ABSTRACT

AN ELECTRON MICROSCOPY AND INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY INVESTIGATION OF GREAT MIAMI RIVER SEDIMENT POLLUTION IN THE INDUSTRIALIZED LANDSCAPE OF HAMILTON, OHIO

by Jennifer L. Tully

The section of the GMR which flows through the city of Hamilton, Ohio is representative of many post industrial cities throughout the Midwest. Sediment samples were collected along the banks of the river and analyzed by ICP-MS, SEM, TEM and STEM. Bulk chemical analysis indicated that anthropogenic metals were concentrated in the ≤40 µm size fraction. SEM analysis identified multiple pollution particulates including lead, barium sulfate, antimony, PbCrO₄ and coal spherules. Additional complexity in the sediment is observed in STEM where correlations between anthropogenic metals and Mn and Fe were observed on clay particles. Statistical analysis of the sample set further confirmed the higher concentrations in the fine fraction of the sediment and identified six metals which were significantly above the concentrations observed in the reference materials: Zn, Sn, Sb, Cu, Pb and Sr. Overall, this study lays the groundwork for a more extensive investigation into the source and extent of pollution within the GMR.
AN ELECTRON MICROSCOPY AND INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY INVESTIGATION OF GREAT MIAMI RIVER SEDIMENT POLLUTION IN THE INDUSTRIALIZED LANDSCAPE OF HAMILTON, OHIO

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Introduction

The city of Hamilton, population 62,477, located in Butler County Ohio, was once an active manufacturing city producing goods from high quality paper to government approved safes (U.S. Census Bureau, 2010). However, in recent years the city has been in decline losing many of its anchor manufacturers. In 2011 Mohawk papers owner of the Beckett Paper Mill announced that the plant would be closing (Todd, 2011). Furthermore the city’s last paper manufacturer SMART Papers (~200+ employees) announced plans to shut down the paper mill in October of 2011 (Livingston, 2012). As one of the oldest industries in Hamilton the loss of the paper business is accelerating the overall decline of the city. Not only is the city in an economic downturn, it is teeming with environmental issues from years as an industrial boom town, including two coal power plants in less than a half mile of each other and one Superfund site, Chem-Dyne. Less than 20 feet below the surface in some locations is the Great Miami River Buried Valley Aquifer (GMRBVA), a designated sole source aquifer by the United States Environmental Protection Agency (USEPA), following the course of the Great Miami River (GMR) which flows through the center of Hamilton (MCD, 2009, GMRBVA). Industry and urbanization crowd the river’s banks vying for use of its natural resources, which makes Hamilton a model city for studying pollution and its effects on the environment. Metal pollution is commonly associated with urban environments and given the manufacturing history of Hamilton and previous work, metal pollution is expected in the GMR. However, this is a very dynamic sedimentary system and whether or not particulate metal pollution is diluted to background levels is unknown. Although surface and groundwater of the GMR and GMRBVA have been investigated and monitored for pollution, to date GMR sediment has not been studied in detail for bulk metal and metal particulate pollution. This study will be the first to investigate the GMR sediment in detail to identify such pollutants and establish a baseline for pollution within this river system.

Background on the GMR and GMRBVA

The Pleistocene glaciations had a profound impact on the topography and natural resources located in southwestern Ohio. Much of the sand and gravel deposits that are mined today originated from alluvial outwash sediments deposited into deep valleys carved by multiple advances and retreats of the Pleistocene glaciations. The buried valley system in Southwestern Ohio through which the GMR flows has been designated a sole-source aquifer by the USEPA; 1.6 million people rely on the water that is pumped from the aquifer (Rowe, 1997). The GMR has its headwaters in Indian Lake located in Logan County, Ohio and flows 170 miles until it drains into the Ohio River (MCD, 2009). Along this path the GMR drains 5,702 square miles of over 6,600 miles of streams; some of this water infiltrates into the GMRBVA and the rest discharges into the Ohio River. (MCD, 2009) As the river flows through Hamilton, Ohio it is ~130 m wide with an average depth of ~19 m (NOAA, 2012) (Figure 1.1). River sediment in this
segment of the river is made up of well-rounded pebble to cobble sized rocks; smaller sediments (sands and clays) fill the pores between the larger cobbles (Figure 1.2).

Figure 1.1: Upstream view of the GMR at the second low-level dam, near the Miami University Hamilton Campus.

Figure 1.2: GMR sediment well rounded pebble to cobble sized rocks with sands and clays.

The city of Hamilton operates both a north and south well field which help to supply the city of Hamilton’s drinking water needs (Figure 1.3). Both well fields pump on average >500
gallons per minute located within the unconsolidated highly conductive sediments of the GMRBVA.

Figure 1.3: Map of production well fields in and around Hamilton, Ohio with corresponding well yields illustrating the buried valley aquifer system (Sheets & Bossenbroek, 2005).
The buried valley itself is 2 miles wide by 150-200 ft in depth and in some places well yield can reach rates of 3,000 gallons per minute (Sheets & Bossenbroek, 2005). Not only does the GMR recharge the crucial GMRBVA to supply residents with drinkable water, the river is also a source of recreation and fishing for the many residents along its banks (Figure 1.4).

**Figure 1.4:** Local residents utilizing the river for fishing, below the second low level dam on the GMR downstream of the Hamilton Municipal Electric Plant (HMEP) and across from the Miami University Hamilton Campus.

**Study Area and History of Hamilton**

This particular segment of the GMR was chosen for this study because of the sprawl of urban industrial development with numerous potential pollution sources. Due to Hamilton’s history from Fort Hamilton in 1791 to an industrial city in the 1900s, there were periods of prosperity and decline as companies cycled through. Beginning in 1850 the first paper mill opened along the GMR which eventually became known as the William Beckett Paper Company (Kinch, 1952). SMART Papers (Figure 1.5), another paper mill, opened in 1893 and before its closure in 2012 this facility operated a 37 mega-watt coal fired power plant which sold approximately 20 mega-watts back to the power grid (Gibson, 2011). The Miami and Erie Canal made Hamilton a stop along the famous shipping route and was in use up until the 1850s when business began to decline, and the canals were phased out in 1900. In place of water shipping
routes came the railroads; first chartered in 1846 as the Cincinnati, Hamilton and Dayton Railroad (Kinch, 1952) this line connected other towns in the area as they expanded.

As Hamilton became more connected to national infrastructure, factories began to open; in the late 1930s 11,800 city residents out of a total population of ~52,176 labored in these factories for the United States Military (Blount, 1995). Shortly after the U.S. entered WWII that number jumped to ~15,000 as the factories were running 24/7 to keep up with demand (Blount, Crout and Shriver, 2000). Many items were made for the war effort: paper for maps, engines for ships, aircraft and work related to the atomic bomb along with many other components (Blount et al., 2000). The Herring-Hall-Marvin Safe Company was also involved with working a mysterious material in their factory in 1943; not until 1993 was it revealed that workers were grinding uranium bars for use in reactors to generate plutonium for the atomic bomb “Fat Man” (Blount, 1995). The U.S. Department of Energy has since remediated the building and in particular the 3rd floor where the uranium was worked and released the site for unrestricted use in 1996 (USDOE, 2011).

After the war ended the first wave of “Industrial Exodus” occurred in the late 1950s and estimates are that 25-43% of available industrial jobs left the city due to shifting markets and dilapidated infrastructure (Blount et al., 2000). As jobs left Hamilton the population declined

**Figure 1.5:** SMART paper plant on the west bank of the GMR in Hamilton, Ohio, almost directly across from the HMEP.
and in the 1970s most of the population growth occurred in the city of Fairfield, as well as in Union and Liberty townships. In 1980 Hamilton had a population of 63,189 and by 1990 the population decreased to 61,436 (Blount et al., 2000). By the 1990s the county’s employment base, which had been largely industrial, was now occupied by mostly local governments, school systems, Miami University and retail/service industries (Blount et al., 2000). Hamilton still maintains industry work within its city limits but the companies are much smaller and many of the factories that operated during WWII are gone. With the closure and auction of the SMART paper mill the industrial dominated chapter of Hamilton’s history will close, while the legacy of industrial pollution will continue. In fact, Hamilton began to experience major environmental issues tied directly to industry during a period of decline in the 1970s in the form of the superfund site Chem-Dyne.

**History of Chem-Dyne**

In the 1970s the company Chem-Dyne began operations on the north side of Hamilton adjacent and south of the Ford Hydraulic Canal and ~1500 ft south of the North Well Field. In 1974 Chem-Dyne began receiving hazardous substances on their 21 acre site as part of their research into reusing the waste for fuels and antifreeze (Blount et al., 2000). The company was fairly unknown to citizens in Hamilton until mishaps began occurring onsite. The first incident occurred on April 24, 1976 when a railroad car with unknown contents began to fume; local firefighters cooled the car with water for ~3 days, until the fuming ceased (Blount et al., 2000). The second major event occurred on August 25, 1979 when an explosion and fire shook the plant, sending waste filled drums and flames 100 feet in the air (Blount et al., 2000). These events brought Chem-Dyne to the attention of local, state, and federal governments along with concerned residents of the city. In 1981 the USEPA listed Chem-Dyne as one of the nation’s worst hazardous waste sites which made it eligible for cleanup under the then newly Congress established Superfund program (Blount et al., 2000). When remediation finally began in May 1983 approximately 8,600 drums, 30 tanks and 2 open top below grade tanks of waste were found onsite with an estimated 463,000 gallons of liquid, 109,000 gallons of sludge and 86,000 gallons of solids (Figure 1.6) (USEPA, 2011).
Figure 1.6: Chem-Dyne Superfund site during the cleanup process. (A) taken in July 1980 (B) taken in June 1982 (C) taken on an unknown date by the Ohio EPA. (McLelland, 2008).

Based on worker’s testimonies, hazardous waste was often spilled and treated improperly. The drums found during cleanup were in a state of disarray with many deteriorating and still leaking their unknown hazardous contents (USEPA, 2011). Due to Chem-Dyne’s lack of diligence in disposing of the hazardous materials between 1976 and 1979 five fish kills in the GMR, upwards to 1 million fish and aquatic animals, were blamed on the company (USEPA, 2011). Materials that were cleaned from the site included: pesticides, pesticide residues, chlorinated hydrocarbons, solvents, waste oils, plastics, resins, polybrominated biphenyl’s (PBB), polychlorinated biphenyl’s (PCB), tris(hydroxymethyl)aminomethane (TRIS), acids, strong bases, heavy metal sludge, cyanide sludge and laboratory chemicals (USEPA, 2011). Several million dollars later the physical cleanup tasks have been completed and according to the Agency for Toxic
Substances and Disease Registry (ATSDR) the soil and air no longer pose a health risk. However, the ATSDR warns that offsite groundwater is still contaminated and could pose a health hazard. Fishing, especially in the Ford Canal which borders the north end of the plant, is discouraged as the fish could still be harboring PCB’s, organic compounds, and metals (ATSDR, 2009).

**Other Sources of Pollution**

In addition to what Chem-Dyne has released into this stretch of the GMR there are several other possible significant sources of pollution. Since 1895 the first Hamilton Municipal Electric Plant (HMEP) has been in operation just south of the current plant which began functioning on January 5, 1929 (“Our City”, 1935)(Figure 1.7). The current plant was first monitored by the EPA on December 31, 1975, and only two years later received its first violation (Envirofacts, HMEP, 2011). HMEP is classified as a major discharger into the GMR and has a permit until July 31, 2014 to discharge a list of chemicals and metals such as Bis(2-ethylhexyl)phthalate, barium, zinc and copper (Envirofacts, HMEP, 2011). As the HMEP is a combustion plant, toxic substances are also released into the air. For the year 2010 HMEP released 275 pounds of barium, 0.156 pounds of dioxin and dioxin-like compounds, 140,000 pounds hydrochloric acid, 20.6 pounds of lead compounds, 2 pounds of mercury and 7,000 pounds of sulfuric acid into the air above Hamilton (Envirofacts, HMEP, 2011). HMEP also transferred barium, lead and mercury compounds (20,400, 1574.2, and 12 pounds respectively) to three landfills: Bavarian Waste, Walton KY, Rumpke, Cincinnati OH, and East Bend Landfill Duke Energy, Rabbit Hash KY (Envirofacts, HMEP, 2011).

![Figure 1.7: HMEP, a coal-fired power plant on the east bank of the GMR in Hamilton. Located just south of the first low-level dam on the GMR and Ford Canal.](image)
On the opposite side of the river from the HMEP rests one of Hamilton’s paper mills, SMART Papers, LLC. In 2010 SMART released 52,750 pounds ammonia, 350,000 pounds hydrochloric acid and 13.5 pounds of lead compounds to the air and transferred 53.11 pounds of lead compounds to the Rumpke landfill (Envirofacts, SMART, 2011).

