



April 4, 2022

Ms. Beth Magee  
Regional Permit Administrator  
NYSDEC – Region 5  
232 Golf Course Road  
Warrensburg, New York 12885

Via Email: [beth.magee@dec.ny.gov](mailto:beth.magee@dec.ny.gov)

Subject: Saratoga Biochar Solutions, LLC  
Request for Additional Information  
NYSDEC Permit Application ID 5-4144-00187/00001  
STERLING File #2020-20

Dear Ms. Magee,

On behalf of Saratoga Biochar Solutions, LLC, Sterling Environmental Engineering, P.C. (STERLING) submits the enclosed additional information and revised Facility documents in response to NYSDEC's technical comments received by email on January 20, 2022.

The following supporting information is enclosed:

- NYSDEC Technical Comments – January 20, 2022
- City of Glens Falls Wastewater Acceptance Letter – February 18, 2022
- WEF Residuals and Biosolids Conference 2021, “Removal and Transformation of PFAS from Biosolids in a High Temperature Pyrolysis System – A Bench Scale Evaluation”
- SBS Small-Scale Thermal Treatment Test PFAS Analytical Data
- Updated Engineering Report
- Updated Facility Manual
- Updated Air State Facility Permit Application Narrative
- Petition for Case-Specific Beneficial Use Determination

For ease of reference, the following responses correspond directly to the enumerated email comments provided by NYSDEC.

### **Response to Comments**

1. The reception pit scalping screens will be sized with 8-inch square openings to remove oversized debris that may be in an incoming load. Since the biosolids feedstock is being obtained from a single contracted supplier directly from wastewater treatment plants, the presence of unauthorized oversized debris is expected to be minimal. The contract with the biosolids supplier holds them responsible for any debris encountered in received loads. If oversized debris is captured on the scalping screens, the first method of removal is manually by personnel with an extension hook. This method of removal is suitable for light debris (e.g., plastics). If large and potentially heavy oversized debris is encountered, a piece of equipment (e.g., excavator or similar) will remove the

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debris. All removed debris will be washed clean of biosolids using the truck wash and placed in a roll-off container for offsite disposal.

- Each biosolids receiving pit has dimensions of 16 feet wide by 52 feet long by 17 feet deep. The width of each pit tapers to a narrower dimension of 8 feet at the base where the conveying augers are located. Each receiving pit provides 427.6 cubic yards of material storage capacity for a total storage capacity of 855.2 cubic yards of received biosolids. This storage capacity is associated with the first process line, and the second and third process lines will each have a biosolids storage silo with a capacity of at least 850 cubic yards. Biosolids reception rates and storage requirements are summarized in the following table:

Received Tons Per Day	Received CY Per Day	Storage Required (CY)	Storage Provided (CY)
720	850	2,550	2,555

Note: Biosolids unit weight assumed at 0.85 tons per CY (63 pounds per cubic foot)

- Each Carbon Fertilizer™ storage silo has a diameter of 24 feet and a height of 44 feet that provides a total storage capacity of approximately 1,230 cubic yards (~615 cubic yards per silo). Each process line has a target production rate of 1 ton of manufactured Carbon Fertilizer™ per hour (i.e., 2.4 cubic yards per hour). Therefore, the silos provide approximately 7 days of storage capacity at full buildout of three process lines. This assumes a Carbon Fertilizer™ density of 0.41 tons per cubic yard.
- The Engineering Report has been updated with equipment types, sizes, and specifications. The Facility Manual has been updated with startup and scheduled/unscheduled shutdown procedures including the actions to be taken in response to significant interruptions to the Facility's normal operations. Key operating parameters are identified in both the Engineering Report and Facility Manual including the normal operating ranges. The following parameters will govern the operation of the carbon manufacturing equipment:
  - Moisture Content of feedstock exiting process input feed pit into the dryer: 23% target
  - Moisture Content of dried feedstock entering the rotary calciner: 5%
  - Dryer Inlet Temperature: 1,100°F
  - Dryer Exhaust Temperature: 240°F
  - Pressure Drop Across Dry Cyclone: 6 in. WC
  - Shell Temperature of Rotary Calciner: 1,200 to 1,300°F
  - Oxygen Content in Rotary Calciner: <3% O<sub>2</sub> by volume
  - Temperature of Thermal Oxidizer: 1,600 to 1,800°F
  - Moisture content of the manufactured Carbon Fertilizer™™: 10%
- SBS has executed an initial 10-year supply contract with Casella Organics to supply all biosolids to the Facility on an exclusive basis. Casella Organics manages over 450,000 tons per year of biosolids regionally. Contracting directly with Casella Organics is preferred over securing multiple contracts with publicly owned treatment plants prior to being operational. The supply contract requires Casella Organics to provide the Facility with required analytical data prior to be allowed to deliver to the Facility. The Facility operating scenarios are designed around the average

characteristics of the biosolids that Casella Organics intends to supply the Facility. In this respect, received biosolids are anticipated to be 75% aerobically digested and 25% anaerobically digested. The average received solids content is anticipated to be 23%, and the Facility has the ability to reject material that is too wet (i.e., less than 19% solids) or too dry (i.e., more than 32% solids). The supply contract also dictates all required reporting to the EPA and NYSDEC is properly documented and followed for each biosolids source, including the onboarding process for new sources. A redacted copy of the executed supply contract is included in the enclosed Petition for a Case-Specific Beneficial Use Determination.

6. Biosolids moisture content primarily affects the drying process, which is the initial step in the Carbon Fertilizer™ manufacturing process. The biosolids dryer reduces the moisture content to 5% prior to thermal treatment in the calciner. This drying process responds to biosolids moisture fluctuations the same way any biosolids dryer does. Procedurally, incoming loads are inspected visually, and historical composition data are reviewed for the load's source. The scale operator may test the moisture content in several areas of the truck bed to determine an average. Based on the moisture content of the load (as determined by source data or onsite testing), the scale operator directs the truck to one of the two receiving pits. This initial screening step aids in moisture control of the feedstock by controlling which receiving pit is used. Following reception, biosolids enter the process input feed pit where wet biosolids are blended with wood feedstock and recirculated dried feedstock from the dryer. The feed proportions in the mixer (i.e., wet biosolids, wood, and dried recirculation) can be adjusted to maintain a consistent moisture content into the dryer. The mixing adjustments are performed by the Facility operator using the PLC and temperature and moisture data from the dryer. Similarly, if the feed mix becomes too dry, the operator will apply moisture with a target of maintaining a consistent 5% moisture content out of the dryer and into the calciner.
7. The site development is subject to requirements under the State Pollutant Discharge Elimination System (SPDES) General Permit for Stormwater Discharges from Construction Activities. A Stormwater Pollution Prevention Plan (SWPPP) has been prepared and submitted to the Town of Moreau for their review. The project will submit a Notice of Intent to NYSDEC Division of Water to obtain permit coverage prior to construction.

The Facility is also subject to requirements of the Multi-Sector General Permit (MSGP) for Stormwater Discharges from Industrial Activities. As currently designed, all industrial activities will be performed under cover and without exposure to stormwater. Therefore, the Facility will submit a No Exposure Certification form to the NYSDEC Division of Water MSGP Coordinator. The No Exposure Certification form must be submitted every five years. If any operational changes occur that expose industrial activity to stormwater, the Facility must obtain MSGP coverage.

The Facility has been in contact with the City of Glens Falls POTW for new connection requirements and to ensure compliance with their industrial pre-treatment program. By letter dated February 18, 2022, Glens Falls has indicated that the treatment plant has adequate capacity to receive the wastewater flow from the Facility and that pretreatment is not necessary. A copy of the Glens Falls letter is enclosed.

8. The biosolids supply contract with Casella Organics includes a provision for managing manufactured Carbon Fertilizer™ that is not otherwise marketed. Casella Organics has access to multiple compost facilities in the region and has agreed to receive the Carbon Fertilizer™ at no cost for incorporation into the composting operations. The Facility will be responsible for transporting the Carbon Fertilizer™ to the regional compost site selected by Casella Organics. A

redacted copy of the executed supply contract is included in the enclosed Petition for a Case-Specific Beneficial Use Determination.

9. The Facility will achieve pathogen and vector attraction reduction through Class A – Alternative 1 (6 NYCRR 361-3.7(a)(1)(i)(b)) by heat drying the feedstock of biosolids and wood waste at a temperature above 80°C to achieve a moisture content less than 10 percent. Product testing must verify that either the density of fecal coliform is less than 1,000 most probable number per gram total solids (dry weight basis) or the density of salmonella bacteria is less than 3 most probable number per 4 grams of total solids (dry weight basis).
10. Sourced biosolids will have been treated and tested by the source prior to receipt at the Facility in accordance with 6 NYCRR 361-3.6. Based on the regional POTWs, sourced biosolids are anticipated approximately 25% anaerobically digested and 75% aerobically digested and otherwise destined for landfill disposal or incineration. Biosolids destined for landfill disposal in New York must meet criteria contained in 6 NYCRR 363-7.1(j); therefore, the composition of received biosolids will be relatively consistent. The anticipated solids content is an average of 23% with a range of 19 to 32%. For each source of biosolids, the Facility will maintain the following information:
  - Name of biosolids generator and quantity received at the Facility.
  - Description of generator's biosolids treatment method (e.g., aerobic digestion).
  - Description of the biosolids quality including information required by 6 NYCRR 361-3.6 and analytical results of the biosolids for the analytes contained in Table 1 of 6 NYCRR 361-3.9.

Outbound material is required to be tested based on the production volume, which is expected to be quarterly for a single production line. As production capacity increases, testing will become more frequent. Furthermore, the Carbon Fertilizer<sup>TM</sup> will be tested at an increased frequency upon startup to establish the guaranteed analysis for registration as a commercial fertilizer. Additional information on product testing is included in the enclosed Petition for a Case-Specific Beneficial Use Determination.

