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THE EFFECT OF THE ANTIBACTERIAL HANDSOAP MATRIX ON THE KINETICS OF TRICLOSAN DISSOLUTION FROM SAND

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By

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THE EFFECT OF THE ANTIBACTERIAL HANDSOAP MATRIX ON THE KINETICS OF TRICLOSAN DISSOLUTION FROM SAND

A THESIS APPROVED FOR THE
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

BY

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Dedication

This written work is dedicated to all of the Native American tribes that have gathered together for this historic moment at Standing Rock, North Dakota. Water is life and we should all strive to be water protectors like everyone involved in this movement. – Dancing Water

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First and foremost, I must thank the almighty, omnipotent Lord for giving me grace, forgiveness, and love. Through you all things are possible and made whole and complete.

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Chapter 1 - Introduction

Trace amounts of many anthropogenic compounds are present in the environment in which we live and thrive. Of great concern is the impact of developed nations' wastewater treatment plant effluent on receiving waters. The low removal efficiency of recalcitrant compounds, such as triclosan, produces residual amounts of pharmaceuticals, personal care products, and industrial chemicals that are frequently below detection thresholds of common methods of analysis. Although some of these compounds degrade rapidly in the aqueous state, many can mechanistically accumulate onto carbon rich sediments and avoid degradation. The mobility and recalcitrance of anthropogenic chemicals within saturated sediments is of great concern in regards to the public health and safety of communities downstream of treated effluents. It is equally important in regards to environmental stewardship, since the more recalcitrant chemicals have the potential to be persistently rereleased into the surrounding water column.

Triclosan, also named as Irgasan as well as 5-Chloro-2-(2,4-dichlorophenoxy)phenol, is a commonly used chemical in many household products such as disinfecting handsoaps, cosmetics, and dental products in the United States. Triclosan is a highly studied endocrine disrupting compound due to its prolific use and subsequent detection in wastewater treatment plant effluent, riverine systems, sediments, and estuaries.

The need to further understand emerging contaminants of concern (ECC) adsorption and dissolution mechanics in river sands is of mounting concern in the scientific community. Adsorption-dissolution kinetics are paramount to ascertaining

anthropogenic impacts on human health, the environment, and water quality of our river systems. The properties of any ECC to solubilize in water and partition onto organic carbon directly affects how mobile or stationary a compound is in the aquatic environment. The rate at which adsorption-dissolution occurs for a given compound can be described as its kinetics and is directly related to its fate and transport. This study examines the dissolution kinetics of triclosan from amended F-65 Ottawa sand. F-65 Ottawa sand is a high-purity silica sand originating from Ottawa, Illinois. It is used for this work as a model river sand. Two sources of triclosan were analyzed, originating from both a high-purity triclosan compound, Irgasan, and from Bac-Down, a triclosan-based antimicrobial hand soap that contains both nonionic and anionic surfactants.

This research produces data that delineates the effects that additives found in personal care products have on dissolution kinetics. Consequently, it adds to the current knowledge of triclosan and provides data in support of models that predict ECC fate in the environment. This thesis also adds to the current body of research on the disolution potential of triclosan in riverine systems. The research goals of this thesis are to: 1) quantify the dissolution kinetic rates of triclosan from amended sand; 2) assess the impact that drought has on the fate and transport of triclosan compounds by examining the dissolution of sand-adsorbed triclosan that has been placed under high, evaporative temperatures; 3) quantify and characterize the effects that additives in personal care products have on the dynamics of triclosan dissolution.

The southwestern United States has a long-standing history of being encumbered by periods of severe drought. Flooding events are also becoming

increasingly disastrous and have recently broken all records in our documented history. To study and ascertain ECC and their mechanisms in the natural systems in which they are placed, under the stressed conditions they are now subjected to, is to invest in our state's mitigation and adaptation strategies involving water reuse, micropollutants, and impacted ecosystems. This body of work proposes potential implications for the utilization of naturally occurring alluvium for attenuation of wastewater treatment plant residuals. Critical periods where a riverine system may be most sensitive and susceptible to endocrine disrupting activity are highlighted. In addition, the use of tertiary treatment systems for reclaimed water reuse is evaluated within the context of this research.

Chapter 2 - Background

2.1 Endocrine Disrupting Compounds

A subcategory of emerging contaminants of concern that have a significant ecological impact are those compounds that disrupt an organism's endocrine system, thereby interfering with normal hormone synthesis and function. Endocrine-disrupting compounds undermine the endocrine system by mimicking or antagonizing (i.e., blocking) endogenous hormones, or by interfering with hormone synthesis, metabolism, or transport (Barrett 2014). An EDC can have a cumulative effect with other varieties of EDCs, observed as an additive whole compounding the biological effect of endocrine disruption (WHO/UNEP 2013). Endocrine disrupting compounds are within the umbrella of ECCs and include a wide range of pharmaceuticals, personal care products, and industrial chemicals. Many of these anthropogenic chemicals are recalcitrant and thus present in publicly owned treatment works (POTW) effluent despite the current

age's great advancement of wastewater treatment processes. These chemical compounds commonly survive in residual amounts and upon reaching a POTW's effluent adsorb to colloidal particles and stream sediments, thus effectively escaping mechanisms of degradation such as photodegradation.

The study of the behavior, fate, and transport of endocrine disrupting compounds have been of paramount concern to the scientific community and many scientists have laid the foundations for future research. Endocrine disrupting compounds are ubiquitous with environmental exposure to EDCs and is viewed to be inevitable for the global population (Fuhrman, Tal and Arnon 2015). Furthermore, endocrine-related diseases and disorders are becoming increasingly observed around the world such as low fertility, genital malformations, thyroid disorders, and endocrine-related cancers. (Freidrich 2013; WHO/UNEP 2013). These health problems are occurring at a rapid rate indicative of non-genetic factors, including anthropogenic chemical exposures (WHO/UNEP 2013).

2.2 Triclosan

Triclosan has been identified as an endocrine disrupting compound that closely resembles anthropogenic estrogens and is known to disrupt and influence the reproductive endocrine system in mammals and aquatic species via three potential mechanisms: disruption of hormones, the displacement of hormones from receptors, and the disruption of steroidogenic enzyme activity (Wang and Tian 2015). Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is a synthesized chlorinated phenoxyphenol (Figure 2.1) that is used as an antimicrobial agent because it inhibits fatty acid synthase in bacteria and has been increasingly used since the 1980's in many personal care

products (Vandhana, et al. 2010). Triclosan is used in formulations of hand soaps, dental care products, cosmetics, detergents and other household products, added at levels typically between 0.1% and 0.3% by weight (Cantwell, et al. 2009). Previous estimations of the combined inputs of triclosan and triclocarban into the U.S. environment has exceeded 600,000 kg/year and has been estimated to approach 10,000,000 kg/year (Miller, et al. 2008).

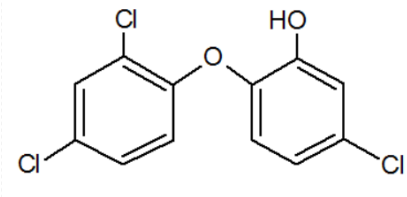


Figure 2.1 Triclosan Chemical Structure

Triclosan is predominantly hydrophobic (log K_{ow} = 4.76) and has low solubility (S_w = 10 mg/L) in water; however, it is still frequently detected in wastewaters and surface waters (Cho, Huang and Schwab 2011). The hydrophobic attribute of triclosan makes it a prime candidate for sorptive processes out of a water matrix and onto solid phases with favorable surfaces such as riverine sediments and colloidal particles. Although pure triclosan solubility is relatively low, observed environmental concentrations of triclosan post-POTW effluent are considerably lower. This implies that even at some of the highest POTW effluent concentrations (5.37 µg/L) all triclosan that enters into a riverine system has the potential to remain in the water matrix without precipitation occurring (Montaseri & Forbes 2016). Given a pKa of 8.1, aqueous pH influences Triclosan's speciation, fate, and its affinity to stay or remain in the aqueous phase (Singer, et al. 2002). Lower pH values than triclosan's pKa constitute hydrogen

ion activity that is strong enough to keep triclosan protonated; therefore, any pH higher than this pKa would dissociate triclosan's critical hydrogen ion, changing this compounds polarity and affinity for sorptive mechanisms.

