5-2006

Facilitated Transport of Triclosan in the Receiving Environment of an Onsite Wastewater Treatment System: Agent of Aquatic Concern

Adrienne L. Roach
University of Tennessee - Knoxville

Recommended Citation

Roach, Adrienne L., "Facilitated Transport of Triclosan in the Receiving Environment of an Onsite Wastewater Treatment System: Agent of Aquatic Concern. " Master's Thesis, University of Tennessee, 2006.
https://trace.tennessee.edu/utk_gradthes/1776

To the Graduate Council:

I am submitting herewith a thesis written by Adrienne L. Roach entitled "Facilitated Transport of Triclosan in the Receiving Environment of an Onsite Wastewater Treatment System: Agent of Aquatic Concern." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Biosystems Engineering Technology.

John R. Buchanan, Major Professor

We have read this thesis and recommend its acceptance:

Jaehoon Lee, Mark Radosevich

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Adrienne L. Roach entitled "Facilitated Transport of Triclosan in the Receiving Environment of an Onsite Wastewater Treatment System: Agent of Aquatic Concern." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Biosystems Engineering Technology.

John R. Buchanan

Major Professor

We have read this thesis
and recommend its acceptance:

Jaehoon Lee

Mark Radosevich

Accepted for the Council:

Anne Mayhew

Vice Chancellor and
Dean of Graduate Studies

(Original signatures are on file with official student records.)

FACILITATED TRANSPORT OF TRICLOSAN IN THE RECEIVING ENVIRONMENT OF AN ONSITE WASTEWATER TREATMENT SYSTEM: AGENT OF AQUATIC CONCERN

A Thesis Presented for the Master of Science Degree
The University of Tennessee, Knoxville

Adrienne L. Roach
May 2006

DEDICATION

This thesis is dedicated to those in pursuit of purpose, not based on the contents of this document but because of what it represents. So, this thesis is dedicated to you. I will leave you with the following quote in hopes that it may be of inspiration to you somewhere along your path:

"The singularity of every man and woman is Jah's [God's] gift. What we struggle to make of it is our sole gift to Jah [God]. The process of what that struggle becomes, in time, [is] the Truth."

- Bob Marley

ACKNOWLEDGEMENTS

First and foremost I would like to thank my Lord God and Savior Jesus Christ for blessing me with this experience. I have truly grown during my time at UT and for that I am truly blessed and thankful. I would like to thank my major professor Dr. John Buchanan for leaving a note one day on my desk a couple of years ago stating: "…see what information you can find on triclosan…." I would have never guessed that through this small piece of information so much would come. I would like to thank my committee members, Dr. Mark Radosevich and Dr. Jaehoon Lee, for their advice and guidance throughout the course of this project. I would like to thank all those who have helped in contributing time, knowledge, support, and/or labor, these include: Galina Melnichenko, Dr. Mike Essington, Dr. John MacCarthy, Dr. Doug Hayes, Julio Gutierrez, Craig Wagoner, Tara Garrett, Youngho Seo, Ipek Celen, and Tyaisha Blount. I would finally, but definitely not lastly, like to thank my family for their continued support.

ABSTRACT

Triclosan (TCS) is an antibacterial found in a host of consumer products ranging from toothpaste to textiles. While initially confined to health care settings, the increased popularity of antimicrobial products has resulted in a surge of products containing this compound and can currently be found in over 700 consumer products. The fate of TCS in wastewater treatment plants (WWTPs) and loss mechanisms once exposed to the environment is a topic that has gained much attention over recent years. However, similar research in onsite systems, where its presence and subsequent persistence can have similar adverse environmental effects, is lacking. It is the objective of this study to examine the interaction of TCS to a sorbing medium in the presence of treated effluent from an onsite wastewater treatment system (OWTS). Experiments conducted to examine factors that govern this behavior were centered around three main points of interest: 1) the interaction of TCS to the sorbing medium in the presence and absence of DOM, 2) the mobility of TCS in the presence and absence of DOM, and 3) the effect DOM with a high and low organic carbon concentrations on sorption and mobility. Laboratory scale batch sorption equilibrium and column transport studies were used to observe the solution interaction of TCS in the presence of a sorptive material, 100% quartz sand. Treatments consisted of three solutions: 1) low organic content (LOC) wastewater filtrate (<0.45µm), 2) high organic content (HOC) wastewater filtrate (<0.45µm), and 3) 5 mM $CaCl_2$ serving as the organic free control (NOC). Human derived wastewater from OWTSs was collected for wastewater treatment solutions. Sorption data fit to the Freundlich isotherm model indicates the greatest amount of TCS sorption to sand in the presence of $CaCl_2$ as compared to LOC and HOC treatments. The Freundlich sorption coefficient (K_F) revealed the least amount of sorption in the LOC treatment. Statistical analysis showed significant differences ($P<0.001$) between all three treatment means. Based on isotherm results, TCS has the potential to be preferentially transported by DOM. Column transport experiments also indicate the potential for facilitated transport by DOM in both LOC and HOC treatments. Breakthrough curves demonstrate earlier breakthrough in DOM treatments as compared to NOC. Although DOM treatments (LOC and HOC) were not found to be significantly different from each other, both were significantly different from the NOC treatment ($P<0.001$). Batch and transport results indicate potential for the facilitated transport of TCS by DOM. However, predicted (batch sorption) and calculated (CXTFIT v2.0) retardation factors did not correlate well with each other. Equilibrium effects were expected to be the dominant factor behind this discrepancy.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PART I

INTRODUCTION AND REVIEW OF LITERATURE

CHAPTER 1

PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN OUR ENVIRONMENT

1.1 INTRODUCTION

Modern advances in medicine, industry, and agriculture offer innumerable benefits to consumers and suppliers. These advances, however, do not come without a tradeoff. Such "improvements" have resulted in the production and accepted use of various chemicals used in the synthesis of medications for human and animal consumption, added as active ingredients to personal care products, and incorporated into textiles for various applications. Collectively, these compounds have been termed pharmaceuticals and personal care products (PPCPs) and will be referred to as such throughout this document. These advances undoubtedly have their place. Developments in science and technology over the past decade have gained sizeable ground in the identification, prevention and treatment of diseases. In exchange for this improvement of human well-being, chemical pollution has been amplified considerably. It is important to note that many of these chemicals have been present in the environment for a number of years. It is their threat as environmental ecotoxical contaminants that are emerging. These threats have been identified due to sensitive analytical methods that are able to detect these compounds at the parts per million and parts per trillion level. This increased sensitivity has highlighted various potential environmental concerns such as their potential ability to cause abnormal physical processes in aquatic life, reproductive impairment in fish, increase in the incidence of cancer, development of antibiotic resistant bacteria, and an increase in potential toxicity when mixed with other chemicals present within an aquatic system (Kolpin et al., 2002).

Digested pharmaceuticals enter the environment after being metabolized by the body and are thus carried in urine and feces. Other compounds are washed down-the-drain if applied or used externally. Many of these compounds have been found to pass through wastewater treatment processes and enter the environment as either the unaltered parent compound or as breakdown products. Once introduced to the environment the effects of these chemicals are largely unknown. A compound's environmental threat is based on the source of the contaminant, its removal rates, and/or its mobility in the environment. How PPCPs are introduced to the environment, their potential impacts, and current status as environmental contaminants is the subject of this chapter.

1.2 IMPORTANCE, EXPOSURE, AND IMPACT

1.2.1 Importance

Pharmaceuticals and personal care products (PPCPs) are an assorted group of chemicals that have, until recently, received only modest consideration as environmental pollutants. The class PPCPs, consist of (but not limited to) all drugs whether prescription or over the counter, nutraceuticals (bioactive food supplements), fragrances, agents in sun-screen, and active ingredients in consumer products (Daughton and Ternes, 1999). Table 1.1 lists the most frequently detected organic wastewater contaminants in U.S. streams (Kolpin et al.,2002). Table 1.2 lists common additives in various personal care products. The components that are found in this large array of products are used specifically for biological activity, either for therapeutic or preventative purposes

Table 1.1 Most frequently detected organic wastewater contaminants in U.S. streams (Kolpin et al., 2002). Table represents a portion of the total 95 compounds of interest in this study.

Chemical	CASRN	Occurrence Percentage (139 streams)	Use
Cholesterol	57-88-5	84.3	Plant/animal steroid
N.N-diethyltoluamide	134-62-3	74.1	Insect repellent
Caffeine	58-08-2	61.9	Stimulant
Triclosan	**3380-34-5**	**57.6**	**Antimicrobial, disinfectant**
Tri(2-chloroethyl) phosphate	115-96-8	57.6	Fire retardant
4-nonylphenol monoethoxylate	-	45.9	Nonionic detergent metabolite
Bisphenol A	80-05-7	41.2	Plasticizer
Cotinine	486-56-6	38.1	Nicotine metabolite
Coprostanol	360-68-9	35.3	Fecal steroid
Fluoranthene	206-44-0	29.4	PAH
1,7-dimethylxanthine	611-59-6	28.6	Caffeine metabolite
Trimethoprim	738-70-5	27.4	Antibiotic
Diazinon	333-41-5	25.9	Insecticide
1,4-dichlorobenzene	106-46-7	25.9	Deodorizer
4-methyl phenol	106-44-5	24.7	Disinfectant
Acteominophen	103-90-2	23.8	Antipyretic
Tetrachloroethylene	127-18-4	23.5	Solvent, degreaser
Erythromycin-H_2O	114-07-8	21.5	Erythromycin metabolite
Estriol	50-27-1	21.4	Reproductive hormone
Lincomycin	154-21-2	19.2	Antibiotic
Chlorpyrifos	2921-88-2	15.3	Insecticide
17β-estradiol	50-28-2	10.6	Reproductive hormone

Table 1.2 Common additives in personal care products (Xi et al., 2005).

Additive compound	Characteristics
Musk ketone	synthetic musks in personal care products
Musk xylene	candles, air fresheners, and aroma therapy, perfumes, cosmetics, and toiletries
Triclosan (2,4,4’-trichloro-2’-hydroxy diphenyl ether)	Bactericide added in detergents, dishwashing detergents, laundry soaps, deodorants, cosmetics, lotions, creams, toothpastes and mouthwashes, footwear, and plastic wear. It interferes with an enzyme crucial to the growth of bacteria
Biphenylol	Bactericide and virucide added in dishwashing detergents, soaps, general surface disinfectants in hospitals, nursing homes, veterinary hospitals, commercial laundries, barbershops, and food processing plants. It is used to sterilize hospital and veterinary equipment
Chlorophene	Bactericide and fungicide added in disinfectant solutions and soaps
DEET (*N,N*-diethyltoluamide)	Pesticide added in insect repellant
Butylparaben (alkyl-*p*-hydroxy-benzoates)	Fungicide added in cosmetics, toiletries, and food
Alkylphenol polyethoxylates	Nonionic surfactants added in detergents
Sodium dodecylbenzenesulfonate	Ionic surfactants added in detergents

(Daughton and Ternes, 1999). Also included in the vast list of PPCPs are drugs used for veterinary purposes and confined animal feeding operations (CAFOs). Animal medications are often not regulated to the level of human drugs and are often administered in larger quantities. The metabolic byproducts of these compounds are, in many cases, directly released to the environment with little to no pre-treatment.

The majority of PPCPs are recalcitrant in wastewater treatment plants and are subsequently released to the environment. However, there are additional exposure routes to the environment. Land application of sewage sludge, wastewater reuse, landfill leachate, are all additional means that these chemicals are introduced to the environment. This document will focus on the contribution of wastewater treatment processes to the presence of PPCPs in the environment with a specific look at one compound in particular, triclosan.

1.2.2 Exposure

Introduction of PPCPs to the environment has no geographic boundaries or climatic limitations as with agrochemicals (Daugthon and Jones-Lepp, 2001). More importantly, these compounds do not necessarily have to be chemically stable to be persistent. Due to their widespread usage and continued output, natural removal rates are often exceeded by their replacement rates. As stated by Daugthon and Jones-Lepp (2001): "…chemical stability is not a prerequisite for environmental persistence".

The levels of PPCPs anticipated in the environment are just as ambiguous as their known effects. The amount that enters the environment is based on various factors: the extent to which a drug is metabolized by the body, the cleaning habits of individuals using various products, which products are used, and the extent in which they are removed from wastewater. The latter factor has been labeled as the primary source of these compounds in the environment. By way of wastewater treatment systems, whether centralized or decentralized, these compounds are continuously introduced to the environment. Since many of these compounds have been found to survive the wastewater treatment process, loss mechanisms once they reach the receiving environment are of primary concern. Natural chemical degradation, biological degradation, and photodegradation determine the rate in which these compounds are removed from the environment. It is therefore, of high importance to study the removal, or non-removal, of these compounds in wastewater treatment facilities and other loss mechanisms that are in the receiving environment.

However, little is known about the ultimate fate of many of these organic chemicals. One reason for this lack of information is the inability of current analytical methods to detect these compounds at levels anticipated in the environment (Kolpin et al., 2002). Complexing this problem is the plethora of compounds that could be present in any given system at any given time. The combined effects, of not only the parent compounds, but also breakdown products and metabolites, add to this issue that is further compounded by the difficulty to predict environmental conditions in both the aquatic and soil environment. Although assessing this situation seems nearly impossible, progress has been made in the ability to detect their presence, quantify their levels of occurrence, and assess their threat to the environment (Herberer, 2002; Boyd et al.., 2003; Kolpin et al., 2004; Oppel et al., 2004; and Bendz et al., 2005).

As of 1999, practically all ecological monitoring studies for PPCPs have been carried out in Europe. Awareness was heightened in Europe due to the restricted ability of their surface water bodies to receive waste due to size limitations, relative to the United States. However, research in Europe concerning their occurrence and behavior in the environment is distributed over a large and often difficult to assess literature base (Daughton and Jones-Lepp, 2001). Over the past five years these compounds have gained substantially more attention in the United States. Research in both Europe and the United States has proven many of these compounds to be persistent and potentially harmful to the environment. Further research has been limited due to the cost of developing methods and conducting analysis.

1.2.3 Impact

Daughton and Jones-Lepp (2001) lists three drivers of ecological change as affected by human activities: 1) habitat disruption and fragmentation, 2) the alteration of community structure, such as, the introduction of alien and nuisance species, and 3) chemical pollution. Chemical pollution by PPCPs is difficult to assess. Annual production of PPCPs can range from a couple of kilograms to thousands of tons. Their use and incorporation into various products is steadily increasing; in many instances, their usage rates are comparable to that of agrochemicals (Daughton and Ternes, 1999). . Concentrations of these compounds in the environment are typically found at extremely low levels (parts per trillion) and effects are expected to be gradual. Complexing the problem are the synergistic effects of multiple compounds.

Some of these compounds serve a dual function as both drugs and as pest-control agents. A few examples are listed as follows: 4-aminopyridine, an avicide and experimental drug for multiple sclerosis; warfarin, a rat poison and anticoagulant; triclosan, a biocide and gingivitis agent used in toothpaste; azacholesterols, antilipidemic drugs and avian/rodent reproductive inhibitor, and acetaminophen, an analgesic and used for the control of brown tree snakes (Daughton and Jones-Lepp, 2001). However, their dual purposes do not directly implicate them as chemical pollutants. Many useful chemicals have dual purpose and one function does not necessarily reflect the other.

With the quantity of compounds of diverse origins detected at measurable concentrations in various compartments of the environment, why have PPCPs gained so much recent attention? Why is their occurrence important? The answer to these questions has been the subject of a variety of papers, symposiums and the like. Research in this area is not solely based on their occurrence and exposure. It is based scientifically on their measurable effects in the aquatic and terrestrial environments as well as effects in the human body. Thus, significant outcomes as to their presence must be weighed against their benefits to consumers. Their presence and abundance is due to the fact that they enter wastewater treatment works and exit either untreated or as various metabolites. Often environmental removal rate are exceeded by replacement rates. This continued out put warrants their persistent classification. Additionally, their simultaneous and sequential exposure of PPCPs to the environment endorses their classification as chemical pollutants.

1.3 OUTLINE OF THESIS

The primary objective of this thesis is to investigate the facilitated transport of triclosan (TCS) by dissolved organic matter (DOM) carried within the treated effluent of an onsite wastewater treatment system (OWTS). A multidisciplinary approach is taken to investigate the many factors involved in the transport of hydrophobic organic compounds (HOCs) in the environment. Using TCS as a probe, this thesis will evaluate the role an OWTS plays to the potential presence of TCS, and possibly other PPCPs, in groundwater and other receiving water bodies. **Chapter 2** introduces the multipart nature of TCS, provides background into its origin, mode of action, and current status as a potential environmental pollutant. **Chapter 3** highlights advances in research in the removal of PPCPs, specifically triclosan, from wastewater treatment plants. Loss mechanisms during wastewater treatment and in receiving environments are also discussed. **Chapter 4** examines the role of organic matter in the environment. It describes the interactions between HOCs and DOM that govern their combined and individual mobility in the environment and factors favoring facilitated transport. **Chapter 5** lists the materials and methods involved in carrying out the experimental procedures. **Chapters 6, 7, and 8** present and discuss the final results of the experiments and concludes with a summary of project findings and list areas for future research.

REFERENCES

Bendz, D., N.A. Paxéus, T.R. Ginn, F.J. Loge. 2005. Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Höje river in Sweden. J. Haz. Mat. 122:195-204.

Boyd, G.R., H. Reemtsma, D.A. Grimm, S. Mitra. 2003. Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. Sci. Total Environ. 311:135-149.

Daughton C.G. and T.A. Ternes. 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environmental Health Perspectives. 107, supplement 6:907-938.

Daugthon, C.G., and T.L. Jones-Lepp. 2001. Pharmaceuticals and personal care products in the environment: scientific and regulatory issues. American Chemical Scociety. Oxford Press.

Herberer, T. 2002. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. J. Hydrol. 266:175-189.

Kolpin D.W., M. Skopec, M.T. Meyer, E.T. Furlong, S.D. Zaugg. 2004. Urban contribution of pharmaceuticals and other wastewater contaminants to streams during differing flow conditions. Sci. Total Environ. 328:119-130

Kolpin D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T.

Buxton. 2002. Pharmaceuticals, Hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A National Reconnaissance. Environ. Sci. Technol. 36:1202-1211.

Oppel, J., G. Broll, D. Löffler, M. Meller, J. Römbke, Th. Ternes. 2004. Leaching behavior of pharmaceuticals in soil-testing-systems: a part of an environmental risk assessment for groundwater protection. Sci. Total Environ. 328:265-273.

Xia, K., A. Bhandari, K. Das, G. Pillar. 2005. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. J. Environ. Qual. 34:91-104.

CHAPTER 2

THE MULTIFACETED TRICLOSAN

2.1 INTRODUCTION

Triclosan (TCS) is a synthetic, non-ionic, broad spectrum antimicrobial agent possessing mostly antibacterial, some antifungal, and antiviral properties. TCS attacks cells by inhibiting membrane synthesis (Singer et al., 2002) and this specific mode of action can encourage microbial resistance. TCS has been used for over 30 years but initially it was confined only to hospitals and health care settings. In the last decade, the use of triclosan containing products has dramatically increased due to marketing schemes and the public's desire for antibacterial labeled products. Currently, TCS can be found in over 700 consumer products, such as, detergents, mouthwash, soaps, cosmetics, socks, sportswear, bed cloths, and even some children's toys. It has gained considerable environmental attention over the past five years and has been labeled as a potentially persistent organic contaminant. In a recent study by the USGS, triclosan was found in 57% of 159 streams and lakes sampled in the U.S. (Kolpin et al., 2002). Similar studies have also detected TCS at quantifiable concentrations in surface waters (Lindström et al., 2002; Balmer et al., 2004; Morrall et al., 2004; Singer et al., 2002; Halden and Paull, 2005; Hua et al., 2005; Sabaliunas et al., 2003; Kolpin et al., 2004). These studies have also raised concerns on the effect of triclosan in the environment. As a result of continued research, triclosan has been found to be both beneficial and potentially detrimental.

This chapter will explore the role of triclosan in antimicrobial resistance, the estrogenic properties of TCS, its use as an effective antimalarial, and potential drug in the treatment of cancer. The purpose of this chapter is to provide useful information as to the many faces of triclosan. Triclosan is used in many products for various purposes. Understanding the benefits and deficiencies in the use of triclosan is essential in understanding the full girth of this controversial issue and assessing its environmental and human impact.

2.2 BENEFITS

2.2.1 Background

TCS was first manufactured by Ciba Specialty Chemicals in Switzerland. Its chemical properties and common uses and benefits (as stated by chemical manufacturer) are listed in tables 2.1. and 2.2, respectively. Less common uses for TCS include its incorporation in certain paints (Meade et al., 2001), plastics used for packaging food (Sanches-Silva et al., 2005), children's toys, toothbrush handles, cutting boards, and surgical drapes (Schweizer, 2001). Ciba Chemical states that TCS is most beneficial when used in hospital and oral hygiene. Hospitals in Australia found a significant reduction of infections in newborn infants caused by methicillin-resistant *Staphylococcus aureus* when soaps containing TCS were used within the maternity ward. TCS has also been proven to reduce cavities and other oral problems due to bacteria by 20-25% when TCS containing toothpaste is used on a regular basis.

Table 2.1 Chemical structure and properties of triclosan

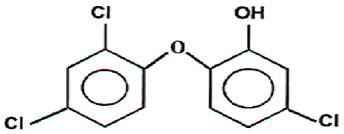
Chemical	Trade Names	Molecular Weight	S_w	Log K_{ow}
2,4,4’-trichloro-2-hydroxydiphenyl ether 	Triclosan Igrasan Microban Lexol 300 Ster-Zac	289.5 g mol^{-1}	10 mg L^{-1}	4.8

Table 2.2 Applications and benefits of using triclosan containing products. Information obtained from manufacturers website, (http://www.cibasc.com/index/ind-index/ind-per_car/ind-pc-ah/ind-pc-triclosan.htm.) Ciba Specialty Chemicals, Switzerland.

