Development of a DART-Mass Spectral Database for 3D-Printed Firearm Polymers, and Airborne Mercury at Three Lakes in North Mississippi

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DEVELOPMENT OF A DART-MASS SPECTRAL DATABASE FOR 3D-PRINTED FIREARM POLYMERS, AND AIRBORNE MERCURY AT THREE LAKES IN NORTH MISSISSIPPI

By

Parker Riley Ball

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College

Oxford

May 2019

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Reader: Dr. Nathan Hammer
ACKNOWLEDGEMENTS

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Finally, I would like to thank my friends and family for their constant support. They have helped me more than they know.
ABSTRACT

This research focuses on two studies: a development towards a DART-mass spectral database for 3D-printed firearm polymers, and a test for airborne mercury concentrations at three lakes in North Mississippi. With the relatively recent developments in 3D-printing technology, 3D-printed firearms have become increasingly prevalent as they have become more accessible to the public. Despite its growing popularity, little research has been done regarding the forensic analysis of evidence from 3D-printed firearms. Using DART-MS in conjunction with thermal desorption techniques, we obtained the mass spectra for 50 different commercially available 3D-printing polymers. Chemometric analysis was done to account for the high variance among DART-MS data for polymer samples. By generating multiple principal component analysis plots, the high dimensionality of the DART-MS data was greatly reduced, allowing us to successfully classify the samples by polymer type. Samples were then further classified by manufacturer and by color. By doing this, we have made the first contribution toward a database of polymer spectra, which can be used to help identify and find the source of unknown 3D-printed firearm-related crime evidence.

The second portion of this research was done in response to an advisory from the Mississippi State Department of Health suggesting that fish in Grenada and Enid Lakes held high concentrations of mercury, a toxic heavy metal. In this study, we measured the atmospheric mercury concentrations at Grenada, Enid, and Sardis Lakes using Mercury Passive Air Samplers, each containing an activated carbon powder to adsorb gaseous mercury. After deploying the samplers and allowing atmospheric mercury to accumulate over time, the samplers were taken back to the lab, where the mercury concentration for
each sample was obtained using a Direct Mercury Analyzer. This was done for one-week, two-week, three-week, and four-week intervals. Though we hypothesized that point sources near Grenada Lake would result in it having the highest atmospheric mercury concentrations, with Enid Lake having the second highest and Sardis Lake having the lowest, our results suggested the opposite. While we suspect this to have been a result of the proximity to industrial areas north of the lakes, the reasons remain unclear, and further research is needed.
Table of Contents

ACKNOWLEDGEMENTS ............................................................................................................. iii
ABSTRACT ................................................................................................................................. iv
LIST OF FIGURES ..................................................................................................................... vii
LIST OF TABLES ......................................................................................................................... viii

CHAPTER 1: 3D-PRINTED FIREARMS ...................................................................................... 1
  1.1 Introduction ....................................................................................................................... 1
      1.1.1 Prevalence of 3D-Printed Firearms ............................................................................. 1
      1.1.2 DART-MS .................................................................................................................. 2
      1.1.3 Chemometric Analysis .............................................................................................. 3
      1.1.4 Prior Research and Purpose of this Study ................................................................. 3
  1.2 Materials and Methods .................................................................................................... 4
      1.2.1 3D-Print Polymer Samples ....................................................................................... 4
      1.2.2 Analysis of 3D-Print Polymers by DART-MS ............................................................ 6
      1.2.3 Application of Chemometrics to Mass Spectra ......................................................... 8
  1.3 Results and Discussion .................................................................................................... 9
      1.3.1 Thermal Desorption DART-MS vs Direct ................................................................. 9
      1.3.2 Chemometric Clustering .......................................................................................... 11
      1.3.3 Identification of Polymers ......................................................................................... 15
  1.4 Conclusion ....................................................................................................................... 17