In addition to infrastructure and factories, urban runoff is a source of unregulated pollution to the GMR. Multiple storm drains discharge directly into the GMR, channeling water from city streets and housing developments into the river during storm events (Figure 1.8). The Ohio EPA has also required the city of Hamilton to eliminate sanitary sewer overflows by 2014 (Wilson, 2009). Within the city there are 5 sewage overflows which can spill untreated wastewater and raw sewage into the natural water systems. One such overflow point is on the banks of the GMR south of the High/Main Street bridge, opposite of downtown Hamilton, which according to the JournalNews article by Richard Wilson released 11 million gallons of overflow into the river in 2008 (Figure 1.9) (Wilson, 2009).

**Figure 1.8:** One of the many storm drains which empty into the GMR. During flood events as shown, water from city streets (dark grey) flows into the GMR (light brown).

**Figure 1.9:** The sewer overflow manhole cover located just above a storm drain and the GMR. This sewer overflow is south of the High/Main Street bridge on the west bank.
Due to the nature of the storm water system in Hamilton, Ohio there exists the possibility for sediments on the streets of Hamilton to easily enter the GMR. Work has been carried out by LeGalley and Krekeler (2013) on the metal and metal particulate pollution present in the street sediments near the HMEP and surrounding areas. That investigation described the complex nature of pollutants found in street sediments collected nearby the HMEP. Street sediments were collected from N. 2nd street which is a densely packed residential road directly adjacent to the HMEP. Sediment was typically sampled from masses 1-3 cm thick from accumulation points on the street and nearby sidewalks. Wind direction data courtesy of the Butler County Regional Airport indicated that stack emissions would be propelled in all directions and around 36% of the data points towards wind directions from the southwest and northwest (LeGalley and Krekeler, 2013). This indicates that airborne pollutants would be dispersed over the entire study area with the potential for high concentrations of coal fired pollution particulate to be accumulated in the small residential community on N. 2nd street. Bulk chemical analysis supported this as LeGalley and Krekeler (2013) observed high concentrations of anthropogenic metals with average concentrations reaching: 25 ppm Cr, 40 ppm Cu, 15 ppm Ni, 215 ppm Pb, and 500 ppm Zn, along with correlations between Ni and Cu ($r^2=0.65$) and Ni and Cr ($r^2=0.44$) (Figure 1.10).

**Figure 1.8:** Correlations with Cu and Cr concentrations and Ni within the street sediment sampled from N. 2nd street (n=13). Adapted from LeGalley and Krekeler (2013).

This data combined with SEM and STEM substantiates the anthropogenic sourcing of metal particulate observed in the sample set, especially concentrations detected in the street sediment are greatly enriched as compared to the background materials (glacial till and local soil) examined by LeGalley et al. (in press). SEM analysis indicated the ubiquitous presence of aluminosilicate coal spherules, which form as a direct result of the coal combustion process. These spherules varied widely in terms of their maturity, size, and surficial morphology while
maintaining the characteristic sphere and high concentrations of Si, Al, Fe, Ca, and O (Figure 1.11).

**Figure 1.9:** Examples of coal spherules observed in street sediment. (A) Spherule ~45 µm in diameter captured at 4,360x (B) Higher magnification image of (A) taken at 23,000x detailing the subhedral to euhedral Fe-rich octahedrons on the surface of the spherule (C) ~13 µm diameter spherule captured at 4,770x (D) 2 µm spherule imbedded in clay particles, captured at 10,750x (E) Mature coal spherule displaying corrosion/alteration textures, captured at 6,800x (F) Higher magnification image of the lower left corner of (E) taken at 25,750x (G) BSD image of an Fe-rich coal spherule with clay particulate attached, captured at 3,000x (H) Higher magnification image of the spherule in (G) displaying the surficial texture indicative of mechanical abrasion, taken at 20,900x. Figure adapted from LeGalley and Krekeler (2013).
Because coal spherules are an indicator for the presence of coal pollution and the HMEP is well documented to have released pounds of multiple metals there is reason to believe that some of the anthropogenic metal pollution is a direct result of coal combustion (Envirofacts, HMEP, 2011).

Additional sources of anthropogenic metal pollution are present especially in an urban environment but can be more difficult to tease out, such as vehicular pollution. LeGalley and Krekeler (2013) determined that Ni-rich, W-rich, and Cr-rich particulates were potentially sourced from HMEP’s infrastructure including potential corrosion of the stack and boilers which are typically composed of steels containing these metals. Pb particles present within the street sediment were found to be 0.3-25 µm in diameter; one pervasive source of Pb pollution within this environment is PbCrO₄, the pigment found in yellow road paint on many of the roads in Hamilton, Ohio (Figure 1.12) (Detherage et al., in review).

**Figure 1.10:** BSD SEM images of PbCrO₄ in samples of yellow road paint taken from the streets of Hamilton, Ohio. (A) PbCrO₄ crystals scattered in an organic paint matrix (B) higher magnification image of the center of (A) captured at 38,000x (C) bright particles of PbCrO₄ (D) 107,000x image of the center of (C) showing rounded PbCrO₄ crystals (E) image captured at 88,000x of euhedral crystals of PbCrO₄ (F) Masses of euhedral PbCrO₄ crystals taken at 86,000x with some crystals displaying rounding. Figure adapted from Detherage et al. in review.
Discrete particles of PbCrO$_4$ were not identified in the SEM analysis performed by LeGalley and Krekeler (2013); however, Pb isotope geochemistry indicated that road paint containing PbCrO$_4$ as a pigment was a wide-ranging source of Pb pollution in the sediments collected (LeGalley et al., in press). Particles of Pb-S were identified in the SEM study and it is possible that the Pb in PbCrO$_4$ is remobilizing and precipitating as the Pb-S rich particles (LeGalley et al., in press). STEM data from LeGalley and Krekeler (2013) further verifies the potential for remobilization of metals within the street sediment as it was found that Cu and Zn preferentially sorbed onto clay particulate (Figure 1.13). As observed in the STEM images Cu, Zn, and P preferentially sorb onto the illite particles whereas no correlation is observed with Hg or Ni.

![STEM images of chlorite and illite aggregate for selected elements](image)

**Figure 1.11**: STEM and STEM/EDS elemental mapping of a representative chlorite and illite aggregate for selected elements. Illite exhibits a strong spatial correlation with Cu and P, while Zn, Ni and Hg are disseminated throughout the aggregate. Adapted from LeGalley and Krekeler (2013).

Not only does this environment contain multiple anthropogenic metals in discrete particle form but the option for mobilization is also present. This allows for metals released into the environment to have a wider reaching effect on the health of individuals living nearby and the ecology. LeGalley et al., (in press) also found that the majority of the anthropogenic metals were concentrated within the fine fraction of the sediment, which indicates another potential avenue for transport, re-suspension. Thus residents nearby could potentially be exposed to fine particulate metals multiple times, first from initial stack emissions and second by wind...
remobilization of previously settled particles some of which may have additional sorbed metals. Exposure to such particulate may cause health-related issues potentially decreasing life expectancy and increasing the risk for cardiopulmonary and lung cancer mortality (eg., Pope et al., 2002, 2009 and LeGalley et al., in press). The street sediment in Hamilton, Ohio is of particular interest as the storm water system provides an avenue for metal laden sediments to enter the GMR. Based on five-year storm water management plan drafted by the city of Hamilton streets in the vicinity of the HMEP are swept once a month while streets in uptown area are swept nightly (City of Hamilton, 2003). Thus, the potential exists for substantial sediment accumulation and transport into natural waterways.

Street sediment has been a neglected area of environmental study that is beginning to gain more attention. Metals/pollutants within the street sediment are mobile, as wind and water transport these particles throughout an environment in a short amount of time. If the metal-laden waters flow into the storm sewer system there is a high probability of those metals ending up in the GMR. Not only street sediment but other urban pollutants such as oil, inorganic and petroleum based chemicals along with solid waste can be deposited into the GMR. The extent of pollutants entering the GMR from street sediment sources had yet to be evaluated until this study. This research investigates the inorganic pollutants present in the GMR sediment collected within the City of Hamilton to determine if street sediment pollution can be detected and if other sources of pollution can be identified. In addition, apparent risks from any resulting pollution found in the GMR will be identified and an assessment of environmental and ecological concern will be produced.

This investigation will test whether or not Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) bulk chemical analysis and Scanning Electron Microscopy (SEM) can act as screening techniques to locate anthropogenic particulate pollution from natural background in a mineralogically complex system. In intricate sedimentary systems such as the GMR, can pollution be detected above geologic background? Further, can metal particulate pollution in this multifaceted system be identified and sourced? If metal particulate pollution can be distinguished from background sedimentation and sourced, are there any changes observed from the source to the GMR? Ultimately this research will establish a baseline of pollution present in the GMR as of the summer of 2012 with potential environmental policy and long-term best management practice implications.
Methods

Sample Collection

A total of 19 river sediment samples were collected along a ~5 km segment of the GMR as it runs through Hamilton, Ohio (GPS coordinates and map in Appendix 4). Additionally 5 reference samples were collected locally of what would be considered natural background in the GMR system (GPS coordinates in Appendix 4, map in Figure 2.1). All samples collected were moist or saturated sediments gathered with clean Powder-Free vinyl gloves and a clean plastic spoon, both of which were discarded after each sample was collected. Sediment was placed into 250 mL Wheaton LDPE bottles, once full excess river water was added to the bottle and the lid was capped tightly as to remove as much oxygen as possible from the container. The bottles were then transported via cooler to a refrigerator (≤6°C) for storage according to QASQA Sample Submission Procedures Revision 12.0 (USEPA).

Sample Separation

Once all samples were collected the sediment was transferred from the refrigerated LDPE bottles to clean 400 mL glass beakers and placed in an oven at 105°C for at least 24 hours. Once dry, the sediment was transferred to labeled Ziploc bags. The sediment was then mixed manually and split within the bag, one half was transferred to a new Ziploc bag designated as “fines” and the other half remained in the original bag. The “fines” bag was mixed manually and split within the bag; one half was poured onto a clean piece of 6x6 inch weigh paper. The weigh paper was then folded in half and a clean spoon scooped off half of the sediment onto another clean piece of weigh paper, the sediment left over was placed into a new bag labeled “bulk”.

Fines Preparation

The other half of the sediment left on the weigh paper was then sieved for “fines” using 40 micron nylon mesh (Nylon 40/26 obtained from Miami Aqua-culture, Inc.) stretched over a plastic embroidery hoop. The hoop was attached to a ring stand and a clean 400 mL glass beaker sat right beneath the hoop with the ring stand height adjusted so that the mesh was touching the top of the beaker. Sediment was poured onto the mesh and rinsed with methanol repeatedly using a clean plastic spoon to agitate the particles. Fines (≤ 40 µm) and methanol were collected in the beaker and the larger particles were removed from the mesh and placed into a clean plastic bag. After each sample the embroidery hoop was cleaned with methanol, the used mesh discarded and a fresh piece of mesh fitted into the hoop. Less than 5 mL of the suspension was pipetted out of the beaker into glass screw top vials for TEM analysis, the beaker was then covered with aluminum foil and set aside to allow the fines to settle out of the methanol suspension. Once settled the methanol was pipetted off and the remaining fines were rinsed with fresh methanol into a 30 mL Wheaton glass vial. These vials were capped with aluminum foil and a pinhole was poked in the foil to allow the methanol to evaporate while the vials were in a fume hood. When the fines in the vials settled (~1 day) a pipette was once again used to carefully remove the excess methanol. The vials were placed back in the fume hood and once the sediment was visibly
dry the vials were transferred to the oven (~90°C) to ensure all methanol had been evaporated. Some samples did not yield enough fines for analysis and the procedure was repeated with the remaining sediments in the “fines” Ziploc.

**Bulk Preparation**

Sediment placed into the “bulk” Ziploc bag was manually agitated and split within the bag. One half of the sediment was poured out onto a sheet of clean 6x6 in weigh paper, larger pebbles were removed manually from the sediment to be milled. The weigh paper was then folded in half and half of the sediment was removed with a clean plastic spoon into an assembled mill. Sediments were milled for 5 minutes in a SPEX tungsten carbide mini-mill and if any large particles remained the sample was milled a second time. The mill was carefully removed and placed on a clean paper towel, opened, and the milled sediment poured onto a clean piece of weigh paper. The sediment was then transferred to a clean 30 mL Wheaton glass vial with a snap cap lid. After removing the sediment the mill was thoroughly cleaned before the next sample was milled.

