5-2016

Effects of cigarette butts on coastal waters: an elemental analysis of seawater from St. Simon’s Island

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Recommended Citation

Adorati, Katherine, "Effects of cigarette butts on coastal waters: an elemental analysis of seawater from St. Simon’s Island" (2016). *Honors Theses.*

Effects of Cigarette Butts on Coastal Waters:

An Elemental Analysis of Seawater from St. Simon's Island

by

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Departmental Honors Thesis

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ABSTRACT

Cigarette litter can have detrimental effects on the environment, specifically when taking into account that over 4.5 trillion cigarette butts are littered every year. Within seawater, trace elements present in cigarettes may leach into the ocean, having damaging effects on the marine ecosystem. The goal of this research was to investigate if elemental contaminants leached from cigarette litter are significant in samples of seawater collected near St. Simon's Island at both high and low tides, surrounding a beach party during the Florida/Georgia football game which occurred on November 1, 2014. Samples were collected in the months prior to and during the event. This project also explored a gallium coprecipitation methodology for elemental isolation. This gallium coprecipitation technique was investigated in order to determine the chemistry behind why gallium is beneficial in the precipitation process as noted by previous research. Samples of gathered seawater were mixed with a gallium standard, and the pH of the solutions were increased to 10 with sodium hydroxide. The formed precipitates were filtered, collected, and re-dissolved with concentrated nitric acid. The concentrated samples were then diluted for elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). The elements of interest were aluminum (Al), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), silver (Ag), strontium (Sr), thallium (Tl), titanium (Ti), and zinc (Zn). The different elemental concentrations that were gathered underwent independent samples t-test to determine if a significant difference in the samples collected was present. Powder X-ray diffraction (power XRD) was also utilized to determine the crystalline composition of samples with and without gallium to explore the gallium coprecipitation technique.

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INTRODUCTION

Significance and Research Objectives

Improperly discarded litter can have damaging effects on the environment.[1] From the known negative effects of air pollution and global warming to the dangers of soil pollution in the food industry, litter can impact almost every aspect of nature.[2] Litter has become such a significant problem that in 2014 the United States taxpayers spent nearly $11 *billion* for litter clean-up across the US, ten times more than the cost of trash disposal.[2] Factors that should be considered when exploring the effects of pollution are litter, chemical runoff, illegal dumping, and tobacco products; all of which can seep into groundwater and affect the water quality.[3] This is especially detrimental for people who rely on wells for their drinking water.[3]

This research further examines litter, but specifically focuses on harmful cigarette waste, which has been observed on city streets, beaches, and even in ocean water.[1] Within seawater, trace elements that are present in the cigarettes may leach into the ocean having damaging effects on the marine ecosystem.[4] This research plans to investigate the hypothesis that contaminants leached from cigarette litter are significant in samples of seawater collected near St. Simon's Island, Georgia (Figure 1), and specifically focuses on a large beach event surrounding the Florida vs. Georgia football game which took place on November 1, 2014. This is an annual event, but samples of seawater were collected in 2014. During that weekend, the St. Simon's Island Beach was "littered" with fans visiting for the game. Once the fans cleared away from the area, trash and litter were left piled all over the beach and in the seawater. At the annual game weekend in 2012, 5,400 pounds of trash and 500 pounds of recyclables were collected around this area.[5]

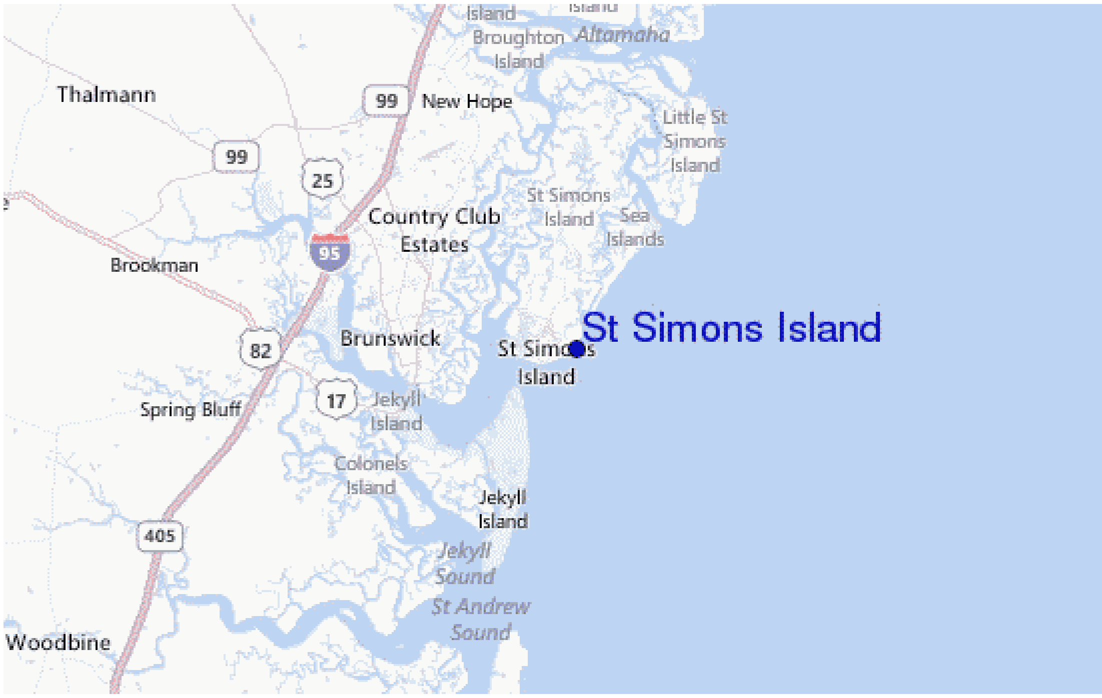

Figure 1: Location of St. Simon's Island, Georgia as indicated by the blue circle[6]

This study is interested in examining the impact this event has on the seawater gathered near the beach using elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). The research objectives will be:

- To study seawater samples collected at high and low tides along the beach in the months prior to and during the Florida/Georgia beach party to investigate if there are significant differences in elemental concentrations in the seawater as determined by an independent samples t-test; and
- To explore a gallium coprecipitation methodology by including the data gathered from the ICP-OES and powder X-ray diffraction (powder-XRD) for elemental isolation in order to determine if the use of gallium is beneficial in the

precipitation process and which types of elemental interactions occur in the process.

A comparative study will also be conducted to observe any deviation from the safe concentration levels provided by the Environmental Protection Agency (EPA) and World Health Organization (WHO) for drinking water. The known concentration of these elements present in seawater will be compared to the results gathered as well. Regarding the experimental approach to the isolation of elements, it is also important to note that gallium precipitation methods have been utilized in other experiments involving seawater, but the mechanism behind the process has not been explored and will be assessed in this research.[7] This project will be conducted in partnership with the University of Georgia (UGa) Marine Extension Service.

Cigarette Litter

Cigarettes are known for their harmful effect on human health and their correlation to the development of cancers.[8] This product is responsible for more than 400,000 premature deaths annually in the United States, clearly indicating a serious health concern.[9] Even though the medical community is highly vocal about this association, cigarette manufacturing continues to be a multibillion-dollar industry.[10] Despite a collaboration of efforts to discourage cigarette smoking in both teens and adults, the Centers for Disease Control and Prevention (CDC) estimated that in 2012, 42.1 million Americans smoked cigarettes.[11] Worldwide, approximately 5.6 trillion cigarettes are smoked every year.[12] Many smokers are unaware of another aspect of cigarettes that should be considered outside of human health, the damaging effects of cigarettes to the environment. People flick out the remains of their cigarette out car windows or throw them down on the ground before entering a building. While one cigarette may seem innocent to an individual, millions and millions of inappropriately discarded cigarette butts wind up throughout the environment in the United States and around the world.[13]

In the US, continuous efforts have been made to raise awareness and reduce the amount of improperly discarded cigarettes. Despite these attempts, cigarette butts are reported to constitute approximately 25-50% of all collected litter in the US.[13] The concerning extent of litter attributed to cigarettes propagates past the US, as the most common form of waste worldwide is cigarette debris.[13] Nearly 4.5 trillion cigarette butts are littered throughout the world every year.[14] This is a large burden on the earth's ecosystems as cigarette butts are not biodegradable, taking up to 12 years to decompose due to the cellulose acetate they contain.[14] Cigarette filters are composed of this cellulose acetate, a type of plastic that can break into smaller pieces but not fully biodegrade.[14]

Cigarettes contribute to pollution in multiple ways, but as mentioned, when focusing on seawater, trace elements that are present in cigarettes can leach out into the water.[4] It has been reported that there are approximately 600 different chemicals found in cigarettes.[15] According to the American Lung Association® (ALA), these include acetone (used as a paint remover), arsenic (used in rat poison), cadmium (active component in battery acid), carbon monoxide (released in car exhaust fumes), formaldehyde (embalming fluid), lead (used in batteries), and many other harmful chemicals.[16] At least 69 of these chemicals are known to cause cancer.[14] The contaminants reported by the ALA are paltry compared to the amount reported by another source, the CRC Press. According to the CRC Press, there are approximately 4,200 chemicals that constitute tobacco products while many others are reported to still be undiscovered.[17] Focusing exclusively on the elements, nearly all of which have been reported to be present in tobacco including alkali, alkaline earth, heavy metals, nonmetals, and rare earth metals.[17] For example, aluminum, arsenic, barium, boron, cesium, chromium, cobalt, copper, fluorine, gold, iodine, iron, lead, lithium, manganese, magnesium, mercury, molybdenum, nickel, platinum, polonium, radium, rubidium, selenium, silicon, silver, strontium, sulfur, titanium, tin, uranium, vanadium, and zinc have been found to be present in cigarettes.[17] Of the 90 naturally occurring elements, nearly 80 have been identified in tobacco.[17] Additionally, 44 isotopes and 24 ions have also been discovered in tobacco.[17] Scientists are curious to understand the role of each element in the tobacco industry, questioning whether these elements aid in plant growth and development or if the elements are used as catalysts both naturally occurring and synthetically added.[17]

This study focuses on 16 elements of interest: Al, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Ag, Sr, Ti, Tl, and Zn, all of which are present in cigarettes.[18] The concentration of these elements varies between cigarette brands, but Table 1 accounts for the average concentration ranges of 12 major cigarette brands as reported by the National Center for Biotechnology Information and as determined by neutron activation.[18,19]

Although thallium has clearly been identified as an ingredient present in both cigarettes and cigarette smoke, there is limited data on thallium concentrations in cigarettes.[20, 21] Silver is also present in cigarettes but the concentration was not reported.[17]

Table 1: Concentration of Elements of Interest Present in Cigarettes[18,19]	
Element	**Concentration (µg/g)**
Al	699-1200
As	<1
Ba	40.7-56.6
Cd	0.77-7.02
Co	<0.01-0.94
Cu	15.6
Cr	<0.1-3.45
Fe	325-520
Mn	155-400
Ni	<2-400
Pb	0.96-2.4
Sr	29.7-49.5
Ti	63.1-149
Zn	16.8-30.5

Cigarette Litter and the Ocean Waters

Cigarette waste is the most common form of waste worldwide, but when specifically focusing on the US shorelines and waterways, cigarette debris is also the most common type of waste collected along the waterways.[12] During the Ocean Conservancy's yearly International Coastal Cleanup in 2009, a total of 2,189,252 cigarettes were collected.[12] This quantity of cigarettes weighs approximately 821 pounds.[12] With this large amount of cigarette waste present near the ocean waters, a fundamental question must be asked: what effects, if any, can cigarette butt waste have in aquatic environments? For example, concentrations of trace elements such as lead, which naturally occurs in water, have risen in recent decades.[22] Reasons for this change can be attributed to oil and gas exploitation, uncontrolled use of fertilizers, climate change, and pollution, such as cigarette butts.[22] Research has shown that leachates from smoked cigarette butts is acutely toxic to the saltwater topsmelt as well as other species at varying concentrations.[12] Possible sources of aquatic toxicity are linked with the filter of cigarettes composed of cellulose acetate fibers, as mentioned.[23] These fibers are treated with titanium dioxide, a delustrant, and packed tightly together with glycerol triacetate as a binding agent to create the filter.[24] These chemicals can leach from the cigarettes into the ocean water as well as the other 600 chemical ingredients and elements present in the cigarettes.[15]

Past research conducted by Jessica W. Moerman and Dr. Gretchen E. Potts has demonstrated that metals (Al, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Sr, Ti, and Zn) do in fact leach into freshwater samples at varying rates.[25] As a result, cigarette litter was found to be a point source for elemental contamination.[25] In the study conducted by Moerman, all metals were detected in leachates as early as one day of soaking.[25] In conclusion, elements present in cigarette wastes are known to leach out as the cigarette waste decomposes and contaminate the waters, altering the elemental concentration present. Moerman’s research was conducted using freshwater, unlike this study which uses saltwater. However, after soaking in ocean water, the possibility of these elements present in cigarettes leaching into the ocean water prevails and may alter the natural concentration of elements in the sea just as in freshwater. The risk of changing and increasing these concentrations makes efficient elemental analysis of ocean water crucial for environmental monitoring.[22]

The concentration of the elements of interest will be compared to drinking water standards set by the Environmental Protection Agency (EPA) and World Health Organization (WHO) in the discussion section as guidelines for the elemental concentrations in seawater has not been established by these agencies. The reported concentrations of elements in the North Atlantic Ocean will also be compared to the results gathered from this study.