Application	**Product features**	**Generic Product Benefits**	**End consumer benefit**
Toothpaste, Mouth-rinse, Oral devices	- Long lasting activity against harmful oral bacteria - Adhesion to teeth enamel and gums - Anti-inflammatory activity - Mouth ulcer reduction	- Anti-gingivitis (bacterial gums disease) - Anti-cavities (bacterial teeth decay) - Anti-plaque (soft bacterial film) - Anti-tartar (hard bacterial film)- Long lasting activity	- One product fights both oral diseases and their precursors
Liquid soap, Dish soap	- Long lasting adhesion - Protection against bacterial contact after hand-wash - Against gram+ (odor) and gram- (infections) bacteria	- Deodorant activity - Broad spectrum antibacterial - Long lasting activity - Hygiene claims	- Fights odor - Protects from contact infections - Adds additional layer of hygiene - Reduces skin irritations
Deodorant	- Long lasting activity against odor forming bacteria - Long lasting adhesion	- Deodorant activity - Broad spectrum antibacterial - Long lasting activity	- Fights odor - Reduces skin irritations - Additional layer of hygiene

2.2.2 Effective Antimalarial

Due to the fact that triclosan specifically attacks lipid biosynthesis, it can be used as an effective drug in the selective treatment of various bacterial born illnesses. Fatty acid synthesis is a fundamental and vital component of the cellular metabolic network. Fatty acids are the essential building blocks for the formation of phospholipids which form the cell membrane. Fatty acid synthase (FAS) is the enzyme system that performs fatty acid synthesis. FAS enzymes are either labeled as type I, found in eukaryotes and some Mycobacteria, or type II, strictly found in prokaryotes. This difference allows FAS to be the most amendable of all biochemical pathways in selective drug therapy. Thus, triclosan can be effective in attacking microbial invaders without affecting the human host.

This discovery has application in combating malaria. The causative bacteria, *Plasmodium falciparum*, have been widely studied in its inhibited growth by triclosan. Here, NAD^+ is the preferred co-factor for the FabI enzyme that is responsible for the delivery of fatty acid intermediates necessary for full lipid synthesis. Triclosan binds directly to FabI which increases its affinity for the oxidized co-factor, NAD^+. This results in the locking of the enzyme in its NAD-bound form, blocking the essential binding of NADH and thus preventing FAS (Figure 2.1). These processes retard cell growth and ultimately cause cell lysis (Roa et al., 2003; Kapoor et al., 2004; Kapoor et al., 2004).

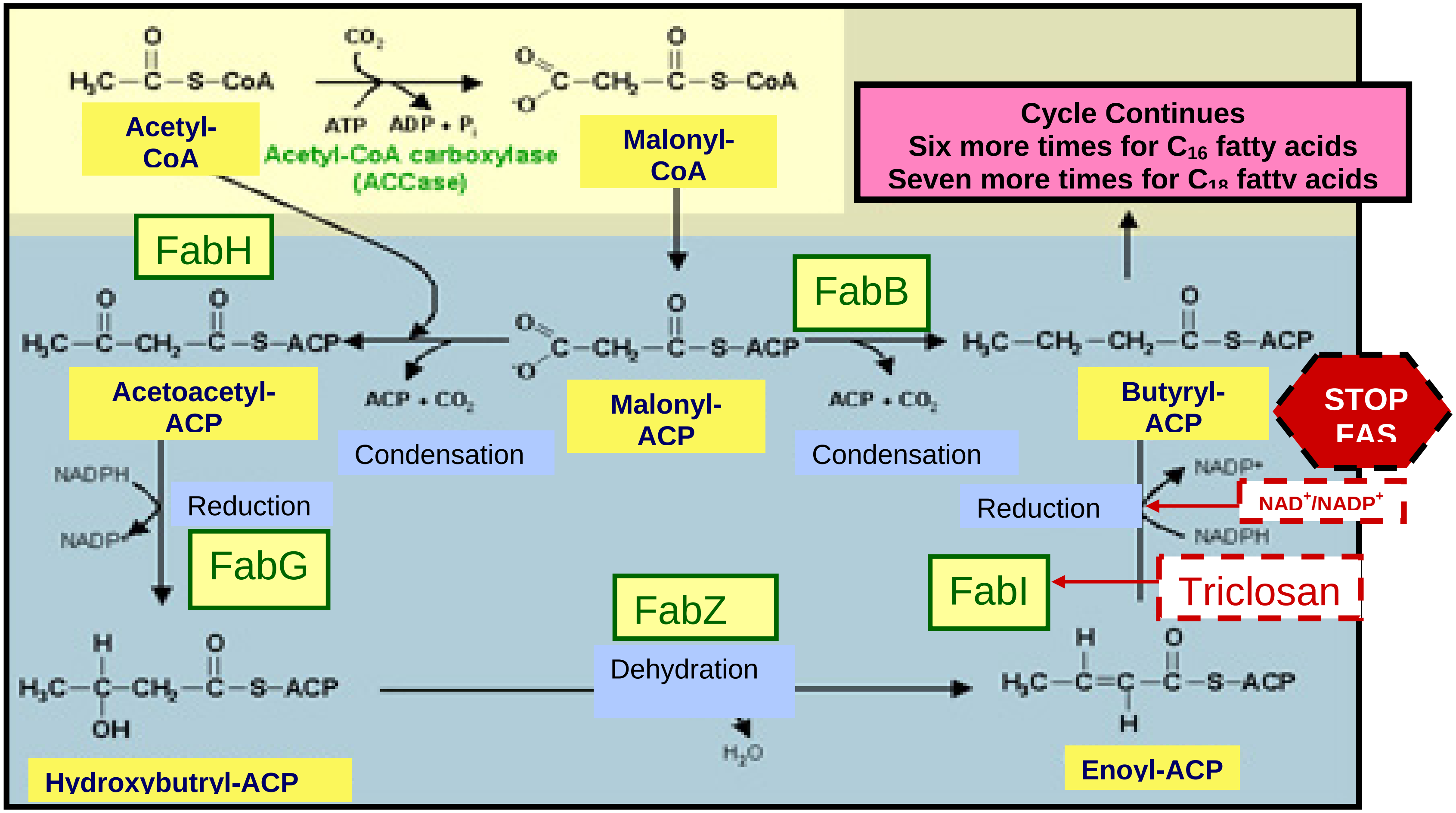


Figure 2.1 Type II fatty acid synthesis. Diagram illustrates the role of the co-enzymes (Fab) in facilitating fatty acid synthesis in a series of oxidaxtion/reduction reactions. Boxes in red/dashed illustrate where TCS interrupts the FAS cycle.

2.2.3 *Chemopreventative Agent*

The discovery of the specific FAS pathway has also led to another beneficial application, possible agent for the chemoprevention of breast cancer. Over expression and high levels of FAS has been found in various cancers of the human body. Often expression levels aid in the transformation to malignant tumors. Studies have shown that FAS expression in malignant breast tumors is associated with an increase in the risk of death (Lu and Archer, 2005; Pizer et al., 1996). In one study, there was a nine fold increase of death when high levels of FAS expression occurred together with high proliferative index >17%. Therefore, FAS expression is expected to play an essential role in the growth and survival of breast cancer cells. FAS inhibitors decrease cell proliferation and induce lysis in breast cancer cell lines. Using triclosan as a FAS inhibitor, Lu and Archer (2005) determined that triclosan suppresses rat mammary carcinogenesis by inhibiting FAS. Thus, FAS is a potential molecular target for the chemoprevention of breast cancer, and as a FAS inhibitor, triclosan has the potential to serve as a chemopreventative agent.

2.3 ADVERSE AFFECTS

2.3.1 *Agent Fostering Antibiotic Resistance*

Due to triclosan's specific mode of action (specifically attacks lipid biosynthesis) its widespread usage has been called into question. Various studies have looked at the link between antibiotic resistance and the use of triclosan and other antimicrobials (McBain et al., 2003; White and McDermott,2001; Levy, 2001; McBain and Gilbert, 2001; Lateef, 2004; Schweizer, 2001; Perencevich et al., 2001; Aiello and

Larson et al., 2003). Even though antibiotic resistance is an age old concern, the responses of bacteria to biocides, in particular triclosan, revived this long established and well researched problem. Many pharmaceuticals attack the same cellular targets. Of concern, is the potential for triclosan to weaken the ability of other pharmaceuticals to treat bacterial diseases that may also function as cell wall inhibitors. This phenomenon is referred to as cross resistance. Fueling this debate is the fact that the presence of triclosan in so many consumer products has not been justified. A number of studies have determined that the inclusion of triclosan is not necessarily an added benefit to consumers (Ayliffe et al., 1988; Larson, 2001; Adolfsson-Erici et al., 2002). The level of protection attained by the addition of triclosan in consumer products is not usually needed in a typical household. This misuse can have a subtle effect, contributing to the progression and persistence of drug resistance within microbial communities (McBain and Gilbert, 2001).

2.3.2 Androgenic Properties

Triclosan is structurally similar to various non-steroidal estrogens. This similarity implies a potential to behave as an environmental estrogen. Foran et al., (2000) examined the effects of triclosan exposure on the development of Japanese medaka as compared to 17-β estradiol, a noted estrogen. Japanese medaka are commonly used as an indicator species of fish. This species is commonly used as a model for endocrine disruption because of their reproduction rates and rapid development time. Sex can be determined phenotypically by visual examination of dimorphic fin characters. Early developmental exposure to estrogen can result in bias sex ratios or intrasex morphology of the gonads. Results from Foran et al., (2000) indicated that changes in fin length and non-significant trends in sex ratio rules triclosan as being weakly androgenic but not estrogenic. Triclosan was used in concentrations of 1, 10, and 100 ug/L and 17-β estradiol at a concentration of 1 ug/L. Exposure of 17-β estradiol to developing Japanese medaka by Nimrod and Benson (1998) produced a 100% female population in concentrations as low as 1 μg/L. Triclosan treatments were not found to be statistically different from controls of an ethanol solution not containing TCS. 17-β estradiol was found to be different, producing 92% females as compared to 56% females at the comparable triclosan level of 1 μg/L. Studies indicate that even though estrogenic properties were not concluded from this preliminary study, triclosan does have the ability to behave as an environmental androgen due to the observed differences in fin length as compared to controls. An androgen is any group of hormones that controls the growth and development of the male reproductive system. Additional research is needed to further explore the sexual effects of TCS exposure to aquatic life.

REFERENCES

Adolfsson-Erici, M., M. Peterson, J. Parkkonen, and J. Sturve. 2002. Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. Chemosphere. 46:1485-1489.

Aiello, A.E. and E. Larson. 2003. Antibacterial cleaning and hygiene products as an emerging risk factor for antibiotic resistance in the community. The Lancet Infectious Diseases. 3:501-506.

Ayliffe, G.A., J.R. Babb, J.G. Davies, and H.A. Lilly. 1988. Hand disinfection: a comparison of various agents in laboratory and ward studies. J. Hosp. Infect. 11, 3:226-243.

Balmer, M.E., T. Poiger, C. Droz, K. Romanin, P. Bergqvist, M.D. Müller, and H. Buser. 2004. Occurrence of methyl triclosan, a transformation product of the bactericide triclosan, in fish from various lakes in Switzerland. Environ. Sci. Tech. 38:390-395.

Foran, C.M., E.R. Bennett, W.H. Benson. 2000. Developmental evaluation of a potential non-steroidal estrogen: triclosan. Marine Environ. Res. 50:153-156.

Halden, R.U., D.H. Paull. 2005. Co-Occurrence if triclocarban and triclosan in U.S. water resources. Environ. Sci. Tech. 39:1420-1426.

Hua, W., E.R. Bennett, R.J. Letcher. 2005. Triclosan in waste and surface waters from the upper Detroit River by liquid chromatography-electrospray-tanem quadrupole mass spectrometry. Environ. Int. 31:621-630.

Kapoor, M., C. Reddy, M. Krishnasastry, A. Surolia, N. Surolia. 2004. Slow-tight-binding inhibition of enoyl-acyl carrier protein reductase from *Plasmodium falciparum* by triclosan. Biochem J. 381:719-725.

Kapoor, M., P. Mukhi, A. Surolia, N. Surolia, K. Suguna. 2004. Kinetic and structural analysis of the increased affinity of enoyl-ACP (acyl-carrier protein) reductace for triclosan in the presence of NAD+. Biochem J. 381:719-725.

Kolpin D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton. 2002. Pharmaceuticals, Hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A National Reconnaissance. Environ. Sci. Technol. 36:1202-1211.

Kolpin, D.W., M. Skopec, M.T. Meyer, E.T. Furlong, S.D. Zaugg. 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Sci. Total Environ. 328:119-130.

Lateef, A. 2004. The microbiology of a pharmaceutical effluent and its public health implications. World J. Microbiol. Biotech. 20:167-177.

Larson, E. 2001. Hygiene of the skin: when is clean too clean? Emerg. Infect. Dis. 7, 2:225-230.

Levy S.B. 2001. Antibacterical household products: Cause for concern. Emerging Infectious Diseases. June. Supplement 7, No. 3.

Lindström A., I.J. Buerge, T. Poiger, P. Bergqvist, M. Müller, H. Buser. 2002. Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. Environ. Sci. Technol. 36:2322-2329.

Lu, S. and M.C. Archer. 2005. Fatty acid synthase is a potential molecular target for the chemoprevention of breast cancer. Carcinogenesis. 26, 1: 1530157.

McBain A.J., P. Gilbert. 2001. Biocide tolerance and the harbingers of doom. International Biodeterioration & Biodegradation 47:55-61.

McBain, A.J., R.G. Bartolo, C.E. Catrenich, D. Charbonneau, R.G. Ledder, B.B. Price, and P. Gilbert. 2003. Exposure of sink drain microcosms to triclosan: population dynamics and antimicrobial susceptibility. Appl. Environ. Microbiol. Sept: 5433-5442.

Meade, M.J., R.L. Wadeell, T.M. Callahan. 2001. Soil bacteria *Pseudomonas putida* and *Alcaligenes xylosoxidans* subsp. *Denitrificans* inactivate triclosan in liquid and solid substrates. FEMS Microbiol. Letters. 204:45-48.

Morrall D., D. McAvoy, B Schatowitz, J. Inauen, M. Jacob, A. Hauk, W. Eckhoff. 2004. A field study of triclosan loss rates in river water (Cibolo Creek, TX). Chemosphere. 54:653-660.

Nimrod, A.C. and W.H. Benson. 1998. Reproduction and development of Japanese medaka following an early life stage exposure to xenoestrogens. Aq. Tox. 44:141-156.

Perencevich, E.N., M.T. Wong, A.D. Harris. 2001. National and regional assessment of the antibacterial soap market: a step toward determining the impact of prevalent antibacterial soaps. Am. J. Infect. Control. Commentary 29:5.

Pizer, E.S., J. Thupari, W.F. Han, M.L. Pinn, F.J. Chrest, G.L. Freywot, C.A. Townsend, F.P. Kuhajda. 1996. Inhibition of fatty acid synthesis induces programmed cell death in human breast cancer cells. Cancer Res. 60:213-218.

Rao, S.P., A. Surolia, N. Surolia. 2003. Triclosan: A shot in the arm for antimalarial chemotherapy. Mol Cell Bio. 253:55-63.

Sabaliunas D., S.F. Webb, A. Hauk, M. Jacob, W.S. Eckhoff. 2003. Environmental fate of triclosan in the River Aire Basin, UK. Water Research. 37:3145-3154.

Sanches-Silva, R. Sendón-García, J. López-Hernández, P. Paseiro-Losada. 2005. Determination of triclosan in food stuffs. J. Sep. Sci. 28:65-72.

Schweizer H.P. 2001. Triclosan: a widely used biocide and its link to antibiotics. FEMS Micro. Letters. 202: 1-7.

Singer H., S. Müller, C. Tixier, L. Pillonel. 2002. Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: Field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ. Sci. Technol. 36:4998-5004.

White D.G., P.F. McDermott. 2001. Biocides, drug resistance and microbial evolution. Current Opinion on Microbiology. 4:313-317.

CHAPTER 3

COMPARATIVE ANALYSIS OF WWTPS AND OWTS IN THE REMOVAL OF TRICLOSAN FROM WASTEWATER

Numerous studies have been conducted on the effectiveness of wastewater treatment plants (WWTPs) in the removal of triclosan from wastewater influent. However, research exploring the effectiveness of onsite wastewater treatment systems (OWTSs) in removing TCS has been neglected. In addition, a full understanding the loss mechanisms associated with the removal of TCS in the environment, i.e., photodegradation, biological and chemical degradation, sorption into soil and sediment, biological methylation, and the formation of dioxin derivatives, are areas not completely explored as well. The main objective of this chapter is to highlight current and past research involving the fate and behavior of triclosan during the wastewater treatment process. Focus will be given to three major loss mechanisms that govern the removal of triclosan from the liquid phase: 1) biodegradation, 2) sorption to sludge, suspended solids and sediment, and 3) photolysis. Loss due to volatilization is considered to be negligible because TCS has a vapor pressure of 4×10^{-6} mmHg at 20°C (Morrall et al., 2004).

Also of concern are transformation byproducts of triclosan during these breakdown processes. In some cases, breakdown products of triclosan have been found to be more harmful than the parent compound and in the case of methlyated triclosan, more bioaccumulative (Lindström et al., 2002; Latch et al., 2003; Balmer et al., 2004).

3.1 FATE AND REMOVAL OF TCS IN WWTPS AND EXPOSURE RATES TO THE AQUATIC ENVIRONMENT

3.1.1 Studies in the United States

McAvoy et al., (2002) studied the fate and removal of triclosan during wastewater treatment at a total of five WWTPs in Ohio. Two plants used activated sludge and three plants had trickling filters. Influent concentrations of triclosan ranged from 3.8 to 16.6 µg/L and were reduced to concentrations of 0.2 – 2.7 µg/L in final effluent. Activated sludge was shown to provide a 96% rate of removal while removal by trickling filters was more variable, ranging in a 58 to 86% reduction in TCS. Results of this study also indicated that triclosan was readily biodegradable under aerobic conditions but not under anaerobic conditions. Biodegradation is thought to be the predominant mechanism for removal within plant operation. This finding is key in the effectiveness in onsite removal of triclosan. Sand filtration was used as a tertiary form of treatment in one of the two trickling filter plants of interest in this study. However, it showed virtually no triclosan removal. During primary treatment, hydraulic retention time was found to have the largest influence on triclosan removal; longer retention times resulted in increased removal. Shorter retention times, due to higher water usage rates within the community, resulted in poor removal. (Table 3.1 summarizes literature concerning the removal of triclosan in WWTPs.)

Hua et al., (2005) assessed the presence of triclosan in the Detroit River watershed of the Great Lakes. This plant serves a population of approximately 80,000 and provides secondary treatment (activated sludge) with ultraviolet (UV) disinfection.

Table 3.1 Literature summary of triclosan removal in WWTPs.

Reference	Location	Treatment(s)/Study Type	Influent TCS Conc. (ng L^{-1})	Effluent/In stream TCS Conc. (ng L^{-1})	Removal	Dominant Removal Mechanism (s)
McAvoy et al., (2002)	Ohio (USA)	Activated sludge Trickling filter	3,800-16,600	200-2,700	96% 58-86%	Biodegradation Hydraulic retention time
Hua et al., (2005)	Detroit River wastershed	Activated sludge w/ UV disinfection	NA	63	22% post UV disinfection	Dilution
Thomas and Foster (2005)	Potomac River (MD, USA)	Activated sludge	NA	13-56	51-99%	Biodegradation during secondary treatment
Morrall et al., (2004)	Cibolo Creek (TX, USA)	River die away rates	NA	119-431 (in stream)	19-28% (in stream)	Sorption, biodegradation, and photolysis
Kolpin et al., (2004)	Iowa (USA)	Contaminant concentrations during varying flow conditions	NA	140 during low flow conditions	NA	Dilution effects during high flows
Kolpin et al., (2002)	U.S. streams	Reconnaissance for 95 organic wastewater contaminants	NA	140-2,300 in 57% of the 139 streams analyzed	NA	NA

Table 3.1 continued

Reference	Location	Treatment/Study Type (s)	Influent TCS Conc. (μg L^{-1})	Effluent/In stream TCS Conc. (μg L^{-1})	Removal	Dominant Removal Mechanism (s)
Federle et al., (2002)	Pennsylvania (USA)	Disturbance in activated sludge processes by TCS	0.04-2	NA	98.5%	Biodegradation (Laboratory scale study)
Thompson et al., (2005)	UK	Rotating biological contactors, trickling filters, and activated sludge	670-5,115	NA	58-98%	Biodegradation; highly dependent upon concentration of dissolved oxygen
Singer et al., (2002)	Switzerland (UK)	Fate in WWTPs, occurrence in surface waters, and lake sediments	NA	0.042-0.213 (effluent); 0.011-0.098 (surface waters); .053 (in utmost sediment layer	79% (WWTP-biological degradation); 15% (sorption to sludge); 6% transported to surface waters	Biodegradation and sorption
Sabaliunas et al., (2003)	Northern Europe	Activated sludge Trickling filter	.022 .008	0.001 0.004	95% in both	Biodegradation
Kanda et al., (2003)	UK	WWTP	NA	3100	0-95%	Biodegradation
Bester (2003)	Germany	Activated sludge	1000	50	80%	Biodegradation and sorption

The main focus of the study was to examine the effects of UV light on TCS removal in wastewater effluent. Effluent samples where collected pre- and post-UV disinfection. Surface water samples were collected at three points, one upstream from discharge and two downstream from discharge. After final UV treatment, effluent concentration was reduced by 22% to an average concentration of 63 ng/L prior to effluent discharge. Triclosan was not found at measurable concentrations at the upstream sample location. Concentrations in sites downstream of plant discharge were reduced to 4 and 8 ng/L. Dilution effects were thought to be the major mechanism behind the reduction in TCS concentration.

