

# USE OF GADOLINIUM TO TRACK SEWAGE EFFLUENT THROUGH THE POUGHKEEPSIE, NEW YORK WATER SYSTEM

A Final Report of the Tibor T. Polgar Fellowship Program

Matthew Badia

Marist College Environmental Science and Chemistry Student Researcher  
matthew.badia1@marist.edu

School of Science, Department of Chemistry, Biochemistry, and Physics  
Marist College  
Poughkeepsie, NY 12601

Project Advisors:

Dr. Neil Fitzgerald  
School of Science, Department of Chemistry, Biochemistry, and Physics  
Marist College  
Poughkeepsie, NY 12601  
Neil.Fitzgerald@marist.edu

Christopher Bowser  
New York State Department of Environmental Conservation  
Hudson River National Estuary Research Reserve  
Chris.bowser@dec.ny.gov

Badia, M., N. Fitzgerald, and C. Bowser. 2021. Use of Gadolinium to Track Sewage Effluent Through the Poughkeepsie, New York Water System. Section I: 1-26 pp. *In* D.J. Yozzo, S.H. Fernald, and H. Andreyko (eds.), Final Reports of the Tibor T. Polgar Fellowship Program, 2019. Hudson River Foundation.

## Abstract

There has been an increase in chemical contaminants in waterways around the world, many of which are released from sewage treatment plants which are incapable of removing most chemical contaminants and are released into the environment where they can accumulate. Current methods of wastewater detection include bacterial analysis, nutrient analysis, chloride analysis, and direct detection; however, each have their own flaws. An alternative method involves the use of gadolinium, an element used in MRI procedures. This study investigated the use of gadolinium as a method of wastewater detection compared to enterococci and chloride analysis. Samples were taken from four locations located along Hudson River near Poughkeepsie, NY: a sewage treatment plant, a water quality monitoring station, and the intake and effluent from a water treatment plant, from June to July 2019. Enterococci were analyzed using the IDEXX Enterolert system. Chloride content was determined using the Mohr titration method. Gadolinium was analyzed using Inductively Coupled Plasma Mass Spectrometry. Enterococci analysis demonstrated high values in wastewater and low levels in the water treatment plant effluent. The bacteria levels in open water were inconsistent between location and sample day. Chloride concentrations decreased from the sewer treatment plant to the water treatment plant intake, and increased after water treatment, likely due to the decomposition of sodium hypochlorite. Gadolinium analysis showed a content averaging approximately 500 ng/L in the sewage treatment plant effluent, followed by a drastic decrease in open water and water treatment plant intake, averaging 15 and 29 ng/L respectively, and a final decrease during the water treatment process to an average of 5 ng/L. Gadolinium appears to be as effective as chloride analysis for detecting wastewater. With a single anthropogenic source and low analysis cost, gadolinium has the potential to replace other methods for tracing wastewater in waterways.

## TABLE OF CONTENTS

|                                 |      |
|---------------------------------|------|
| Abstract.....                   | I-2  |
| Table of Contents.....          | I-3  |
| List of Figures and Tables..... | I-4  |
| Introduction.....               | I-5  |
| Methods.....                    | I-9  |
| Results.....                    | I-15 |
| Discussion.....                 | I-20 |
| Conclusion.....                 | I-23 |
| Acknowledgements.....           | I-24 |
| References.....                 | I-25 |

**LIST OF FIGURES AND TABLES**

Figure 1 – Map of sample locations..... I-10

Figure 2 – Enterococci levels throughout the experiment ..... I-16

Figure 3 – Chloride levels for the data obtained by the Mohr method of titration  
..... I-17

Figure 4 – Comparison between the chloride levels and gadolinium levels  
throughout the experimental period ..... I-18

Figure 5 – Comparison of the three methods of wastewater detection..... I-20

## INTRODUCTION

The Hudson River Estuary (HRE) extends from the Battery on Manhattan Island, to the Federal Dam in Troy, New York. The HRE is a vital ecological and economic resource for the state of New York and the surrounding area. The river itself is 315 miles in length with its source at Lake Tear of the Clouds in the Adirondack Mountains, before joining with the Mohawk River at Schenectady, New York. The Hudson River Watershed covers 13,400 square miles, as far east as Vermont, Massachusetts, and Connecticut, and as far south as New Jersey (NYSDEC HREP 2009). The HRE is a vital local resource, providing economic and recreational benefits for thousands. The HRE ecosystem is essential for a multitude of species, including the American Eel and the Atlantic Sturgeon, which is endangered in the Hudson River.

Pharmaceuticals and Personal Care Products (PPCPs) are bio-accumulators, meaning that concentration of the chemical increases in tissues as the chemical moves up the food chain (Stahl 2016). According to the EPA, significant waterways around the country, including the Hudson River, are contaminated with PPCPs, heavy metals, and bacteria (Stahl 2016). A substantial contributor to the contamination of US Waterways is from sewage treatment plants (STPs) (Daughton 2009). PPCPs originate in sewage from the biological waste of people taking pharmaceuticals, or the compound being sent down the drain, either intentionally or unintentionally (Daughton 2009). STPs make efforts to remove contaminants from sewage; however, methods are inadequate for the complete removal of PPCPs and other chemical pollutants (Daughton 2009). Consequently, concentrations of various PPCPs accumulate into the nation's waterways (Daughton 2009).