Gallium Preconcentration Technique

Ocean water contains a delicate and complex mixture of water, dissolved salts, gases, and inorganic and organic materials.[22] Sodium chloride (NaCl) is the main salt component in seawater while other ions also exist in a high concentration such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}.[22] Inorganic carbon, bromine, boron, and fluoride are found to be present in lower concentrations.[22] The analysis of salt-containing samples can be a challenge for ICP-OES, the chosen instrument for analysis. Salts may accumulate in the nebulizer tip, changing the nebulization efficiency, and resulting in signal drift and high variability.[22] Since most of the instrumental analytical methods currently available do not possess the selectivity, sensitivity, or freedom from matrix interferences, trace elements in natural seawaters must be extracted from the saltwater matrix prior to analysis in order to reduce interferences.[26] Therefore, precipitation steps were necessary in order to remove the elements of interest from the saltwater matrix. Furthermore, since the concentrations of trace elements in seawater are extremely low (see Table 42, Discussion section), preconcentration prior to analysis was required.[27]

Previous research used a gallium coprecipitation technique with seawater.[7, 27] This published method aids in elemental precipitation and isolation from the saltwater matrix.[7, 27] The advantage of using gallium was reported to be little spectral interference. However, the research did not include how gallium coprecipitated with the elements or how this technique worked. Further examination of this gallium preconcentration step was investigated to determine the chemical interactions behind this coprecipitation step.

Synthetic Seawater

Due to limited amounts of the collected St. Simon's Island seawater samples, three different types of commercial seawaters were utilized to examine the research methodology and to further explore and focus on the preconcentration technique which uses gallium. This was tested by spiking purchased standard samples of seawater, including Top Fin® liquid saltwater concentrate (used for home aquariums), RICCA Chemical Company® synthetic seawater, and Carolina seawater that was collected off the coast of the Atlantic Ocean and sold through Fisher Scientific. For simplicity, these three samples of seawater will be referred to as the "synthetic seawater samples". These samples were spiked with the elements of interest to a known elemental concentration of 0.1 ppm and precipitated with and without gallium. These prepared samples then underwent the same analytical procedure as the St. Simon's Island samples and were analyzed by ICP-OES to determine if using gallium proved to be beneficial. To further examine the coprecipitation technique, some of these samples were also analyzed by powder X-ray diffraction to determine the composition of these samples.

INSTRUMENTATION

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentrations.[28, 29] ICP-OES is a highly sensitive technique, allowing low detection limits of parts per million.[29] High plasma temperatures ranging from 3,000 – 7,000 Kelvin (K) allows for an easy excitation of atoms.[28, 29]

ICP utilizes the simple characteristic of excited species emitting wavelengths of certain energy in order to obtain measurements. Electrons of an atom can either be in the ground (unexcited) state or in an upper energy level state, referred to as the excited state. In order for an electron from a substance to be promoted from the normal ground state to one or more higher energy excited state, absorption must occur.[29] Absorption is a process in which energy is transferred to the species, in this case, an atom of an element.[29] According to quantum theory, atoms, molecules, and ions have only a limited number of discrete energy levels, and thus, for absorption of energy to occur, the energy of the exciting species must exactly match the energy difference between the ground state and one of the excited states of the absorbing element.[29] Thermal excitation of this electron to higher orbitals can be brought about by an electric arc, spark, heat of a flame, or in this case, plasma.[29]

The ICP-OES detection, however, does not focus on absorption, but rather on the *emission* processes, as indicated by its name. Once an electron has absorbed energy, it is in the excited state, which has a brief lifetime, often just 10^{-8} seconds, before returning to the ground state.[28] Returning to the ground state is achieved through photon emission.[29] The instrument acquires information about the analyte, or element, by measuring the electromagnetic radiation emitted as it returns to the ground state since this type of radiation is produced when excited electrons relax to lower energy levels by giving up their excess energy as photons. The radiant intensity emitted is proportional to the element's concentration.[29] The wavelength of the radiation produced is characteristic of each element, since each element emits light which possesses a unique wavelength.[29] This allows the instrument to distinguish between different elements that could be present, although some elements can emit radiation with extremely similar wavelengths. The absorption and emission processes are demonstrated by the energy diagram in Figure 2.

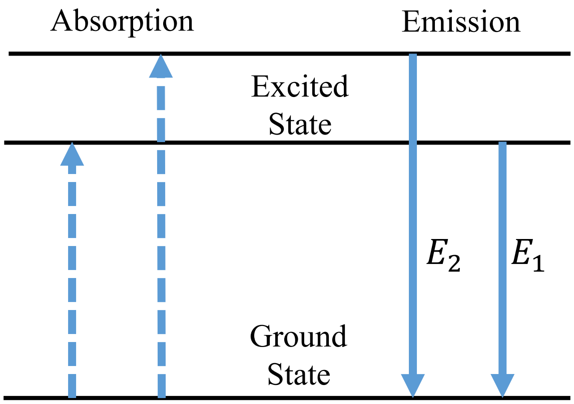

Figure 2: Energy level diagram indicating absorption and emission processes[29]

ICP-OES utilizes a plasma, a highly ionized gas that is macroscopically neutral, as the source to excite the electrons of the elements to a higher energy state.[29] With the Jobin-Yvon Ultima ICP-OES, the gas that is used to generate the plasma is argon.[29] It is necessary to supply external energy in the form of an electrical field in order to ionize the gas and to sustain the plasma, which will in turn, transmit some of its energy to the sample in order to excite the electrons present to higher energy levels.[29] The source is a torch consisting of three concentric quartz tubes surrounded by induction coils that are connected to a radiofrequency (RF) generator as illustrated in Figure 3.[29]

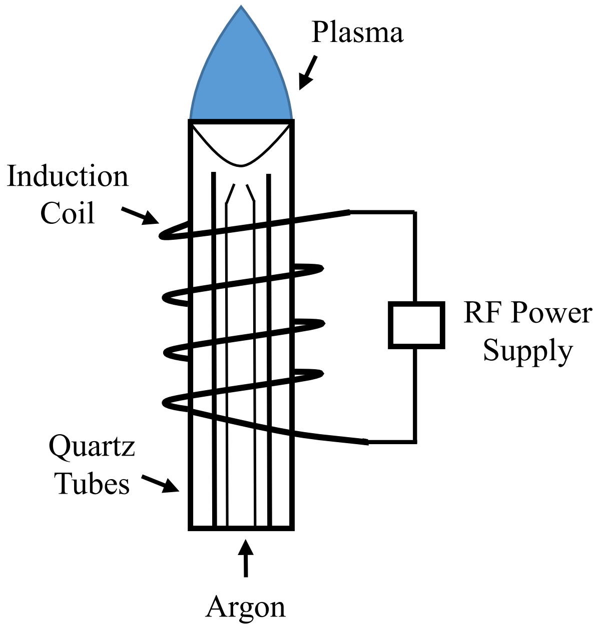

Figure 3: Induction coil surrounding quartz tube of plasma torch[29]

These tubes allow argon gas to flow. Also present is a coolant, typically water or ethylene glycol, which prevents overheating and flows along a circular path through the coils (Figure 3). Ionization of the flowing argon is initiated by a spark from a Tesla coil.[29] The argon ionizes according to Equation 1 where Ar is the elemental symbol for argon and e^- signifies an electron.

$$\text{Ar} + \text{energy} \rightarrow \text{Ar}^+ + e^- \qquad \text{Eqn. 1}$$

The resulting ions and electrons interact with a fluctuating magnetic field produced by the RF induction coil.[28] This interaction produces ions and electrons that flow in a closed annular paths (Figure 4).[29] There is resistance to flow by these ions and electrons causing ohmic heating of the plasma. Thus, argon ions, once formed in a plasma, can absorb sufficient power from an external source to maintain the temperature at a level where further ionization sustains the plasma indefinitely.[29]

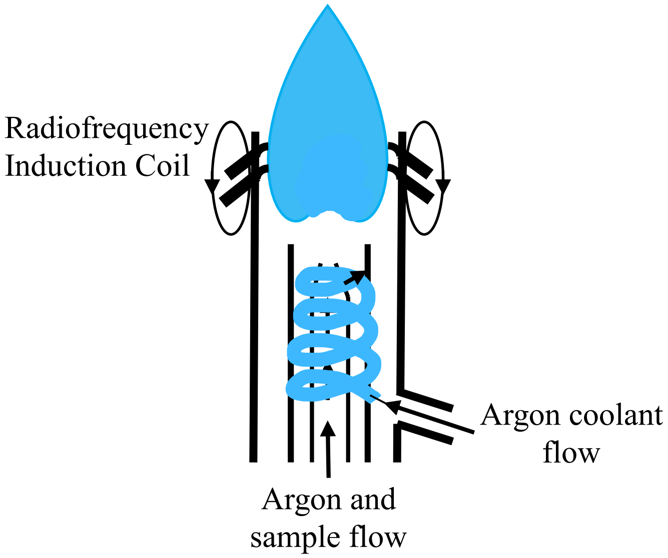

Figure 4: Typical ICP torch configuration[29]

Samples are introduced into the ICP by argon flowing through the central quartz tube (Figure 4).[29] First, the sample goes through a nebulizer. The nebulizing gas flows through an opening that surrounds the capillary which holds the liquid sample.[29] This causes a reduced pressure and aspiration of the sample which breaks up the solution into a fine mist.[29] Once the sample is in aerosol form from the nebulizer, it passes into the plasma. At the high temperatures of the plasma, the electrons in the atoms will become excited, and subsequently, relax to the ground state, emitting characteristic radiation. In ICP-OES, temperatures can reach up to 10,000 K, which thus increases the number of atoms that exist in an excited state. The population of excited atoms relative to the number of ground state atoms is expressed by the Boltzmann equation (Equation 2),

$$\frac{N_j}{N_O} = \frac{g_j}{g_O} \exp\left(\frac{-E}{kT}\right) \qquad \text{(Eqn. 2)}$$

where N_j and N_0 are the number of atoms present in an excited state, and ground state, respectively, and k is the Boltzmann's constant (1.38 x 10^{-23} J/K).[29] Absolute temperature is indicated by T, and as mentioned, the higher the temperature, and thus the higher the N_j/N_0 ratio, the higher the number of atoms that exist in the excited state. This results in a greater number of emissions as these atoms return to ground state The statistical weights, g_j and g_o, are determined by the number of states which possess equal energy at each quantum level.[29] E is the energy difference between the excited and ground atomic particles, which can be calculated according to Equation 3,

$$E_1 - E_O = h\Delta v = \frac{hc}{\Delta\lambda} \qquad \text{(Eqn. 3)}$$

where E_1 and E_0 are the energy of the higher state and lower state, respectively.[29] The term c is the speed of light while h is Planck's constant. The wavelength, λ, and frequency, v, of emitted radiation are also used in order to find the energy difference between the two states.

The radiation emitted at the unique wavelength is recorded by a monochromator which allows the researcher to select the wavelength of interest. The monochromator utilizes two small mirrors and a grating in order to allow only the desired wavelength to pass through to the detector.[29] The wavelength chosen for each element in this experiment is recorded in Table 7 (see Data and Calculations section).

The emitted radiation from the monochromator enters the photomultiplier tube (PMT), the detector, which amplifies the signal. The PMT contains a photoemissive cathode which emits electrons when exposed to radiation.[29] The tube contains additional electrodes, called dynodes, which also emit more electrons.[29] Each dynode is charged more positive than the previous, and as a result, the electrons are accelerated to the next dynode. Since there are multiple dynodes, by the time the process has been completed, $10^6 – 10^7$ electrons have been generated from each incident photon.[29] This cascade of electrons is collected at the anode and the resulting signal is processed using a computer and software. The signal produced for each element is compared to the signal produced from the calibration standards. From this, the concentrations of each element in a sample can be derived.

