# THE DEVELOPMENT OF A POINT-OF-USE BIOLOGICAL SAND FILTER WITH AN ADDED ACTIVATED CARBON LAYER FOR APPLICATIONS IN THE MEKONG DELTA

By

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#### ABSTRACT

# KRISTEN WYCKOFF THE DEVELOPMENT OF A POINT-OF-USE BIOLOGICAL SAND FILTER WITH AN ADDED ACTIVATED CARBON LAYER FOR APPLICATIONS IN THE MEKONG DELTA

Under the direction of DR. LAURA LACKEY

The Mekong Delta is home to a network of waterways. The water is polluted with wastes from five other countries in addition to Vietnam's own agricultural pollution. Water in the Mekong Delta is prone to high turbidity, total suspended solids, and salinity. Drinking water standards for Vietnam are of equal or lesser strictness of those set by the World Health Organization. Seventy five percent of urban and 35% of suburban residents benefit from state provided drinking infrastructure; the rest of the population of the Mekong Delta obtains drinking water from surface water, groundwater, and rainwater.

In this study, point-of-use filtration technologies were explored as potential solutions to the drinking water availability problem in the Mekong Delta. A biological sand filter (BSF) was designed to include a layer of activated carbon for pretreatment. The activated carbon layer was made from mangrove charcoal obtained from Vietnam, and was activated with a 25% NaCl m/m solution. Two nearly identical BSFs were constructed following guidelines from Aqua Clara. One was operated as a control; the other included

mangrove carbon pre-treatment. This design was chosen over others for its low cost, simplicity, and the lack of available mangrove charcoal.

Filters were operated daily for two and a half months. Each filter was loaded with 5 L of synthetic water made from river water containing  $2.95 \times 10^{-6}$  M imidacloprid, a common insecticide in Vietnam. Filters were monitored at four points throughout the process; the influent, carbon bed effluent, control filter effluent (Filter 1), and hybrid filter effluent (Filter 2). Parameters monitored included absorbance, COD, total coliforms, turbidity, conductivity, temperature, pH, total solids, and flow rate. Parameter analysis was completed at 95% confidence with Tukey's multiple comparisons, paired t-tests, and confidence interval t-tests. No performance based statistical differences were found between the two filters other than flow rate, where Filter 1 had a higher flow rate than Filter 2. It was found that the filters effectively removed COD, total coliforms, and turbidity. Future work should include studies about placement of activated carbon in the filter scheme, activation techniques, and the characterization of pesticide adsorption on activated mangrove charcoal.

# CHAPTER 1

#### INTRODUCTION

# The Drinking Water Problem

It is estimated that 2.6 billion people around the world lack access to sanitation, with 1.1 billion lacking access to an improved drinking water source [1], [2]. Without access to clean drinking water and sanitation, people are at risk for a variety of health problems. Predominant health problems associated with limited or no access to clean drinking water, sanitation, and hygiene include diarrheal diseases, helminthes, schistosomiasis, heavy metal poisoning, and trachoma [2]. It is estimated that 90% of the 3.4 million deaths annually attributed to lack of clean drinking water and poor sanitation are children under the age of 5 [2].

# Vietnam's Water Situation

Vietnam has access to plentiful sources of water, with approximately 255 billion m<sup>3</sup> (6.73 x 10<sup>13</sup> gallons) available per year from the 2360 rivers flowing through the country [3]. Unfortunately, the available water is not safe for drinking purposes without first treating it, and minimal appropriate potable water infrastructure exists. The surface waters that often serve as drinking water sources are contaminated with various industrial and agricultural wastes and pollutants, as well as other chemical pollutants, including northern Vietnam's high natural arsenic concentrations [3], [4].

#### The Mekong Delta

Currently, there are about 2.1 million poor families in South Vietnam who live on boats or floating houses along the Hau and Mekong Rivers and Southeast areas of Vietnam where they put trash and feces to the river. The inhabitants rely predominately on rainwater, surface water, and groundwater sources for drinking water applications [5], [6]. Only 75% of urban and 35% of suburban residents have access to drinking water infrastructure provided by the state [6]. Groundwater is the major source of drinking water during the dry season, which runs from December to April, but there are risks of groundwater contamination and salt water intrusion [6–8]. Every year, there are about 2,100 children and elderly patients who die from gastrointestinal infection and diarrhea resulting from intake water from the rivers in South Vietnam (Can Tho General Hospital, Vietnam). Figure 1 and Figure 2 show examples of living conditions in Vietnam, including boats and floating houses as well as water collection from the Mekong River.



Figure 1. Boat Houses in the Mekong Delta [9].



Figure 2. Water collection in the Mekong Delta [10].

#### Water Contaminants in the Mekong River

The Mekong River runs through five countries before Vietnamese residents gain access to the water source [11]. These countries have varying laws on pollution handling and dumping, leaving the bulk of the population of the Mekong Delta at risk of exposure to contamination from the upstream activity. The Mekong Delta is one of the world's largest producers of rice [6–8]. Due to high agricultural water usage, associated water contaminants include herbicides, insecticides, and pesticides. Industrial wastes, especially from processing, also contribute to the pollution of the river system [3], [6], [8], [12–15]. In addition to chemical contaminants, physical contaminants are also causing problems in the area. High turbidity and total suspended solids (TSS) in the water contaminate the drinking water sources [6], [7]. During the dry season, the salinity of the surface water becomes a serious problem, forcing the use of ground water sources as the primary water source [5–8].

#### Regulations

Most countries have their own set of regulatory guidelines and laws for management of wastewater and drinking water. The United States follows guidelines set by the Environmental Protection Agency (EPA), while other countries without federally regulated drinking water strategies tend to follow guidelines set by the World Health Organization (WHO). In Vietnam, the Vietnam Committee on Large Dams (VNCOLD) provides guidelines for drinking water, but these guidelines are not strictly enforced or followed [3]. Some regulations enforced by EPA are more stringent than those of the WHO, including turbidity. Guidelines provided by both the EPA and WHO are more strict than the VNCOLD; parameters of specific interest include total coliforms and turbidity [3], [16], [17].

#### Point-of-Use Water Filtration

In an effort to address the enormous task of household water treatment and safe storage (HWTS) in developing countries containing minimal infrastructure, many creative ideas have been developed and implemented. Technologies proven to be effective at reducing diarrheal disease include chlorination using a dilute solution of sodium hypochlorite that is often produced locally [18], [19], solar disinfection (SODIS) [20], [21], coagulation and flocculation [22], [23], biosand filtration, and ceramic filtration [24–26]. A commonly used coagulation and flocculation scheme was developed through reverse engineering a water treatment plant by the Proctor & Gamble Company in conjunction with the Center for Disease Control and Prevention; this technology is trademarked PUR Purifier of Water<sup>TM</sup>. Individual PUR sachets contain powdered ferric sulfate that serves as a flocculant and calcium hypochlorite as the disinfectant; one package is capable of treating up to 10 L of water [27]. Another technique is a ceramic filter impregnated with colloidal silver that was designed by Potters for Peace is widely accepted. These filters, which are shaped like a flower pot, are often manufactured locally at ceramic facilities [28].

Biosand filtration is another promising point-of-use technology used to treat water for drinking and cooking. Biosand Filters (BSFs) were developed at the University of Calgary by Richard Manz in the 1980s [29]. Slow sand filtration, which is commonly used in developed countries' water treatment systems, provided inspiration for the BSF design. Dr. Manz co-founded the Center for Affordable Water and Sanitation Technology (CAWST) that is focused on BSF development and worldwide distribution [30]. In addition to CAWST, other companies such as Aqua Clara International [31], Tiva Water and Hydraid Biosand Water Filter [32] are also focused on BSF design improvement and distribution.