Thomas and Foster (2005) tracked triclosan, caffeine, and five acidic pharmaceuticals (ibuprofen, naproxen, mefenamic acid, ketoprofen, and diclofenac) through the wastewater treatment process. Their aim was to identify the specific stage associated with the highest amount of triclosan removal during wastewater purification. WWTPs with similar treatment processes and design were chosen. All plants consisted of a primary settling process, biological nutrient removal by activated sludge, and advanced treatment consisting of phosphorous removal, gravity filtration, and disinfection. Three plants were chosen, each discharging into tributaries of the Potomac River (MD, USA). Secondary treatment was found to remove the majority of the influent tricloan load with removal percentages ranging from 51-99%. During secondary treatment microbes, in a mixture of aerobic and anaerobic zones, degrade a majority of the remaining organic matter that passes through primary treatment. The concentration of triclosan was also found to be strongly influenced by suspended matter. One of the three plants studied had a consistently higher concentration of suspended matter resulting in less removal of TCS in all stages of treatment. Thus, understanding the interaction between triclosan and suspended matter would provide helpful information as to the mobility of triclosan in a treatment system.

Cibolo Creek in Texas was chosen by Morrall et al., (2004) as an ideal site to study rate loss of triclosan in river water post sewage treatment. Trickling filter plants with low dilution factors were desired to obtain samples above the analytical detection limit of triclosan. Activated sludge plants were not desired because of their overall high TCS removal. Trickling filter plants that had other effluent inputs within 8 km downstream of discharge were eliminated. Also eliminated were locations of highly variable weather conditions. Thus, Cibolo Creek, a moderate sized stream located in South Central Texas was chosen. Cibolo Creek Municipal Treatment Plant is a trickling filter plant with dual media filtration as tertiary treatment. A sodium bromide tracer was used to track the movement of a parcel of water as it exited the plant and was transported downstream. Samples for triclosan concentration were collected upstream of the sewage treatment plant, at the plant discharge, and within an 8 km river stretch down steam of the discharge point. Mathematical modeling was used to account for triclosan loss due to sorption and settling based on various chemical parameters. Triclosan concentration in the first reach declined from 431 to 223 ng/L, 59 ng/L of this loss was thought to be due to sorption and settling of solids. In the second reach, 119 ng/L was lost but only 3 ng/L predicted to be due to sorption and settling. These findings reflect a loss of 28% in the first reach and 2% loss of TCS in the second reach due to sorption and settling. The overall loss of TCS due to sorption and settling was predicted to be 19% over the entire 8 km river stretch. Cibolo Creek was described as having low water clarity due to deeper pools and turbulent riffles. Thus, the authors concluded that biodegradation was expected to be the major loss mechanism rather than photodegradation.

Kolpin et al., (2004) examined the concentrations of pharmaceuticals and various organic wastewater contaminants in urban streams in Iowa (USA) during varying flow conditions. Their objective was to determine the contribution of urban centers to contaminant concentrations in relation to high, normal, and low flow conditions. Twenty-three stream locations were chosen upstream and downstream of 10 cities in Iowa. Water samples were collected from each location three times during high, normal and low streamflow conditions. A total of 105 compounds, including triclosan, were analyzed in each water sample using three analytical methods developed by the USGS (United States Geological Survey). The number of detected compounds decreased as streamflow increased. Triclosan was only detected during low flow conditions. It was found in 10% of all the samples collected with a maximum concentration of 0.14 μg/L. It was concluded that the urban contribution of organic contaminants to streams is strongly dependent on flow conditions. Dilution effects during high flow accounts for the majority of reduction; concentrations are muted and below instrument detection limits.

An earlier study (Kolpin et al., 2002) found that TCS was one of the most frequently detected organic wastewater contaminants in the aquatic environment. This groundbreaking study was the first national reconnaissance in the United States for the occurrence of 95 wastewater contaminants in a total of 139 streams across 30 states. Sites for stream sampling were chosen in locations susceptible to wastewater contamination. Triclosan was found in 57% of the streams tested, and the concentrations ranged from 0.14 μg/L to 2.3 μg/L. Aside from TCS, a number of other wastewater contaminants were detected in a single sample. An average of seven, but as many as 38 wastewater contaminants were identified in a single water sample. The authors highlight concerns about the unknown synergistic effects of the combination of these contaminants in an aquatic environment.

Because WWTPs depend on microorganisms to degrade organic pollutants, another concern is whether TCS can affect treatment in plant performance. Federle et al., (2002) exclusively looked at the fate and effects of triclosan in activated sludge. Their objectives were as follows: determine if triclosan is degraded in activated sludge, establish the extent of sorption and biodegradation on the removal of TCS from activated sludge treatment, and to assess adverse effects of triclosan on the treatment process. Triclosan was radiolabeled with ^{14}C in the 2, 4-dichlorophenoxy ring in laboratory batch mineralization experiments and bench-top continuous activated sludge (CAS) systems. Sludge from an activated-sludge system (PA, USA) was collected and used in experiments. Results showed that triclosan was extensively biodegraded and removed in activated-sludge systems. It was also found that triclosan is unlikely to disturb sewage treatment processes at concentrations expected from household and manufacturing wastewaters. Increasing concentrations of triclosan were used throughout laboratory experiments to observe shock and the potential effects of abrupt increases of triclosan levels. These sudden increases in triclosan influent concentrations had no major adverse effects on measured wastewater treatment parameters, such as, chemical oxygen demand, biological oxygen demand, and ammonia removal. The authors conclude that variable amounts of triclosan are expected to escape wastewater treatment and its presence represents little risk to sewage treatment operation.

3.1.2 European Studies

Influent concentrations of triclosan can vary considerably in wastewater treatment works. Thompson et al., (2005) found influent concentrations of triclosan in three wastewater treatment plants in the United Kingdom ranging from 670 and 5115 ng/L. Removal efficiencies varied depending on methods of treatment. Plants examined in this study included rotating biological contactors, trickling filters, and activated sludge. Triclosan removal ranged from 58-96%, 86-97%, and 95-98% respectively. When sufficient dissolved oxygen was available, these authors found that biodegradation provided the maximum removal. Plants maintaining dissolved oxygen levels between 1.5 and 2.0 mg/L during the activated sludge process showed consistently high removal. In cases where dissolved organic concentrations were lower, such as trickling filters and rotating biological contactors, sorption was noted as the predominant mechanism of removal. Also cited is the role of biomass in contaminant removal. Changes in biomass makeup, such as the level of microbial maturity, can affect the amount of triclosan that is sorbed. This is highly important to plant operation and regulations.

Singer et al., (2002) observed the occurrence and fate of triclosan in wastewater treatment plants, surface waters, and lake sediments. In addition, they developed analytical methods for quantifying triclosan in various matrices such as surface waters, wastewater, sediment, and sludge. The catchment area of Lake Greifensee in Switzerland, receiving effluent from seven surrounding wastewater treatment plants was the area of interest. All plants had similar BOD and/or COD removal efficiency. Effluents from all seven plants were collected and analyzed for triclosan concentration. Two main tributaries leading into the lake, AaUster and Aabach Moenchaltorf, were sampled and vertical concentration profiles were taken directly in the lake. A sediment core was also taken from the lake and cut into annual layers based on various dating techniques. Core samples were analyzed to get a sediment depth profile that represented a time range of 1960-1993. During the wastewater treatment process triclosan was removed at overall percentages of 79% by biological degradation, 15% from sorption to sludge, and 6% transported to receiving surface water. The transport of triclosan by particles was calculated as being approximately 10% because a filtration stage within each plant resulted in a suspended solid concentration of 10 mg/L in collected effluent samples. Only the dissolved fraction of triclosan was analyzed in these effluent samples. Triclosan effluent concentrations ranged from 42 to 213 ng/L with corresponding triclosan loads between 0.2 and 3.2 g/day. Assuming that the sources of triclosan was from domestic use only, the output load by treated effluents correspond to 30-210 mg of triclosan/1000 inhabitants per day. Concentration in the two rivers receiving plant effluent reflected fairly constant triclosan concentrations. However, triclosan concentrations in Aa Uster increased by a factor of 5 during high water events. The authors noted that this increase could possibly be due to the discharge of untreated wastewater from combined sewer overflows directly into the river during rain events. The other river sampled, Aabach Moenchaltorf, did not show as much impact from untreated wastewater during rain events as reflected in triclosan concentrations. A fairly constant concentration of 20 ng/L was observed throughout the period of the study for this river, even during high water events.

Sabaliunas et al., (2003) measured environmental loadings, concentrations, and removal of triclosan during wastewater treatment and in river water under conditions in

Northern Europe. The purpose of this study was to increase the understanding of the fate of triclosan in the aquatic environment and to generate data needed for site-specific and regional exposure assessments. The removal of triclosan was observed during wastewater treatment at two plants, one operating by trickling filter and the other by activated sludge. In-stream removal was based on effluent concentrations of triclosan in a stream receiving treated effluent from the wastewater treatment plants. A fluorescent dye was released at the WWTP discharge points to visually follow the plug downstream and mark sampling points at peak dye concentrations. In-stream samples were taken at five sampling site along the river stretch, 50 m upstream, 20, 750, 1500, and 3500 m downstream from the discharge point. During wastewater treatment, influent triclosan concentration was removed by approximately 95% during both activated sludge and advanced trickling filter methods. In-stream removal of triclosan was also found to be rapid. Triclosan was eliminated from effluent entering the receiving stream, Mag Brook, at a rate of 0.21-0.33 h^{-1}. As a result, these authors state that triclosan was not a threat to the aquatic environment nor is it persistent in the aquatic environment. However, various parameters have an effect on triclosan concentration in the environment. Study conditions are site specific and cannot necessarily be extrapolated to other environments.

A study by Kanda et al., (2003) was carried out to survey and determine the levels of PPCPs in crude sewage and removal rates during passage through sewage treatment works in the United Kingdom. A total of 6 plants, all primarily receiving domestic waste, were observed during the course of the study. Triclosan was detected in all crude sewage samples and in all effluent samples. A maximum effluent concentration of 3100 ng/L was obtained within the plants tested. Removal efficiencies were highly variable among the plants, ranging from 0% to 95%. However, on average, the removal rate was found to be approximately 90%. The authors explain the low removal was due to a new plant with immature biofilm.

Bester (2003) examined triclosan concentrations in an activated sludge wastewater treatment plant in Germany. Samples were collected from the influent, sludge, and effluent. The purpose of this study was to obtain systematic data on balances of triclosan concentration and movement within a sewage plant. Sludge from other plants (20) was also compared to get an idea of plant to plant variability. Triclosan was found at average concentrations of 1000 ng/L in influent, 1200 ng/g in sludge, and 50 ng/L in effluent. Mass balances were calculated and it was determined that 30% of triclosan is sorbed to sludge and approximately 5% is transported as a dissolved species in the out-flowing water. The authors noted that the transformation of triclosan to various metabolites could be an additional explanation for loss. However, methyl-triclosan, a bio-breakdown product, was not detected. The authors stated that triclosan should be considered a major issue in German sewage plants, due to unaccounted loss within the treatment process.

3.2 Loss Mechanisms in the Aquatic Environment and Derivative Formation

While the concern of triclosan's presence in surface waters and other environments has considerably increased over the past five years, triclosan byproducts are also receiving increasing attention as well. Triclosan is stated as being non-toxic and safe by its manufacturers (Ciba Specialty Chemicals). However, some derivatives of triclosan are highly toxic and can bioaccumulate. In order to assess the threat of triclosan derivatives, the conditions favoring their formation must be better understood. Two prominent by-products, methyl-triclosan and 2,8-dichlorodebenzo-*p*-dioxin, are shown in figure 3.1. This section will focus on the two main mechanisms behind the formation of these by-products, 1) biological methylation and 2) photochemical conversion to dioxins.

3.2.1 Biological Methylation and Dioxin Formation

Photolysis accounts for the majority of triclosan loss in surface waters (Latch et al., 2003; Singer et al., 2002; Lindström et al., 2002; Morrall et al., 2004; Reiss et al., 2002) For example, photolysis accounted for 80% of triclosan dissipation in Lake Greifensee (Singer et al., (2002)). Following this observation, Latch et al., (2003) studied the factors leading to the transformation of triclosan to 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) in sunlight-irradiated surface waters. The role of pH and irradiation wavelength was investigated in the formation of dioxins. Mississippi River water and buffered water were used throughout laboratory experiments. Results indicated that 2,8-DCDD was produced in both buffered and natural water due to irradiation. Formation percentages ranged from 1 to 12% under various conditions tested. All tests were carried out at a pH of 8 or greater. Triclosan with a pKa of 8.1 is only photodegradable in its dissociated form. Results also indicated that even though loss due to dioxin formation is significant, it is not the dominant one. Polymers derived from triclosan are likely to be the main reaction products. Another concern for future research is the stability of the formed dioxin in the natural environment.

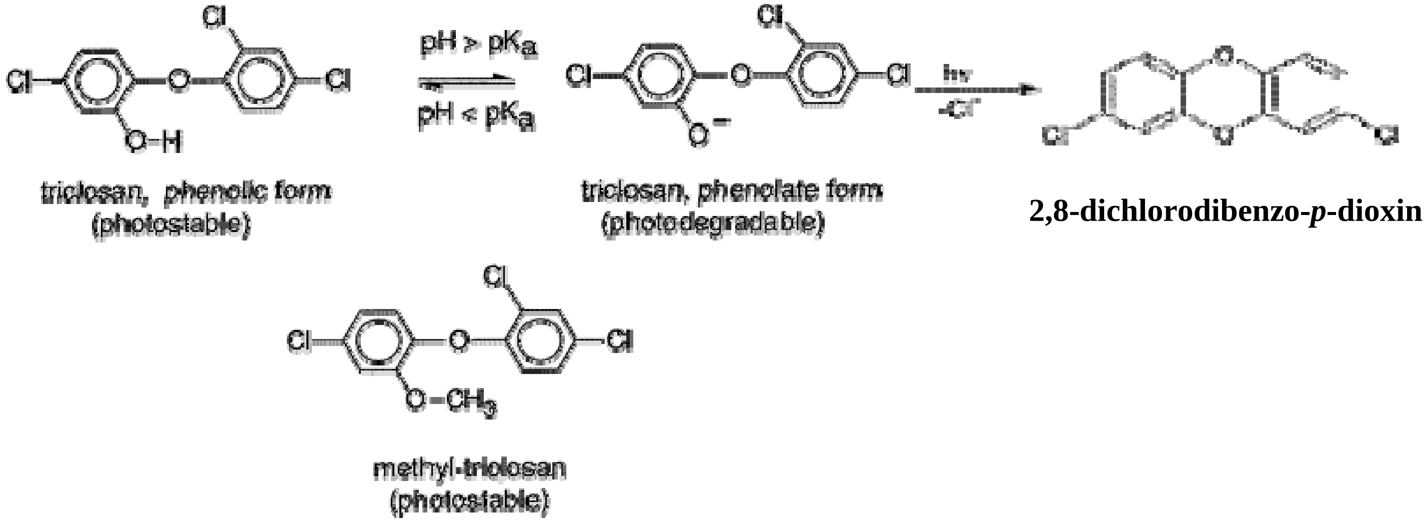


Figure 3.1 Factors governing the formation of methyl-triclosan and 2,8-dichlorodibenzo-*p*-dioxin. Triclosan has a pK_a of 8.1. (Lindström et al., 2002; Latch et al., 2003).

Lindstrom et al., (2002) assessed the occurrence of both triclosan and methyl-triclosan in the aquatic environment of Lake Greifensee in Switzerland. Since previous studies (Singer et al., 2002) indicated the majority of triclosan loss from photogedradation, the presence of methyl triclosan was of concern because it is stable against photodegradation. Methyl-triclosan was less than 2% of the total triclosan effluent load. However, its concentration increased to 30% relative to triclosan post discharge into receiving rivers. This finding indicates that triclosan has the ability to environmentally transform into methyl-triclosan, a more lipophilic and bioaccumlative by-product.

3.3 FATE AND REMOVAL OF ORGANIC WASTEWATER CONTAMINANTS IN OWTSS

Research exploring the effectiveness of OWTS in removing organic wastewater contaminants (OWCs) in particular, PPCPs and TCS, has been neglected with the exception of a few studies. Rudel et al., (1998) characterized the impact of endocrine-disrupting chemicals on groundwater quality from an OWTS. These authors studied EDCs in drinking water resources. (Triclosan was not one of the compounds of interest in this study.) EDCs were found at total influent concentrations of 1350-11,000 ug L^{-1}. Concentrations were reduced to 30μg/L in treated effluent. The results of this study indicate that septic systems may be a significant source of OWCs to groundwater.

In order to understand the fate of chemicals released in the environment it is important to study both their removal in wastewater treatment processes as well as loss mechanisms once they reach the receiving environment. The subsurface soil receiving effluent from an OWTS is a vital component in the treatment of wastewater effluent before reaching groundwater or other receiving water bodies. Figure 3.2 illustrates the

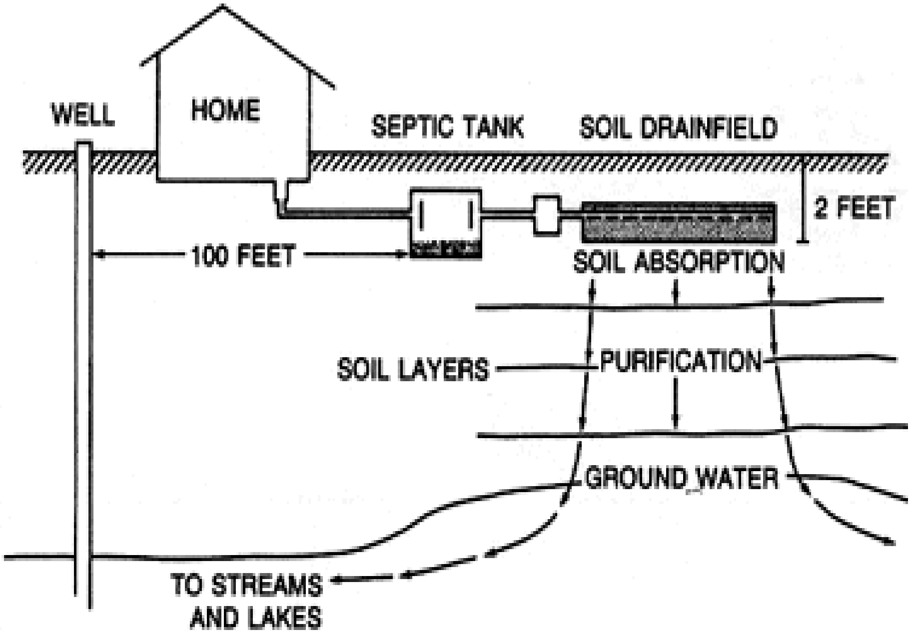


Figure 3.2 Schematic of an OWTS. (http//ees.soil.nesu.edu/soilscience/publication/Soilfacts/AG-439-13)

Basic schematic of an OWTS. The subsurface soil matrix functions as a barrier in prohibiting the entrance of contaminants to the receiving aquatic environment of an OWTS. The physical, chemical, and biological properties of the soil define and control this impact. As stated, limited data is available concerning the transport mechanisms of PPCPs in soils and sediment. Even less information is available for triclosan. This understanding is vital in accessing the transport and fate of TCS through an OWTS. Singer et al., (2002) measured the vertical concentration profile of TCS in a lake sediment core of Lake Greifensee in Switzerland. A high amount of TCS was found in the 30-year-old sediment layer indicating that degradation is slow in the sediment under study conditions. This finding also reflected the increased use of TCS over the past 30 years. These findings make the assumption that TCS is fairly persistent in the sediment, but were not verified with additional data. A study by Lindstrom et al., (2002) found that the removal rate of TCS by sorption/sedimentation is slower than by water exchange. Mathematical modeling indicated that sorption and settling accounted for approximately 19% of total TCS loss in a study of a creek in Texas (Morrall et al., 2004). Only one of these studies obtained data from actual soil analysis and that the latter two reflect estimations from mathematical models and rate loss equations.

Of utmost concern in an OWTS, is the ability of the soil to retain contaminants dissolved within the wastewater. The longer the retention period the longer the time for these contaminants to be broken down by a combination of physical, chemical, and biological reactions. However, if this retention time is reduced, groundwater and other receiving water bodies are potentially at risk. One example of the reduction of retention time is the facilitated transport of contaminants through the soil matrix Components within wastewater that can function as contaminant carriers are dissolved organic matter (DOM). DOM is known to reduce the affinity of various hydrophobic organic compounds (HOCs) to soil and thus enhance their transport. However, DOM can also increase this affinity of HOCs to soil by providing additional sites for sorption. The behavior of DOM in solute-soil systems and its interaction with HOCs is the subject of the next chapter.

REFERENCES

Balmer, M.E., T. Poiger, C. Droz, K. Romanin, P. Bergqvist, M.D. Müller, and H. Buser. 2004. Occurrence of methyl triclosan, a transformation product of the bactericide triclosan, in fish from various lakes in Switzerland. Environ. Sci. Tech. 38:390-395.

Bester, K. 2003. Triclosan in a sewage treatment process – balances and monitoring data. Water Res. 37:3891-3896.

