

Fate of Micropollutants During Pyrolysis of Biosolids

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FATE OF MICROPOLLUTANTS IN BIOSOLIDS DURING PYROLYSIS

by

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ABSTRACT

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John Ross

Marquette University, 2014

Approximately 250 tons of organic micropollutants, including pharmaceuticals, antimicrobials, and hormones, are discharged to the environment during land application of wastewater biosolids. Reusing wastewater biosolids is vital to the sustainability of wastewater treatment, but current treatment processes do not remove micropollutants from biosolids in an efficient manner. Pyrolysis—the heating of biomass to temperatures between 400 and 800 °C under oxygen-free conditions—was proposed as a biosolids treatment process that could produce a beneficial soil amendment product, biochar, and remove micropollutants. The objective of this research was to determine the effect of pyrolysis temperature and residence time on the removal of micropollutants in biosolids as well as to characterize the ultimate fate of micropollutants following pyrolysis. Batch pyrolysis experiments were conducted on i) sand samples spiked with micropollutants to quantify the fate and breakdown products in a clean system and on ii) biosolids to determine removal in an actual biosolids matrix. Triclosan, triclocarban, nonylphenol and estradiol were selected for analysis because of their high abundance in biosolids and variable chemical properties. Extraction methods were developed using an Accelerated Solvent Extractor and samples were quantified via liquid chromatography-mass spectrometry. Pyrolysis of biosolids was conducted for 60-minutes and removal of triclosan and triclocarban (to below quantification limit) was achieved at 300 °C and 200 °C, respectively. Substantial removal (>90%) of nonylphenol was achieved at 300 °C, but 600 °C was required to remove nonylphenol to below the quantification limit. The pyrolysis reaction time to remove 90% of micropollutants was later determined to be less than 5 minutes at 500 °C. Micropollutant fate studies revealed that pyrolysis both volatilizes and degrades micropollutants. Micropollutants with high vapor pressure were more likely to volatilize before undergoing transformations. Reductive dehalogenation was a suspected degradation pathway for chlorinated organic compounds as dechlorinated triclocarban products and suspected dechlorinated triclosan products were identified. Results from the pyrolysis experiments demonstrate that micropollutants can be removed (to below quantification limit) from the biochar and transferred to the pyrolysis gas and oil where they are destined for combustion. In summary, pyrolysis is a viable biosolids management technology to mitigate the discharge of micropollutants to the environment when land applying biosolids.

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DEDICATION

I would like to dedicate this thesis to my wife, for her support, encouragement, and insight throughout this project, and to my parents for their continual support of my academic pursuits.

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1 INTRODUCTION

1.1 Motivation

Biosolids are the carbon and nutrient-rich residual solids generated from municipal water resource recovery facilities (WRRFs), and are widely land applied as a soil amendment. Though land application of biosolids offers many benefits, it is increasingly a source of public concern due to the presence of anthropogenic organic compounds, a.k.a micropollutants (MPs). Increased public concern over the land application of biosolids has sparked interest in developing alternative biosolids management practices to land application.

Pyrolysis is an emerging biosolids management technology that captures energy from organics in biosolids and produces a value-added solid product, biochar, that can be used as an adsorbent or as a soil amendment (see Figure 1.1). If MPs are reduced during biochar production, WRRFs would be able to produce a value-added product while minimizing the spread of MPs into the environment. Previous research has not yet explored the impact of pyrolysis on the fate of MPs in biosolids, but pyrolysis has been shown to remove chlorinated pollutants from other waste streams.

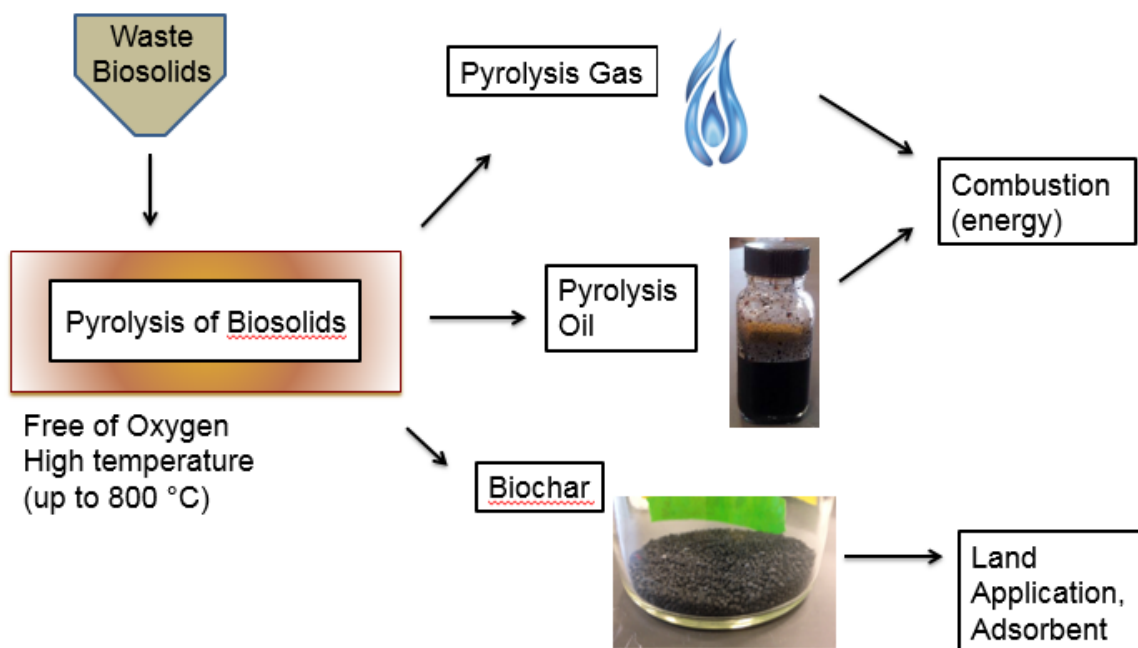


Figure 1.1: Pyrolysis of Biosolids Defined. Pyrolysis in this experiment utilizes dried biosolids that otherwise would be land applied and produces pyrolysis gas, oil, and biochar. Biochar can be land applied or utilized like an activated carbon (adsorbent).

1.2 Pyrolysis of Biosolids

Pyrolysis is the thermal processing of organic substances under oxygen-free conditions. Pyrolysis of biosolids occurs at temperatures between 400 and 800 °C and produces three main products: pyrolysis gas, pyrolysis oil, and biochar. During pyrolysis, MP compounds have three potential outcomes, as depicted in Figure 1.2: (i) they do not undergo any change in chemical structure, (ii) they partially decompose or transform, or (iii) they undergo complete decomposition to single carbon gases. The parent compounds and transformation products may remain in the biochar, or partition to the pyrolysis oil or pyrolysis gas.

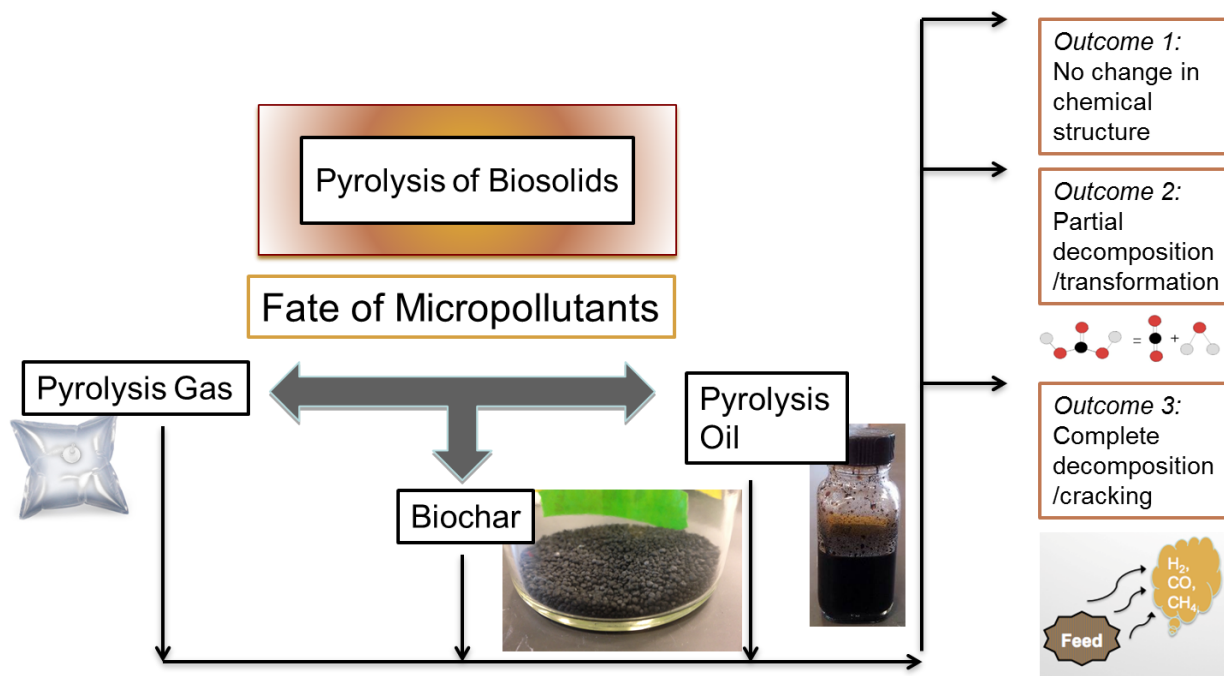


Figure 1.2: Potential fate of micropollutants during pyrolysis. Following pyrolysis of biosolids, MPs could be associated with the pyrolysis gas, pyrolysis oil, or biochar. The MPs could remain as the parent compounds, partially decompose into transformation products, or mineralize to single carbon gases.

1.3 Objectives

The main objective of this research was to determine the impact of pyrolysis on the fate of MPs in biosolids. Pyrolysis is operated at different temperatures and retention times, and there is potential for transformation of MPs during pyrolysis to occur. The 3 specific objectives were to:

- Determine the effects of pyrolysis temperature on the removal of MPs during the pyrolysis of biosolids.
- Determine the effect of pyrolysis reaction time on the removal of MPs during the pyrolysis of biosolids.

- Establish the potential for transformation of MPs during the pyrolysis of biosolids.

1.4 Approach

This research focused on four prevalent MPs found in biosolids. Triclosan (TCS) and Triclocarban (TCC) are antimicrobials and were selected for this research because they are often found in the highest abundance in biosolids and have very different vapor pressures. Nonylphenol (NP) is a detergent metabolite and is also found in high abundance, and Estradiol (E2) is a natural hormone that is a potent estrogen. Experiments were designed to test the stated objectives. In each case, a theoretical hypothesis was formulated and then tested.

Methods were developed to extract the MPs from biosolids and biochar samples and to quantify the MPs in the extracts using liquid chromatography – mass spectrometry. The recovery of MPs using these methods was determined for quality control/quality assurance (QA/QC) purposes. Robust cleaning methods were developed to minimize background contamination of the extraction equipment.

For the pyrolysis experiments, biosolids were introduced into a muffle furnace under anoxic conditions to study the effects of varying temperature and residence time on MP removal. Finally, contrived fate studies where sand was spiked with MPs were conducted to determine if the MPs were destroyed or volatilized during pyrolysis.

1.5 Thesis Structure

The following chapters provide an in-depth description of the research conducted to determine the impact of pyrolysis on the fate of MPs in biosolids. A thorough look at external literature relevant to this project is presented in Chapter 2. The experimental

methods are presented in Chapter 3 to provide specific details regarding how the results were obtained. The experimental results are presented and discussed in Chapter 4. Finally, the conclusions in Chapter 5 provide a summary of the work and its relation to existing literature. Data from experimental results that are presented in figures throughout the thesis are provided in the Appendix.

2 LITERATURE REVIEW

2.1 Biosolids

Biosolids are the residual solids generated from municipal WRRFs. They are rich in carbon and nutrients and are widely applied as a soil conditioner to improve and maintain productive soils and stimulate plant growth (US EPA, 2014). The U.S. Environmental Protection Agency (US EPA) estimates that approximately 6.9 million dry tons of biosolids are produced annually in the U.S, and over half of these biosolids are land applied as a soil amendment (Epstein, 2003). Land application of biosolids takes place in all 50 states to grow agricultural crops; fertilize gardens, golf courses, and parks; and reclaim mining sites (US EPA, 2014). Biosolids reduce the need for chemical fertilizer because they contain nutrients such as nitrogen, phosphorus, and potassium, as well as other trace elements required for the growth of agricultural crops (Cogger, Bary, Kennedy, & Fortuna, 2013; Jaramillo-López & Powell, 2013). Land application of biosolids also enriches the natural carbon cycle by recycling the organic carbon found in biosolids into the terrestrial environment.

Though biosolids offer many benefits as a soil amendment, they are increasingly a source of public concern due to the presence of organic compounds, a.k.a. MPs. For the remainder of this thesis, the term MPs will be used to represent organic compounds generated from anthropogenic sources found at low concentrations ($\leq \mu\text{g/L}$) in the environment (e.g. pharmaceuticals and personal care products [PPCPs], brominated flame retardants (BFRs), plastics and plasticizers, surfactants, and musks and fragrances). A study analyzing biosolids-related articles from newspapers in Florida, Virginia, and California from 1994 to 2004 found that articles were three times more likely to express

concern over undesirable compounds in biosolids than to espouse the benefits of biosolids land application (Goodman, 2006). More recently, communities such as Kern County, CA and Wheatfield, NY, have voted to ban land application of biosolids, while natural and organic grocer Whole Foods instituted a policy banning the sale of produce grown in soil that has received biosolids (eNews Park Forest, 2014; Jerome, 2014; The Bakersfield Californian, 2013). Concern over land application of biosolids is generated from documented and supposed risks posed by the presence of MPs in biosolids. Biosolids that contain less MPs would likely be a more marketable product, which ultimately would allow WRRFs to turn more ‘waste’ into value-added product.

2.2 Micropollutants

Everyday use of chemicals in a variety of consumer products leads to MPs entering the wastewater conveyance system (Andaluri, Suri, & Kumar, 2012; Halling-Sørensen et al., 1998; Michael et al., 2013). MPs discharged to the wastewater conveyance system converge at urban wastewater treatment plants where they are either mineralized, transformed, or unaffected prior to being discharged to the environment with liquid and solid effluents. Many MPs, including PPCPs, steroids and hormones, and surfactants are recalcitrant to conventional wastewater treatment technology (Carballa, Omil, Ternes, & Lema, 2007; Le-Minh, Khan, Drewes, & Stuetz, 2010; US EPA Office of Water, 2010). Several MPs are readily degraded under aerobic conditions found in activated sludge, but, due to their hydrophobic nature, sorb to solids in primary sedimentation and are not readily degraded in anaerobic digesters (Carballa et al., 2007; Chen et al., 2011; Giger, Brunner, & Schaener, 1984). The MPs that sorb to biosolids during wastewater treatment are retained within the solid matrices throughout solids

treatment and land application (Citulski & Farahbakhsh, 2010; Clarke & Smith, 2011; La Guardia et al., 2004; McClellan & Halden, 2010). In fact, over 200 metric tons of MPs are discharged to the environment through the land application of biosolids each year (McClellan & Halden, 2010). In the USEPA National Sewage Sludge Survey, 38 PPCPs were detected in at least one composite biosolids sample; composite samples being made of 21 to 24 biosolids samples from WRRFs across America (McClellan & Halden, 2010). The antimicrobials TCC and TCS were the most abundant MPs detected in the National Sewage Sludge Survey. Other highly abundant compounds in biosolids include NP and natural and synthetic estrogens (La Guardia, Hale, Harvey, & Mainor, 2001; Temes, Andersen, Gilberg, & Bonerz, 2002).

TCS is a widely used antimicrobial agent with cause for concern because it affects a wide variety of organisms (Heidler & Halden, 2007; McAvoy, Schatowitz, Jacob, Hauk, & Eckhoff, 2009). TCS has been detected in municipal WRRF biosolids at concentrations up to 133 mg/kg of dried biosolids (US EPA, 2009). TCS reduces indicators for reproductive success in mosquitofish and tadpoles, substantially affects behavior of fathead minnows and muscle functioning in mice, and alters estrogen metabolism in humans (Jacobs, Nolan, & Hood, 2005; Raut & Angus, 2010; Schultz, Bartell, & Schoenfuss, 2012; Zhang et al., 2012). In addition to its endocrine-disrupting effects, TCS also inhibits the growth of aquatic organisms, including algae, phytoplankton and zebra fish at low $\mu\text{g/L}$ levels (Clarke & Smith, 2011; DeLorenzo & Fleming, 2008; La Guardia et al., 2004; Oliveira, Domingues, Koppe Grisolia, & Soares, 2009; Orvos et al., 2009). TCS is a biologically active compound that was designed to target a broad-spectrum of bacteria. Therefore, its presence in the environment also has

potential to alter environmental microbial communities (McNamara & Krzmarzick, 2013; Stasinakis et al., 2008). Sub-lethal exposure to TCS has been demonstrated to increase cross-resistance to other antimicrobials and potentially the number of antimicrobial resistance genes (ARGs) in a given environment (Chen, Pi, Zhou, Yu, & Li, 2009; Chuanchuen, Karkhoff-Schweizer, & Schweizer, 2003; Ghosh, Cremers, Jakob, & Love, 2011; McMurry, Oethinger, & Levy, 1998; McNamara, LaPara, & Novak, 2014). TCS-resistant bacteria exhibiting resistance to other antimicrobials have been identified in waters impacted by urban WRRF discharge, and it is possible that TCS could select for antibiotic-resistant strains in soils amended with biosolids (Middleton & Salierno, 2013)

TCC is another widely used and widely dispersed antimicrobial agent. TCC has been detected in municipal WRRF biosolids at concentrations up to 433 mg/kg of dried biosolids (US EPA, 2009). TCC was incorporated into personal care products, such as bar soaps, beginning in the 1950s (Miller et al., 2008). While less is known about TCC relative to TCS, TCC toxicity and bioaccumulation studies pertaining to aquatic indicator organisms (fish, crustacea, algae, and microorganisms) demonstrate that TCC can enact acute and chronic toxicity, decrease egg health, cause endocrine disruption, and lower reproductive rates for the target aquatic species (Ahn et al., 2008; Chalew & Halden, 2009; Coogan, Edziyie, La Point, & Venables, 2007; Giudice & Young, 2010; Higgins, Paesani, Abbott, & Halden, 2009; Miller, Colquhoun, & Halden, 2010).