11. The Waste Control Plan has been updated to indicate only unadulterated wood is authorized and that unauthorized wood waste includes wood products that are painted, chemically treated (e.g., pressure-treated wood or railroad ties), or manufactured with chemicals such as glues or adhesives (e.g., plywood or particle board).
12. Unit price sources have been added to the Closure Cost Estimate included in the Facility Manual.
13. PFAS compounds that may be in the source biosolids will pass through the dryer and will be separated from the solids in the pyrolysis process and are not expected to be present in the final manufactured Carbon Fertilizer<sup>TM</sup>. The current understanding of the fate of PFAS compounds during thermal treatment is described in the enclosed proceedings from the 2021 WEF Residuals and Biosolids Conference, which confirmed the removal of between 98.9% and 100% of all PFAS compounds analyzed from the solid phase (i.e., biosolids to biochar) when thermally treated through pyrolysis at 500°C to 700°C. The study analyzed concentrations of 28 PFAS compounds in the source biosolids and in the resulting biochar, oils, and syngas following pyrolysis. 31 PFAS compounds were analyzed in the syngas based on the ability of the analytical method for this media. The results indicated that remaining PFAS compounds after pyrolysis were detected primarily in

the syngas. The study supports the conclusion that PFAS compounds are first desorbed from the solids phase (i.e., the biosolids) and then transformed and/or destroyed when in the gas or oil phase, with greater desorption and transformation/destruction occurring at higher pyrolysis temperature.

The findings of the WEF conference proceedings are supported by independent testing performed by SBS during design of the Facility. SBS performed a small-scale thermal treatment test using biosolids from the North Shore Water Reclamation District's Zion Wastewater Treatment Plant located on the north shore of Chicago. The dried biosolids were tested for 21 PFAS compounds prior to thermally treating in a pyrolysis kiln at approximately 450°C for 20 minutes and then testing the resulting biochar. The raw dried biosolids had detections of 15 PFAS compounds, while the small-scale thermal treatment test resulted in the removal of all PFAS compounds to below quantification limits except for PFOS, which was reduced by 72%. A copy of the analytical data for the raw dried biosolids and the produced biochar is enclosed.

The Facility design intends to operate the pyrolysis kiln to achieve a material temperature of 900°F to 1,150°F (482°C to 621°C), which is higher than SBS's small-scale test and within the range evaluated in the WEF conference proceedings. The higher temperature is expected to result in greater removal of PFAS compounds from the solid phase. As indicated in the WEF conference proceedings, desorbed PFAS compounds are expected to be present in the syngas; however, the SBS Facility will thermally oxidize the syngas for heat recovery at a temperature of 1,600°F to 1,800°F (871°C to 982°C), which is expected to result in additional destruction of PFAS compounds. The Facility will perform stack testing upon startup to quantify actual emissions, including PFAS compounds. Currently, there are no promulgated PFAS air emissions limits; however, the Facility acknowledges the emerging science and has included space in the Facility floor plan to install carbon treatment if additional polishing is needed for the process emissions prior to exhaust.

14. The requested marketing and distribution plan and written letters of intent are included in the enclosed Petition for a Case-Specific Beneficial Use Determination.
15. Storage capacities for inbound and outbound materials are described in Responses 2 and 3.
16. A Petition for a Case-Specific Beneficial Use Determination is enclosed and is also being submitted to Kathleen Prather, P.E., of the Bureau of Solid Waste Management at NYSDEC's Central Office.
17. Casella provides turnkey solid waste services to municipalities, commercial operations, industrial facilities and directly to homeowners. As such, Casella manages wood products on a regular basis and will work with the Facility to supply wood waste. A copy of Casella's letter of intent is included in the enclosed Petition for a Case-Specific Beneficial Use Determination.
18. A description of the product bagging area and storage silos has been added to the Engineering Report. The product bagging area is located outdoors and under roof cover between the process area and Carbon Fertilizer™ silos. The bagging area is for filling super sacks only with a capacity of 1 to 2 CY. The bagging line intercepts Carbon Fertilizer™ that is being conveyed from the process area to the Carbon Fertilizer™ storage silos. The Carbon Fertilizer™ will be hydrated to 10% moisture after the jacketed cooling conveyor and prior to storage to eliminate dust throughout. In addition, a dust chute will be used at the end of the bulk loading conveyor for dust control when loading trucks. To mitigate combustion risks from combustible dusts, the process and conveyance equipment include dust ports for dust removal as well as nitrogen purging to eliminate a combustible atmosphere. Recovered dust is fed into the dryer exhaust prior to the dry cyclone for reclamation into the Carbon Fertilizer™™ manufacturing process. The entire process area will be

outfitted with sprinkler systems as a secondary form of fire control in accordance with fire protection requirements.

19. A description of the dust control provisions has been added to the Engineering Report. Dust associated with Carbon Fertilizer™ storage and loading is contained in stages. Dried biosolids are sifted before entering the calciner to remove oversized particles. These oversized particles are reduced to fines through the use of a hammermill and returned to the dry material bin. The pyrolysis process further shrinks particles, but also constantly agglomerates the particles to form the granular Carbon Fertilizer™ particles. The agglomeration step helps to avoid dust in the final product. The Carbon Fertilizer™ is cooled prior to adding moisture to re-hydrate the Carbon Fertilizer™ to 10% moisture content prior to bagging and storage to eliminate dust. Dust control associated with the bagging and storage areas are further described in the prior Response 18.
20. A product information sheet is included in the enclosed Petition for a Case-Specific Beneficial Use Determination.
21. As indicated in the NYSDEC document “Biosolids Management in New York State” (March 2018), about 68% of generated biosolids is landfilled and approximately 11% is landfilled out of state. By creating a new in-state management option, emission associated with long-haul disposal options may be avoided depending on the source and current disposal location. Avoided CO<sub>2e</sub> emissions associated with disposal transportation is just one aspect of the project where greenhouse gas emissions can be reduced. The major category of GHG emission reductions will be associated with reduced methane generation associated with landfill disposal. A quantitative assessment of GHG emissions has been added to the enclosed updated Air State Facility Permit Application Narrative to demonstrate consistency with the Climate Leadership and Community Protection Act (CLCPA). The Facility will monetize GHG emission reductions through the carbon credit market. A lifecycle analysis is underway to develop the preliminary carbon intensity (CI) score that is required to generate carbon credits. A comprehensive lifecycle analysis will be prepared with actual operational data following Facility startup.
22. Each process line will produce syngas at a rate of 4,056 to 4,141 lb/hr and a temperature of 630°F to 651°F. The range is based on the evaluated operating scenarios of feedstock composition. The maximum pressure within the calciner will be up to 1 in. WC, and the syngas will be produced at atmospheric pressure.
23. At completion of all three phases, the Facility natural gas demand will be approximately 15 MMBTU/hr and the electrical demand will be approximately 1,500 kW/hr.
24. Final engineering drawings and stamped P&ID will be provided prior to construction and are anticipated to be completed in approximately 15 weeks.
25. NYSDEC Division of Air requested that AERSCREEN dispersion model be revised using the lower exhaust temperature of 76.9°C and that a CLCPA consistency assessment be provided. The enclosed Air State Facility Permit Application Narrative includes revised model output using a lower exhaust temperature and a detailed CLCPA consistency assessment.
26. NYSDEC indicated that the applications would remain incomplete pending the SEQR determination by the Town Planning Board. The Town Planning Board issued a Negative Declaration on March 7, 2022 which was submitted to NYSDEC on March 14, 2022. A copy of Parts 1, 2, and 3 of the Full EAF is included in the enclosed updated Engineering Report.

We trust that this letter and enclosed documentation satisfies NYSDEC's review comments and provides a complete application. Please contact me should you have any questions or comments.

Very truly yours,  
STERLING ENVIRONMENTAL ENGINEERING, P.C.



Andrew M. Millspaugh, P.E.  
Vice President

[Andrew.Millspaugh@sterlingenvironmental.com](mailto:Andrew.Millspaugh@sterlingenvironmental.com)

Email/FedEx  
Enclosures

cc: Raymond Apy, Saratoga Biochar Solutions, LLC. (email)  
Bryce Meeker, Saratoga Biochar Solutions, LLC. (email)  
Kevin Wood, P.E., NYSDEC (email)  
Katelyn White, NYSDEC (email)  
Mike Sundberg, P.E., NYSDEC (email)  
Kathleen Prather, P.E., NYSDEC (email)

**NYSDEC TECHNICAL COMMENTS – JANUARY 20, 2022**



## Andrew Millspaugh

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**From:** Magee, Beth A (DEC) <beth.magee@dec.ny.gov>  
**Sent:** Thursday, January 20, 2022 1:44 PM  
**To:** Raymond Apy; Andrew Millspaugh  
**Cc:** Wood, Kevin (DEC); White, Katelyn M (DEC); Sundberg, Mike (DEC)  
**Subject:** DEC Application # 5-4144-00187/00001: Saratoga Biochar Solutions, LLC: Moreau (T)

Good afternoon.

Staff with our Division of Materials Management have reviewed the referenced Solid Waste Management permit application and provide the following comments. Please update the application documents to address the following:

1. How will the scalper overs be removed, stored and disposed?
2. What are the dimensions of the sludge receiving pits?
3. What are the size(s) of the vertical carbon silos?
4. Please include the following: equipment sizes and specifications, system descriptions and standard operating procedures, including startup and scheduled and unscheduled shutdown procedures. Identify the key operating parameters that will be monitored in the control room and what the normal operating ranges will be. Describe the actions to be taken in response to significant interruptions to the facility's normal operations.
5. Identify the specific biosolids source(s) and provide letters of interest and the required analytical data from those sources.
6. How will varying biosolids moisture contents affect the operation? Specifically, what operating parameters will be monitored and adjusted to account for this?
7. Please follow-up with the Division of Water on any required stormwater / MSGP permitting that may be necessary, and follow-up with the City of Glens Falls POTW to ensure compliance with their industrial pre-treatment program.
8. Provide written communication with disposal facilities agreeing to provide contingency disposal of biochar not meeting standards and excess biosolids which may need to be removed during unexpected downtime.
9. Indicate which methods will be used to demonstrate the pathogen and vector attraction reduction criteria will be met, and the monitoring and testing that will occur to demonstrate compliance.
10. Provide specifics on inbound and outbound material testing - who will perform it, what parameters will be included, what frequency, how will it be recorded and tracked to shipments, etc.?
11. List the wood waste types prohibited from acceptance at the facility in your waste control plan.
12. Provide the sources of your unit costs for your closure cost estimates.
13. There's a potential for PFAS compounds to be present in the inbound biosolids. Please explain what the fate of those compounds will be through the process and whether they'll remain in the product.
14. Provide a marketing and distribution plan for the biochar fertilizer identifying: 1) specific end users by written letters of intent, 2) categories of users and approximate quantity of product each user is expected to take (i.e. landscapers, farmers, etc.), 3) the frequency and method(s) of distribution, and 4) provisions in place for periods when marketing is limited (i.e. winter)?
15. The storage capacities for inbound and outbound materials at the facility should be provided.
16. Please submit a BUD petition for the biochar end use(s).
17. Provide letters of interest from potential wood sources.
18. Sheet No. A101 depicts a product bagging area and two fertilizer silos which are not discussed in the engineering report. Please include descriptions of these operations. The silo storage of dried biosolids has led to fires at other facilities. If silos are to be used, the controls that will be used to minimize fire risk and actions that will be taken if fires occur must be described.
19. The dust control provisions should include a discussion of dust from the storage and loading of the biochar product.
20. Provide a product information sheet for the fertilizer which includes recommended use, application rates, etc.