CHAPTER 2: Airborne Mercury ................................................................................................. 18
  2.1 Introduction ....................................................................................................................... 18
      2.1.1 Mercury and its Sources ........................................................................................... 18
      2.1.2 Prior Research and Purpose of this Study ............................................................... 19
  2.2 Materials and Methods ................................................................................................... 20
      2.2.1 Sampling Sites and Deployment .............................................................................. 20
      2.2.2 Mercury Passive Air Samplers ............................................................................... 22
      2.2.3 Background on the Analytical Instrumentation Used ............................................. 24
  2.3 Results and Discussion .................................................................................................. 25
  2.4 Conclusion ....................................................................................................................... 28

REFERENCES .......................................................................................................................... 29
LIST OF FIGURES

Figure 1: DART-MS Schematic .................................................................2
Figure 2: Plastic Sample Display ..................................................................6
Figure 3: Direct Analysis of Polymer by DART ................................................7
Figure 4: Thermal Desorption DART interface ................................................7
Figure 5: DART-MS to TD-DART-MS Comparison .........................................10
Figure 6: Thermal Desorption 3D Plot ..........................................................11
Figure 7: PCA Plot of TD-DART-MS data ....................................................13
Figure 8: PCA Plot of DART-MS data ..........................................................13
Figure 9: PCA Plot- ABS by Color ..............................................................14
Figure 10: PCA Plot- ABS by Manufacturer ..................................................14
Figure 11: Positive Identification- Sample 48 ...............................................16
Figure 12: Positive Identification- Sample 44 ...............................................16
Figure 13: Mississippi Map .......................................................................19
Figure 14: Setup at Enid Lake ..................................................................21
Figure 15: Setup at Grenada Lake ..............................................................22
Figure 16: MerPas Sampler Components .....................................................23
Figure 17: Photo of DMA .....................................................................24
Figure 18: DMA Schematic .....................................................................25
Figure 19: Graph of Results ....................................................................27
LIST OF TABLES

Table 1: 3D-Print Polymers Analyzed by DART-MS..........................................................5
Table 2: TD-DART-MS Parameters (JEOL, Peabody MA)..................................................8
Table 3: DART-MS Parameters (University of Mississippi) ..............................................8
Table 4: Total Mercury Levels and Concentrations Over Time .........................................26
CHAPTER 1: DEVELOPMENT OF A DART-MASS SPECTRAL DATABASE
FOR 3D-PRINTED FIREARM POLYMERS

1.1 Introduction

1.1.1 Prevalence of 3D-Printed Firearms

The threat of 3D-printed firearms has become increasingly evident in recent years. With recent technological advancements and growth in the 3D-printing market, it has now become easier for people to self-manufacture their own firearms, avoid the proper licensing and registration, and potentially bypass current security measures such as metal detectors. Availability of these firearms is evident in the ongoing federal effort to combat Defense Distributed, a nonprofit organization that has gained much publicity since 2013 for distributing downloadable 3D-printed gun models online for free. In addition, these particular firearms can be created without a serial number, which would keep it from being traced. To exacerbate the matter, news stories have told of an association of 3D-printed guns with drug and gang-related crimes outside of the United States, signifying that this has become an issue on a global scale (Black and Cizdziel, 2019).

Note: The forensic research involving DART-MS and 3D-printed polymers was a partnership with graduate student Oscar Black; my role was primarily data analysis and interpretation.
1.1.2 DART-MS

Direct analysis in real time - mass spectrometry (DART-MS) is an analytical technique used to obtain mass spectra under ambient conditions, ionizing a sample instantly with little to no sample preparation. With a DART ion source, a gas, He or N₂, passes through a discharge chamber where an electric current is applied to generate a glow discharge, producing excited neutral chemical species called metastables. A perforated electrode removes ions from the gas stream as it travels through a second chamber. In a third chamber, the gas is then heated, and the sample is ionized by reacting with the metastables and causing desorption. By using DART in tandem with a mass spectrometer, the system can then utilize a chemical’s unique ionization and fragmentation patterns in order properly identify a sample. A general schematic for DART can be seen in Figure 1 (Cody et al., 2005).

