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# DETECTING POLLUTION IN SURFACE WATERS IN LORRAINE, FRANCE

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By


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# ABSTRACT

The purpose of this MQP was to determine if and how gray and yellow water discharges could be tracked and distinguished from one another. A further goal was to determine whether the sources of pollution in the Meurthe and Moselle Rivers could be identified and tracked using fluorescence. It was determined that contaminants can be easily distinguished from one another and tracked to their source using this method.

# AUTHORSHIP PAGE

Both of the authors of this report contributed equally to the writing of this report.

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TABLE OF CONTENTS

TABLE OF FIGURES

LIST OF TABLES

# CHAPTER 1: INTRODUCTION

Nancy, France is a city of 100,000 inhabitants, located in the Lorraine region of northeastern France. Greater Nancy, which is composed of approximately 20 municipalities, has about 410,000 inhabitants. Two rivers – the Meurthe and the Moselle – flow through Lorraine and, as can be expected in an area supporting such a large number of people, these rivers contain significant levels of pollution. As Europe and the rest of the world continue to become more environmentally conscious, the issues of water pollution and the consequent necessity of river decontamination move towards the forefront of both national and international concern.

## *1.1 Meurthe River*

The Meurthe River originates in the Vosges Mountains of France, near Col de la Schlucht, at 1190 meters above sea level, and flows 159 kilometers to its terminus in the Moselle River in Pompey.

A large wastewater treatment facility is located along the river in Nancy and various stages of treated effluent and overflow from the plant are discharged directly into the water during rainy conditions. Contamination by this only partially-treated wastewater has a dramatic effect on the quality of the river water.

Effluent and overflow are not the only causes of pollution in this river. In 1997, 21 tons of nonylphenol ethoxylate were released into the Meurthe. A tank in a riverside paper manufacturing plant was unintentionally filled with the toxic substance that was mistaken for washing water by the supplier of the water. The error went unnoticed until the liquid was dumped into the rain drainage system, which eventually flows into the Meurthe. The nonylphenol ethoxylate polluted the river as far as 15 kilometers downstream from the point of discharge and resulted in the death

of 1 ton of fish (Christou, 2000).

Whether intentional or unintentional, substances discharged into the river have a large impact on many water characteristics such as ammonium content, turbidity and chemical oxygen demand, as well as overall water quality. The Meurthe River is a tributary of the Moselle River and thus the pollution of the Meurthe adds to the pollution in the Moselle.

## *1.2 Moselle River*

The Moselle River originates in the Vosges Mountains, flows through Luxembourg and terminates 545 kilometers away in Koblenz, Germany, as a left tributary of the Rhine River. Its source is located at the base of Ballon d'Alsace, one of the mountains in the Vosges, at 715 meters above sea level, and the river continues west of the mountain range through the Lorraine region.

In France, the Moselle passes through a number of towns including Épinal, Pont-á-Mousson, and Metz. Several active paper mills are located near Épinal and these mills discharge substantial amounts of wastes, namely humic acid from paper production, directly into the river. This presence of this discharge, which is acidic and brownish-yellow in color, contributes significantly to the pollution level of the river. Additional industries located along the river are steel and iron manufacture, cement production and coal mining, all of which also have considerable impact on the water quality of the Moselle.

Tributaries of the Moselle are quite numerous and include the Rupt de Mad, the Orne, the Madon, the Moselotte, the Baybach and the aforementioned Meurthe River. These branches flow into the Moselle from both the right and the left.

In the early 1800s, the river was pristine and fish were plentiful. Lush

vegetation grew along the banks and the water was clean and clear. With the discovery of microbes in the mid-1800s, medical professionals became more concerned with the spread of disease associated with the present sewer system of the time. Many cities, including Nancy, revamped their sewage disposal practices by creating unified systems that collected the wastewater and discharged it into the Moselle – waste disposal that was carried out at the expense of the water quality of the river.

In the 1870s, river pollution gained widespread recognition as a serious problem. Consequently, a management strategy was implemented that employed a fairly lax method of regulation by enforcing a so-called 'command and control' policy. The basis of this policy was that details regarding the specific amounts of pollution from every plant be provided to the prefect, who was allowed to close any plant he deemed was discharging more than the acceptable pollution amount. However, this step was rarely, if ever, taken; as long as the pollution was 'discreet', meaning large quantities of discharge were not released into the river at any one time; authorities did not consider the pollution harmful to the aquatic environment (Garcier, 2007).

In the first half of the 20$^{th}$ century, water pollution problems took a backseat to more pressing issues such as the war and the economy; however, when lack of clean water sources for human use and consumption became a problem, the severely polluted Moselle was once again at the forefront of both national and international concern. According to public records, there were only three wastewater treatment facilities along the entire Moselle River in 1946 and two of those three had been out of order for at least six years prior to the count, likely shut down due to the war. By 1960, the organic pollution levels were higher than ever, due to years of effluence,

canalization and industrialization. In 1963, France, Luxembourg and Germany created the International Commissions for the Protection of the Moselle and the Sarre, an important first step in the protection of these international rivers. Although the organization was not nearly as effective as originally expected, pollution levels began to decrease due to a reduced number of domestic effluents. (Garcier, 2007). The Water Law of 1964, designed originally to avert water shortages, also played a part in the augmented protection of the rivers. Levels of organic pollution continued to decline at a mediocre pace until 1990, when the rate of reduction increased considerably; today, organic pollution levels are lower than they were in the 1860s (Garcier, 2007). However, monitoring and reducing pollution levels is still a priority and there are many organizations devoted to these initiatives.

## *1.3 Identification of Contamination Sources*

Although any given sample of polluted water can contain a large number of different impurities, many of these contaminants can be easily distinguished from one another using basic laboratory tests. The first priority of this MQP was to determine if and how gray and yellow water discharges could be tracked and distinguished from one another. The second goal of this project was to determine whether the sources of pollution in the Meurthe and Moselle Rivers could be tracked using simple methods.

Optical brighteners, which are added to cleaning solutions such as laundry soaps in order to provide a whitening effect, are found in gray water from washing. These additives absorb light in the ultraviolet and violet region of the electromagnetic spectrum and also emit light in the blue region, which hides yellow and brown tones to make clothing appear whiter (Panda, 2006). The presence of optical brighteners in

a water sample can be easily detected by first generating a synchronous fluorescence spectrum and subsequently exposing the sample to UV light, which generally results in the photo decay of the optical brightener's fluorescence. An additional synchronous spectrum can then be generated and used for comparison purposes to determine the amount of photo decay that has taken place, and a large amount of photo decay suggests the presence of optical brighteners in the sample.

By following such a process, we were able to positively identify the presence of optical brighteners in many water samples collected from the Meurthe River. The amount detected in the water from the Moselle River was substantially less, yet nonetheless undoubtedly present.

Tryptophan, found in urine, can also be identified in a water sample by a similar method; however, tryptophan does not photo decay. Therefore, a large peak around 290 nm that does not decrease after exposure to UV light can be identified as tryptophan. The ability to differentiate between tryptophan and optical brightener peaks enabled us to distinguish between gray and yellow wastewaters.

After confirming this capability to differentiate between wastewaters, it was possible to use the aforementioned technique to determine what types of contamination were present in the samples taken from the Meurthe and Moselle rivers.

# CHAPTER 2: BACKGROUND

## *2.1 Managing/Tracking Water Quality*

Fecal contamination in surface waters can result from numerous sources of fecal pollution, including human sewage, manure from livestock operations, indigenous wildlife, and urban runoff (Griffith et al., 2003). The ability to identify the origin of fecal pollution is essential for evaluating the risks to those that may be affected by this pollution. This is imperative in order to take the proper action should a problem arise (Graves et al., 2007). The impact of fecal contamination reaches many spectrums of human societies as well as ecological systems. For example, human illness may occur if water polluted with fecal matter by human and human wastes is ingested (Palladino, 2005). Microbial source tracking [MST] involves microbiological, genotypic, phenotypic, and chemical methods by which fecal pollution is tracked (Scott et al., 2007). MST has developed rapidly over the past several years, resulting in several publications and over 20 different methods for source-tracking (Graves et al., 2007).

The issue of fecal contamination is becoming more apparent as the number of livestock has increased in the past several years (Baker, 2002). Likewise, this trend has led to an increase in waste products from livestock. If not discharged properly, the organic waste products lead to a rapid growth of river micro-organisms, resulting in a heightened biological oxygen demand (BOD). Increases in BOD lead to a decrease in river oxygen and hence, the death of aquatic life (Baker, 2002).

BOD is closely related to chemical oxygen demand (COD), which is a

measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of ammonia and nitrite ("Chemical Oxygen Demand", 2008). The COD value can be used as an indication of the level of organic pollutants in a water sample, which allows for an approximation of water quality. Since COD levels are closely correlated with pollution levels, they are regulated by the government in many countries. Maximum COD levels are set and these standards must be adhered to in order for wastewater treatment plants to return treated water to the environment. If COD is above the imposed maximum, water must undergo additional treatment until the allowed COD conditions are met (Clescerl et. al, ND).

## *2.2 Fluorescence Characterization*

Fluorescence occurs when electrons in a molecule absorb energy, rise to their 'excited' state, and then release the absorbed energy in the form of light. The ground state is the energy level at which the electron exists in preferentially, and is the most stable. When an electron absorbs a photon, it gains energy and rises to a higher energy state. Since this more excited state is also more unstable, the electron will release energy rather quickly, falling back down to the ground state. It is due to this release of energy that the luminescence known as fluorescence is produced (Baker, 2002).

Since the fluorescent characteristics of a particular molecule are a direct result of its chemical structure and composition, it is possible to use fluorescence applications to determine the identity of molecules of an unknown substance. By comparing the fluorescent activity of a known substance to that of an unknown molecule, the identity of the latter can be inferred (Baker, 2002).

One of the most important fluorescent characteristics of matter is the amount of conjugated double or triple bonds present in a molecule of the substance.

Conjugated double bonds are consecutive double bonds separated by a single bond, and conjugated triple bonds are similar in that they are consecutive triple bonds separated by a single bond. Conjugation of bonds leads to increased fluorescence because the electrons involved in the aforementioned bonds are in π orbitals, instead of the Σ orbitals that single bonds are composed of. Electrons in π orbitals are able to move more easily between energy levels than electrons in Σ orbitals and, therefore, absorb and release energy more frequently. This leads to an increased amount of fluorescence (Baker, 2002). Aromatic compounds, which are ringed molecules composed of conjugated bonds that exhibit stronger stabilization than regular conjugated molecules, also fluoresce due to electron movement in the π orbitals. The presence of nitrogen and oxygen atoms, as well as that of double bond-containing substituent groups, also serves to increase the intensity of fluorescence (Baker, 2005). Fluorescent materials can be classified in one of two main groups: compounds containing humic-like or fulvic-like substances, and protein fluorescence (mainly tryptophan-like fluorescence). The former category is made up of molecules which have a high content of carboxylic groups and aromatic and conjugated structures; it is the carboxylic groups and conjugation characteristics that are referred to as the humic and fulvic-like (Baker, 2002). The second category is proteins that fluoresce, due in large part to tryptophan, one of the 20 standard amino acids (University of Hawaii, 1999). Tryptophan is the molecule responsible for the majority of the fluorescence emissions of proteins and has been found to have excitation at 220-230 nm and 270-280 and emission at approximately 350 nm (Baker, 2005).

### 2.2.1 Quenching

Fluorescence quenching is a process which decreases the intensity of the fluorescence emission. The accessibility of groups on a protein molecule can be

measured by the use of quenchers to perturb fluorophores. Quenching by small molecules, either in the solvent or bound to the protein in close proximity to the fluorophore, can greatly decrease the quantum yield of a protein. Quenching may occur through the following means: (1) collisional or dynamic quenching; (2) static quenching; (3) quenching by energy transfer; (4) charge transfer reactions (University of Hawaii, 1999).

## *2.3 Spectroscopic Techniques*

Fluorophores, a category of functional groups that includes fulvic- and humic-like substances, tryptophan, and tyrosine, are the components of molecules that cause them to fluoresce. The aforementioned property of fluorescence makes possible a variety of tests and techniques, from which the composition of the molecule under consideration can be deduced. This capability is especially useful in the investigation of contaminated surface water, such as lakes and rivers located nearby chemical and wastewater treatment plants. By analyzing water samples taken from contaminated regions, the actual source of the pollution can be identified. From there, steps can be taken to ensure that the cause of the contamination is discontinued.

Fluorescence is of particular interest when identifying and sourcing contaminated waters that contain human urine. Tryptophan and creatine are components of urine and, since they exhibit a broad peak for $\lambda_{ext}$ = 310 nm – $\lambda_{em}$ = 370 nm, are easily identifiable (Pons, 2004). This greatly simplifies the task of recognizing the presence of urine in water.

### 2.3.1 Excitation-Emission Matrix

An important tool for identifying water contamination sources is Excitation-Emission Matrix (EEM) fluorescence spectroscopy. This technique yields

fluorescence spectra of samples at a variety of different excitation wavelengths, producing a unique fluorescent 'fingerprint' specific to each water sample (Yan, 2000). The different locations of spectral peaks of diverse water samples yield valuable information about the fluorophores present in each sample. Unknown fluorophores in a sample can be identified by comparison to known fluorescent fingerprints, and the distinct ratios of fluorescence intensity of separate components provide scientists with the ability to distinguish between differing waste sources.

One critical advantage of EEM is the speed at which it can be performed. Water samples can be analyzed rapidly, within minutes, and the sample size required for analysis is relatively small compared to amounts necessary for other testing techniques (Baker, 2002). An additional advantage of fluorescence techniques over other methods of identification is that fluorescence is less affected by such factors like the turbidity of the water sample (Wu, 2006). However, samples containing fluorescent organic compounds can degrade over time and therefore must be analyzed in a timely fashion. Degradation can occur as a result of microbial action or by fluorophores (foreign to the original sample) entering the water, thereby skewing the spectra. Another risk to sample quality is the possibility of photodegradation, which occurs in the presence of UV light (Yan, 2000). For these reasons, it is best to take fluorescence readings within 24 hours of collection (Baker, 2002).

### 2.3.2 Synchronous Spectroscopy

Synchronous spectroscopy is a more recently developed method that provides a greater range of data than does EEM spectroscopy. In the synchronous technique, both the emission wavelength and the excitation wavelength (represented as $\lambda_{emm}$ and $\lambda_{exc}$, respectively) are scanned concurrently, while the fluorescence signal is recorded

and a constant wavelength interval is maintained between the $\lambda_{emm}$ and $\lambda_{exc}$ throughout the scan (Liu, 2007). This technique is used to enhance selectivity when assaying various samples, since it is possible to obtain a very resolved spectrum by keeping the wavelength interval constant.

### 2.3.3 Ultraviolet and Visible Light Spectroscopy

UV-vis spectroscopy (ultraviolet and visible spectroscopy) is a somewhat older method, used since the 1930's to characterize both natural water and wastewater. This technique, unlike EEM spectroscopy, is sensitive to turbidity of the sample (Pons, 2004). It is useful in identifying compounds that are highly conjugated, since conjugated molecules absorb UV light and yield useful spectra for analysis. The UV-vis spectrophotometer works by measuring the intensity of light passing through a sample (a value termed *I*) and comparing it to the intensity of light before it passes through the sample. The latter value is known as $I_{O.}$ The ratio of *I* to $I_{O,}$ symbolized by the formula $I/I_{O,}$ represents the transmittance of the sample. The concept can be summarized by the equation $T = I/I_{O,}$ with 'T' standing for transmittance. The numerical value of T is expressed as a percentage, and the value of absorbance (*A*) can be determined using the equation $A = -\log(T)$. Although absorbance does not have technical units, it represents the amount of light a material absorbs (Blauch, 2001).

In actual laboratory use of UV-visible spectroscopy, the 200-300 nm range is especially important. It is within this range that many detergents exhibit a broad absorption band, which is crucial for identification purposes (Pons, 2004). Using this method, the presence of anionic detergents, nitrates, and suspended and colloidal matter can be traced (Thomas, 1996).

In order to optimize the detection capabilities of spectroscopy techniques, it is

possible to combine different methods. For instance, UV-visible spectroscopy can be merged with synchronous fluorescence spectroscopy in an effort to increase optical spectroscopic potential (Wu, 2006). With the continued investigation of various combinations of techniques, it is likely that new and improved spectral detection processes will soon become an important part of water contamination studies.

## *2.4: Applications of Ultraviolet Light and Spectroscopy*

The term 'spectroscopy' embodies a broad collection of various techniques, many of which are viable for determining the composition of soil and water samples. These applications are very valuable in environmental lab work, when it is necessary to ascertain the identity of components of a given sample in order to decide upon further actions to be taken.

### 2.4.1 Fingerprinting

The presence of fecal contamination in water presents a threat to human health. Detecting sources and pathways of fecal contaminations is an essential step in determining appropriate measures for counteracting the pollution (Boving et al., 2004). Boving et al. (2004) studied a rapidly growing coastal area experiencing water quality degradation; in order to pinpoint the source of the problem, a fingerprinting technique was developed. This method allowed the research group to identify the precise source of pollution and then begin to take the appropriate steps in cleaning up.

Dissolved organic carbon (DOC) is typically used as a means to measure the level of organic content in water. However, this parameter fails to predict the character of the organic matter in water. Therefore, it cannot differentiate between fecal contamination and optical brighteners (Bengraine, 2001). A study by Orlove (1995) shows spectrofluorescence as an excellent diagnostic of pollution in an open

sea. Therefore, spectrofluorescence seems to be a promising alternative to DOC.

In addition, Boving has described several methods for identifying fecal bacteria, including microbiological and chemical methods. However, the costs of most of these methods were so high that they wouldn't be feasible to use for rapid detection. One of the most inexpensive and frequently used methods for fingerprinting is based on the fluorescence of optical brighteners. Developed in the 1930's and added to laundry detergents after World War 2, optical brighteners absorb UV light and fluoresce blue light in the visible spectrum. Figure 1, shows the chemical structure of one particular optical brightener commonly used in detergents for cotton and wool fabrics.

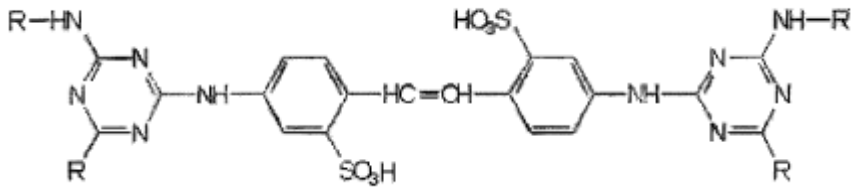


**Figure 1: 4,4-bis-(triazinylamino)-stilbene-2–2-disulfonic acid**

This fluorescent whitening agent is an example of a group of FWAs commonly used for cotton, wool, and polyamides fabrics.

These optical brighteners are detectable in aqueous solutions by the use of fluorescence. The suggestion of using optical brighteners has been questioned since the 1970 with research performed by Smart and Laidlaw (1977). In more recent studies, Stoll and Ginger (1998) used the principle of identifying graywater influent into a Swiss lake. In their studies, they found that optical brighteners are photochemically stable during treatment. However, over a 28-day period, concentrations were reduced by photodegredation.

Despite its promise, detection of optical brighteners as a means to identify the

presence of fecal contamination in surface waters may be complicated due to the existence of other fluorescent compounds in the water (Bovel et al., 2003). Some of those compounds include humic acid, tannic acid, and other dissolved organic compounds.

### 2.4.2 Spectroscopic Techniques for Facilitation of Water Quality Monitoring

Water is essential to human life, as it comprises about 70% of the human body. Thus, water quality and wastewater treatment are important issues when human health is of concern. There are many variables that characterize pollution, such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), and Total Nitrogen (TN). The time that is required for these tests render them adequate for rapid monitoring of water or wastewater. Furthermore, some of these tests require harmful reagents such as mercury and cadmium (Pons et al., ND).

As a result, spectroscopy has been used for several years as a basis for non-invasive and non-destructive means to measure pollution parameters. In particular, Infra-red, UV-Visible and fluorescence spectroscopies have been used for monitoring water quality (Baker, 2002). However, infra-red spectroscopy does not work well for substances in small concentrations. (Pons et al., ND). It has been used in wastewater treatment for monitoring and controlling an anaerobic digester, where the concentration of pollutants is high (Steyer et al, 2002).

On the contrary, UV spectroscopy is able to detect substances such as nitrates, nitrites, and various others at low concentrations. UN spectroscopy collects data in the wavelength range of 200 nm to 600 nm, approximately. Correlations between Chemical Oxygen Demand and absorbance at 254 nm are usually found since many

pollutants appear to have an absorption band close to this wavelength. Many compounds such as proteins, steroids, phenols, oils, surfactants, vitamins, humic and fulvic acids emit fluorescence after excitation by near-UV light. Since these substances have fluorescent centers in the same general vicinity, Natural Organic Matter (NOM) has been characterized using excitation-emission matrices (EEM) in several bodies of water. Synchronous fluorescence achieves better resolution for emission and excitation fluorescence (Andrade-Eiroa, 2000). In consequence, UV-visible and synchronous fluorescence spectroscopic techniques offer a quick and reagent-free characterization of the water quality in natural water bodies, drinking water, and bottled water samples.

### 2.4.3 Determining Human Fecal Contamination Using UV-light

Microbial source tracking identifies sources of fecal contamination in bodies of water. Hartel et al. (2007) describes one potentially inexpensive MST method for identifying human fecal contamination by detecting optical brighteners, easily identifiable substances which typically originate from laundry detergents and other washing fluids. The idea of differentiating optical brighteners from human sewage stems from the fact that household plumbing systems mix effluent from washing machines and toilets (Boving et al., 2004).

Hence, the ultimate goal is to evaluate the feasibility of differentiating between optical brighteners in graywater and fecal contamination in wastewater. This combination results in four possible scenarios: (1) high concentrations of optical brighteners and high counts of fecal bacteria, which suggests a malfunctioning septic drainfield or leaking field pipe, (2) high concentrations of optical brighteners and low counts of fecal bacteria, which suggests graywater in the storm water system, (3) low

concentrations of optical brighteners and high counts of fecal bacteria, which suggests other warm-blooded animals as a source, and (4) low concentrations of optical brighteners and low counts of fecal bacteria, which suggests no source of fecal contamination (Hartel et al., 2007).

Furthermore, Hartel et al. (2007) describe three possible approaches for detecting optical brighteners in water, including the use of a fluorimeter, an inexpensive, easy-to-use instrument with excellent sensitivity. However, results were contradictory when fluorimetry was combined with counts of fecal bacteria. There were several instances when this technique was successful (Kerfoot and Skinner, 1981; Hagedorn et al., 2005; McDonald et al., 2006), and others when they were unsuccessful (Close et al., 1989; Wolfe, 1995). Wolfe (1995) has attributed many of the unsuccessful cases to other organic compounds contributing to background fluorescence.

In addition, organic matter in water has been long known to fluoresce when exposed to UV light (Kalle, 1949). This fact is advantageous because optical brighteners photo decay in a matter of hours when exposed to sunlight (Kramer et al., 1996). Therefore, it may be possible to differentiate between optical brighteners and fecal contamination through the differences in their respective photo decaying rates.

# CHAPTER 3: METHODOLOGY

## *3.1 Detergent and Optical Brightener Tests*

One liter of each of the following stock solutions was prepared: Diaminostilbene (DAS), Fluorescent Brightener 28 (FB28), Tinopal CBS-X and Tinopal DMA-X. 27.3 mg of DAS, 27.7 mg of FB28, 21.3 mg of CBS-X and 28.3 mg of DMA-X were placed in separate flasks and 1000 ml of de-ionized water was added to each flask; 25 cl of each mixture was stored.

A 5 ml sample of each of the aforementioned solutions was diluted to a concentration of 1/1000 and the emission fluorescence of each of was measured in an F-2500 Fluorescence Spectrophotometer, beginning with a set emission wavelength of 250 nm and increasing the measurement settings by 10 nm for each subsequent measurement until peaks went out of range of the spectra. Analysis of the resulting electron-emission matrices (EEMs) determined that since readings for each of the four samples surpassed 10,000, the solutions must be further diluted to 1/10,000. EEMs were generated from the 1/10,000 samples and saved for analysis.

1/10,000, 1/1000 and 1/100 concentration DMA-X were prepared from stock solution for testing with irradiation treatment using a UV light box. Eight cuvettes containing 2-ml samples were prepared for each concentration of DMA-X and were irradiated in the UV box: samples were exposed to UV light for 15 minute intervals and after each interval, one cuvette (‘sample 1’) was removed; remaining cuvettes were rotated a quarter turn for a total duration of 2 hours. Irradiated cuvettes were tested in the fluorescence spectrophotometer for synchronous fluorescence to evaluate the effect of UV light degradation versus time; the setting for the starting emission wavelength was 280 nm with an excitation wavelength of 230 nm.

Similar experiments, using 1/1000 and 1/100 concentrations, were performed with the DAS, CBS-X and FB28 optical brighteners to test for fluorescence and the occurrence of photodecay. These compounds were tested by the exact same procedure as the DMA-X solution and the collected data was recorded and graphed.

1000 mL of de-ionized water was added to 10 mL of carwashing detergent in a 1-liter flask; 50 cL of solution was stored. Stock solution was diluted to 1/1000 and 1/100 concentrations and eight 2-mL cuvettes of each dilution were placed inside the UV irradiation box; the aforementioned protocol was followed using these two solutions. It was determined that UV-light degradation did not occur within a 2-hour experiment and a longer period of exposure was needed; one cuvette was removed each half hour for a total experiment duration of 4 hours.

After it was concluded that the original UV irradiation box was not resulting in sufficient sample photodecay, the experimental protocol was altered and a more intense UV light was used in place of the box. The new light was used in all subsequent experiments.

1/1000 and 1/100 concentrations of DAS, CBS-X, FB28 and Ariel (a brand of laundry detergent) were irradiated for 2 hours, with 15 minute intervals as previously described and synchronous fluorescence spectroscopy was performed to determine the occurrence of any photodecay.

Solutions of three laundry detergents were made: 19.1 mg of Rit Whitener & Brightener, 23.8 mg of Rit White Wash and 21.0 mg of Rit Color Brightener were each dissolved in 1 L of de-ionized water. 1/1000 concentrations of each of the three solutions irradiated according to the previously described protocol.

1 L of de-ionized water was added to 20 mL of tryptophan to make a stock

solution that was diluted to 1/1000 for use in following experiments. A 1/1000 dilution of each of the four optical brighteners (CBS-X, DAS, DMA-X and FB28) was mixed with the 1/1000 tryptophan dilution in a 50/50 ratio. The optical brightener/tryptophan mixtures were placed into cuvettes (8 cuvettes for each separate optical brightener) and exposed to UV irradiation and tested in the F-2500 fluorescence spectrophotometer according to the previously mentioned protocol.

The same procedure was followed using a 1/100 dilution of the carwash stock solution, a 1/1000 dilution of the Ariel stock solution, a 1/1000 dilution of the Rit Whitener & Brightener stock solution, a 1/1000 dilution of the Rit Color Brightener stock solution and a 1/1000 dilution of the Rit White Wash stock solution.

Data from the aforementioned tests was used to distinguish and identify any trends in the photodecay and/or fluorescence of the optical brighteners and tryptophan.

## *3.2 Site Sample Collection and Analysis*

Samples were gathered from the Meurthe River for each of 7 days. Samples 0 and 1 were taken from bridges upstream from the wastewater treatment plant. Sample 2 was taken from the area of overflow from the plant's primary treatment; sample 3 was taken directly from the effluent of the plant; sample 4 was taken further down the river from the effluent and sample 5 was taken from a pipe approximately 10 meters downstream from sample 3. Samples of the plant overflow (2 and 5) were only taken when actual overflow was present. Each sample was filtered to remove particulate matter and synchronous spectra of each were generated. Samples were then exposed to UV light for 2 hours and after their removal from the light, another synchronous spectrum of each was generated which can be compared to the pre-UV irradiation spectrum of the sample to determine the occurrence of photodecay and hence, the

presence or absence of tryptophan.

Non-irradiated samples of river water from each collection point were tested for ammonium content in terms of mg/L by adding 2 drops of mineral stabilizer, 2 drops of dispersing agent and 400 µl of Nessler Reagent to each sample. Ammonium content was determined by measuring the absorbance at 425 nm of every sample and the resulting calibration curve was used to determine the ammonium content (in mg/L) for each sample.

Samples were then collected from a variety of sites along the Moselle River on two separate days, approximately 40 samples each day. These samples were then analyzed in the same fashion as the water from the Meurthe River: filtration, synchronous spectra, UV irradiation and then additional (post-UV) synchronous spectra were generated to determine the amount of photodecay. Ammonium content of these samples was also determined, in the manner previously mentioned.

Raw wastewater samples were collected from the treatment plant along the Meurthe over 2 24-hour periods, in both 30- and 15-minute intervals. These were analyzed by aforementioned procedures to determine the COD and ammonium content, as well as the presence or absence of optical brighteners and tryptophan.

# CHAPTER 4: RESULTS

This section summarizes the results of UV Irradiation Tests of several optical brighteners, laundry detergents, and washing liquids. In addition, results of UV irradiation tests, UV spectrums, and nitrate calculations from the field samples of the Meurthe and Moselle Rivers are presented in this section.

## *4.1 UV Irradiation Tests*

The UV Irradiation tests allowed insight into the sensitivity of optical brighteners and, thus, cleaning liquids that eventually contribute to gray waters. Furthermore, it provided information regarding any trends, if any, of photodegredation.

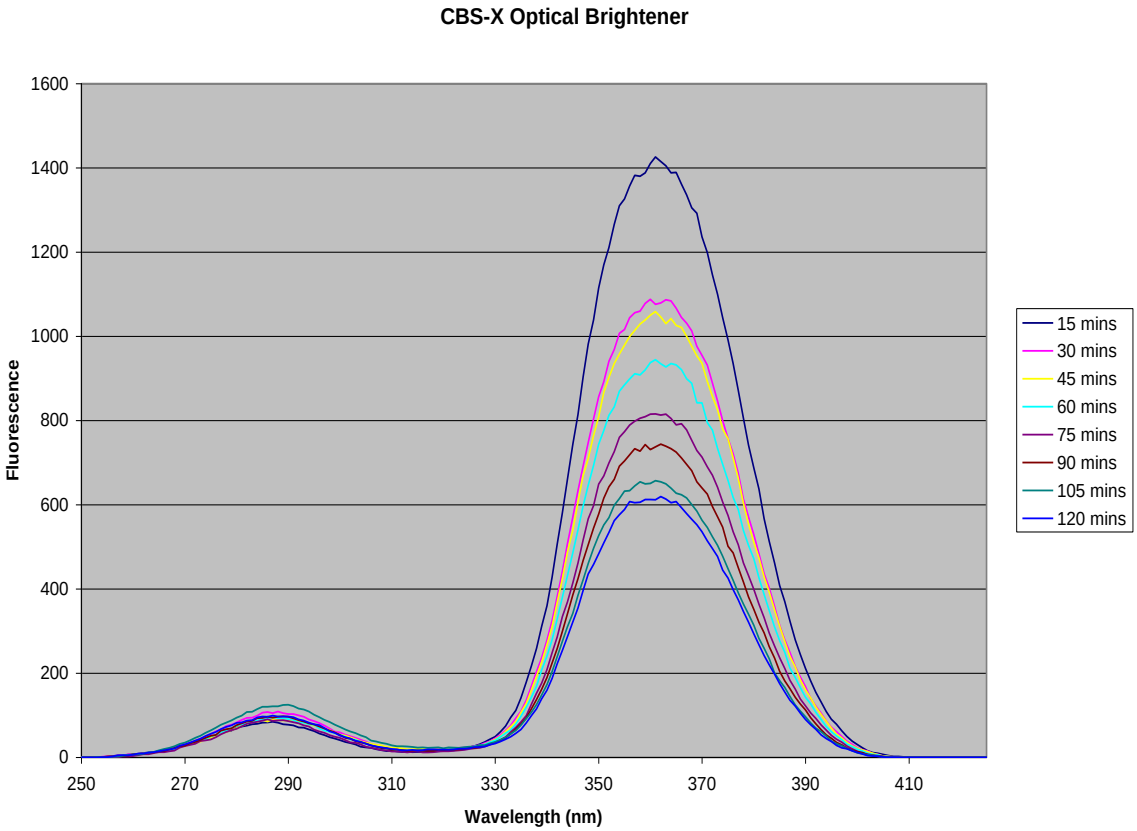


Figure 2: CBS-X Optical Brightener Dilution 1000 UV Irradiation Test

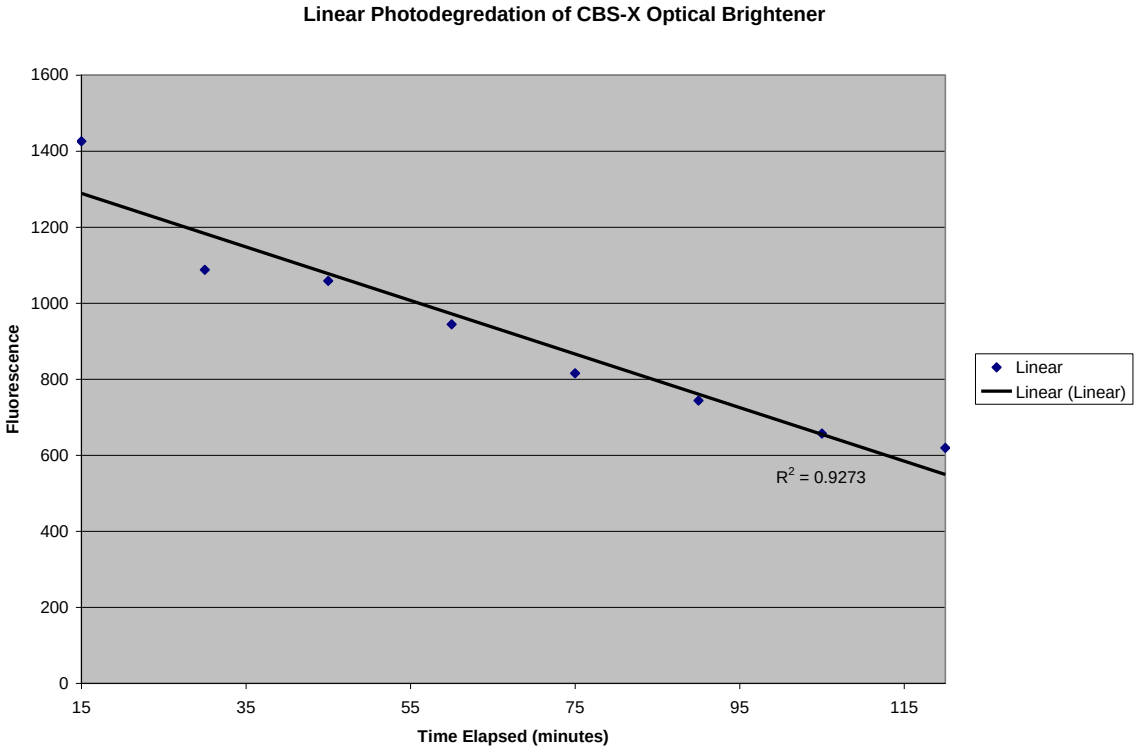


Figure 3: Linear photodegredation of CBS-X Optical Brightener

The use of ultraviolet light irradiation to observe any trends in photodegredation properties of optical brighteners revealed that most optical brighteners showed sensitivity to ultraviolet light. However, some optical brighteners showed no sensitivity, such as FB28. This result can be seen in Figure 8 of Appendix E. The DAS and CBS-X optical brighteners each showed a pattern of degradation when subjected to UV Irradiation. Furthermore, the DAS and CBS-X optical brighteners showed a linear trend of photodegredation, as seen in Figures 2 and 3 for DAS (refer to Appendix E), and as seen in Figures 6 and 7 for CBS-X. The results from the optical brighteners mean that the presence of optical brighteners in gray and yellow waters is able to be detected through means of UV Irradiation.

### 4.1.1 Meurthe River

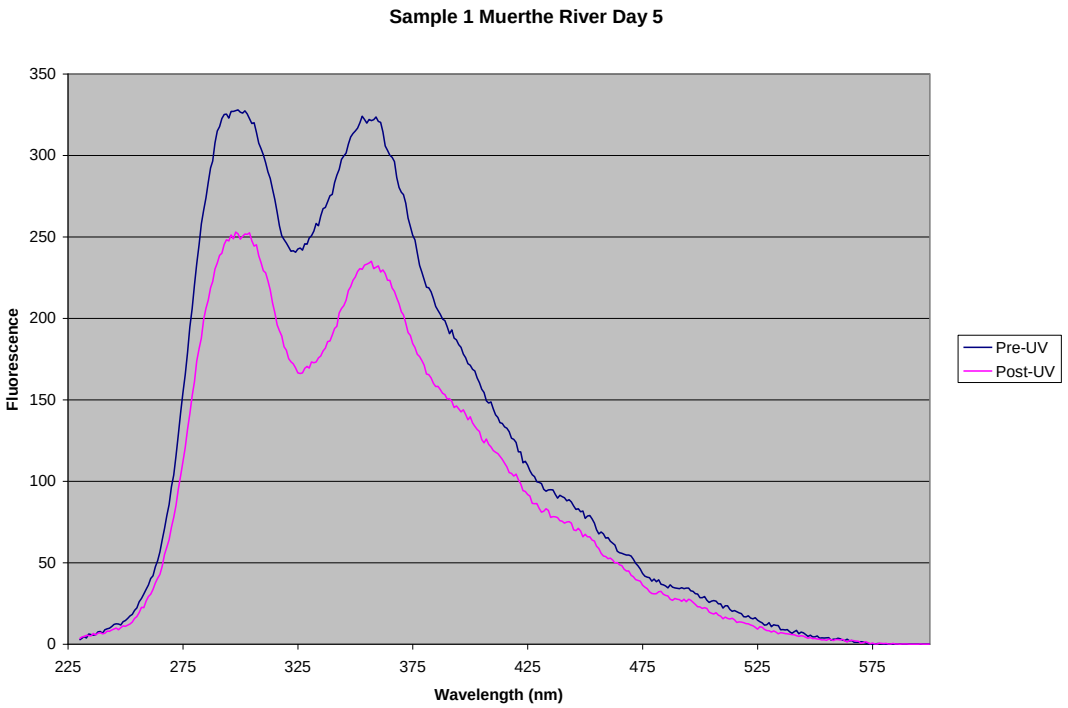


Figure 4: Site Sample 1 from the Meurthe River Day 5

Optical brighteners are present in a vast majority of laundry detergents and washing liquids. Therefore, these products were subjected to the same UV irradiation tests as the optical brighteners in order to detect their existence in these products. The laundry color brightener, whitener and brightener, and whitewash detergents showed no clear linear degradation after UV irradiation. The same was also the case for the carwash detergent, meaning there are no optical brighteners in these products that are sensitive to UV irradiation. The Ariel clothes washing liquid, however, did show sensitivity to the irradiation (refer to Figure 4). In fact, the photodegredation trend was linear, as seen in Figure 5. This means that there is a presence of irradiation-sensitive brighteners in Ariel cloth washing liquid. Hence, it was possible to detect the presence of optical brightener and, therefore, washing liquids in gray waters through the use of UV irradiation and UV spectroscopy.

### 4.1.2 Moselle River

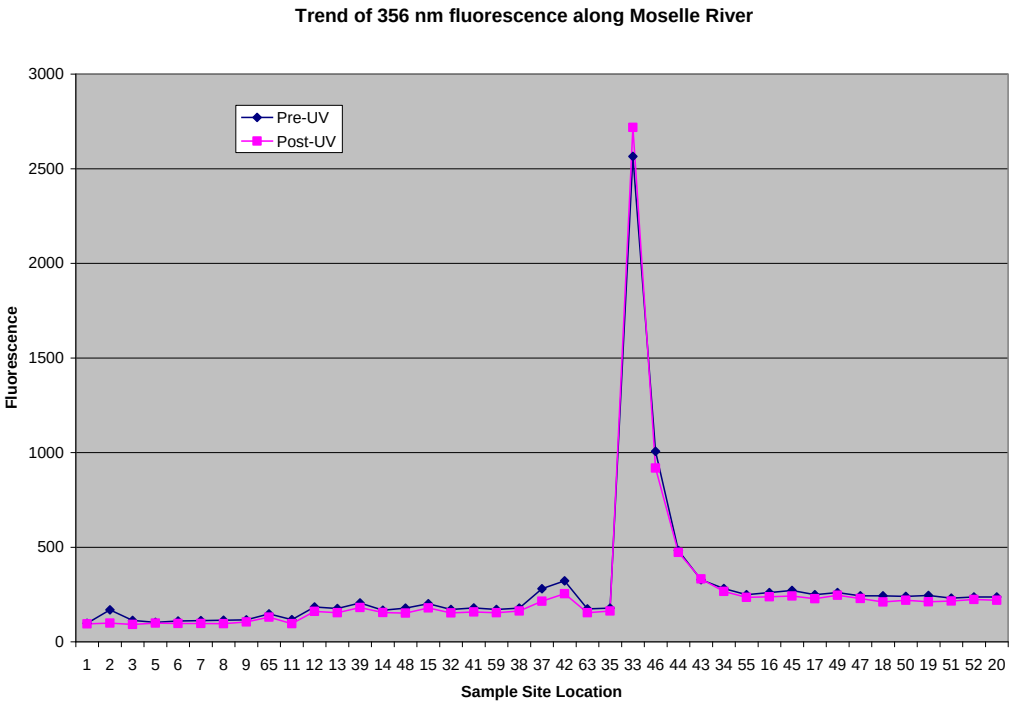


Figure 5: Sequential trend for fluorescence at 356 nm along the Moselle River

The Moselle River was tracked sequentially at 290 nm and 356 nm wavelengths in order to determine the areas of greatest tryptophan and humic acid content along the river. The points that had the highest peaks for tryptophan were at the Site Samples 42 and 37, as evident in Figure 60. Site Sample 42 is the urban wastewater discharge plume and Site Sample 37 is directly upstream from that; therefore, it was a clear indication of the presence of tryptophan at those points along the river. The points showing the strongest evidence for the presence of humic acid were Site Samples 33, 46, and 43, as evident from Figure 61. Site Sample 33 is the discharge from the paper mill wastewater treatment plant. The very large fluorescence peak at Site Sample 33 is due to the humic acid found in wood. The tryptophan-like

fluorescence at these peaks is likely due to the humic acids, as well as the overlapping of peaks.

Table 1: Data for Moselle River Tributaries

| Pollution Information for Tributaries along the Moselle River | | | | |
|---|---|---|---|---|
| Tributary | 290 nm (Before Decay) | 356 nm (Pre-Decay) | COD Surrogate at 254 nm | Ammonium Content |
| AF01 | 164.1 | 150.1 | 0.0661 | 1.5852 |
| AF02 | 236.1 | 171.7 | 0.1056 | 1.6541 |
| AF03 | 234.1 | 240.9 | 0.1876 | 0.6203 |
| AF04 | 237.9 | 186.3 | 0.0989 | 1.0338 |
| AF48 | 140.8 | 108.4 | 0.0296 | 1.3784 |
| AF05 | 251.9 | 183.6 | 0.1265 | 1.3095 |
| AF06 | 231 | 169.5 | 0.1112 | 2.4811 |
| AF07 | 213.6 | 163.4 | 0.0659 | 1.7230 |
| AF08 | 270.1 | 162 | 0.0879 | 1.3784 |
| AF10 | 246.7 | 152.1 | 0.0514 | 0.8270 |
| AF12 | 133 | 125.5 | 0.0365 | 1.4473 |
| AF13 | 270.1 | 849.4 | 0.1149 | 0.8960 |
| 67 | 182.8 | 196.6 | 0.0695 | 0.8270 |
| 70 | 160.5 | 151.6 | N/A | 1.2406 |

As seen in Table 2, the tributaries that run into the Moselle River contributed a higher amount of fluorescence, on average, than what was found in the river itself. The amount of tributary fluorescence at 356 nm, which is indicative of optical brighteners and humic acid, was about the same as that from the river; therefore, the tributaries were not deemed contributing factors to the presence of humic acids or optical brighteners. Additionally, since the relative volumes of the tributaries accounted for are exponentially less than that of the main river, it was determined that tributary fluorescence did not contribute notably to the overall fluorescence in the Moselle River.

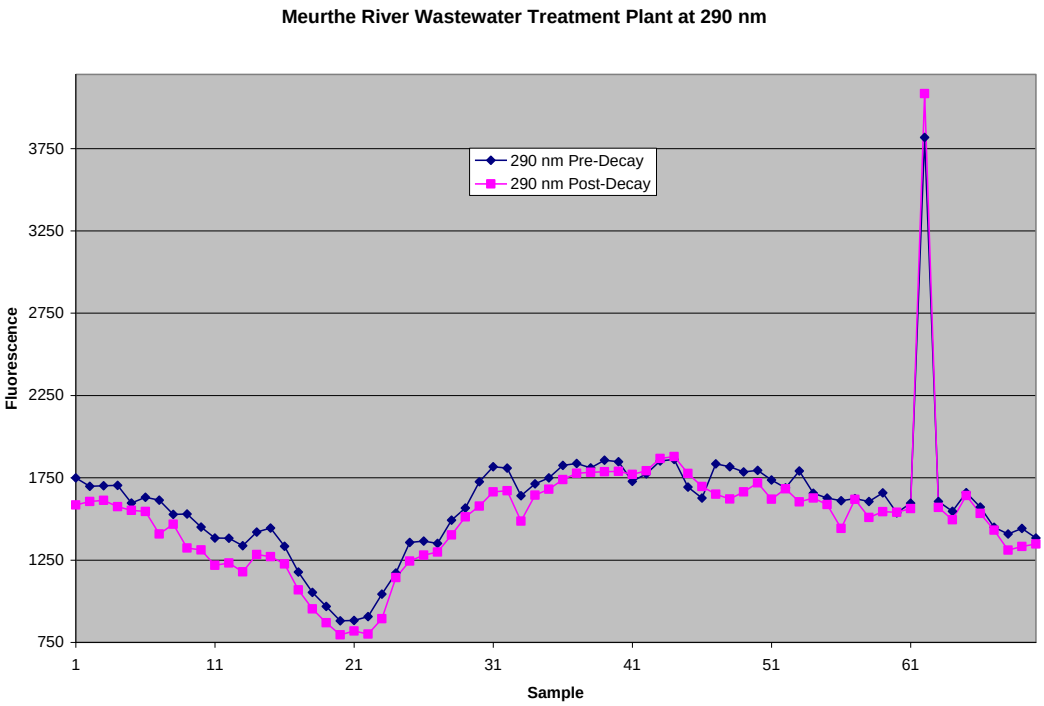


Figure 6: Fluorescence Trend versus Time at 290 nm for the Meurthe River Wastewater Treatment Plant

The presence of tryptophan was characterized by a peak of fluorescence at a wavelength of 290 nm in the synchronous spectra. There are also some optical brighteners that have peaks at this same wavelength. In order to differentiate between the presence of optical brightener and tryptophan in an actual sample of water, UV irradiation tests were performed. The presence of tryptophan was confirmed when there was little to no obvious photodegredation over time at the 290 nm peak in any of the products and optical brighteners tested, since tryptophan is not sensitive to UV irradiation. There was slight photodegredation with the DAS and CBS-X optical brighteners and Ariel clothes washing liquid, as expected. However, the total amount of degradation decreased significantly with the presence of tryptophan as seen in Figures 12, 13, and 16, suggesting that UV irradiation is an effective method to differentiate between yellow and gray wastewaters.

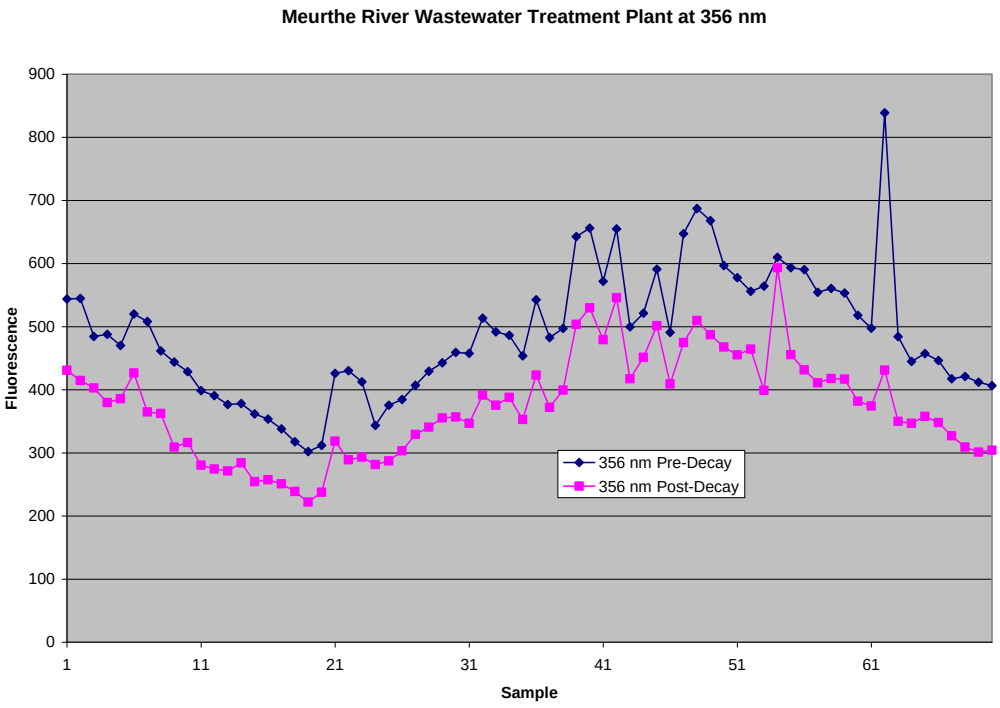


Figure 7: Fluorescence Trend versus Time at 356 nm for the Meurthe River Wastewater Treatment Plant

As evident in Figure 64, the fluorescence levels at 290 nm varied throughout the course of a day. The sampling began at 9 p.m. when the fluorescence was 1750. Fluorescence exhibited a steady decrease throughout the course of the night until 7 a.m., correlating with typical water usage. After 7 a.m., the fluorescence increased steadily until 1:30 p.m., at which point it began to decrease slightly and continued to throughout the afternoon and evening. After subjection of the samples to UV irradiation, each of them showed only marginal to no decrease in fluorescence, suggesting the presence of yellow water or optical brighteners not sensitive to UV irradiation.

Fluorescence levels at 356 nm also varied throughout the duration of one day of raw wastewater sampling. As with the fluorescence at 290 nm, the fluorescence at 356 nm decreased steadily from 9 p.m. until 7 a.m. From 7 a.m. on, the fluorescence

levels increased more steeply than that of 290 nm, until 2:45 p.m. at which they drop off. This was also consistent with typical water usage timing. In addition to yellowwater, UV irradiation data suggested the presence of graywaters in the raw wastewater samples.

The ammonium content for the wastewater treatment plant samples followed a similar trend as those found in the UV spectra and fluorescence data. As seen in Figure 67 in Appendix E, the ammonium trend decreases from 9 p.m. until 7 a.m., at which point it increases again until mid-day, followed by another steady decrease.

# CHAPTER 5: Conclusions and Recommendations

Although the scope of experimentation was limited to just two rivers in France, it was possible to make some valuable determinations that can be applied to a variety of different waterways, regardless of surface water type or location.

Initially, samples were taken from the Meurthe River and analysis yielded a significant amount of tryptophan, characteristic of yellow water. In addition to tryptophan, a number of peaks attributable to optical brighteners were identified by synchronous fluorescence combined with the photo decay technique, suggesting that the samples included gray water as well as yellow. These findings were confirmed by the presence of a large wastewater treatment plant along the Meurthe that discharges effluent directly into the river, and thus it was concluded that both gray and yellow waters were present and that it is possible to distinguish between the two.

The validity of this means to track sources of contamination was further corroborated by experiments done on samples from the Moselle River. We were able to identify optical brighteners by the same methods as used for the Meurthe River samples and from that, concluded that there is gray water present in the river. In addition to optical brighteners, a number of spectral peaks did not exhibit decay in the post-UV comparison. This component of the sample was therefore differentiable from the decayed optical brighteners in the water. As there is a paper mill located alongside the Moselle that discharges large quantities of waste into the water, these peaks were deemed to be representative of humic acid, which, like tryptophan, does not decay.

Since the non-decaying tryptophan (or humic acid) can be easily distinguished from the decayed optical brighteners after UV exposure, identification of separate

components is a simple and straightforward process. Once a sample is exposed to UV irradiation and a post-exposure synchronous fluorescence spectrum is generated and compared to the pre-exposure spectrum, optical brighteners can generally be distinguished from tryptophan, which does not photodecay.

DAS, one of the two key optical brighteners found in 98% of laundry detergents, is one of the many brighteners that decay in the presence of UV light. However, FB28, the second key optical brightener, does not exhibit any substantial decay even after a significant amount of time under UV light. FB28 and other brighteners that do not photo decay cannot yet be detected by simple methods such as those outlined above.

UV irradiation combined with fluorescent detection proved to be a simplistic and conclusive method of identifying contamination sources. Although further technological development is necessary in order to take advantage of the full capabilities of this tracking technique, the combination of these methods is still a very valuable tool at present to detect and differentiate the presence of yellow and gray wastewaters.