Similar to TCC and TCS, NP is a MP found at mg/kg levels in biosolids. NP is formed when NP ethoxylates (NPEOs), household surfactants, are biodegraded in wastewater treatment plants (Ahel, Giger, & Schaffner, 1994; Giger et al., 1984; Liu, Tani, Kimbara, & Kawai, 2006). NP has been detected in municipal WRRF biosolids at

concentrations over 850 mg/kg of dried biosolids (La Guardia et al., 2001). NP is a xenobiotic compound with endocrine disruption capabilities that can affect the hormonal system of a wide variety of organisms (Soares, Guieysse, Jefferson, Cartmell, & Lester, 2008). NP was linked to developmental abnormalities in freshwater prawns, has a demonstrated ability to alter steroid hormone metabolism in aquatic species, and decreased mice reproduction in a laboratory study. (Baldwin, Graham, Shea, & LeBlanc, 1997; Kyselova, Peknicova, Buckiova, & Boubelik, 2003; Sung & Ye, 2009). NP is also an estrogenic compound, which has detrimental consequences on fish population and reproduction (Kidd et al., 2007; Masuyama et al., 2014; Vajda et al., 2008). The EU has banned the use and production of NPEOs due to the many harmful effects of its degradation products, and NPEOs are strictly monitored in many other countries such as Canada and Japan (Soares et al., 2008). Increasing concern regarding the presence of NP in biosolids could result in additional bans or restrictions on the use of NPEOs within the EU or elsewhere (McNamara et al., 2012).

In addition to chemicals used in consumer products, hormones excreted from humans and animals also pose a risk to environmental systems, and of specific concern are environmental estrogens. Estrone (E1), E2, estriol (E3), and 17 α -ethynylestradiol (EE2) are common estrogens that end up in wastewater treatment plants and have documented impacts on environmental systems. In municipal WRRF biosolids, E1 and E2 have been detected at up to 0.037 mg/kg and 0.049 mg/kg, respectively, and EE2 up to 0.017 mg/kg of dried biosolids (Temes et al., 2002). Environmental estrogens can imbalance many different organisms' innate endocrine regulatory system, including humans, at concentrations as low as the ng/L level (Colborn, Saal, & Soto, 1993;

Harrison, Holmes, & Humfrey, 1997). Research has demonstrated sexual inhibition or reversion in a number of aquatic species, including, turtles, trout, and minnows, by the presence of natural estrogens (Irwin, Gray, & Oberdo, 2001; Khanal et al., 2006; Panter, Thompson, & Sumpter, 1998; Tabata et al., 1997). Endocrine-disruption indicators in white suckers (*Catostomus commersoni*), consistent with exposure to estrogenic wastewater contaminants, were identified in white suckers downstream of a WRRF outfall (Vajda et al., 2008). Kidd et al. (2007) demonstrated that seven years of chronic exposure to low concentrations (5-6 ng/mL) of EE2 led to feminization of male fathead minnows to such an extent that the species neared extinction in the lake.

2.3 Current Biosolids Management Strategies

Increased public concern over the land application of biosolids has sparked interest in developing alternative biosolids management practices to land application (Andrade et al., 2014; Epstein, 2003; National Research Council, 2002; Reimers et al., 2013). Landfilling and incineration are two typical disposal practices for biosolids that prevent land application, but are falling out of favor (North East Biosolids and Residuals Association, 2007; US EPA, 1993). Disposal to landfills is increasingly seen as unattractive because it fails to recycle the carbon and nutrients in biosolids. Incineration also has limited application for the same reason, as well as the fact that it commonly operates at a net negative energy balance due to the typically high moisture content in biosolids (Wang et al., 2008). Along with valuable nutrients, biosolids from secondary and primary settling tanks contain a volatile organic fraction that yields energy in anaerobic digestion. In anaerobic digestion, bacteria break down organics in biosolids in an oxygen-free environment, producing methane that can be recovered to generate

electricity (Zaks et al., 2011). However, not all of the carbon available for energy is captured during anaerobic digestion (Wang et al., 2008). Additionally, many MPs, including PPCPs, estrogenic compounds, and NP, are persistent during anaerobic digestion (Carballa et al., 2007; Citulski & Farahbakhsh, 2010; Hospido et al., 2010; Le-Minh et al., 2010). For biosolids management strategies to be sustainable, energy capture and nutrient recovery should be optimized while the impacts of MPs on the environment are minimized.

2.4 Pyrolysis as Biosolids Treatment

Pyrolysis is an emerging biosolids management technology that captures energy from organics in biosolids and produces a value-added solid product, biochar, which can also be used as a soil amendment and adsorbent. Pyrolysis is the thermal processing of organic substances under oxygen-free conditions, and occurs at temperatures between 400 and 800 °C. Three main products are produced during pyrolysis: pyrolysis gas, pyrolysis oil, and biochar (Karayildirim, Yanik, Yuksel, & Bockhorn, 2006). A portion of the pyrolysis gas contains heavier organics that can be condensed, forming pyrolysis oil that is convenient to store and has potential for refining into a usable fuel (Marker, Felix, Linck, & Roberts, 2011). Pyrolysis gas requires less process configuration and refining than pyrolysis oil for use in spark ignition or compression ignition engines (Hossain & Davies, 2013).

Biochar can be used as an adsorbent for wastewater and remediation schemes, and as a soil conditioner. Chen and Chen (2009) demonstrated that biochar made from orange peels removes nonpolar (naphthalene) and polar (1-naphthol) hydrophobic organic compounds from water. Biochar can also be used to sorb pesticides and heavy metals

from wastewater (Biswas et al., 2008; Li et al., 2008; Zheng, Guo, Chow, Bennett, & Rajagopalan, 2010). Biosolids were demonstrated as suitable feed for the production of an effective biochar adsorbent, based on sorption tests analyzing the capacity of biosolids-derived biochar to remove two synthetic dyes (Tracid orange GS and Direct fast turquoise blue GL) from an aqueous solution (Wen et al., 2011). Zhang, Nriagu and Itoh (2005) analyzed biochar production from biosolids using H_2SO_4 , H_3PO_4 , and ZnCl_2 as chemical activation reagents and determined the application was effective and practical for utilization in industrial wastewater treatment for mercury removal. Biochar is also a chemically stable organic carbon source that is both an effective soil amendment and, upon land application, a means to increase long-term soil carbon sequestration (Hossain, Strezov, Chan, & Nelson, 2010; Yao, Gao, Chen, & Yang, 2013). If MPs are reduced during pyrolysis production, WRRFs could produce a value-added product while minimizing the spread of MPs into the environment.

2.5 Pyrolysis for Organic Pollutant Control

Previous research has not yet explored the impact of pyrolysis on MPs in biosolids, but the impact of pyrolysis on other organic compounds has been investigated. Pyrolysis can eliminate organic pollutants from solid phases by volatilization and decomposition reactions. Bridle, Hammerton, and Hertle (1990) operated a pilot-scale pyrolysis reactor at 450 °C for 30 minutes using municipal WRRF biosolids as a feed. The authors demonstrated removal of polychlorinated biphenyls (PCBs) and hexachloronene (HCB) from average concentrations in the biosolids of 1.3 and 0.32 mg/kg, respectively, to non-detectable levels (less than 0.004 and 0.012 mg/kg, respectively) in the biochar. Hu et. al. (2007) operated a lab-scale pyrolysis reactor at

800 °C at retention times of 30, 60, and 90 minutes that achieved removal of dioxins and PCBs from contaminated sediment at removal efficiencies greater than 99.9%. The authors of both studies stated partial and complete decomposition of the organic pollutants were probable, but were unable to demonstrate proof of the organic pollutant decomposition. Bridle, Hammerton, and Hertle cited work conducted by Bayer (1990) demonstrating reductive dehalogenation of chlorinated dioxins occurs under pyrolytic conditions. The authors reasoned that the pyrolysis temperature of 450 °C, above the boiling point of HCB and PCB, would transfer these compounds into the vapor state of the reactor. The gas, containing a hydrogen and carbon dioxide fraction, would generate a reductive environment for reductive dehalogenation to occur. Since HCB and PCB are regarded as thermally stable compounds (in an oxidative environment) the authors postulated that their results were indicative of what would be achieved for other less stable organic compounds. Hu et al. (2007) conducted a fate study of dioxins within their pyrolysis system and recovered 99.5% of the dioxins originally present in the raw sediment in the pyrolysis gas and pyrolysis oil. Though the authors stated that the dioxins could undergo decomposition at 800 °C, the dioxins likely evaporated and escaped the system before high enough temperatures were reached for dioxin decomposition. This result may be attributed to the 1,000 ml/min flow of nitrogen gas blown through the system.

Since these studies, researchers have continued to explore dehalogenation under pyrolytic conditions (Hinz et al., 1994; Hornung, Balabanovich, Donner, & Seifert, 2003; Zanaveskin & Averyanov, 1998). Various pyrolysis designs to induce dehalogenation have been developed for pyrolysis of waste electrical and electronics equipment.

Miskolczi et al. (2008) designed a lengthened tube reactor to extend the residence time of organobromines in the hot zone of the pyrolysis reactor. Under this system a greater amount of organic bromine was converted into non-toxic inorganic bromine products compared to typical fluidized bed and fixed bed pyrolysis reactors. Pyrolysis in conjunction with zeolite and metal catalysts has been found to improve dehalogenation of brominated organics during pyrolysis (Blazsó & Czégény, 2006; Brebu et al., 2005). Other research has focused on conducting catalytic hydrodehalogenation methods to remove halogens in pyrolysis oils when no dehalogenation is conducted in the pyrolysis process. Hornung et. al. (2003) found that pyrolysis conducted at a temperature of 350 °C at a residence time of 20 minutes was optimal for performing catalytic hydrodehalogenation of brominated phenols using polypropylene as a reductive source.

Based on the above work, it was hypothesized that MPs, especially chlorinated organics like TCS and TCC, would undergo transformation reactions within pyrolysis. It was predicted that the vapor pressure (VP) of each compound would play an important role, as the primary transformation mechanisms would likely correlate to the retention time of the MPs within the hot zone of the reactor. Compounds having a larger VP would be more likely to volatilize and exit the reactor quickly, avoiding the retention time and temperature required for transformation reactions. Also, a reductive source would be required for reductive dehalogenation of the chlorinated organics.

2.6 Summary of Research Needs

Existing literature suggests that organic MPs are likely to be removed from biosolids during pyrolysis, but to what extent and their ultimate fate remain unknown. If pyrolysis produces a biochar product that is void of MPs, pyrolysis of biosolids will offer

great potential as a biosolids management technology in its production of a value-added product that mitigates risks associated with land application of MPs. In this study, research was conducted to determine the effect of pyrolysis temperature and residence time on the removal of MPs in biosolids during pyrolysis as well as to characterize the ultimate fate of the MPs within the system. Based on the ability of pyrolysis to eliminate organic pollutants from biosolids and contaminated sediment, it is hypothesized that pyrolysis substantially removes MPs from the solid phase and produce biochar that has significantly less MPs than biosolids.

Three hypothesis were tested that correspond to the three research objectives:

Objective 1. Determine the effects of pyrolysis temperature on the removal of MPs during the pyrolysis of biosolids.

Hypothesis: An increase in pyrolysis temperature (above the melting point of the MPs) will remove MPs from the solid product during pyrolysis.

Objective 2. Determine the effect of pyrolysis reaction time on the removal of MPs during the pyrolysis of biosolids.

Hypothesis: Substantial removal of MPs from the solid product during the pyrolysis of biosolids happens rapidly (at less than 10 minutes of pyrolysis).

Objective 3. Establish the potential for transformation of MPs during the pyrolysis of biosolids.

Hypothesis: Pyrolysis will partially or fully decompose MPs and will be more likely to decompose those MPs that reside in the reactor for the longest amount of time.

3 METHODOLOGY

3.1 Micropollutant Removal from Biosolids

3.1.1 Impact of Temperature on Micropollutant Removal

Batch pyrolysis experiments were performed to determine the impact of pyrolysis temperature on the removal of MPs from biosolids. Biosolids were a heat-dried blend of anaerobically digested biosolids and waste activated sludge biosolids. Biosolids pellets were approximately 2 millimeters in diameter. Experiments were performed in triplicate using replicate flasks; approximately 1.5 grams of biosolids were added to 50 mL flasks for each temperature step experiment. The flasks were sparged for 5 minutes with argon, covered with aluminum foil, and then introduced into a Fischer-Scientific Isotemp® Muffle Furnace. After sparging, the three flasks containing biosolids were heated at 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, or 600 °C for one hour. A time of one hour was selected so as not to limit the removal of micropollutants by retention time, as removal of MPs was expected to occur at a retention time of less than an hour. Three flasks also underwent the sample preparation described above, but were held at room temperature (22 °C) for an hour as a control. The resulting biochar products were extracted and analyzed for TCS, TCC, NP and E2.

The ability of the experimental setup to maintain anaerobic conditions within the flask was validated. Sparged and un-sparged flasks containing biosolids were introduced into the muffle furnace and the solid product generated was evaluated. The product generated without having been sparged differed dramatically in color (it turned orange) from the biochar (black color), indicating that the un-sparged product had undergone combustion, while the biochar had not. This confirmed that if oxygen was available,

combustion of the biosolids would occur, but the sparging method prevented combustion, indicating that anaerobic conditions were maintained.

3.1.2 Impact of Time on Micropollutant Removal

Batch pyrolysis experiments were performed to determine the impact of pyrolysis reaction time on the fate of MPs in biosolids. Biosolids utilized as feed were as described above, and samples were prepared in the same manner. Experiments were performed in triplicate; flasks were heated at 500 °C for 2.5, 5, or 10 minutes. Three flasks also underwent the sample preparation described above, but were held at room temperature (22 °C) for an hour as a control. The resulting biochar products were extracted and analyzed for TCS, TCC, NP and E2.

3.2 Micropollutant Fate Studies

A separate set of laboratory-scale pyrolysis experiments were performed to determine if the MPs were transferred from the biosolids to the pyrolysis gas and pyrolysis oil. A stainless steel reactor was loaded with sand and spiked with 1 mg each of TCS, TCC, NP, and E2 in a stock solution of methanol. The reactor was left overnight for the methanol to evaporate. Sand was used as an inert carrier so that the MPs were the only organic compounds in the pyrolysis system, enabling greater accuracy in MP detection. Spiking the sand with a methanol solution partitioned the MPs to the sand more similar to how they would partition to biosolids in a WRRF, as compared to adding dry MP compounds directly. The reactor was sealed and placed in a Lindberg tube furnace (240 volts, maximum temperature 1,200°C). For each pyrolysis run, the furnace was kept at 500°C for two hours. Argon gas was passed through the reactor at a flow rate of 60 ml/min through stainless steel piping leading into the reactor. Stainless steel piping

leading out of the reactor was connected to norprene tubing leading into impingers, each filled with methanol. The gas traveling through the reactor transferred the MPs that had volatilized into the impingers, where they partitioned into the methanol. The experimental setup is illustrated in Figure 3.1.

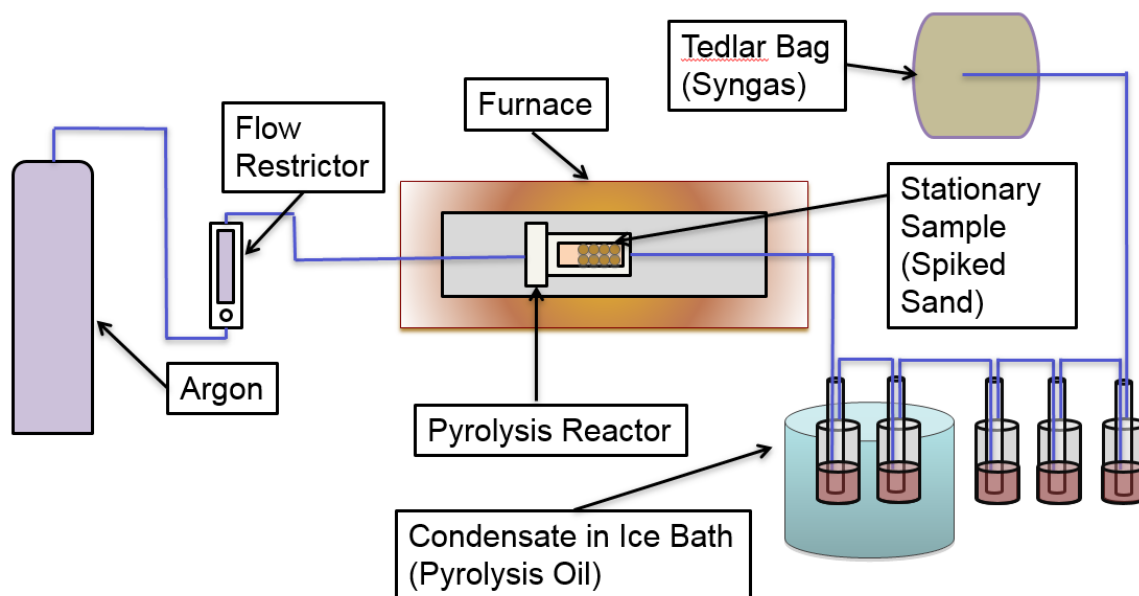


Figure 3.1: Micropollutant fate study experimental setup. Stainless steel piping introduces argon into pyrolysis reactor and carries volatilized micropollutants into impingers to partition to methanol.

