# ANALYSIS OF SURFACTANT COMPOSITION AND INORGANIC IONS IN LAKE WATER USING ATR-FTIR SPECTROSCOPY AND ION CHROMATOGRAPHY

by

GABRIELLE DWYER
(Under the Direction of Amanda Frossard)

## ABSTRACT

Surfactant molecules in lake water can alter the rate of exchange of gases at the air-water interface and increase the solubility of pollutants. Here, a method was developed to characterize the organic composition of surfactants using Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) spectroscopy. This method was also used to investigate the effects of photochemistry on the composition of surfactant molecules. Surfactants and other large organic molecules were extracted from water samples collected at Lake Herrick at the University of Georgia. Irradiation of lake water samples had little effect on the total organic composition measured with ATR-FTIR. However, samples collected during the day and night showed spectral differences, suggesting other processes, possibly biological, may impact the composition of surfactants and organics in the lake water. The concentration of major ions in the lake water samples was measured using Ion Chromatography, and the results showed elevated $K^+$ and $Cl^-$ concentrations.

INDEX WORDS: Surfactants, Attenuated Total Reflectance–Fourier Transform Infra-Red Spectroscopy, Ion Chromatography

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May 2022

# DEDICATION

I'm dedicating my thesis to Edward Shakes. He was a great educator and an even greater grandpa. He would have loved to learn about my research. Finishing graduate school without him was challenging, but he would have wanted me to persevere. He is greatly missed, and I wish he were here. Thank you for your wisdom, generosity, and love.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Surfactants in Aerosol Particles

Aerosols impact our environment in different ways, such as cloud formation, visibility, air quality, and respiratory health.[1-3] The function of an aerosol particle is dependent on its features, such as chemical composition.[4] Organic molecules such as surfactants can affect aerosol particles' chemical and physical properties.[5] Surfactants are amphiphilic compounds - They have a hydrophilic head group and a hydrophobic tail.[6] They can be classified based on the charge of the hydrophilic head group. There are three types of surfactants: cationic, anionic, and non-ionic. Cationic surfactants are positively charged, anionic surfactants are negatively charged, and non-ionic surfactants have no charge. Natural sources of surfactants in aerosol particles include sea spray aerosols and lake spray aerosols that are produced from breaking waves.[4, 7] Combustion from vehicles and emissions from biomass burning are anthropogenic sources of surfactants in aerosol particles.[8, 9] Surfactants aid in cloud condensation nuclei (CCN) activation by lowering the surface tension and allowing particles to form cloud droplets at the critical supersaturation of the atmosphere.[5]

## 1.2 Surfactants in Lake Water

Surfactants have been found in environmental samples around lake ecosystems.[10] These organic substances can affect aquatic systems in different ways. Surfactants in lake water can form a monolayer film that acts as a barrier at the surface.[11] This film can limit the rate of gas exchange at the air-water interface, which can have implications on climate models that predict the flux of $CO_2$ in the atmosphere.[11] Surfactants in lake water can also increase the solubility of organic and inorganic pollutants that accumulate at the surface because of their ability to reduce surface tension.[12] This can negatively impact organisms and processes that affect lake ecosystems.

Lakes contain dissolved organic matter (DOM), some of which have surface-active properties.[12] DOM is a complex mixture of dissolved organics that can be made up of decomposed plant material and other organisms.[13] Humic-like substances (HULIS) around lake ecosystems decompose to form natural surfactants.[10, 14] Biological surfactants can be generated from algae and phytoplankton present in lake water.[14] Surfactants can also be naturally derived from volatile organic compounds (VOCs) emitted from soil and vegetation surrounding lake ecosystems through chemical processing.[12] Anthropogenic contributions in lakes include synthetic surfactants present in personal care products, pesticides, and waste from industrial sites.[14]

Razak et al.[14] investigated the concentration of surfactants in the surface microlayer of Lake Chini, Malaysia, using colorimetry. The study showed that anionic surfactants were more abundant than cationic surfactants in the lake. High concentrations of anionic surfactants can be attributed to the domestic practices of the people who reside close to the lake and fuel leaks from petrol-powered boats.[14] Additionally, untreated wastewater can contribute to elevated concentrations of cationic surfactants in lakes.[14]

Characterizing surfactants in lake water is essential because of their ability to increase the solubility of pollutants and their influence on the rate of air-water gas exchange.[15] Previous research has shown that surface-active organic compounds in lake water include carbonyls and carboxylic acids.[10] Even though surfactants have a significant impact on lake ecosystems, the chemical composition of surfactants in lake water is poorly characterized.[12]

### 1.3 Previous Studies on Characterizing Surfactants

There are limited studies on characterizing surfactants because there are insufficient suitable methods that analyze surfactant composition with good sensitivity.[6] Mecozzi et al.[16] analyzed surfactant characteristics of marine foams using UV-Vis and FTIR spectroscopy and found that the chemical structure of surfactants is similar to biomolecules such as lipids, carbohydrates, and proteins. Also, Sasi et al.[6] did a study on Lake Vembanad in India that used mass spectrometry to identify surfactants in lake water. The study related the chemical composition of the surfactants to their physicochemical properties (pH, salinity, temperature, etc.) to assess water quality. This study identified the following types of surfactants in lake water: linear alkylbenzene sulfonates, alcohol ethoxy sulfates, and alcohol ethoxylates.[6] Based on previous research, ATR-FTIR spectroscopy is a suitable method for analyzing functional groups in surfactants.[16]

### 1.4 Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) Spectroscopy for Functional Group Analysis for Surfactants

The hydrophobic tail of a surfactant consists of an aliphatic/aromatic hydrocarbon chain.[6] Anionic surfactants consist of linear alkylbenzene sulfonates, cationic surfactants consist of quaternium ammonium molecules, and non-ionic surfactants consist of ethoxylated linear alcohols, ethoxylated phenols, and fatty acid esters.[6, 17] The chemical composition of surfactants can be analyzed by use of Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) spectroscopy.[18] Infrared (IR) waves from a light source in the instrument pass through the ATR crystal and the sample at an angle greater than the critical angle causing total internal reflection.[19]As a result, evanescent waves form at the inflection points. The interaction with the evanescent waves and the sample gives information about the functional groups present in the sample.[19] This information is sent to the detector, and spectra are generated.[19] The spectra can then be used for functional group analysis based on the absorbance values and wavenumbers that correspond with different peaks in absorption. The advantages of using ATR-FTIR spectroscopy include only needing a small sample size for analysis, little to no sample preparation, and a wide range of samples that can be analyzed.[20] The types of samples that can be analyzed include solids, liquids, pastes, and powders.[21] Also, the instrument is user-friendly, and the ATR crystal is easy to clean.[21] The factors that should be considered when using the ATR-FTIR for functional group analysis for surfactants include limits of detection, choice of solvent, and drying time for solvent.

### 1.5 Photolysis of Organic Molecules

Limited research has been done on the photolysis of organic molecules in lake water.[22] The surface microlayer of marine and freshwater sources is enriched with organics, including surfactants.[12] The surface microlayer is exposed to higher radiation than the underlying bulk water due to light intensity decreasing exponentially as the depth of the water increases.[23] UV radiation occurring at the air-water interface can lead to photodegradation of the organic molecules.[24] Additionally, the chemical structure and concentration of the surfactants in lake water can be altered by the photochemical reactions involving organic molecules.[22, 23]

### 1.6 Use of Ion Chromatography for Characterizing Atmospheric Aerosols

Ion chromatography (IC) is an analytical technique used to measure the ionic composition of atmospheric species.[8] It is a form of liquid chromatography that utilizes an ions' affinity to charged resin (stationary phase) in the columns to achieve separation.[25] For a cation exchanger, the molecule of interest is positively charged, and the resin is negatively charged.[25] For an anion exchanger, the molecule of interest is negatively charged, and the resin is positively charged.[25] This technique is an efficient method for characterizing the inorganic components of aerosols due to its high selectivity and sensitivity.[26] The ionic species that can be measured with Ion Chromatography include atmospheric alkylamines, water-soluble organics, and inorganic ions.[27, 28] A field study investigated the effect of $SO_2$, $NO_{x,}$ and VOCs (volatile organic compounds) on the concentration of the ionic composition of secondary aerosols in Chicago, Illinois. It was found that the concentrations of the ions were dependent on factors such as temperature and wind direction. IC results can also be used for source apportionment of atmospheric aerosols.[29] High potassium concentrations have been traced to biomass burning, and high sodium and chloride ions concentrations have been associated with sea spray aerosols.[29] The presence of sulfate and nitrate ions in aerosol particles has been attributed to localized pollution emitted from anthropogenic sources.[29]

## 1.7 Use of Ion Chromatography for Ionic Composition Analysis for Lake Water

Ion chromatography has been used in previous studies to determine the concentration of the major ions in lake water. The physicochemical properties of lake spray aerosols (LSA) and sea spray aerosols (SSA) are different even though they are generated through the same mechanism - breaking waves and bubble bursting.[30, 31] The average salinity of seawater is 35‰ (35 g of salt dissolved in 1000 g of seawater).[32] However, salinity measurements for lakes are inconsistent because the salinity of lake water is heavily dependent on the environmental factors affecting the surrounding area.[33] The major inorganic cations commonly present in lake water include $Mg^{2+}$, $Ca^{2+}$, $Na^+$, $K^+$, and the anions include $Cl^-$, $HCO3^-$, and $SO_4^{2-}$.[33-35] Weathering of rocks, municipal wastewater, limestone, and carbonate rocks contributes to the $Ca^{2+}$

concentration in lake water.[33, 35] Generally, as the mineral content ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$) of lake water increases, so does the $Cl^{-}$ concentration.[33]

Lakes are subject to natural input such as precipitation, soil erosion, and weathering of rocks. Anthropogenic pollutants such as surface runoff containing synthetic surfactants, fertilizers, and domestic and industrial effluents can deposit into lakes.[33] Substantial input from watersheds and short water residence times can increase the variability of the concentration of major ions in lake water.[35] Furthermore, chlorophyll production is dependent on magnesium, a known growth factor for phytoplankton.[33] Additionally, nitrate is a fertilizer for phytoplankton; therefore, elevated nitrate can increase phytoplankton production.[33]

## 1.8 Motivation for Research Project

There are limited studies on the chemical composition of surfactants in aquatic systems. I aim to develop a method to measure the functional group composition of total organics and surfactants in lake water using Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR). Samples were collected from Lake Herrick at the University of Georgia. The lake was shut down in 2002 due to bacterial contamination, and recreational practices such as swimming and canoeing were prohibited.[36] However, after restoration was completed, the lake was reopened in 2018.[36] Two tributaries feed the lake with runoff originating from domestic and woodland areas, which could contribute to the surfactant composition in the lake.[36] Lake Herrick is a nearby source of surfactants and organics used to test the developed method. Due to its history, the sample area is of interest, and samples were readily available in the lab.

There is limited literature on the sun's solar radiation/photochemical effects on the composition of surfactants. UV radiation from the sun can photodegrade organic molecules into smaller particles, contributing to the molecules' environmental impact, including lifetimes for atmospheric particles.[37] Analysis of the functional groups of surfactants in aquatic systems improves our understanding of how surfactants facilitate processes that affect our environment and climate. It is predicted that the peaks in absorption for the irradiated morning samples will have lower maximums than the original morning samples. Additionally, it is predicted that the afternoon samples' absorption peaks will have lower maximums in absorption than the morning samples. The change in absorbance could be attributed to the photodegradation of surfactants/organics into smaller organic molecules.

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# CHAPTER 2

# DETERMINATION OF SURFACTANT AND IONIC COMPOSITION OF LAKE HERRICK USING ATR-FTIR SPECTROSCOPY AND ION CHROMATOGRAPHY

## 2.1. Methods

### 2.1.1 Sample Collection

Water samples were collected at Lake Herrick twice a day from January 20, 2020, to February 9, 2020, by the Frossard Lab group members (Jaci Hawkins and Ariana Deegan). These samples were collected at the floating dock towards the back of the lake (Figure 1). This location was chosen because it is the furthest away from anthropogenic influences, including car exhaust from the parking deck and runoff from the intramural fields. Sample collection took place every day in the morning (before sunrise at 7 AM) and in the afternoon (before sunset at 4 PM). The samples were collected in precleaned 300 mL and 120 mL amber glass bottles. The bottles were rinsed with the lake water three times before collecting samples. The bottles were then wrapped in foil and placed in the freezer until analysis was performed - to prevent degradation of the surfactants and organics in the lake water samples (n=42).

### 2.1.2 Irradiation of Lake Water Samples

One of seven sample pairs (morning samples) was transferred to a jacketed beaker with a quartz lid and irradiated with a Suntest CPS (Atlas) solar simulator with a 1.5 79 kW Xenon lamp. A solar simulator is designed to simulate natural sunlight under controlled laboratory conditions.[1] The morning samples (collected just before sunrise) were exposed to 3000 W/m$^2$ (3 suns = 3000 W/m$^2$) of radiation for two hours.[2] The irradiated and non-irradiated samples were compared to investigate the effects of UV radiation on the chemical composition of the surfactants and organics in the lake water samples. The irradiation and extraction of the morning samples were done by Amelia Dalton, a past member of the Frossard lab.

