PROJECT DESIGN AND SAMPLING PLAN

PFAS in Biosolids: Characterization and Fate

Department of Natural Resources and Environmental Control

Division of Water

89 Kings Highway
Dover, DE 19901

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1.0 INTRODUCTION AND BACKGROUND

The Clean Water Act (CWA) of 1972 and its amendments govern water pollution in the United States. One aspect of the CWA is section 405(d) that requires the EPA to establish requirements and management practices for the use and disposal of sewage sludge (biosolids). In 1993 EPA issued regulations 40 CFR Part 503, Standards for the Use or Disposal of Sewage Sludge. Prior to development of the regulations, a survey was conducted to identify contaminants of concern found in biosolids. A comprehensive risk assessment was then conducted to determine which of these contaminants found in biosolids posed risk to public health and the environment. Ultimately numeric limits and management practices were developed to limit exposure to these contaminants. Every 2 years, the EPA is required to refine its risk assessments and reevaluate contaminants that are present in biosolids and develop new numeric limits and management practices that protect public health and the environment from reasonably anticipated adverse effects of chemical and microbial pollutants during the use or disposal of biosolids.

A group of emerging contaminants of concern are per- and polyfluoroalkyl substances (PFAS) which are a large group of man-made chemicals that include perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). PFAS have been used since the 1950's as stain and soil repellents for carpets and clothing textiles, oil and grease resistance for food contact paper and surfactants in firefighting foams. PFAS are highly persistent in the environment and some bioaccumulate in humans. There is evidence that continued exposure above specific levels to certain PFAS may lead to adverse health effects.

According to existing data, PFAS are found in virtually all biosolids at varying concentrations (PCWR et. al, 2020; Bogdan, 2021). Analytical methods continue to be developed to better detect PFAS compounds and to determine which PFAS compounds are the most impactful to human health and the environment. The EPA has dedicated many resources towards developing risk-based action levels for PFAS but the initial risk assessment is only focused on PFOA and PFOS and the EPA is not scheduled to complete the risk assessment for biosolids until the winter of 2024. Thus, federal PFOA and PFOS action levels will not likely be developed until 2025. As the EPA's initial risk-based action levels are limited to PFOA and PFOS, many uncertainties related to other PFAS compounds will remain and more scientific data is needed to develop these other risk-based action levels.

While research is ongoing at federal and state levels, wastewater and biosolids continue to be applied within the State of Delaware in accordance with the requirements of existing Department of Natural Resources and Environmental Control (DNREC) regulations and permits and periodically DNREC receives requests to issue new permits for the land application of biosolids. In 2021 Delaware generated approximately 21,000 dry tons of biosolids, and about 12,900 dry tons of biosolid were land applied in Delaware including 600 dry tons (5%) from out of state sources. Roughly 8,700 dry tons of Delaware generated biosolids were land applied in Pennsylvania.

As the current understanding of the impacts of PFAS is limited, a science based approached to regulate the compounds is not possible at this time and the Department's appropriate regulatory path is difficult to determine. Environmental advocacy groups have also raised concerns related to PFAS and the land application of biosolids.

To examine PFAS in the waste stream DNREC developed this project design and sampling plan to investigate the concentrations of certain PFAS compounds in wastewater influent, effluent, and biosolids at selected wastewater treatment plants (WWTPs) across the state. To further investigate the fate of PFAS, DNREC has selected a biosolids land application facility and will also sample selected (wastewater) groundwater discharge facilities (i.e., spray irrigation sites and rapid infiltration basins) ato characterize PFAS and better understand potential PFAS impacts from these sites to soil and groundwater. This document only covers sampling of soil and groundwater related to the biosolids study site and biosolids from selected WWTPs throughout the state . A Project Design and Sampling Plan for the influents and effluents from WWTPs is under preparation and is expected to be finalized-released in mid-2023.

Section 2.0 presents the sampling plan for biosolids and the groundwater and soils at a biosolid land application site; Section 3.0 discusses quality assurance and quality control; Section 4.0 shows the tentative project schedule; and Section 5 summarizes the proposed activities.

2.0 BIOSOLIDS AND LAND APPLICATION

This phase of the biosolids sampling will entail the examination of PFAS in biosolids prior to land application along with soil and groundwater monitoring of an existing application site.