For the first experiment, two impingers, containing 20 and 100 mL of methanol each (exact volume determined gravimetrically), were utilized. To ensure that all the MPs that had volatilized partitioned to the methanol three more impingers were added for the next two experiments, each with approximately 100 mL of methanol (exact volume determined gravimetrically). MPs captured in methanol represent the MPs that would be present in the pyrolysis oil or pyrolysis gas following pyrolysis of biosolids. The first two impingers were situated in an ice bucket to cool the gas and capture the volatilized MPs. After the pyrolysis run was complete, the system was left to cool overnight. The

next day the sand was extracted and analyzed for the presence of TCS, TCC, NP, and E2. The stainless steel piping and norprene tubing leading to and from the reactor in the pyrolysis system was rinsed to recover MPs that may have settled in the piping and tubing. Several rinses utilizing 15 mL of methanol were conducted after the first pyrolysis run to determine the appropriate volume of methanol required to capture the MPs within the piping and tubing. It was found that 15 mL and 90 mL of methanol were adequate to rinse the piping and tubing to and from the reactor, respectively. Samples from the impingers and piping and tubing rinse were analyzed for the presence of TCS, TCC, NP, and E2. In total, three replicate fate experiments were performed.

Two control runs were conducted to ensure that removal of MPs was from the pyrolysis process and not experimental artifacts. A positive control was conducted to validate that MPs would still be present in the sand after two hours when no heat was applied. The pyrolysis system was setup as described above, but no heat was applied. A negative control was conducted in which the pyrolysis system was setup as described above, except that no MPs were spiked into the sand. For this control, the furnace was kept at 500 °C for two hours. For the positive and negative control, the typical rinsing and analysis was performed on the piping and tubing to and from the reactor, the methanol in the impingers, and on the sand after the reaction to validate that any removal from pyrolysis experiments was due to pyrolysis and not other abiotic removal mechanisms such as sorption or volatilization.

3.3 Sample Processing and Quantification

3.3.1 ASE Extraction Method

A solids extraction method was developed to ensure optimal extraction efficiency of TCS, TCC, NP and E2 using an accelerated solvent extractor (ASE). Extraction methods were developed on a Dionex ASE 350, shown in Figure 3.1 below.



Figure 3.2: Dionex ASE 350 Accelerated Solvent Extractor

Relevant ASE literature was reviewed to identify adequate operational parameters for MP extraction. The operational parameters selected for use throughout the experiment were: oven temperature of 60 °C, a pressure of 1500 psi, an oven heating time of 5 minutes followed by a static time of 5 minutes, and a flush volume of 60% of the extraction cell volume. Five ASE methods were tested to determine the optimal recovery of TCS, TCC, NP and E2 from sand during extraction. Solvent type (methanol or dichloromethane [DCM]) and extraction cycles (1 or 2) were varied between five tests;

temperature and pressure were constant between the five methods tested, as described above. The five ASE cycles tested were: (1) single extraction cycle with DCM, (2) double extraction cycle with DCM, (3) double cycles with a 1:1 mixture of DCM and methanol, (4) single extraction cycle with methanol, and (5) double extraction cycles with methanol. One ml of a stock solution containing 400 µg/ml of TCS, TCC, NP, and E2 in methanol was spiked into sand placed in an ASE extraction cell so that 400 µg of each MP was present in each cell. The extraction cells were then left to sit overnight to evaporate the methanol while the MPs remained in the sand. On the next day, the cells were filled with sand and capped. This spike was conducted in duplicate for each extraction method. The extraction collection cells were measured gravimetrically to determine the volume of the extract. Because the LC-MS/MS method requires a 1:1 ratio of methanol and deionized (DI) water, an aliquot from each of the DCM and DCM:methanol extraction vials was removed after the extraction process to undergo a blow down procedure with air to volatilize the DCM; MPs were re-suspended in approximately 2 mL of methanol. The exact volume of methanol suspension was measured gravimetrically. All samples were analyzed by LC-MS/MS to determine which solvent and run cycle generated the greatest recovery with the smallest standard deviation between duplicates. The optimal extraction method was selected and used for subsequent experiments. Both the sand and extraction collection vials used in this experiment (and all consequent extractions) had been baked at 550 °C for four hours prior to use to minimize background contamination.

3.4 Quality Assurance/Quality Control

3.4.1 Spike and Recovery on Biosolids and Biochar

Spike-and-recovery experiments were conducted on biosolids and biochar samples to determine recovery efficiencies of TCS, TCC, NP, and E2 in biosolids and biochar. A central goal of this project was to determine the impact of pyrolysis on the fate of MPs; therefore, spike-and-recovery experiments were conducted to ensure that an absence of MPs in biochar products could be attributed to pyrolysis, as opposed to an experimental artifact, such as poor extraction recovery. An aliquot of biosolids was divided into two portions, with one portion sampled as the “influent” to pyrolysis and the other portion of biosolids undergoing pyrolysis at 500 °C to produce biochar, or “effluent”. The biosolids feed sample was then divided evenly into six sub-samples and the same was done for the biochar product. Then 10 µg each of TCS, TCC, NP, and E2 were spiked onto three of the sub-samples in the biosolids sample group and three of the sub-samples in the biochar sample group. Spiking occurred on solid samples placed in a glass tube previously baked at 550 °C using a MP stock solution. The spiked samples sat overnight to allow the solvent carrier to evaporate while the MPs remained. The six biosolids feed sub-samples (three spiked, three not-spiked) and six biochar sub-samples (three spiked, three not-spiked) then underwent ASE extraction, and the extracts were analyzed for TCS, TCC, NP and E2 concentrations using an LC-MS/MS. Recovery efficiencies of TCS, TCC, NP and E2 were calculated for both biosolids and biochar by subtracting the average mass of MPs detected in samples that had not been spiked by the amount of MPs detected in the spiked samples. This value was divided by the mass of MPs that were spiked into the samples.

$$\text{Recovery efficiency} = \frac{\text{Mass of MP in sample} - \text{Mass of MP in baseline sample}}{\text{Mass of MP spiked into sample}} * 100\%$$

3.4.2 Extraction Control with Crushed Samples

A set of batch pyrolysis experiments were conducted to ensure that MP removal results were not altered by extraction difficulties from the complex matrices of the solid samples. The solids samples from the temperature and time experiments were not ground before extraction. An additional experiment was performed to determine if grinding and crushing the biosolids and biochar samples would result in an increase in MP concentration. Three biosolids samples and three biochar samples that had been pyrolyzed at 500 °C for 60 minutes were ground with a mortar and pestle for 15 minutes. After grinding, the samples were extracted and analyzed for TCS, TCC, NP and E2. Results were compared to those obtained from the temperature pyrolysis experiments to determine if MPs were trapped in samples that were not ground.

3.4.3 ASE Extraction Cell Equipment Cleaning Procedure

A robust cleaning procedure was developed to minimize background concentrations and cross-contamination between extractions. Simple cleaning methods proved to be insufficient in removing background contamination between extractions. Five cleaning methods, ranging in sophistication, were performed on ASE extraction cells that previously had been used to extract solid samples containing TCS, TCC, NP, and E2 to determine how many cleaning steps were required for reliable results. The first stage consisted of simply rinsing the components with DI water, and the next four methods consecutively built upon the water rinse in complexity. These methods are shown in Table 3.1.

Table 3.1: ASE Cell Cleaning Procedures Tested

<i>Method 1</i>	Triple rinse ASE cell bodies and end cap components with DI water
<i>Method 2</i>	Method 1 + triple rinse ASE cell bodies and end cap components with methanol
<i>Method 3</i>	Method 2 + sonicate ASE end cap components for ten minutes in acetone then triple rinse ASE end cap components with methanol
<i>Method 4</i>	Method 3 + bake equipment used to clean ASE cells at 550 °C for four hours
<i>Method 5</i>	Method 4 + sonicate ASE cell bodies and end cap components for ten minutes in acetone then triple rinse ASE cell bodies and end cap components with methanol

After the ASE extraction cells had undergone one of the five cleaning procedures, the ASE extraction cells underwent extraction. The extracts were analyzed on the LC-MS/MS for the presence of TCS, TCC, N2, and E2 and the optimal cleaning method was selected. Once a cleaning method was established, each subsequent round of extractions performed included a sand blank extraction that underwent the same cleaning procedure as the samples to determine background contamination for each set of extractions.



Figure 3.3: Cleaning method was developed to clean the ASE cell between runs; an ASE cell is shown on top with one cell deconstructed.

3.5 Quantification with LC-MS/MS and LC-MS

A method was developed to quantify TCS, TCC, NP, and E2 using an LC-MS/MS at the University of Wisconsin-Milwaukee Zilber School of Public Health Aquatic and Environmental Microbiology and Chemistry Lab. This method was used to determine the ASE extraction method, ASE extraction cell equipment cleaning procedure, spike and recovery results for biosolids and biochar, and the impact of temperature on MP removal from biosolids. TCS, TCC, NP, and E2 were analyzed in a single LC-MS/MS run operating in negative mode with electrospray ionization. LC-MS/MS samples were analyzed in a 1:1 mixture of methanol and DI water in 1.5 mL amber screw thread vials. Detection methods were developed on an AB Sciex 4000 QTRAP coupled to a Shimadzu Prominence HPLC. Compounds were separated using a Phenomenex Luna C18 column in a linear gradient of 70% to 100% methanol over 20 minutes using a total flow of 0.3 mL/min. Identification of target analytes is based on the presence of two transition ions eluting from the column at the same retention time as standards. Quantification is based on a linear regression analysis of sample peak area to that of five to seven standard samples. Transition ions for TCS are 288 m/z parent ion to daughter ions 35 and 37 m/z. Transitions ions for TCC are 312 m/z parent ion to daughter ions 160 and 126 m/z. Transitions ions for NP are 219 m/z parent ion to daughter ions 133 and 147 m/z. Transitions ions for E2 are 271 m/z parent ion to daughter ions 145 and 183 m/z. Detection limits for TCC and TCS using a signal-to-noise ratio of 3:1 are 0.05 ug/L and 0.5 ug/L or 1 and 10 pg on column, respectively. Quantification limits for TCS, TCC, NP, and E2 using a signal-to-noise ratio of 10:1 are 10ug/L for all compounds.

After purchasing a LC-MS/MS at the Marquette University Water Quality Center part-way through the project, a method was developed to quantify TCS, TCC, NP, and E2 using this piece of equipment. This method was used to determine the impact of time on MP removal, extraction results from crushed control samples, and MP fate studies. TCS, TCC, NP, and E2 were analyzed in a single LC-MS/MS run operating in negative mode with electrospray ionization. LC-MS/MS samples were analyzed in a 1:1 mixture of methanol and DI water in 1.5 mL amber screw thread vials. Detection methods were developed on a Shimadzu LCMS-2020. Compounds were separated using a Phenomenex Luna C18 column in a linear gradient of 80% to 100% methanol over 13 minutes using a total flow of 0.4 mL/min. Identification of target analytes is based on the presence of parent compounds eluting from the column at the same retention time as standards. Quantification is based on a linear regression analysis of sample peak area to that of five to seven standard samples. The mass to charge ratio used for TCS is 288 m/z, 312 m/z for TCC, 219 for NP, and 271 m/z for E2. Quantification limits for TCS, TCC, NP, and E2 using a signal-to-noise ratio of 10:1 are 10 ug/L for TCS and TCC and 25 ug/L for NP and E2.

4 RESULTS AND DISCUSSION

4.1 Method Development and Data Quality Assurance/Quality Control

The goal of this research was to determine the impact of pyrolysis on the fate of MPs in biosolids. Prior to conducting pyrolysis experiments, methods were developed for extracting biosolids, and the recovery of MPs using these methods was determined for quality control/quality assurance (QA/QC) purposes. Due to the low concentrations (ng/mL) analyzed in this research and the ubiquitous presence of some MPs, such as TCS and TCC, in common commercial products, robust cleaning methods were developed to minimize background contamination.

4.1.1 ASE Extraction Method

ASE methods were varied to determine the optimal extraction of TCS, TCC, NP and E2. Solvent type (methanol or DCM) and extraction cycles (1 or 2) were varied between the five tests; temperature and pressure were constant between the five methods tested, as described in Section 3.2.1. Figures 4.1-4.5 illustrate the average extraction efficiency achieved for each solvent configuration when the ASE extractions were performed in duplicate runs on sand spiked with TCS, TCC, NP and E2.

The extraction efficiencies when using dichloromethane as the solvent at one extraction cycle are shown in Figure 4.1. Due to the low E2 recovery of $25\% \pm 13\%$ this method was not selected.

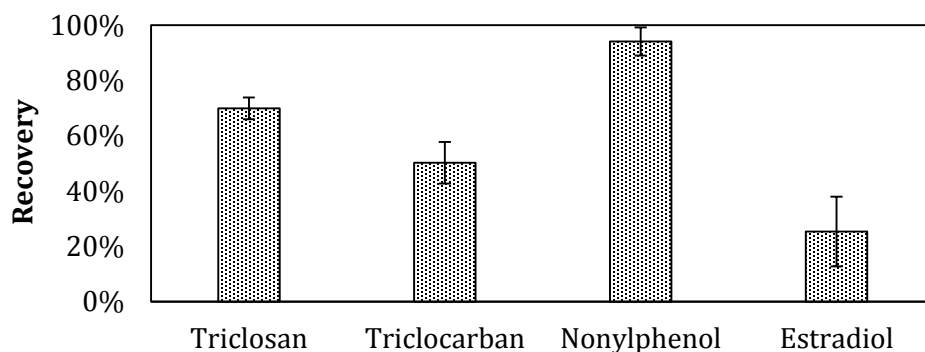


Figure 4.1. Extraction efficiency using dichloromethane and one extraction cycle. Vertical bars represent average recovery and the error bars represent the standard deviation between duplicate runs.

The extraction efficiencies when using dichloromethane as the solvent at two extraction cycles are shown in Figure 4.2. TCS, TCC, and NP recovery were similar to the one-cycle method, and while E2 recovery improved, this method was not selected because of the low E2 recovery. The NP recovery is greater than 100% because the results indicated more NP was in the sample than what was spiked into the sample, indicating inaccuracy in the method.

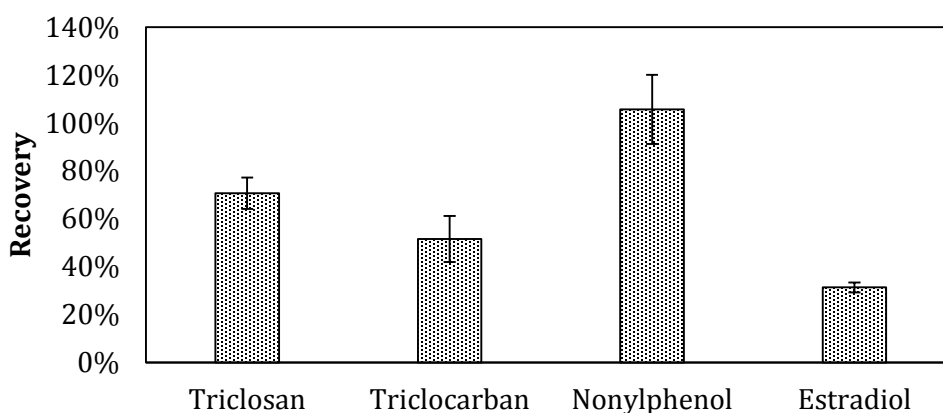


Figure 4.2: Extraction efficiency using dichloromethane and two extraction cycles. Vertical bars represent average recovery and the error bars represent the standard deviation between duplicate runs.

The extraction efficiencies when using dichloromethane and methanol in a one to one ratio as the extraction solvent mixture at two extraction cycles are shown in Figure 4.3. This method improved TCC recovery up to 77%, but the TCC standard deviation was 24%. TCS recovery was only 30%, and no E2 was recovered. Overall recovery efficiencies varied greatly between compounds and reproducibility was poor.

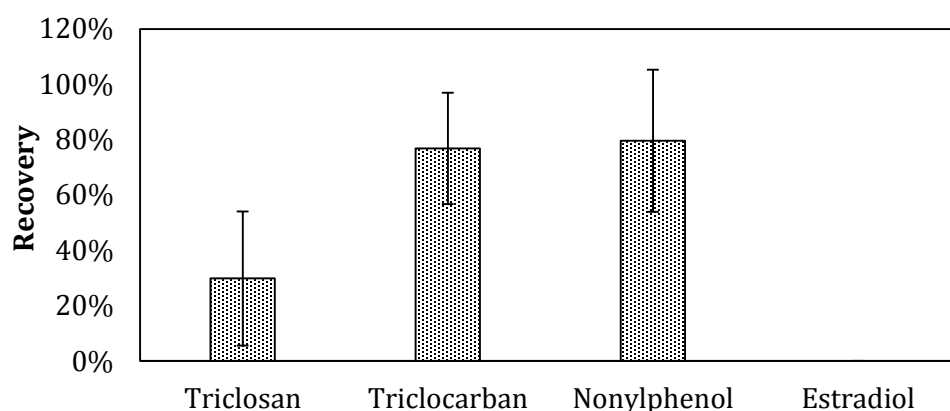


Figure 4.3: Extraction efficiency using 1:1 methanol:dichloromethane at two cycles. Vertical bars represent average recovery and the error bars represent the standard deviation between duplicate runs.

The extraction efficiencies when using methanol as the solvent at one extraction cycle are shown in Figure 4.4. Average recovery for TCS, NP, and E2 was 70% or greater, but the standard deviations for recovery on these three compounds was at least 15%. TCC recovery was $44\% \pm 16\%$. While this method would suffice for recovering MPs, two cycles of methanol were attempted to optimize this method.