# Appendix A: Excitation Emission Matrices

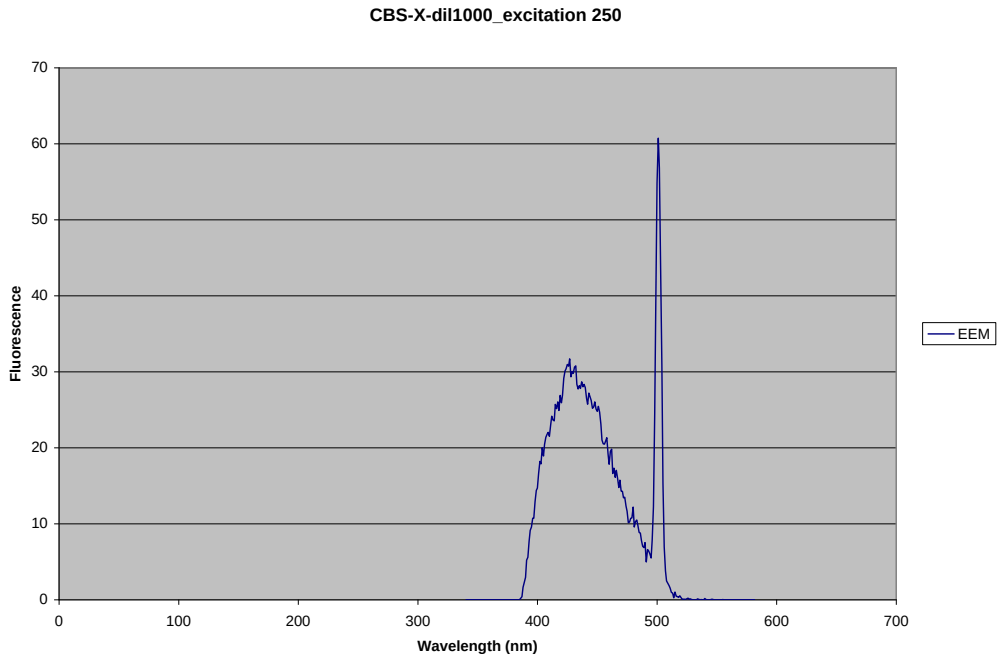


**Figure 8: Excitation Emission Matrix of CBS-X at 250 nm**

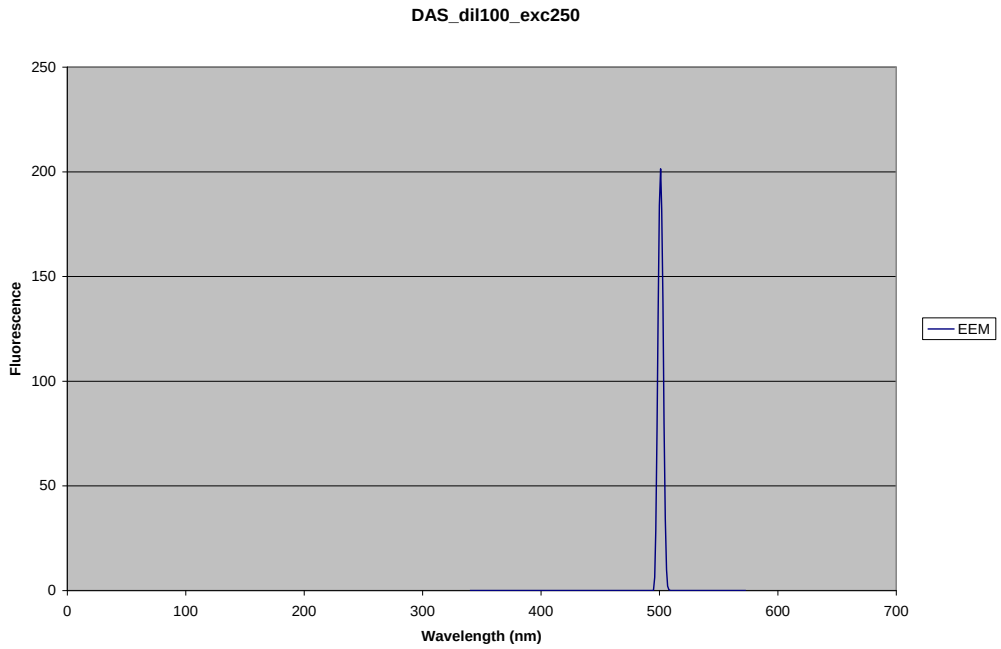


**Figure 9: Excitation Emission Matrix of DAS at 250 nm**

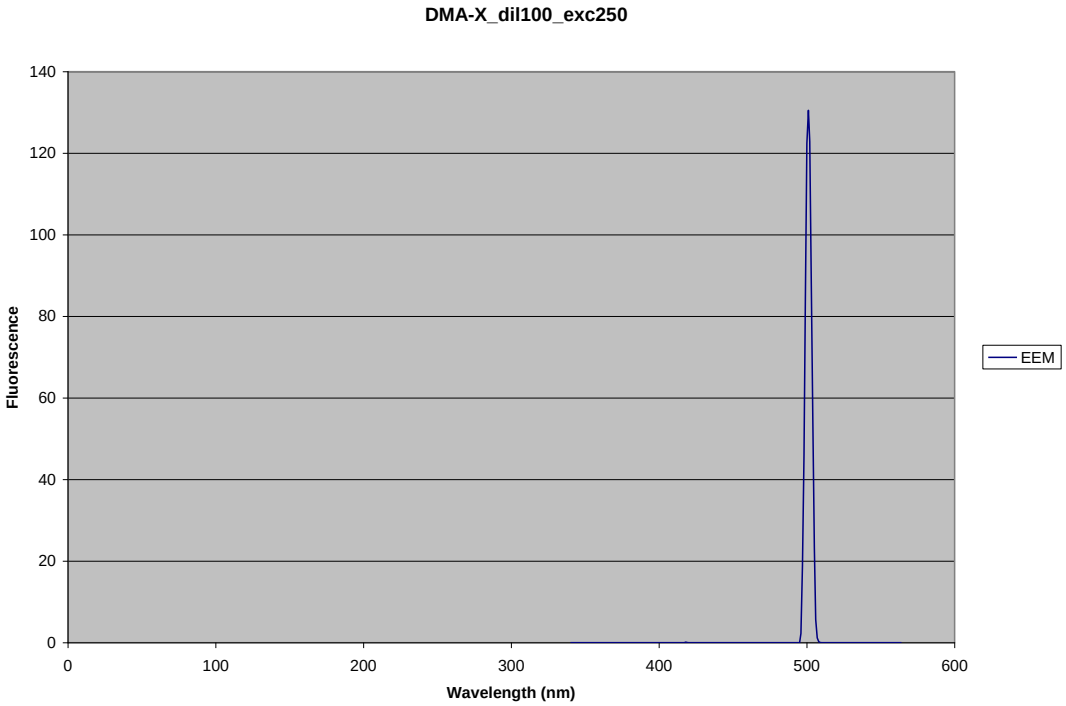


**Figure 10: Excitation Emission Matrix of DMA-X at 250 nm**

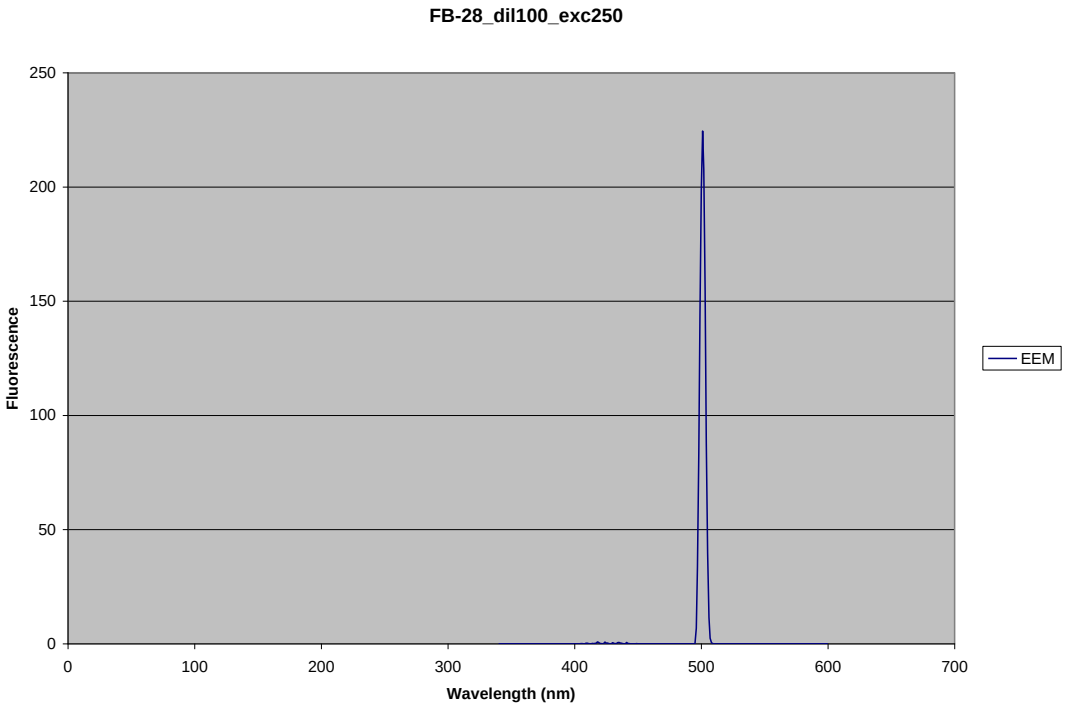


**Figure 11: Excitation Emission Matrix of FB-28 at 250 nm**

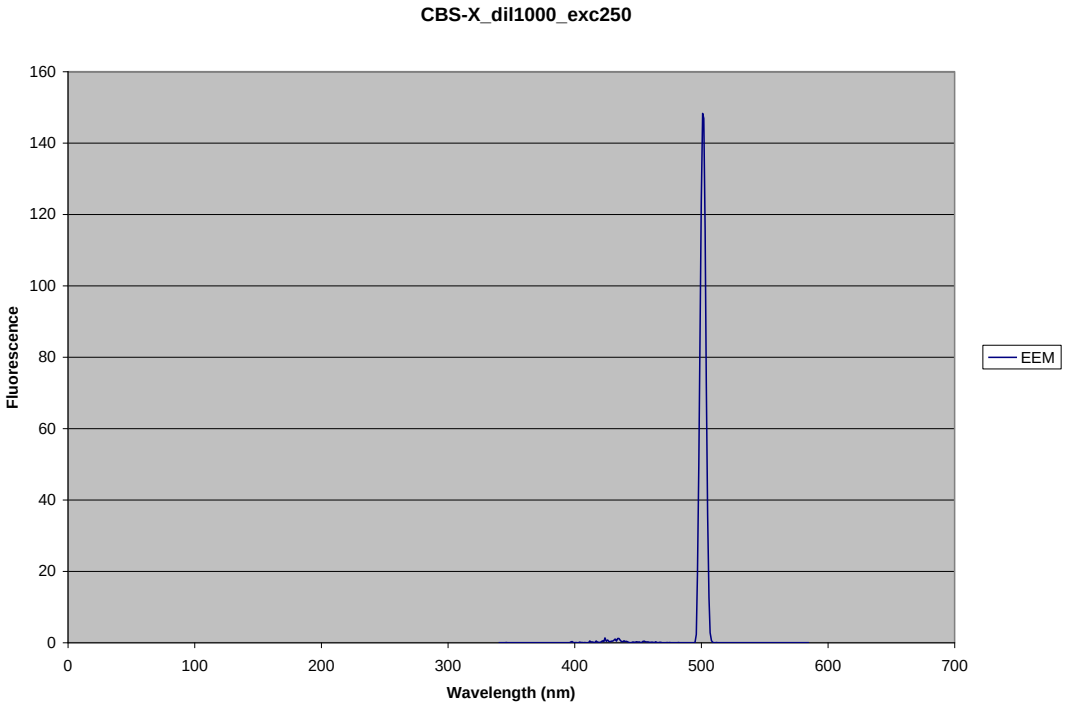


**Figure 12: Excitation Emission Matrix of CBS-X at 250 nm**

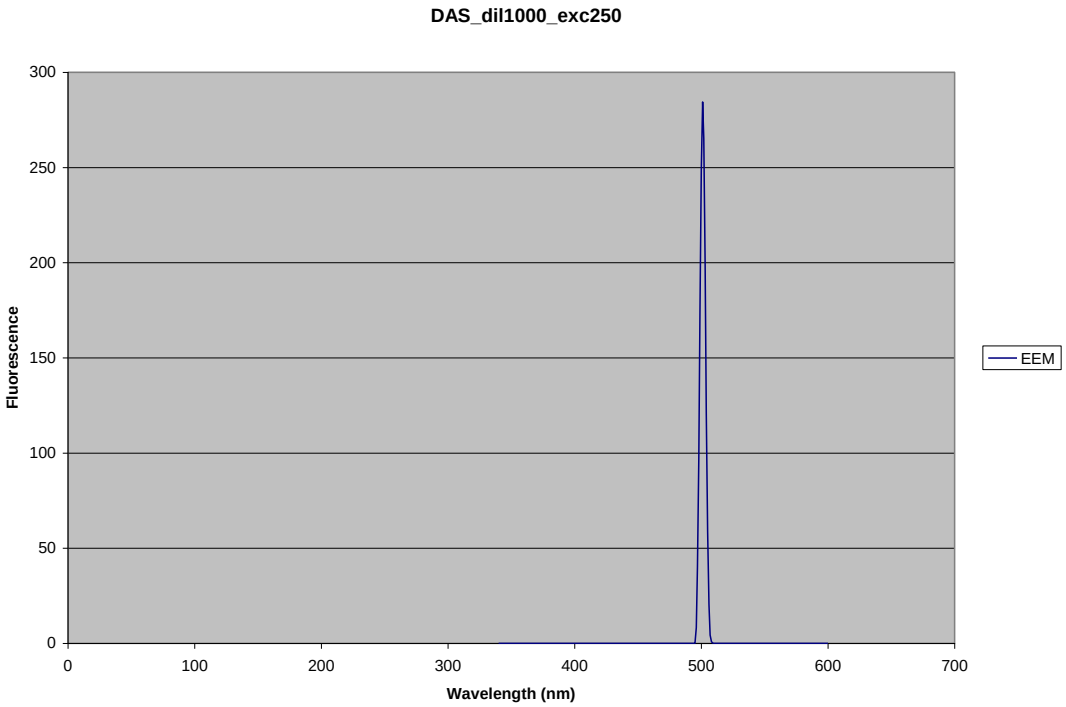


**Figure 13: Excitation Emission Matrix of DAS at 250 nm**

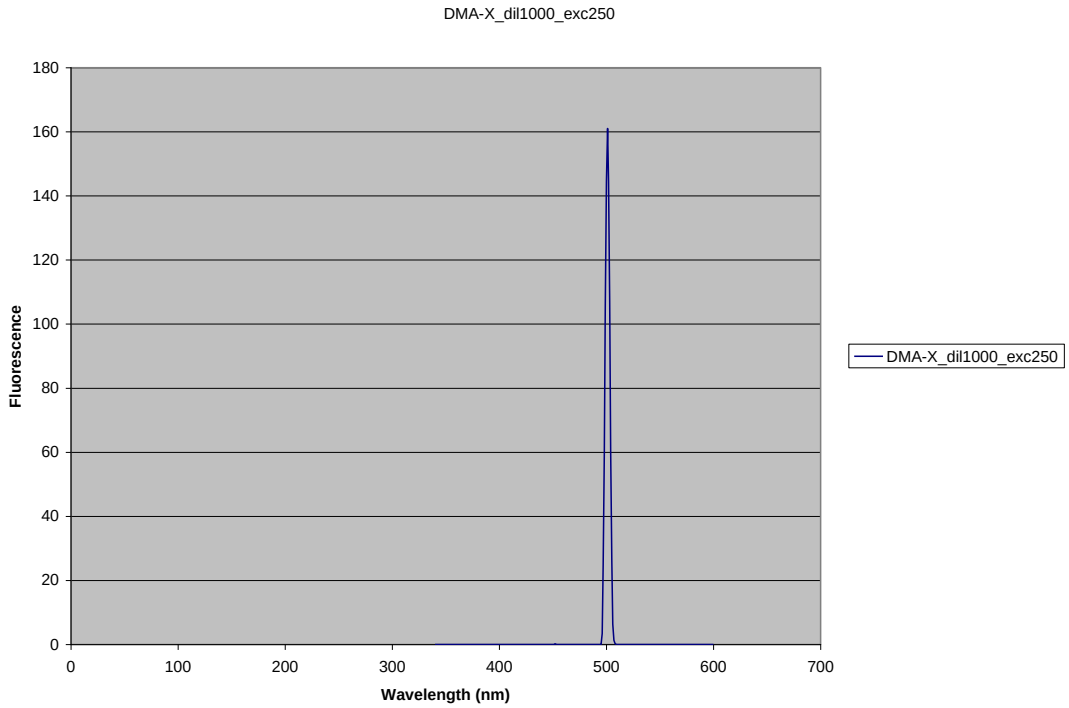


**Figure 14: Excitation Emission Matrix of DMA-X at 250 nm**

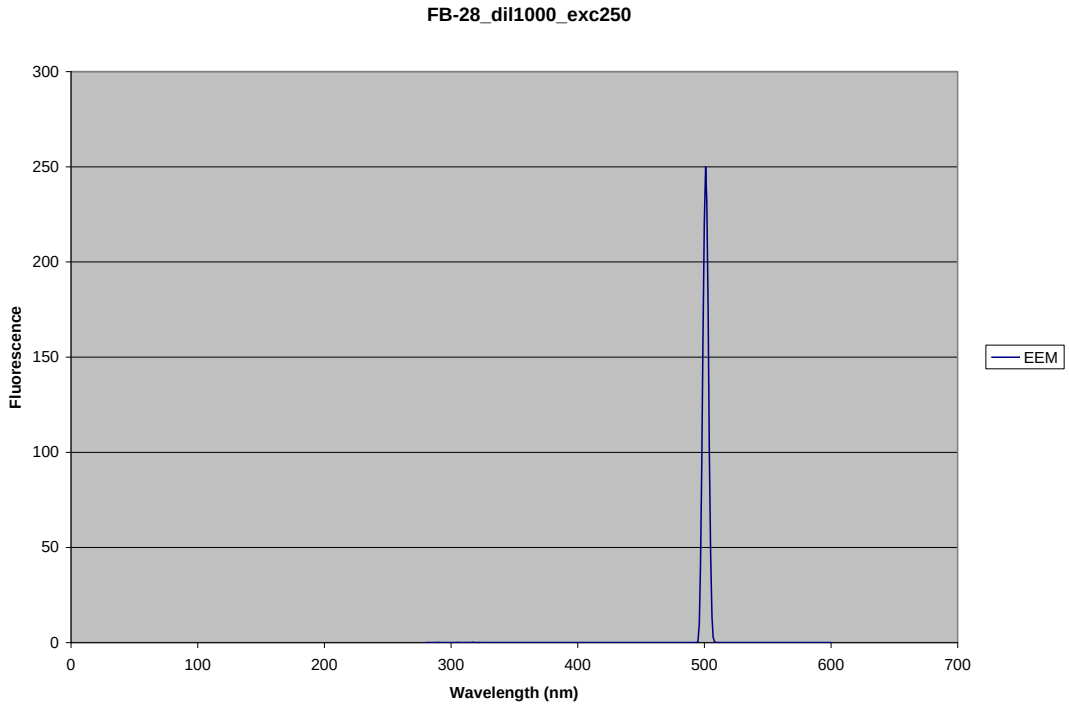


**Figure 15: Excitation Emission Matrix of FB-28 at 250 nm**

# Appendix B: Site Sample Locations for the Moselle River

| Number | Location | GPS Position |
|---|---|---|
| 1 | Source | 47°53.22 N 6°53.32 E |
| 2 | Les sources (Source Marie) | 47°53.21 N 6°52.42 E |
| 3 | Bussang | 47°53.10 N 6°51.25 |
| 4 | Entrée Saint-Maurice | |
| 5 | Pont Jean | 47°51.54 N 6°48.33 E |
| 6 | Croix de la Barange (Fresse) | 47°52 N 6°47.78 E |
| 7 | Le Thillot | 47°52.62 N 6°4.89 E |
| 8 | Ramonchamp | 47°53.53 N 6°44.38 E |
| 9 | Ferdrupt | 47°54.52 N 6°42.35 E |
| 10 | Rupt (Longchamp) | 47°54.46 N 6°39.45 E |
| 65 | Maxonchamp | 47°56.25 N 6°38.43 E |
| 11 | Vecoux (sortie) | 47°59.20 N 6°37.32 E |
| 12 | Eloyes | 48°05.57 N 6°36.46 E |
| 13 | Jarménil | 48°06.64 N 6°34.47 E |
| 39 | Saut du Broc | 48°07.32 N 6°32.56 E |
| 31 | Saut du Broc (amont plage) | 48°07.27 N 6°32.61 E |
| 30 | Saut du Broc (plage) | 48°07.28 N 6°32.69 E |
| 14 | Arches - Archettes | 48°07.34 N 6°31.9 E |
| 48 | Pont N57, amont Soba | 48°08.53 N 6°30.59 E |
| 40 | Stade rugby | 48°08.58 N 6°28.7 E |
| 15 | Passerelle entrée Epinal | 48°09.32 N 6°27.12 E |
| 32 | Passerelle aval Pont Patch | 48°10.39 N 6°26.85 E |
| 41 | Pont République | 48°11.04 N 6°26.65 E |
| 59 | Pont canal | 48°12.44 N 6°26.54 E |
| 58 | Aval DO | 48°12.85 N 6°26.12 E |
| 38 | Aval Michelin | 48°12.84 N 6°26.05 E |
| 37 | Amont Step Epinal | 48°12.90 N 6°26.62 E |
| 42 | Rejet Step Epinal | 48°12.92 N 6°26.62 E |
| 36 | Aval Step Epinal | 48°13.36 N 6°26.58 E |
| 62 | Aval Step Epinal | 48°12.95 N 6°26.65 E |
| 61 | Aval Step Epinal | 48°12.97 N 6°26.65 E |
| 60 | Aval Step Epinal, bras principal | 48°13.08 N 6°26.68 E |
| 35 | Amont rejet NSK | 48°13.45 N 6°26.57 E |
| 33 | Rejet NSK | 48°13.47 N 6° 26.56 E |
| 46 | Panache rejet NSK (Pont autoroute) | 48°13.51 N 6°26.57 E |
| 44 | Panache rejet NSK | 48°13.54 N 6°26.58 E |
| 43 | Panache rejet NSK | 48°13.58 N 6°26.59 E |
| 34 | Aval rejet NSK | 48°13.62 N 6°26.61 E |
| 53 | Amont écluse de Chavelot | 48°14.04 N 6°26.42 E |
| 54 | Aval écluse de Chavelot | 48°14.12 N 6°26.40 E |
| 55 | Passerelle bras Moselle | 48°14.22 N 6°26.36 E |

| | | |
|---|---|---|
| 56 | Aval barrage de Chavelot | 48°14.22 N 6°26.40 E |
| 57 | Face à STEP Thaon | 48°1419 N 6°26.12 E |
| 16 | Thaon-Girmont | 48°15.27 N 6°25.87 E |
| 45 | Amont Châtel – aval Durbion | 48°18.50 N 6°24.15 E |
| 17 | Châtel | 48°18.75 N 6°24.47 E |
| 49 | Portieux | 48°20.73 N 6°20.42 E |
| 47 | Charmes | 48°22.52 N 6°17.79 E |
| 18 | Bainville | 48°26.33 N 6°16.91 E |
| 50 | Bayon | 48°28.68 N 6°18.37 E |
| 19 | Velle | 48°31.78 N 6°16.47 E |
| 51 | Tonnoy | 48°33.04 N 6°14.78 E |
| 52 | Flavigny (intérieur village) | 48°34.02 N 6°11.44 E |
| 20 | Flavigny | 48°34.70 N 6°10.81 E |
| AF01 | Archettes (Ruiss. d'Argent) | 48°07.50 N 6°31.98 E |
| AF02 | Girmont (St Adrian) | 48°15.44 N 6°26.21 E |
| AF03 | Vaxoncourt (Durbion) | 48°17.58 N 6°24.75 E |
| AF04 | Noméxy-Frizon (Avière) | 48°18.61 N 6°22.66 E |
| AF48 | Petit apport près du point 48 | 48°08.53 N 6°30.59 E |
| 66 | Bréhavillers (Moselotte) | 48°01.31 N 6°41.10 E |
| 67 | Jarménil (Vologne) | 48°06.87 N 6°34.27 E |
| 68 | Chéniménil (Vologne) | 48°08.05 N 6°36.22 E |
| 69 | Docelles (Vologne) | 48°08.67 N 6°37.02 E |