### 2.1.3 Extraction of Surfactants

Surfactants and large organics in the Lake Herrick samples were extracted using solid-phase extraction. The extraction method used was optimized by Burdette et al.[3] The frozen lake water samples were first thawed overnight and filtered with a 25 mm syringe filter with a 0.45 µm polyethersulfone membrane to remove the lake sediments such as dirt/soil. The filtered samples were then transferred to new clean bottles. ENVI-Carb graphitized carbon (EnviCarb) and Envi18 C18 polymerically bonded octadecyl (Envi18) cartridges were used for the extraction process. The cartridges were conditioned with 6 mL of acetonitrile (ACN) and 12 mL of ultrapure water using a syringe. EnviCarb cartridges have high extraction efficiencies for cationic and non-ionic surfactants from water samples.[3] The Envi18 cartridges have high extraction efficiencies for anionic and non-ionic surfactants from water samples.[3] After the cartridges were conditioned, 75 mL of the lake water samples were processed through each of the cartridges. ACN was used as the elution solvent to elute the surfactants and organics attracted to the cartridges. The surfactants and organics were desorbed and collected into a small vial.

### 2.1.4 ATR-FTIR Analysis of Surfactants

Standard surfactant solutions were used to develop the method for analyzing the composition of surfactants using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy. The detection limit was determined for the following standard surfactant solutions: sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), benzyldimethylhexadecylammonium chloride (BAC), cetrimonium chloride (CTAC), brij, and genapol using the Frossard Lab ATR-FTIR (Thermo Scientific Nicolet iS50). I did serial dilutions using 1mM standard surfactant solutions in ACN. Standard solutions with concentrations of 1.0, 0.5, 0.25, 0.125, 0.0625, and 0.03125 mM were analyzed to determine the lowest concentration that can reasonably be detected with the ATR-FTIR. Two µL of each surfactant solution was used for analysis. The solutions were dried on the ATR crystal for 4 minutes, and the spectra were collected at a resolution of 2 cm$^{-1}$ and a scan number of 120.

The drying time for ACN was previously determined experimentally by Amelia Dalton. Two µL of a standard surfactant solution (1 mM sodium dodecyl sulfate dissolved in ACN) was analyzed with an ATR-FTIR using different drying times. The spectrum for the dried standard solution was compared to the spectrum for pure ACN. When a 4-minute or longer drying time was used, no ACN peaks were present in the spectra for the standard solutions. Therefore, 4 minutes was chosen as the optimum drying time for ACN.

The spectroscopic properties of the extracted surfactants/organics from the lake water dissolved in acetonitrile were analyzed using an ATR-FTIR. Two µL of each sample was dispensed onto the ATR crystal using a micropipette. The sample was left to dry for 4 minutes allowing the ACN to evaporate - leaving only the surfactants and organics in the sample on the ATR crystal. The pressure tower compressed the sample, and spectra were collected at a resolution of 4 cm$^{-1}$ and a scan number of 120. The Harrop Lab ATR-FTIR (Thermo Scientific Nicolet 6700) was used to analyze all Lake Herrick samples. All the samples were analyzed around the same time.

### 2.1.5 Data Analysis for ATR-FTIR spectra

The Thermo Scientific OMNIC software was used to normalize the scale of the y-axis of the spectra collected - the lowest absorbance peak was set to 0, and the highest absorbance peak was set to 1. This normalization was done because some of the spectra had negative peaks in absorption. The normalized scale spectra for the Lake Herrick samples were then normalized to the last point (the last absorbance peak was set to 1) and plotted using Igor. This post-processing (normalizing spectra to the last point) was done to show all the spectra starting at the same point.

#### 2.1.5.1 Cosine similarity

Cosine similarity is used to measure the similarity between two vectors. It is determined by calculating the cosine of the angle between the two vectors. The results can range from 0 to 1. The closer the result is to 1, the more similar the vectors are. The normalized scale spectra (resolution = 4 $cm^{-1}$ and scan number =120) from 2800 $cm^{-1}$ to 3600 $cm^{-1}$ were used to calculate the cosine similarity between non-irradiated morning and irradiated morning samples and between samples extracted with Envi18 and EnviCarb cartridges.[4] This region was chosen to omit noisy regions of the spectra (1900 – 2300 $cm^{-1}$ and 3601 – 4000 $cm^{-1}$) and focus on the alcohol and alkane peaks.

I used cosine similarity because the similarity between two variables is altered if there is a constant change to one of the variables as opposed to a correlation comparison. It is also advantageous because it measures the angle between vectors and not the magnitude. For ATR-FTIR spectroscopy, two samples can be the same while having different concentrations, making cosine similarity a suitable method to assess the similarity between two ATR-FTIR spectra. The samples are considered very similar if the cosine similarity between the two spectra is above 0.95.[5]

#### 2.1.5.2 Absorbance Ratios

Absorbance ratios were used to relatively compare the alkane to alcohol functional groups for the organics in the Lake Herrick samples. For FTIR spectroscopy, higher peaks in absorption indicate the presence of more functional groups that absorb in a specific region.[6] The absorption region for aliphatic $CH_x$ stretching is 2850 to 2950 $cm^{-1}$.[7] The absorption region for hydroxyl stretching (carbohydrate) is 3450 to 3300 $cm^{-1}$.[7] ATR-FTIR spectra for surfactants showed that these organics have high peaks in absorption for alkane functional groups and low peaks in absorption for hydroxyl functional groups. Therefore, the absorbance ratios may be related to how surfactant-like the organics in the Lake Herrick samples are.

The normalized scale spectra were used to calculate absorbance ratios for morning and afternoon samples. The absorbance ratios for the four alkane peaks relative to the alcohol peak followed similar trends for each sample type (See Appendix Figure A1). For this work, the peak in absorption corresponding to 2950 $cm^{-1}$ (alkane) was divided by the peak in absorption for 3382 $cm^{-1}$ (hydroxyl). Absorbance ratios ($A_{2950/3382}$) were calculated and compared for all sample types.

#### 2.1.5.3 Principal Component Analysis (PCA):

Principal Component Analysis (PCA) is a dimensionality reduction technique used for a more straightforward analysis of a dataset.[8] PCA uses a series of linear equations on the original dataset to assign new variables representing the principal components (PC).[8] The normalized scale spectra from 2500 $cm^{-1}$ to 4000 $cm^{-1}$ for all Lake Herrick Samples were used to perform PCA. The PCA function in MATLAB automatically centers the data, and the dataset was additionally normalized to unit area. Preprocessing (normalizing ATR-FTIR spectra to scale and normalizing dataset to the unit area) of the dataset was done for baseline correction purposes. The PCA function was set to return each principal component's loadings, scores, and percent variance. A scatter plot of PC1 (1st principal component) and PC2 (2nd principal component) was created to show the variance within the samples. The loadings for PC1 and PC2 were plotted against the wavenumbers (variables) to assess the importance of each peak in absorption.

### 2.1.6 Ion Chromatography (IC) Analysis for Lake Herrick Samples

The ionic composition of the Lake Herrick samples was analyzed using Ion Chromatography (Thermo Scientific Dionex Integrion HPIC). Calibration curves were created using standard solutions of salts. Cationic and anionic standard solutions were made for calibration purposes. The cationic standard solution consisted of 0.0223 g of KCl (120 mg/L $K^+$), 0.0043 g of $CaCl_2$ (15 mg/L $Ca^{2+}$), 0.0024 g of $MgCl_2$ (5 mg/L $Mg^{2+}$), 0.0018 g of NaCl (5 mg/L $Na^+$) dissolved in 100 mL of ultrapure water. The anionic standard solution consisted of 0.2540 g of NaCl (150 mg/L $Cl^-$) dissolved in 100 mL of ultrapure water. Another standard solution containing 0.0096 g of $(NH_4)_2SO_4$ in 100 mL of ultrapure water (7 mg/L $SO_4^{2-}$) was used to quantify $SO_4^{2-}$ in the samples.

## 2.2 Results and Discussion

### 2.2.1 ATR-FTIR Method Development for Surfactant Analysis

Few studies have analyzed the detailed chemical composition of surfactants in seawater/lake water due to the lack of appropriate methods.[9] In this study, a method was developed to analyze the chemical composition of surfactants using solid-phase extraction and ATR-FTIR spectroscopy.

Standard surfactants were used to test the method and determine the detection limit before surfactants from the lake water samples were analyzed. The detection limit ranges from 0.03125 mM to 0.12500 mM (Table 1). Standard surfactants were dissolved in acetonitrile, placed on the ATR crystal, and left to dry for 4 minutes. This drying time allowed acetonitrile to evaporate completely, leaving only the surfactant on the crystal. Figure 2A shows that the 4-

minute drying time for ACN is sufficient. There are no peaks in absorption that overlap with the standard SDBS solution and ACN. The standard SDBS solution was compared to the SDBS solid standard (Figure 2B). The prominent peaks in absorption for both samples overlap, and there are no shifts in the peaks in absorption, which shows that the proposed evaporation and drying method does not alter the composition of the analyte.

### 2.2.2 ATR-FTIR Spectroscopic Characteristics of Surfactants and Large Organics Extracted from Lake Herrick Water

The composition of surfactants consists of a polar head group and a non-polar end. The non-polar region is comprised of a (saturated/non-saturated) hydrocarbon chain, and the polar head group is made up of a non-ionic or ionic group.[9] The functional group assignments for the Lake Herrick samples are consistent with the characteristics of surfactants (Table 2).[7] This study mainly focuses on the ATR-FTIR spectral region of 2500 $cm^{-1}$ to 4000 $cm^{-1}$ (Figure 3). The prominent peaks in absorption for the Lake Herrick samples include peak locations at 3382, 2950, 2925, 2869, and 2855 $cm^{-1}$. The alkane peaks in absorption (2950, 2925, 2869, and 2855 $cm^{-1}$) may be characteristic of surfactants' hydrophobic tail or organics with alkane functional groups.[7, 10] The organic hydroxyl peak in absorption (3382 $cm^{-1}$) could represent the hydrophilic head group of surfactants or organics with alcohol functional groups.[7, 10]

Also, the organic hydroxyl peak location is consistent with the hydroxyl peak location for disaccharides ($3383 \pm 4$ $cm^{-1}$).[7, 11] Mecozzi et al.[7] did a study that confirmed the presence of carbohydrates in marine foams. Carbohydrates significantly contribute to dissolved organic matter (DOM) composition in freshwater sources.[12] Sources of carbohydrates in lake water include exudates from phytoplankton, macrophytes, and algae.[12] Carbohydrates and surfactants stabilize organic films at the surface, which can impact gas exchange occurring at the air-water interface.[7, 13] This can have implications on the flux of $CO_2$ in the atmosphere.[14]

### 2.2.3 Photochemical Effects on Chemical Composition for Lake Herrick Samples

ATR-FTIR spectra for the morning samples and irradiated morning samples were compared to investigate the photochemical effects on the composition of surfactants. Morning samples (collected before sunrise) were irradiated because they were exposed to the least amount of natural sunlight. There is little difference between the spectra for irradiated and non-irradiated morning samples (Figure 4). The cosine similarity of the spectra for irradiated and non-irradiated samples was calculated to assess the similarity between the composition of the samples (Table 3). The cosine similarity values range from 0.9890 to 0.9991. These values indicate that the irradiated and non-irradiated samples have very similar organic signatures and that the photochemical effects are negligible when considering the composition of surfactants and organics.[5] The expectation was that organics in the irradiated samples would be broken down, and the functional groups would have lower maximums in absorption.[15, 16]

The ATR-FTIR spectra for the afternoon, morning, and irradiated morning samples extracted with Envi18 cartridges were compared to investigate the effects of the time of day the samples were collected (Figure 5). Based on the ATR-FTIR spectra shown in Figure 4, photochemical effects did not significantly impact the absorbance values and chemical composition of the surfactant and organic molecules extracted from the Lake Herrick samples. Compared to the morning samples, the afternoon samples demonstrate the impact of effects other than the photochemical effects. Stolle et al.[14] suggest that there could be biological production of surfactants predominantly occurring at night which could explain why the alkane peaks in absorption for the morning samples are higher than the alkane peaks in absorption for the afternoon samples.

### 2.2.3.1 Absorbance Ratios for Samples Extracted with Envi18 Cartridges

Surfactants have been characterized by having high hydrogen to carbon ratios (H/C) and low oxygen to carbon ratios (O/C).[3] Alkane functional groups contribute to high H/C ratios, and hydroxyl functional groups contribute to high O/C ratios.[17] $A_{2950/3382}$ represents the absorbance ratio between the alkane peak in absorption (2950 $cm^{-1}$) and the alcohol peak in absorption (3382 $cm^{-1}$) for the Lake Herrick samples. $A_{2950/3382}$ is a relative ratio of alkane to hydroxyl functional groups in the samples. Absorbance values obtained from the FTIR spectra are not directly related to concentration. So, the calculated absorbance ratios are used for comparison purposes instead of quantitative analysis. Samples with relatively higher $A_{2950/3382}$ may have organic molecules that are more surfactant-like in composition when compared to samples with lower $A_{2950/3382}$. However, because FTIR is a bulk measurement that gives information on chemical composition but not structural information, it is not the most suitable method to quantify H/C and O/C ratios. It is possible that the organic hydroxyl and alkane functional groups are externally mixed.