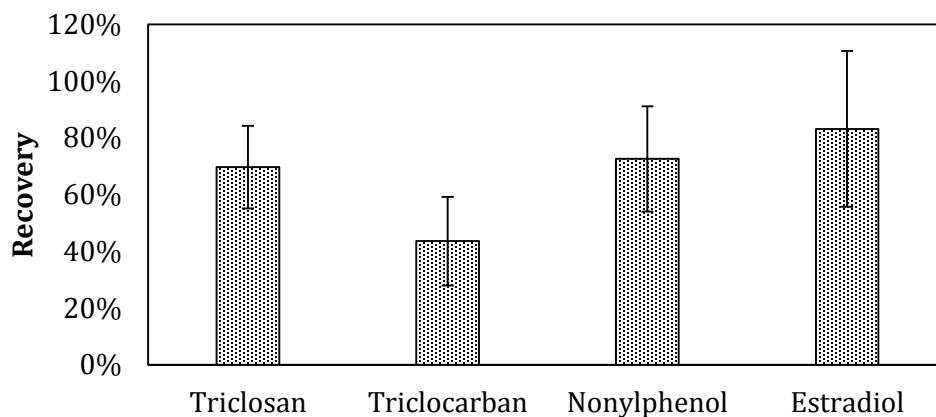


Figure 4.4: Extraction efficiency using methanol at one cycle. Vertical bars represent average recovery and the error bars represent the standard deviation between duplicate runs.

The extraction efficiencies when using methanol as the solvent with two extraction cycles are shown in Figure 4.5. For this method, recoveries for each MP were greater than 50%. Furthermore, this method proved to be more reproducible as the relative standard deviation for the recovery of each compound was less than 10%. This extraction method provided the optimal combination of extraction efficiency and reproducibility and was selected as the extraction method for the subsequent experiments.

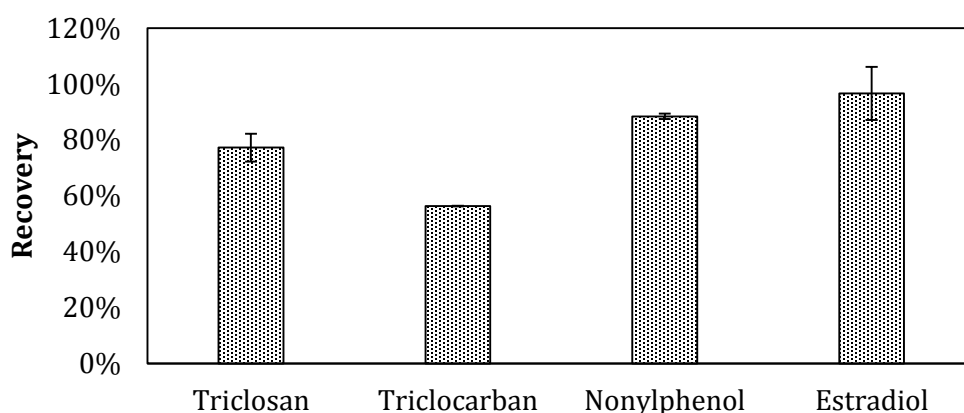


Figure 4.5: Extraction efficiency using methanol at two cycles. Vertical bars represent average recovery and the error bars represent the standard deviation between duplicate runs.

4.1.2 ASE Extraction Cell Equipment Cleaning Procedure

A robust cleaning procedure was developed to minimize background concentrations and cross-contamination between extractions. Five different cleaning methods were tested. The average concentrations of each MP following 1 of the 5 cleaning procedures of the ASE cells are shown in Figure 4.6. In theory all concentrations should be zero because these are sample blanks; any MPs present indicates contamination of the blank sample. The robustness of the cleaning method increased from methods 1 to 5 (See Table 3.1 for description), with each cleaning method adding one additional step. The background contamination levels decreased as the robustness increased. The first cleaning method, in which the ASE extraction cell equipment only received a triple rinse with DI water, resulted in MP detects in the extract ranging from 9.3 to 48 ng/mL. The second cleaning method, which included a triple rinse of the ASE extraction cell equipment with methanol after the DI rinse still had MPs in the blank ranging from 4.9 to 19 ng/mL. The third cleaning method, which added to the second method a sonication step of the ASE end cap components (excluding the ASE cell body) for ten minutes in acetone followed by a triple rinse of methanol for the ASE end cap components, still yielded positive detects of TCS, ESD, and NP. The fourth cleaning method, which built on the third cleaning method by using laboratory equipment that had been baked in a Fischer Scientific Isotemp® Muffle Furnace, resulted in detects of NP and ESD. The fifth cleaning method, which included sonicating the ASE cell bodies and rinsing them with methanol, eliminated TCC, TCS, and ESD in the blank and only NP was detected at 6.6 ng/mL.

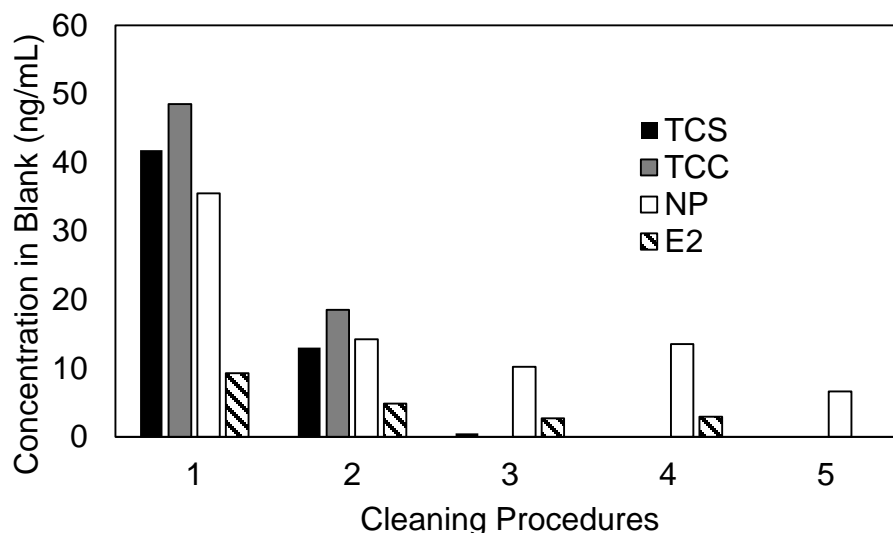


Figure 4.6: Impact of cleaning steps on ASE blank extraction. Vertical bars represent micropollutant concentration in extract between duplicate runs. See Table 3.1 for description of cleaning methods 1-5.

Method 5 was selected for use to clean the ASE extraction equipment for all experiments. Cleaning methods 1, 2, and 3 demonstrated a decreasing trend in MP background contamination as the cleaning methods increased in sophistication and effort. Differences in MP background contamination between methods 3 and 4 were negligible, but a further reduction in MP background contamination was observed in method 5. While NP was still detected in method 5, the levels were substantially lower than levels detected in actual samples (on the order of 100's of ng/mL). After consistent use of cleaning method 5, background contamination of ASE cells was negligible for the actual experiments.

4.1.3 Spike and Recovery on Biosolids and Biochar

Recovery of TCS, TCC, NP, and E2 from biosolids and biochar samples were calculated from spike and recovery experiments. The recovery efficiency results (Figure 4.7) indicate that the MPs can adequately be detected on both the biosolids and biochar

samples. Recovery efficiencies were greater for biosolids samples than for biochar samples, but MPs were still detected in all of the biochar samples. The recovery of TCS, TCC, NP and E2 was 70% or greater in biosolids samples, and the relative standard deviation for each of these recoveries was less than 20%. The recovery of MPs in biochar was between 30% and 70%, and the relative standard deviation was between 5% and 40%. The low recoveries in biochar indicate that a decrease of MPs in biochar of about 50% could not be safely attributed to pyrolysis, but high removals (>90%) would very likely be due to pyrolysis.

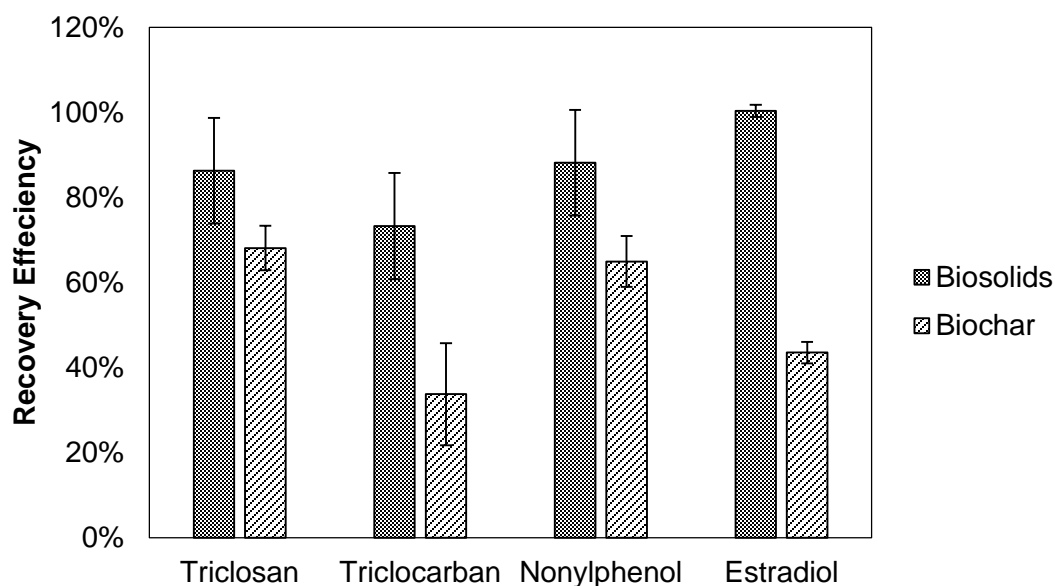


Figure 4.7. Micropollutant Recovery Efficiency from Biosolids and Biochar. Vertical bars represent average recovery and the error bars represent the standard deviation between triplicate runs.

4.2 The Impact of Pyrolysis on Micropollutant Removal from Biosolids

4.2.1 Impact of Temperature on Micropollutant Removal

Pyrolysis temperature greatly impacted the removal of MPs from biosolids.

Pyrolysis experiments were carried out at temperatures ranging from room temperature

controls (22 °C) to 600 °C. MPs were removed at 300 °C and above. E2 was not detected at quantifiable levels in the biosolids feed and was not analyzed in this section. Figures 4.8-4.10 illustrate the effect of a given temperature under pyrolytic conditions on the presence of TCS, TCC, and NP in the biochar.

4.2.1.1 Impact of Temperature on TCS Removal

Removal of TCS (to below quantification limit) was achieved at a temperature of 300 °C. The impact of temperature on TCS concentration in the solid product is shown in Figure 4.8. The average concentrations of TCS in the biosolids samples was 2.40 mg/kg \pm 0.58 mg/kg. The large standard deviation of TCS concentrations at temperatures less than or equal to 200 °C is likely due, in part, to the inherent variability of MPs found in biosolids. While large variability persists at lower temperatures, at 300 °C and above, variability is minimized along with TCS concentrations. All biochar samples obtained from pyrolysis at 300 °C, 400 °C, 500 °C, and 600 °C did not contain TCS at levels at or above the quantification limit (0.08 mg/kg for all samples, except those obtained at 500 °C and 600 °C, for which the quantification limit was 0.10 mg/kg). In short, pyrolysis removes TCS at a minimum temperature of 300 °C. The difference between concentrations in influent biosolids and the solid product formed at 100 °C and 200 °C is not significantly different at a 95% level (t-test, p-value = 0.34 and 0.43, respectively).

A room temperature control was performed to ensure that heat was the actual cause for loss of TCS. In this control, argon was used to purge the beaker as was done for the other experiments, and the beaker sat at room temperature for 60 minutes. The average concentrations of TCS in the room temperature control was 3.05 mg/kg \pm 0.15 mg/kg, which did not demonstrate a reduction in TCS.

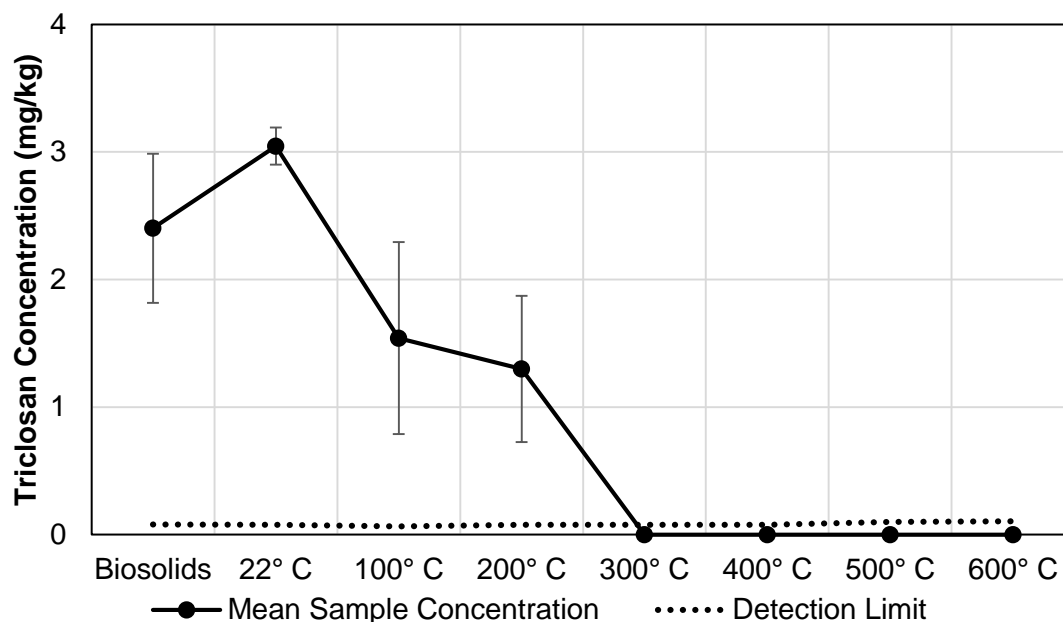


Figure 4.8. Impact of temperature on removal of triclosan during pyrolysis. Data points represent the average concentration and error bars represent the standard deviation between the triplicate runs.

4.2.1.2 Impact of Temperature on TCC Removal

Removal of TCC (to below quantification limit) was achieved at a temperature of 200 °C. The impact of temperature on TCC concentration in the solid product is shown in Figure 4.9. The average concentrations of TCC in the biosolids samples was 4.36 mg/kg \pm 2.36 mg/kg. While large variability persists at lower temperatures, at 200 °C and above, variability is minimized along with TCS concentrations. All biochar samples obtained from pyrolysis at 300 °C, 400 °C, 500 °C, and 600 °C did not contain TCC at levels at or above the quantification limit (0.08 mg/kg for all samples, except those obtained at 500 °C and 600 °C, at which the quantification limit was 0.10 mg/kg). In short, pyrolysis removes TCS at 200 °C. The difference between concentrations in the influent biosolids and the solid product formed at 100 °C is not significantly different at a

95% level (t-test, p-value = 0.97) The average concentrations of TCC in the room temperature control was $6.00 \text{ mg/kg} \pm 0.34$, which did not demonstrate a reduction in TCC.

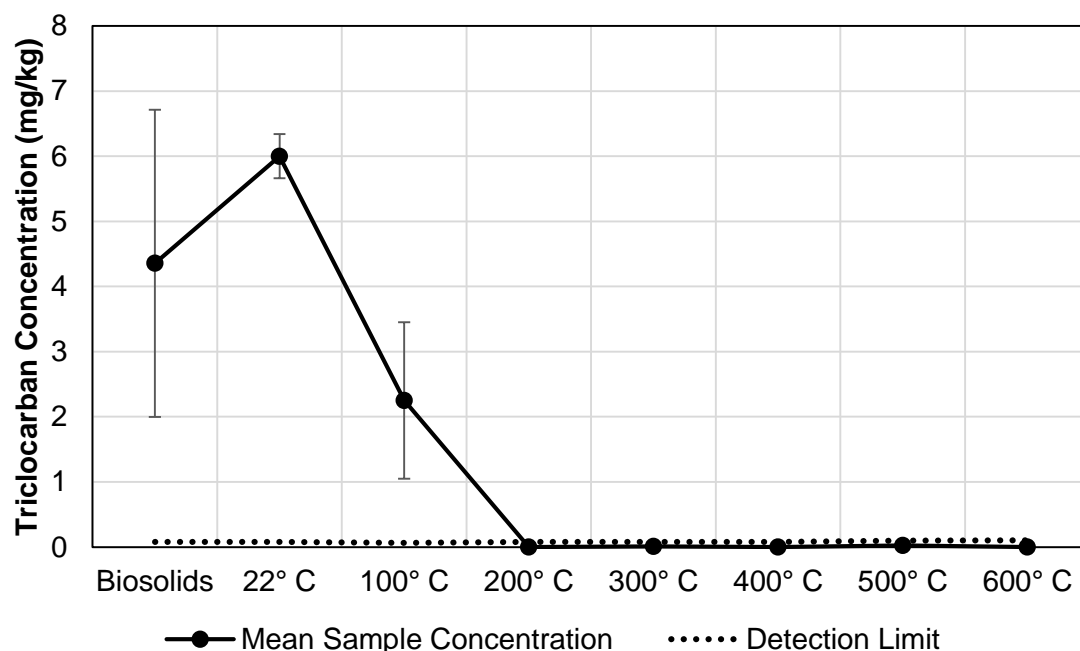


Figure 4.9: Impact of temperature on removal of triclocarban during pyrolysis. Data points represent the average concentration and error bars represent the standard deviation between the triplicate runs.

4.2.1.3 Impact of Temperature on NP Removal

Removal of NP (to below quantification limit) was achieved at a temperature of 600 °C. The impact of temperature on NP concentration in the solid product is shown in Figure 4.10. The average concentration of NP in the biosolids samples was $35.0 \text{ mg/kg} \pm 12.0 \text{ mg/kg}$. While large variability persists at lower temperatures, at 300 °C and above, variability is minimized along with NP concentrations. The average concentration of NP in the biochar samples produced at 300 °C, 400 °C, and 500 °C represented greater than 97 percent removal. Biochar samples obtained from pyrolysis at 600 °C did not contain

NP at levels at or above the quantification limit (0.10 mg/kg). In short, pyrolysis removes NP at 300 °C to levels near the quantification limit, and at 600 °C, to below the quantification limit. The difference between concentrations in the influent biosolids and the solid product formed at 100 °C and 200 °C is not significantly different at a 95% level (t-test, p-values = 0.34 and 0.43, respectively). The average concentration of NP in the room temperature control was 31.7 mg/kg \pm 2.01 mg/kg, which did not demonstrate a reduction in NP.

