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Emerging investigators series: pyrolysis removes common microconstituents triclocarban, triclosan, and nonylphenol from biosolids†

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Reusing biosolids is vital for the sustainability of wastewater management. Pyrolysis is an anoxic thermal degradation process that can be used to convert biosolids into energy rich py-gas and py-oil, and a beneficial soil amendment, biochar. Batch biosolids pyrolysis (60 minutes) revealed that triclocarban and triclosan were removed (to below quantification limit) at 200 °C and 300 °C, respectively. Substantial removal (>90%) of nonylphenol was achieved at 300 °C as well, but 600 °C was required to remove nonylphenol to below the quantification limit. At 500 °C, the pyrolysis reaction time to remove >90% of microconstituents was less than 5 minutes. Fate studies revealed that microconstituents were both volatilized and thermochemically transformed during pyrolysis; microconstituents with higher vapor pressures were more likely to volatilize and leave the pyrolysis reactor before being transformed than compounds with lower vapor pressures. Reductive dehalogenation products of triclocarban and suspected dehalogenation products of triclosan were identified in py-gas. Application of biosolids-derived biochar to soil in place of biosolids has potential to minimize organic microconstituents discharged to the environment provided appropriate management of py-gas and py-oil.

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Water impact

Reuse of biosolids is critical for sustainable water resource recovery. Biosolids carry organic microconstituents, such as pharmaceuticals, antimicrobials, and other consumer product chemicals, that cause concern when land applying biosolids. This research demonstrates that pyrolysis could be used to remove organic microconstituents from biosolids.

Introduction

Land application of wastewater biosolids is often an economical and beneficial way to reuse nutrients.¹ Although land application can be beneficial, constituents other than nutrients are released to the environment.^{2,3} Many organic microconstituents, including antimicrobials, surfactants, hormones, pharmaceuticals, and personal care products are not removed during conventional biosolids handling processes, such as anaerobic digestion, and are discharged to the environment following land application of biosolids.^{4–9} The fate of microconstituents is variable following land application as they remain in soil,¹⁰ are sequestered by plants,^{10–13} biodegraded,¹⁴ transferred in runoff,¹⁵ and bioaccumulate into earthworms.¹⁶ New solids management processes that

remove microconstituents and produce a beneficial soil conditioner would provide wastewater treatment utilities with a viable option if they desired to reuse biosolids while minimizing release of these organic microconstituents to the environment.

Pyrolysis is a thermal process that occurs in the absence of oxygen and is gaining interest for biosolids management.^{17,18} Pyrolysis produces a beneficial soil conditioner, biochar, as well as pyrolysis-gas and pyrolysis-liquid (a.k.a. bio-oil), both of which have energy content and can be used as fuel.^{19–21} Depending on operating conditions and feedstock volatile solids concentration, the pyrolysis gas can yield enough energy to offset the energy required for the pyrolysis process.²² The energy available in py-gas and py-oil is enough to cover the energy costs of the pyrolysis process and offset some of the energy required to dry biosolids.²³ Biochar is used for different land-application purposes than biosolids because biochar has less available nutrients and carbon.²⁴ Still, biochar has many benefits when used as a soil conditioner. For instance, biochar contributes to carbon