# Appendix C: Pre- and Post-UV Data from the Moselle River

Date of Samples: February 14th, 2008

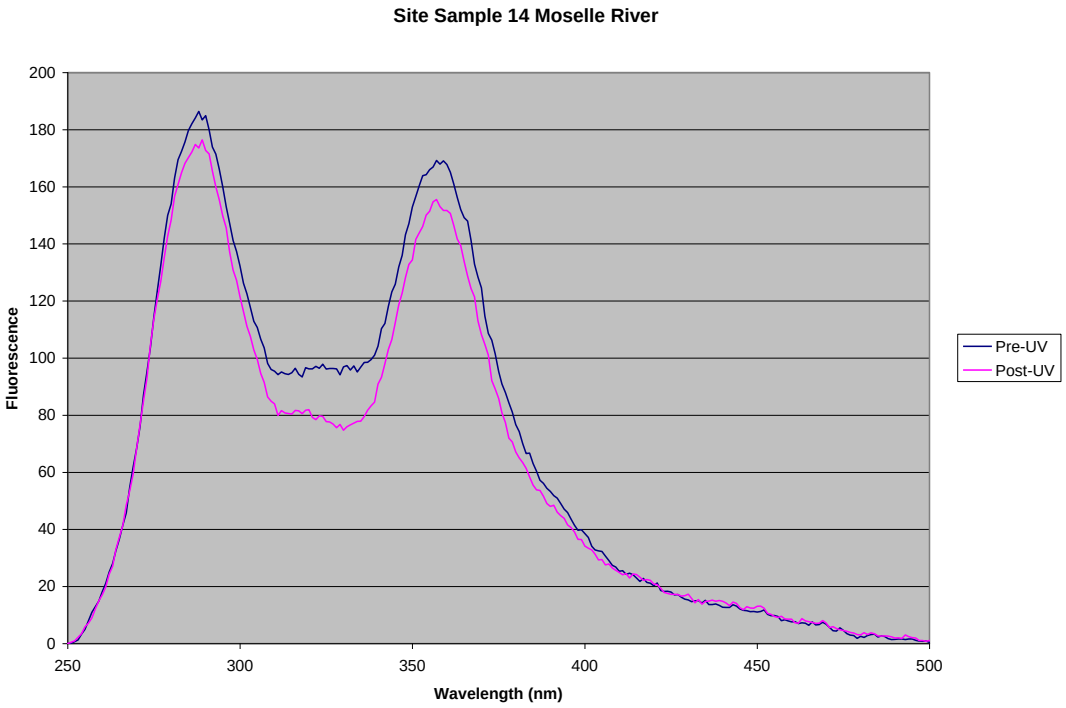


Figure 16: Pre- and Post-UV Comparison of Site Sample 14

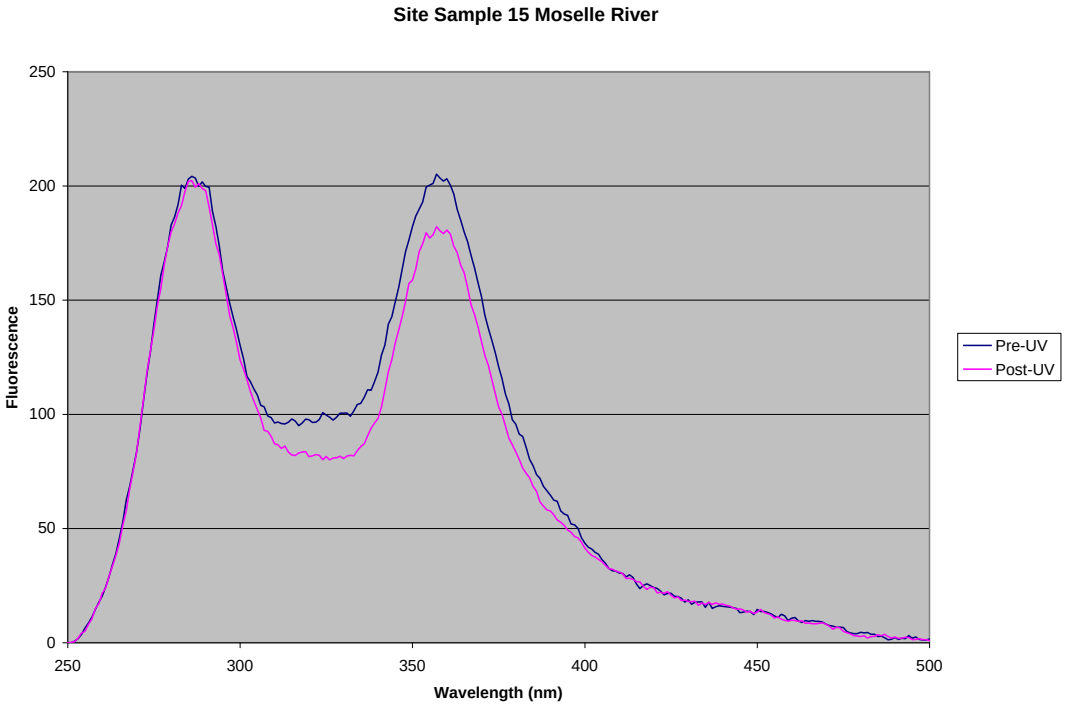


Figure 17: Pre- and Post-UB Comparison of Site Sample 15

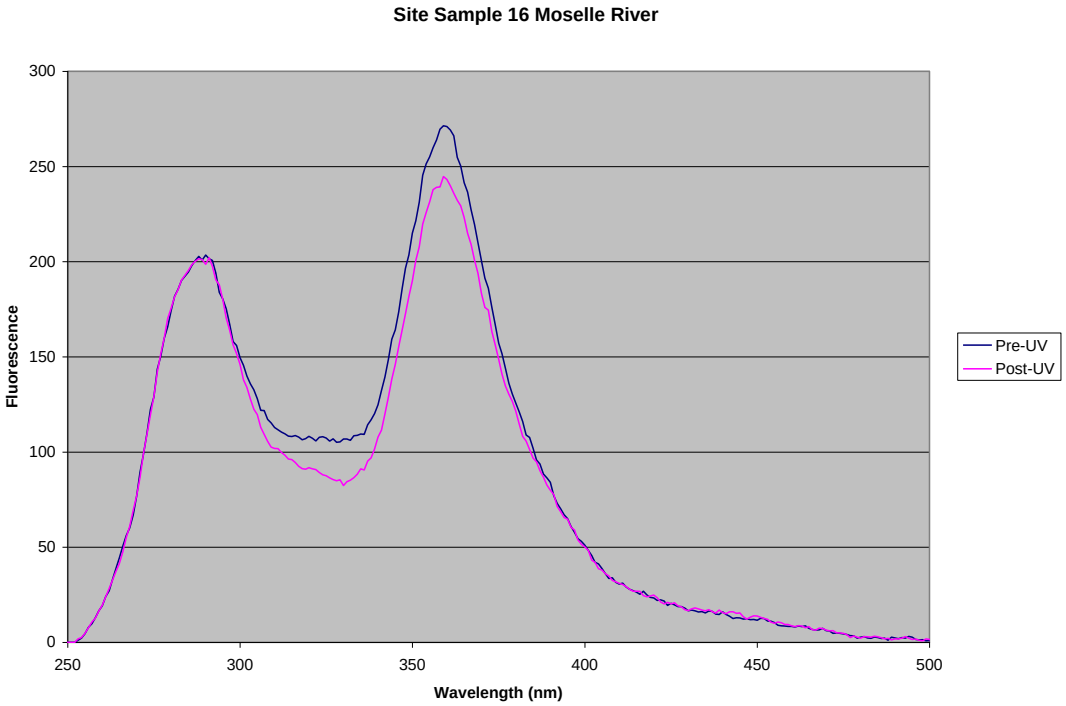


Figure 18: Pre- and Post-UV Comparison of Site Sample 16

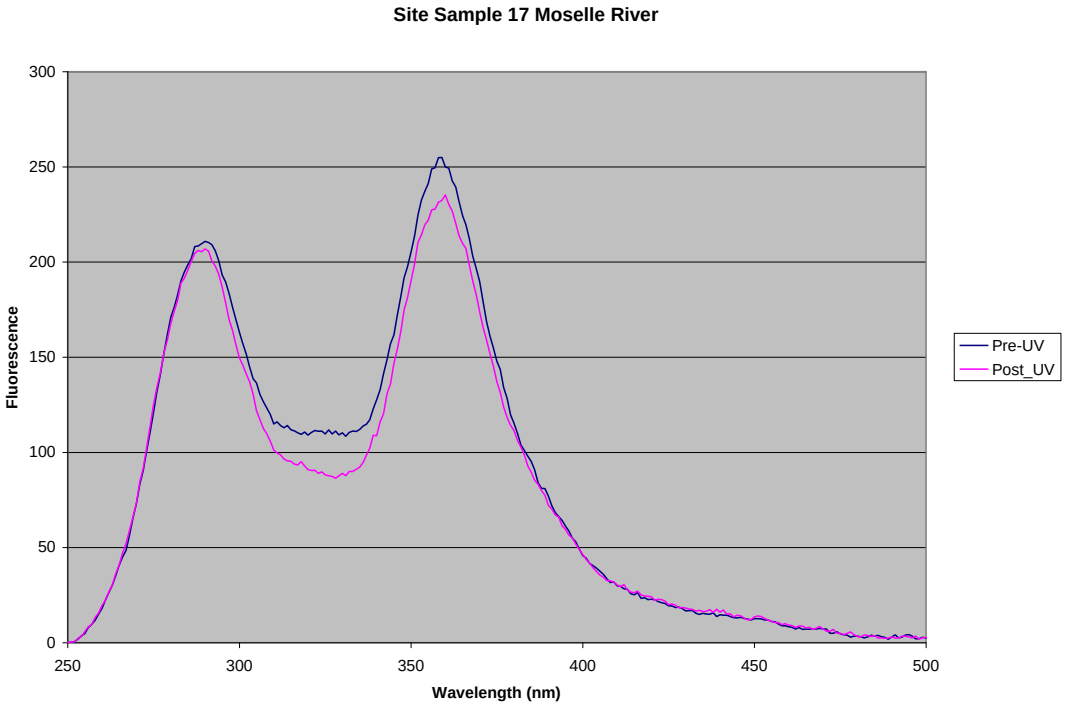


Figure 19: Pre- and Post-UV Comparison of Site Sample 17

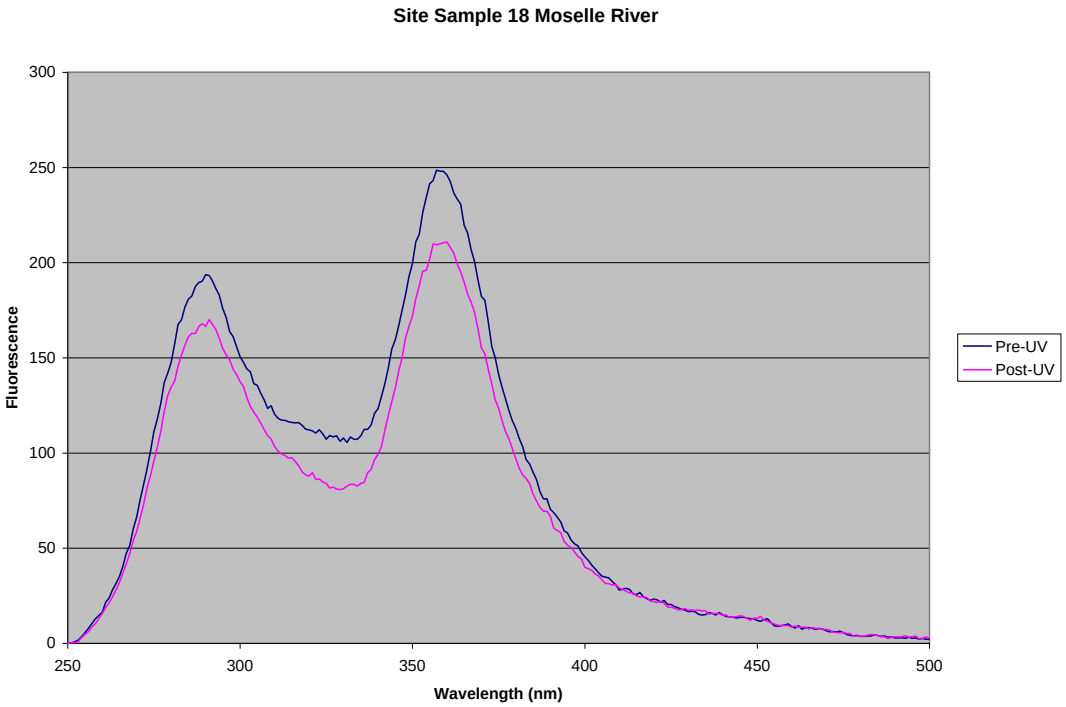


Figure 20: Pre- and Post-UV Comparison of Site Sample 18

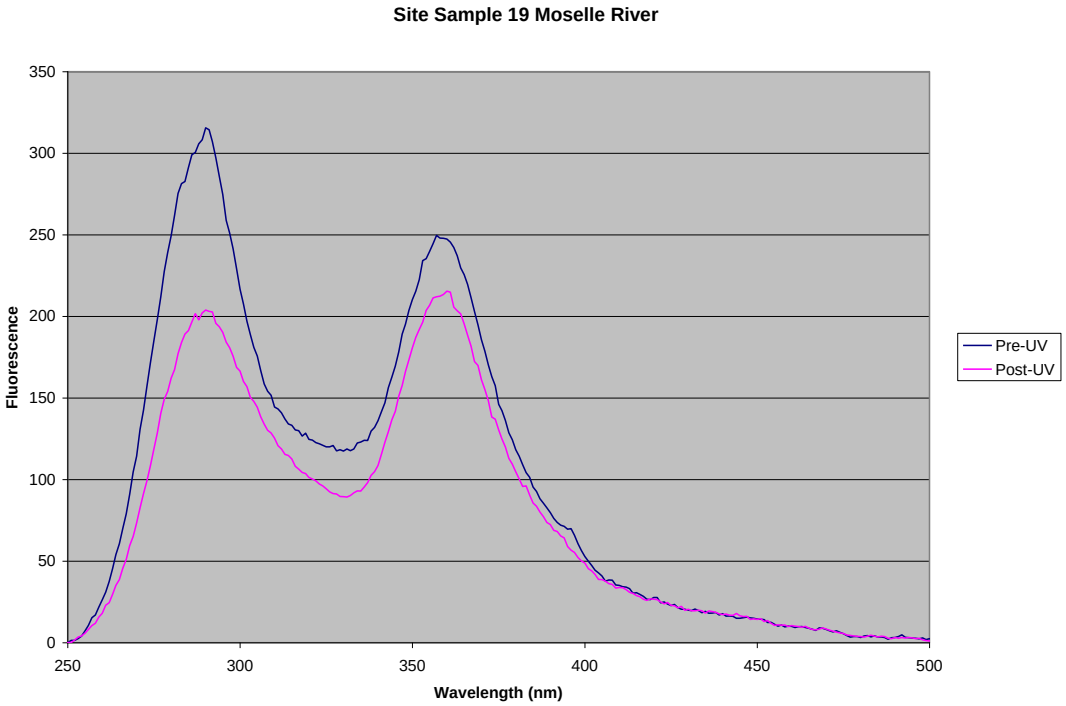


Figure 21: Pre- and Post-UV Comparison of Site Sample 19

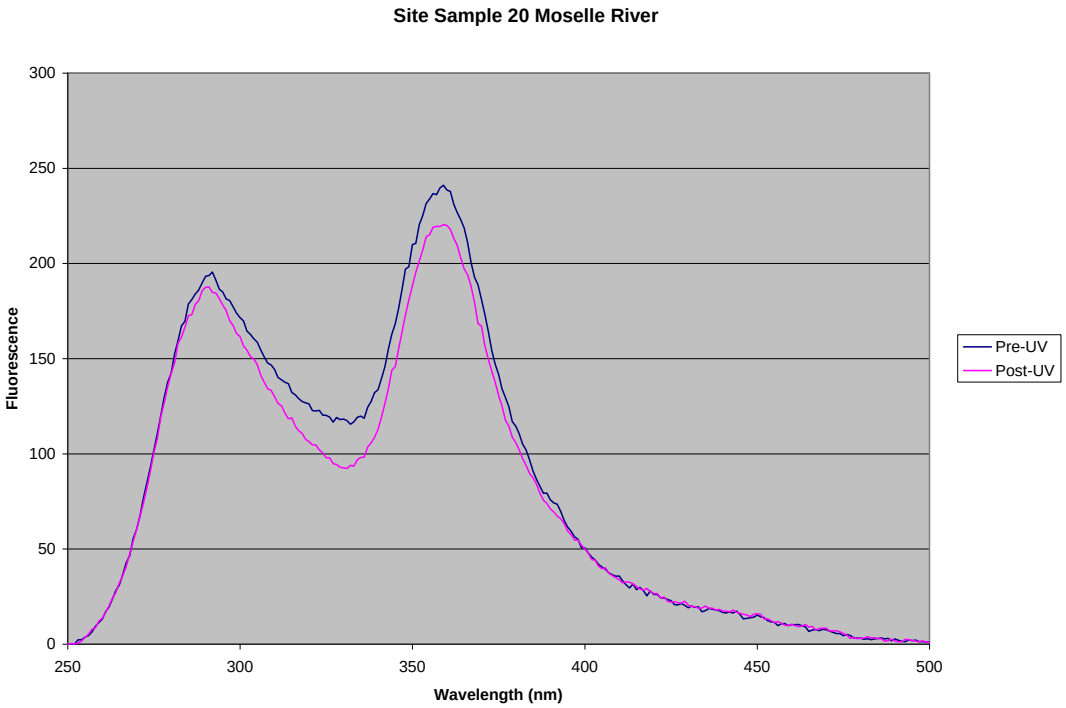


Figure 22: Pre- and Post-UV Comparison of Site Sample 20

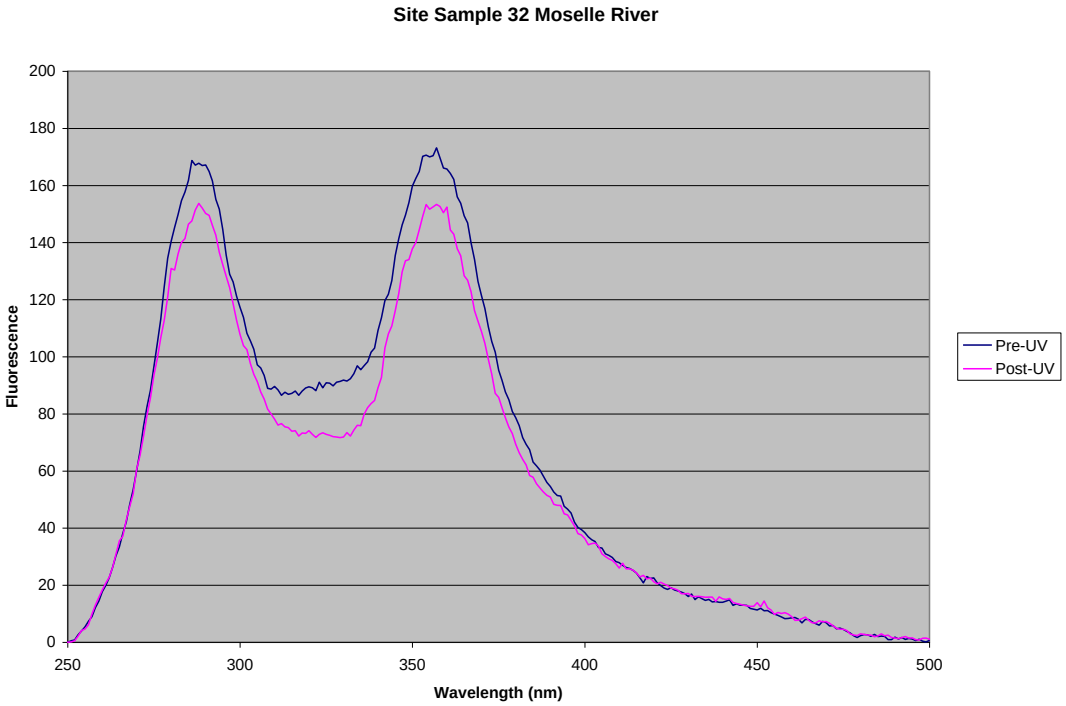


Figure 23: Pre- and Post- UV Comparison of Site Sample 32

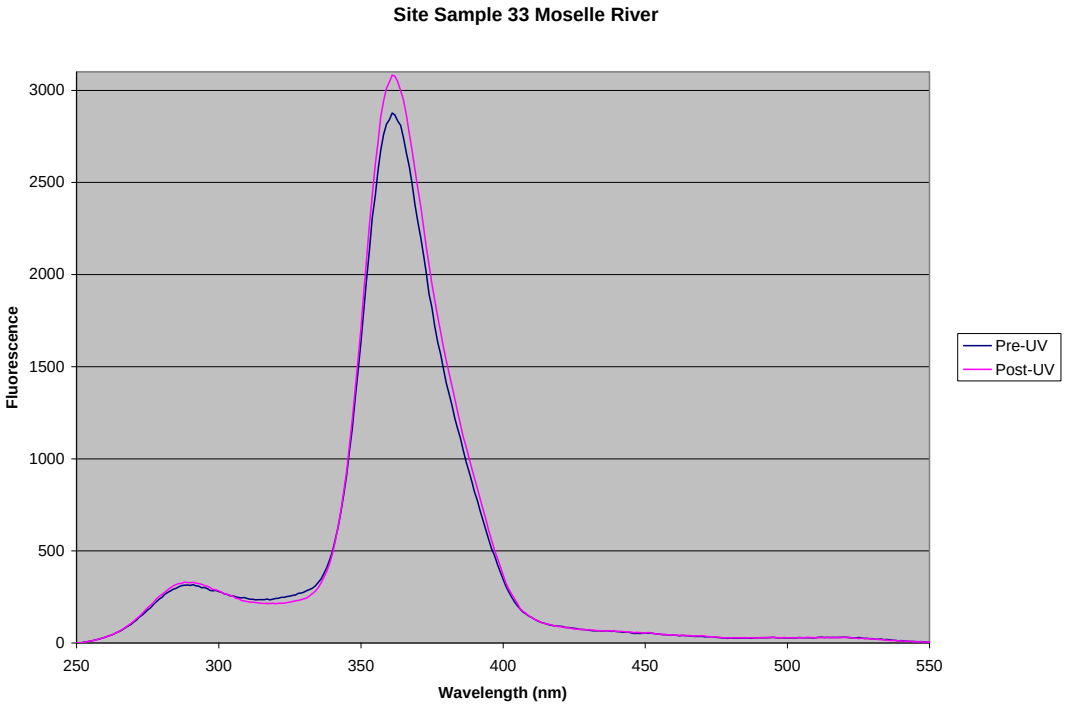


Figure 24: Pre- and Post-UV Comparison of Site Sample 33

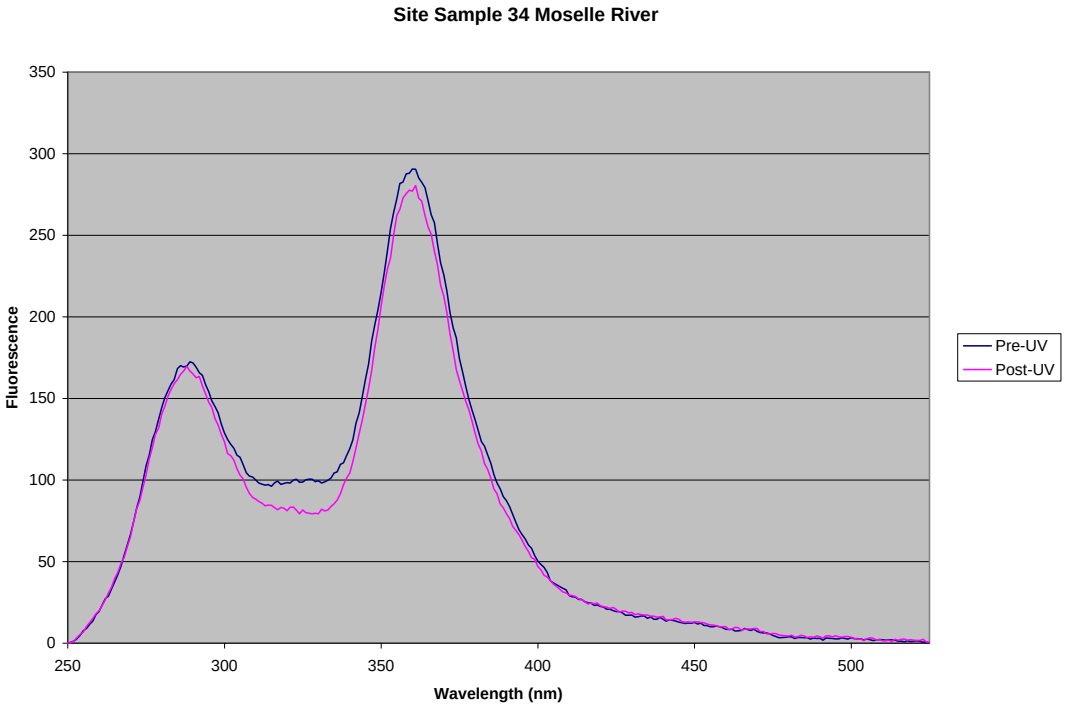


Figure 25: Pre- and Post-UV Comparison of Site Sample 34

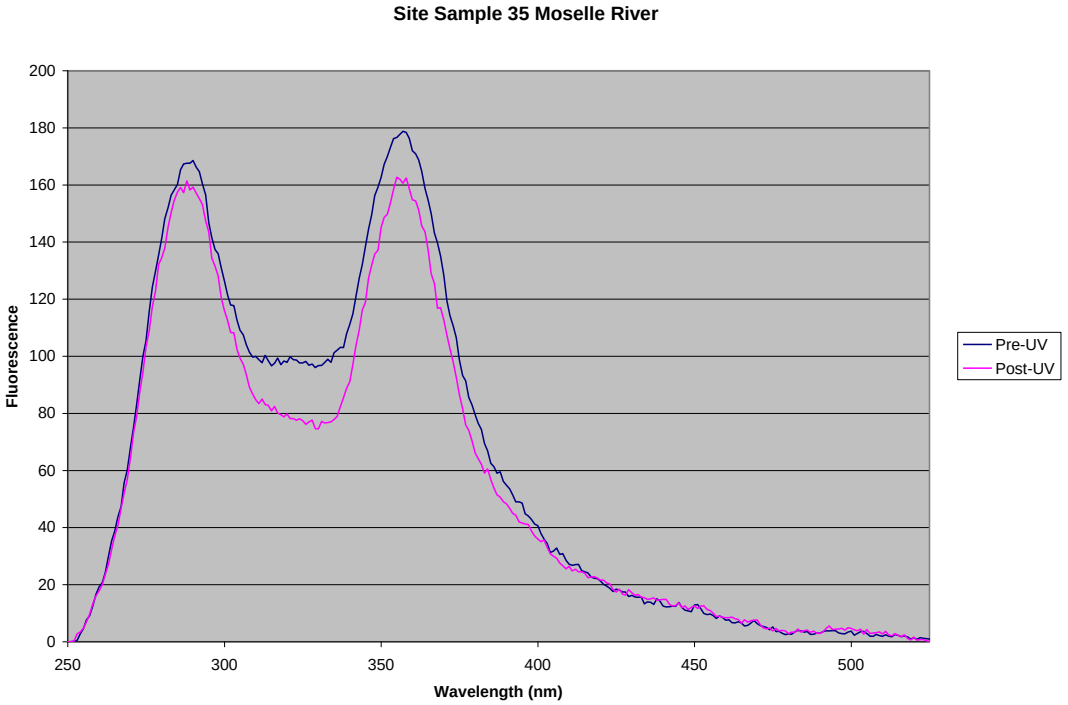


Figure 26: Pre- and Post-UV Comparison of Site Sample 35

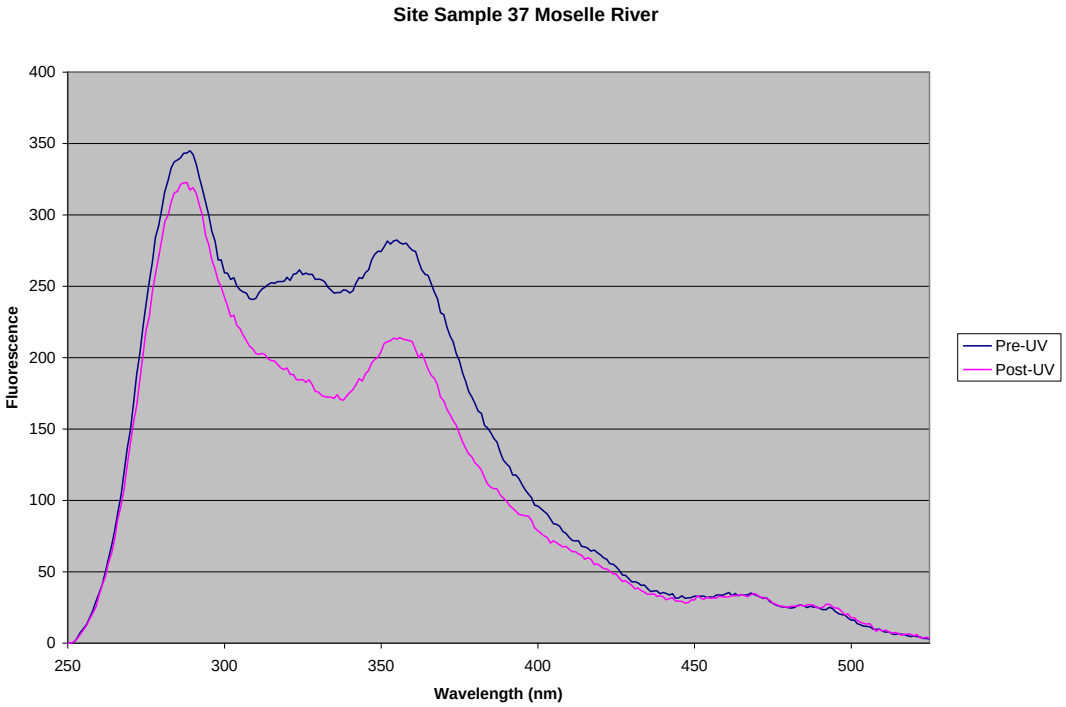


Figure 27: Pre- and Post-UV Comparison of Site Sample 37

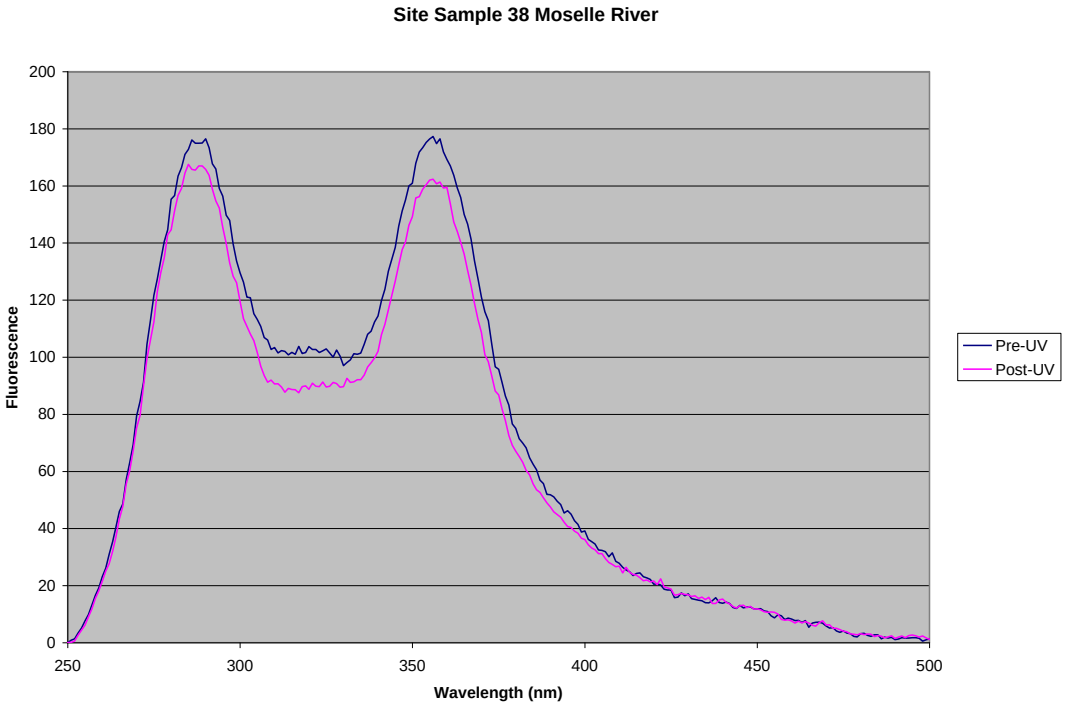


Figure 28: Pre- and Post-UV Comparison of Site Sample 38

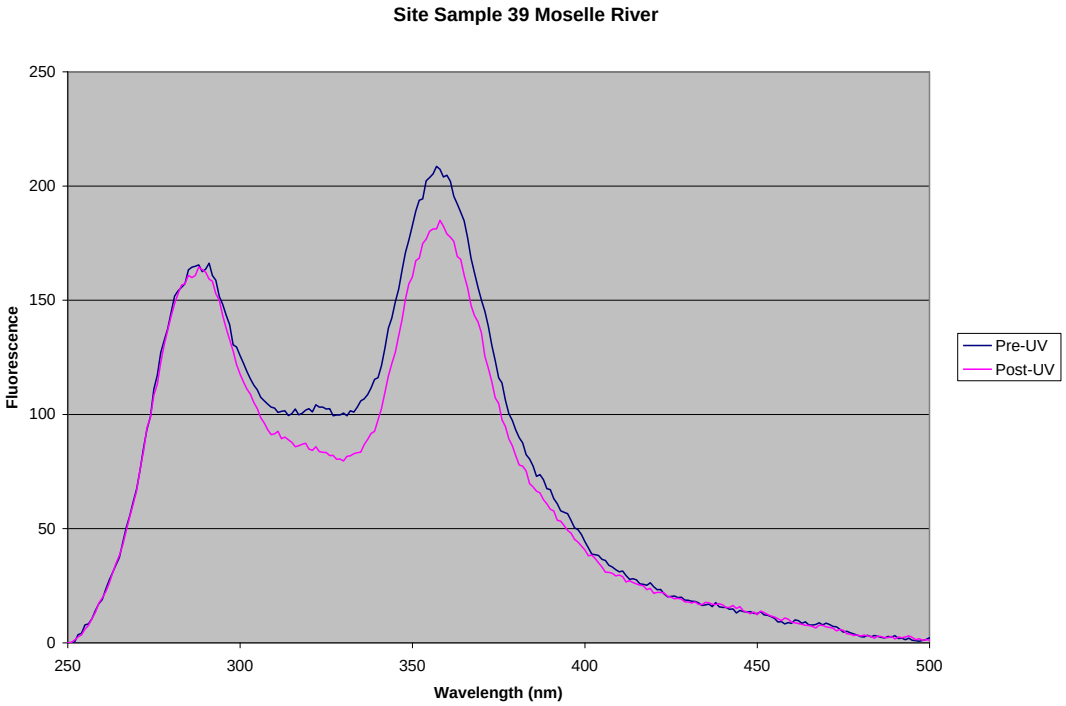


Figure 29: Pre- and Post-UV Comparison of Site Sample 39

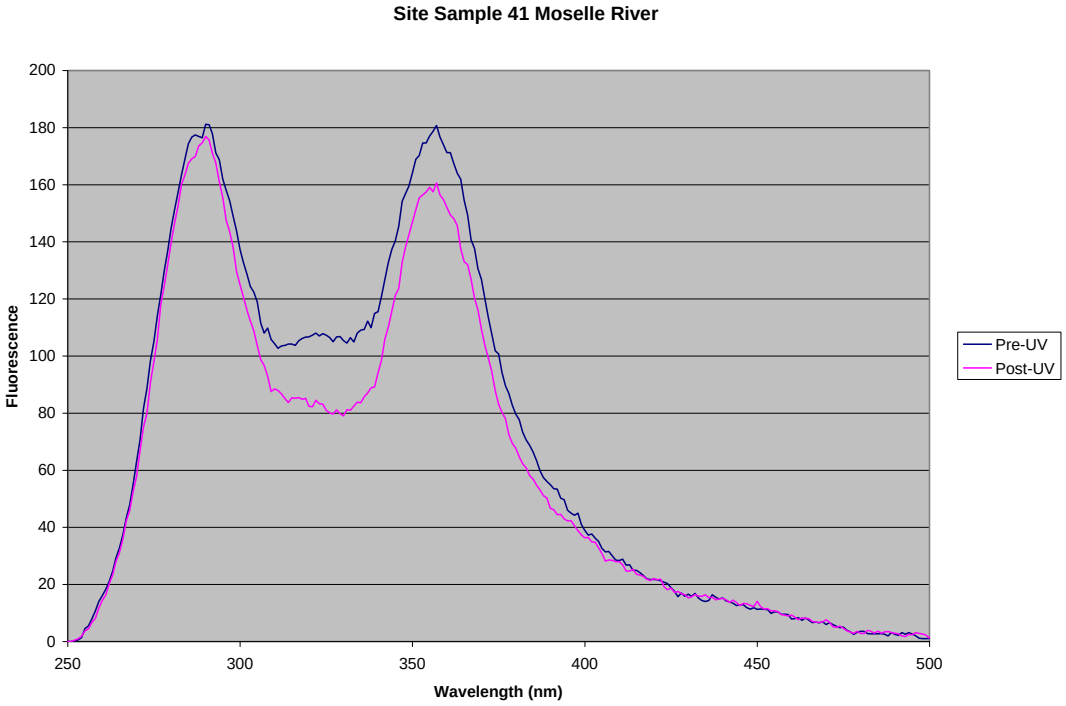


Figure 30: Pre- and Post-UV Comparison of Site Sample 41

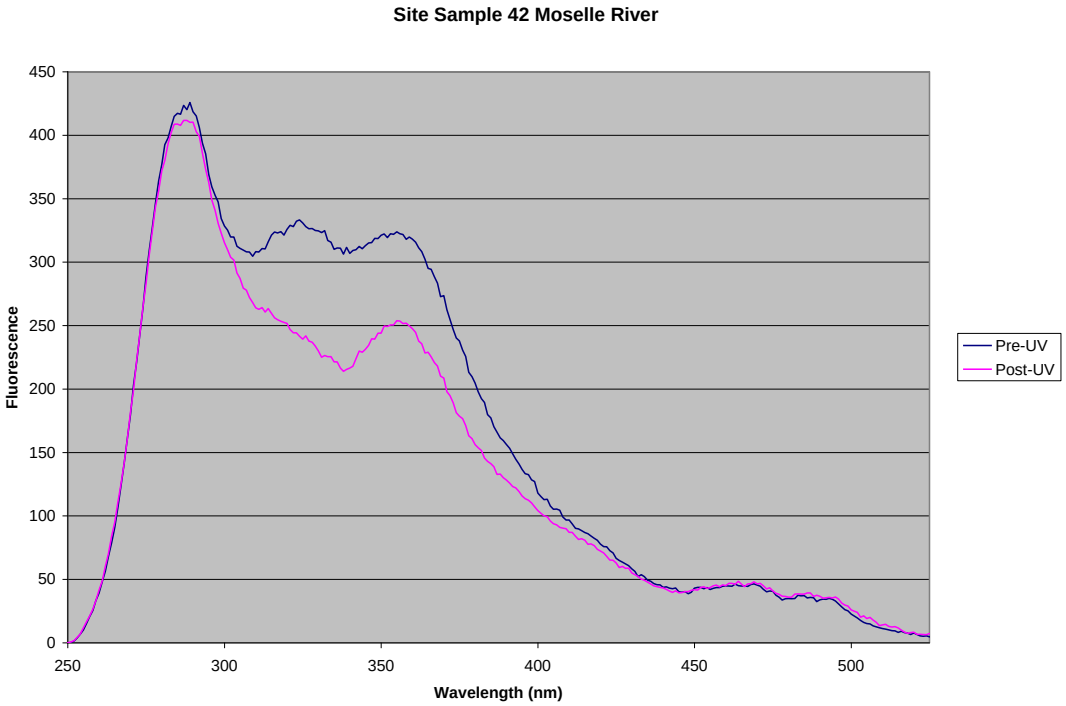


Figure 31: Pre- and Post-UV Comparison of Site Sample 42

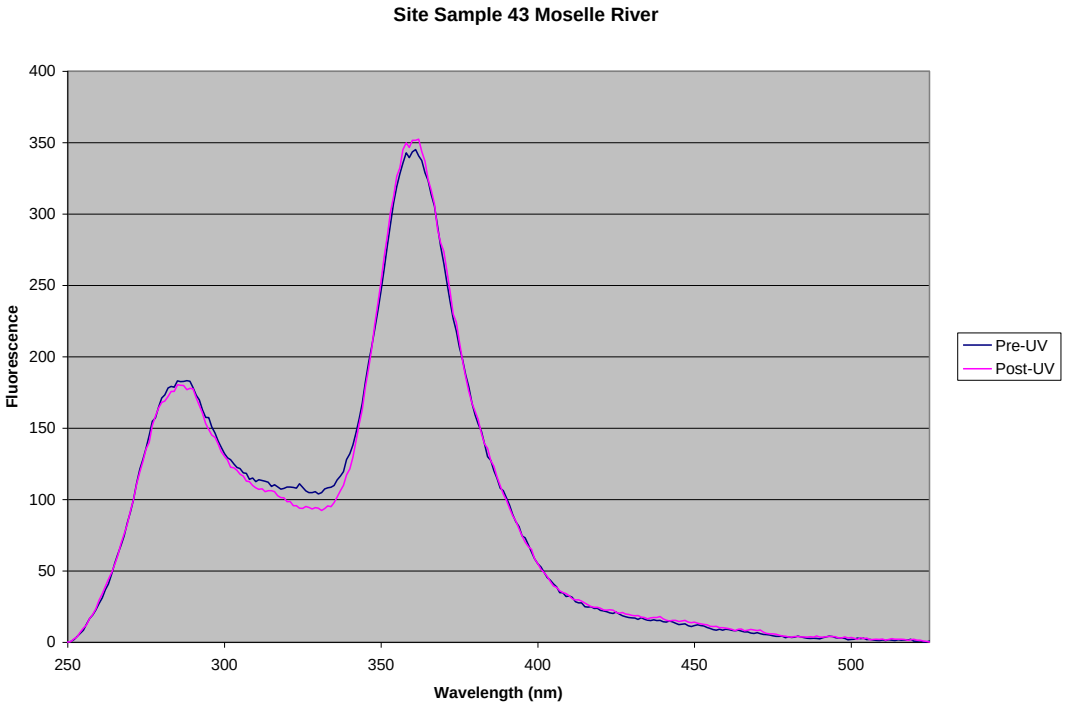


Figure 32: Pre- and Post-UV Comparison of Site Sample 43

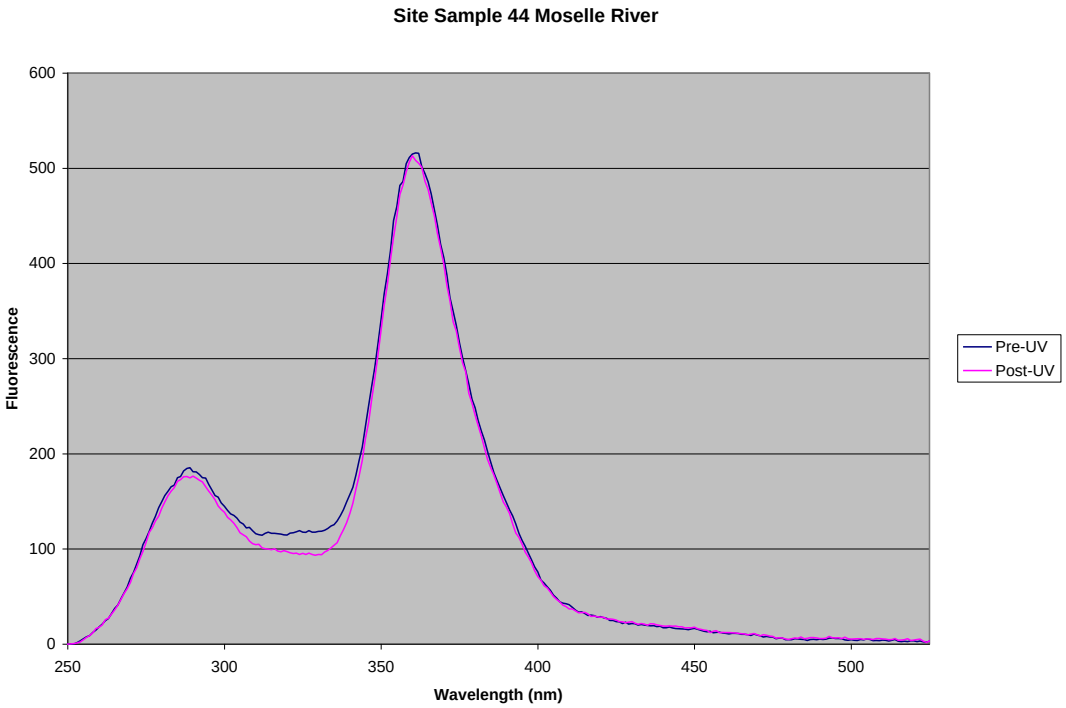


Figure 33: Pre- and Post-UV Comparison of Site Sample 44

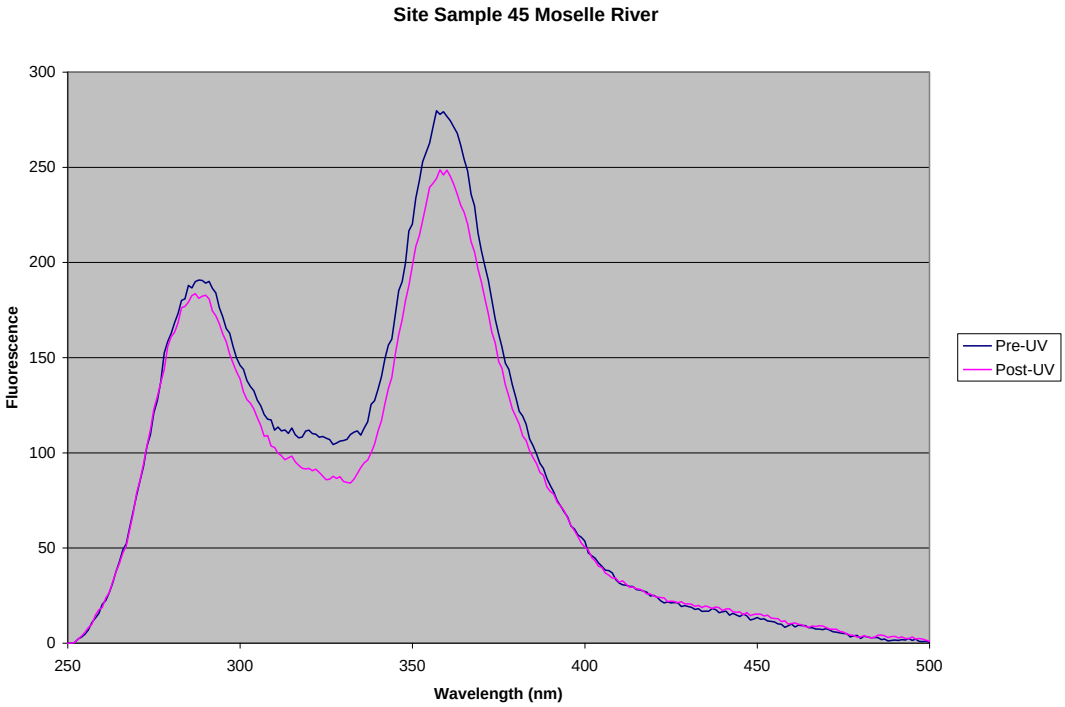


Figure 34: Pre- and Post-UV Comparison of Site Sample 45

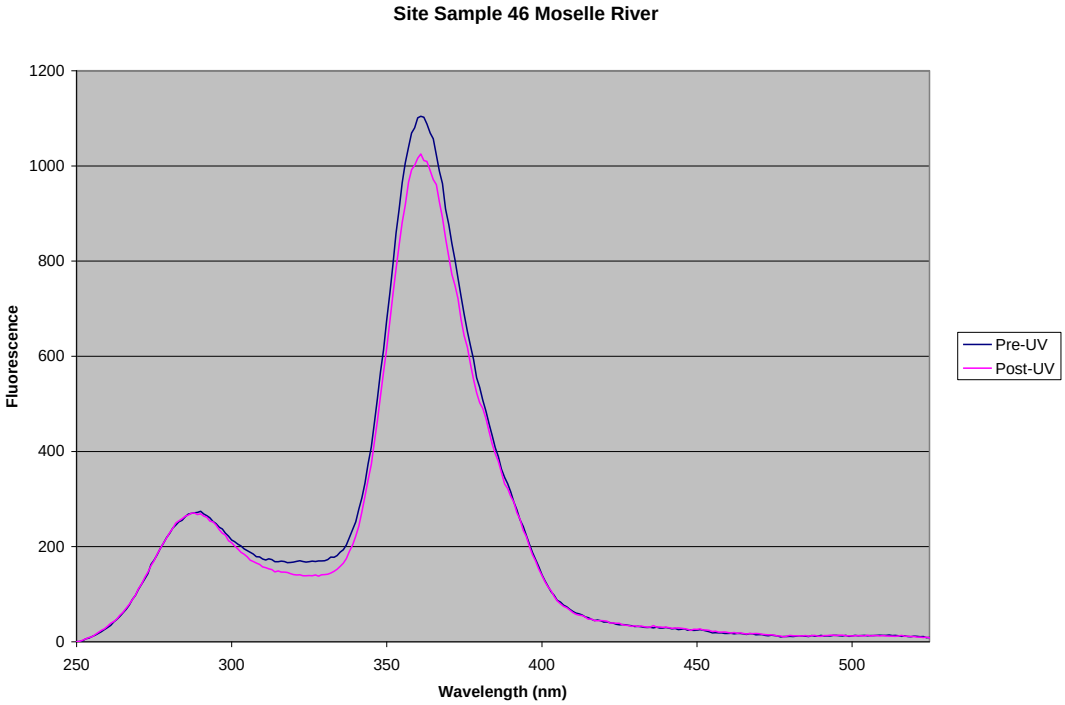


Figure 35: Pre- and Post-UV Comparison of Site Sample 46

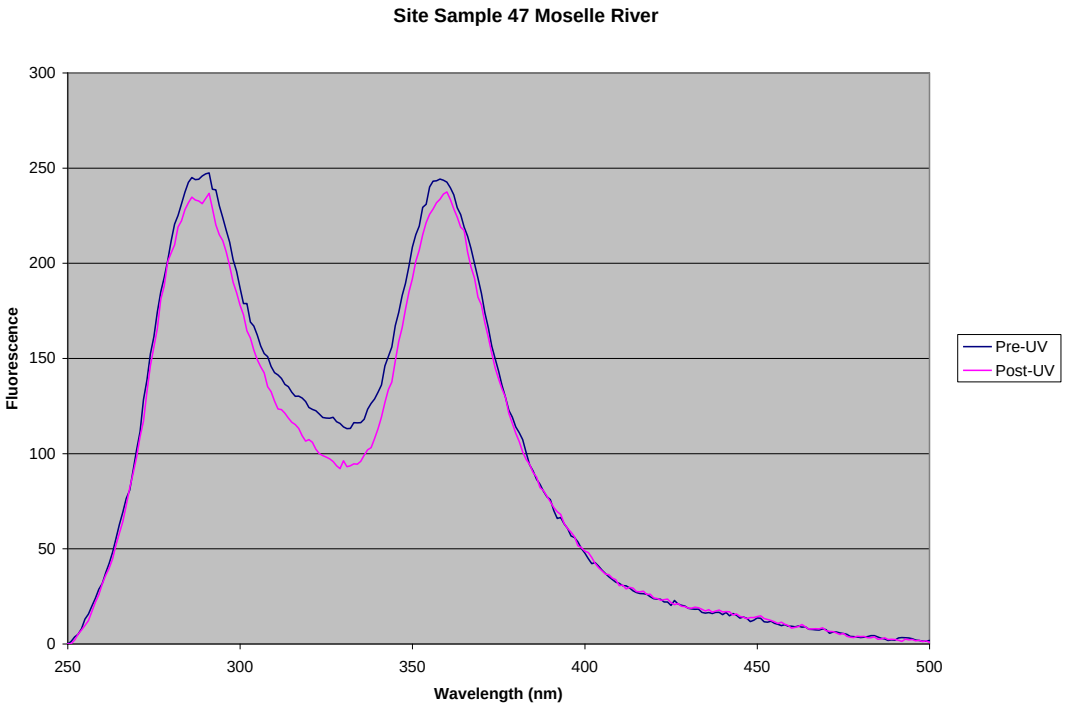


Figure 36: Pre- and Post-UV Comparison of Site Sample 47

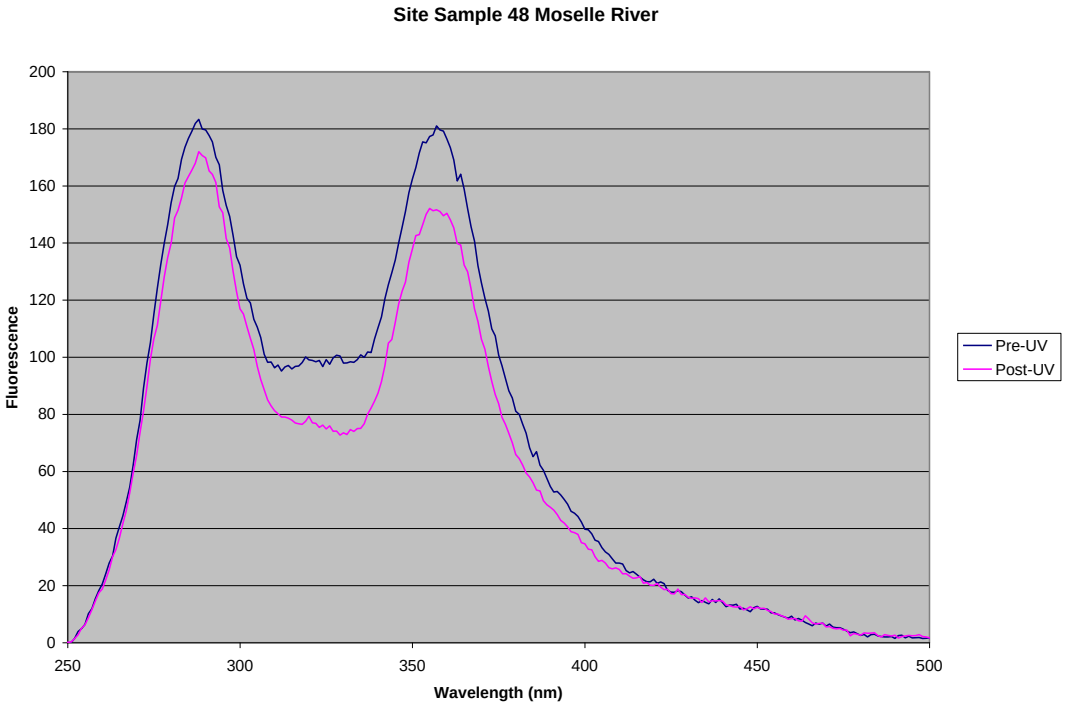


Figure 37: Pre- and Post-UV Comparison of Site Sample 48