The $A_{2950/3382}$ for Envi18 morning (original), Envi18 morning (irradiated), Envi18 afternoon, and EnviCarb afternoon samples were compared (Figure 6). Except for the samples collected on 2/2/2020 – 2/4/2020, the absorbance ratios for Envi18 morning (original) correspond to the absorbance ratios for Envi18 morning (irradiated) that were collected on the same day. The corresponding absorbance ratios signify how comparable the composition of samples is. Morning samples may consist of more surfactant-like molecules than afternoon samples due to their higher absorbance ratios. As stated previously, this may be attributed to the biological production of surfactants.[14] Also, standard surfactants had absorbance ratios of 5.7 and 4.2 (see Appendix Figure A5).

#### 2.2.3.2 PCA of ATR-FTIR Spectra Showing Variability Explained by the Time of Day for Sampling

PCA was used to assess the variability of the chemical composition for Lake Herrick samples. The ATR-FTIR spectral region of 2500 $cm^{-1}$ to 4000 $cm^{-1}$ used for PCA is shown in Figure 3. This region emphasizes the samples' main organic components (organic hydroxyl and saturated alkane) and excludes the ATR crystal noise (between 1900 $cm^{-1}$ and 2300 $cm^{-1}$).[18] Figure 7 shows the scatter plot of the scores for PC1 and PC2. The total variability explained by PC1 and PC2 is 89.2%. PC1 explains 51.2 % variability within the data. The majority of samples with positive PC1 scores are morning samples, and the majority of samples with negative PC1 scores are afternoon samples**.** Most of the variance is explained by the time of day the samples were collected. Diurnal variability has been observed with other environmental samples containing surfactants as well.[14] This variance could also be explained by when the samples were extracted, considering the morning samples were extracted before the afternoon samples. Additionally, irradiated and non-irradiated morning samples cluster together, reiterating their similarity. This outcome suggests that potential biological effects or other non-photochemical sources may significantly influence the composition of surfactants and organics than photochemical effects.[14]

Figure 8 represents the loadings for each PC and is used to interpret the importance of each peak in absorption. PC1 loadings have positive values at wavenumbers 2950, 2925, 2869, and 2855 $cm^{-1}$ - indicating that samples with high alkane peaks in absorption represent the samples with positive PC1 scores. These samples, which are predominantly morning samples, may be consistent with molecules that have high H/C ratios and are more surfactant-like.[3]

### 2.2.4 ATR-FTIR Analysis for Afternoon Lake Herrick Samples Extracted with Envi18 and EnviCarb Cartridges

The ATR-FTIR spectra for samples extracted using EnviCarb and Envi18 cartridges were compared to analyze the difference in composition between cationic and anionic surfactants, respectively (Figure 9). EnviCarb cartridges extract cationic and non-ionic surfactants efficiently, while Envi18 cartridges extract anionic and non-ionic surfactants efficiently.[3] The overall maximums in absorption for the alcohol peaks are higher for the samples extracted with Envi18 cartridges when compared to samples extracted with EnviCarb cartridges. The spectra imply that the samples' anionic surfactants may have more functional groups that absorb at that wavenumber (3382 $cm^{-1}$) or the Envi18 cartridges extract organics with that functional group more efficiently. There is also variability between the samples shown in the spectra' fingerprint region (400 $cm^{-1}$ and 1500 $cm^{-1}$). The cosine similarity of the spectra for samples extracted with EnviCarb and Envi18 cartridges ranges from 0.9689 to 0.9994 (Table 4). These values indicate that the chemical composition of the samples extracted with Envi18 and EnviCarb cartridges are similar.[5]

#### 2.2.4.1 Absorbance Ratios for Afternoon Samples

The absorbance ratios for the EnviCarb afternoon sample and Envi18 afternoon sample collected on 1/28/2020 are equivalent (Figure 6). However, there is a variation in the absorbance ratios for most EnviCarb and Envi18 afternoon samples collected on the same day. Although the cosine similarity values indicated that chemical composition for afternoon Envi18 and afternoon EnviCarb samples are similar, samples extracted with EnviCarb cartridges have higher absorbance ratios than samples extracted with Envi18 cartridges. This comparison also confirms that the Envi18 cartridges extract the organic components that absorb at 3382 $cm^{-1}$ more efficiently.

#### 2.2.4.2 PCA of ATR-FTIR Spectra Shows Variability Explained by the Type of Cartridges used for Extraction

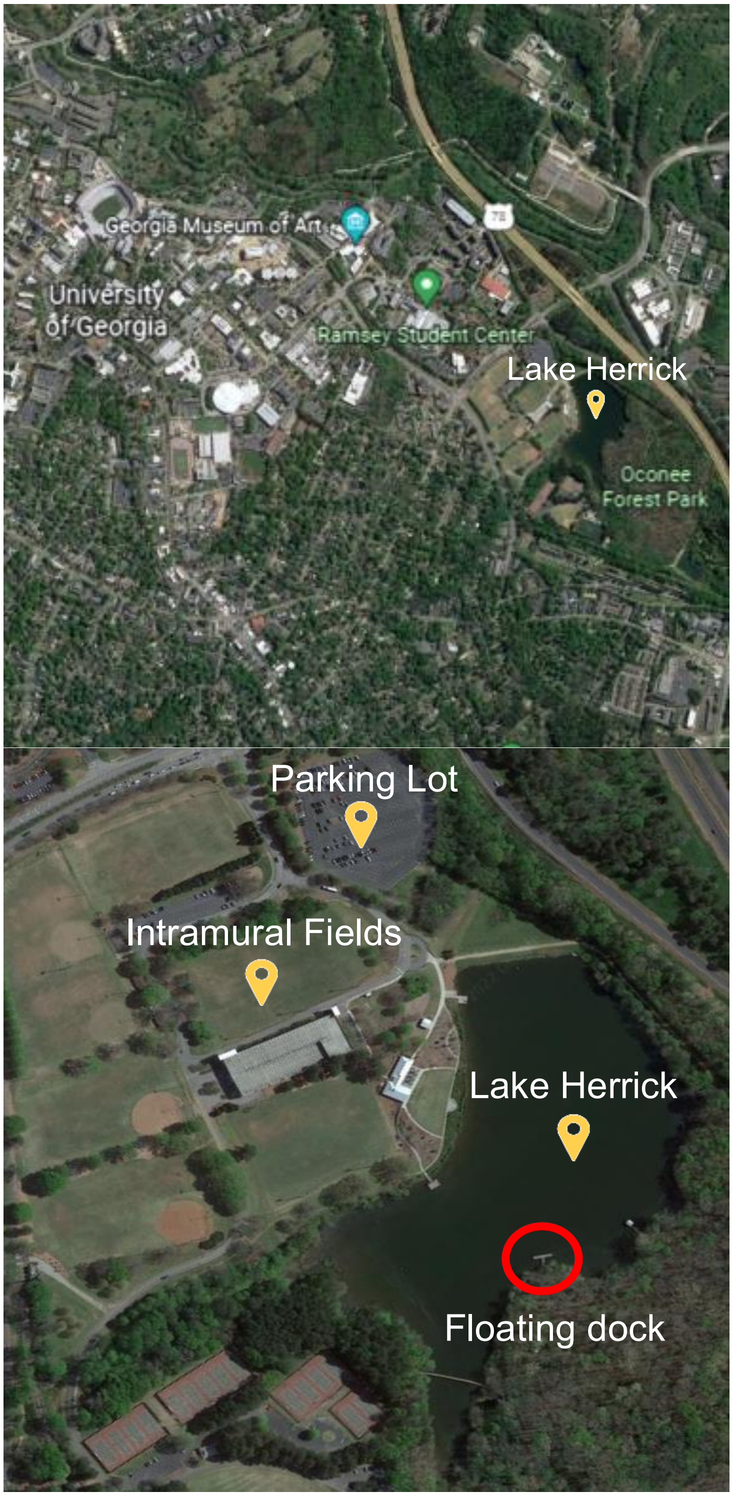
The loadings for PC2 have negative values at 2950, 2925, 2869, 2855, and 3382 $cm^{-1}$ (Figure 8). However, the alkane peaks in absorption (2950, 2925, 2869, 2855 $cm^{-1}$) for PC2 loadings have a lower magnitude than the alkane peaks for PC1 loadings. Also, the hydroxyl peak in absorption (3382 $cm^{-1}$) associated with loadings for PC2 has a higher magnitude when compared to the hydroxyl peak for the PC1 loadings. Samples with negative PC1 and PC2 scores have high maximums in absorption for the hydroxyl group and low maximums in absorption for the alkane groups. These samples, mainly Envi18 afternoon samples, may be consistent with molecules with high O/C ratios. The cartridge used for extraction explains the second most variance (38%) within the data (Figure 7). The majority of the samples extracted with EnviCarb cartridges have positive PC2 scores. In contrast, most samples extracted with Envi18 cartridges have negative PC2 scores. This variation may be caused by classes of surfactants (cationic, anionic, and non-ionic) clustering together.

### 2.2.8 Correlation Between Ionic and Surfactant Composition of Lake Herrick Samples

Ion chromatography was used to determine the concentration of the major ions present in Lake Herrick water samples. I expected to see $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, and $Cl^-$ and $SO_4^{2-}$ present in the samples.[19] The detected ions include $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Cl^-$, and $SO_4^{2-}$. Other peaks were present in the ion chromatogram for the Lake Herrick samples; hence future analysis could include quantifying ions such as $NO_3^-$ and $PO_4^{3-}$. The average concentrations for each major ion are: 47.0 mg/L ($K^+$), 44.0 mg/L ($Cl^-$), 3.0 mg/L ($Ca^{2+}$), 2.0 mg/L $SO_4^{2-}$, 2.0 mg/L ($Na^+$) and 1.5 mg/L ($Mg^{2+}$). The concentration of ions in most of the samples followed a trend of $K^+ > Cl^- > Ca^{2+} > SO_4^{2-} > Na^+ > Mg^{2+}$ except for samples collected on 2/6/2020 06:52, 2/7/2020 06:50, and 2/9/2020 07:05 (Figure 10). Precipitation has a dilution effect on the salinity of aquatic systems.[20] The effect of precipitation on the salinity of the samples is shown in Figure 11. On days when it rained (2/6/2020 6:52 and 2/7/2020 06:50), the $K^+$ and $Cl^-$ concentrations decreased significantly. Precipitation occurring on the previous day could have affected the salinity of the sample collected on 2/9/20 at 07:05 due to the dilution effect.

Figure 10 shows that $K^+$ and $Cl^-$ have the highest concentrations. The results for these ions were unexpected. When compared to the ionic composition of surface water samples from areas in and close to Athens, Georgia, the Lake Herrick IC results were not comparable for some ions. $Ca^{2+}$, $Mg^{2+}$, and $Na^+$ in the Lake Herrick samples had concentrations consistent with the surface water measurements (Figure 11). However, the concentrations for $K^+$ in the Lake Herrick samples are exceedingly higher than the concentrations in the surface water measurements. The concentrations for $K^+$ and $Cl^-$ have a 1:1 ratio for the Lake Herrick samples. This ratio reflects that those ions probably originated from the same source. Chemicals such as fertilizers (Potash) from agricultural runoff or water softener effluents could be the source of $K^+$ and $Cl^-$ in the lake.[21, 22] Armadillo and Birdsong are the two tributary streams that feed Lake Herrick (Figure 12).[23] Sample collection took place close to these tributaries. Accordingly, high salt concentrations from the tributaries' inflow could be influencing the $K^+$ and $Cl^-$ concentrations in the lake.[22]

The relationship between the absorbance ratios for the organic and surfactant composition and the concentration of $K^+$ and $Cl^-$ was evaluated. If the two variables (surfactants and organics and concentration of $K^+$ or $Cl^-$) have a positive correlation, they could potentially be originating from the same source.[24] However, no correlation was found between the $A_{2950/3382}$ for samples extracted with Envi18 cartridges and the concentration of $K^+$ and $Cl^-$ (Figure 13).



Source: Google Earth

**Figure 1.** Map of the sampling site for Lake Herrick samples. The bottom panel is a close-up version of the top panel. The circle represents the sampling location.