![Figure 1: A schematic diagram of a DART ion system (Credit: Dr. Chip Cody)](image)

DART-MS is also nondestructive, allowing for the analyzed trace evidence to be stored and reused for further analysis, a useful advantage in the forensic field. Due to the “fingerprint” mass spectra obtained with this method, DART-MS has been applied to multiple forensic investigations, including the identification of controlled substances and
trace evidence analysis, as well as several others (Cody et al., 2005; Lesiak and Shephard, 2014; Laramée et al., 2007).

1.1.3 Chemometric Analysis

Multivariate analysis is a necessary tool for finding relationships over the multiple variables between chemically complex samples and spectra. Chemometric analysis offers a means of converting chemical information into more comprehensive digital data, and principal component analysis (PCA) is a form of multivariate analysis that reduces the dimensionality of samples that range over many different chemical variables. These methods allow one to project data of high dimensionality into a two- or three-dimensional matrix. PCA utilizes data cluster analysis, in which a set of data objects of similar quality are placed in a group, or a cluster, closer together on a plot than the more dissimilar data objects. This provides a statistical analysis that can allow one to find the source for a particular sample being tested (Houck, 2015).

1.1.4 Prior Research and Purpose of this Study

Though the prevalence and potential threat of 3D-printed firearm crimes have steadily increased, not much scientific research has been done to develop forensic investigation methods for these firearms. In addition, though many forensic applications for DART-MS have been established in recent years, little research has been done to apply this method to gunshot residue and other trace evidence from firearms.

The purpose of the current study was to analyze the chemical composition of various plastic samples often used for 3D-printing using direct analysis in real time – mass spectrometry (DART-MS). Specific objectives were to obtain the mass spectra for
50 different samples at varying temperatures and classify them using principal component analysis (PCA). This information can then contribute to the creation of a forensic database, which will play a crucial part in criminal investigations. Given a situation in which a 3D-printed firearm was used in a crime, an unknown residue sample can be collected and compared to this database in order to potentially identify the specific plastic particle found using chemometric analysis. By matching distinguishable qualities between the sample and the known reference data, one may be able to ascertain the source of a particular polymer, thus narrowing the potential suspect pool through purchase history (Black, 2019).

1.2 Materials and Methods

1.2.1 3D-Print Polymer Samples

Samples from 50 different plastics (varying in brand, color, etc.) were obtained from the University of Mississippi Center for Manufacturing Excellence and analyzed using a DART-MS at the JOEL laboratory in Peabody, Massachusetts. The main polymer types among the samples, polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate glycol (PETG), and nylon, were chosen due to their strong prevalence in the 3D-printing market, allowing us to adequately replicate the trace evidence potentially obtained in a 3D-printed firearm case. Manufacturers for the polymer samples include Makergeeks, Matterhackers, Matterhackers, Ninjaflex, Hatchbox, Flashforge, Makeshaper, Ultimaker, and ESUN, as well as several others. All sample names are listed in Table 1, and a polymer display is provided in Figure 2.
<table>
<thead>
<tr>
<th>PLA</th>
<th>ABS</th>
<th>PETG</th>
<th>Miscellaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.</td>
<td>31. Makeshaper Blue</td>
<td>16. Hatchbox Blue</td>
<td>35. nGen Black Copolyester</td>
</tr>
<tr>
<td>5.</td>
<td>32. Matterhackers White</td>
<td>18. Makeshaper Grey</td>
<td>38. HT copolyester</td>
</tr>
<tr>
<td>8.</td>
<td>37. IC3D Blue</td>
<td>34. ESUN Red</td>
<td>40. Yoyi Black Flexible Filament 7</td>
</tr>
<tr>
<td>9.</td>
<td>48. 3D-Universe White</td>
<td>46. Matterhackers Green</td>
<td>41. GizmoDorks Black Carbon Fiber</td>
</tr>
<tr>
<td>10.</td>
<td>43. Filament Express Black ASA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Makeshaper Orange</td>
<td>44. Taulman Natural Nylon 645</td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>ESUN Silver</td>
<td>45. Verbatim White BVOH</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Matterhackers Gold</td>
<td>49. Lulzbot Natural Bridge Nylon</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>Makeshaper White</td>
<td>50. Taulman Natural Bridge Nylon</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>ESUN Brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>Matterhackers White</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>Makeshaper Black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.</td>
<td>Matterhackers Blue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.</td>
<td>Makerseries Black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>Makeshaper Blue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.</td>
<td>Ultimaker Silver</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.</td>
<td>Makeshaper Blue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.</td>
<td>ColorFabb Woodfill</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.</td>
<td>Ultimaker Clear</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2: A display including 30 of the plastic samples analyzed for this study

