

PUR[®] PACKET EFFECTIVENESS IN THE PRESENCE OF PESTICIDES AND
INCREASED ORGANIC MATTER

By

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To my Nana

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Abstract of Thesis Presented to the Graduate School
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Point of use drinking water treatment has proven itself to be highly effective in regions where only primitive techniques, such as boiling water, were the only means of treating water. One product in particular, the PUR[®] packet, is widely known for treating water within the United States and abroad. Very little testing of this product, however, has been done outside of Procter & Gamble© to prove the overall effectiveness of this product. One particular area of interest was the PUR[®] packet's ability to remove pesticides from water. With this product being advertised for use during hiking and camping trips, this is a serious concern especially in agriculture watersheds.

Water from Lake Alice on the University of Florida Campus was selected for treatment. This source water was spiked with Humic Acid, Toluene, and Atrazine to create a more competitive environment for adsorption. This was also done to increase the Natural Organic Matter concentration. Atrazine was the primary pesticide focused on because it is widely used throughout America, particularly in the Midwestern Corn Belt. A series of tests were run to see if the PUR[®] packet alone was enough to combat this contaminant or if the addition of Activated Carbon was necessary for acceptable removal.

CHAPTER 1 INTRODUCTION

Water is one of the most basic necessities of every human being. For centuries, people have worked effortlessly to treat and purify their drinking water to improve their health. In ancient times, it was assumed that clear, good tasting water was clean water¹. With advancements in technology and modern medicine, this truth was dispelled by the uncovering of several contaminants, including bacteria and viruses, that impact drinking water quality and, in turn, impact human health. These findings prompted the need for safer drinking water treatment practices and fueled the creation of more advanced drinking water treatment systems.

Today, a large amount of complex drinking water treatment plants that provide superior drinking water to their customers exist throughout the world; however, this is not so in all regions. Underdeveloped nations that lack the resources and finances of their urbanized counterparts are deprived of this exceptional drinking water quality. This disparity has brought about the creation and application of a number point of use (POU) drinking water treatment devices in several third world countries. Even though these systems are not completely comparable to the types of water treatment available in urbanized nations, they are helping close the gap on the 1.1 billion people who do not have access to safe drinking water² throughout the world.

Point of use treatment has proven itself to be highly effective in regions where only primitive techniques, such as boiling, were the only means of treating water. The initial success of POU treatment has in turn sparked new developments in this area which are constantly being implemented in underdeveloped communities around the world. The impact of these efforts, however, is at times slighted by the lack of community

acceptance or financial status of the target customers. With financial strain being one of the driving forces behind the lack of use, it has become more important now more than ever to find a more cost efficient way to treat water for people with limited resources. The use of activated carbon has proven to be very effective in previous years but, with the push for a more sustainable approach to water treatment, new tactics are on the rise.

One of the most noteworthy projects carried out throughout the past decade has been conducted by Dr. Greg Allgood. He, in collaboration with Procter & Gamble© (P&G™), PUR® , and numerous other partners, helped to start a global initiative known as the Children's Safe Drinking Water Program (CSDW)³. The CSDW is a program that strives to reduce sickness and death as a result of consuming contaminated drinking water. The program has provided aid to more than 40 developing countries to date. Although this organization is not the first to undertake such a great endeavor, they have a new and innovative approach to an ever present problem. The only purification system needed for their treatment process is the powdered contents of a packet similar to the packet used to make Kool-Aid®. This invention is known as the PUR® packet.

The PUR® packet is the ingenious product of Dr. Allgood's work and research through P&G™. The powdered mixture in these packets removes dirt, cysts, bacteria and viruses from contaminated water and turns it into safe, clean drinking water. Just one of these little packets can disinfect 10 liters of water which could potentially supply one person with 5 days worth of clean drinking water. The entire process takes only 30 minutes and requires fairly simple tools. To produce the clean water you need 2 containers that can hold 2.5 gallons of water, a PUR® packet, a stirring spoon (or similar

apparatus), and a 100% cotton cloth filter⁴. One thing that makes the packet such a great resource is that it is so compact. Unlike sending cases of bottled water or building an entire treatment system, the packets are fairly inexpensive to ship and put in place. Their size makes it easy to send several at one time which is a great stride in helping solve the world's water crisis. Dr. Allgood's cause has already donated over 2 billion liters of clean water to several underdeveloped nations and has pledged to donate more than 4 billion liters by the year 2012.

The PUR[®] packet is also recommended for use during recreational activities such as camping, hiking, backpacking, fishing, and hunting. With the high use of pesticides such as Atrazine throughout the United States, there is always a growing concern of these pollutants leaching into water systems. This work focuses on the interaction of the PUR[®] packet in the presence of increased organic matter and trace contaminants. As steps to analyze the effectiveness of the PUR[®] packet in this environment, the following hypotheses and objectives were identified.

Hypotheses:

- The PUR[®] packet will create disinfection byproducts from the water purification procedure
- The PUR[®] packet's removal capabilities are very well defined on the packaging, therefore, it was expected that the product would not remove Atrazine.

Objectives:

- To test the PUR[®] packet for color and turbidity removal
- To determine if disinfection byproducts are formed
- To determine whether trace contaminants, such as Atrazine, are removed
- To determine if the addition of an easily produced activated carbon could aid in water purification

CHAPTER 2 LITERATURE REVIEW

2.1 PUR[®] Packets

The PUR[®] packet is the brain child of Dr. Greg Allgood and Procter & Gamble[©] (P&G[™]). In the late 1990s, they decided to help tackle the world's water crisis with the creation of this powder treatment source. Several undeveloped nations have to deal with waterborne illnesses that leave their people vulnerable to sickness and even death. Tainted water also makes life extremely difficult for individuals with compromised immune systems who may be suffering from diseases such as HIV/AIDS. Waterborne illnesses have been a problem for centuries, even in some of the most developed regions. The increased risk of such diseases was taking such a large toll on people worldwide that in the early 1900s people finally decided to figure out a way to disinfect their water.

In 1908, chlorine was used to disinfect a U.S. municipal water supply in Jersey City, NJ⁵. By the 1920s and 1930s, chlorine stopped most epidemics due to waterborne disease and chlorination seemed like the way to go for appropriate disinfection. However, people in developing nations that did not have access to such treatment facilities were still consuming unhealthy, contaminated drinking water. The cholera outbreak of 1991 in Peru is ultimately what led P&G[™] to develop their own drinking water treatment process. To help combat cholera in Latin America, the Center for Disease Control (CDC) provided people with chlorine bleach solutions to treat contaminated drinking water throughout the region. This was administered in specially designed bottles that allowed people to effectively treat one jerry can of water using the bottle's cap as the appropriate dose. Although chlorine bleach is commonly known as a

powerful disinfectant and it effectively eliminates viruses and bacteria, it still left the water looking dirty due to the presence of suspended particles. With P&G™ being the main manufacturer of chlorine bleach, the company decided to take on the challenge of improving this treatment process. This new process would remove suspended solids in addition to disinfecting the water. Thus, the PUR® packet was born.

2.1.2 Coagulation and Flocculation

The main additions P&G™ made to the already effective process of chlorine disinfection were coagulation, flocculation and filtration. The coagulant of choice for their process is iron sulfate (ferric iron), of which the packet contains 352 mg. The total list of packet ingredients includes ferric sulfate, bentonite, sodium carbonate, chitosan, polyacrylamide, potassium permanganate, and calcium hypochlorite⁶. One study by Reller et al (2003) showed that the use of these ingredients was favored over the use of chlorine bleach alone for disinfection. The study showed a 29% decrease in the incidence of diarrhea of a few rural households in Guatemala. This study also showed that participants preferred this type of treatment over traditional chlorine disinfection alone because it removed some of the sediments that disinfection left behind.

Coagulation and flocculation is one of the most effective and widely used treatment processes used today and its use dates back several centuries. The Ancient Egyptians are credited with the first use of these two methods. They developed their own techniques which are considered to be the first clarifying devices known to man. Their system was pictured in the tombs of both Amenophis II and Rameses II, inscribed in the 15th and 13th century BC, respectively⁷. Through this process the Egyptians are noted as the first to discover coagulation. They added alum to water in order to remove suspended solids, a method still in use today.

After the Renaissance period brought an end to scientific discovery, the world entered what is known as the Dark Ages. Water treatment was fairly stagnant and the same methods were being used until the brilliant discoveries of three Dutchmen. In 1590, Hans Janssen and his sons, Zacharias and Hans, saw that objects could be magnified by putting a piece of concave glass in a tube⁸. This became known as a compound microscope. The microscope brought light to a dimension of life that had never been seen before. Their invention was used for almost a century until it was perfected by a Dutch naturalist. In the late 16th Century, Antony van Leeuwenhoek created what is known as the first microscope⁹. Surprisingly, one of the main objects he chose to study was water. He was the first to see organisms living in water and brought these invisible impurities to the attention of others. He was able to achieve magnifications up to 270 times greater than the original object. After reporting his findings to the Royal Society, they were published throughout Europe and sparked the next evolution of drinking water treatment.