Powder X-Ray Diffraction (Powder-XRD)

Diffraction techniques, particularly those which utilize X-rays, are some of the most important techniques available for the determination of crystal structures.[30] This method can be used to determine the positions of atoms and ions that make up a solid compound, and thus, provide details of the unit cell.[30] Diffraction is the interference between waves that occurs as a result of an object being in their path.[30] When focusing on X-ray diffraction, X-rays are scattered with no change in energy by the electrons within atoms, and diffraction can occur.[30] This results in scattering from atoms in a crystal with spacings that are similar to the wavelength of the radiation.[30] Diffraction can be quantized according to Bragg's equation (Equation 4) since scattering can be regarded as the equivalent to reflection from two parallel planes of atoms separated by a distance, d.[30] The angle θ at which a constructive interference occurs between waves is

$$\sin\theta = \frac{n\lambda}{2d} \qquad \text{(Eqn. 4)}$$

where n is an integer and λ is wavelength.[30] Thus, an X-ray beam imposing on a crystalline compound with an ordered array of atoms will produce a set of diffraction patterns.[30] The sample is rotated through all angels at which Bragg's equation is satisfied. Usually, recording X-ray intensities involves a crystal rotating in the imposing X-ray beam.[30] The diffraction pattern produced is characteristic of the peak positions and types of atom present in the crystalline compound.[30] Furthermore, the measurement of X-ray diffraction angles and intensities can provide structural information.[30]

Powder-XRD is primarily used for phase identification and the determination of lattice parameters and types.[30] Powder-XRD is the only method that is applicable to all crystalline substance and the entire spectrum can be recorded on a short strip of film to give an X-ray "fingerprint" of the compound.[30] A powdered (polycrystalline) sample contains a large amount of small crystallites which are randomly oriented.[30] When an X-ray beam strikes the powdered sample, the beam is dispersed in all directions, and at specific angles, reflecting those given by Bragg's equation, constructive interference occurs.[30] As a result, each set of atoms with lattice spacing d gives rise to a cone of diffraction intensity.[30] A powder diffractometer has an electronic detector mounted on a goniometer, which is utilized to measure the angles of the diffracted beams.[30] Scanning the detector around the sample cuts through the diffraction cones formed and the intensity of the X-rays detected is recorded in relation to the detector angle.[30] The number and positions of the reflections are dependent upon various factors including: cell parameters, crystal system, lattice type, and wavelengths used to collect the data.[30] The peak positions correspond to the types of atoms present and their intensities.

Nearly all crystalline solids have a unique, characteristic powder-XRD pattern. In a compound mixture, each crystalline substance present contributes to the overall powder diffraction pattern.[31] Typically, the method is sensitive enough to detect small levels (5–10% by mass) of a particular crystalline component within the mixture.[32] Many of the powder diffraction data sets collected have been compiled into a database and can serve as a reference for comparison when trying to identify unknown components.[30] This database contains over 50,000 powder-XRD patterns and can be used to determine a material’s identification simply by observing and comparing its powder pattern.[30] Other sources report as many as 815,000+ unique patterns that can be used to identify compounds.[33]

The diffractometer contains a goniometer, which serves to measure diffraction angles, as well as a number of electric circuits crucial for determining the intensity of diffraction at any angle.[32] The goniometer consists of a large flat sample combined with a parafocusing arrangement to increase the intensity of diffraction.[32] Also, within the goniometer is an X-ray counter tube in place of film to detect the diffracted radiation.[32] The counter serves to transform the radiation spectrum which is emitted by the sample into a pulse spectrum which produces a graphic record of intensity plotted against the diffraction angle.[32] As mentioned, the spectra produced is matched with a database to determine the identities of the substances that are present. Thus, the procedure in analyzing the powder spectrum of an unknown compound can be summed as consisting of measuring the diffraction angles, calculating the spacings of the reflections, and then inferring the dimensions of the unit cell in order to determine the unknown identities of the components.[32]

Experimental

Sample Collection

The St. Simon's Island seawater samples were collected along the beach at both high and low tides at the end of each month beginning on July 31, 2014 and ending on October 31, 2014 by collaborators at the University of Georgia Marine Extension Service as indicated in Table 2. After collection in plastic containers, the seawater was filtered through 0.45 µm filters and acidified to a pH of about 1.6 with trace metal grade nitric acid. Samples were then frozen and shipped overnight to the University of Tennessee at Chattanooga where they were kept refrigerated until analysis.

TABLE 2: Collection Dates of St. Simon's Island Samples

Collection Date (2014)	High/Low Tide
7/31	High
7/31	Low
8/31	High
8/31	Low
10/1	High
10/1	Low
10/31	High
10/31	Low

Note: GPS data was not provided by UGa Marine Extension Service

Materials

TraceMetal Grade Concentrated Nitric Acid (Fisher Scientific)

pH Probe (Vernier)

pH 4.00 and 7.00 buffer solutions (Fisher Scientific)

47 mm All-Glass Vacuum Holder (Millipore)

0.45 µm Express Plus 47 mm Discs filter paper (Millipore)

RICCA Chemical Company® Synthetic Seawater (Fisher Scientific)

Top Fin® Liquid Saltwater Concentrate (PetSmart)

Carolina Seawater (Fisher Scientific)

0.22 µm Clarity High Performance 25 mm Syringe Filters (Environmental Express)

SPEX Certiprep 1,000 ppm standards (Fisher Scientific)

Inorganic^{TM} Ventures 10,000 ppm gallium standard (Fisher Scientific)

Submicron Filtered HPLC Grade water (Fisher Scientific)

HPLC Grade water (Fisher Scientific)

Safety precautions: Gloves were worn while handling nitric acid and sodium hydroxide and transfers of these chemicals were conducted in the fume hood.

Preparation of Standards

Standards were prepared for instrument calibration. The standards were prepared in groups, with four elements in each group. The groups were divided as shown in Table 3.

TABLE 3: Elemental Groups Analyzed by ICP-OES	
Group	**Elements**
1	Al, Cr, Co, Cu
2	Fe, Mn, Ni, Zn
3	Cd, Pb, Ag, As
4	Ba, Ti, Tl, Sr

Standards were prepared at 0.01 ppm, 0.1 ppm, 1.0 ppm, and 10.0 ppm, diluted from 1,000 ppm stock standards. The necessary amount of stock standard was pipetted into a 100 mL volumetric flask using an automatic pipette and the solutions were diluted with Millipore water. The solution was stoppered and mixed by inverting, and then poured into an appropriately labeled high density polyethylene (HDPE) plastic storage bottle. This procedure was repeated until all standards were prepared.

Preparation of Gallium Standard

A gallium coprecipitation technique was utilized to isolate the elements prior to analysis for increased sensitivity. A 100 mg/L gallium standard solution was first prepared by pipetting 1.0 mL of 10,000 mg/L gallium into a 100 mL volumetric flask and diluting to mark with Millipore water. The standard was mixed by inverting and transferred to an appropriately labeled HDPE plastic storage bottle.

Research Methodology using Synthetic Seawater Samples

The synthetic seawater samples (Top Fin® liquid saltwater concentrate, RICCA Chemical Company® synthetic seawater, and Carolina seawater) were spiked to a known concentration of 0.1 ppm with the element of interest. These samples were prepared in the following manner after all glassware to be used was cleaned. To make a single elemental sample, 20.0 μL of the element of interest was pipetted using an automatic pipette to a 200 mL volumetric flask, diluted with Millipore water, and mixed. The sample was then transferred to a 400 mL beaker and moved to a fume hood. Next, the gallium standard was added to some of the solutions by pipetting 5 mL of the 100 ppm gallium standard. The pipette tip was washed with the gallium standard before use. The resulting solution was mixed with a stirring rod and remained colorless. The initial pH was then measured using a pH probe. While stirring, 1.0 M NaOH was added dropwise to adjust the pH of the sample to around 10, and 0.1 M NaOH was added for fine adjustment to reach the desired pH of 10. During the addition, the solution transformed from colorless (transparent) to a cloudy white liquid and a white precipitate began to form as the elements of interest precipitated out of the saltwater matrix.

The solution was then allowed to sit overnight (24 hour period) in the fume hood to allow the precipitate to settle to the bottom of the beaker. After the solution and precipitate had stood overnight, the Millipore vacuum holder was utilized to filter the samples. The precipitate was collected on the filter paper and washed with Millipore water. This process required 2-4 hours depending on the amount of precipitate present. The filter paper with the precipitate was then transferred onto a watch glass using forceps, covered with a separate watch glass, and allowed to dry in the hood. Once the precipitate was dried (1-3 hours depending on mass of precipitate), the filter paper and the precipitate were placed in a Büchner funnel and dissolved with 1.5-3.0 mL of concentrated nitric acid. Larger precipitated samples required a higher volume of nitric acid, while smaller samples dissolved with only 1.5 mL of nitric acid. The filtrate was quantitatively transferred into a 25 mL volumetric flask and diluted to the 25 mL line with HPLC grade water. The filtrate was mixed through inversion and then syringe filtered into HDPE plastic storage bottles for analysis by the ICP-OES.

Samples were also prepared to have all 16 elements of interest present with and without gallium. The same procedure was followed as above, but 20 μL of all the elements were added to the 200 mL volumetric flask. The samples that contained gallium had 5.0 mL of the 100 mg/L gallium standard added as mentioned above while this step was withheld for the samples that were not to contain gallium. Additionally, no elements were added for samples that were to serve as blanks. All the samples prepared with synthetic seawater are summarized in Table 4, demonstrating the elements present in each sample and if gallium was added.

Research Method with St. Simon’s Island Seawater Samples

The same procedure for gallium precipitation was followed with the St. Simon’s Island samples. There were two differences in procedure from the prepared synthetic seawater samples. First, the St. Simon’s Island collected samples were not spiked with any elements. Secondly, the coprecipitation technique was utilized in all samples of the St. Simon’s Island seawater to isolate the elements prior to analysis for increased sensitivity, and thus, gallium was added to all samples of seawater. This step differs from the synthetic seawater samples where some samples contained gallium while others did not. The procedure was repeated for all sample collection dates. The seawater collected on 7/31/2014 was prepared by a previous research student, Veronica Hubble.

Preparation for Samples Undergoing Powder-XRD

Samples of synthetic seawater were prepared to be analyzed by powder X-ray diffraction. These samples underwent the same methodology previously explained, but the precipitates were not re-dissolved with nitric acid. Instead, these samples were allowed to dry for longer periods of time than the others (a minimum of one week). Then, the samples were crushed using an agate mortar and pestle. Once the samples were a fine powder, they were collected in vials until analysis by powder-XRD.

Analysis

The standards and sample solutions were analyzed by ICP-OES. The operating conditions for the instrument are listed in Table 5. The selected wavelengths for each element that were utilized by the ICP-OES are listed in Table 7 (see Data and Calculations). The powdered samples were analyzed by powder-XRD. The instrument parameters are listed in Table 6.

TABLE 4: Synthetic Seawater Samples Prepared

Synthetic Seawater	Gallium Present	Elements Present
Top Fin	Yes	None
Top Fin	Yes	Al, Cr, Co, Cu
Top Fin	Yes	Fe, Mn, Ni, Zn
Top Fin	Yes	Cd, Pb, Ag, As
Top Fin	Yes	Ba, Ti, Tl, Sr
Top Fin	Yes	All
RICCA	Yes	None
RICCA	Yes	Al, Cr, Co, Cu
RICCA	Yes	Fe, Mn, Ni, Zn
RICCA	Yes	Cd, Pb, Ag, As
RICCA	Yes	Ba, Ti, Tl, Sr
RICCA	Yes	All
RICCA	No	None
RICCA	No	Al, Cr, Co, Cu
RICCA	No	Fe, Mn, Ni, Zn
RICCA	No	Cd, Pb, Ag, As
RICCA	No	Ba, Ti, Tl, Sr
RICCA	No	All
Carolina	Yes	None
Carolina	Yes	Al, Cr, Co, Cu
Carolina	Yes	Fe, Mn, Ni, Zn
Carolina	Yes	Cd, Pb, Ag, As
Carolina	Yes	Ba, Ti, Tl, Sr
Carolina	Yes	All
Carolina	No	None
Carolina	No	Al, Cr, Co, Cu
Carolina	No	Fe, Mn, Ni, Zn
Carolina	No	Cd, Pb, Ag, As
Carolina	No	Ba, Ti, Tl, Sr
Carolina	No	All

TABLE 5: Operating Conditions for ICP-OES	
Plasma Observation	Axial
RF Generation	1250 W
Flow Rate	400 µL min^{-1}
Plasma Gas Flow Rate	12 L min^{-1}
Carrier Gas Flow Rate	1.0 mL min^{-1}
Monochromator	Czerny-Turner, 1.0 m
grating	2,400 grooves/mm, holographic
Detector	PMT

TABLE 6: Operating Conditions for Powder-XRD	
Peak positions defined by	Minimum of 2nd derivative
Minimum peak tip width (°2Theta)	0.00
Maximum peak tip width (°2Theta)	1.00
Peak base width (°2Theta)	2.00
Radiation	Cu Kα1, λ=1.54056 Å
X-ray tube	PW2273 long fine-focus X-ray tube
Accelerating potential	40 kV
Filament current	40 mÅ
Incident beam slits	1 degree divergence slit
Diffracted beam slits	0.2 mm receiving slit, soller slits, and a 1 degree antiscatter slit
Scan range	13 – 65 degrees
Step size	0.015 degrees
Counting time	2 seconds
Resulting scan time	2 hours and 4 minutes

DATA AND CALCULATIONS

Standard Preparation

The ICP-OES was calibrated using standards prepared with known concentrations of 0.01, 0.1, 1.0, and 10 mg/L or parts per million (ppm). The amount of stock standard (1,000 ppm) that was used to make the necessary standards was calculated using Equation 5

$$M_1V_1 = M_2V_2 \quad \text{(Eq. 5)}$$

where M represents the concentration in ppm and V is the volume required or needed in μL.