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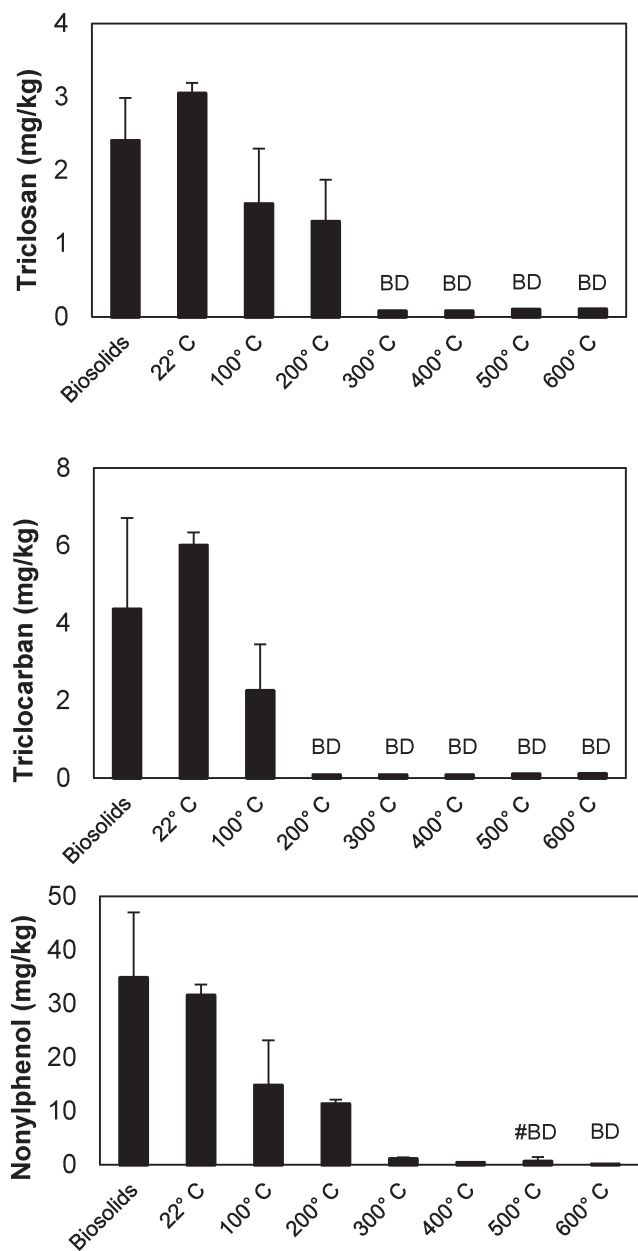


Fig. 2 Impact of temperature on removal of triclosan (top), triclocarban (middle), and nonylphenol (bottom) during thermal processing/pyrolysis. Data points represent the average concentration and error bars represent the standard deviation among the triplicate experiments ($n = 3$). The “biosolids” bar represents the feed biosolids that was not pyrolyzed ($n = 9$). Non-detects were plotted as detection limits and are marked with “B.D.” to indicated below detection limit. The #BD marker indicates that two of the three samples were below detection limit.

for 30 minutes removed more than 85% of PCB's.²⁸ Pyrolysis of sediment also removed dioxins by volatilization, albeit these experiments were performed at 800 °C for 30 minutes²⁹ Biosolids pyrolysis would most likely be conducted at temperatures of at least 450 °C with retention times of five minutes or more to optimize production of biochar and py-gas.^{39,41} Based on results from this study, biosolids pyrolysis systems

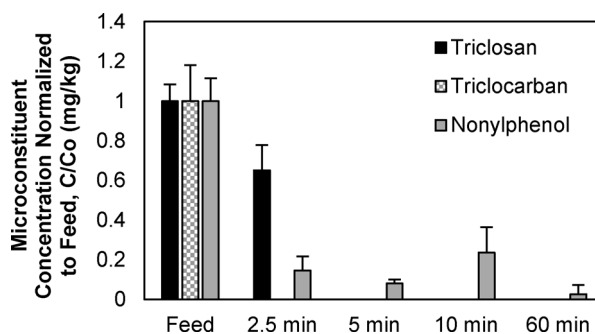


Fig. 3 Impact of pyrolysis reaction time on removal of TCS, TCC, and NP from biosolids during pyrolysis at 500 °C. Data points represent the average concentration and error bars represent the standard deviation among the triplicate experiments ($n = 3$).

would remove organic microconstituents from solids to create a beneficial biochar soil amendment that contains substantially less microconstituent mass compared to dried biosolids. In a full-scale system, the amount of time required for pyrolysis would be dependent on the mass of biosolids processed, and a longer pyrolysis reaction time may be required depending on the amount of biosolids processed. Additionally, more energy inputs would initially be required to heat more biosolids, but there is potential that the energy available in py-gas and py-oil would offset energy needs for pyrolysis. The enthalpy of pyrolysis of biosolids was previously estimated to be -1130 kJ kg^{-1} at 500 °C,²³ and other work found that pyrolysis of biosolids can be exothermic or endothermic.²² More research should be conducted to determine how energy inputs and outputs of pyrolysis change as a function of temperature.