21. Page 19 of the engineering report states: "In summary, the carbon fertilizer manufacturing process potentially achieves a negative carbon footprint based on 1) replacing chemical fertilizers, 2) decreasing biosolids hauling,..." Please explain further item 2, how hauling to the Biochar facility is different from hauling the biosolids to other facilities.
22. Part 362-1.4(a)(1)(ii) requires a summary of the pressure, temperature, and pounds per hour of all steam to be generated and used at the facility be described. It is understood that the facility won't generate steam, but it will generate syngas. Please include a summary of the pressure, temperature, and pounds per hour of all syngas to be generated and used at the facility.
23. Please provide estimates of how much natural gas and electricity will be consumed from the operation.
24. Provide final engineering drawings and P&IDs stamped by a New York State licensed professional engineer.

Please be reminded that the DEC Division of Air also provided technical comments on this permit application via email on 12/1/21 and that the application is currently incomplete pending the SEQR determination by the Town Planning Board.

Please feel free to contact me with any questions.

Thank you,

**Beth A. Magee**

Deputy Regional Permit Administrator, Division of Environmental Permits

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**CITY OF GLENS FALLS WASTEWATER ACCEPTANCE LETTER – FEBRUARY 18, 2022**

Raymond Apy  
Chief Executive Officer  
Northeastern Biochar Solutions

Feb. 18, 2022

Mr. Apy

Per our discussion on December 14, 2021, the City of Glens Falls Wastewater Treatment Plant can receive the profile and volume of wastewater as stated in said meeting.

At this time your facility would not be considered a categorical industrial user but as with all industrial customers that send wastewater to the City of Glens Falls Wastewater Treatment Plant, you will be required to meet the Glens Falls City Code 177 Article VII, Discharge Requirements. Pretreatment will not be necessary unless the profile of your wastewater does not meet the Glens Falls Local Limits or causes pass through or interference with the wastewater treatment plant process.

I would like to reiterate that based on the data we have; the Town of Moreau is presently discharging around 75,000 gpd to the City of Glens Falls WWTP and the Town of Moreau's purchased capacity is 190,000 gpd. However, I do not know how that capacity is allocated among Moreau's 5 sewer district extensions. That is a question that you would have to ask the folks in Moreau as it is the responsibility of the Town of Moreau to appoint capacity in each of their sewer districts.

If you have any questions or need clarification, please contact me.

Thank you,



Christopher S. Miller  
Chief Operator  
City of Glens Falls Wastewater Treatment Plant  
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**WEF RESIDUALS AND BIOSOLIDS CONFERENCE 2021, "REMOVAL AND  
TRANSFORMATION OF PFAS FROM BIOSOLIDS IN A HIGH TEMPERATURE  
PYROLYSIS SYSTEM – A BENCH SCALE EVALUATION"**

## **Removal and Transformation of PFAS from Biosolids in a High Temperature Pyrolysis System - A Bench Scale Evaluation**

Todd O. Williams, PE, BCEE, Jacobs Engineering

Scott Grieco, PhD, PE, Jacobs Engineering

Bahman Bani, PhD, PE, Jacobs Engineering

Andrew Friedenthal, CharTech Solutions

Andrew White, CharTech Solutions

### **ABSTRACT**

Jacobs and CharTech Solutions (CharTech) recently partnered to investigate the application of CharTech's High Temperature Pyrolysis Technology for biosolids management, and its efficacy in eliminating PFAS from the solid fraction. In addition, the transformation or elimination of PFAS compounds by measuring concentrations in the resultant bio-oil and pyrogas produced from the pyrolysis process were evaluated. This is one of the first analyses done using dried biosolids which captured PFAS data from the all output matrices including the resultant char, bio-oil and pyrogas fractions resulting from the pyrolysis of biosolids. Bench scale testing was performed in a continuously fed pyrolysis unit to compare the PFAS removal performance at 500°C and 700°C pyrolysis temperatures.

Dried biosolids tested in the bench scale test were derived from un-stabilized waste activated sludge produced from two Water Resource Recovery Facilities (WRRFs) operated by Jacobs. The solids were previously dewatered with belt filter presses to approximately 20 percent solids and subsequently dried in a batch thermal dryer fired with natural gas to evaporate water, resulting in a biosolids product that was approximately 95 percent solids. The dried biosolids material previously met Class A Exceptional Quality biosolids product status by achieving all pathogen and vector-attraction reduction requirements, as well as meeting the concentration limits of heavy metals according to the U.S. Environmental Protection Agency's (EPA) 40 Code of Federal Regulations (CFR) Part 503 Rule.

To better understand the PFAS fate through the pyrolysis process, mass balance analysis on biochar, bio-oil and pyrogas streams were conducted and removals of PFAS were estimated. The result of mass balance analysis indicated a total measured PFAS mass removal of 84.4% and 95.6% for 500°C and 700°C, respectively for all the PFAS tested in this study.

This paper describes in detail the testing apparatus and procedures used and provide a full description of the results measured. The information will be useful for engineers, planners, scientists, utilities, regulators and others interested in the evaluation of pyrolysis as a potential biosolids management alternative to minimize PFAS in biosolids.

### **KEYWORDS**

Per- and Poly-Fluoroalkyl Substances (PFAS), biosolids, pyrolysis, carbonization

### **INTRODUCTION**

Per- and Poly-Fluoroalkyl Substances (PFAS) are a large family of organic compounds, including more than 4,000 synthetic fluorinated organic chemicals used since the 1940s. PFAS have unique surfactant properties that make them repel both water and oil. Because of these properties, they have been used extensively in firefighting foams, surface coatings, and protectant formulations for consumer products, including paper and cardboard packaging products, carpets, leather products and clothing, construction materials, and nonstick coatings (ITRC, 2020). Manufacturers of these items often discharge to Water Resource Recovery Facilities (WRRFs). Landfill leachate discharge and household sewage are also common sources of PFAS in WRRF influent. Conventional WRRFs have proven to be relatively ineffective in removal of PFAS and discharge from WRRF is considered a major source of PFAS in the environment (Ahrens 2011, Chen et al., 2018). There is mounting evidence that continued exposure above specific levels of certain PFAS may lead to adverse health effects (USEPA 2016a, 2016b, ATSDR 2018a).

PFAS concentrations in wastewater and sludge or biosolids are mass loading based. Long chain PFAS compounds discharged into WRRFs partition to the solids and end up in the resulting sludge or biosolids. The presence of PFAS in WRRF biosolids has raised a concern in the recent years for beneficial land application programs as PFAS could mobilize in soil, leach into run-off, infiltrate into groundwater or be taken up by biota (Sepulvado et al. 2011). Within the PFAS family of compounds, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are the two most common compounds and are a focus of Federal and State drinking water and environmental regulations. These compounds were commonly used in the manufacture of aqueous film forming foams (AFFF) for fighting aircraft fuel fires and other industrial and commercial products. In February 2019, the US EPA developed an action plan to limit human exposure to potentially harmful levels of PFAS in the environment. The short-term action plan includes testing for measurable PFAS and PFAS precursors in biosolids. The action plan was updated in February 2020 indicating that EPA is developing a risk assessment to better understand the potential public health and ecological risks associated specifically with PFOA and PFOS in land-applied biosolids.

With mounting concern about the presence of PFAS in biosolids and the lack of specific guidance from the US EPA regarding the risks of these compounds within biosolids, some states have begun their own evaluations on this topic with suggested concentration limits of PFAS in biosolids used for land application. However, state regulatory agencies do not have a consistent approach to managing PFAS in biosolids. These concerns coupled with lack of consistent guidelines from the US EPA and state regulators has caused utilities to consider alternatives to eliminate the presence of PFAS in biosolids to minimize their risk exposure to potential future regulatory standards. As a result, technologies which can effectively destroy PFAS in biosolids based products are being investigated. One such technology is pyrolysis. Pyrolysis is the conversion or cracking of biomass or biosolids at high temperatures in the absence of oxygen. As most organics are thermally unstable, they can be split in a pyrolysis process by a combination of thermal cracking and condensation reactions into gaseous (pyrogas), liquid (bio-oil), and solid (biochar) fractions. With limited research available on the ability of pyrolysis to eliminate PFAS from biosolids and the fate of PFAS in the resulting effluents (solids, liquid, and air), there is a need to provide actual data for engineers and planners to evaluate as to the actual performance of the pyrolysis process with respect to PFAS reduction and fate.

Jacobs and CharTech Solutions (CharTech) partnered to investigate the application of CharTech's High Temperature Pyrolysis Technology for biosolids management, and its efficacy in eliminating PFAS from the solid fraction. In addition, the transformation or elimination of PFAS compounds by measuring concentrations in the resultant bio-oil and pyrogas produced from the pyrolysis process were evaluated. This is one of the first analyses done using dried biosolids which captured PFAS data from the all output matrices including the resultant char, bio-oil and pyrogas fractions resulting from the pyrolysis of biosolids. Bench scale testing was performed in a continuously fed bench scale pyrolysis unit at Western University Institute for Chemicals and Fuels from Alternative Resources (ICFAR) to compare the PFAS removal performance at 500°C and 700°C pyrolysis temperatures. ICFAR, along with third party labs including ORTECH Consulting, Inc. (ORTECH), ALS Environmental (ALS) and E3 Laboratories, Inc. (E3), analyzed the feedstock and biocarbon/bio-oil/gas outputs for PFAS, as well as conduct proximate & ultimate analysis, ash characterization, and calorific value analysis on the biocarbon outputs.