Federle, T.W., S.K. Kaiser, and B.A. Nuck. 2002. Fate and effects of triclosan in activated sludge. Environ. Toxicol. Chem. 21, 7:1330-1337.

Hua, W., E.R. Bennett, R.J. Letcher. 2005. Triclosan in waste and surface waters from the upper Detroit River by liquid chromatography-electrospray-tanem quadrupole mass spectrometry. Environ. Int. 31:621-630.

Kanda, R., P. Griffin, H.A. James, and J. Fothergill. 2003. Pharmaceutical and personal care products in sewage treatment works. J. Environ. Monit. 5, 5:823-830.

Kolpin D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton. 2002. Pharmaceuticals, Hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A National Reconnaissance. Environ. Sci. Technol. 36:1202-1211

Kolpin, D.W., M. Skopec, M.T. Meyer, E.T. Furlong, S.D. Zaugg. 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Sci. Total Environ. 328:119-130.

Latch, D.E., J.L. Packer, W.A. Arnold, K. McNeill. 2003. Photochemical conversion of triclosan to 2,8-dichlorodibenzo-p-dioxin in aqueous solution. J. Photochem. Photobiol. 158:63-66.

Lindström A., I.J. Buerge, T. Poiger, P. Bergqvist, M. Müller, H. Buser. 2002. Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. Environ. Sci. Technol. 36:2322-2329.

McAvoy, D.C., A.J. DeCarvalho, A.M. Nielsen, M.L. Cano. 2002. Investigation of an onsite wastewater treatment system in sandy soil: modeling the fate of surfactants. Environ. Tox. Chem. 21, 12:2623-2630.

Morrall D., D. McAvoy, B Schatowitz, J. Inauen, M. Jacob, A. Hauk, W. Eckhoff. 2004. A field study of triclosan loss rates in river water (Cibolo Creek, TX). Chemosphere. 54:653-660

Rudel, R.A., S.J. Melly, P.W. Geno, G. Sun, and J.G. Brody. 1998. Identification of alkylphenols and other estrogenic phenolic compounds in wastewater, septage, and groundwater on Cape Cod, Massachusetts. Environmental Science and Technology. 32:861-869.

Sabaliunas D., S.F. Webb, A. Hauk, M. Jacob, W.S. Eckhoff. 2003. Environmental fate of triclosan in the River Aire Basin, UK. Water Research. 37:3145-3154.

Singer H., S. Müller, C. Tixier, L. Pillonel. 2002. Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: Field measurements in wastewater treatment plants, surface waters, and lake sediments. Environ. Sci. Technol. 36:4998-5004

Thomas, P.M., and G.D. Foster. 2005. Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process. Environ. Toxicol. Chem. 24, 1:25-30.

Thompson, A., P. Griffin, R. Stuetz, E. Cartmell. 2005. The fate and removal of triclosan during wastewater treatment. Water Environ. Research. 77, 1:63-67.

CHAPTER 4

DISSOLVED ORGANIC MATTER AND HYDROPHOBIC ORGANIC COMPOUNDS: PROPERTIES, CHARACTERISTICS, AND INTERACTIONS IN SOIL SYSTEMS

Organic matter is ubiquitous in the environment, being found in all terrestrial and aquatic environments. The sorption of hydrophobic organic compounds (HOCs) by dissolved organic matter (DOM) is of critical importance in the understanding of the solubility, fate, and impact of contaminants in the environment. It is recognized that dissolved organic matter plays a major role in the sorption of HOCs in soil systems. Generally, the apparent aqueous solubility of an organic compound is increased by DOM. The result is decreased sorption to non-dissolved solids, therefore, enhancing contaminant transport of HOCs within a soil profile. The ability of microorganisms to degrade these compounds can also be hindered by DOM. However, much is still unknown regarding the behavior of DOM in the environment. The complex and heterogeneous nature of DOM accounts for this lack of understanding. Although it is difficult to predict the behavior of DOM, several factors that contribute to the fate of contaminants associated with DOM have been determined based on general characteristics. Of prime importance are the following factors: 1) the identity and concentration of dissolved organic matter, 2) the nature of the interaction between the contaminants, DOM, and sorbing medium, and 4) the mobility of the colloidal matter (DOM) within an aquifer.

4.1 HISTORICAL BACKGROUND

Humic substances are a major soil component and have been studied for over two centuries. Much of the early and current research was dominated by soil scientists. The term humic acid was coined by Achard in 1786 when peat was extracted with alkali and precipitated upon acidification (Aiken et al., 1985). This term was not commonly used until 1839. Berzelius, a Swedish soil scientist, isolated humic substances from surface waters. He studied various extracts and gained insight into their elementary composition and their ability to form metal complexes. It was not until the early 20th century (1914) when Oden, a soil scientist, classified humic substances into the groups of humus coal, humic acid, hymatomelanic acid (named by Hoppe-Seyler), and fulvic acid (Aiken et al., 1985). Oden was recorded as the first scientist to use term fulvic acid to describe the alkali-soluble and acid-soluble humic fraction. Later Shmuk examined the formation of humic substances by soil microorganisms. In 1930 he also demonstrated the presence of esters which indicated the presence of COOH (carboxylic acid) groups by the process of esterification. He expressed humic acids as being “a nitrogenous body of an acid nature, the acidity being due to both its power of adsorption, as a result of the colloidal condition of the humic acid, and to the presence of COOH groups” (Aiken et al., 1985).

Despite the information that has been gained from the first recorded experiments with humic matter, there are still many unknowns and doubts in the origins, role, nature, and function of humic matter in the environment. These uncertainties form differences of opinions by scientists. A multidisciplinary approach is needed to accurately observe the various roles of these compounds as they relate to the global carbon cycle, public health, and soil health. Aiken et al., (1985) stated that: "For this reason, [no definitive answers for longstanding fundamental questions] the study of humic substances is a bona fide academic exercise per se and does not necessarily require practical applications or geochemical significance to lend it justification."

4.2 PROPERTIES OF HUMIC MATTER

Terminology used in defining humic substances varies from author to author and from scientist to scientist. This was a major difficulty encountered in the early study of humics. Currently, consistent definitions exist for each major fraction of humics. The general category, humic substances, refers to all natural organic substances that are of high molecular weight, are heterogeneous in nature, and made up of the decomposition of plant and animal tissues (Gaffney et al., 1996). The major three fractions of humic substances, humin, humic acid, and fulvic acid, are defined operationally on the basis of aqueous solubility as a function of pH. Humin is typically strongly bound to metals and clays and therefore insoluble at all pH values. Humic acids are insoluble at pH values of 2 or less, but soluble at higher pH values. Fulvic acids are soluble in water at all pH values. Typically, humic and fulvic acids are what is left after the humin fraction has beed removed (Gaffney et al., 1996). Water solubility is an effective criterion for separation because it is dependent upon acidic functional group content, molecular weight, aromaticity, and other chemical characteristics. Molecular size can also be used as a technique in defining fractions and separation. Humic matter ranges in size from a few hundred to several hundred thousand atomic mass units (Gaffney et al., 1996). Generally, fulvic acids are lower in molecular weight than humic acids. Because of the larger size and greater sorption site availability, humic acids are thought to contribute most to the binding of HOCs.

The presence of functional groups greatly contributes to the polarity of the organic matter. Humic materials are made up of a backbone of alkyl/aromatic units cross-linked predominately by oxygen and nitrogen groups. Major functional groups include carboxylic acid, phenolic and alcohol hydroxyls, ketone, and quinine groups. Fulvic acids contain more carboxylic acid, phenolic, and ketonic groups than humic acids. Structurally, they are more aliphatic and less aromatic than humic acids, which accounts for their higher solubility in water at all pH values. Because humic acids are more aromatic, they become insoluble when carboxylate groups are protonated at low pH values (Gaffney et al., 1996). This property allows humic material to bind to both hydrophobic and hydrophilic materials. Therefore, in combination with their colloidal properties, humic and fulvic materials are effective agents in transporting both organic and inorganic contaminants in the environment.

4.3 COLLOIDAL CHARACTERISTICS

Organic colloids are formed when humic and fulvic acids aggregate due to their surface active properties. This aggregation leads to the formation of micellular structures that are responsible for the complexation of HOCs in aqueous environments. A micelle has a hydrophobic core and a charged surface. Hydrophilic functional groups orient themselves out in the bulk solution, while the hydrophobic functional groups orient themselves inward away from the aqueous environment. This hydrophobic core acts as a second, nonaqueous phase and increases the water solubility of hydrophobic organic compounds. Organic molecules must be amphiphilic in order for a micelle to form. Meaning, one portion of the molecule must be more hydrophobic while the other needs to be more hydrophilic. From these requirements, arrangements of functional groups on the molecules can be implied and indicate the specific binding interactions present. However, certain criteria are required for micelle formation.

Micelles form as a result of hydrophobic effects. Micelle formation is dependent on the concentration of surfactant, the hydrophobic portions of the molecule. The required surfactant concentration is termed the “critical micelle concentration” (CMC) (Gaffney et al., 1996). At levels lower than the CMC, the surfactant molecules drift to the solution-air interface and interfere with the structural arrangement of the water molecules. The result is a decrease in surface tension of the solution. Increasing the amount of surfactant will support the formation of additional micelles, but the surface tension will remain constant once the CMC has been achieved. The occurrence of a constant surface tension and abrupt solubilization of a HOC is a definitive test for micelle formation.

4.4 HOC COMPLEXATION

Increased aqueous solubility, decreased sorption, and enhanced transport resulting from the complexation of hydrophobic compounds with dissolved/colloidal organic matter have been heavily researched. The degree to which DOM will complex with organic chemicals is dependent upon the nature and source of the DOM as well as properties of the organic compound in question (Nelson et al., 1998). The majority of the research has concentrated in the movement of pesticides. Micropollutants such as triclosan and other PPCPs have been overlooked with the exception of a few studies. Although generalizations can be made, differences in functional groups and polarity play a major role in the behavior of these compounds in the environment. The effect of DOM on sorption and possible transport is dependent on the nature of the solute, soil, and DOM as well as the competition between solute-soil, solute-DOM, and DOM-soil interactions (Kan and Tomson, 1990).

4.4.1 Nature of the Solute

The preference of a compound for a certain phase in a soil-water system can indicate the likelihood of its mobility and behavior in a soil system. Partition parameters such as K_{ow}, K_{oc}, and K_d are commonly used to quantitatively express this preference. K_{ow}, the *n*-octanol water partition coefficient, is the ratio of the dissolved concentration of a chemical in octanol and in water at equilibrium. Octanol serves as a surrogate for the binding of organic compounds instead of the aqueous phase in solution. This coefficient can be used to predict the extent that a contaminant will likely bioaccumulate in living organisms. The soil organic partition coefficient, K_{oc}, can be defined as the concentration ratio of a solute sorbed onto the soil phase and in the aqueous phase at equilibrium. Prediction of K_{oc} from hydrophobic parameters is widely used because typically, soil organic matter (SOM) is considered the dominant sorptive phase for organic compounds. K_d is the distribution coefficient of a given solute in solid and solution phase. K_d has wide application in any system where the preference of a compound to one phase over another is desired. Understanding the affinity of a solute to the soil or solution phase in the natural environment is essential for assessing the impact and probability of contaminant exposure to humans and or wildlife.

4.4.2 Nature of the Soil

Soil can be described as a dual-function sorbent where mineral matter sorbs a contaminant by adsorption (surface interaction) while soil organic matter (SOM) sorbs the contaminant by partition. Mineral matter acts as an adsorbent under fairly dry conditions where organic compounds are held on the surface of mineral particles. However, competition of sorbing compounds to mineral matter can arise in the presence of water and the presence of various organic contaminants in a system. Sorption of HOCs by organic matter generally predominates over sorption to minerals, because clay minerals in soils are typically hydrated (Carmo et al., 2000). In the presence of water, mineral matter prefers to adsorb water due to their similar molecular polarities. SOM prefers to sorb the contaminants, thus decreasing the sorption of organic contaminants to mineral matter (Chiou and Kile, 2002). Because organic contaminants partition (or complex) into the SOM independently, it is important to understand the function of the SOM and how partition processes affect the fate of organic contaminants.

SOM partition coefficients (K_{om}) as well as organic carbon coefficients (K_{oc}), discussed previously, are commonly used to predict the distribution of organic contaminants within the soil environment as it relates to the amount of organic matter present. Use of these coefficients to predict contaminant distribution based on variations of SOM properties in different soils, minimizes the time and effort expended in the experimental process of obtaining data. However, use of K_{om} values to predict the soil-water distribution of contaminants ignores the potential contribution of soil minerals to sorption (Chiou and Kile, 2000). The intensity that mineral matter versus organic matter sorbs a particular compound, determines the retention of HOCs in soil. Hydrophobic interactions facilitate the adsorption of neutral organic molecules on mineral surfaces, smectite in particular. Depending on surface charge, hydrophobic nanosites located within the inner cavity of smectie clays can greatly influence sorption of organic compounds (Laird et al., 1999). The large surface area of smectites (600-800 m^2g) as well as their range and abundance in a wide variety of soils greatly influences the environmental fate of HOCs (Laird et al., 1999). Sheng et al., (2001) determined that for certain pesticides, expandable soil clays have the potential to be an equal or dominant sorptive phase when compared to SOM for pesticide retention in soil. This study used K-saturated and Ca-saturated semectite and SOM in the form of a muck soil to determine the sorption strength of various pesticides. Adsorption was affected by the type of clay and its charge, the type of exchange cation present, and the type and position of substituents on the aromatic ring of a given compound. Sorption strength is an important determinant in accessing the bioavailability, persistence, and potential for leaching of a compound with in the soil environment.

4.4.3 Nature and Source of DOM

The degree that DOM will complex with organic chemicals is dependent upon the nature and source of the DOM (Nelson et al., 1998). The effect of DOM on the solubility and sorption of organic compounds is determined by the concentration, source, size, polarity, and molecular configuration of the DOM. Chiou et al., (1986) carried out solubility enhancement studies on HOCs and found their affinity to associate with DOM as follows: soil-derived humics > soil-derived fulvics > aquatic humics > and aquatic fulvics. However, not examined in this study are solubility enhancements of DOM derived from sewage sludge or effluent. Studies involving the use of sewage wastes suggest that sewage-derived organic matter can possibly enhance herbicide transport (Nelson et al., 1998). Hassett and Anderson (1982) found municipal sewage-borne particulate matter to be a more effective adsorbent to organic compounds than river borne particulate matter. In a study by Graber et al., (1995) enhanced atrazine transport in soil irrigated with secondary effluent implied that sewage derived DOM might have been the cause of facilitated transport. Typically the larger surface area of humics, in relation to fulvic acids, are more responsible for the binding of organic compounds.

4.5 INSTRUMENTATION USED IN WASTEWATER CHARACTERIZATION

4.5.1 NMR Spectroscopy

Carbon is the element central to organic chemistry. Therefore, ^{13}C nuclear magnetic resonance (NMR) spectroscopy plays an important role in determining the structure of unknown organic molecules. Although complete structural information cannot be determined, NMR provides an indication of the distribution of various types of carbons (Rocha et al., 1999). It offers information concerning the number of different types of carbon atoms present in a molecule and the electronic environment of the different types of carbons present within a compound (Figure 4.1). Recently, ^{13}C NMR spectroscopy has been a helpful tool for characterizing organic matter, soil organic matter (SOM) in particular. However, the heterogeneity and complexity of organic matter limits

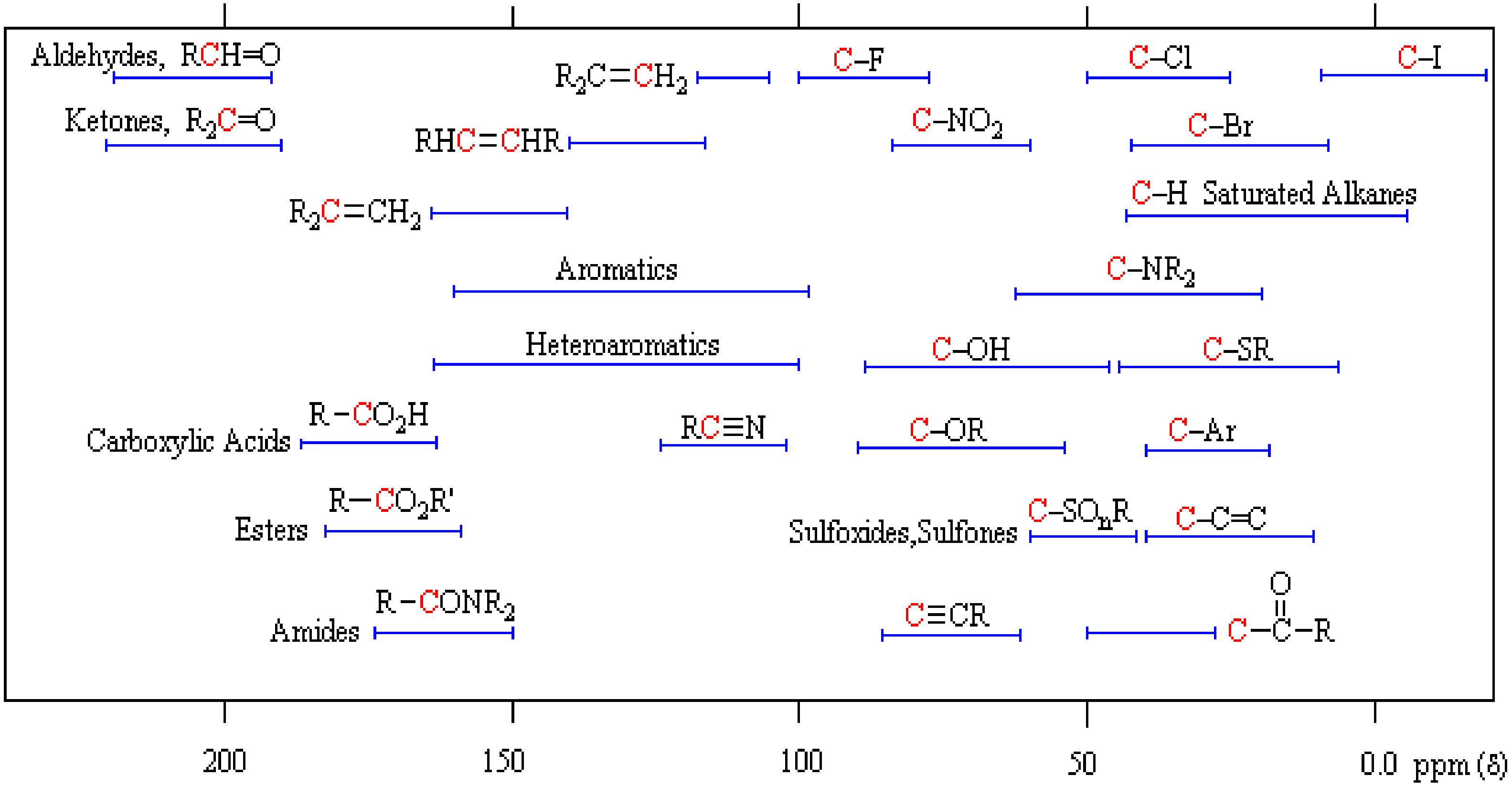


Figure 4.1 Chemical shift ranges in ^{13}C NMR. (generated by William Reusch)

the level of detail available from ^{13}C NMR. The information obtained from carbon analysis is typically limited to broad functional group classes such as aromatics and aliphatics in bulk spectroscopic analysis (Wong et al., 2002). Even with this limiting factor, bulk spectroscopic properties can provide much information due to the fact that aromatic functional groups are typically thought to be responsible for the binding capacity of organic matter. Certain predictors, such as K_{oc} values, already exist and are used extensively in predicting the sorption of organic contaminants, pesticides in particular. However, use of these values assumes uniform behavior of organic matter within soil. Identifying the composition of organic matter will aid in determining its role in the binding and transport of organic contaminants. Uniform behavior is unlikely because the structure and composition of organic components are likely to vary significantly among soils. The use of K_{oc} values alone can lead to inaccurate predictions about the fate of contaminants (Ahmad et al., 2001). Ahmad et al., (2001) determined that the use of averaged K_{oc} values are inadequate in assessing a soils' sorption capacity. The relationship between K_{oc} and structural variations of SOM from two regions, Australia and Pakistan, were studied. Two pesticides were of interest, carbaryl and phosalone. Variations in the structural composition of the SOM were observed for both soils studied. The variations in K_{oc} could only be explained when variations in the aromatic components of the SOM were taken into account. Correlations between SOM and K_{oc} values indicated that the aromatic component of SOM is a good predictor of a soils ability to bind the nonionic pesticides studied.

The majority of organic matter characterization studies have focused on SOM derived from terrestrial and aquatic sources. Spectroscopic characterization of organic matter derived from wastewater is also a helpful tool, but seldom studied. Dignac et al., (2001) observed this discrepancy and conducted experiments to study the changes in the organic composition of wastewater during treatment using a combination of three spectroscopic techniques: 1) solid state CPMAS ^{13}C NMR, 2) liquid state ^{1}H NMR, and IR. Changes in the organic matter during biological treatment were highlighted. ^{13}C and ^{1}H NMR indicated that aromatic carbons are minor constituents within wastewater. The most noted difference between wastewater and treated wastewater was that alkyl chains exhibited a more highly branched character in treated water. Long chain aliphatic carbons were more present in raw wastewater. This finding is highly important in studying the fate of HOCs in the environment. As stated previously, aromatic functional groups are most noted for their binding capacity.