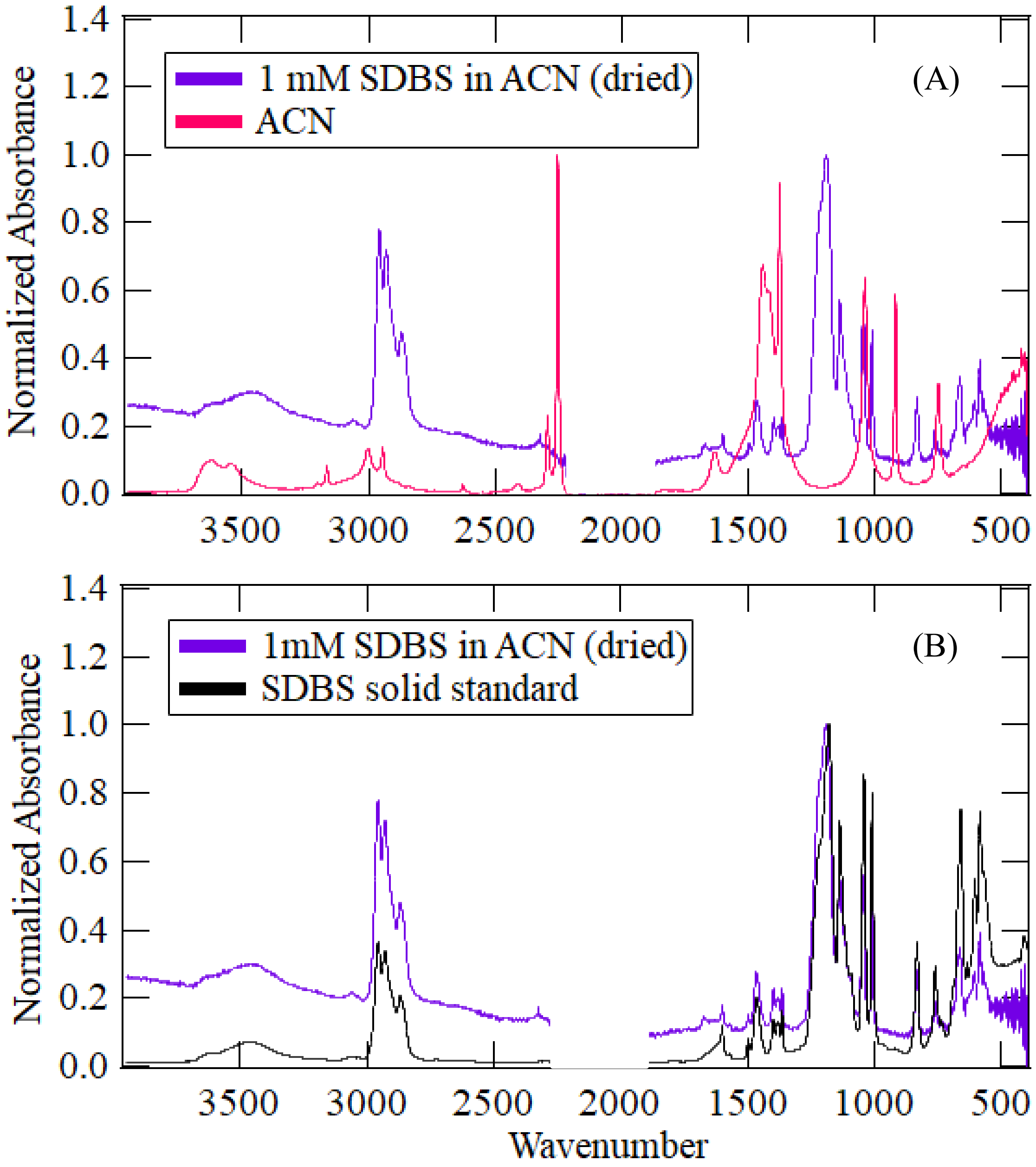


**Figure 2.** Comparison of ATR-FTIR spectra for standard surfactant sodium dodecylbenzene sulfonate (SDBS) solution and acetonitrile (ACN) (A) and SDBS solid standard (B) using 4-minute drying times.

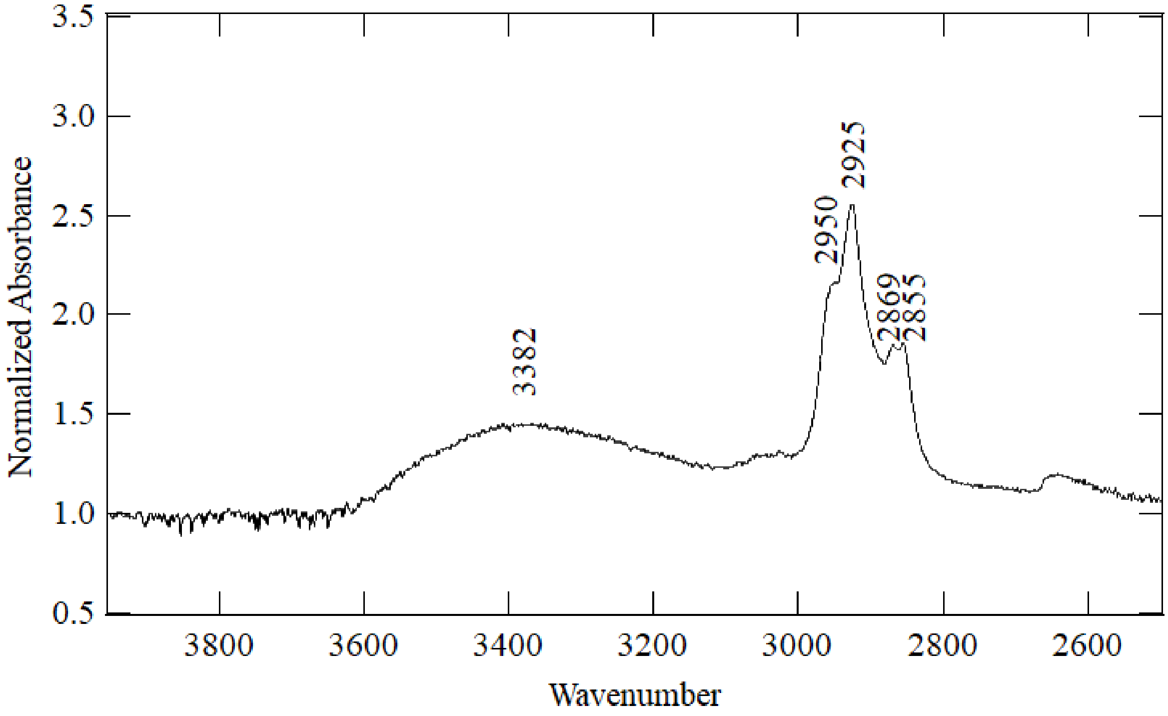


**Figure 3.** Representative ATR-FTIR spectrum (2500 cm$^{-1}$ to 4000 cm$^{-1}$) for Lake Herrick samples. Hydroxyl (3382 cm$^{-1}$) and alkane (2950, 2925, 2869, 2855 cm$^{-1}$) functional group absorbance peaks are labeled.

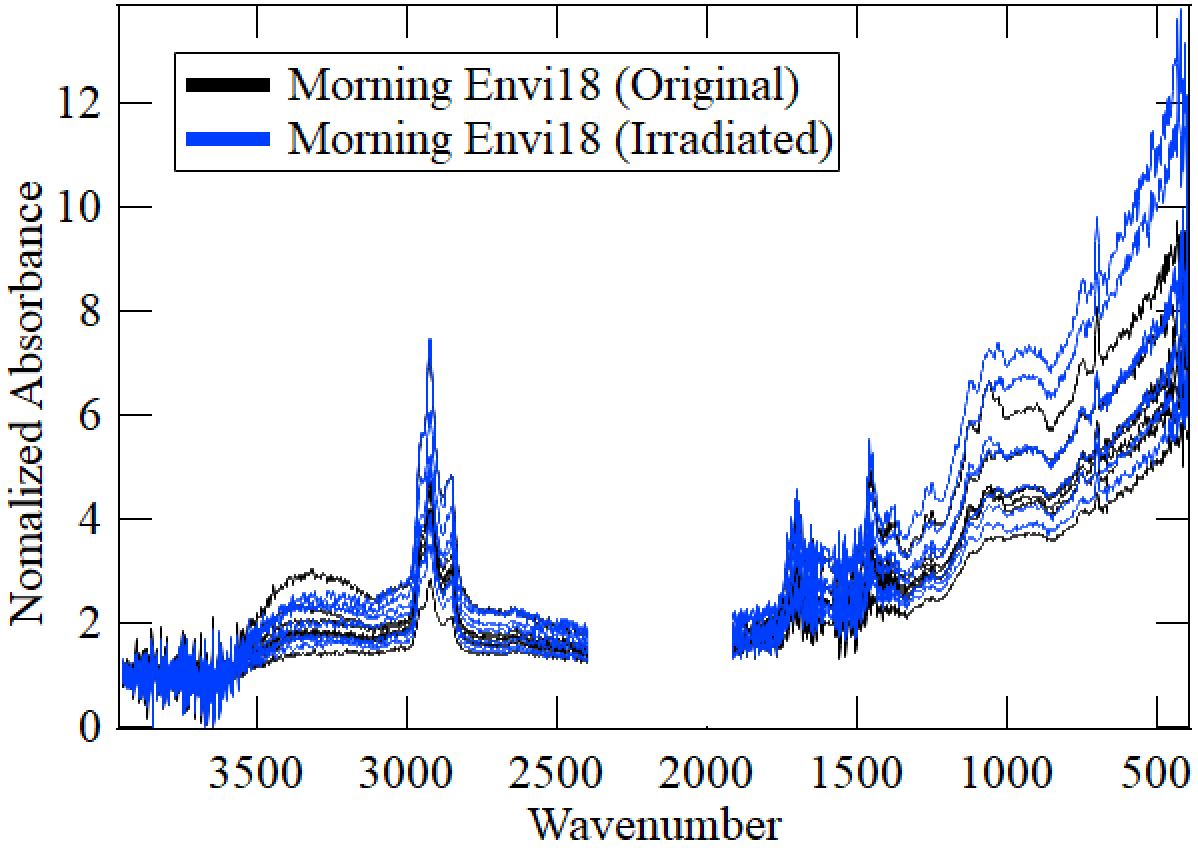


**Figure 4.** ATR-FTIR spectra comparison of irradiated (blue) and non-irradiated (black) morning Lake Herrick samples. Organics were extracted with Envi18 cartridges.

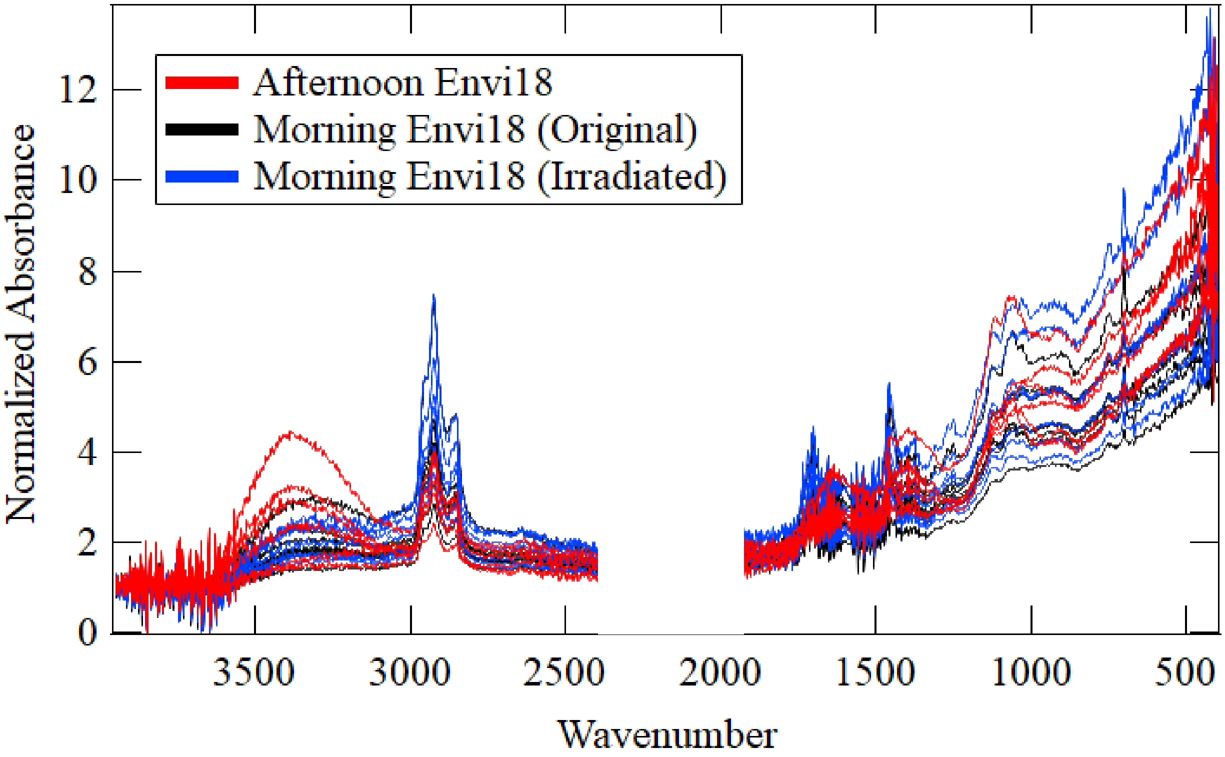


**Figure 5.** ATR-FTIR spectra comparison of afternoon, morning, and irradiated morning Lake Herrick samples. Organics were extracted with Envi18 cartridges.