Many studies have indicated that triclosan is retained and recalcitrant in soils and sediments. An outdoor mesocosm study of 72 PPCPs, which included triclosan, Walters et al. (2010) indicated that although degradation of PPCPs occur over time many of the compounds persist in agricultural soils years after biosolid application and triclosan remained detectable for 858 days. It is then apparent that triclosan can remain preserved in soils with adequate organic fractions for well over two years.

Research has also shown triclosan is mobile once in riverine systems, most of which ultimately end up depositing their waters into an oceanic system. Sediment core samples of multiple urbanized estuaries in the United States were studied by Cantwell et al. (2010) to assess spatial and temporal triclosan concentrations. The study concluded that triclosan has long-term stability in estuary sediments, a marked increase of triclosan in sediments since its 1964 patent was issued, and unique site variability dependent on industrial activity and wastewater treatment technology. Marine sediment column mesocosm studies were also performed by Ho et al. (2012) that noted the negative impact of increasing triclosan concentrations on marine benthic organisms and gave warning to the increasing usage and subsequent discharge of triclosan. Sangster et al. (2014) suggested the possibility of aquatic organisms' absorbing biologically active steroids (i.e. estrogenic compounds) that were associated with colloidal material. It can then be seen there is a lack of knowledge regarding the dissolution mechanisms involving the relationship of triclosan and riverine sediments.

The occurrence and fate of triclosan in wastewater, wastewater treatment sludge, effluent receiving surface water, and lake sediments was observed by Singer et al. (2002). It was found that that although surface waters had triclosan levels (50 ng/L) below a predicted no-effect concentration, the concentrations detected in lake sediments indicated the persistence of triclosan in the aquatic environment. It expressly warned of the increasing urban use of triclosan despite advancements in WWTP technology that occurred in the mid-1970s.

2.3 Publicly Owned Treatment Works

In the United States pharmaceuticals, personal care products, and industrial chemicals are mostly removed from wastewater through a series of biological processes that occur in publicly owned treatment waterworks (i.e. POTWs). The reduction and/or transformation, of these contaminants vary, from the type of treatment technology implemented to the physicochemical properties of an individual ECC (Stanley 2014) such as that of triclosan.

The conventional wastewater treatment process is defined in this work as consisting of one or more series of coagulation, flocculation, sedimentation, and operational units, including biological digestion. Key removal mechanisms of triclosan include adsorption to activated sludge, biological degradation, and advanced treatment technologies (e.g. Ozonation/H_2O_2) (Ahmed et al. 2016). Advanced treatment technologies are more scarcely seen due to the cost associated with improving existing POTWs within municipalities across the United States.

With the lack of widespread use of advanced and hybrid treatment technologies, mass loadings of residual triclosan into riverine systems occur on a regular basis. These concentrations in the water column (up to 86 µg/L) are often below common, simple methods of detection and require advanced, expensive analyses to quantify (Salvatierra-Stamp et al. 2015). The continual loading of residual ECC from conventional wastewater treatment plants (i.e. lacking advanced or hybrid treatment technology) into riverine sediments of commonly dry, low precipitation regions, such as the southwestern United States, frames an issue that continual augmentation of rivers allows for the accumulation and mobility of triclosan (from 0.1 - 53.0 mg/L) in riverine sediment (Montaseri & Forbes 2016).

2.4 Adsorption

Triclosan concentrates onto riverine sediments by way of adsorption. Triclosan in the aqueous form is protonated below a pH value equivalent to its pKa value (pKa = 8.1). Under these conditions, triclosan can adsorb onto riverine sediments at the outfalls of a POTW by accumulating on the surface of the sediments and forming a film. The adsorption process is limited by the extent of particle exposure through agitation and the available surface area that is effective in partitioning triclosan out of the water column. Adsorption of this kind would occur from ion exchange between aqueous triclosan and sediment particles, as well as Van der Waals electrostatic forces (Zaghtiti 2009).

During periods of drought, riverine systems are altered and placed under greater amounts of stress from human activity. Water flows are minimized due to less precipitation and higher evapotranspiration rates. Larger surface areas of river banks are dried and expose large tracts of riverine sediments. The input of POTW effluent

into riverine systems becomes a greater portion of a river's volumetric flow rate during these periods. This decreases the typical dilution of trace ECC that enter the natural environment when mean river flows are present. Studies performed germane to the impact of drought on wastewater contaminants in Lake Mead, which lies on the state borders of Arizona and Nevada, by Benotti et al. (2010) illustrated that drought would cause an increase in wastewater treatment residual contaminants due to a marked decrease in dilution capacity of the receiving rivers. These sediments become largely unsaturated over the period of the drought and have a greater affinity to adsorb trace ECC from POTWs at effluent concentrations. Therefore, times of drought are seen as critical periods to the saturation and preservation of ECC, including triclosan, in riverine systems.

2.5 Dissolution

Dissolution occurs when sediment particles that have interacted with a contaminant come into nonequilibrium with the surrounding environment and the aqueous chemical species are formed (Zhao 2014). Likewise, once triclosan is associated with a sand grain it will continuously attempt to maintain equilibrium with the surrounding water column. The dissolution process is driven by undersaturation within a water matrix and begins to slow as saturation is approached (Cornell 2004). Rate limiting mass transfer between an aqueous phase and an insoluble compound can dampen the dissolution process (Soerens 1998).

Dissolution and desorption are two distinct processes that are worth contrasting in this body of work. Desorption is the process by which a compound is detached from an available, active site of a solid particle. Dissolution occurs when a compound

transitions from a solid phase to a liquid phase, typically moving through a diffuse layer that is driven by a concentration gradient between that of the solid phase's surface concentration and that of the surrounding bulk solution. In the context of this research the dissolution process is observed and quantified.

The dissolution process can be depicted by graphing the change of a compound of concern's concentration in solvent through time. Dissolution from a solid compound is governed by the Noyes-Whitney equation (1) which states that the dissolution kinetic rate is first-order and proportional to the difference of the dissolved concentration at a given time to that of the compounds ultimate solubility concentration (Dokoumetzidis et al. 2006).

$$\frac{dC}{dt} = k(C_s - C) \qquad (1)$$

The Noyes-Whitney equation presented is based on Fick's Law of Diffusion. This equation is derived from the Fickian diffusion concept that concentration gradients drive the flux of dissolution from high concentrations to lower concentrations in the natural order of establishing dynamic equilibrium. This can be substituted into the equation yielding the following equation (2) that solves for the dissolved concentration of a substance in dissolution at a given time:

$$C(t) = C_s(1 - e^{(-kt)}) \qquad (2)$$

Where k represents the kinetic dissolution rate constant which shall remain constant, as long as the system is under the conditions of constant temperature, solvent volume, and agitation (Hattori et al. 2013).