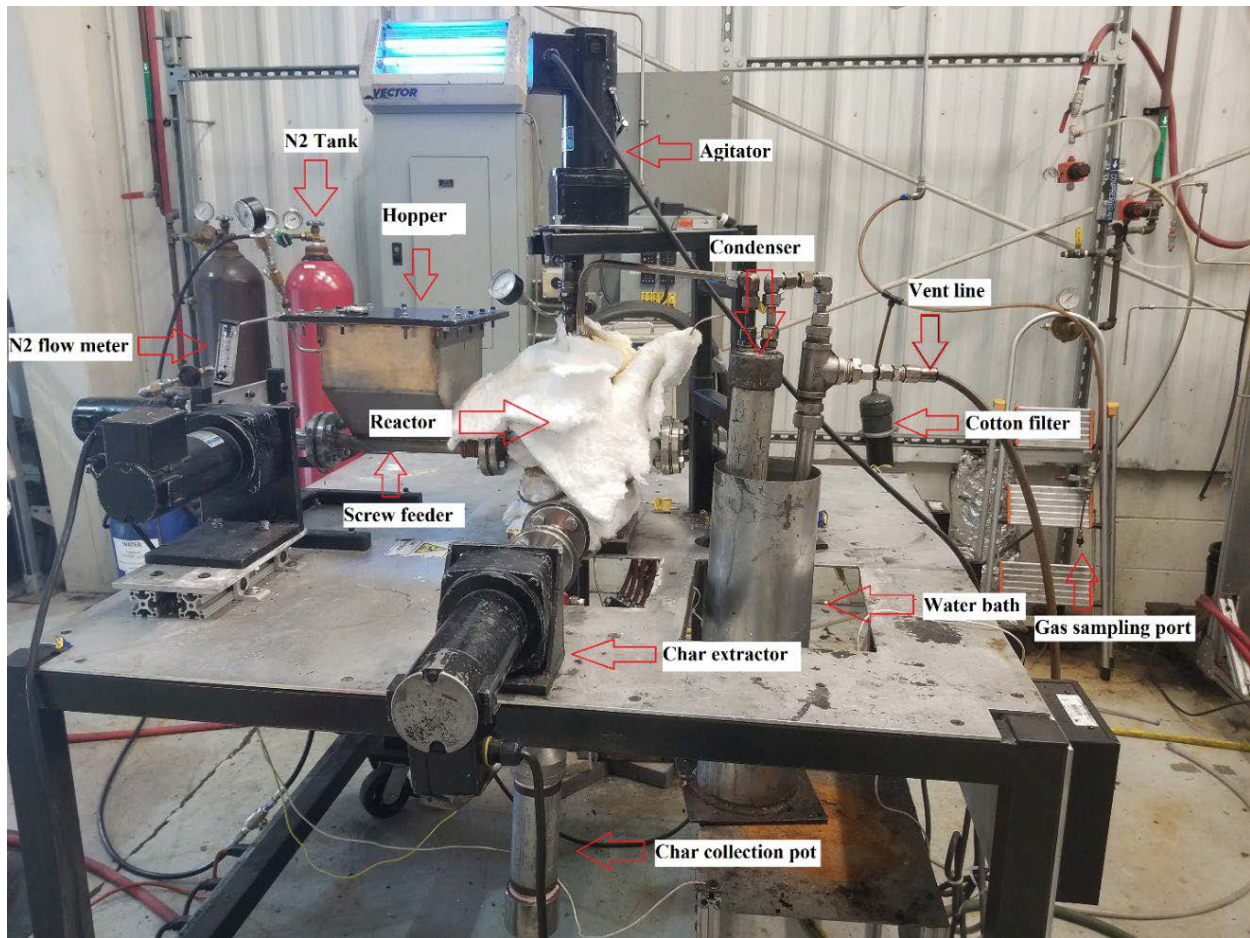
## **METHODOLOGY AND QUALITY CONTROL**

### **Bench Scale Pyrolysis Kiln**

ICFAR identified the bench-scale pyrolysis kiln known as “Baby MFR” as the best system to process a biosolid feedstock at 500°C and 700°C. The Baby Mechanically Fluidized Reactor (MFR) reactor seen in Figure 1 is composed of two main sections: the reactor and condensation system. The reaction section is composed of a medium size mechanically fluidized reactor, cylindrical, 15 cm in diameter and 25.4 cm in height. It has two band heaters controlled by a Watlow's controller. Five hundred (500) grams of feedstock are precisely weighed and then introduced into the hopper. A screw at 25 g/min rate conveys the feedstock from the hopper to the reactor. The feedstock is well mixed inside the reactor at 500°C and 700°C via an agitator. The condenser apparatus is composed of two condensers placed in a water bath. A mixture of ice and water is used for cooling. After a second condenser, the residual gas goes through a filter and to the exhaust line. A screw connected to the bottom of reactor is used to extract the biochar and is collected in a biochar container.



Figure 1- Baby Mechanically Fluidized Reactor



### Gas Sampling

Sampling for PFAS was conducted using the sampling procedures detailed in Modified Method 0010 “Method for Determining HFPO-DA and Other Method 537 PFAS Compound Emissions in Stack Gas”. There currently is no promulgated emission testing and analysis method for PFAS, although the US EPA is in the process of developing these methods. The sampling approach used by ORTECH was based on discussions and feedback from technical contacts, including the US EPA OAQPS (Office of Air Quality Planning and Standards) and ALS, the laboratory which prepared the sampling media and conducted the analysis following sample collection by ORTECH as seen in Figure 2.

The sampling method involved withdrawing a sample of the stack gas ( $\approx 3$  liters per minute) through a sampling line containing a glass wool plug to remove particulate material. The sample was then passed through a water-cooled condenser and a XAD-2 adsorbent tube, as the primary collection device. Condensate was collected in a series of impingers initially containing DI water and the sample was then drawn through a backup XAD-2 adsorbent tube. The sampled gas stream then passed through a silica gel trap to remove any remaining traces of moisture prior to the rotameter, pump and dry gas meter. ORTECH started and stopped each test as instructed by the operator.

Figure 2- Gas Sampling Train Arrangement



Following the conclusion of each run, the tubes were removed from the train, capped and placed in appropriately labeled test tubes which were also capped. The probe and condenser were rinsed in triplicate with a methanol/5% NH<sub>4</sub>OH solution into a sample container. The impinger solution and collected condensate were transferred into a separate sample container. The sample containers were sealed and sent to ALS for PFAS analysis. The analytical laboratory analyzed three sample fractions (probe/condenser rinse, XAD-2 tube and impinger solution) separately for thirty-one measured gas phase PFAS compounds. A blank of each sample fraction was also collected and analyzed to assess background contamination, if any. The amounts collected in each fraction were combined to determine the total collected for the sample. The analytical detection limit was used to determine the total collected and emission data, for those compounds reported as less than the analytical detection limit (<). Of the thirty-one PFAS compounds included in the test program, only seven were detected in quantities greater than the analytical detection limit in at least one of the samples.

#### **Analyses Performed and QA/QC**

ALS Labs conducted the PFAS analysis on the raw biosolids, biochar at 500°C and biochar at 700°C using MOECC E3506 Method. Samples were extracted with alkaline organic solvent. Dilute organic extract with water (10% organic/water) then passed through SPE. Final extract of Perfluorinated compounds were analyzed by Liquid Chromatography with tandem mass spectrometry (LC/MS-MS).

ICFAR conducted the Ultimate Analysis, Proximate Analysis (ASTM D1762-84), and the Calorific Value Determination using a bomb calorimeter (C200, IKA, Germany) with 2 replicates per sample set. The calibration process before measuring was carried out in the sample vessel using pelletized benzoic acid (IKA C 723, IKA, Germany). Benzoic acid (Heat of combustion of 26.454 MJ/Kg) was used as a standard to calibrate the bomb calorimeter.

Elemental analysis of carbon, hydrogen, nitrogen and sulfur was undertaken using the CHNS analyzers model Thermo Flash EA 1112 series. Samples were combusted at 900°C in a stream of helium with a measured amount of oxygen. This produced N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub> which were then separated and quantified by gas chromatography using a 5 mm diameter steel (length of 2 m) packed column, a helium carrier gas with a flow rate of 140 mL/min, and detected with a Propack model thermal conductivity detector (TCD). The oxygen content was calculated by the mass difference. BBOT (1-2 mg) is used as a standard to calibrate the system in CHNS configuration. The calibration was repeated for every new set

of samples. Also, BBOT (1-2 mg) is used as an unknown sample for quality control purposes with each set of samples.

Ash characterization was undertaken by E3 Labs for the analysis of metals using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Mass balance analysis was conducted by measuring the mass, volume and concentration of each product stream (biochar, biooil and pyrolysis gas). Five hundred (500) grams of biomass was precisely weighed, and after each test biooil and biochar were collected and weighed by a balance with 0.1 g accuracy. The accuracy of balance is checked regularly. The yields of biochar, biooil and pyrolysis gas was then calculated as shown below. The gas yield was calculated by the weight difference:

Biooil Yield = (g bio-oil/g biosolid) \* 100

Biochar Yield = (g bio-char/g biosolid) \* 100

Non-condensable gas Yield = 100 – biooil yield – biochar yield

The total mass of PFAS in each of the product streams was calculated by multiplying the PFAS concentrations by the total mass processed (500 grams) and by the applicable yields.

A comprehensive internal quality assurance/quality control (QA/QC) program was completed by the laboratories and ICFAR during testing and analysis.

## **PFAS RESULTS AND DISCUSSION**

A summary of the results is presented in Table 1. As noted in Table 1, the PFAS components that are measurable in any of the phases or samples tested are bolded, while the full suite of samples tested is presented. Also, of note Perfluorononane sulfonic acid (PFNS) was only tested in the pyrogas, and not the solids, while Perfluorobutanoic acid (PFBA) was only tested in the solids and biooil, not the pyrogas. As reported by ALS, PFNS is a newer compound that has not been validated for their soil (solid) matrix method yet and is only available in the water phase. For PFBA, ALS experienced issues with contamination and it was omitted from the air report as the method blanks were contaminated.

It is important to note that there are cases where the concentration appears to increase from the initial biosolids sample to the measured output. In some cases (6:2 FTS, PFDA, PFNA, PFOA and PFPeA), it appears as though the concentration increases from below detection limit in the biosolids to a detectable level in the outputs. This can be attributed to either the overall mass balance, as the three output (biochar, biooil, pyrogas) all derive from the same feedstock. Therefore, if all of the PFAS component remains in one of the forms (for example, biochar) during the process, it will in effect be concentrated. The other reason for an increase in some of the PFAS increase in the pyrogas can be due to precursor degradation and transformation, indicating some compounds may be the result of the partial degradation of, or reaction with, other PFAS components.