Figure 3 shows a schematic of a typical BSF. From the figure, note the layers of media that are typically used in a BSF. From the bottom of the filter container moving upwards, layers of filter media include 3 to 5 cm diameter rocks, river gravel, course sand, and fine sand.



Figure 3. Typical Biological Sand Filter Layering Schematic.

## **Project Goals**

The motivation for this research stemmed from the desire to develop a new Mercer On Mission (MOM) Program to Vietnam. The new MOM Vietnam program is focused on improving the health of those that live in floating houses and rely on surface water for drinking. In support of this effort, the primary goal for this project was to design a cost effective, point-of-use water filter for home use in Vietnam's Mekong Delta. Inexpensive materials considered for construction were ones that could be procured locally in the Mekong Delta. Mangrove charcoal (Duoc charcoal) was available for use in the BSF design and is both plentiful and cheap throughout Vietnam. Mekong Delta River water

was imitated by spiking Ocmulgee River water with a pesticide that is commonly used in Vietnam.

BSF technology is considered a cost effective and appropriate technology for treating surface water in developing countries. Unfortunately, BSFs are not recommended to treat water characterized by high turbidity or organic contamination [33]. Considering these limitations of BSF technology and the source water characteristics commonly observed in the Mekong Delta, a BSF alone is not a good option for treating the targeted water.

A variety of one and two-container hybrid BSF designs that incorporated activated carbon were considered for use in this study. Four of the most promising design alternatives are outlined below. The pros, cons, and feasibility of each design are addressed in Table 1.

Designs Alternatives Considered Include:

- 1. A one-container system that includes two or more 3 to 5-cm layers of activated carbon within the traditional fine sand layer of the BSF.
- 2. A one-container system that includes a single 5 to 10-cm layer of activated carbon that replaced the top 5 to 10-cm of fine sand.
- 3. A two-container system, in which one container is packed with activated carbon while the other is built and operated as a typical BSF. In this option, both the

activated carbon and the BSF containers are characterized with the same lag phase between loadings.

- a. Incorporate the activated carbon container as a pre-filter for the BSF
- b. Incorporate the activated carbon container after the BSF to serve as a polishing filter
- 4. A one-container system that houses the activated carbon in the BSF diffuser.

_			Feasible with
Design	Advantages	Disadvantages	Available Bosourcos
1	-Relatively small footprint -Relatively low cost; a one container system -Potential to incorporate biofilm on activated carbon; combine removal mechanisms of adsorption with biological decay -contact time with activated carbon is equal to the filter lag time	<ul> <li>Difficult to replace saturated activated carbon without removing filter packing.</li> <li>Schmutzdecke disrupted when activated carbon is replaced; high probability of lowering turbidity and pathogen removal</li> </ul>	Yes
2	-Relatively small footprint -Relatively low cost; a one container system -Potential to incorporate biofilm on activated carbon; combine removal mechanisms of adsorption with biological decay -contact time with activated carbon equals filter lag time	-An uncertainly of developing a schmutzdecke layer	Yes
3	-Potential to incorporate biofilm on activated carbon; combine removal mechanisms of adsorption with biological decay -Potential to incorporate a large volume of activated carbon -Contact time with activated carbon is equal to the filter lag time; a relatively large time -Relatively easy to replace activated carbon when saturated	-Relatively large footprint -Relatively large cost; a two container system	No
4	<ul> <li>-Relatively small footprint</li> <li>-Relatively small cost; a one container system</li> <li>-Potential to incorporate a relatively large volume of activated carbon</li> <li>-Easy to replace saturated carbon</li> </ul>	-Contact time with activated carbon is relatively very short -A relatively low potential to incorporate biofilm on activated carbon	Yes

Table 1. Pros and Cons of Hybrid BSF Designs Considered in this Study.

Designs 1 and 2 were eliminated, since disruption of the schmutzdecke would occur each time the activated carbon was replaced in the system. Additionally, those designs were also considered less user friendly than designs 3 and 4. Design 3 was characterized with many advantages, but was deemed infeasible due to the small about of mangrove charcoal available for use in this laboratory study. Design 4 that incorporated the activated charcoal in the BSF diffuser was chosen for this study.

The overarching goal of this project was to compare the performance of a traditional BSF to a hybrid BSF that incorporated activated mangrove charcoal housed in the BSF diffuser to treat surface water contaminated with an organic pesticide. In addition to evaluating the design and performance of the hybrid BSF, other research goals included:

- 1. Determining an effective and relatively low cost method to activate the mangrove charcoal,
- 2. Comparing performance of activated mangrove charcoal to non-activated mangrove charcoal.

If the aforementioned research goals are met, a better BSF for use in the Mekong Delta may result.

## CHAPTER 2

## LITERATURE REVIEW

#### Drinking Water Quality Standards

Drinking water standards have been established by many different agencies all over the world. In the United States, the Environmental Protection Agency (EPA) regulates and creates laws about drinking water. Many of Vietnam's drinking water quality laws set parameters equal to or lower than World Health Organization (WHO) guidelines.

### Environmental Protection Agency

The EPA was established 2 December, 1970, under President Nixon with the initial purpose of research, monitoring, setting standards, and enforcement [34]. Nixon stated "the 1970s absolutely must be the years when America pays its debt to the past by reclaiming the purity of its air, its waters, and our living environment [34]." The entire process of starting up the EPA took almost an entire calendar year.

Today, the EPA primarily deals with air and water pollution, waste, cleanup, toxics and other chemicals, and green technologies [35]. Regulations on drinking water follow and are enforced by The Safe Drinking Water Act (SDWA). The SDWA was passed by Congress in 1974 to regulate public drinking water supply, and was amended in 1986 and in 1996 in order to also protect water sources [36]. water contaminants can be broken into six groups: disinfectants, disinfection byproducts, inorganic chemicals, microorganisms, organic chemicals, and radionuclides [16].

## World Health Organization

The WHO was formed in 1948 and functions as the United Nation's authority on global public health and policy [37]. To protect public health, WHO provides standards for air, water, waste, and more. Water criteria are segmented into chemical, microbial, and radiological aspects, each with its own set of standards.

#### Drinking Water in Vietnam

Only 40-50% of residents in the Mekong Delta have access to treated drinking water provided by the state. The remainder get drinking water from rainwater, surface, and groundwater sources [6]. Rainwater is only a drinking water source during the monsoon season. Seventy percent of the rainfall in Vietnam falls between August and October [6], [7]. Drinking water standards for state provided water do exist, however contaminants are still present in the treated drinking water. Surface and ground water sources also serve purposes for laundry, agriculture, food preparation, travel, and as human waste receptacles, further contaminating the drinking water sources [6]. The Mekong Delta is Vietnam's largest producer of rice and has 17 million inhabitants. *Drinking water standards*. The Vietnam Committee on Large Dams has developed drinking water standards which are based on standards from the EPA, Germany, and Thailand. Table 2 shows drinking water comparisons between the WHO and VNCOLD. From the table it is apparent that standards are lower for Vietnam than for the WHO. One difference among the EPA, WHO, and VNCOLD standards is the total coliform count allowed in treated drinking water. It is likely that this is due to lack of infrastructure, appropriate water sources, and funding to get clean drinking water programs started from within the country. In addition to in state efforts, options for providing clean drinking water require support from UNICEF or other not for profit aid organizations.

Table 2. Comparisons among the EPA, WHO and VNCOLD Drinking Water Standards [3], [16], [17].

