



Elimination of microplastics, PFAS, and PPCPs from biosolids via pyrolysis to produce biochar: Feasibility and techno-economic analysis

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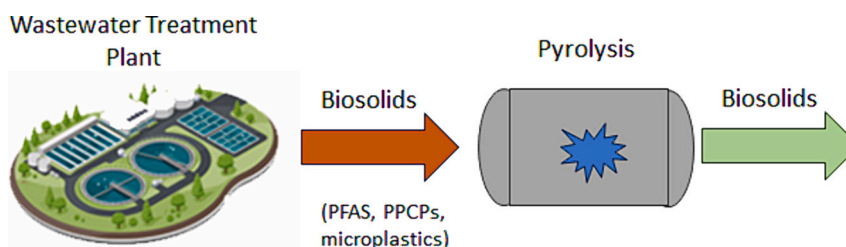
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HIGHLIGHTS

- Pyrolysis eliminates >99 % of PFAS, microplastics and PPCPs from biosolids.
- Biochar from biosolids high in Fe and P
- Pyrolysis can generate revenue for wastewater treatment plant.
- Revenue dependent on scale of unit and market for biochar

GRAPHICAL ABSTRACT



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ABSTRACT

Biosolids from municipal wastewater treatment contain many contaminants of emerging concern, including microplastics (MPs), per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and chemicals from personal care products (PPCPs). Many of these contaminants have very slow biotic or abiotic degradation rates and have been shown to have human and ecological health impacts. Application of biosolids to agriculture, a common disposal method, can result in extended environmental contamination. An approach for eliminating the contaminants is pyrolysis, which can also generate biochar, enhancing carbon sequestration as a side-benefit. We pyrolyzed biosolid samples from an operating facility at various temperatures from 400 to 700 °C with a 2-hour residence time. We then evaluated contaminant removal, which in many cases was 100 %, with only a few residuals. No trace of PFAS was detectable even at 400 °C. Overall mass removal of PPCPs, including PFAS, was over 99.9 %. MP removal via pyrolysis ranged from 91 to 97 %. The biochar contains significant amounts of Fe and P, which make it a useful fertilizer amendment. The techno-economic analysis indicates that pyrolysis may generate significant cost savings, and revenue from the sale of biochar, sufficient to more than cover the investment and operating costs of the dryer and pyrolysis unit.

1. Introduction

Microplastics (MPs), per- and polyfluoroalkyl substances (PFAS),

pharmaceuticals and other chemicals from personal care products (PPCPs), released from a myriad products used in residential, commercial, and industrial activities into wastewater accumulate to a significant

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extent in biosolids (Hall et al., 2021; Martín et al., 2012; Xia et al., 2005; Crossman et al., 2020). The application of biosolids to agriculture, a practice that is used around the world as a useful way to recover and reuse nitrogen (N) and phosphorus (P), can result in the accumulation of the contaminants in agricultural soils (Lu et al., 2012; Clough and Condron, 2010). This then becomes an important pathway for their dispersal via wind erosion, runoff, and even groundwater, leading to widespread contamination (Johnson, 2022; Kolpin et al., 2021; Kinney and Heuvel, 2020). In addition, there is evidence that the organic compounds can be taken up by crop plants (Wu et al., 2015; Ghisi et al., 2019), resulting in an exposure pathway for humans. Given the increasing concern about the implications for human and ecological health of these pollutants, there is a need to develop alternative approaches for dealing with biosolids.

While biotic and abiotic degradation of MPs, PFAS, and PPCPs can occur, many of these chemicals have very long-residence times in the environment, in some cases on the scale of decades or even centuries (Xu et al., 2009; Berhanu et al., 2023; Dickman and Aga, 2022; Othman et al., 2021; Corcoran, 2022). There are major research efforts to accelerate their degradability, but at this stage the reality is that these compounds will continue to accumulate in soils, sediments, organisms, and waterbodies. Their “dilution” using compost or other natural materials, to reduce the concentrations at which they are applied does not solve the problem, since the loading is still the same, even if the mixed material contains a lower concentration.

Pyrolysis of biosolids offers a solution to this problem (Fig. S1). Heating the dried biosolids to high temperatures under anoxic conditions is expected to eliminate all three of these classes of contaminants (Ni et al., 2020; Paz-Ferreiro et al., 2018; Elkhailifa et al., 2022; McNamara et al., 2016). A benefit of employing pyrolysis is that the end product, biochar, is still rich in P and other elements (e.g., Ca, Mg) that are important for plant growth (Adhikari et al., 2019; Marmiroli et al., 2022). Biochar has been shown to have several other benefits for agriculture, including carbon sequestration and increasing soil organic matter, as well as additional nutrient and moisture retention (Spokas et al., 2012). Biochar is closely related to activated carbon, and thus can also be used to remove organic pollutants from water. It could thus be used to decrease the concentrations of PFAS and PPCPs in finished wastewater treatment effluent, and then be pyrolyzed again to eliminate these compounds.

To date, the role of pyrolysis for eliminating MPs, PFAS, and PPCPs from biosolids has not been studied in detail, and the studies have been mostly focused on just one class of contaminants. A study on the use of pyrolysis for mitigation of MPs in biosolids focused on the role of pyrolysis temperature, although the study was limited to 500 °C (Ni et al., 2020). The authors found that MPs were reduced from 551–961 particles/g to 1.4–2.3 particles/g at 500 °C, or a 99.75 % removal on average. Pyrolysis was very effective at removing polyolefins (e.g. polyethylene and polypropylene), and the residues at 500 °C were mostly polyvinyl butyral and polycaprolactone.