Eriksson et al., (2004) also found that aliphatic carbon was more important in hydrophobic partitioning than aromatic carbon. This study examined the binding of 2,4,6-trinitrotoluene (TNT), aniline, and nitrobenzene to dissolved and particulate soil organic matter. Using a combination of sorption parameters and spectroscopic analysis, specific biding information was obtained. In turn, characteristics of sorption isotherms defined by mixed Langmuir and linear model were explained by ^{13}C NMR and XPS spectroscopy (X-ray photoelectron spectroscopy). It was ultimately determined that in contaminated soils characterized by continuous leaching of DOM, TNT and its related derivatives, have the ability to be transported to ground waters and surface waters due to their preference for specific functional groups in DOM.

Triclosan has also been studied by spectroscopic analysis. Hundt et al., (2000) was interested in the breakdown products of TCS by two fungi, *Trametes versicolor* and *Pycnoporus cinnabarinus*. HPLC provided quantitative information while ^{13}C NMR and FTIR provided qualitative and structural information. The fungi were able to degrade triclosan to various metabolites. Toxicity tests determined that these metabolites exhibited lower cytotoxic and microbial activity as compared to parent TCS. However, *P. cinnabarinus* was noted as methylating the hydroxyl group of TCS during cultivation. Methylated triclosan, as mentioned earlier (Ch 3.), is a known biotransformation product being found in various environmental compartments and also more bioaccumulative than parent TCS. This study recognized one possible source of its environmental occurrence.

Guillén et al., (2004) used ^{13}C NMR spectroscopy to study the location and orientation of TCS in phospholipids model membranes. This was of interest because the original theory of Regös and Hitz (1974) on TCS mode of action has been overshadowed by the current mechanism of fatty acid synthesis inhibition in microbial cells. The study of Regös and Hitz (1974) stated that TCS causes membrane lesions that compromise cell integrity and ultimately cause cellular contents to leak. Even though fatty acid inhibition is a well recognized mechanism of TCS, identifying its orientation within phospholipids membranes has wide application in completely understanding its full mode of action. Using egg yolk lecithin as model membranes, Guillén et al., (2004) determined that TCS is located in the proximity of carbons C1/C4 of the phospholipid molecule and that TCS is likely aligned perpendicular to phospholipids. ^{13}C NMR spectroscopy can be used in gaining specific compositional information on the carbon makeup of organic matter, identifying specific trends in compositional change during the wastewater treatment process, and in obtaining compound specific information.

4.5.2 UV-Visible Spectrophotometry

The degree of hydrophobicity in humic substances controls the molecular absorptivity of humic matter in ultraviolet (UV) spectroscopy (Piccolo et al., 2000). The use of UV analysis for qualitative and quantitative information on the composition of dissolved organic carbon is becoming increasingly popular and found to be a useful nondestructive tool (Piccolo et al., 2000; Her et al., 2003; Dunnivant et al., 1992; Guo and Chorover, 2002; Chin et al., 1994; Gu et al.,1994). Her et al., (2003) used UV analysis along with other methods a combination to characterize DOM originating from groundwater, surface water, and secondary wastewater effluent. Their major objective was to develop a rapid analytical method to aid in water and wastewater treatment optimization requiring only minimal sample volume. The ability to analyze bulk water samples as opposed to samples subjected to isolation, fractionation, and concentration was of prime importance. Results indicated a mixture of polysaccharide and protein-like substances for the surface and wastewater samples and minimal amounts of fluvic-like substances were found in the wastewater effluent

Dunnivant et al., (1992) used laboratory columns to investigate the dominant processes controlling the transport of naturally occurring DOC in aquifer sediments using surface water. Of major importance was the adsorption of subcomponents within DOC. Certain fractions of DOC have been found to be preferentially adsorbed while other fractions have been found to be preferentially transported. Dunnivant et al., (1992) separated the DOC into three subgroups, total hydrophilic, hydrophobic acid, and hydrophobic neutral. These subgroups, varying concentrations of DOC were used in column experiments. Column effluent samples were characterized by light absorbance at 260, 330, and 435 nm. Absorptivity (absorbance divided by DOC concentration, L $kg^{-1}cm^{-1}$) was plotted against pore volume. Absorbance at these wavelengths was desired to observe compositional changes in DOC during transport experiments. Both fractionated and unfractionated DOC was used in experiments. Spectroscopic analysis of column effluent showed significant changes in absorptivity during initial breakthrough. Changes became negligible during the tailing portion of breakthrough curves generated in the study. However, size exclusion experiments indicated that the composition of mobile organic carbon changed during DOC breakthrough. Hydrophobic components were found to preferentially adsorb while hydrophilic components were rapidly transported through columns. These differences in mobility play a major role in the subsurface transport of organic and inorganic contaminants. Mobile hydrophilic components may be effective in transporting metals and radionuclides. Organic contaminants are expected to bind preferentially to hydrophobic components but will bind differently to the acidic and neutral subcomponents, depending on characteristics of the contaminant (Dunnivant et al., 1992). Compositional analysis of DOM is essential in truly characterizing its behavior and thus organic contaminants in the terrestrial and aquatic environment.

Chin et al., (1994) also determined that bulk spectroscopic analysis can be used to quickly estimate the size of humic substances and their aromatic content. Molar absorptivity at 280 nm is frequently used to index the aromaticity of DOM (Guo and Chorover, 2003). At this wavelength π-π* electron transitions occur in the UV range from 270-280 nm (Figure 4.2). Another advantage of using this method is that nitrate does not absorb radiation at 280 nm and does not interfere with analysis (Chin et al., 1994). Another commonly used as an indicator of humification is the E4/E6 (465 and 665 nm) ratio.

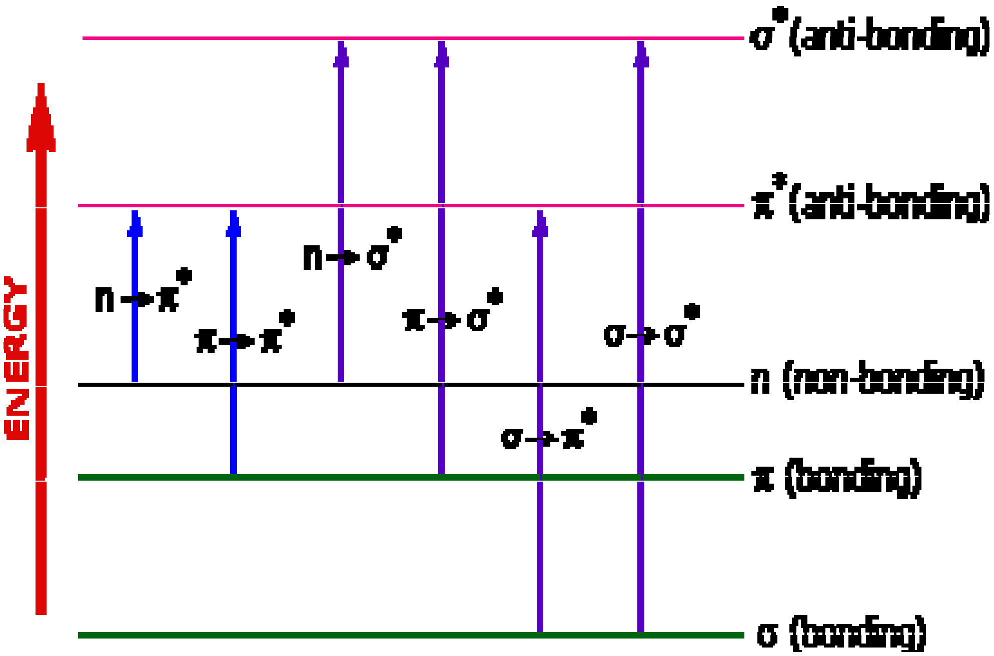


Figure 4.2 Electron transitions in UV-Visible spectrophotometry. The π-π* transition is an index if aromaticity corresponding to absorbance at 280 nm. The σ-σ* transition is characteristic of low molecular weight carbon atoms, typically corresponding to absorbencies at 224 nm.

REFERENCES

Ahmad, R., R.S. Kookana, A.M. Alston, and J.O. Skjemstad. 2001. The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by ^{13}C CPMAS NMR Spectroscopy. Environ. Sci. Technol. 35:878-884.

Aiken, G.R., D.M. McKnight, R.L. Wershaw, and P. MacCarthy. 1985. Humic substances in soil, sediment, and water: Geochemistry, isolation, and characterization. Wiley Interscience.

Carmo, A.M., L.S. Hundal, and M.L. Thompson. 2000. Sorption of hydrophobic organic compounds by soil materials: application of unit equivalent Freundlich Coefficients. Environ. Sci. Technol. 34:4363-4369.

Chin, Y., G. Alken, E. O'Loughlin. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ. Sci. Technol. 28:1853-1858.

Chiou, C.T.,and D.E. Kile. 2002. Contaminant sorption by soil and bed sediment, Is there a difference?. USGS Fact Sheet. June. 087-00.

Chiou, C.T., R.L. Malcom, T.I. Brinton, and D.E. Kile. 1986. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. Environ. Sci. Technol. 20:502-508.

Dignac, M.F., P. Ginestet, A. Bruchet, J.M. Audic, S. Derenne, C. Largeau. 2001. Changes in the organic composition of wastewater during biological treatment as studied by NMR and IR spectroscopy. Water Sci. Technol. 43, 2:51-58.

Dunnivant, F.M., P.M. Jardine, D.L. Taylor, J.F. McCarthy. 1992. Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. Soil. Sci. Soc. Am. J. 56, 2:437-444.

Eriksson, J., S. Frankki, A. Shchukarev, and U. Skyllberg. 2004. Binding of 2,4,6-trinitrotoluene, aniline, and nitrobenzene to dissolved and particulate soil organic matter. Environ. Sci. Technol. 38:3074-3080.

Gaffney, J.S., N.A. Marley, S.B. Clark. 1996. Humic and Fulvic Acids: Isolation, Structure, and Environmental Role. American Chemical Society.

Graber, E.R., Z. Gerstl, E. Fischer, G.U. Mingel. 1995. Enhanced transport of atrazine under irrigation with effluent. Soil Sci. Soc. Am. J. 59, 6:1513-1519.

Gu, B., J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy. 1994. Adsorption and desorption of different organic matter fractions on iron oxide. Geochimica. et Cosmochimica. Acta. 59, 2:219-229.

Guillén, J., A. Bernabeu, S. Shapiro, J. Villalaín. 2004. Location and orientation of triclosan in phospholipid model membranes. Eur. Biophys. J. 33:448-453.

Guo M., and J. Chorover. 2003. Transport and fractionation of dissolved organic matter in soil columns. Soil. Sci. 168, 2: 108-118.

Hassett, J.P., and M.A. Anderson. 1982. Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river-and sewage-borne particles. Water Res. 16:681-686.

Her, N., G. Amy, D. McKnight, J. Sohn, Y. Yoon. 2003. Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and f fluorescence detection. Water Res. 37:4295-4303.

Hundt, K. D. Martin, E. Hammer, U. Jonas, M.K. Kindermann, and F. Schauer. 2000. Transformation of triclosan by Trametes versicolor and Pycnoporus cinnabarinus. Appl. Environ. Microbiol. 66, 9:4757-4160.

Kan, A.T., and M.B. Tomson. 1990. Ground water transport of hydrophobic organic compounds in the presence of dissolved organic matter. Environ. Chem. 9:253-263.

Laird, D.A., and P.D. Fleming. 1998. Mechanisms for adsorption of organic bases on hydrated smectite surfaces. Environ. Tox. Chem. 18, 8:1668:1672.

Nelson, S.D., J. Letey, W.J. Farmer, C.F. Williams, and M. Ben-Hur. 1998. Facilitated transport of napropamide by dissolved organic matter in sewage-sludge-amedned soil. J. Environ. Qual. 27:1194-1200.

Piccolo, A., P. Conte, A. Cozzolino. 2000. Chromatographic and spectrophometric properties of dissolved humic substances compared with macromolecular polymers. Soil Sci. 166, 3:174-185.

Regös, J. and H.R. Hitz. 1974. Investigations on the mode of action of triclosan, a broad spectrum antimicrobial agent. Zentralbl. Bakteriol. Abt. Orig. A. 226:390-401.

Rocha, J.C., É. Sargentini, I.A.S. Toscano, A.D. Rosa, and P. Burba. 1999. Multi-method study on aquatic humic substances from the “Rio Negro”-Amazonas State/Brazil. Emphasis on molecular-size classification of their metal contents. J. Braz. Chem. Soc. 10, 3:169-175.

Sheng, G., C.T. Johnson, B.J. Teppen, and S.A. Boyd. 2001. Potential contributions of smectite clays and organic matter to pesticide retention in soils. J. Agric. Food. Chem. 49:2899-2907.

Wong, S., J.V. Hanna, S. King, T.J. Carroll, R.J. Eldridge, D.R. Dixon, B.A. Bolto, S. Hesse, G. Abbt-Braun, and F.H. Frimmel. 2002 Fractionation of natural organic matter in drinking water and characterization by 13C cross-polarization magic-angle spinning NMR spectroscopy and size exclusion chromatography. Environ. Sci. Technol. 36:3497-3503.

PART II

EXPERIMENTAL SECTION

CHAPTER 5

METHODS FOR DETERMINING THE SOLID-SOLUTION INTERACTION OF TRICLOSAN IN POROUS MEDIA

This section presents experiments conducted to observe the solid-solution interaction of triclosan in porous media as a means to determine the potential for facilitated transport by dissolved organic matter (DOM). Experiments were carried out in two phases: 1) batch sorption equilibrium and 2) column transport. Isotherms were developed in batch sorption experiments as an initial step to observe the sorption behavior of TCS. Pulse input breakthrough curves were generated under saturated conditions to observe the mobility of TCS in re-packed laboratory columns. The sorption characteristics and mobility of TCS in quartz sand, was analyzed using three treatment solutions. These consisted of primary wastewater filtrate (<0.45μm) collected from an onsite wastewater treatment system (OWTS) of 1) low and 2) high organic carbon (HOC) concentration and 3) 5mM $CaCl_2$ (NOC) serving as an organic free control. An additional objective was to characterize the wastewater by spectroscopic compositional analysis. This was accomplished using ^{13}C NMR (carbon 13 nuclear magnetic resonance) spectroscopy and UV-Visible spectrophotometry (UV-Vis). Instrumentation, materials and theoretical considerations for each experimental phase are presented in this chapter.

5.1 Wastewater Collection and Site Characteristics

Two sites were chosen for wastewater collection. Both sites are located in residential subdivisions where waste is collectively treated by a community based decentralized system. Wastewater is collected, treated, and dispersed identically in both locations. All waste received by systems were primarily of domestic origin. Wastewater from each home is collected in an individual septic tank for primary treatment, i.e., liquid/solid separation. Effluent from these individual tanks is transported to a community based recirculating sand filtration system (Figures 5.1 (a) and (b)). The recirculating sand filter, serving as secondary treatment, is an aerobic treatment mechanism that serves to reduce the organic carbon content of the wastewater and thus biochemical oxygen demand (BOD). In both cases, wastewater for use in laboratory experiments, was collected prior to secondary treatment by sand filtration. These samples consisted of primary treated effluent from all the homes served by the system. This sampling location was chosen because it represents the level of treatment achieved by a basic septic tank. Nationwide, many homes on decentralized treatment do not operate with an additional means of treatment. In the majority of onsite systems, primary treated waste is transported to the receiving environment, typically subsurface soil, where final treatment occurs. Wastewater used in experiments were collected in three, 20 gallon plastic carboys at each site. Carboys were filled with effluent by use of a sample pump. Upon arrival at the laboratory, wastewater was homogenized and stored in a refrigerator at 4°C prior to use. Wastewater was generally used within two weeks of collection.

Site 1 is located in Blount County (TN) and serves a subdivision of 20+ homes. Development in this subdivision is new and currently expanding. Site 2 is located in Rutherford County (TN) and serves 100+ homes. Preliminary experiments indicated that site 2 (Figure 5.1 (c)). Because of this large difference, differences in DOC-TCS

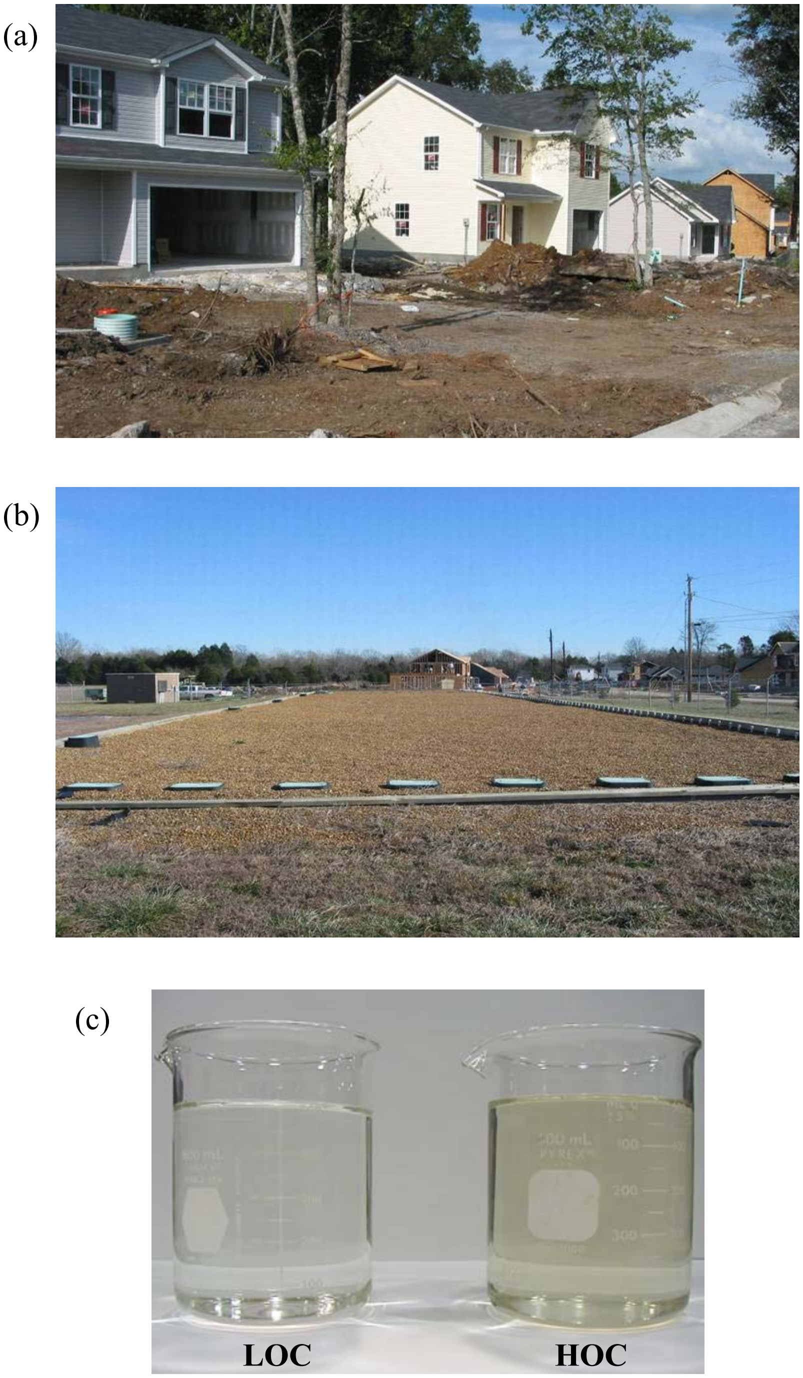


Figure 5.1 Wastewater collection sites. (a) Residential subdivision (site 2), (b) Sand filtration unit, and (c) wastewater filtrate (<0.45 μm) from site 1 and 2 (LOC and HOC, respectively).

interactions were also expected. One factor attributing to the differences in DOC content are dilution effects in site 1. Residents in this subdivision use water on a more leisurely basis as compared to site 2. The majority of homes have swimming pools, saunas, and/or hot tubs. Water drained from these facilities are primarily transported to the septic tank. Wastewater was collected during the summer months, the peak time for recreational water usage.

5.2 ADSORBATE

One hundred percent quartz sea sand (crystalline silica; silicone dioxide - SiO_2) was used as the adsorbate for both batch and column studies (Fisher Scientific, GA). Prior to use, sand was washed through a No. 200 mesh sieve to remove fines that could pass through the mesh strain the at bottom of the transport column. After repeated washes with tap water, the sand was rinsed multiple times with distilled water and allowed to air dry. Organic carbon was measured on the sand at a mass concentration of 0.02 mg kg^{-1} prior to pre-treatment by solid organic combustion.

Sand was chosen as the sorption medium for various reasons. It is structurally well defined. Carbon content is minimal and thus not expected to contribute to the sorption of TCS; sorption of TCS will be due to the sand itself or components within treatment solutions. Also, sand filtration serves as the media for fixed-film secondary treatment in the subdivisions of sites 1 and 2. The sorption and mobility of TCS in these experiments will give an indication as to the extent of TCS removal before final dispersal to soil. Removal and/or non-removal of TCS can also give an indication as to the behavior of other organic wastewater contaminants present within effluent.

5.3 CHEMICALS AND SOLUTIONS

All reagents were of analytical or reagent grade. High pressure liquid chromatography (HPLC) grade TCS was purchased from Sigma-Aldrich (St. Louis, MO) as its trade name, Irgasan, with a purity of 97% and used as received. Primary stock solutions of TCS were prepared in HPLC grade acetonitrile. Intermediate standard solutions were prepared in HPLC grade acetonitrile and water at a 70:30 volume/volume ratio. Standards were held at 4°C by refrigeration. Other analytes, KBr and $CaCl_2$ were all reagent grade. KBr was used as a conservative tracer in column transport experiments. 5mM $CaCl_2$ was used as an ionic solution base for the NOC treatments in both sorption and transport experiments. (Preliminary studies indicated chloride to be the major anion within the LOC and HOC wastewaters.) Laboratory-generated distilled water was used throughout the study.