**ICP-MS Sample Preparation**

Both the bulk and fine samples in Wheaton glass vials were prepared for ICP-MS bulk chemical analysis. One carbon crucible was cleaned thoroughly with a Kimwipe for each sample analyzed. ~50 mg of sample was weighed out onto clean weigh paper and an additional ~75 mg of Spectroflux 100A, lithium metaborate. The weigh paper was then carefully removed from the scale and a clean spatula was used to thoroughly mix the LiBO$_2$ and sample together until homogeneous. The mixture was then carefully poured into a clean carbon crucible. Batches of 6 crucibles were fused at a time, once the muffle furnace (1400 Furnace Barnstead Thermolyne, programmable) had reached 950°C the crucibles were loaded into the furnace and left for 20 minutes. Clean 125 mL PP bottles were filled with ~125 mL of 1% nitric acid for each sample; all bottles were labeled and weighed with the mass of nitric acid recorded for each bottle. Once the samples had been fused, one crucible was removed from the oven with tongs and the bead was poured into the corresponding bottle filled with acid. That bottle was then capped tightly, manually swirled, and placed onto a shaker table at medium speed for at least 8 hours. This procedure was then carried out for all of the remaining crucibles in the furnace. After at least 8 hours the bottles were checked for the extent of dissolution, if the bead had not completely dissolved those bottles were placed in a sonicator for ~45 minutes. Some samples had to be remade as complete dissolution of the bead was not achieved. The final solution was then transferred to 16x125 mm polypropylene test tubes for analysis on a Varian 810 ICP-MS against 10 geological standards: BE-N, DNC-1, RGM-1, SY-2, GSP-2, AGV-2, DR-N, BHVO-2, STM-1 and BCR-2.
ICP-OES

Inductively Couple Plasma-Optical Emission Spectroscopy (ICP-OES) analysis used the final solutions obtained in the ICP-MS analysis procedure except with an additional dilution. ~10 mL of 1% nitric acid was pipetted into a BD Falcon 15 mL polypropylene conical tube and its mass was recorded. Then ~1 mL of the ICP-MS final solution was pipetted into the BD Falcon tube, the mass of the solution was recorded and the solution was homogenized. These diluted samples were then analyzed on an Agilent Technologies 700 Series ICP-OES against 10 geological standards: BE-N, DNC-1, RGM-1, SY-2, GSP-2, AGV-2, DR-N, BHVO-2, STM-1 and BCR-2. ICP-OES major elements were measured as weight percent (wt%) oxides and converted to ppm using equation 1.

\[(\text{wt\% oxide} \times 10,000)(\text{molar fraction of major element}) = \text{major element (ppm)}\]

**Equation 1:** Conversion of weight percent oxides to ppm

Statistics

Statistical analysis of the GMR sediment samples is assisted and in part provided by Dr. Byran Smucker’s Data Analysis Practicum class (STA 475). The class compared the concentrations of 28 elements (Al, Sb, As, Ba, Be, Bi, Cd, Ce, Cs, Cr, Co, Cu, Fe, La, Pb, Mn, Ni, Rb, Sr, Th, Sn, Ti, W, U, V, Y, Zn and Zr) in the fine fraction of the GMR sediments to the fine fraction of the 4 reference materials by creating box plots (Representative plots in Appendix 7). This exploratory data analysis (EDA) indicated that some elements were significantly higher in the GMR sediment as opposed to the references. The data was then subjected to a Welch two-sample one-tailed t-test which only identified scenarios in which the GMR elemental concentrations were greater than those in the references. To control the compounding error rate the Benjamini-Hochberg (BH) procedure was used which controls the proportion of false discoveries (Benjamini and Yekutieli, 2001; Benjamini and Hochberg, 1995). Using the BH procedure, the proportion of false discoveries is held at 0.05 in that 5% of the significant conclusions drawn from the data set are expected to be false discoveries. Further, the independence of the samples was evaluated through the use of regression models with correlation structures and compared using Akaike Information Criterion (AIC). All samples were also re-checked using the same methods for the t-test and BH adjustment with significant outliers in Bi, Cu, Mn, Ni, Pb, Sr, Sn and W removed.

SEM

Scanning electron microscopy was performed on samples identified by the ICP-MS data to have high concentrations of anthropogenic metals. The fine sediments were chosen for analysis and the dried sediment was affixed to carbon adhesive tabs on aluminum stubs, no conductive coating was applied. All samples were analyzed using a Zeiss Supra 35 VP FEG SEM operated at 20 kv equipped with an EDAX Genesis 2000 XEDS. Back-scatter detection was used to identify particles of interest and energy dispersive spectra (EDS) were collected to
determine the composition of those particles. The EDAX Genesis 2000 XEDS has a detection limit of ~0.1 wt% for the majority of elements analyzed.

**TEM/STEM**

Vials of the fines and methanol suspensions were used to prepare the transmission electron microscopy (TEM) grids for analysis. The vial was agitated thoroughly and allowed to stand for 10 minutes then a small amount was pipetted off from the top 5 cm of the solution. One drop was then placed on a 300 mesh lacey carbon coated titanium TEM grid (obtained from Ladd Research, VT, USA) and allowed to dry under ambient air conditions covered in a plastic petri dish. All samples were analyzed using a JEOL JEM 2100 LaB₆ TEM/STEM operated at 200 kV with a beam current of 107 mA. Scanning Transmission Electron Microscopy (STEM) elemental hypermaps were obtained using a Bruker silicon drift XEDS detector with count rates generally between 0.1 and 0.2 kcps and scan times from ~15-30 minutes. Quantitative analyses of the spectra obtained were carried out using the Elementlist PB-ZAF method with a 1 sigma error and excluding Ti and C (as both are predominately grid materials).

**XRD**

X-Ray diffraction was performed on select representative reference and unknown fine sediment samples. Due to low sample volumes less than 3 g of the fine sediment was mixed with methanol to make a slurry. From the slurry a small amount was pipetted off the top of the settling mixture and transferred to a zero background slide. Care was taken to spread the sample evenly over the entire slide and create a uniform opaque film for analysis. Each sample was then run on a Scintag X1 Powder X-Ray Diffractometer with scan parameters of 2-65° 2θ, step size of 0.02° and a dwell time of 2 seconds which yielded run times of approximately 1 hour and 45 minutes. Powder diffraction patterns were processed and analyzed using the program MDI Jade 9.
Results

Bulk ICP-MS data for trace element composition was collected for the fine and bulk fraction of all samples and references (Appendix 1, 2, and 3 respectively). Initially a conservative approach was taken to define natural background material within the river environment. Because the majority of the river sediment is derived from glacially derived local Ordovician bedrock mixed with weathered metamorphic and igneous rocks ultimately from the bedrock of northern Michigan, USA and Canada, anthropogenic sources need to be distinguished from natural sources.

Reference Material

A total of 5 reference materials were collected representing naturally occurring materials in the GMR valley including: sediment from Four Mile Creek (tributary to the GMR), an abandoned stream, residential stormwater runoff, glacial till and the Russell soil series (RWB2) (Figure 2.1).

Figure 2.1: Google map view of the 5 reference samples collected for analysis.

The Russell soil series was selected because it is one of the most dominant soil types in Butler County, Ohio and thus components would potentially be present in the GMR. Similarly, glacial till which was collected from Peffer Park in Oxford, Ohio is abundant in this area due to the glacial impacts of the Pleistocene. Samples of Four Mile Creek sediment were collected to represent background concentrations of metals coming from the natural areas surrounding Hamilton, Ohio. Four Mile Creek has its headwaters in Preble County, Ohio and flows to Acton Lake, past Oxford, Ohio, and joins the GMR just north of the city of Hamilton. With a smaller
watershed than the GMR, Four Mile Creek drains 322 square miles the majority of which is cultivated crop land (~53%) with only ~10% developed land (OHEPA, 2013). The abandoned stream sediment was selected because it appears to be a dry channel, only active during heavy storm events. It is likely that these sediments are rarely reworked by water thus, they have potentially only accumulated airborne pollutants. The residential stormwater runoff was selected to represent the potential concentrations of anthropogenic metals that could be entering the GMR during a storm event from Black Road Subdivision northeast of Ross, Ohio and similar housing complexes.

In order to define background the reference samples, fines and bulk were evaluated to determine elemental concentrations of interest. A total of 8 samples of bulk and fines for 4 of the 5 reference samples were evaluated. The reference sample of residential stormwater runoff was omitted from this evaluation as it was assumed to contain high concentrations of anthropogenic particulate pollution.

Reference samples exhibited characteristic geochemical correlations with $r^2$ values > 0.7 between Ti/Zr, Ba/Sr, La/Ce (Figure 2.2).

**Figure 2.2**: Correlations between Zr and Ti (A), Ba and Sr (B) and Ce and La (C) according to ICP-MS data taken from reference samples (excluding stormwater runoff).
Of these elements the highest concentrations were observed in the fine fraction of the sediment except for Ba and Sr which had the highest concentration in the bulk fraction, 428 ppm and 232.6 ppm respectively. Relationships were also observed between Al/Fe, Zn/Ti and Ti/Al with $r^2$ values > 0.5 (Figure 2.3).

![Graphs A, B, C](image)

**Figure 2.3:** Correlations between Al and Fe (A), Zn and Ti (B) and Ti and Al (C) according to ICP-MS data taken from reference samples (excluding stormwater runoff).

Fe, Al, Zn and Ti all had the highest elemental concentrations measured in the fine fraction of the sediment: 908.4, 2162.6, 69.3 and 279.9 ppm respectively. All correlations are consistent with natural geochemical trends. Reference samples are assumed to represent natural geochemical background and concentrations of all elements are consistent with the glacial till, Russell soil, abandoned stream channel deposits and sediment from Four Mile Creek. XRD analysis on the Russell soil indicated a composition of quartz and feldspars while the glacial till was observed to have a composition of quartz, calcite and dolomite (Appendix 5). Once compared with unknown samples of GMR sediment it was found that sites within the GMR had higher concentrations of many of the metals analyzed. After applying the conservative approach to determining natural background, many sampling sites plotted above background concentrations.
Sediment Samples-Natural Background

Samples displayed expected geochemical correlations; however, some correlations were stronger in particular fractions of the sediment (bulk vs. fines). Sr and Ba were found to have a weak correlation in the bulk samples \((r^2=0.56)\) and no correlation if all samples were considered \((r^2=0.12)\) (Figure 2.4).

**Figure 2.4:** ICP-MS data for bulk and fine GMR sediment samples. A weak correlation is observed in the bulk sediments with no correlation in the fine sediments.

Al and Ti also exhibited a correlation in the bulk samples once Ti outliers (345.24 and 254.43 ppm) were removed from the data set \((r^2=0.63)\) with no correlation in the fines \((r^2=0.10)\) (Figure 2.5).
Figure 2.5: ICP-MS correlations between Ti and Al with two bulk sample outliers removed for excessive Ti concentrations. A moderate correlation is observed within the bulk sediments.

Concentrations of Ti exceeded maximum concentrations observed in the reference materials with values as high as 345.2 ppm whereas the maximum reference concentrations was 279.9 ppm. Ti correlated well with both Zr and Fe displaying an overall $r^2$ value of 0.88 with Fe (Figure 2.6a) and a bulk $r^2=0.70$/fines $r^2=0.55$ with Zr (Figure 2.6b). These relationships were also observed regularly in SEM imaging and EDS data collection as euhedral particles rich in Ti and Fe were regularly identified. These particles varied in size from 20-60 µm in length and 5-35 µm in width. They were composed of mainly Fe and Ti, were largely euhedral to subhedral and were interpreted to be ilmenite (Figure 2.7).

Figure 2.6: (A) ICP-MS correlations between Ti and Fe for all GMR sediments sampled. (B) ICP-MS correlations between Ti and Zr separated into bulk and fine samples with both size fractions showing relatively moderate correlations with one another.
Higher concentrations of both Fe and Ti were observed in the river sediment samples as compared with the reference materials. Fe and Al also exhibited a good correlation ($r^2 = 0.8$) in all samples once two Fe outliers, 1557.6 and 1017.71 ppm were removed from the sample set (Figure 2.8).

Figure 2.7: (A) Eucleral Fe and Ti-rich particle interpreted as ilmenite 16.5 μm in length and ~4 μm in width (B) EDS spectra (keV along the x-axis) of the particle in (A). (A) is captured in back-scatter detection mode (BSD) at a working distance of 8.4 mm, 25 kV, 18.73 KX and a scale bar = 1 μm.