For PFAS, a pilot study considered 41 different compounds, of which 21 could be detected (Thoma et al., 2022). The initial concentrations of these PFAS in biosolids ranged from 2 to 85 µg/kg. The temperature within the pyrolysis reactor ranged from 649 °C ± 6 °C at the front end to 586 °C ± 32 °C at the exit, or an average of 617.5 °C, with a residence time of 19.1 min. The authors found no PFAS residues within the resulting biochar. Another study considered 41 PFAS compounds, of which 25 were detected in four different biosolids feedstocks (Sørmø et al., 2023). The total PFAS concentrations ranged from 56 to 441 µg/kg in the biosolids feedstocks, mostly composed of perfluoropentanoic acid (PFPeA), perfluorooctanesulfonic acid (PFOS), and 4:2 fluorotelomer sulfonic acid (4,2 FTS), with perfluorobutanoic acid (PFBA) also found in significant amounts in one feedstock (40 %). The study considered temperatures between 500 °C and 800 °C with a residence time of 20 min for most feedstock. Removal efficiency increased with temperature, from 96.93 % at 500 °C to 98.35 % at 800 °C for the “worst” performing

feedstock. For other biosolids feedstocks, removal was 99.55 % or better even at 500 °C. The most recalcitrant compounds were perfluoroalkyl sulfonic acids (PFASs) and perfluoroalkyl carboxylic acids (PFCAs). PFAS were detected in the flue gas in particle and gaseous fractions at concentrations ranging from < limit of detection (LOD) to 100 ng/m³ with a mean of 50 ± 70 ng/m³. In a third study, pyrolysis was conducted at 500 °C, 650 °C, and 800 °C, with a retention time of 20 min (McNamara et al., 2023a). The authors collected the vapors from the pyrolysis process, which were then condensed to a mixture of water and organic liquid phases, as well as organic vapors. PFAS removal was >99 % in biochar at 500 °C or above, with influent total PFAS ranging from 4 to 16 µg/kg. However, PFBA was detected in the condensed pyrolysis liquid, and it appears that it was produced during the transformation of PFBA precursors, particularly at 500 °C. The mass of *N*-ethyl perfluorooctane sulfonamidoethanol (NetFOSE), and *N*-methyl perfluorooctane sulfonamidoethanol (NMeFOSE) also increased by over two orders of magnitude in the condensed pyrolysis liquid, compared to their mass in the original biosolids. Thus, post-treatment of the effluent gases is likely warranted. Complete destruction of all PFAS in the exhaust gases may require an afterburner operating at 1000 °C or greater (Winchell et al., 2021), but the pyrolysis unit could still be operated at a much lower temperature to eliminate PFAS from the biosolids. There have been several additional studies on the removal of PFAS (Garg et al., 2023; Zhang et al., 2023; Wallace et al., 2023; Kundu et al., 2021), including a very useful perspective on the benefits and limitations by McNamara et al. (2023b).

A recent study considered pyrolysis of biosolids to eliminate PPCPs at 450 °C and 600 °C (Alipour et al., 2022). Although the study considered 27 different compounds, only 8 were found in the biosolids using gas chromatography–mass spectrometry, with a total concentration of 45.31 µg/kg. After pyrolysis at 450 °C, only 0.71 µg/kg remained (>98 % removal), mostly from saccharine, and at 600 °C none of the 8 PPCPs were detectable. The study also demonstrated that polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) were completely removed at 600 °C. Another study found that out of a target of 27 PPCPs commonly found in wastewater, 9 were detected in the biosolids at concentrations ranging from 0.1 to 50 µg/kg (Moško et al., 2021). None of the PPCPs were detected in the biochar after pyrolysis at 400 °C for 2 h. The study also demonstrated high removal of PCBs, generally as a function of pyrolysis temperature, although no PCBs were detected at 400 °C, but were detected at decreasing concentrations at 500–800 °C, eventually reaching 99.9 % removal efficiency. Similarly, PAHs were increasingly removed at higher temperatures.

Although there have been techno-economic analyses of the use of pyrolysis for production of biofuels (e.g., methanol, biooil) and biochar, the focus has been on the use of agricultural waste, woody materials, and other forestry residues (Zhu et al., 2022; Zhang et al., 2021; Li et al., 2019; Shabangu et al., 2014). A techno-economic analysis of the production of biochar from biosolids has not been conducted, to explore this not only as an approach for dealing with many contaminants in wastewater residue streams, but also to justify the investment.

In this study, we first evaluated the feasibility of removing MPs, PFAS, and PPCPs during the pyrolysis of biosolids to generate biochar, at different temperatures and residence times, and then conducted a techno-economic analysis of the costs and benefits associated with the implementation of a large-scale pyrolysis treatment system, under various scenarios.

2. Materials and methods

2.1. Materials

PPCP analytical standards and three isotope-labeled internal standards (trimethoprim-D9, fluoxetine-D5 and ibuprofen-D3) were purchased from Sigma Aldrich (St. Louis, MO, USA). PFAS analytical standards (EPA-537PDSL-R1) were purchased from Wellington

Laboratories (Guelph, ON, Canada). High-performance liquid chromatography (HPLC)-grade water, methanol, acetone and acetonitrile were purchased from Honeywell Burdick & Jackson (Muskegon, MI, USA). Dispersive sorbent C18 and primary secondary amine (PSA) QuEChERS kits were purchased from Agilent Technologies, Santa Clara, CA.

