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Degradation of triclosan and triclocarban and formation of transformation products in activated sludge using benchtop bioreactors

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ABSTRACT

Benchtop bioreactors were run aerobically with activated sludge samples collected from a large municipal wastewater treatment plant (WWTP) to understand how increased hydraulic retention time (HRT), sludge retention time (SRT), and varying treatment temperatures (21 °C and 30 °C) impact concentrations of the endocrine disrupting antimicrobials triclosan (TCS), triclocarban (TCC), and their transformation products. Samples from the reactors were collected periodically over a 122–196 h period and the solid and liquid fraction were separately quantitated for TCS, TCC, and methyltriclosan (MeTCS) and scanned qualitatively for six other transformation products. Results indicated that TCS, TCC and MeTCS were predominately associated with the solids fraction of the activated sludge with only nominal concentrations in the liquids fraction. TCS was degraded in the solids fraction, with increased rates at 30 °C ($-0.0224 \pm 0.007\ h^{-1}$) when compared to reactors run at 21 °C ($-\ 0.0170 \pm 0.003\ h^{-1}$). Conversely, TCC concentrations did not significantly change in solids samples from reactors run at 21 °C, while an increase in reactor temperature to 30 °C resulted in TCC degradation at an average rate of $-\ 0.0158 \pm 0.012\ h^{-1}$. Additionally, MeTCS formation in the solids fraction was observed in three out of four reactors run - indicating a notable transformation of TCS. Qualitative appearance of 2,4-dichlorophenol and 4-chloroanaline was observed in the liquids fraction of all reactor samples. The remaining four qualitatively scanned compounds were not detected. These experiments demonstrate that increased HRT, SRT, and temperature result in enhanced removal of TCS and TCC from wastewater during the activated sludge process. Furthermore, a substantial formation of TCS into MeTCS was observed.

1. Introduction

Triclosan [5-chloro-2-(2,4-dichlorophenoxy) phenol] (TCS) and triclocarban [1-(4-chlorophenyl) − 3-(3,4-dichlorophenyl) urea] (TCC) are antimicrobial organic chemicals present in a variety of consumer products, particularly personal care products (Halden, 2014). Heavy use of these compounds has resulted in their detection in both environmental (Gautam et al., 2014; Maruya et al., 2014) and biotic samples (Kinney et al., 2008; Macherius et al., 2014; Pycke et al., 2014a; Schebb et al., 2012), which has drawn concern due to the toxicological properties of TCS and TCC, most notably endocrine disruption (Ahn et al., 2008; Chen et al., 2008; Hinther et al., 2011; Zorrilla et al., 2008). These environmental and toxicological concerns have lead the United States Food and Drug Administration to issue a ruling restricting the use of these compounds in consumer products (FDA, 2016). One such source of these antimicrobials to the environment is the wastewater treatment (WWT) process, where they are typically only partially degraded and, therefore, present in wastewater effluent (Lozano et al., 2013), untreated sludge (Verlicchi and Zambello, 2015), and treated sludge or biosolids (Andrade et al., 2015; Armstrong et al., 2017b; Verlicchi and Zambello, 2015). While degradation of TCS and TCC can occur during WWT, the extent to which this takes place is dependent on the treatment methods utilized by the WWT plant (Armstrong et al., 2017b; Pycke et al., 2014b).

TCS has been demonstrated to transform biologically into several compounds, including methyltriclosan (MeTCS), 2,4-dichlorophenol (2,4-DCP), and 4-chlorocatechol (Chen et al., 2015; Do Gyun Lee et al., 2012; Gangadharan Puthiya Veetil et al., 2012; Lozano et al., 2013). TCC, meanwhile, can be biologically transformed into carbanilides, including 4,4′-dichlorocarbanilide (DCC), 1-(3-chlorophenyl) − 3-phenylurea (MCC), and carbanilide (NCC), or either biologically or abiotically into 4-chloroaniline (4-CA) (Miller et al., 2010). Like their parent

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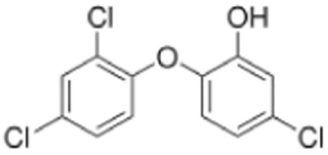
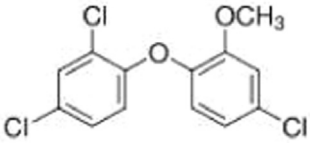
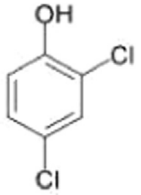
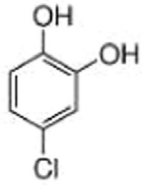
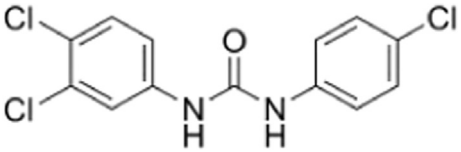
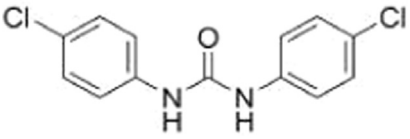
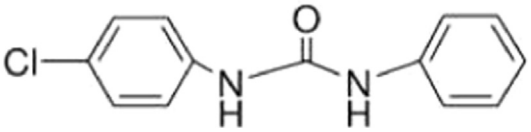
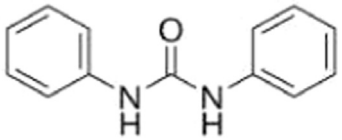
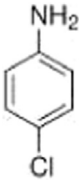
Table 1
Compounds Analyzed and Their Structures.

Compound	Structure
Triclosan (TCS)	
Methyl Triclosan (MeTCS)	
2,4-Dichlorophenol (2,4-DCP)	
4-chlorocatechol	
Triclocarban (TCC)	
4,4′-Dichlorocarbanilide (DCC)	
1-(3-Chlorophenyl) – 3-phenylurea (MCC)	
Carbanilide (NCC)	
4-Chloroaniline (4-CA)	

compounds, TCS and TCC transformation products, provided in Table 1, have themselves demonstrated undesirable environmental and health characteristics. MeTCS has been demonstrated to be more persistent than TCS (Lozano et al., 2012) and, like TCS, possesses endocrine disrupting capabilities (Hinther et al., 2011). Additionally the carbanilide analogs of TCC have also demonstrated the ability to impact the endocrine system (Ahn et al., 2008).

TCS and TCC degradation and the formation of transformation products have been shown to occur in the wastewater treatment process (Lozano et al., 2013; Pycke et al., 2014b). This research aims to simulate the activated sludge process in a controlled environment by using benchtop bioreactors, allowing for degradation rates and formation of degradation products to be determined under varying operational conditions. Changes in concentrations of TCC, TCS, and MeTCS were determined in two reactors run simultaneously over a 122–196 h time period at fixed-temperatures of 21 °C and 30 °C and degradation or