Surfactants are additives commonly used in household products, such as soaps and detergents. Surfactants can increase the solubility of hydrophobic organic compounds or lower the interfacial tension to enhance the mobility of hydrophobic organic compounds (Zhang 2013). Accordingly, surfactants are used to increase the solubility of triclosan in antibacterial hand soaps. Similarly, many additives that currently are in use for these products can enhance or slow the dissolution process. Although the solubility of the compound is affected by the surfactant, this described change in physical kinetics can cause alterations in a compound's dissolution, which could be reflected in changes to its dissolution rates.

In the natural environment, the aquatic chemistry is rarely at an equilibrium. Many hydrological inputs and outputs are constantly changing; therefore, riverine water column and sediment concentrations would rarely see physicochemical equilibrium. Intense precipitation overburdens urban infrastructure, POTWs, and the natural environment alike. The current trend of increasing storm intensity has caused larger storm water runoff volumes from urban developments and can overload POTW systems to the point where they must bypass untreated water into a riverine system. Wilson et al. (2015) observed and tested the Rio Grande River during a large flooding event and indicated that flooding can cause WWTP effluent residuals to contaminate floodwaters and infiltrate bank sediments, most noticeably through particle adsorption and deposition, and that PPCPs can persist in riparian soils post-flooding. Unfortunately, the occurrence of these severe storms during periods of prolonged severe drought do little to salve the situation. Penetration of rainwater into the ground's water table is a slow process that causes a large majority of intense storm waters to become runoff,

increasing a watershed's volumetric flows, and ultimately causing flooding of urban areas, floodplains, and river systems. Of highest concern in this body of work is the agitation of triclosan contaminated river alluvium, dissolution of desiccated, preserved triclosan within river sands, and the subsequent transport of triclosan throughout the natural environment from these "desiccation-saturation cycles". Triclosan is continuously released into the environment as a result of incomplete removal efficiencies at POTWs. Thus, triclosan is believed to pose the risk to be transported in floodwaters during flooding events, potentially impacting floodplains (Wilson, Addo-Mensah and Mendez 2015).

Chapter 3 - Methodology

3.1 Research Overview

This study examines and quantifies the dissolution process of triclosan in amended F-65 Ottawa sand. This study looked at three concerns regarding the dissolution process triclosan: 1.) the quantification of dissolution kinetic rates of triclosan amended in the sand with and without surfactant addition; 2.) the quantification and characterization of the effects that increasing amounts of triclosan mass loadings and surfactants have on triclosan's dissolution kinetics; 3.) the correlation between triclosan's dissolution kinetic rate and triclosan's aqueous solubility.

The dissolution process was observed through UV-photospectroscopy and statistical analysis. F-65 was washed and the dried under high evaporative temperatures. F-65 was then amended with triclosan stock solutions and allowed to dry at varying temperatures. Each sample was weighed and then allowed to dissolve through agitation

within the water column of a nylon cell. Light absorbance was measured for each sample across a range of wavelengths during the dissolution process through UV-photospectroscopy. Prior to dissolution, standards were made for both the effect of F-65 agitation in deionized water and for a known concentration of triclosan stock solution. Each individual triclosan dissolution was statistically fitted to the known standards and a dissolution curve was produced with aqueous concentration versus time. By solving the Noyes-Whitney equation, triclosan dissolution kinetic rates and triclosan aqueous solubility concentration were obtained for each sample.

Dissolution kinetics were quantified and characterized for pure triclosan and surfactant-based triclosan samples. Samples were performed in triplicates. Samples that were amended with pure triclosan were compared to samples amended with surfactant-based triclosan of equivalent concentrations. Samples with surfactant-based triclosan were also performed with a range of concentrations obtained through stock dilution. The results of these samples were compared with one another to observe the effect of increased surfactant concentration and mass loadings. The kinetic dissolution rates of these samples were compared with the initial concentrations of the stock solutions used to amend the sands to evaluate the possibility of correlation. Triclosan dissolution rates were also compared with observed aqueous saturation concentrations better quantify the correlation between the two.

3.2 F-65 Washing Methods

The model sediment selected for this study is F-65 Ottawa sand. F-65 is a quarry Ottawa, Illinois supplied by US Silica. As a high-purity silica sand, F-65 was selected with the purpose of studying the dissolution process in a model sand with a low

organic fraction. F-65 is known to have a net negative surface charge at a range pH values that are common in riverine systems, and has been observed to retain a negative zeta potential from a pH range of 4.5 up to 10 (Fujita & Kobayashi 2016). F-65 was first washed to remove fine particles that have settling velocities small enough to remain suspended in solution. F-65 was washed and drained with tap water in a 1 L graduated cylinder ten times. This was followed with 15 rinses with deionized water. The F-65 was then placed in an aluminum foil vessel and dried at 110°C in a Blue-M OV-12A Stabil-Therm Gravity Oven for 24 hours. The and was then removed from the oven and covered while being allowed to cool prior to use.

3.3 Triclosan Stock Preparation

Pure triclosan stock solution was created by dissolving Irgasan, ≥97.0%, as determined by HPLC, (Sigma Aldrich) in Acetonitrile, HPLC-ACS-grade (Fisher Scientific). A 100 mL stock solution of acetonitrile was prepared in a 100 mL Erlenmeyer flask to a concentration of 500 mg/L Irgasan. Stock solution was securely sealed and agitated for 24 hours by use of a Barnstead Thermolyne M49235 Orbital Lab Rotator. When not in use the stock solution was completely covered in aluminum foil during storage in order to eliminate any possible photodegradation.

Bac-Down stock solution was created by dissolving Bac-Down antimicrobial handsoap (0.5% w/w) in deionized water. A 250 mL stock solution was prepared in a 250 mL erlenmeyer flask to a concentration of 500 mg/L. Stock solution was securely sealed and agitated for 24 hours by use of the orbital lab rotator. This stock solution was also completely covered in aluminum foil during storage order to eliminate any possible photodegradation.

The pH of stock dilutions were measured with an AR60 dual channel pH/ION/Conductivity/DO meter (Fisher Scientific). The pH of the stock dilutions were observed due to the pK_a of triclosan (8.1).

3.4 Sample Preparation

Pure triclosan experimental samples were prepared by weighing 16 g of F-65 sand into a 1 and 3/8 fl. Oz fluted aluminum weighing dish (Fisher) in triplicates. The 500 mg/L stock solution was diluted to 250 mg/L. Each sample was amended with 4 mL of this solution in order to saturate the sand. Each sample was then mixed in order to ensure homogenous cover. The samples were then placed into a fume hood to dry at room temperature (20~22^{o}C) for 24 hours prior to use.

Bac-Down triclosan samples prepared by weighing 56 g of F-65 Sand into a fluted aluminum weighing dish in triplicates. The 500 mg/L stock solution was diluted to concentrations of 333 mg/L, 250 mg/L, and 167 mg/L. Sample triplicates were amended with 14 mL of either 500 mg/L, 300 mg/L, 250 mg/L, or 167 mg/L. These samples were placed in a IS-41 American gold series Incubator (American scientific products) to dry at 60°C for 24 hours prior to use.

3.5 Dissolution in Nylon Cell with Fiber Optic UV-spectrophotometer

Dissolution experiments were performed in a custom-made nylon cell that was fashioned to hold and seal a fiber optic spectrometer while creating a continuously stirred tank reactor. The cell is cylindrical in shape with two flat surfaces cut into the cylinder parallel to each other (Figure 3.2). On both sides of these surfaces are threaded holes fashioned to hold and seal the fiber optic needles 1.52 cm from the top of the cell.

In the center of the cell is a well that is 3.81 cm in diameter 3.81 cm in depth. The total height of the cell is 4.45 cm.