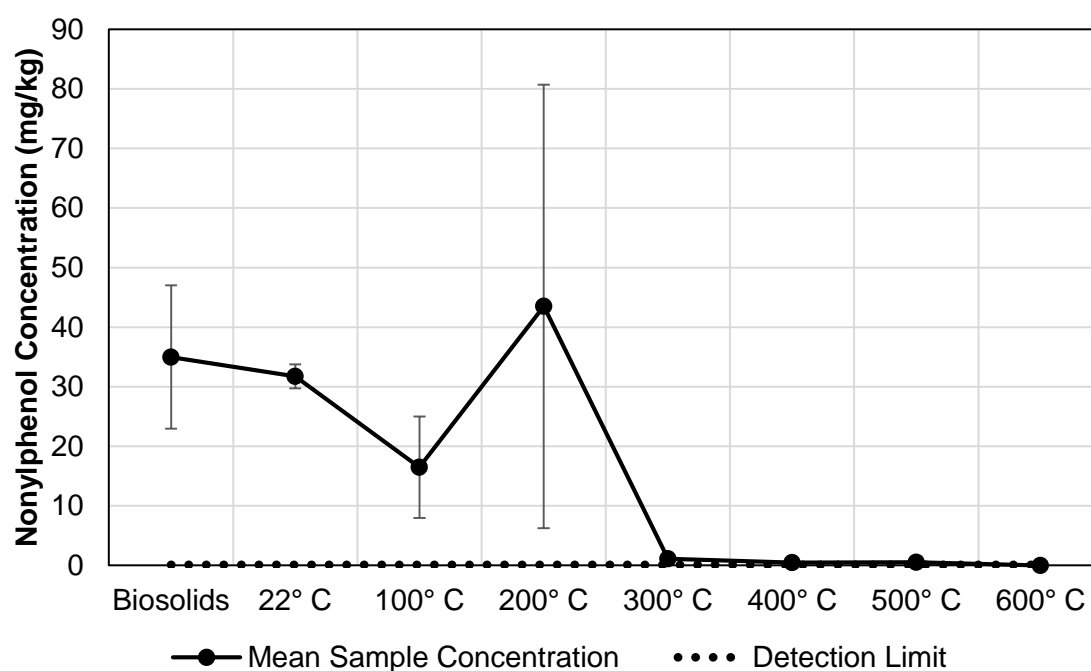


Figure 4.10: Impact of temperature on removal of nonylphenol during pyrolysis. Data points represent the average concentration and error bars represent the standard deviation between the triplicate runs.

4.2.2 Impact of Time on Micropollutant Removal

The temperature experiments describe in Section 3.1.2 were all performed as 60 minute batch experiments. Additional experiments were performed to determine how long it took to achieve MP concentrations below quantification limit. Experiments were

performed at 500 °C for 2.5, 5, and 10 minutes. The effect of pyrolysis run time on the average concentration of TCS, TCC, and NP in the biochar is shown in Figure 4.11. TCC was removed to below the quantification limit by 2.5 minutes, i.e., it was only present at quantifiable levels in the feed. TCS was still present at 2.5 minutes, but at a reduced concentration. The difference between the concentration at 2.5 minutes and the feed concentration was statistically significant at the 95% level (t-test, p-value = 0.02). By 5 minutes TCS was removed (to below quantification limits). The NP concentrations at 2.5, 5, 10, and 60 minutes were statistically different from the feed, but the difference was not statistically significant at the 95% level between each other (ANOVA, p-values = 0.01 and 0.16, respectively). The average concentration of NP in the biochar samples produced at 2.5, 5, 10, and 60 minutes represented greater than 97 greater removal. In general, at 500 °C the removal of MPs happens very fast, i.e., less than 5 minutes. Pilot-scale experiments should be operated to determine removal in continuous flow-experiments.

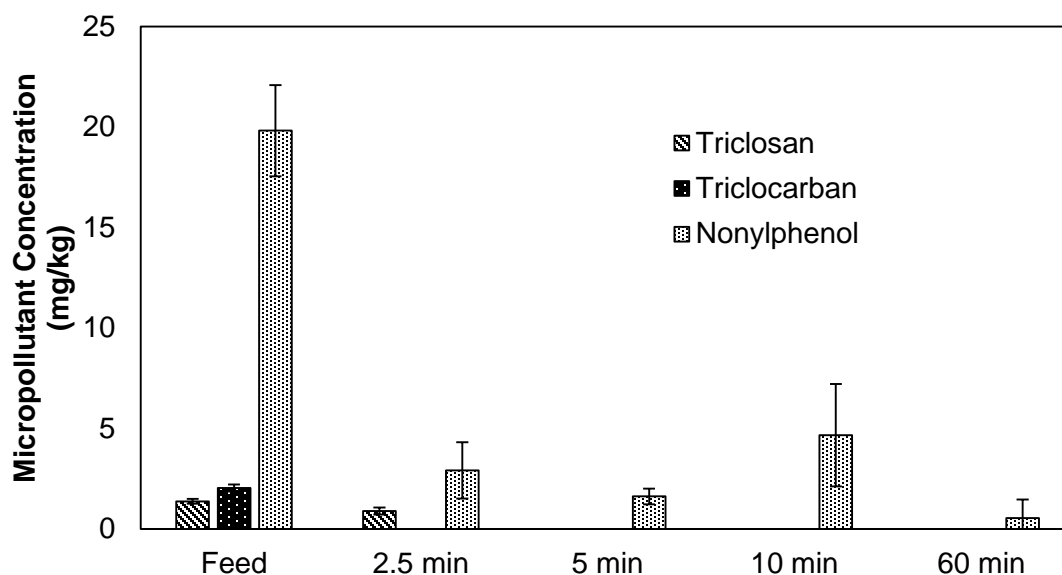


Figure 4.11. Impact of time on removal of triclosan, triclocarban, and nonylphenol during pyrolysis. Estradiol was not detected in the biosolids feed and so was not analyzed in this section. The error bars represent the standard deviation between the triplicate runs.

4.2.3 Extraction Control with Crushed Samples

For the previously described experiments solid samples were extracted by putting the solids samples directly into the ASE cells. A set of experiments were conducted to ensure that MP removal was not due to difficulty detecting MPs trapped inside the solid matrix. Pyrolysis experiments were performed and biosolids and biochar samples were crushed prior to extraction. MP were still found in the feed, but not in the biochar following pyrolysis at 500 °C for one hour (see Table 4.1). These results corroborate what was described above, i.e., that pyrolysis removes MPs. The biosolids concentrations in Table 4.1 are slightly higher than the biosolids concentrations obtained from the temperature and time controlled experiments. The difference in values may be due to the variable nature of the sample. Of importance for this test were the results obtained for the biochar sample. For the biochar samples, both TCS and TCC were not found at or

above the quantification limit. NP was detected in the biochar at an average concentration lower than that determined in the time and temperature controlled events, demonstrating a greater than 99 percent removal. These results demonstrate that TCS, TCC, and NP were not hidden in the solid matrices during extraction, and confirms the removal observed during the other experiments was a result of pyrolysis.

Table 4.2: Results from Extractions of Three Biosolids and Biochar Samples

	Triclosan	Triclocarban	Nonylphenol
Biosolids Sample A	4.58	7.10	51.2
Biosolids Sample A	4.63	7.38	51.9
Biosolids Sample A	4.66	7.23	51.0
Mean	4.63	7.24	51.4
Standard Deviation	0.04	0.14	0.43
Biochar Sample A	<0.10	<0.10	0.22
Biochar Sample B	<0.10	<0.10	0.25
Biochar Sample C	<0.10	<0.10	0.22
Mean	<0.10	<0.10	0.23
Standard Deviation	N/A	N/A	0.022

4.3 Micropollutant Fate Studies

After determining that pyrolysis removed MPs, contrived fate studies were conducted to determine if the MPs were destroyed or volatilized during pyrolysis. In these experiments sand was spiked with 1 mg of each MP and methanol condensers were connected to the pyrolysis reactor to catch volatilized products.

4.3.1 Micropollutant Recovery during Pyrolysis

Analyses following pyrolysis of sand spiked with TCS, TCC, NP, and E2 demonstrated that pyrolysis both volatilizes and degrades these compounds. The fractions of MPs recovered after pyrolysis in the sand sample, in the methanol used to rinse the tubing, and in the methanol in the impingers are shown in Figure 4.12. A

substantial portion of TCS and NP volatilized and was recovered in the system, but less than 5% of TCC and E2 were recovered. An average of $41\% \pm 6\%$ of TCS was recovered from the system in the triplicate runs. NP was recovered at an average of $45\% \pm 18\%$ between the total mass recovered in the triplicate runs. None of the MPs were present in the sand which corroborates with the above experiments that found pyrolysis removes MPs from solid matrices. The incomplete mass balance is likely due to destruction of parent compounds in addition to minor losses during the extraction process.

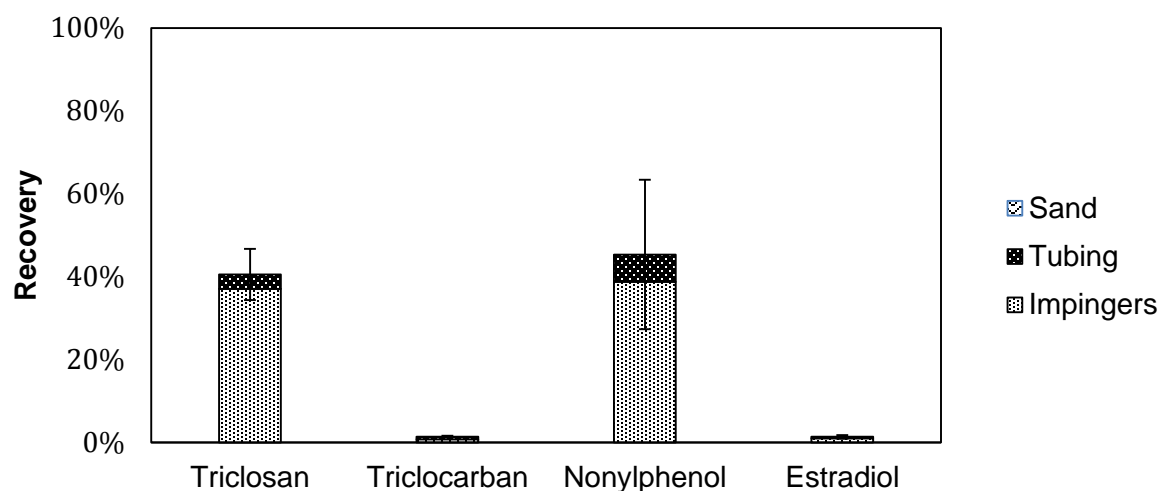


Figure 4.12: Micropollutant recovery in pyrolysis products. The error bars represent the standard deviation observed between the total amounts of mass recovered for each micropollutant between the triplicate runs.

Negative controls (pyrolysis with no MPs added) and positive controls (MPs spiked with no heat added) provided assurance that the system configuration was not responsible for leaching MPs or the transfer and transformation of the MPs. The negative control did not result in detection of any of the MPs. These results confirm that nothing within the system, such as tubing, produced products that would appear as TCS, TCC, NP, and E2 or the degradation products analyzed. The positive control (MPs spiked in

the sand, but no heat applied) resulted in detection of MPs within the sand after the experiment without any detection of MPs in the system tubing or impingers. The positive control results are shown in Figure 4.13. TCS, TCC, NP, and E2 were detected in the sand at approximately 40 to 65% of the original mass added. The incomplete mass balance is likely due to losses during the extraction process due to the large mass of MPs in the system. These results demonstrate that the transfer of the MPs from the sand to the tubing and impingers was not an artifact of the pyrolysis configuration and was due to the thermochemical reactions occurring during pyrolysis.

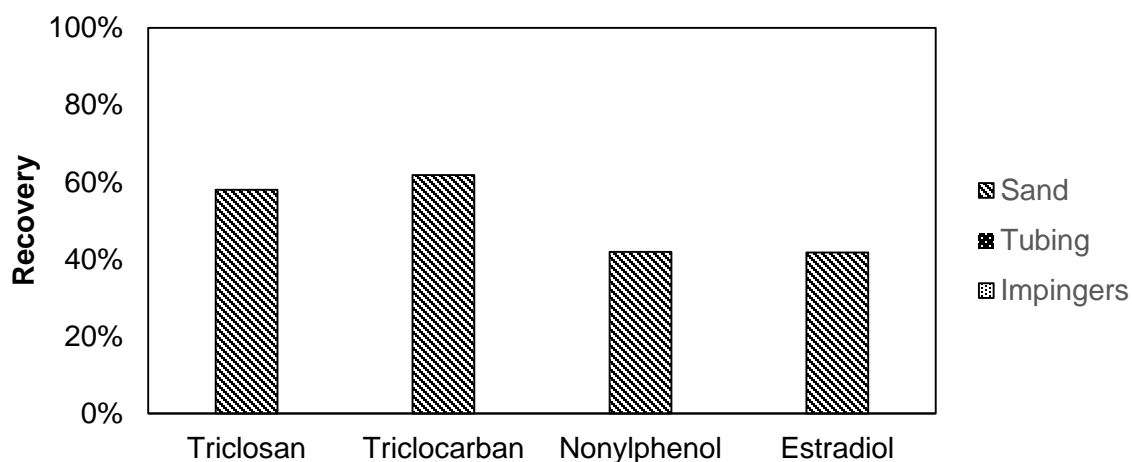


Figure 4.13: Micropollutant recovery in positive control. Micropollutants were spiked into sand and held in the system at room temperature.

4.3.2 Potential Micropollutant Transformation Products

Based on the incomplete recovery of MPs from the above experiments, it was expected that pyrolysis was transforming the parent compounds. Indeed, partial degradation of the MPs occurred during pyrolysis and potential transformation products

were identified. Potential breakdown pathways for TCC and TCS are shown in Figures 4.14 and 4.15.