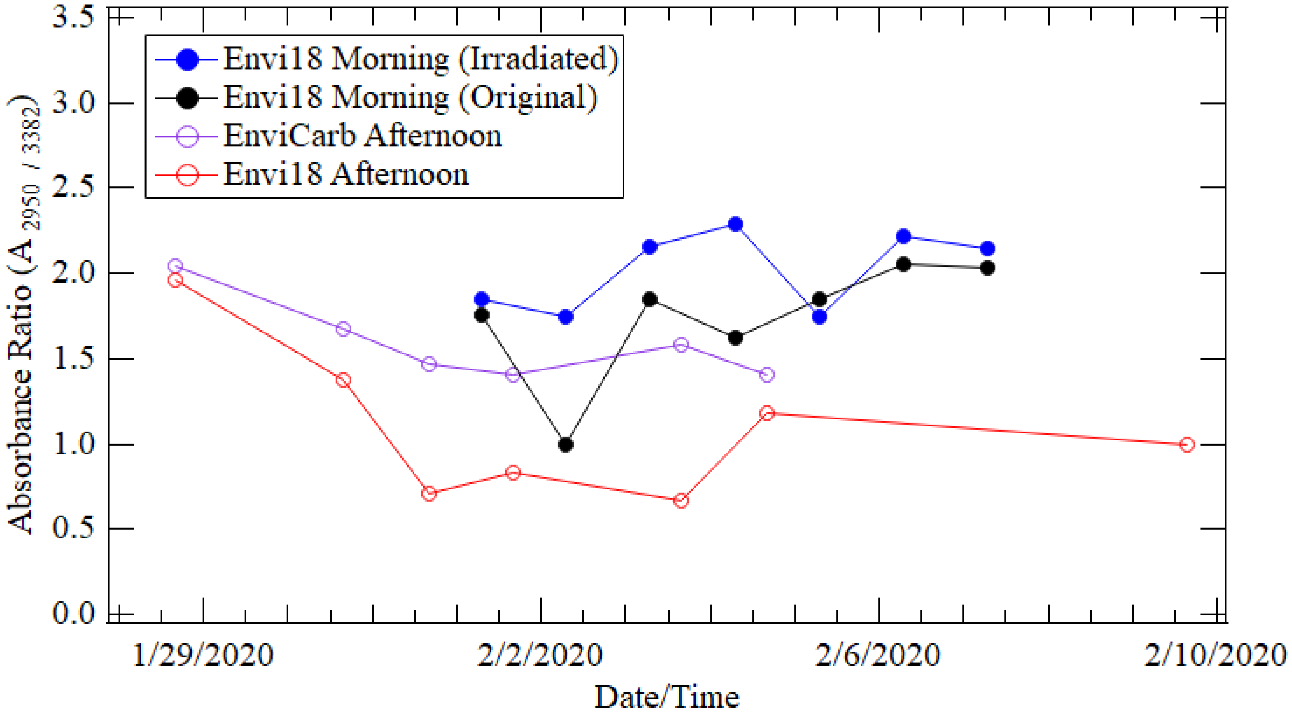


**Figure 6.** Absorbance ratio ($A_{2950/3382}$) obtained from ATR-FTIR spectra for afternoon, morning, and irradiated morning Lake Herrick samples.

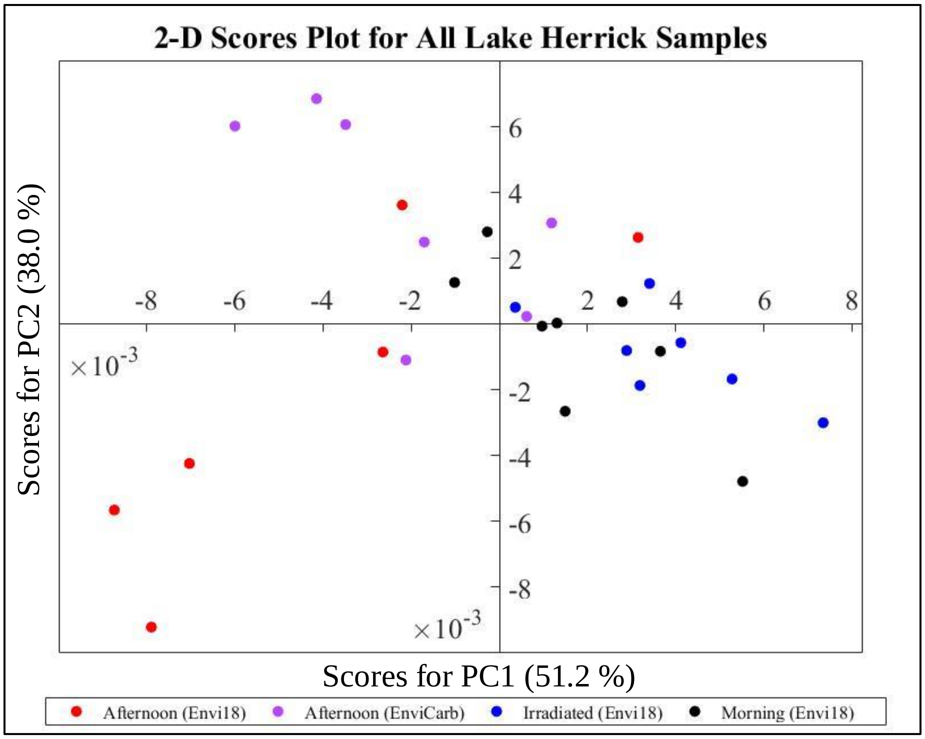


**Figure 7.** PCA of ATR-FTIR spectra (2500 cm$^{-1}$ to 4000 cm$^{-1}$) for afternoon, morning, and irradiated morning Lake Herrick samples. Organics were extracted with both Envi18 and EnviCarb samples, as indicated.

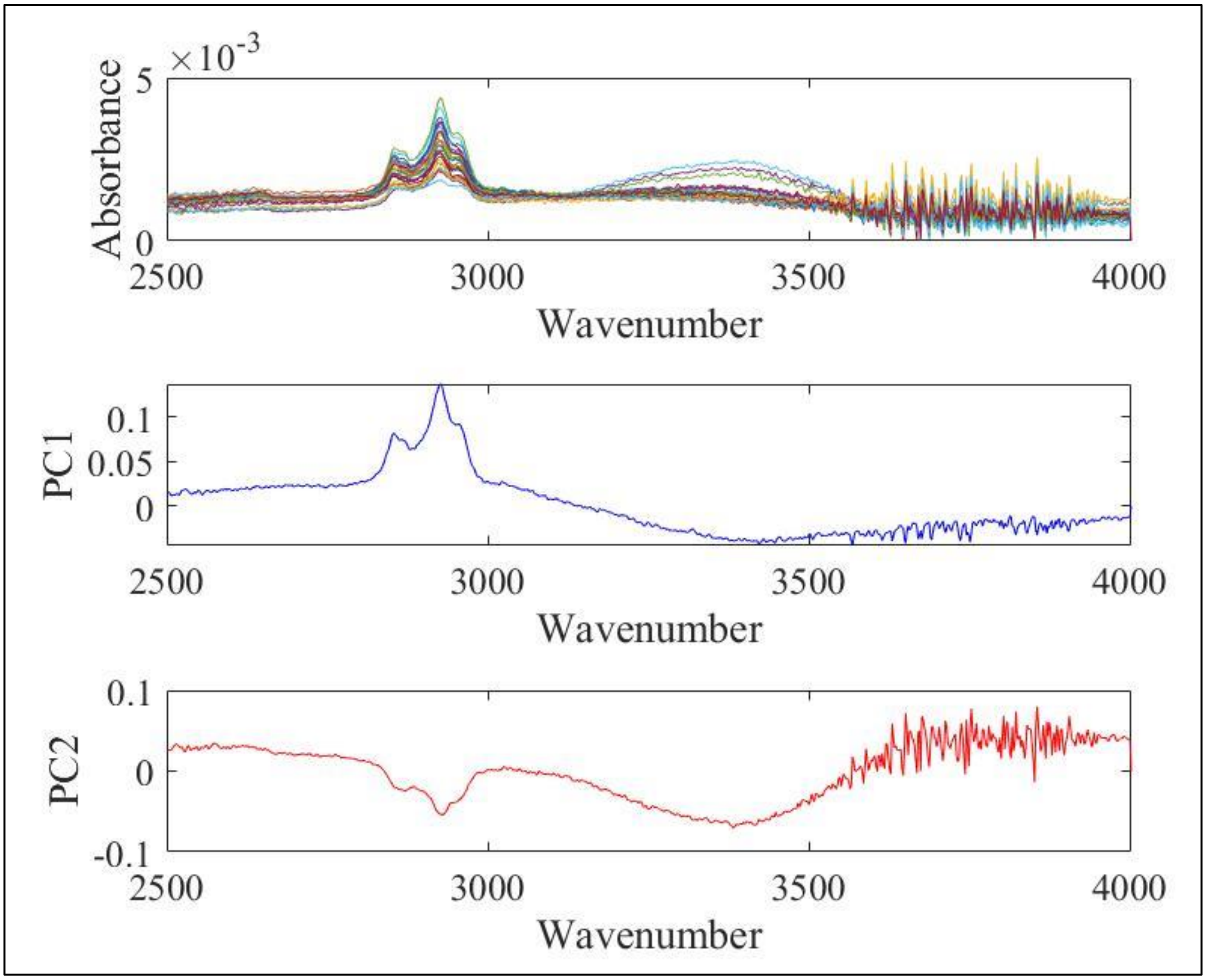


**Figure 8.** Loadings profile for PC1 and PC2 for the PCA of ATR-FTIR spectra (2500 cm$^{-1}$ to 4000 cm$^{-1}$) for afternoon, morning, and irradiated morning Lake Herrick samples for both extraction types.

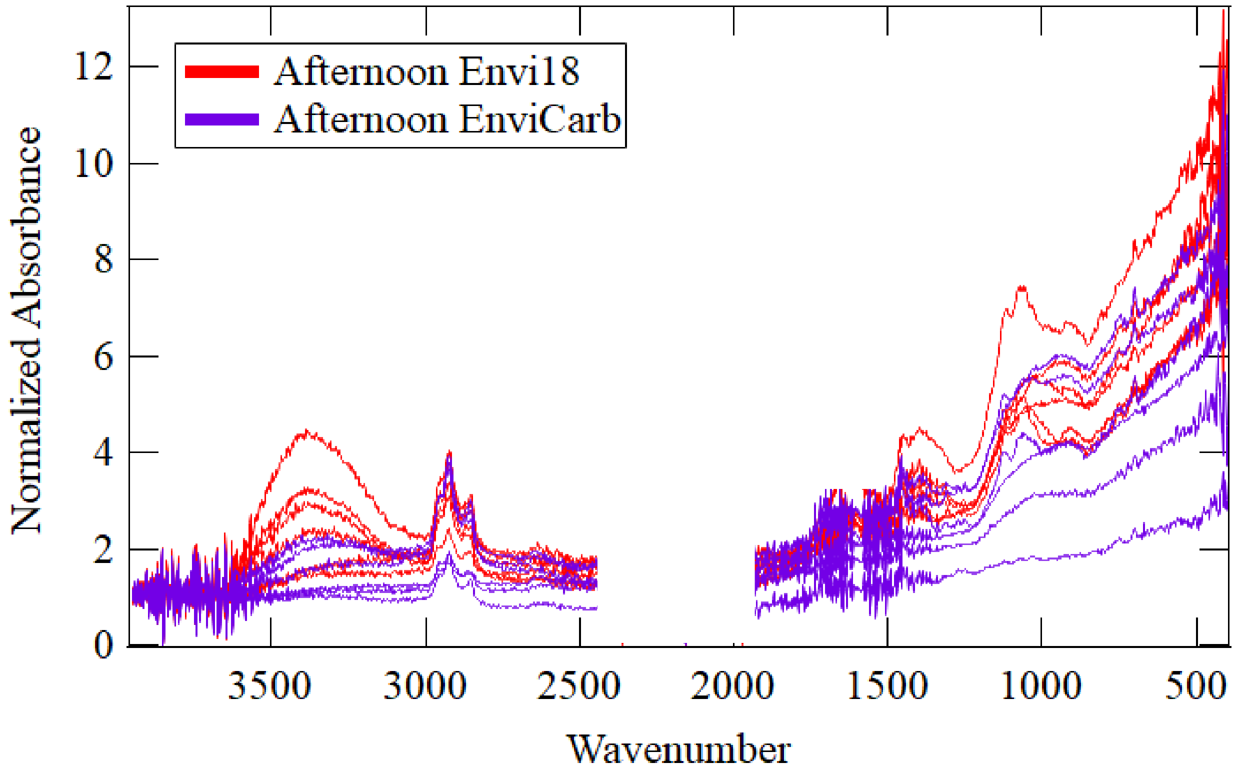


**Figure 9.** ATR-FTIR spectra comparison of afternoon Lake Herrick samples. Organics were extracted with Envi18 (red) and EnviCarb (purple) cartridges.