After the discovery of microorganisms, a widespread implementation of filtration systems took place. During the 1700s, filtration was recognized as an effective way of removing microscopic impurities. In 1703, Parisian scientist Phillipe La Hire brought forth the first idea of point of use drinking water treatment for all¹⁰. He proposed a plan that would provide sand filters and rain water cisterns in every household. Later in 1749, a Frenchman, Joseph Amy, was issued the first patent for a water filter¹¹. His device, comprised of both sponges and sand filters, became the first standard for filtration systems. During this period the first patent was also issued for a household filter designed by a potter, Johanna Hempel. Although filtration became known as the most

effective way of removing particles from water, the degree of its effectiveness was still not understood. It would take more scientific exploration to shed light on how clean drinking water was becoming. All of these advancements are what helped fuel a need for better contaminant removal practices. The microscope led scientists to physically examine the pathogens in the water that were making people sick and thus helped them find a way to tackle these impurities. After years of testing and technological growth, it was determined that the combined processes of coagulation, flocculation and filtration were some of the best ways to combat these microscopic threats.

Coagulation is the process of adding a chemical to water to stabilize the charges of suspended solids and particulate matter present in the source. With most particles in contaminated water being negatively charged, ferric iron, which has a 3+ charge, is a good coagulant. One reason an iron based coagulant may have been selected over an aluminum one is because the ferric flocs are a lot heavier than alum flocs causing them sink. For the PUR[®] packet's purposes, this makes it easier for consumers to see the amount of contaminants that are actually being removed from the water. Coagulation immediately promotes the formation of microflocs which in turn grow throughout the mixing process. The rapid mixing during coagulation is what stimulates particle collision thus helping them to stick together and grow. Flocculation is what allows these microflocs to agglomerate into large flocs which makes it easier to remove contaminants. Flocculation is what occurs during the settling phase after rapid mixing. There is still a certain amount of gentle mixing that takes place during the settling phase which helps entrap any remaining contaminants left in solution. After creating the floc, it

is necessary to separate it from the solution. The PUR[®] packet process accomplishes this through a method that was used quite some time ago.

In ancient times, the methods of coagulation and flocculation were the only ones upheld until a well known Greek physician linked water attributes to human health. Around 400 BC, Hippocrates emphasized the importance of filtering water and its direct effect on one's health¹². Seeing water's healing power, Hippocrates developed a special filtration device that would remove solids such as sediment, something that was not focused on during that period of time. This invention later became known as the "Hippocratic Sleeve". The sleeve was simply a piece of cloth that water was strained through to remove particles. This was used in addition to boiling to provide advanced contaminant removal. With coagulation, flocculation and cloth filtration having such a long history in drinking water treatment, it is no surprise that they are the main components of the PUR[®] packet's water treatment process.

First the powder substance is added to 10 liters of contaminated water. The mix is then stirred for five minutes and allowed to settle for five minutes. Small flocs will immediately begin to form during the mixing process resulting in a large floc at the end of the settling process. A 100% cotton cloth is then placed over a second container which can also hold 10 liters of water and the newly treated water is filtered into an empty container that can also hold 10 liters of water. The floc is trapped on top of the cloth and is then disposed of in a latrine or on the ground. This process can be seen in Figure 1. The combination of these processes has effectively provided the removal of dirt, cysts, and pollutants and effectively kills viruses and bacteria.

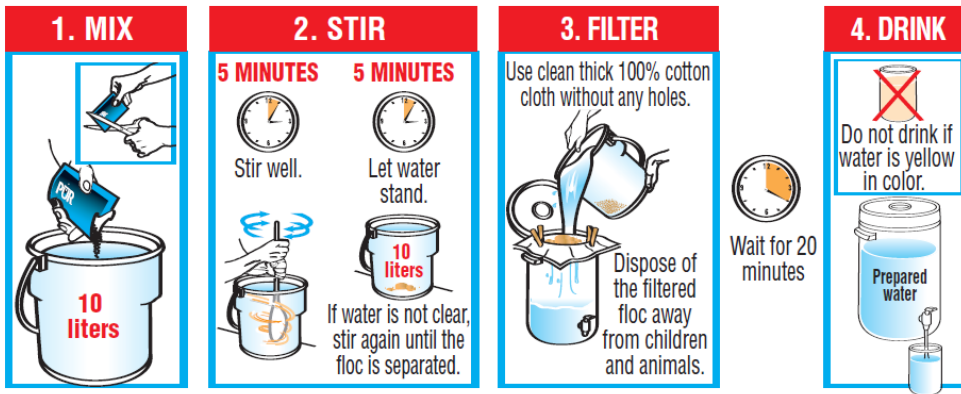


Figure 2-1. PUR[®] Purifier of Water Directions for Use (Source: http://www.purpurifierofwater.com/downloads/pur_packet_instructions.pdf)

2.1.3 Current Application

The PUR[®] packets use throughout developed nations has been very well documented. Since its first distribution in 2004, Dr. Allgood has traveled all over the world helping combat issues such as diarrhea, cholera, and other waterborne illness through use of the PUR[®] packet. To date, the program's efforts have already provided over 2 billion liters of clean water to people in underdeveloped nations and the group is seemingly on track to fulfill their goal of providing 4 billion liters of water to these regions by the year 2012.

A six-month pilot project in Northeastern Uganda¹³ put the PUR[®] packets to work with highly favorable results. This project selected 1500 people to participate in the implementation of household water purification and sanitation systems. The coupled sanitation system was necessary because poor drinking water quality is often the result of improper sanitation conditions in these regions. Similar plans have been used in others parts of the third world including Pakistan¹⁴. In several incidences good hygiene practices often predict the ultimate success of a drinking water treatment plan. The end

result of this study was the significant removal of E-coli in several sample water sources.

With 2 million deaths of children being attributed to waterborne illnesses or diseases, it only makes sense to try and educate the children. This is exactly what P&G™ did in a study conducted in the Democratic Republic of Congo¹⁵. This is a region where nearly 80% of the population does not have potable drinking water. Delivering the information directly to the children was extremely beneficial because they are often times the water carriers of the family. After educating the children about the PUR® packets, they brought that knowledge home. By the end of the study, 95% of households knew how to sanitize their water and 91% were washing their hands before and after meals. This caused a drastic decrease in the incidence of diarrhea in households. Similar studies have been conducted in Liberia¹⁶, Kenya¹⁷ and Guatemala (Reller et al 2003).

In the wake of the devastation that hit Haiti in 2010, the PUR® packets have also shown one of their alternative purposes. In addition to providing clean water to developing nations, the packets are also used for relief efforts after natural disasters. As seen with the earthquake in Haiti, the few clean sources of water that the nation did possess were completely obliterated. P&G™ and PUR® immediately sprung into action delivering 6 million packets to the country which provided a 3 month supply of clean water for 340,000 people¹⁸. The device was used for a similar situation in Honduras back in 2008¹⁹. With the help of Catholic Relief Services, PUR® packets were distributed to families without access to safe drinking water after a Tropical Depression struck the region in October of that year.

Furthermore, the supplier recommends that this product also be used for recreational purposes such as camping, hiking, hunting, and backpacking. However, there has been very little research done to test the effectiveness of the product in these environments.

2.2 Activated Carbon

The use of Activated Carbon (AC) for drinking water treatment dates all the way back to ancient civilizations. One of the earliest known recordings of drinking water treatment dates back to 4000 BC²⁰. This was the first documentation of taste and odor control, two things that AC is often used to treat today. These ancient Greek and Sanskrit writings suggested filtering water through charcoal, exposing it to sunlight, boiling, and straining²¹. Around 2000 BC, a Sanskrit document called the Sus'ruta Samhita sited impure water as the source of several medical concerns²². This document also suggested two new treatment methods: dipping a heated rod into the water or filtering it through coarse sand or gravel.

The activated carbon has also made a name for itself in the medical industry. Patients who are victims of chemical poisoning from household products are treated with AC because of its ability to absorb toxins. It has also been noted that AC was used in 1500 BC to combat odors from gangrene wounds. Activated Carbon has also made strides in the air purification industry and has been in use there for quite some time as well. The exposure of soldiers to poisonous gases during World War 1 led to the mass production of respirators with AC filters. Carbon filters are also found in several home and office air purifiers.