![Figure 2.7](image)

\[ y = 1.63x + 418.47 \]
\[ R^2 = 0.8 \]

Figure 2.8: ICP-MS correlations between Al and Fe with two bulk sample outliers removed for excessive Fe concentrations (1557.6 and 1017.71 ppm). A strong correlation is observed amongst all size fractions.
Additional natural Fe and Ti textures were observed throughout the samples. One such distinctive texture was a characteristic triangular formation interpreted to be magnetite (Figure 2.9 and 2.10). Both masses are rich in Fe and O, have a total size of ~13 µm and display an equilateral triangular morphology consistent with spinels. This morphology is more defined in Figure 2.9 which constrains the sides of the triangles (arrows) to be ~1 µm in length. In Figure 2.10 the triangular morphology is less defined and triangles appear to have side lengths of ~3.3 µm. Other Fe-rich particles are much larger (30-40 µm in size) and tabular. Figure 2.11 illustrates such a tabular particle (~1 µm thick) which exhibits an undulating surface displaying signs of potential differential weathering. The image in Figure 2.12 also displays a subhedral particle with visible differential weathering, pitting and mechanical abrasion evident on its surface. This particular grain is found to contain high concentrations of Fe and O with additional peaks representative of background material such as Si, Al, Ca, K and Mg (Figure 2.12C).

**Figure 2.9:** The above image displays an iron and oxygen rich particle ~13.5 µm in width with a distinctive equilateral triangular morphology (arrows). The triangles have side lengths of ~1 µm and are similar to textures observed in spinel magnetites. Data is captured in BSD mode at a working distance of 8.6 mm, 25 kV, 15.64 KX and a scale bar = 1 µm.
Figure 2.10: Image (A) is a compact particle ~13 µm in length, ~9 µm in width with EDS data indicating high concentrations of Fe and O with lesser amounts of Si, Al, Ca, and K. This particle displays a similar triangular texture to the mass in Figure 2.9, which is characteristic of spinel magnetite. Micrograph (B) depicts an equilateral triangle indicated by the orange outline which has side lengths of ~3.3 µm and would be considered the (111) face. The micrograph in (A) is taken in BSD mode at a working distance of 8.5 mm, 25 kV, 14.85 KX and a scale bar = 1µm. Micrograph (B) is a higher magnification image of the center portion of the mass imaged in (A), magnification of 33.07 KX and scale bar = 1 µm.

Figure 2.11: The above micrograph is of a tabular particle with high Fe and O concentrations by EDS, interpreted to be magnetite or hematite. The particle itself is 40 µm in length and ~1 µm thick with an undulating upper surface potentially the result of differential weathering. Data is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 4.38 KX and a scale bar = 10 µm.
Multiple masses and single particles of framboidal pyrite are found throughout all samples analyzed indicating the probability of localized anoxic microbial activity within the river sediment. In Figure 2.13A the mass of framboidal pyrite is located in the center of the micrograph and individual crystals of the same brightness can be found away from the larger mass in all directions. Intact large masses of framboidal pyrite are characterized up to 40 µm in length and 25 µm in width. Each crystal is euhedral and typically ≤1 µm in size, actual framboids were also identified and found to be smaller than the aggregates with a diameter of 6 µm (Figure 2.14). In terms of chemical purity the spherical crystals are found to be mainly composed of S and Fe with lesser amounts of Mg, Al, Si, Ca and K. Also, due to the size of the crystals some as small as 0.4 µm the signals for Mg, Al, Si, Ca and K are most likely originating from the surrounding material.
Figure 2. 13: The micrograph in (A) displays a partially disseminated mass of probable frambooidal pyrite ~40 µm in length and around 25 µm in width. The mass is composed of individual spherical euhedral crystals ≤1 µm. Micrograph (B) is a higher magnification image of the center region pictured in (A). The micrographs are captured in BSD mode at a working distance of 8.5 mm, 25 kV, 4.31 KX (A), 11.57 KX (B) and a scale bar = 10 µm (A) 2 µm (B).

Both masses of frambooidal pyrite were composed of spherical microcrystals which had a maximum size of ~ 1 µm with many falling into much smaller size categories (Figure 2.13).

Figure 2. 14: The image above is of a frambooid of pyrite with a diameter of approximately 6 µm (A). The frambooid is composed of spherical crystals ~0.4 µm in size, and these textures are consistent with biological origin. (B) illustrates the EDS which indicates that the chemistry of this frambooid is relatively pure with high peaks for both Fe and S (keV along the x-axis). The image is captured at a working distance of 8.5 mm, 25 kV, 33.76 KX and a scale bar = 1 µm.
Relationships among the rare earth elements were also observed within the ICP-MS data set and are consistent with geochemical trends; the only source of REEs present in this environment should be naturally occurring as there are no known sources of anthropogenic REEs in this region. La and Lu exhibited weak correlations in both the bulk and fine fractions and an overall $r^2$ value of 0.50 (Figure 2.15).

![Figure 2.15: Correlation between Lu and La using ICP-MS data for all size fractions.](image)

La and Ce on the other hand were strongly correlated with an $r^2$=0.98 (Figure 2.16) which was also documented in the SEM data collection as particles rich in La and Ce were frequently observed. These particles were between 2-4 µm in length with an average of 1 µm in width and displayed very prominent La and Ce peaks within the EDS spectra (Figure 2.17-2.20). In addition, reference sample correlations between La and Ce also had a high $r^2$ value 0.99 indicating very little change in the relationship between these two elements in reference and GMR sediment samples.
Figure 2. 16: A strong correlation between Ce and La was observed throughout all size fractions after one outlier with excessive Ce concentration (125.63 ppm) was removed from the sample set.

Figure 2. 17: The above image shows a subhedral to euhedral REE phosphate mass containing cerium and lanthanum. Particles are ~2 µm in length and ~300 nm in width with some rounding on the edges. The data is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 46.30 KX and a scale bar = 200 nm.
Figure 2. 18: The micrograph above is taken of a subhedral REE phosphate ~3.5 µm in length ~2.2 µm in width. Data is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 36.61 KX and scale bar = 1 µm.

Figure 2. 19: The above image is a subhedral La and Ce phosphate. This particle is 4 µm in length and 1.2 µm in width; crosshairs indicate the point of EDS analysis. The data is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 14.25 KX and a scale bar = 2 µm.
Figure 2.20: The above micrograph is an anhedral La and Ce phosphate, 3.5 µm in length and 2.5 µm in width. This data is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 28.28 KX and scale bar = 1 µm.

ICP-MS REE data was plotted against the North American Shale Composite (NASC) (Figure 2.21). This provided more evidence that the GMR sediment is not systematically geochemically enriched or depleted in elements or has an unusual source component expressed. Additionally, XRD data indicates that no exotic mineral phases are present within three representative GMR sediment samples, the samples yield diffraction peaks characteristic of: quartz, feldspar, calcite and dolomite (Appendix 5). The Igpet plot illustrates that the fine fraction of the sediment (green triangles) is more enriched in REE as opposed to the bulk fraction of the sediment. Trends of higher concentrations in the fines as opposed to the bulk were also evident in the ICP-MS data. Co, Ce, La, As, Zn, Ni, Cr, Cu and W all displayed significantly higher concentrations in the fine fraction as opposed to the bulk for the majority of the samples. Representative plots for selected elements of Zn and Ni are presented in Figure 2.22.
Figure 2.21: Igpet (2005) plot of all GMR sediment samples. Green triangles represent the fine samples whereas the blue circles represent the bulk sediment.
Figure 2.22: ICP-MS data for all 19 sample sites separated into the fine and bulk fraction at each sampling site. (A) Zn concentration is greater in the fine fraction (red squares) as opposed to the bulk (blue diamonds). (B) Ni concentration is greater in the fine fraction as opposed to the bulk.

Some samples display a higher concentration in the bulk fraction of the sediment in comparison to the fines. Cd (not shown) and Ba both had 6 separate samples containing a higher concentration in the bulk as opposed to the fine counterpart of the particular sample. For many of the other elements this discrepancy is much lower; Pb, Mn, Sn and Zr only 3 samples have a higher concentration in the bulk, only 2 samples for Fe and Cr, and 1 sample for both W and Cu (Figure 2.23). Overall, the majority of the metals are concentrated in the fine fraction of the sediment but higher bulk concentrations do exist in selected samples.
Figure 2. 23: ICP-MS data for all 19 sample sites separated into the fine and bulk fraction at each sampling site. (A) Ba concentration (B) Sn concentration.

Further characterization of this sediment in terms of extent of weathering was also examined. Utilizing an index of chemical alteration (CIA) defined by equation 2 the extent of weathering was determined for all analyzed samples.
Equation 2: Index of chemical alteration taken from McLennan, 1993. CaO* indicates Ca in the silicate fraction only.

Samples were evaluated based on the following criteria set forth by McLennan, 1993: CIAs of 45-55 indicate little to no weathering, 100 indicates intense weathering, ~61 indicates average sediment and an average shale ranges from 65-70. CIAs were calculated for all samples and averages were taken of the fines, bulk and references. The results indicated that the fines (average CIA=70.5) were moderately weathered, the bulk (average CIA=64.8) represented average sediment and the references (average CIA=68.5) were representative of average shale. Overall these sediments had not undergone extensive chemical weathering which agrees with the provenance of GMR sediment. The majority of these sediments are glaciogenic. Thus, the sediments have not undergone the typical route of chemical weathering and have instead been mechanically weathered through by the erosive force of ice (McLennan, 1993). Further sediment yield rates calculated using equation 3 confirms the glacial derivation and anthropogenic impacts of river control according to Figure 2.24 taken from McLennan, 1993.

Sediment Yield (t/km$^2$/yr) = (2.25 * 10$^5$) * (10$^{-0.0435[CIA]}$)

Equation 3: Equation for sediment yield using previously calculated CIA values. Taken from McLennan, 1993.

Figure 2.24: Adapted from McLennan, 1993. (A) shows sediment yields and CIA values for selected rivers around the world. Solid squares for the Colorado, Columbia, Indus, Mississippi and Nile Rivers represent pre-dam values. Open squares connected to all except the Colorado and Nile are current sediment yields, both the Colorado and Nile have essentially zero yields. (B) Diagram indicating how anthropogenic and natural processes result in different weathering relationships.
Average CIA values for bulk, fines and reference samples were used to calculate the sediment yield, equation 3 generated 341.9, 193.1 and 242.2 t/km$^2$/yr respectively. This coupled with the average CIA values indicates that these sediments fall mainly into the moderately weathered category in Figure 2.24. This is to be expected as GMR sediment is glacially derived and the GMR has been altered in order to control flooding issues, thus anthropogenic forces could be at work accelerating the rates of erosion in some sections of the GMR.

**Sediment Samples—Probable Anthropogenic Pollution**

Potential anthropogenic particulate pollution was identified through the use of ICP-MS data and particulate morphology. If sediment samples had high concentrations of an element, above the conservative background quantity it was interpreted that those concentrations represented anthropogenic contamination. Multiple samples were screened using the SEM and TEM to determine how particular metals occur within the GMR sediment. Through SEM imaging and EDS data, contaminants such as Pb, Ba sulfate, Cu sulfide, Sb, As, coal spherules, Co, W, Cr along with potential anthropogenic particulates containing Fe and Ti were identified. Coal spherules from fly ash were most easily recognized as a contaminant due to their morphology, a direct result of the coal combustion process. The spherules identified in this study demonstrate the smaller size fraction as they vary in size from 2-27 µm and have an assortment of surficial textures. Since all SEM work was performed on the fine fraction of the sediment (≤40 µm) spherules may exist in larger sizes but were removed from this particular sample set during sample preparation. Figure 2.25-2.33 illustrate the diversity of coal spherules seen within the GMR sediment.

**Figure 2.25:** A representative iron, silica and aluminum-rich mature coal spherule with an ~4.5 µm diameter, the spherule exhibits blocky subhedral components. Data is captured in BSD mode at a working distance of 8.5 mm, 20 kV, magnification of 22.60 KX and a scale bar = 1 µm
Figure 2.26: (A) A representative iron, silica, aluminum and oxygen rich coal spherule ~ 27 µm in diameter displaying a thatched fabric. Smaller particles and an additional coal spherule ~2 µm in diameter (arrow) are adhered to the spherule. The image is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 4.63 KX and a scale bar = 10 µm. (B) Higher magnification image of the spherule in (A) captured at 9.70 KX and a scale bar = 2 µm.