Fate of microconstituents during pyrolysis

TCS, TCC, and NP were spiked into a reactor loaded only with sand and heated for two hours at 500 °C to determine if the microconstituents volatilized and/or transformed during pyrolysis. A room temperature control experiment was conducted; the recovery of TCS, TCC, and NP in the sand was 58%, 62%, and 42%, respectively, and none of the microconstituents were detected downstream in the methanol collection system (see ESI,† section ES4, Fig. ES6). After pyrolysis at 500 °C, none of the microconstituents were detected in the sand, which corroborates the findings above that biosolids pyrolysis removed these organic microconstituents from the solid phase. In the sand-spiked experiments, a substantial portion of TCS and NP mass was recovered in methanol within the impinger system (approximately 40%), but less than 5% of TCC was detected in the methanol (Fig. 4).

The substantially lower recovery of TCC may be a result of chemical transformation during pyrolysis. The recovery of microconstituents in the experimental system after pyrolysis, a potential indicator of transformation, correlated to the vapor pressures of the microconstituents. Microconstituents with higher vapor pressures volatilized and were recovered in





Fig. 4 The impact of pyrolysis on the fate of microconstituents spiked into sand. No microconstituents were detected in sand following pyrolysis at 500 °C for two hours. Following pyrolysis the mass recovered in the methanol collection system (tubing + impingers) was highest for NP and TCS which had the highest vapor pressures. The error bars represent the standard deviation observed among the total amounts of mass recovered for each microconstituent between the triplicate runs ($n = 3$).

the methanol collection system at rates similar to the negative control experiments (approximately 40%), while microconstituents with lower vapor pressures were barely recovered (<2%) in the methanol collection system (see Fig. 4 and Table 1). The lower vapor pressures of TCC may result in TCC having longer retention times under pyrolytic conditions because they do not volatilize as quickly and are therefore exposed to higher temperatures for extended periods of time. The reaction time for transformations to occur would be greater for low-vapor-pressure microconstituents compared to high-vapor-pressure microconstituents. More complete transformation would result in a decrease in recovery for low-vapor-pressure microconstituents. Hu *et al.* (2007) attributed the high pollutant recovery in their pyrolysis system to the quick volatilization and exiting of the compounds from the pyrolysis reactor.²⁹ They postulated that, if the pollutants remained in the reactor longer, then the pollutants would have transformed during the higher temperatures at longer reaction times. Miskolczi *et al.* (2008) also found that flame retardant plastics underwent dehalogenation to a greater extent in a lengthened pyrolysis tube reactor when compared to typical fluidized bed and fixed bed reactors due to long residence times achieved in tube reactors.⁴²

Reductive dechlorination was a suspected chemical transformation mechanism for TCC and TCS. Both compounds are polychlorinated (see Table 2) and susceptible to biological reductive dehalogenation,^{43–46} implying that they could also

Table 1 Microconstituent estimated vapor pressure from the US EPA Estimations Program Interface Suite (EPI Suite v4.11)

Microconstituent	Vapor pressure (mm Hg)
Nonylphenol	6.86×10^{-4}
Triclosan	4.65×10^{-6}
Triclocarban	3.61×10^{-9}