Table 1 – PFAS Component Concentrations

Parameter	Biosolids (µg/kg)	Test 1 - 500°C			Test 2 - 700°C		
		Biochar (µg/kg)	PyroGas (µg/kg)	Biooil (µg/kg)	Biochar (µg/kg)	PyroGas (µg/kg)	Biooil (µg/kg)
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>6:2 Fluorotelomer sulfonic acid (6:2 FTS)</b>	<b>BDL</b>	<b>BDL</b>	<b>0.11</b>	<b>BDL</b>	<b>BDL</b>	<b>0.12</b>	<b>BDL</b>
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>10:2 Fluorotelomer sulfonic acid (10:2 FTS)</b>	<b>1.2</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>
Perfluorobutane sulfonic acid (PFBS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>Perfluorohexane sulfonic acid (PFHxS)</b>	<b>BDL</b>	<b>0.45</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>
Perfluorotridecanoic acid (PFTrDA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>Perfluorooctane sulfonic acid (PFOS)</b>	<b>26.6</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>
Perfluoropentane sulfonic acid (PFPeS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamide (EtFOSA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamidoethanol (EtFOSE)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>N-Et PFO sulfonamidoacetic acid (EtFOSAA)</b>	<b>5.3</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>
N-Me PFO sulfonamide (MeFOSA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>N-Me PFO sulfonamidoacetic acid (MeFOSAA)</b>	<b>2.9</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>
N-Me PFO sulfonamidoethanol (MeFOSE)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroheptane sulfonic acid (PFHpS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorooctane sulfonamide (FOSA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorodecane sulfonic acid (PFDS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorobutanoic acid (PFBA)	BDL	BDL	N/A	BDL	BDL	N/A	BDL
<b>Perfluorodecanoic acid (PFDA)</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>BDL</b>	<b>0.042</b>	<b>BDL</b>
Perfluorododecanoic acid (PFDoDA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroheptanoic acid (PFHpA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>Perfluorohexanoic acid (PFHxA)</b>	<b>2.2</b>	<b>0.39</b>	<b>19.49</b>	<b>BDL</b>	<b>BDL</b>	<b>1.44</b>	<b>BDL</b>
<b>Perfluorononanoic acid (PFNA)</b>	<b>BDL</b>	<b>BDL</b>	<b>1.68</b>	<b>BDL</b>	<b>BDL</b>	<b>1.21</b>	<b>BDL</b>
<b>Perfluorooctanoic acid (PFOA)</b>	<b>BDL</b>	<b>0.23</b>	<b>2.45</b>	<b>BDL</b>	<b>BDL</b>	<b>0.61</b>	<b>BDL</b>
<b>Perfluoropentanoic acid (PFPeA)</b>	<b>BDL</b>	<b>BDL</b>	<b>4.94</b>	<b>BDL</b>	<b>BDL</b>	<b>1.04</b>	<b>BDL</b>
Perfluorotetradecanoic acid (PFTeDA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
<b>Perfluoroundecanoic acid (PFUnDA)</b>	<b>1.8</b>	<b>BDL</b>	<b>0.47</b>	<b>BDL</b>	<b>BDL</b>	<b>0.281</b>	<b>BDL</b>
Perfluorononane sulfonic acid (PFNS)	N/A	N/A	BDL	N/A	N/A	BDL	N/A

Note: Components that registered concentrations above detection limits are bolded.

The results as determined by the laboratories for the biosolids feedstock, the biochar/biocarbons and biooils are all presented as concentrations on a mass basis. For the pyrolysis gas (pyrogas), however, the absolute values from three test sources (probe/condenser, XAD2 and impinger solution) are provided in nanogram (ng). Therefore, a conversion was required for PFAS in the pyrogas to measure concentration on a mass basis.

The percentage contribution of the various PFAS components in the biosolids, biochar at 500°C, pyrogas at 500°C and pyrogas at 700°C are presented in Figure 3, Figure 4, Figure 5 and Figure 6, respectively. There are no percentage contributions for biochar at 700°C, or biooil at any temperature, as the components tested were below detection limits.

Figure 3 - PFAS Components by Percentage in Biosolids

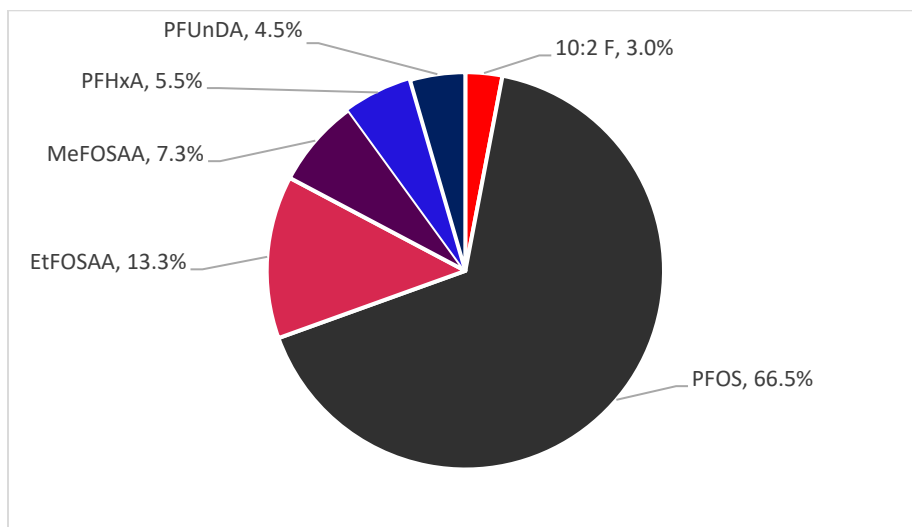


Figure 4 - PFAS Components by Percentage in Biochar at 500°C

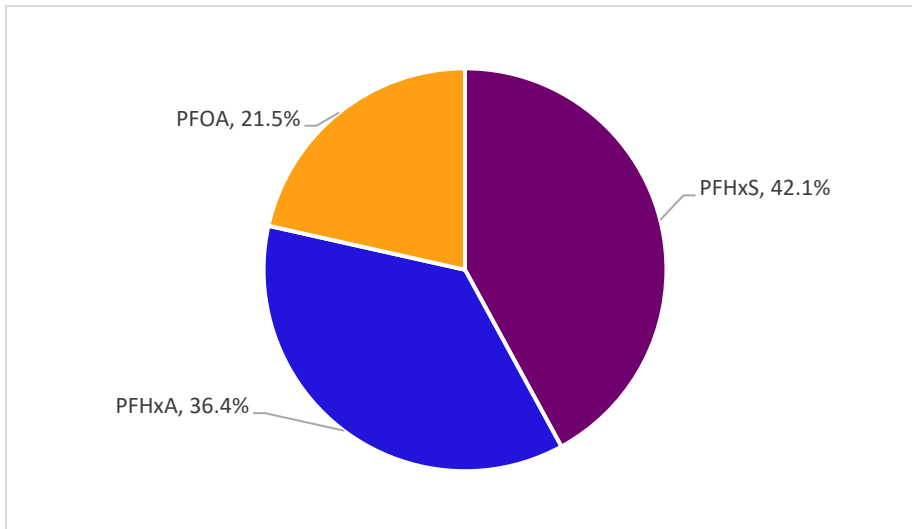


Figure 5 - PFAS Components by Percentage in PyroGas at 500°C

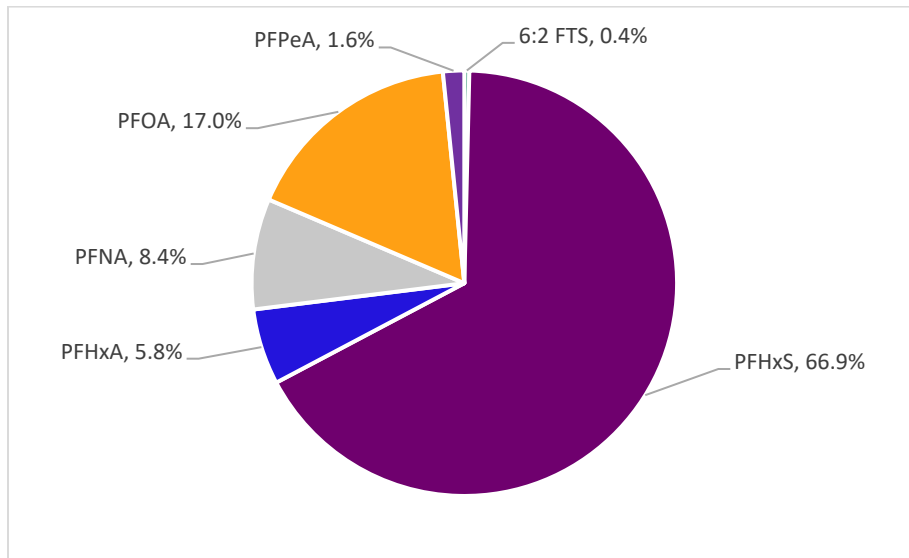
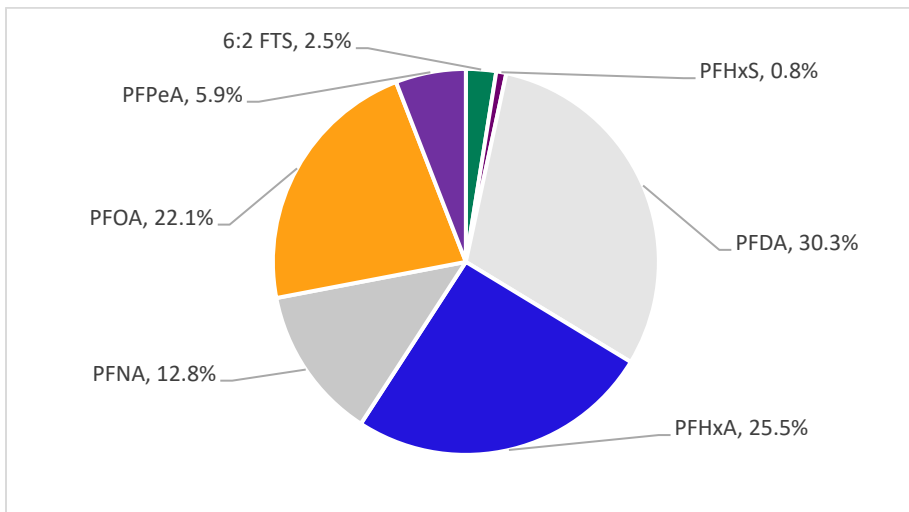