Figure 2.27: The above micrograph is of an immature coal spherule only 3 µm in diameter. This image is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 21.45 KX and scale bar = 1 µm.
Figure 2. 28: This image is taken of an iron, silica and oxygen-rich mature coal spherule with a 3.5 µm diameter. The data is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 26.69 KX and a scale bar = 1 µm.

Figure 2. 29: Micrograph depicting a representative relatively un-weathered coal spherule that has a diameter of 6 µm. The data is captured in BSD mode, at a working distance of 8.5 mm, 25 kV, 28.52 KX and a scale bar = 1 µm.
Figure 2.30: The above micrograph is a coal spherule with an ~19 µm diameter displaying a conglomeritic texture. This coal spherule appears relatively un-weathered with some smaller clay particles adhered to the surface. The image is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 8.42 KX and a scale bar = 2 µm.

Figure 2.31: Image depicting a 9 µm diameter coal spherule, displaying a smooth outer texture with an abraded window into a spiny inner sphere (arrow). EDS spectra indicates high concentrations of Si, Al and O with lesser amounts of Ca, K, Mg, Fe, and Ti. The data is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 15.97 KX and a scale bar = 2 µm.
Figure 2.32: The above micrographs portray a mature 15 µm diameter coal spherule with a chemical composition rich in Fe, Si, O, Al and Ca, with minor amounts of K, Mg, and Ti. Image (A) is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 13.10 KX and a scale bar = 2 µm. Image (B) is a higher magnification image of the center of the coal spherule from (A) magnification 28.57 KX and scale bar = 1 µm. Image (C) is a 41.12 KX image of the middle right of image (B) with a scale bar = 1 µm. The equilateral triangle (outlined by orange triangle in C) has sides equal to ~0.6 µm and is a texture consistent with spinels.
Figure 2.33: The above image (A) shows a mature coal spherule with an overall diameter of 10 µm. This spherule displays a “bird’s nest” structure with acicular fragments composing the majority of the structure. EDS analysis indicates high concentrations of Al, Si, and O with lesser amounts of Fe, Ti, Ca, and K. The data is captured in BSD mode at a working distance of 8.4 mm, 25 kV, 22.82 KX, and a scale bar = 2 µm. The EDS of this coal spherule pictured above is in (B) with keV along the x-axis.

Most spherules were rich in Fe, Si and O with fluctuating amounts of Fe, Al, Ca, K and Ti. Figure 2.33A is of a spherule which had Al as its most abundant element followed by Si, O and Fe which is opposite of many of the other spherules profiled (Figure 2.33B). Transition metals such as Ni, Cr and V, which commonly occur in spinel-rich spherules at concentrations of ~100 to 1000 ppm, were not observed in any coal ash spherules in the GMR.

Numerous particles interpreted as being anthropogenic in origin were identified in the SEM with the aid of BSD and EDS. This research aimed to identify anthropogenic metal-rich particles within the GMR sediment thus BSD supported this effort in simplifying the search process for these metals. Numerous particles of Ba sulfate were found, many of which displayed the effects of mechanical weathering within the river environment (Figure 2.34-2.40).
Figure 2.34: The two micrographs above display barium and sulfur-rich particulate surrounded by silica and calcium-rich particles. This barium and sulfur particle is ~28 µm in length and ~14 µm in width and displays pitting and abrasion textures. Image (A) is captured in BSD mode at a working distance of 8.4 mm, 25 kV, 11.30 KX and a scale bar = 1 µm. Image (B) is a 14.30 KX image of the bottom left of the particle imaged in (A).

Figure 2.35: This electron micrograph is an anhedral barium and sulfur-rich particle which is ~2 µm in width and displays potential mechanical abrasion and weathering. The image is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 37.61 KX and scale bar = 1 µm.
Figure 2. 36: The image above illustrates a subhedral barium and sulfur-rich particle which is 2.7 µm in width ~3.4 µm in length. Rounding and some pitting is visible on the particle which indicate potential weathering effects. The data is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 21.68 KX and a scale bar = 1 µm.

Figure 2. 37: The image in (A) is a mass of Ba and S-rich euhedral to subhedral particles with the center particle (arrow) having a length of 9 µm and an ~2 µm width. The image and spectra are captured in BSD mode, with a working distance of 8.5 mm, 25 kV, 11.03 KX and a scale bar = 2 µm. The EDS in (B) with keV along the x-axis is collected from the particle imaged in (A). Note the 1:1 ratio of Ba to S and the high O peak, indicating this is potentially a particle of barite (BaSO₄).
Figure 2.38: The above images portray an unconsolidated mass of Ba and S-rich particles, most of which display either rounding or pitting. Image (A) is captured in BSD mode with a working distance of 8.5 mm, 25 kV, 23.47 KX and a scale bar = 1 µm. Image (B) is a 34.85 KX image of the mass imaged in (A) with a scale bar = 1 µm.

Figure 2.39: Image (A) illustrates an anhedral to subhedral Ba and S-rich particle which has a length of 5.6 µm and a width of ~2.2 µm (excluding the longer limbs). The micrograph is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 39.78 KX and a scale bar = 200 nm. (B) is the corresponding energy dispersive spectra to the particle imaged in (A) with keV along the x-axis. The signal for both Ba and S are 1:1 which could be indicative of barite (BaSO₄).
Figure 2.40: Micrograph (A) is a Ba-rich particle (barite) that is 20 µm in length and 8 µm in width at the widest section, surrounded by aggregates of Ca- and Si-rich grains. The Ba-rich particle appears to be mechanically weathered with pitting noticeable on the upper left side of the particle in (B). Both micrographs are captured in BSD mode, working distance = 8.5 mm, 25 kV and scale bars = 1 µm. Image (A) was taken at a magnification of 11.10 KX while image (B) is a higher magnification image of the upper left hand corner of (A), captured at 22.28 KX.

These particles ranged in size from 28-3.4 µm in length and 14-2 µm in width with the majority of particles having a width between 2 and 3 µm. Chemically, these particles are rich in Ba and S according to the EDS spectra with peaks for Si, Al, Ca and O interpreted to be from the background substrate.

Pb is another contaminant regularly identified within the samples varying from small anhedral particles at 550 nm to larger particles of Pb ~10 µm in diameter. Most Pb particles are anhedral and some display rounding, potentially from mechanical weathering or dissolution (Figure 2.41 and 2.42). One subhedral diamond-shaped particle profiled (Figure 2.43) is the largest lead-rich particle identified in the sample set at 8 µm in width and 10 µm in length. This particular grain also has smaller ~0.5 µm crystals of similar brightness adhered to its edges. Since this micrograph is taken in BSD crystals of a similar brightness most likely indicate crystals of similar chemical composition. The larger diamond-shaped mass and the smaller euhedral crystals are most likely lead-rich according to EDS, which indicates a high lead peak with lesser peaks for Si, O, Ca, Mg and Fe. The majority of particles are composed of mainly Pb and are interpreted to be Pb metal particles or corroded Pb metal; one however, did have an EDS peak for P (Figure 2.44).
**Figure 2.41:** The image in (A) is of an anhedral rounded lead particle which is 2.2 µm in length and 1.5 µm in width surrounded by calcium and silica rich background material. (B) is the EDS of the particle imaged in (A) which depicts strong Pb peaks with keV along the x-axis. This image is captured in BSD mode at a working distance of 8.5mm, 20kV, magnification 61.97 KX with a scale bar = 200 nm.

**Figure 2.42:** The above image is of a weathered anhedral lead particle on a silica and calcium-rich background. The lead-rich particle is ~550 nm in width and is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 160.08 KX and a scale bar = 200 nm.
Figure 2.43: The above micrographs are of a subhedral to euhedral Pb-rich particle that is 8 µm in width and 10 µm in length and surrounded by Ca and Si-rich material. Image (A) is taken in BSD mode at a working distance of 8.4 mm, 25 KV, 7.40 KX and scale bar = 2 µm. Image (B) is a higher magnification image (25.77 KX, scale bar = 1 µm) of the upper half of the particle imaged in (A), (B) shows ~0.5 µm euhedral crystals exhibiting an equivalent highlight as seen in the larger particle (arrows). EDS is shown in (C) for the particle imaged in (A), note the strong Pb peak.
In addition to discrete particles of Pb, the compound PbCrO$_4$ was identified in the river sediment samples. The morphology of these particles is characteristic as crystals of PbCrO$_4$ were found to be embedded within a calcium/silica matrix. A previous study by Detherage et al., in review, identified PbCrO$_4$ in multiple samples of yellow road paint taken from the streets of Hamilton. 13 yellow paint samples were collected and PbCrO$_4$ was identified in 10 of those samples using the SEM. Particles were characterized to be 125 to 350 nm in length and 75 to 200 nm in width, occurring as subhedral to euhedral crystals within an organic polymer matrix (Detherage et al., in review)(Figure 1.12). River sediment bulk chemical analysis indicated a weak correlation in the sample set between Pb and Cr. (Figure 2.45)
Figure 2.45: Correlation between Pb and Cr using ICP-MS data for all size fractions. The trend excludes the outlier which had a higher concentration of Pb in comparison to the other samples.

Similar masses of PbCrO$_4$ were identified in GMR sediment both as apparent paint matrixes and as single crystals. One potential particle of yellow road paint appeared as an isosceles triangle with a base ~9.5 µm in length and legs ~8.2 µm in length (Figure 2.46).

Figure 2.46: Yellow road paint aggregate in the shape of an isosceles triangle with a base ~9.5 µm in length and legs ~8.2 µm in length. Bright PbCrO$_4$ crystals ~600 nm in length and ~100 nm in width are embedded within a dull Ca and organic rich matrix. Data is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 22.97 KX and a scale bar = 1 µm.
SEM images taken in BSD mode illustrate bright euhedral PbCrO$_4$ crystals embedded within a dull matrix very similar to what was observed in the Detherage et al. study. PbCrO$_4$ crystals range in length from ~300 nm to over 600 nm in length with many crystals falling in the >600 nm category. Crystals within Figure 2.46 are ~600 nm in length and ~100 nm in width on average. All crystals exhibit high peaks for both Pb and Cr while spot EDS analysis on the matrix exhibits lower Pb and Cr peaks with higher EDS peaks for Ca, Si, Al and O (Figure 2.47 and 2.48).

Figure 2.47: A high magnification image of PbCrO$_4$ crystals (A) with accompanying EDS data (B) for crosshairs pictured in (A). The EDS indicates relatively high concentrations of both Pb and Cr with additional signal coming from the surrounding matrix (Ca, Si, Al, O). Micrograph (A) was taken in BSD mode at a working distance of 8.5 mm, 25 kV, 78.34 KX and a scale bar = 200 nm.
Figure 2. 48: Image (A) is a micrograph with crosshairs over a region of matrix to the immediate left of the PbCrO$_4$ crystal aggregate profiled in Figure 2.47. The EDS data in (B) is for the crosshairs pictured in (A) with keV along the x-axis, this data indicates a higher concentration of Ca, Si, Al and O with lesser concentrations of Pb and Cr. Image data is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 44.22 KX and a scale bar = 1µm.

An additional mass of PbCrO$_4$ crystals was also found without a prevalent matrix. These crystals appeared to have undergone more weathering and most displayed broken ends with only one side of the crystal coming to a termination point. Due to this the average length of the crystals varied from ~320 nm to ~420 nm with more consistent widths from 50 nm to ~100 nm, mimicking the widths of the crystals identified in Figure 2.46 (Figure 2.49 and 2.50).

Figure 2. 49: An aggregate of PbCrO$_4$ crystals is imaged in the center of the above micrograph with an additional PbCrO$_4$ crystal in the upper right of the image. These crystals vary in length from ~420 nm to ~320 nm with more consistent 50 nm to 100 nm widths. Data is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 60.30 KX and a scale bar = 200 nm.
Figure 2.50: Above is a higher magnification image of the center PbCrO$_4$ crystal aggregate that is imaged in Figure 2.49. Here evidence for potential dissolution is more evident with significant rounding visible on the ends of multiple PbCrO$_4$ crystals and the appearance of faint thin halos (~30 nm in width) around the crystals (arrows). The micrograph is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 193.21 KX and a scale bar = 100 nm.

Figure 2.51: The above micrograph is a high magnification image of two crystals of PbCrO$_4$ the crystal to the right (yellow bracket) is ~420 nm in length and ~130 nm in width with a termination point on the right end. Data is collected in BSD mode at a working distance of 8.5 mm, 25 kV, 338.74 KX and a scale bar = 100 nm.
The PbCrO$_4$ crystals in Figures 2.49 and 2.50 appear to be significantly rounded with halos around the edges of individual crystals, suggesting some degree of dissolution. Rounding to this degree was not observed in the paint chips analyzed by Detherage et al. or in the embedded crystals of Figure 2.46. Figure 2.51 is another micrograph of isolated euhedral PbCrO$_4$ crystals located nearby the mass of crystals in Figure 2.49. The main crystal in this image with the termination on the right is 420 nm in length and ~130 nm in width, also displaying potential dissolution as evidenced by rounding.