2.2.1 Manufacture. Carbon can be activated through physical or chemical processes. Physical reactivation can occur in one of two ways. The first involves

carbonization in which the material is pyrolyzed or heated in the absence of oxygen. The second is exposing the carbonaceous material to an oxidizing atmosphere such as steam. These two methods can also be combined to improve pore size and surface area. Chemical activation requires impregnating the material with a chemical and then carbonizing it at lower temperatures. Both processes have been proven to be effective in producing AC's of various pore sizes and surface areas. The pore sizes of activated carbon are measured in angstroms (Å). One angstrom is equal to 1×10^{-10} m which is the equivalent to a grain of sugar. AC pore structures are characterized with three size distinctions: Micropores (0-20 Å), Mesopores (20-500 Å), and Macropores (>500 Å). AC surface areas are normally in excess of 500m^2 for 1 gram of carbon.

One technique for creating AC in ancient times was by using charcoal kilns. Such devices are still in use today throughout the developing world. A project in Indonesia studied the effective yield of carbon between six types of charcoal kilns used in the region²³. Similar devices are used throughout Asia, Africa, and South America. These kilns are normally made of soil, clay, brick, or stone and are constructed by hand. The systems in urbanized nations are more advanced but achieve the same goal. The activation process normally takes place in either a rotary kiln, shaft kiln (multiple hearth furnace), or a fluidized bed²⁴. These devices allow for better control of temperature which directly effects pore structure development. Achieving a desired pore size and surface area can be accomplished through both of the physical and chemical processes discussed.

Activated carbon can be produced from a number of materials. A lot of these source materials come from the food and forestry industries. These are businesses that

tend to produce a fair amount of waste and have now found an environmentally friendly way to dispose of it. There are several studies that show how waste from farming processes have been used to create activated carbon. Some of these studies include examining sawdust²⁵, rice husks^{26, 27}, nutshells^{28, 29}, pomegranate seeds³⁰, and sago waste³¹.

2.3 Atrazine

Atrazine is a well known herbicide in the world of agriculture and lawn care. This fact is proven by the 74-80 million pounds of Atrazine that are used each year in the United States³² alone. Despite its ban for use in the European Union in 2003³³, it is still one of the most widely used herbicides in the world. Atrazine is mainly used in agriculture and more specifically on corn crops. It is credited with being capable of eliminating or preventing the growth of both broadleaf and grassy weeds, plants thought to be a nuisance in this industry. This product is also used for the cultivation sorghum, guava, hay, macadamia nuts, pasture grasses, and winter wheat³⁴. On the non-agricultural side, Atrazine is also used for golf courses, landscape maintenance, forests, and recreational areas normally in Florida and other Southeastern states. The highest use of Atrazine, however, is in the Midwestern region of the United States.

Once Atrazine is applied for these purposes it is very slow to break down in the environment. This is largely due to its triazine structure which can be seen below in Figure 2. The large size of this compound is what prevents it from easily breaking down. The triazine structure is one that promotes Hydrogen donating and accepting because of the presence of several Hydrogen and Nitrogen molecules. The duality of the compound is what makes it dissolve readily in water and have a low tendency to adhere to soil particles. This ultimately results in a large contamination of streams, rivers, lakes, and

drinking water supplies as a whole. Contamination levels normally spike in the spring when large amounts of the herbicide are applied to agricultural crops. Two sources, rain runoff and ground infiltration, allow the product to enter waterways and groundwater supplies. Once Atrazine is in the environment it can persist for long periods of time.

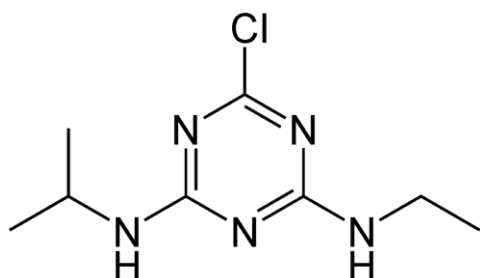


Figure 2-2. Chemical Composition of Atrazine

Although drinking water is one of the main sources of exposure to Atrazine, there are also a few others that are not commonly recognized. Children playing on lawns or in soil that have recently been sprayed are at risk for direct exposure. It is also important to note that Atrazine can persist in soil for an extended period so a child playing on a lawn that was treated months ago is still at risk. During application there is a certain amount of drift that may occur. The drift of Atrazine causes it to become airborne and it has been found in dust particles at low levels in homes throughout the Midwest^{35, 36, 37} and in California³⁸. These studies also found that people residing in households with farmers or individuals who apply the pesticide are at an extremely high risk because the contaminant may be in the clothes or shoes of that person when they reenter the home. Atrazine residues have also been detected in food samples^{39, 40} but these levels were beneath the EPA's maximum contaminant level (MCL).

2.3.1 Health effects. One of the things that makes Atrazine a contaminant of concern are the number of adverse health effects associated with it. One study by Ochoa-Acuña et al in 2009⁴¹ found that exposure to Atrazine during pregnancy produced a significant increase in the amount of babies born small-for-gestational-age. This means that the birth weight, length, or head circumference of the child was below the 10th percentile for a specific gestational age. In 2004, occupational exposure to Atrazine was linked to causing increased risk of infertility and adverse pregnancy outcomes such as miscarriages, preterm delivery, and birth defects⁴². Atrazine has also been found to effect infant mortality and morbidity rates.

There are also several health risks for adults exposed to Atrazine. In 2004, Swan found that Atrazine exposure contributed to reduced sperm quality of men in Missouri. Another study also linked the pesticide to diminished sperm motility⁴³. Atrazine has also been shown to potentially affect the heart, brain, and lungs^{44, 45}. There is still a large debate as to whether or not Atrazine can be linked to any forms of cancer. The EPA reports that there is no correlation but several epidemiological studies are now exploring the possible link to the agricultural uses of Atrazine to various types of cancer. It has, however, been documented that the endocrine disrupting properties of Atrazine have shown to effect fish, amphibians, and reptiles⁴⁶. It is in turn feared that this herbicide is a risk factor for reproductive cancers in humans and other mammals.

CHAPTER 3 MATERIALS AND METHODS

3.1 PUR[®] Packets

The PUR[®] packets were obtained from an online retailer (Walmart[®]) which supplies the treatment kit. These packets were used to treat raw water from Lake Alice on the University of Florida campus. Lake Alice was chosen for the ease of access to the water source and the amount of natural organic matter (NOM) thought to be present in the water. To increase the quantity of experiments that could be performed using a single PUR[®] packet, the powder was split into tenths, thus allowing for 10 experiments to be performed from each packet. Therefore, 0.4 g of PUR[®] powder was used to treat 1 liter of water in every experiment. Although there was no research found about the scalability of the PUR packet, the powder was thoroughly mixed to increase the potential of each component making it into the scaled treatment process. However, it will be helpful for future experiments to determine the concentrations of each component to ensure each is present in the modified treatment process. The water treated in these experiments was only used for analysis. None of it was consumed after treatment. The directions for use of the PUR[®] packet were modified for this reason. The edited directions for use are as follows:

1. Mix
 - Measure out 0.4 grams of PUR[®] powder.
 - Add the powder to a clean beaker holding 1 liter of source water.
2. Stir
 - Stir the powder vigorously in the water for 5 minutes using a magnetic stir rod and stir plate. Be sure a vortex is created when stirring. Then, let the water stand for 5 minutes or until it becomes clear.
3. Filter

- Once the water looks clear, and the floc is at the bottom of the beaker, filter the water through a vacuum filter into a clean storage container.
- The filter must be a clean, 0.45 um membrane filter, without holes, that prevents the floc from passing through. The floc will be left behind in the bottom of the container and in the membrane filter.
- Discard the floc from the water treatment process in a trash receptacle.

All of the experiments were carried out in progression; meaning that duplicate experiments were not performed for this analysis. This was because after the PUR[®] packet proved its effectiveness at one level, the packet was then tested at the next level. After the water was treated, samples were sent to Engineering Performance Solutions (EPS - Gainesville, Florida) for water quality analysis. More detailed pictures of the treatment process can be seen in Appendix A: PUR[®] Packet Treatment Photos.

The first set of experiments was designed to test the PUR[®] packet's ability to remove color and turbidity from the water and also examine whether or not the packet produced disinfection byproducts (DBPs). This test was also designed to check for Atrazine in the source water from Lake Alice. The water was treated using the modified directions given above. The mixing was done on a magnetic stir plate at a medium setting. After vacuum filtration, 200 mL samples of source water and treated water was sent to EPS for analysis.