The sewage treatment process is broken down into two steps. In the first step, waste is passed through a screen which removes large objects that would damage equipment. The waste then passes through a grit chamber where sediment and small stones settle to the bottom. The waste then passes into a sedimentation tank where the velocity of the water decreases to allow finer particulate matter to settle. The second step involves removing much of the organic matter. The primary method of this is aeration and activated sludge. This process uses bacteria to breakdown the organic matter into byproducts. The bacteria and microorganisms are reused and the water is passed onto a disinfecting stage. It is common to use sodium hypochlorite for this process (Daughton 2009).

The water treatment process is more sophisticated than the sewage treatment process. Water treatment begins with a process called flocculation. During this step, a coagulant is added to the water which removes sediments and particulate matter. In many instances, the sediment is collected as sludge and is sold to fertilizer companies. The water then is passed through a series of filters containing gravel, sand, and activated carbon. Water then must be disinfected. In the Poughkeepsie Water Treatment Facility, this disinfection is accomplished in three stages. The first stage, water is exposed to ultraviolet light. A solution of sodium hypochlorite is then added to the water for further sterilization. Finally, ozone is passed through the water as a final step in the disinfecting process. Water throughout the process is routinely sampled for basic water chemistry and sent out for chemical analysis to ensure safe drinking water for the community.

Combined Sewage Overflows (CSOs) also contribute to the presence of pharmaceuticals in urbanized waterways (Rechenburg et al. 2006). CSOs occur during

significant rainfall events when sewer systems become overwhelmed by the volume of water. As a result, the system releases untreated sewage along with the overflow of water into the nearby waterway. During this process, a high concentration of contaminants, including PPCPs and bacteria, is released.

The identification and tracking of these anthropogenic pollutants are imperative in the determination of the potential detrimental effects on human health. Identification of these organic compounds has previously focused on direct quantification using High-Performance Liquid Chromatography (HPLC), Gas Chromatography-Mass Spectrometry (GC-MS), and Liquid Chromatography-Mass Spectrometry (LC-MS). All of these methods require complicated extraction procedures and are expensive.

It is possible to use nutrients as a chemical tracer for wastewater. Nitrate and phosphate are commonly used for this purpose (Katz and Griffin 2008). Both nitrate and phosphate arise from the decomposition of organic matter, including human waste. There are several methods used for the detection of nitrate and phosphate ranging from colorimetric methods to electronic probes. These nutrients have several anthropogenic and non-anthropogenic sources. The two most prominent are runoff from agriculture or municipal land using fertilizer, and from runoff from animal waste. Both of these have the potential of producing increased levels of nitrate and phosphate. This becomes an issue in regions such as the Hudson Valley, which have a large agricultural economy.

Bacteria is a commonly used method of wastewater detection. Enterococci are most commonly used (Wéry et al. 2010). These bacteria, depending on the species, form either symbiotic or pathogenic relationships with humans. In either case, these bacteria can be detected in small quantities in sewage treatment plant effluents as the water

leaving the system is not completely sterile. There are several other sources of enterococci including waterfowl and agricultural animals. As a result, many of the common tests for enterococci detect non-human species.

There are several options for the detection of wastewater using chemical contaminants. Chloride is a popular method for wastewater detection (Wolf et al. 2012). Chloride has several sources in water. In wastewater, chloride can arise from the human diet in the form of sodium chloride, or from water softeners in the form of sodium or potassium chloride. Chloride can also arise from the use of road salt during winter to melt ice. As the ice melts, runoff brings this salt into waterways. Calcium chloride is commonly used in this purpose. Lastly, chloride can appear in waterways as the result of natural decay of sediments. Heavy metals can also be used as a tracer of wastewater; however, many have non-anthropogenic sources.

Gadolinium (Gd) is a rare earth element whose presence in the waterways has been previously reported as negligible. The primary use of gadolinium is as an Magnetic Resonance Imaging (MRI) contrast agent. In the body, gadolinium can enhance the quality of images. These compounds are processed by the kidneys with a half-life of 2 hours. Once in the sewer system, gadolinium functions similarly to other PPCPs and are not broken down by the water treatment process (Verplank et al. 2005). By itself, gadolinium is a toxic heavy metal, but gadolinium (III) can also be encased in an organic molecule called a chelate. These chelates are organic molecules that encase the gadolinium ion to protect the human body from the toxicity. This allows for the nearly 1 gram of gadolinium to pass harmlessly through the human body. Additionally, the chelate can be modified to a certain portion of the body (Caravan et al. 1999).



Recent studies have reported the presence of what is referred to as gadolinium anomalies (Verplank et al. 2005; Caravan et al. 1999; Rabiet et al. 2009; Williams et al. 2013). These anomalies are classified as environmental gadolinium levels higher than expected. Anomalies in the expected presence of gadolinium were first published in 1996 and has since been attributed to the contrast used in MRI. A study conducted in Boulder Creek conducted by Verplank et al. (2005) investigated the chelate itself as opposed to the gadolinium. It was reported that gadolinium chelates are a signature of urban wastewater. Other studies around the world have investigated the impact of municipal water on gadolinium content. These studies have concluded gadolinium anomalies are the result of MRI facilities; however, these studies nearly exclusively focus on surface water, whereas this study focuses on open water, a water treatment plant and a water treatment facility (Verplank et al. 2005; Caravan et al. 1999; Rabiet et al. 2009; Williams et al. 2013).