	EPA	WHO	VNCOLD
Total Coliforms	0	0 per 100 mL sample	2 MPN/100 mL
Fecal Coliforms	0	0 per 100 mL sample	0 MPN/100 mL
Turbidity (NTU)	0.3	<1	<5
pН	6.5-8.5	6.5-8.5	6-8.5

Drinking water quality. The Mekong River is a major waterway of Southeast Asia, running through China, Burma (Myanmar), Thailand, Laos, and finally through Vietnam [11]. Vietnam is at the mercy of the other countries that the river runs through. When the river reaches the Vietnam border its waters are already polluted and of suspect quality. The Mekong Delta is a mass of waterways branching off of the Mekong River in Southwest Vietnam. Water that reaches the Mekong Delta is highly contaminated with arsenic, insecticides, pesticides, and herbicides, and is highly saline [6]. In addition to the chemical contaminants, the Mekong River is very turbid and characterized by high total suspended solids (TSS) [7]. The solids in the water negatively impact both the quality and appearance of the potential drinking water. Figure 4 shows a map of the Mekong River traversing through various countries until it reaches the Mekong Delta in Southwest Vietnam. The arrow at the bottom labeled Mekong is showing both the end of the Mekong River and the area known as the Mekong Delta.



Figure 4. Map of the Mekong River's Path of Flow through China, Burma, Thailand, Laos, and Cambodia to the Mekong Delta in South West Vietnam [38].

#### **Biological Sand Filtration**

The Biological Sand Filter was developed by Dr. David Manz at the University of Calgary in Alberta, Canada in 1990. The BSF was based off of the slow sand filter routinely used in water treatment schemes in the United States. The primary operational difference between the two technologies is the pause period; the BSF was designed for intermittent, point-of-use purposes, whereas the slow sand filter is watered continuously [39]. There are many adaptations of the BSF, with two of the primary adaptations stemming from work done by the Centre for Affordable Water and Sanitation Technology (CAWST) and Aqua Clara. Large scale BSFs for use in communities versus point of use filtration inside the home have been explored [29]. The primary difference between a CAWST and an Aqua Clara filter is the inclusion of a metallic biocide in the bottom fine sand layer by Aqua Clara; the outlet piping of the two filters are also significantly different. Since CAWST filters do not utilize a metallic biocide, disinfection is still necessary after filtration.

#### Center for Affordable Water and Sanitation Technology

The Center for Affordable Water and Sanitation Technology was founded in 2001 in Alberta, Canada. CAWST is a non-profit organization, co-founded by Dr. David Manz, which trains and consults with organizations that work with providing clean drinking water to developing countries. As biofilter technologies improve, CAWST updates their biosand filter design, and is currently on Version 10 [30]. Version 10 of the CAWST

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filter is a cement filter which is layered from the bottom up with drainage gravel, separation gravel, sand, a biolayer, and a diffuser. The tubing used to drain filtered water is 1 cm (3/8 inch) in diameter [40]. The CAWST biosand filter has been proven to remove up to 100% of helminthes and protozoa, 98.5% of bacteria, and 70-99% of viruses in lab conditions. Users are encouraged to have a pause time of at least 1 hour and up to no more than 48 hours. CAWST implements teaching and using natural resources for the 63 different countries in which it operates with other non-governmental organizations (NGOs) [30].

#### Aqua Clara International

Aqua Clara International is an international not-for-profit organization based in Michigan that is dedicated to providing water at WHO standards for developing countries. By 2007, Aqua Clara had developed a standard template for biosand filters [41]. Aqua Clara filters are to be built out of Polyvinyl Chloride (PVC) to provide at least 40 L of water per day for less than \$0.001 per liter. The filters utilize a biolayer, sand filtration and a brass biocide. Filter layering from the bottom up includes stone, gravel, coarse sand, fine sand plus the biocide, and fine sand. In the top 1-10 millimeters of the fine sand layer, typically the top 3 mm, a schmutzdecke or biolayer develops when the filter is properly used. A layer of water approximately 2.5 cm (1 inch) thick covers the schmutzdecke [42]. A diffuser is used to prevent destruction of the biolayer when water is poured into the filter. Aqua Clara recommends at least a thirty day period to develop the schmutzdecke, before which the water should be considered unclean. A12-hour pause period is recommended between loadings [31].

Aqua Clara promotes the use of native resources. All sand and gravel should be from the location where the filters are being installed. Local people should be taught how to build and use the filters with only simple tools. A sieve is used to separate course and fine sand, and gravel into separate piles. After separation, the sand and gravel are washed to remove organics, dust, soil, and silt, and are laid out to dry under the sun [31].

## Bronze and Copper as Metallic Biocides

The biocide in a BSF is used as a final precautionary measure to neutralize any microorganisms that are not removed from the source water by the schmutzdecke or through mechanical means from fine-sand filtration. Metallic biocides have many applicable uses today, but a primary use is for water purification and disinfection. The first recorded use of a metallic biocide was in 400 BCE in ancient Greece, where copper was utilized for its anti-fouling, anti-bacterial, and water purification abilities [43]. However the use of metallic biocides for microbial control of drinking water did not start until the 19<sup>th</sup> century [44].

Copper has many uses today. One of the most common uses is as a biocide for the reduction of *Escherichia coli* (*E. coli*) in kitchen and water purification settings [43], [45]. Copper is also recognized because of its antiviral and anti-fouling capabilities and

as a fungicide, algicide, molluscicide, nematocide, alcaricide, and bactericide [43]. These capabilities, along with the toxic effects of copper on microorganisms, make copper a strong agent for use in water purification technologies [43]. Once past the cell wall, copper's oxidative states act as a catalyst for reactions which destroy a cell's proteins, nucleic acid, and lipids [43], [45].

Many different alternatives to copper for use as a metallic biocide are available. The most common alternatives to copper are stainless steel, and copper alloys, including but not limited to bronze and brass. Each metal has different strengths and weaknesses for assisting in microbial control. For instance, it has been found that the performance of bronze is statistically better than that of stainless steel for the reduction of *E. coli* and *Staphylococcus epidermis* (*S. epidermis*) [46]. Brass and bronze did not exhibit a statistically significantly difference in biocidal performance during a two hour test period.

Aluminum bronze allows for the removal of tin from the copper alloy, lowering the overall cost. Copper-aluminum alloys are also known for their strengthening effects, while copper-lead alloys perform better at lower temperatures [47]. Dangers of using bronze over copper include the leaching of iron into the drinking water, but the additional metals in copper alloys could possibly help remove and reduce microorganisms that are resistant to copper.

#### Activated Carbon

Almost any solid substance can be used as an adsorbent. One of the most commonly used adsorbents is activated carbon. Activated carbon has a large specific surface area, reaching up to approximately  $1000 \text{ m}^2\text{g}^{-1}$  [48]. It is the preferred choice for adsorption for wastewater and drinking water applications due not only to the large specific surface area, but its ability to remove organic compounds. Alternatives to activated carbon include synthetic resins, activated alumina, aluminum hydroxide floc, soil organic carbon, and soil minerals [48]. Adsorbents easily attract high molecular weight organics, low and non-polar compounds and ions. Low molecular weight, highly polar compounds are not as readily adsorbed [49]. Two categories of activated carbon based on particle diameter are commonly used. Adsorbent particles greater than approximately 0.3 mm in diameter are considered granular activated carbon (GAC) and diameters smaller than 0.3 mm are considered powdered activated carbon (PAC).