3.2 Humic Acid and Toluene Studies

The purpose of these tests was to see how the PUR[®] packet would behave in the presence of increased organic matter and another organic substance. Instead of adding viruses and bacteria to the raw water, Toluene was selected as the additional contaminant. Actual viruses and bacteria such as Hepatitis A and Coliform were not added because they are very dangerous to handle. Toluene was used to simulate the

increased competitive adsorption environment that this packet is normally used to treat. Just like viruses and bacteria, Toluene is able to bind to organic material in aqueous environments, increasing its longevity in these systems.

These experiments were also still testing the hypothesis of the PUR[®] packet producing DBPs. The total organic carbon (TOC) level of Lake Alice was initially 8 mg/L. It was desired to increase this concentration to 10, 15, and 20 mg/L in three different beakers. This was done by adding 2, 7, and 12 mg of Humic Acid to the beakers, respectively. The Humic Acid was obtained from the International Humic Substance Society (St. Paul, Minnesota). The type of Humic Acid used was Suwannee River Humic Acid Standard II. Then, a 10 uL dose of Toluene was added to each beaker. The beakers were then thoroughly mixed by hand with a stirring apparatus and a 200 mL sample was extracted from each for water quality analysis. The substance in each beaker then underwent the modified treatment process. Three new sample mixtures were created using the same contaminants and dosages as listed above. These mixtures were allowed to undergo treatment for 60 minutes instead of the recommended 5 minutes. This was done to see if extended exposure to the PUR[®] powder would create more DBPs. They were then vacuum filtered and 200 mL samples from each were extracted. All nine samples collected from this process were then sent to EPS for water quality analysis.

3.3 Atrazine Studies

The experiments conducted with Atrazine followed a similar pattern to the Humic Acid and Toluene experiments. Just as before, there were three beakers with 1 liter of water, 10 uL of Toluene and 2,7, or 12 mg of Humic Acid. Each beaker was then spiked with 20 uL of Atrazine. With no Atrazine being detected in the raw source water from the

first set of experiments, it was necessary to analyze whether or not the PUR[®] packet could actually remove this substance. The Atrazine was obtained from SPEX CentriPrep (Metuchen, NJ) through Fisher Scientific Company. A 200 mL aliquot was removed from each beaker and all beakers were then treated according to the modified directions. A 200 mL sample was then obtained from each of the treated beakers and all 6 samples were sent to EPS for water quality analysis.

3.4 Activated Carbon Production

The activated carbon used in these experiments was created from sawdust. The first step of this process was nitrogen pyrolysis. The sawdust was charred in batches of 1.5 grams per sample. This process took place in a furnace set to a temperature of 450°C with a Nitrogen flowrate of 30 mL/min for 15 minutes. These pyrolyzed samples were then compiled into one large batch. The furnace temperature was then increased to 700°C for steam activation. The newly pyrolyzed sawdust was activated in four batches each containing 1.5 g of material. Two samples were activated at a steam flowrate of 0.2 mL/min for 15 and 30 minutes. A second set of samples was activated at a steam flowrate of 0.5 mL/min for 15 and 30 minutes. A small portion of each sample (0.2 g) was analyzed using the Quantachrome Instruments NOVA 2200e surface area analyzer. Three of these activated carbons were selected for use in the next set of experiments.

3.5 PUR[®] and Activated Carbon Treatment

For this process, 1 liter of water was added to three 1500 mL beakers. There were then 3 mg of Humic Acid added to each beaker. They were all spiked with 10 uL of Toluene and 20 uL of Atrazine. The first beaker was treated with activated carbon first and then the PUR[®] powder. The second beaker was treated with activated carbon and

the PUR[®] powder at the same time. The third beaker was treated with the PUR[®] powder first and then activated carbon. In every case the activated carbon was used in accordance with the modified directions used for the PUR[®] packet. This process was completed a total of six times using 20 mg and 100 mg doses of each carbon. Each mixture was vacuum filtered in the final stage and eighteen 200 mL samples were sent to EPS for analysis.

3.6 Total Organic Carbon

There were several needs for this type of testing. It was thought that TOC played a fairly vital role in the effectiveness of the PUR[®] packet. Therefore, several TOC tests were conducted at various stages in the experimentation process. It was first necessary to determine the amount of TOC reduction the PUR[®] packet and the activated carbon were capable of. This was done by testing the TOC of the water during the PUR[®] and activated carbon treatment experiments. Testing was also necessary to determine if any of the treatment agents in the PUR[®] packet were creating organic carbon. All TOC analysis was carried out on a Tekmar Dohrmann Apollo 9000 Combustion TOC/TN analyzer. This machine required a 40 mL vial from each treated sample which was extracted after the vacuum filtration.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Raw Water Tests

The first set of experiments was used to determine the quality of raw water obtained from Lake Alice and the ability of the PUR[®] packet to treat this water. The water quality parameters examined were color, turbidity, Atrazine, and disinfection byproducts (expressed as TTHMs). The results for this test can be seen below in Table 4-1. The “Raw” column refers to the source water from Lake Alice. The “Clean” column represents the water sample taken after treating Lake Alice water with the PUR[®] powder.

Table 4-1. Raw water test results

Specification	Raw	Clean
Color (Pt-Co)	22	3
Turbidity (FAU)	70	24
Atrazine (ug/L)	ND	ND
TTHM (ug/L)	ND	2.09

**5 minutes of contact time*

ND = Below detection limit of 0.5 ug/L for Atrazine

ND = Below detection limit of 0.5 ug/L for TTHMs

From the table it can be seen that the PUR[®] packet had removal in both color and turbidity. With no Atrazine being detected in the source water it is reasonable for there to be none detected in the treated water. Although some disinfection byproducts were created during the cleaning process, the detected amount of 2.09 ug/L is still approximately 40 times lower than the EPA’s maximum contaminant level (MCL) of 80 ug/L.

4.2 Humic Acid and Toluene Studies

After seeing the PUR[®] packet’s ability to perform well it was time to test its effectiveness in the presence of increased organic matter and another contaminant.

Each beaker was spiked with Humic Acid to increase the TOC concentration and Toluene to introduce an additional pollutant. Once again the PUR[®] packet combated color and turbidity well, even with the excess organic matter present. The packet was also effective in removing Toluene. Again, a small amount of DBPs were formed in the process but they still were not significant. The results of this are displayed in Table 4-2. The parameters examined in these tests were color, turbidity, Toluene, and TTHMs.

Table 4-2. Humic Acid and Toluene water test

Sample ID	Color (Pt-Co)	Turbidity (FAU)	Toluene (ug/L)	TTHM (ug/L)
Raw 10 mg/L	146	87	2830	ND
Raw 15 mg/L	143	46	525	0.9
Raw 20 mg/L	231	22	513	0.9
Clean 10 mg/L 5 min	7	0	1329	1.4
Clean 10 mg/L 60 min	25	0	61	1.2
Clean 15 mg/L 5 min	14	0	289	2.1
Clean 15 mg/L 60 min	30	1	15	1.5
Clean 20 mg/L 5 min	24	0	64	1.6
Clean 20 mg/L 60 min	21	0	2	ND

ND = Below detection limit of 0.5 ug/L for Toluene and TTHMs

The Raw 10, 15 and 20 mg/L represent the three different beakers that were spiked with 2, 7, and 12 mg of Humic Acid, respectively. Each of these samples was also spiked with 10 uL of Toluene. All of the sample ID's starting with clean as the subject were samples taken from the treated Lake Alice water. For example, "Clean 10 mg/L 5 min" was taken after treating the Raw 10 mg/L beaker with the PUR[®] powder. The endings notations of 5 and 60 minutes denote how long each beaker was allowed to mix with the PUR[®] powder.

The removal of color, turbidity, and Toluene can be seen in Table 4-3. The percent removal of Toluene was almost 100% after 60 minutes of treatment for all three

samples (i.e., when starting with 10, 15, and 20 mg/L of TOC). Turbidity removal was 100% for all samples except for one which was relatively close at 97% removal.

Table 4-3. Percent removal from Humic Acid and Toluene test

Sample ID	Color (%)	Turbidity (%)	Toluene (%)
Clean 10 mg/L 5 min	95	100	53
Clean 10 mg/L 60 min	83	100	98
Clean 15 mg/L 5 min	90	100	45
Clean 15 mg/L 60 min	79	97	97
Clean 20 mg/L 5 min	90	100	88
Clean 20 mg/L 60 min	91	100	100

4.3 Atrazine Studies

During the Atrazine tests, color and turbidity were still removed but an interesting phenomenon occurred when Toluene and Atrazine were both present in the water. In the presence of Atrazine the removal efficiency of Toluene was greatly diminished. The removal of Atrazine itself was almost nonexistent (Table 4-4). The percent removal (Table 4-5) shows how little of both substances were removed in comparison to Table 4-3.