1.2.2 Analysis of 3D-Print Polymers by DART-MS

The following method using DART-MS and chemometric application was in collaboration with Oscar Black et al. (2019). Samples were analyzed both directly by DART-AccuTOF (Figure 3) and by using a Biochromato IonRocket Thermal Desorption (TD) unit paired with the DART-AccuTOF (Figure 4). For TD-DART-MS analysis, portions (approximately 1 mm) of each of the 50 polymers was cut with a scalpel and placed in the TD well of the IonRocket. A glass T-junction was used to direct the vaporous decomposition products of the polymers into the heated DART stream (Figure 4). Direct analysis was done for 34 of the samples as well, samples of approximately 1 cm each were held directly in the DART beam using forceps. Parameters for TD-DART-MS and DART-MS are shown in Table 2 and Table 3, respectively.
Figure 3: Direct analysis of 3D-Print Polymer

Figure 4: Thermal Desorption unit coupled to DART source at the MS inlet
### Table 2. TD-DART-MS Parameters (JEOL, Peabody MA)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrumentation</td>
<td>IonSense DART source, JEOL AccuTOF LC-plus mass spectrometer, Biochromato IonRocket Thermal Desorption unit</td>
</tr>
<tr>
<td>Detector Voltage</td>
<td>2100V</td>
</tr>
<tr>
<td>Acquisition time</td>
<td>1 second</td>
</tr>
<tr>
<td>Orifice 1: 20V</td>
<td>Grid Voltage: 350V/150V</td>
</tr>
<tr>
<td>Orifice 2: 20V</td>
<td>RF Ion Guide: 450V</td>
</tr>
<tr>
<td>Ring Lens: 5V</td>
<td>Mass Range: 50-1000 amu</td>
</tr>
<tr>
<td>DART source temp</td>
<td>250°C</td>
</tr>
<tr>
<td>Ramp: 50°C - 600°C in 5 min.</td>
<td>Hold temp at 600°C for 1 min.</td>
</tr>
<tr>
<td>Mass Range: 50-1000 amu</td>
<td>DART source temp: 250°C</td>
</tr>
</tbody>
</table>

Table 2: Used with permission from Oscar Black (2019)

### Table 3. DART-MS Parameters (University of Mississippi)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrumentation</td>
<td>IonSense DART source, JEOL AccuTOF 4G mass spectrometer</td>
</tr>
<tr>
<td>Detector Voltage</td>
<td>2100V</td>
</tr>
<tr>
<td>Acquisition time</td>
<td>1 second</td>
</tr>
<tr>
<td>Orifice 1: 20V</td>
<td>Grid Voltage: 350V/150V</td>
</tr>
<tr>
<td>Orifice 2: 20V</td>
<td>RF Ion Guide: 450V</td>
</tr>
<tr>
<td>Ring Lens: 5V</td>
<td>Mass Range: 50-1000 amu</td>
</tr>
<tr>
<td>DART source temperature</td>
<td>250°C</td>
</tr>
</tbody>
</table>

Table 3: Used with permission from Oscar Black (2019)

### 1.2.3 Application of Chemometrics to Mass Spectra

Treatment of all DART mass spectra was conducted using msAxel Data Processing software. All samples were background subtracted against the first 10 seconds of analysis where no samples were introduced to the sample inlet. Background subtracted spectra were exported as “centroided text files” for use in Mass Mountaineer, designed by Dr. Chip Cody. All chemometric evaluations (principal component analysis [PCA]) were conducted within Mass Mountaineer, after which 3D-plots were generated. Spectral data was also converted into NIST format .MSP files within Mass Mountaineer and exported to NIST MS Search Program for the generation of two user libraries. Thermal desorption
spectral data was exported to Origin in order to create 3D plots of m/z vs. intensity, resolved by temperature (z-axis 50°C to 650°C with 100°C increments).