#### The History of Activated Carbon

The first recorded use of activated carbon for water treatment was in 1875 in rapid filters. Patents for the use of activated carbon in filtration techniques began appearing in the early 1900s. 1920 brought the use of activated carbon specifically for the control and removal of taste and odor. PAC was the preferred form of activated carbon from the 1920s until the 1960s when the Advanced Water Treatment Research Program was formed by the U.S. Public Health Association [48], [49]. Attempts at using activated carbon adsorption techniques to replace biological treatment in the 1930s failed, but systems were modified to current day techniques utilizing both technologies in sequence [48]. Either order of technologies is possible and can efficiently treat the desired water source, but the most typical configuration utilizes biological treatment before activated carbon filtration. Using activated carbon filtration before biological treatment is not the preferred method due to the more frequent need for backwashing with highly turbid sources and the overloading of the activated carbon with biological films. Activated carbon does have the ability to grow a biolayer. This can potentially increase the ability of the activated carbon to treat the water.

Today, activated carbon is used for drinking water, industrial and municipal wastewater, and groundwater treatment. Applications of activated carbon for these purposes include the removal of organic matter, especially natural organic matter (NOM), synthetic organic compounds (SOC), total organic carbon (TOC), as well as particulates, metal ions, odor, taste, and excess chlorine [48]. Removal is modeled using isotherms, typically Freundlich or Langmuir. The Freundlich isotherm is used more frequently because it requires less data, but the Langmuir isotherm can be derived from equilibrium or statistics from data [48].

#### Sources of Charcoal and Activation Methods

Many carbonaceous sources are available for raw materials for the manufacture of activated carbon, including wood, coal, peat, lignin, nutshells, bone, and coconut shells

[48], [50]. The most common industrial sources of AC are coal or lignocellulosic materials [51]. These raw sources must first be turned into charcoal, and then activated using one of many available processes. There is little difference between any carbonization processes, but different activation processes are plentiful.

Activation is the generation of porosity, increasing surface area [51]. Activation processes are categorized by two primary subsets, physical and chemical. The primary step in physical preparation of activated carbon is carbonization. Carbonization removes volatiles, excess oxygen, and excess hydrogen, increasing the pure carbon proportion in the raw source [48], [50]. Typical carbonization processes occur around 800°C [48], [50], [52]. Carbonization is followed by activation with carbon gasification reactants, which needs to take place at temperatures between 600-1200°C [48], [50], [51].

Chemical activation can be accomplished using a variety of different activating agents including alkali metal hydroxides, alkali metals, alkali metal carbonates, and transition metal salts, all of which typically utilize dehydrating agents [51]. Chemical activation is achieved with a lower process temperature than the physical processes and tends to develop a better porous structure [51].

Of the three primary chemical activation techniques, alkali metal hydroxides are the most effective, and the most dangerous. Alkali metal hydroxides typically utilized include KOH, and NaOH. They are capable of creating high specific surface area, but are

corrosive, and hazardous to both people and the environment. KOH is generally considered the best option when using alkali metal hydroxides for activation [51].

The second option listed above that describes using alkali metal carbonates for activation is much safer. Carbohydrate salts containing Li, Na, K, Rb, and Cs are common choices for activation. Physical properties of elements and adsorbents determine the final textural properties. Potassium is frequently cited as the best choice due to its ability to interject itself into layers of adjacent carbon layers. The potassium is then removed with washing, leaving voids that increase surface area and pore volume [51].

The use of transition metal salts to promote activation achieves a result similar to physical activation.  $ZnCl_2$ , NaCl, and  $CaCl_2$  are commonly used transition metal salts, although  $ZnCl_2$  is by far the most popular choice. Transition metal salts promote the formation of tar, blocking pores created in char, but remove hydrogen and oxygen molecules, in turn increasing pore space [51].

# Statistical Analyses

Statistical analyses applied to data obtained from this study include confidence interval t distributions, paired t-tests, and Tukey's multiple paired comparisons. Percent removal, log removal, and moving averages were also used to interpret data. Tukey's test was used to compare differences between each treatment pair. Studentized range distribution tables were used to find the critical coefficient. A benefit to Tukey's method
is if the sample sizes for all treatments are the same, the confidence is exactly as calculated [53], [54].

## CHAPTER 3

## METHODOLOGY

## Carbon Source and Activation

## Carbon Source

Mangroves cover approximately 2% of Vietnam, 50% of which can be found in the Mekong Delta [55]. Mangrove forests are an important part of Vietnam's cultural and economic ecosystems, supplying sources of charcoal, timber, and firewood [56]. Although previous destruction of Vietnam's mangrove forests has prompted preservation and re-planting projects, mangrove trees still remain a top supplier of the Mekong Delta resident's carbon and charcoal sources.

### Activation and Equilibrium Adsorption Capabilities

Mangrove, or "Duoc" was retrieved from Vietnam in the summer of 2012 as unactivated chunks of charcoal. The charcoal was crushed and sieved. Particles retained ranged in diameter from 0.425 to 5 mm. Charcoal pieces that passed through the #40 sieve were removed.

Physical and chemical techniques can be used to convert charcoal into activated carbon. Chemical activation techniques are typically more effective than physical

techniques due to the ability of the chemicals to reach more of the pore spaces of the charcoal. One negative aspect of using chemical activation is the need to wash and dry the carbon sources after activation [51].

Two transition metal salts were explored for mangrove activation in this study. Three 1 L salt solutions were prepared in distilled water that contained 25% CaCl<sub>2</sub>, 50% NaCl, and 25% NaCl on a mass basis. Approximately 10.5 g of carbon particles were immersed in each salt solution for 24 hours. The activated mangrove was then rinsed with DI water for approximately 5 min. A series of beakers containing 40 mL of a p-nitrophenol solution characterized with an initial absorbance of 2.393 absorbance units were prepared. 0.5, 1, 2, 3, and 4 g of activated mangrove were placed into the beakers containing the p-nitrophenol solution and placed on a shaker table operating at 100 rpm for 48 hours. The control experiment was similarly designed, run in parallel and used unactivated mangrove charcoal.

The absorbance values obtained from the p-nitrophenol solution for the mangrove treated in CaCl<sub>2</sub> and two NaCl solutions were compared values obtained from untreated mangrove. All three activated solutions performed similarly. The cheapest and most environmentally friendly method, the 25% NaCl m/m solution, was the chosen method for activating the mangrove for the filters.

#### Filter Construction

Two identical BSFs were constructed from 19 liter (5 gallon) buckets. Each bucket contained 1.27 cm (0.5 in.) PVC piping in the shape of an 'x' on the bottom of the filter as shown in Figure 5. Each of the four pipe sections on the bottom of the bucket had three 0.32 cm (1/8 in.) holes, 1.75 cm (11/16 in.) apart, all the way through the piping.



Figure 5. Bottom Piping Schematic for both Filter 1 and Filter 2.

Five cm (2 in.) of rocks were used to cover the piping, and this layer was covered by 2.5 cm (1 in.) of pebbles. The layer of pebbles was covered by 2.5 cm (1 in.) of fine sand followed by 2.5 cm (1 in.) of fine sand mixed with 25 g of bronze shavings. Aluminum Bronze 954 was purchased from onlinemetals.com, this particular bronze is comparable to ASTM B505. Aluminum bronze, the type of metallic biocide used in this study, is composed of 83% copper, 10-11% aluminum and 3-5% iron. A final 12.7 cm (5 in.) of fine sand was added on top of the sand and bronze mixture. The top of this final layer of fine sand was approximately 2.5 cm (1 in.) below the effluent pipe.

The sand used in construction was cleaned and sieved. Results from the sieve analysis are shown in Table 3. 10% of the sand diameter was smaller ( $D_{10}$ ) than 0.45 mm, with a uniformity coefficient of 1.8.