Figure 6 - PFAS Components by Percentage in PyroGas at 700°C



### PFAS Mass Balance Results

With varying operating temperatures, the yields of biochar, biooil and pyrolysis gas will also vary, as seen in Figure 7. For each pyrolysis test, 500g of feedstock was processed. At 500°C, this led to output yields of 40% biochar, 40% biooil and 20% pyrolysis gas (pyrogas). As expected, as the temperature increases, the yield begins to favour the formation of pyrogas, with the yields at 700°C being 30% biochar, 33% biooil and 37% pyrogas. All yields are as reported by ICFAR. At the higher temperature, more of the volatile species in the solid feedstock are volatilized. In addition, at higher temperatures, the longer chain hydrocarbons which are volatilized from the biosolids, but would condense on cooling for the 500°C run, are further cracked into their non-condensable (permanent) structure within the kiln at 700°C. Yields are shown in Table 3. It should be noted that the lab testing is on a “once-through”



basis. On scale-up to a full commercial system, the biooil is recycled back to the kiln for further processing into pyrogas, and therefore at a scope boundary of the system, there are only two product streams, biochar and pyrogas. The recycling of biooil is demonstrated at full-scale at a number of installations operating around the world.

Figure 7 - Biosolids/Biooil/Biocarbon Samples

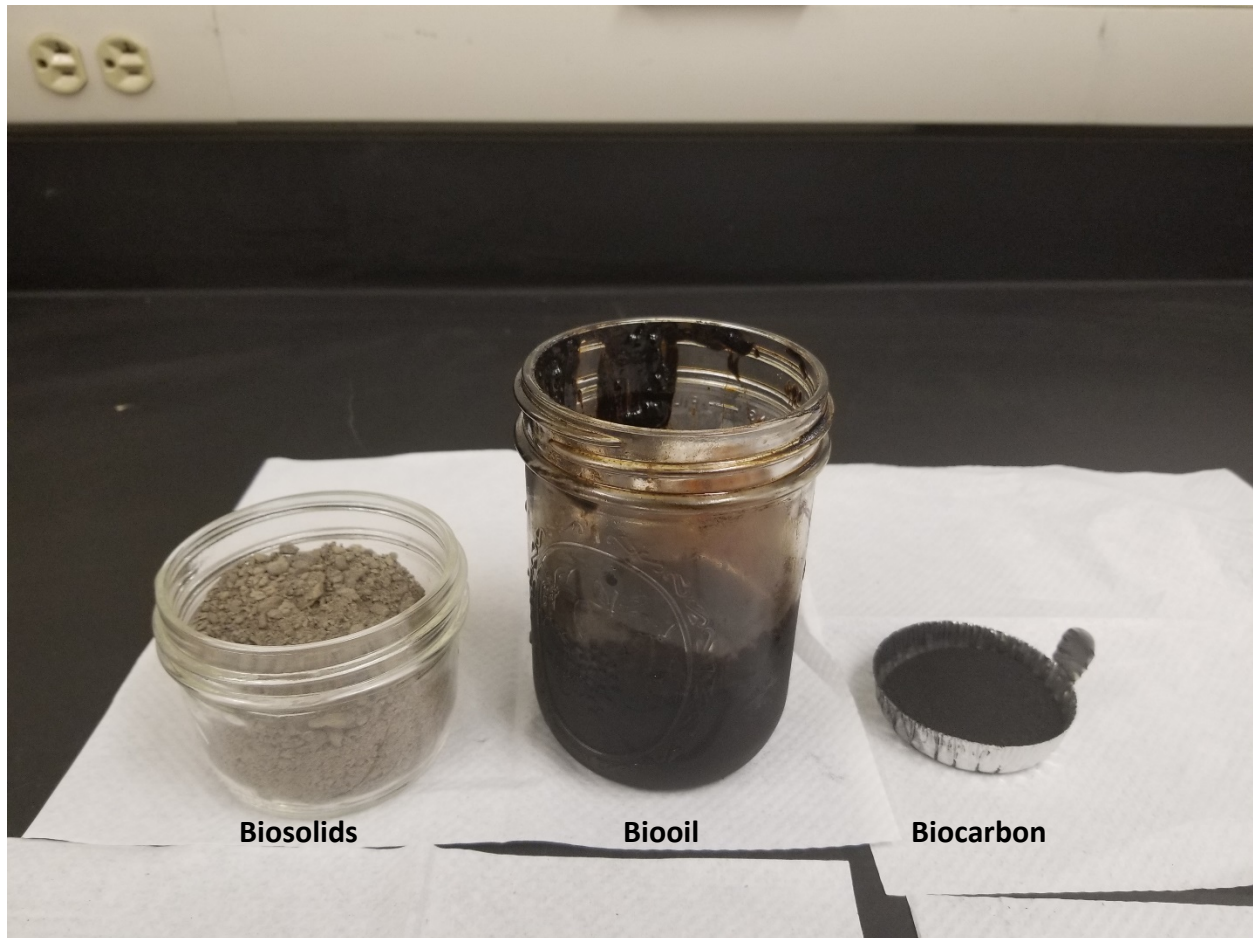


Table 2 - Product Yields from Biosolids Pyrolysis

Sample	Biochar		Biooil		Pyrogas	
	%	grams	%	grams	%	grams
Biochar (500°C)	40	200	40	200	20	100
Biochar (700°C)	30	150	33	165	37	185

One of the principal objectives of this study was to determine the fate of the various PFAS components during the pyrolysis of biosolids. The absolute value (or quantity) of PFAS in the biosolids is determined knowing the total biosolids processed was 500g. Therefore, the concentration values of the various



PFAS components presented in Table 1 for biosolids can be multiplied by 0.5kg to determine the absolute amount in the biosolids feedstock. To determine the PFAS in each of the product streams, the concentrations in Table 1 for each stream is multiplied by 0.5kg (the total mass processed) and by the yields presented in Table 3. The results of this calculation are presented in Table 4. Of note in Table 4, only the constituents which were detectable are presented for clarity. The remainder of the mass balance is determined in the column “destroyed/converted” for both the 500°C run and the 700°C run. In this context, destroyed is an amalgamation of desorption from the solid phase, and further decomposition in the gas phase.

Overall, the mass of all PFAS components remaining in all product streams (biochar, biooil and pyrogas) for the 500°C run is 15.6%, and further reduced to just 4.4% remaining for the 700°C run.

Of the PFAS constituents which are measurable in the biosolids, 10:2 FTS, PFOS, EtFOSAA, MeFOSAA are all desorbed from the solids phase at both test temperatures, and additionally are not present in the pyrogas or biooil, indicating desorption, decomposition or transformation.

PFHxS is below detection limits in the biosolids (Table 1), however it is measured in the biochar at 500°C, indicating that there is no, or only partial, desorption at 500°C. Its presence in the biochar is theorized to be due to a concentrating effect, as the overall solid mass decreases (Table 3), if the PFHxS does not desorb its mass is therefore fixed, increasing its concentration. There is no PFHxS present in the pyrolysis gas at 500°C, further indicating that there is no desorption at 500°C. At 700°C, there is no PFHxS present in any of the streams, therefore desorption and decomposition can be postulated to have occurred.

PFOA is below detection limits in the biosolids but is present in both the biochar (0.046 µg) and pyrogas (0.245 µg) at 500°C, indicating that while some desorption is occurring, it is not possible to quantify due to the concentration occurring in multiple streams. Similar to PFHxS, the presence of PFOA in the biochar at 500°C indicates a concentrating effect as the mass of the total solids decreases relative to the fixed mass of PFOA in the solids or transformation of precursors. However, at this time, the only conclusion is that desorption may begin in the range of 500°C. At 700°C, there is no PFOA remaining in the biochar, indicating that thermal desorption has occurred, while there is a reduction in amount in the pyrogas versus the 500°C run, indicating some thermal decomposition occurs between 500°C and 700°C.

For components 6:2 FTS, PFDA, PFNA, PFOA and PFPeA, a mass balance is not possible as these components are below detection limit in the biosolids. Although these components are below detection limits in the biosolids, they are present in the pyrolysis gas in various amounts. There are two suspected drivers behind the presence of PFAS components in the pyrogas that are below detection limits in the biosolids. First, similar to PFHxS in the biochar, there is a concentrating effect when PFAS components are only present in one of the product streams, as the total mass of the product stream is related to the yield, but the mass of the PFAS component is fixed. Second, there has been research conducted by others showing that certain PFAS components are precursors for other components. Therefore, the presence of certain components in the pyrogas only could also be an indicator of partial degradation at the processing temperature.

For 6:2 FTS, it is present in small quantities in the product pyrogas stream (0.01 µg and 0.02 µg for the 500°C and 700°C runs, respectively), as is PFDA (0.007 µg in the pyrogas at 700°C only). For PFNA, values in the pyrogas increase slightly from 500°C to 700°C. As 6:2 FTS, PFDA and PFNA are all below detection limits in the biosolids, are only present in the pyrogas product stream, and show a slight increase in

amount as the temperature is increased, they are the primary candidates for future work to determine their role as precursors. PFEeA is also only present in the pyrogas and shows a decrease in quantity from 0.494  $\mu\text{g}$  at 500°C to 0.194  $\mu\text{g}$  at 700°C, indicating that as the pyrolysis temperature approaches 700°C, there is thermal decomposition of PFEeA occurring.

PFHxA is present in the biosolids sample at 1.1 $\mu\text{g}$ . At 500°C, only 0.078  $\mu\text{g}$  is present in the biochar, however 1.95  $\mu\text{g}$  are present in the pyrogas, more than is present in the original biosolids feedstock. Therefore, PFHxA is another candidate for further work in the gas phase degradation process. PFUnDA is completely desorbed at both temperatures, and approximately 0.005% remains in the pyrolysis gas at either temperature tested.