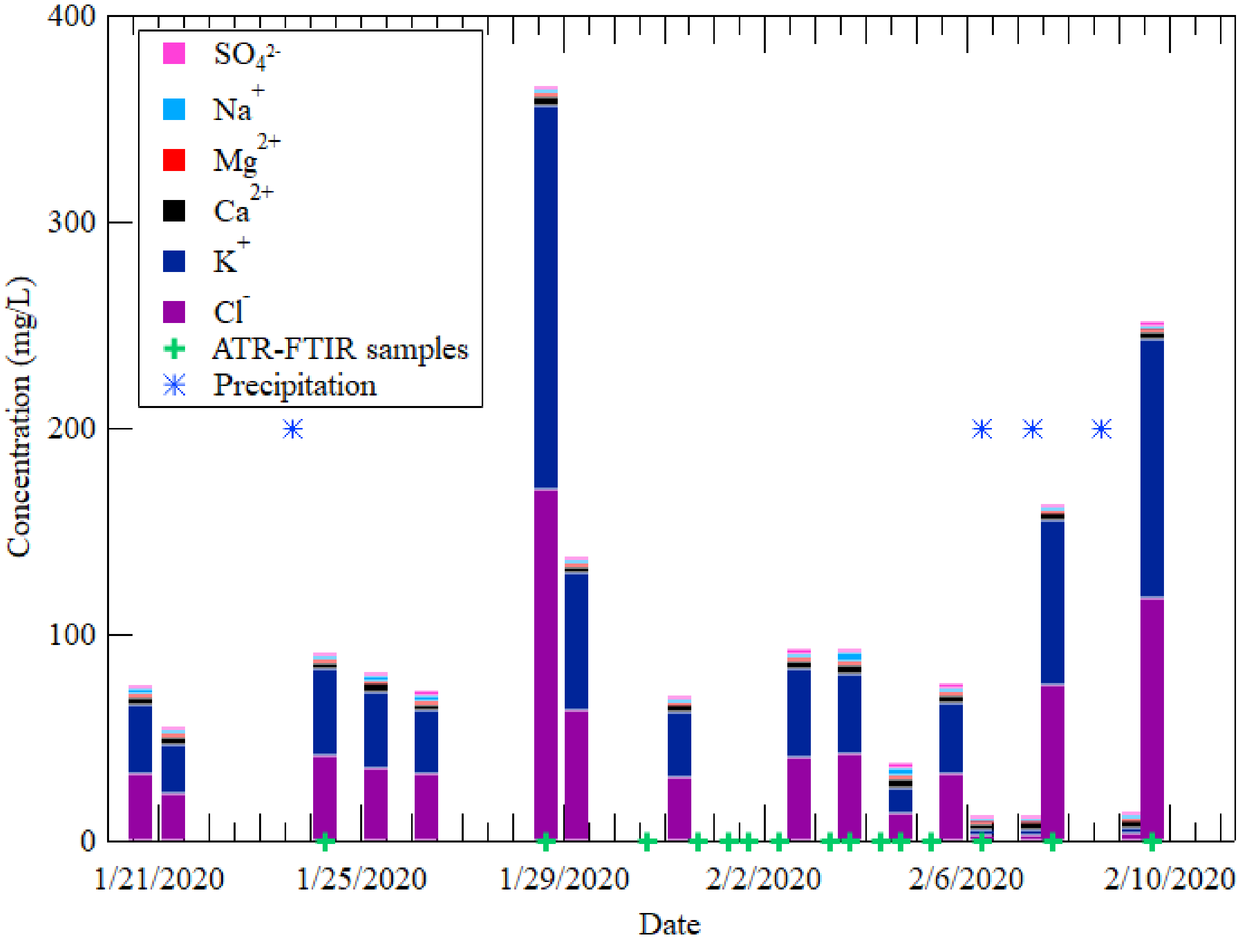


**Figure 10.** Concentrations of major ions measured in Lake Herrick samples over the sampling period. Sampling times with concurrent precipitation and corresponding ATR-FTIR measurements are noted.

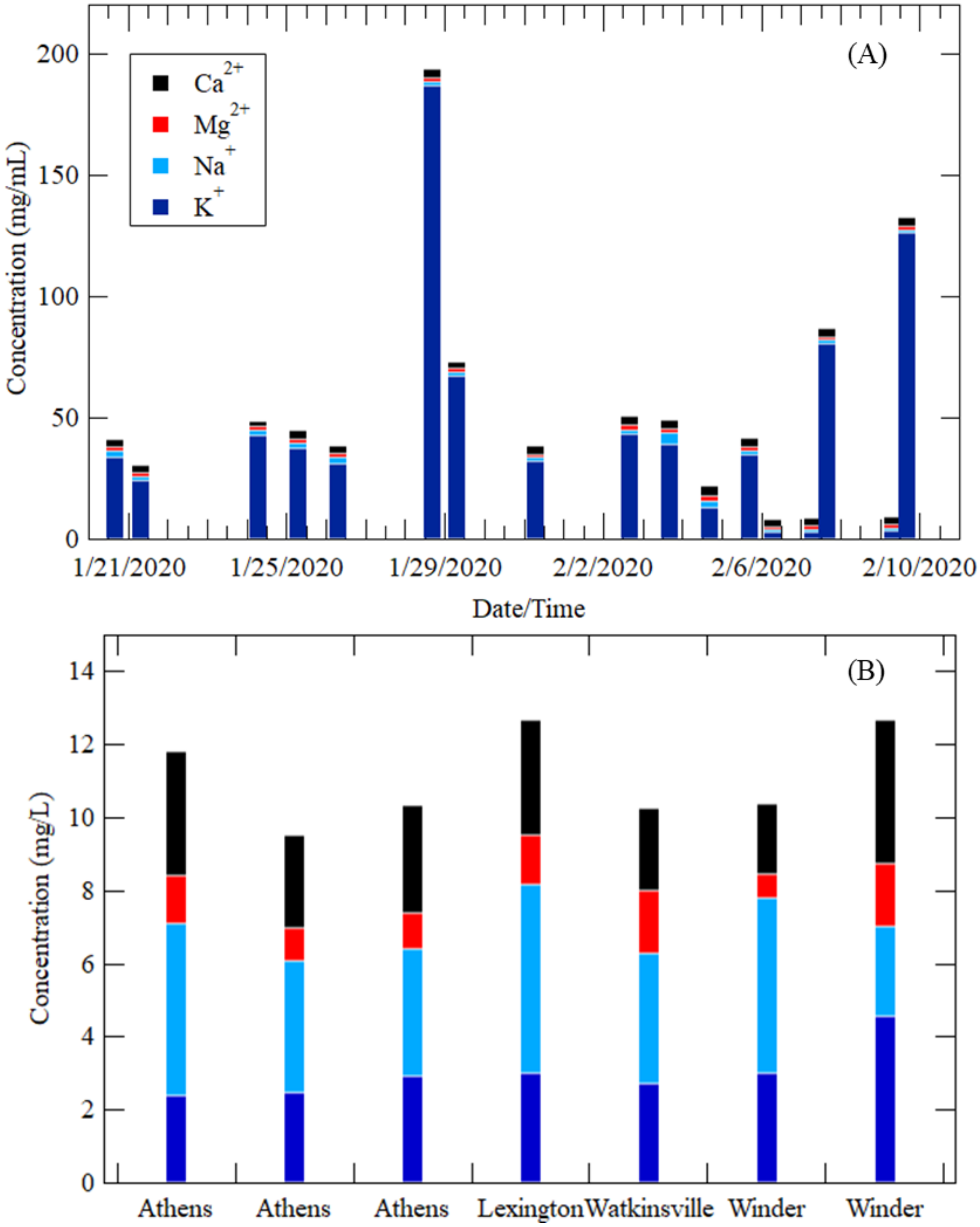
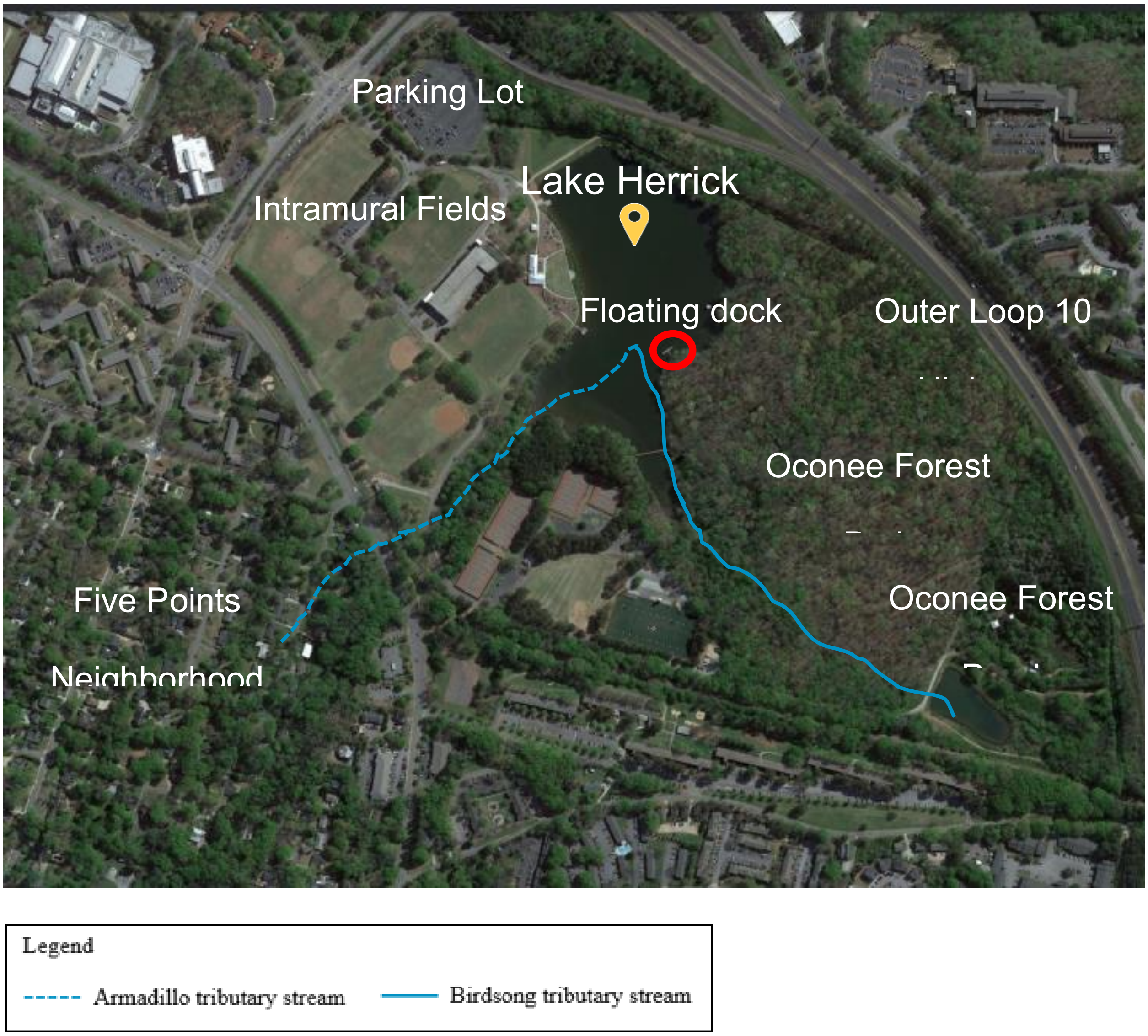


**Figure 11.** Comparison of the ionic composition of Lake Herrick samples (A) and the ionic composition of surface water samples collected in Athens, Georgia, and surrounding areas (B) (data provided by: UGA Agricultural and Environmental Services Laboratories).[25]



Source: Google Earth

**Figure 12.** Location of tributaries that feed Lake Herrick (data are from ref 23)[23]

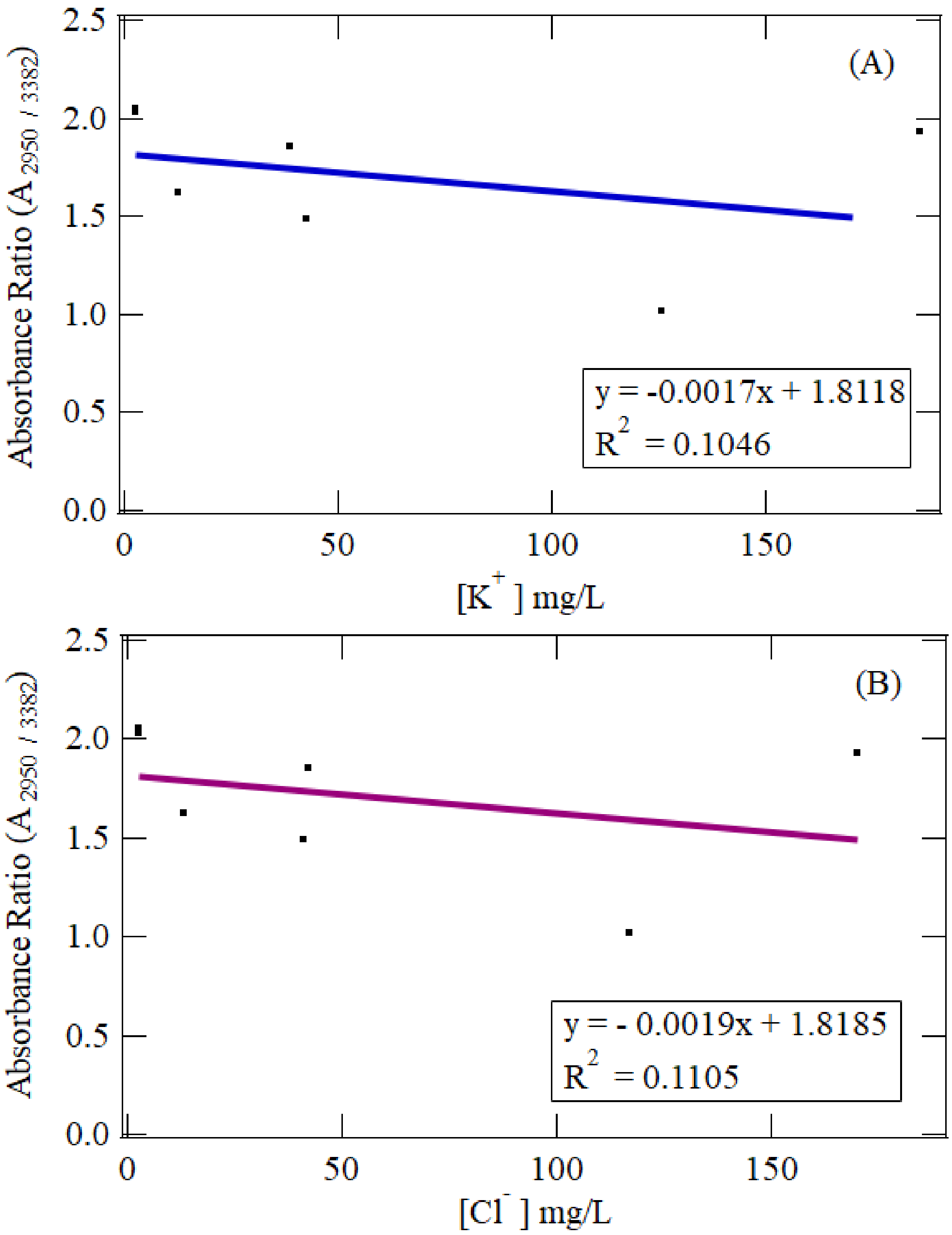


**Figure 13.** Correlations of $K^+$ concentrations (A) and $Cl^-$ concentrations (B) with the $A_{2950/3382}$ for organics extracted from Lake Herrick samples with Envi18 cartridges.