The standards were prepared as described in the Experimental section. These standards, along with Millipore water (which was assigned a concentration of zero ppm), were used to generate calibration curves by plotting the background subtracted intensity (cts) against the concentration of the element of interest. Once these curves were generated, the calibration equations were derived. These equations, along with the correlation coefficient, are reported in Table 7 for each element investigated.

Limit of Detection and Limit of Quantitation

Listed in Table 7 is the limit of detection (LOD) and limit of quantitation (LOQ) for each element. The LOD and LOQ are derived using Equations 6 and 7, respectively.[28, 29]

$$\text{LOD} = \frac{3\sigma_{blank}}{m} \quad \text{(Eq. 6)}$$

$$\text{LOQ} = \frac{10\sigma_{blank}}{m} \quad \text{(Eq. 7)}$$

In these equations, σ_{blank} refers to the standard deviation of the blank and m is the slope of the calibration curve for each specific element that was found from the standards.

The LOD is the concentration at which the instrument can discriminate between small differences in analyte concentration. In other words, the LOD is the minimum concentration of analyte that can be detected at a known 95% confidence level.[29] The LOQ, however, represents the lowest concertation at which measurements can be reliably detected and be quantitatively meaningful.[29] The ICP-OES detected concentrations for the unknowns (St. Simon's Island samples) that were higher than the LOD for all elements (see Data and Calculations section, even numbered Tables 8-38). The concentrations for most of the elements were also above the LOQ. The concentrations of aluminum, arsenic, cadmium, and thallium did not contain detected concentrations higher than the LOQ for the unknowns.

Table 7: Emission Wavelengths, Slopes, Correlation Coefficients, Limit of Detections and Limit of Quantitations for Elements of Interest

Element	Wavelength (nm)	Slope	r^2	LOD (ppm)	LOQ (ppm)
Aluminum	308.215	5.77×10^4	0.9996	0.00684	0.0228
Arsenic	193.696	1.09×10^5	0.9999	0.0145	0.0484
Barium	455.403	3.98×10^6	0.9976	0.000184	0.000613
Cadmium	226.502	9.39×10^5	0.9999	0.00151	0.00502
Chromium	267.716	1.18×10^6	0.9996	0.00141	0.00470
Cobalt	228.616	1.03×10^6	0.9998	0.000489	0.00163
Copper	324.754	5.68×10^6	0.9990	0.000442	0.00147
Iron	259.940	1.90×10^6	0.9999	0.000986	0.00329
Lead	220.353	1.46×10^5	0.9999	0.00319	0.0106
Manganese	257.610	9.63×10^6	0.9993	0.000179	0.000598
Nickel	231.604	6.60×10^5	0.9994	0.00102	0.00339
Silver	328.068	4.01×10^6	0.9995	0.000216	0.000722
Strontium	407.771	2.90×10^6	0.9970	0.0000353	0.000118
Thallium	190.864	3.05×10^4	0.9975	0.0406	0.135
Titanium	334.941	4.40×10^6	0.9983	0.000346	0.00115
Zinc	213.856	5.15×10^6	0.9991	0.000273	0.000911

Elemental Concentrations

To find the concentration of the elements, the data generated from the ICP-OES was utilized. The reported intensity (counts) was divided by the slope (m) and multiplied in order to account for the precipitation dilution factor as is indicated in Equation 8.

$$\text{Concentration (ppm)} = \frac{Intensity}{m} \times \frac{25}{200} \quad \text{(Eqn. 8)}$$

Tables 8-39 report the concentration of the elements of interest in parts per million of the St. Simon’s Island samples and the spiked synthetic seawater samples. The St. Simon’s Island samples are organized by the dates collected. The spiked samples are divided into the type of seawater used (Top Fin, RICCA, or Carolina seawater) and whether gallium was or was not added. Those samples that have the phrase “No Ga” included indicate that no gallium was added to that specific sample while the other samples did have gallium added. The samples labeled “blank” did not have any spiked elements added, while those that contain the phrase “spiked”, were spiked with the element of interest. Lastly, some samples were spiked with all 16 elements. This is indicated by the samples that have the phrase “all” in the sample name. These found concentrations were used to assess whether or not the samples that contained gallium had elements precipitating out of the saltwater matrix with a higher efficiency.

Aluminum Data

Table 8: Concentration of Aluminum in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.0163	0.000738
8/31	High	0.0163	0.00142
10/1	High	0.0171	0.000826
10/31	High	0.0170	0.000456
7/31	Low	0.0164	0.00133
8/31	Low	0.0156	0.000319
10/1	Low	0.0164	0.000735
10/31	Low	0.0164	0.00130
Average		0.0165	0.000890

Table 9: Spiked Concentration of Aluminum in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.0251	0.000176
Top Fin Spiked	0.0755	0.000745
Top Fin All Elements	0.0790	0.00958
RICCA Blank No Ga	0.0194	0.000974
RICCA Blank	0.0167	0.000436
RICCA Spiked No Ga	0.119	0.00161
RICCA Spiked	0.160	0.00241
RICCA All Elements No Ga	0.120	0.00404
RICCA All Elements	0.167	0.0116
Carolina Blank No Ga	0.0197	0.000518
Carolina Blank	0.0266	0.000204
Carolina Spiked No Ga	0.135	0.00240
Carolina Spiked	0.147	0.000991
Carolina All Elements No Ga	0.141	0.00534
Carolina All Elements	0.149	0.00410

*Spiked concentration = 0.1 ppm

Arsenic Data

Table 10: Concentration of Arsenic in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.0185	0.00130
8/31	High	0.0150	0.000391
10/1	High	0.0148	0.00114
10/31	High	0.0145	0.000523
7/31	Low	0.0171	0.000428
8/31	Low	0.0148	0.000804
10/1	Low	0.0154	0.000715
10/31	Low	0.0147	0.000779
Average		0.0156	0.000761

Table 11: Spiked Concentration of Arsenic in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.0172	0.000524
Top Fin Spiked	0.0879	0.000672
Top Fin All Elements	0.0844	0.000922
RICCA Blank No Ga	0.0128	0.000715
RICCA Blank	0.0135	0.000251
RICCA Spiked No Ga	0.175	0.00236
RICCA Spiked	0.132	0.000296
RICCA All Elements No Ga	0.124	0.000935
RICCA All Elements	0.173	0.00282
Carolina Blank No Ga	0.0164	0.000330
Carolina Blank	0.0155	0.000245
Carolina Spiked No Ga	0.150	0.00161
Carolina Spiked	0.166	0.00374
Carolina All Elements No Ga	0.160	0.00114
Carolina All Elements	0.166	0.000773

*Spiked concentration = 0.1 ppm

Barium Data

Table 12: Concentration of Barium in Samples of St. Simon’s Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00654	0.00244
8/31	High	0.262	0.0225
10/1	High	0.219	0.0495
10/31	High	0.273	0.0136
7/31	Low	0.00813	0.00581
8/31	Low	0.287	0.0200
10/1	Low	0.247	0.0152
10/31	Low	0.269	0.0130
Average		0.196	0.0178

Table 13: Spiked Concentration of Barium in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.155	0.000616
Top Fin Spiked	0.164	0.000234
Top Fin All Elements	0.175	0.00133
RICCA Blank No Ga	0.237	0.00104
RICCA Blank	0.230	0.000388
RICCA Spiked No Ga	0.222	0.000601
RICCA Spiked	0.249	0.00178
RICCA All Elements No Ga	0.207	0.000333
RICCA All Elements	0.234	0.00180
Carolina Blank No Ga	0.158	0.000881
Carolina Blank	0.182	0.000908
Carolina Spiked No Ga	0.194	0.000624
Carolina Spiked	0.212	0.00183
Carolina All Elements No Ga	0.191	0.00100
Carolina All Elements	0.171	0.00106

*Spiked concentration = 0.1 ppm

Cadmium Data

Table 14: Concentration of Cadmium in Samples of St. Simon’s Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00284	0.000373
8/31	High	0.00310	0.000149
10/1	High	0.00307	0.000227
10/31	High	0.00299	0.000185
7/31	Low	0.00308	0.000350
8/31	Low	0.00317	0.000609
10/1	Low	0.00297	0.0000888
10/31	Low	0.00288	0.000271
Average		0.00301	0.000282

Table 15: Spiked Concentration of Cadmium in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Topfin Blank	0.00329	0.000106
Topfin Spiked	0.0710	0.0000305
Topfin All	0.0702	0.000636
RICCA Blank No Ga	0.00250	0.0000721
RICCA Blank	0.00237	0.0000521
RICCA Spiked No Ga	0.109	0.000540
RICCA Spiked	0.113	0.000304
RICCA All No Ga	0.110	0.000351
RICCA All	0.145	0.00212
Carolina Blank No Ga	0.00265	0.0000681
Carolina Blank	0.00239	0.0000304
Carolina Spiked No Ga	0.101	0.00102
Carolina Spiked	0.130	0.000238
Carolina All No Ga	0.138	0.00149
Carolina All	0.138	0.000553

*Spiked concentration = 0.1 ppm

Chromium Data

Table 16: Concentration of Chromium in Samples of St. Simon’s Island Seawater

Sample	Tide	Concentration (ppm)	Standard Deviation (ppm)
7/31	High	0.00444	0.000238
8/31	High	0.00453	0.000640
10/1	High	0.00563	0.00148
10/31	High	0.00477	0.000612
7/31	Low	0.00424	0.000464
8/31	Low	0.00442	0.000518
10/1	Low	0.00446	0.0000918
10/31	Low	0.00441	0.000702
Average		0.00461	0.000594

Table 17: Spiked Concentration of Chromium in Different Saltwater Samples

Sample Name	Concentration (ppm)	Standard Deviation (ppm)
Topfin Blank	0.00329	0.000181
Topfin Spiked	0.0710	0.000590
Topfin All Elements	0.0703	0.000237
RICCA Blank No Ga	0.00248	0.000142
RICCA Blank	0.00236	0.0000685
RICCA Spiked No Ga	0.109	0.000792
RICCA Spiked	0.113	0.00122
RICCA All Elements No Ga	0.109	0.00120
RICCA All Elements	0.145	0.0221
Carolina Blank No Ga	0.00264	0.0000720
Carolina Blank	0.00239	0.0000482
Carolina Spiked No Ga	0.101	0.00256
Carolina Spiked	0.129	0.00142
Carolina All Elements No Ga	0.138	0.00364
Carolina All Elements	0.137	0.000847

*Spiked concentration = 0.1 ppm

Cobalt Data

Table 18: Concentration of Cobalt in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00321	0.000229
8/31	High	0.00289	0.000105
10/1	High	0.00289	0.0000843
10/31	High	0.00288	0.0000818
7/31	Low	0.00358	0.000746
8/31	Low	0.00277	0.000230
10/1	Low	0.00295	0.000143
10/31	Low	0.00288	0.000263
Average		0.00301	0.000235

Table 19: Spiked Concentration of Cobalt in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.00796	0.0000812
Top Fin Spiked	0.0819	0.00121
Top Fin All Elements	0.108	0.000752
RICCA Blank No Ga	0.00394	0.000126
RICCA Blank	0.00539	0.000190
RICCA Spiked No Ga	0.109	0.000981
RICCA Spiked	0.142	0.00109
RICCA All Elements No Ga	0.112	0.000793
RICCA All Elements	0.143	0.00339
Carolina Blank No Ga	0.00502	0.0000305
Carolina Blank	0.00465	0.0000359
Carolina Spiked No Ga	0.108	0.00152
Carolina Spiked	0.150	0.00119
Carolina All Elements No Ga	0.142	0.000983
Carolina All Elements	0.153	0.00258