Figure 3.1 Nylon Cell with Fiber Optic UV-spectrophotometer

To gather and collect data during for these experiments a PX-2 pulsed xenon light source (Ocean Optics Inc.) and a SD 2000 fiber optic spectrometer (Ocean Optics Inc.) was fastened and sealed to the nylon cell's threaded holes. The fiber optic needles were aligned to face each other for proper calibration and function. One fiber optic cable was aligned and measured to extend 0.585" from the well's inner circumference. The other fiber optic cable was aligned and measured to extend 0.883" from the well's inner circumference as well. These measurements were checked prior to each dissolution experiment in order to ensure accuracy and precision of data collection.

A calibration was performed for the fiber optic system prior to each dissolution experiment. The calibrations were performed on the PcS_Scan ver. 4.8.4 (Chen et al. 2007) program used to measure and collect the experiment data. First, the cell was

filled with deionized water and the PcS_Scan program was initialized. A dark spectrum reading is taken, followed by turning on the strobe light, allowing the system to equilibrate for 30 seconds, and then taking a reference spectrum sample to capture absorbance in the cells medium (deionized water). Next the cell is emptied and "snapshots" were taken of solutions that were to be used as references to fit the dissolution curves after the dissolution experiment is performed. Two references were made by taking snap shots. The first reference was for a known stock dilution of 7 mg/L of pure triclosan in deionized water. The second reference was an F-65 sand reference where 15 g of F-65 had been continuously stirred in deionized water for 80 minutes in order to assess the impact that agitated F-65 has on the measured light absorbance for these experiments. Continuous stirring is accomplished with a magnetic stirring bar and a Thermolyne climarec 1 magnetic stirring plate. The two references created were then processed in a conversion program called Spec2Abs (Kibbey et al. 2009). Spec2Abs converted the .spec reference snapshots into .abs files that could then be utilized to fit every set of dissolution experiment data.

Dissolutions experiments were prepared identically for each amended sand sample. From each sample 15 g of amended F-65 was weighed into a fluted aluminum weighing dish. After calibrating the fiber optic system and emptying the nylon cell of any deionized water, the amended sand is added into the cell's well along with a magnetic stirring rod. The cell is then placed on the magnetic stirring plate and is filled with deionized water while simultaneously initiating the data sampling sequence. The magnetic stirring plate was set to its dialed labeled "1" and was recorded to at 110 rotations per minute (rpm). Each dissolution was allowed to run for 3,600 - 4,800

seconds (1 – 1.33 hours). The mass of deionized water used for each experiment sample was recorded.

3.6 Decontamination

A process of decontamination was followed in order to ensure removal of triclosan from instruments, beakers, and the nylon cell. Decontamination began with five deionized water rinses. The nylon cell would then receive a Methanol, HPLC-grade (Fisher Scientific) rinse. Instruments and beakers utilized received a 2-Propanol, HPLC-grade (Fisher Scientific) rinse. These desorption rinses were then followed by ten deionized water rinses. The nylon cell and beakers would then be filled with deionized water which was then immediately discarded. Items were either placed back into use or allowed to dry for at least 12 hours.

Erlenmeyer flasks that were used to house Irgasan and Bac-Down stock solutions were soaked for 24 hours at the end of each stock's use. Alconox powder precision cleaner (Alconox Inc.) was prepared to specifications. Flasks were then soaked overnight for 24 hours. After soaking the flasks were washed 15 times with tap water, followed by 10 washes with deionized water. Flasks were then placed to dry until further use.

3.7 Analysis of Dissolutions

After each sample was analyzed with a UV-spectrophotometer to measure light absorbance across a spectrum of 200 to 550 nm, a program created to fit known references to analyzed dissolution data, SpectrumFit (Kibbey et al. 2009), was used. Each dissolution experiment was fit with four references. Using PcS_Scan a dark

spectrum and reference spectrum was produced and used for each dissolution individually in the SpectrumFit analysis. Two prior Snapshots taken for the F-65 sand reference and the characteristic 8 mg/L triclosan solution (Figure 3.2) in PcS_Scan were converted from a .spec file to a .abs file and utilized for all dissolution fitting in SpectrumFit. Each dissolution was fitted for a wavelength range of 240 – 400 nm. This range was selected since it captured the triclosan's characteristic curve, as well as removed the noise that is commonly experienced at the upper and lower ends of the wavelength range (i.e. $\leq$ 220 nm, $\geq$ 450 nm).

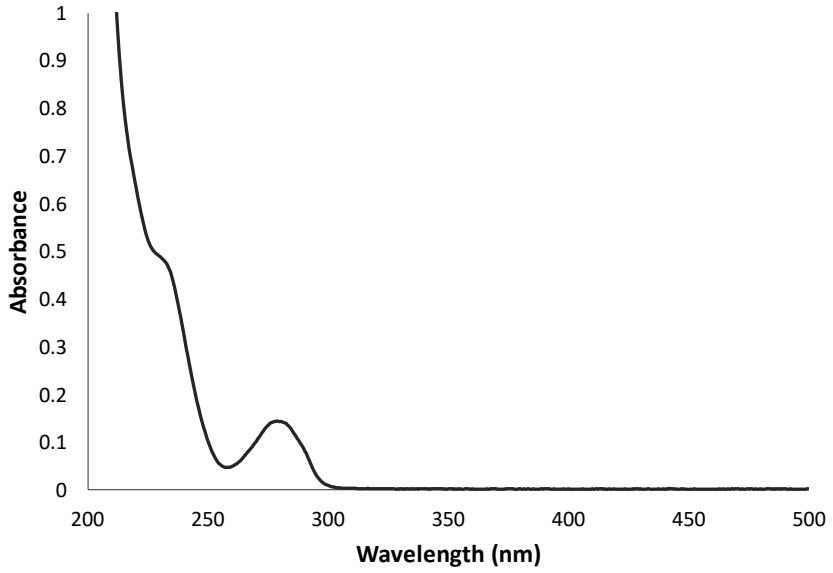


Figure 3.2 10 mg/L Pure Triclosan in Deionized Water - 240 Seconds

SpectrumFit produced data that provided dissolution curves from the dissolution of amended F-65 sand experiments. The concentration of triclosan detected in the water column was plotted versus time to produce the curves. By solving the Noyes-Whitney equation, performing residual sum of squares analysis, (Eqn. 2) and optimizing iterations to minimize observed error in the Solver function of Excel, kinetic rates of the

dissolutions were calculated. ANOVA statistical analyses were performed on this triplicate data to ascertain the kinetic dissolution rate average, variance, and test of significance producing confidence intervals.

Chapter 4 – Results & Discussion

4.1 Irgasan Dissolution Curves

The SpectrumFit program was used to produce dissolution curves for 250 mg/L pure triclosan triplicates (Figure 4.1). The pH of this stock dilution was observed to be 6.60, which is below triclosan's pK_a of 8.1. Triclosan thus stays protonated and retains its affinity for adsorption to F-65 sand's negative surface charge. The average solubility concentration was 9.59 mg/L which approached known triclosan aqueous solubility limits of 10 mg/L. The kinetic dissolution rate was determined to be 0.0065 s^{-1}. Both descriptive characteristics were determined by optimizing the system of equations through minimizing the cumulative error from residual sum of squares analysis and allowing these two variables to change in the solver function, precisely fitting a dissolution curve to the data produced by the dissolution experiment (Figure 4.2).