Table 4-4. Humic Acid, Toluene, and Atrazine test

Sample ID	Color (Pt-Co)	Turbidity (FAU)	Toluene (ug/L)	Atrazine (ug/L)
Raw 10 mg/L	56	4	2145	40
Raw 15 mg/L	134	6	494	22
Raw 20 mg/L	180	5	476	14
Clean 10 mg/L, 5 min	16	2	2020	34
Clean 15 mg/L, 5 min	8	0	322	24
Clean 20 mg/L, 5 min	7	0	307	14

The sample IDs of Raw 10, 15, and 20 mg/L still represent the three different beakers that were spiked with 2, 7, and 12 mg of Humic Acid, respectively. Each beaker was also spiked with 10 uL of Toluene and 20 uL of Atrazine. The samples labeled

clean are samples of treated water from that corresponding beaker (i.e. Clean 15 mg/L was treated from Raw 15 mg/L).

Table 4-5. Toluene and Atrazine percent removal

Sample ID	Color (%)	Turbidity (%)	Toluene (%)	Atrazine (%)
Clean 10 mg/L, 5 min	71	50	5.9	14
Clean 15 mg/L, 5 min	94	100	35	8.8
Clean 20 mg/L, 5 min	96	100	36	2.1

Diminished removal of all four parameters was seen in this set of experiments. This could possibly be related to the number of contaminants present in the water. Toluene, color, and turbidity were all removed quite well before Atrazine was added to the system. The large chemical structure of Atrazine could have also contributed to its lack of adsorption and also the lack of adsorption of the other two contaminants. A more in depth depiction of the Humic Acid and Toluene structures can be seen in Appendix B: Chemical Structures. After discovering this lack of removal, it was necessary to examine the possible effect activated carbon might have on the mixture.

4.4 Activated Carbon Creation

Only 1.5 g of saw dust was used during Nitrogen pyrolysis and steam activation to ensure all of the material had the ability to fully react. During pyrolysis there was at least 40% mass loss in every sample (Table 4-6). This value of mass loss is typical when using this process because non carbonaceous material is burned off.

Table 4-6. Nitrogen pyrolysis of sawdust

Sample ID	Mass Before (g)	Mass After (g)	Mass Loss (%)
1	1.5	0.889	40.7
2	1.5	0.846	43.6
3	1.5	0.856	42.9
4	1.5	0.864	42.4
5	1.5	0.848	43.5
6	1.5	0.877	41.6
7	1.5	0.886	41.0
8	1.5	0.896	40.2
9	1.5	0.875	41.7

During steam activation each sample experienced a mass loss greater than 50%, which is also typical for this process (Table 4-7). It was expected that the mass loss would be greater from 15 minute to 30 minute activation times but it was discovered that the increase in mass loss was very small. Using 0.2 mL/min of steam the mass loss increased from 53.7% to 54.2% (a minor difference of 0.5%). Using 0.5 mL/min of steam the mass loss increased from 55.0% to 55.9% (a difference of 0.9%).

Table 4-7. Steam Activation of Pyrolyzed Sawdust

Sample ID	Mass Before (g)	Mass After (g)	Mass Loss (%)	Steam Flowrate (mL/min)	Time (min)
# 1	1.5	0.687	53.7	0.2	30
# 2	1.5	0.694	54.2	0.2	15
# 3	1.5	0.661	55.9	0.5	30
# 4	1.5	0.675	55.0	0.5	15

Analyzing each sample on the NOVA 2200e gave a more in depth look at the carbon capacity and pore size (Table 4-8). The maximum surface area achieved was 416 m²/g and the minimum was 168 m²/g. The pore volume followed a similar trend with the largest pore volume residing in the 416 m²/g sample and the smallest pore volume residing in the 168 m²/g sample. The average pore size however had a different result. The pore size for Carbon #1, #3, and #4 were all around 9 Å while the pore size for Carbon #2 (which had the smallest surface area) was 12.8 Å.

Table 4-8. Activated Carbon particle analysis

Sample ID	Sample Mass (g)	Surface Area (m ² /g)	Pore Size (Å)	Pore Volume (cm ³ /g)
#1*	0.183	327	9.2	0.15
#2*	0.194	168	12.8	0.11
#3	0.181	398	9.0	0.18
#4*	0.167	416	9.1	0.19

* Carbon was selected for final treatment process

4.5 PUR[®] and Activated Carbon Treatment Results

Color and turbidity were still effectively taken care of in these experiments. With the addition of activated carbon, it was expected that there would be increased removal of both Atrazine and Toluene. Its presence, however, was almost unrecognizable in the results. The two contaminants added to the water were still removed in relatively small percentages (Tables 4-9 through 4-14). Though these percentages were small, it was apparent that use of activated carbon in conjunction with the PUR[®] packet would be a possible solution to combating these contaminants.

The sample labeled “Raw Spiked” contained 3 mg of Humic Acid, 10 uL of Toluene and 20 uL of Atrazine. The sample IDs starting with “AC Before” mean that the sample was first treated with activated carbon and then the PUR[®] powder. Sample IDs starting with “AC During” were treated with AC and PUR[®] powder at the same time. Samples starting with “AC After” were treated first with the PUR[®] powder and then AC. The endings of 20 mg and 100 mg represent the dose of carbon used to treat that sample.

Table 4-9. Carbon #1 treatment results

Sample ID	Color (Pt-Co)	Turbidity (FAU)	Toluene (ug/L)	Atrazine (ug/L)
Raw Spiked	109	32	308	37
AC Before 20 mg	6	0	256	26
AC During 20 mg	8	0	261	33
AC After 20 mg	8	0	88	28
AC Before 100 mg	10	2	19	16
AC During 100 mg	10	0	285	24
AC After 100 mg	15	1	171	27

Table 4-10. Percent removal Carbon #1

Sample ID	Toluene (%)	Atrazine (%)
AC Before 20 mg	17	30
AC During 20 mg	15	10
AC After 20 mg	72	25
AC Before 100 mg	94	57
AC During 100 mg	8	34
AC After 100 mg	44	28

Table 4-11. Carbon #2 treatment results

Sample ID	Color (Pt-Co)	Turbidity (FAU)	Toluene (ug/L)	Atrazine (ug/L)
Raw Spiked	109	32	308	37
AC Before 20 mg	10	0	256	26
AC During 20 mg	12	0	278	32
AC After 20 mg	11	0	228	21
AC Before 100 mg	10	0	171	29
AC During 100 mg	25	2	274	32
AC After 100 mg	15	0	244	34

Table 4-12. Percent removal Carbon #2

Sample ID	Toluene (%)	Atrazine (%)
AC Before 20 mg	17	30
AC During 20 mg	10	15
AC After 20 mg	26	43
AC Before 100 mg	44	22
AC During 100 mg	11	14
AC After 100 mg	21	8

Table 4-13. Carbon #4 treatment results

Sample ID	Color (Pt-Co)	Turbidity (FAU)	Toluene (ug/L)	Atrazine (ug/L)
Raw Spiked	109	32	308	37
AC Before 20 mg	11	0	260	33
AC During 20 mg	10	9	101	28
AC After 20 mg	12	1	308	30
AC Before 100 mg	13	1	177	33
AC During 100 mg	13	1	278	29
AC After 100 mg	13	2	184	31

Table 4-14. Percent removal Carbon #4

Sample ID	Toluene (%)	Atrazine (%)
AC Before 20 mg	16	15
AC During 20 mg	67	25
AC After 20 mg	0	18
AC Before 100 mg	43	12
AC During 100 mg	10	23
AC After 100 mg	40	18

For the “AC Before” and “AC After” samples, the first treatment method was completely removed from solution before using the second method (i.e. activated carbon was completely filtered out before using PUR[®] in the “AC Before” samples and PUR[®] was completely filtered out before using activated carbon in the “AC After” samples).

From these results it was observed that the best removal of Toluene when using a 100 mg dose was found by using AC before the PUR[®] packet. With the 20 mg dose Carbon #1 and #2 performed better by using carbons after the PUR[®] packet while Carbon #4 performed well in conjunction with the PUR[®] packet. The best removal of Atrazine using either a 20 mg or 100 mg dose was using AC before the PUR[®] packet in Carbon #1 and #2. The best removal of this contaminant using Carbon #4 was found using it during the PUR[®] treatment process. It is duly noted that none of these carbons were able to provide adequate removal to meet EPA standard for Atrazine of 3 ug/L but it is a good indicator that a larger surface area, more porous carbon may be able to eliminate it from the system.