Table 3 - Mass Balance of PFAS Constituents

Feedstock/Output	Test 1 - 500°C						Test 2 - 700°C				
	Biosolids	Biochar	PyroGas	Biooil	Destroyed/Converted		Biochar	PyroGas	Biooil	Destroyed/Converted	
<b>Total Mass (g)</b>	500	200	100	200	N/A		150	185	165	NA	
<b>Parameter</b>	(µg)	(µg)	(µg)	(µg)	(µg)	(%)	(µg)	(µg)	(µg)	(µg)	(%)
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	BDL	BDL	0.011	BDL	- <sup>2</sup>	- <sup>2</sup>	BDL	0.022	BDL	- <sup>2</sup>	- <sup>2</sup>
10:2 Fluorotelomer sulfonic acid (10:2 FTS)	0.60	BDL	BDL	BDL	0.60	100%	BDL	BDL	BDL	0.60	100%
Perfluorohexane sulfonic acid (PFHxS)	0.09 <sup>1</sup>	0.09	BDL	BDL	0.00	0%	BDL	BDL	BDL	0.09	100%
Perfluorooctane sulfonic acid (PFOS)	13.3	BDL	BDL	BDL	13.3	100%	BDL	BDL	BDL	13.3	100%
N-Et PFO sulfonamidoacetic acid (EtFOSAA)	2.65	BDL	BDL	BDL	2.65	100%	BDL	BDL	BDL	2.65	100%
N-Me PFO sulfonamidoacetic acid (MeFOSAA)	1.45	BDL	BDL	BDL	1.45	100%	BDL	BDL	BDL	1.45	100%
Perfluorodecanoic acid (PFDA)	BDL	BDL	BDL	BDL	- <sup>2</sup>	- <sup>2</sup>	BDL	0.007	BDL	- <sup>2</sup>	- <sup>2</sup>
Perfluorohexanoic acid (PFHxA)	1.10	0.078	1.95	BDL	-0.93	-84.3%	BDL	0.266	BDL	0.8336	75.8%
Perfluorononanoic acid (PFNA)	BDL	BDL	0.168	BDL	- <sup>2</sup>	- <sup>2</sup>	BDL	0.224	BDL	- <sup>2</sup>	- <sup>2</sup>
Perfluorooctanoic acid (PFOA)	BDL	0.046	0.245	BDL	- <sup>3</sup>	- <sup>3</sup>	BDL	0.113	BDL	- <sup>3</sup>	- <sup>3</sup>
Perfluoropentanoic acid (PFPeA)	BDL	BDL	0.494	BDL	- <sup>2</sup>	- <sup>2</sup>	BDL	0.194	BDL	- <sup>2</sup>	- <sup>2</sup>
Perfluoroundecanoic acid (PFUnDA)	0.90	BDL	0.047	BDL	0.85	94.8%	BDL	0.052	BDL	0.8482	94.24%
<b>Total</b>	<b>20.09</b>	<b>0.21</b>	<b>2.915</b>	<b>0.00</b>	<b>16.96</b>	<b>84.4%</b>	<b>0.00</b>	<b>0.878</b>	<b>0.00</b>	<b>19.21</b>	<b>95.6%</b>

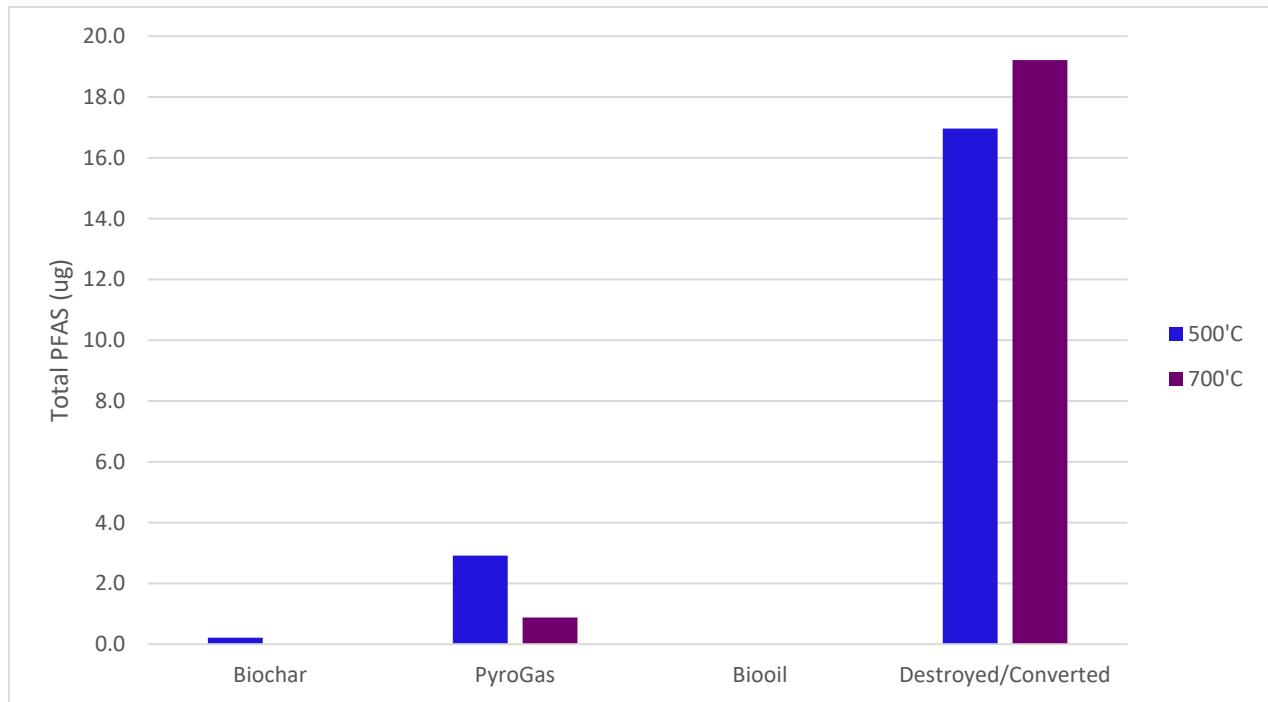
<sup>1</sup>PFHxS was below detection limits in the biosolids feedstock – therefore the absolute value was assumed to be the same as present in biochar at 500°C.

<sup>2</sup>Where the PFAS component is below detection limits and is only present in the pyrogas, it is not possible to estimate the amount destroyed or converted.

<sup>3</sup>PFOA is below detection limits in the biosolids feedstock, but as it presents in both the biochar and pyrogas at 500°C, the same estimates as note (1) are not applicable.

The total distribution of PFAS mass after pyrolysis at both temperature ranges is illustrated further in Figure 8 .

Figure 8 - Total Measured PFAS Mass Balance at 500°C and 700°C



### PFAS Testing Summary

Twenty eight of the most commonly measured PFAS compounds were analyzed in the feed biosolids, biochar, bio-oil and 31 PFAS compounds were analyzed in the pyrogas. Only six PFAS compounds (10:2 Fluorotelomer sulfonic acid, PFOS, N-Et PFO sulfonamidoacetic acid, N-Me PFO sulfonamidoacetic acid, Perfluorohexanoic acid, and Perfluoroundecanoic acid) were measured above the detection limits in the feed biosolids. Three PFAS compounds were detected in the biochar at the 500°C pyrolysis temperature (Perfluorohexane sulfonic acid, Perfluorohexanoic acid, Perfluorooctanoic acid), all at less than 0.5 ppb (dry weight). No PFAS compounds were detected in biochar at the 700°C pyrolysis temperature. PFOS was measured at 26.6 ppb in the feed biosolids but not detected in the biochar, bio-oil or pyrogas at either pyrolysis temperature. Although not detected in the dried biosolids, PFOA was detected at very low concentrations in biochar and pyrogas indicating a lack of complete destruction and/or transformation of precursor compounds during pyrolysis. Higher concentration of Perfluorohexanoic acid (PFHxA) in pyrogas at 500°C compared to 700°C was observed, suggesting greater removal of PFHxA at a higher temperature.

### Additional Biochar Analysis

In addition to PFAS testing, energy density & elemental analysis (Table 4), proximate analysis (Table 5) and biochar and biooil analysis (Table 6) were conducted on the biosolids feedstock, the biochar produced at 500°C and the biochar produced at 700°C. These parameters are important in the design of a full-scale pyrolysis system, as well as in the determination of the best market opportunity for the resultant biochar.

The higher heating value (HHV, presented in table 4) of the biosolids is relatively high at 18.5 MJ/kg (as a reference, typical wood materials range from 16 to 20). As the material is pyrolyzed, the HHV decreases to 11.6 for the 500°C run, and 10.3 for the 700°C. There are two factors that contribute to the decrease in HHV. First is yield and ash concentration (as presented in Table 3 and 4). As the total amount of solid material decreases during pyrolysis, the ash concentrates in the solid biochar. While the total mass of ash doesn't change, its concentration does, increasing from 17.88% in the biosolids, to 61.43% in the biochar at 500°C and 69.66% in the biochar at 700°C. From an energy density perspective, ash is an inert, and therefore drastically increasing its concentration will decrease the energy density. The other contributing factor is the decrease in volatile matter. As the pyrolysis kiln temperature increased, the decrease in volatile matter in the solid fraction is a benefit from an overall pyrolysis system perspective as the volatile matter becomes present as various permanent gas components in the pyrogas stream (Table 3). Therefore, as the temperature increases, the energy balance increasingly favors the pyrogas stream, allowing for sufficient energy being available to allow the system to not only operate exclusively on the pyrogas it generates, but also the opportunity for excess pyrogas being available for other uses. The decrease in volatile matter in the biocarbon stream does result in less energy rich volatile matter in the biocarbon, which in turn decreases the contribution from the volatile matter in the biocarbon towards its energy density.