**Table 1.** Limit of detection for ATR-FTIR analyses of standard surfactants (using Nicolet iS50 ATR-FTIR).

| **Surfactant** | **Surfactant Type** | **Limit of Detection (mM)** |
|---|---|---|
| Sodium dodecyl sulfate (SDS) | Anionic | 0.06250 |
| Sodium dodecylbenzene sulfonate (SDBS) | Anionic | 0.06250 |
| Benzyldimethylhexadecylammonium chloride (BAC) | Cationic | 0.06250 |
| Cetrimonium chloride (CTAC) | Cationic | 0.12500 |
| Brij | Non-ionic | 0.12500 |
| Genapol | Non-ionic | 0.03125 |

**Table 2.** Major functional group assignments for ATR-FTIR spectra relevant to the organics in the Lake Herrick samples.

| **ATR-FTIR wavenumber ($cm^{-1}$)** | **Functional group** |
|---|---|
| 3382 | Organic Hydroxyl (C-OH) |
| 2950 | Alkane (C-C–H) |
| 2925 | Alkane (C-C–H) |
| 2869 | Alkane (C-C–H) |
| 2855 | Alkane (C-C–H) |

**Table 3.** Cosine similarity of the organic spectra for non-irradiated and irradiated morning Lake Herrick samples (using Nicolet 6700 ATR-FTIR).

| Sample Collection Date/Time | Cosine Similarity of Spectra for Morning and Irradiated Morning Lake Water Samples |
|---|---|
| 2/1/2020 6:50 | 0.9985 |
| 2/2/2020 6:55 | 0.9987 |
| 2/3/2020 6:55 | 0.9977 |
| 2/4/2020 6:55 | 0.9890 |
| 2/5/2020 6:51 | 0.9992 |
| 2/6/2020 6:52 | 0.9965 |
| 2/7/2020 6:50 | 0.9991 |

**Table 4.** Cosine Similarity of the spectra for Lake Herrick samples extracted with EnviCarb and Envi18 cartridges (using Nicolet 6700 ATR-FTIR).

| Sample Collection Date/Time | Cosine Similarity of the Spectra for Samples Extracted with EnviCarb and Envi18 Cartridges |
|---|---|
| 1/24/2020 6:48 | 0.9994 |
| 1/28/2020 15:53 | 0.9976 |
| 1/30/2020 15:56 | 0.9980 |
| 2/1/2020 15:45 | 0.9832 |
| 2/3/2020 15:44 | 0.9689 |
| 2/4/2020 15:55 | 0.9951 |

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# CHAPTER 3

# CONCLUSION

My research aimed to develop a method to analyze surfactants in lake water using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and to characterize and compare the organic species in the lake water samples collected from Lake Herrick. The concentrations of major ions were measured with Ion Chromatography. Water samples were collected at two points during the day – morning (before sunrise) and afternoon (before sunset). These sampling times and the irradiation experiments were done to test the influence of time of day and photochemistry on the composition of organics in the lake water.

The ATR-FTIR spectroscopy analysis showed that the surfactants and large organic molecules extracted from the Lake Herrick water samples consisted of large fractions of organic hydroxyl and saturated hydrocarbons. Ratios of absorbance values in the alkane (2950 $cm^{-1}$) and hydroxyl (3382 $cm^{-1}$) absorbance regions were compared across samples. These absorbance ratios ($A_{2950/3382}$) were consistent across all samples, indicating little variability in the organic composition.

Samples were also extracted with different solid-phase extraction cartridges to compare the spectra composition of different types of surfactants targeted in these extractions. Envi18 cartridges have high extraction efficiencies for anionic and non-ionic surfactants, while EnviCarb (graphitized carbon) cartridges have high extraction efficiencies for cationic surfactants. The cosine similarity values for the spectra of organics extracted with the Envi18 and EnviCarb cartridges were high, demonstrating that the spectral composition of the organics extracted with these cartridges is similar. The principal component analysis (PCA) and absorption ratios ($A_{2950/3382}$) showed some variability between the spectra of the organics extracted with the different cartridges, with the organic spectra from the Envi18 cartridge extractions having lower ratios of alkane to hydroxyl than those extracted with the EnviCarb cartridges.

Spectra of the organics extracted from the irradiated samples were compared to those of the nighttime samples to assess the effects of photochemistry. The cosine similarities of the paired original morning and irradiated morning samples were very high, indicating that there was very little change in the organic composition caused by the irradiation. This may be due to the type of analysis. Even if some of the molecules were fragmented, the total functional group composition might remain the same because ATR-FTIR measured the total organics.

The spectra for morning samples show characteristics of molecules with a high H/C ratio and low O/C ratio compared to the afternoon samples. This is indicated by the higher ratio of alkane absorbance to hydroxyl absorbance observed in the afternoon samples. The PCA also shows that the most variance within the dataset is due to the time of day that the samples were collected. Together with the irradiation experiments, this indicates that a process other than irradiation contributes to the differences in the organic spectral composition.

The concentrations of major ions in the Lake Herrick water samples were measured using Ion Chromatography. The samples contained concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $SO_4^{2-}$, and $Cl^{-}$ above the detection limit. The concentrations of these ions were consistent over the whole sampling time and for the different times of the day. The $K^{+}$ and $Cl^{-}$ concentrations were significantly higher than concentrations found in surface waters around Athens, Georgia. High concentrations of ions from nearby tributaries that feed Lake Herrick could be the source of elevated $K^+$ and $Cl^-$ in Lake Herrick. Additionally, there was also no correlation between the surfactant composition and the ionic composition of Lake Herrick.

Future work and further analyses can be done to expand this work and investigate some of the findings. For example, surface tension measurements could be done to confirm the presence of surfactants and compare the relative surfactant strengths in the morning, afternoon, and irradiated samples as well as those extracted from the Envi18 and EnviCarb cartridges. This could give more insight into their surface-active properties. Furthermore, more samples could be collected over a range of seasons. A larger sample size would improve the correlation analysis to compare the ionic composition and organic composition. Samples collected over a range of seasons would also give insight into the sources of the organics and the major ions present in the lake water. Further analyses could also be done at bodies of water upstream and downstream of Lake Herrick to investigate the sources and sinks of organics. In addition, high-resolution mass spectrometry could fully identify the composition of surfactants and organics present in the lake water by measuring the mass to charge ratio of components in the samples. Also, an additional extraction method could be developed to target surfactant molecules selectively for further analysis.

# APPENDIX

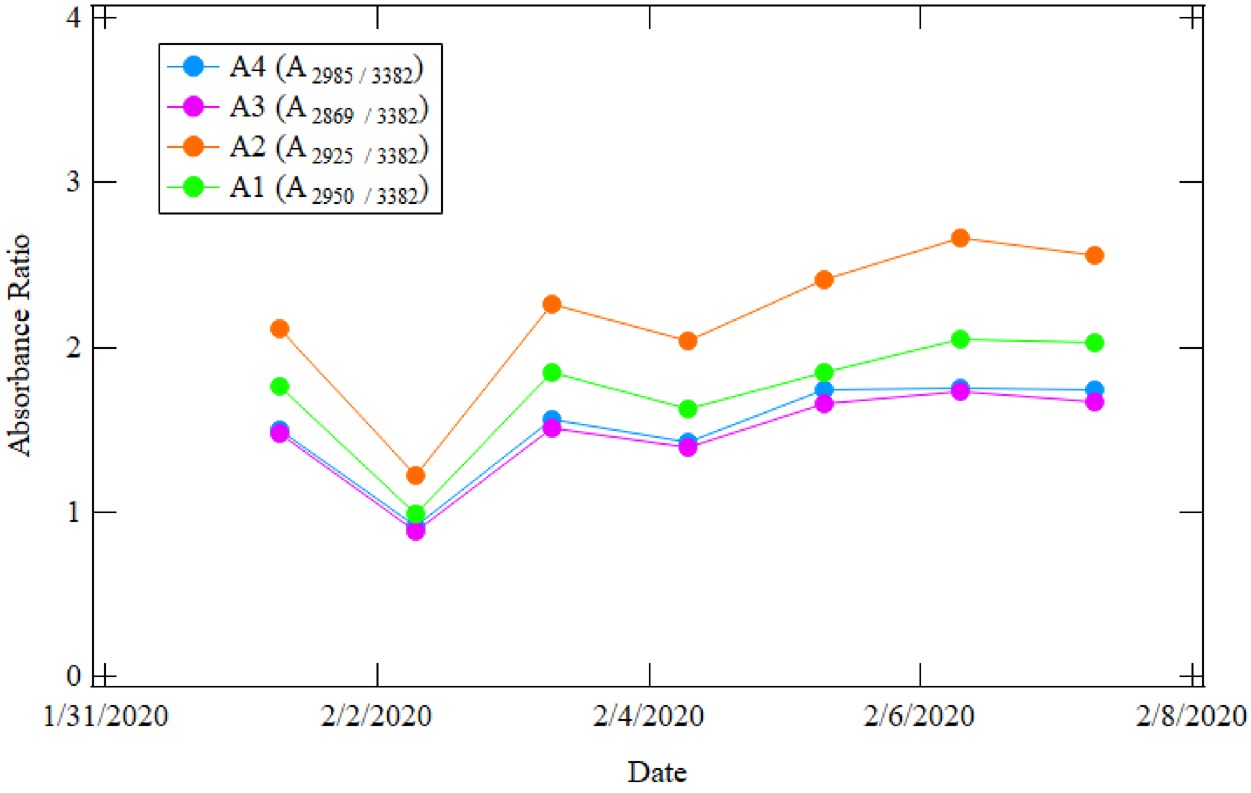

**Figure A1.** Absorbance ratios (alkane peak at four different locations to hydroxyl peak at 3382 cm$^{-1}$) calculated for morning samples across the sampling period.

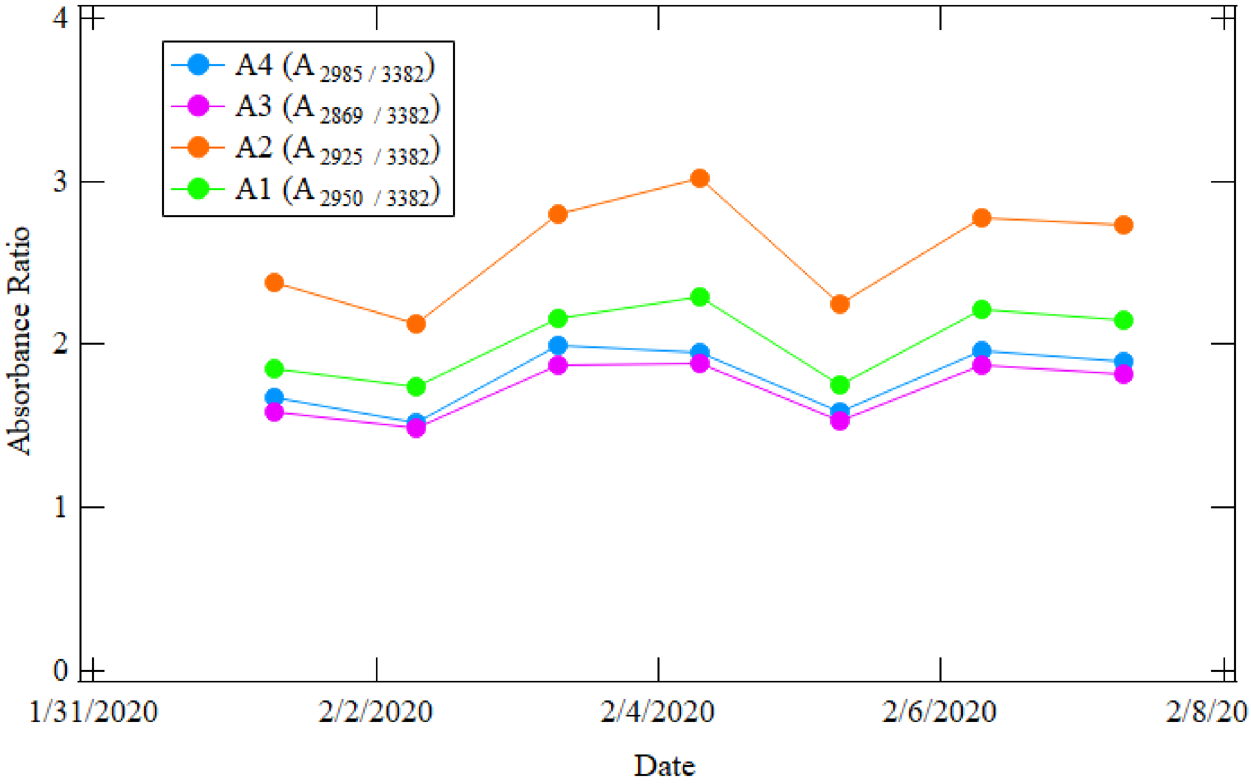

**Figure A2.** Absorbance ratios (alkane peak at four different locations to hydroxyl peak at 3382 cm$^{-1}$) calculated for irradiated morning samples across the sampling period.