Solutions for both the LOC and HOC treatments were prepared identically. Collected wastewater was sequentially filtered by vacuum filtration. Pore size decreased in the order of 1mm>1.6µm>0.8µm>0.45µm. Whatman and Millipore glass fiber pre-filters were used for the 1mm and 1.6µm fractions, respectively. Fisherbrand nitrocellulose filters were used for the 0.8µm and 0.45µm fractions, respectively. If not used immediately, wastewater filtrate was stored in 4L amber glass containers and refrigerated at a temperature of 4°C, prior to use, but used within 48 hours after filtration.

5.4 INSTRUMENTATION

5.4.1 HPLC

Triclosan identification and quantification was carried out on a Shimadzu VP Series High Performance Liquid Chromatography system (HPLC). The instrument consisted of a quaternary pump, solvent degasser, autosampler, and a diode array UV detector. Triclosan separation was achieved on a 150 × 4.6 mm Econosphere (Alltech Associates, Inc.) C_{18} column with a 5 µm particle size. HPLC conditions for separation were as follows: mobile phase of 70:30 acetonitrile:water, 1 mL/min flow rate, 50 µL injection volume, and UV adsorption at 220nm for detection. Calibration was achieved using five calibration standards ranging from 0.1 to 10 mg L^{-1}. Calibration standards were analyzed at the beginning of each sample set and exhibited linearity (r^2 of 0.9994 - 0.9999) throughout the course of the study. Matrix spikes and calibration standards were performed every 15 - 20 samples to ensure proper instrument operation and peak integration.

5.4.2 ^{13}C NMR

A carbon "fingerprint" of the wastewater was obtained via ^{13}C NMR (carbon 13 Nuclear Magnetic Resonance) spectroscopy. Although complete structural information cannot be determined, it provides an indication of the distribution of various types of carbon functional groups (Rocha et al., 1999). Peaks of main concern were within the aromatic chemical shift band between 110 - 160 ppm and the non-aromatic, or aliphatic, chemical shift band between 0 - 45 ppm. Isolating peak identification to these regions gives a first qualitative look into the composition of the LOC and HOC wastewaters.

Prior to NMR analysis, wastewater was dehydrated on a Labconco 4.5 freeze dry system. Approximately 72 hours of drying time was needed for a 600 mL sample of wastewater filtrate. 600 mLs of wastewater yielded approximately 100 mg of solid residue. The residue collected was dissolved in deuterated chloroform ($CDCl_3$; Cambridge Laboratories, 99% purity) with a 0.5% internal tetramethylsilane (TMS) standard. In cases where the residue did not fully dissolve, the solution was centrifuged at 3200 rpm for 10 minutes and supernatant was transferred to an NMR tube. ^{13}C NMR spectra were recorded on a Varian 300MHz NMR. 29,696 scans (15 hours) were acquired for wastewater samples to produce the most intense signal and clearly defined peaks. Chemical shifts were expressed relatively to chloroform (middle peak of triplet set at 77.0 δ).

5.4.3 UV-Visible Spectrophotometer

A Genesys™ 6 UV-Visible spectrophotometer was used as an additional means of wastewater characterization. Bulk spectroscopic properties can be used to quickly estimate the size, aromatic content, and other characteristics of humic substances (Chin et al., 1994). Column effluent samples in transport experiments were placed in 1 cm quartz window cuvettes and analyzed at the following wavelengths: 224, 280, 465, and 665 nm. Absorbance at these wavelengths can provide information as to the degree of humification and aromaticity of organic carbon. Absorbance at 224 nm is characteristic of low molecular weight organic carbon (Chin et al., 1994), absorbance at 280 is a direct index of aromaticity, and absorbencies at 465 and 665 nm is expressed as a ratio – E4/E6 – is an indication of the degree of humification. A plot of molar absporptivity (ε, L mol^{-1}

cm^{-1}) against pore volume is a potential indicator of changes in wastewater composition during transport experiments. Molar absorptivity is calculated by the following equation:

$\varepsilon = A/cl$

where A is absorbance at a given wavelength, c is the concentration of organic carbon per sample (mol L^{-1}) and l is the length of the light path through the cuvette (1 cm). This information can also be used to confirm ^{13}C NMR findings.

5.5 BATCH SORPTION EQUILIBRIUM EXPERIMENT

5.5.1 Theory

An isotherm approach was taken to observe the sorption behavior of TCS. Adsorption isotherms are commonly used as a non-mechanistic approach to assess the adsorption of a compound by an adsorptive material. The sorption isotherm is a graph of the equilibrium surface excess or amount of a compound adsorbed in units of mmol/kg or mg/kg designated by *q* which is the amount of substance sorbed, calculated by the following equation:

$q = V_l\,(C_{in}-C_{eq})/m_s$

where V_l = volume of liquid (L), C_{in} = initial compound concentration (mg L^{-1}), C_{eq} = equilibrium solution concentration (mg L^{-1}), m_s = mass of adsorbent material (kg) (Essington, 2003). At equilibrium, the amount of substance that has disappeared from the solution phase is assumed to be adsorbed by the solid. The Freundlich model is commonly used to describe this phenomenon. The Freundlich model accounts for the variation in *q* (the amount sorbed computed by difference) as a function of C_{eq} (the equilibrium solution concentration) and is described by the equation

$q = K_F C_{eq}^N$

where K_F, the Freundlich coefficient, is the overall sorption capacity of the system. N is the heterogeneity of the sorbing surface (0, very heterogeneous and 1, very homogenous) and also described as the deviation from isotherm linearity. The amount of compound sorbed (q) in mg kg $^{-1}$ is plotted against the equilibrium solution concentration (C_{eq}) in mg L^{-1}. In order to determine if the Freundlich model describes the data, the equation is transformed into the linear expression,

$\log q = \log K_F + N \log C_{eq}$.

Plotting $\log q$ against $\log C_{eq}$ will form a straight line with slope of N and a y-intercept of $\log K_F$, if the model describes the data (Essington, 2003).

The sorption of hydrophobic organic compounds (HOCs) in the presence of organic matter is often described by the linear partition theory. Isotherms described by this model are often linear up to high adsorbate concentrations, i.e., they exhibit C-type (linear) isotherm behavior. The linear partition theory is identical to the Freundlich model when N=1 and quantified with the following expression

$q = K_p C_{eq}$

where K_p is the partition coefficient. K_p can be described as the distribution of adsorbate in the solid-solution phase. However, non-linearity is also a common observance in the sorption of organic compounds. In these cases, the Freundlich isotherm is often useful, but only when N<1.

Retardation factors (R) can be estimated using batch experiments. R is directly related to the soil distribution coefficient, K_F in our case. R will vary with soil type and properties as well as solute type and properties. Establishing a reliable method for the estimation of R with batch studies is favored because batch experiments are less cumbersome to carry out in the laboratory and require less time and materials than column studies. The following equation was used to calculate a predicted R based on batch sorption parameters:

$R = 1 + (\rho_b/\theta)\, K_d$.

Where R is the retardation factor, ρ_b is solid bulk density (g cm^{-3}), θ is porosity [where $\theta = 1-(\rho_b/\rho_p)$, where ρ_p is particle density and equal to 2.65 g cm^{-3}], and K_d is the distribution coefficient [q/C_{eq}]. A uniform bulk density of 1.44 g cm^{-3} and uniform porosity of 0.430 was used for all predicted R calculations and K_d was determined as the ratio of q to C_{eq} at a TCS input concentration of 1 mg L^{-1}. One mg L^{-1} was chosen because it represents the middle concentration value within the concentration range used in batch studies.

5.5.2 Experimental Setup

The batch studies used washed and air dried quartz sand at a 1:10 (4 g: 40 mL) sand/solution ratio. Three treatments were applied, LOC, HOC, and NOC (three replicates for each treatment). TCS was added at six concentrations (0.25, 0.5, 1, 2, 3, and 5 mg L^{-1}). TCS was dissolved in 100% acetonitrile and added to each batch sample. Less than 0.3 % co-solvent of acetonitrile was used and expected to have minimal effect on sorption. Wheaton (GA, USA) borosilicate glass EPA vials (40 mL capacity) supplied with a closed teflon lined screw cap were used throughout the duration of batch studies. Samples were allowed to equilibrate for 48 hours on a reciprocating shaker set at 200 rpm. Aliquots from each sample were centrifuged at 3200 rpm for 10 minutes and analyzed by HPLC. Zero-sand controls were created for each batch experiment. These controls allowed for the quantification of losses other than sorption. To observe differences between treatments and differences within treatments, a complete randomized design (CRD) with replication and sampling was used and data analyzed by SAS (statistical analysis software).

5.6 COLUMN TRANSPORT EXPERIMENT

5.6.1 Theory

Breakthrough curves (BTCs) are plots of relative solute concentration versus time, or more commonly, pore volume. The relative concentration can be defined as the ratio of the measured concentration of the out flowing solution to its initial input concentration. The shape and characteristics of the curve are directly related to soil texture, composition, and eluting solution. Ideally, the curves should be sigmoidal in shape and symmetrical about the front of the eluting solution (Hillel, 1998). However, as the soil texture gets finer, these curves diverge from this idealistic symmetrical shape. This can be owed to various interactions within the matrix of a fine-textured soil such as sorption of the eluting solution into soil particles, the irregular velocity due to non-uniform pore spacing, biodegradation, and other physical and chemical interactions. The purpose of carrying out a BTC column experiment in our study, was to compare sorption parameters calculated from the batch isotherm study and measured values from columns.

The transport of DOC in soils can be described by a convection-dispersion model where the retardation factor is one of the important coefficients. Retardation is the delay in solute transport as compared to a non-adsorbed or conservative solute. Column experiments can also be used to estimate retardation for a specific soil and solute when steady-flow is reached. A conventional inverse curve fitting method (CXTFIT) is commonly used to calculate retardation (Lee et al., 2000; Kamra and Lennartz, 2005; Tilahun et al., 2005; Pang et al., 2002; Lee et al., 2001; Li and Shuman, 1997). In our study, CXTFIT (v.2.0) was used to estimate triclosan transport parameters in sand columns using a nonlinear least-squares parameter optimization method (Toride et al., 1999).

5.6.2 Experimental Setup

Step input breakthrough curves were generated under saturated conditions. The experimental configuration is shown in figure 5.2. Stainless steel columns (30.5 cm × 6.3 cm i.d.) were packed with washed, air dried quartz sand to a bulk density of 1.4 g cm^{-3}. Columns were purchased from Geotechnical Services, Inc. (CA, USA). Stainless steel plate was machined to bottom of tubes upon receipt to laboratory. A 0.64 cm hole was tapped in the center of the plate to provide an attachment site for the collection of column effluent. All materials used in column construction were either stainless steel or teflon.

Prior to treatment application, columns were saturated from the bottom with a background solution matching that of input solution with the exception of TCS and a KBr conservative tracer. Through separate columns, three treatments were applied after

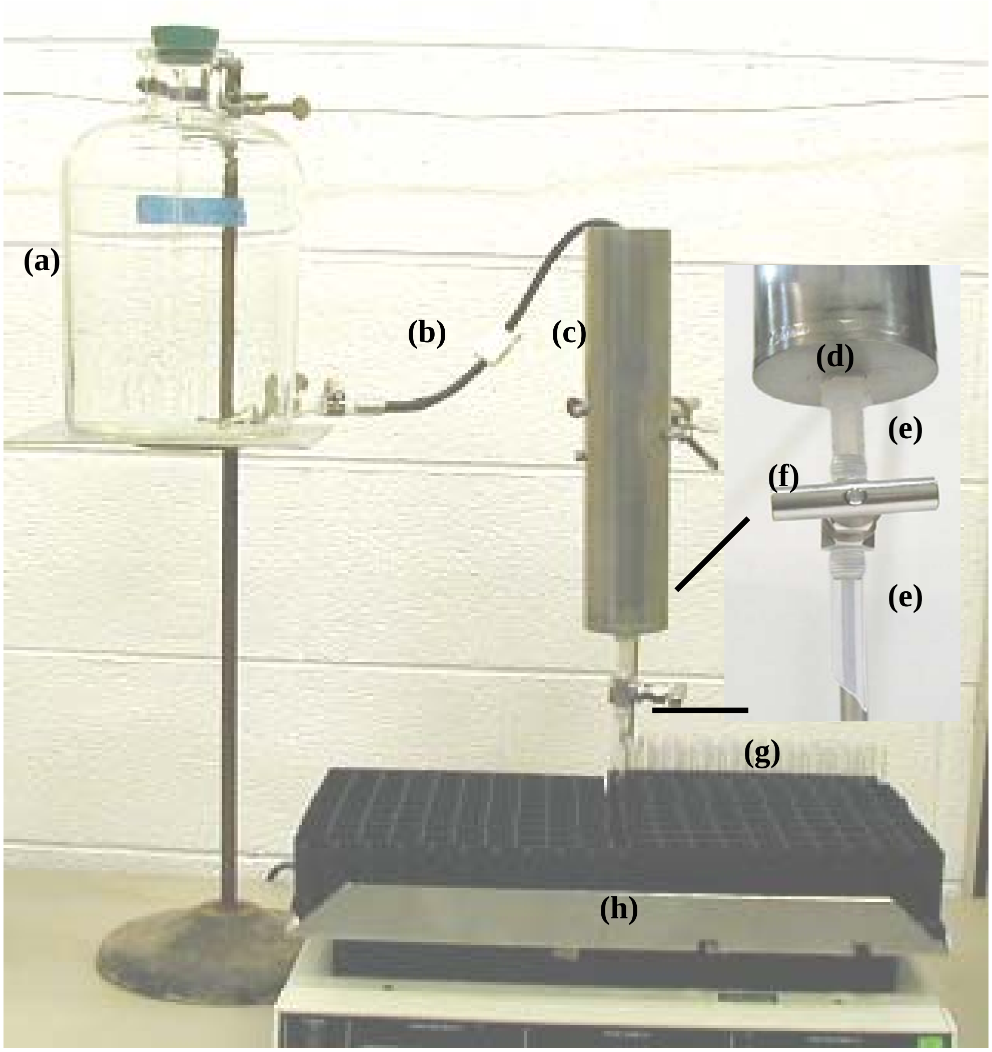


Figure 5.2. Breakthrough curve experimental configuration. (a) mariotte bottle and input solution, (b) fluoroelastomer tubing to transport input solution, (c) stainless steel sand column (30.5 cm × 6.3 cm i.d.) with a sand height of 22.9 cm, (d) base of column consisting of teflon barbed fitting for connection to tubing and threaded top (.635 cm) for connection to base of column, (e) Teflon tubing to transport column eluent to stop valve and fraction collector, (f) stainless steel stop valve to regulate flow rate, (g) 12 ml broscillate glass tubes to collect column eluent, and (h) fraction collector.

establishing steady state conditions with the background solution. For both background and input solutions, a constant head was established and maintained by use of a mariotte device. Input solution for the NOC treatment was made up in distilled water and input solutions for LOC and HOC treatments were made up in filtered wastewater effluent (<0.45 μm). A TCS concentration of 1 mg L^{-1} was used for all treatments. TCS standards dissolved in acetonitrile was added to bulk solutions. Less than 0.3% co-solvent of acetonitrile was used to achieve desired TCS concentration in input solutions and sorption and transport effects were expected to be minimal. Flow rate of solution exiting the column was controlled by a stainless steel valve at base of column that maintained a constant flow rate of 10 mL min^{-1} (±0.5). Teflon tubing and fluoroelastomer tubing was used to transport the input solution and outflowing solution from the column. A range of samples were selected for HPLC analysis based on the number of pore volumes passed throughout the column. BTC is plotted as the relative TCS concentration (RC_{TCS}) against pore volume (PV). RC_{TCS} is calculated from analyzed column effluent samples as follows:

$RC_{TCS} = C/C_o$

where C is the concentration of TCS in the sample and C_o is the initial concentration of TCS in the eluding solution. Pore volume is determined as follows:

$PV = \theta \times V$

where θ is porosity and V is the volume of the column. Data for RC_{TCS} based on pore volume was regressed by the CXTFIT (v.2.0) computer model to estimate the retardation of TCS within the columns. The reliability of batch experiments in the prediction of TCS retardation was determined by comparing predicted batch retardation coefficients to those measured by column transport experiments.

REFERENCES

Chin, Y., G. Alken, and E.O'Loughlin. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ. Sci. Technol. 28:1853-1858.

Essington, M.E. 2003. Soil and Water Chemistry: An Integrative Approach. CRC Press, Boca Raton, FL.

Hillel, Daniel. 1998. Environmental Soil Physics. Academic Press.

Lee, J., R. Horton, K. Noborio, D.B. Jaynes. 2001. Characterization of preferential flow in undisturbed, structured soil columns using a vertical TDR probe. J. Contam. Hydrol. 51:131-144.

Lee, J., R. Horton, D.B. Jaynes. 2000. A time domain reflectometry method to measure immobile water content and mass exchange coefficient. Soil Sci. Soc. Am. J. 64, 6:1911-1917.

Li, Z. and L.M. Shuman. 1997. Estimation of retardation factor of dissolved organic carbon in sandy soils using batch experiments. Geoderma. 78:197-206.

Kamra, S.K. and B. Lennartz. 2005. Quantitative indices to characterize the extent of preferential flow in soils. Environ. Model. Software 20:903-915.

Pang, L., M. Close, D. Schneider, G. Stanton. 2002. Effect of pore-water velocity on chemical nonequilibrium transport of Cd, Zn, and Pb in alluvial gravel columns. J. Contam. Hydrol. 57:241-258.

Rocha, J.C., É. Sargentini, I.A.S. Toscano, A.D. Rosa, and P. Burba. 1999. Multi-method study on aquatic humic substances from the "Rio Negro"-Amazonas State/Brazil. Emphasis on molecular-size classification of their metal contents. J. Braz. Chem. Soc. 10, 3:169-175.

Tilahun, K., J.F. Botha, A.T.P. Bennie. 2005. Transport of bromide in the Bainsvlei soil: Field experiment and deterministic/stochastic model simulation. II. Intermittent water application. Australian J. Soil Res. 48:81-85.

Toride, N., F.J. Leij, M. van Genuchten. 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, version 2.1. Research report no. 137, U.S. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture: Riverside California. 1999, p. 119.

PART III

RESULTS, DISCUSSION, AND CONCLUSIONS

CHAPTER 6

SORPTION CHARACTERISTICS OF TRICLOSAN IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

6.1 BATCH SORPTION EXPERIMENT

6.1.1 Results

Sorption isotherms of triclosan (TCS) on quartz sand in three treatment solutions were fit to the Freundlich isotherm model and are shown in figure 6.1. Sorption parameters are listed in table 6.1. Isotherm shape can give qualitative information as to the sorption characteristics in a given system. The relationship between the amounts sorbed to the solid phase versus the amount dissolved in solution post equilibrium is characteristic of various sorption phenomena. Based on qualitative analysis, TCS sorption in the LOC treatment on quartz sand exhibits an S-shape (figure 6.2a). This isotherm is characterized by a small slope at low TCS concentrations that increases as TCS concentration increases. This sorption behavior is commonly present in soils with high dissolved organic concentrations (Essington, 2003). The affinity of the quartz surface for TCS is less than that of the aqueous solution when TCS concentration is low. As TCS concentrations increase and exceed the complexation capacity of the DOC, the quartz surface gains preference and L-type behavior is evident. Based on our study, the DOC present in the LOC treatment, although at low concentrations, is able to complex TCS to a greater extent as compared to the quartz surface. Once the TCS concentration is high enough, these interactions with the DOC are overcome and sorption to the sand predominates and eventually plateaus once binding sites on the sand are filled.

.

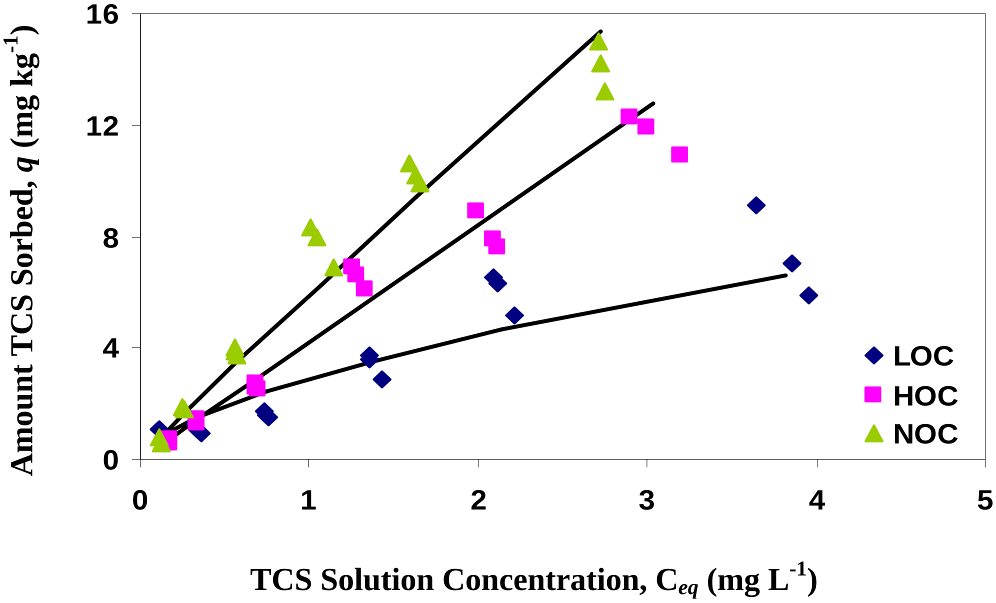


Figure 6.1 Sorption isotherms of LOC, HOC, and NOC treatment solutions illustrating the retention of TCS by sand. Freundlich fit in bold lines. Treatment means significantly different ($P<0.05$).