4.6 Total Organic Carbon Studies

The lack of removal of Toluene and Atrazine after adding activated carbon to the experiment prompted a desire to investigate TOC levels in the water. The observed

concentration could explain the lack of adsorption which could possibly be linked to a potentially more competitive environment due to the increased amount of contaminants. High TOC values would also indicate a possible lack of removal of Humic Acid as well. TOC was first examined from the PUR[®] and AC tests. The three carbons presented varied results. Carbon #1 (Figure 4-1) exhibited better TOC removal with the 100 mg dose. The removal before, during, and after with this carbon was consistently lower than the 20 mg dose. This was expected to be the trend in all three carbons but the other two had different outcomes. Carbon #2 (Figure 4-2) showed better removal with the 20 mg dose. This may be attributed to the small surface area of 168 m²/g of the material. The carbon may have been dealing with too many competing particles, preventing it from effectively absorbing organic matter as it did in Carbon #1.

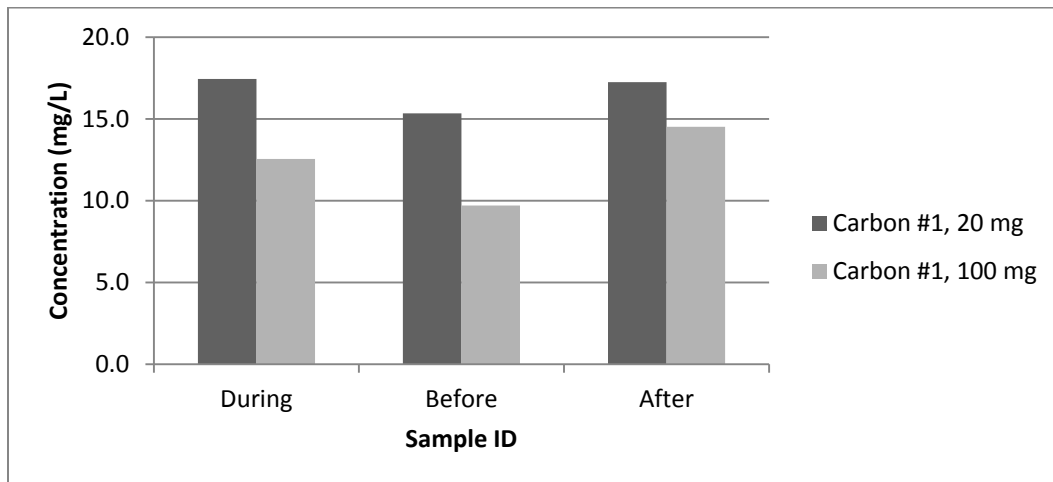


Figure 4-1. TOC concentration for Carbon #1

Carbon #4 (Figure 4-3) had very little difference in TOC concentration before, during, or after the PUR[®] treatment process. This was the most surprising result because this carbon possessed the largest surface area (416 m²/g) and the highest pore volume (0.19 cm³/g) of all three ACs.

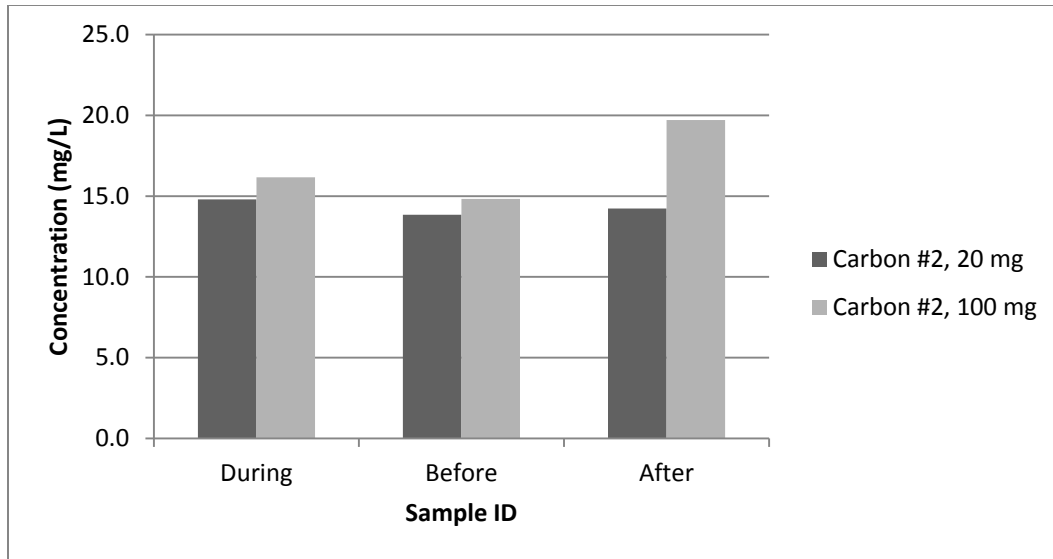


Figure 4-2. TOC concentration for Carbon #2

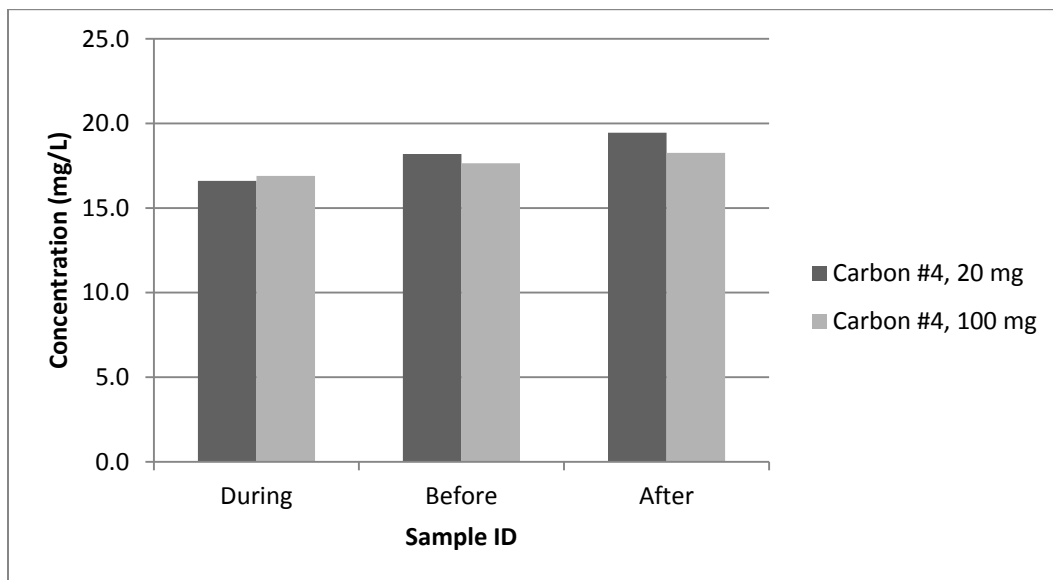


Figure 4-3. TOC concentration for Carbon #4

With most of the TOC values being above the assumed starting concentration of 8 mg/L, it was necessary to investigate the possible effect the PUR[®] packet might have had on the water. In Figure 4-4 and Table 4-15, the effect of the PUR[®] packet on TOC concentration was examined.

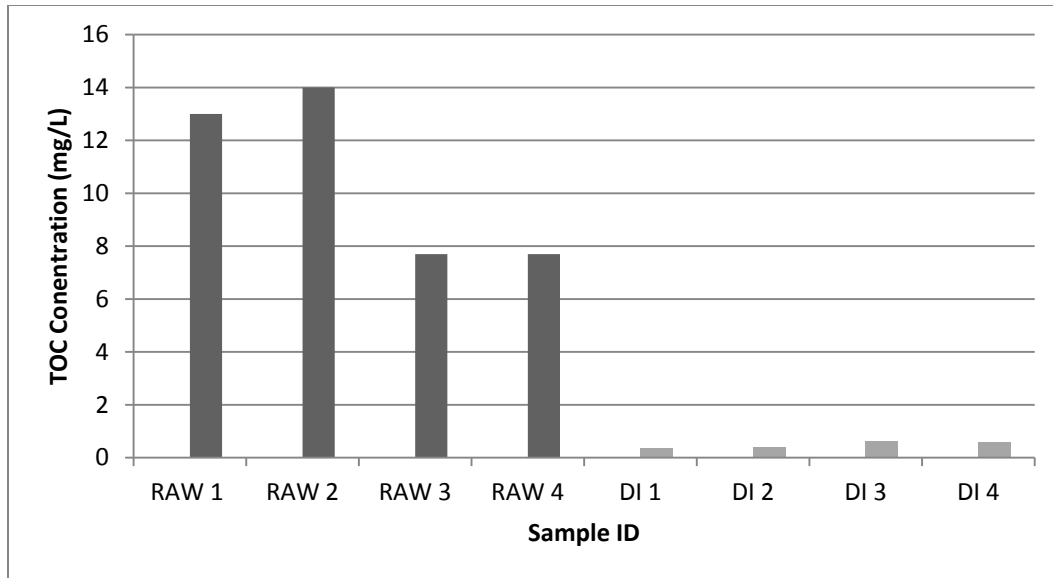


Figure 4-4. Raw and DI water TOC concentration

Table 4-15. Raw & DI water TOC concentration

Sample ID	Concentration (mg/L)
RAW 1	13
RAW 2	14
RAW 3	7.7
RAW 4	7.7
DI 1	0.37
DI 2	0.40
DI 3	0.64
DI 4	0.60

Raw 1 and 2 were samples from the Lake Alice source water without any additional chemicals. DI 1 and 2 were samples of deionized water. There is an evident decrease in TOC concentration observed in Raw 3 and 4 at 7.70 mg/L and 7.71 mg/L, respectively. There is a slight increase in TOC concentration for DI 3 and 4 but this difference is negligible. The increase can possibly be credited to the coagulant aids present in the PUR[®] packet's powder. It was also observed that the actual starting TOC concentration of the Lake Alice source water was around 13 mg/L. This could be due to

the different season in which the water was collected causing a slight change in water quality.

