 2022 NDCAP meeting, the analytical parameter list was generated by selecting parameters that reflect the EPA priority pollutants, parameters in the NPDES Permit and other parameters identified from a literature review by MassDEP. GEL Laboratories was not able to analyze the samples for whole effluent toxicity, tolytriazole and asbestos, so these parameters were removed from the analytical parameter list.

In all, 239 parameters were analyzed and the list included the following:

- pH
- temperature
- oil and grease
- total residual chlorine
- total dissolved solids
- metals (Al, As, Be, B, Cd, total Cr, Co , Fe, Pb, Ni, K, Se, Ag, Th and Zn)
- cyanide
- nitrogen, nitrate/nitrite
- semi-volatile organic compounds/polycyclic aromatic hydrocarbons (129 different compounds)
- volatile organic compounds (56 different compounds)
- per- and polyfluoroalkyl substances (PFAS – 25 different compounds)
- Polychlorinated Biphenyls (PCBs – 7 different compounds)

The full list of all the parameters analyzed is in the analytical data report (attached).

SAMPLE RESULTS

The temperatures of the three samples were measured at the time of sampling and were as follows: 93.88° F for the sample from the Dryer Separator Pit, 93.93° F for the sample from the Spent Fuel Pool and 57.03° F for the sample from the Torus.

Twenty-two (22) of the 239 parameters that were analyzed were detected above the method detection limit (including estimated values) in at least one of the three samples. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. These detections are summarized in Table 1. No other parameters were detected in the samples.

Holtec provided MassDEP with a table of the parameters that were detected above the MDL in the samples Holtec collected. These results were added to Table 1 for comparison.

COMPARISON WITH HOLTEC RESULTS

The analytical results for the samples collected by MassDEP compare within expected ranges to the analytical results for the samples collected by Holtec indicating that the two sets of samples are acceptable split samples/duplicates.

Relative Percent Difference

The comparison of split samples, or duplicates, is commonly undertaken by expressing the duplicate results as the Relative Percent Difference (RPD) using the following equation:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

Where: RPD is relative percent difference
C_1 is the concentration of analyte from sample 1
C_2 is the concentration of analyte from sample 2

According to the EPA, an RPD of ≤ 20% is considered an acceptable result for split/duplicate aqueous samples provided the result is five to ten times the detection limit. In those circumstances where the result is close to the detection limit, RPD may exceed 20%. In addition, the acceptable RPD is strongly influenced by the analyte and matrix.

The range of the RPDs for the comparable results is 0 to 20.2%, indicating that the samples collected and transported by Holtec are acceptable duplicates with the samples collected and transported by MassDEP. The one parameter with a RPD of 20.2% was the PFAS perfluorohexane sulfonic acid (PFH_xS).

Table 1
Non-Radioactive Split Sampling Results
for
MassDEP and Holtec Samples
(detections only)
Pilgrim Station
April 2023

Parameter	Dryer Separator		Spent Fuel Pool		Torus	
	MassDEP Results	Holtec Results	MassDEP Results	Holtec Results	MassDEP Results	Holtec Results
Per- and polyfluoroalkyl substances (PFAS – results in nanograms per liter (ng/L) or parts per trillion – (ppt))						
Perfluorobutane sulfonic acid (PFBS)	<[1]0.578	<0.591	<0.591	<0.577	1.09 J[2]	0.951 J
Perfluorobutanoic acid (PFBA)	<0.701	NA[3]	<0.716	NA	2.62	NA
Perfluorohexane sulfonic acid (PFH_xS)	<0.578	<0.591	<0.591	<0.577	8.71	7.11
Perfluorohexanoic acid[4] (PFH_xA)	<0.701	<0.716	<0.716	<0.699	5.14	4.49
Perfluorooctane sulfonic acid (PFOS)	<0.701	<0.716	<0.591	<0.699	1.26 J	1.13 J
Perfluorooctanoic acid (PFOA)	<0.701	<0.716	<0.716	<0.699	1.77 J	1.75 J
Perfluoropentane sulfonic acid (PFP_eS)	<0.578	NA	<0.591	NA	1.25 J	NA
Perfluoropentanoic acid (PFP_eA)	<0.578	NA	<0.591	NA	2.04	NA
Perfluoroheptanoic acid (PFH_pA)	<0.578	<0.591	<0.591	<0.577	<0.602	0.778 J
Metals (results are in micrograms per liter (µg/L) or parts per billion (ppb))						
Boron	194	200	174	181	165	166
Cobalt	<3.00	NA	<3.00	NA	0.313 J	NA
Copper	NA[4]	<3.00	NA	<3.00	NA	0.629 J
Iron	<330	<330	<330	<330	149	144
Nickel	<6.00	<6.00	<6.00	<6.00	2.94	3.01
Potassium	1,010	1,040	993	960	2,620	2,710
Zinc	366	380	364	356	1,460	1,460
Cyanide	<8.35	<8.35	<8.35	<8.35	<1.67	1.74 J
General chemistry (results are in milligrams per liter (mg/L) or parts per million (ppm), except pH which is in Standard Units (SU))						
Nitrogen/nitrate	0.938	0.897	0.928	0.909	1.21	1.22
Oil & grease	<1.51	2.65 J	2.16 J	2.16 J	1.82 J	1.60 J
pH	7.49	NA	7.40	NA	7.59	NA
Total dissolved solids	<4.76	NA	<4.76	NA	2,600	NA
Chlorine (total residual)	<0.0170	0.0207 HJ	<0.0170	<0.0170 HU	0.0283 H[5]J	<0.0170 HU
Semi-volatile organic compounds (SVOCs – results are in µg/L or ppb)						
Bis(2-ethylhexl) phthalate	<1.50	NA	<1.50	NA	0.324 J	NA
Volatile organic compounds (VOCs – results are in micrograms per liter (µg/L) or parts per billion (ppb))						
Acetone	4.21 J	NA	2.56 J	NA	2.53 J	NA
Methylene chloride	0.790 B[6]J	0.810 BJ	9.79 BJ	0.900 BJ	0.890 BJ	0.880 BJ

Notes:

1. < denotes results are below the method detection limit. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The value give is the detection limit for that analyte.
2. The "J" qualifier is used to note that the reported concentration is considered estimated. The "J-flag" is used whenever the measured concentration is lower than the reporting limit but above the method detection limit. The reporting limit is the lowest concentration of the substance tested that can be reported reliably under normal laboratory conditions.
3. NA = Not analyzed
4. H – Analytical holding time was exceeded
5. B – The targeted analyte was detected in the associated blank.

Analytical Data Report