Sieve #	Total Sieved Mass (g)	% Mass
6	4.58	0.20
20	816.50	35.83
40	1311.33	57.54
60	92.22	4.05
100	40.15	1.76
230	11.53	0.51
Excess	2.57	0.11

Table 3. Percentage and Total Mass of Three Sieve Runs for a Sand Sieve Analysis.

A 25% solution of NaCl was used to activate 2 L of granular mangrove charcoal. After activation, the carbon was thoroughly rinsed in DI water to remove the salt. A bowl that contained a series of 0.32 cm (1/8 in.) diameter holes housed the activated carbon. The carbon-filled bowl rested on top of one of the traditional BSFs and provided pretreatment to the BSF influent water. In this study, the traditional BSF (the BSF without an activated carbon source) is referred to as Filter 1 and the BSF with activated carbon pretreatment is referred to as Filter 2. A bowl with a series of 0.32 cm (1/8 in.) drilled holes was used as a diffuser for Filter 1. Designed BSF schematics for Filters 1 and 2 can be seen in Figure 6 and Figure 7 respectively.



Figure 6. Filter Layering Schematic for Filter 1.



Figure 7. Filter Layering Schematic for Filter 2.

#### Filter Watering

#### Water Collection

Influent water was collected from the same point along the Ocmulgee River in Macon, Georgia. Filters were loaded with 5 L of water every 24 hours from 11 October, 2012 until 1 January, 2013. A starvation period was initiated from 24 December, 2012 through 27 December, 2012. During this time the filters were not loaded.

## Water Dosing

In an effort to synthetically represent river water conditions in Vietnam, the collected Ocmulgee River water was dosed with 0.2835 g L<sup>-1</sup> imidacloprid. Imidacloprid is a commonly used insecticide throughout the world. Pelletized Bayer Ant and Insect Killer served as the source of imidacloprid in this study. A stock solution of the insecticide was prepared by shaking 189g pelletized insecticide until dissolved in 1 L de-ionized (DI) water. The insoluble shell of the pellets that served as the insecticide carrier was removed from the stock solution through filtration. Initial solution filtration was conducted with Biodesign Inc. NSC Cell Microsieves of 8, 15, 20, 35, and 50  $\mu$ m. The solution was then filtered with a final pore size of 1.5  $\mu$ m using 934-AH filter papers from Hach.

#### Sampling, Testing, and Analysis

### Water Sampling

Beakers used for sample collection were autoclaved after each sampling event. For consistency, daily effluent grab samples of approximately 100 mL were obtained from each BSF after 2 L of water had passed through the individual filter. Effluent from the basin housing the activated carbon was also routinely sampled after 2-3 L had passed through the carbon bowl. On 26 November, 2012, approximately one-third of the Filter 2 schmutzdecke was disrupted by a dropped beaker.

## Sample Testing

Parameters tested for all water samples included pH, temperature, turbidity, conductivity, chemical oxygen demand (COD), soluble COD (COD<sub>S</sub>), coliforms and *E. coli*, flow rate, absorbance, and solids. Filters were tested every day from 11 October, 2012 to 15 November, 2012. Subsequently, the influent and effluent water parameters were characterized twice per week.

*Temperature and pH.* Temperature and pH were measured using an Accumet model 25 pH/ion meter. Samples were allowed to stabilize before readings were taken. The meter was rinsed with DI water before and after each reading.

*Turbidity*. Turbidity was measured with a Hach 2100P Turbidimeter. The turbidimeter was calibrated before use on a testing day with DI water. The turbidity vial was rinsed with DI water between each sample.

*Conductivity*. Conductivity was measured with an HM digital EC/TDS/Temp COM-100. The probe was rinsed with DI water before each measurement was taken. Conductivity was measured in µS KCL.

*Chemical Oxygen Demand and Soluble Chemical Oxygen Demand.* Both COD and COD<sub>S</sub> analyses were conducted in accordance with Hach COD procedures. Low range COD vials were used and incubated in a Hach COD reactor, and measurements were taken on a Hach DR 2800 using the Low Range COD program. All COD<sub>S</sub> samples were prepared using a filter characterized with 1.5  $\mu$ m pore openings (935-AH Hach filter paper). The filter holder was rinsed between samples. Both COD and COD<sub>S</sub> analysis utilized 2 mL of sample, which were measured with a Hamilton 0.01-1.00 mL micropipette with 1 mL single-use, sterile tips. Soluble COD was measured for all samples from 13 November, 2012 until 31 December, 2012.

*Coliform and E. coli Measurement.* All materials used for coliform and *E. coli* testing were sterile. The magnetic filtration apparatus and forceps were sterilized using the ON-01E Oven Lab Companion Autoclave. Pall Corporation sterile petri dishes with absorbent pads were used. Sterilized filter papers from Pall Corp. (0.45 µm GN-6 grid) were used until the beginning of December. From December on, 0.45 µm GN-6 Sterile Metricel

filter papers were used. Two different types of media were used. From 19 October, 2012 through 29 October, 2012 m-endo broth ampules from Hach were used. The remainder of the experiment used m-ColiBlue 24 broth from Hach. Coliform tests were stored overnight at 35°C in a Hach Portable Incubator. Typical sample volumes used to complete coliform testing were 0.1 mL for the influent and carbon samples, and 5 mL for effluent samples taken from both Filter 1 and Filter 2. Coliform testing was completed following instructions provided by the US EPA [57].

*Flow rate*. Flow rate was determined by measuring the time it took the filter to process two liters of water. Each filter was loaded with river water to the capacity of available freeboard, and head was allowed to decrease. Once 2 liters had passed through the BSF, the filtration time was recorded.

*Absorbance*. Absorbance was measured using an Ocean Optics USB 2000 USB-ISS-UV/VIS Spectrophotometer with a range of 200-1100 nm. Unfiltered samples were poured into 3 mL cuvettes and wiped before analysis. A standard using river water and imidacloprid was analyzed so that absorbance levels, both entering and leaving the filters, could be compared and measured on a percent removal basis.

*Solids*. Solids analysis was completed in compliance with the 18<sup>th</sup> Edition of Standards Methods, using Solids 2540 [58]. Seventy milliliter solids trays were used to measure total solids, volatile solids, and fixed solids. An Amsco Eagle Tent oven was held at 105°C, and a Vulcan A-550 furnace was used for incineration at 550°C. A Mettler Toledo A6245 scale was used to quantify the mass of the solids, and a Cole Parmer 1-5 mL micropipette was used to disperse 40 mL of sample into the solids trays.

#### Statistical Evaluation Techniques

Experimental data were compared using a variety of techniques. Techniques include paired t-tests [59], Tukey's Method for Multiple Comparisons [54], and two-sided t-tests [60]. Table values were used for Tukey's studentized range values [61], and t-values for the paired and two-sided t-tests [62]. Equation 1, Equation 2, and Equation 3 represent two-sided t-tests, paired t-tests, and Tukey's method respectively. All comparisons were conducted at a confidence level of  $\alpha$ =0.05.

$$\overline{y} - s_{\overline{y}} t_{\alpha/2} < \eta < \overline{y} + s_{\overline{y}} t_{\alpha/2} \tag{1}$$

where  $\overline{y}$  is the sample mean,  $s_{\overline{y}}$  is the sample standard deviation, t is the studentized t statistic, and  $\eta$  is the true mean.

$$\overline{d} - s_{\overline{d}} t_{\alpha/2} < \delta < \overline{d} + s_{\overline{d}} t_{\alpha/2} \tag{2}$$

where  $\overline{d}$  is the average of the paired differences,  $s_{\overline{d}}$  is the standard error of the average of the paired differences, t is the studentized t-statistic, and  $\delta$  is the true mean of differences.