Recognizing the PUR[®] packet did not have a significant impact on the TOC levels, the effect of Humic Acid was then evaluated. Four samples were extracted from a beaker of raw water spiked with 3 mg of Humic Acid. The result showed a significant increase in TOC concentration (Figure 4-5, Table 4-16). The error bars present in Figure 4-5 represent the standard deviation between the samples. The average concentration was observed to be 22.7 mg/L with a maximum of 23.7 mg/L and a minimum of 22.2 mg/L. This was a fairly notable increase of approximately 10 mg/L from the previously observed average raw water concentration of 13.5 mg/L. It was assumed that the adding 3 mg of Humic Acid to the system that the TOC concentration would increase by no more than 3 mg/L. Knowing that approximately half of the composition of organic matter is carbon, it was expected that only a 1.5 mg/L increase would be observed.

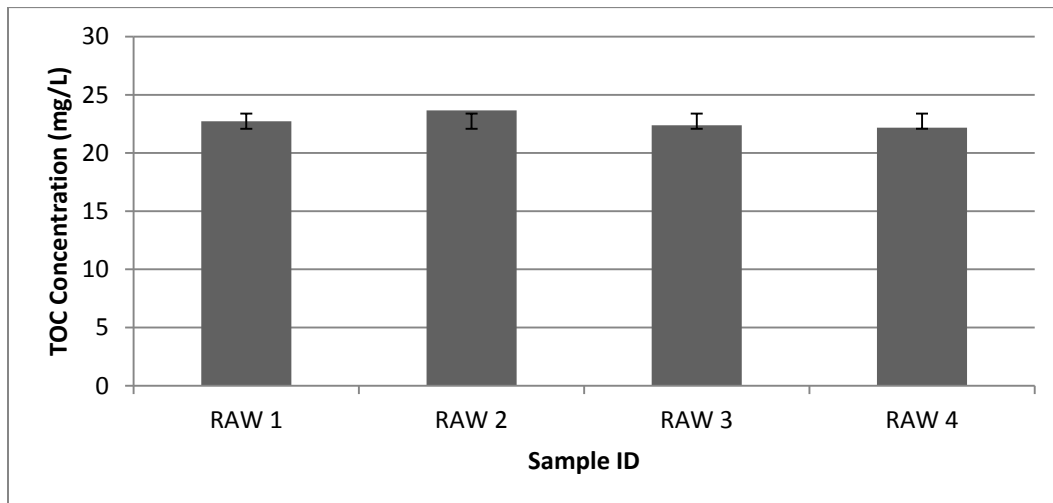


Figure 4-5. Raw + Humic Acid TOC concentration

Table 4-16. Raw + Humic TOC concentration

Sample ID	Concentration (mg/L)
RAW 1	22.7
RAW 2	23.7
RAW 3	22.4
RAW 4	22.2

From all of these TOC tests it was determined that the PUR[®] packet was in fact decreasing TOC instead of creating it as previously thought. This can be confirmed by comparing the average concentration in the raw water spiked with Humic Acid to the values obtained from treating the contaminated water with PUR[®] and AC (Figure 4-6). All values obtained after treating water were below the spiked concentration of 23 mg/L.

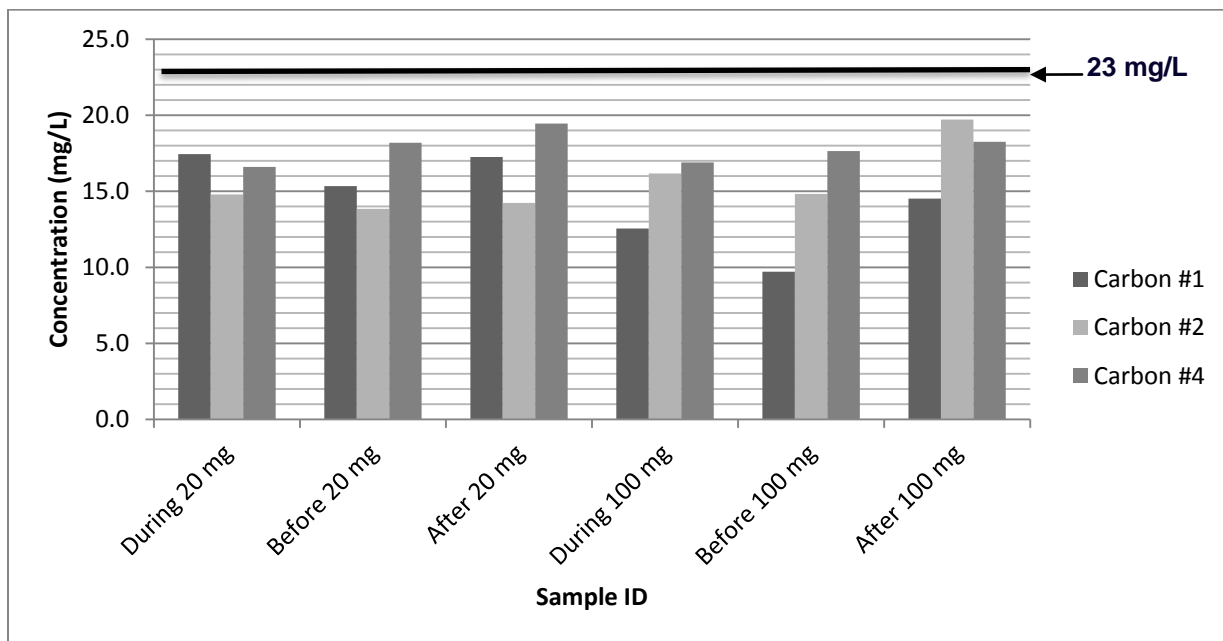


Figure 4-6. Raw vs. treated TOC concentration

CHAPTER 5 SUMMARY AND CONCLUSIONS

The PUR[®] packet was examined for its potential to create disinfection byproducts and its ability to remove Atrazine from drinking water. Humic Acid and Toluene were also added to the water to analyze the PUR[®] packet's ability to combat increased contaminant loadings in the water. As suspected, the PUR[®] packet aided in color and turbidity removal from the contaminated water. Testing the water at both its raw and saturated conditions did not yield a significant amount of disinfection byproducts. Although some DBPs were created, their concentration was well below the EPA's regulated limit.

As hypothesized the PUR[®] packet was not effective in removal of Atrazine in the presence of increased contaminants and organic matter. This is likely due to the increased competition for adsorption by the other compounds present. Although it is unclear how all of the components of the PUR[®] packet work, it was assumed that with the presence of so many treatment chemicals within the powder it would potentially be more effective in combating Atrazine and Toluene. With these results proving that the packet does not perform well in this setting, it suggests a need for more work to be done to investigate the purpose of each component of the PUR[®] powder. It may not be practical to list this product for use during recreational activity if it does not remove likely potential hazards from the water.

It was also found that an easily produced activated carbon was not sufficient in aiding the removal of Toluene or Atrazine. This may be due to the short contact time or the very high level of TOC in the water. It is known that commercially ready activated carbons are effective in removing both Toluene and Atrazine from water. The purpose

of this experiment, however, was to create a low cost activated carbon from a natural resource which could be incorporated with the PUR[®] packet's normal use. Most people in developing regions, as well as those in remote areas of developed countries, do not have access to these commercially prepared ACs. If activated carbon is not feasible to pair with PUR[®] there are other alternatives such as ion exchange treatment that have done well with Atrazine removal in solution⁴⁷. Regardless, something needs to be done to improve the PUR[®] packet's efficiency in this area before it is marketed for further recreational uses.