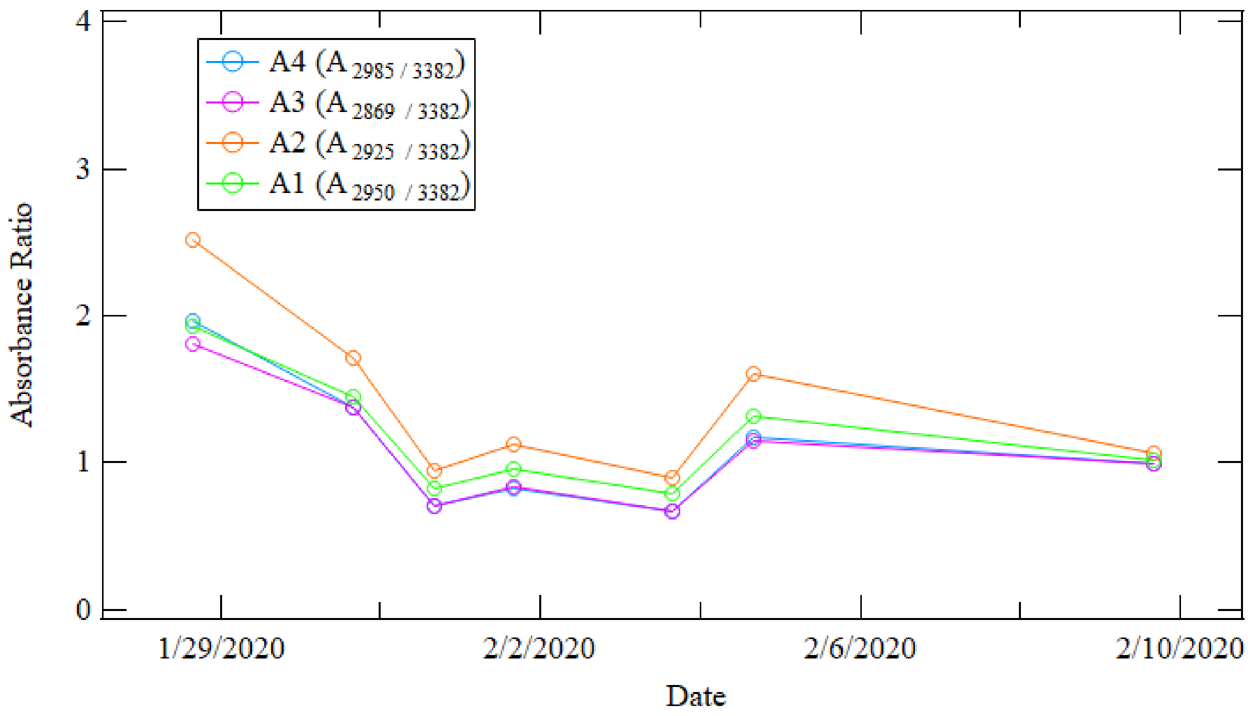

**Figure A3.** Absorbance ratios (alkane peak at four different locations to hydroxyl peak at 3382 cm$^{-1}$) calculated for E18 afternoon samples across the sampling period.

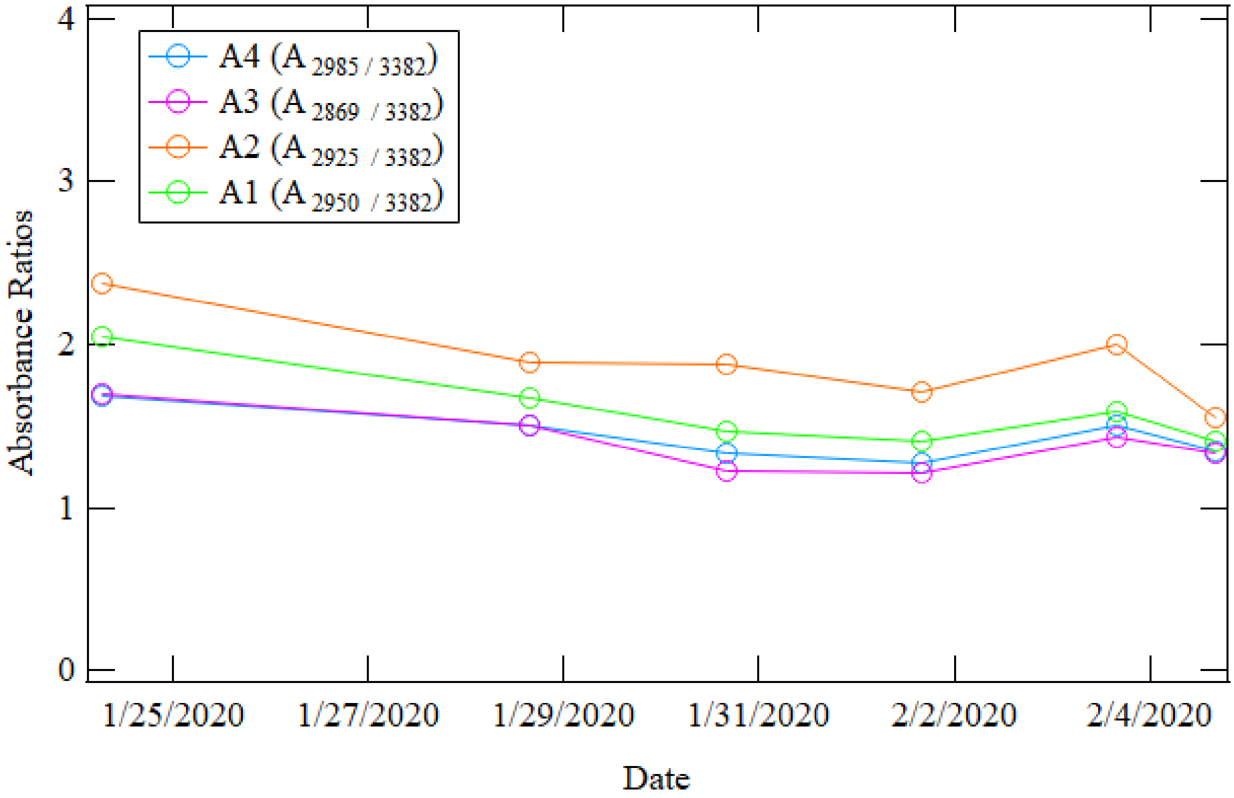

**Figure A4.** Absorbance ratios (alkane peak at four different locations to hydroxyl peak at 3382 cm$^{-1}$) calculated for EnviCarb afternoon samples across the sampling period.

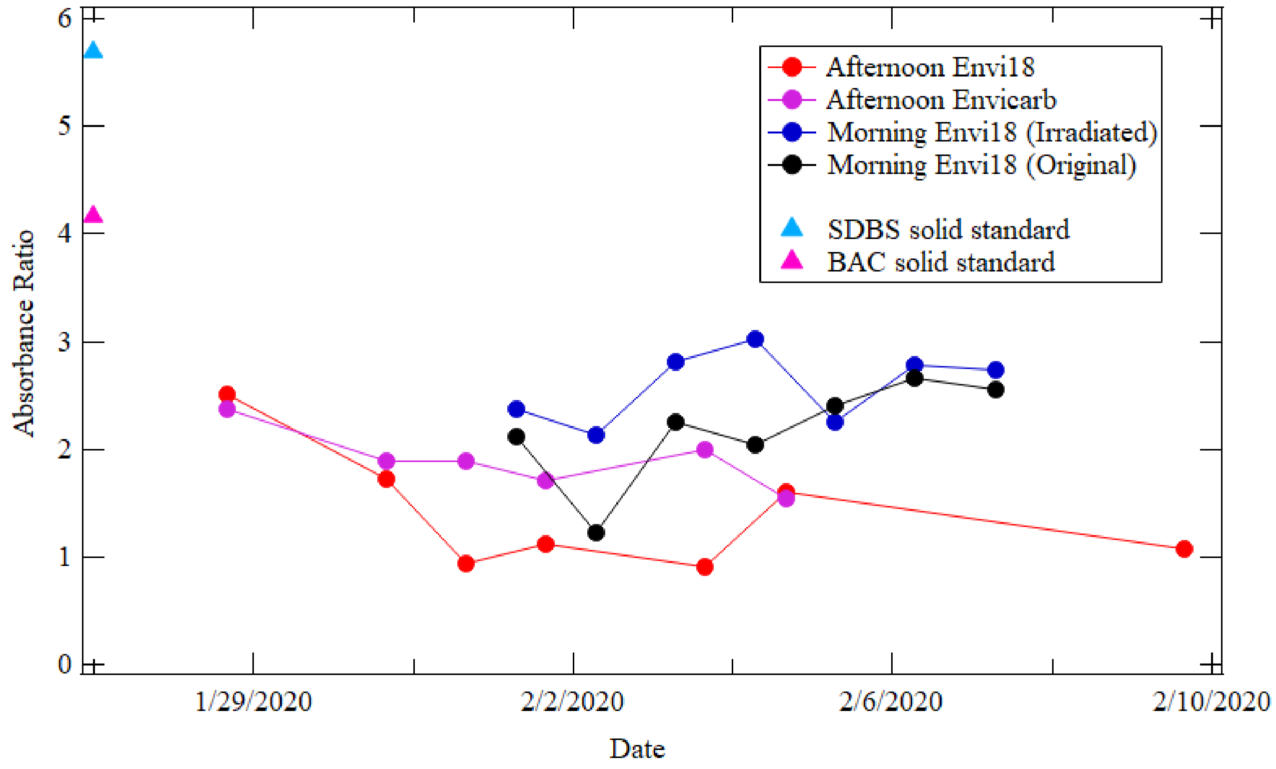

**Figure A5.** Absorbance ratios (alkane peak at 2950 $cm^{-1}$ to hydroxyl peak at 3382 $cm^{-1}$) for standard surfactants and all Lake Herrick samples.

**Table A1.** Concentration of major ions in Lake Herrick samples

| **Date/Time** | **$Na^+$ (mg/L)** | **$K^+$ (mg/L)** | **$Mg^{2+}$ (mg/L)** | **$Ca^{2+}$ (mg/L)** | **$Cl^-$ (mg/L)** | **$SO_4^{2-}$ (mg/L)** |
|---|---|---|---|---|---|---|
| 1/20/20 15:51 | 2.3186 | 33.6676 | 1.4898 | 3.5038 | 32.4475 | 2.0713 |
| 1/21/20 6:57 | 1.7267 | 23.7303 | 1.4817 | 3.5283 | 23.0684 | 1.7794 |
| 1/24/20 6:48 | 1.8508 | 42.7038 | 1.4902 | 2.5050 | 41.0169 | 1.8427 |
| 1/25/20 6:55 | 2.0988 | 37.1023 | 1.6208 | 3.8006 | 35.0733 | 2.0708 |
| 1/26/20 6:47 | 2.8248 | 30.6429 | 1.7494 | 2.8465 | 32.0813 | 2.3487 |
| 1/28/20 14:53 | 1.7956 | 186.2821 | 1.7807 | 3.7082 | 170.2697 | 1.8843 |
| 1/29/20 6:42 | 1.6294 | 67.1608 | 1.5027 | 2.5499 | 62.9341 | 1.9040 |
| 1/31/20 6:53 | 1.6560 | 31.6279 | 1.4616 | 3.4302 | 30.3237 | 1.9595 |
| 2/2/20 15:48 | 1.9333 | 42.9505 | 1.6452 | 3.7177 | 40.1501 | 2.1872 |
| 2/3/20 15:44 | 4.4807 | 38.9588 | 1.6888 | 3.7026 | 42.0816 | 2.3389 |
| 2/4/20 15:55 | 3.0226 | 12.6271 | 1.8839 | 4.2485 | 13.1657 | 2.7649 |
| 2/5/20 16:18 | 1.8391 | 34.4645 | 1.5784 | 3.4993 | 32.5312 | 2.1527 |
| 2/6/20 6:52 | 1.2630 | 2.5284 | 1.1647 | 3.1397 | 2.5398 | 1.5257 |
| 2/7/20 6:50 | 1.3108 | 2.6073 | 1.2189 | 3.1260 | 2.6458 | 1.7007 |
| 2/7/20 15:45 | 1.3567 | 80.3350 | 1.4000 | 3.3049 | 75.0051 | 1.8080 |
| 2/9/20 7:05 | 1.4718 | 2.9933 | 1.3915 | 3.4007 | 3.1348 | 1.9315 |
| 2/9/20 15:45 | 1.4592 | 125.7667 | 1.4793 | 3.4685 | 117.2422 | 1.9435 |