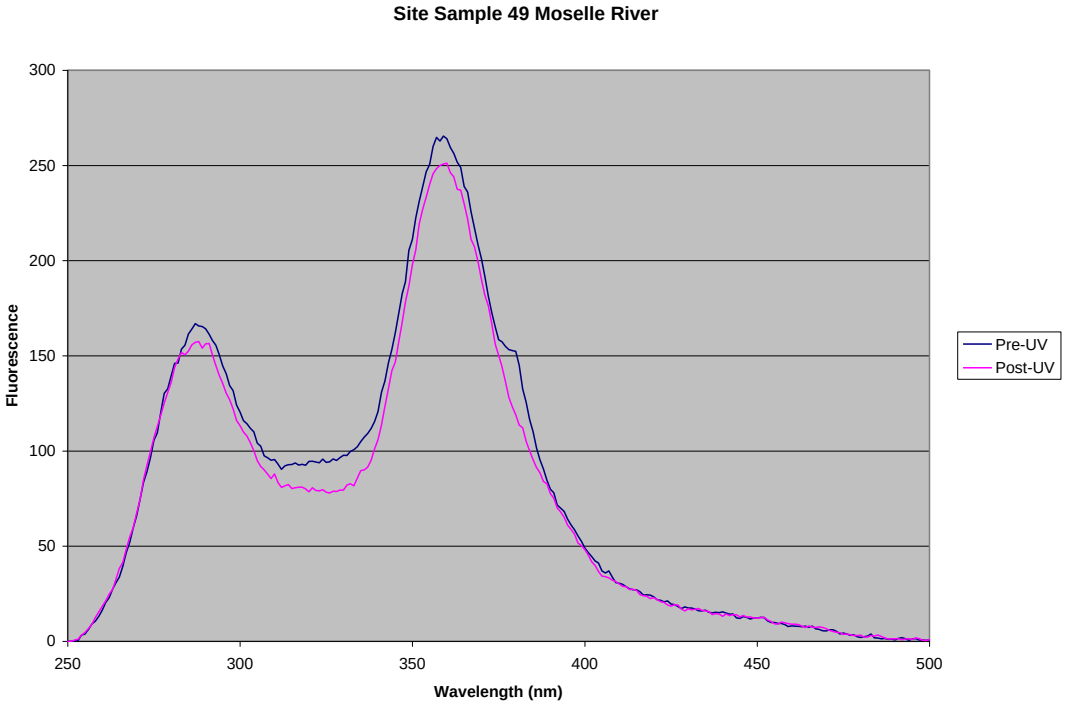


Figure 38: Pre- and Post-UV Comparison of Site Sample 49

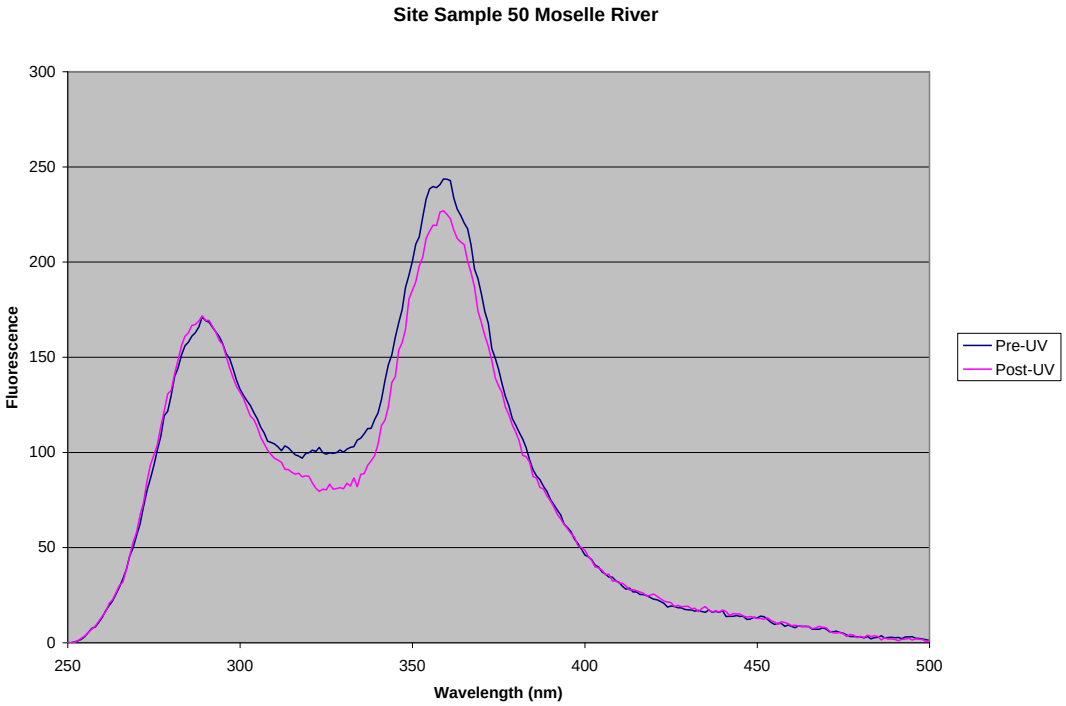


Figure 39: Pre- and Post-UV Comparison of Site Sample 50

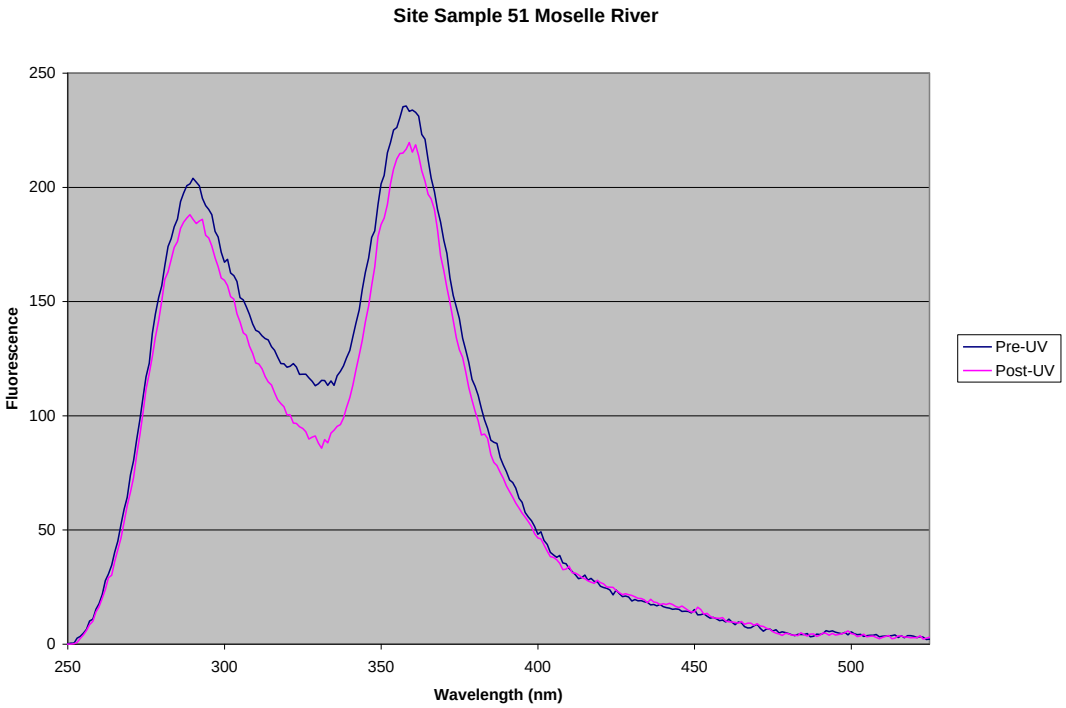


Figure 40: Pre- and Post-UV Comparison of Site Sample 51

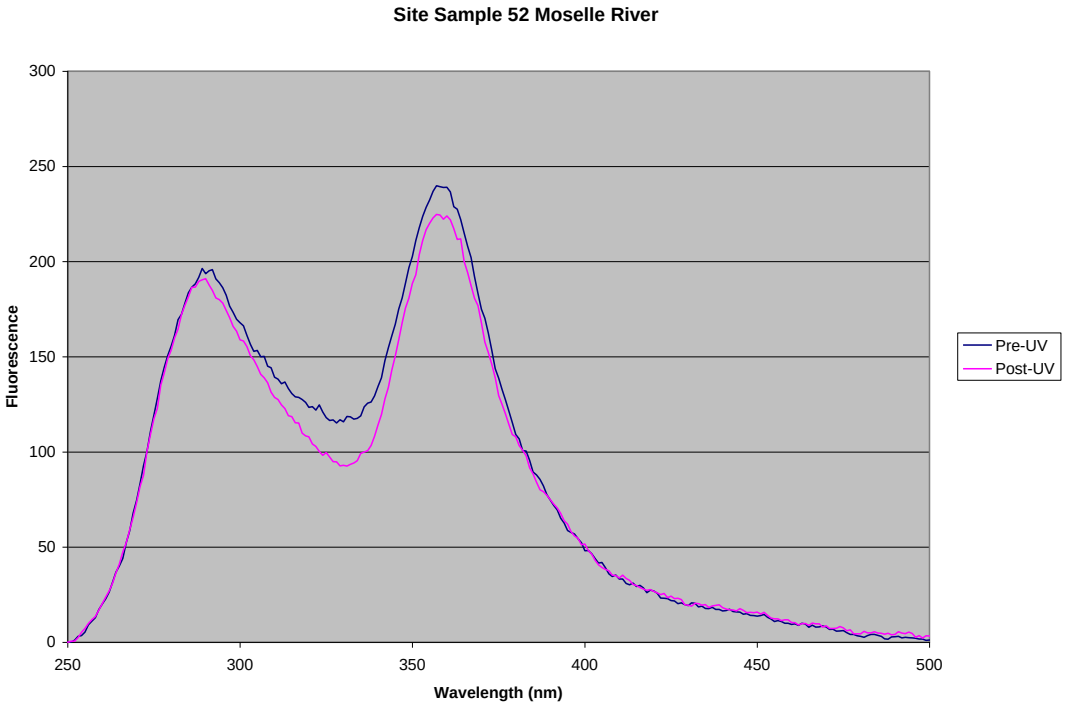


Figure 41: Pre- and Post-UV Comparison of Site Sample 52

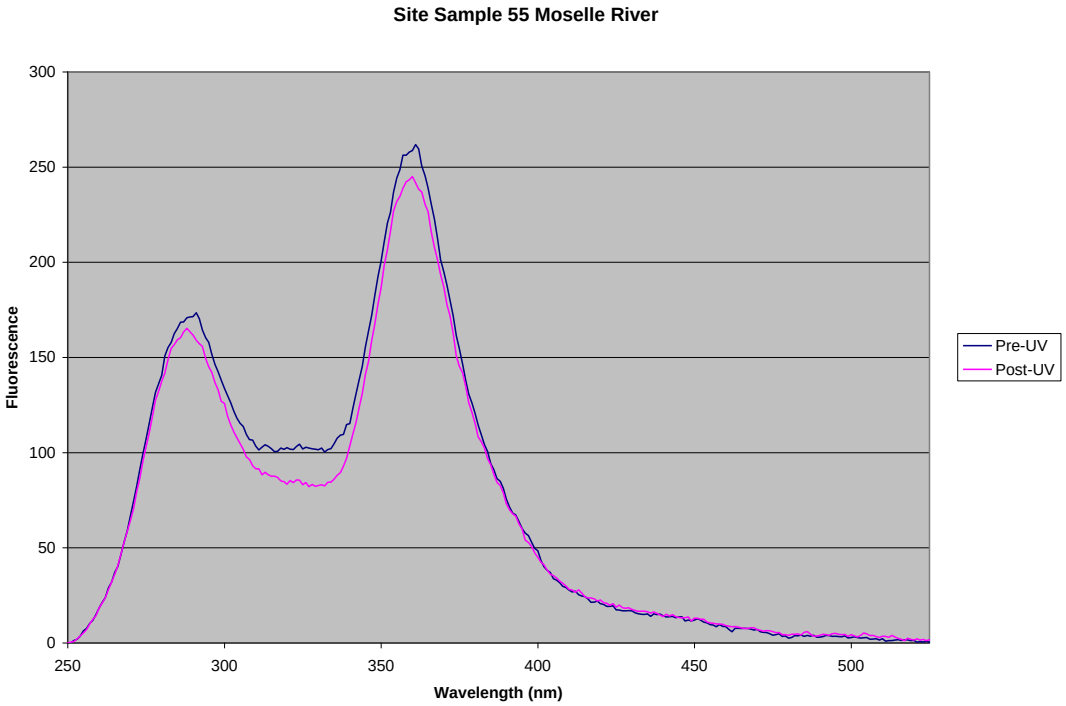


Figure 42: Pre- and Post-UV Comparison of Site Sample 55

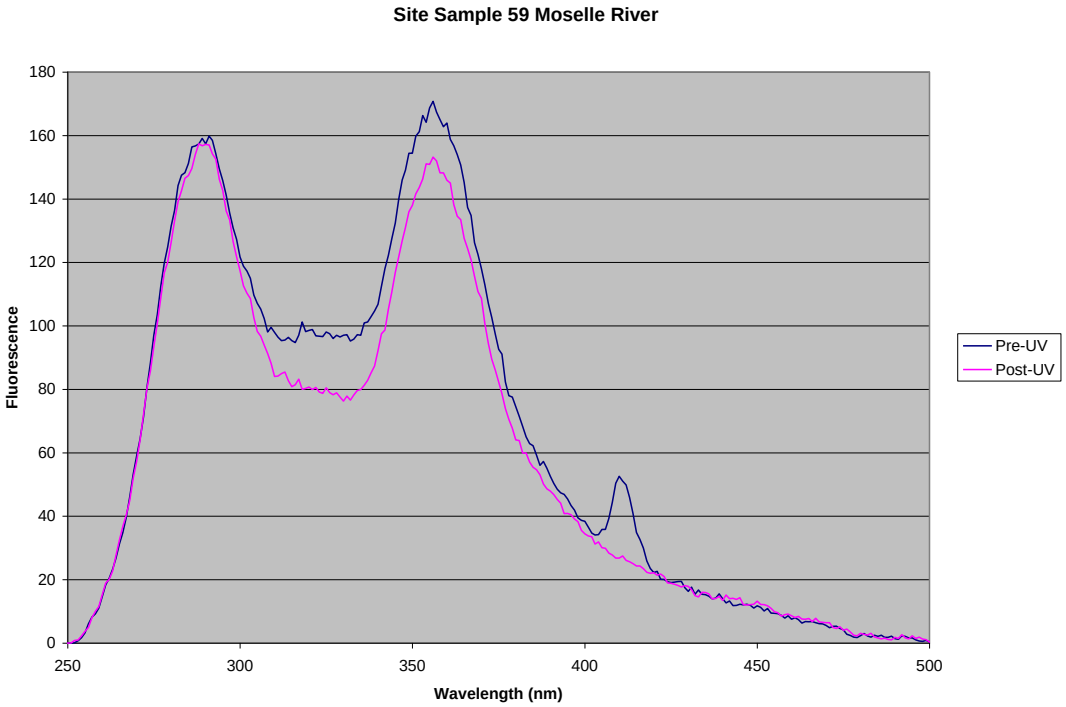


Figure 43: Pre- and Post-UV Comparison of Site Sample 59

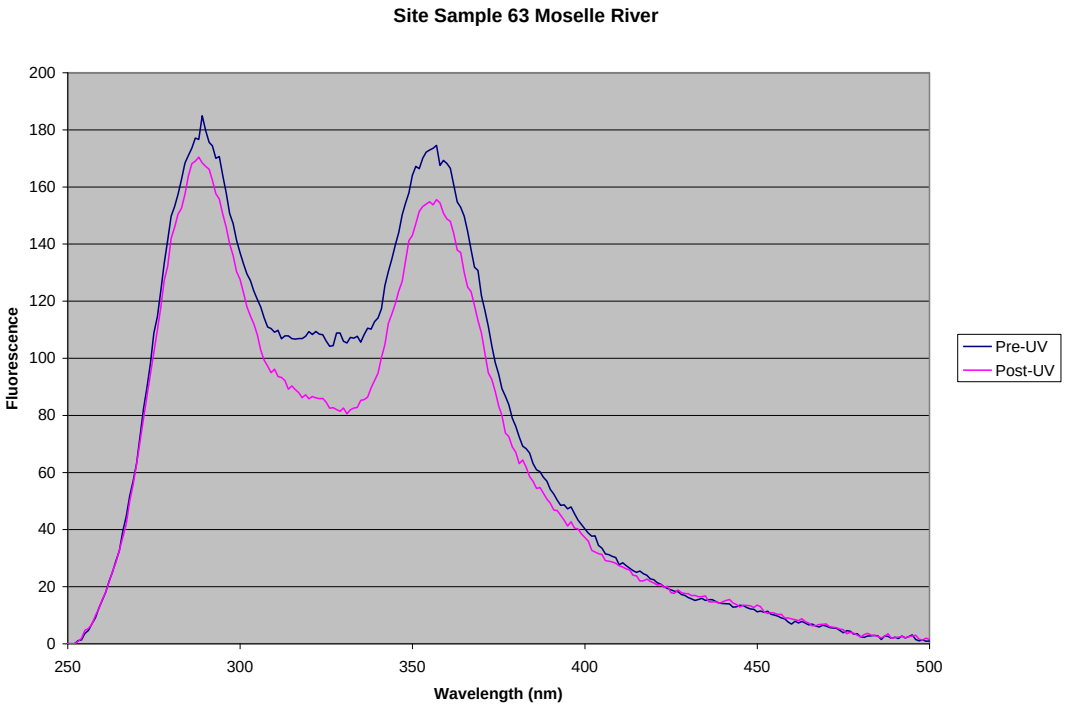


Figure 44: Pre- and Post-UV Comparison of Site Sample 63

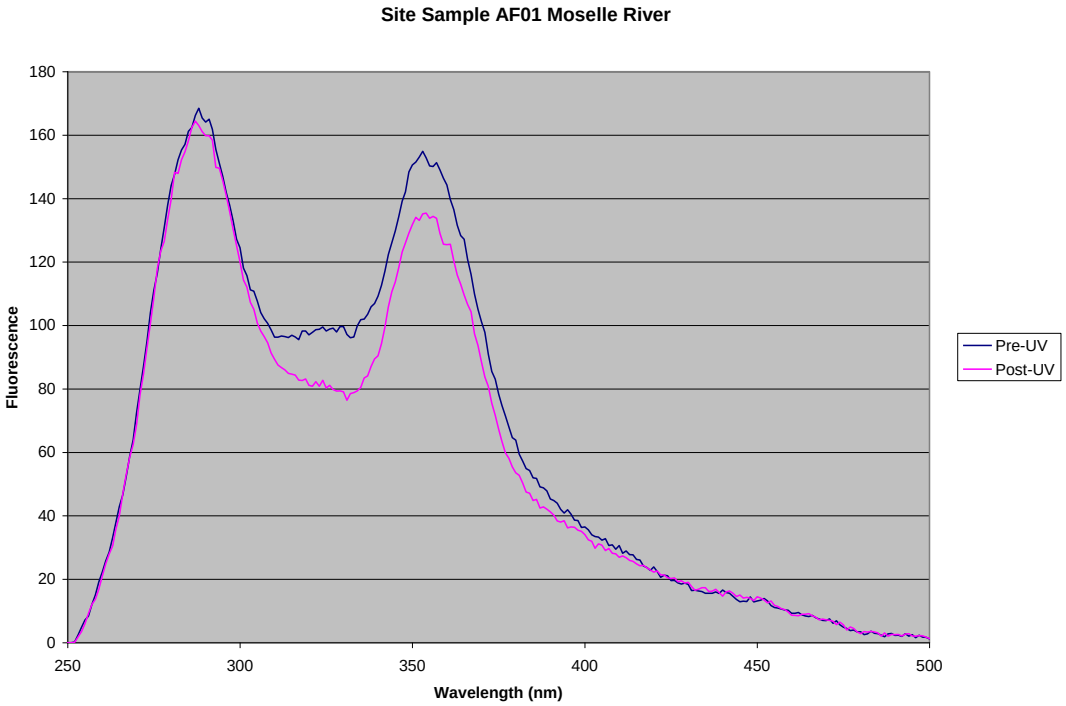


Figure 45: Pre- and Post-UV Comparison of Site Sample AF01

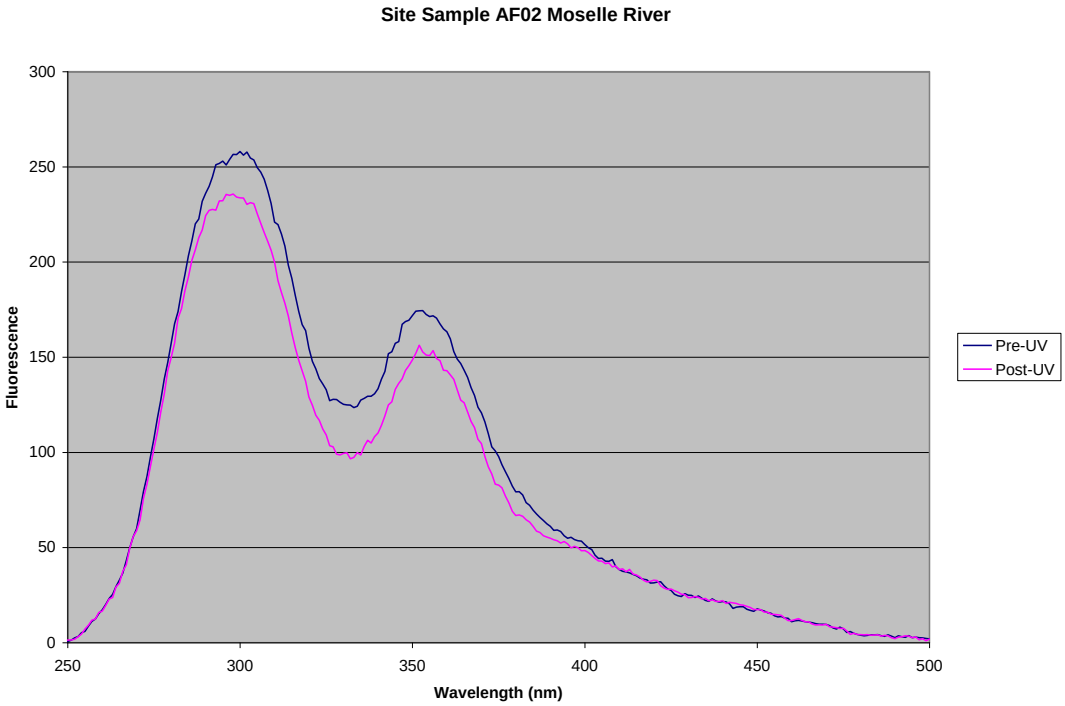


Figure 46: Pre- and Post-UV Comparison of Site Sample AF02

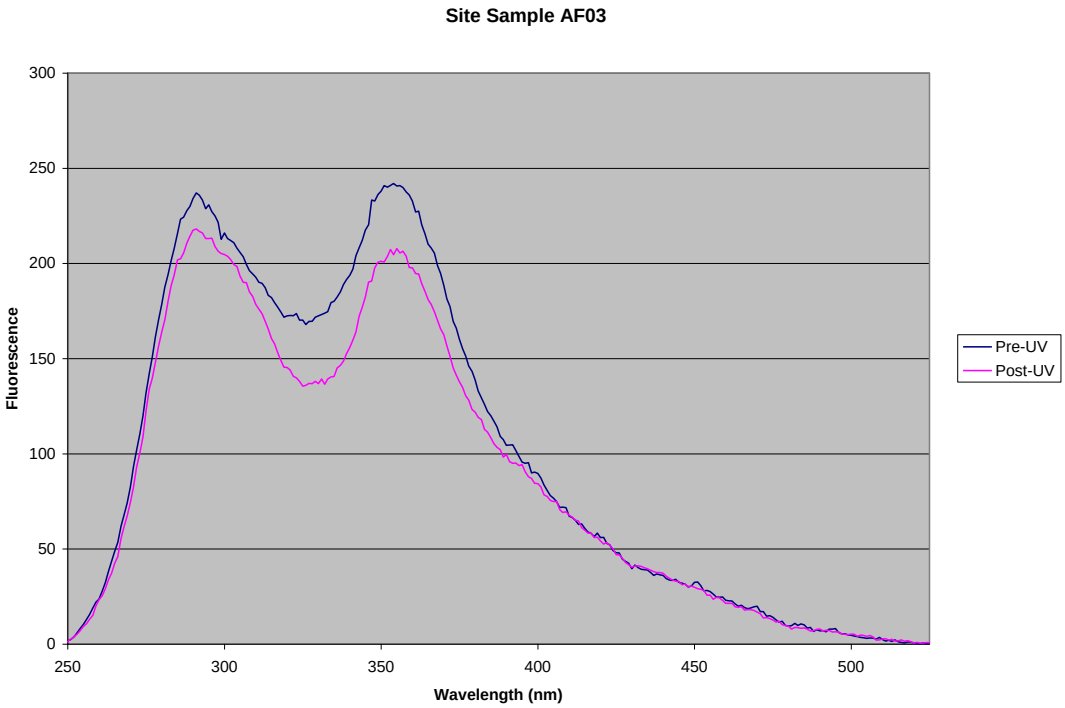


Figure 47: Pre- and Post-UV Comparison of Site Sample AF03

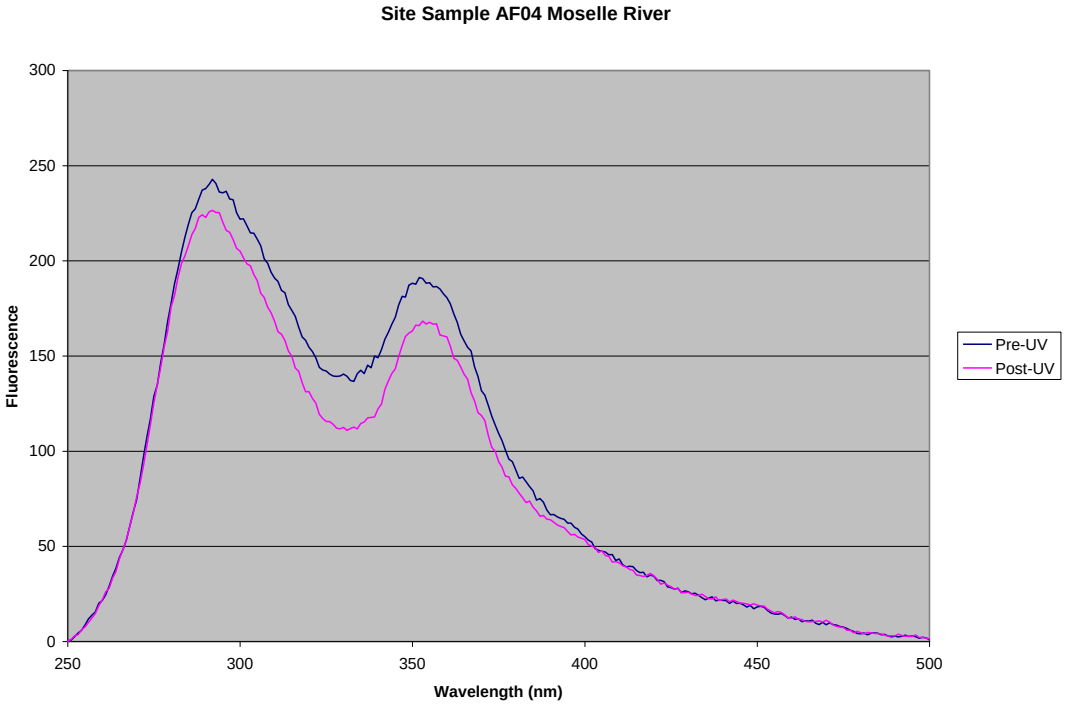


Figure 48: Pre- and Post-UV Comparison of Site Sample AF04

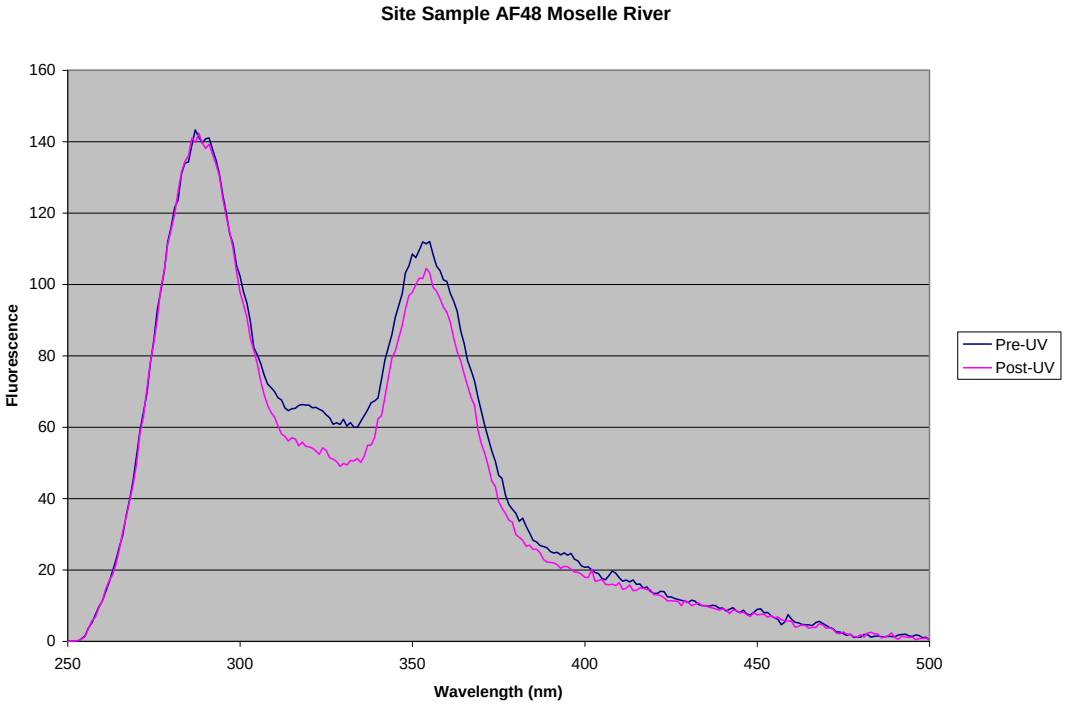


Figure 49: Pre- and Post-UV Comparison of Site Sample AF48

Date of Samples: February 19th, 2008

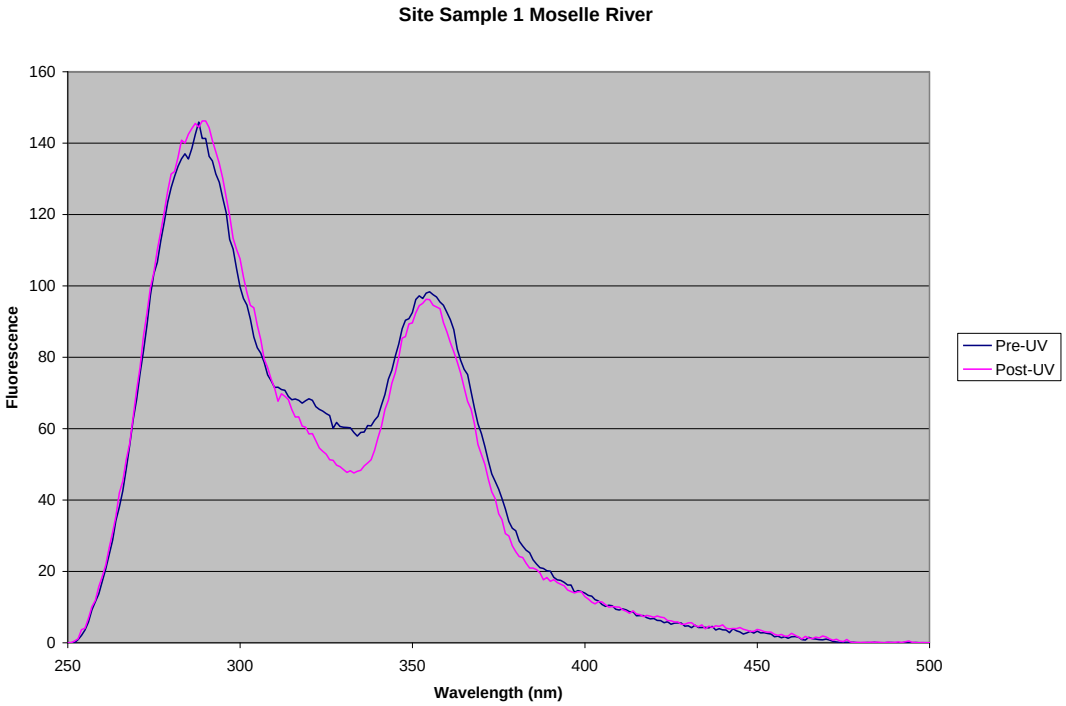


Figure 50: Pre- and Post-UV Comparison of Site Sample 1

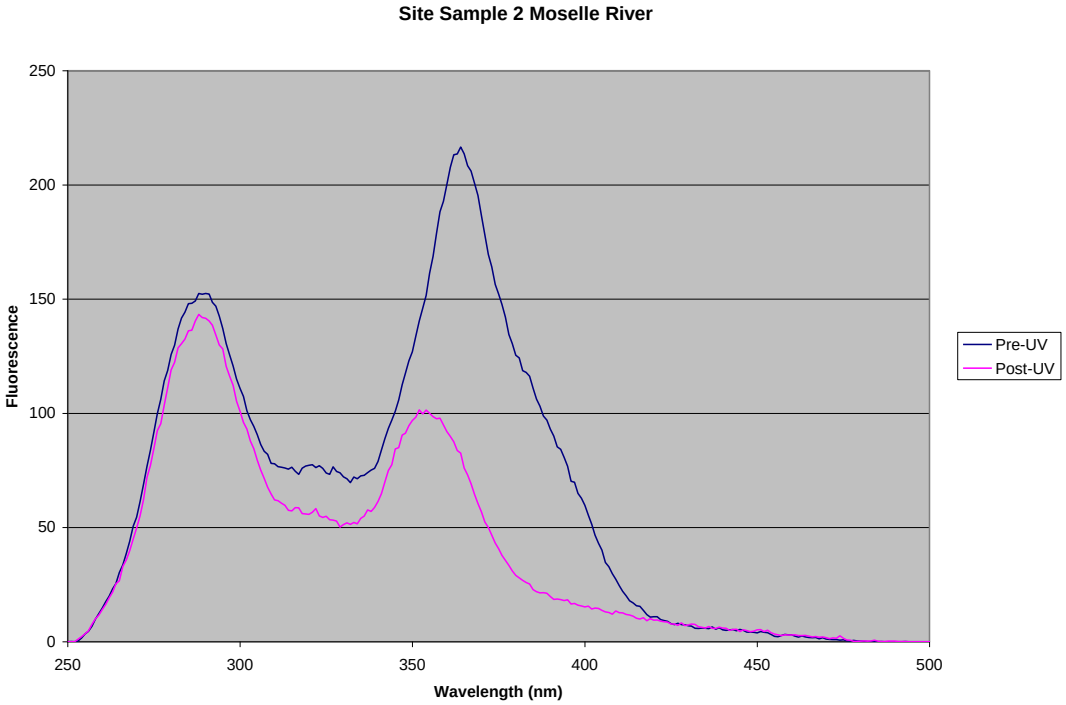


Figure 51: Pre- and Post-UV Comparison of Site Sample 2

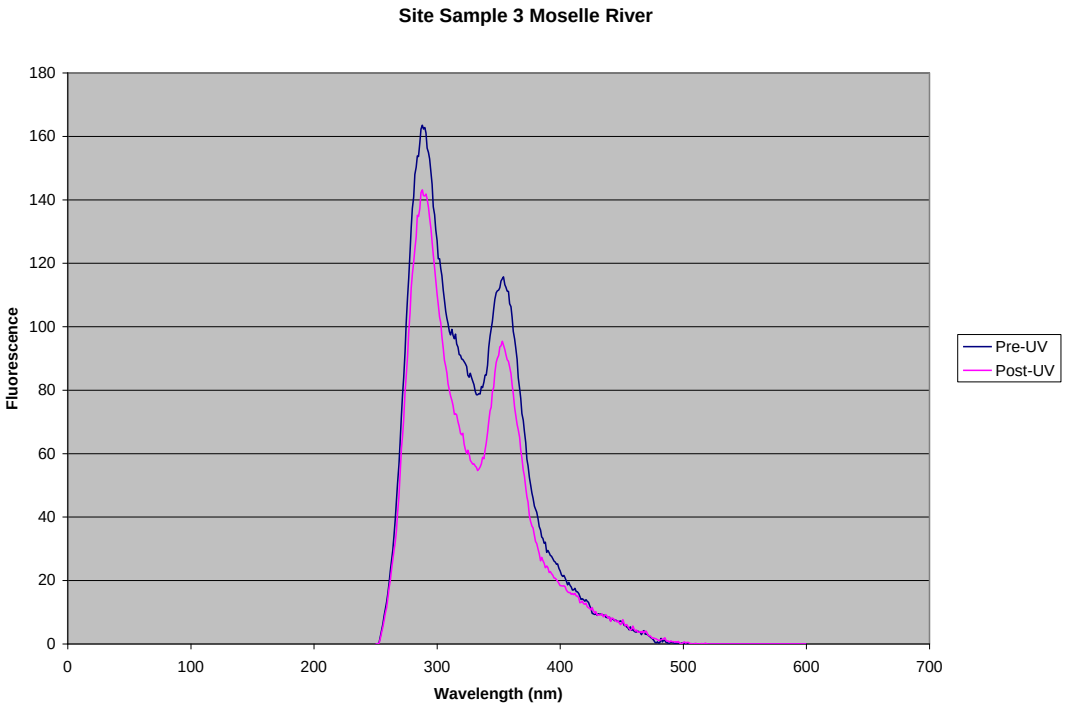


Figure 52: Pre- and Post-UV Comparison of Site Sample 3

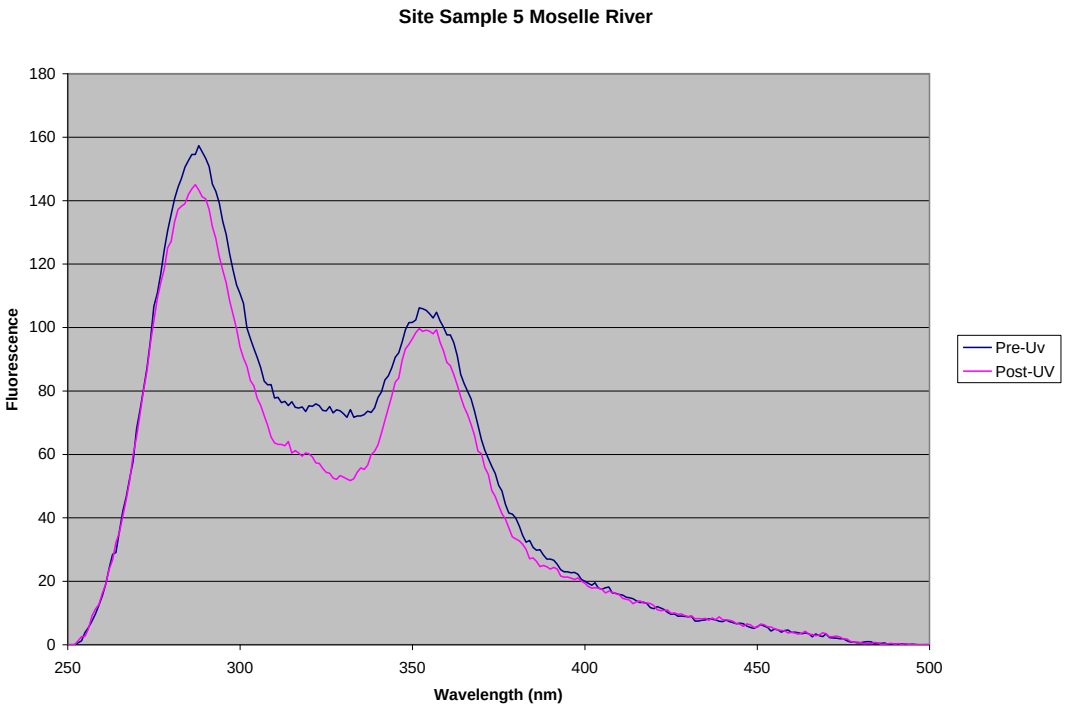


Figure 53: Pre- and Post-UV Comparison of Site Sample 5

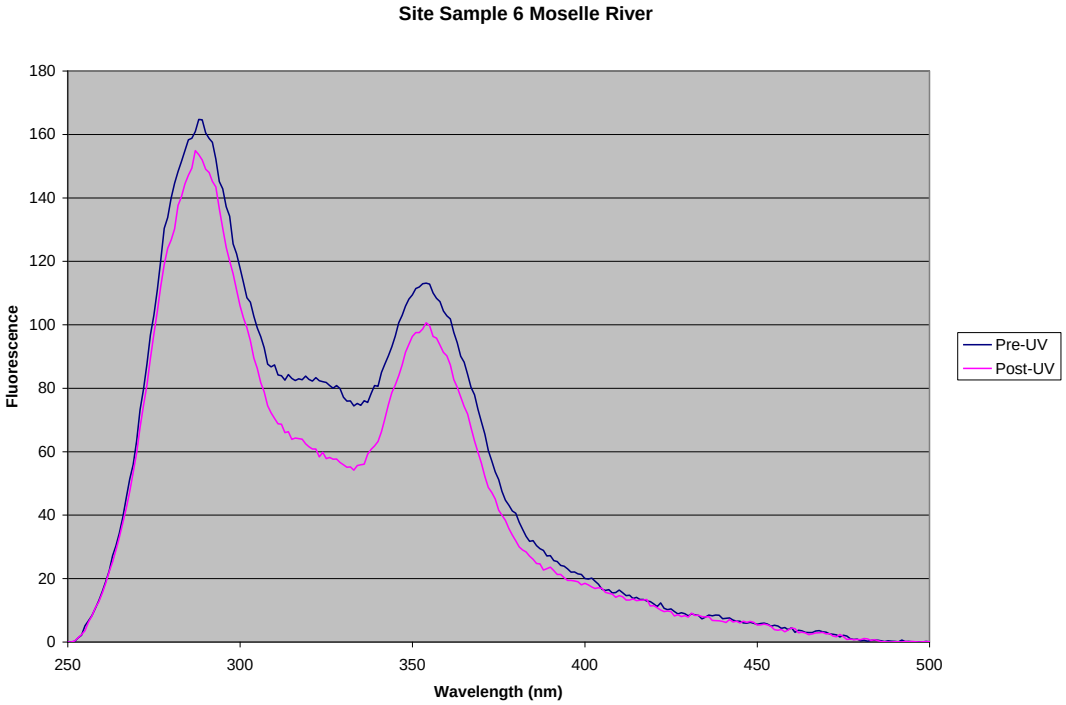


Figure 54: Pre- and Post-UV Comparison of Site Sample 6

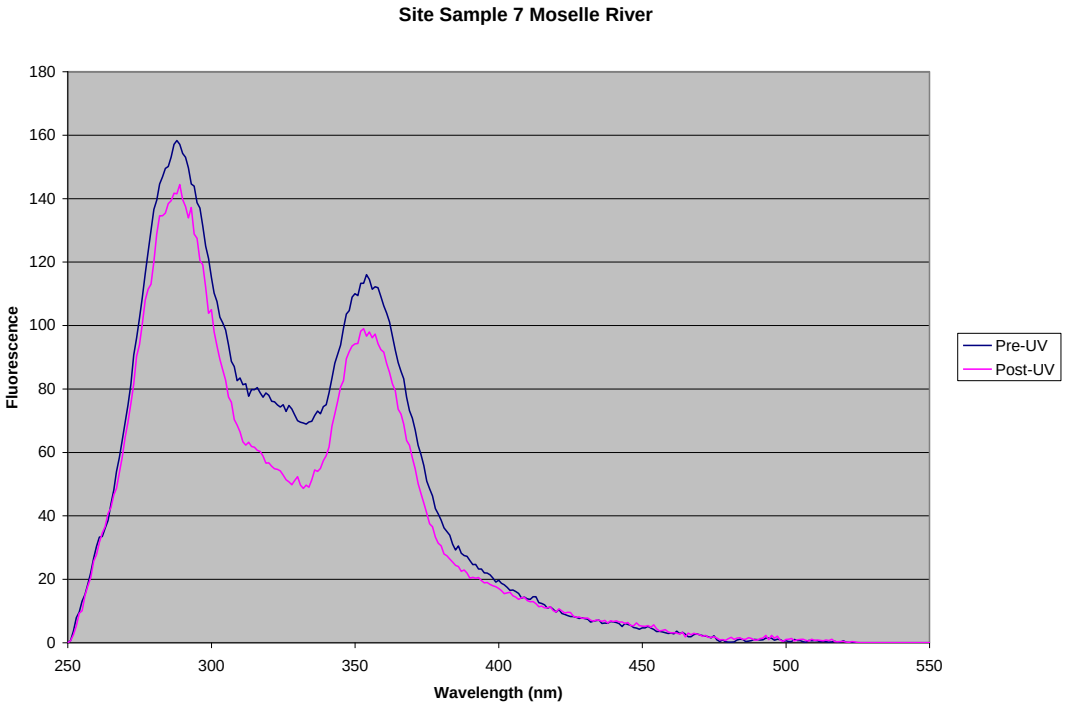


Figure 55: Pre- and Post-UV Comparison of Site Sample 7

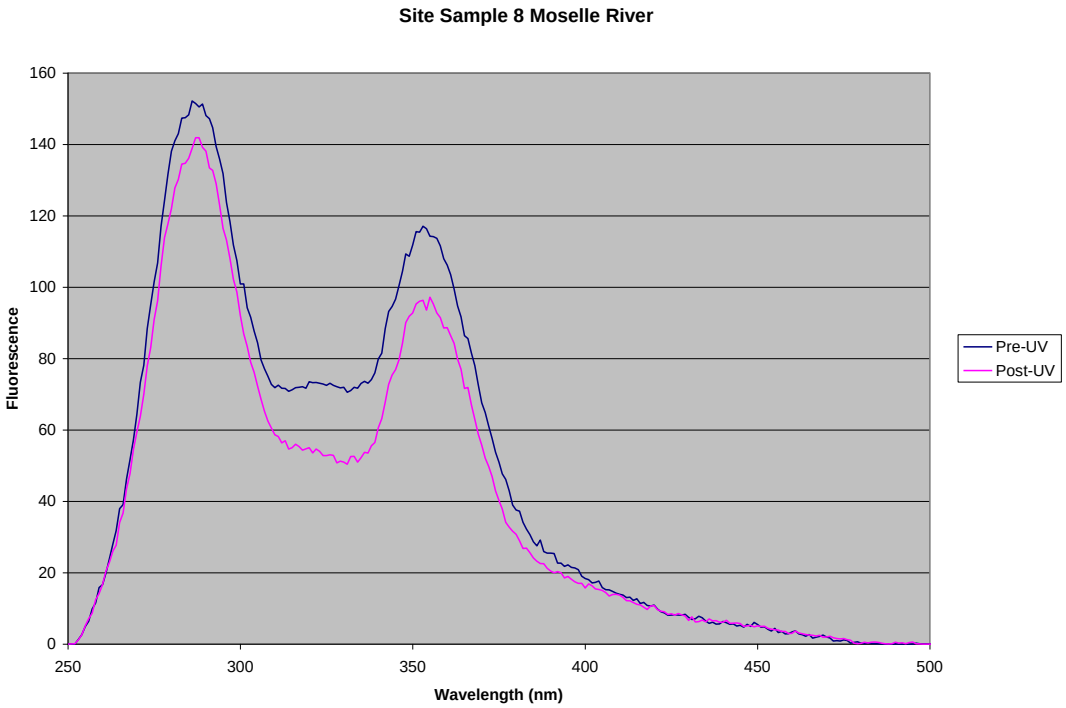


Figure 56: Pre- and Post-UV Comparison of Site Sample 8

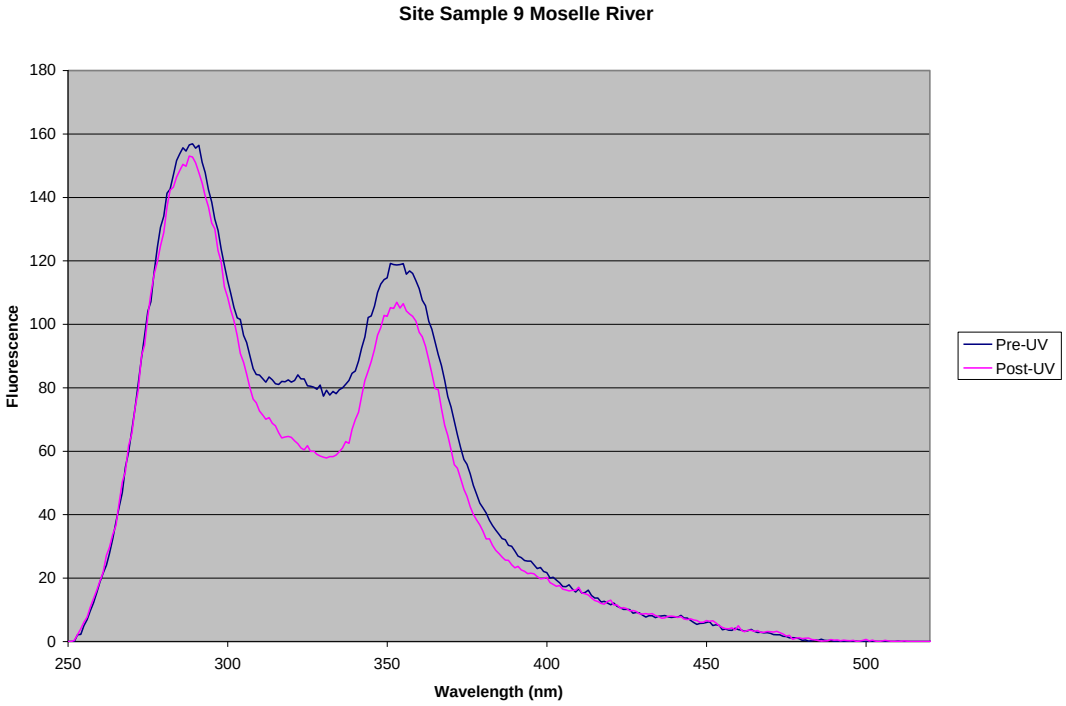


Figure 57: Pre- and Post-UV Comparison of Site Sample 9

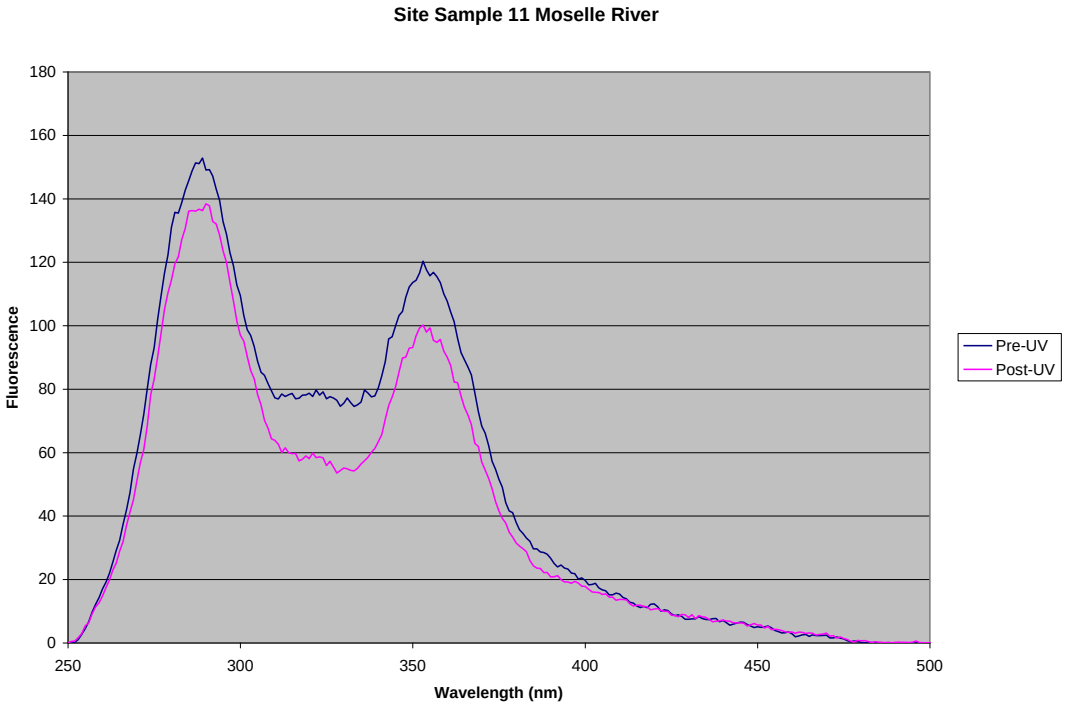


Figure 58: Pre- and Post-UV Comparison of Site Sample 11

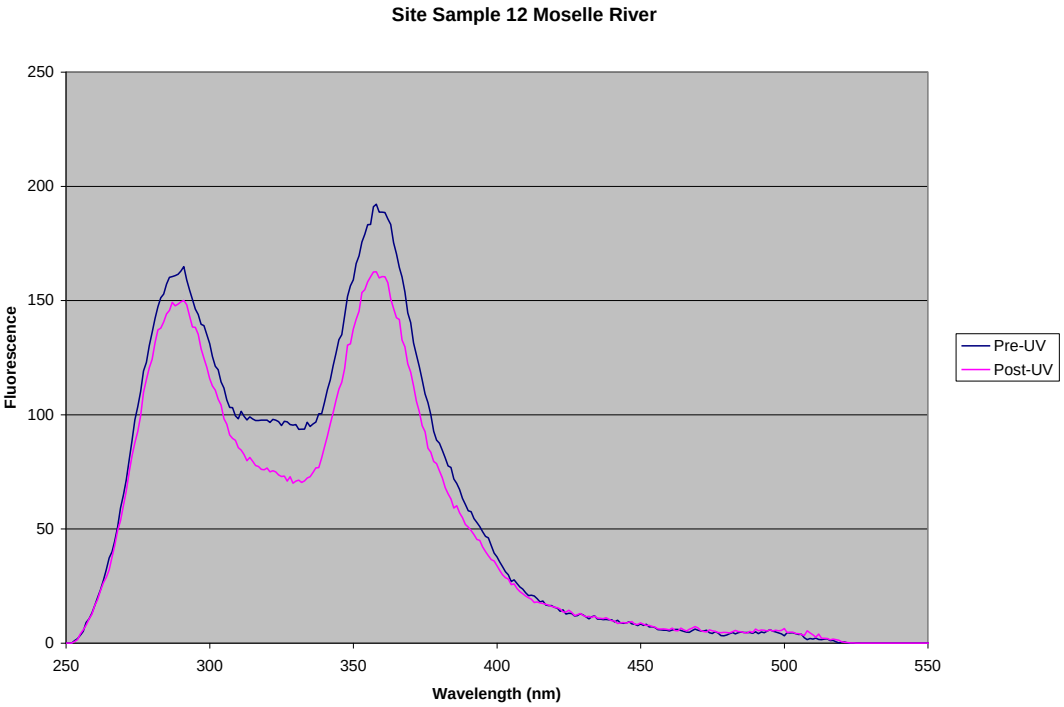


Figure 59: Pre- and Post-UV Comparison of Site Sample 12

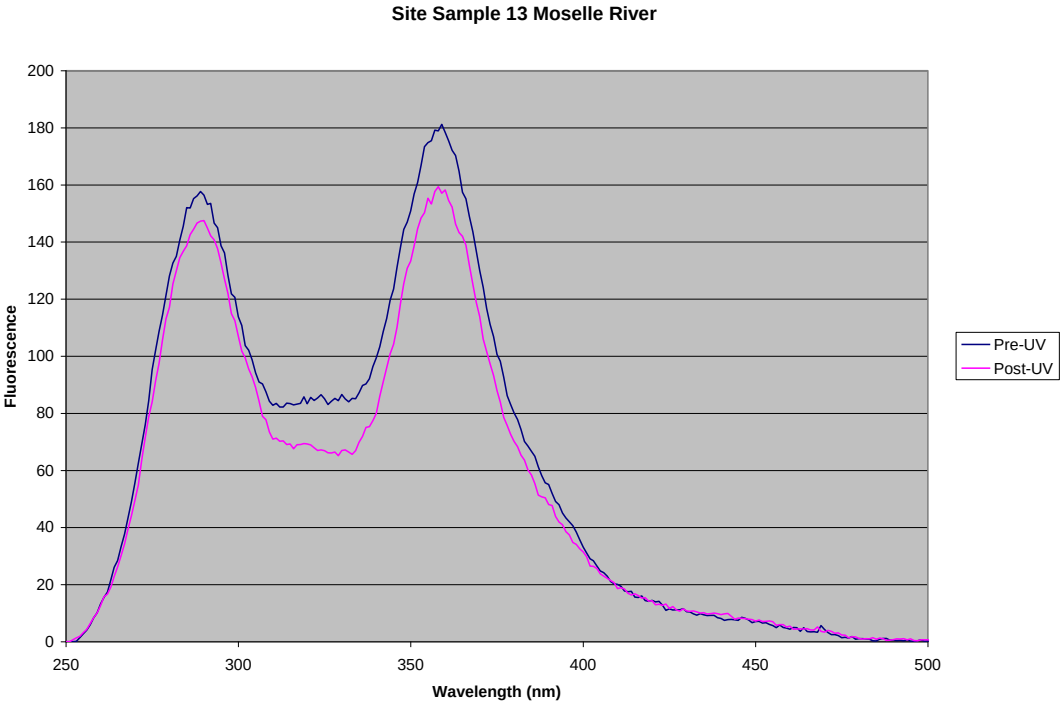