The goal of this study was to determine the effectiveness of Gd as a tracer for wastewater in the Hudson River. This was accomplished by comparing the results of Gd analysis to the results of chloride and enterococci analysis, two previously accepted methods of wastewater detection.

## **METHODS**

### **Sampling**

Samples were collected from four locations: Arlington Wastewater Treatment Plant, the Hudson River Environmental Conditions Observing Systems (HRECOS) station located at Marist College, and both the intake and the effluent from the Poughkeepsie Joint Water Treatment Facility.



**Figure 1: Map of Sample locations showing the Sewage Treatment Plant (STP), the HRECOS station, the intake of the Water Treatment Plant (WTP in), and the Water Treatment Plant effluent (WTP eff).**

#### Site Characterization

The Poughkeepsie Municipal area is serviced by two sewage treatment facilities, the Arlington Wastewater Treatment Plant and the Poughkeepsie Water Pollution Control Plant. The Arlington Wastewater Treatment Plant services the City and Town of Poughkeepsie. The Poughkeepsie Water Pollution Control Plant, located off of Marist College campus, also serves the Town and City of Poughkeepsie. There are approximately 100,000 residents within the limits of the city and town. The sewer system is designed for each facility to share the sewage from the municipality.

The Arlington Wastewater Treatment Plant serves the approximate 26,000 residents of the Town of Poughkeepsie. While the town does not contain many medical facilities within the town limits, there are as many as eighteen individual MRI facilities within the City of Poughkeepsie. The plant averages a discharge rate of 4.6 million

gallons per day. Samples were taken near the end of the treatment process before water enters the river.

The drinking water plant is jointly owned by the City and Town of Poughkeepsie and the Dutchess Water Authority. The facility serves approximately 100,000 people in the City and Town of Poughkeepsie, the Dutchess County Water Authority, and the Town of Hyde Park, just to the north. The plant produces nearly 9.5 million gallons per day (mgd) of treated drinking water with a maximum capacity of around 11 mgd. The plant is sourced directly from the Hudson River. A pipe submerged 10 meters below the surface of the river located off Longview Park in Poughkeepsie pumps water from the river to the facility located slightly uphill.

HRECOS is a network of near real-time environmental monitoring stations. The network is operated by governmental, academic, and private institutions throughout the Hudson River Watershed. The stations are located from Battery Park in New York City, to the Port of Albany, and along the Mohawk River. The stations are equipped with a variety of sensors that monitor water quality and weather patterns every 15 minutes year-round. This data is freely available to the general public on the HRECOS website. The station located at Marist College is jointly operated by the Cary Institute of Ecosystems Studies, Marist College, and the United States Geological Survey. Unlike most other stations, the Marist College station samples both surface and from a depth of 10 meters in the hyporheic zone. Samples were taken from the hyporheic zone directly from the Marist pump station.

### Sample Collection

Samples were taken from four locations, the Arlington Wastewater Treatment Plant, hereby referred to as the sewage treatment plant, the HRECOS station located at Marist College, referred to as the HRECOS station, and the intake and effluent from the Poughkeepsie Water Treatment Plant. Samples from the sewage treatment plant were taken from the final stage of treatment in the open holding pond by means of a dip-stick. Water samples from the HRECOS station were taken from a holding tub that continuously cycles the sample water. Lastly, the water treatment plant has a sampling lab that samples water directly from various points during the treatment process on tap.

Samples were collected at slack tide, the point at the end of one tide cycle, and the beginning of another where the water does not move in either direction. Five samples were taken at the end of low tide, and five samples were taken at the end of high tide. Extra samples were taken on the last day of sampling and sent for PPCP analysis. Samples were collected in plastic bottles cleaned with dilute nitric acid. Sampling occurred between June and July 2019. The temperature, time of collection, and current weather conditions were recorded.

### Initial Sample Processing

Immediately upon the collection of samples, the pH was measured using a pH probe. Samples were then taken for enterococci analysis. For heavy metal analysis, 30 mL of each sample was filtered at 0.45  $\mu\text{m}$  using vacuum filtration. These samples were then acidified to 1% nitric acid (Thermo Fisher Scientific) in acid cleaned storage vessels. These, and the remaining samples, were refrigerated until analyzed.

### Enterococci Analysis

Enterococci levels were measured using the IDEXX Enterolert system. Enterolert is a US EPA approved method for the detection of enterococci within sewer and water systems. The samples were analyzed immediately after being collected. From each sample, 100 mL was added to the collection vessel along with reagent and shaken. The sample was then added to a Quanti Tray and hermetically sealed. The sample was incubated at  $41 \text{ degrees} \pm 0.5$  for 24 hours. The samples were viewed under UV, and the fluorescing wells counted. For this method, any blue fluorescence was counted as a positive. The total number of bacteria was then estimated using the most probable number of bacteria. A 95% confidence interval was calculated using the most probable number calculator provided by IDEXX. Enterolert detects a variety of species including *E. faecalis*, *E. faecium*, *E. avium*, *E. gallinarum*, *E. casseliflavus*, and *E. durans* among other species acknowledged, but not listed by the manufacturer. Enterolert is not capable of detecting individual species of bacteria (IDEXX 2019).