2.2. Sample collection and preparation

Biosolid samples were collected from an operating large wastewater treatment plant in Southern California. The samples were stored in glass jars and kept at 4 °C until preparation. To minimize volatilization of organic compounds, the biosolids were freeze-dried for 24 h using a commercial freeze dryer (HarvestRight), to reduce water content. The freeze-dried samples were ground using a pestle and mortar and liquid nitrogen.

2.3. Pyrolysis process

Biosolid samples were separated into four different groups, for pyrolysis at different temperatures: 400 °C, 500 °C, 600 °C, and 700 °C. Within each group, the samples were evenly distributed into three ceramic crucibles to generate triplicates, and the pre-pyrolysis weights were recorded. Sample weights ranged from 19.64 to 26.03 g. After the crucibles were loaded into a Cole-Parmer StableTemp furnace at room temperature, the door was closed and nitrogen gas was allowed into the furnace to remove oxygen via the exhaust vent. After 1 min, the N₂ flow was adjusted to 170 mL/min, to maintain a nitrogen atmosphere within the furnace. Then, the furnace was turned on and adjusted to reach the target temperature. Once the oven reached the temperature, it was held constant for 2 h. Then the oven was turned off and allowed to cool back down to room temperature while keeping the nitrogen valve open at the controlled rate. The biochar samples were removed from the oven, and the post pyrolysis weights of each bowl were recorded. These samples were stored at −20 °C until extraction to prevent degradation of the compounds of interest.

2.4. Extraction of PPCPs and PFAS from biosolids and biochar

Freeze-dried samples were ground with mortar and pestle and filtered through a 0.5 mm sieve. This process removed any large particle, which mainly consisted of unbreakable mineral materials (i.e., small rocks), allowing for more consistent particles and identical replicate samples. Method validation was performed to discover the most effective approach of extracting PPCPs and PFAS compounds from the biosolids and biochar. Two methods were used in this study: Solid-Phase Extraction (SPE) based on EPA Method 1694 (Ferrer et al., 2010) and the Agilent Single Extraction (ASE) method (Moodie et al., 2021). The details of the extraction methods, as well as the recoveries are presented in the Supporting Information. Overall, the ASE method performed better, but not for the same compounds, so both methods were used and the results are reported using both extraction methods.

2.5. LC-MS/MS method for PPCPs and PFAS analysis

An Agilent Technologies 1290 HPLC coupled with a 6470 Triple Quad LC/MS was used to perform quantitative analysis of 30 PPCPs and 16 PFAS concentrations in the samples (Supporting information Table S2). An Agilent C18-Ether column with gradient mobile phase (A: 0.1 % (m:v) ammonium formate and 0.1 % (v:v) formic acid in water; B: 1:1 (v:v) methanol: acetonitrile) was used to separate the compounds. The total run time for each sample was approximately 30 mins. Six levels of calibration standards at 10, 100, 250, 500, 750, and 1000 ng/ml were employed. Method limits of detection (LODs) are provided in the Supporting Information.

2.6. Microplastics extraction and quantification

The details of the microplastics analysis are provided in the Supporting information. In brief, care was taken to avoid contamination when handling the samples. All samples were freeze-dried using a Harvest Right freeze dryer. Dried biosolids (150 g) were sieved through a 2 mm stainless steel sieve and both size fractions were collected and subjected to microplastic analysis. The <2 mm size fraction underwent organic matter digestion and density separation for microplastic extraction, while the >2 mm size fraction was visually examined for plastic particles using a stereomicroscope (Olympus SZ40) at 40× magnification. Samples derived from the <2 mm fraction were partitioned into 3 portions and placed in glass beakers to undergo treatment with Fenton's reagent for organic matter digestion. The samples were resuspended in 300 ml of CaCl₂ suspension (1.4 g/cm³) used for extraction, then centrifuged at approximately 1600g for 1 h (SH-3000 Swinging Bucket Rotor, Sorvall). The supernatant was filtered through a 10-μm PCTE filter followed by a 1.6-μm glass fiber filter using a glass filtration apparatus.

Microplastics were visually identified using a stereomicroscope (Olympus SZ40) at 40× magnification to count the number of microplastic-appearing particles. A random sample of particles representing approximately 4 % of total particles were collected for polymer identification using an ATR-FTIR microscope (Thermo Fisher Scientific Nicolet iN10 Infrared Microscope) equipped with a mercury-cadmium-telluride (MCT) detector. IR spectra were analyzed using the Thermo-Fisher OMNIC Picta software and identified by searching established spectra databases in the software, as well as the Open Specy polymer database.

For comparison, samples from normal commercial and organic commercial composting were also processed as above and analyzed.

2.7. Elemental analysis

Inductively-coupled plasma with mass spectrometry (ICP-MS) was employed to determine elemental composition of the biosolids and biochars, targeting 24 elements. About 0.1 g samples were placed in 50 ml digestion tubes, and 10 ml of concentrated trace-metal grade HNO₃ (Fisher Scientific, Hampton, NH) was added into each tube. The suspension was heated at 80 °C for 2 h and 125 °C for 1 h on a Versa-Bath hot block digestion system (S Model 224, Fisher Scientific). At the end of the digestion process, the digestates volumes were adjusted to 10 ml with Milli-Q water (18.2 MΩ cm) and centrifuged at 18,000 g for 15 min (Southwest Science SC1024R, Hamilton Township, NJ) to separate the solid residues. The supernatants were further diluted and acidified with 2 % trace-metal grade HNO₃ prior to ICP-MS analysis (Agilent Technologies 7900 ICP-MS). ICP-MS calibration standard solutions (0.5 μg/L to 2000 μg/L) were prepared with a NIST Traceable standard (SPEX, Metuchen, NJ). An internal standard solution (Alfa Aesar, Haverhill, MA) was continuously injected during the ICP-MS analysis to correct for instrument drift during analysis.