**Figure 60: Pre- and Post-UV Comparison of Site Sample 13**

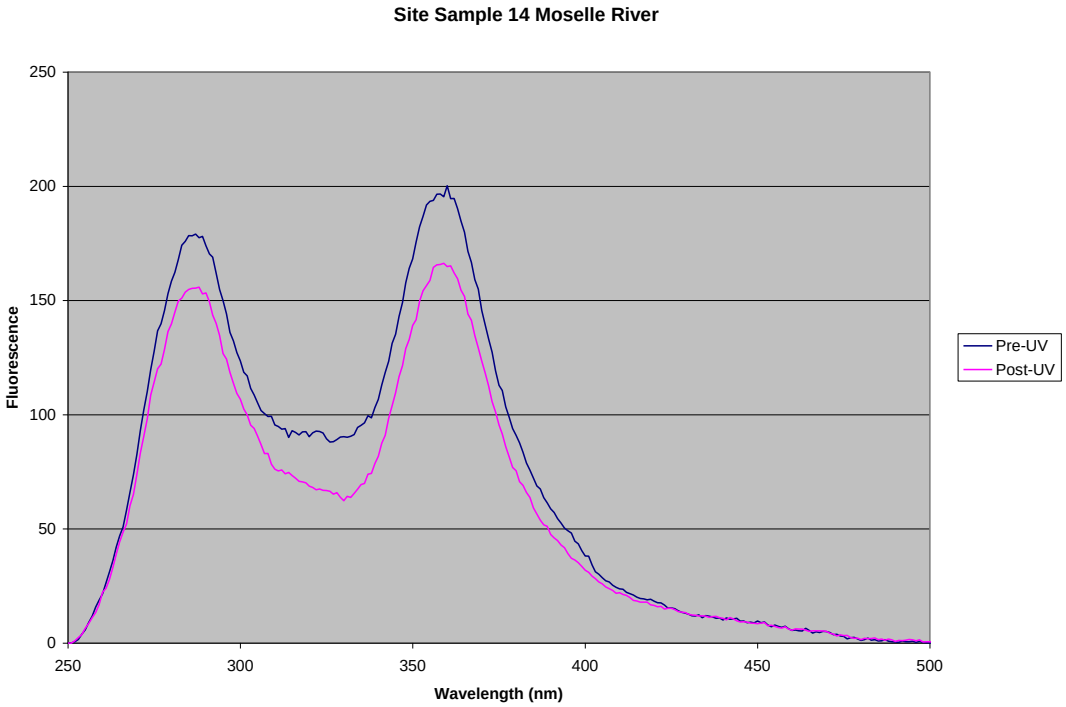


Figure 61: Pre- and Post-UV Comparison of Site Sample 14

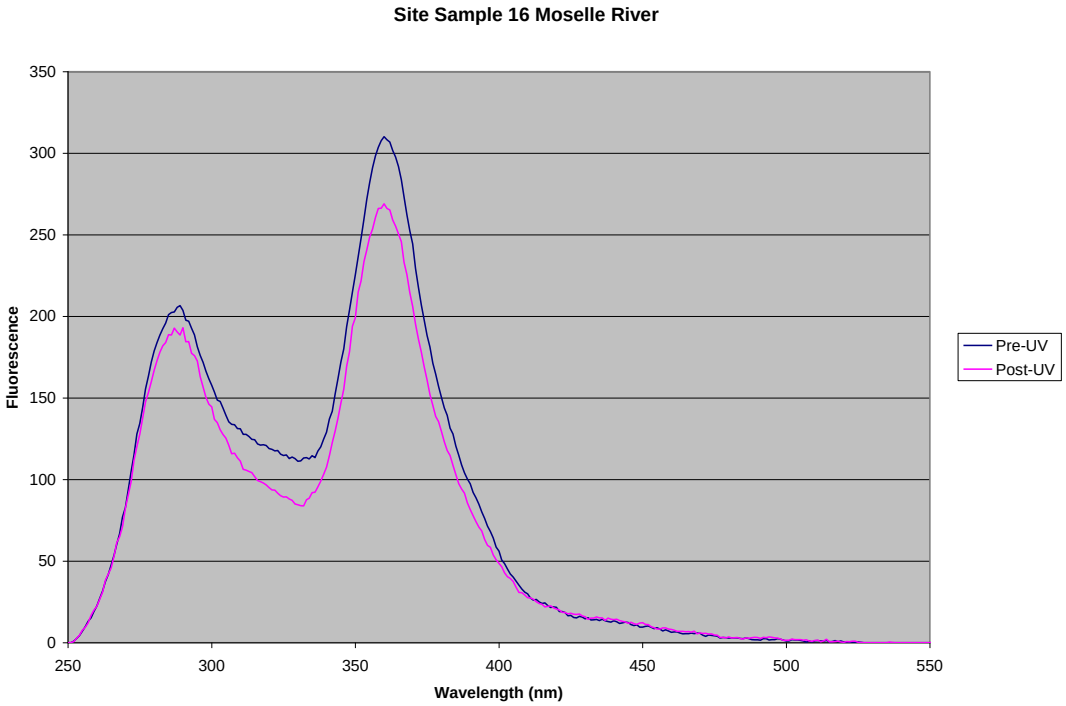


Figure 62: Pre- and Post-UV Comparison of Site Sample 16

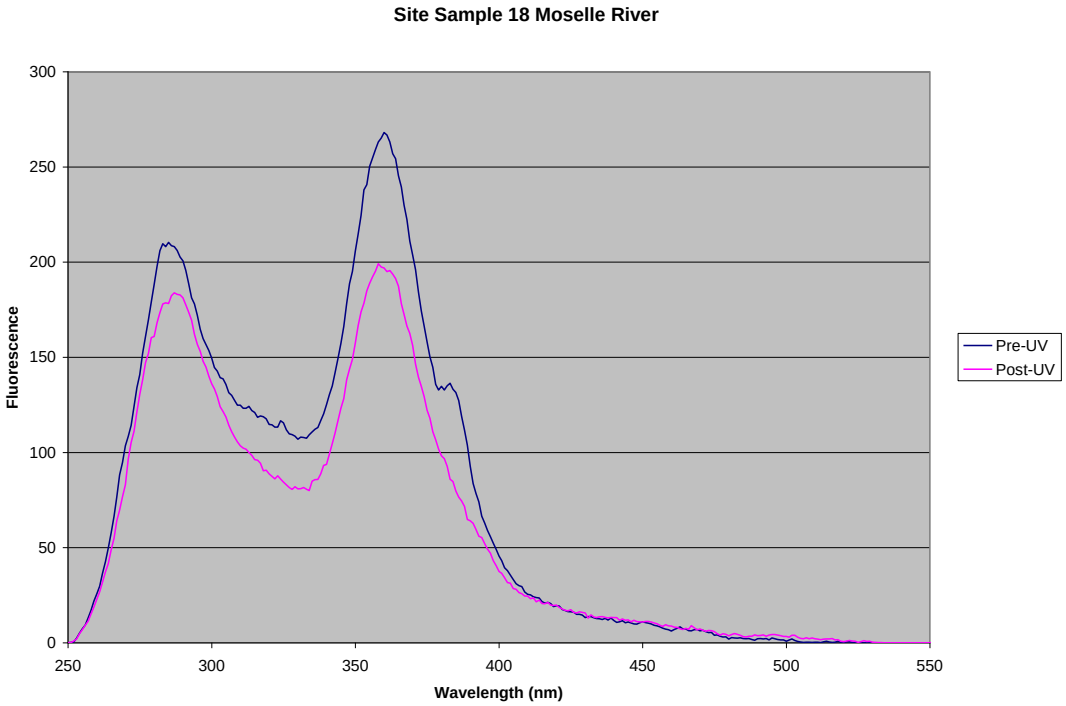


Figure 63: Pre- and Post-UV Comparison of Site Sample 18

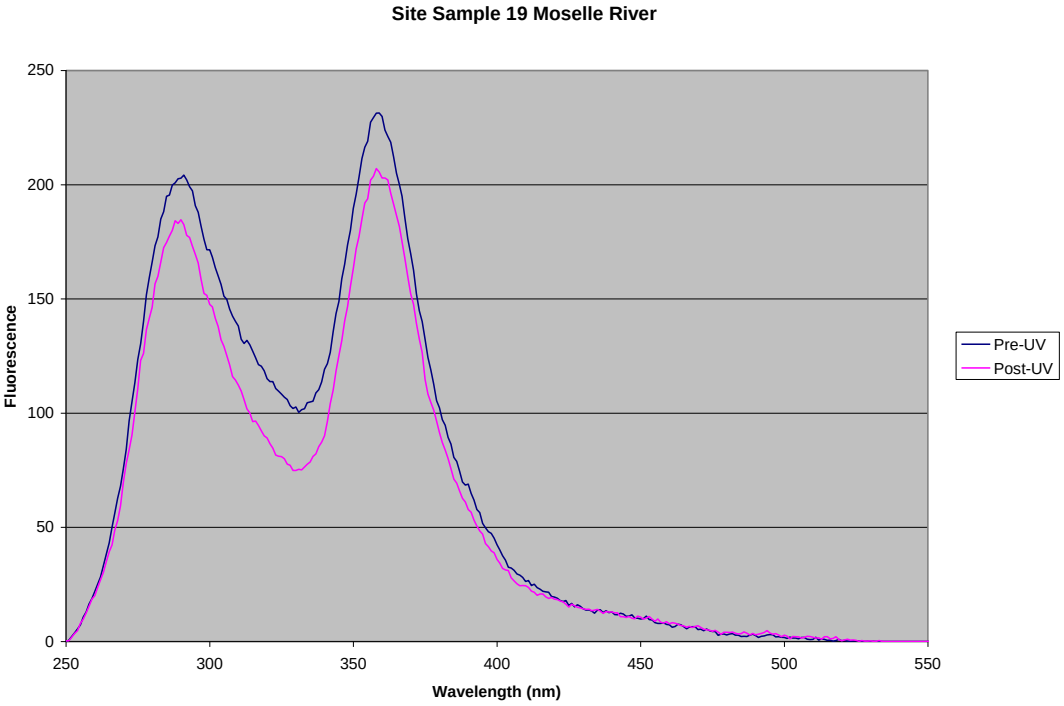


Figure 64: Pre- and Post-UV Comparison of Site Sample 19

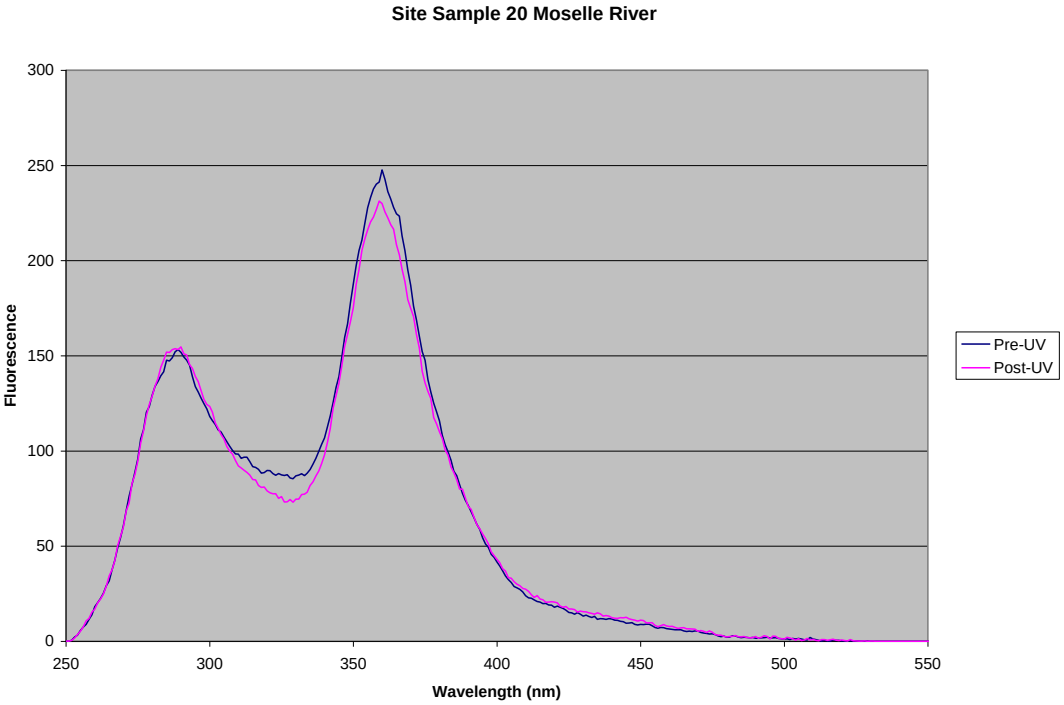


Figure 65: Pre- and Post-UV Comparison of Site Sample 20

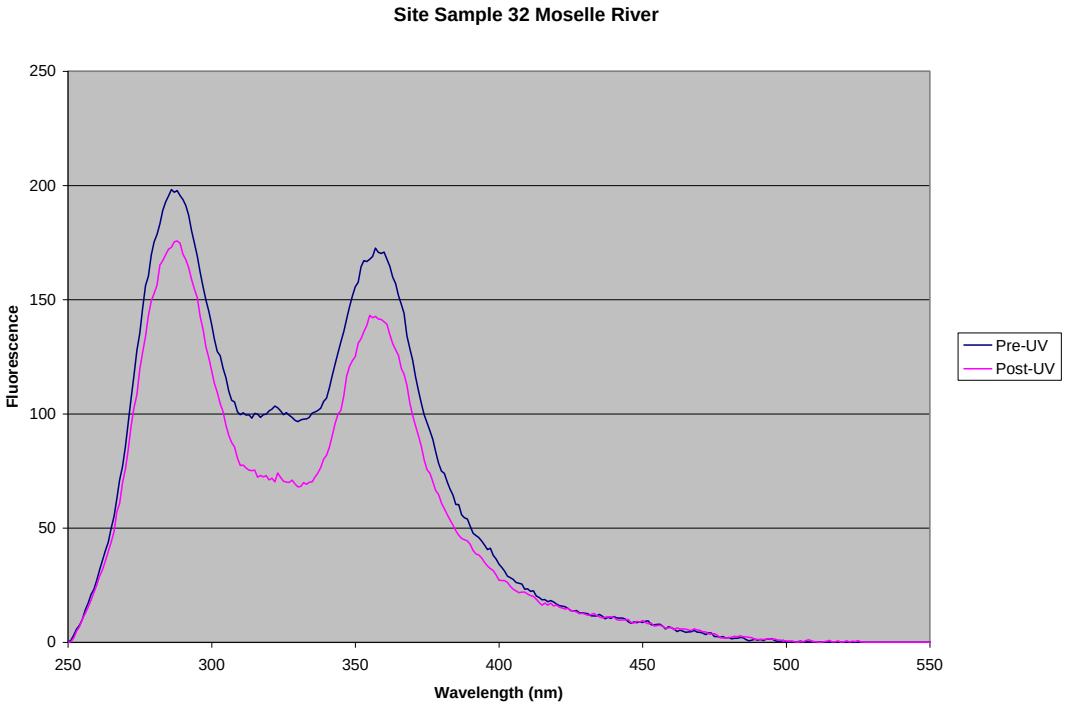


Figure 66: Pre- and Post-UV Comparison of Site Sample 32

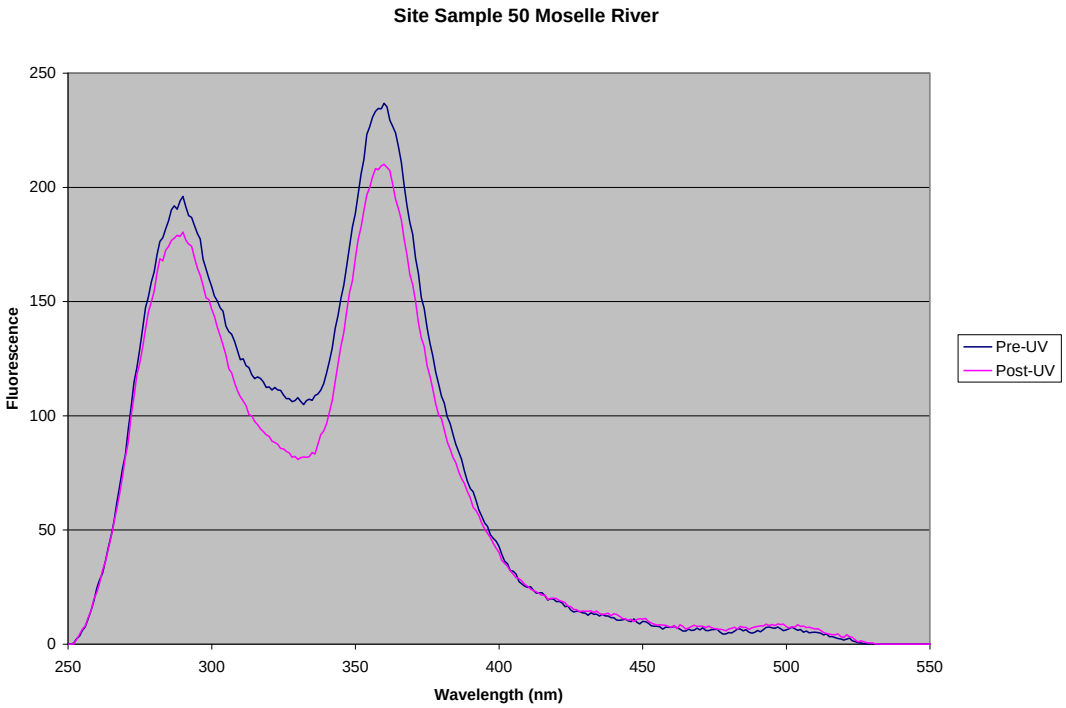


Figure 67: Pre- and Post-UV Comparison of Site Sample 50

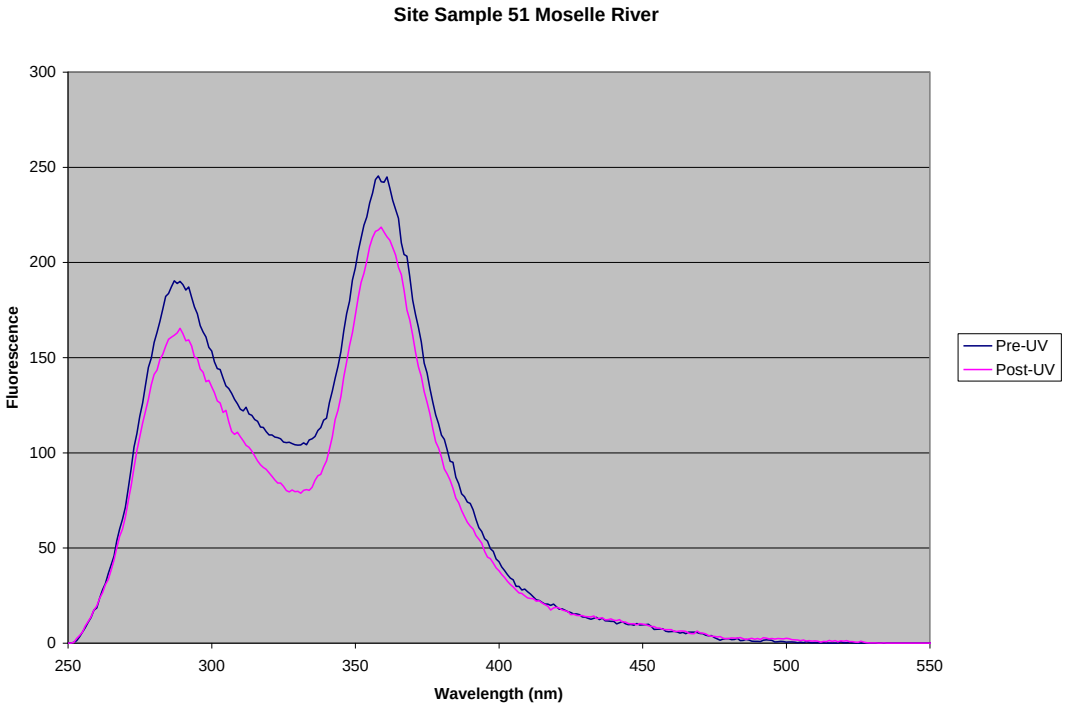


Figure 68: Pre- and Post-UV Comparison of Site Sample 51

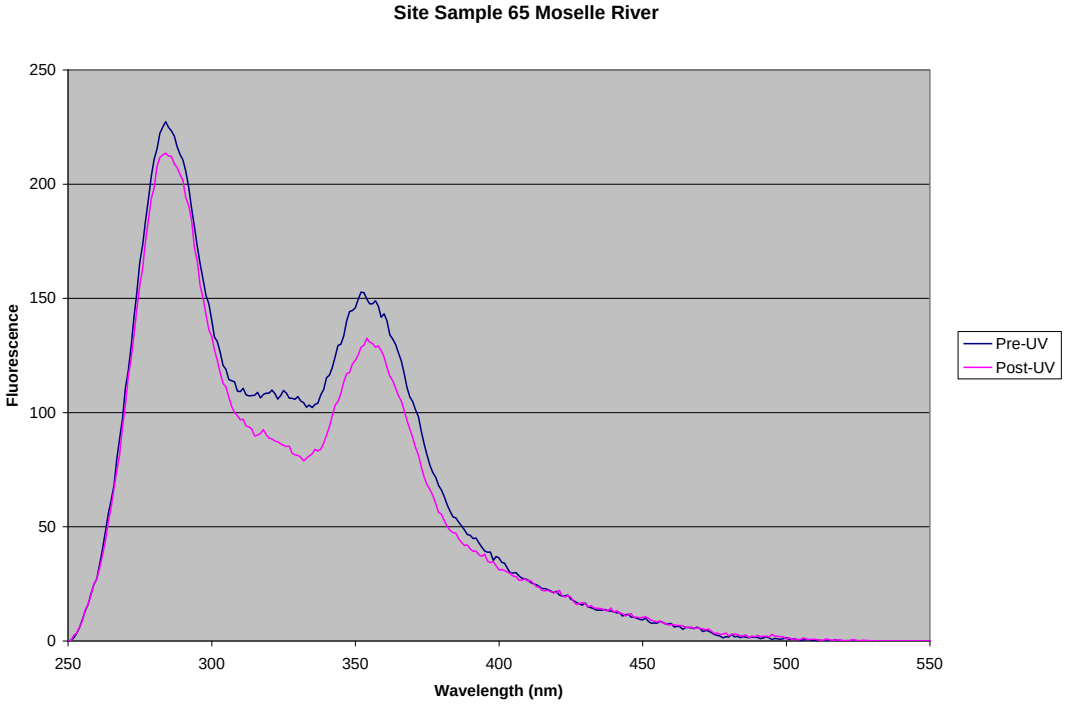


Figure 69: Pre- and Post-UV Comparison of Site Sample 65

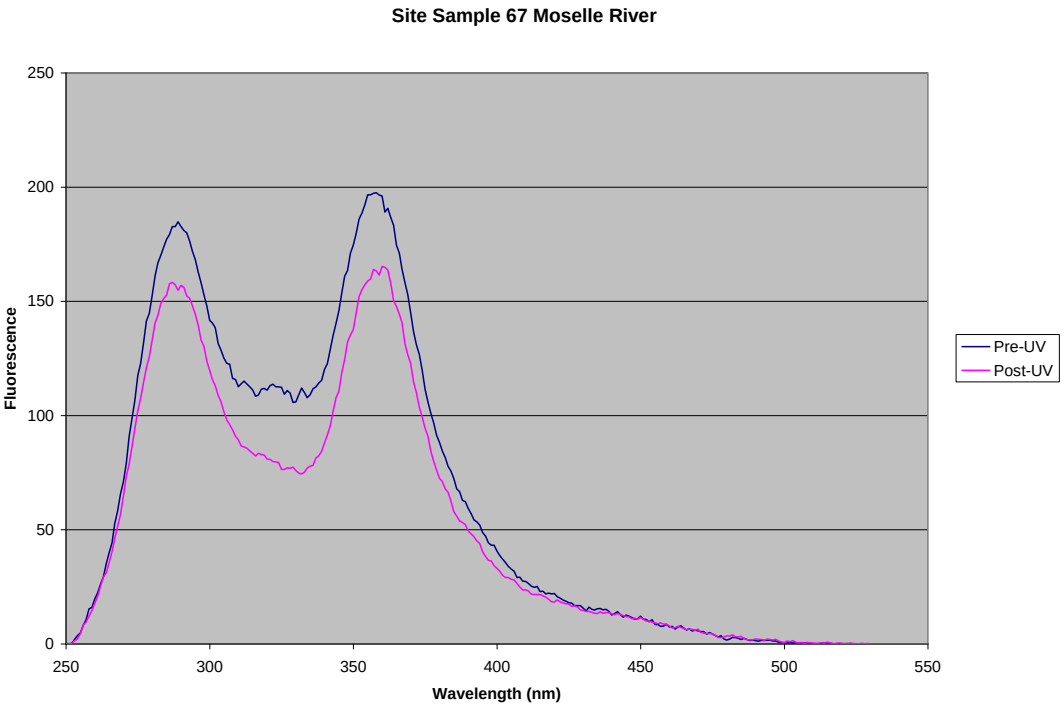


Figure 70: Pre- and Post-UV Comparison of Site Sample 67

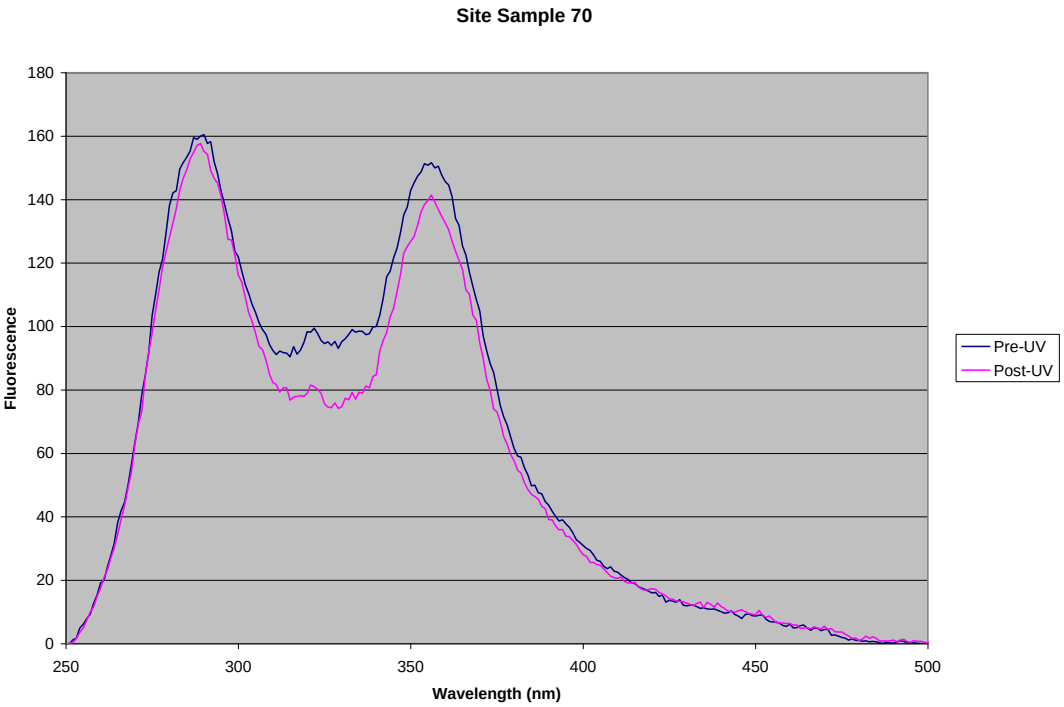


Figure 71: Pre- and Post-UV Comparison of Site Sample 70

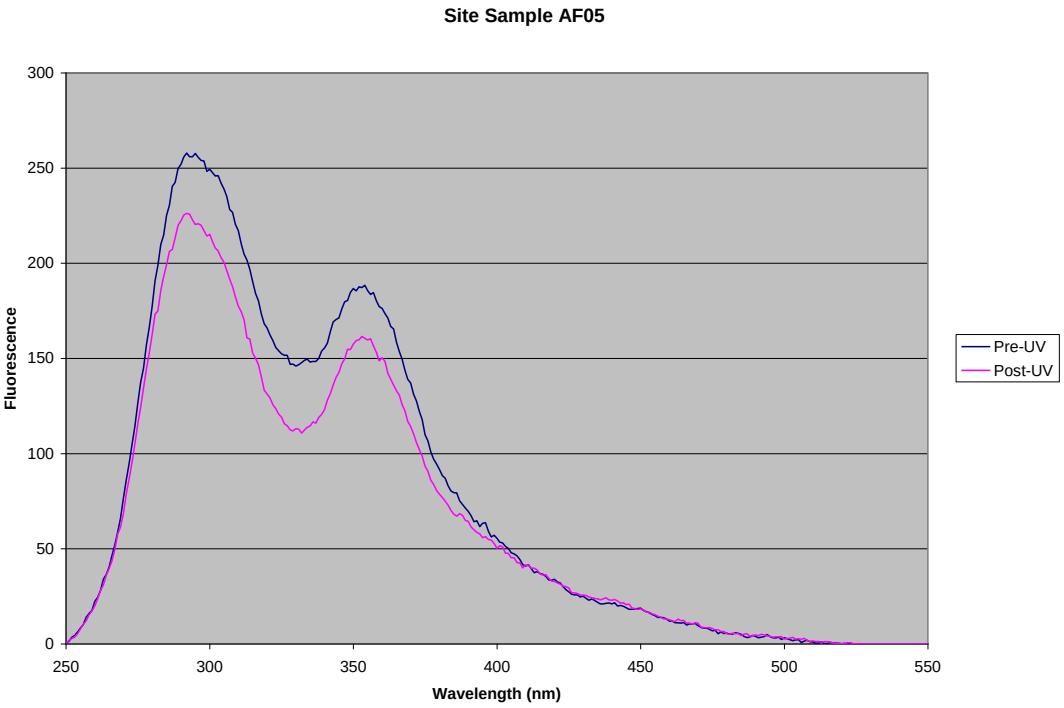


Figure 72: Pre- and Post-UV Comparison of Site Sample AF05

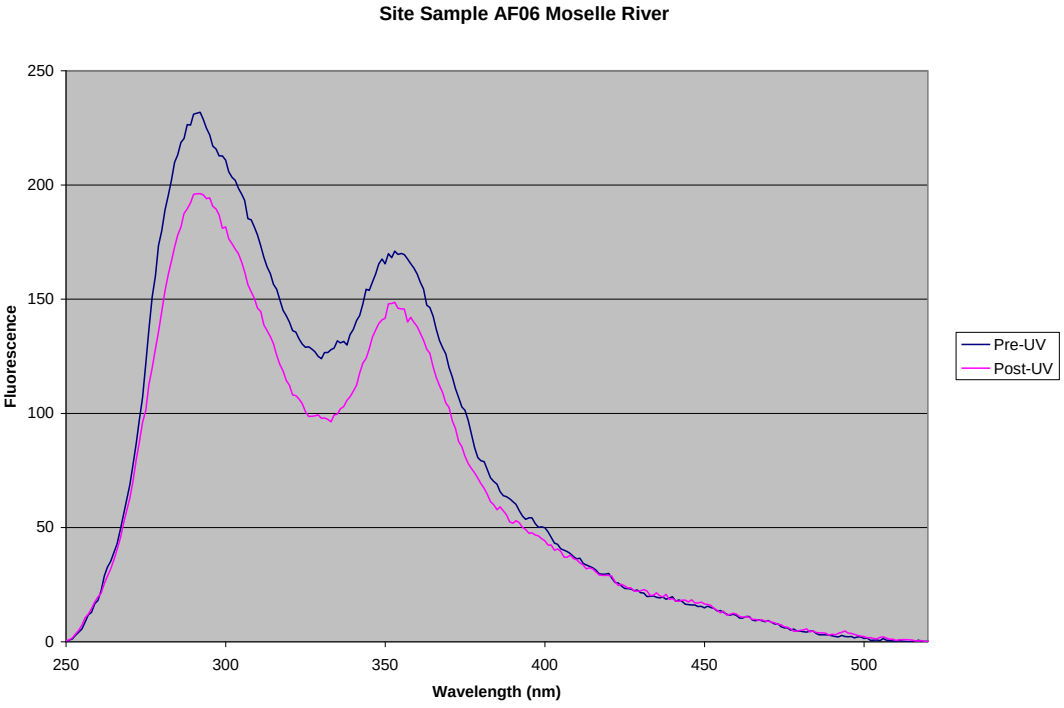


Figure 73: Pre- and Post-UV Comparison of Site Sample AF06

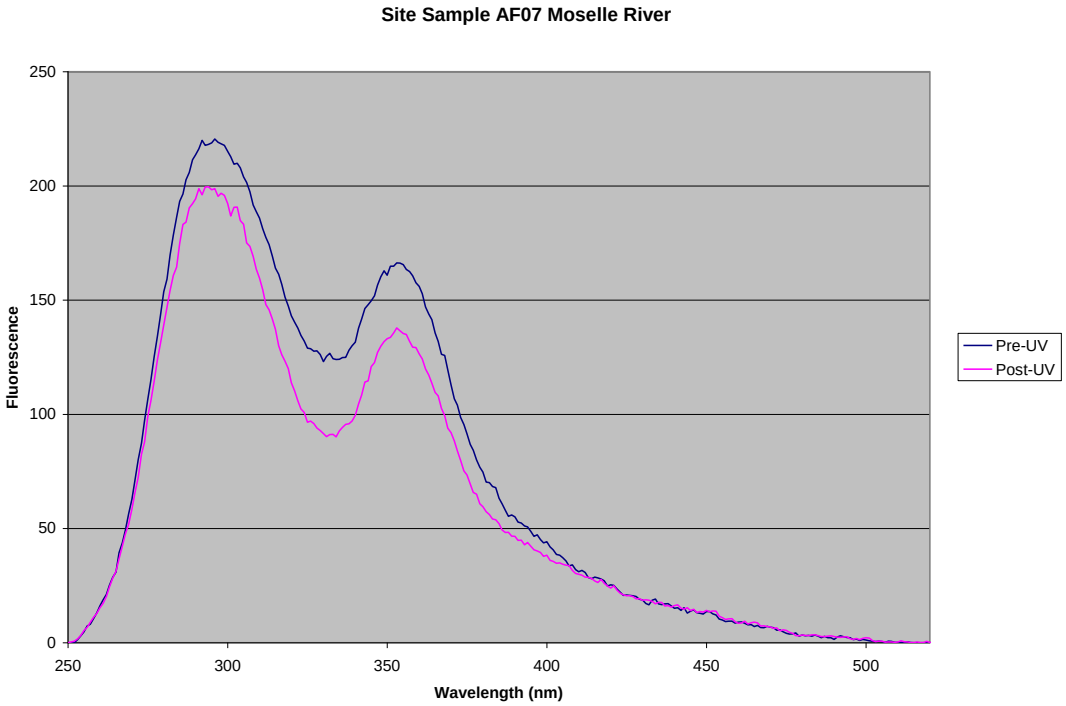


Figure 74: Pre- and Post-UV Comparison of Site Sample AF07

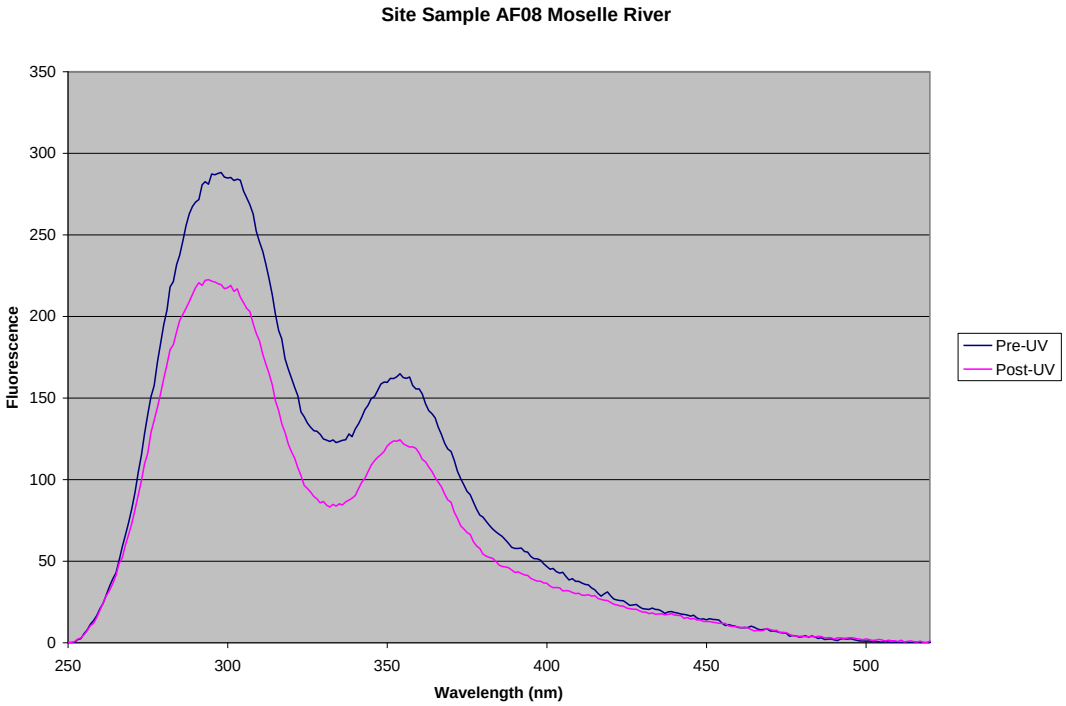


Figure 75: Pre- and Post-UV Comparison of Site Sample AF08

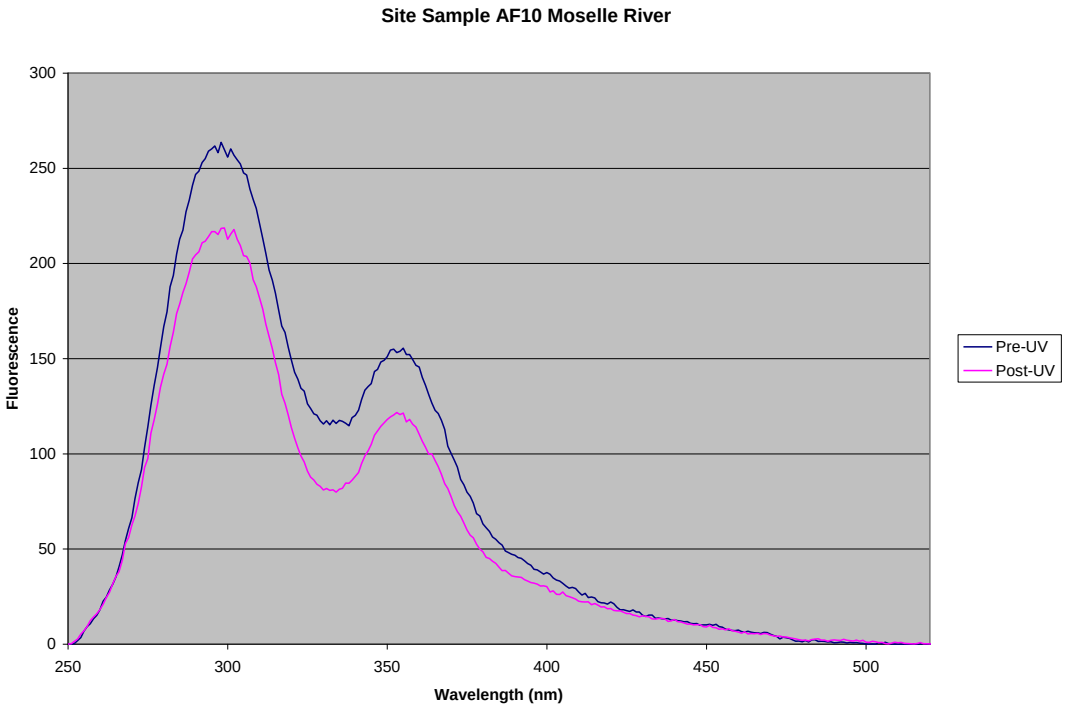


Figure 76: Pre- and Post-UV Comparison of Site Sample AF10

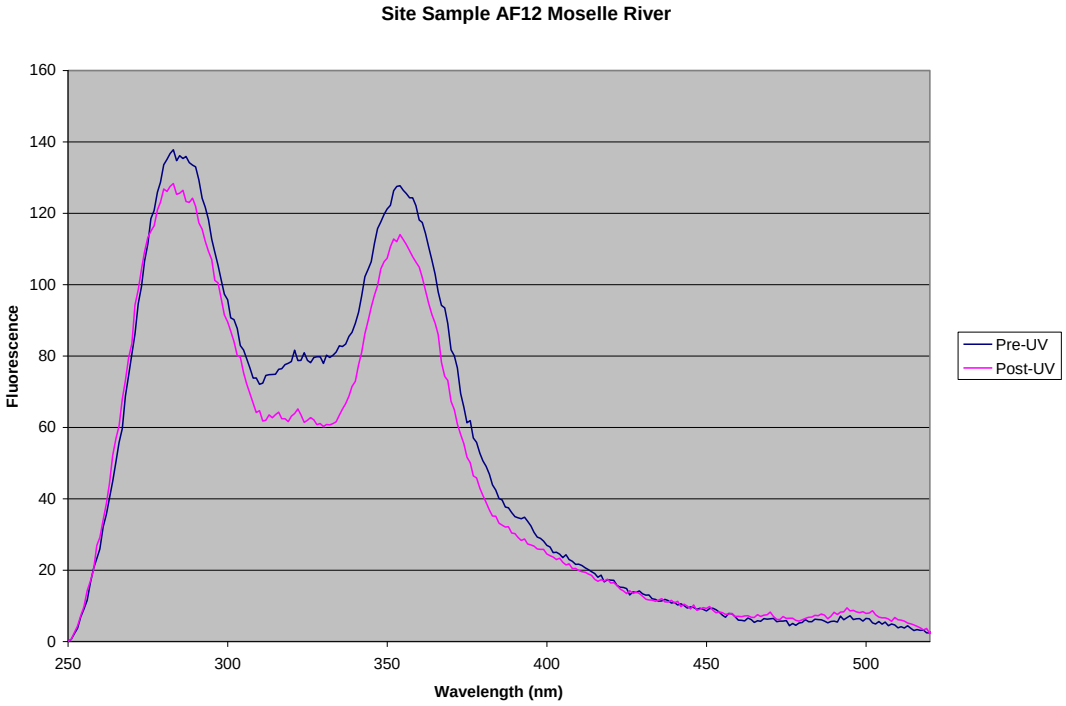


Figure 77: Pre- and Post-UV Comparison of Site Sample AF12

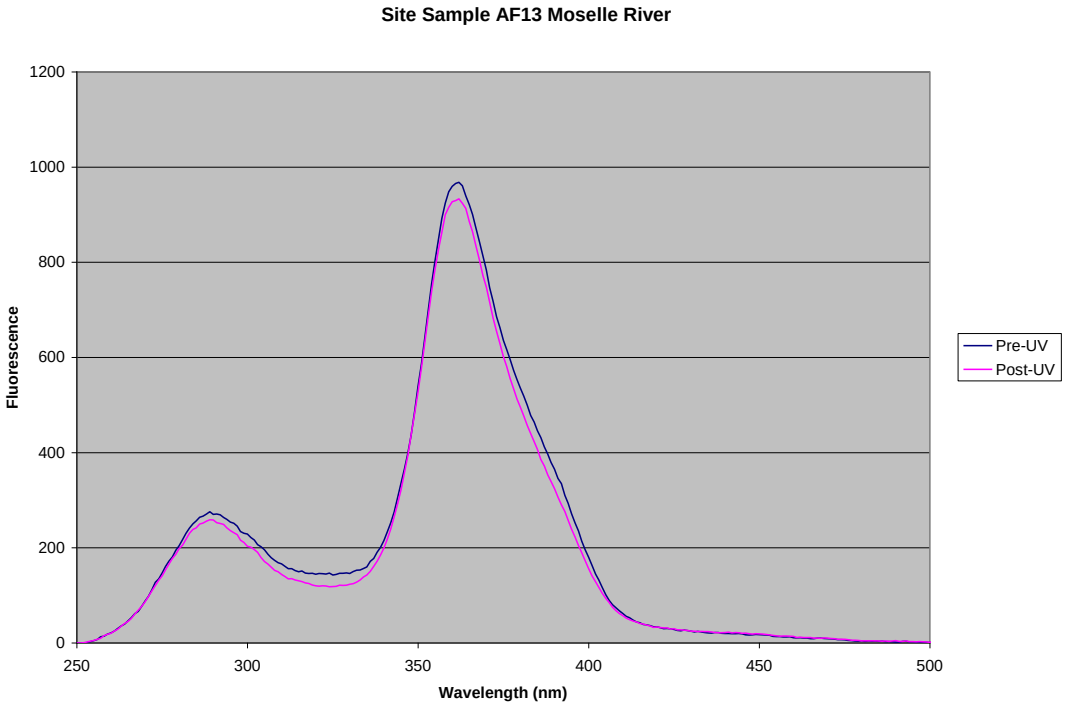


Figure 78: Pre- and Post-UV Comparison of Site Sample AF13

# Appendix D: UV Spectra Data from the Moselle River

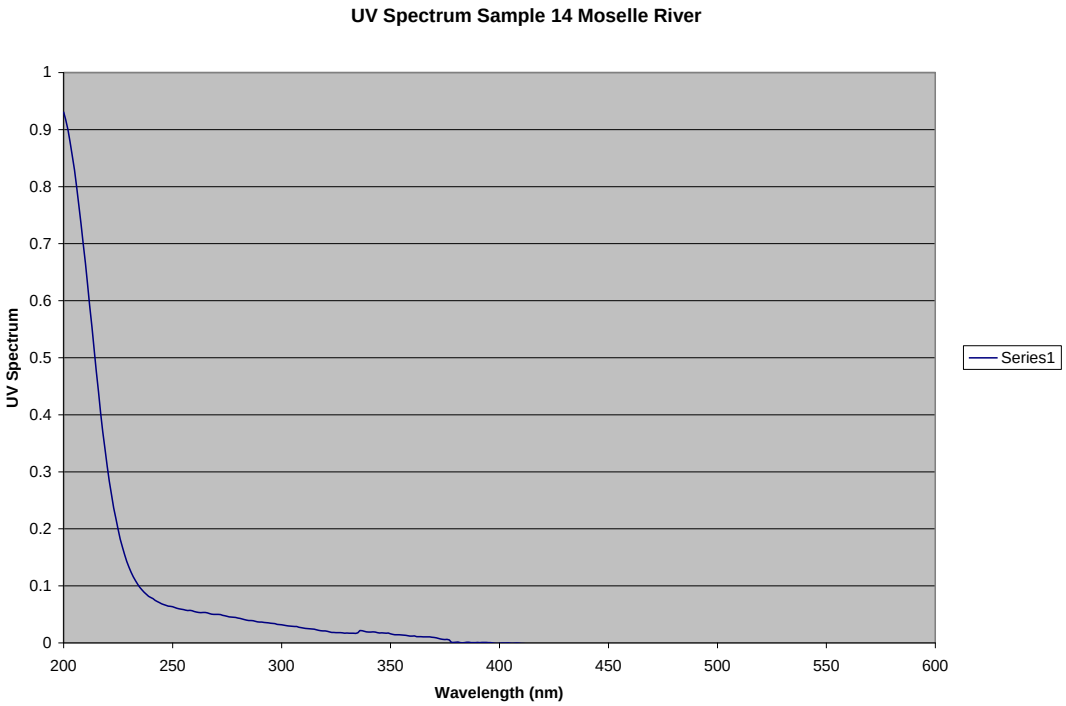


Figure 79: Site Sample 14

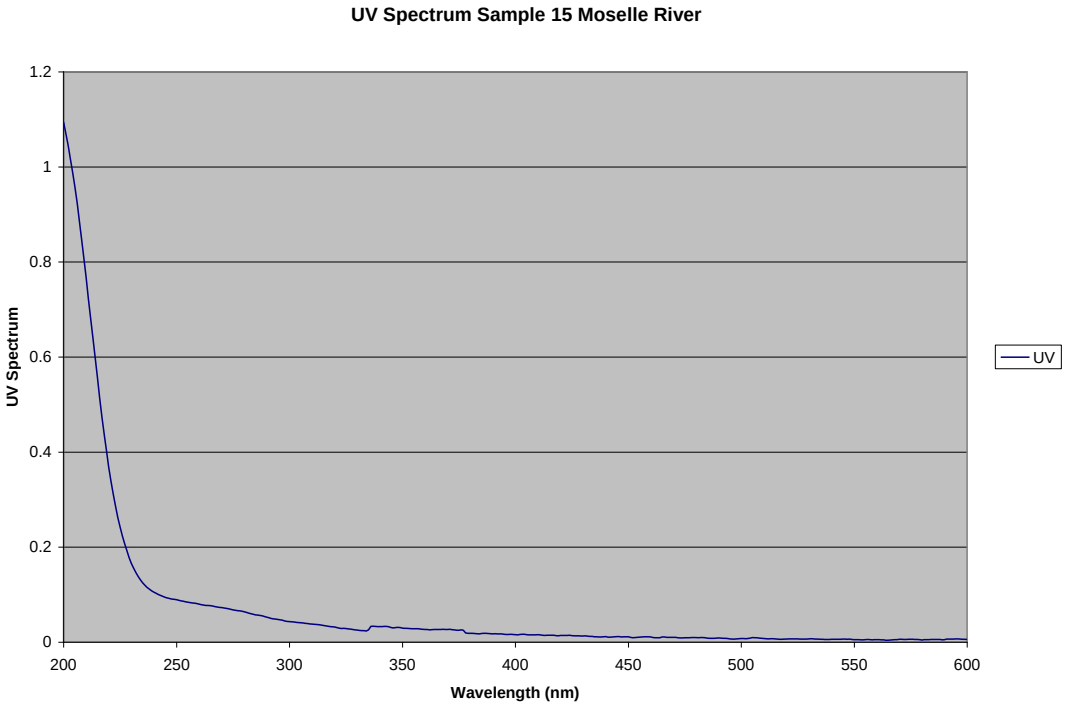


Figure 80: Site Sample 15

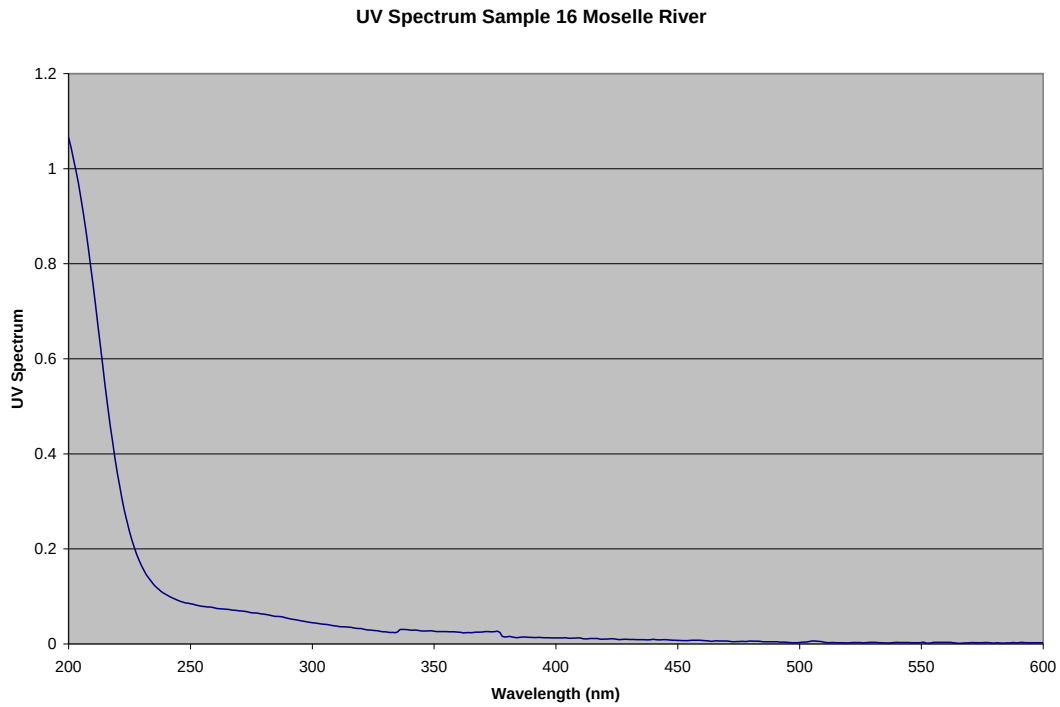


Figure 81: Site Sample 16

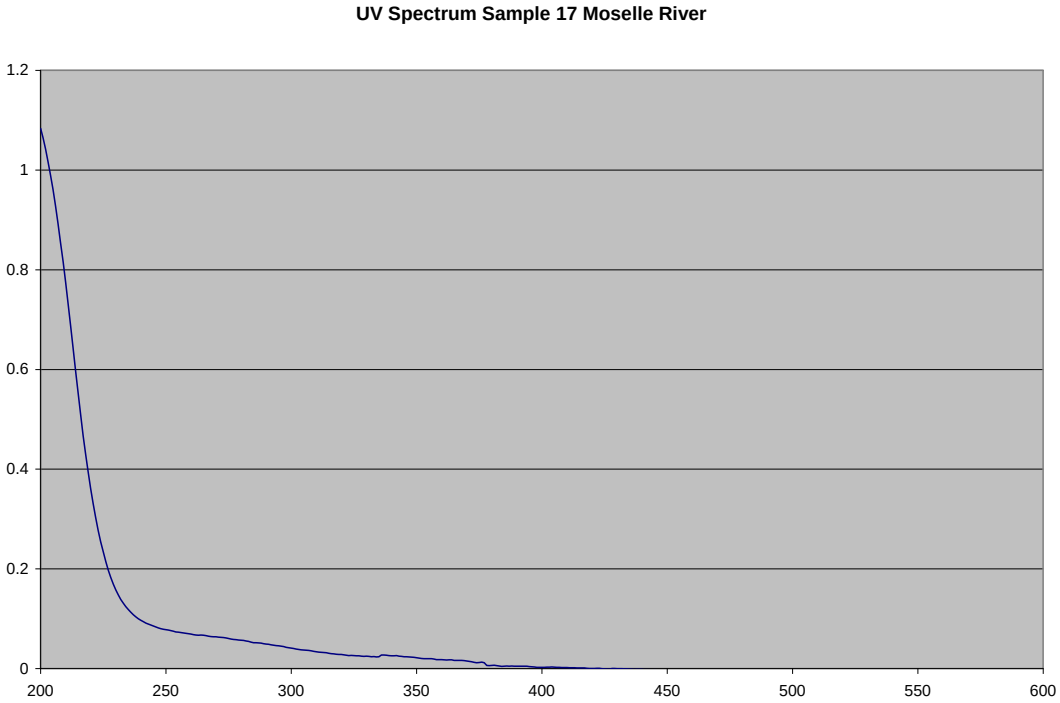


Figure 82: Site Sample 17

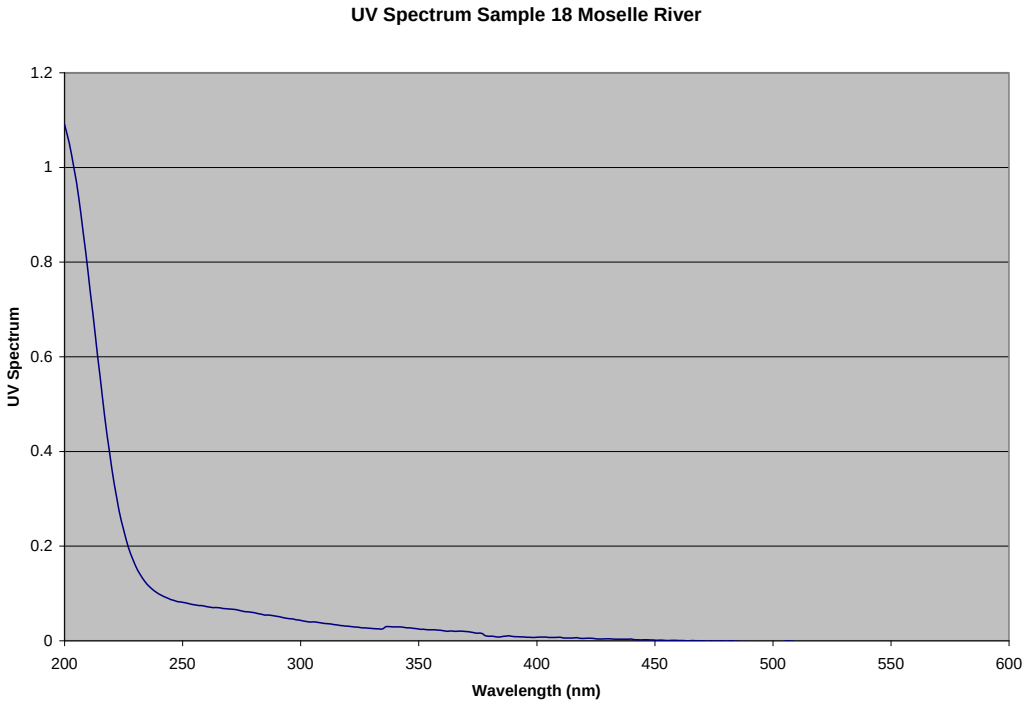


Figure 83: Site Sample 18

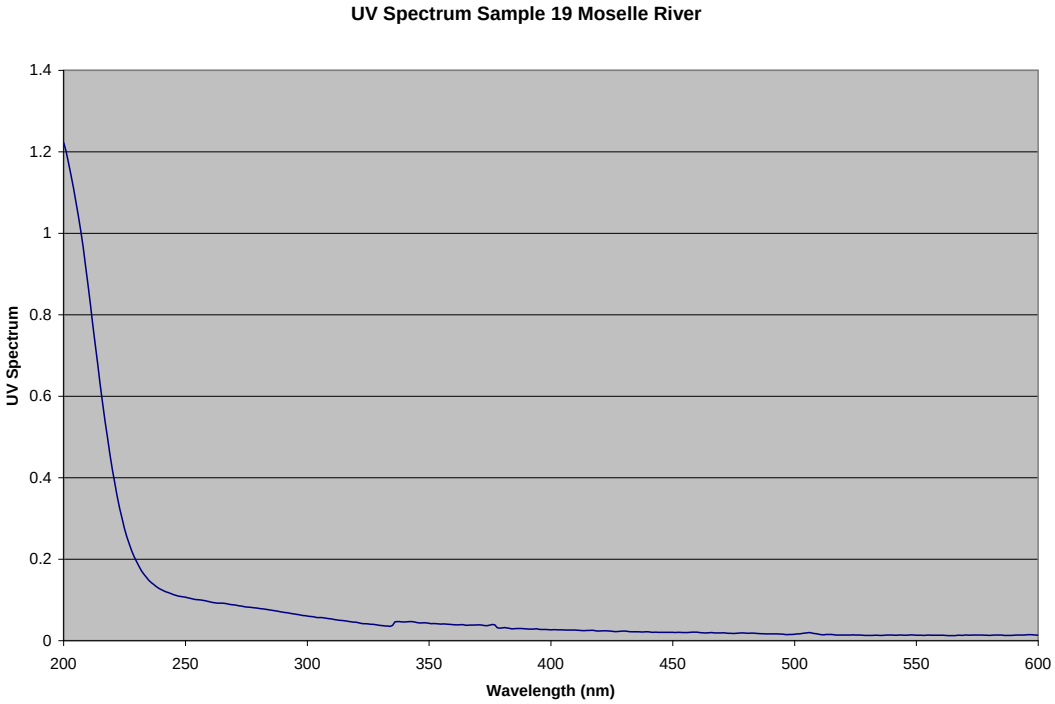


Figure 84: Site Sample 19