2.1 Biosolids Land Application

A biosolid land application site operated by the City of Rehoboth has been selected for the biosolid PFAS study. The City of Rehoboth's wastewater treatment plant's influent is mostly comprised of residential and commercial sources with little to no industry wastewater inputs. The plant treats approximately 1.2 million gallons per day (MGD) and produces roughly 200 dry tons of sludge (biosolids) annually. Stabilized sludge from the City of Rehoboth Wastewater Treatment Facility has been applied to 85-acres of farmland, located approximately 6 miles southeast of Milford, Delaware since 1989. Figure 1 shows the regional location of the permitted land treatment site and Figure 2 shows the detailed layout of land application fields and the monitoring wells installed at the site.

Figure 1: Land Application Site Location

Figure 2. Land Application Fields (F1-F8) and Monitoring Wells (W1-W8) at the Site Location
*(*Monitoring wells selected for this PFAS study are discussed in Section 2.1.2)*

Biosolids were applied by subsurface injection at a depth of up to 10 inches beneath the soil surface. Initially Fields 1-5 were permitted and land application of biosolids and application activities started in 1989, use of Fields 6 and 7 began in 1991, and Field 8 in 1995. Annual application records of biosolids on each field are available from 2002 through 2021 (Table 1).

A cumulative loading analysis was performed based on available biosolids loading data from 2002 to present (2007 loading was *interpolated* from application records in the years before and after). As shown in Figure 3, the differences in the total per acre amount of the biosolids applied onto the 8 fields for the time period are similar. However as noted earlier there were more than 10 years of loading prior to record keeping and Fields 6 and 7 were permitted 2 years after F1-F5 and Field 8 permitted 4 years after F1-F5.

Year	Acres applied onto	Total dry tons applied	Average dry tons/ac.	Fields applied onto
2021	55	186	3.4	1, 2, 6, 7, 8
2020	65	254	3.9	3, 4, 5, 6, 7, 8
2019	50	232	4.6	1, 2, 3, 4, 5
2018	55	235	4.3	1, 2, 3, 6, 7
2017	50	203	4.1	1, 3, 4, 5, 8
2016	45	194	4.3	1, 2, 6, 7
2015	50	229	4.6	2, 3, 4, 5, 8
2014	45	210	4.7	1, 6, 7, 8
2013	50	241	4.8	1, 2, 3, 4, 5
2012	45	214	4.8	5, 6, 7, 8
2011	50	202	4.0	1, 2, 3, 4, 5
2010	42.5	223	5.2	5, 6, 7, 8
2009	40	190	4.8	1, 2, 3, 4
2008	45	213	4.7	1, 2, 6, 7
2007*	-	-	-	-
2006	42.5	181	4.7	1, 2, 3, 7
2005	55	201	3.7	4, 5, 6, 7, 8
2004	40	176	4.4	1, 2, 3, 4
2003	45	161	3.6	5, 6 ,7 ,8
2002	40	169	4.2	3, 4, 5, 8

* 2007 records could not be located.