*Spiked concentration = 0.1 ppm

Copper Data

Table 20: Concentration of Copper in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00731	0.00496
8/31	High	0.00344	0.000592
10/1	High	0.00438	0.00223
10/31	High	0.00240	0.0000760
7/31	Low	0.00541	0.00193
8/31	Low	0.00339	0.00128
10/1	Low	0.00262	0.000124
10/31	Low	0.00257	0.000245
Average		0.00394	0.00143

Table 21: Spiked Concentration of Copper in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.0172	0.0000234
Top Fin Spiked	0.0878	0.000870
Top Fin All Elements	0.0844	0.0164
RICCA Blank No Ga	0.0128	0.0000126
RICCA Blank	0.0135	0.00000933
RICCA Spiked No Ga	0.174	0.000490
RICCA Spiked	0.131	0.00175
RICCA All Elements No Ga	0.123	0.000549
RICCA All Elements	0.173	0.00266
Carolina Blank No Ga	0.0164	0.00000800
Carolina Blank	0.0155	0.0000236
Carolina Spiked No Ga	0.149	0.00201
Carolina Spiked	0.166	0.00174
Carolina All Elements No Ga	0.160	0.00257
Carolina All Elements	0.165	0.00141

*Spiked concentration = 0.1 ppm

Iron Data

Table 22: Concentration of Iron in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.0185	0.00130
8/31	High	0.0592	0.0559
10/1	High	0.0605	0.0485
10/31	High	0.117	0.0751
7/31	Low	0.0170	0.000428
8/31	Low	0.0900	0.0688
10/1	Low	0.0606	0.0451
10/31	Low	0.0571	0.0327
Average		0.0601	0.0410

Table 23: Spiked Concentration of Iron in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.131	0.000505
Top Fin Spiked	0.117	0.000346
Top Fin All Elements	0.116	0.000319
RICCA Blank No Ga	0.0385	0.0000712
RICCA Blank	0.0275	0.000113
RICCA Spiked No Ga	0.176	0.00198
RICCA Spiked	0.171	0.000297
RICCA All Elements No Ga	0.245	0.00217
RICCA All Elements	0.179	0.00108
Carolina Blank No Ga	0.0236	0.000258
Carolina Blank	0.0168	0.0000782
Carolina Spiked No Ga	0.234	0.00169
Carolina Spiked	0.220	0.000600
Carolina All Elements No Ga	0.242	0.00282
Carolina All Elements	0.131	0.00205

*Spiked concentration = 0.1 ppm

Lead Data

Table 24: Concentration of Lead in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.0131	0.00114
8/31	High	0.0223	0.000673
10/1	High	0.0198	0.00164
10/31	High	0.0187	0.000904
7/31	Low	0.0147	0.00240
8/31	Low	0.0210	0.00371
10/1	Low	0.0190	0.000232
10/31	Low	0.0189	0.00153
Average		0.0184	0.00153

Table 25: Spiked Concentration of Lead in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.0251	0.0000753
Top Fin Spiked	0.0755	0.000253
Top Fin All Elements	0.0790	0.00145
RICCA Blank No Ga	0.0194	0.000391
RICCA Blank	0.0167	0.0000786
RICCA Spiked No Ga	0.119	0.00108
RICCA Spiked	0.160	0.00191
RICCA All Elements No Ga	0.120	0.000230
RICCA All Elements	0.167	0.00137
Carolina Blank No Ga	0.0197	0.000417
Carolina Blank	0.0265	0.000152
Carolina Spiked No Ga	0.135	0.00111
Carolina Spiked	0.147	0.000710
Carolina All Elements No Ga	0.141	0.000992
Carolina All Elements	0.149	0.00162

*Spiked concentration = 0.1 ppm

Manganese Data

Table 26: Concentration of Manganese in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.000842	0.00602
8/31	High	0.00177	0.000371
10/1	High	0.00174	0.000609
10/31	High	0.00472	0.00196
7/31	Low	0.00115	0.00346
8/31	Low	0.00420	0.000479
10/1	Low	0.00252	0.00178
10/31	Low	0.00191	0.000557
Average		0.00236	0.00190

Table 27: Spiked Concentration of Manganese in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.477	0.00155
Top Fin Spiked	0.521	0.00489
Top Fin All Elements	0.501	0.00168
RICCA Blank No Ga	0.0373	0.000313
RICCA Blank	0.0376	0.000118
RICCA Spiked No Ga	0.129	0.000700
RICCA Spiked	0.163	0.000966
RICCA All Elements No Ga	0.169	0.000481
RICCA All Elements	0.181	0.00112
Carolina Blank No Ga	0.00122	0.0000264
Carolina Blank	0.00126	0.0000161
Carolina Spiked No Ga	0.131	0.000397
Carolina Spiked	0.136	0.000574
Carolina All Elements No Ga	0.145	0.000688
Carolina All Elements	0.133	0.000373

*Spiked concentration = 0.1 ppm

Nickel Data

Table 28: Concentration of Nickel in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00769	0.00113
8/31	High	0.00587	0.000352
10/1	High	0.00558	0.000480
10/31	High	0.00642	0.00105
7/31	Low	0.0107	0.00562
8/31	Low	0.00515	0.000397
10/1	Low	0.00540	0.000154
10/31	Low	0.00535	0.000300
Average		0.00652	0.00119

Table 29: Spiked Concentration of Nickel in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.0145	0.000519
Top Fin Spiked	0.0803	0.000350
Top Fin All Elements	0.0701	0.000251
RICCA Blank No Ga	0.0230	0.000215
RICCA Blank	0.00892	0.000254
RICCA Spiked No Ga	0.134	0.00240
RICCA Spiked	0.165	0.00177
RICCA All Elements No Ga	0.143	0.000715
RICCA All Elements	0.129	0.0000676
Carolina Blank No Ga	0.00959	0.000384
Carolina Blank	0.0102	0.000206
Carolina Spiked No Ga	0.175	0.000321
Carolina Spiked	0.168	0.000509
Carolina All Elements No Ga	0.164	0.000878
Carolina All Elements	0.178	0.00128

*Spiked concentration = 0.1 ppm

Silver Data

Table 30: Concentration of Silver in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00186	0.000135
8/31	High	0.00304	0.0000560
10/1	High	0.00287	0.000195
10/31	High	0.00307	0.000575
7/31	Low	0.00192	0.000249
8/31	Low	0.00396	0.000878
10/1	Low	0.00269	0.0000292
10/31	Low	0.00275	0.000361
Average		0.00277	0.000310

Table 31: Spiked Concentration of Silver in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.00734	0.0000396
Top Fin Spiked	0.00679	0.0000266
Top Fin All Elements	0.00221	0.0000730
RICCA Blank No Ga	0.00325	0.0000290
RICCA Blank	0.00595	0.0000084
RICCA Spiked No Ga	0.00396	0.0000643
RICCA Spiked	0.00552	0.0000450
RICCA All Elements No Ga	0.00458	0.0000935
RICCA All Elements	0.00214	0.0000178
Carolina Blank No Ga	0.00211	0.0000357
Carolina Blank	0.00621	0.0000353
Carolina Spiked No Ga	0.00558	0.0000704
Carolina Spiked	0.00540	0.0000301
Carolina All Elements No Ga	0.00752	0.0000345
Carolina All Elements	0.00228	0.0000997

*Spiked concentration = 0.1 ppm

Strontium Data

Table 32: Concentration of Strontium in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.7680	0.651
8/31	High	0.00927	0.000991
10/1	High	0.00870	0.00182
10/31	High	0.00838	0.000809
7/31	Low	0.39774	0.413
8/31	Low	0.00621	0.00183
10/1	Low	0.00957	0.00313
10/31	Low	0.00889	0.00109
Average		0.152	0.134

Table 33: Spiked Concentration of Strontium in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.00450	0.0000336
Top Fin Spiked	0.0339	0.000265
Top Fin All Elements	0.0319	0.000194
RICCA Blank No Ga	0.915	0.00273
RICCA Blank	0.679	0.00374
RICCA Spiked No Ga	0.612	0.00494
RICCA Spiked	0.171	0.00292
RICCA All Elements No Ga	0.106	0.000830
RICCA All Elements	0.110	0.000638
Carolina Blank No Ga	0.406	0.00382
Carolina Blank	0.431	0.00286
Carolina Spiked No Ga	0.369	0.00123
Carolina Spiked	0.141	0.00105
Carolina All Elements No Ga	0.0389	0.000131
Carolina All Elements	0.0510	0.000195

*Spiked concentration = 0.1 ppm

Thallium Data

Table 34: Concentration of Thallium in Samples of St. Simon’s Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.0825	0.00333
8/31	High	0.0439	0.00104
10/1	High	0.0457	0.00218
10/31	High	0.0457	0.00122
7/31	Low	0.0816	0.00577
8/31	Low	0.0429	0.00407
10/1	Low	0.0465	0.00148
10/31	Low	0.0451	0.00393
Average		0.0543	0.00288

Table 35: Spiked Concentration of Thallium in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.0816	0.00156
Top Fin Spiked	0.101	0.00152
Top Fin All Elements	0.0949	0.00396
RICCA Blank No Ga	0.0610	0.00254
RICCA Blank	0.0627	0.00213
RICCA Spiked No Ga	0.0701	0.00153
RICCA Spiked	0.0649	0.00320
RICCA All Elements No Ga	0.0802	0.000864
RICCA All Elements	0.0912	0.00458
Carolina Blank No Ga	0.0740	0.00298
Carolina Blank	0.0674	0.000819
Carolina Spiked No Ga	0.0748	0.000655
Carolina Spiked	0.0676	0.00141
Carolina All Elements No Ga	0.0929	0.00237
Carolina All Elements	0.0898	0.00179

*Spiked concentration = 0.1 ppm

Titanium Data

Table 36: Concentration of Titanium in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.00203	0.000137
8/31	High	0.00285	0.000378
10/1	High	0.00280	0.000615
10/31	High	0.003121	0.000388
7/31	Low	0.00138	0.000218
8/31	Low	0.00321	0.000349
10/1	Low	0.00303	0.000597
10/31	Low	0.00291	0.000117
Average		0.00267	0.000350

Table 37: Spiked Concentration of Titanium in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.00182	0.00000870
Top Fin Spiked	0.0623	0.000333
Top Fin All Elements	0.0641	0.000442
RICCA Blank No Ga	0.00194	0.0000102
RICCA Blank	0.00184	0.0000165
RICCA Spiked No Ga	0.0998	0.000974
RICCA Spiked	0.146	0.000694
RICCA All Elements No Ga	0.103	0.000990
RICCA All Elements	0.158	0.00274
Carolina Blank No Ga	0.00170	0.0000135
Carolina Blank	0.00165	0.0000201
Carolina Spiked No Ga	0.119	0.000964
Carolina Spiked	0.123	0.000823
Carolina All Elements No Ga	0.132	0.00165
Carolina All Elements	0.132	0.00149

*Spiked concentration = 0.1 ppm

Zinc Data

Table 38: Concentration of Zinc in Samples of St. Simon's Island Seawater			
Sample	**Tide**	**Concentration (ppm)**	**Standard Deviation (ppm)**
7/31	High	0.0185	0.00130
8/31	High	0.0150	0.000391
10/1	High	0.0148	0.00114
10/31	High	0.0148	0.000523
7/31	Low	0.0171	0.000428
8/31	Low	0.0148	0.000804
10/1	Low	0.0154	0.000715
10/31	Low	0.0147	0.000779
Average		0.0156	0.000761

Table 39: Spiked Concentration of Zinc in Different Saltwater Samples		
Sample Name	**Concentration (ppm)**	**Standard Deviation (ppm)**
Top Fin Blank	0.132	0.000971
Top Fin Spiked	0.199	0.00154
Top Fin All Elements	0.188	0.00182
RICCA Blank No Ga	0.160	0.000304
RICCA Blank	0.136	0.000712
RICCA Spiked No Ga	0.237	0.00103
RICCA Spiked	0.236	0.00179
RICCA All Elements No Ga	0.398	0.000862
RICCA All Elements	0.245	0.00283
Carolina Blank No Ga	0.0855	0.000775
Carolina Blank	0.126	0.000517
Carolina Spiked No Ga	0.193	0.00160
Carolina Spiked	0.324	0.00215
Carolina All Elements No Ga	0.264	0.00105
Carolina All Elements	0.281	0.000848

*Spiked concentration = 0.1 ppm

Comparison of Experimental Means: t-Test

From the results gathered from the St. Simon's Island samples, a t-test was performed in order to calculate if there was a significant difference between the samples collected on 10/31 (event day) and the samples collected on 7/31, 8/31, and 10/1 of 2014. Equation 9 was used to find the standard deviation, which is subsequently used to find the t-value. Equation 10 shows the formula used for the t-test.[34]

$$s^2 = \frac{(n_1-1){s_1}^2 + (n_2-1){s_2}^2}{(n_1+n_2-2)} \quad \text{(Eqn. 9)}$$

$$t = \left| \frac{(\bar{x}_1 - \bar{x}_2)}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \right| \quad \text{(Eqn. 10)}$$

In these formulas, $\bar{x}_1$ is the average concentration of an element at a date (either 7/31, 8/31, or 10/1) while $\bar{x}_2$ is the average concentration of the element on 10/31. Standard deviation is indicated by s while n is the degrees of freedom. The ICP-OES measures three intensity readings for each sample and the standard deviation was calculated from these three readings and are reported in the even numbered Tables 8-38. The degrees of freedom used for these calculations was six.