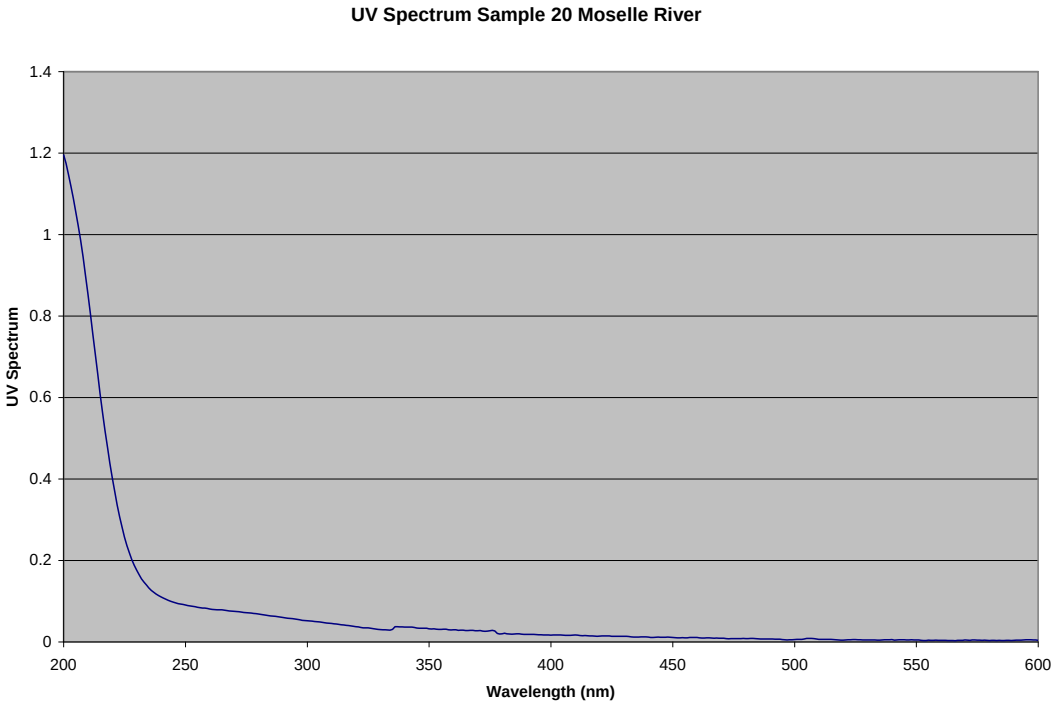


Figure 85: Site Sample 20

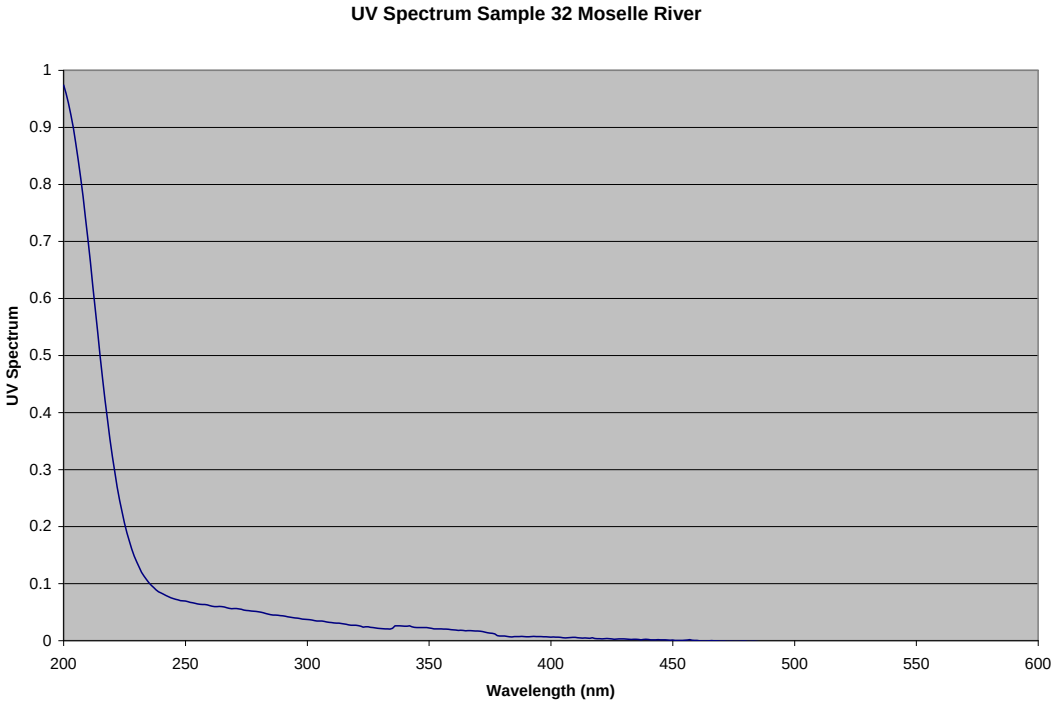


Figure 86: Site Sample 32

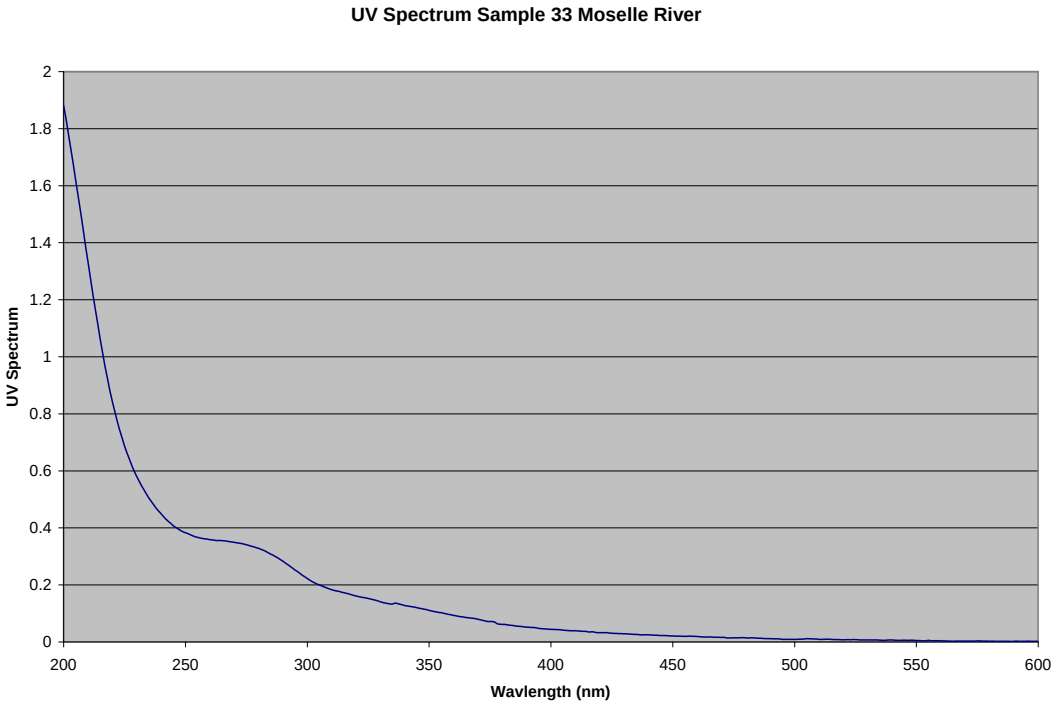


Figure 87: Site Sample 33

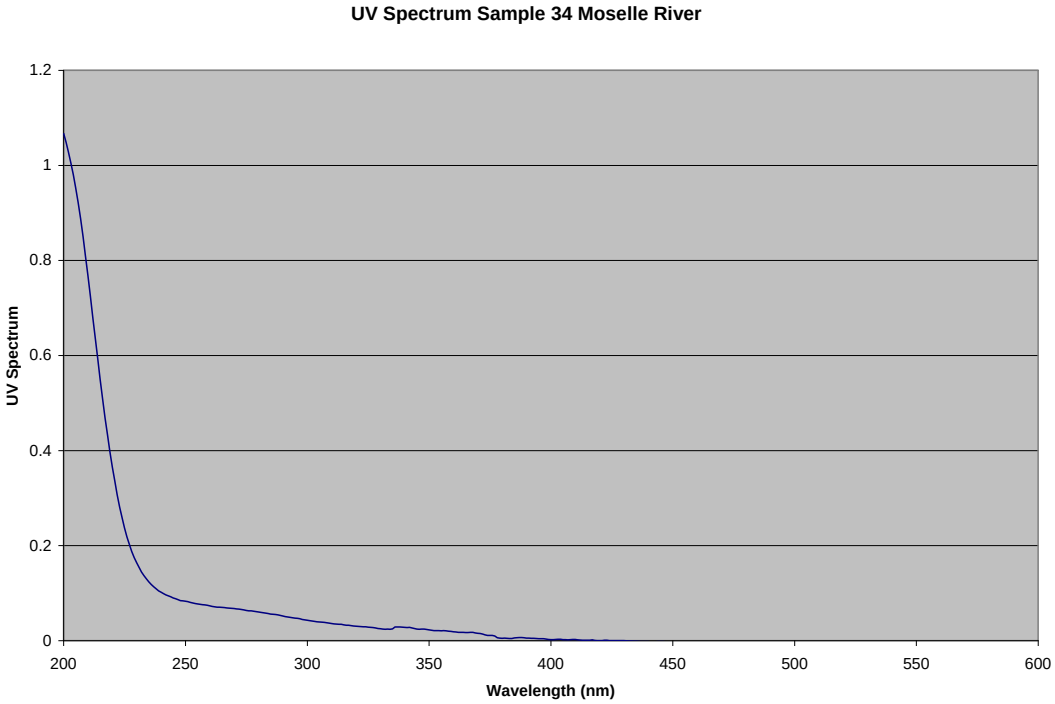


Figure 88: Site Sample 34

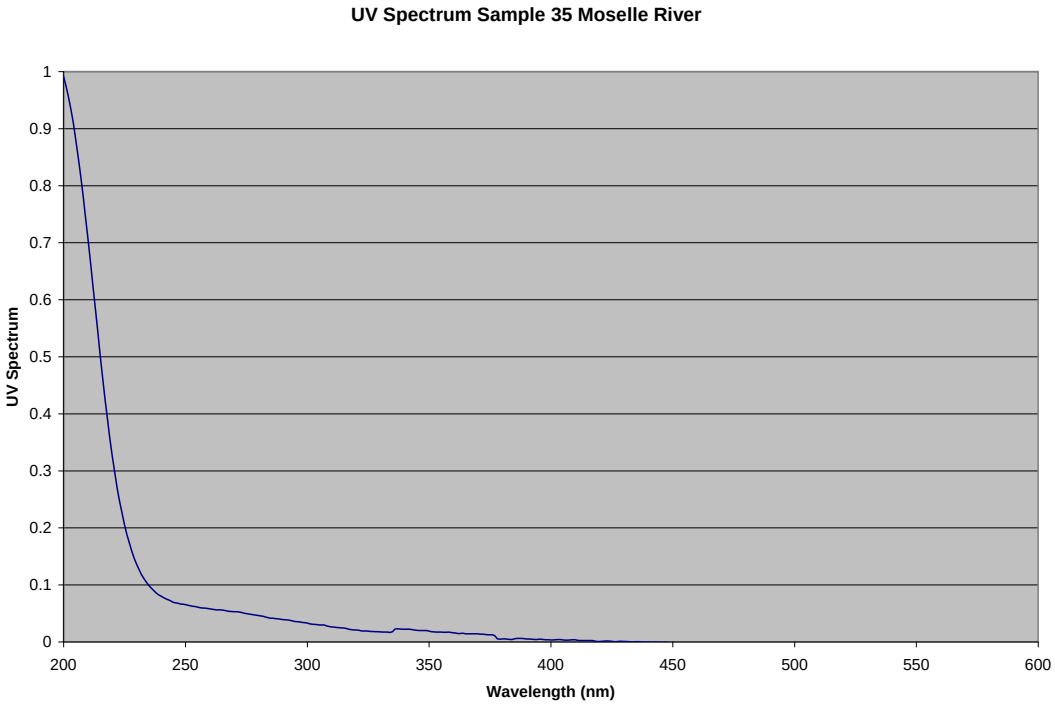


Figure 89: Site Sample 35

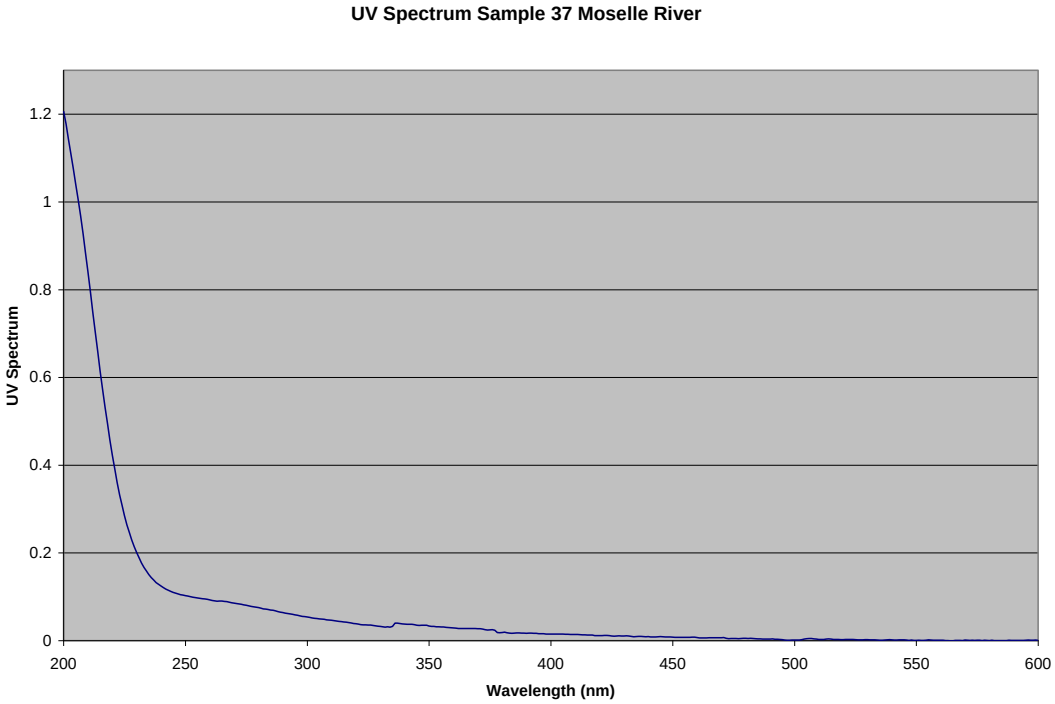


Figure 90: Site Sample 37

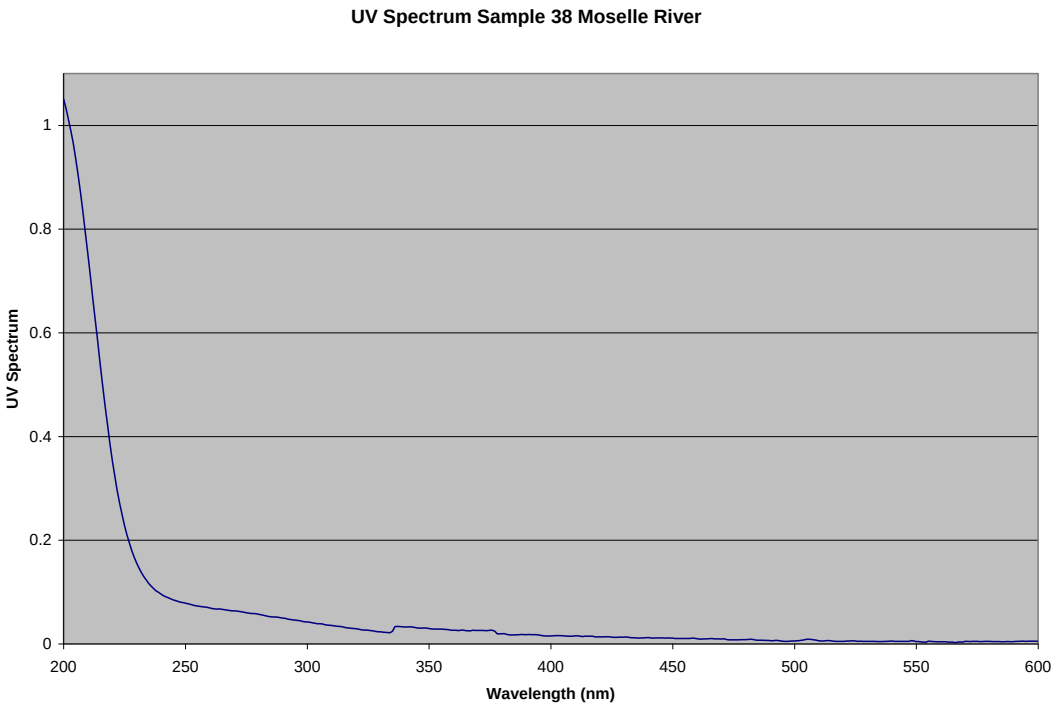


Figure 91: Site Sample 38

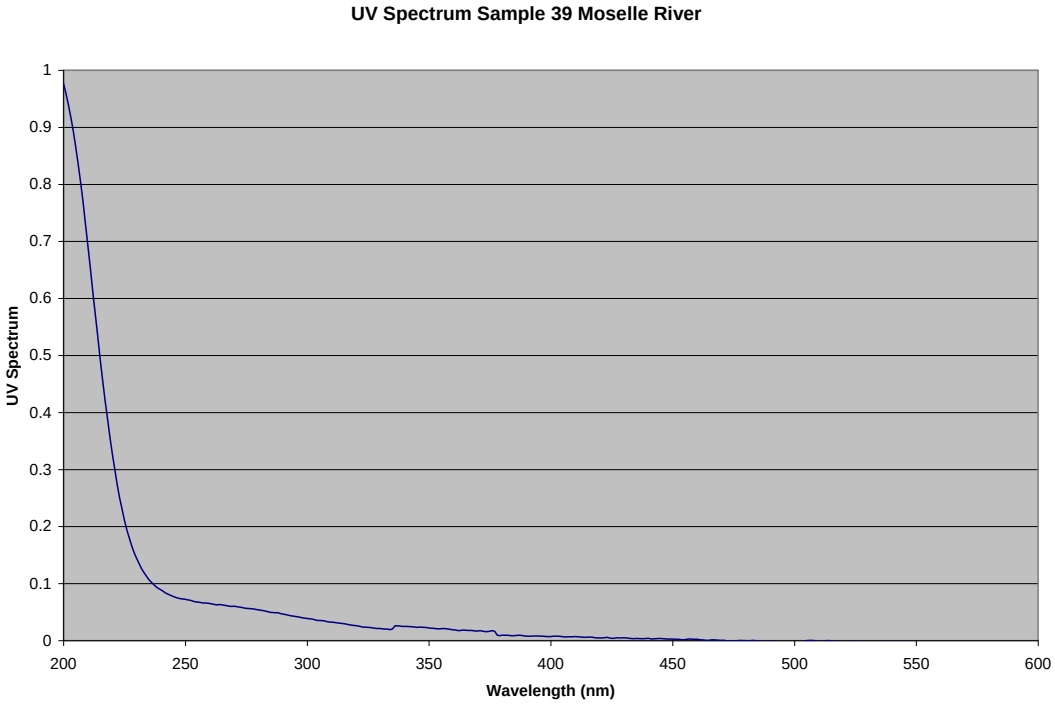


Figure 92: Site Sample 39

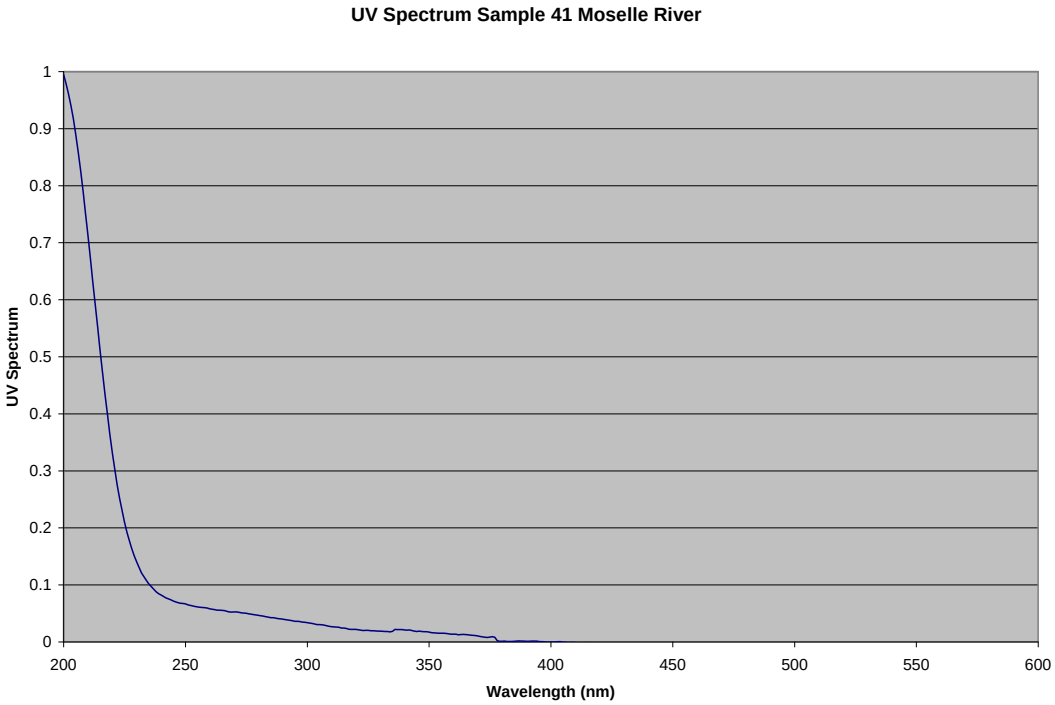


Figure 93: Site Sample 41

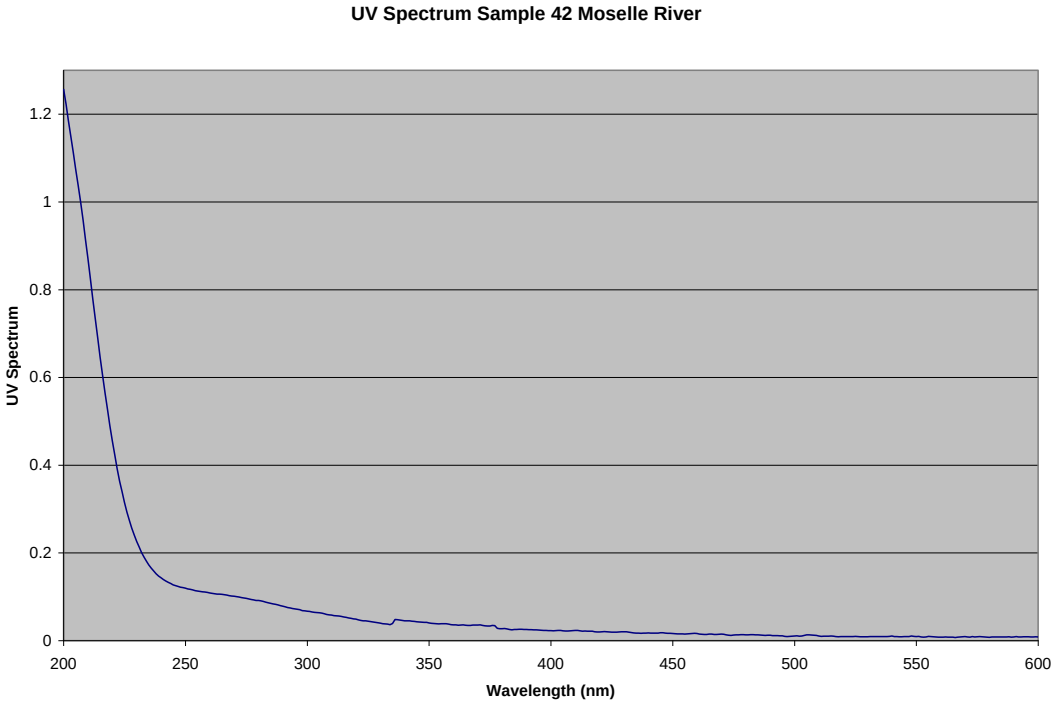


Figure 94: Site Sample 42

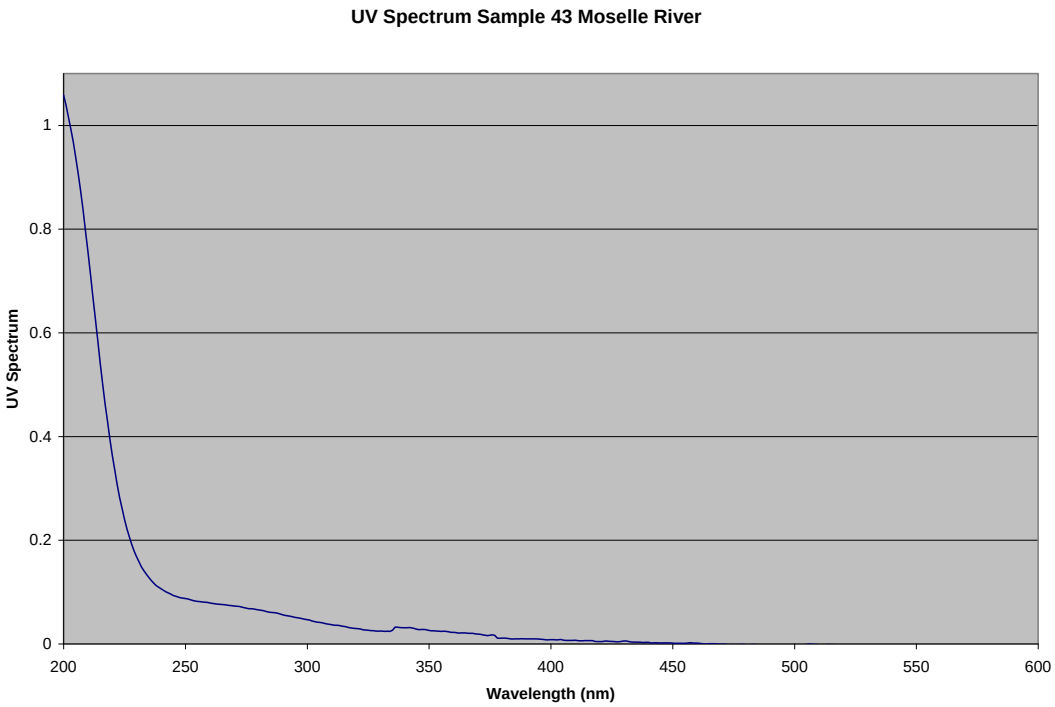


Figure 95: Site Sample 43

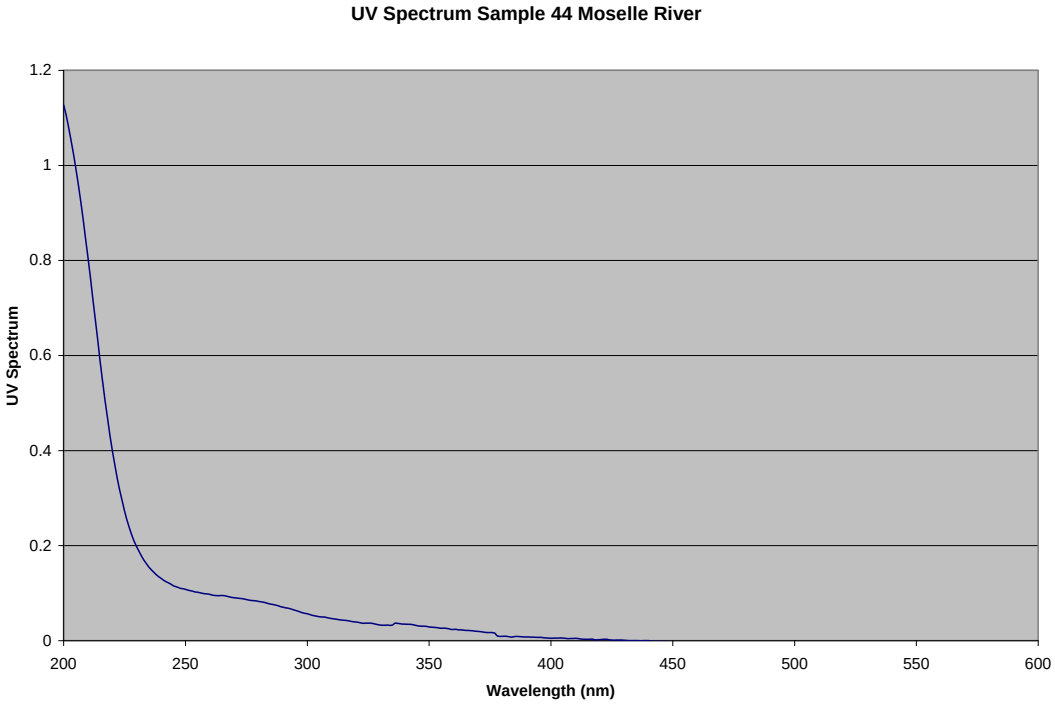


Figure 96: Site Sample 44

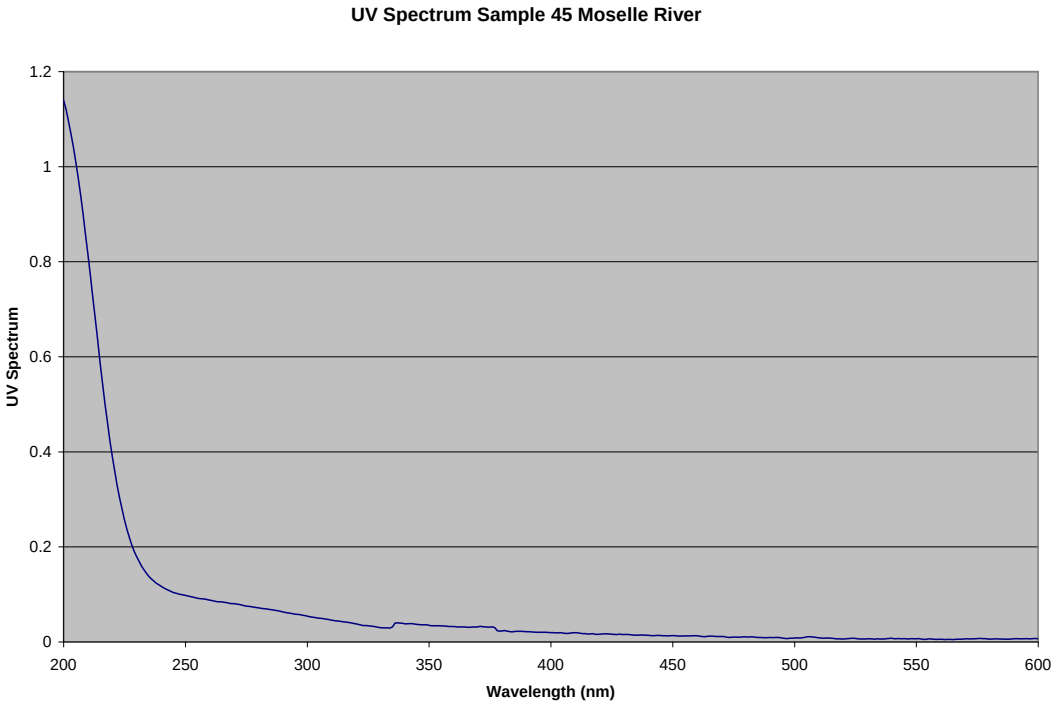


Figure 97: Site Sample 45

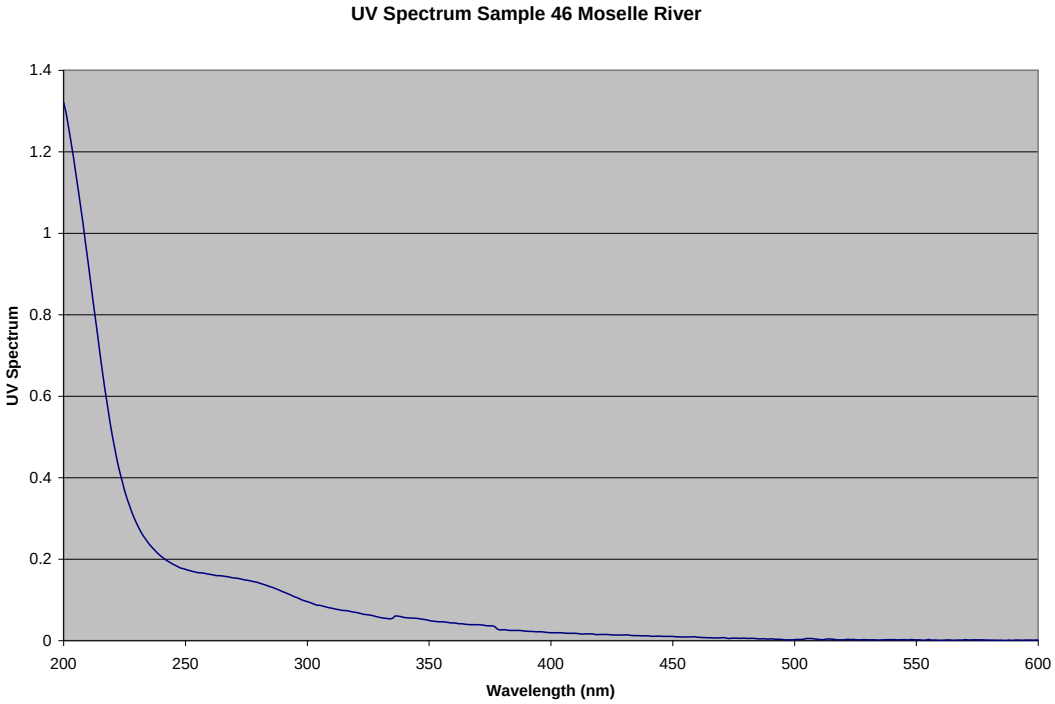


Figure 98: Site Sample 46

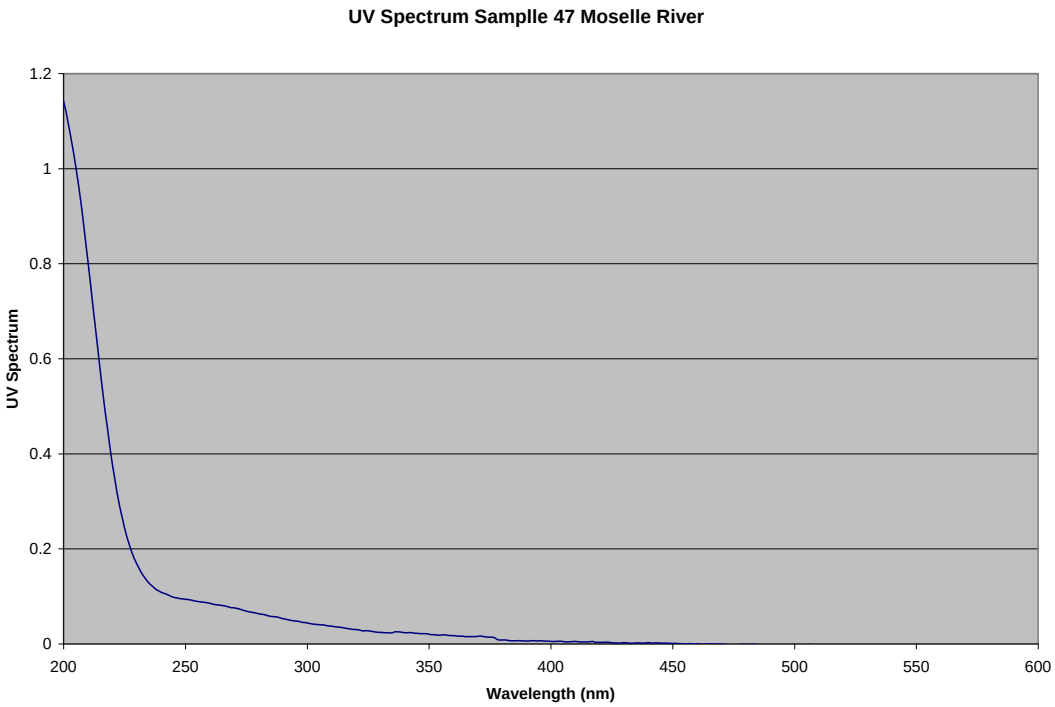


Figure 99: Site Sample 47

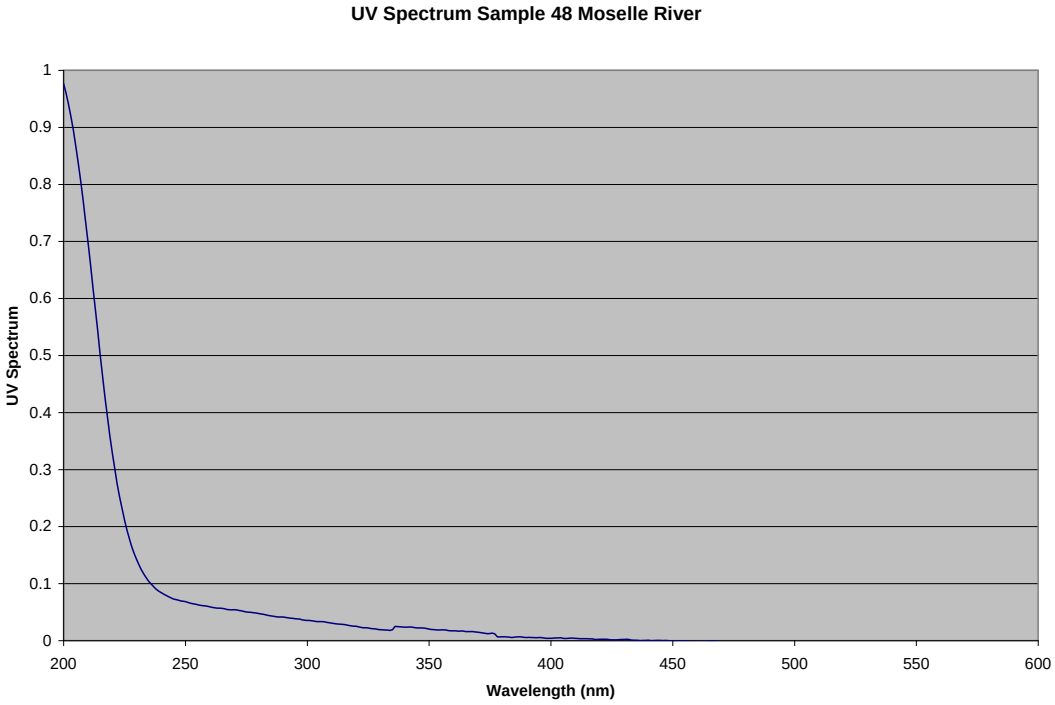


Figure 100: Site Sample 48

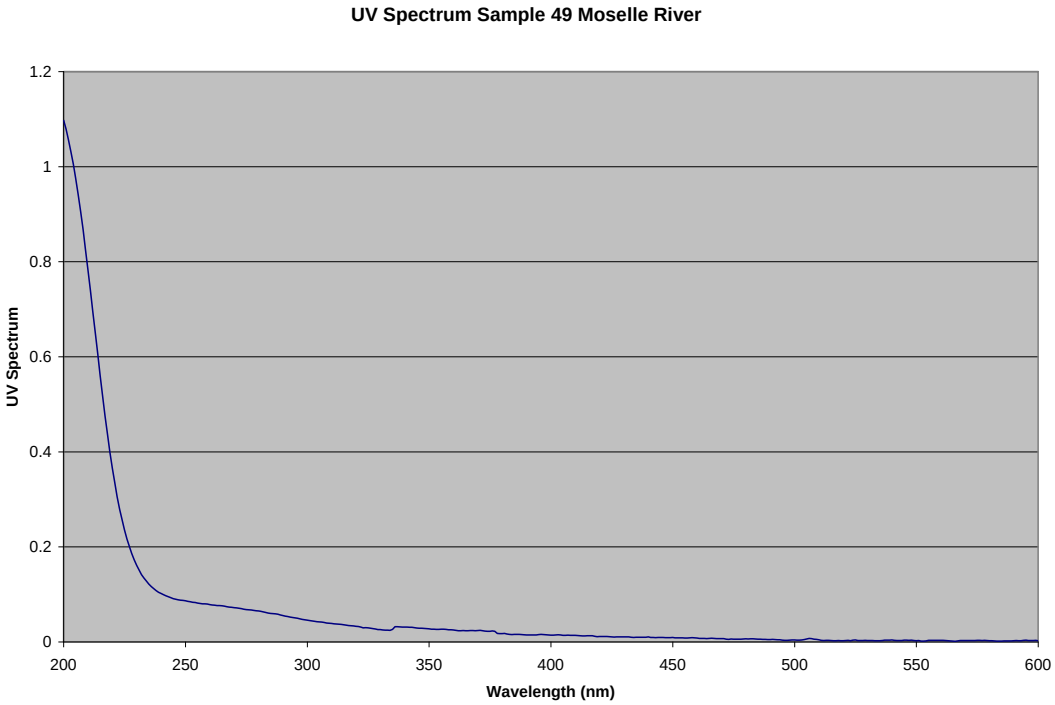


Figure 101: Site Sample 49

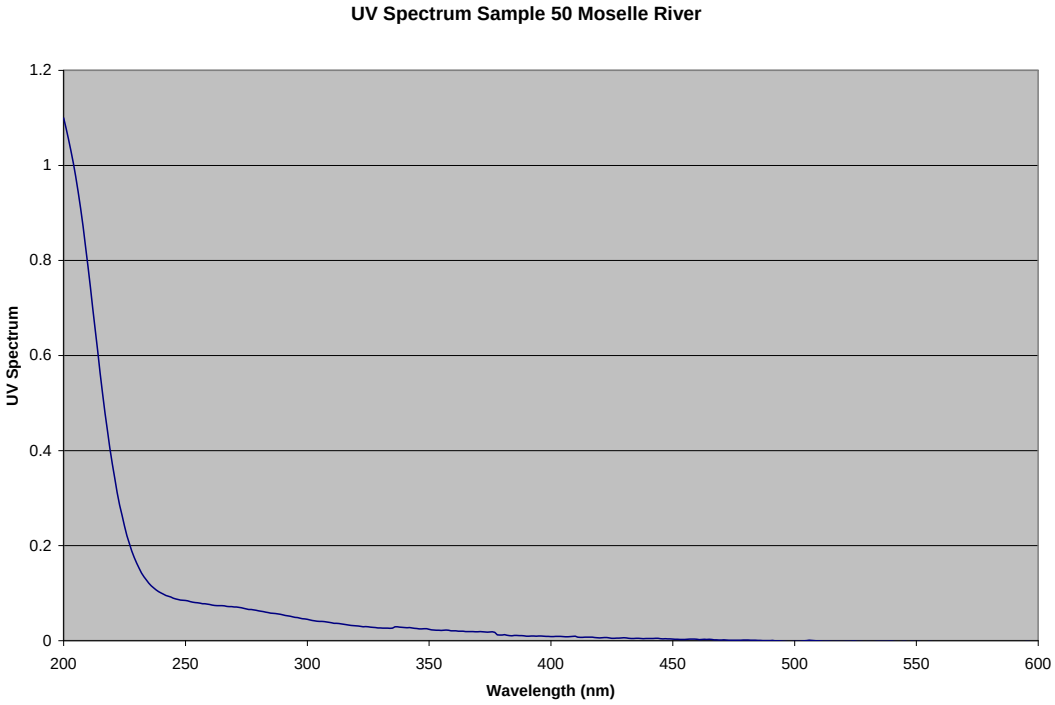


Figure 102: Site Sample 50

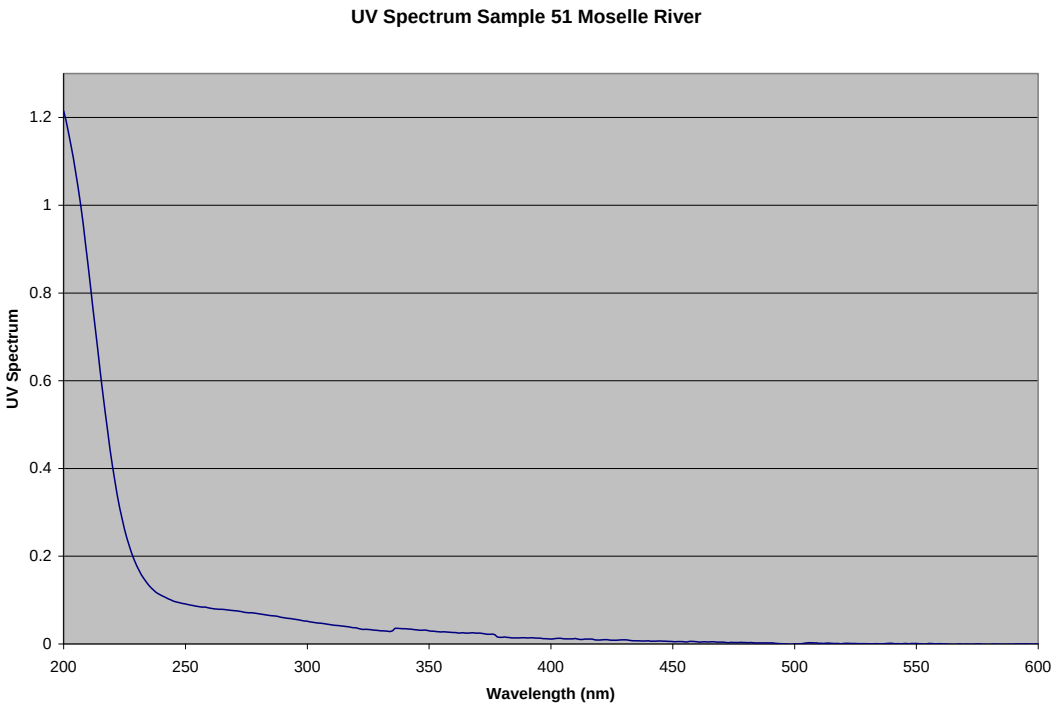


Figure 103: Site Sample 51

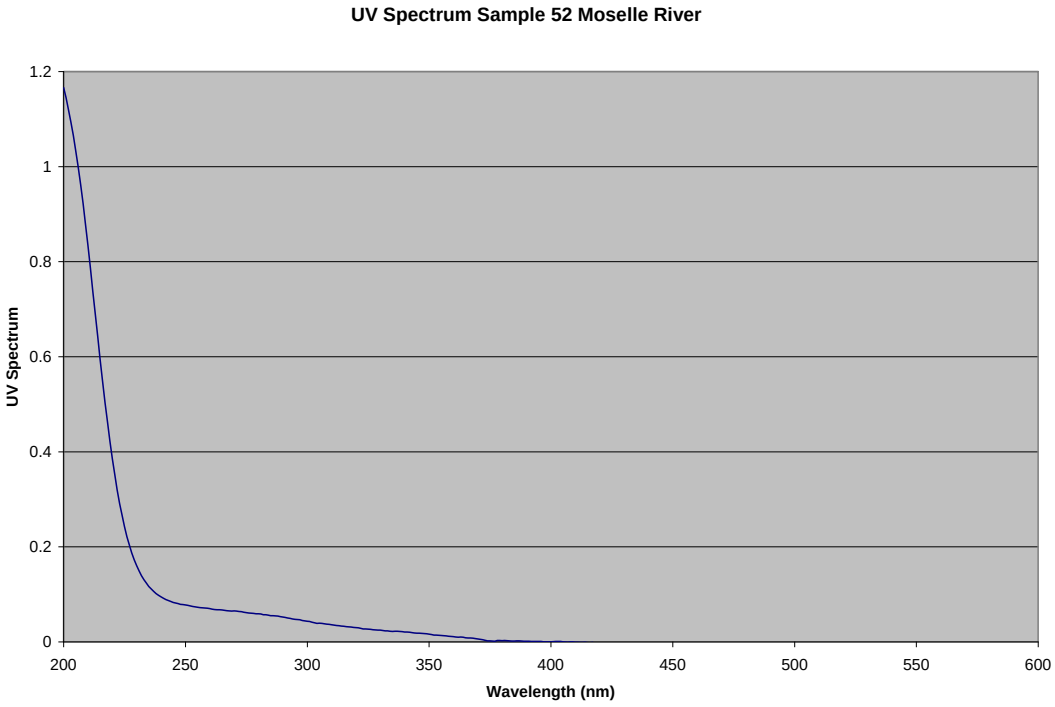


Figure 104: Site Sample 52

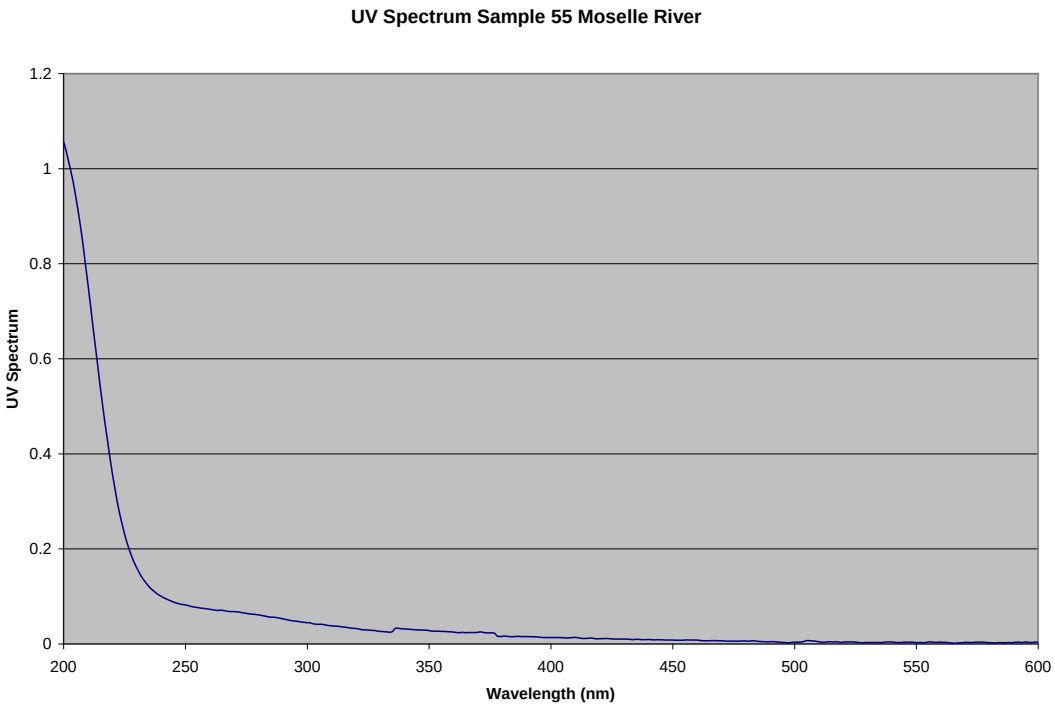


Figure 105: Site Sample 55

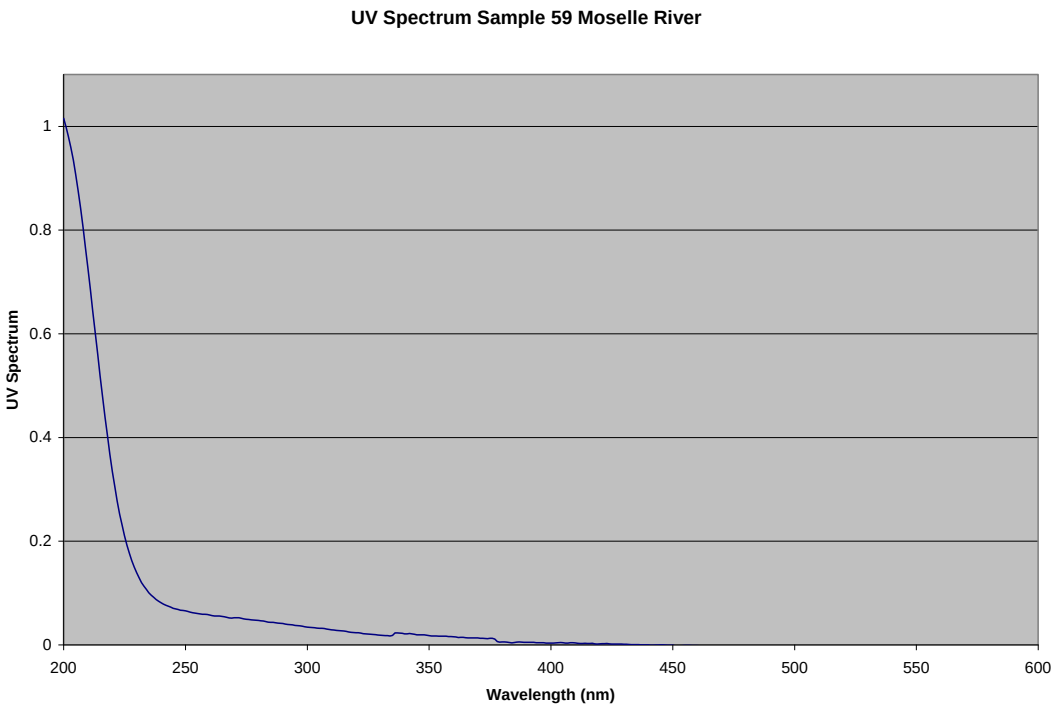


Figure 106: Site Sample 59

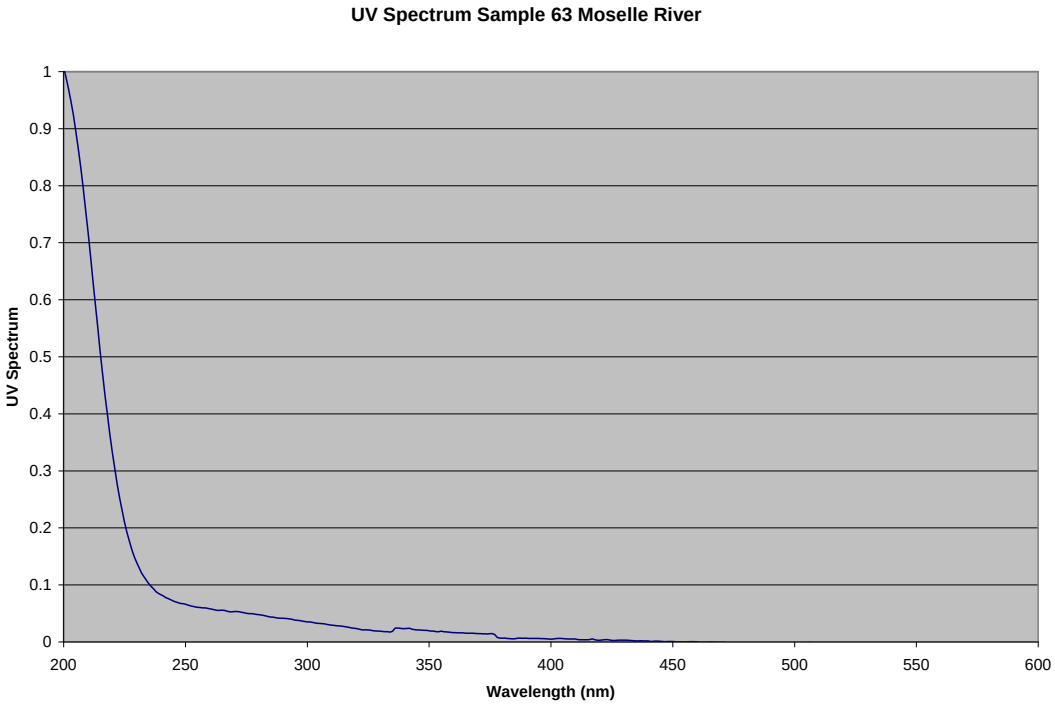


Figure 107: Site Sample 63

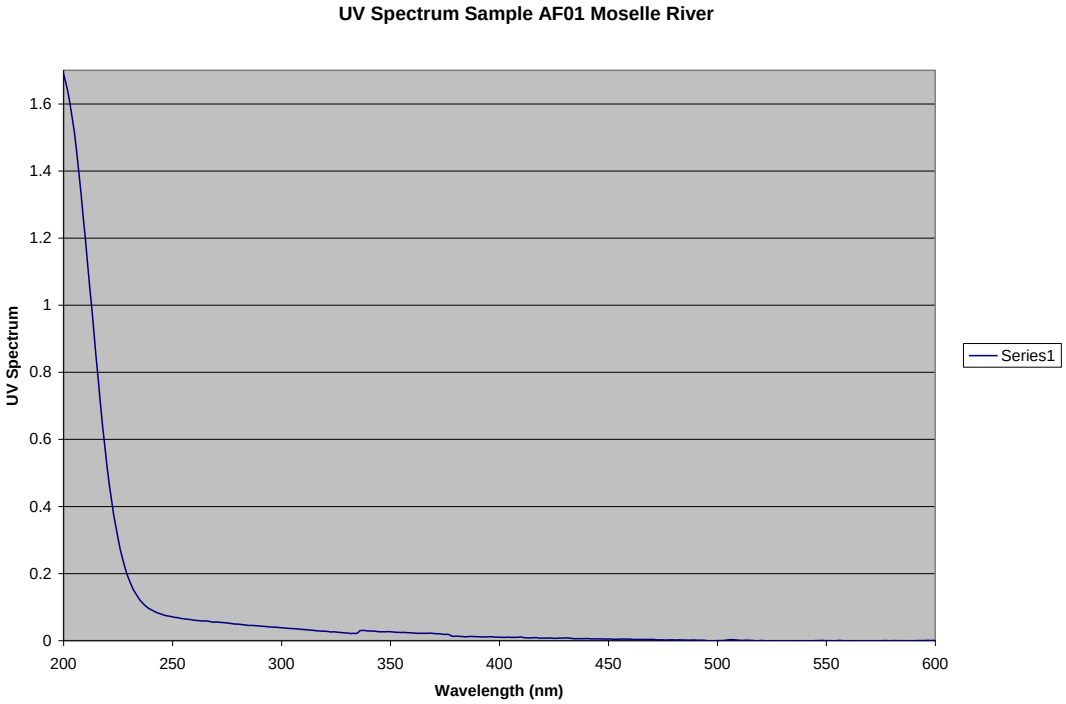


Figure 108: Site Sample AF01

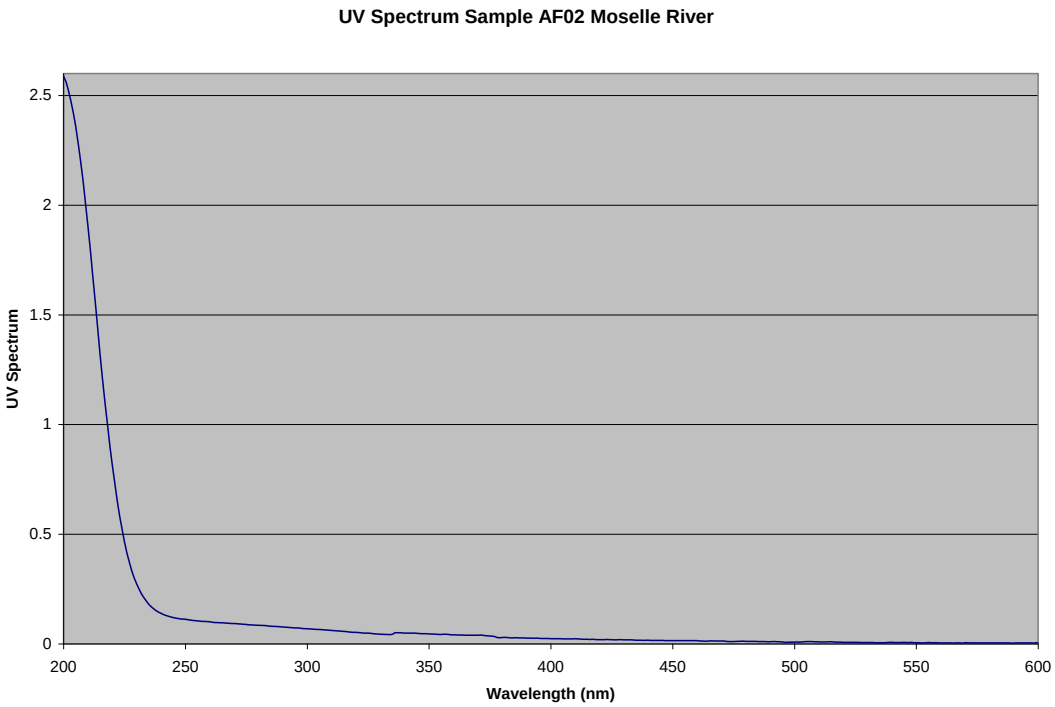


Figure 109: Site Sample AF02

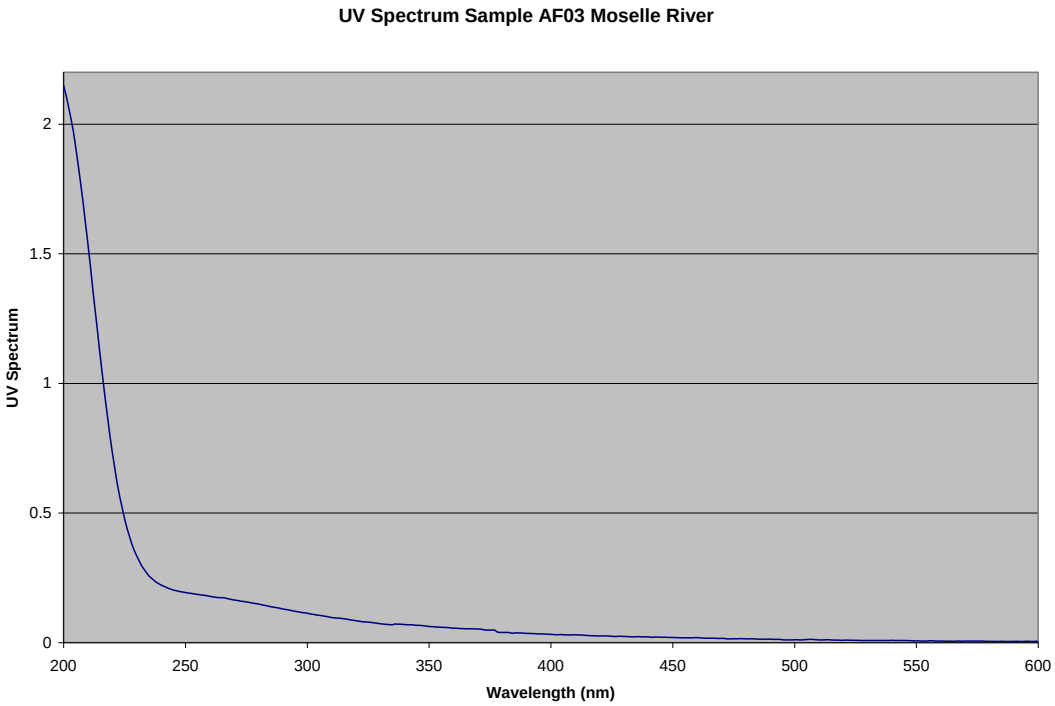


Figure 110: Site Sample AF03

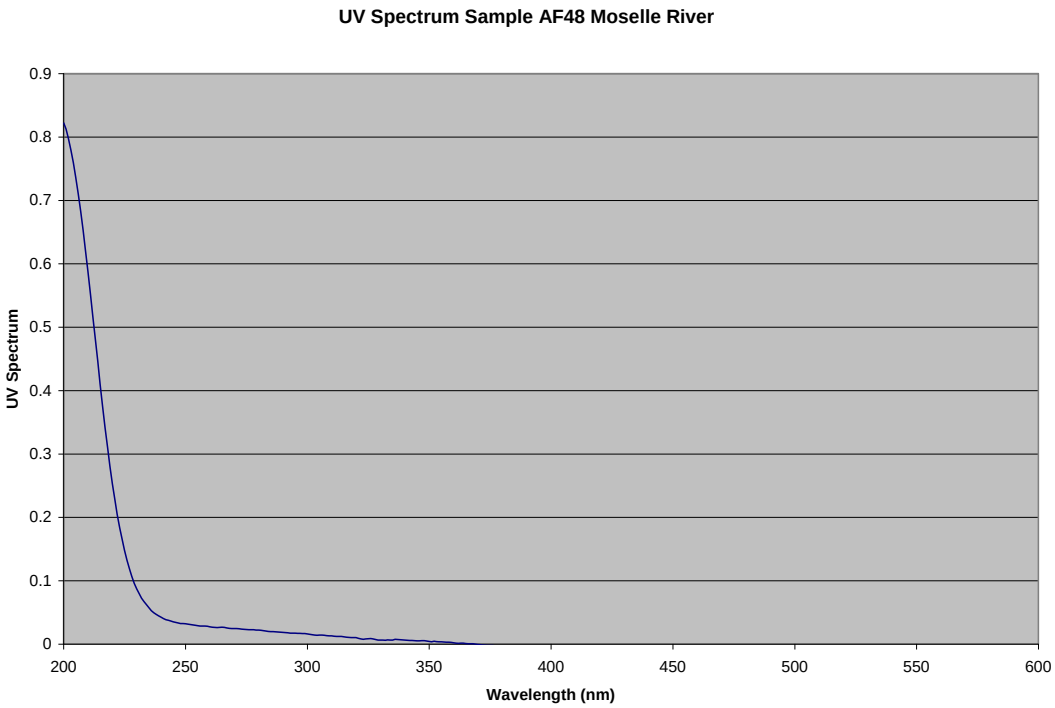


Figure 111: Site Sample AF48

The surrogate chemical oxygen demand values were tracked sequentially along the Moselle River to corroborate the evidence in the fluorescence data, which indicated the presence of both tryptophan and humic acid. The largest COD values were found at Sample Sites 33, 46, and 42 – consistent with the fluorescence peaks found at 356 nm. This was expected because COD levels rise with the presence of organic compounds.