Spectra were generated for each of the polymer classes (PLA, ABS, PETG, Nylon, Other), and each polymer class was also further separated by color and also by manufacturer. By classifying the polymers by type, color, and manufacturer, we were able to generate multiple methods to aid in the classification of an unknown polymer. In the case of an unknown, the sample would be analyzed using DART-MS and then compared to a database of spectra to see if the unknown falls within the grouping of a common polymer type. Once the polymer type is obtained, the sample can then be further classified by color and manufacturer within that polymer subcategory. This information could then potentially lead to the source and type of polymer, for which a purchase history could then be investigated, including potential suspects in the area. Overall, this statistical technique further validates the direct interpretation of DART-MS data. Though the spectra themselves can be used to identify and classify polymers, expert interpretation of complex numerical data is required; our database provides the same (or potentially better, less subjective) discriminatory power, eliminating the need for expert input.

1.3 Results and Discussion

1.3.1 Thermal Desorption DART-MS vs Direct

Mass spectra were obtained both by direct analysis of polymers and by thermal desorption, which led to a strong difference in spectra. As shown in Figure 5, mass spectra from TD-DART-MS appeared to be significantly cleaner. Direct analysis is not
penetrative, meaning it only obtains mass spectra for the surface of the polymer; the thermal desorption technique breaks down the polymer, obtaining mass spectra for more than just the surface. Noting the differences in their respective data, both analysis techniques can be useful when creating a database of DART-mass spectra.

The thermal desorption spectral data was used to generate 3D plots for each of the 50 samples. These plots (example in Figure 6) show that fragments of high mass-to-charge ratios decomposed at higher temperatures, beginning at around 300-350°C. Obtaining desorption data for samples over a wide range of temperatures allows for stronger differentiation between polymers, thus offering a better means of identifying an individual polymer sample in the future.

Figure 5: Comparison of Makeshaper Black PLA by DART-MS (Red) and TD-DART-MS (Blue)
Figure 6: 3D Plot displaying the thermal desorption spectra for Polylite Blue PLA (Sample 4)

1.3.2 Chemometric Clustering

By generating multiple PCA plots, we were able to successfully separate and classify the 50 samples by their respective polymer types. Further, each type was successfully separated by color and again by manufacturer. This supports the initial hypothesis that the polymers from 3D-printed firearms can be grouped by their distinguishable characteristics using DART-MS and chemometric analysis. When comparing the TD-DART-MS data plots with the direct DART data plots, as shown in
Figure 7 and Figure 8, respectively, it is evident that TD-DART-MS provided tighter clusters for the various polymer types. PCA allowed us to successfully reduce the high dimensionality of the spectra data, providing plots that accounted for 60-80% of the variance within the data set (Black, 2019). Of the various polymers used in the study, PLA appeared to have the broadest spread relative to the others (Figure 7 and Figure 8). This is likely due to the fact that there was a wide variety of colors sampled (samples categorized as “Blue” could have actually been blue, crystal blue, navy, aqua, etc.). In addition, the reason for the high separation amongst “Blue” ABS samples (Figure 9) is that while the two samples are both technically blue, one of the samples is actually navy. The reliability of this method is further exemplified by the successful separation of ABS samples into color and manufacturer classes shown in Figure 9 and Figure 10, respectively.
Figure 7: PCA plot of TD-DART-MS data: all polymers (n=40)

Figure 8: PCA plot of DART-MS data: all polymers (n=34)
Figure 9: PCA plot of TD-DART-MS data: ABS by color (n=7)