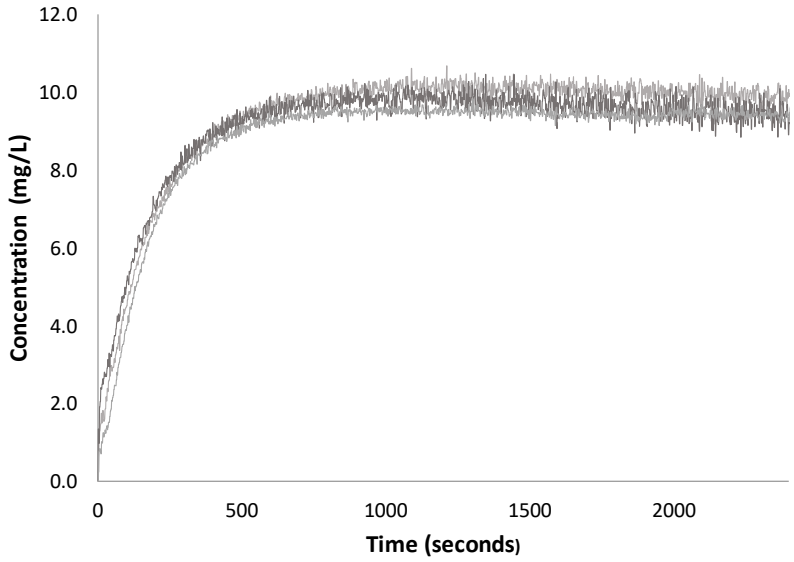


Figure 4.1 250 mg/L Pure Triclosan Dissolutions in Nylon Cell - Composite

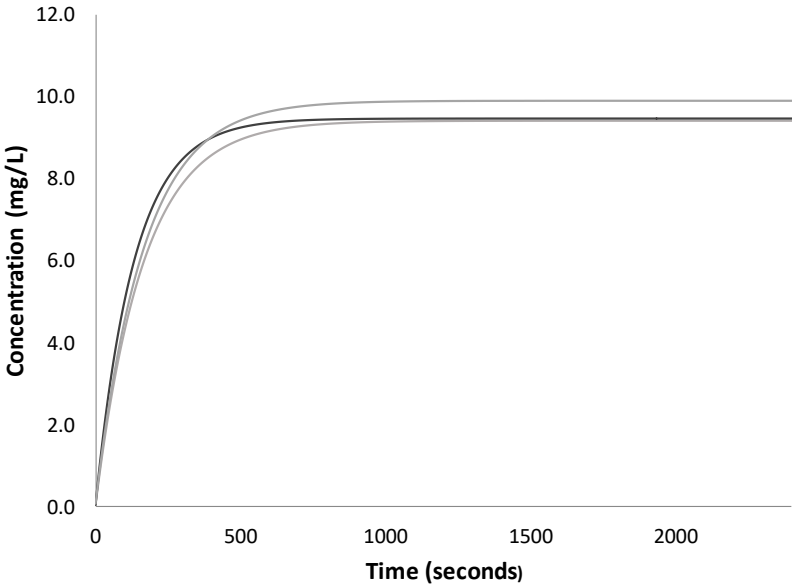


Figure 4.2 250 mg/L Pure Triclosan Dissolutions in Nylon Cell Fit-curves – Composite

4.2 Bac-Down Dissolution Curves

Dissolution curves were created for Bac-Down amended F-65 triplicates for varying concentrations of 167, 250, 333, and 500 mg/L. The pH of the 500 mg/L stock solution was 7.01 and the subsequent stock dilutions with deionized water retained a circumneutral pH. The solubility concentration and dissolution kinetic rates were derived for these experiments in the same fashion as the Irgasan amended triplicates. The average kinetic dissolution rates and the average solubility concentration of each dissolution triplicate is provided in Table 4.1. One dissolution in the 167 mg/L triplicates was removed from analysis due to induced error by premature addition of deionized water into the cell as the acting solvent. Triplicate dissolution curves produced through executed dissolution experiments and dissolution fit-curves for 167, 250, 333, and 500 mg/L concentrations of the Bac-Down amended F-65 experiments compiled in Appendix A.

Table 4.1 Bac-Down Dissolution Parameters

Triclosan Source	C_{spiked} (mg/L)	Mass Loading (mg/kg)	C_{sol} (mg/L)	$k_{dissolution}$ (s^{-1})	Std. Deviation
Bac-Down	500	3018.87	34.08	0.0106	0.00291
Bac-Down	333	2010.57	24.39	0.0100	0.00137
Bac-Down	250	1509.43	19.93	0.0085	0.00401
Bac-Down	167	1008.30	11.52	0.0079	0.00194

The average kinetic dissolution fit-curves were crafted and compared (Figure 4.3). Increasing concentrations of Bac-Down amended F-65 sand was directly related to increased dissolution kinetics despite desiccation of the 56g sand samples at 60^{o}C. The increase of the mass loading of Bac-Down was strongly correlated with an increase in dissolution kinetic rates (Figure 4.4) and was illustrated by an R^2 value of 0.915. This establishes the foundation that some triclosan-based antimicrobial hand soaps

possess the ability to persist in drying sand beds with high, desiccating temperatures. The implications of this evidence enhance the argument that triclosan can be drought-tolerant in the sub-surface of river alluvium that avoids photodegradation.

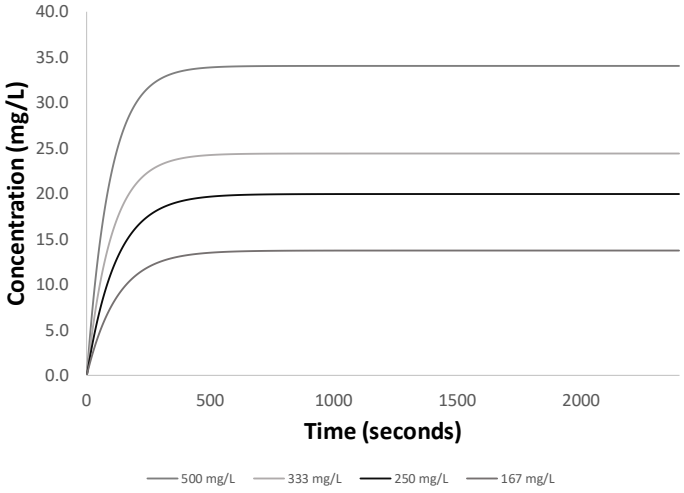


Figure 4.3 Bac-Down Antimicrobial Hand Soap Average Kinetic Dissolution Fit-curves

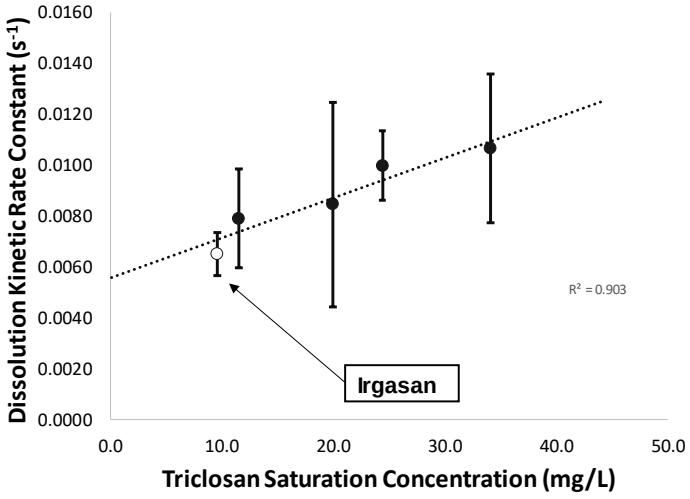


Figure 4.4 Bac-Down Kinetic Dissolution Rates Versus Triclosan Mass Loading Rates

Increased mass loading of Bac-Down triclosan is proportional to an increase of anionic and nonionic surfactant mass loading of the sample. The concentration of the amended Bac-Down F-65 experiments had a strong correlation to the dissolution kinetic rate that was identical to its mass loading, as it is essential to view these two concepts as the same process. The increase in Bac-Down mass loading of triclosan illustrated an even stronger correlation to the saturation concentration of detected triclosan with an R^2 value of 0.980 (Figure 4.5). This correlation is most likely attributed to the increased application of Bac-down's surfactant additive when applied to the F-65 samples. This would provide evidence that an increase in concentration, or use of, a triclosan product that contains surfactant additives would produce a linear increase in triclosan's aqueous saturation concentration equally proportional to the amount of product used for a given volume of water.