Particles containing Sb (Figure 2.52 and 2.53), Cu sulfide (Figure 2.54), Co (Figure 2.55), and As (Figure 2.56) were less common, occurring only a few times throughout the sample set. Sb particles were identified in two samples (JT 18 and 19) using the SEM. Sample JT 18 ICP-MS data indicated Sb concentration was at 0.91 ppm while JT 19 had the highest Sb concentration of all the fine samples at 1.22 ppm. One particle identified in JT 18 appears to be characteristic of elemental Sb with multiple crystals displaying a pseudocubic habit embedded in a Si, O and Al rich matrix (Figure 2.52).

**Figure 2.52:** Image (A) illustrates the pseudocubic habit of multiple Sb-rich crystals with the largest cube (arrow) being ~600 nm in size and all the smaller crystals around 200 nm. These crystals are embedded in a Si, O, and Al-rich matrix as is shown by the EDS in (B) (keV along the x-axis), the pseudocubic crystals impart the high Sb peak. The image is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 47.09 KX and a scale bar = 1 µm.
The pseudocubic crystals observed in this SEM image are approximately 200 nm across with the larger cube ~600 nm across. Another particle located in JT 19 contains Sb but not as the main element, instead, (in decreasing abundance) this particle contained Si, Al, and K-rich material. (B) is the associated EDS for the particle imaged in (A), which indicates that the particle is not only rich in Sb but also in Pb and Fe (keV along the x-axis). Data collected in BSD mode at a working distance of 8.5 mm, 25 kV, 34.10 KX with a scale bar = 1 µm.

Figure 2.53: Image (A) is a micrograph of a massive anhedral Sb-rich particle that is 0.7 µm in width and 1 µm long surrounded by Si-, Al- and K-rich material. (B) is the associated EDS for the particle imaged in (A), which indicates that the particle is not only rich in Sb but also in Pb and Fe (keV along the x-axis). Data collected in BSD mode at a working distance of 8.5 mm, 25 kV, 34.10 KX with a scale bar = 1 µm.

The pseudocubic crystals observed in this SEM image are approximately 200 nm across with the larger cube ~600 nm across. Another particle located in JT 19 contains Sb but not as the main element, instead, (in decreasing abundance) this particle contained Si, O, Al, Pb, Sb, Fe, K and Mg (Figure 2.53). This particle is 0.7 µm in width and 1 µm in length and instead of displaying a pseudocubic habit this particle is massive and anhedral. One striking crystal rich in Cu and S was found within the sample set and is interpreted to be a copper sulfide due to its elemental abundance of Cu and S and the low solubility of such a compound in an aqueous river environment. The euhedral crystals were observed to be ~ 5 µm in length and 2 µm in width with smaller subhedral crystals aggregated around the base of the larger crystals (Figure 2.54).
Figure 2.54: The above image is of euhedral copper sulfide crystals ~5 µm in length and ~2 µm in width (white arrows) with smaller subhedral to euhedral crystals at the base (black arrows). This micrograph is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 15.22 KX and a scale bar = 1 µm.

Another unique particle having high concentrations of Co, Cr, Si, W, Ca, K, Al and Pb was identified with the SEM; this particle appeared to be subhedral and tabular in shape. A clean image was difficult to obtain for this particular particle as it was buried beneath other platy particles; however, jagged outside edges, potentially indicating weathering or particle texture are visible (Figure 2.55).

Figure 2.55: The micrograph in (A) is a tabular particle containing multiple metals and displaying jagged potentially weathered edges. (B) is the corresponding EDS spectra (keV along
the x-axis) which shows that this particle is rich in Cr, Co, Pb, W, and Fe, with additional peaks for Ca, K, Al and Si most likely representing the surrounding material. Image (A) is captured in BSD mode at a working distance of 8.5 mm, 25 kV, 48.08 KX and a scale bar = 1 µm.

One particle containing As was distinguished amongst natural clay particulate. 1.8 µm in length by 1 µm in width, this particle appeared to be rounded and displayed EDS peaks for Fe and As along with the expected Si, O, Al, Ca and K signatures potentially from the surrounding particulate (Figure 2.56).

![Figure 2.56: The above image (A) is an anhedral rounded particle 1.8 µm in length and 1 µm in width, surrounded by platy aggregates. The particle itself contains a significant amount of As and Fe with the surrounding particulate contributing a Si, Al, Ca, and K signal (B, keV along the x-axis). The image is taken in BSD mode at a working distance of 8.5 mm, 25 kV, 109.26 KX and scale bar = 100 nm.](image)

**Bright Field TEM**

Selected natural phyllosilicate clay particles within the sample set were also analyzed using TEM. This technique allows for a more detailed analysis of the finest particles present within the GMR sediment. The complexity of the sediment is further realized through this study as discrete particles on the nanometer scale were found in aggregates only a few micrometers in length. Selected area electron diffraction (SAED) of the aggregates reveals both single crystal and polycrystalline material. EDS from these aggregates reveal compositions analogous to illite, calcite and Fe-oxides; all of which are expected natural constituents of river sediment.
along ~104 and the discrete diffraction net indicates that this is a single crystal of calcite. Image H is a mass of Fe-oxide settled on an illite particle, the Fe-oxide aggregates are ~60 nm in length and ~10 nm in width, scale bar = 50 nm. SAED pattern G corresponds to the Fe-oxide aggregate in H and illustrates diffraction cones which have d-spacings consistent with goethite and hematite.
Figure 2.57B shows multiple euhedral laths of illite with widths ranging from ~40 nm to ~170 nm with the longest lath around 0.95 µm in length. Fe-oxides occupy the bottom portion of this micrograph and tend to be around 50 nm or less in length. The EDS spectra is especially significant for this aggregate as a distinct Zn peak is present. It is expected that the Zn is in association with the Fe-oxide aggregate. Anhedral illite is shown in Figure 2.57D with Fe-oxide aggregates adhering around the edge of the illite and in the upper portion of the micrograph. In 2.57C the ring of diffraction spots is indicative of a stacking disorder amongst the platy illite crystals. Figure 2.57E and F illustrate a calcite crystal imaged along the 104 crystallographic face, E indicates that a single crystal is present owing to single discrete diffraction spots. The softening along the edge of the calcite crystal in F indicates dissolution. Image 2.57H is a micrograph of an Fe-oxide aggregate adhered to an illite crystal, the individual Fe-oxide crystals appear to be similar in size to those imaged in Figure 2.57B having lengths around 60 nm and 10 nm widths. The diffraction cones shown in Figure 2.57G generated by this mass of Fe-oxide and illite yield d-spacings consistent with a mixture of goethite and hematite.

Additional examples of illite are provided in Figure 2.58 with examples of euhedral and subhedral illite crystals. Figure 2.58B is an excellent example of platy euhedral illite which appears to exhibit several layers along with attached Fe-oxide particles the largest of which is 100 nm in length and ~60 nm in width. Additionally Figure 2.58A confirms that the particle in B is a single crystal as the SAED image shows a pseudohexagonal net with discrete diffraction spots. Figure 2.58C and D also illustrate an illite but the SAED pattern indicates that multiple slightly offset illite crystals make up the particle. This particular illite is also subhedral and appears to have a small ~60 nm long Fe-oxide particle adhered it its edge at the bottom right hand corner of the image.
Figure 2.58: The two bright field TEM images and SAED patterns above were taken from GMR fine sediment sample JT 10. SAED pattern A illustrates a single psuedohexagonal net taken along hk0 of the crystal in B. Micrograph B is a euhedral particle of illite exhibiting some overgrowths and adhered Fe-oxide masses, scale bar = 50 nm. Image D is representative of a subhedral illite particle with a scale bar = 50 nm. The corresponding SAED pattern is shown in C, it was taken down ~hk0 of the illite particle and shows that this particular particle consists of multiple crystals.
Figure 2. 59: The above SAED patterns and bright field TEM images were taken from GMR fine sediment sample JT 18. Micrograph B appears to be a subhedral illite particle with attached aggregates of Fe-oxide, scale bar = 0.1 µm. The SAED pattern in A corresponds to the aggregate in B and indicates that two crystals are present and overlapping. D appears to be an aggregate of illite crystals which appear to be subhedral, scale bar = 20 nm. Image C is the SAED pattern of D taken along ~hk0 and looks as if it is of a single crystal. Micrograph F is a subhedral to euhedral particle ~1.2 µm long and ~0.9 µm wide (scale bar = 0.1 µm) with a chemical composition pointing towards calcite. The SAED pattern for this crystal is shown in E and indicates that a single crystal is present. Multiple masses of Fe-oxide ~80 nm in size are visible in H along with what appears to be platy particles of illite, scale bar = 20 nm. The SAED of this image is shown in G and the distinct rings indicate that the particles are stacked and slightly offset from one another.
Figure 2.59 continues to demonstrate the diversity of illite and calcite particles observed in the sample set. SAED pattern in 2.59A and the EDS taken from the particle in B is consistent with the presence of two crystals of illite as evidenced by the double diffraction spots. This micrograph of illite is subhedral to anhedral and also includes adhered Fe-oxide aggregates ranging in size from 50 nm to 0.22 µm. Figure 2.59 C and D appear to display several layers of subhedral illite which are all part of a single crystal as the SAED pattern exhibits discrete diffraction spots in a diamond shaped net. The particle imaged in Figure 2.59F appears to be a single crystal of calcite. The SAED pattern in E displays discrete well-spaced diffraction spots that form a diamond shaped net which indicates that only one crystal is present. The calcite crystal itself is euohedral to subhedral ~0.9 µm wide and ~1.2 µm in length and displays some rounding on the edges indicative of potential dissolution. Finally, Figure 2.59H illustrates another aggregate consistent with anhedral illite with attached aggregates of Fe-oxide masses that are ~80 nm in size. The SAED pattern in G signifies that multiple crystals are present as double diffraction spots are visible.

**STEM/Elemental Mapping**

Elemental associations at higher magnifications and resolutions were determined using scanning transmission electron microscopy (STEM). Representative images and corresponding elemental maps are provided for: JT 2, JT 10 and JT 18. These elemental maps provide representative examples of the natural elemental associations and spatial associations of pollutants on clay aggregates within the sample set. STEM allows for nanometer elemental associations to be mapped on micrometer-sized particles. This technique allowed for clay particle identification and contaminant association along with illustrating the complex nature of environmental samples. Two particles were determined to be mainly of natural origin (Figure 2.60 and 2.61) with each exhibiting its own unique composition. Figure 2.60 is predominately dolomite (CaMg(CO₃)₂) with a ~750 nm long crystal of kaolinite and a small fragment of Fe-rich material. This mass also displays disseminated phosphorus and a ~200 nm particle of concentrated amounts of Fe and Mn. Figure 2.61 on the other hand illustrates the variety of phyllosilicate minerals present within the river sediment with a main particle consisting of mainly smectite with some illite. This particular mass displays multiple natural particles all within one aggregate less than 2 µm in length. A grain interpreted as apatite (Ca₅(PO₄)₃) appears in the lower left of elemental maps Ca and P. A void is visible in both the Ca and P maps, in which Mn appears to be occupying along with some S. One particle of Ti-oxide appears surrounded by an Fe-oxide with some association with disseminated Mn. Also evident in this STEM image are the crystalline Fe oxides (stars) which stand out against the polycrystalline background material. These crystals are interpreted to be goethite based on morphology, which is a common naturally occurring Fe oxide. Both of the samples previously described illustrate natural materials and elemental associations within the GMR sediment. Associations between Al, K, Mg, Si, Ca and O typically indicate phyllosilicate minerals, Mn tends to follow heavy metals, and natural occurring apatites and Fe oxides are prevalent.
Figure 2. 60: The above micrographs are STEM and STEM/elemental maps for a representative natural particle composed of mainly dolomite. Strong positive spatial correlations are observed between Al and Si along with Mg, O, and Ca. STEM images and elemental maps are captured at 60,000 x, 200 keV and the scale bar = 500 nm.
**Figure 2.61:** The above images are STEM and STEM/elemental maps for a representative natural particle containing goethite indicated by the positive correlation observed in the Fe and O maps. Additional strong correlations exist between Ca and P in addition to correlations between Si, K, Mg, and Al. STEM images and elemental maps are taken at 100,000 x, 200 keV with a scale bar = 300 nm.
Several elemental maps exhibited relationships which can be interpreted to be anthropogenic. Figure 2.62 appeared to be one particle; however, STEM mapping indicated that several discrete materials are present. The main particle in Figure 2.62 is interpreted to be dolomite as it is rich in Ca and Mg, oxygen exhibits an affinity to the right rim of the particle which also coincides with greater signal for both Ca and Mg. Al appears to only correlate with Si (kaolinite) in the upper right hand corner of the image. There is a strong correlation between Cu and S. Overall Mn appears disseminated throughout the particle but does correlate with some of the Fe and Cu present in the sample.
Figure 2.62: Micrographs of STEM and STEM/elemental maps for a sediment particle containing anthropogenic pollution. The bulk of the particle consists of Ca, Mg and O (dolomite) with an Al-rich region. Cu and S are observed to have a strong correlation to one another and a correlation is observed between Fe and Mn. Micrographs were captured at 60,000 x, 200 keV and a scale bar = 400 nm.