To be considered significantly different at the 95% confidence level, the sample must have a t-value greater than 2.45, at six degrees of freedom.[34] Table 40 contains the elements on the dates indicated that had a significant difference in concentration when compared to the concentration present on the 10/31/14 samples. Notice the trend which follows the cooling of the weather. More values are statistically different during the summer months from the main collection date of 10/31/14. This could also be attributed to sample preparation of 7/31 by another student. This does not explain the values from 8/31 or 10/1.

Table 40: t-Value for Elemental Concentration Difference from 10/31			
Element	**High/low tide**	**Date**	**t-value**
Ag	High	7/31	3.419
Ag	Low	7/31	3.349
As	High	7/31	5.253
As	Low	7/31	4.858
Ba	High	7/31	32.725
Ba	Low	7/31	31.768
Co	High	7/31	2.527
Cu	Low	7/31	3.000
Pb	High	7/31	7.375
Pb	Low	7/31	2.799
Ti	High	7/31	4.527
Ti	Low	7/31	12.504
Tl	High	7/31	20.752
Tl	Low	7/31	10.036
Zn	High	7/31	3.436
Ag	Low	8/31	2.560
Cu	High	8/31	3.598
Mn	High	8/31	2.516
Mn	Low	8/31	5.976
Pb	High	8/31	5.868
Zn	Low	8/31	2.826
Zn	Low	10/1	2.583

Note: t-value = 2.45 at 95% confidence level

Powder-XRD Figures

In order to further examine the gallium coprecipitation technique, some samples were analyzed by powder X-ray diffraction. This instrument allowed for comparison of the unknown sample to a library of known compounds. Figure 5 and 6 show the composition of RICCA seawater which was not spiked with any elements. Figure 5 (labeled “ricca1”) does contain gallium while Figure 6 (labeled “ricca2”) does not contain gallium. These two figures demonstrate what the unknown samples’ compositions most likely match, aragonite and halite. These diagrams were combined in order to show a side-by-side comparison, indicated in Figure 7.

The Carolina seawater also underwent analysis by powder-XRD. Figure 8 and 9 demonstrate the crystalline composition matches of these two samples. Figure 8 (labeled Carolina_1ga) demonstrates the results obtained when gallium was added, while Figure 9 corresponds to the Carolina sample that was not spiked with gallium (labeled Carolina _1). Figure 10 demonstrates a comparison of both of these samples.

For further comparison, the RICCA and Carolina spectra were combined to show a side by side contrast of the crystalline compositions of each. Figure 11 demonstrates RICCA and Carolina samples with gallium while Figure 12 demonstrates a comparison of the two samples without gallium added.

RICCA 1 and RICCA 2 Synthetic Seawater Powder-XRD

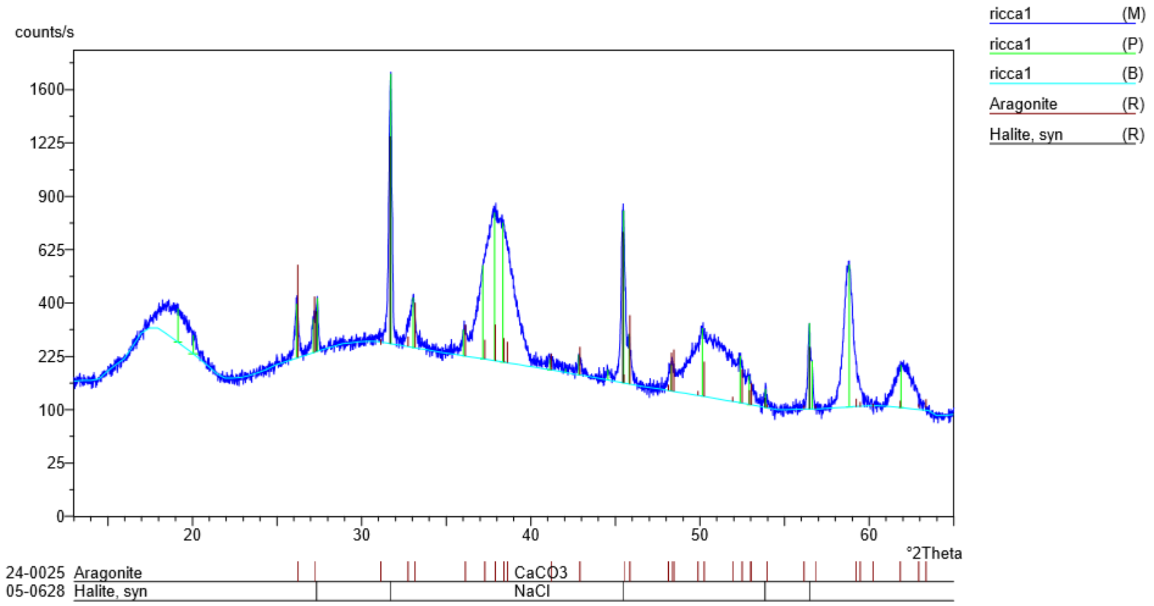

Figure 5: Powder-XRD spectra of RICCA synthetic seawater with gallium, showing accepted reference patterns

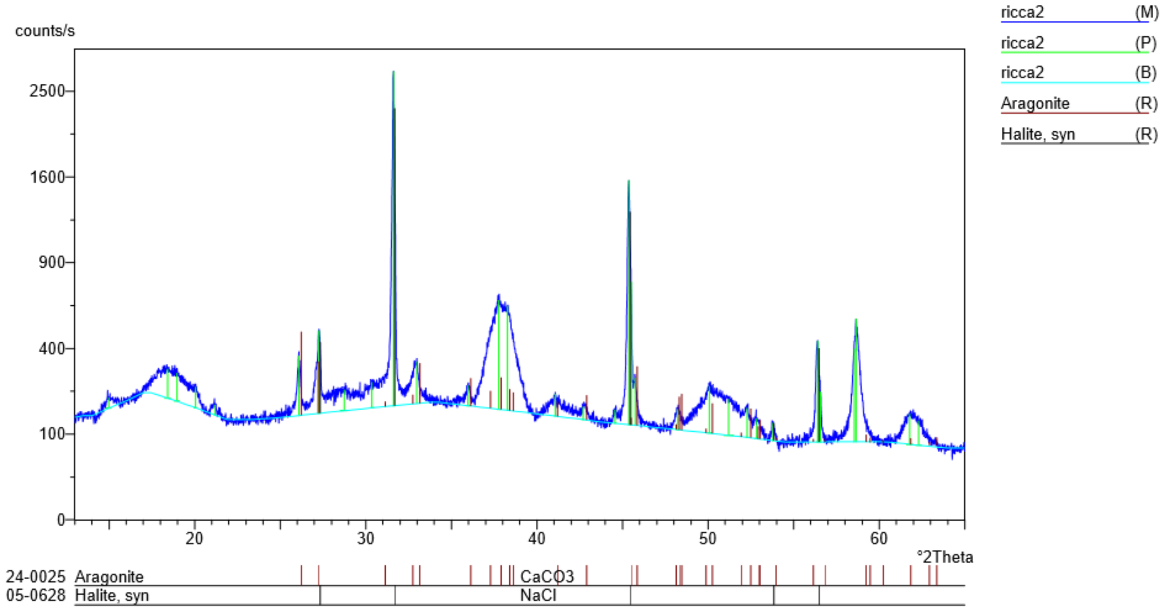

Figure 6: Powder-XRD spectra of RICCA synthetic seawater without gallium, showing accepted reference patterns

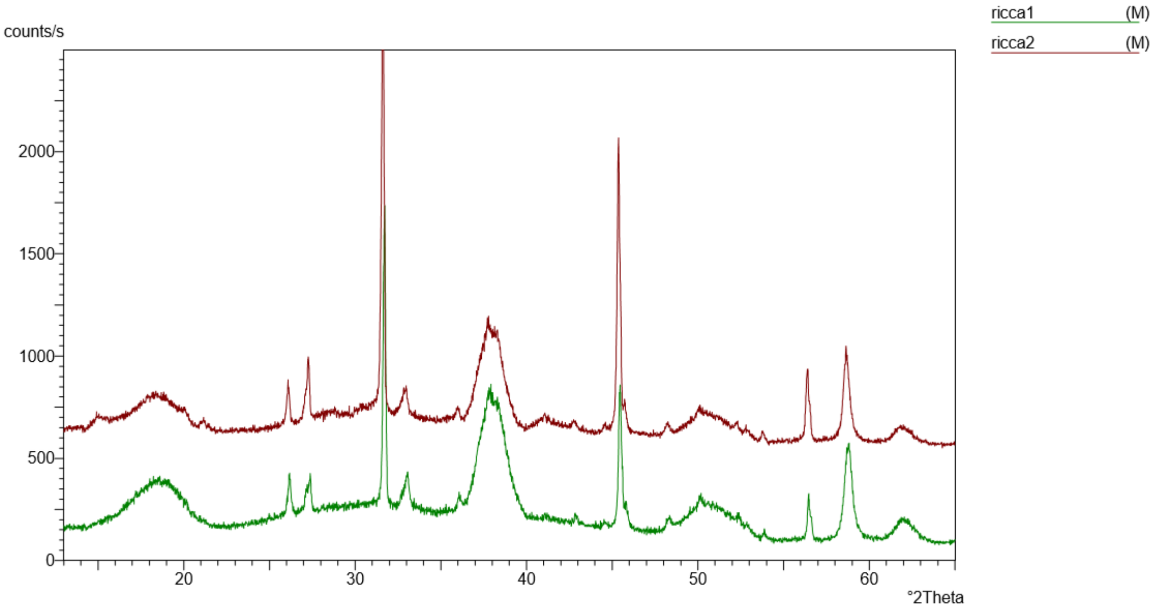

Figure 7: Comparison of RICCA synthetic seawater powder-XRD spectra without (red line above) and with gallium (green line below)

Carolina Seawater Powder-XRD

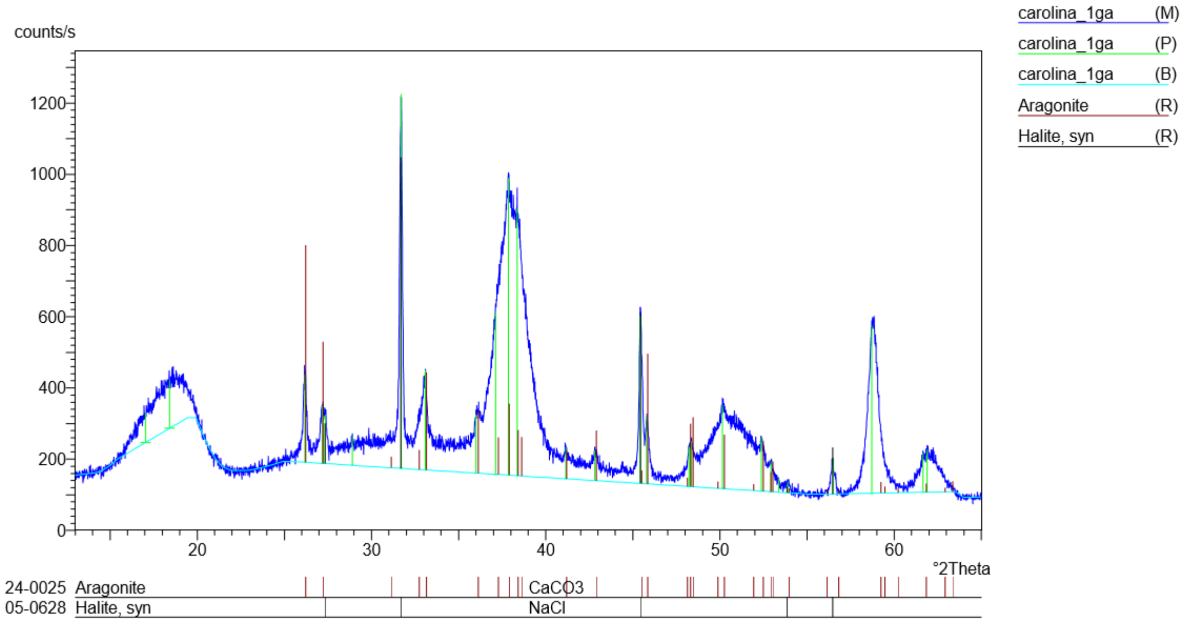

Figure 8: Powder X-ray diffraction spectra of Carolina seawater with gallium, showing accepted reference patterns