Table 6.1 Sorption isotherm parameters and predicted retardation factors for LOC, HOC, and NOC treatment solutions. Values represent triplicate means. Values in parentheses represent data range about the triplicate mean value.

Treatment	K_F mean separation	N	r^2	Predicted R
LOC *(n=18)*	**2.9^a (±0.1)**	**.620 (±0.18)**	**.870 (±0.04)**	**7.72 (±0.5)**
HOC *(n=18)*	**4.2^b (±0.3)**	**1.00 (±0.1)**	**.990 (±0.02)**	**12.9 (±0.6)**
NOC *(n=18)*	**5.9^c (±0.6)**	**.950 (±0.12)**	**.970 (±0.01)**	**19.6 (±0.6)**

n = number of samples
K_F = Index of sorption capacity
mean separation ($P<0.05$)
N = Deviation from isotherm linearity
r^2 = Model fit
R = Predicted retardation factor [$R = 1+(\rho_b/\theta)K_d$]
(R calculated for K_d at 1 mg L^{-1}; middle input value in batch sorption study)

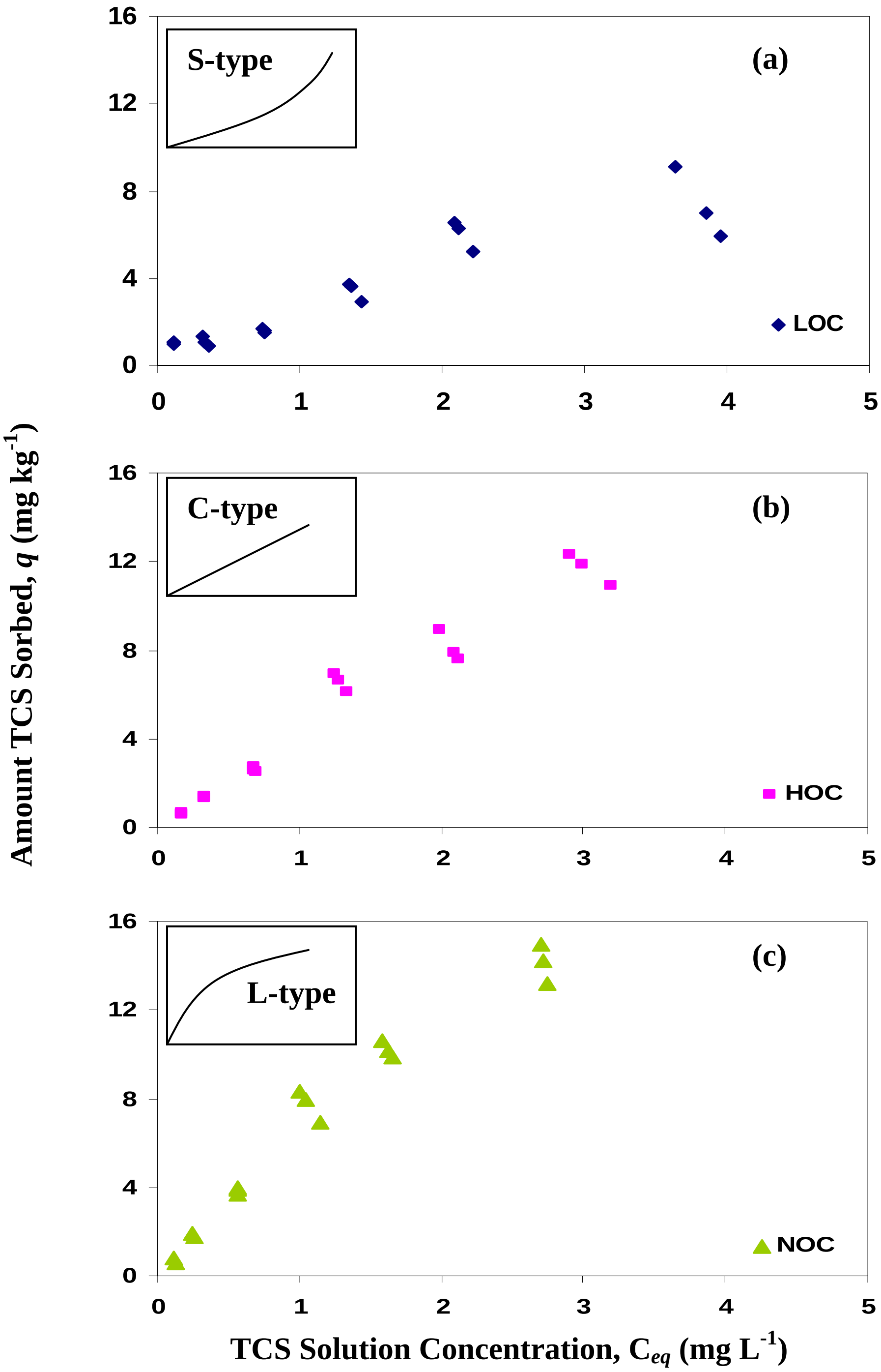


Figure 6.2 Individual sorption isotherms for (a) LOC exhibiting an S-curve, (b) HOC exhibiting a C-curve, and (c) exhibiting an L-curve.

S-curves are also associated with the adsorption of neutral organic compounds. Initial adsorption is low because the ionic (charged) environment of the soil surface is not compatible with the nonionic character of the organic compound. As adsorbate concentration increases and greater amounts of the organic compound are forced onto the soil surface, the surface becomes stabilized (essentially becoming nonionic).

The shape of the HOC treatment isotherm exhibits C-type characteristics (figure 6.2b). This type of isotherm is associated with the adsorption of nonionic and hydrophobic organic compounds (HOCs) (Essington, 2003). Initial slope remains independent of surface coverage until some maximum adsorption capacity is achieved. This is also termed constant partitioning, linear portioning, or hydrophobic sorption. Typically, these isotherms are linear up to relatively high adsorbate concentrations. The shape of the HOC isotherm is relatively linear and no apparent TCS sorption maxima is observed within this system. As compared to the other two treatments, LOC and NOC, this could possibly be due to the increased concentration of organic carbon (OC). OC concentration for this system is approximately 60 mg L^{-1} versus 5 mg L^{-1} for the LOC treatment. This indicates that the increased OC content provided additional sites for TCS to partition, exceeding the natural holding capacity of the quartz sand.

The shape of the isotherm in the NOC treatment exhibits L-type characteristics (figure 6.2c). L-type is the most commonly encountered type of isotherm in soil chemistry (Essington, 2003) and clearly illustrated in the NOC treatment isotherm (figure 6.2c). This isotherm indicates that TCS has a relatively high affinity for the quartz surface at low concentrations. As TCS concentration increases, the affinity of TCS for the quartz surface decreases and sorption plateaus. Although not extremely pronounced, the slope of the line is greatest at the lower two TCS concentrations. An indication in sorption plateau is evident at the higher two TCS concentrations. This indicates that quartz has the ability to sorb TCS at low concentrations until surface sites are filled in an organic free environment.

Prediction of the fate of contaminants often relies on constants derived from sorption isotherms (Carmo et al., 2000). Sorption isotherms provide information about the quantity of a sorbed substance (Nemeth-Konda et al., 2002). The calculated sorption parameters for the Freundlich isotherm model are listed in table 6.1. The Freundlich model adequately described the sorption of TCS by quartz under three treatment solutions. K_F, the Freundlich coefficient, is an index of the sorption capacity of a sorbent. N indicates the degree of deviation from isotherm linearity. Data show that sorption of TCS on quartz decreases in order of NOC> HOC>LOC. The slopes ($n<1$) of the LOC and NOC treatments indicate that as the initial concentrations of TCS increased, the percentage sorbed by the soil decreased. However, the slope of the curve for the HOC treatment is equal to one ($n=1$). In this case, the Freundlich model becomes the linear partition theory, indicative of constant TCS sorption to the quartz surface.

The fundamental goal of the sorption experiment was to acquire a predicted retardation factor for use in column experiments (Table 6.1). Retardation factors increased in the order of LOC<HOC<NOC. This increase in values indicates the likelihood for facilitated transport of TCS by DOM, due decreased sorption. The major factors attributing to the increased solubility of TCS are thought to be due to the presence of DOM based on reasons previously explained. Solution pH is another contributing

factor affecting the sorption behavior of TCS. Solution pH for both the LOC and HOC treatments ranged from 7.0 to 7.5, while solution pH for the NOC treatment ranged from 6.0 to 6.5. TCS has a pKa of 8.1 (Figure 6.3). At a pH of 7, the majority of TCS in solution is in its dissociated form, the negative charge on the hydroxyl group will likely act conservatively to the quartz surface, possibly resulting in the decreased sorption of TCS at this solution pH. At a pH of 6, the majority of TCS in solution is in its neutral form, the hydroxyl group is protonated and more responsive to the quartz surface. Therefore, it is very likely that solution pH contributed to the sorption behavior of TCS in our system. However, the pH of the LOC and HOC treatments fall within the range of typical wastewater pH. Adjusting the pH of the NOC treatment to match that of the wastewater treatments would not be reflective of behavior in an organic free system; the organic matter within the wastewater contributes to the overall pH of the solution.

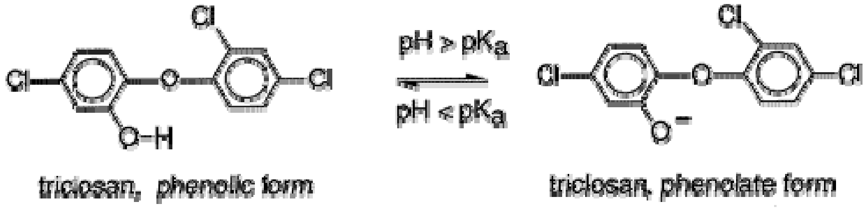


Figure 6.3 Conversion of TCS to its undissociated (phenolic) and dissociated (phenolate) forms at pH values above and below its pK_a of 8.1. (Lindström et al., 2002)

REFERENCES

Carmo, A.M., L.S. Hundal, M.L. Thompson. 2000. Sorption of hydrophobic organic compounds by soil materials: application of unit equivalent Freundlich coefficients. Environ. Sci. Technol. 34:4363-4369.

Essington, M.E. 2003. Soil chemistry: an integrative approach. Boca Raton. CRC Press.

Lindström A., I.J. Buerge, T. Poiger, P. Bergqvist, M. Müller, H. Buser. 2002. Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. Environ. Sci. Technol. 36:2322-2329.

Nemeth-Konda, L., G. Füleky, G. Morovjan, P. Csokan. 2002. Sorption behavior of acetochlor, atrazine, carbendazim, diazinon, imidacloprid, and isoproturon on Hungarian agricultural soil. Chemosphere. 28:545-552.

CHAPTER 7

ENHANCED TRANSPORT OF TRICLOSAN BY DISSOLVED ORGANIC MATTER IN SATURATED LABORATORY COLUMNS

7.1 COLUMN TRANSPORT EXPERIMENT

7.1.1 Results

Complete breakthrough of TCS was achieved in all three treatments. Figure 7.1 illustrates the breakthrough of TCS in treatment solutions, LOC, HOC, and NOC. Bromide (Br^-, 10 mg L^{-1}), used as a conservative tracer throughout the duration of the column transport study, is also plotted. Data are plotted as relative concentrations (C/Co, where C is the effluent TCS concentration and Co is the influent TCS concentration) vs. pore volume of treatment solution passed through each column. Data are presented as triplicate means. Relative to the Br^- tracer, TCS breakthrough was delayed for several pore volumes for the LOC and HOC treatments and further delayed in the NOC treatment. The results of the CXTFIT (v.2.0) regression for column experiments are presented in table 7.1. Predicted retardation factors calculated from the batch studies over estimated retardation factors determined by the model based on measured column data. The most likely reason for this discrepancy is the difference between the nature of the solid-solution interactions within each study. The batch study represents sorption at equilibrium, whereas, the column is a flow through system representing sorption in a dynamic environment. This disagreement is often encountered when using batch studies in comparison with column studies (Li and Shuman, 1997). Additionally, TCS breakthrough in both the LOC and HOC treatments were not found to be significantly ($P<0.05$) different from each other. This indicates that the transport of TCS in our system

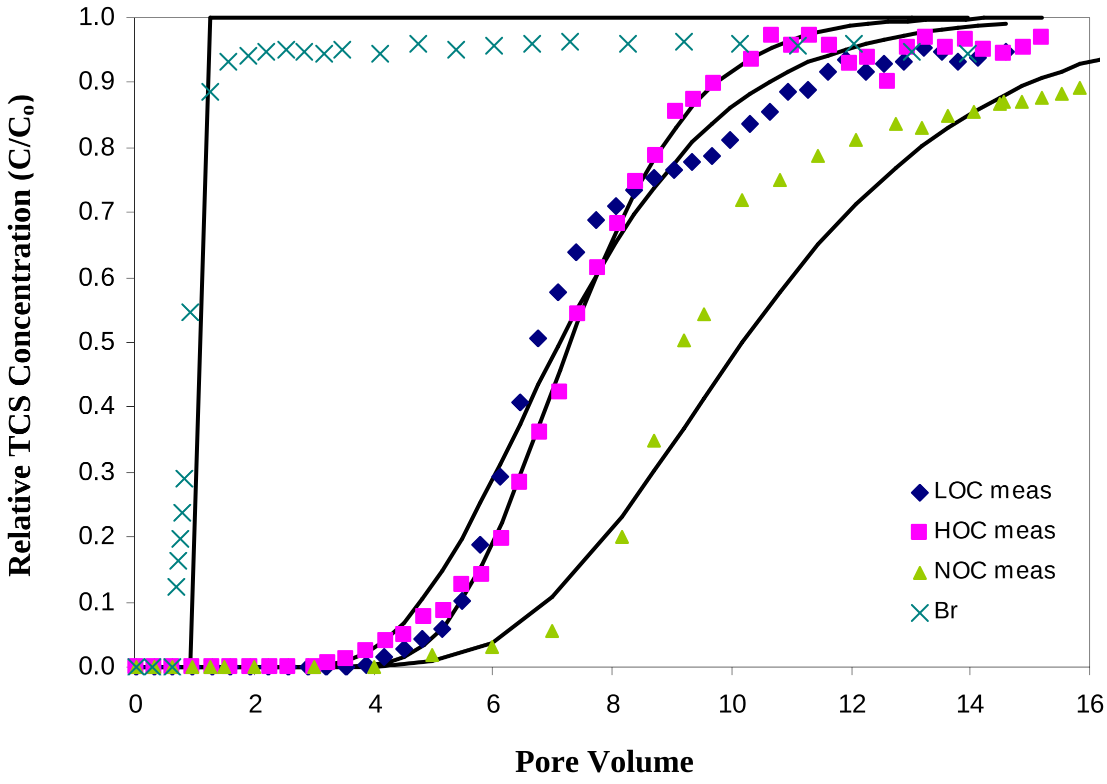


Figure 7.1 Breakthrough Curves of TCS for LOC, HOC, and NOC treatment solutions. Relative TCS concentration (C/Co) of treatments and conservative tracer is plotted against solution pore volume. Bold lines represent CXTFIT model regression. Data plots represent triplicate means (LOC and HOC not different ($P<0.05$)).

Table 7.1 Physical properties of laboratory transport columns.

Treatment	Influent DOC Conc. (mg/L)	Sand Column height	Bulk Density (g cm^{-3})	Water Content/ Porosity	Pore water velocity (cm/h)	Calculated Retardation Factor by CXTFIT	Predicted Retardation Factor
LOC	5 (±1.0)	22.86	1.50	.436	42.6	7.42	7.72
LOC	5 (±1.3)	22.86	1.52	.426	42.7	7.57	8.24
LOC	5 (±1.8)	22.86	1.52	.426	42.6	7.21	7.22
HOC	60 (±3.7)	22.86	1.52	.428	44.2	7.67	12.2
HOC	60 (±4.1)	22.86	1.52	.427	43.6	7.72	13.5
HOC	60 (±3.2)	22.86	1.52	.427	43.6	7.70	12.9
NOC	0	22.86	1.51	.431	43.0	10.2	23.5
NOC	0	22.86	1.50	.435	42.6	10.0	21.4
NOC	0	22.86	1.51	.429	42.2	10.5	22.9

is possibly independent of organic carbon concentration. Compositional analysis of bulk wastewaters, LOC and HOC, are presented in the following chapter as a means to address compositional differences within the wastewater as opposed to differences in organic carbon concentration.

In addition to retardation in the treatments, tailing of the BTCs in comparison to the Br^- tracer is also evident. TCS breakthrough can be described by an initial rapid concentration increase, followed by a delay in concentration increase, and ending in tailing. Processes responsible for retardation are dominated by sorption kinetics. Dunnivant et al. (1992) lists three processes that contribute to extended tailing of DOC in transport columns, 1) the possible nonlinear features of the DOC isotherm, 2) time-dependent adsorption during transport, and 3) the occurrence of multiple adsorption processes during transport. Nonlinearity of the TCS sorption isotherms described previously, provide an explanation as to the shape of TCS BTCs. Parker and Jardine (1986) noted that isotherm nonlinearity is known to cause tailing in BTCs.

Sorption isotherms for both the LOC and HOC treatments displayed non-linearity. NOC treatment was linear, which may explain its sharper TCS breakthrough as compared to the other two treatments. Chemical interactions are expected to be the dominant processes affecting the transport of TCS. The presence of DOM, in particular that generated from an OWTS, greatly influences sorption of TCS and can create an environment for facilitated transport. This has implications for not only TCS but for other hydrophobic organic compounds (HOCs) present on onsite treatment.

Totsche and Kögel-Knabner (2004) lists the following conditions for enhanced mobility: soil horizons that are equilibrated and saturated with DOM, soil horizons that can potentially sorb DOM but are partially saturated with DOM, and sediments with high inputs of DOM. These conditions are similar to the receiving environment of an OWTS. In this environment, solid phase materials are "pre-equilibrated" with DOM creating an environment favoring transport. Even though this environment is not easily defined, generalizations can be made. Biodegradation and chemical reactions reduce the organic content of the DOM as well as contaminate concentrations, but inputs of DOM and contaminants are continuously reestablished. Depending on the nature of the organic matter present as well as properties of the sorbing medium, the continuous input of DOM can create more sorption sites and allow extra sorption capacity of the soil or fill sites and conservatively "pass" through.

Totsche and Kögel-Knabner (2004) also present case studies to explain the effects of contaminant mobility as it relates to organic mobility and situations favoring enhanced or reduced contaminant mobility. Three main scenarios are presented that affect transport in porous media: 1) cotransport, 2) cosorption, and 3) cumulative sorption. All relate to the interaction of DOM with the immobile solid phase. In our case, the quartz sand solid phase is not expected to have much interaction with the DOM, meaning the quartz surface is nonreactive to the DOM and transport is expected to dominate. Since the DOM does interact with TCS, cotransport is exhibited in the LOC and HOC treatment columns. TCS breaks through twice as fast as compared to the organic free control. However, break through in DOM treatments are not completely due to cosorption which is evident when compared to the conservative Br- tracer. LOC and HOC treatments to not begin to break through until approximately 5 pore volumes after tracer. This retardation is due to sorption of TCS to the solid phase. Cosorption would increase TCS sorption to the sand and reduce mobility. This phenomena, however, is evident in the sorption experiment. Due the higher sorption coefficient values, the HOC treatment was expected to be more retarded that the LOC in columns. This discrepancy could indicate that equilibrium was not achieved in columns.

REFERENCES

Dunnivant, F.M., P.M. Jardine, D.L. Taylor, J.F. McCarthy. 1992. Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. Soil. Sci. Soc. Am. J. 56, 2:437-444.

Li, Z. and L.M. Shuman. 1997. Estimation of retardation factor of dissolved organic carbon in sandy soils using batch experiments. Geoderma. 78:197-206.

Parker, J.C., and P.M. Jardine. 1986. Effects of heterogeneous adsorption behavior on ion-transport. Water Res. Research. 22, 8:1334-1340.

Totsche, K.U. and I. Kögel-Knaber, 2004. Mobile organic sorbent affected contaminant transport is soil: numerical case studies for enhanced and reduced mobility. Vadose Zone J. 3:352-367.