### Chloride Analysis

Chloride content in samples was measured by a Mohr Method of Titration. This method involves two steps, a standardization method, then the analysis of each sample. This is a crude but effective method for the detection of chloride and other halides in water samples by the titration of the sample against silver nitrate with potassium chromate. Solutions of 0.0141 M silver nitrate (Ward's) and 0.25 M potassium chromate (Thermo Fisher Scientific) were prepared. For standardization, 0.0200 g sodium chloride (Sigma Scientific) was dissolved in 100 mL of deionized water. To this solution, 1.0 mL of the potassium chromate was added. This solution was titrated against the solution of

silver nitrate. This process was repeated until two values were achieved with less than a 1% difference. The endpoint was reached when the color of the solution changed from bright yellow to a deep orange. From this, the concentration of silver nitrate was calculated from the average volume of silver nitrate used as follows:

$$Molarity AgNO_3 = \frac{\frac{Weight NaCl (g)}{58.449 \frac{g}{mol}}}{Volume AgNO_3 (L)}$$

Exactly 100.00 mL of each sample was taken and the pH was adjusted to between 7-10. To this solution, 1.0 mL of the potassium chromate was added, and the solution was titrated against the now known concentration of silver nitrate. The endpoint is reached when the solution changes color from yellow to orange. The total concentration of chloride was then be calculated from the total volume of silver nitrate calculated as follows:

$$M_{Ag^{2+}}(V_{AgNO_3}) = mol_{Ag^{2+}} = mol_{Cl^{-}}$$

$$mol_{Cl^{-}} * 35.45 \frac{g}{mol} = g Cl^{-}$$

$$g Cl^{-} * 1000 = mg Cl^{-}$$

$$\frac{mg Cl^{-}}{0.1 L} = \frac{mg}{L} Cl^{-}$$

### Gadolinium Analysis

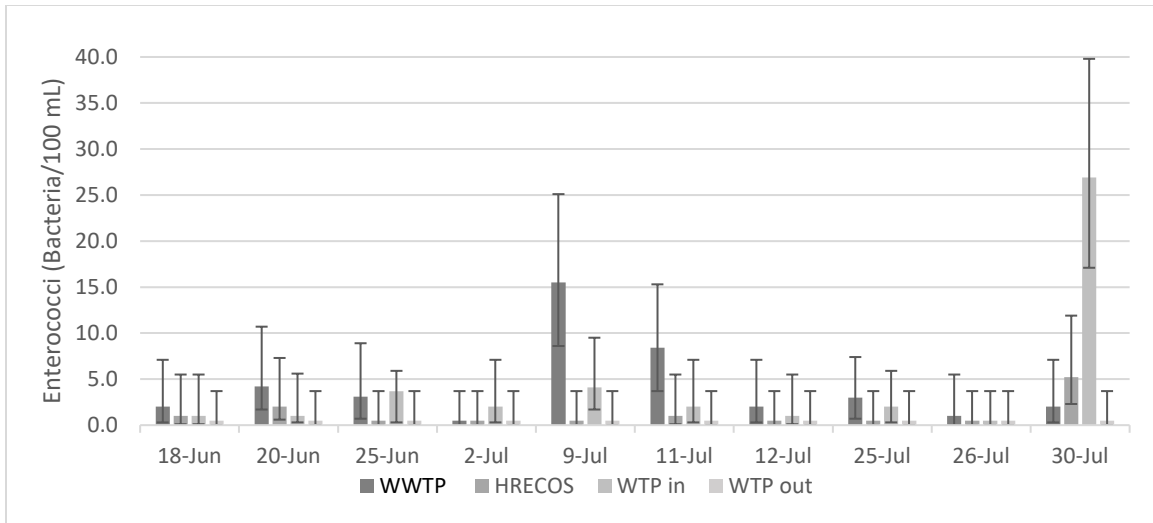
Gadolinium standards were made in concentrations of 1, 2, 10, 100, and 500 ng/L (ppt) (SPEX CertiPrep). Standards were made in deionized water and acidified to 1% nitric acid. Gadolinium analysis was conducted using Inductively Coupled Plasma Mass

Spectrometry (ThermoScientific iCap RQ). The analysis was conducted with Terbium as a reference. Samples were run against a 1% nitric acid blank.

## **RESULTS**

### Enterococci

In general, enterococci content varied between sample date and location. Figure 2 shows the enterococci levels with the 95% confidence intervals determined experimentally by IDEXX. Most of the sampling dates demonstrated the highest level of enterococci at the sewage treatment plant, with an average of 4.2 bacteria per 100 mL of sample. The bacteria levels for the HRECOS station and the water treatment plant intake were similar, consistent with predictions given the proximity of the two sampling locations with an average of 1.2 and 4.4, respectively. There were, on occasion, variations to this pattern where the difference between the level of bacteria in the HRECOS station and the WTP intake was significant, these differences were inconsistent. Consistently over the sampling period, no bacteria were detected in the effluent of the water treatment plant. The highest recorded bacteria level was seen on the final day of sampling at the WTP intake reading at approximately 26 bacteria per 100 mL of sample, far higher than any of the other samples.