In addition, biosolids and biochar samples were dried and finely ground before being sent to the analytical lab for C, H, and N analysis. The analysis was performed using a CEC 440 Elemental Analyzer and the Dumas combustion method. Each sample, weighing 2 mg, was carefully loaded into silver capsules using a microbalance for analysis. Three replicates of each sample were analyzed. The results are reported in the Supporting Information.

2.8. Economic analysis

Preliminary cost information for the biosolids drying and pyrolysis full-scale equipment was obtained from manufacturers, including capital expenses, installation costs, and operational parameters. Cost information for labor, electricity, natural gas, transportation of biosolids, and other inputs was obtained from an operation in Southern California.

3. Results and discussion

3.1. Pyrolysis

The average water content in the biosolids before freeze drying and homogenization was 80.33 %. After pyrolysis, the average weight loss for biochar pyrolyzed to 400 °C, 500 °C, 600 °C, and 700 °C was 73.83 %, 74.83 %, 75.27 %, and 75.85 %, respectively. There was only a significant difference between the weight loss percentages at 400 °C and 700 °C (Fig. S2). There was also a noticeable color change of the biochar as the pyrolysis temperature increased; the initial untreated biosolid was dark brown, and as temperature rose to 700 °C the biochar turned progressively darker red. This was likely due to the oxidation of iron naturally present in the biosolids, producing iron oxides.

3.2. Analysis of PPCPs and PFAS in biosolids and biochar

Of the 30 PPCPs considered in the analysis, 23 were detected in the biosolids (Fig. 1A), although the concentrations varied depending on the extraction method (Appendix, Table S1). The concentrations ranged from around 1 ng/g to over 900 ng/g for one PPCP (erucylamide, a food additive that is also used in polymer formulations). Total PPCPs represent around 1.9 µg/g in the biosolids based on the ASE method and 0.72 µg/g based on EPA Method 1694. For PFAS, the concentrations ranged

from 0.3 to 21.7 ng/g using the ASE method, for a total PFAS concentration (considering only the compounds in this study) of 47.7 ng/g using ASE and 12.1 ng/g using EPA Method 1694 (Fig. 1B). These are low concentrations, but within the range detected in biosolids. For example, PFOS, the most commonly detected PFAS in biosolids, has been detected at concentrations ranging from 0.13 ng/g (Berger et al., 2004) to 5383 ng/g (Guo et al., 2008). Perfluorooctanoic acid (PFOA), another common PFAS, has been detected at levels from 0.09 ng/g (Sindik et al., 2013) and 4780 ng/g (Li et al., 2019).

None of the PFAS considered in this study were detected in biochar, regardless of pyrolysis temperature. Unexpectedly, three PPCPs were detected in biochar (DEET, linagliptin, and n-butylparaben) at most pyrolysis temperatures (Fig. 2). In some cases, these compounds were not completely degraded even at 700 °C, although in general there was a decreasing trend with temperature. For n-butylparaben, there was an overall decrease in concentration as temperature increased, with an unexplainable increase at 500 °C using the EPA method, which was not observed using the ASE method. For DEET, there was an immediate decrease to very low concentrations (0.13 to 0.53 ng/g) at all pyrolysis temperatures using either method. For linagliptin, there was an immediate decrease to nearly zero concentration (non-detect to 0.03 ng/g) at all pyrolysis temperatures (Fig. 2).

3.3. Analysis of microplastics in biosolids and biochar

While biosolids contained 15.1 particles/g, biochar contained only 0.4 to 1.4 particles/g. This is a 91–97 % reduction in microplastic particles. Most of the particles in biosolids were in the 10–250 µm range (Fig. 3A), followed by particles in the 1.6–10 µm range. In biochar, no particles >250 µm were observed. For comparison, a sample from municipal compost contained 7.59 particles/g, with similar size distribution as biosolids, and a sample from organic compost had 0.727 particles/g, mostly in the 1.6–10 µm range. Thus, the level of microplastics in biochar produced at 400 °C is similar to those in organic compost. Fibers were in general the most common morphology, followed by fragments, except in biosolids where fragments represented a slightly higher fraction than fibers (Fig. 3B). Beads and fiber bundles were rarely observed in the samples. In terms of composition, polystyrenes, polyester, and polyhaloolefins (e.g., polyvinyl chloride) were the most common microplastics in biosolids (Fig. 3C), while in biochar (400 °C) the dominant composition was cellulose derived fibers, followed by polyester (Fig. 3D). Organic matter was detected, but was not likely from synthetic polymers.