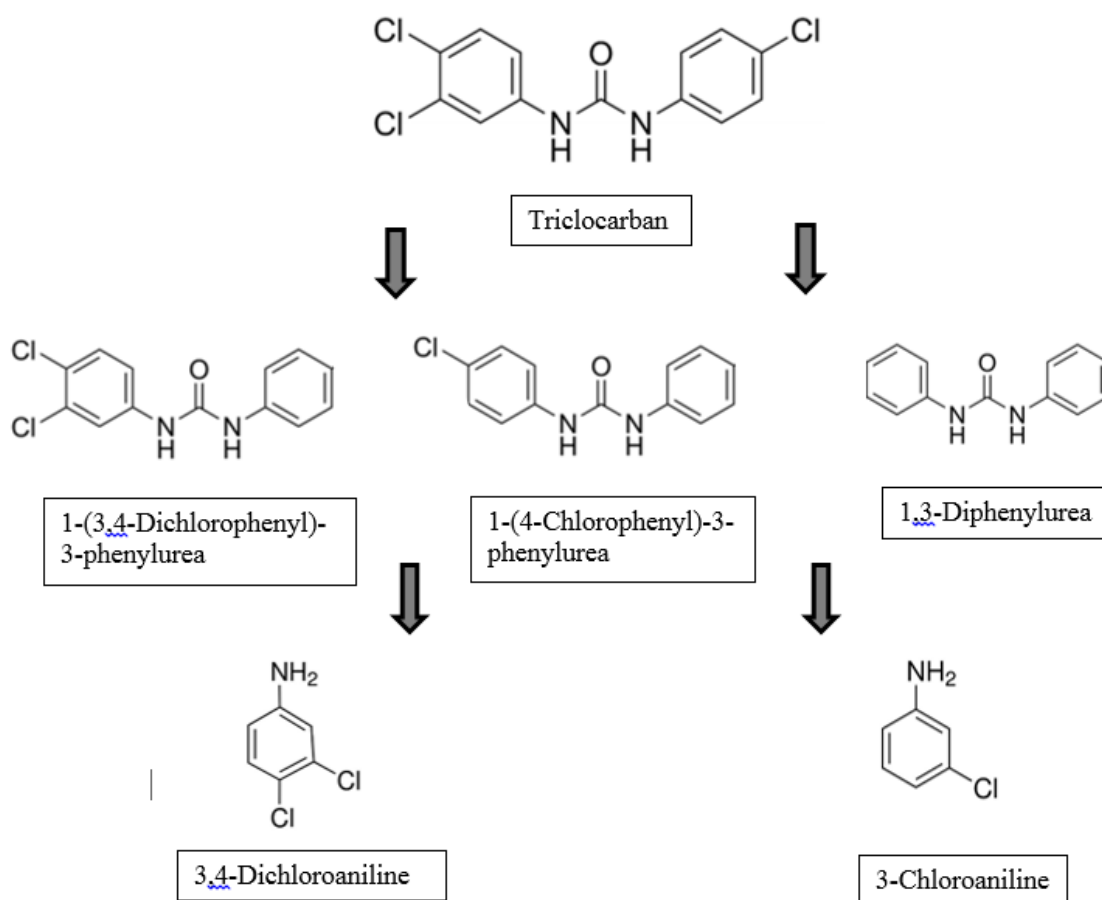


Figure 4.14: Triclocarban transformation products

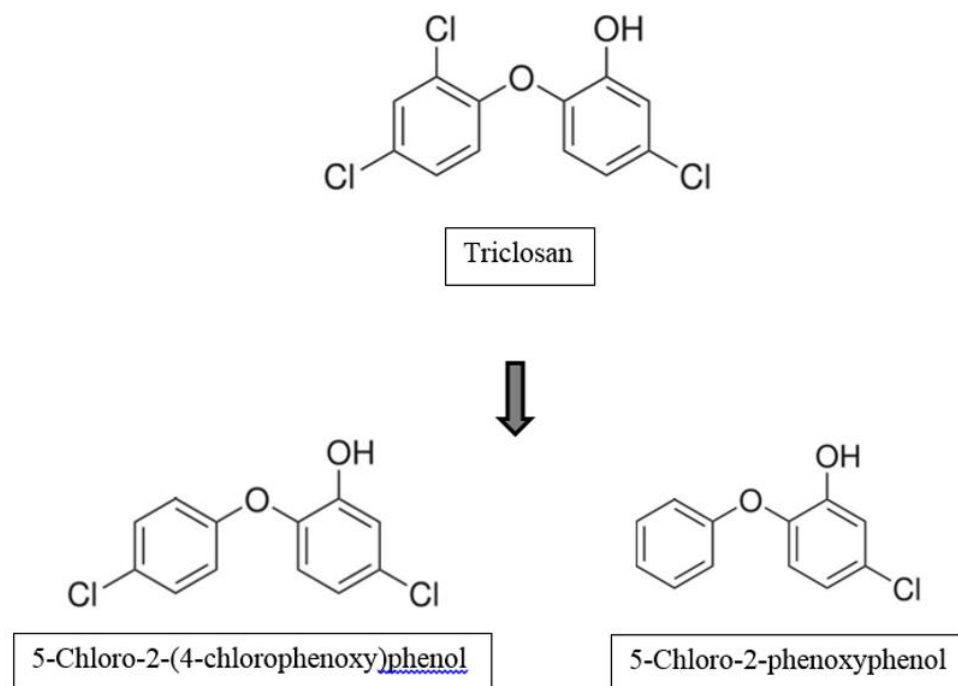
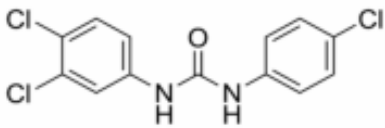
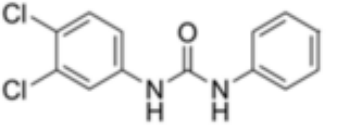
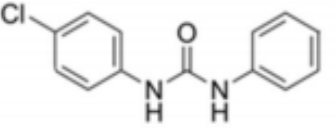
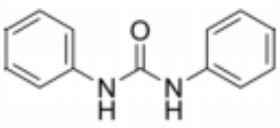
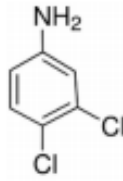
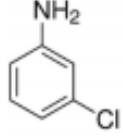
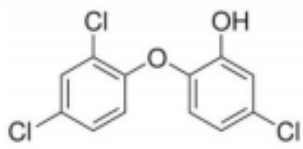
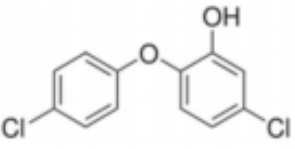
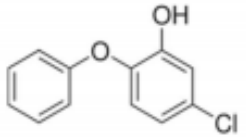


Figure 4.15: Triclosan Transformation Products

From the literature, it was expected that TCC could undergo dehalogenation in which one, two, or three chlorine ions would be cleaved and replaced with a hydrogen atom, forming 1-(3,4-dichlorophenyl)-3-phenylurea, 1-(4-chlorophenyl)-3-phenylurea, and 1,3-diphenylurea respectively (Miller et al., 2008). TCC and its dehalogenated products were also suspected to undergo separation between their aromatic structures, forming 3,4-dichloroaniline and 3-chloroaniline (Miller et al., 2010). Similarly, TCS was expected to undergo dehalogenation reactions forming 5-chloro-2-(4-chlorophenoxy)phenol and 5-chloro-2-phenoxyphenol (Anger et al., 2013).

Table 4.3: Triclosan and Triclocarban Products

Compound	Molecular Weight (g/mol)	Structure
Triclocarban	315	
1-(3,4-Dichlorophenyl)-3-phenylurea	281	
1-(4-Chlorophenyl)-3-phenylurea	247	
1,3-Diphenylurea	212	
3,4-Dichloroaniline	162	
3-Chloroaniline	127	
Triclosan	289	
5-Chloro-2-(4-chlorophenoxy)phenol	255	
5-Chloro-2-phenoxyphenol	221	

4.3.3 Triclocarban and Triclosan Product Identification

TCC and likely TCS products were identified in the samples collected during the fate study. TCC products were identified by correlating the retention time of peaks generated for the respective product's mass to charge ratio from standards to those obtained from experimental samples. For example, Figures 4.16-19 illustrate peaks of the parent TCS and TCC compounds generated from standards and then from samples collected during the fate study.

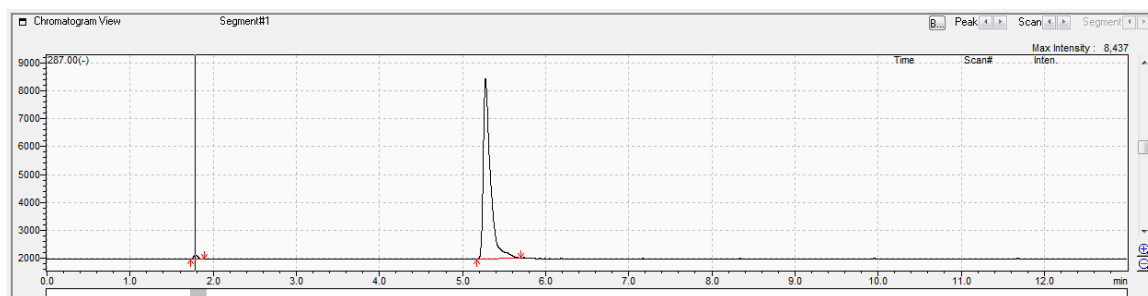


Figure 4.16: Triclosan chromatogram from standard

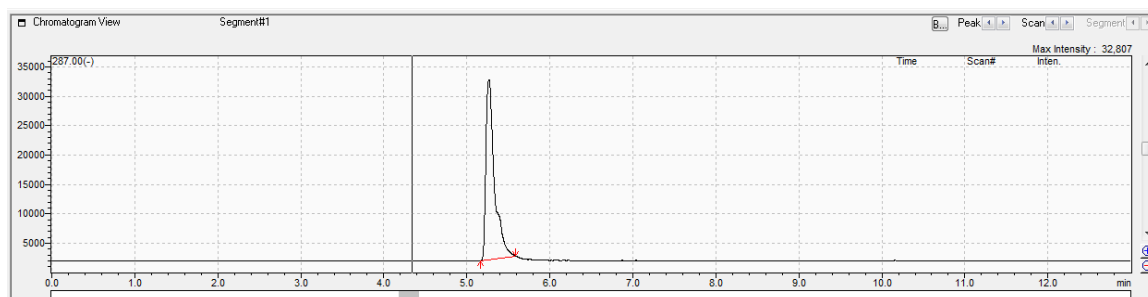


Figure 4.17: Triclosan chromatogram from impinger sample

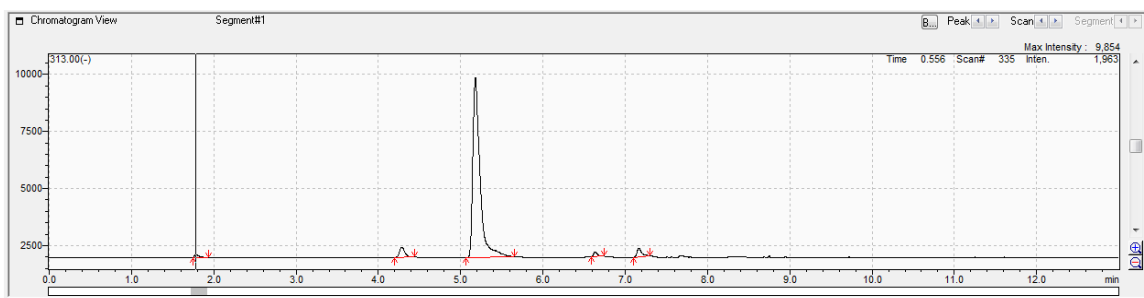


Figure 4.18: Triclocarban chromatogram from standard

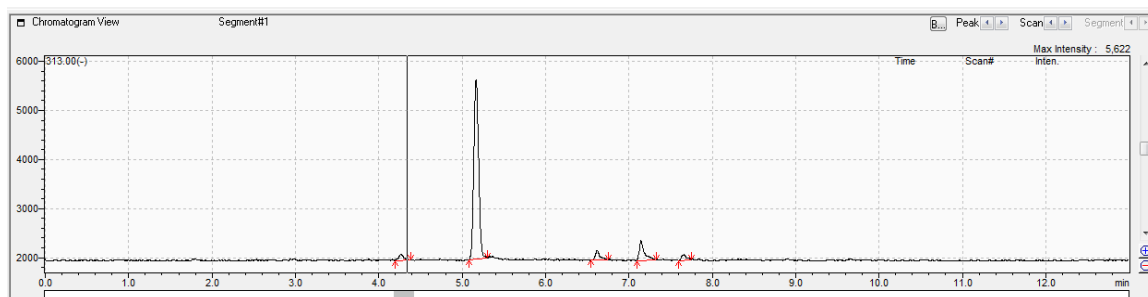


Figure 4.19: Triclocarban chromatogram from impinger sample

TCC undergoing dechlorination of both one and two chlorines was identified in the same way. Figures 4.20-4.23 illustrate peaks of 1-(3,4-dichlorophenyl)-3-phenylurea and 1-(4-chlorophenyl)-3-phenylurea in chromatograms generated from standards and from samples collected during the fate study. The presence of the three other TCC products was unable to be confirmed, as no peaks were observed at the same retention time as the standards. While the mass represents less than 5% of the total carbon added, this result demonstrates that breakdown products were formed.

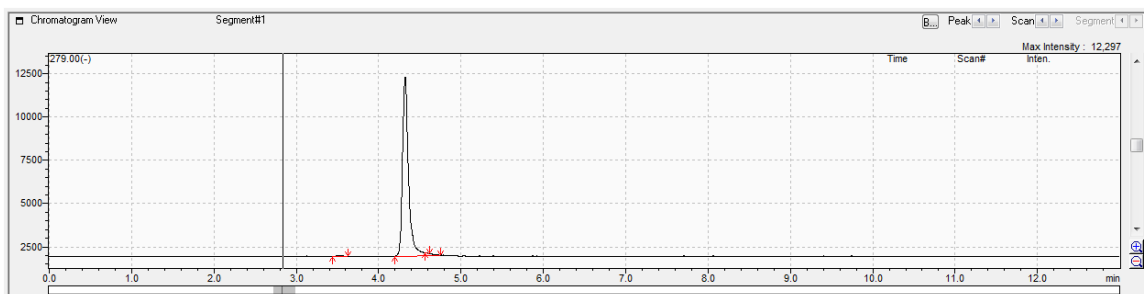


Figure 4.20: 1-(3,4-Dichlorophenyl)-3-phenylurea chromatogram from standard

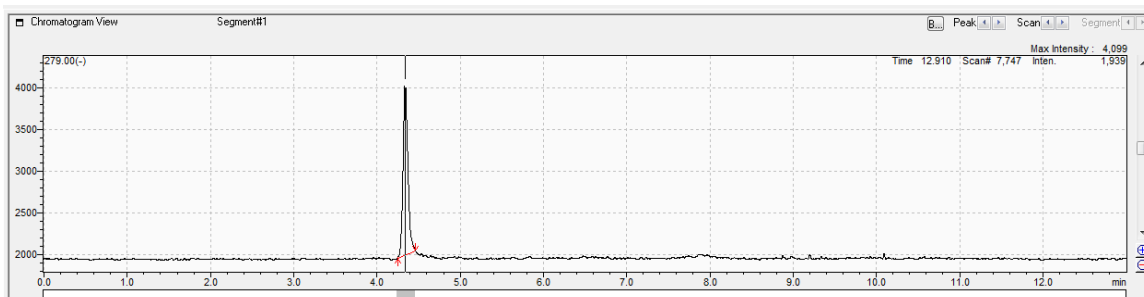


Figure 4.21: 1-(3,4-Dichlorophenyl)-3-phenylurea chromatogram from impinger sample

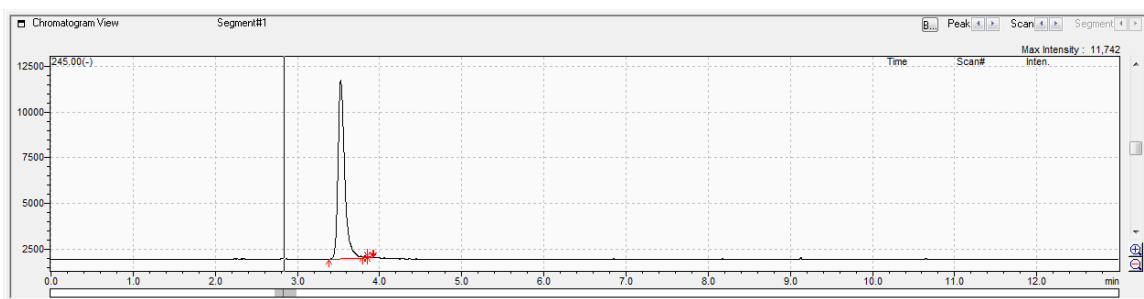


Figure 4.22: 1-(4-Chlorophenyl)-4-phenylurea chromatogram from standard

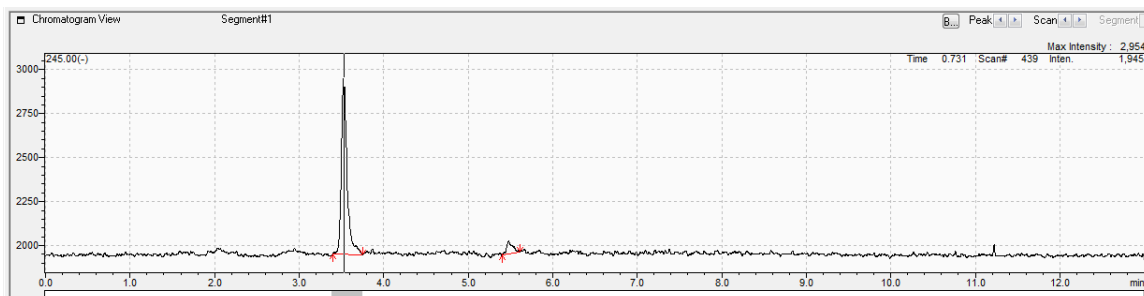


Figure 4.23: 1-(4-Chlorophenyl)-3-phenylurea chromatogram from pyrolysis system tubing rinse

Although no standards were available to confirm the retention time of the dechlorinated TCS products, the chromatograms generated at the corresponding mass to charge ratio show peaks that are likely the respective TCS products. This supposition is strengthened by the incremental decrease in retention times in the predicted product chromatograms which demonstrates an increase in polarity compared to TCS, as would be expected from the loss of a chlorine atom. Figures 4.24-4.25 illustrate suspected peaks of 5-chloro-2-(4-chlorophenoxy)phenol and 5-chloro-2-phenoxyphenol in chromatograms generated from samples collected during the fate study.

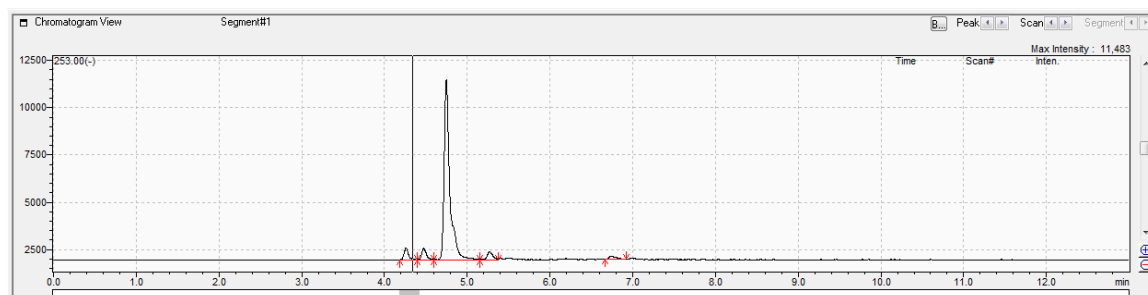


Figure 4.24: Likely 5-Chloro-2-(3-chlorophenoxy)phenol chromatogram from impinger

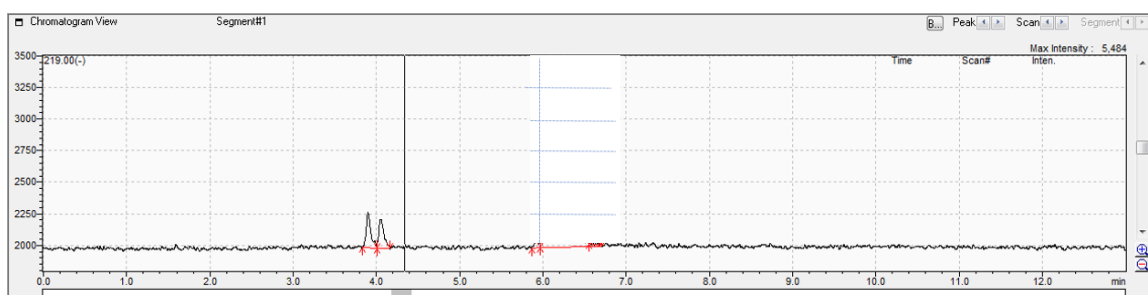


Figure 4.25: Likely 5-Chloro-2-phenoxyphenol chromatogram from impinger

4.3.4 Micropollutant Fate Discussion

The transformation (or lack thereof) of MPs during pyrolysis was correlated to the vapor pressures (VPs) of the MPs. The observed recovery of each MP from the fate experiments are shown in Table 4.3 along with each compound's VP, estimated using the

software Estimations Program Interface (EPI) Suite version 4.11 from the US EPA. The difference in recovery values between TCS and NP, as well as between TCC and E2, is not statistically significant at a 95% level (t-test, p-values = 0.67 and 0.69, respectively). The VP values for the four compounds follow a similar relationship to that of the recovery values: TCS and NP are both similar and have VPs orders of magnitude larger than TCC and E2. These VP values suggest that during pyrolysis, TCS and NP quickly volatilize and exit the reactor faster than TCC and E2. The lower VPs of TCC and E2 imply that they remain in the reactor for a longer period of time. The longer retention time of TCC and E2 under pyrolytic conditions provides longer reaction time for transformation to occur, which could account for the decrease in recovery values for these compounds. Hu et. al. (2007) attributed their large recovery of pollutants in their pyrolysis system to the quick volatilization and exiting of the compounds from the pyrolysis reactor. They postulated that, if the pollutants remained in the reactor longer, they would have been exposed to higher temperatures at longer reaction times required for transformation. This postulation was supported in the work of Miskolszi et. al. (2008) who found that flame retarded plastics underwent dehalogenation to a greater extent in a lengthened pyrolysis tube reactor when compared to typical fluidized bed and fixed bed pyrolysis reactors due to long residence times achieved in the tube reactor.