# Appendix E: Irradiation Tests

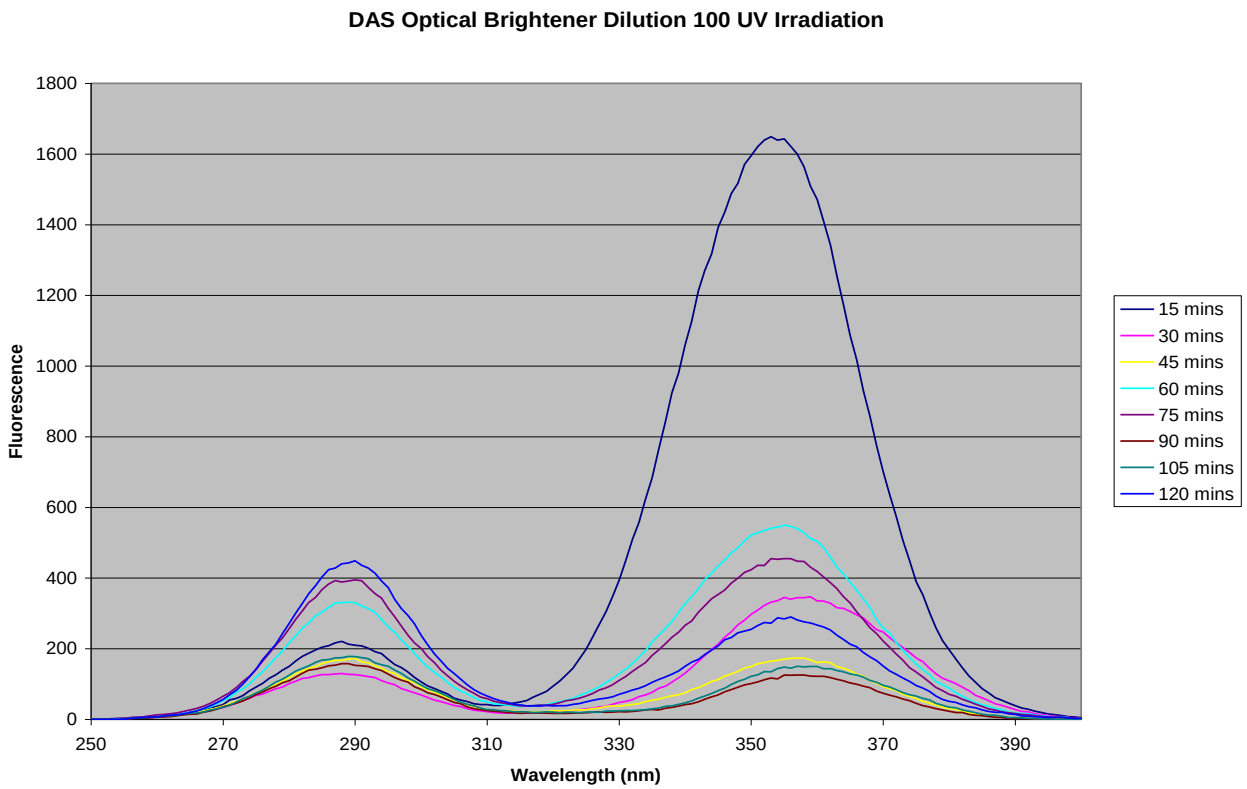


Figure 112: DAS Optical Brightner UV Irradiation

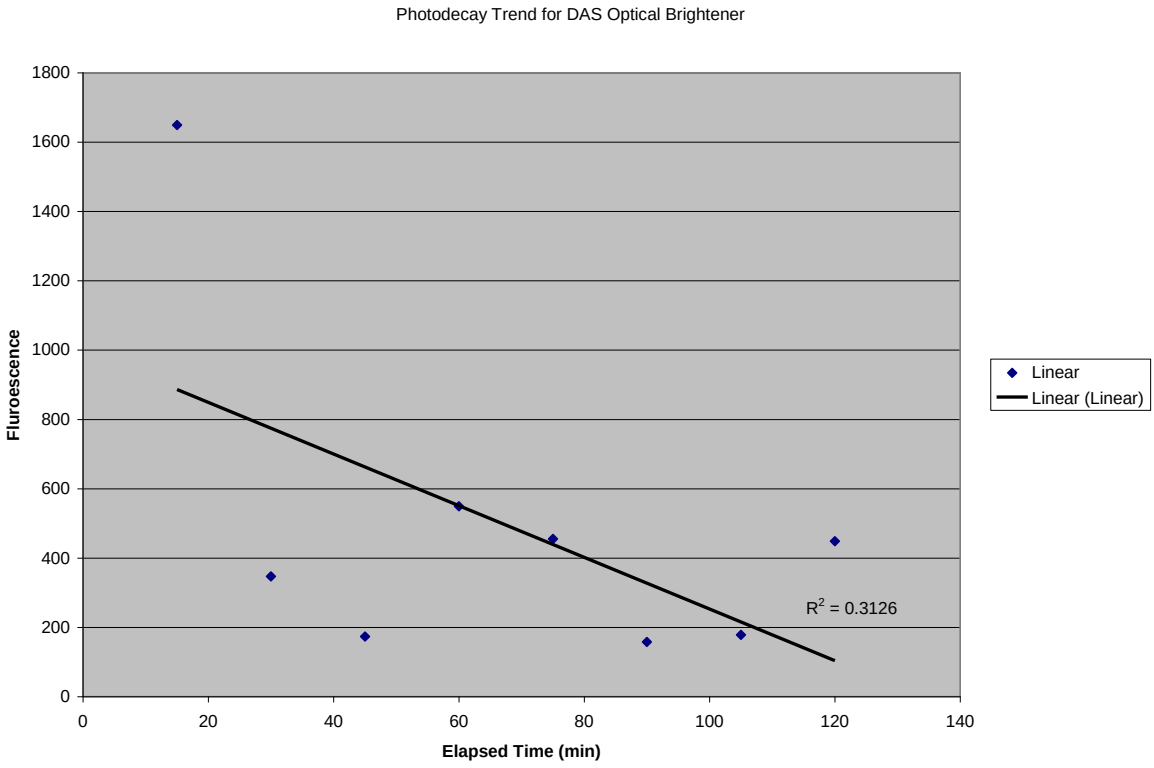


Figure 113: Linear trend of photodegredation for DAS Optical Brightener Dilution

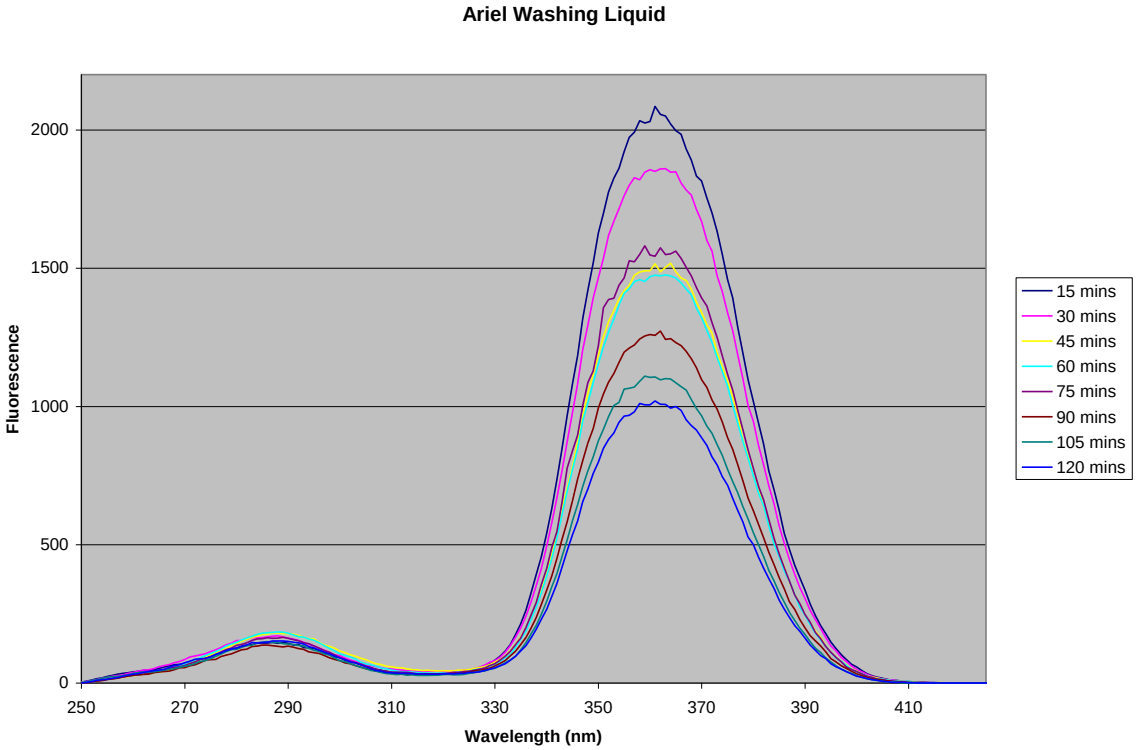


Figure 114: Ariel Washing Liquid Dilution 1000 UV Irradiation Test

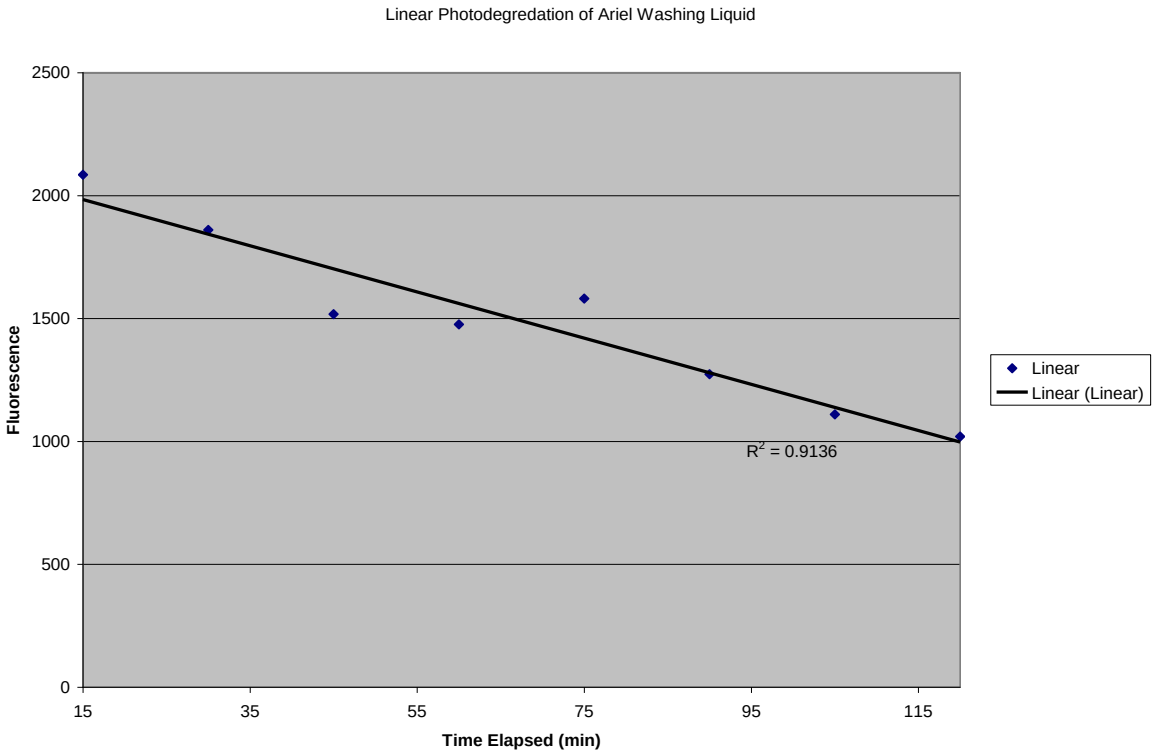


Figure 115: Linear trend of photodegredation for Ariel washing liquid

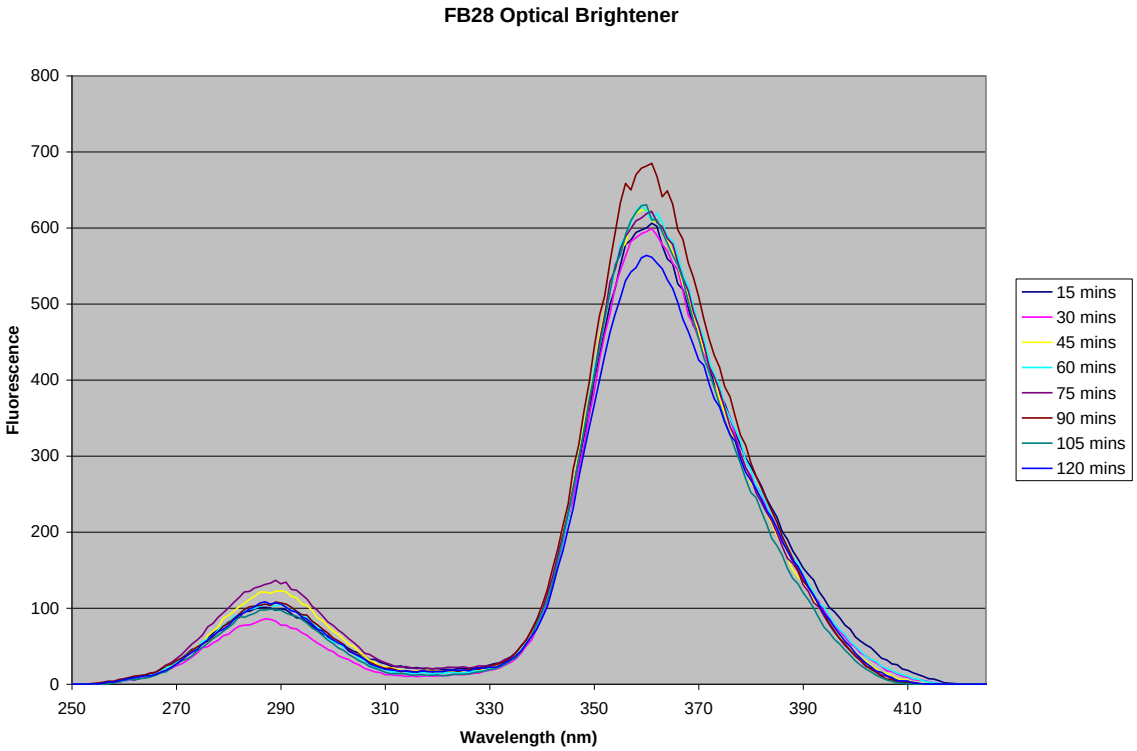


Figure 116: FB28 Optical Brightener Dilution 100 UV Irradiation Test

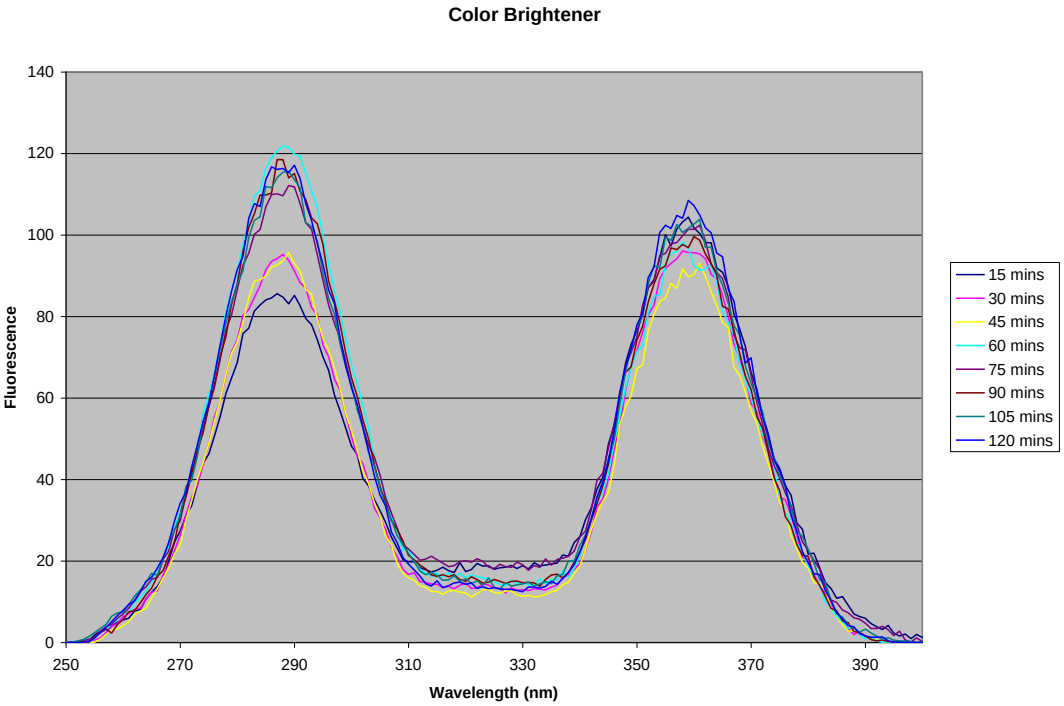


Figure 117: Color Brightener Detergent Dilution 1000 UV Irradiation Test

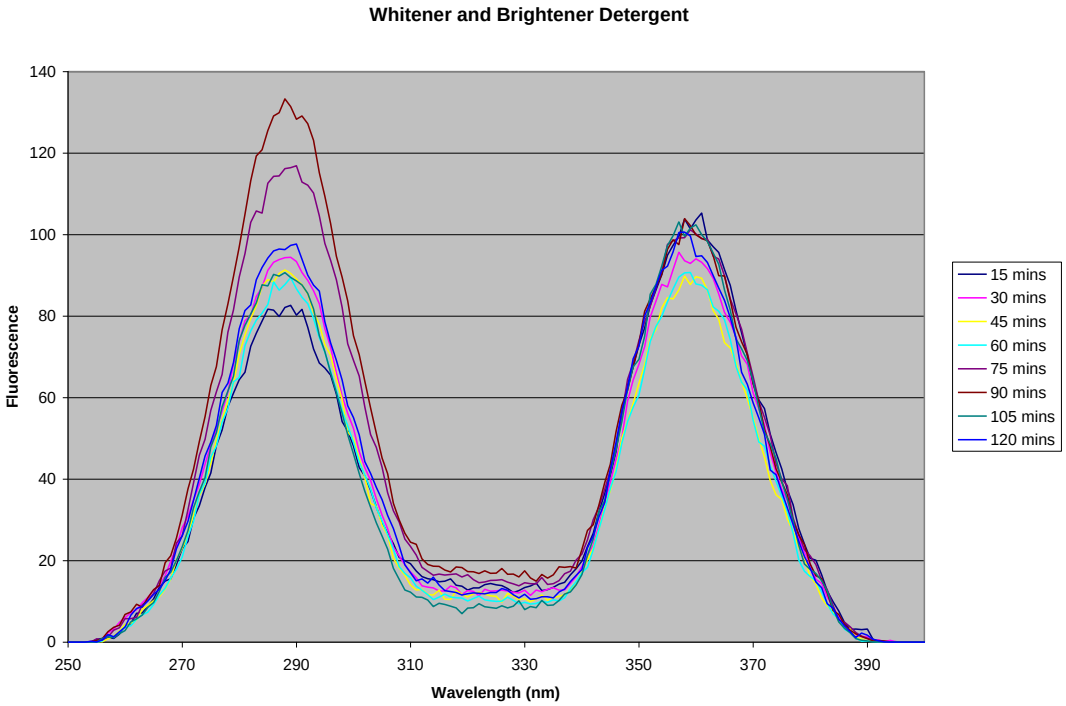


Figure 118: Whitener and Brightener Detergent Dilution 1000 UV Irradiation Test

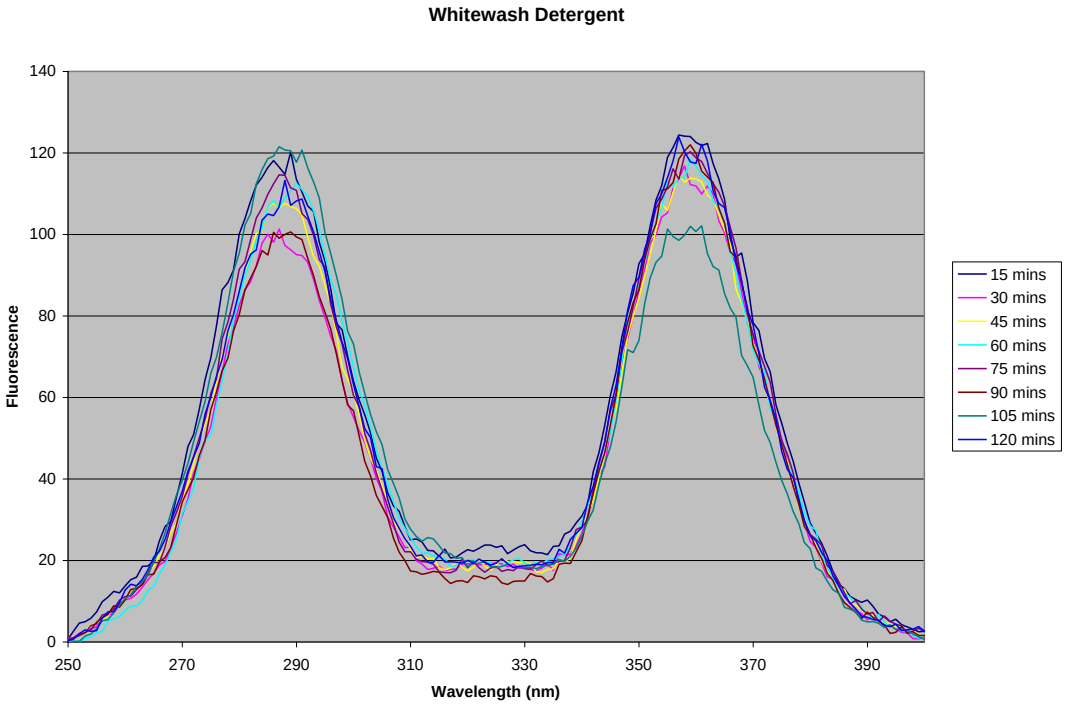


Figure 119: Whitewash Detergent Dilution 1000 UV Irradiation Test

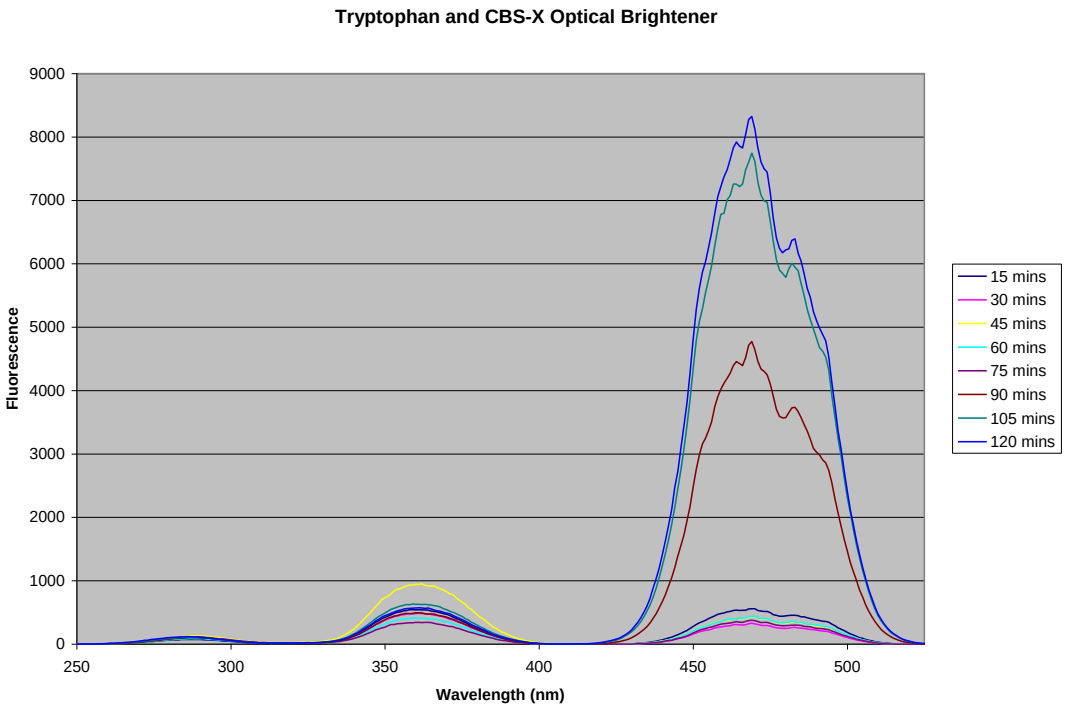


Figure 120: Tryptophan and CBS-X Optical Brightener UV Irradiation Test

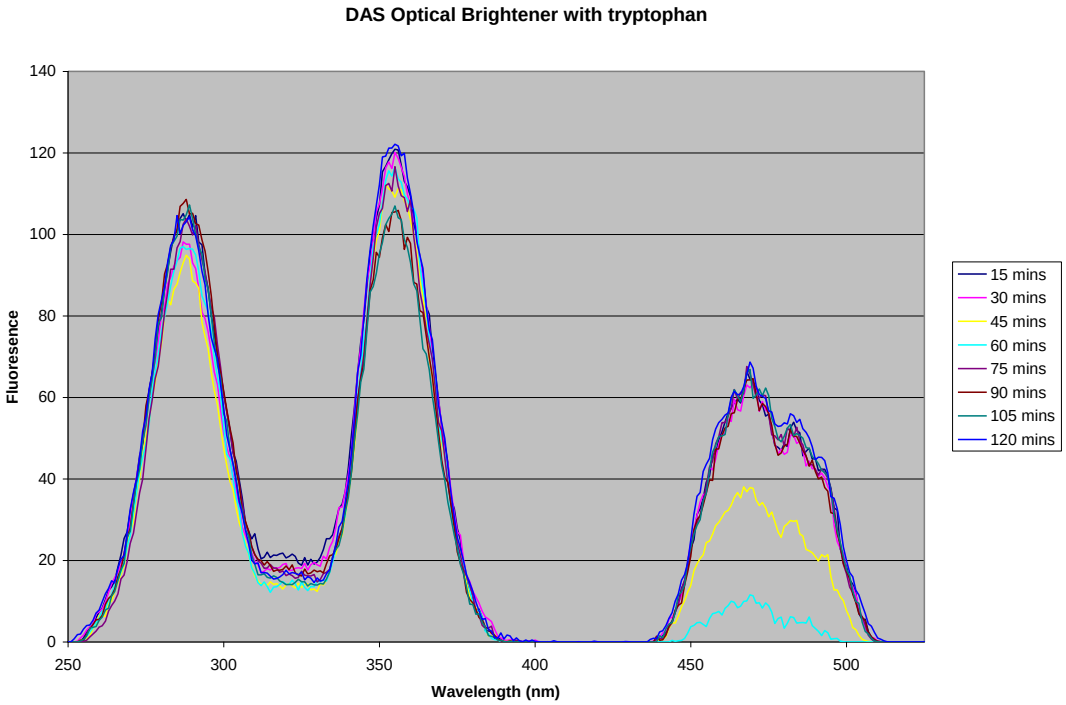


Figure 121: DAS Optical Brightener with Tryptophan UV Irradiation Test

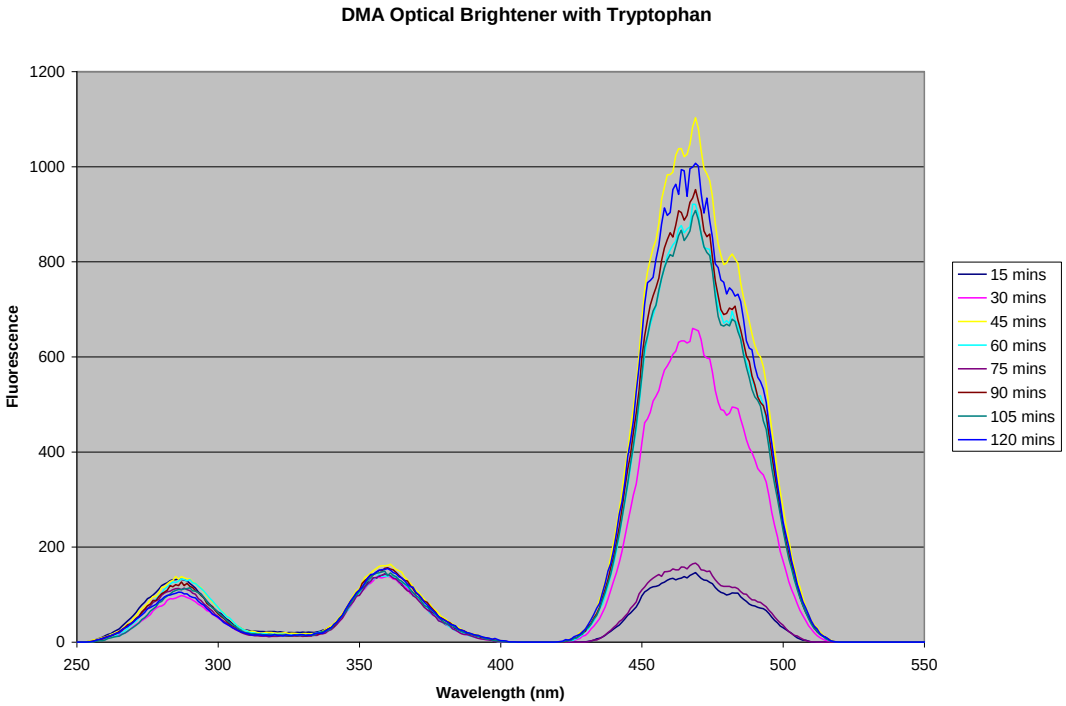


Figure 122: DMA Optical Brightener with Tryptopohan UV Irradiation Test

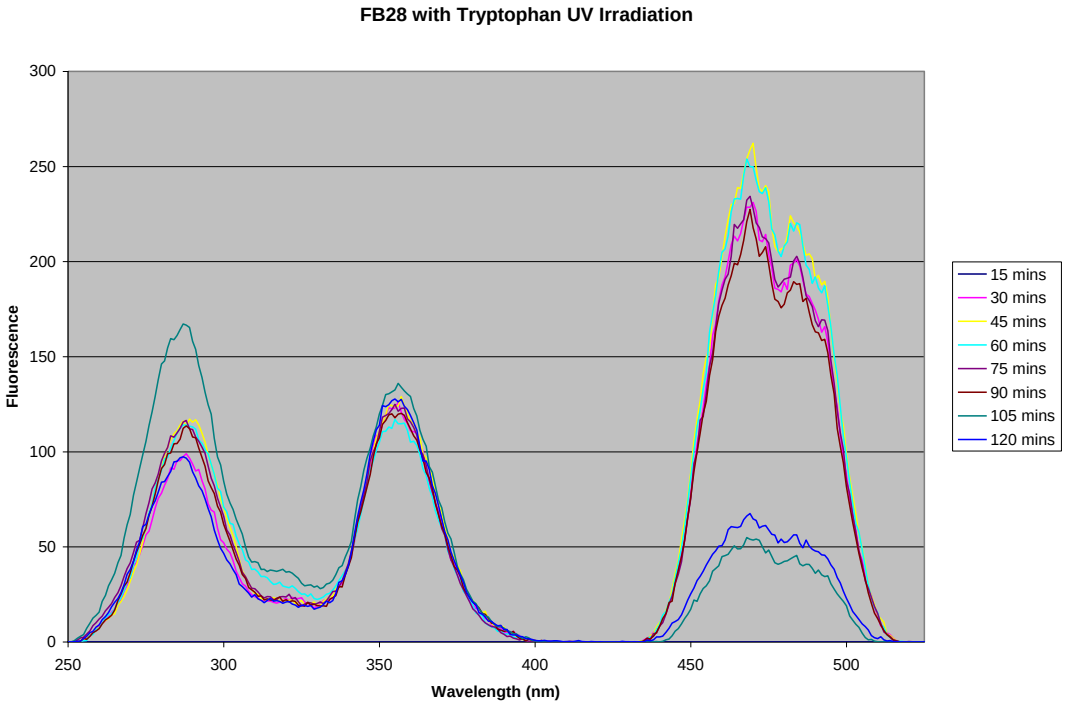


Figure 123: FB28 with Tryptophan UV Irradiation Test

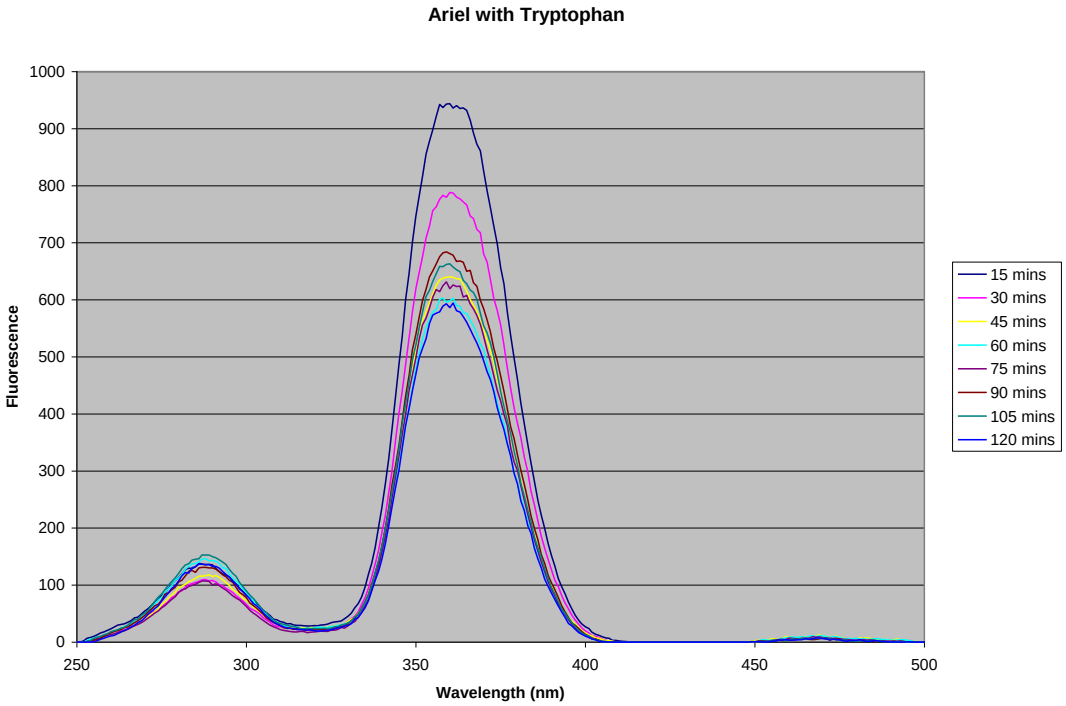


Figure 124: Ariel Washing Fluid with Tryptophan UV Irradiation

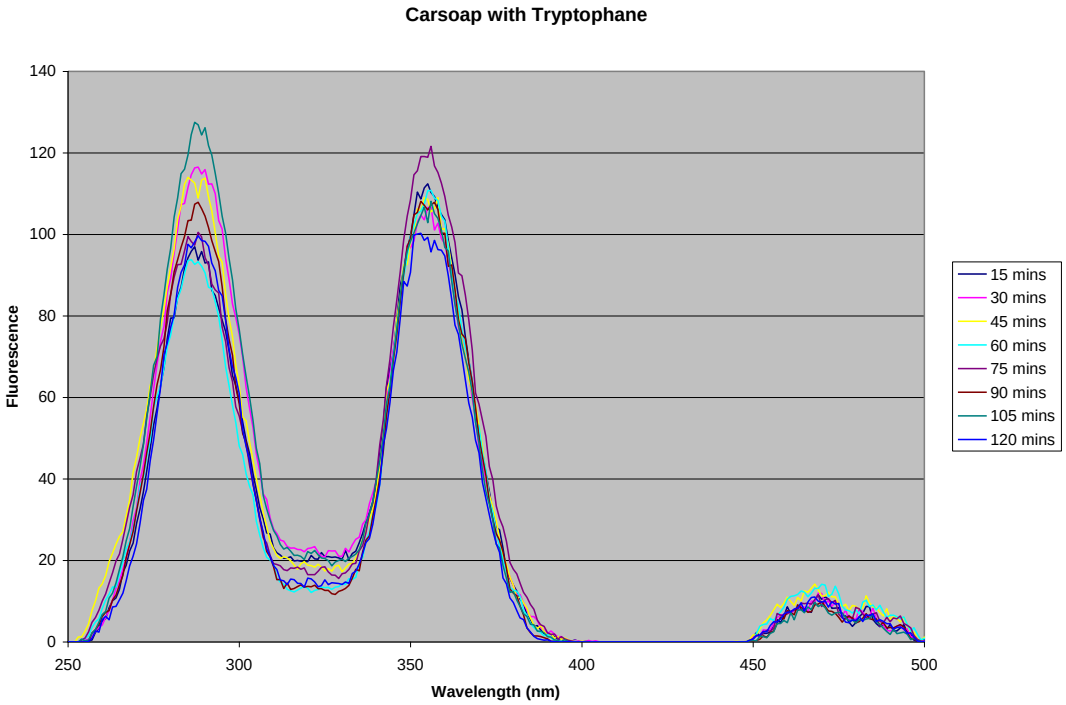


Figure 125: Carsoap with Tryptophan UV Irradiation Test

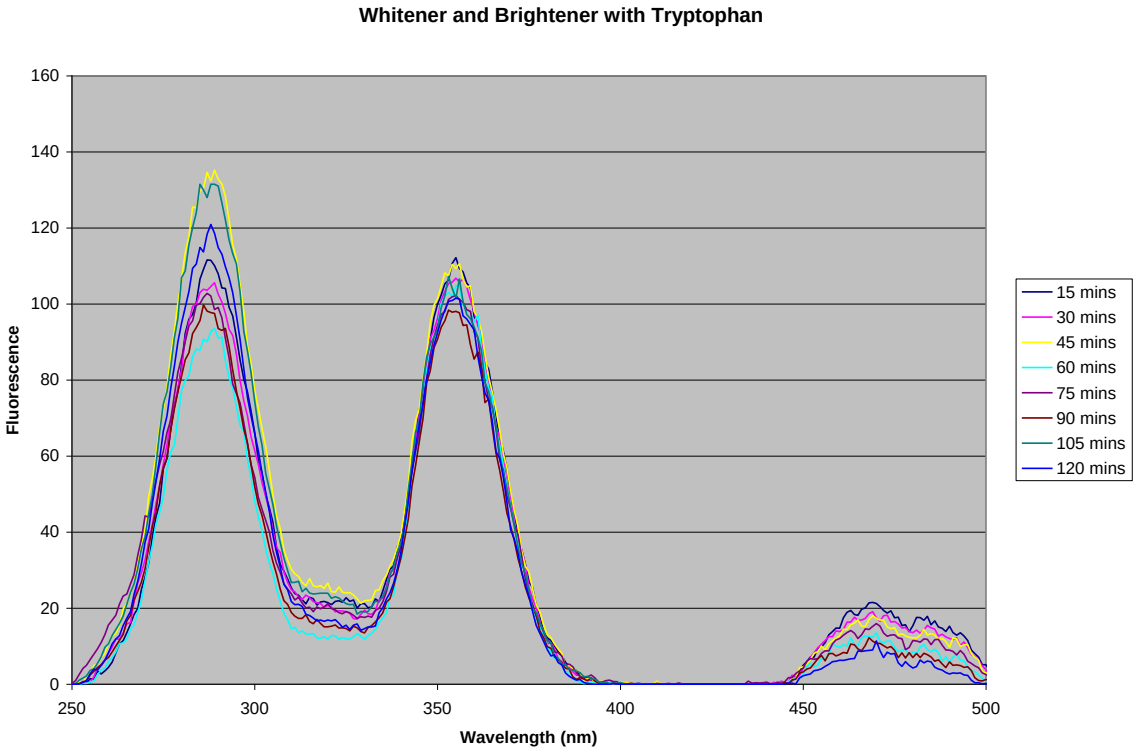


Figure 126: Whitener and Brightener with Tryptophan UV Irradiation Test

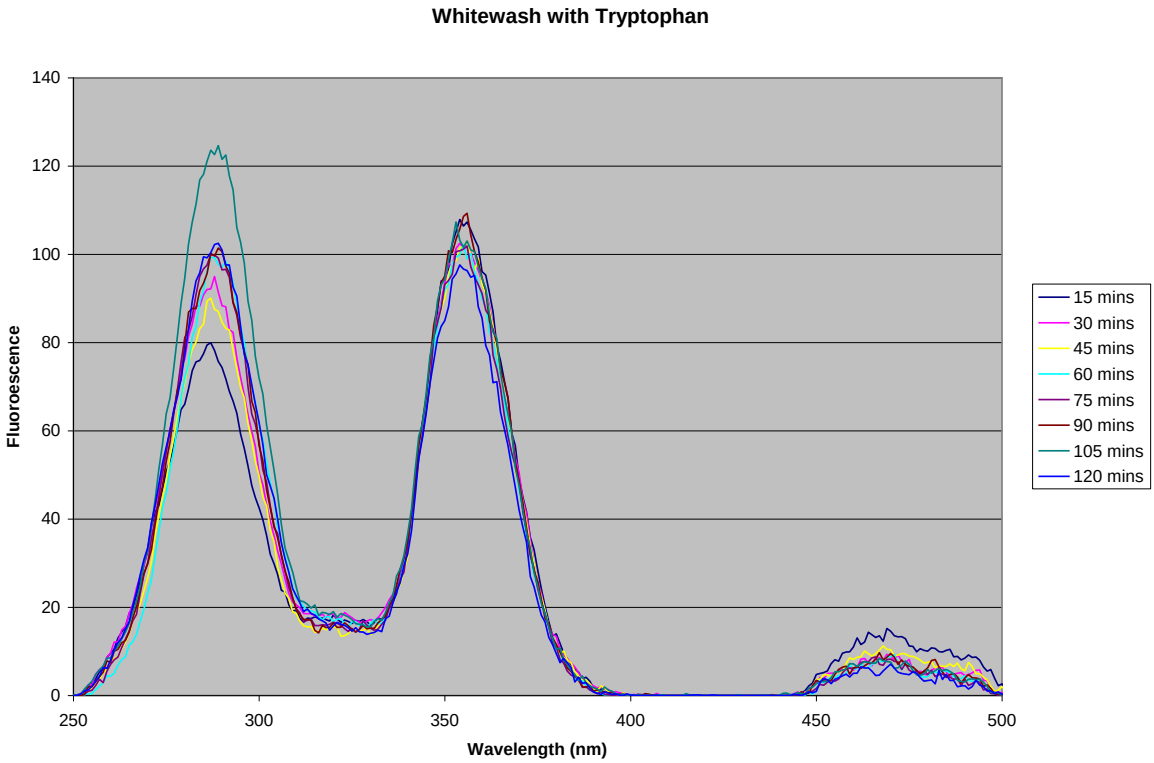


Figure 127: Whitewash Detergent with Tryptophan UV Irradiation Test

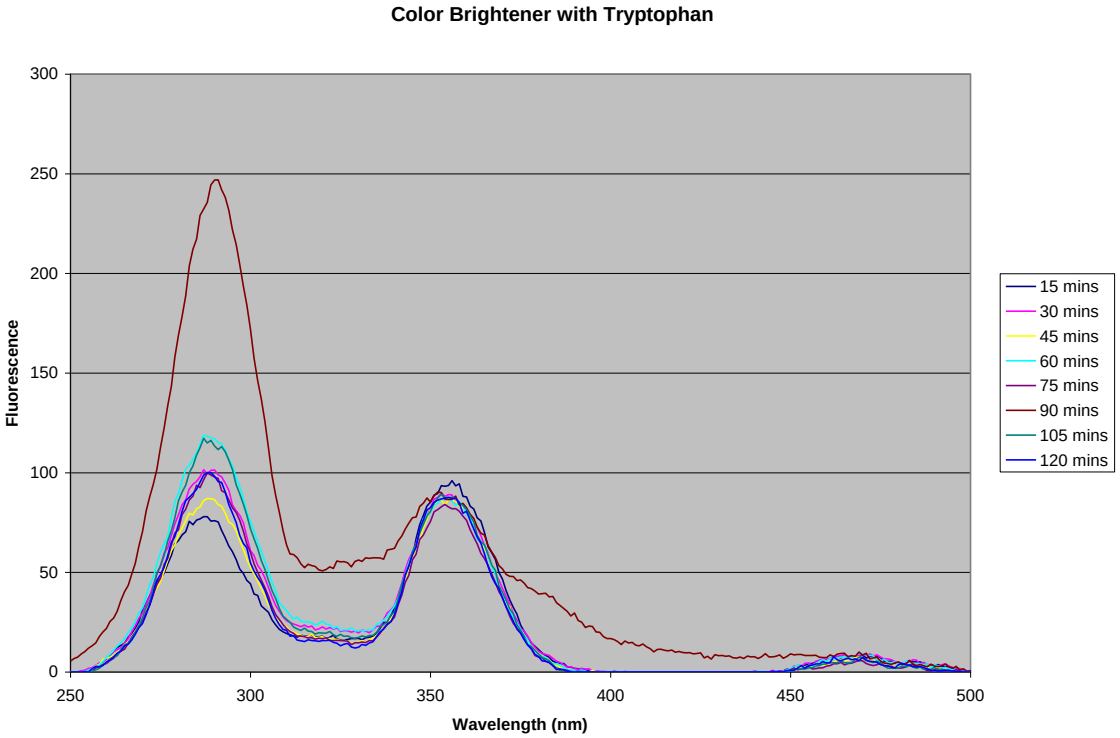


Figure 128: Color Brightener Detergent with Tryptophan UV Irradiation Test

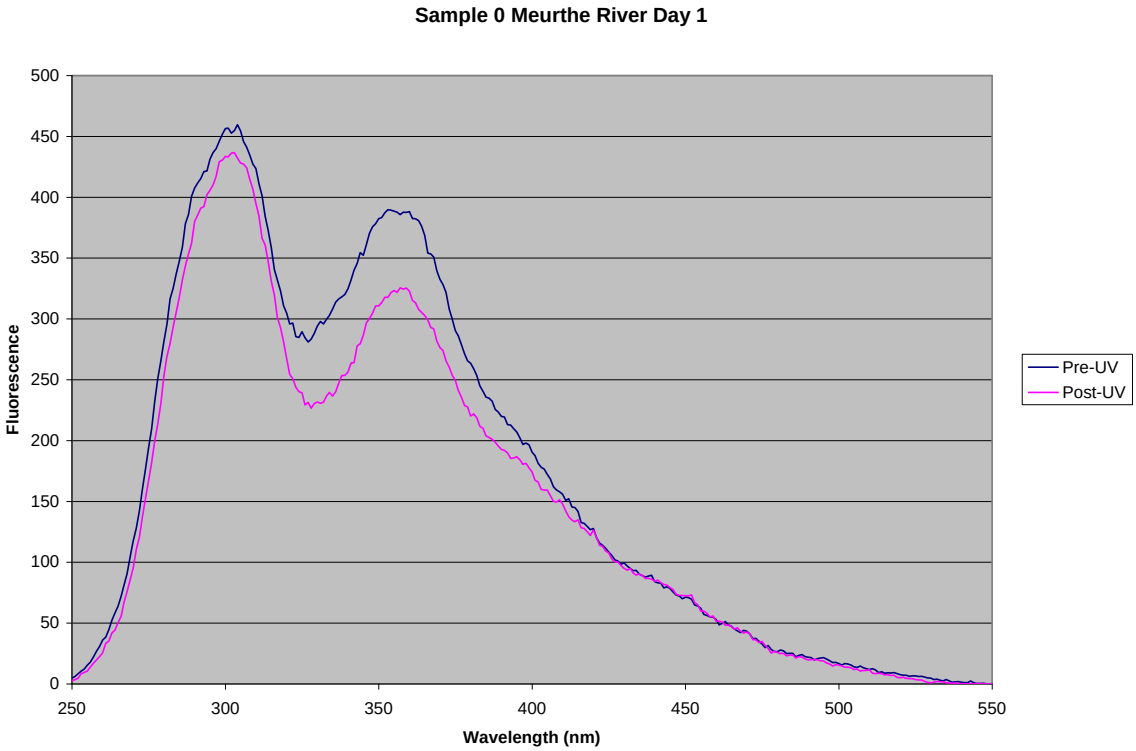


Figure 129: Site 0 Sample from the Meurthe River on Day 1

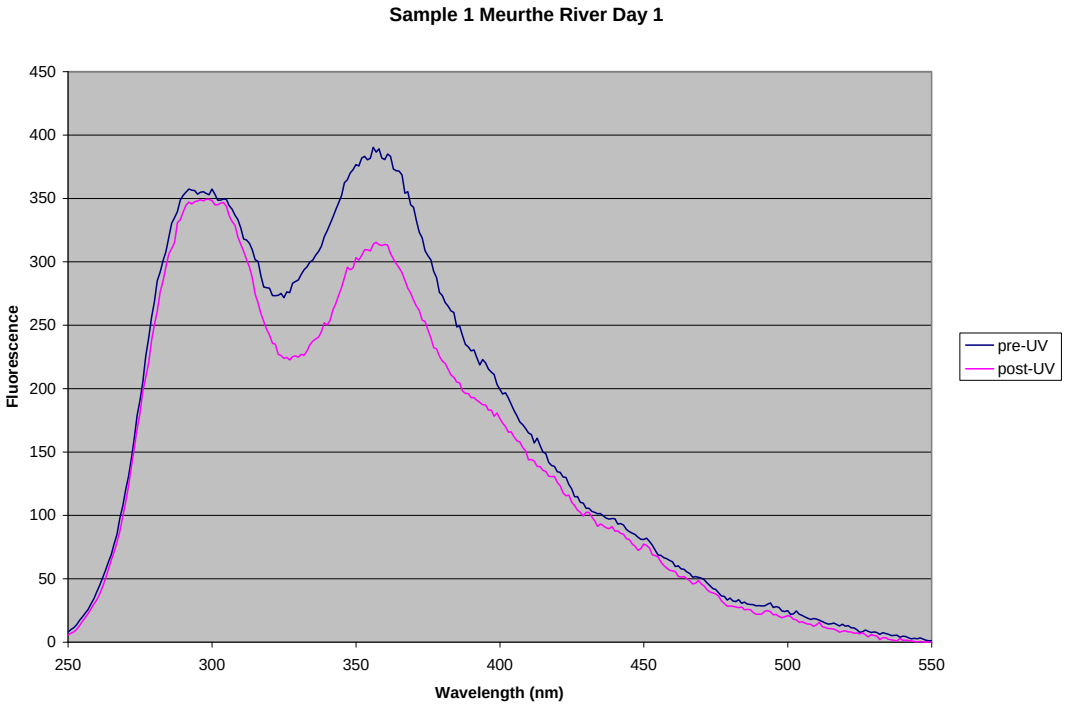


Figure 130: Site 1 Sample from the Meurthe River Day 1

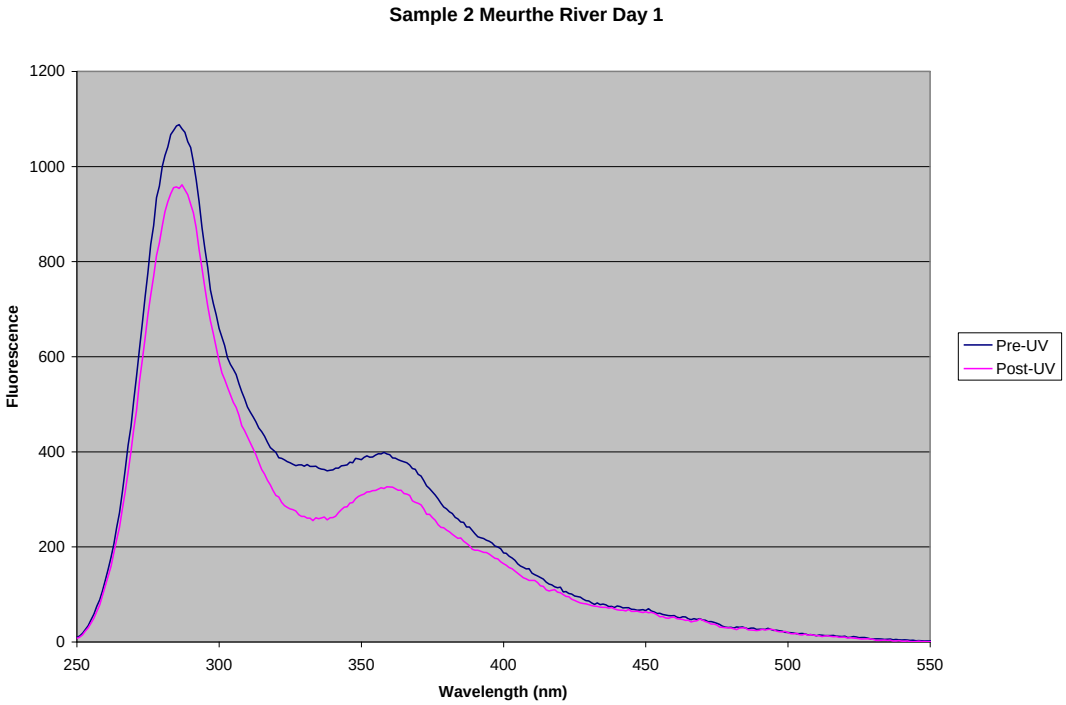


Figure 131: Site Sample 2 from the Meurthe River Day 1

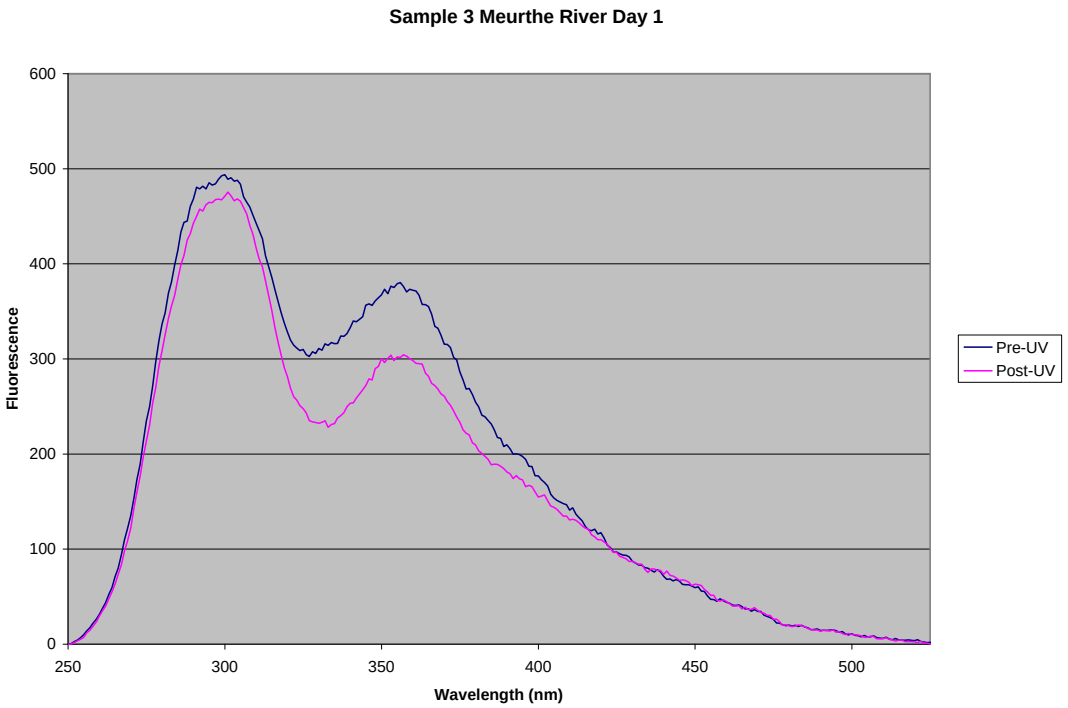


Figure 132: Site Sample 3 from the Meurthe River Day 1

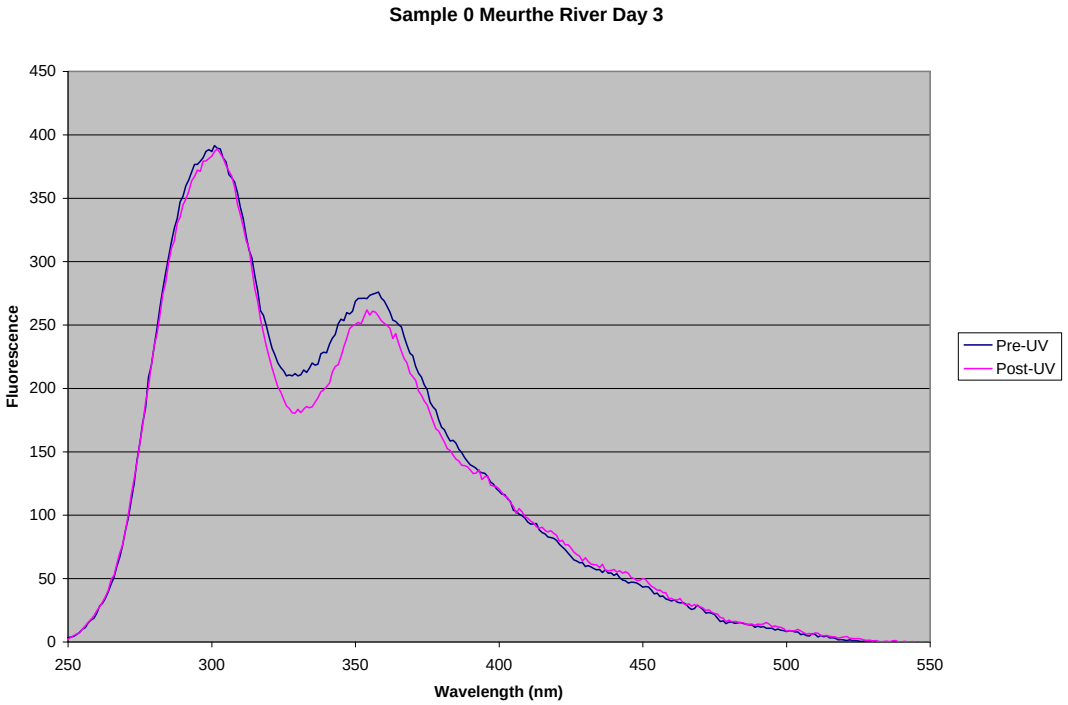


Figure 133: Site Sample 0 from the Meurthe River Day 3

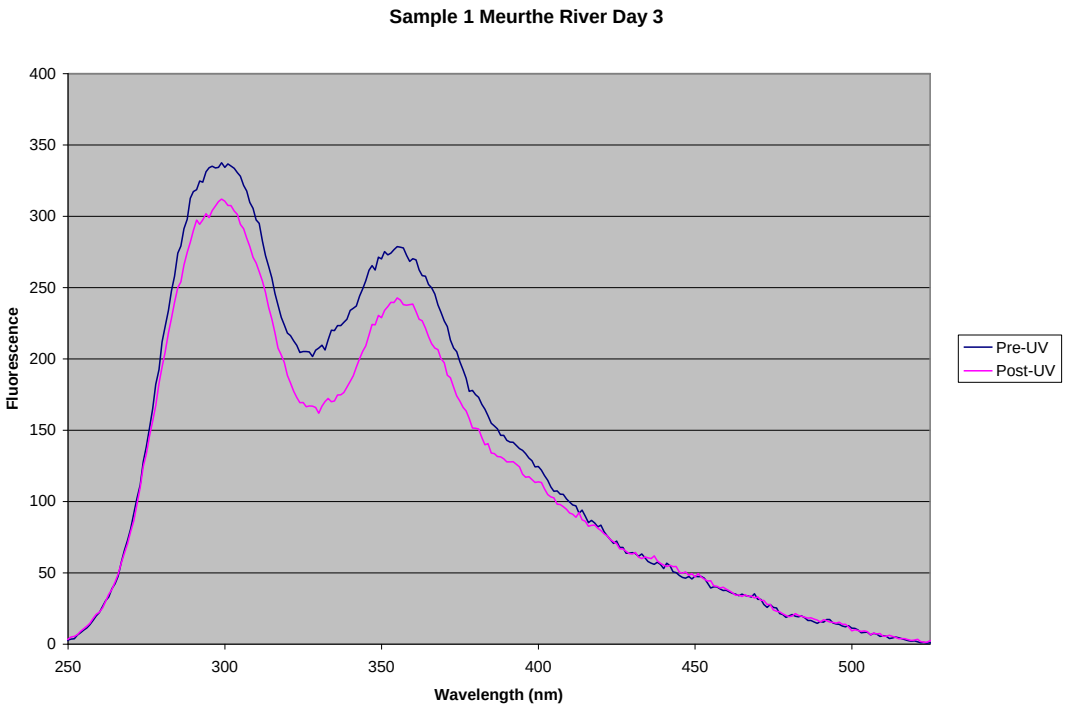


Figure 134: Site Sample 1 from the Meurthe River Day 3

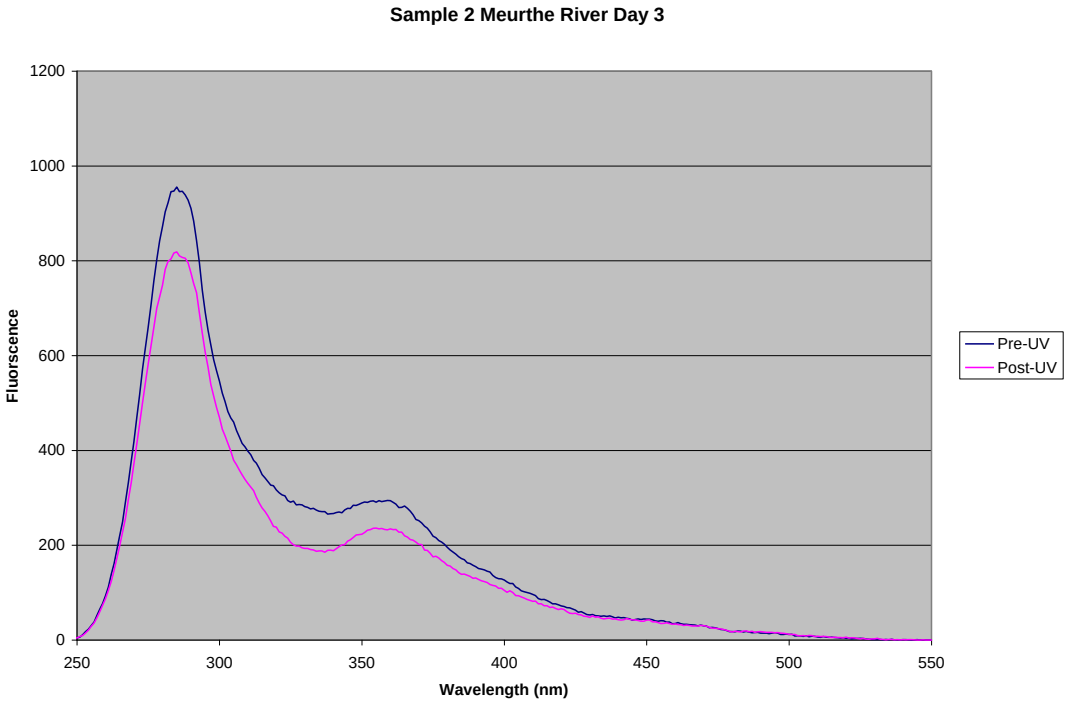


Figure 135: Site Sample 2 from the Meurthe River Day 3

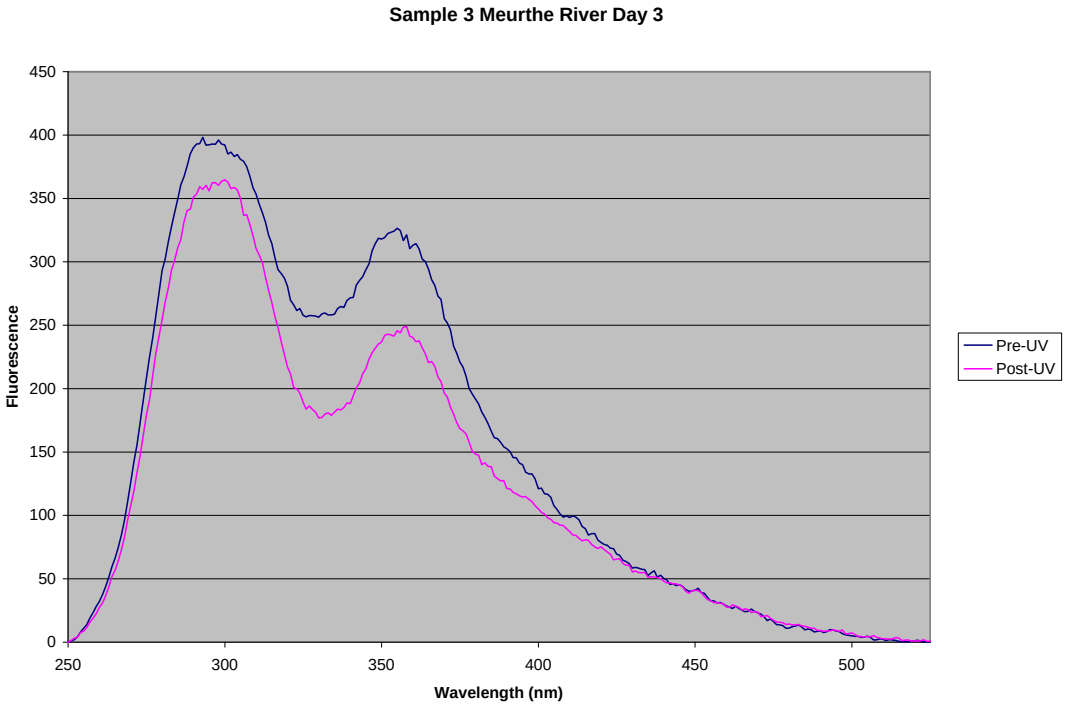


Figure 136: Site Sample 3 from the Meurthe River Day 3

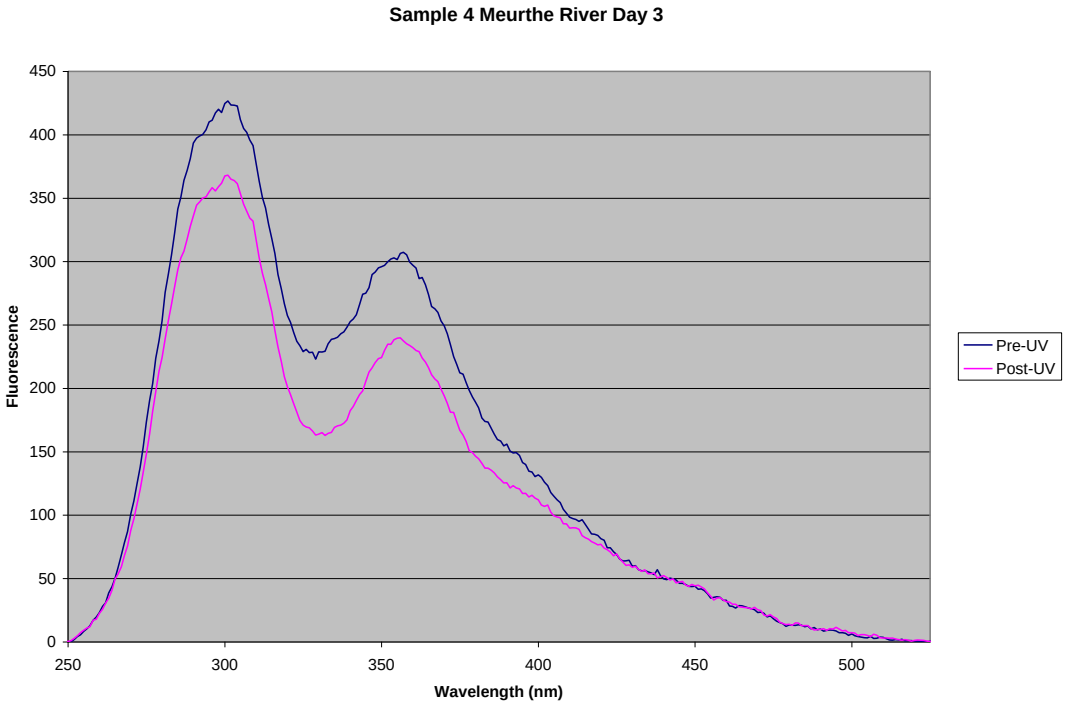


Figure 137: Site Sample 4 from the Meurthe River Day 3

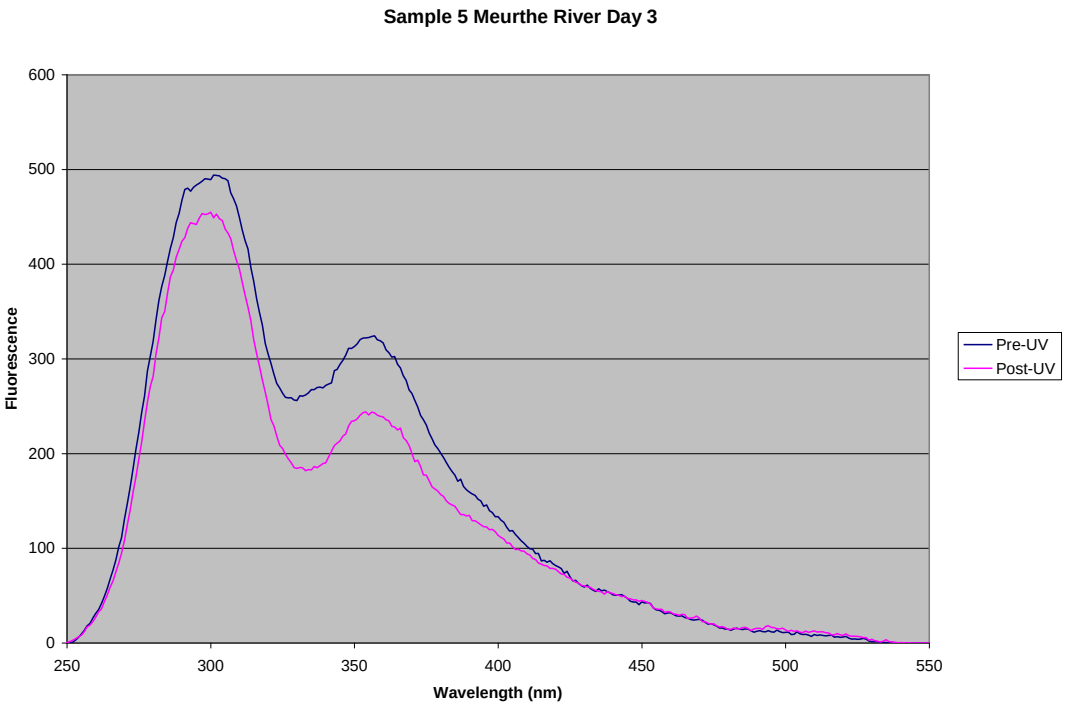


Figure 138: Site Sample 5 from the Meurthe River Day 3

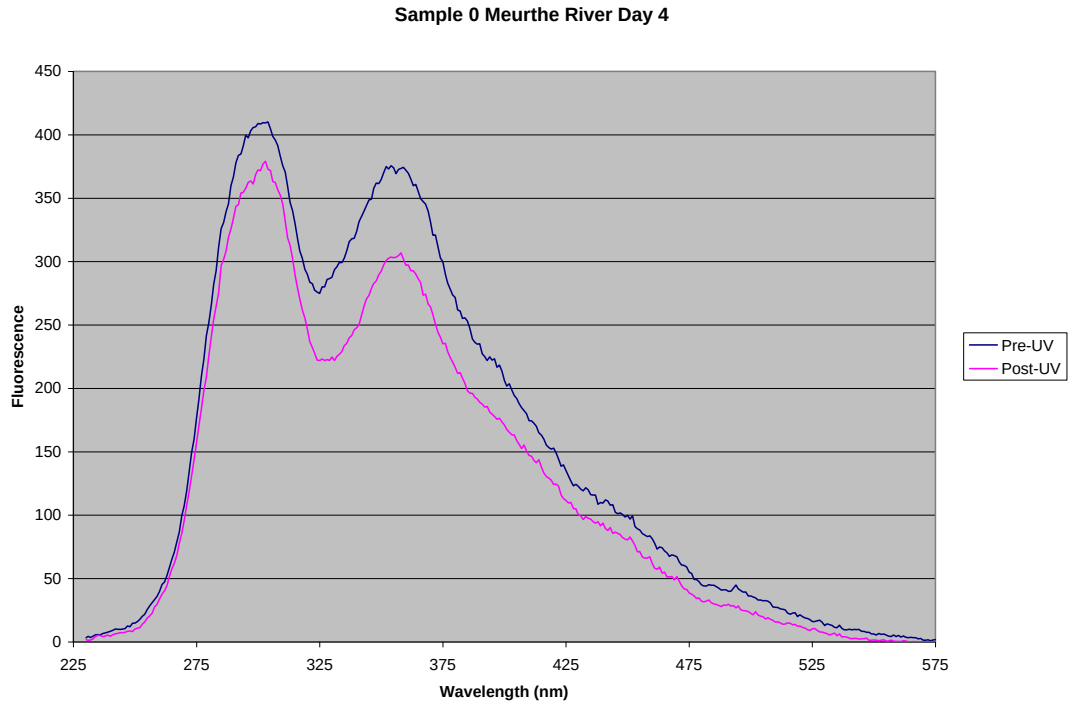


Figure 139: Site Sample 0 from the Meurthe River Day 4

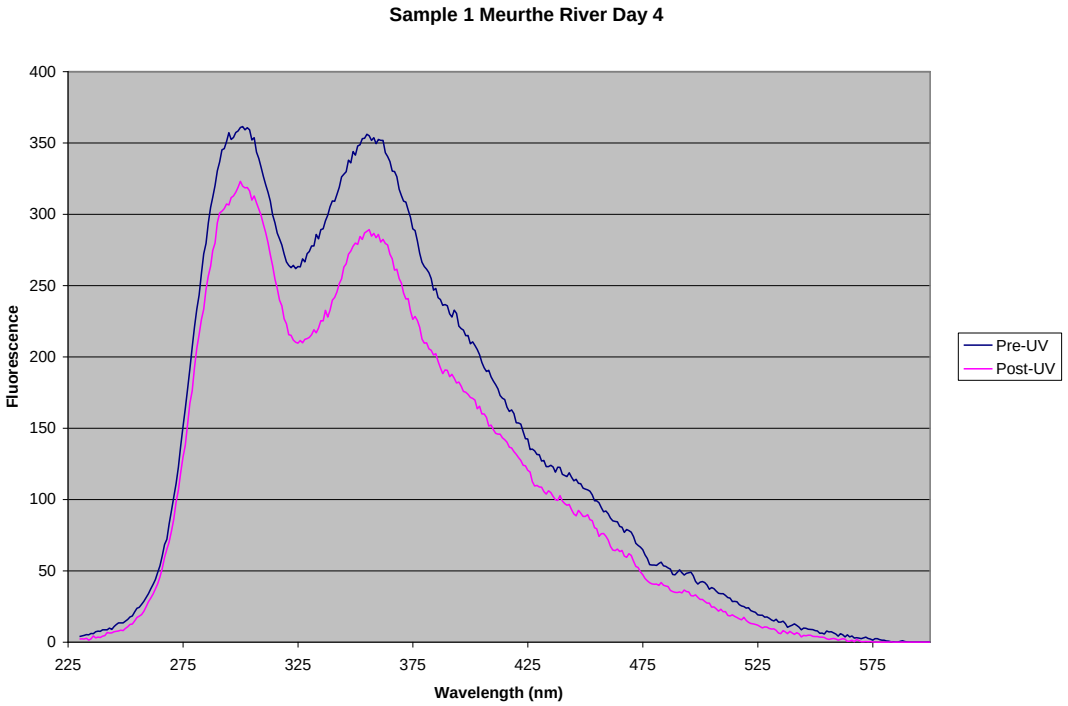


Figure 140: Site Sample 1 from the Meurthe River Day 4

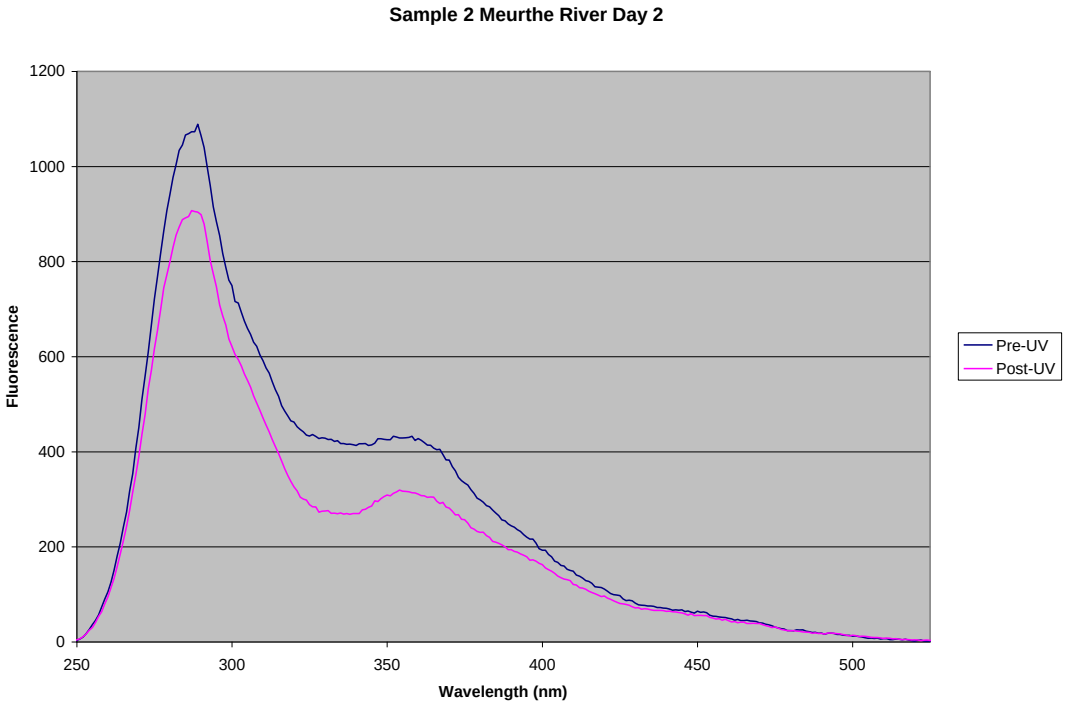


Figure 141: Site Sample 2 from the Meurthe River Day 4

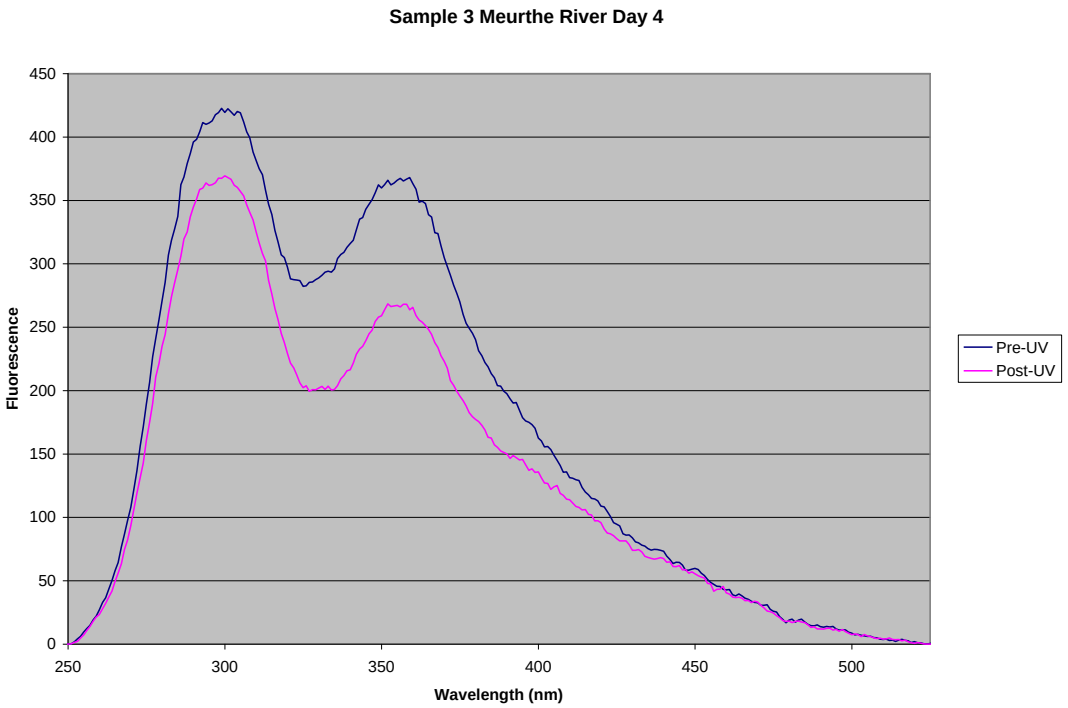


Figure 142: Site Sample 3 from the Meurthe River Day 4

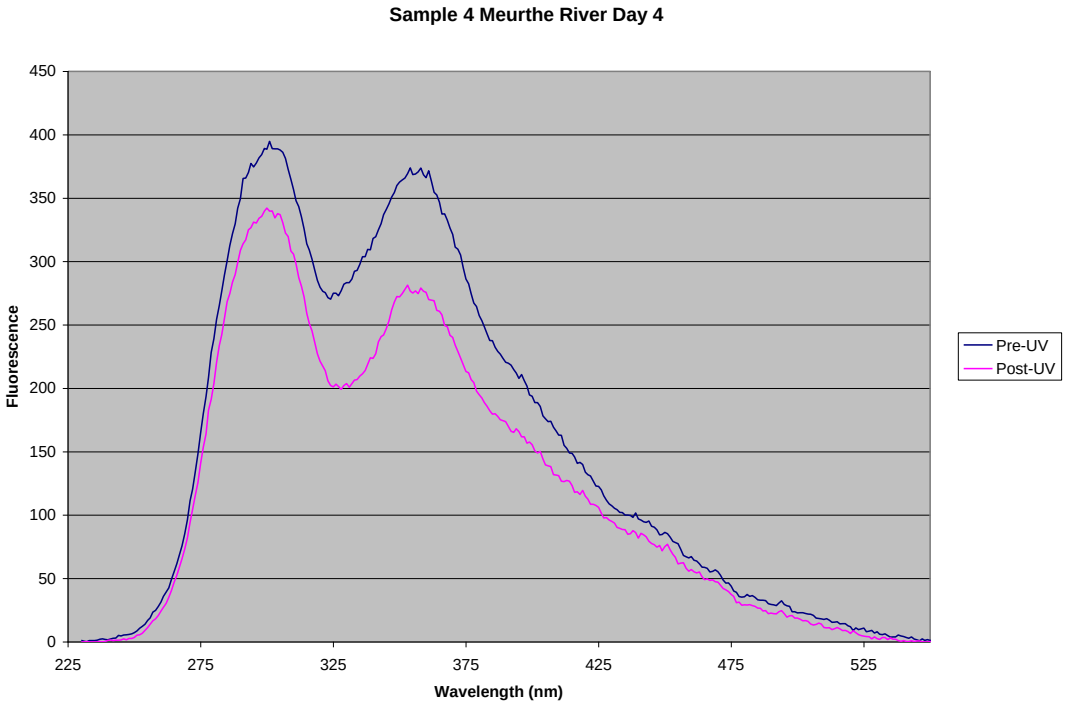


Figure 143: Site Sample 4 from the Meurthe River Day 4

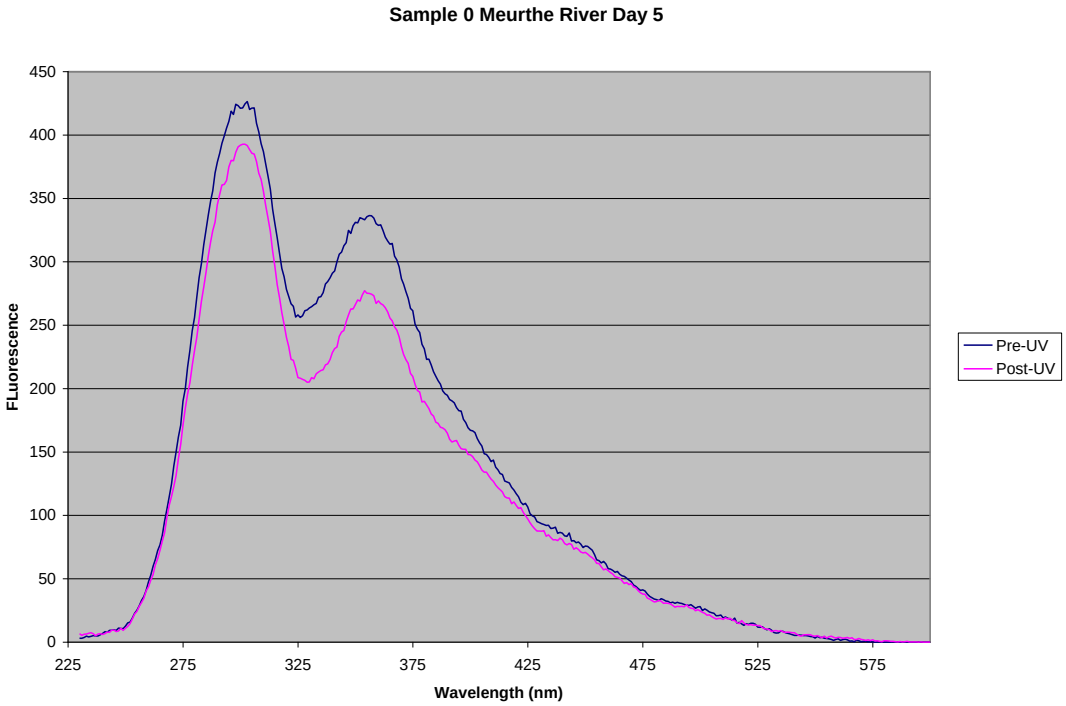


Figure 144: Site Sample 0 from the Meurthe River Day 5

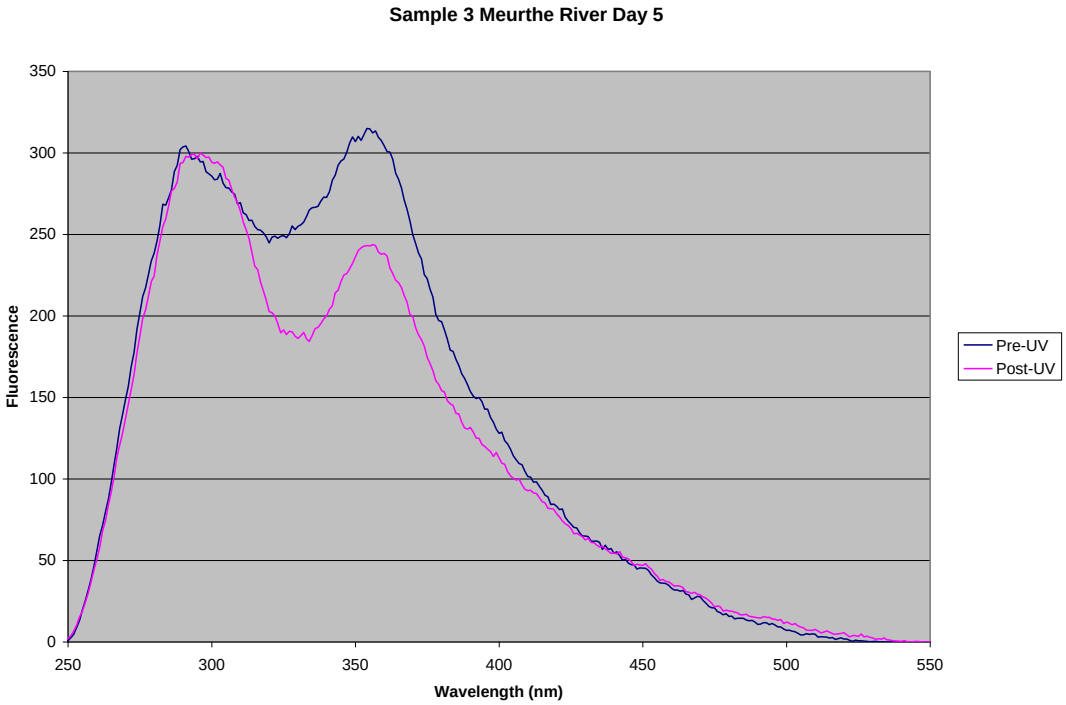


Figure 145: Site Sample 3 from the Meurthe River Day 5

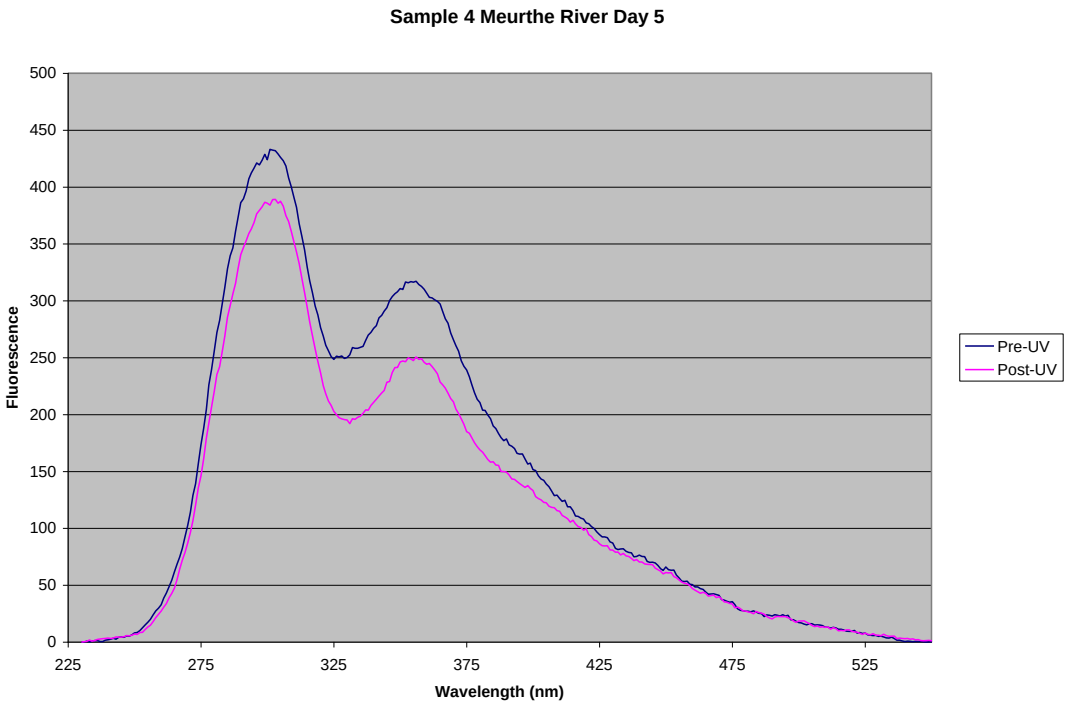


Figure 146: Site Sample 4 from the Meurthe River Day 5

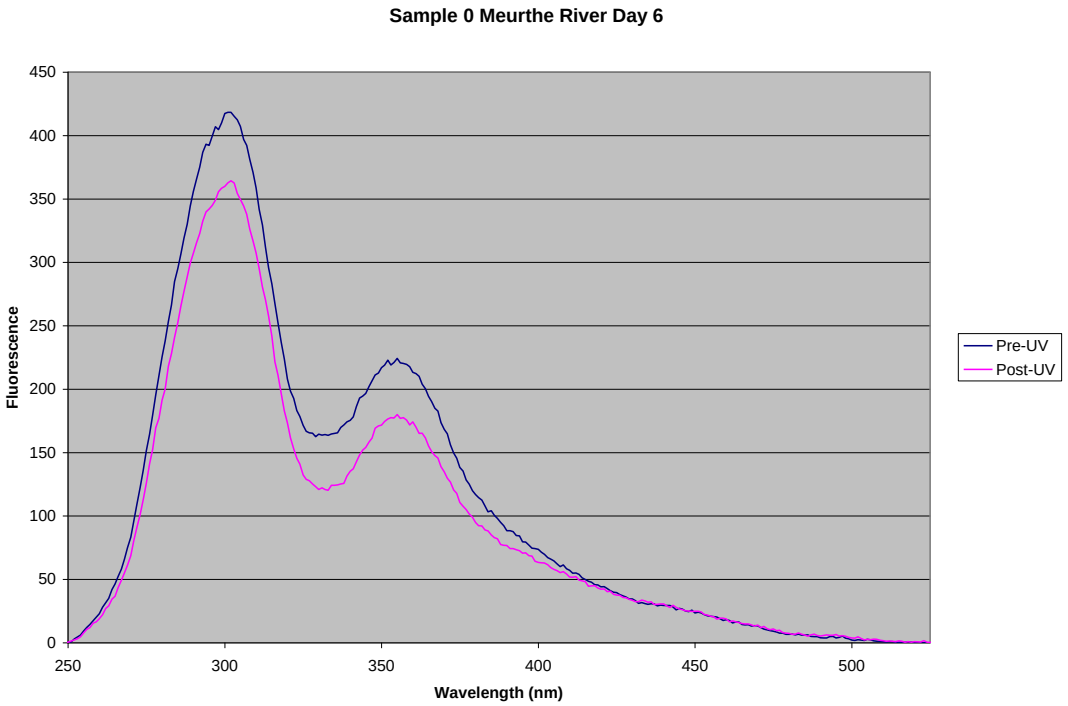


Figure 147: Site Sample 0 from the Meurthe River Day 6

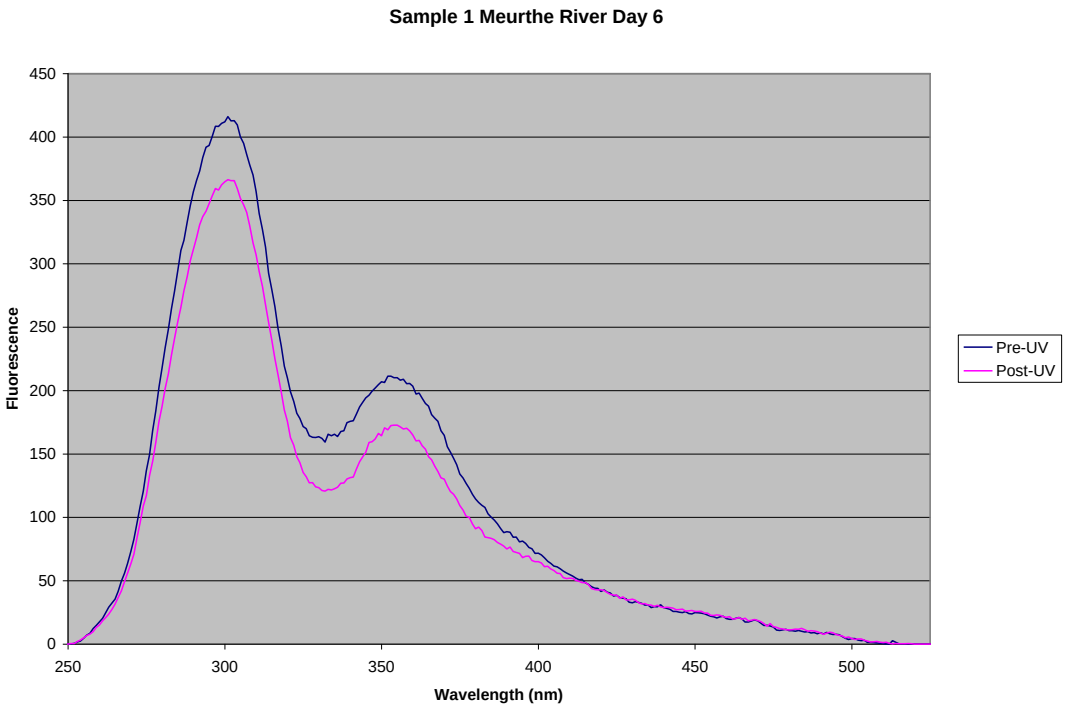


Figure 148: Site Sample 1 from the Meurthe River Day 6

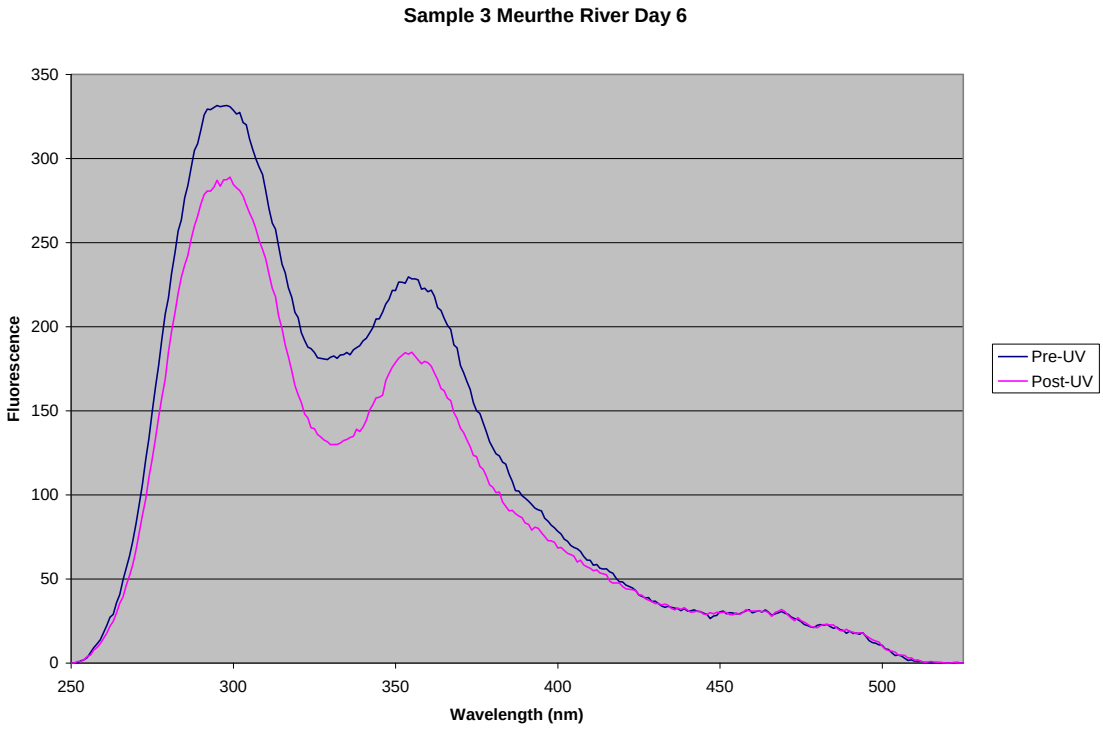


Figure 149: Site Sample 3 from the Meurthe River Day 6

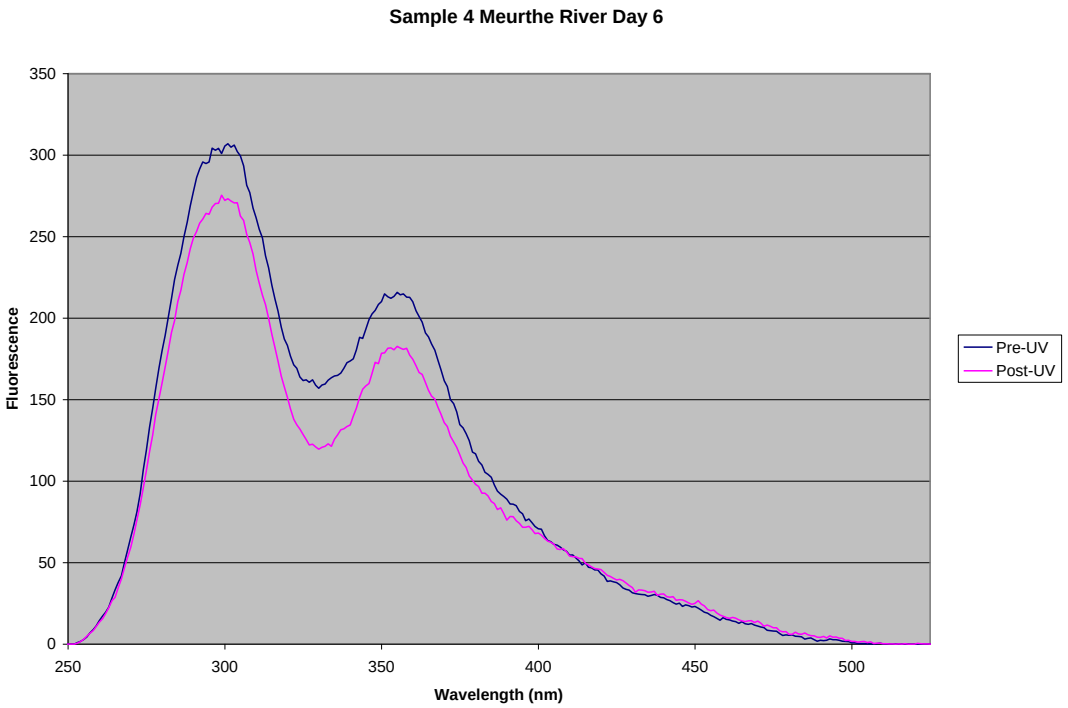


Figure 150: Site Sample 4 from the Meurthe River Day 6

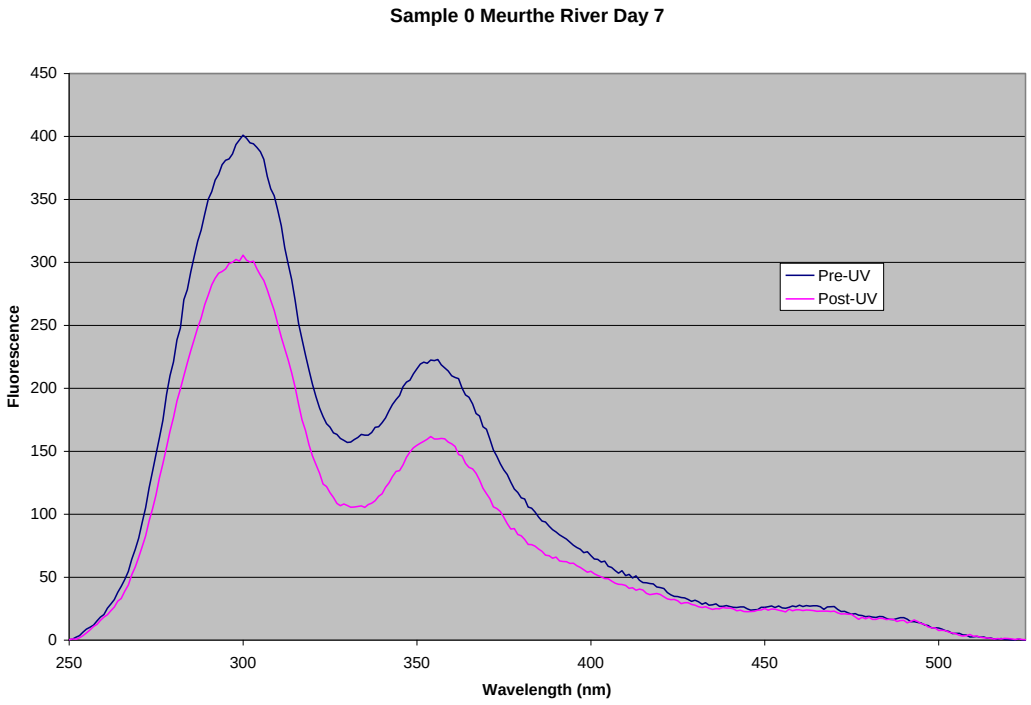


Figure 151: Site Sample 0 from the Meurthe River Day 7

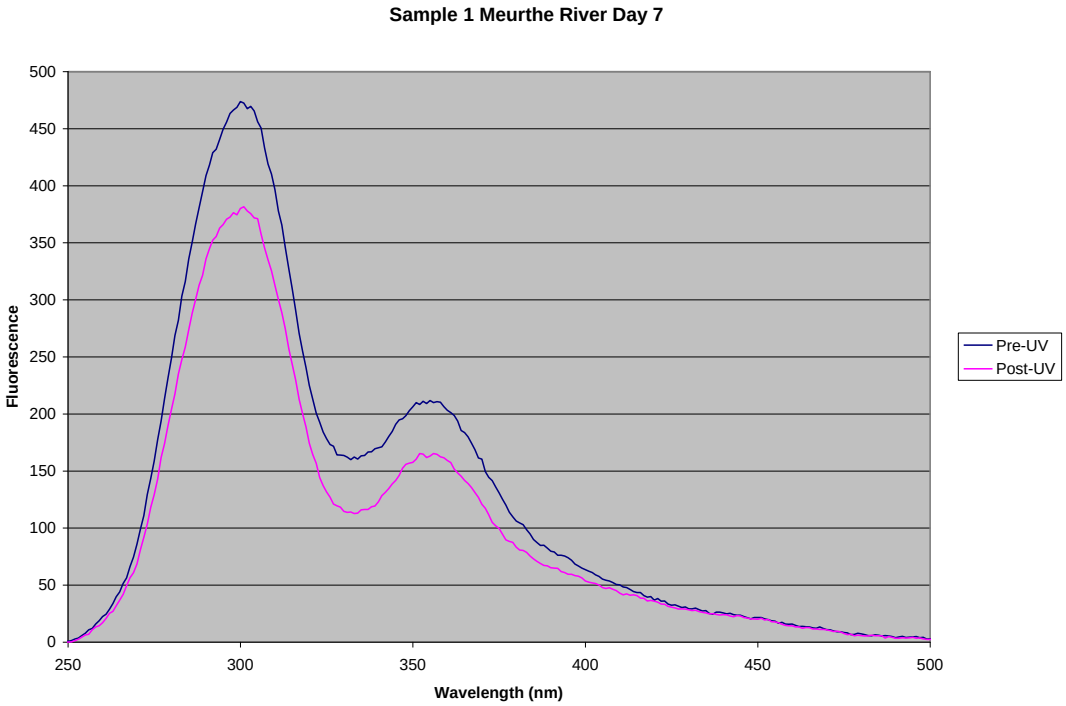


Figure 152: Site Sample 1 from the Meurthe River Day 7

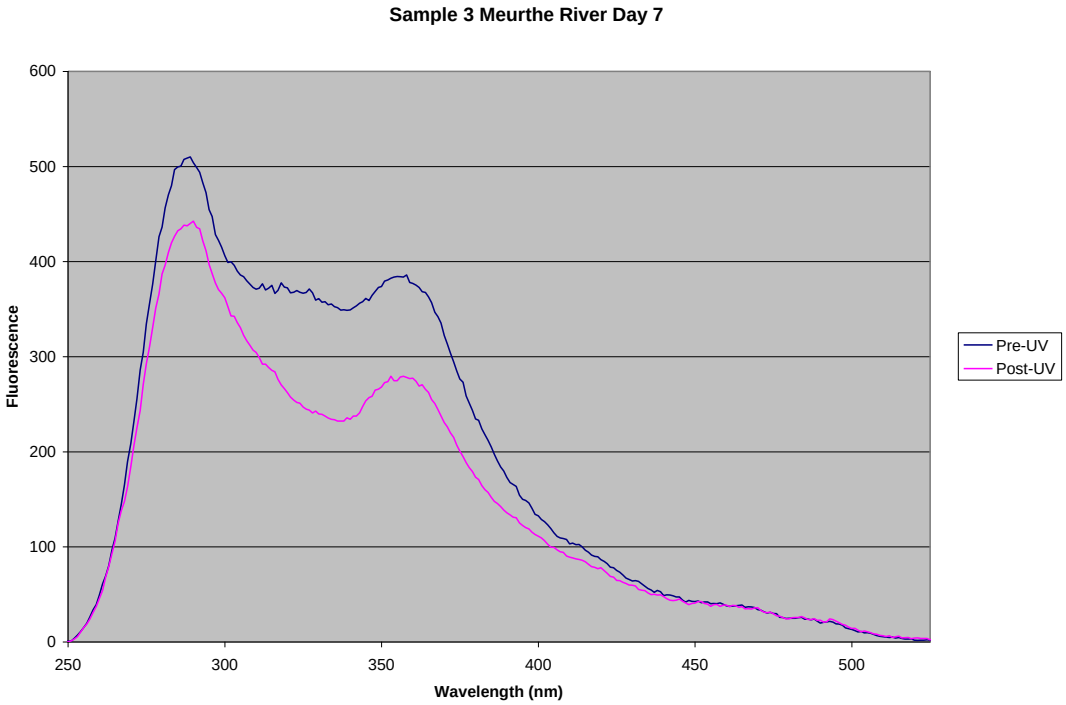


Figure 153: Site Sample 3 from the Meurthe River Day 7

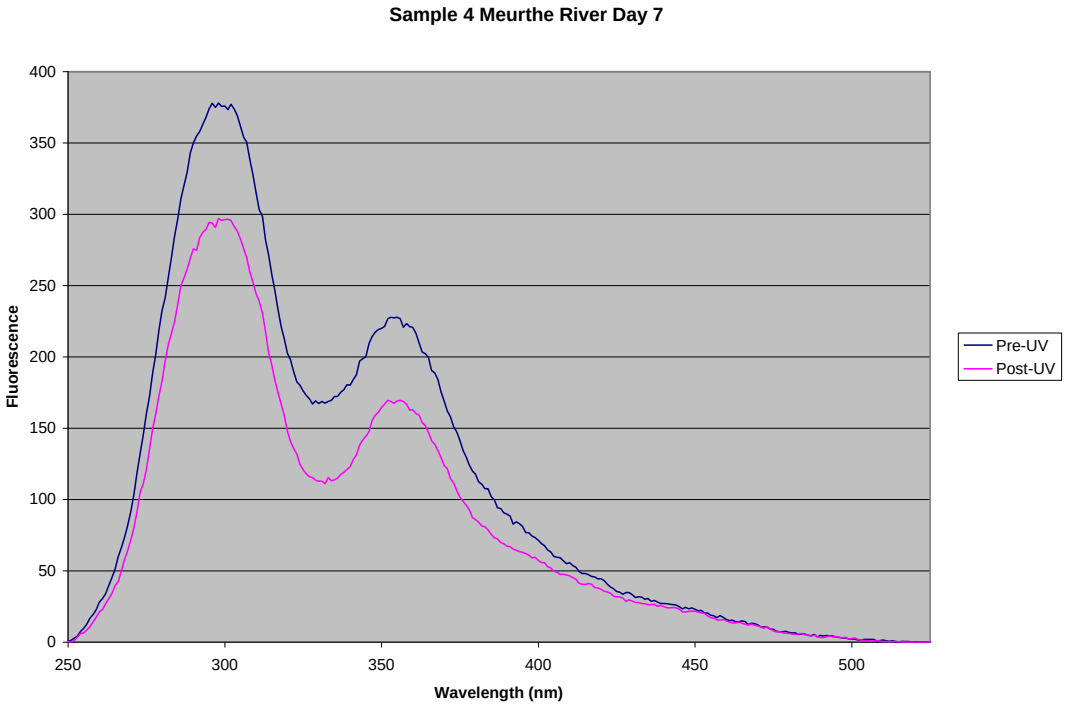


Figure 154: Site Sample 4 from the Meurthe River Day 7

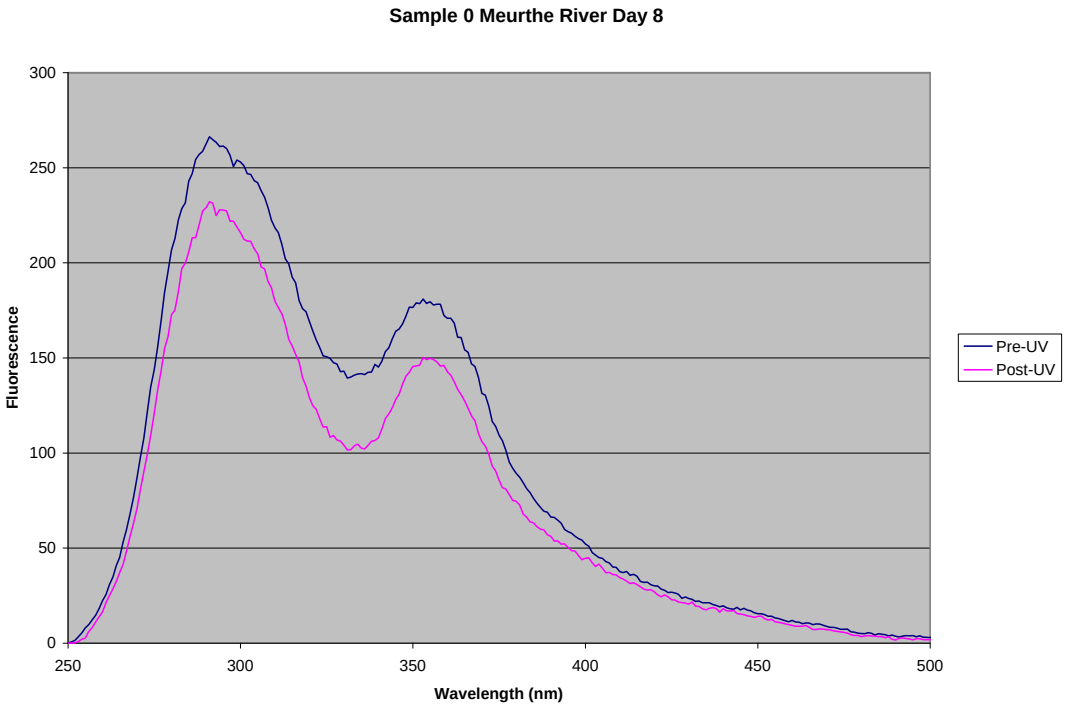


Figure 155: Site Sample 0 from the Meurthe River Day 8

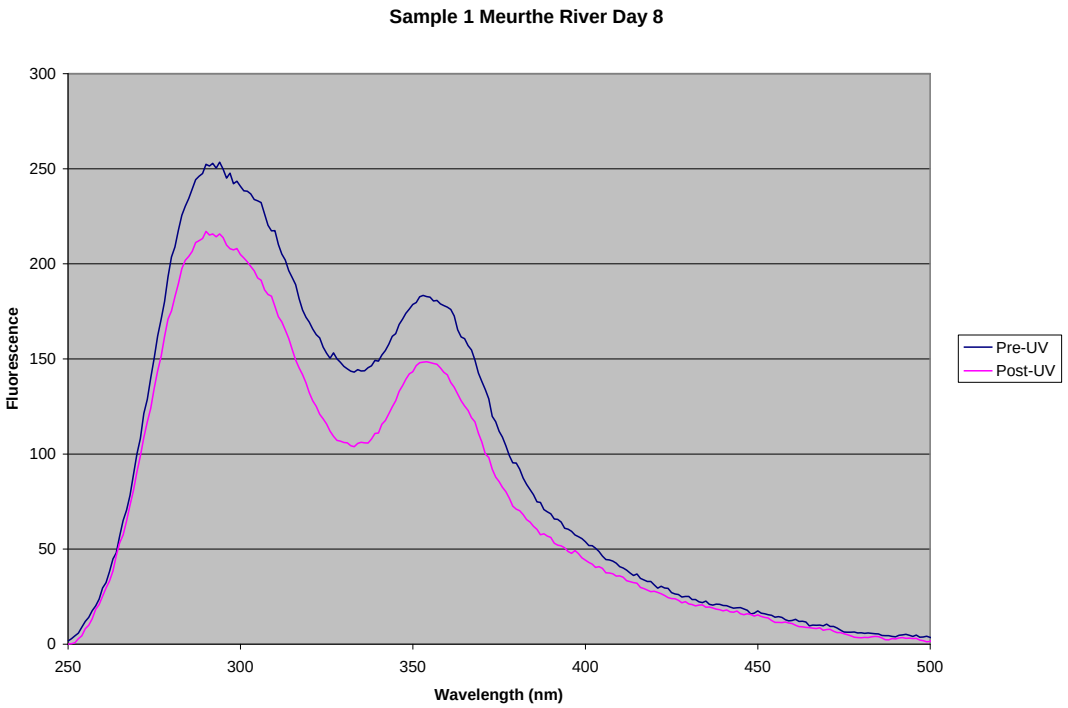


Figure 156: Site Sample 1 from the Meurthe River Day 8

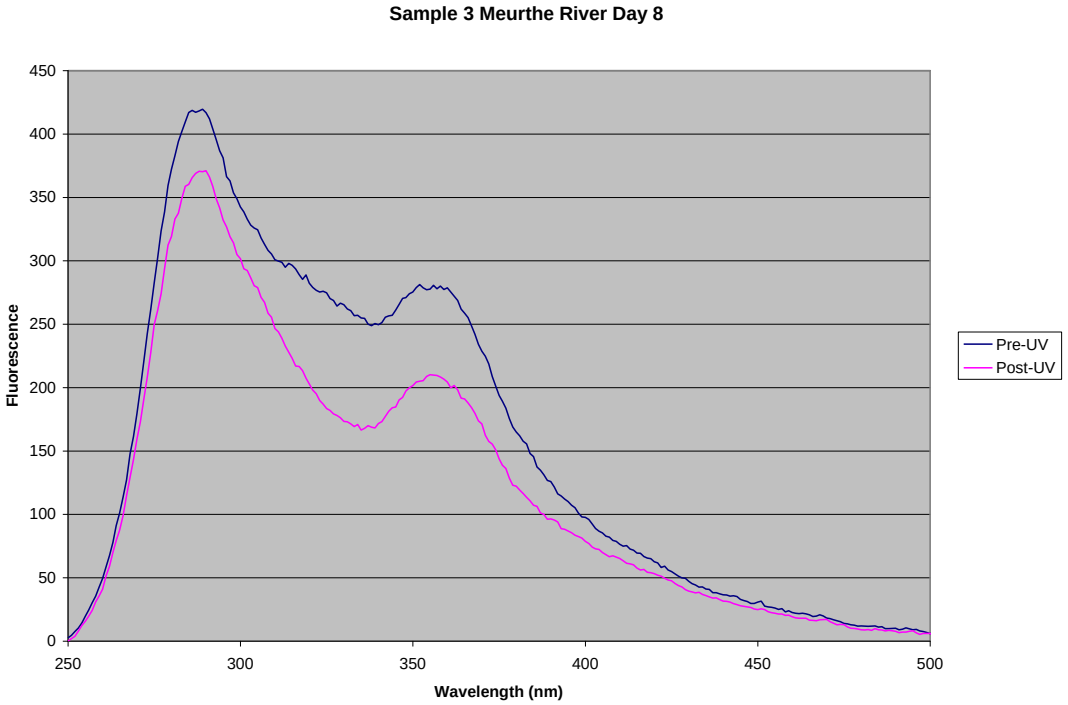


Figure 157: Site Sample 3 from the Meurthe River Day 8

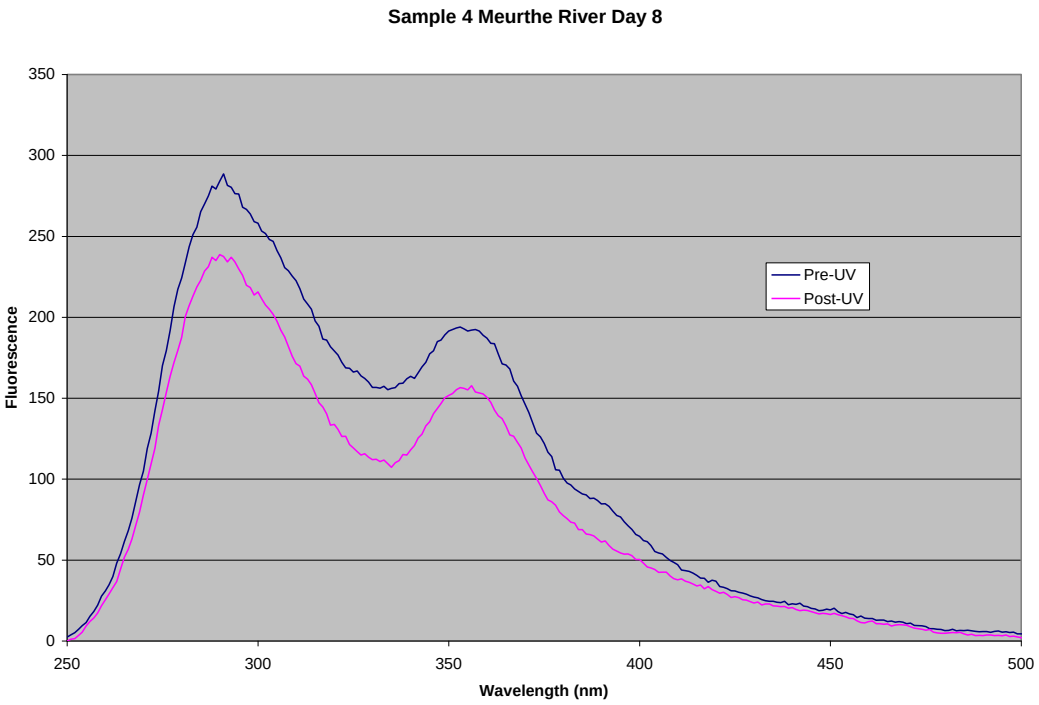


Figure 158: Site Sample 4 from the Meurthe River Day 8

### 5.4.1.1 Day One

The Meurthe River was sampled over a period of eight days and at several pre-determined sample sites to determine affect of weather conditions and position along the river. All of the fluorescence shows that each of the samples analyzed on all eight days showed peaks at both 290 nm and 356 nm. The first day of sampling at the Meurthe River shows that at Sample Sites 0 and 1 (Figures 21 and 22) shows that there is no degradation at 290 nm after UV Irradiation. Site Sample 2 (Figure 23) shows some degradation and Site Sample 3 (Figure 24) shows marginal degradation. This means that there is a likely a presence of tryptophan or optical brighteners that are non-sensitive to UV-Irradiation. Sample 2 shows the most degradation because it is overflow from only primary treatment at the wastewater treatment plant. Sample 3 is the effluent from the wastewater treatment plant; therefore, it is reasonable that the degradation at 290 nm is less than that of Sample 2 but more than that of Samples