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$$\left(\overline{y}_{i} - \overline{y}_{j}\right) \mp \frac{q_{k,\nu,\alpha/2}}{\sqrt{2}} s_{pool} \sqrt{\frac{1}{n_{i}} + \frac{1}{n_{j}}}$$
(3)

where  $(\overline{y}_i - \overline{y}_j)$  is the true difference between two means,  $q_{k,\nu,\alpha/2}$  is the upper significance level of the studentized range for k means and  $\nu$  degrees of freedom,  $s_{pool}$  is the pooled sample standard deviation, and n is the number of observations.

Images in this document are presented in color.

#### CHAPTER 4

## **RESULTS AND DISCUSSION**

## Summary of Results

The efficacy of two point-of-use filtering schemes to treat river water artificially contaminated with a pesticide was investigated. Filter 1, which served as the experimental control, was designed, constructed and operated following guidelines provided by Aqua Clara [31]. Filtering system 2 contained two distinct processes that operated in series; an adsorption bed was the first unit operation used to treat the river water. An Aqua Clara biosand filter (constructed as similarly as possible to Filter 1) treated the effluent from the adsorption bed. The filtering schemes were loaded daily with river water spiked with 0.2835 g  $L^{-1}$  imidacloprid.

## Activation of the Mangrove Charcoal

The activated carbon used in Filter 2 was made from mangrove charcoal obtained from Vietnam. Many activation techniques exist for charcoal. Activation with a salt is one of the cheapest, safest methods. Practical activation techniques include soaking granulated mangrove charcoal in a 25% m/m NaCl solution, a 50% m/m NaCl solution, and a 25% m/m CaCl<sub>2</sub> solution. The activation effect of each salt treatment was quantified using a batch, equilibrium adsorption study. A  $6.85 \times 10^{-5}$  M p-nitrophenol solution was added to a series of 200 mL beakers that contained a known mass of activated mangrove charcoal.

Figure 8 shows the change in absorbance measured at equilibrium conditions and represents the relative adsorption capacity of p-nitrophenol resulting from the different activation salt solutions. Using the paired t-test method at  $\alpha$ =0.05, it was shown that the mangrove charcoal activated by the 25% (m/m) NaCl solution adsorbed more p-nitrophenol than the untreated charcoal, but was statistically similar to the two other treatment techniques. Since the three activation techniques were statistically indistinguishable, the cheapest, most feasible option, soaking in a 25% (m/m) NaCl solution, was chosen to activate the charcoal used in Filter 2.



Figure 8. Change in Absorption Capabilities of Various Activation Methods for Mangrove Charcoal.

#### Filter Performance Data

The influent and effluent water quality from both filter systems was characterized daily from 11 October, 2012 to 15 November, 2012 and biweekly until 31 December, 2012. Grab samples from the influent and the effluents of the activated carbon bed and both BSFs were evaluated to quantify performance for Filters 1 and 2. The samples collected were characterized by absorbance, temperature, conductivity, total coliforms, solids, turbidity, COD, and pH. Flow rates for Filter 1 and Filter 2 were also measured.

## Filter Flow Rates

Flow rates were monitored every testing day throughout the project. Figure 9 shows the average flow rates for Filter 1 and Filter 2 were 21.1 and 9.97 Lhr<sup>-1</sup>respectively, which are statistically different at  $\alpha$ =0.05. The flow rate through Filter 2 was impeded by the flow through the activated carbon housed in the diffuser, and theoretically should have increased the treatment imparted on water moving through the BSF [63].



Figure 9. Filter Flow Rate Trends for Filter 1 and Filter 2.

## Absorbance

Absorbance was measured to monitor the removal of imidacloprid from the influent river water. Every day, the river water was dosed with 0.2835 g  $L^{-1}$  imidacloprid. Figure 10 shows an example of a daily comparison of influent water to the water treated by the mangrove activated carbon, Filter 1, and all of Filter 2. The peak around 250 nm is the imidacloprid in the water. Figure 11 shows a four day moving average of absorbance trends from 13 October, 2012 to 31 December, 2012. Trends for both filter effluents are similar for this time period. Filter 1 and 2 effluent imidacloprid concentrations occasionally exceeded the inlet pesticide concentration. This anomaly remains unexplained.



Figure 10. Example of one Daily Absorbance Trend: 2 November, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.



Figure 11. Four Day Moving Average Percent Removal of Absorbance through Filters 1 and 2. Il represents the percent removal from the influent through Filter 1; I2 represents the percent removal from the influent through Filter 2.

Tukey's test was used to compare the percent removal for Filter 1 to all of Filter 2, water treated only by the carbon bed of Filter 2, and removal through only the BSF portion of Filter 2. Using a 95% confidence interval, it was found that there was a statistical difference and the carbon portion of Filter 2 removed more imidacloprid than the BSF portion of Filter 2. A paired t-test, also at a confidence interval of 95%, proved that there was no statistical difference between the treatment of Filter 1 and Filter 2 as a whole.

### Temperature

Influent and effluent water temperatures for both filter systems were compared using t-tests to find the 95% confidence interval. Table 4 shows the confidence intervals, means, and standard deviations for the influent, and Filter 1, carbon bed, and Filter 2 effluents. Several data points fall outside the confidence intervals, but all temperatures stayed within a few degrees of each other, and near room temperature throughout the entire testing period.

		Standard		
	Mean (°C)	Deviation	Low (°C)	High (°C)
Influent	20.90	0.80	20.67	21.13
Filter 1 Effluent	21.13	0.50	20.98	21.27
Charcoal				
Effluent	20.42	0.83	20.18	20.66
Filter 2 Effluent	20.98	0.45	20.85	21.11

Table 4. Mean, Standard Deviation, and 95% Confidence Intervals for Temperature from 11 October to 31 December, 2012.

### Conductivity

Conductivity is the measure of a water's ability to pass an electrical current, and is greatly affected by temperature and dissolved salts [64]. Figure 12 shows the conductivity trend over the entire treatment period. A dip in conductivity occurred in mid November, however no drastic change in temperature occurred. As mentioned previously, a few temperature data points did fall outside of the 95% confidence interval, but are not different enough to cause a significant increase in conductivity.

Tukey's multiple paired comparison technique was used to interpret conductivity data. It was determined that at a 95% confidence interval, the conductivity of Filter 2 effluent was higher than effluents from Filter 1 and the carbon bed, and higher than the influent. The conductivity effluents from Filter 1 and the carbon bed were also both higher than the influent, but were statistically similar to each other. The increased conductivity in Filter 2 cannot be explained due to temperature, but it is possible that NaCl ions not properly removed from the carbon bed during rinsing slipped into the filter. The sand used for this study was also previously used in another BSF project which used KCl tracers.



Figure 12. Conductivity Trend from 15 October to 31 December, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.

## Total Coliforms

Coliforms were measured by counting colonies grown over a twenty-four hour period. Every testing period, with the exception of tests prepared between 18-28 October which used m-endo broth ampules, was prepared using m-ColiBlue 24 broth. Using m-ColiBlue 24 Broth allows for coliforms and *E.coli* to be separately enumerated. Tests using the mendo broth ampules were counted as total coliforms. Total counts from all other dates were summed to form the total coliform data. Total coliform counts are shown in Figure 13. On average, 1 log removal of total coliforms was achieved for both filters. Typically, it is desired to achieve between 2 and 4 log removal for BSFs [39], [65]. No significant differences between filter performances exist, but filter influent coliform counts are higher than both filter effluents at a 95% confidence interval. Table 5 shows the percentage at which Filters 1 and 2 each achieved <1, 1-2, 2-3, >3 log removal.