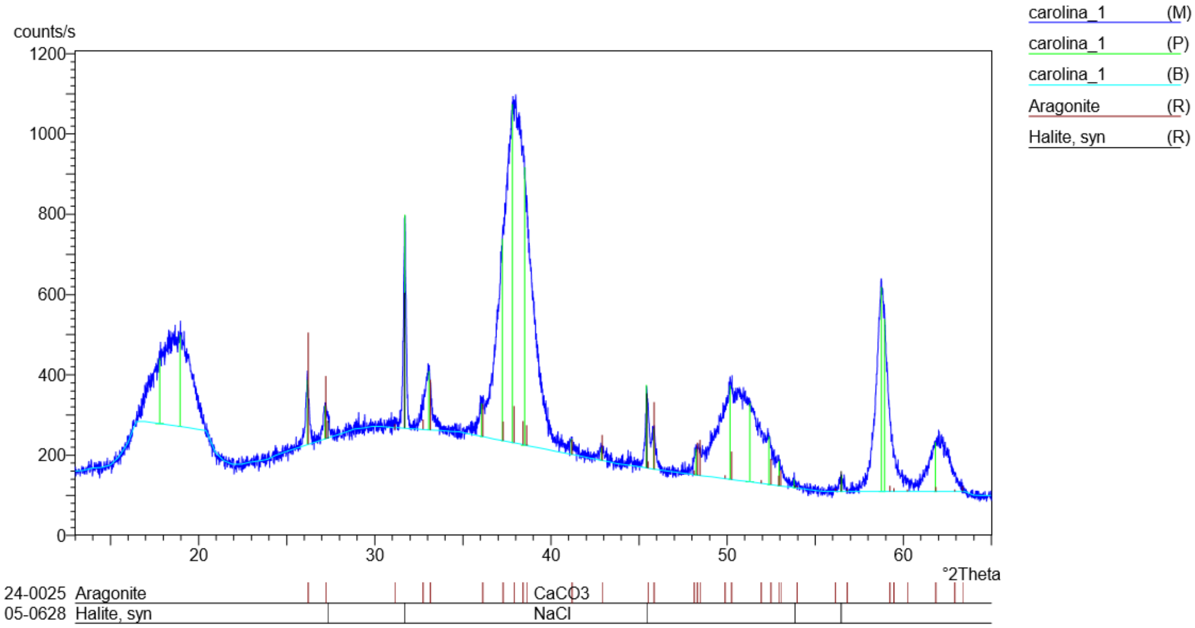

Figure 9: Powder X-ray diffraction spectra of Carolina seawater without gallium, showing accepted reference patterns

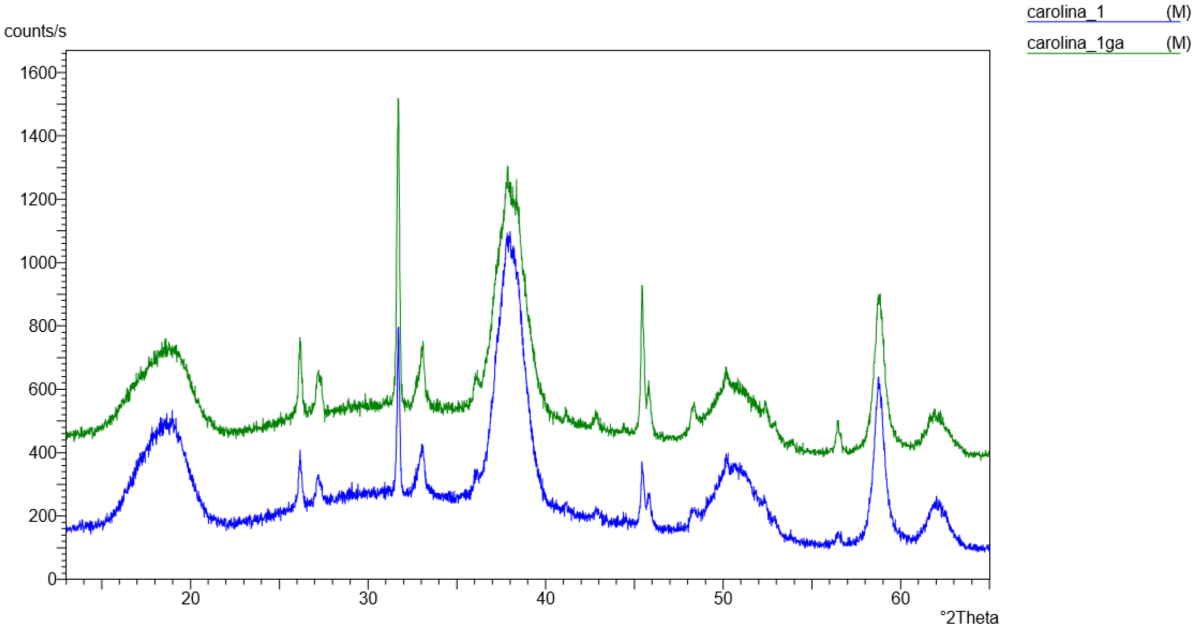

Figure 10: Comparison of the spectra for Carolina seawater with gallium (green line above) and without gallium (blue line below)

RICCA synthetic seawater comparison to Carolina seawater Powder-XRD

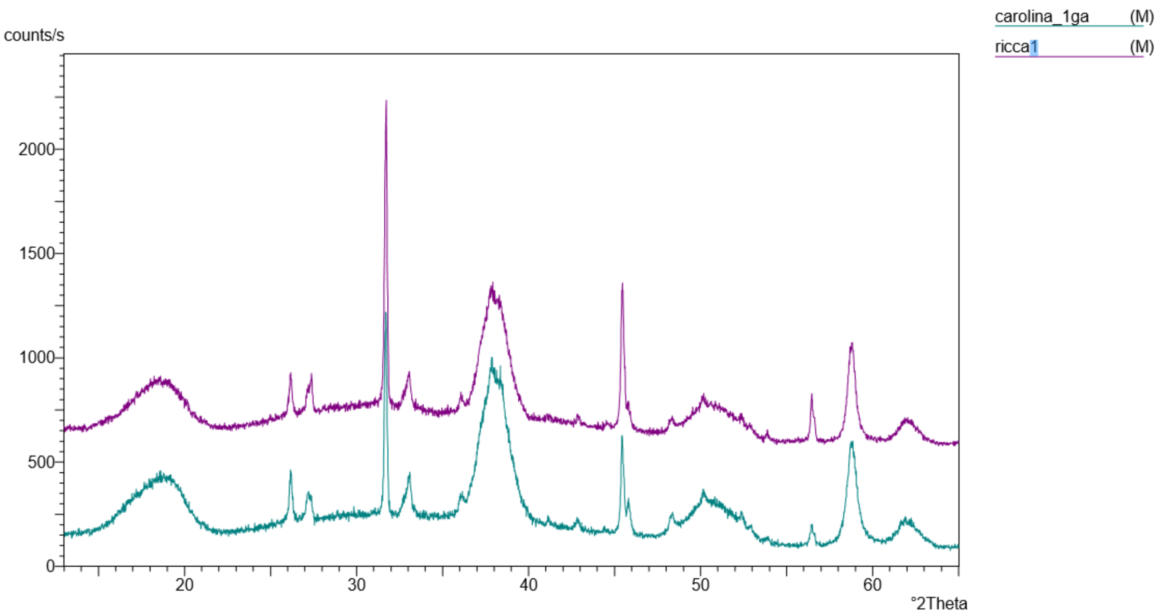

Figure 11: Comparison of spectra for Carolina seawater (blue line below) and RICCA synthetic water (purple line above) with gallium

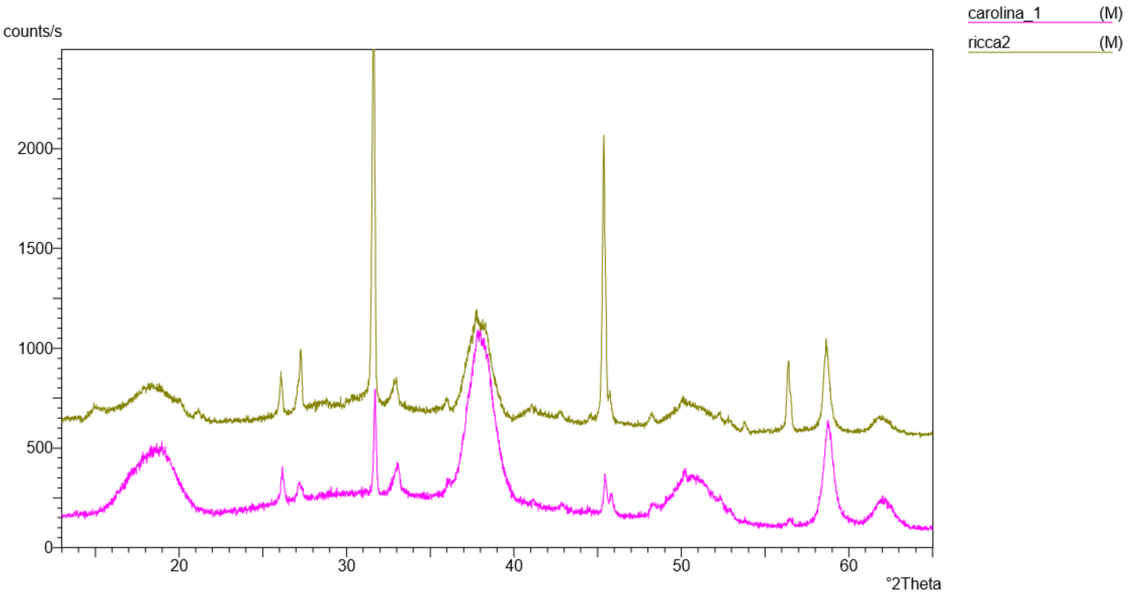

Figure 12: Comparison of spectra for Carolina seawater (pink line below) and RICCA synthetic seawater (tan line above) without gallium

DISCUSSION

St. Simon's Island Samples

The concentrations of the elements present in St. Simon's Island samples are listed in the *even numbered tables* beginning with Table 8 and ending with Table 38. These concentrations can be compared to the standards set by the Environmental Protection Agency (EPA) and the World Health Organization (WHO) for drinking water. Although seawater is clearly not drinking water, it is of interest to compare these guidelines to the acquired results. The EPA regulatory standards for elements in drinking water are in Table 41.[35, 36, 37] Also present in this table are the standards set by WHO for comparison.[38]

Table 41: EPA and WHO Reported Concentrations of Elements in Drinking Water

Element	EPA Concentration (ppm) [35, 36, 37]	WHO Concentration (ppm) [38]
Aluminum	0.2	0.2
Arsenic	0.01	0.01
Barium	2.0	0.7
Cadmium	0.005	0.003
Chromium	0.1	0.2
Cobalt	0.002	N/A
Copper	1.3	2.0
Iron	0.3	0.3
Lead	0.015	0.01
Manganese	0.05	0.05
Nickel	0.1	0.07
Silver	0.1	0.05
Strontium	N/A	N/A
Thallium	0.002	N/A
Titanium	N/A	N/A
Zinc	5.0	3.0

Regulations for titanium and strontium were not reported by the EPA. WHO also reported their available data was inadequate to permit a derivation of a guideline value for cobalt, strontium, thallium, and titanium. The averages of the concentrations determined from the collections 7/31, 8/31, 10/1, and 10/31 at high and low tides were averaged for each element as indicated by the even numbered tables in Tables 8 – 38. Comparing these averages to the drinking water safety regulations, aluminum, barium, cadmium, chromium, copper, iron, manganese, nickel, silver, and zinc had concentrations present in seawater lower than the reported safe drinking limits of drinking water. The concentrations of arsenic, cobalt, lead, and thallium were higher than is allowed from the drinking water standards. According to the EPA, arsenic has been linked to a variety of different forms of cancer including cancer of the bladder, kidney, liver, prostate, lungs, nasal passages, and skin.[39] Arsenic is also responsible for some non-cancer effects including nausea, vomiting, diarrhea, blindness, and partial paralysis.[39] In 2001, the Arsenic Rule was established in order to reduce the levels of arsenic in drinking water.[39] Similarly, WHO and the EPA report that thallium and lead can be linked to numerous health problems such as damage to various systems of the body including the nervous, reproductive, and urinary systems.[40, 41] Both thallium and lead can also lead to birth defects.[40, 41] Increased contact and ingestion of cobalt was reported to lead to severe lung damage and cancer.[42] These four elements (arsenic, lead, thallium, and cobalt), which were found to be in higher concentrations in the St. Simon’s Island seawater, are a potential source of poisoning when exposure levels are high.