Table 4 - Energy & Elemental Analysis (Dry Basis)

Parameter	Biosolids	Biochar 500°C	Biochar 700°C
HHV (MJ/kg)	18.5	11.6	10.3
Carbon (%)	39.95	26.69	23.95
Nitrogen (%)	5.87	0.15	0.08
Hydrogen (%)	5.83	1.63	0.56
Sulphur (%)	0.54	0.54	0.86
Oxygen & Ash (%)	47.82	71.00	74.55

Table 5 - Proximate Analysis (As Received)

Parameter	Biosolids	Biochar 500°C	Biochar 700°C
-----------	-----------	------------------	------------------

Water (%)	4.48	0.12	2.12
Volatile Matter (%)	65.01	10.8	1.66
Fixed Carbon (%)	12.62	27.63	26.55
Ash (%)	17.88	61.43	69.66

As with the other biochar parameters, the concentration of the specific ash components (mg of ash per kg of sample) increases as the ash concentrates in the biochar (Table 5). Some ash however does carry through into the condensate (biooil). Of note, both arsenic and selenium are eliminated to below detection limits in the biochar but are present in the biooil. The ash remaining in the biochar will be an important factor in determining the biochar's marketability, as some ash components are viewed as having a positive impact on the biocarbon's marketability due to their beneficial properties as a soil amendment or fertilizer (such as calcium, potassium and phosphorous, which are present but not measured as part of this analysis), whereas other ash components are seen as a negative from a marketability perspective, and therefore it is important to ensure they are below local, regional and federal regulatory or other limits. As an example of one set of regulatory limits, the ash components that could be of concern are compared to the EPA limits for Exceptional Quality Standards for biosolids in Table 6.

Table 6 – Biochar and Biooil Analysis

Parameter	Biosolids (mg/kg)	Test 1 - 500°C		Test 2 - 700°C		EPA Limits <sup>1</sup> (mg/kg)
		Biochar (mg/kg)	Biooil (mg/kg)	Biochar (mg/kg)	Biooil (mg/kg)	
Arsenic	4	BDL	6.18	BDL	7.81	41
Cadmium	2.2	4.0	0.419	3.2	0.079	39
Chromium	51.6	82.1	2.47	69.00	0.36	-
Cobalt	3.62	6.10	BDL	6.96	BDL	-
Copper	493	853	18.8	886	2.5	1,500
Lead	77.1	137	2.78	146	0.47	300
Mercury	0.88	0.19	0.634	BDL	0.330	17
Molybdenum	14.6	24.2	0.558	23.3	0.113	-
Nickel	24.1	40.8	2.16	43.9	0.51	420
Selenium	1	BDL	5.53	BDL	4.13	100
Zinc	872	1,430	37.7	1,510	7.4	2,800

<sup>1</sup>Pollutant limits from US EPA for Exceptional Quality Standards for biosolids

## CONCLUSIONS

At a high-level, the overall purpose of this study was to assess the ability of high temperature pyrolysis to reduce PFAS components present in biosolids. On a mass basis, the measured detectable PFAS in the solid stream (biosolids to biochar) is reduced by 98.9% at a processing temperature of 500°C, and to no detectable concentration at a processing temperature of 700°C. When looking at all product streams (biochar, biooil and pyrogas), PFAS is reduced by 84.4% at 500°C, and 95.6% at 700°C. Therefore, high temperature pyrolysis is an effective process to drastically reduce the presence of PFAS from biosolids, resulting in no detectable concentration in the biocarbon output at 700°C. From the initial results presented in this study, there are various PFAS components which are below detection limits in the biosolids, however are present in the pyrolysis gas (at low concentrations). Therefore, these components have either concentrated in the pyrogas, or are part of a precursor compound/degradation pathway of certain PFAS components.

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**SBS SMALL-SCALE THERMAL TREATMENT TEST PFAS ANALYTICAL DATA**



Sample Description: **Biosolids Grab Sample**

Ultra Compost Inc.

Project Name: **Biochar**

ELLE Sample #: **SW 1051834**

ELLE Group #: **2042698**

Matrix: **Solid Waste**

Submittal Date/Time: **05/08/2019 08:30**

Collection Date/Time: **05/06/2019 10:20**

CAT No.	Analysis Name	CAS Number	Dry Result	Dry Limit of Quantitation*	Dry Method Detection Limit	Dilution Factor
<b>LC/MS/MS Miscellaneous EPA 537 Version 1.1 Modified</b>			ng/g	ng/g	ng/g	
14027	6:2-Fluorotelomersulfonic acid	27619-97-2	< 2.1	2.1	0.64	1
14027	8:2-Fluorotelomersulfonic acid	39108-34-4	< 2.1	2.1	0.64	1
14027	NEtFOSAA	2991-50-6	2.8	2.1	0.53	1
NEtFOSAA is the acronym for N-ethyl perfluorooctanesulfonamidoacetic Acid.						
14027	NMeFOSAA	2355-31-9	5.3	2.1	0.53	1
NMeFOSAA is the acronym for N-methyl perfluorooctanesulfonamidoacetic Acid.						
14027	Perfluorobutanesulfonic acid	375-73-5	< 0.64	0.64	0.21	1
14027	Perfluorobutanoic acid	375-22-4	2.2	2.1	0.64	1
14027	Perfluorodecanesulfonic acid	335-77-3	1.1	1.1	0.32	1
14027	Perfluorodecanoic acid	335-76-2	11	0.64	0.21	1
14027	Perfluorododecanoic acid	307-55-1	6.6	0.64	0.21	1
14027	Perfluoroheptanesulfonic acid	375-92-8	< 0.64	0.64	0.21	1
14027	Perfluoroheptanoic acid	375-85-9	1.4	0.64	0.21	1
14027	Perfluorohexanesulfonic acid	355-46-4	< 0.64	0.64	0.21	1
14027	Perfluorohexanoic acid	307-24-4	16	0.64	0.21	1
14027	Perfluorononanoic acid	375-95-1	1.9	0.64	0.21	1
14027	Perfluorooctanesulfonamide	754-91-6	< 0.64	0.64	0.21	1
14027	Perfluorooctanesulfonic acid	1763-23-1	4.6	0.95	0.32	1
14027	Perfluorooctanoic acid	335-67-1	20	0.64	0.21	1
14027	Perfluoropentanoic acid	2706-90-3	2.2	0.64	0.21	1
14027	Perfluorotetradecanoic acid	376-06-7	2.0	0.64	0.21	1
14027	Perfluorotridecanoic acid	72629-94-8	2.4	0.64	0.21	1
14027	Perfluoroundecanoic acid	2058-94-8	8.8	0.64	0.21	1

The recovery for injection standard 13C2-PFDA is outside of QC acceptance limits as noted on the QC Summary. The recovery for injection standard 13C2-PFDA is also outside of QC acceptance limits in the associated matrix spike and matrix spike duplicate samples, thus indicating a matrix effect.

<b>Wet Chemistry</b>		<b>SM 2540 G-2011</b>	%	%	%	
		<b>%Moisture Calc</b>				
00111	Moisture	n.a.	5.6	0.50	0.50	1
Moisture represents the loss in weight of the sample after oven drying at 103 - 105 degrees Celsius. The moisture result reported is on an as-received basis.						

### Sample Comments

State of New York Certification No. 10670

\*=This limit was used in the evaluation of the final result

Sample Description: **Biochar Grab Sample**

Project Name: **Biochar**

Ultra Compost Inc.  
ELLE Sample #: **SW 1051835**  
ELLE Group #: **2042698**  
Matrix: **Solid Waste**

Submittal Date/Time: 05/08/2019 08:30

Collection Date/Time: 05/06/2019 10:20

CAT No.	Analysis Name	CAS Number	Dry Result	Dry Limit of Quantitation*	Dry Method Detection Limit	Dilution Factor
<b>LC/MS/MS Miscellaneous EPA 537 Version 1.1 Modified</b>			ng/g	ng/g	ng/g	
14027	6:2-Fluorotelomersulfonic acid	27619-97-2	< 2.0	2.0	0.59	1
14027	8:2-Fluorotelomersulfonic acid	39108-34-4	< 2.0	2.0	0.59	1
14027	NETFOSAA	2991-50-6	< 2.0	2.0	0.49	1
NETFOSAA is the acronym for N-ethyl perfluorooctanesulfonamidoacetic Acid.						
14027	NMeFOSAA	2355-31-9	< 2.0	2.0	0.49	1
NMeFOSAA is the acronym for N-methyl perfluorooctanesulfonamidoacetic Acid.						
14027	Perfluorobutanesulfonic acid	375-73-5	< 0.59	0.59	0.20	1
14027	Perfluorobutanoic acid	375-22-4	< 2.0	2.0	0.59	1
14027	Perfluorodecanesulfonic acid	335-77-3	< 0.98	0.98	0.29	1
14027	Perfluorodecanoic acid	335-76-2	< 0.59	0.59	0.20	1
14027	Perfluorododecanoic acid	307-55-1	< 0.59	0.59	0.20	1
14027	Perfluoroheptanesulfonic acid	375-92-8	< 0.59	0.59	0.20	1
14027	Perfluoroheptanoic acid	375-85-9	< 0.59	0.59	0.20	1
14027	Perfluorohexanesulfonic acid	355-46-4	< 0.59	0.59	0.20	1
14027	Perfluorohexanoic acid	307-24-4	< 0.59	0.59	0.20	1
14027	Perfluorononanoic acid	375-95-1	< 0.59	0.59	0.20	1
14027	Perfluorooctanesulfonamide	754-91-6	< 0.59	0.59	0.20	1
14027	Perfluorooctanesulfonic acid	1763-23-1	<b>1.3</b>	0.88	0.29	1
14027	Perfluorooctanoic acid	335-67-1	< 0.59	0.59	0.20	1
14027	Perfluoropentanoic acid	2706-90-3	< 0.59	0.59	0.20	1
14027	Perfluorotetradecanoic acid	376-06-7	< 0.59	0.59	0.20	1
14027	Perfluorotridecanoic acid	72629-94-8	< 0.59	0.59	0.20	1
14027	Perfluoroundecanoic acid	2058-94-8	< 0.59	0.59	0.20	1

**Wet Chemistry**

**SM 2540 G-2011  
%Moisture Calc**

CAT No.	Analysis Name	Method	Trial#	Batch#	Analysis Date and Time	Analyst	Dilution Factor
00111	Moisture	n.a.	2.0		0.50	0.50	1
Moisture represents the loss in weight of the sample after oven drying at 103 - 105 degrees Celsius. The moisture result reported is on an as-received basis.							

**Sample Comments**

State of New York Certification No. 10670

**Laboratory Sample Analysis Record**

CAT No.	Analysis Name	Method	Trial#	Batch#	Analysis Date and Time	Analyst	Dilution Factor
14027	Biosolid NY 21 PFAS	EPA 537 Version 1.1 Modified	1	19129012	05/18/2019 00:43	Jason W Knight	1
14090	PFAS Solid Prep	EPA 537 Version 1.1 Modified	1	19129012	05/09/2019 16:00	Anthony C Polaski	1

\*=This limit was used in the evaluation of the final result