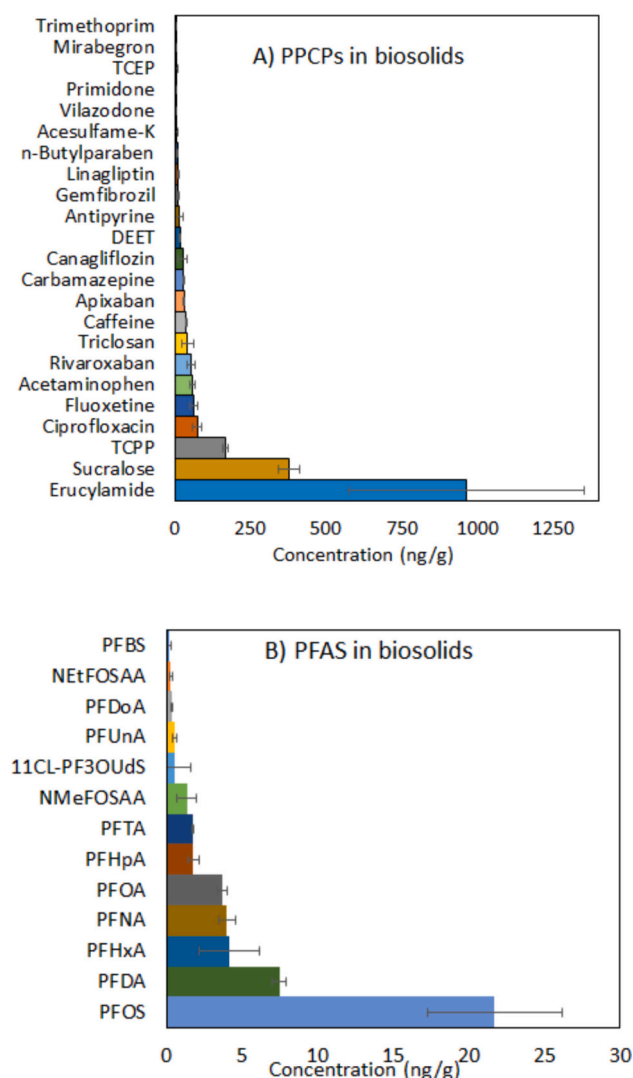


Fig. 1. Concentration in biosolids of (A) PPCPs; and (B) PFAS.

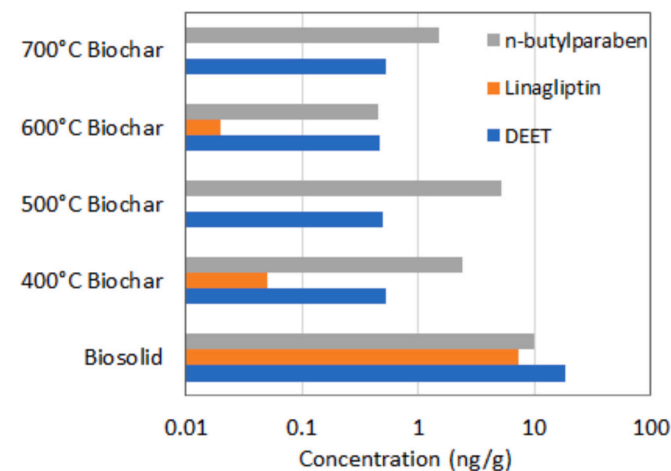


Fig. 2. Concentration of DEET, Linagliptin, and n-butylparaben in biosolids and biochar.

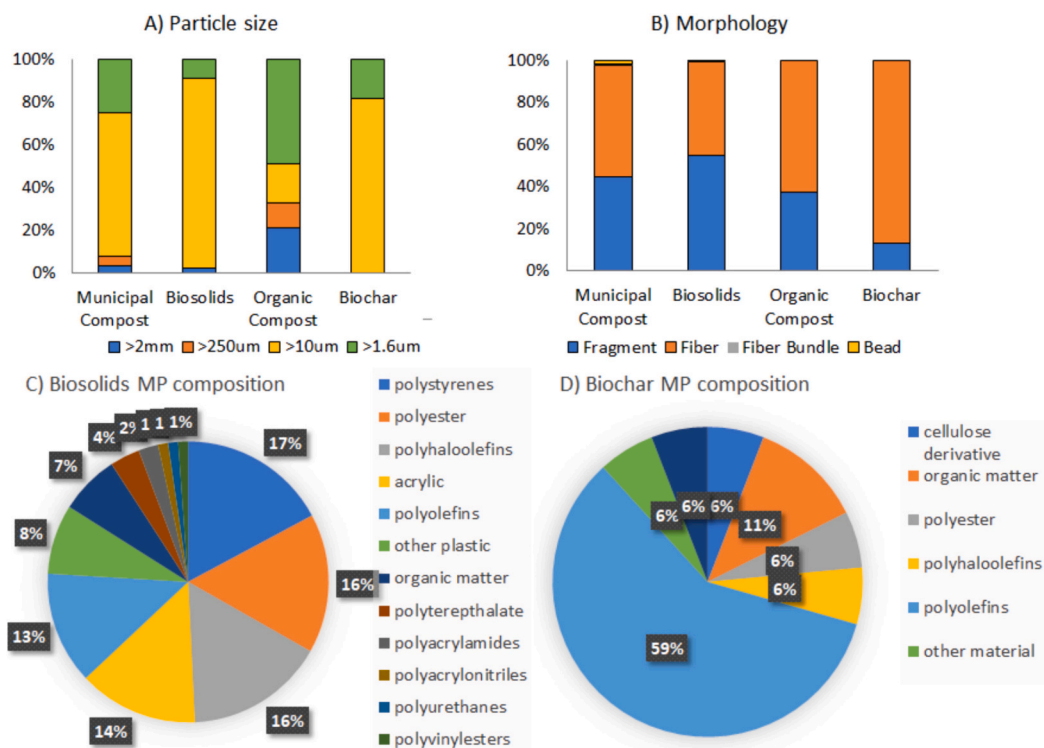


Fig. 3. Characterization of microplastic (MP) particles in biosolids and biochar, in terms of (A) size; (B) morphology; (C) composition in biosolids; and (D) composition in biochar.