Figure 10: PCA plot of TD-DART-MS data: ABS separated by manufacturer (n=7)
1.3.3 Identification of Polymers

After obtaining PCA plots that properly separated the polymer samples, those chemometric parameters were then used in order to test an “unknown” sample and determine whether or not it falls into the correct cluster of data points. Results (Figure 11 and Figure 12) demonstrate the positive identification of “unknown” polymer samples, which supports our initial hypothesis that DART-MS can provide a foundation for the identification of unknown polymer evidence from 3D-printed firearms. Our research found that PCA plots generated from TD-DART-MS data were more reliable than those generated from direct DART analysis, given that the former creates a more enclosed environment for samples, which leads to a reduction of background noise.

In future studies, more polymer spectra can be contributed toward the further development of a database, and the parameters for PCA analysis can be modified for maximum efficiency. It is recommended that unfamiliar polymer samples be excluded from the PCA plots to avoid skewing the data point clusters produced by the more common polymers (PLA, ABS, PETG, and nylon) and potentially limiting the efficacy of the identification test (Black, 2019).
Figure 11: Positive identification of Sample #48 ABS (pink square) when treating it as an unknown (n=40)

Figure 12: Positive identification of Sample #44 Nylon (pink square) when treating it as an unknown (n=40)
1.4 Conclusion

The results from this study show strong potential for the classification and identification of unknown polymer evidence as the 3D-print polymer database continues to grow. Chemometric analysis of mass spectral data allowed for the successful classification of various 3D-print polymer samples, and thermal desorption techniques provided an even stronger basis for this classification. It is recommended that another full study be done in the future, with a focus on modifying the parameters used in the chemometric analysis of polymers for potentially stronger separation when generating PCA plots. These parameters should be improved over time as more contributions are made to the database. It is suspected that stronger discrimination could result from the specific selection of particular m/z peaks in each individual sample, particularly in peaks of high intensity, as these peaks may contribute to the high chemical variance amongst samples. Future studies can also utilize different types of plots to complement the visual data plots, such as score and loading plots to assign numerical value (Black, 2019).
CHAPTER 2: AIRBORNE MERCURY AT THREE LAKES
IN NORTH MISSISSIPPI

2.1 Introduction

2.1.1 Mercury and its Sources

Mercury (Hg) is a toxic heavy metal that is present throughout the environment. It has three forms: elemental (liquid) mercury, inorganic mercury, and organic mercury (methylmercury). Natural sources of mercury include volcanoes, forest fires, and fossil fuels, while common anthropogenic sources include power plants, smelters, and incinerators (Tweedy). Once it has been introduced into the environment, chemical transformations of mercury species allow for them to persist throughout the atmosphere as well as aquatic ecosystems. The primary source of mercury exposure for humans is the consumption of fish containing methylmercury, the most toxic of the three forms, which bioaccumulates along the food chain. Human exposure to high levels of mercury can lead to damage in the immune and nervous systems, and it can cause neurodevelopmental issues in unborn children. Due to its many adverse health effects, measuring airborne mercury concentration in the atmosphere is vital, as it would allow for a greater understanding of its deposition, sources, and trends (USGS, 2009; Tekran, 2019).

Note: The mercury research was a partnership with graduate student Byunggwon Jeon; my role was primarily sampling, data analysis and interpretation.
2.1.2 Prior Research and Purpose of this Study

The Mississippi State Department of Health (MSDH) has issued a fish consumption advisory for Enid and Grenada Lakes, recommending limited consumption of fish from these lakes as a precaution from harmful mercury exposure levels; however, Sardis Lake does not have an advisory. A map of the lakes can be seen in Figure 13.

Figure 13: A map of Mississippi, showing the relative locations of Sardis Lake (top), Enid Lake (middle), Grenada Lake (bottom) as well as the Red Hills Power Plant (indicated by the red dot) (Wolff et al., 2016)
Several studies have been conducted since the fish consumption advisories were issued, investigating the mercury levels at the three lakes. One study found that the mercury levels in fish were highest at Grenada Lake, followed by Enid and then Sardis (Wolff et al., 2016). Another previous study done by one of Dr. Cizdziel’s previous research students (Ruiqi Feng) had found the highest mercury deposition levels at Sardis Lake, then Enid Lake, then Grenada Lake; however, the study left much room for improvement in regards to lowering the blank concentrations of samples as well as improving the overall uncertainty of the experiment.