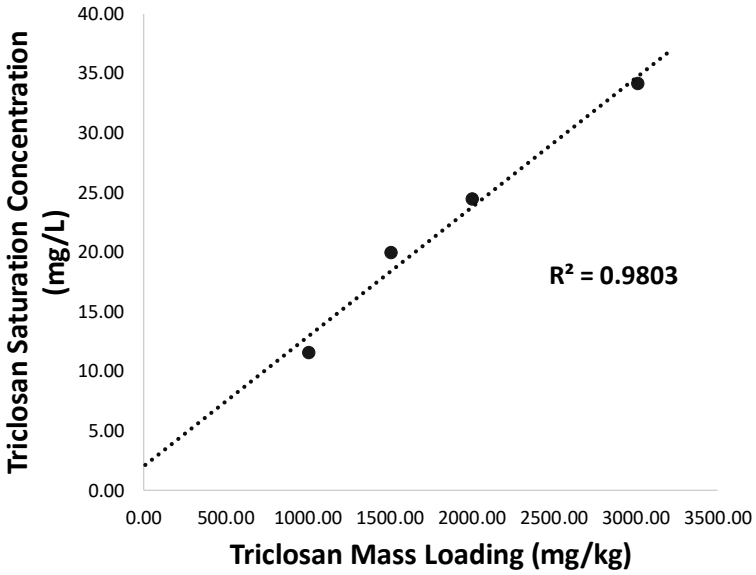


Figure 4.5 Bac-Down Triclosan Saturation Concentration Versus Triclosan Mass Loading Rates

4.3 Surfactant Analysis

The effects of surfactant in triclosan amended F-65 sand was analyzed by contrasting and comparing the kinetic dissolution of 250 mg/L Irgasan experiments with that of the kinetic dissolution of 250 mg/L Bac-Down experiments. The comparison of the two sets of triplicates' kinetic dissolution fit-curves (Figure 4.6) and the average kinetic dissolution fit-curves (Figure 4.7) produced significant contrast. Since the mass loading of triclosan is similar in both experiments, the effects of surfactant additives present in Bac-Down dissolution triplicates were able to be distinguished from pure triclosan dissolution triplicates.

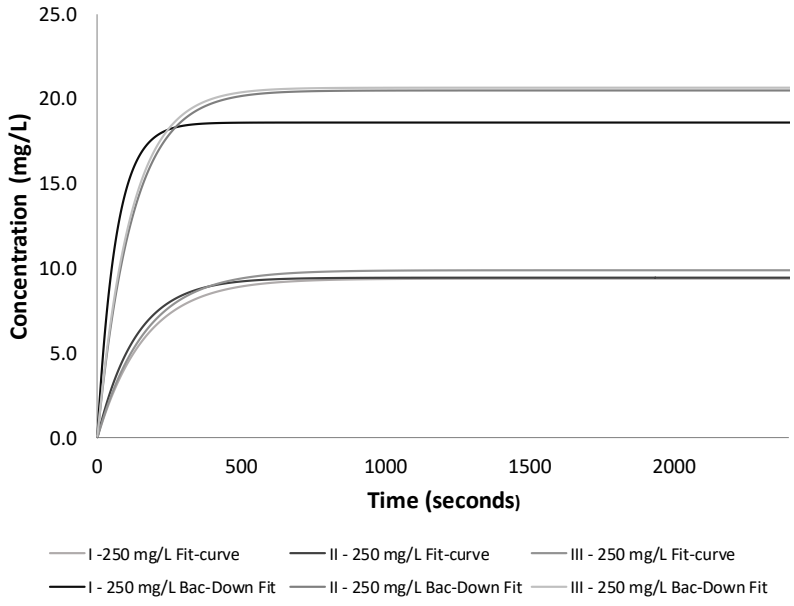


Figure 4.6 250 mg/L Pure Triclosan & Bac-Down Dissolutions - Composite

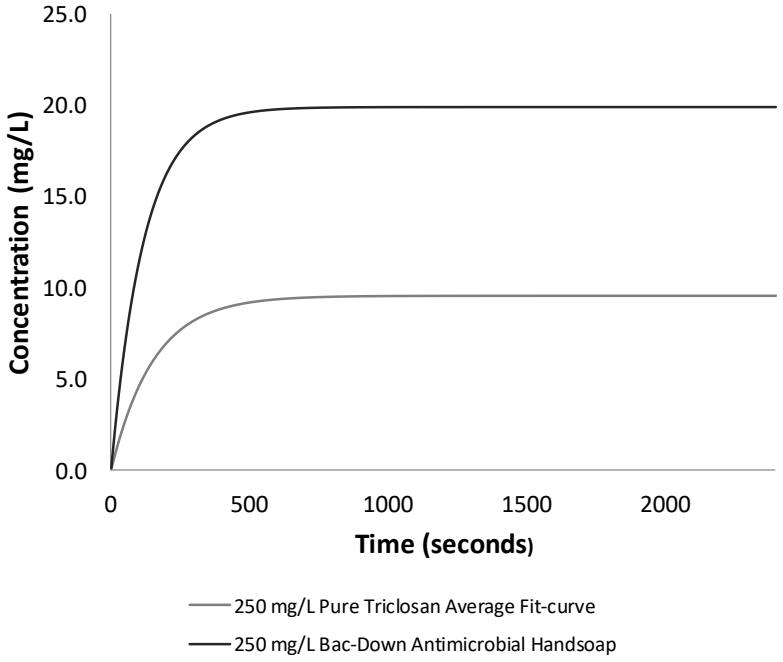


Figure 4.7 250 mg/L Pure Triclosan & Bac-Down Dissolutions Average Kinetic Fit-curves

A strong increase in triclosan's water solubility and a moderate increase in the kinetic dissolution rate was observed for triclosan in the presence of the surfactant-based Bac-Down. The average kinetic dissolution rates and average aqueous solubilities for both pure and surfactant-based experiments were compared (Table 4.2). The observed average aqueous solubility of triclosan was doubled for Bac-Down, as opposed to Irgasan dissolutions. An increase in the average kinetic dissolution rate of 31% was also calculated, respectively.

Table 4.2 Irgasan & Bac-Down Kinetic Dissolution Parameters

Triclosan Source	C_{spiked} (mg/L)	Mass Loading (mg/kg)	C_{sol} (mg/L)	$k_{dissolution}$ (s^{-1})	Std. Deviation
Irgasan ≥97.0% HPLC	250	1509.43	9.59	0.0065	0.00085
Bac-Down	250	1509.43	19.93	0.0085	0.00401

To assess the relationship of the dissolution kinetic rates with triclosan's saturation concentration of the Irgasan amended F-65 dissolution experiment was compared with all Bac-Down amended F-65 experiments (Figure 4.8). A strong correlation was maintained with a value for R^2 of 0.916. In this study, triclosan's dissolution kinetic rate has a positive linear relationship with the saturation concentration. An increase in the saturation concentration through the addition or increase of surfactants would therefore be likely to result in a proportional increase in the dissolution kinetic rates.