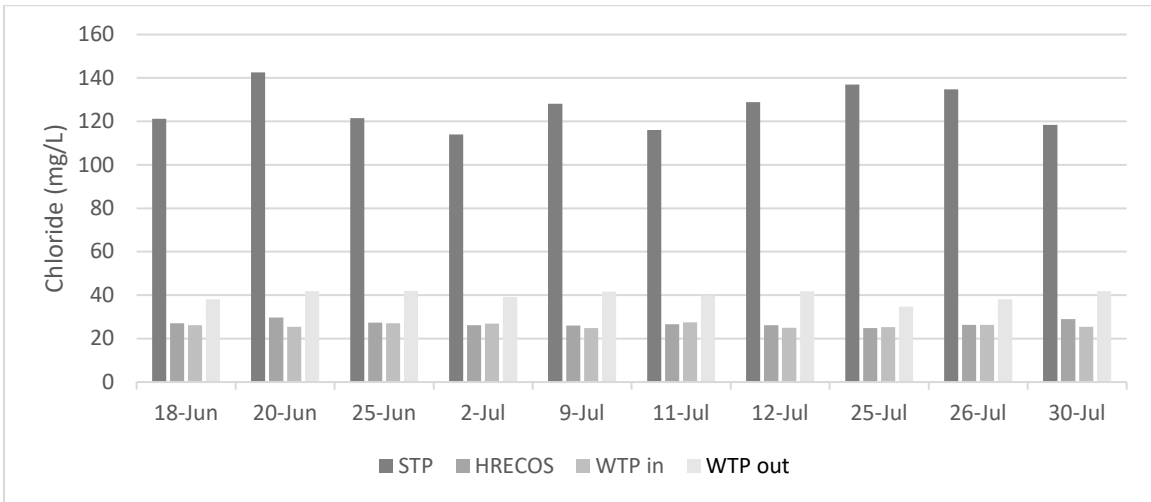


**Figure 2: Enterococci levels throughout the experiment. The bacteria level is measured in the number of bacteria per 100 mL seen on the primary vertical axis. The primary horizontal axis shows the date of sample collection. From left to right on a given sample day, the bars can be read as the sewer treatment plant, the HRECOS station, the water treatment plant intake, and the water treatment facility effluent. The error bars represent a 95% confidence interval provided by IDEXX.**

Chloride levels followed a more predictable pattern throughout the sampling period shown in Figure 3. The data shows a trend of periodic fluctuations in chloride content; however, the sampling period is too small and too widespread over the summer to conclude a potential pattern. The highest levels of chloride were seen on the second day of sampling. This appeared to correspond to an increase in chloride for all four sampling locations on June 20<sup>th</sup>. The highest levels of chloride were seen in the sewer treatment plant with an average of 126 mg/L. This is followed by relatively consistent levels of chloride in the HRECOS station and the water treatment plant intake with an average of 26.9 and 26.0 mg/L, respectively. A slight increase in the chloride levels was detected with an average of 39.9 mg/L in the water treatment plant effluent. In general, the data follow the predicted pattern, despite the increase in chloride after the water



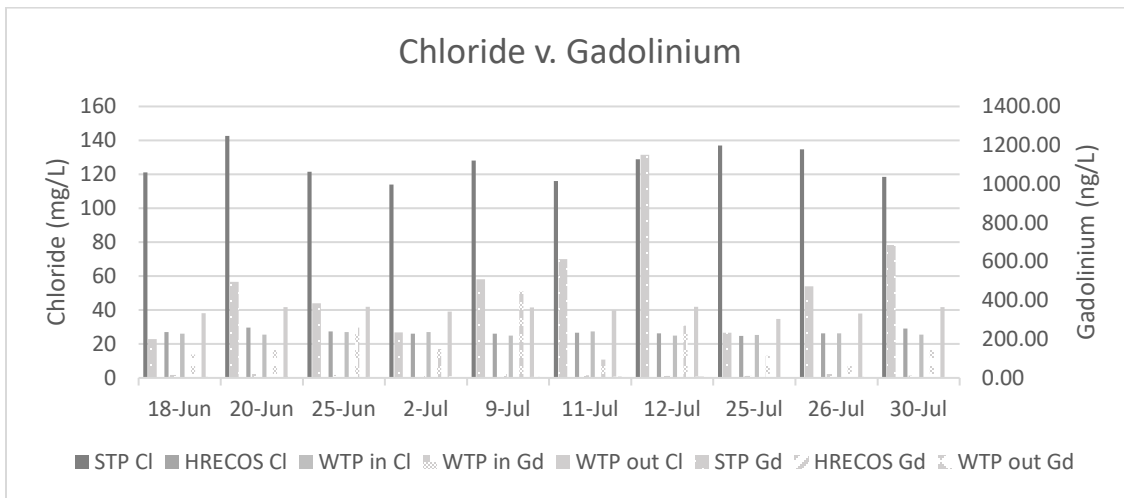
treatment process. It is anticipated these unusual values are due to the addition of sodium hypochlorite during the water treatment process.



**Figure 3: Chloride levels for the data obtained by the Mohr method of titration. The primary vertical axis shows the chloride levels measured in mg/L. The primary horizontal axis shows the date of sample collection. From left to right on a given sample day, the bars can be read as the sewer treatment plant, the HRECOS station, the water treatment plant intake, and the water treatment facility effluent.**

Figure 4 shows a graph of chloride content measured in mg/L and gadolinium measured in ng/L, or parts per trillion. The purpose of this graph is to compare the effectiveness of the novel method, gadolinium, to the known method of detection, chloride. In general, gadolinium content appears to show a similar pattern as chloride. Gadolinium content is consistently the highest in the sewer treatment plant effluent. The concentration then decreases at the HRECOS station and the water treatment plant intake. Unlike chloride, gadolinium levels appear to be more variable between the HRECOS station and the water treatment plant intake. The gadolinium levels then decrease significantly during the water treatment process. The highest level of gadolinium was detected from the sewer treatment plant on July 12<sup>th</sup> with a concentration of 1150.96