Figure 13. Total Coliform Count Trends from 11 October to 31 December, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.

Log Removal	Filter 1	Filter 2
R<1	31.0%	33.3%
1≤R<2	28.6%	40.5%
2≤R<3	28.6%	19.1%
R≤3	11.9%	7.1%

Table 5. Log Removal in Percentage for Filter 1 and Filter 2, where R is Log Removal (Log Influent- Log Respective Filter).

## Solids

Solids were analyzed weekly until November 15, 2012. After which point, they were analyzed biweekly. Total and volatile solids concentrations were measured, and were subsequently used to determine fixed solids. Figures 14 and 15 show the lack of significant trends in total or volatile solid concentrations. Tukey's analysis showed no significant differences between filter influent and effluent for either total or volatile solids at 95% confidence. Unexpectedly, the analysis did show statistical differences, an increase in fixed solids concentration in both filter effluents over the primary influent concentration. These results are shown in Appendix A. WHO standards for total solids do not exist and are instead represented as total suspended solids. VNCOLD total solids standards are set for  $0.15 \text{ gL}^{-1}$ [3], [17].



Figure 14. Total Solids Trends from 24 October to 31 December, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.



Figure 15. Total Volatile Solids Trends from 24 October to 31 December, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.

#### **Turbidity**

Turbidity standards for WHO and VNCOLD are <1 NTU and <5 NTU, respectively [3], [17]. The average effluent turbidity for Filter 1 and Filter 2 were 1.39 and 0.98 NTU, respectively. Using Tukey's multiple comparison test at a 95% confidence level, it was found that the effluent turbidity from Filter 1 and Filter 2 were not statistically different. Average turbidity values were 3.41 NTU for the influent, 3.875 NTU for the activated carbon bed effluent, 1.39 NTU for the effluent of Filter 1, and 0.98 NTU for the effluent of Filter 2. Average percent removal efficiencies for Filters 1 and 2 from the influent are 45.7% and 60.6% respectively. The mean turbidity of the influent and the adsorption bed effluent were similar and were higher than both effluents from Filter 1 and the BSF associated with the Filter 2 process. Figure 16 shows these trends. Notice from the figure that the effluent turbidity from the adsorption bed used in Filter 2 was atypically high during the first week of experimentation. Although the mangrove activated charcoal was sieved and rinsed prior to use in the adsorption bed associated with Filter 2, it is assumed and was visually confirmed that residual particles continued to rinse from the charcoal during initial use and caused the relatively high turbidity measurements observed until 18 October, 2012. After this date, turbidity was similar between the influent and the adsorption bed effluent.



Figure 16. Turbidity Trends from 11 October to 31 December, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.

#### Chemical Oxygen Demand (COD)

Chemical Oxygen Demand is used to measure the amount of oxygen required to oxidize materials in a sample with a strong oxidant. Total COD contains both particulate and soluble COD. Particulate COD is easily removed by physical operations, while removing soluble COD requires a biological or chemical process. BSFs primarily utilize biological processes to remove contaminants, including COD, from the water source.

COD trends in Figure 17 show that COD concentrations leaving the activated carbon bed are higher than those in the influent for the first 2 weeks of experimentation. During that time period, the effluent COD concentration from Filter 2 trended higher than from Filter 1.

Tukey's tests were used to evaluate COD concentration trends during three unique time periods of the experiment: (1) the entire data set, (2) the first month of data (12 October- 13 November) when COD effluent concentrations from the adsorption bed are higher than influent concentrations, and (3) all data collected after 13 November, 2012. An evaluation of the complete data set and for the first month of experimentation (until 13 November) indicates that the activated carbon bed effluent had a higher COD concentration than the influent, Filter 1 effluent, and Filter 2 effluent. For all three data periods evaluated, the influent COD concentrations were higher than Filter 1 and Filter 2 effluents. When only the data collected after the first month of testing was considered, the COD concentrations in the influent and the activated carbon bed effluent were similar. Also during this time period, statistical differences were shown to exist between the influent and both filter effluents and adsorption bed effluent COD concentrations. For all three data collection periods evaluated, Filter 1 and Filter 2 were found to be statistically similar at a 95% confidence level.



Figure 17. Six Day Moving Average for COD Data from 16 October to 14 November, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.

Figure 18 compares COD removal of the sand in Filter 2 to that of Filter 1. The figure shows the percent COD removal between the influent and Filter 1, the influent and Filter 2, and the carbon bed and the sand of Filter 2. These comparisons were required to observe the location from which COD was being removed in Filter 2. It can be seen that removal between the influent and Filter 1, and the carbon bed and the sand of Filter 2 is similar, but inconclusive. Average COD removal for Filter 1, the entire Filter 2 system

(BSF plus carbon bed), and the BSF portion of Filter 2 are 25%, 26%, and 36% respectively.



Figure 18. Percent Removal COD for the Influent through Filter 1 and Filter 2 and Water Treated by the Activated Mangrove Charcoal through Filter 2. I1 represents the percent removal from the influent through Filter 1; I2 represents the percent removal from the influent through Filter 2; D2 is the percent removal from the effluent of the carbon bed to the effluent of Filter 2.

Soluble COD (COD<sub>S</sub>). COD<sub>S</sub> measurements began on 10 November, 2012. Figure 19

shows the COD<sub>S</sub> trends. No visible difference is observed between influent and activated

carbon bed effluent COD<sub>S</sub> concentrations, which was confirmed statistically using

Tukey's test at a 95% confidence level.



Figure 19. CODs from 10 November, 2012 to 31 December, 2012. The influent water is labeled as I; 1 represents the effluent from Filter 1; D is the effluent from the charcoal bed associated with Filter 2; 2 is the effluent from the entire Filter 2 system.

# pH

According to the EPA, WHO, and VNCOLD, pH should be 6.5-8.5 for drinking water applications [3], [16], [17]. Statistical analysis at 95% confidence demonstrated that pH always fell within the 'safe' range. Sample means, standard deviations, and confidence intervals are shown in Table 6 for all sampling points.

		Standard		
	Mean	Deviation	Low	High
Influent	7.20	0.21	7.14	7.26
Filter 1 Effluent	6.95	0.15	6.90	7.00
Carbon Effluent	7.19	0.21	7.12	7.25
Filter 2 Effluent	6.92	0.15	6.88	6.97

Table 6. Mean, Standard Deviation, and 95% Confidence Intervals for pH from 11 October to 31 December, 2012.

### Filter Effluent and WHO Comparisons

Table 7 shows the comparisons of Filter 1 and Filter 2 effluent values to WHO and VNCOLD standards. COD, turbidity, total solids, and Total Coliforms are average values for the entire testing period. The data demonstrates that effluent from both filters meet pH and turbidity regulations. On average, effluent total coliform and total solids concentrations exceed recommended VNCOLD standards.

	WHO [17], [66]	VNCOLD [3]	Filter 1	Filter 2
pН	6.5-8.5	6.5-8.5	6.9-7.0	6.88-6.97
COD (mg/L)	10	Х	40.93	42.28
Turbidity (ntu)	<1	<5	1.39	0.98
Total Coliforms	0	2	422	644
(MPN/100 mL)				
Total Solids	Х	750-1500	1590	1640
(mg/L)	(1500 TDS)			

Table 7. WHO and VNCOLD Standards Compared to Filter 1 and Filter 2 Effluents.

\*X denotes a where a standard has not been provided by the respective authority.

Table 8 shows the percentage of effluent samples tested from Filter 1 and Filter 2 that meets treatment requirements for specific drinking water guidelines provided by WHO and VNCOLD. It can be seen that turbidity has the highest pass percentage for both sets of standards. Neither filter meets WHO standards set for COD. Filter 2 has higher pass rates for turbidity and total coliforms than Filter 1, while Filter 1 has higher pass rates for total solids than Filter 2.