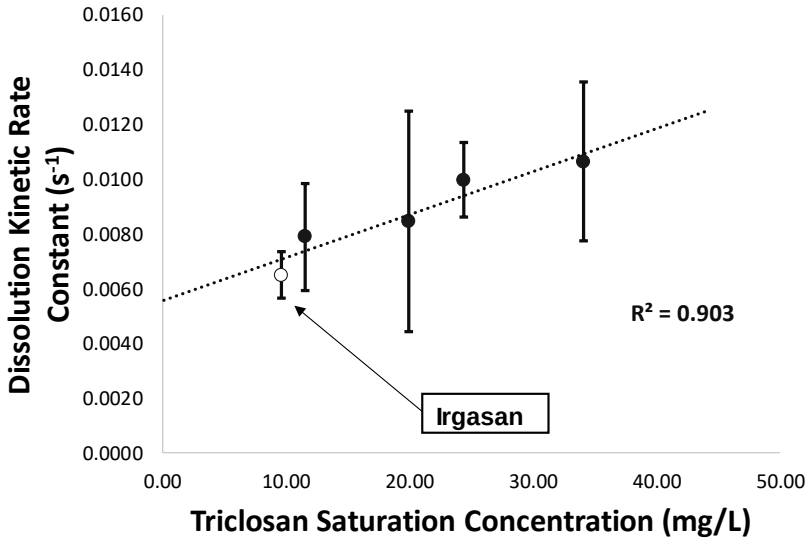


Figure 4.8 Irgasan & Bac-Down Dissolution Kinetic Rates Versus Triclosan Saturation Concentration

A relationship was was assessed between triclosan's dissolution kinetic rates and with triclosan's mass loadings of the Irgasan amended F-65 dissolution experiment compared with all of the Bac-Down amended F-65 experiments (Figure 4.9). A mild correlation was observed with a value for R^2 of 0.592. In this study, triclosan's dissolution kinetic rate has a positive linear relationship with the amended triclosan

concentration (i.e. mass loading). The increase in the dissolution kinetic rates through the increase of triclosan mass loading appears to be likely.

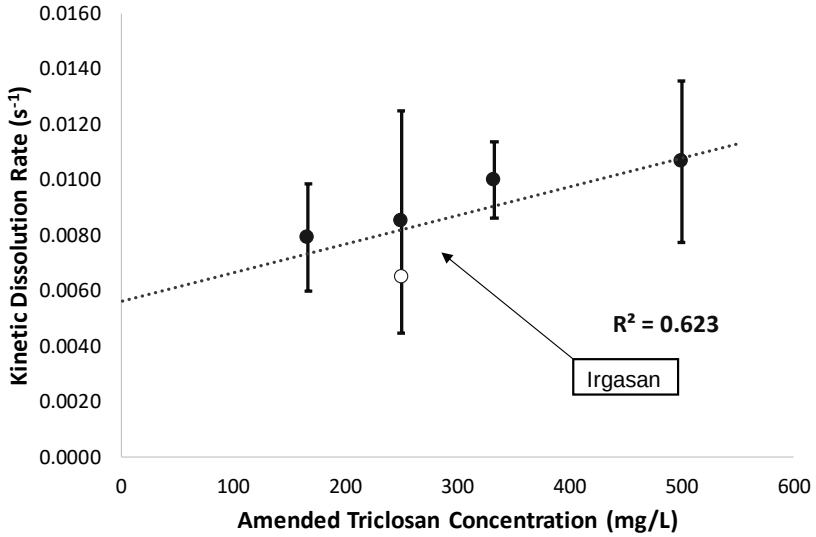


Figure 4.9 Irgasan & Bac-Down Kinetic Dissolution Rates Versus Triclosan Mass Loading Rates

Overall, it is evident that the surfactants present in Bac-Down have a much stronger correlation to the kinetic dissolution rate and triclosan's aqueous solubility than with the dissolution rate and mass loading. A large enough mass loading could not only coat F-65 sand grains, but also form triclosan precipitate interstitially. This would increase the effective surface area of triclosan for dissolution and thus increase the kinetic dissolution rate constant. However, since the correlation to triclosan's aqueous solubility was much higher than that of mass loading, a much more likely explanation for the trends observed in this series of data would be that the surfactants found in Bac-Down elevate triclosan's solubility concentration limit and this subsequently results in a proportional increase in its kinetic dissolution rate.

4.4 Nylon Cell Adsorption

When approaching the end of this study, a phenomenon was observed in dissolution curves that extended beyond 3600 seconds (1 hour) and was further investigated. The dissolution curves of concern experienced a slight decrease in the saturation concentration plateau around the 3600 second marker. The material of the nylon cell was then studied to observe adsorption potential of the cell's inner walls.

A pure triclosan stock dilution of 7 mg/L was created to fill the nylon cell and observe triclosan's concentration over time. This concentration was selected as it was below the saturation concentration of Irgasan (10 mg/L) and as such would not precipitate out of solution. The cell was decontaminated prior to this experiment as described in methods section. It was observed that over the duration of the dissolution experiments of 2400 seconds a decrease of 3 mg/L in solution was observed (Figure 4.10).

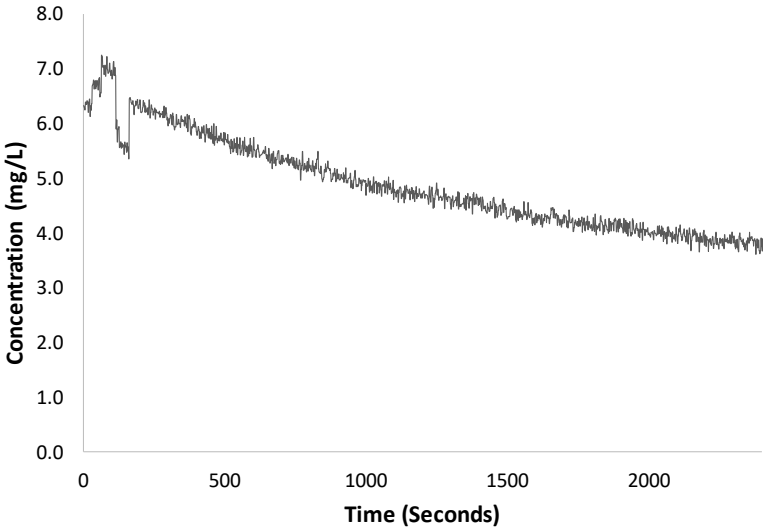


Figure 4.10 Triclosan Concentration in Nylon Cell with Time

The nylon cell has adsorptive potential with the compound triclosan. This mechanism could potentially be addressed by solving the Noyes-Whitney equation with a second adsorption constant (k_{ads}):

$$\frac{dC}{dt} = k(C_s - C) - k_{ads}(C) \quad (3)$$

Chapter 5 – Conclusions

The dissolution mechanisms of triclosan in a model river sand was observed and quantified. Kinetic rates were formulated based on drug dissolution theory involving the Noyes-Whitney equation. This study determined the effects that the saturation-desiccation cycle has on the dissolution mechanisms of surfactant-based triclosan. Surfactant-based triclosan was subjected to high evapotranspiration temperatures and was found to have negligible effects on the compound and its dissolution mechanics. Surfactants that are commonly found in triclosan-based consumer hand washing products increase the solubility of this compound in water and the kinetic dissolution rate. An increased dissolution rate could potentially lead to a greater mobility of this compound within the aquatic environment.