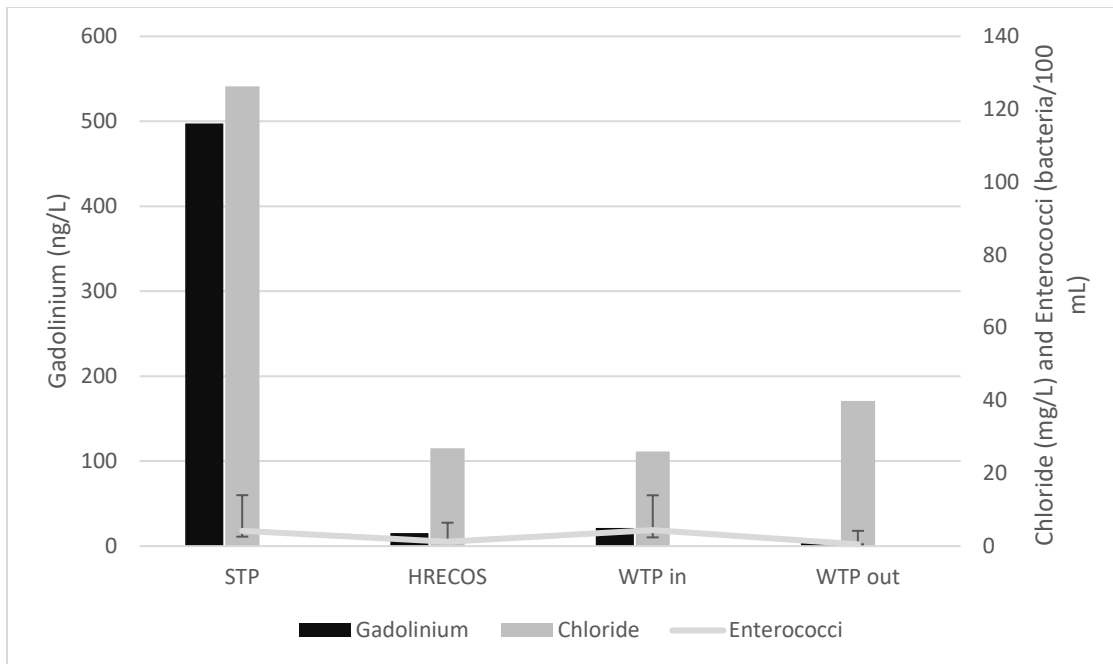
ng/L. This is much higher than the next highest level which occurred on July 11<sup>th</sup> at 613.11 ng/L. The maximum values in the HRECOS station was 19.84 ng/L on July 9<sup>th</sup> and the water treatment plant was 50.95 ng/L on July 9<sup>th</sup>. The lowest concentration of gadolinium was found in the water treatment plant effluent on July 25 with a concentration of 3.75 ng/L.



**Figure 4:** Comparison between the chloride levels and gadolinium levels throughout the experimental period. The primary vertical axis shows the chloride content measured in mg/L. The secondary vertical axis shows the gadolinium content in ng/L. From left to right on a given sample day, the bars can be read as the sewer treatment plant chloride and the sewer treatment plant gadolinium, the HRECOS station chloride and the HRECOS gadolinium, the water treatment plant intake chloride and the water treatment plant gadolinium, and the water treatment facility effluent chloride and water treatment facility effluent gadolinium.

Figure 5 shows a graph of the average gadolinium, chloride, and enterococci content. This graph shows the effectiveness of gadolinium as a tracer compared to the two accepted methods of detection for wastewater. The graph demonstrates changes in gadolinium that correspond to changes in chloride. Gadolinium appears to have a much

larger dilution factor in open water than chloride. Gadolinium concentrations in the sewer treatment plant average 497.61 ng/L. This value is diluted in open water to an average of 15.19 ng/L at the HRECOS station and 21.39 ng/L at the water treatment plant intake. This is in comparison to an average of 15.91 ng/L in the HRECOS station and 21.39 ng/L in the water treatment plant intake. This is compared to an average chloride value of 126.23 mg/L in the sewer treatment plant which was only diluted to an average of 26.91 mg/L in the HRECOS station and 26.0 mg/L in the water treatment plant intake. This may simply be due to the naturally higher levels of chloride in the Hudson River. Additional discrepancies between gadolinium and chloride were seen at the water treatment plant effluent. Gadolinium levels further decrease during the treatment process to an average of 5.9 ng/L; however, chloride levels increased to 39.89 mg/L after the water treatment process. This increase is believed to be due to the water treatment process.



**Figure 5:** Comparison of the three methods of wastewater detection used in this study. The average of each measure was taken for the individual sampling locations. Gadolinium and chloride content are shown as bars whereas enterococci levels are shown as a line. The error bars represent the average 95% confidence interval for each measurement. The primary vertical axis shows the gadolinium content at each location measured in ng/L (ppt). The secondary vertical axis shows the chloride content measured in mg/L and enterococci levels, measured in bacteria/100 mL. The horizontal axis shows the four sampling locations in order of appearance on the river, the sewer treatment plant, the HRECOS station, the water treatment plant intake, and the water treatment plant effluent.