Figure 2.63 is a higher magnification image of the particle imaged in Figure 2.62 which demonstrates a positive spatial relationship between Mn and heavy metals such as Ni, Cr, and Fe. There also appears to be a correlation between Cu, Fe, S, Mn and Ni with the strongest correlation between Cu, Fe and S. These relationships appear on a dolomite particle (Ca and Mg maps) with significantly smaller crystals of kaolinite (right edge of particle, Al and Si rich).
Figure 2.63: The above STEM and STEM/elemental maps are higher magnification images of the area containing Cu in the sediment particle imaged in Figure 2.62. Strong natural spatial correlations are observed between Ca, Mg and O (dolomite) in addition to Al and Si sharing an affinity to one another (kaolinite). Mn appears to correlate with some of the pollutants: Cr, Ni and Fe; while a strong correlation is observed between S and Cu with some affinity to Mn and Fe. STEM images are collected at 200,000 x, 200 keV and a scale bar = 200 nm.

Figure 2.64 is an aggregate of particles the bulk of which appears to be rich in Fe, Ca, Cl and O. One particle in the lower right which is composed of Al, O and Si is a fragment of kaolinite, a particle directly above the kaolinite on the opposite edge of the mass is consistent with the composition of a smectite. There appears to be some correlation between Fe and Mn in this particular particle, while Cu and P appear disseminated with no apparent correlation to Fe.
Figure 2.64: The above images are low magnification STEM and STEM/elemental maps for a particle which appears to contain anthropogenic pollutants. Cu, P and S are disseminated throughout the particle while a strong correlation is observed between Si, Al and O and between Mg and Ca. Fe appears along the left edge of the particle in discrete clusters that are not observed to correlate well with any of the other mapped elements. These micrographs are taken at 25,000x, 200 keV with a scale bar = 1 µm.
STEM Detailed Elemental Analysis

The distribution of Fe varied amongst the samples analyzed with STEM/EDS elemental mapping. Discrete particles of high concentration were observed along with disseminated distributions. Overall for Fe, non-standardized EDS spectra from the maps indicate concentrations are typically 0.01 to 2.2 wt % Fe. The discrete particles appear to be around 300 nm or less in size with a blocky or crystalline shape. Fe tends to correlate spatially with O and Mn, along with Cu, Cr and Ni if present. Goethite was observed in the presence of smectite in Figure 2.61 whereas disseminated Fe with concentrated masses that did not display the high crystallinity of those in Figure 2.61 were found to be in association with dolomite.

Titanium composes the TEM grids which were used for analysis, thus background Ti EDS peaks were observed in every sample. However, Figure 2.61 illustrates one particle which displays the presence of a Ti-rich mass within a dominantly smectite particle. Due to the omnipresence of Ti as a result of the grid metal, quantitative analysis was not performed on the EDS spectra. This particular Ti mass is around 300 nm in length, almost completely surrounded by Fe with a close spatial association with O. Significant quantities of Ti are not present in any of the other images presented, however, small masses similar to the one in Figure 2.61 were observed on various other particles within the sample set.

Concentrations of Mn based on non-standardized EDS spectra from the elemental maps indicate that the average concentration is less than 0.06 wt % Mn with the highest value being 0.17 wt % Mn on the particle imaged in Figure 2.60. Mn appears disseminated throughout the majority of the particles mapped but does tend to concentrate into areas which are shown to contain other metals such as Cu and Fe as well as S. Spatially the relationship between Fe and Mn is relatively consistent over the STEM images presented.

S is disseminated throughout multiple particles unless significant Cu is present. When concentrated regions of Cu appear in the particle, S is observed to be in close spatial association. Figure 2.62 and 2.63 illustrate the affinity of S to Cu when a concentrated mass (~300 nm) of Cu is present, this relationship is not as evident when Cu is disseminated, such as in Figure 2.64. Otherwise the S appears to be spread across the entire particle similar to the distribution of Mn and Fe (Figures 2.60, 2.61 and 2.64). S exhibits concentrations of 0.14 wt % to 1 wt % S according to non-standardized EDS spectra collected from the STEM maps with an average of 0.46 wt % S observed among all the images presented.

For Cu, non-standardized EDS spectra obtained from the STEM elemental maps indicate concentrations are typically between 0.01 and 0.03 wt % Cu. Cu is visible in 3 of the STEM images presented, Figure 2.62 is a low magnification image (60,000 x) and Figure 2.63 is a higher magnification image (200,000 x) of a concentrated pocket of Cu. Cu was also found to be disseminated such as in Figure 2.64 where Cu is found throughout the majority of the mapped dolomite particle. The Cu particle in Figure 2.62 and Figure 2.63 is around 300 nm, and is
closely associated with S. There appears to be a correlation of Fe and Mn to Cu as well but this relationship is not as pronounced as the association observed between Cu and S. Cu has been found to be associated with dolomite as the concentrated Cu pocket was located on a dolomite rich mass and the disseminated Cu in Figure 2.64 shows higher concentrations on the dolomite particle as opposed to the adhered kaolinite particles.

Figure 2.62 and 2.63 illustrate an additional complexity, scale. Figure 2.63 is a high magnification image of the upper right hand side of Figure 2.62 where a concentrated mass of Cu is located. In the higher magnification image it is evident that not only Cu but traces of Cr and Ni are present which were not identifiable in the lower magnification image. Evident peaks for both Cr and Ni are present on the EDS spectra, however, the quantification of these peaks returns values too low. Cr is strongly associated with Fe, Mn and Ni and appears to have no affinity to the region with Cu and S. The elemental map for Cr is observed to be most similar to that of Fe concentration, as intensities of the two elements match except for when Fe is associated with Cu and S. An apparent higher concentration can be observed in the elemental maps for Ni as it is more plentiful then Cr with a distribution similar to Fe and Mn. Fe, Mn and Ni have comparable dissemination across the mapped particle and appear to be associated with the Cu and S-rich mass which then has no association to Cr. Both Cr and Ni have a closer association with the dolomite particle as opposed to the kaolinite in the sample as none of the metals appear to be related to the kaolinite particle at the edge of the mapped area.

Concentrations of Cl observed in Figure 2.64 using non-standardized EDS spectra from the elemental map indicates that the concentration is around 0.42 wt % Cl. The particle in Figure 2.64 is ~6 µm in length and ~3.7 µm in width and Cl is observed to be disseminated across the entire area which is composed of mainly dolomite with discrete particles of kaolinite and smectite. Cl appears to follow a similar pattern as Cu, Mn, P and S displaying an even distribution across the particle with no areas in which a higher concentration pocket is observed. There does appear to be a slight decrease in Cl concentration around the kaolinite particles.

For P, non-standardized EDS spectra from the elemental maps of 3 particles indicate concentrations range from 0.57 to 1.1 wt % P. In Figure 2.61 P is observed in close association with Ca with the highest concentration of P occurring with Ca in a ~180 nm mass which is interpreted to be an apatite (Ca₅(PO₄)₃). Elsewhere in the same image P appears to follow Ca dissemination and does not exhibit an affinity to any particular region of this phyllosilicate. Figures 2.60 and 2.64 show P disseminated across the entire dominantly dolomite-rich particle. In neither case does P associate more strongly with the Ca present in the particle as was observed in Figure 2.61. The disseminated P does not exhibit a particular affinity to any of the other elements mapped with it, nor does it exhibit an affinity to a specific region of the particle. P seems to be distributed evenly over the particles with no apparent attraction to any other characteristics in the particles.
Statistical Analysis- Bulk Chemical Data

After performing the statistical t-tests with the BH adjustment a total 6 elements were discovered to be higher in the GMR sediment than in the reference samples: Zn, Sn, Sb, Cu, Pb and Sr (Table 1). The last column in Table 1 indicates the difference in sample means, thus Pb concentrations in the GMR sediment are ~12 ppm higher than that observed in the reference samples. The GMR sediment samples are also considered independent observations as a more complex regression model with correlation structures had relatively the same AIC value as the model without a correlation structure indicating that the observations were independent. However, normality is still assumed within the sample set as that particular component could not be conclusively analyzed with a small number of reference samples. Additionally, sample concentration outliers had no effect on the outcome of the t-tests. Outliers were removed for Bi, Cu, Mn, Ni, Pb, Sr, Sn and W and the t-test with the BH adjustment was re-run; resulting p-values were found to still indicate the same significant elements as previously identified.

Table 1: Results of the Welch one-tailed t-test with BH adjustment.

<table>
<thead>
<tr>
<th>Element</th>
<th>Benjamini-Hochberg adjusted p-value</th>
<th>( \bar{y}<em>{GMR} - \bar{y}</em>{Ref} ) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>&lt;0.0001</td>
<td>62.86</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0016</td>
<td>1.27</td>
</tr>
<tr>
<td>Sb</td>
<td>0.0089</td>
<td>0.32</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0137</td>
<td>9.01</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0151</td>
<td>12.14</td>
</tr>
<tr>
<td>Sr</td>
<td>0.0259</td>
<td>124.18</td>
</tr>
</tbody>
</table>
Discussion

Natural Background

Establishing natural background levels of metals within an environment is fundamentally important. The GMR is a complex system with a combination of background materials from local bedrock (Ordovician limestone and shale) and glacial deposits derived from a variety of igneous, sedimentary and metamorphic rocks. These source rocks complicate identifying anthropogenic pollution. Four local reference materials were chosen to be the most representative of natural material in the area and through the use of multiple experimental techniques and statistics a general background determination was made.

It was determined through several geochemical correlations and comparison to the NASC that sediment samples within the GMR are comparable to the average sediment composite compiled in the study by Gromet et al. (1984). The majority of the river sediment samples plot slightly below 1 in comparison to the NASC (Figure 2.21), a value of 1 would indicate that sediments are equal in concentration to the shales sampled in Gromet et al.’s 1984 study. The NASC is proposed to be a representative sample of continental crust that has undergone the effects of weathering and erosion (Gromet et al., 1984). The wide geographical genesis of the sediments within the GMR allows the comparison of sediment sample’s REE concentrations to the NASC. In addition to relating the sample set to the NASC, the extent of weathering is characterized by defining the index of chemical alteration for each river sediment sample. Here the NASC results are further validated by the reference materials which yield an average CIA=68.5, representative of a typical shale. Separately Russell Soil (fines and bulk) and glacial till fines are considered moderately weathered with CIA values greater than 70. Four Mile Creek and the abandoned stream reference bulk materials are considered average sediments and glacial till bulk, abandoned stream and Four Mile Creek fines are representative of an average shale. There is also a distinct divide between the bulk and fine fraction of the sediment samples as the bulk fraction displays a CIA=64.8 (average sediment) and the fines a higher CIA=70.5 indicating increased weathering in that fraction of the sediment.