Sites 0 and 1. All of these samples sites showed moderate degradation at 356 nm wavelength, which indicates the presence of both humic acids, as well as optical brighteners sensitive to UV Irradiation.

#### 5.4.1.2 Day Three

On day three of sampling the Meurthe River, all of the sites were analyzed. Site Sample 0 showed no degradation at 290 nm, indicating the presence of tryptophan or optical brighteners not sensitive to UV irradiation. Site Sample 1 showed marginal degradation, indicating the same situation as with Sample Site 0. Site Samples 2 and 3 showed more degradation at 290 nm, indicating the likelihood of the optical brighteners being present. Site Sample 4 showed a larger degradation than that of 0 and 1, due to the fact that it is down the river from the wastewater treatment plant. Site Sample 5 was similar to that of 3, which was expected since it was simply overflow from the tertiary treatment of the plant.

All of the site samples showed a decrease in fluorescence at 356 nm, confirming the presence of optical brighteners. As expected, the largest presence of optical brighteners appeared to be at the wastewater effluent as seen in Figure 29 and at Site Sample 4 in Figure 30.

#### 5.4.1.3 Day Four

All of the site samples showed a slightly decreased amount of fluorescence overall from the previous days, likely due to improved weather conditions. Samples 0, 1, 2, 3, and 4 (Figures 31-35) showed degradation in fluorescence at 290 nm, signifying both the presence of optical brighteners as well as yellow water. All of the samples also displayed degradation at 356 nm, indicating the presence of both optical brighteners and humic acid. The largest degradations were at Sample Site 3 and Sample Site 4, as expected.

#### 5.4.1.4 Days Five to Eight

Days 5-8 all had similar weather conditions; consequently, results from these four days were similar. Site Samples 0 and 1 showed degradation at 290 nm, as expected. Sample Site 3 showed no degradation at 290 nm, likely attributable to the presence of yellow water or optical brighteners not sensitive to UV irradiation. All of the sample site (0, 1, 3, and 4) data indicated the presence of gray water, evidenced by large degradations of fluorescence at 356 nm.

In summary, as seen in Figure 64, Sample Site 2 always had the greatest presence of yellow water, followed by Sample Site 3, 4, 5, 1 and 0, respectively. Figure 65 shows the heightened existence of optical brighteners at the wastewater treatment effluent and points further down the river.

# Appendix E: Irradiation Tests

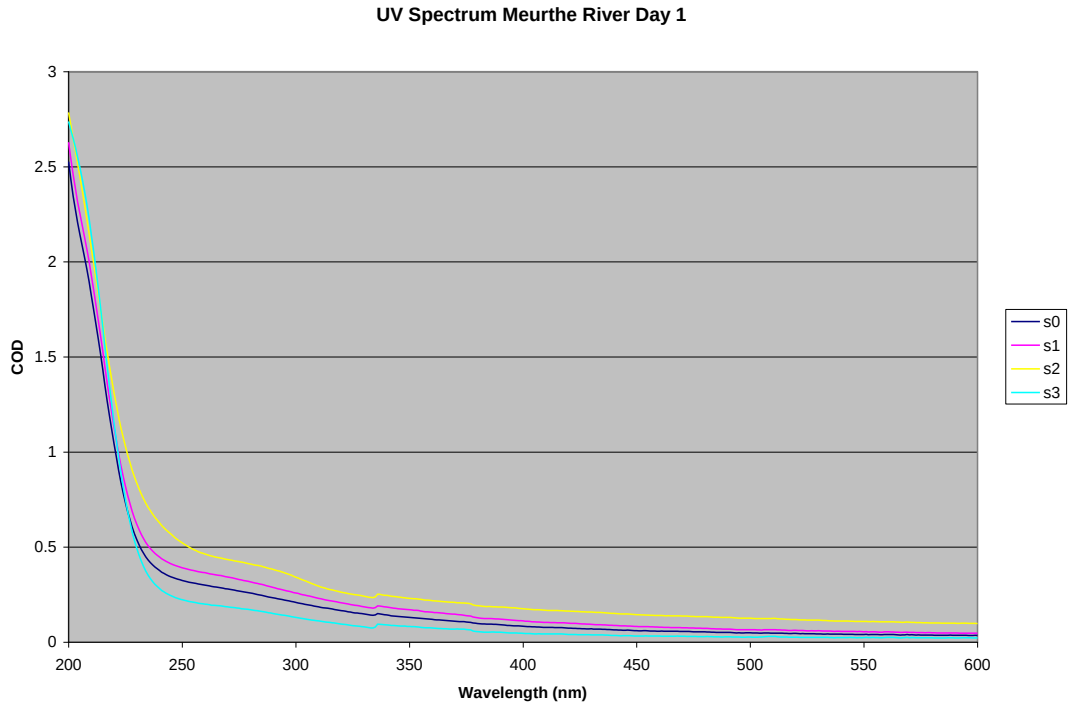


Figure 159: UV Spectrum for Meurthe River Day 1

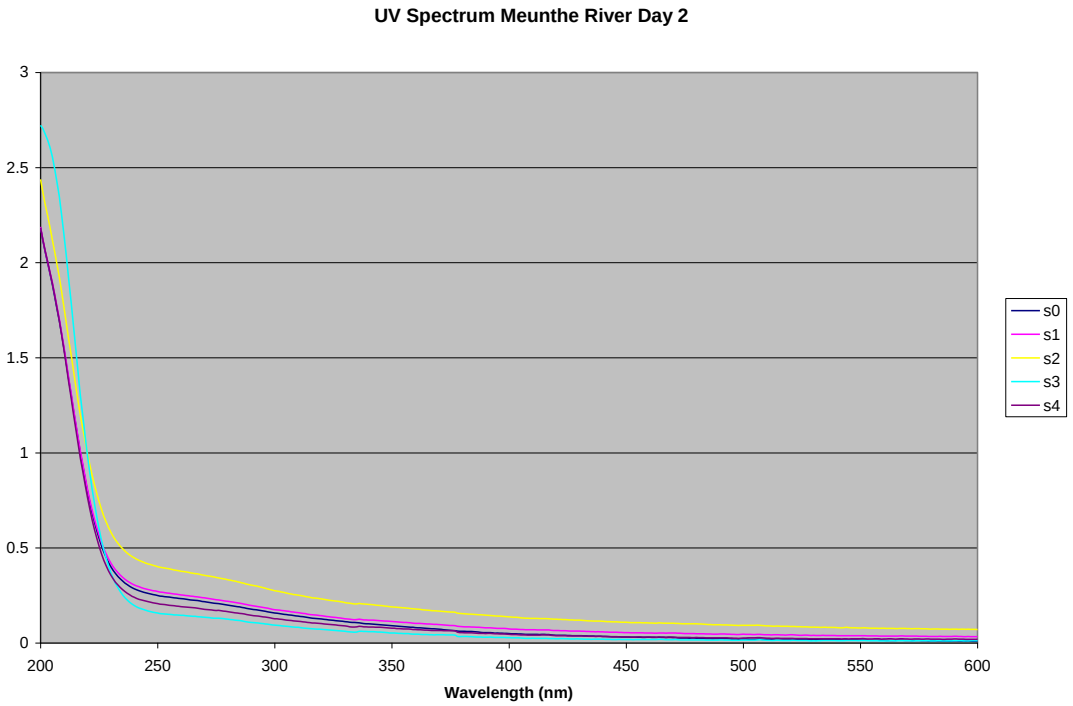


Figure 160: UV Spectrum for Meurthe River Day 2

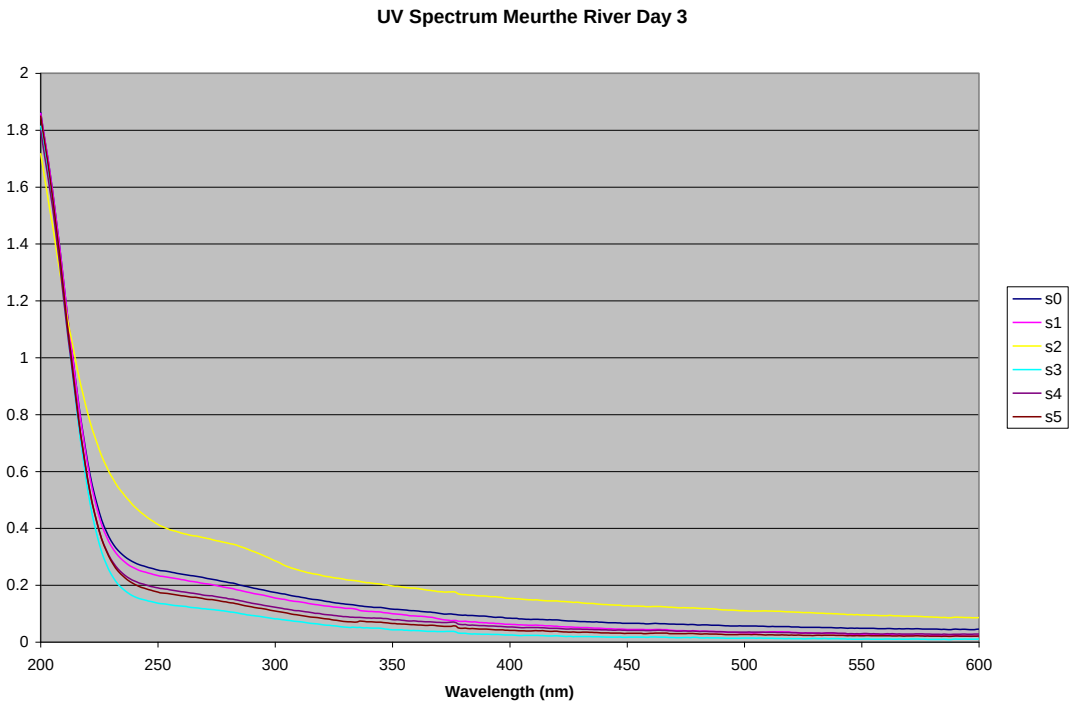


Figure 161: UV Spectrum for Meurthe River Day 3

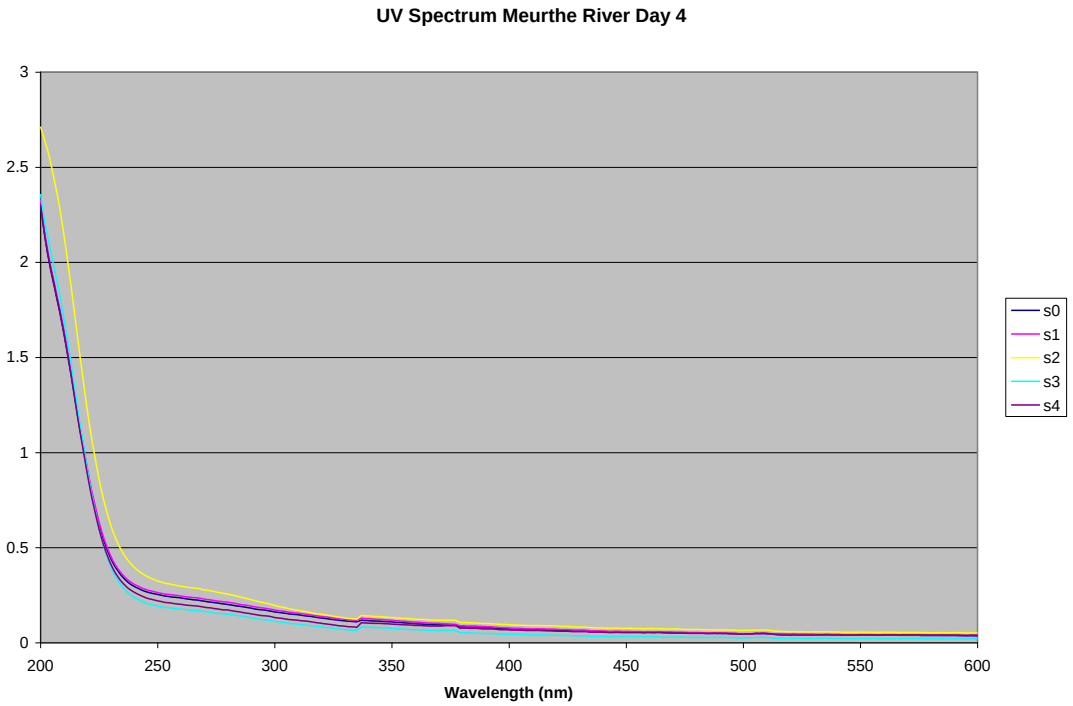


Figure 162: UV Spectrum for Meurthe River Day 4

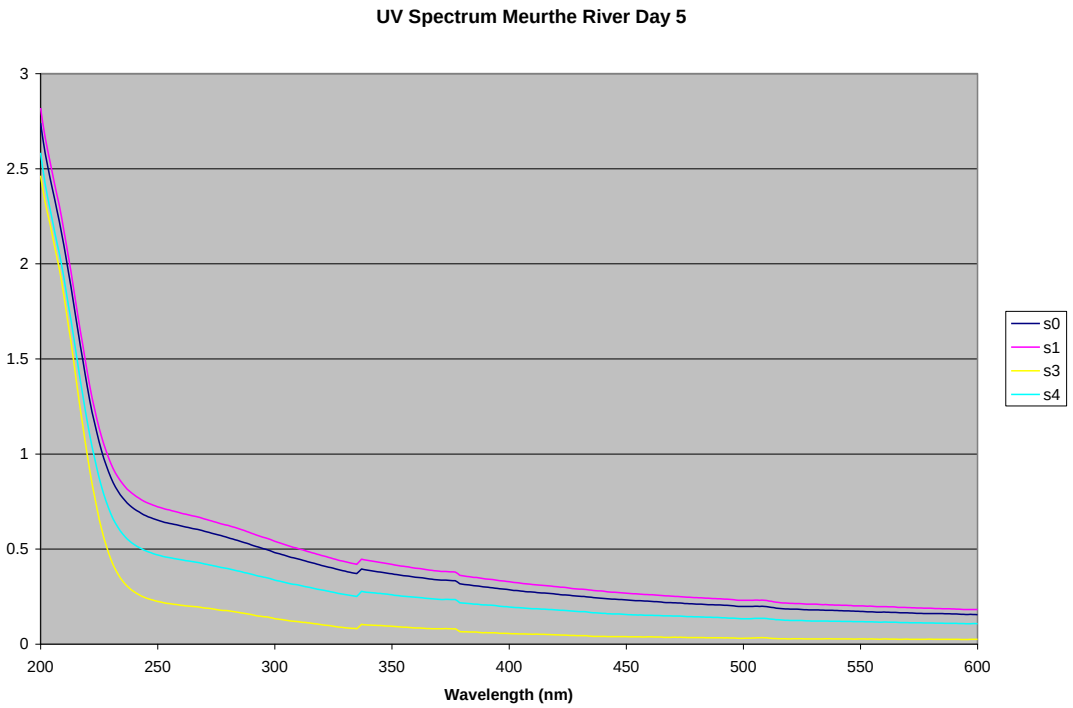


Figure 163: UV Spectrum for Meurthe River Day 5

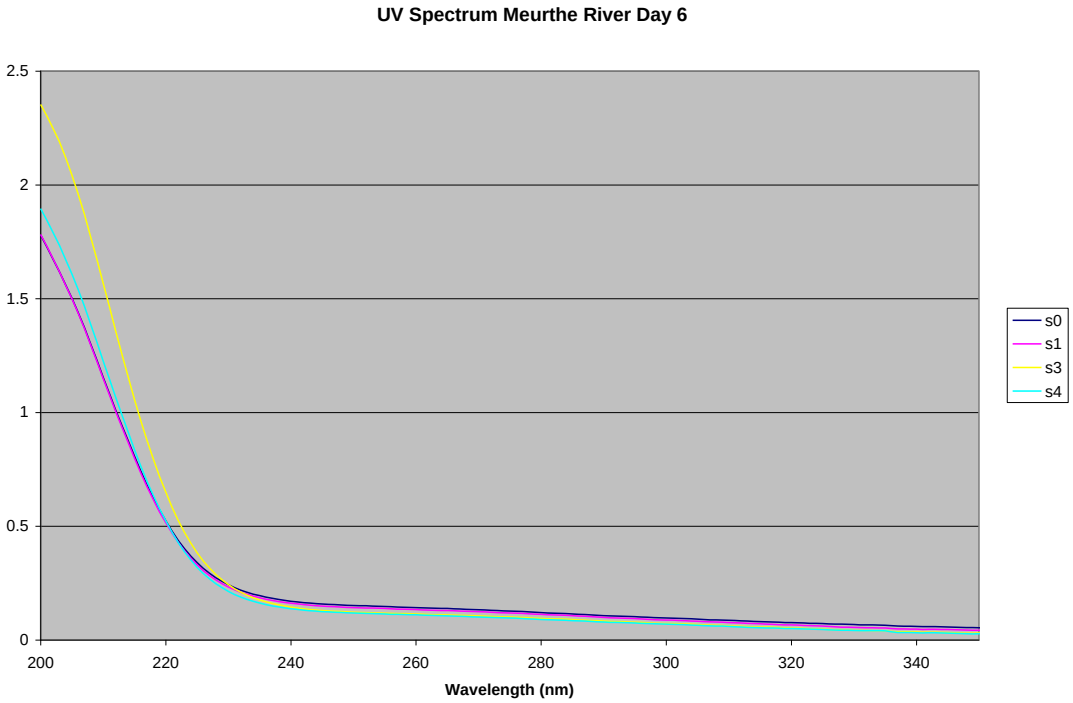


Figure 164: UV Spectrum for Meurthe River Day 6

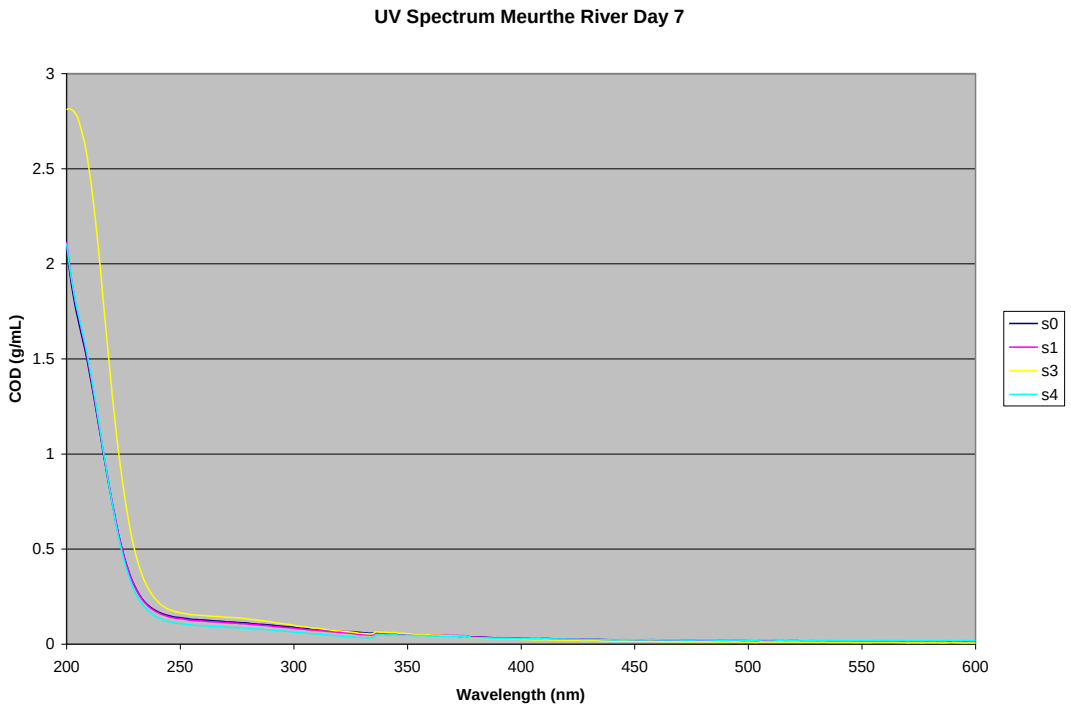


Figure 165: UV Spectrum Meurthe River Day 7

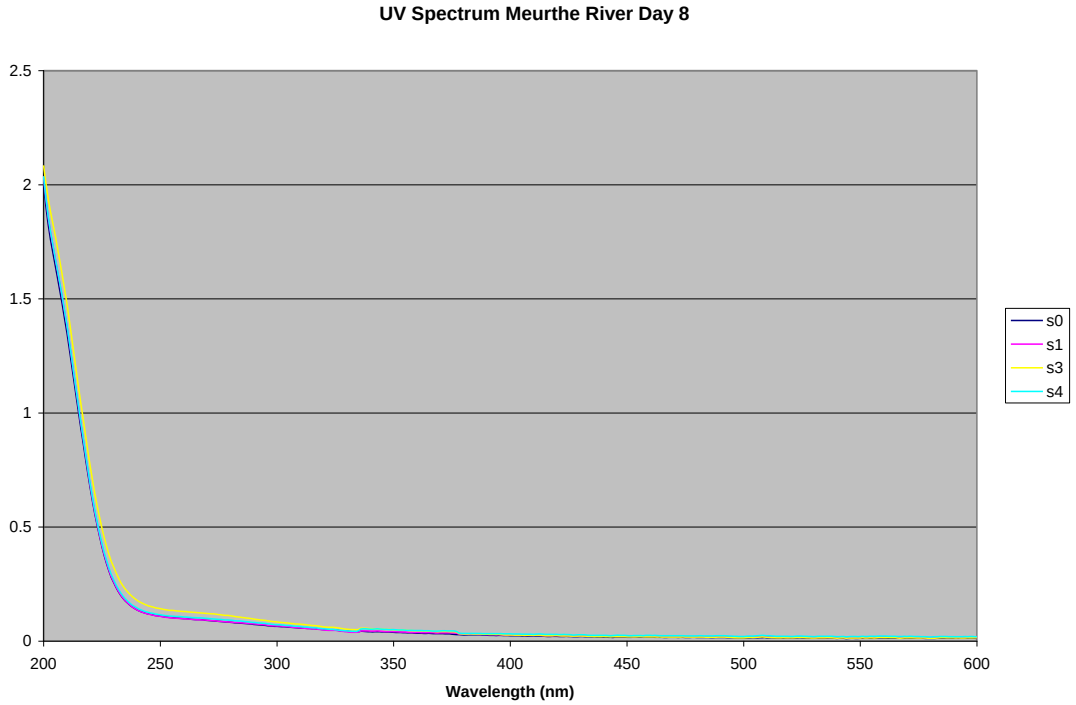


Figure 166: UV Spectrum Meurthe River Day 8

The UV spectrum data from the Meurthe River gave a picture of the chemical oxygen demands (CODs) at the sample sites along the river along the course of several days and weather patterns, as indicated in Table 1. The highest chemical

oxygen demand was at Sample Site 2, as expected, since it contained the highest amount of pollution. This was consistent with the synchronous fluorescence spectroscopy. The wastewater treatment plant effluent, Sample Site 3, showed the lowest COD on average. Sample Sites 0, 1, and 4 were very inconsistent, as some days had a very low COD while other days, the values were very high. This could be explained by the possible fecal contamination from the local fauna. Sample Site 5 was only collected on one day, and the COD level for that was higher than that of the effluent but lower than that of the other sample sites. COD levels were apt indicators of yellow waters and were consistent with the interpretation of the fluorescence data.

Table 2: COD Measurements at 254 nm Wavelength of the Meurthe River

| COD Measurements at 254 nm Wavelength | | | | | | |
|---|---|---|---|---|---|---|
| Day | Sample 0 | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
| 1 | 0.313 | 0.379 | 0.493 | 0.212 | Not Collected | Not Collected |
| 2 | 0.243 | 0.263 | 0.392 | 0.152 | 0.2 | Not Collected |
| 3 | 0.249 | 0.228 | 0.399 | 0.133 | 0.186 | 0.171 |
| 4 | 0.244 | 0.255 | 0.311 | 0.185 | 0.211 | Not Collected |
| 5 | 0.638 | 0.708 | Not Collected | 0.215 | 0.457 | Not Collected |
| 6 | 0.148 | 0.14 | Not Collected | 0.119 | 0.115 | Not Collected |
| 7 | 0.132 | 0.127 | Not Collected | 0.156 | 0.102 | Not Collected |
| 8 | 0.104 | 0.103 | Not Collected | 0.135 | 0.110 | Not Collected |

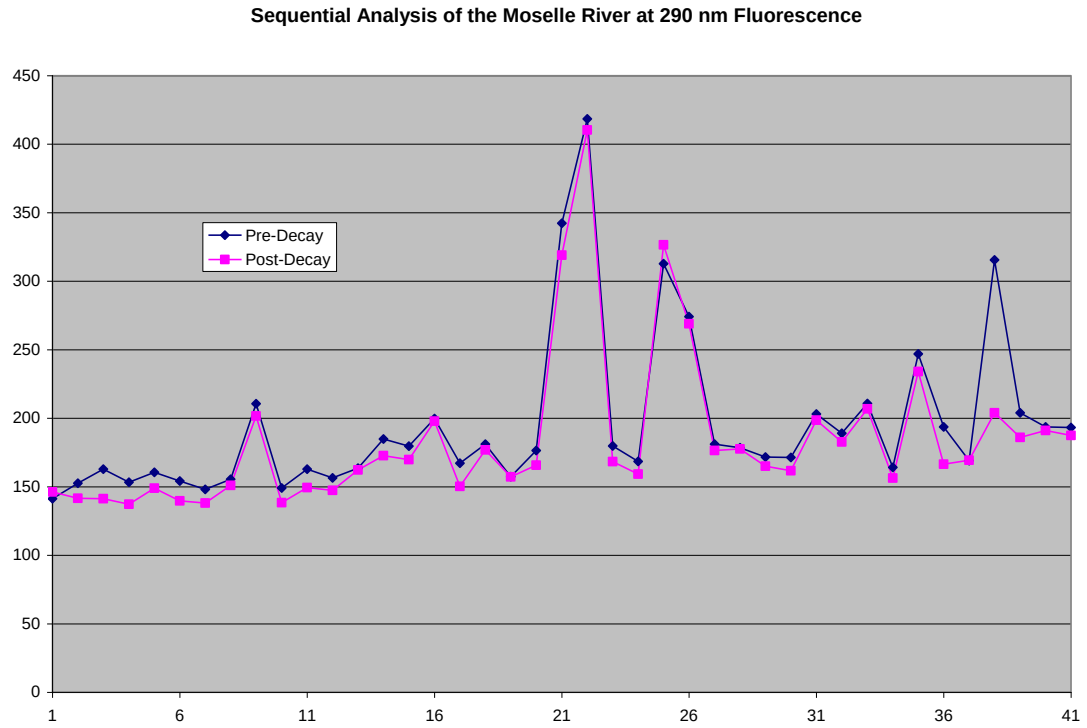


Figure 167: Fluorescence Trend along Moselle River at 290 nm

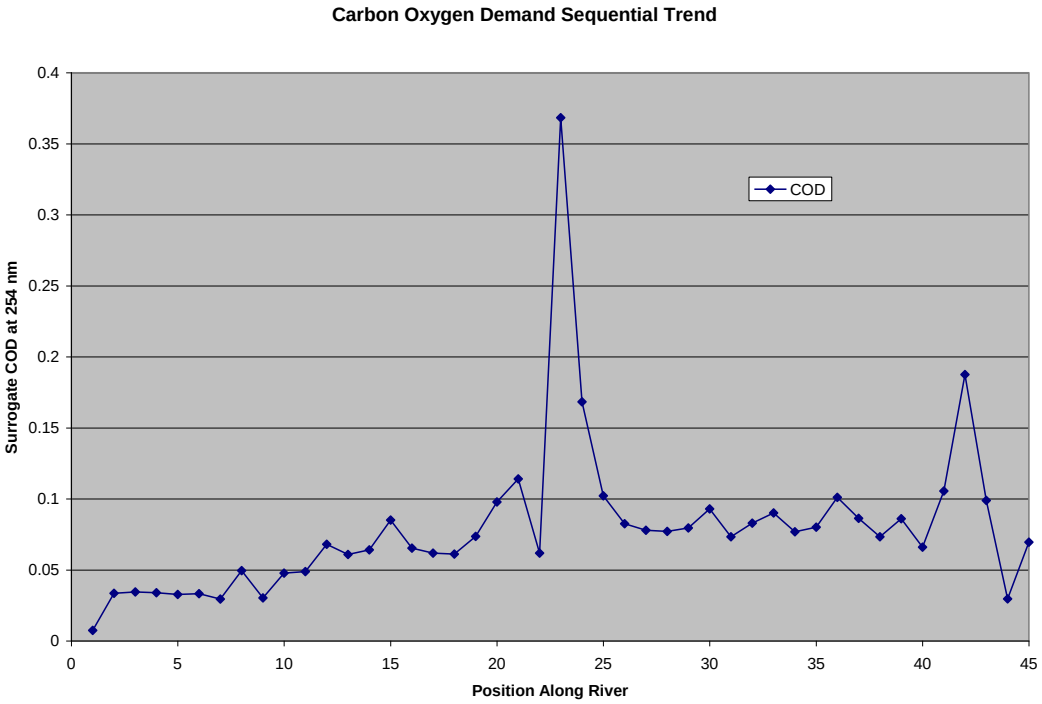


Figure 168: Sequential trend of surrogate COD for the Moselle River

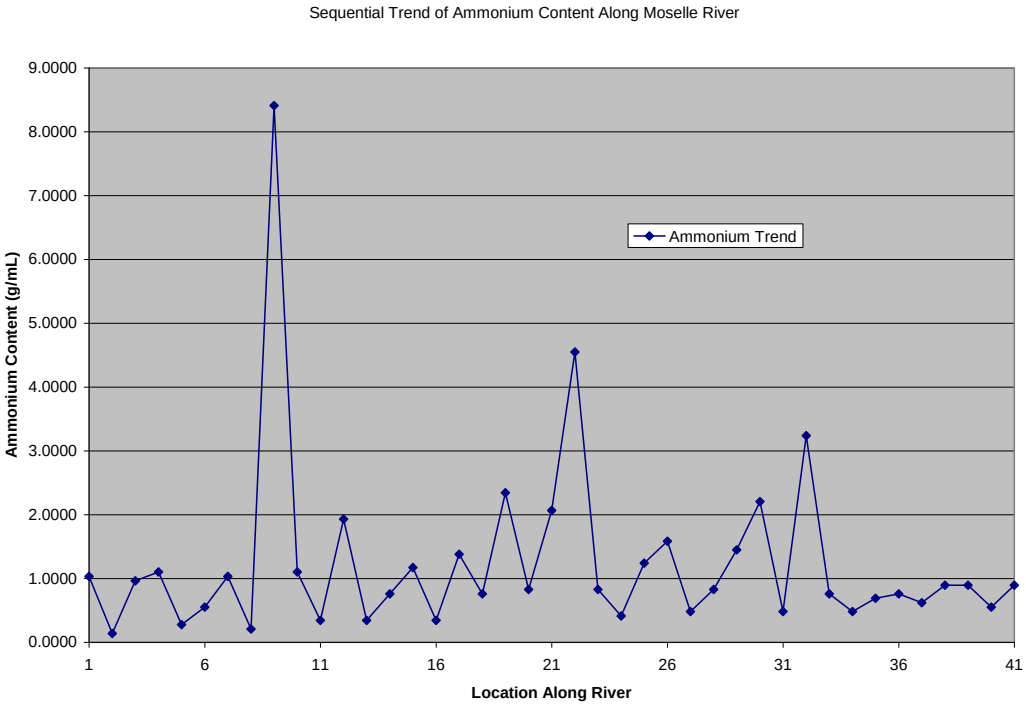


Figure 169: Sequential Trend of Ammonium Content along the Moselle River

# Appendix G: Meurthe River Wastewater Treatment Plant Trends

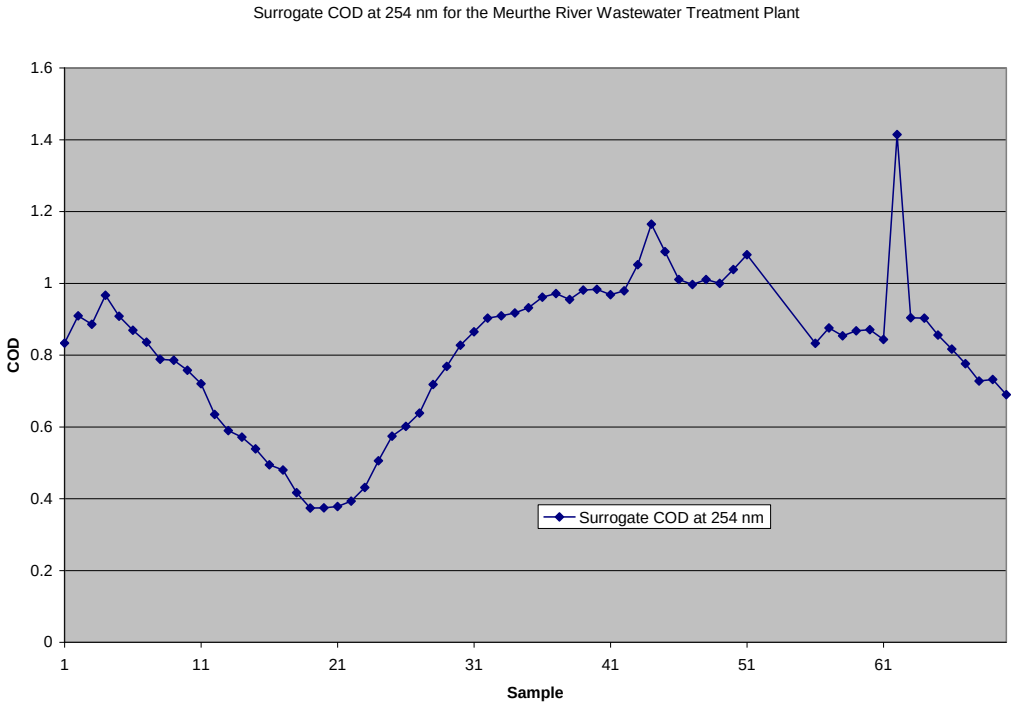


Figure 170: Surrogate COD Trend versus Time for the Meurthe River Wastewater Treatment Plant

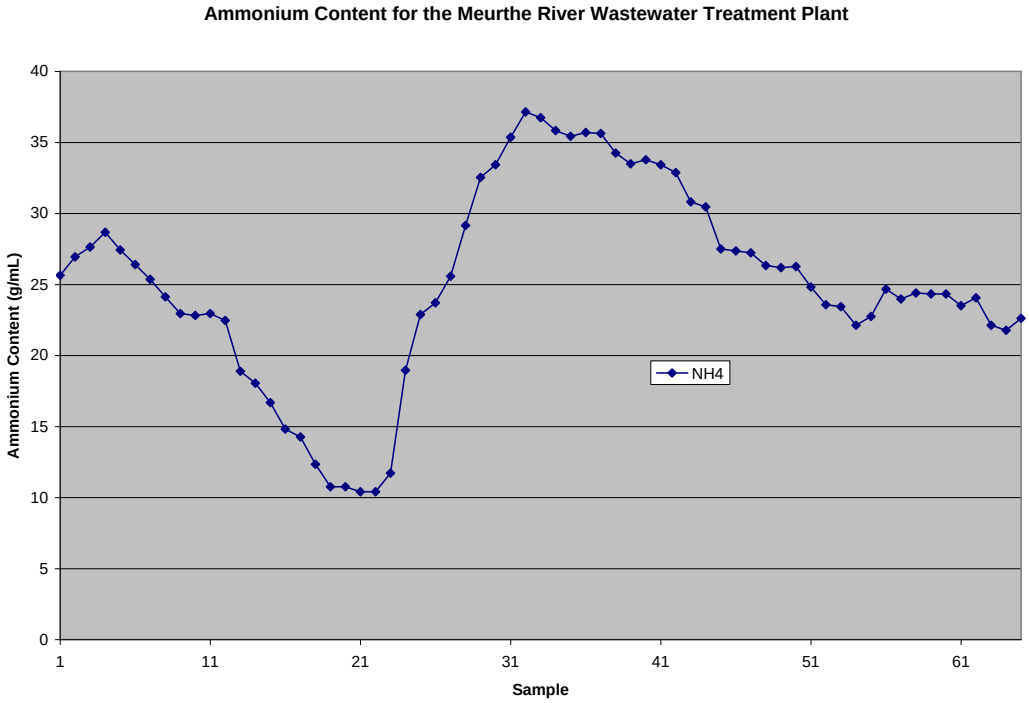


Figure 171: Ammonium Content Trend versus Time for the Meurthe River Wastewater Treatment Plant

The presence of ammonium is an indication of the presence of urine. The ammonium content trend can be found in Figure 63. The content of ammonium shows peaks at Sample Sites 11, 35, and 49. The highest of these is at Sample Site 11, followed by 35 and 49, respectively.

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