Table 4.3: Micropollutant recovery and estimated vapor pressure from the US EPA Estimations Program Interface Suite (EPI Suite v4.11)

Micropollutant	Vapor Pressure (mm Hg)	Recovery
Nonylphenol	6.86E-04	45%
Triclosan	4.65E-06	41%
Triclocarban	3.61E-09	1.4%
Estradiol	6.38E-09	1.4%

Dehalogenation of halogenated organics is a common transformation mechanism in pyrolysis studies. It is not surprising to see the presence of dechlorinated TCC products and likely dechlorinated TCS products in the experiments described in this work. For dechlorination to occur, a reductive source is required. It is interesting to consider the reductive source for the replacement of the chlorine ions in this work for which no catalyst was added. Hydrogen or hydrocarbons (methane, *n*-hexane) must have been available for exchange with chlorine in the TCC and TCS structures for dechlorination to take place (Hornung et al., 2003). These experiments were carried out with MPs spiked into sand, so in theory the only hydrogen or hydrocarbon source available would be from fragments of other decomposed MPs within the system. It is possible that the reaction rate was limited by the reductive source. In actual biosolids, it is likely that dehalogenation of MP during pyrolysis would occur more rapidly because the organic fraction of biosolids would undergo decomposition and transfer more hydrogen and hydrocarbons into the gas phase.

4.4 Environmental Implications

Overall, this work demonstrates that pyrolysis of biosolids could minimize the spread of MPs into the environment. Results from the temperature and time pyrolysis experiments demonstrate pyrolysis can achieve greater than 95 percent removal of TCS, TCC, and NP from biosolids. The main goal of the fate analyses was to determine if transformation of MP is possible in pyrolysis, and if transformation was more likely to occur for MPs that are retained within the reactor for a longer amount of time. The fate studies were not designed to identify the fraction of MP that transferred to the pyrolysis oil relative to the fraction that transferred to the pyrolysis gas, or elucidate all of the MP

degradation pathways. Also, it is expected that the partitioning of MPs into the pyrolysis gas or oil would be dependent on each pyrolysis reactor configuration and operation (temperature, inert gas flow rate, pyrolysis gas composition, etc.). If the partitioning of MPs into the oil or gas fraction is desired for a particular operation, a pilot-scale system should be constructed and analyzed to obtain accurate results. Of central importance to the topic of MP control, however, is that both the pyrolysis gas and oil are destined for combustion within an internal combustion engine. If complete combustion occurs, the MPs in the oil and gas should therefore be mineralized. Future work should be conducted on the combustion of pyrolysis gas or oil to ensure the destruction of MP within the pyrolysis gas or oil occurs during combustion. Future work should also be conducted to elucidate the transformation capacity of pyrolysis for specific MPs over a range of operational parameters. In summary, these results indicate that land application of biochar would result in less MPs being returned to the environment than land application of biosolids.

5 CONCLUSIONS

The goal of this research was to determine the impact of pyrolysis on the fate of MPs in biosolids. TCS, TCC, NP, and E2 were selected for analysis in this experiment due to their relative abundance in biosolids, MP class diversity, and differing vapor pressures. An in-depth understanding of the behavior of TCS, TCC, NP and E2 during pyrolysis with respect to system temperature, residence time, and transformation potential was necessary to postulate theories for the impact of pyrolysis on the fate of MPs in biosolids. These conclusions are based on laboratory-scale experiments performed at the Marquette University Water Quality Center.

1. Pyrolysis of biosolids can minimize the spread of MPs into the environment.

Results from the pyrolysis experiments demonstrate that MPs can be removed (to below quantification limit) from the biochar and transferred to the pyrolysis gas and oil as the parent compound or a transformation product. Both the pyrolysis gas and oil would be destined for combustion for energy. If complete combustion occurs, the MPs in the oil and gas would be mineralized.

2. Pyrolysis will remove MPs from biochar, but will not necessarily destroy MPs.

Analyses of TCS, TCC, NP, and E2 following pyrolysis of sand spiked with TCS, TCC, NP, and E2 demonstrated that pyrolysis both volatilizes and degrades these compounds. A substantial portion of TCS and NP volatilized and was recovered in the system (greater than 40%), but less than 5% of TCC and E2

were recovered. The missing mass balance is likely due to destruction of parent compounds in addition to losses during the extraction process.

3. Volatile MPs are less likely to be transformed during pyrolysis. The transformation (or lack thereof) of MPs during pyrolysis was correlated to the VPs of the MPs, i.e., MPs with higher vapor pressures were volatilized and were recovered with condensate while MPs with lower vapor pressures were not recovered in the condensate. The lower VPs of TCC and E2 cause them to remain in the reactor for a longer period of time, which provides a longer reaction time for transformation to occur.
4. Pyrolysis can lead to the destruction of chlorinated MPs through reductive dehalogenation. Dechlorinated TCC products and likely dechlorinated TCS products were identified in the MP fate experiments. This finding demonstrates that dehalogenation of halogenated organics occurred. Dehalogenation is a common transformation mechanism in pyrolysis. Further work should be conducted to elucidate the parameters that govern this mechanism during pyrolysis.
5. Pyrolysis temperature greatly impacts the removal of MPs from biosolids. Removal of TCS and TCC (to below quantification limit) was achieved at temperatures of 300 °C and 200 °C, respectively. Substantial removal of NP

was achieved at 300 °C, but a temperature of 600 °C was required to remove NP to below the quantification limit.

6. The pyrolysis reaction time to remove MPs is less than 5 minutes. TCS and TCC were removed (to below quantification limit) after 5 minutes of pyrolysis at 500 °C. The NP concentrations at 2.5, 5, 10, and 60 minutes were statistically different from the feed, but were not statistically different from each other (ANOVA, p-values = 0.01 and 0.16, respectively); average removal at all temperatures was almost 90%. Pilot-scale experiments should be operated to confirm removal in continuous flow-experiments.

In summary, pyrolysis is a viable biosolids management technology to mitigate the discharge of MPs to the environment when land applying biosolids.

6 BIBLIOGRAPHY

- Ahel, M., Giger, W., & Schaffner, C. (1994). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment—II. Occurrence and transformation in rivers. *Water Research*, 28(5), 1143–1152.
- Ahn, K. C., Zhao, B., Chen, J., Cherednichenko, G., Sanmarti, E., Denison, M. S., ... Hammock, B. D. (2008). In vitro biologic activities of the antimicrobials triclocarban, its analogs, and triclosan in bioassay screens: receptor-based bioassay screens. *Environmental Health Perspectives*, 116(9), 1203–10.
- Andaluri, G., Suri, R. P. S., & Kumar, K. (2012). Occurrence of estrogen hormones in biosolids, animal manure and mushroom compost. *Environmental Monitoring and Assessment*, 184(2), 1197–205.
- Andrade, N. a., Lozano, N., McConnell, L. L., Torrents, A., Rice, C. P., & Ramirez, M. (2014). Long-term trends of PBDEs, triclosan, and triclocarban in biosolids from a wastewater treatment plant in the Mid-Atlantic region of the US. *Journal of Hazardous Materials*.
- Anger, C. T., Sueper, C., Blumentritt, D. J., Mcneill, K., Engstrom, D. R., & Arnold, W. A. (2013). Quantification of Triclosan, Chlorinated Triclosan Derivatives, and their Dioxin Photoproducts in Lacustrine Sediment Cores. *Environmental Science & Technology*, 47, 1833–1843.
- Baldwin, W. S., Graham, S. E., Shea, D., & LeBlanc, G. A. (1997). Metabolic androgenization of female *Daphnia magna* by the xenoestrogen 4-nonylphenol. *Environmental Toxicology and Chemistry*, 16(9), 1905–1911.
- Biswas, B. K., Inoue, J., Inoue, K., Ghimire, K. N., Harada, H., Ohto, K., & Kawakita, H. (2008). Adsorptive removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel. *Journal of Hazardous Materials*, 154(1-3), 1066–74.
- Blazsó, M., & Czégény, Z. (2006). Catalytic destruction of brominated aromatic compounds studied in a catalyst microbed coupled to gas chromatography/mass spectrometry. *Journal of Chromatography. A*, 1130(1), 91–6.
- Brebu, M., Bhaskar, T., Murai, K., Muto, A., Sakata, Y., & Uddin, M. A. (2005). Removal of nitrogen, bromine, and chlorine from PP/PE/PS/PVC/ABS–Br pyrolysis liquid products using Fe- and Ca-based catalysts. *Polymer Degradation and Stability*, 87(2), 225–230.
- Bridle, T. R., Hammerton, I., & Hertle, C. K. (1990). Control of Heavy Metals and Organochlorines using the Oil from Sludge Process. *Water Science & Technology*, 22(12), 249–258.

- Carballa, M., Omil, F., Ternes, T., & Lema, J. M. (2007). Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge. *Water Research*, 41(10), 2139–50.
- Chalew, T. E. A., & Halden, R. U. (2009). ENVIRONMENTAL EXPOSURE OF AQUATIC AND TERRESTRIAL BIOTA TO TRICLOSAN AND TRICLOCARBAN 1, 45(1).
- Chen, B., & Chen, Z. (2009). Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, 76(1), 127–133.
- Chen, X., Nielsen, J. L., Furgal, K., Liu, Y., Lolas, I. B., & Bester, K. (2011). Biodegradation of triclosan and formation of methyl-triclosan in activated sludge under aerobic conditions. *Chemosphere*, 84(4), 452–6.
- Chen, Y., Pi, B., Zhou, H., Yu, Y., & Li, L. (2009). Triclosan resistance in clinical isolates of *Acinetobacter baumannii*. *Journal of Medical Microbiology*, 58(Pt 8), 1086–91.
- Chuanchuen, R., Karkhoff-Schweizer, R. R., & Schweizer, H. P. (2003). High-level triclosan resistance in *Pseudomonas aeruginosa* is solely a result of efflux. *American Journal of Infection Control*, 31(2), 124–127.
- Citulski, J. a., & Farahbakhsh, K. (2010). Fate of endocrine-active compounds during municipal biosolids treatment: a review. *Environmental Science & Technology*, 44(22), 8367–76.
- Clarke, B. O., & Smith, S. R. (2011). Review of “emerging” organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environment International*, 37(1), 226–47.
doi:10.1016/j.envint.2010.06.004
- Cogger, C. G., Bary, A. I., Kennedy, A. C., & Fortuna, A.-M. (2013). Long-Term Crop and Soil Response to Biosolids Applications in Dryland Wheat. *American Society of Agronomy*, 42(6), 1872–1880.
- Colborn, T., Saal, F. S., & Soto, A. M. (1993). Developmental Effects of Endocrine-Disrupting Chemicals in Wildlife and Humans, (July).
- Coogan, M. a, Edziyie, R. E., La Point, T. W., & Venables, B. J. (2007). Algal bioaccumulation of triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment plant receiving stream. *Chemosphere*, 67(10), 1911–8.
- DeLorenzo, M. E., & Fleming, J. (2008). Individual and mixture effects of selected pharmaceuticals and personal care products on the marine phytoplankton species

- Dunaliella tertiolecta. *Archives of Environmental Contamination and Toxicology*, 54(2), 203–10.
- eNews Park Forest. (2014). Town Bans Land Application of Sewage Sludge, or Biosolids. *eNews Park Forest*. Retrieved from <http://www.enevnews.com/latest-news/science/science-a-environmental/54922-town-bans-land-application-of-sewage-sludge-or-biosolids.html>
- Epstein, E. (2003). *Land Application of Sewage Sludge and Biosolids*. Boca Raton, Florida: CRC Press LLC.
- Ghosh, S., Cremers, C. M., Jakob, U., & Love, N. G. (2011). Chlorinated phenols control the expression of the multidrug resistance efflux pump MexAB-OprM in *Pseudomonas aeruginosa* by interacting with NalC. *Molecular Microbiology*, 79(6), 1547–56.
- Giger, W., Brunner, P. H., & Schaener, C. (1984). Nonylphenol in Sewage Sludge. *Science*, 225(August), 623–625.
- Giudice, B. D., & Young, T. M. (2010). The antimicrobial triclocarban stimulates embryo production in the freshwater mudsnail *Potamopyrgus antipodarum*†. *Environmental Toxicology and Chemistry*, 29(4), 966–970.
- Goodman, J. R. (2006). Beneficial or biohazard? How the media frame biosolids. *Public Understanding of Science*, 15(3), 359–375.
- Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P. F., Ingerslev, F., Holten Lützhøft, H. C., & Jørgensen, S. E. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment- A review. *Chemosphere*, 36(2), 357–393.
- Harrison, P. T. C., Holmes, P., & Humfrey, C. D. N. (1997). Reproductive health in humans and wildlife : are adverse trends associated with environmental chemical exposure ?, 205, 97–106.
- Heidler, J., & Halden, R. U. (2007). Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere*, 66(2), 362–9.
- Higgins, C. P., Paesani, Z. J., Abbott, T. E., & Halden, R. U. (2009). Pharmaceuticals and Personal Care Products in the Environment BIOACCUMULATION OF TRICLOCARBAN IN LUMBRICULUS VARIEGATUS. *Environmental Toxicology and Chemistry*, 28(12), 2580–2586.
- Hinz, B., M., H., Pohlmann, K., S., S., Schimmel, I., & Sinn, H. (1994). Dehalogenation of pyrolysis products. *Journal of Analytical and Applied Pyrolysis*, 30(1), 35–46.

- Hornung, a., Balabanovich, a. I., Donner, S., & Seifert, H. (2003a). Detoxification of brominated pyrolysis oils. *Journal of Analytical and Applied Pyrolysis*, 70(2), 723–733.
- Hornung, a., Balabanovich, a. I., Donner, S., & Seifert, H. (2003b). Detoxification of brominated pyrolysis oils. *Journal of Analytical and Applied Pyrolysis*, 70(2), 723–733.
- Hospido, A., Carballa, M., Moreira, M., Omil, F., Lema, J. M., & Feijoo, G. (2010). Environmental assessment of anaerobically digested sludge reuse in agriculture: potential impacts of emerging micropollutants. *Water Research*, 44(10), 3225–33.
- Hossain, a. K., & Davies, P. a. (2013). Pyrolysis liquids and gases as alternative fuels in internal combustion engines – A review. *Renewable and Sustainable Energy Reviews*, 21, 165–189.
- Hossain, M. K., Strezov, V., Chan, K. Y., & Nelson, P. F. (2010). Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). *Chemosphere*, 78(9), 1167–71.
- Hu, Z., Navarro, R., Nomura, N., Kong, H., Wijesekara, S., & Matsumura, M. (2007). Changes in chlorinated organic pollutants and heavy metal content of sediments during pyrolysis. *Environmental Science and Pollution Research International*, 14(1), 12–8. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/17352123>
- Irwin, L. K., Gray, S., & Oberdo, E. (2001). Vitellogenin induction in painted turtle , *Chrysemys picta* , as a biomarker of exposure to environmental levels of estradiol, 55, 49–60.
- Jacobs, M. N., Nolan, G. T., & Hood, S. R. (2005). Lignans, bacteriocides and organochlorine compounds activate the human pregnane X receptor (PXR). *Toxicology and Applied Pharmacology*, 209(2), 123–33.
- Jaramillo-López, P. F., & Powell, M. A. (2013). Application of stabilized biosolids and fly ash mixtures as soil amendments and their impact on free living nematodes and carrot (*Daucus carota*) yield. *International Journal Of Recycling of Organic Waste in Agriculture*, 2(22).
- Jerome, S. (2014). Whole Foods Bans Sludge Fertilizer. *Water Online*. Retrieved from <http://www.wateronline.com/doc/whole-foods-bans-sludge-fertilizer-0001>
- Karayildirim, T., Yanik, J., Yuksel, M., & Bockhorn, H. (2006). Characterisation of products from pyrolysis of waste sludges. *Fuel*, 85(10-11), 1498–1508.
- Khanal, S. K., Xie, B., Thompson, M. L., Sung, S., Ong, S.-K., & van Leeuwen, J. (Hans). (2006). Fate, Transport, and Biodegradation of Natural Estrogens in the

- Environment and Engineered Systems. *Environmental Science & Technology*, 40(21), 6537–6546.
- Kidd, K. a, Blanchfield, P. J., Mills, K. H., Palace, V. P., Evans, R. E., Lazorchak, J. M., & Flick, R. W. (2007). Collapse of a fish population after exposure to a synthetic estrogen. *Proceedings of the National Academy of Sciences of the United States of America*, 104(21), 8897–8901.
- Kyselova, V., Peknicova, J., Buckiova, D., & Boubelik, M. (2003). Effects of p-nonylphenol and resveratrol on body and organ weight and in vivo fertility of outbred CD-1 mice, 10, 1–10.
- La Guardia, M. J., Hale, R. C., Harvey, E., Bush, E. O., Mainor, T. M., & Gaylor, M. O. (2004). Organic Contaminants of Emerging Concern in Land-Applied Sewage Sludge (Biosolids). *Journal of Residuals Science & Technology*, 1(2), 111–122.
- La Guardia, M. J., Hale, R. C., Harvey, E., & Mainor, T. M. (2001). Alkylphenol ethoxylate degradation products in land-applied sewage sludge (biosolids). *Environmental Science & Technology*, 35(24), 4798–804. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/11775155>
- Le-Minh, N., Khan, S. J., Drewes, J. E., & Stuetz, R. M. (2010). Fate of antibiotics during municipal water recycling treatment processes. *Water Research*, 44(15), 4295–323.
- Li, X., Tang, Y., Cao, X., Lu, D., Luo, F., & Shao, W. (2008). Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 317(1-3), 512–521.
- Liu, X., Tani, A., Kimbara, K., & Kawai, F. (2006). Metabolic pathway of xenoestrogenic short ethoxy chain-nonylphenol to nonylphenol by aerobic bacteria, Ensifer sp. strain AS08 and Pseudomonas sp. strain AS90. *Applied Microbiology and Biotechnology*, 72(3), 552–9.
- Marker, T. L., Felix, L. G., Linck, M. B., & Roberts, M. J. (2011). Integrated Hydropyrolysis and Hydroconversion for the Direct Production of Gasoline and Diesel Fuels or Blending Components from Biomass, Part 1: Proof of Principle Testing. *Environmental Progress & Sustainable Energy*, 31(2), 191–199.
- Masuyama, H., Hiramatsu, Y., Kunitomi, M., Kudo, T., Macdonald, P. N., Gynecology, H. M., & Pxr, P. X. (2014). Endocrine Disrupting Chemicals , Phthalic Acid and Nonylphenol , Activate Pregnane X Receptor- Mediated Transcription, (October), 421–428.