Table 1. Historical records of biosolid application at the City of Rehoboth site

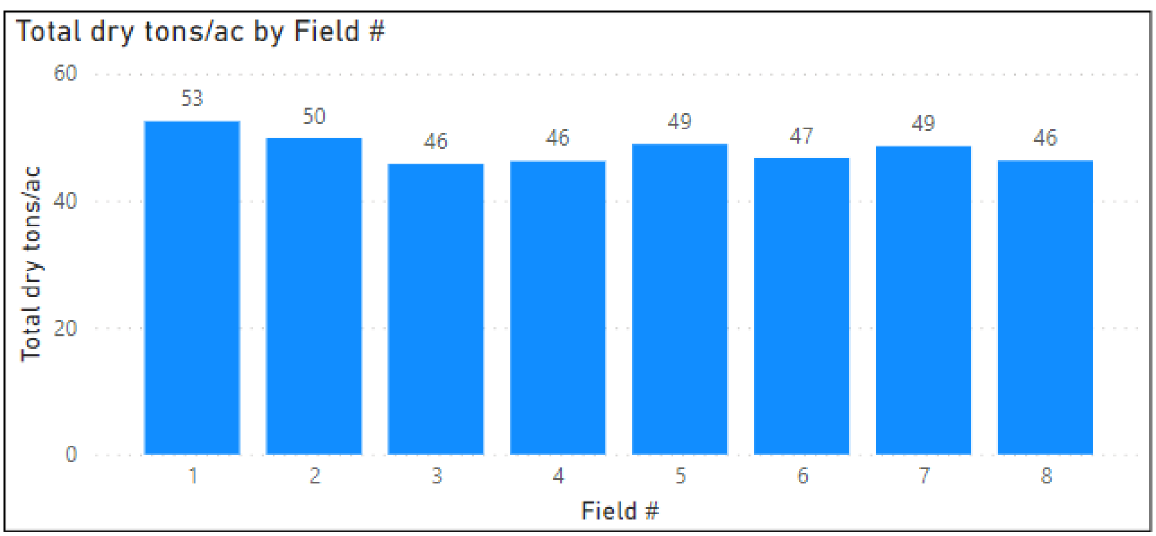

Figure 3. Accumulative Loading of Biosolids in Each of the Fields

Soil samples from the different fields of the land treatment site, water samples from selected monitoring wells, as well as the biosolids will be collected for this portion of the study. Details on each type of sampling are presented in the sections below.

2.1.1 Soil Sampling

A total of 14 soil sampling locations are located within the eight land application fields and two outside of the application area (Figure 4). Based on the average loading rate (as shown in Table 1), F1-5 could have received at least 10 tons more than F8. It was therefore decided that sampling locations should be evenly distributed, as a result of F8 being slightly denser than other fields, to better characterize the youngest field. At each sampling location, samples will be collected at depths of 1 foot, 3 feet and 6 feet below the surface. Based on the water-level measurements from on-site monitoring wells, groundwater levels in the northern 1/3 of the site should be greater than 9 feet below the surface but decrease seasonally to as low as two or three feet below the surface towards southern boundary. If the surficial groundwater table is encountered before reaching the desired depth, the last obtainable depth (1 or 3 feet) will be the final sampling depth at that location. A total of 48 soil samples is possible for the study (14 in-application area at 3 depths and 2 out of application area at 3 depths). Sample ID for samples collected inside the application area will be assigned in the format of F(*field number*)-(*sample number*)(*depth code*). With depth code classified as: a=1 foot, b=3 feet, c=6 feet. For example, F5-1c is the sample location 1 collected from Field 5 at a depth of 6 feet. The two sample locations outside the application area will be WF8-1(*a,b,c*) for the sample location west of field 8 and NF3-1(*a,b,c*) for the sample location north of filed 3.

Soil samples will be collected once in the Fall of 2022 for this study. The thirty-seven PFAS parameters to be analyzed for in the soil samples are shown in Table 2.

Figure 4. Soil Sampling Site Locations

11Cl-PF3OUdS	Perfluorododecanoic acid (PFDoA)	PFEESA
4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	Perfluoroheptanesulfonic Acid (PFHpS)	PFMBA
4:2 FTS	Perfluoroheptanoic acid (PFHpA)	PFMPA
6:2 FTS	Perfluorohexanesulfonic acid (PFHxS)	5:3 FTCA
8:2 FTS	Perfluorohexanoic acid (PFHxA)	6:2 FTCA
9Cl-PF3ONS	Perfluorononanoic acid (PFNA)	6:2 FTUCA
HFPO-DA (GenX)	Perfluorooctanesulfonic acid (PFOS)	Hydro-PS Acid
NEtFOSAA	Perfluorooctanoic acid (PFOA)	PFMOAA
NFDHA	Perfluoropentanesulfonic acid (PFPeS)	PFO2HxA
NMeFOSAA	Perfluoropentanoic acid (PFPeA)	PFO3OA
Perfluorobutanesulfonic acid (PFBS)	Perfluorotetradecanoic acid (PFTeA)	PPF Acid
Perfluorobutanoic acid (PFBA)	Perfluorotridecanoic acid (PFTrDA)	
Perfluorodecanoic acid (PFDA)	Perfluoroundecanoic acid (PFUnA)	

Table 2. PFAS Compounds to be Analyzed for Soil Samples
*(after *Method 537(M) DNREC REM Compound List, 2022*)

2.1.2 Groundwater Sampling

Three monitoring wells were selected for this study (see Figure 2 for locations): W-1, W-5, W-6 and W-8 (downgradient). Samples will be collected quarterly for a year for a total of 16 groundwater samples for the study.

Sample ID will be assigned in the format of W (*well number*)-(*quarter number*). For example, W5-3 is the third quarter sample collected from well W-5. Parameters to be analyzed for groundwater samples will be the same as those analyzed for soil (see Table 2).

2.1.3 Biosolid Sampling

Four samples of biosolids will be collected quarterly for a year to estimate loading on the fields. Samples may be collected either at the site prior to application or at the Rehoboth City WWTP during loading for transport to the project site. Parameters to be analyzed for groundwater samples will be the same as those analyzed for soil (see Table 2).