The fate and transport of triclosan within river and soil sediments under periods of extreme weather such as drought, flood, and the saturation-desiccation cycle needs to be further studied. Due to the relatively high cost of analyzing trace residuals in effluent receiving waters, this research created a low cost method of ECC observation and analysis by utilizing concentrations of these compounds that are higher than would be observed in the environment, ultimately establishing relationships with constituent behavior and extreme weather events. Based on this study, the dissolution potential of

triclosan is great enough to persist in riverine systems and travel down-gradient from the point of discharge. Surface waters are jeopardized by the saturation-desiccation cycle and some areas of the United States are projected to have changes in precipitation and surface water flow patterns as a result of global climate change (Benotti, Stanford and Snyder 2010). The ban on triclosan from consumer antiseptic washing products produced by the FDA on September 2nd, 2016 will greatly reduce the complex social, environmental, and economic risk from surfactant-based products containing triclosan.

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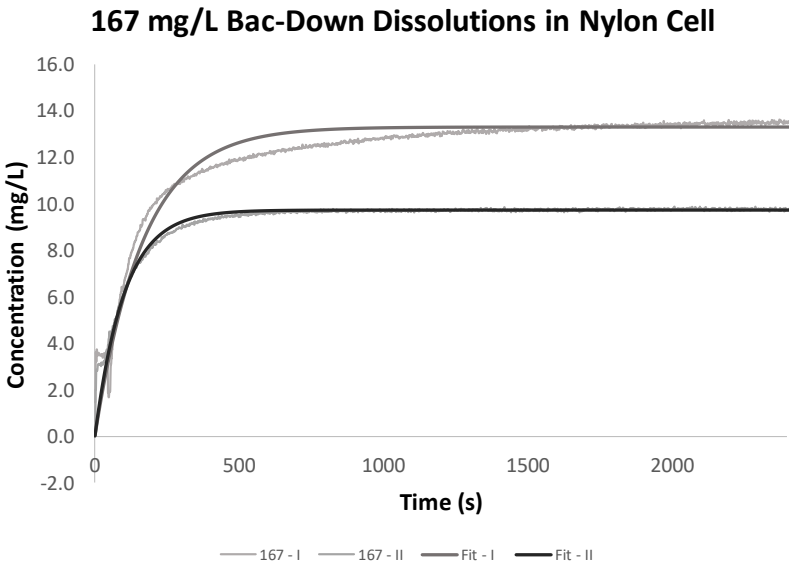
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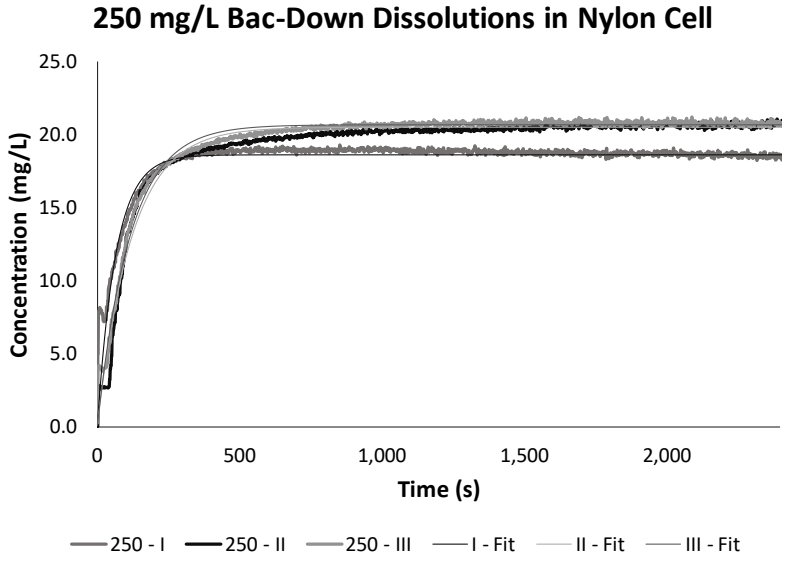
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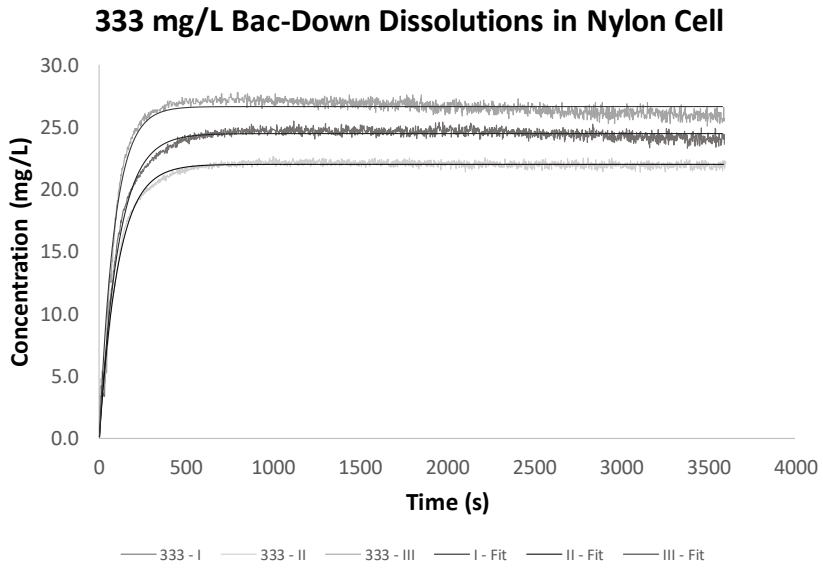
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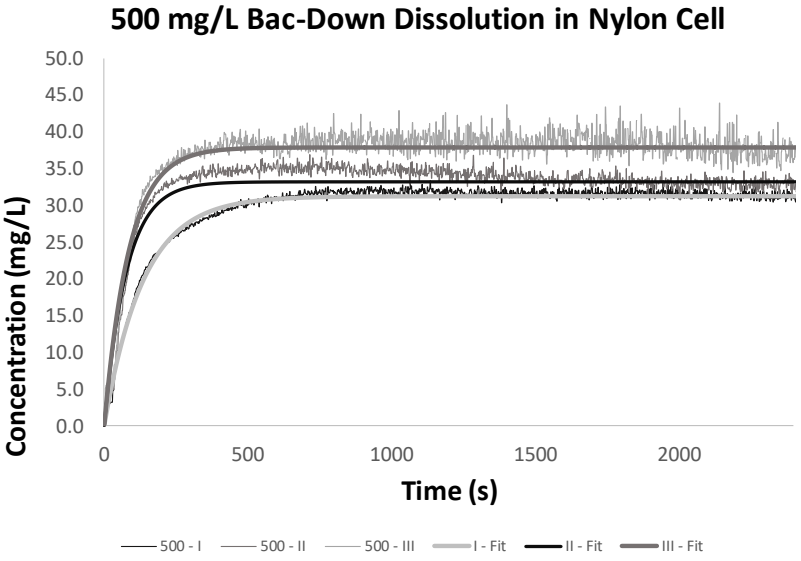
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Appendix A


167 mg/L Bac-Down Dissolutions in Nylon Cell
Concentration (mg/L)
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
0
500
1000
1500
2000
Time (s)
167 - I
167 - II
Fit - I
Fit - II


250 mg/L Bac-Down Dissolutions in Nylon Cell
Concentration (mg/L)
25.0
20.0
15.0
10.0
5.0
0.0
0
500
1,000
1,500
2,000
Time (s)
250 - I
250 - II
250 - III
I - Fit
II - Fit
III - Fit


333 mg/L Bac-Down Dissolutions in Nylon Cell
Concentration (mg/L)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
500
1000
1500
2000
2500
3000
3500
4000
Time (s)
333 - I
333 - II
333 - III
I - Fit
II - Fit
III - Fit


500 mg/L Bac-Down Dissolution in Nylon Cell
Concentration (mg/L)
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
500
1000
1500
2000
Time (s)
500 - I
500 - II
500 - III
I - Fit
II - Fit
III - Fit