CHAPTER 8

BULK WASTEWATER CHARACTERIZATION BY ^{13}C NMR AND UV-VISIBLE SPECTRAL ANALYSIS

8.1 ^{13}C NMR

Chromatograms of LOC and HOC filtrate obtained from ^{13}C NMR analysis are illustrated in figures 8.1 and 8.2, respectively. Chromatograms are separated into two distinct chemical shift regions, aromatic carbon (110-160 ppm) and non-aromatic (aliphatic) carbon (0-45 ppm). Table 8.1 provides a peak summary of both wastewater samples based on peaks identified in the designated chemical shift regions. Based on ^{13}C NMR chromatograms, aromatic C is the major constituent carbon class in the LOC wastewater. Aliphatic C is the major carbon constituent class in the HOC wastewater. Peaks in the aromatic C region are also present in the HOC wastewater. These results agree, in part, with the findings of Dignac et al., (2001) where treated wastewater was found to have minor aromatic character as compared to aliphatic C. This finding is important in our study because the sorption of TCS in the LOC treatment exhibited the least amount of sorption capacity in the batch experiment but has more aromatic character than the HOC treatment. This suggests that aromatic C is responsible for the enhanced mobility of TCS in the column transport experiment, but should be confirmed with additional studies examining the sole interaction of TCS to DOC within each treatment. Additionally, greater sorption of TCS in the HOC treatment as compared to the LOC treatment suggest that sorption capacity is reliant on the presence of aliphatic C. However, similar transport characteristics in both the LOC and HOC treatments in the

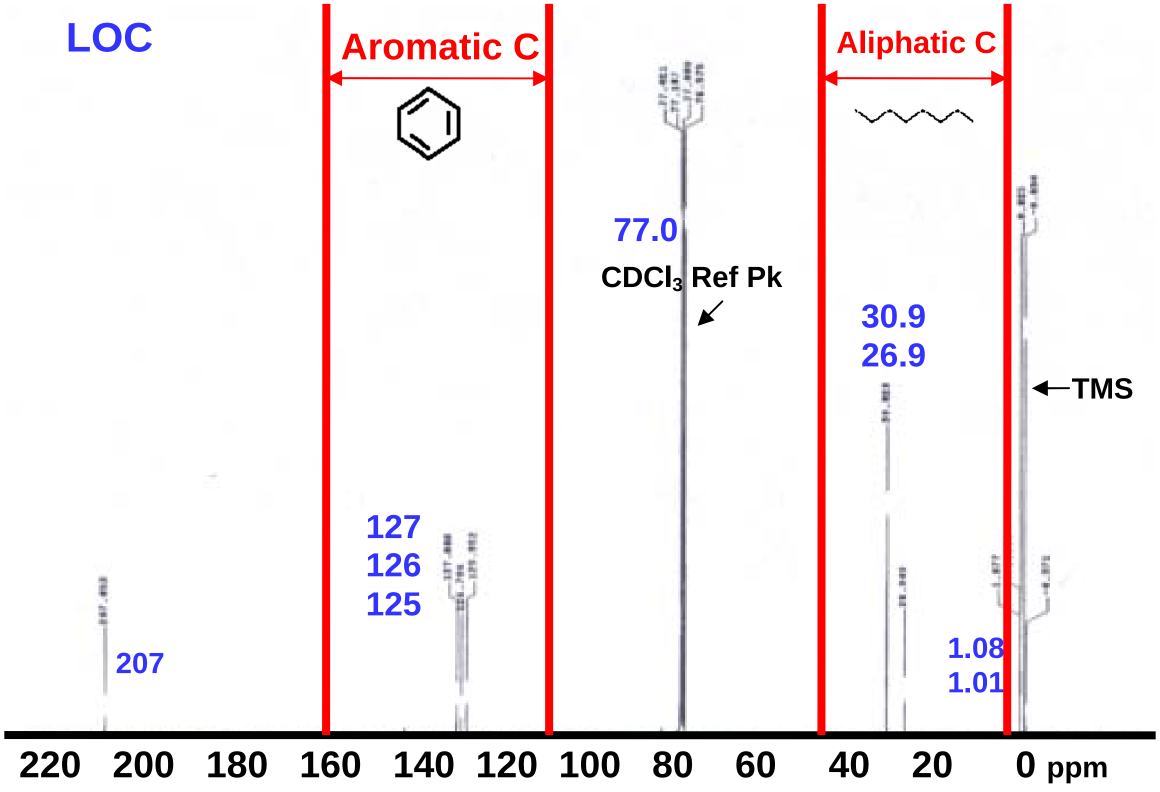


Figure 8.1 ^{13}C NMR chromatogram of the LOC wastewater filtrate (<0.45 μm).

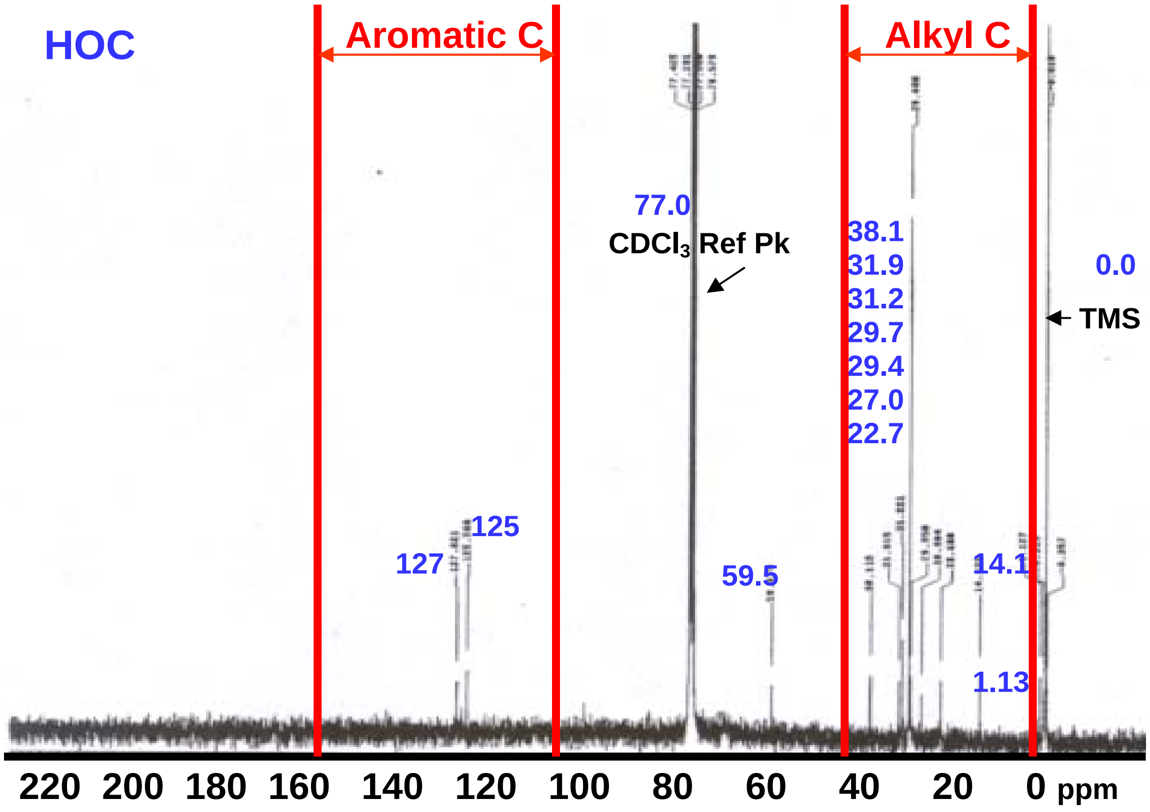


Figure 8.2 ^{13}C NMR chromatogram of the HOC wastewater filtrate (<0.45 µm).

Table 8.1. Summary of ^{13}C NMR analysis on LOC and HOC wastewaters. Region assignment is based on five main chemical shift bands: alkyl C (0-45 ppm), alkyl C bonded to heteroatoms (N and O) (45-110 ppm), aromatic and olefinic C (110-160 ppm), carboxyl C (160-190 ppm), and carbonyl C (190-210 ppm) (Dignac et al., 2001).

Sample	TOC (mg/L)	Resonance Signal (ppm)	Region
LOC	5	1.0	Alkyl C (0-45)
		1.0	
		27	
		31	
		125	Aromatic C (110-160)
		126	
		127	
		207	Carbonyl C (190-210)
HOC	60	0.32	Alkyl C (0-45)
		1.1	
		14	
		22	
		26	
		29	
		29	
		31	
		31	
		38	
		59	Alkyl C bonded to heteroatoms (N and O)
		126	Aromatic C (110-160)
		128	

column study suggest that mobility of TCS in the presence if HOC is due to the presence of aromatic C as well.

8.2 UV-VISIBLE SPECTROPHOTOMETRY

In an effort to observe the preferential adsorption or transport of subcomponents in the DOM treatments (LOC and HOC), column effluent samples were analyzed by ultraviolet-visible spectrophotometry (UV-Vis). Light absorbance was measured at 224, 280, 435, and 645 nm and were converted to molar absorptivity by dividing absorption value by organic carbon concentration. Molar absorptivity (ε) at 224, 280, 465, and 645 nm were used to confirm the results of ^{13}C NMR analysis. Plotting ε versus pore volume (Figure 8.3) also provided information as to the possible compositional changes of subcomponents within wastewater during the column transport experiment. Low molecular weight carbons, or less humified structures, are absorbed at 224 nm with greater intensity than higher molecular weight carbons. Comparing absorbance at 224 nm with absorbance at 280, the index of DOM aromaticity, can give a fair indication of the abundance of aromatic or non-aromatic carbon functional groups (Figure 8.3). Plotting the ratio 465/645, also gives an indication as to the degree of humification/aromatic content (Figure 8.4). Chin et al., (1994) states that bulk spectroscopic properties can be used to quickly estimate the size of humic substances and their aromatic contents. Both of which are important in understanding their mobility and ability to react with organic contaminants.

The intensity of absorbance at 280 nm for the LOC wastewater was consistently greater than that for the HOC wastewater during the column transport experiments

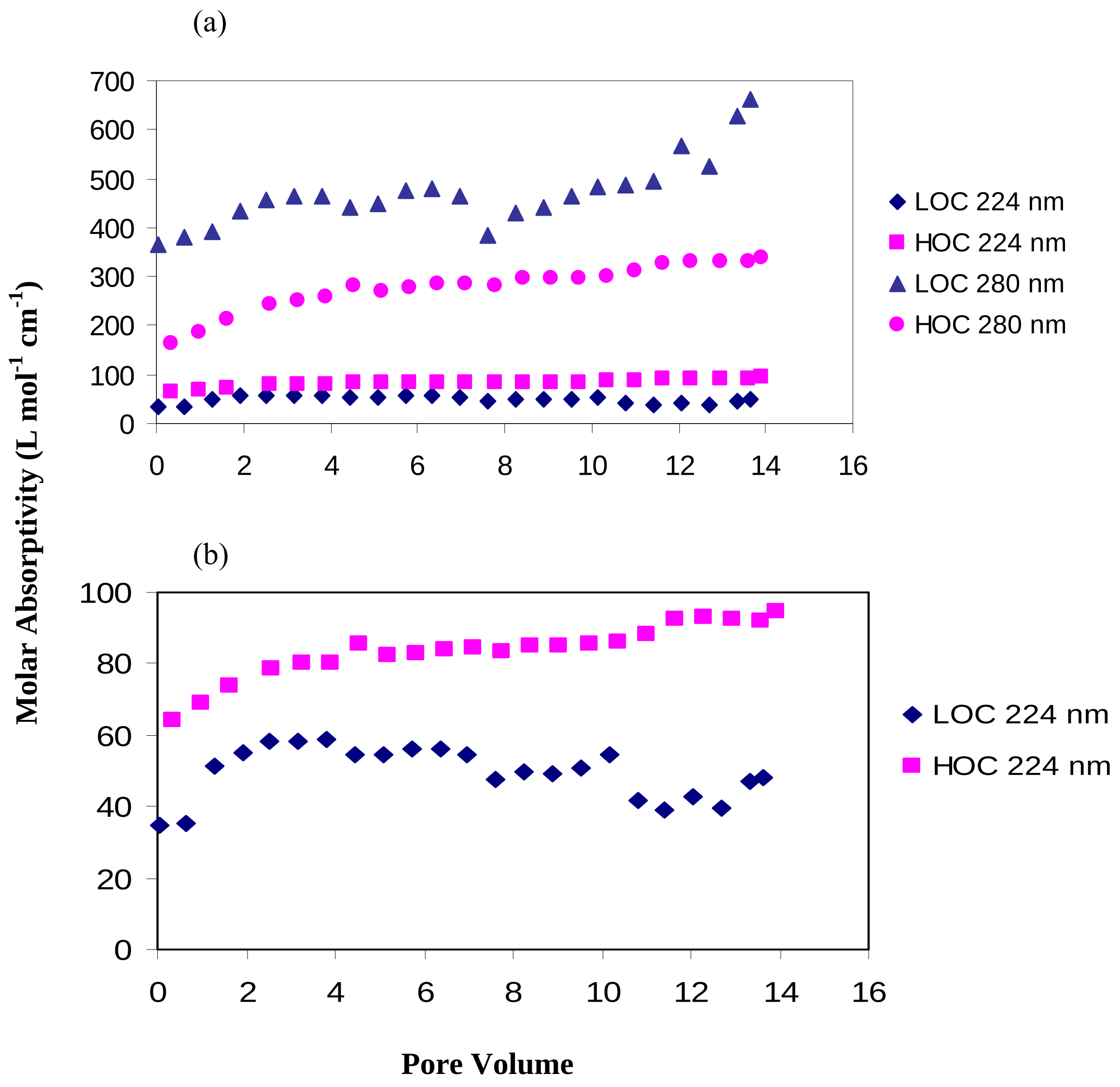


Figure 8.3 Molar absorptivity of LOC and HOC plotted against pore volume. (a) Molar absorptivity at wavelengths, 224 nm and 280 nm against pore volume. (b) Molar absorptivity at 224 nm, expanded version of (a). Data points represent triplicate means.

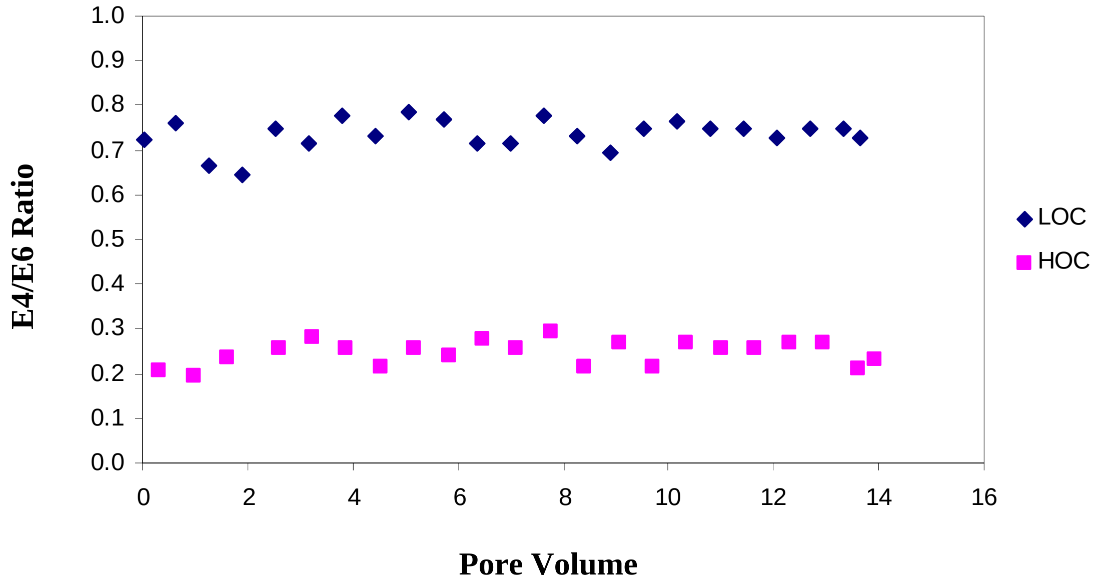


Figure 8.4 E4/E6 ratio plotted against pore volume. Magnitude of E4/E6 is related to the degree of humification. A low ratio is indicative of high molecular size and weight and directly related to aromatic content, whereas a high ratio indicates the presence of large portions of aliphatic structures (Kononova, 1967). Data points represent triplicate means.

indicating that the LOC wastewater has a higher proportion of aromatic carbon. These findings are consistent with the ^{13}C NMR results. Conversely, absorbance at 224 nm was consistently more intense for the HOC wastewater indicating the presence of low molecular weight organic carbon. The E4/E6 ratio plotted against pore volume also suggests that the LOC wastewater has a higher presence of aromatic carbon as compared to the HOC wastewater. Based on the fluctuations in absorbance, changes in organic carbon composition during the column transport experiment is slightly evident during the LOC treatment, but more pronounced at later pore volumes. Absorbance values were more stable during the HOC treatments. Guo and Chorover (2003) found that the transport of DOM in soil columns, specific for their study, resulted in the selective uptake of high molecular weight and aromatic molecules. Smaller compounds were preferentially eluted. Even though this phenomenon was not observed in our study, the transport of HOCs is governed by the hydrophobic effects of the DOM and sorbing medium. Based on the sorption study, the retention of TCS is based on the abundance of aliphatic carbon as reflected in the HOC treatment. This indicates that TCS is transported by aromatic carbon in the LOC treatment given the lowest degree of sorption capacity in conjunction with its greater proportion of aromatic carbon.

8.3 STUDY CONCLUSIONS

The concentrations and distribution of triclosan in the aquatic environment are governed by its consumer use pattern, removal rate during wastewater treatment, and removal once exposed to the receiving environment. Understanding the processes that determine the fate of triclosan in the aquatic and terrestrial environment is useful in predicting its environmental exposure. The primary effort of this study was to observe the potential for the facilitated transport of triclosan by DOM contained within wastewater effluent. This determination can provide a means to assess the potential for the leaching of TCS to groundwater, and thus, the threat to surface waters. Based on batch sorption and column transport studies, there is a potential for the facilitated transport of TCS. In order for facilitated transport to occur, the interaction between DOM and TCS has to be able to overcome the interaction of TCS to the solid phase. Sorption capacity as defined by the Freundlich coefficient (K_F) indicated the greatest amount of TCS sorption to sand in the presence of $CaCl_2$ as compared to LOC and HOC treatments with the least amount of sorption in the LOC treatment. The Freundlich exponent (N) expressed the greatest deviation from isotherm linearity in the LOC treatment. Breakthrough curves showed earlier breakthrough in both the LOC and HOC treatments as compared to the NOC treatment. However, predicted and measured retardation factors did not correlate well. The main conclusion to this discrepancy is thought to be due to the different environments of the sorption and transport studies. The batch sorption experiment represents sorption at equilibrium where as transport studies represent a dynamic environment. Other process might also be contributing factors, but not explored within this study.

Spectral analysis provided an opportunity to look at compositional differences between each wastewater treatment since characterization by organic carbon concentration did not fully explain the sorption and transport behavior of TCS in our study. ^{13}C NMR revealed that the LOC wastewater had the greatest amount of aromatic carbon and the least amount of aliphatic carbon as compared to the HOC wastewater.

This finding in combination with batch results suggests that aliphatic carbon is more responsible for the binding of TCS to quartz sand in the presence of DOM. In order to confirm this finding, additional studies are needed in observing sorption of TCS to subcomponents within the wastewater, mainly the hydrophobic and hydrophilic components. Ultra-violet (UV) data confirms the findings of the ^{13}C NMR analysis. Greater absorbance at 280 nm in the LOC treatment as compared to the HOC, confirms the presence of aromatic carbon in the LOC wastewater. Conversely, absorbance at 220 nm in the HOC wastewater confirms the greater amount of aliphatic carbon. Based on these results, the potential for the facilitated transport of TCS by DOM in the receiving environment of an onsite wastewater treatment system is a likely. Thus, the potential for the transport of other organic contaminants is a potential threat. One method of controlling this threat to groundwater from an OWTS is the inclusion of aerobic treatment zones to encourage rapid microbial degradation. The primary method of triclosan removal during treatment in wastewater treatment plants is biodegradation.

As reflected in this paper, triclosan has many uses, some beneficial and some potentially detrimental. Understanding the effects of this compound in the environment, aquatic life, wildlife, as well as human life is essential in truly assessing its threat to the global environment. Through this understanding informed decisions can be made as to the widespread usage of TCS. The following is an excerpt from Daughton and Jones-Lepp (2001) that reflects the interconnectedness of individuals to the global environment:

" It is difficult for the individual to perceive their small-scale activities as having any measurable impact on the larger environment; personal actions, activities, and behaviors

are often deemed minuscule or inconsequential in the larger scheme…A factor making it difficult for the individual to perceive the interconnectedness of their lives and the health of the environment is the immediacy of any adverse effects, because most actions have delayed consequences, obscuring the ultimate causes. The direct impact of the individual consumer in adding to the potential pollutant load on the environment is a concept that has not been well appreciated…the occurrence of PPCPs [pharmaceuticals and personal care products] *in the environment highlights the intimate, inseparable, and immediate connection between the actions, activities, and behaviors of individual citizens and the environment in which they live…PPCPs enjoy true worldwide usage…their introduction to the environment has no geographic boundaries or climate-use limitations* [as with many pesticides]*…they are discharged to the environment wherever people live or visit, regardless of season…emphasis needs to be given to the likelihood of environmental persistence coupled with the potential to elicit biological effects at low exposure levels-not just in humans, but also in wildlife."*

REFERENCES

Chin, Y., G. Alken, E. O'Loughlin. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ. Sci. Technol. 28:1853-1858.

Dignac, M.F., P. Ginestet, A. Bruchet, J.M. Audic, S. Derenne, C. Largeau. 2001. Changes in the organic composition of wastewater during biological treatment as studied by NMR and IR spectroscopes. Water Sci. Technol. 43, 2:51-58.

Daughton, C.G., and T.L. Jones-Lepp. 2001. Pharmaceuticals and personal care products in the environment: scientific and regulatory issues. American Chemical Society. Washington, D.C.

Guo M., and J. Chorover. 2003. Transport and fractionation of dissolved organic matter in soil columns. Soil. Sci. 168, 2: 108-118.

Kononova, M.M. 1967. Methods of determining humus composition and rationalization. Soviet Soil Sci. 7:894-902.

VITA

Adrienne Lysandra Roach was born on August 25, 1979, in Rochester, New York. In 1985 she, along with her family, moved to Huntsville, AL where she later attended Sparkman High School and graduated in 1997. She entered Alabama A&M University in August of 1997 and graduated with a Bachelor's of Science in Biology with a minor in Chemistry in 2001. Upon graduation she relocated to Knoxville, TN where she worked as an intern and later employee of Shaw Environmental and Infrastructure. In August of 2003, she entered graduate school at the University of Tennessee in Knoxville as a Master's student in Biosystems Engineering Technology. Her main area of focus was carrier mediated chemical transport in porous media and onsite wastewater technology. Adrienne received her degree in May, 2006.