- McAvoy, D. C., Schatowitz, B., Jacob, M., Hauk, A., & Eckhoff, W. S. (2009). Measurement of triclosan in wastewater treatment systems. *Environmental Toxicology and Chemistry*, 21(7), 1323–1329.
- McClellan, K., & Halden, R. U. (2010). Pharmaceuticals and personal care products in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. *Water Research*, 44(2), 658–68.
- Mcmurry, L. M., Oethinger, M., & Levy, S. B. (1998). Triclosan targets lipid synthesis, (Mic), 531–532.
- McNamara, P. J., & Krzmarzick, M. J. (2013). Triclosan enriches for Dehalococcoides-like Chloroflexi in anaerobic soil at environmentally relevant concentrations. *FEMS Microbiology Letters*, 344(1), 48–52.
- McNamara, P. J., LaPara, T. M., & Novak, P. J. (2014). The impacts of triclosan on anaerobic community structures, function, and antimicrobial resistance. *Environmental Science & Technology*, 48(13), 7393–400.
- McNamara, P. J., Wilson, C. a, Wogen, M. T., Murthy, S. N., Novak, J. T., & Novak, P. J. (2012). The effect of thermal hydrolysis pretreatment on the anaerobic degradation of nonylphenol and short-chain nonylphenol ethoxylates in digested biosolids. *Water Research*, 46(9), 2937–46.
- Michael, I., Rizzo, L., McArdell, C. ., Manaia, C. ., Merlin, C., Schwartz, T., ... Fatta-Kassinos, D. (2013). Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review. *Water Research*, 47(3), 957–95.
- Middleton, J. H., & Salierno, J. D. (2013). Antibiotic resistance in triclosan tolerant fecal coliforms isolated from surface waters near wastewater treatment plant outflows (Morris County, NJ, USA). *Ecotoxicology and Environmental Safety*, 88, 79–88.
- Miller, T. R., Colquhoun, D. R., & Halden, R. U. (2010). Identification of wastewater bacteria involved in the degradation of triclocarban and its non-chlorinated congener. *Journal of Hazardous Materials*, 183(1-3), 766–72.
- Miller, T. R., Heidler, J., Chillrud, S. N., Delaquil, A., Ritchie, J. C., Mihalic, J. N., & Bopp, R. (2008). Fate of Triclosan and Evidence for Reductive Dechlorination of Triclocarban in Estuarine Sediments. *Environmental Science & Technology*, 42(12), 4570–4576.
- Miskolczi, N., Hall, W. J., Angyal, A., Bartha, L., & Williams, P. T. (2008). Production of oil with low organobromine content from the pyrolysis of flame retarded HIPS and ABS plastics. *Journal of Analytical and Applied Pyrolysis*, 83(1), 115–123.

- National Research Council, C. on T. and P. in B. A. to L. (2002). *Biosolids Applied to Land: Advancing Standards and Practices* (p. 368). Washington, D.C.: National Academy of Sciences.
- North East Biosolids and Residuals Association. (2007). *A National Biosolids Regulations, Quality, End Use & Disposal Survey – Final Report*.
- Oliveira, R., Domingues, I., Koppe Grisolia, C., & Soares, A. M. V. M. (2009). Effects of triclosan on zebrafish early-life stages and adults. *Environmental Science and Pollution Research International*, 16(6), 679–88.
- Orvos, D. R., Versteeg, D. J., Inaue, J., Capdevielle, M., Rothenstein, A., & Cunningham, V. (2009). Aquatic toxicity of triclosan. *Environmental Toxicology and Chemistry*, 21(7), 1338–1349.
- Panter, G. H., Thompson, R. S., & Sumpter, J. P. (1998). Adverse reproductive effects in male fathead minnows (*Pimephales promelas*) exposed to environmentally relevant concentrations of the natural oestrogens , oestradiol and oestrone, 42, 243–253.
- Raut, S. A., & Angus, R. A. (2010). Triclosan has endocrine-disrupting effects in male western mosquitofish, *Gambusia affinis*. *Environmental Toxicology and Chemistry*, 29(6), 1287–1291.
- Reimers, R. S., Xu, Y., Pillai, S. D., Fitzmorris-Brisolara, K. B., Oleszkiewicz, J. A., & Seidl, G. (2013). Future Directions Biosolids Management of The Second Decade of the 21st Century. In *Disinfection and Public Health 2013 - Water Environment Federation* (pp. 1–23).
- Schultz, M. M., Bartell, S. E., & Schoenfuss, H. L. (2012). Effects of triclosan and triclocarban, two ubiquitous environmental contaminants, on anatomy, physiology, and behavior of the fathead minnow (*Pimephales promelas*). *Archives of Environmental Contamination and Toxicology*, 63(1), 114–24.
- Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., & Lester, J. N. (2008). Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environment International*, 34(7), 1033–49.
- Stasinakis, A. S., Mamais, D., Thomaidis, N. S., Danika, E., Gatidou, G., & Lekkas, T. D. (2008). Inhibitory effect of triclosan and nonylphenol on respiration rates and ammonia removal in activated sludge systems. *Ecotoxicology and Environmental Safety*, 70(2), 199–206.
- Sung, H.-H., & Ye, Y.-Z. (2009). Effect of nonylphenol on giant freshwater prawn (*Macrobrachium rosenbergii*) via oral treatment: toxicity and messenger RNA expression of hemocyte genes. *Aquatic Toxicology (Amsterdam, Netherlands)*, 91(3), 270–7.

- Tabata, A., Kashiwada, S., Ohnishi, Y., Ishikawa, H., Miyamoto, N., & Itoh, M. (1997). Estrogenic influences of estradiol-17 β , p-nonylphenol and bis-phenol-A on Japanese Medaka (*Oryzias latipes*) at detected environmental concentrations, *1*, 109–116.
- Temes, T. a, Andersen, H., Gilberg, D., & Bonerz, M. (2002). Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS. *Analytical Chemistry*, 74(14), 3498–504. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/12139060>
- The Bakersfield Californian. (2013). Kern seeks high court sludge review. *The Bakersfield Californian*. Retrieved from <http://www.bakersfieldcalifornian.com/business/local/x568090143/County-asks-for-state-Supreme-Courts-review-on-sludge-ban>
- USEPA. Standards for the Use or Disposal of Sewage Sludge; Final Rules (1993).
- USEPA. (2009). *Targeted National Sewage Sludge Survey Overview Report*. Washington, D.C.
- USEPA. (2014). Water: Sewage Sludge (Biosolids) - Frequently Asked Questions. Retrieved from <http://water.epa.gov/polwaste/wastewater/treatment/biosolids/genqa.cfm>
- USEPA Office of Water. (2010). *Treating Contaminants of Emerging Concern: A Literature Review Database* (pp. 1–27).
- Vajda, A. M., Barber, L. B., Gray, J. L., Lopez, E. M., Woodling, J. D., & Norris, D. O. (2008). Reproductive disruption in fish downstream from an estrogenic wastewater effluent. *Environmental Science & Technology*, 42(9), 3407–14.
- Wang, H., Brown, S. L., Magesan, G. N., Slade, A. H., Quintern, M., Clinton, P. W., & Payn, T. W. (2008a). Technological options for the management of biosolids. *Environmental Science and Pollution Research International*, 15(4), 308–17.
- Wang, H., Brown, S. L., Magesan, G. N., Slade, A. H., Quintern, M., Clinton, P. W., & Payn, T. W. (2008b). Technological options for the management of biosolids. *Environmental Science and Pollution Research International*, 15(4), 308–17.
- Wen, Q., Li, C., Cai, Z., Zhang, W., Gao, H., Chen, L., ... Zhao, Y. (2011). Study on activated carbon derived from sewage sludge for adsorption of gaseous formaldehyde. *Bioresource Technology*, 102(2), 942–7.
- Yao, Y., Gao, B., Chen, J., & Yang, L. (2013). Engineered Biochar Reclaiming Phosphate from Aqueous Solutions: Mechanisms and Potential Application as a Slow-Release Fertilizer. *Environmental Science & Technology*.

- Zaks, D. P. M., Winchester, N., Kucharik, C. J., Barford, C. C., Paltsev, S., & Reilly, J. M. (2011). Contribution of anaerobic digesters to emissions mitigation and electricity generation under U.S. climate policy. *Environmental Science & Technology*, 45(16), 6735–42.
- Zanaveskin, L. N., & Averyanov, V. A. (1998). Polychlorobiphenyls : problems of the pollution of the environment and technological neutralisation methods. *Russian Chemical Reviews*, 67(8), 713–724.
- Zhang, F.-S., Nriagu, J. O., & Itoh, H. (2005). Mercury removal from water using activated carbons derived from organic sewage sludge. *Water Research*, 39(2-3), 389–95.
- Zhang, R., Bannister, R. A., Timofeyev, V., Li, N., Fritsch, E. B., Feng, W., ... Cherednichenko, G. (2012). Correction for Cherednichenko et al., Triclosan impairs excitation-contraction coupling and Ca²⁺ dynamics in striated muscle. *Proceedings of the National Academy of Sciences*, 109(40), 16393–16393.
- Zheng, W., Guo, M., Chow, T., Bennett, D. N., & Rajagopalan, N. (2010). Sorption properties of greenwaste biochar for two triazine pesticides. *Journal of Hazardous Materials*, 181(1-3), 121–6.

APPENDIX

A.1 Micropollutant Removal and Fate during Pyrolysis of Biosolids

Table A4: Impact of Temperature on Micropollutant Removal from Biosolids

Sample	NP (mg/kg)	TCS (mg/kg)	TCC (mg/kg)
Feed A	50.6	1.8	3.4
Feed B	55.3	2.1	3.6
Feed C	39.9	2.2	3.5
Feed D	31.5	3.0	7.8
Feed E	36.2	3.3	7.8
Feed F	33.5	3.1	6.5
Feed G	22.8	1.7	2.1
Feed H	22.3	2.1	2.1
Feed I	22.7	2.2	2.4
Control A	29.5	2.9	5.7
Control B	32.5	3.2	5.9
Control C	33.3	3.1	6.4
100 °C A	19.9	2.0	2.8
100 °C B	22.8	2.0	3.0
100 °C C	6.8	0.7	0.9
200 °C A	11.4	0.6	<0.2
200 °C B	84.3	1.7	<0.2
200 °C C	34.7	1.6	<0.2
300 °C A	1.3	<0.2	<0.2
300 °C B	1.2	<0.2	<0.2
300 °C C	0.8	<0.2	<0.2
400 °C A	0.4	<0.2	<0.2
400 °C B	0.5	<0.2	<0.2
400 °C C	0.4	<0.2	<0.2
500 °C A	<0.3	<0.3	<0.3
500 °C B	1.6	<0.3	<0.3
500 °C C	<0.3	<0.3	<0.3
600 °C A	<0.3	<0.3	<0.3
600 °C B	<0.3	<0.3	<0.3
600 °C C	<0.3	<0.3	<0.3

Table A2: Impact of Pyrolysis Time on Micropollutant Removal from Biosolids

Sample	NP (mg/kg)	TCS (mg/kg)	TCC (mg/kg)
Feed A	22.4	1.2	2.2
Feed B	18.8	1.5	2.1
Feed C	18.2	1.4	1.8
2.5 min A	3.9	0.9	<.2
2.5 min B	1.3	0.7	<.2
2.5 min C	3.5	1.1	<.2
5 min A	1.2	<0.2	<0.2
5 min B	1.7	<0.2	<0.2
5 min C	1.9	<0.2	<0.2
10 min A	1.7	<0.3	<0.3
10 min B	6.0	<0.3	<0.3
10 min C	6.3	<0.3	<0.3
60 min A	<0.3	<0.3	<0.3
60 min B	1.6	<0.3	<0.3
60 min C	<0.3	<0.3	<0.3
Cntrl A	18.3	1.2	1.6
Cntrl B	26.9	2.1	2.6
Cntrl C	20.5	2.4	3.1

Table A3: Fate of Micropollutants During Pyrolysis, Micropollutant Recovery

Sample	NP	E2	TCS	TCC
Run 1 Impingers	59%	1.0%	32%	1.3%
Run 1 Tubing	3%	0.2%	2%	0.2%
Run 1 Sand	<0.05%	<0.05%	<0.02%	<0.02%
Run 2 Impingers	31%	0.9%	36%	0.6%
Run 2 Tubing	12%	0.5%	5%	0.8%
Run 2 Sand	<0.05%	<0.05%	<0.02%	<0.02%
Run 3 Impingers	26%	1%	44%	0%
Run 3 Tubing	5%	<0.05%	3%	1%
Run 3 Sand	<0.05%	<0.05%	<0.02%	<0.02%

Table A4: Fate of Micropollutants during Pyrolysis, Positive Control, Micropollutant Recovery

Sample	NP	E2	TCS	TCC
Impingers	<0.05%	<0.05%	<0.02%	<0.02%
Tubing	<0.05%	<0.05%	<0.02%	<0.02%
Sand	58%	62%	42%	42%

Table A5: Fate of Micropollutants during Pyrolysis, Negative Control, Micropollutant Detection (ng/mL)

Sample	NP	E2	TCS	TCC
Impingers	<0.25	<0.25	<0.10	<0.10
Tubing	<0.25	<0.25	<0.10	<0.10
Sand	<0.25	<0.25	<0.10	<0.10

B.1 Quality Assurance/Quality Control

Table B1: Micropollutant Recovery From ASE Extraction Methods Test

Extraction Method	TCS	TCC	NP	E2
DCM 1 cycle A	73%	45%	91%	34%
DCM 1 cycle B	67%	56%	98%	16%
DCM 2 cycles A	75%	58%	116%	30%
DCM 2 cycles B	66%	45%	95%	33%
DCM:Methanol A	47%	91%	98%	<0.05%
DCM:Methanol B	13%	63%	61%	<0.05%
Methanol 1 cycle A	59%	33%	60%	64%
Methanol 1 cycle B	80%	55%	86%	103%
Methanol 2 cycles A	74%	56%	88%	90%
Methanol 2 cycles B	81%	56%	89%	103%

Table B2: Spike and Recovery Data for Biosolids Samples

Sample	TCS (mg/kg)	TCC (mg/kg)	NP (mg/kg)	E2 (mg/kg)
Biosolids A	2.2	2.7	19.4	<0.2
Biosolids B	2.0	2.8	16.7	<0.2
Biosolids C	2.7	3.5	19.1	<0.2
Spiked Sample A	19.3	16.9	70.8	3.5
Spiked Sample B	15.4	13.6	49.4	3.5
Spiked Sample C	17.9	17.3	74.7	3.6
MP addition A	17.5	17.5	52.6	3.5
MP addition B	18.0	18.0	54.0	3.6
MP addition C	17.5	17.5	52.4	3.5
Recovery A	97%	79%	100%	100%
Recovery B	73%	59%	57%	99%
Recovery C	89%	82%	107%	102%

Table B3: Spike and Recovery Data for Biochar Samples

Sample	TCS (mg/kg)	TCC (mg/kg)	NP (mg/kg)	E2 (mg/kg)
Biosolids A	<0.2	<0.2	<0.2	<0.2
Biosolids B	<0.2	<0.2	<0.2	<0.2
Biosolids C	<0.2	<0.2	<0.2	<0.2
Spiked Sample A	15.0	5.0	47.9	1.8
Spiked Sample B	12.7	7.3	43.0	2.0
Spiked Sample C	13.4	10.2	39.4	2.0
MP addition A	22.4	22.4	67.1	4.5
MP addition B	22.4	22.4	67.2	4.5
MP addition C	22.1	22.1	66.3	4.4
Recovery A	66%	22%	71%	41%
Recovery B	56%	33%	64%	44%
Recovery C	60%	46%	59%	46%

Table B4: ASE Cell Cleaning Method Test Data

	TCS (ng/mL)	TCC (ng/mL)	NP (ng/mL)	ESD (ng/mL)
Cleaning Method 1	41.8	48.5	35.5	9.3
Cleaning Method 2	13.0	18.5	14.2	4.9
Cleaning Method 3	0.5	<0.5	10.2	2.7
Cleaning Method 4	<0.5	<0.5	13.5	2.9
Cleaning Method 5	<0.5	<0.5	6.6	<0.5