2.2 Biosolids Characterization

To examine the concentration of PFAS from differing sources of influent, DNREC is proposing to collect additional biosolid samples from four more wastewater treatment facilities within the State and added to the Rehoboth facility biosolids data. To provide a variety of influent types, facilities were selected based on industrial, municipal, or mixed sources. The additional facilities are:

- City of Wilmington: The largest wastewater treatment plant in the State of Delaware treating approximately 67 MGD daily average discharge rate of wastewater and consists of industrial, commercial, and residential wastewater. This wastewater treatment plant receives the largest contributions of wastewater from industry in the state and treats landfill leachate.

- Kent County: This wastewater treatment plant is the second largest in the state of Delaware treating approximately 13 MGD daily average discharge rate of wastewater and consists of industrial, commercial, and residential wastewater. Additionally, the Kent County wastewater treatment plant treats landfill leachate.

- City of Seaford: This wastewater treatment plant is medium sized and treats approximately 1.1 MGD of wastewater and consists of industrial, commercial, and residential wastewater. Formerly this plant treated wastewater generated from many chemical companies and is believed to have several historical contributors of PFAS to the wastewater treatment plant. While much of the heavy industry has left the area, sampling the City's sludge will help determine if PFAS levels in the sludge is currently elevated. The City of Seaford treats landfill leachate.

- Beaver Creek: The Beaver Creek Regional Wastewater Treatment Facility currently treats up to 150,000 gallons/day of residential waste that is generated by dwellings located in the Meadows of Beaver Creek community in Milton, Delaware. The influent is treated by a Sequencing Batch Reactor (SBR) system and disposed of into six (6) Rapid Infiltration Basins (RIB). Biosolid-sludge sampling from this facility will help characterizing PFAS in residential wastes (sewers).

- Rehoboth: The City of Rehoboth's wastewater treatment facility treats approximately 1.2 MGD of wastewater comprised mostly of residential and commercial sources with little to no industry wastewater inputs.

Four biosolid samples will be collected from each facility listed above (quarterly sampling for a year); and therefore, there will be 16 additional biosolid samples not including Rehoboth for a total of 20 biosolid samples.

Samples will be named in the format BS(*Site Code*)-(*Quarter*) where BS=Biosolids, Site Code is R=Rehoboth, W=Wilmington, K=Kent County, S=Seaford, B=Beaver Creek and the Quarter is the 1-4 corresponding to chorological order of the quarter sampled. For example, BSK-3 would be the 3rd quarter biosolid sample taken from Kent County Treatment. Parameters to be analyzed are the same as those for soil samples (see Table 2).

3.0 QUALITY ASSURANCE AND QUALITY CONTROL

A Quality Assurance Project Plan (QAPP) will be developed for this study prior to the start of sampling. DNREC will select qualified contractors and laboratories to perform sample collection and analysis. These contractors will be required to submit Standard Operating Procedures (SOPs) and Quality Assurance and Quality Control Plans (QA/QC) to DNREC for approval prior to contracting.

4.0 PROJECT SCHEDULE

This sampling plan will be finalized in October 2022. Sampling team(s) will be selected from State certified-listed contractors in November 2022 when communication with selected facilities should also be finalized. It is anticipated that field sampling would first occur in late November – early December 2022.

5.0 SUMMARY

DNREC- Division of Water intents to conduct a study on PFAS in wastewater influent, effluent, and from biosolids generated during the treatment of wastewater. Biosolids from five Wastewater Treatment Plants (WWTP) will be collected. The land application site that has been utilized for the application of biosolids from the City of Rehoboth Beach WWTP since 1989 will be used to examine the movement of PFAS in the soil and groundwater. Up to 48 soil samples, and 16 groundwater samples from monitoring wells will be collected from the Rehoboth facility. A total of 20 biosolids samples will be analyzed from five WWTPs. All samples will be analyzed for 37 PFAS compounds.

DELAWARE DEPARTMENT OF NATURAL RESOURCES AND ENVIRONMENTAL CONTROL

Reference

Bogdan D., 2021. Evaluation of PFAS in Influent, Effluent, and Residuals of Wastewater Treatment Plants (WWPTs) in Michigan: Michigan Department of Environment, Great Lakes, and Energy, April 2021 (pp. 119)

PCWR et. al., 2020. PFAS in Biosolids- A Southern Arizona Case Study: Pima County Wastewater Reclamation, Jacobs Engineering, the University of Arizona, and the National Science Foundation, October 2020 (pp. 32)