Table 8. Filter 1 and Filter 2 Effluent Quality Pass Rate Comparisons to WHO and VNCOLD Standards.

	WHO		VNCOLD	
Parameter	Filter 1	Filter 2	Filter 1	Filter 2
COD	0%	0%	Х	Х
Turbidity	29.17%	45.83%	100%	100%
Total Coliforms	2.27%	3.41%	2.27%	3.41%
Total Solids	27.78%	5.56%	27.78%	5.56%

\*x denotes a where a standard has not been provided by the VNCOLD for COD.

#### CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

## Conclusion

Biological sand filtration is an appropriate technology for point-of-use water treatment in developing countries. It is an inexpensive and effective way to clean and treat water. The use of adsorption technologies in conjunction with biological treatment is common in both Europe and the United States. Activated carbon working in tandem with a BSF can be used to remove organisms and compounds that cannot be removed by biological treatment alone, including pesticides, insecticides, and herbicides.

Two filters were designed for this project. Filter 1 was the control filter; a traditional BSF following standards set by Aqua Clara, Int. Filter 2 was comprised of two components, an activated mangrove charcoal layer, activated with a 25% m/m NaCl solution, and a traditional Aqua Clara BSF that was constructed as similar to Filter 1 as possible. In order to compare performance between the two filters, water quality analysis was performed at four points, including the influent, and effluents from the carbon bed, Filter 1, and Filter 2.

Statistical analysis of the experimental data demonstrated that each filter removed COD, total coliforms, and turbidity during treatment. During the formation of the

individual filter schmutzdeckes, COD and turbidity exiting the activated carbon bed were higher than those observed in the influent water. It is theorized that this unexpected increase in COD concentration is due to small pieces of mangrove activated charcoal that were released in the carbon bed effluent. These granular pieces of charcoal potentially carry adsorbed imidacloprid. Similarly, the initial increase in turbidity is attributed to excess salt and charcoal particulates rinsing from the activated carbon bed and passing into the BSF portion of Filter 2. This would also explain why Filter 2 had a higher conductivity than all other effluents and the influent. Other than conductivity, no statistical differences were found between the effluent water quality of the filters.

#### **Recommendations for Future Work**

Due to the inability to statistically differentiate between filter effluent quality, primary recommendations for future work focus on filter design. In typical schemes used for large scale water treatment, activated carbon filtration follows biological treatment. Although Design 3 outlined in Chapter 1 has a larger footprint than all other designs considered for use in this study, it is the simplest remaining option to consider for future work. Experiments conducted using the Design 3 duel-container system should compare two filter systems where the activated carbon is utilized either before or after biological treatment. A control BSF is easy to simulate in this experimental scenario. This dual-container design allows for an increase in the amount of activated carbon used, which

could potentially improve filter performance to more regularly meet WHO and VNCOLD drinking water standards.

It is also recommended to explore additional pesticides, herbicides, and insecticides commonly found in water sources in Vietnam and incorporate them in the synthesis of the filter influent water. Deference should be given to those chemicals characterized with different peak absorbance wavelengths on a UV-VIS Spectrophotometer in order to separately monitor removal rates. Finding chemicals still allowed for use in the United States that are currently a significant problem in Vietnam's waterways is difficult, so additional investigation would be necessary.

Additional research efforts should focus on exploring the efficacy of various cost effective carbon activation methods. A series of batch, small-scale experiments could be used to characterize the chemical specific equilibrium adsorption capacity for mangrove charcoal that is activated using different techniques. The kinetics of adsorption could also be studied using similar experimental protocols. Results from this type of study would provide additional insight to the potential of incorporating activated carbon in a BSF, as well as the timing required to reactivate or replace the carbon. This study may also explain the increase in absorbance through the carbon bed which was seen during this study.

# APPENDIX

# A. DATA

Table 9. Tukey's Statistical Analysis for COD at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	89.73	mgL <sup>-1</sup>	I (54.49)	1 (40.93)	D (63.42)
Spool	9.47	1 (40.93)	13.55814		
q	4.01	D (63.42)	-8.93023	-22.4884	
$(y_i - y_j)$	5.79	2 (42.28)	12.2093	-1.34884	21.13953

Table 10. Tukey's Statistical Analysis for Soluble COD at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	120.63	mgL <sup>-1</sup>	I (46.94)	1 (36.63)	D (47.94)
Spool	10.98	1 (36.63)	10.31		
q	4.124	D (47.94)	-1.00	-11.31	
$(y_i - y_j)$	11.32	2 (37.44)	9.50	-0.81	10.50

Table 11. Tukey's Statistical Analysis for Total Coliforms at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	9.65E+11	colonies	I (1198646)	1 (47987.4)	D (936196)
Spool	982541	1 (47987.4)	1150658		
q	4.01	D (936196)	262449	-888209	
$(y_i - y_j)$	600842	2 (65403)	113324	-17416	870794

Table 12. Tukey's Statistical Analysis for Conductivity at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	156.66	μS KCL	I (185.70)	1 (194.95)	D (196.28)
Spool	12.52	1 (194.95)	-9.26		
q	4.01	D (196.28)	-10.58	-1.33	
$(y_i - y_j)$	7.65	2 (204.84)	-19.14	-9.88	-8.56

Table 13. Tukey's Statistical Analysis for Total Suspended Solids at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	0.000242	gL <sup>-1</sup>	I (0.150)	1 (0.159)	D (0.159)
Spool	0.0156	1 (0.159)	-0.009		
q	4.115	D (0.159)	-0.009	0.000	
$(y_i - y_j)$	0.0151	2 (0.164)	-0.014	-0.005	-0.005

Table 14. Tukey's Statistical Analysis for Volatile Suspended Solids at  $\alpha$ =0.05.

$s^2_{pool}$	0.0002	gL <sup>-1</sup>	I (0.047)	1 (0.043)	D (0.051)
Spool	0.0141	1 (0.043)	0.004		
q	4.115	D (0.051)	-0.003	-0.007	
$(y_i - y_j)$	0.0137	2 (0.045)	0.002	-0.002	0.006

Table 15. Tukey's Statistical Analysis for Fixed Suspended Solids at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	0.000158	$gL^{-1}$	I (0.103)	1 (0.116)	D (0.109)
Spool	0.0126	1 (0.116)	-0.013		
q	4.115	D (0.109)	-0.006	0.007	
$(y_i - y_j)$	0.0122	2 (0.0.119)	-0.016	-0.003	-0.010



Figure 20. Total Fixed Solids Trends.
Table 16. Tukey's Statistical Analysis for Turbidity at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	4.63	NTU	I (3.41)	1 (1.39)	D (3.88)
Spool	2.15	1 (1.39)	2.03		
q	4.00	D (3.88)	-0.46	-2.49	
$(y_i - y_j)$	1.27	2 (0.98)	2.43	0.40	2.89

Table 17. Tukey's Statistical Analysis for Absorbance at  $\alpha$ =0.05.

s <sup>2</sup> <sub>pool</sub>	158.25	% removal	I1 (11.27)	I2 (12.36)	ID (15.27)
Spool	12.58	I2 (12.36)	-1.59		
q	4.00	ID (15.27)	-0.89	0.70	
$(y_i - y_j)$	7.42	D2 (10.95)	7.23	8.81	8.11

Table 18. Paired t-Test Analysis for Flow Rate at  $\alpha$ =0.05.

mean	11.21
std	3.42
n	45
sdbar	0.51
t	2.0168
high	10.18
low	12.24

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