For future work it would be interesting to examine the interactions between Humic Acid and Atrazine, Humic Acid and Toluene, and Atrazine and Toluene. Some research suggests that the presence of natural organic matter hinders the removal of Atrazine⁴⁸ and it would be interesting to see if this is also true for the other interactions previously mentioned. There would also be examination of the molecular structures of Humic Acid, Toluene, and Atrazine to determine what molecular forces occur within each and what exchanges occur between them. Lastly, a deeper look will be taken at possibly creating a simple AC that would have a greater effect on removing contaminants from drinking water that the PUR[®] packet is unable to conquer.

APPENDIX A
PUR[®] PACKET TREATMENT PHOTOS

These are various shots taken throughout the PUR[®] Packet water treatment process.



Figure A-1. Floc forming just after PUR[®] mixing process



Figure A-2. Settled floc after allowing mixture to settle for the recommended 5 minute period



Figure A-3. Front view of PUR[®] treatment of Raw and DI water for the TOC concentration test (Raw water from Lake Alice on the left, Deionized water on the right)

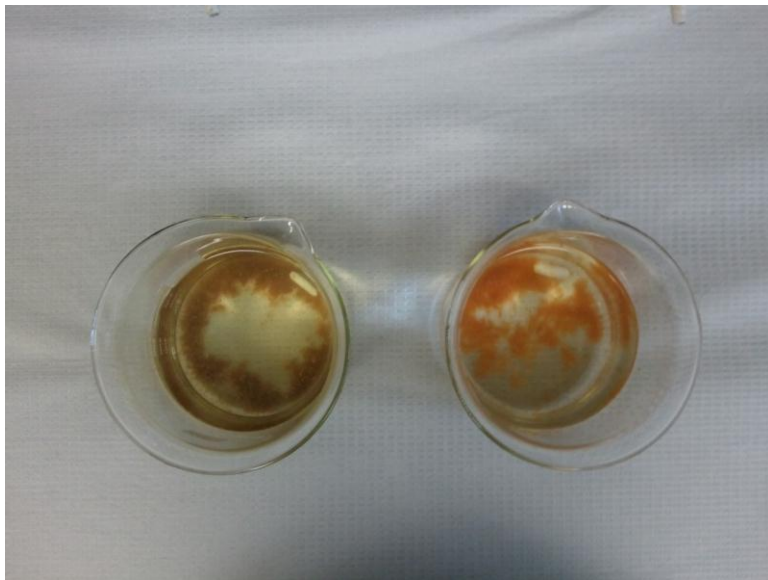


Figure A-4. Top view of Raw and DI water after PUR[®] treatment process (Raw Lake Alice water on the left, Deionized water on the right)



Figure A-5. Filters after vacuum filtering the Raw and DI treated water (Raw water filter is on the left, DI water filter is on the right)

APPENDIX B
CHEMICAL STRUCTURES

Toluene, Atrazine, Humic Acid (several types)

B.1. Toluene

MW: 92.14 g/mol

Empirical Formula: C_7H_8 or $C_6H_5CH_3$

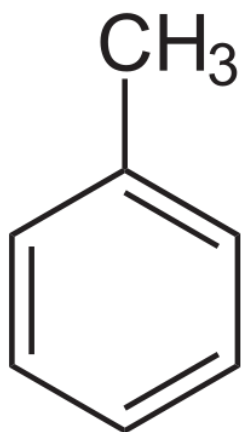


Figure B-1. Basic Toluene chemical structure

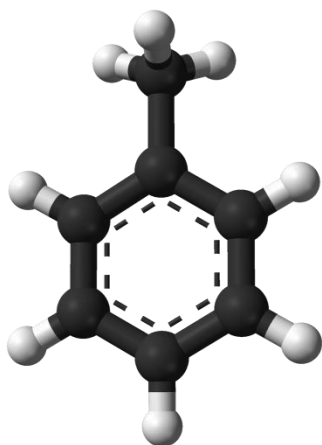


Figure B-2. 3-D Toluene structure created with Crystal Maker 8.1 and Accelrys DS Visualizer (Source: Ben Mills)

B.2. Humic Acid

Humic Acids come in several shapes and sizes. These are just a few examples of the various types of Humic Acid. Their large size and different compositions all create varying molecular weights and empirical formulas.

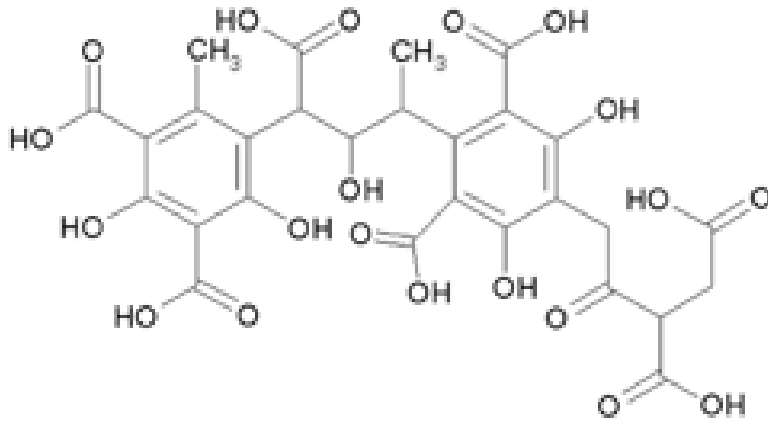


Figure B-3. Humic Acid structure #1

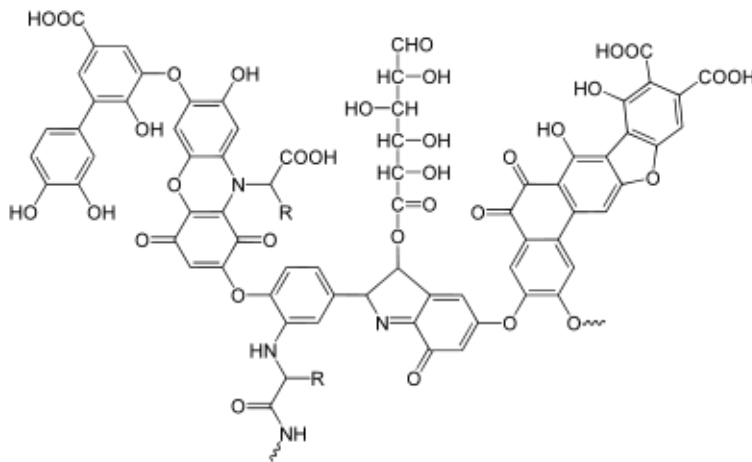


Figure B-4. Humic Acid structure #2

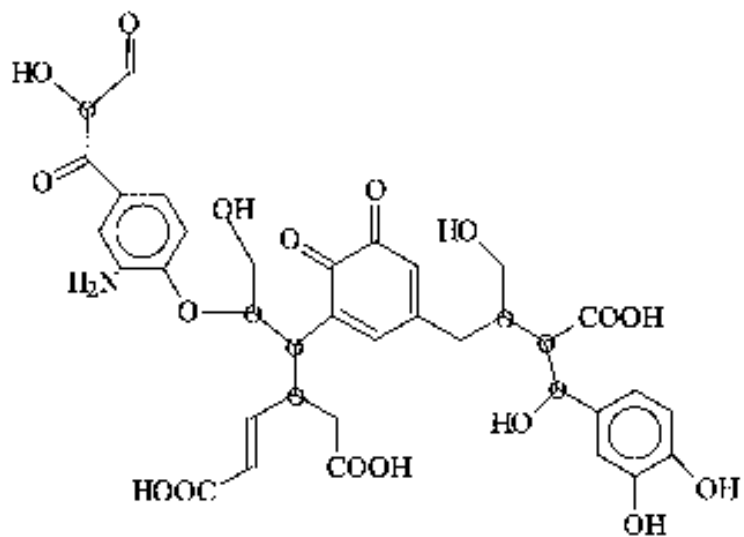


Figure B-5. Humic Acid structure #3

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BIOGRAPHICAL SKETCH

Taccara Nakia Williams was born in May of 1987 in Waterbury, CT. She graduated from Crosby High School in 2005 with honors and went on to pursue an engineering degree at Temple University in Philadelphia, PA. Craving a more challenging and intimate learning environment she transferred to North Carolina Agricultural and Technical State University in Greensboro, NC in the Fall of 2006. Here she earned her Bachelor of Science degree in civil engineering and graduated Magna cum Laude in May of 2009. She also received a Waste Management Certificate during her matriculation. Her desire to get a more in depth understanding of water quality and quantity issues led her to pursue a graduate degree in environmental engineering at the University of Florida. In the future, she hopes to use the knowledge she has acquired in her educational career to help improve the water quality and quantity issues of the world.