## DISCUSSION

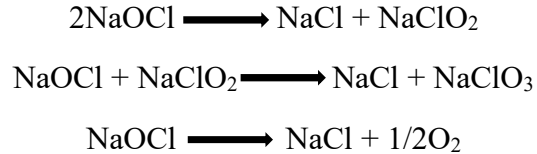
The main issue with the use of enterococci analysis is the broad range of species for which this test targets. There is a total of six species listed on the manufacturer's website, including *E. faecalis*, *E. faecium*, *E. durans*, *E. gallinarum*, *E. casseliflavus*, *E. avium* (IDEXX 2019). *E. faecalis* and *E. faecium* are commonly found in the human microbiome (Lebreton et al. 2014). *E. durans* is frequently seen as a pathogen in foals,

calves, piglets, and puppies (Orsini and Divers 2014). *E. gallinarum* and *E. casseliflavus* are both suspected to be pathogenic in humans and other mammals (Patel et al. 1993). Lastly, *E. avium* is most commonly found in the digestive tract of a variety of species of birds (Monticelli et al. 2018). Many of these species can also be found in symbiosis or as pathogens in a wide variety of species of both mammals and birds. Of all the species, only two are usually found in the human microbiome, while two other species are found in common animals. As a result, it is possible many of the positives represent bacteria that are not a result of human activity. For instance, agriculture is vital to the economy of the Mid-Hudson Valley. Dutchess County is ranked number one in the state for the number of horses, a host of several species of enterococci (Dutchess County Government 2019). Additionally, there is a Canada Geese population of 200,000 within New York State (NYSDEC 2019), many of which are located around major bodies of water including the Hudson River. The fecal matter of these animals, domestic and wild, may contain various species of enterococci, many of which are detectable by IDEXX Enterolert. Therefore, it is possible many of the bacteria seen in this study did not originate from humans, but rather animals.

In general, the chloride data follows the expected pattern of the highest values seen in the sewer treatment facility, followed by lower levels located at the HRECOS station and the water treatment plant intake. The higher levels of chloride seen in the water treatment plant effluent were initially confounding. After further research, it was determined the rise in chloride levels were most likely due to the spontaneous decomposition of bleach which is added as a part of the water treatment process. Sodium hypochlorite will spontaneously react with itself to form sodium chloride, oxygen gas,

sodium chlorate, and small amounts of sodium chlorite. It is predicted this level of sodium chloride that is formed is enough to increase the total chloride content in the water treatment plant effluent. While these levels of chloride are elevated, it is important to note water will not begin to taste salty until a chloride content of approximately 180 mg/L.

The average gadolinium content, when compared to chloride, demonstrates its potential effectiveness as a tracer. Gadolinium levels were found to be the highest in the sewer treatment plant, which was expected as samples from this site should have unaltered levels of gadolinium straight from the source. The large dilution of gadolinium seen from the sewer treatment plant and the HRECOS station and the water treatment plant intake. Once leaving the sewer treatment facility, any contaminants will be homogenized throughout the river due to the sheer volume of the Hudson. It appears that there is a near 30-fold dilution of gadolinium concentration between the STP and the open water; however, there is an apparent lower dilution factor for chloride. The differences in the dilution factors between gadolinium and chloride suggests chloride is more abundant in the Hudson River than gadolinium. Lastly, in regards to the water treatment plant, there are discrepancies in the chloride levels. Chloride levels unexpectedly increased during the water treatment process. The water treatment involves the addition of sodium hypochlorite, bleach (Church 1994). Bleach can undergo spontaneous reduction with three pathways proposed in figure 5 (Lister 1956). In each pathway, sodium chloride is produced which is detectable by the Mohr Method.



In contrast to the increase in chloride, gadolinium concentrations in the water treatment plant effluent decreased during the treatment process. This can be attributed directly to the water treatment process. During the flocculation step of the water treatment process, a flocking agent is added as noted previously to help facilitate the settling of sediments from the water. The sludge is then collected and can be sold as fertilizer. Chemical analysis from the Poughkeepsie Water Treatment Facility shows higher concentrations of heavy metal such as aluminum, copper, and zinc, higher in sludge than in the effluent. It is expected gadolinium will follow a similar pattern as other heavy metals, settling out of solution with sediment and ending up with the sludge. This may produce issues with the selling of the sludge. High heavy metal concentrations could prove dangerous when used with agricultural crops, or could pollute the environment. The Poughkeepsie Water Treatment Plant does not have this issue and regularly checks for contaminants and the sludge is regarded as safe.

## CONCLUSION

Several organic gadolinium complexes are used as a contrasting agent in MRI procedures. These complexes enhance imaging power of MRI procedures. Gadolinium complexes are extremely stable and are not broken down by the sewer treatment process. This allows for the potential of gadolinium to be used as a tracer for sewage in areas with high urban density, or with populations that utilize MRI facilities. This study suggests gadolinium is as effective as other methods of detection. Gadolinium levels within the

study area change in a similar fashion as chloride. Levels of both gadolinium and chloride are the highest within sewer treatment facilities. These levels decrease significantly in the open water of the Hudson River. Lastly, gadolinium levels appear to decrease during the water treatment process. Results from this and other studies suggest the efficacy of gadolinium as a tracer of municipal wastewater. The data suggests a positive gadolinium anomaly in the Hudson River. By sampling various points between a sewage treatment plant and a drinking water path, the gadolinium anomaly was traced to wastewater. Unlike other methods of detection, gadolinium has a single anthropogenic source. Chloride has several sources including water softeners, road salt, and the natural salt front in tidal estuaries such as the Hudson. The only anthropogenic source for gadolinium is sewage treatment plants. Further work needs to be conducted to confirm the effectiveness of gadolinium as a tracer for sewage not only in open water, but through water treatment systems. This study was conducted over a short period of time in a specific circumstance where the primary sewer treatment plant is located relatively close to the primary water treatment facility.