The purpose of this study was to monitor the mercury concentrations in the atmosphere around three lakes in North Mississippi: Sardis Lake, Enid Lake, and Grenada Lake. We hypothesized that point sources, particularly the Red Hills Power Plant near Grenada Lake, may be a primary source of the mercury for the three lakes, causing higher concentration levels in Grenada Lake, followed by Enid and then Sardis. This trend would be consistent with the mercury levels found in fish.

2.2 Materials and Methods

2.2.1 Sampling Sites and Deployment

The passive samplers were deployed on the dams at Sardis, Enid, and Grenada Lakes in order to compare the airborne mercury concentration at each site. All three lakes are open to the public for recreational uses, including swimming and fishing, which has led them to be of interest to the Mississippi State Department of Health (MSDH), particularly with regards to mercury exposure from fish consumption. The main point
sources that we suspected to affect mercury levels at these lakes are the Red Hills Power Plant in Ackerman, Mississippi, and the Resolute Forest Products paper mill in Grenada, Mississippi, both of which are in relatively close proximity to Grenada Lake. For each field site, an apparatus was assembled by drilling metal brackets into a block of wood and attaching the wood to two metal poles that could then be hammered securely into the soil. The metal brackets allowed for the secure attachment of multiple samplers at a time. While nearly all samplers were deployed with mesh lids to allow for gas exchange, one sampler at Grenada Lake was kept sealed to be used as a blank measurement. The samplers were left to accumulate airborne mercury over various time intervals: one week, two weeks, three weeks, and four weeks. The time and date was recorded at the time of each deployment and again at the time of collection. Experimental setups for Enid Lake and Grenada Lake can be seen in Figure 14 and Figure 15, respectively.

Figure 14: The experimental setup at Enid Lake
2.2.2 Mercury Passive Air Samplers

Air monitoring for this study was done using the Mercury Passive Air Sampler (MerPAS) made by the Tekran Instruments Corporation. These are a useful tool for monitoring mercury in the atmosphere at a relatively low cost. The samplers are passive, meaning they can be deployed and left to accumulate chemical pollutants over time in a variety of environments. Gaseous mercury is obtained by the sampler (shown in Figure 16) by diffusing through a radial housing chamber and adsorbing onto an activated carbon powder. The carbon is impregnated with sulfur, which allows for the attraction of airborne mercury species. To ensure protection in the storage and transport of samples, the housing chamber is screwed into a protective jar, which can be sealed using a plastic lid. Alternate lids were used as each sampler was deployed; these lids contained a mesh
covering to allow for gas exchange rather than the typical seal (McLagan et al., 2015; MerPAS, 2018).

Figure 16: Schematic (left) and photo (right) of the MerPAS sampler and its individual components (McLagan et al., 2015)

One of the benefits of passive sampling is that it allows for the collection of desired chemical species over a larger time frame, allowing one to determine a rate of accumulation in a variety of different environments and locations. In addition, passive sampling does not need to be supervised nor does it require the use of a pump to facilitate air movement as it would with active sampling methods, making it more convenient and less expensive than active sampling methods (Sigma-Aldrich).
2.2.3 Background on the Analytical Instrumentation Used