Table 2 Triclosan, triclocarban, and dechlorinated product structures

Compound	Structure	Percent of moles found in condenser system normalized to moles of parent compound spiked
Triclocarban		1.3 ^a
1-(3,4-Dichlorophenyl)-3-phenylurea		0.97 ^b
1-(4-Chlorophenyl)-3-phenylurea		0.02 ^b
Triclosan		40.7 ^a
5-Chloro-2-(4-chlorophenoxy)phenol		NA ^c
5-Chloro-2-phenoxyphenol		NA

^a Denotes triplicate runs. ^b Denotes duplicate runs. ^c NA denotes standards not available.

be susceptible to abiotic reductive dehalogenation under appropriate conditions. Indeed, lesser chlorinated TCC homologs, 1-(3,4-dichlorophenyl)-3-phenylurea and 1-(4-chlorophenyl)-3-phenylurea, were detected in methanol in the impinger system after pyrolysis (Table 2). Standards for these chemicals were available (Sigma Aldrich, St. Louis, MO) to confirm the peaks on the LC-MS, and are shown in the ESI,† section ES5. The moles of 1-(3,4-dichlorophenyl)-3-phenylurea recovered were nearly equal to the moles of TCC recovered (Table 2). The moles of dechlorinated products recovered in the condenser system did not account for a substantial portion of the parent compound molar mass spiked into the system, but their detection indicated that thermochemical reductive dehalogenation occurred during pyrolysis.

Lesser chlorinated TCS homologs, 5-chloro-2-(4-chlorophenoxy)phenol and 5-chloro-2-phenoxyphenol, were also suspected in methanol in the impinger system (see ESI,† section ES6). Standards were not commercially available for these two TCS homologs, but LC-MS analytes were detected having mass/charge (m/z) ratios expected for these lesser chlorinated homologs. The analyte retention times were shorter than TCS, indicating a decrease in hydrophobicity that would be expected when chlorine atoms are replaced by hydrogen atoms. These compounds ostensibly are more soluble than their parent compounds and, if released, more easily transported throughout the environment; therefore, management of the py-oil and py-gas is important to minimize the release of microconstituents back to the environment. These transformation products were not detected in the biochar.

A hydrogen source is required for reductive dechlorination of TCC and TCS to occur.³¹ These experiments were carried out with microconstituents spiked into sand, so hydrogen



available to exchange with chlorine during dechlorination would be from fragments of other decomposed microconstituents within the system. The dechlorination reaction rate may have been limited by the lack of hydrogen. In actual biosolids, dechlorination of microconstituents during pyrolysis could occur more rapidly because the organic fraction of biosolids would undergo decomposition and release more hydrogen into the gas phase. While the results from these experiments indicate that organic microconstituents are removed from biosolids by either thermochemical transformation or volatilization, future work should investigate the role of biosolids constituents, such as metals and organic matter, on chemical transformation products.

Finally, in the negative control heat was applied to the system but sand was not spiked with microconstituents; microconstituents were not detected in impinger methanol or piping/tubing extracts, indicating that heating the system did not yield an experimental artifact in which microconstituents were produced. The negative control and room temperature experiments along with the pyrolysis heated experiments confirmed that pyrolysis was responsible for removing microconstituents from the sand and transporting parent compounds and transformation products to the py-gas.

Conclusions

Pyrolysis of biosolids could minimize the discharge of microconstituents to the environment *via* land application of the residual solids. Microconstituents can be removed from the resulting biochar when 1.5 g of heat-dried biosolids are pyrolyzed at 500 °C for 2.5 minutes. In a full-scale system, the microconstituents detected would be transferred to the pyrolysis gas and pyrolysis oil as either the parent compound or a transformation product. Both the pyrolysis-gas and pyrolysis-oil could be combusted for energy recovery if properly refined. If complete combustion occurs, then the microconstituents in the oil and gas would be mineralized. Future work should be conducted to determine the fate of microconstituents during combustion of pyrolysis-gas and pyrolysis-oil to ensure that these microconstituents are not released to the environment during handling of these pyrolysis products. In summary, pyrolysis could be added as a biosolids processing step that reduces the amount of organic microconstituents discharged to the environment with residual solids.

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