3.4. Analysis of metal residues in biosolids and biochar

Biosolids contain around 100 g/kg of metals and other elements (Fig. 4). Iron (Fe) and phosphorus (P), most likely as phosphate, represent almost 75 % of the other elements present (Fig. 4A), followed by magnesium (Mg), potassium (K), aluminum (Al), and sodium (Na). This is as expected, since these elements are conserved during pyrolysis. The composition of biochar pyrolyzed at different temperatures reflects a similar distribution, although with some variation likely due to the heterogeneous nature of biosolids. The higher concentration of all of these elements reflects the loss of significant amounts of carbon and other light elements. In terms of minor elements, zinc (Zn) and copper (Cu) represent the most significant fraction (Fig. 4B), together adding up to 1654 mg/kg in biosolids. Lead (Pb) is present at 17 mg/kg in biosolids, arsenic (As) is at 3.6 mg/kg, while cadmium (Cd) is only 2.0 mg/kg. These concentrations are well below the regulatory ceiling concentrations determined by the USEPA (40 CFR § 503.13) for biosolids.

3.5. Techno-economic analysis of biochar production from biosolids

We conducted the techno-economic analysis for wastewater treatment ranging from 1000 to 20,000 metric tons/yr of dewatered sludge. For illustration purposes, only the calculations for the 20,000 tons/yr operation are presented. The analysis assumes that the current operation produces sludges from various stages of the wastewater treatment, which are then processed in anaerobic digestors. These are then press-dried, to produce biosolids with approximately 80 % moisture content.

3.5.1. Energy and mass balance

Prior to pyrolysis, the moisture content must be reduced to approximately 20 %, using thermal energy in part generated by the pyrolysis process (Fig. S1). Understanding the energy requirements for the overall drying and pyrolysis processes is pivotal for assessing the financial viability of this approach. Commercial drying systems require 800–850 thermal kWh (McNamara et al., 2016) and 40 electrical kWh per metric

ton of water removed from the biosolids. The electrical energy is used for fans, conveyor belt motors, and controls, not for heating. A wastewater treatment facility processing 20,000 tons of press-dried sludge annually must remove 16,000 metric tons of water. Therefore, 704,000 kWh of electricity and 13,200,000 kWh of thermal energy are required to reduce the moisture content to 20 %.

The pyrolysis equipment takes in the dried biosolids and produces thermal energy and biochar. Both outputs depend on the organic content of the biosolids, which can range from ~55 % to 70 % (Torrecillas et al., 2013), with a calorific value from 11.5 to 15 MJ/kg dry solids (Elkhalifa et al., 2022; Hakeem et al., 2022; Kan et al., 2016). For the calculations we assumed an average conversion of 53.5 % from dry biosolids to biochar, generating 2140 metric tons of biochar per year. Since the biosolids contain a significant amount of energy, the pyrolysis process generates 1.29–1.46 thermal kWh per kg of dried biosolids (Winchell et al., 2021). This depends on the composition of the biosolids. Other feedstocks, such as woodchip (mulch) or green waste have a greater (30–40 %) calorific value. An average yield of 1.375 kWh of thermal energy per kg dry biosolids was considered, generating 5,500,000 kW thermal/yr. Since these are key factors, a sensitivity analysis was conducted on these parameters, presented below in the economic analysis. Thus, a net 7,700,000 kWh thermal/yr are required, which can be supplied either from biogas produced in the anaerobic digestion of the sludges, or from purchased natural gas. The power demand of the pyrolysis equipment is 48 electrical kW, with an annual electrical consumption of 384,000 kWh.

3.5.2. Costs

All costs are in US dollars (\$). The following cost components were considered:

- **Capital and Installation Costs:** Costs are based on information from equipment providers. Drying equipment is modular, with $y = 0.1231 + 0.0017x$, where x = evaporation capacity in kg H₂O/h and y = capital cost (million \$), with ± 15 % based on country of

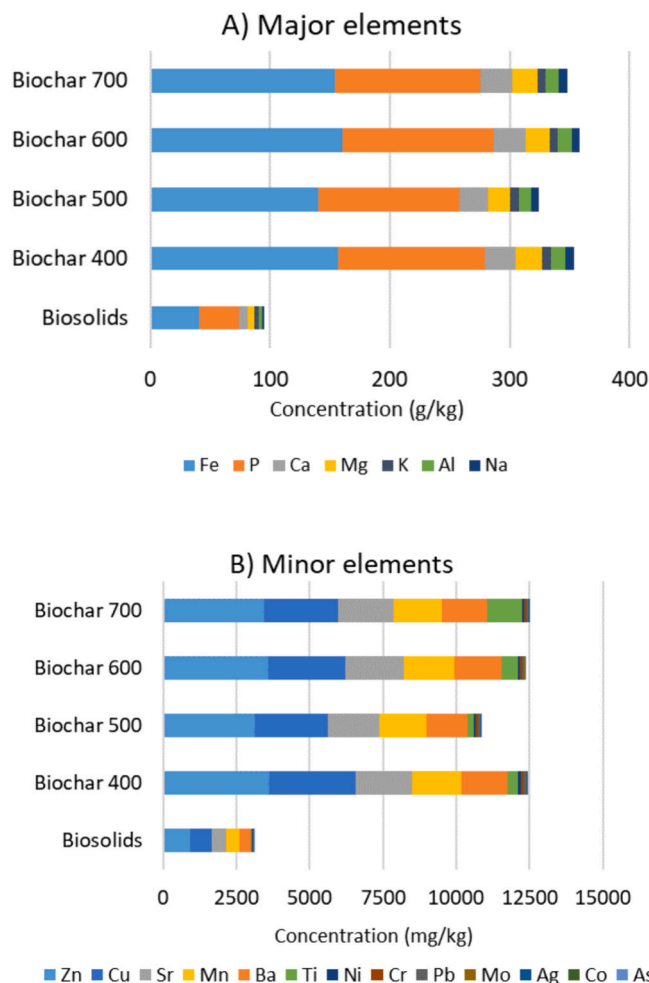


Fig. 4. Concentration of (A) major (g/kg); and (B) minor (mg/kg) elements in biosolids and biochar.

manufacture. Installation costs of 15 % of capital costs included, although this can vary depending on site specific conditions. Pyrolysis equipment is not available in modules, which means that the equipment may be oversized for the amount of biosolids available, and would thus be operated at <100 % of the 8000 h/yr typically considered. For the analysis, $y = 1.015 + 0.0006x$, where x = dry biosolids annual input (ton/yr) and y = capital cost (million \$), with ± 15 % based on country of manufacture.