Figure 17: Photo of the Direct Mercury Analyzer (DMA) used in this experiment

Once the samplers were retrieved from their respective locations and brought back to the lab at the University of Mississippi, the activated carbon from each sampler was carefully removed and measured for the mercury concentration using a Direct Mercury Analyzer (Milestone DMA-80). This instrument is particularly useful for quantifying mercury in various sample matrices without needing to isolate the analyte (Milestone, Inc.). The DMA used in this study was first calibrated using several mercury standards available in the lab. Samples of approximately 0.5 g of activated carbon were loaded into quartz boats.
Since the lifetime of the DMA catalyst tube can be decreased with high exposure to sulfur, approximately 0.2 grams of Na$_2$CO$_3$ was added to the top of each sample boat to help avoid catalyst depletion. Sample boats were introduced into the instrument upon their placement in an autosampler (a schematic is shown in Figure 18). Samples are placed in a furnace, where they are dried and combusted under oxygen flow. Upon release, mercury and other combustion products are carried through a catalyst furnace, which removes interfering compounds and converts mercury species to elemental mercury vapor (Hg$_0$). Gold amalgamation is utilized in order to trap the mercury released from the samples; the amalgamation furnace is then heated so the gaseous mercury can be carried to an atomic absorption spectrophotometer, in which the elemental mercury absorbs a photon at 253.65 nm and transitions between electron quantum states. Using Beer’s Law, the absorbance of the material is proportional to its analyte concentration (Milestone, Inc.).

![Figure 18: A schematic diagram of a DMA system. (Credit: Milestone, Inc.)](image-url)
2.3 Results and Discussion

### Table 4. Total Mercury Levels and Concentrations Over Time

<table>
<thead>
<tr>
<th></th>
<th>1 week</th>
<th>2 weeks</th>
<th>3 weeks</th>
<th>4 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg (ng)</td>
<td>SE</td>
<td>Conc. (ng/m³)</td>
<td>SE</td>
</tr>
<tr>
<td></td>
<td>Conc. (ng/m³)</td>
<td>SE</td>
<td>Hg (ng)</td>
<td>SE</td>
</tr>
<tr>
<td>Conc. (ng/m³)</td>
<td>SE</td>
<td>Hg (ng)</td>
<td>SE</td>
<td></td>
</tr>
<tr>
<td>Grenada</td>
<td>1.16</td>
<td>0.08</td>
<td>1.24</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>2.12</td>
<td>0.07</td>
<td>1.11</td>
<td>0.04</td>
</tr>
<tr>
<td>Enid</td>
<td>1.09</td>
<td>0.08</td>
<td>1.50</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>2.13</td>
<td>0.23</td>
<td>1.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Sardis</td>
<td>1.18</td>
<td>0.06</td>
<td>1.67</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>2.24</td>
<td>0.20</td>
<td>1.18</td>
<td>0.11</td>
</tr>
</tbody>
</table>

From the data shown in **Table 4**, it is evident that a consistent trend appeared among the concentration measurements. Sardis Lake showed to have the highest mercury concentration (in ng/m³), with Enid Lake having the second highest and Grenada Lake having the lowest concentration. This trend is consistent in the data for all four time intervals tested. The data for total accumulated mercury in the samples (**Figure 19**) also supports this general trend, with an increasing difference among the three lakes as the sampling time was increased. While a clear trend can be seen in our data, it should be
noted that the differences between the most measurements were not statistically different (p > 0.05).

Figure 19: Accumulation of mercury at the three lakes over time, ranging from one to four weeks. Error bars = ±1 S.E.
2.4 Conclusion

Although not statistically significant, concentrations of airborne mercury were consistently higher at Sardis Lake, the northern-most lake, and tended to be lowest at Grenada Lake, the southern-most lake. The trend is most apparent in the samples acquired over the longest duration (4-week period). Although this north-south concentration gradient was opposite to what was expected, it is consistent with a report that mercury concentrations can be elevated when the wind stems from industrial areas in the north such as Memphis (Jiang et al., 2013). It is also speculated that inconsistent weather and temperature changes may have had an effect on our results, particularly for the shorter duration samples. The Red Hills Coal-Fired Power Plant near Grenada Lake does not seem to be impacting the airborne mercury at the lake’s dam. However, the lake’s watershed extends many miles to the east and deposition from the CFPP may be greater in those areas. In any case, the reason for higher concentration at Grenada is still unclear. More research should be done in order to determine the cause for higher concentrations of Hg in fish from Grenada Lake compared to Sardis Lake.
REFERENCES