The known/reported elemental composition of seawater, specifically, those elements involved in this research, are reported in Table 42.[26, 43, 44, 45] The abundance of these trace elements or any particular element present in the ocean can vary according to both time and space.[44] The middle column of Table 42 has the elemental concentrations in seawater. The right column, however, has the concentrations of the elements in the North Atlantic Ocean specifically, as provided by another source. These concentrations are of interest since St. Simon's Island faces the North Atlantic Ocean, perhaps making this a more reliable comparison. These concentrations were derived as surface level distributions, and some values are reported as ranges.

Table 42: Concentration of Trace Elements of Interest in Ocean Waters

Element	**Average Concentration (ppm) in Seawater[43, 44, 45,]**	**Average Concentration (ppm) in North Atlantic Ocean Surface[26]**
Al	1×10^{-2}	$4 \times 10^{-4} – 1.1 \times 10^{-2}$
As	3×10^{-3}	1.5×10^{-2}
Ag	4×10^{-5}	N/A
Ba	3×10^{-3}	N/A
Cd	1.1×10^{-4}	$1.1 \times 10^{-7} – 1.1 \times 10^{-6}$
Co	5×10^{-4}	$1.1 \times 10^{-6} – 1.8 \times 10^{-5}$
Cr	5×10^{-5}	1.8×10^{-4}
Cu	3×10^{-3}	$6.4 \times 10^{-4} – 8.3 \times 10^{-4}$
Fe	1×10^{-2}	$2.8 \times 10^{-6} – 5.6 \times 10^{-6}$
Mn	2×10^{-3}	$5.5 \times 10^{-5} – 1.6 \times 10^{-4}$
Ni	2×10^{-3}	1.2×10^{-4}
Pb	3×10^{-5}	$2.1 \times 10^{-5} – 3.1 \times 10^{-5}$
Sr	8	N/A
Ti	1×10^{-3}	$1.4 \times 10^{-6} – 2.9 \times 10^{-6}$
Tl	$<1 \times 10^{-5}$	$1.2 \times 10^{-5} – 1.4 \times 10^{-5}$
Zn	1×10^{-2}	$6.5 \times 10^{-6} – 1.3 \times 10^{-5}$

The concentrations for silver, barium, and strontium were not reported for the North Atlantic Ocean. The averages of the concentrations for the St. Simon's Island samples, as mentioned, are reported in the even numbered tables in Tables 8 – 38. Out of the 16 elements investigated, 15 of these had higher concentrations than the average reported in Table 42. The only element that was found to be present in lower concentrations was strontium. Aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, thallium, titanium, and zinc all had higher concentrations than previously reported studies.

One of the main components of this study, however, was to investigate whether the concentrations of certain elements in seawater differs in samples collected near St. Simon's Island, GA, during and in months leading up to a beach event surrounding the Florida vs. Georgia football game. The samples were collected on 7/31, 8/31, 10/1, and 10/31 of 2014. In order to determine if there is a significant difference in the concentration levels, an independent samples t-test was conducted comparing the concentrations on 7/31 to that of 10/31, and similarly, the concentrations on 8/31 and 10/1 to that of 10/31 using IBM SPSS software. To be considered significantly different at the 95% confidence level, the independent samples t-test must have yielded a t-value greater than 2.45, at six degrees of freedom.[34] The element symbol, tide at which the sample was collected, and date, along with the t-value, are reported in Table 40 for those elements that did have a significant difference from the samples collected on 10/31. The higher the t-value corresponds to the higher the difference in concentration of these samples.

Interestingly, the number of significant differences is highest for the dates furthest away from 10/31. There were more samples with significant differences when the concentrations of 10/31 were compared to that of 7/31, than with any other date. These samples were prepared by another undergraduate researcher, Veronica Hubble (now at North Carolina State University). Differences due to personal lab technique may have resulted. However, this trend continues with the other two sample collections in August and early October. More samples contained significant elemental differences for 8/31 when compared to 10/31 than when 10/1 was compared to 10/31. Thus, more values were statistically different the further away the sample was collected from the main collection date of 10/31. Explanations for this may vary, but could include different events that were going on during the time. During the summer months, since there is a larger crowd present, there may be an increased amount of trash pick-up/clean-up done by the city. During the cooler months, since less people attend the beaches, trash pickup may decrease. Another potential reason for this trend of increased concentration of elements in warmer months may be explained through global warming. According to earth scientist Dr. Julie Kerr Casper, “Global warming hypotheses suggest that ocean evaporation will increase as Earth’s temperature does.”[46] If during higher temperatures, there is increased evaporation, this could lead to a higher concentration of elements to be detected rather than when the ocean is more “diluted”, or in other words, when there is less evaporation occurring.

Overall, however, there does not appear to be a difference from the elemental concentrations of samples collected prior to and during the beach event on 10/31.

Spiked Samples and Gallium Coprecipitation

The other main interest of this study focused on the use of gallium as a coprecipitating agent. Gallium, an amphoteric metallic element, dissolves in aqueous solution at both high and low pH regions.[27] Gallium usually precipitates between pH 5–6 and above pH 9 in seawater.[27] The equilibria and dissociation constants of gallium hydroxide are as given by Equations 11 and 12.[27]

$$Ga(OH)_3\ (s) \leftrightarrow Ga^{3+} + 3OH^- \qquad K = 5x10^{-37} \qquad \text{Eqn. 11}$$

$$Ga(OH)_3\ (s) \leftrightarrow GaO_2^- + H^+ + H_2O \qquad K = 10^{-15} \qquad \text{Eqn. 12}$$

Not only was adjusting the pH to 10 necessary to precipitate the elements, but also to ensure the added gallium would also precipitate. Research conducted at The University of Tokyo found that the gallium coprecipitation method can be efficiently used for trace metal preconcentration in seawater.[27] There was a heavy dependence on a cooperative interaction between gallium and magnesium in order for the precipitate to form.[27] Since the concentration of magnesium in seawater is high (1,272 ppm), enough magnesium was present to form this interaction with gallium.[47] The research failed to discuss why gallium was beneficial to precipitation. Multiple studies have found the use of gallium to be useful for the concentration step, but the details for this is unclear.[7, 27, 48] The spiked samples of synthetic seawater analyzed by ICP-OES and powder-XRD were investigated to determine the chemistry behind this benefit.

The *odd numbered tables* in Tables 9 – 39 indicate the detected concentrations of the elements with and without the use of gallium for RICCA® and Carolina seawaters as determined by ICP-OES. The Top Fin samples all contained gallium. These samples were spiked to a known concentration of 0.1 ppm. Some of these samples have a higher concentration while others have lower concentrations. Furthermore, although some samples had higher concentrations while using gallium, the increase was not consistent as some samples had lower concentrations detected with gallium. From these samples, there is no clear indication that the use of gallium was beneficial.

To further examine this issue, the precipitates were studied by powder X-ray diffraction (powder-XRD). Specifically, the precipitates of Carolina seawater that contained the added gallium were compared to a control Carolina precipitate that did not have the added gallium. The RICCA® water samples also underwent this same analysis with powder-XRD.

Unfortunately, the powder-XRD detected identical major components in both samples of Carolina and RICCA® seawater: aragonite and halite (Figures 5 – 12). These minerals have chemical formulas of $CaCO_3$ and NaCl, respectively. This indicates that the gallium concentration was not high enough to be detected. Interestingly, aragonite and halite are two different types of ionic compound, with NaCl being a salt. As mentioned previously, it was necessary to isolate the elements from the saltwater matrix, however, salts are the major components present in the samples. Furthermore, the samples that contained gallium and did not contain gallium are almost identical in their spectra. When comparing RICCA® and Carolina results, the spectra are almost identical as well as indicated by Figures 11 and 12. Powder-XRD was not sensitive enough to detect the small changes in elemental concentration when large concentrations of seawater matrix are still present. Though the gallium precipitation was supposed to facilitate removal of the matrix, no difference is seen between the two samples. The spectra of these samples as well as the results from the ICP-OES analysis of spiked samples indicates that the use of gallium does not appear to be beneficial during the precipitation process to remove the saltwater components.

Errors in Methodology and Other Possibilities of Errors

There are a variety of factors that could have led to errors in the concentrations that were determined by ICP-OES. The high temperature of the plasma may excite electrons within atoms and form ions that emit radiation at a different wavelength than the one selected. However, this is unlikely as plasma itself serves as an ionization suppressor due to the high concentration of electrons present from the ionization of argon gas, thus pushing the equilibrium of the elements to remain in the unionized form.[29]

Spectral interferences are also a possibility. Elements can emit radiation at hundreds of different wavelengths.[29] Since the number of emission lines for any given element can be enormous, a spectral interference could occur where a different element also emits a line at the same wavelength of another element. Thus, a higher concentration is recorded due to this interfering species. This could lead to a falsely high concentration of an element. Furthermore, due to the high temperatures and increased excitation of the chemical species, there can be a wider range of emitted lines and a higher chance of a spectral interference to occur. For example, a vanadium line at 308.211 nm interferes in the determination of aluminum based on its emission line at 308.215 nm, which is the wavelength that was selected for analysis by ICP-OES.[29] Thus, if any vanadium was present within any of the samples, this could lead to a falsely high concentration of aluminum. This phenomena could occur with any of the wavelengths chosen for the elements.

Another chance of error could be that the standards used for calibration were not prepared in seawater like the rest of the samples. There is a possibility that a substance present in the saltwater matrix affected the determined concentrations of the elements. This could be by forming refractory compounds or altering the elements in some way which yields different emission lines rather than the emission line selected. An internal standard, a substance that responds to uncontrollable variables in the same way as the analyte, could have been added to the standards to correct this.[29] In other words, the standards could have been prepared in such a way to account for this variable. Another factor of potential error, specifically when focusing on the unknown St. Simon’s Island samples, was that the sample “sit” time, or storage time, varied from a few months after collection to up to seven months. After the seawater had spent months in the storage containers, settling of elements may have occurred, or other phenomena could have occurred while in the storage container that altered the concentration. Shaking or mixing the seawater in the storage containers prior to beginning the procedure may have alleviated this problem.

CONCLUSION

The purpose of this study was to investigate if elemental contaminants leached from cigarette litter are significant in samples of seawater collected near St. Simon's Island. The concentrations of elements (Al, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Ag, Sr, Tl, Ti, and Zn) in the seawater samples were determined by ICP-OES. These values were first compared to the safe drinking water levels determined by the EPA and WHO. Out of the 16 elements, arsenic, cobalt, lead, and thallium had higher concentrations than is allowed from the drinking water standards. These concentrations were then compared to the reported known elemental values of elements in seawater, out of the 16 elements investigated, 15 of these had higher concentrations. Strontium was the only element present in lower concentrations.

An independent samples t-test was also conducted to determine if the elemental concentrations on 7/31, 8/31, and 10/1 differed from those on 10/31, which was the weekend of the Florida/Georgia football game beach party. To be considered significantly different at the 95% confidence level, the independent samples t-test must have yielded a t-value greater than 2.45, at six degrees of freedom. While some elements had a t-value of 2.45 or greater, there was not an overall consistent difference in elemental concentrations in these months. Reasons for these differences could include variations in trash pick-up during the warmer and cooler months or changes in temperature.

This project also aimed to explore a gallium coprecipitation methodology for elemental isolation through investigation by the ICP-OES, powder-XRD, and synthetic seawaters, Carolina and RICCA® seawater. The ICP-OES detected that some spiked samples of the synthetic seawater had higher concentrations while using gallium, while the increase was not consistent as some samples had lower concentrations detected with gallium. From these samples, there is no clear advantage as to why the use of gallium was beneficial. Powder-XRD detected identical major components in both of these seawaters, regardless of whether gallium was or was not added. The results gathered from the ICP-OES and powder-XRD indicate that the use of gallium does not appear to be beneficial during the precipitation process to remove the saltwater components.

In conclusion, although the elemental concentrations in seawater did not significantly differ during the Florida/Georgia football game party on St. Simon's Island and previous months, the found concentrations were higher for almost all the elements of interest, except for strontium, when compared to known reported values of elements in the ocean. It is likely that this could be contributed to elemental contaminants leaching from cigarette litter into the seawater. At the annual game weekend in 2012, 5,400 pounds of trash and 500 pounds of recyclables were collected around St. Simon's Island Beach. Among the litter collected were cigarette butts, which is not surprising since 4.5 trillion cigarette butts are littered every year worldwide. The large amount of improperly discarded cigarette litter has the possibility of polluting ocean waters and increasing elemental contamination.

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