- **Annual Maintenance Costs:** based on information from the equipment providers, maintenance costs were estimated at 2.5 % of capital costs for each system.
- **Labor Costs:** the equipment providers estimate 4–6 h of daily labor for operating and maintaining the equipment. An additional 10 % was considered for maintenance due to start-up and shutdown. Integrated labor rates (salary + benefits) in California range from \$50–70/h.
- **Utility Costs:** the average cost of electricity is 0.18–0.22 \$/kWh, and 0.65–0.81 \$/therm for natural gas.
- A 3 % discount rate was applied to compute the present value of recurring costs over a 20-year period, assuming this is the typical lifetime for the equipment.

An example for a 15,000 metric tons/yr wet biosolids system is presented in Table 1. Fig. 5 presents the present value of costs for systems from 1000 to 20,000 metric tons wet biosolids/yr, total (Fig. 5A) and normalized by throughput (Fig. 5B). Clearly, economies of scale are important. Net Present Value (NPV) of costs converges to around

Table 1

Capital and recurring costs for 15,000 metric tons/yr wet biosolids system, and present value of total costs over 20 years.

	Low	Medium	High
Capital and installation costs			
Biosolids dryer	\$2,470,000	\$2,840,000	3,270,000
Pyrolysis	\$2,450,000	\$2,820,000	3,240,000
Total	\$4,920,000	\$5,660,000	6,510,000
Annual recurring costs			
Maintenance costs (\$/year)	\$123,000	\$141,000	\$163,000
Labor (\$/year)	\$75,000	\$113,000	\$158,000
Electricity (\$/year)	\$165,000	\$180,000	\$198,000
Natural gas (\$/year)	\$133,000	\$145,000	\$160,000
Total	\$496,000	\$579,000	\$679,000
Present value costs			
Recurring costs over 20 years	\$9,930,000	\$11,600,000	\$13,600,000
Discounted recurring costs	\$7,390,000	\$8,620,000	\$10,100,000
Total present value costs	\$12,300,000	\$14,300,000	\$16,600,000

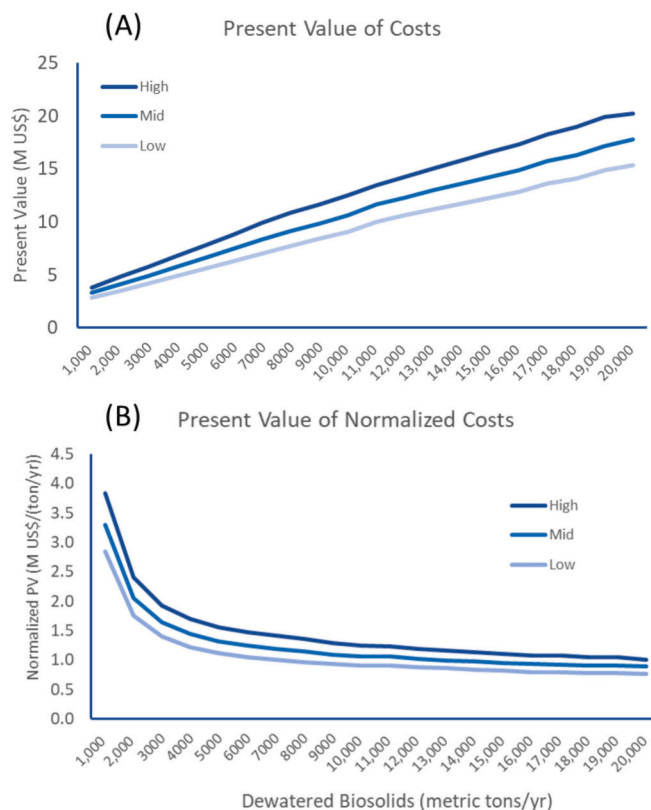


Fig. 5. (A) Total present value of costs; and (B) normalized present value of costs (present value divided by the wet biosolids throughput in metric tons/yr).

\$900,000 per metric ton/yr for the larger systems.

The four factors for recurring costs have similar weight, although labor costs can have the most variation. These costs are for coastal California, which is a rather expensive region for labor and utilities. The costs are indicative, but a full evaluation of each project should be conducted.

3.5.3. Revenue and savings

The final component of the economic analysis involves calculating potential revenue from the sale of biochar and savings associated with elimination of transport of wet biosolids to agricultural locations. Since the wastewater treatment plant is usually at the lower end of the

watershed(s) and within city limits, the distance to agricultural sites where biosolids would be normally applied can be 25–50 km. In some cases, wet biosolids can be transported over 200 km to agricultural sites. The distance is very site specific, but for the analysis distances of 50 and 200 km round-trip were considered. Transportation costs are in the range of 0.20–0.26 \$/km-metric ton. There is a wide range of prices for biochar, depending on region, quality and amount sold, with lower prices for large shipments, with a range of 200–1000 \$/metric ton (Elias et al., 2022). For the analysis we considered a range from 400 to 800 \$/metric ton. The present value of the sale of biochar and savings is highly dependent on the price of biochar, and the distance to the disposal site of wet biosolids (Fig. 6A), while the transportation costs were less significant.