### **ACKNOWLEDGEMENTS**

Special thanks go to the Tibor T. Polgar Fellowship and the Hudson River Foundation for funding. Dr. Raymond Kepner of Marist College for the use of his laboratory for microbial analysis. Dr Allison Spodek and Karen Wovklich of Vassar College for the use of their ICP-MS for analysis. Lastly, thanks go to Steve Segna of the Arlington Sewer Treatment Plant and Dottie DiNobile of the Poughkeepsie Water Treatment for their assistance in sample acquisition.



## REFERENCES

- Caravan, P., J.J. Ellison, T.J. McMurry, and R.B., Lauffer. 1999. Gadolinium (III) chelates as MRI contrast agents: structure, dynamics, and applications. *Chemical Reviews* 99:2293-2352.
- Church, J.A. 1994. Kinetics of the uncatalyzed and copper (II)-catalyzed decomposition of sodium hypochlorite. *Industrial & Engineering Chemistry Research* 33: 239-245.
- Daughton, C.G. 2009. "Introduction to Pharmaceuticals and Personal Care Products (PPCPS)" United States Department of Environmental Protection (USEPA). [https://cfpub.epa.gov/si/si\\_public\\_record\\_report.cfm?Lab=NERL&TIMSType=&count=10000&dirEntryId=142077&searchAll=&showCriteria=2&simpleSearch=0&startIndex=20001](https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&TIMSType=&count=10000&dirEntryId=142077&searchAll=&showCriteria=2&simpleSearch=0&startIndex=20001) (accessed December 16, 2019).
- Dutchess County Government 2019. Dutchess County Government. Retrieved from <https://www.dutchessny.gov/>.
- IDEXX. 2019. Retrieved from <https://www.idexx.com/en/water/water-products-services/enterolert/>
- Katz, B.G., and D.W. Griffin. 2008. Using chemical and microbiological indicators to track the impacts from the land application of treated municipal wastewater and other sources on groundwater quality in a karstic springs basin. *Environmental Geology* 55: 801-821.
- Lebreton, F., R.J. Willems, and M.S. Gilmore. 2014. Enterococcus diversity, origins in nature, and gut colonization. Enterococci: from commensals to leading causes of drug resistant infection [Internet]. Massachusetts Eye and Ear Infirmary.
- Lister, M.W. 1956. Decomposition of sodium hypochlorite: the catalyzed reaction. *Canadian Journal of Chemistry* 34: 479-488.
- Monticelli, J., A. Knezevich, R. Luzzati, and S. Di Bella. 2018. Clinical management of non-faecium non-faecalis vancomycin-resistant enterococci infection. Focus on *Enterococcus gallinarum* and *Enterococcus casseliflavus/flavescens*. *Journal of Infection and Chemotherapy*: 24 237-246.
- New York State Department of Environmental Conservation (NYSDEC). 2019. Nuisance Canada Geese. Retrieved from <https://www.dec.ny.gov/animals/7003.html>.
- New York State Department of Environmental Conservation Hudson River Estuary Program (NYSDEC HREP). 2009. Hudson River Watershed Map. Retrieved from <https://www.dec.ny.gov/education/63069.html>.

- Orsini, J.A., and T.J. Divers. 2014. *Equine emergencies: treatment and procedures*. Elsevier Saunders, St. Louis, MO.
- Patel, R., M.R. Keating, F.R. Cockerill III, and J.M. Steckelberg. 1993. Bacteremia due to *Enterococcus avium*. *Clinical Infectious Diseases* 17: 1006-1011.
- Rabiet, M., F. Brissaud, J.L. Seidel, S. Pistre, and F. Elbaz-Poulichet. 2009. Positive gadolinium anomalies in wastewater treatment plant effluents and aquatic environment in the Hérault watershed (South France). *Chemosphere* 75: 1057-1064.
- Rechenburg, A., C. Koch, T. Claßen, and T. Kistemann. 2006. Impact of sewage treatment plants and combined sewer overflow basins on the microbiological quality of surface water. *Water Science and Technology* 54: 95-99.
- Stahl, L. 2016. Pilot Study of Pharmaceuticals and Personal Care Products in Fish Tissue. Retrieved September 19, 2016, from <https://www.epa.gov/fish-tech/pilot-study-pharmaceuticals-and-personal-care-products-fish-tissue>
- Verplank, P.L., H.E. Taylor, D.K. Nordstrom, and L.B. Barber. 2005. Aqueous stability of gadolinium in surface waters receiving sewage treatment plant effluent, Boulder Creek, Colorado. *Environmental Science & Technology*. 39: 6923-6929.
- Wéry, N., C. Monteil, A.M. Pourcher, and J.J. Godon. 2010. Human-specific fecal bacteria in wastewater treatment plant effluents. *Water Research* 44: 1873-1883.
- Williams, M., A. Kumar, C. Ort, M.G. Lawrence, A. Hambly, S.J. Khan, and R. Kookana. 2013. The use of multiple tracers for tracking wastewater discharges in freshwater systems. *Environ. Monit. Assess.* 185: 9321-9332.
- Wolf, L., C. Zwiener, and M. Zemann. 2012. Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks. *Science of the Total Environment* 430: 8-19.