The resulting net present value (benefits – costs) is highly dependent on the scale of the pyrolysis operation, the market price of biochar, the capital costs, the distance (50 or 200 km) for disposal of wet biosolids, and to a lesser extent the operational costs (Fig. 6B). Smaller operations (<4000 metric tons of wet biosolids/yr) may not be economically sustainable, in which case thinking about a regional operation to serve various communities may be an approach. There is a significant difference in net present value between the potential lower and higher end of costs and biochar prices. If the price of biochar is below around \$600/metric ton, the investment could be justified based on elimination of pollutants going to agricultural fields; carbon credits may also offset the costs, although this was outside the scope of this study. At this stage, there are only a few operations worldwide processing biosolids via pyrolysis, but as the number of installations increases, it is very likely that the capital costs will decrease significantly.

4. Conclusions

Pyrolysis is a promising approach for dealing with MPs, PFAS, and PPCPs in wastewater biosolids. Pyrolysis at all temperatures tested, from 400 to 700 °C, was successful removing all PFAS and most PPCPs in biosolids, with the exception of traces of DEET, linagliptin, and n-butylparaben. For linagliptin, removal ranged from 99.3 % to 100 %, while for DEET removal was slightly lower, from 97.1 % to 99.0 %. Surprisingly, n-butylparaben was the most resistant to pyrolysis, although the concentrations ranged from 0.67 to 5.14 ng/g in biochar, depending on the pyrolysis temperature and the method of analysis. For the PFAS analyzed and detected in the biosolids, removal was 100 %, with no detectable concentrations. MP removal via pyrolysis ranged from 91 to 97 %. It should be noted that our study employed a two-hour residence time, while most commercial pyrolysis units operate with shorter residence times. Thus, further work is needed to determine the effect of residence time. The gases from pyrolysis need to be treated to remove any residual pollutants of concern, including PFAS degradation products.

The techno-economic analysis considered the energy produced by pyrolysis, as heat, for partially drying the biosolids before their pyrolysis. Although additional fuel is needed to dry the biosolids to 20 % moisture, in the form of natural gas, the contribution of heat from the pyrolysis of biosolids is substantial. Taking into consideration the cost savings from not transporting so much water embedded in the biosolids to the composting facility, and the revenue generated from the sale of biochar, the operation can quickly cover the investment and operating costs, considering a 20-year lifetime. The favorable outcome can be increased by considering a more inclusive approach, in which either nearby or regional wastewater treatment facilities send biosolids to a common drying and pyrolysis facility.

CRediT authorship contribution statement

Arturo A. Keller: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

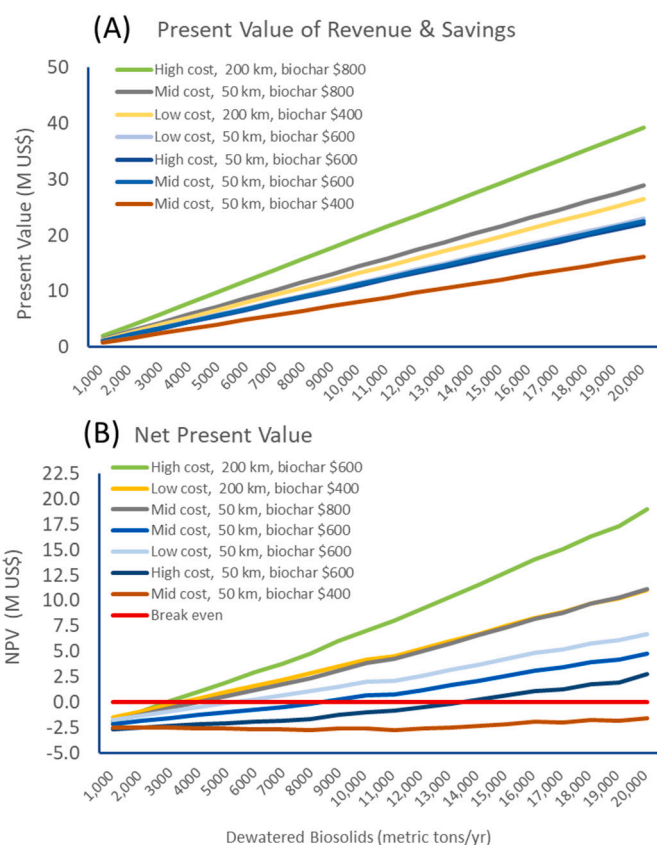


Fig. 6. (A) Present value of revenue and savings; and (B) net present value (NPV). The red “break even” line reflects a zero NPV.

Weiwei Li: Writing – review & editing, Investigation, Formal analysis, Data curation. **Yuki Floyd:** Writing – review & editing, Investigation, Formal analysis, Data curation. **James Bae:** Writing – review & editing, Data curation. **Kayla Marie Clemens:** Writing – review & editing, Formal analysis, Data curation. **Eleanor Thomas:** Writing – review & editing, Formal analysis, Data curation. **Ziwei Han:** Writing – review & editing, Formal analysis, Data curation. **Adeyemi S. Adeleye:** Writing – review & editing, Project administration, Methodology, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Provides additional details on the methods of analysis of PPCPs,

PFAS, and MPs, and two tables with data on the analysis of PPCPs and PFAS. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.174773>.

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