Geochemically, the reference materials display expected trends with a variety of elements in both the bulk and fine fractions of the samples (Figures 2.2 and 2.3). Trends illustrated in Figure 2.2 display strong correlations between Zr and Ti, Ba and Sr along with Ce and La. One of those correlations Ce and La, is also observed in the river sediment samples which display an excellent relationships amongst the bulk and fine fractions of the sediments (Figure 2.16). The relationship between Ce and La was reinforced with the SEM data as particles rich in Ce and La were frequently observed. Many particles are subhedral to euhedral, associated with phosphate, under 4 µm in length and interpreted to be monazites (Ce, La, Nd, Th)PO₄ (Figure 2.17-2.20). Even though SEM analysis is only conducted on the fine fraction of the sediment (particle size ≤ 40 µm), no particles larger than 4 µm were identified within the sample set. Thus, it appears as though the REEs dominantly exist as the mineral monazite within the fine subset of the samples.
River sediment samples generally did not display the same trends represented in the reference samples aside from the Ce and La correlation. Plots for Ce and La in the GMR sediment samples yield a positive slope of 2.08; similarly the references also display a positive slope of 1.91. The association of Ba and Sr in the reference samples (fines and bulk) exhibits an $r^2=0.82$ (Figure 2.2 B), whereas the same correlation in the river sediment samples is found to be non-existent for the fine fraction of the sediment and moderate for the bulk fraction ($r^2=0.56$) (Figure 2.4). Associations are also found to differ between Fe and Ti, which in the reference sediments display a weak correlation ($r^2=0.37$) and in the river sediment samples exhibit an excellent correlation $r^2=0.88$ (Figure 2.6 A). SEM data indicates that ilmenite (FeTiO$_3$) is the dominant Fe-oxide present in river sediment samples. STEM elemental mapping indicates that discrete micrometer scale titanium oxides do occur (Figure 2.61) and this may explain the variability observed in the correlation.

Fe sulfide is also present in multiple samples and is found as individual spherical particles disseminated throughout multiple samples as discrete single crystals and also as aggregates of framboidal pyrite (Figure 2.14) (Popa et al., 2004). Figure 2.13 illustrates a mass of framboidal pyrite and how the individual crystals are disseminated throughout the sample. The crystals maintain a relatively pure composition of Fe and S along with displaying excellent continuous crystallinity throughout the sediment samples. However, determining whether or not these pyrite crystals are biogenic or authigenic is difficult to prove with the evidence collected in this study. Additionally the literature does not provide a clear picture on the formation of pyrite framboids; however, S isotope studies appear to shed some light on whether the process is biotic but this topic has yet to be resolved as a whole (Schieber and Riciputi, 2005; Popa et al., 2004; Boughriet et al., 1998; Kohn et al., 1998; Mann et al. 1990). Reducing conditions are required for pyrite stability and several studies interpret the textures observed as biogenic (Schieber and Riciputi, 2005; Popa et al., 2004). Owing to the delicate textures exhibited in the framboidal pyrite aggregates they are interpreted as forming from biogenic processes in reducing conditions.

Elemental associations were critical in identifying phases in the SEM and STEM analysis. Particulates observed in the SEM and STEM could be identified by apparent crystallinity, size and texture; however, these physical features may not provide enough information to definitively identify a particle. Additionally, EDS was used to evaluate the relative concentrations of particular elements present within a particle. REE phosphates were identified by their chemical makeup, generally significant amounts of La, Ce and P along with their typical euhedral to subhedral appearance (Figure 2.7). Moreover, natural Fe- and Ti-rich oxide particles were identified by their significant Ti and Fe concentrations by EDS which also follows the observed trend in the ICP-MS data (Figures 2.6 and 2.7). Clay particulate was identified in the TEM by comparing the elemental associations observed between different STEM elemental maps. Strong correlations between Al, Si and O indicated kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), correlations between Mg, Ca and O indicated dolomite (CaMg(CO$_3$)$_2$) while associations among K, Al, Mg and Si indicate illite (K(Al, Mg, Fe)$_2$(Si, Al)$_4$O$_{10}$$\cdot$OH$_2$).
In terms of bulk mineralogy according to the CIA the GMR fine sediments have experienced moderate weathering while bulk sediments are more typical of average sediment. This is reaffirmed multiple times in this study using various experimental techniques. According to XRD data collected for representative GMR fine sediment samples and reference materials, there are 4 dominant mineral phases: quartz, feldspars, calcite and dolomite (Appendix 5). These minerals reappear in the SEM data and were also plentiful in the TEM/SAED data. Figures 2.57-2.59 show several particles of calcite which were identified using EDS and SAED patterns from fine fraction GMR sediment samples. These figures also illustrate multiple illite particles which arise from the weathering of source rocks. Additionally, the STEM/EDS elemental mapping has verified the consistency of the bulk mineralogy in which multiple illite, kaolinite and dolomite particles have been profiled (Figures 2.60-2.64). Not only is this data consistent with the XRD data, but it also coincides with the CIA calculated for the fines and bulk based on bulk chemical ICP-MS analyses. Based on the CIA values weathering products (such as illite) are expected to be plentiful in the fines along with components of average sediment such as: quartz, feldspars, dolomite and calcite.

**Anthropogenic Input**

ICP-MS data indicates the majority of anthropogenic metals are found to be concentrated in the fine fraction of the river sediment (Figure 2.22). Some elemental correlations involving copper (Cu/Ni, Cu/Zn, Cu/Al) are strong when all samples (bulk and fines) are considered. However, when observing the size fractions separately a weak correlation is observed with those same elements amongst the fines and a stronger correlation is observed in the bulk fraction. The fines do not always yield close associations amongst different metals even though the fines contain on average the highest concentrations of those particular metals (Appendix 6). There appear to be some associations which are stronger in the fines, some which are stronger in the bulk and others which are throughout both fines and bulk.

This incidence of higher concentrations of anthropogenic metals in the fine fraction of the sediment has also been noted in other pollution studies (Chabukdhara and Nema, 2012; Elless et al., 2007; Jain, C.K., 2004; Kļaviņš et al., 2000; Rubio et al., 2000; Birch and Taylor, 1999; Soares et al., 1999; Sakai et al., 1986). In a study most comparable to the present work conducted by Rubio et al. (2000) two subgroups of river sediments were evaluated: sandy samples with less than 10% mud and samples with a high concentration of mud. It was found that in the muddy samples the average concentrations of Al, Fe, Ti, Cu, Pb, Cr, Ni, Co, and As were higher than the concentrations observed in the mainly sandy samples (Rubio et al., 2000). Average concentrations for Al, Fe, Ti, Cu and Zn were significantly higher in the muddy sediments, up to 7 times greater than the amount identified in the sand and gravel-rich samples (Rubio et al., 2000). In the study by Rubio et al. (2000) Fe was above background levels thus indicating potential contamination within this particular environment. Al, however, was utilized as a tracer and in a normalization technique and did not have a concentration above background levels. Sakai et al. (1986) also observed an increase in metal concentration with finer sediment particles,
observing that some of the highest concentrations of metals fall into the \( \leq 460 \, \mu m \) size category. In this particular study the sediments that were \( \leq 71 \, \mu m \) were found to contain higher concentrations of: Cd, Mn, Zn, and Pb, in comparison to sediments in the 1680-810 \( \mu m \) fraction (Sakai et al., 1986). Additional river sediment studies by-pass analyzing the entire sediment and instead design the study to focus on the finer fraction of the sediment. Chabukdhara and Nema (2012) published a study on India’s Hindon River in which river sediments were collected and sieved through \(<2 \, \text{mm mesh} \) before analysis. While a study by Kļaviņš et al. (2000) analyzed a fraction of the river sediment \(<63 \, \mu m \). Both studies were able to identify metals that were potentially a result of anthropogenic pollution. Thus, it has been noted in multiple studies that anthropogenic metals tend to accumulate within the fine fraction of the sediment; however, the definition of the fine fraction varies for each particular study.

In this study the fine fraction of the sediment is limited to particles \( \leq 40 \, \mu m \). This separation of bulk and fine sediments yields two distinct populations and aids in the constraint of potential anthropogenic particulate. The fine fraction of the sediment is the main focus of this pollution study because these samples present the highest concentration of anthropogenic metals. Fine fraction samples which have some of the highest anthropogenic metal concentrations were chosen for SEM analysis; and with the bulk of the sediment removed, locating and profiling anthropogenic particles in the SEM is a straightforward task. Through the use of the back-scatter detector (BSD) dense or metal-rich particulates are identified within the sample set and characterized by energy dispersive spectroscopy (EDS). By means of identifying samples with high concentrations of anthropogenic metals, and further imaging and characterizing those samples in the SEM multiple potential pollution products were identified including: Pb, Ba sulfate, Cu sulfide, Sb, As, Co, W, Cr, and coal spherules.

Coal spherules have characteristic spherical morphology that allows for them to be easily recognized amongst clay and silica-rich particles as nothing else in the sediment displays such a shape. Due to their distinctive traits and omnipresence amongst the sample set, coal spherules are a direct indicator of coal combustion pollution. Within the fine GMR sediments multiple textures and sizes of coal spherules were identified. The largest and smallest coal spherules (27 \( \mu m \) and 2 \( \mu m \) respectively) were identified together with the smaller spherule attached to the larger spherule (Figure 2.26A). In a previous study by LeGally and Krekeler (2013) coal spherules were recognized in street sediment samples from Hamilton, Ohio (Figure 1.11). That study also displayed the wide variety of textures and sizes that can arise in coal spherules as a result of combustion. Another study by Magiera et al. (2011) also depicts the complexity, in which some spherules were found to be magnetic composed of mainly iron oxides while others were hollow consisting of only an outer crust. A range of sizes was observed as well as surficial textures (rough to smooth) and some spherules were found to have a silicate or aluminosilicate core with an outer layer of silica, magnetite or maghemite (Magiera et al. 2011).
All of the coal ash spherules identified in the GMR sediment are solid spheres with some showing significant signs of weathering consistent with those observed in Hamilton street sediment by LeGallely and Krekelar (2013) (Figure 2.31, 2.33). LeGallely et al. (2013) identified spherules ranging in size from 50-100 µm, of varying surficial textures and with chemical compositions of O, Si, Al, Mg and Ca. The spherules observed in the GMR sediment could come from a variety of sources; one local source is the HMEP which sits on the banks of the GMR and has operated as a coal combustion power plant since the early 1900s. However, since this pollution can end up in the GMR directly through air deposition, indirectly from sources upstream or from street sediment that is washed into the river a definite source for this particular pollution cannot be distinguished. Potential does exist to trace coal spherules back to a general source as the specific conditions in which the spherules are created dictate the morphology and mineralogy of the resulting particle (Magiera et al., 2011). This coupled with magnetic properties of the spherule (also a function of formation and initial material) can give an indication of what coal was burned initially which in turn can help to narrow down the potential sources. One example of this is in Magiera et al. (2011) which found that lignite combustion products had lower magnetic susceptibilities than harder coals. By comparing the mineralogy and textures of coal spherules, future investigations may be able to track coal pollution along the GMR. Results of this investigation demonstrate the durability of coal spherules in the river sediment environment and may prove to be useful for provenance studies.

Another coal combustion product identified in the GMR sediment is barite (BaSO₄). These anhedral to subhedral particles are found to be rich in Ba and S by EDS analysis (Figure 2.37B, 2.39B). Although not as simple to identify as coal spherules, these particles are found regularly throughout the GMR sediments examined in the SEM. Most of the particles imaged occur as small discrete particles amid the background material such as Figure 2.35 and 2.39. Others appear to be larger less cohesive aggregates of Barite (Figure 2.34 and 2.38). In a previous study of Hamilton, Ohio road paint by Detherage et al. (in review) it was found that blue road paint was composed of mainly calcite and barite with barite particles being ≤10 µm and anhedral. Thus, it is possible although not likely that some of the barite particles identified could be originating from blue road paint applied to the streets of Hamilton. However, anhedral particles are not texturally distinct which complicates matters in determining a source and blue traffic paint is a minor source, estimated to be <0.1 % of all road paint in Hamilton.

A more probable genesis is coal combustion as barite is a common constituent in coals because it is “part of an abiotic deposition-dissolution cycle that is activated by organic materials” (Jablonska et al., 2001, p. 941). A study by Jablonska et al. (2001) examined barite in atmospheric dust over the upper Silesian industrial region in Poland where coal combustion is common. Results of this study indicated two potential origins of the barite sampled in atmospheric dust: barite was present in the coal and survived the coal combustion process or barite formed as a result of the combination of atmospheric sulfuric acid (another by-product of coal combustion) and airborne dust (Jablonska et al., 2001). Potentially the barium sulfate
observed in the GMR sediment is primary barite that survived the coal combustion process as Jablonska et al. (2001) describes those particles as being angular and between 1-25 µm. Neogenic barite from the reaction of sulfuric acid and dust particulate would yield more well-formed crystals (Jablonska et al., 2001). None of the barite particles observed in the GMR appear to be ideally formed crystals, instead most appear to be aggregates or fragments. According to the MSDS sheet published by Sigma-Aldrich barium sulfate has a melting point of 1,580°C, thus if the furnace did not reach high enough temperatures barium sulfate would survive the combustion and could potentially be ejected with the rest of the ash and air particulate (Sigma-Aldrich, Barium Sulfate, 2012). Additionally barite has also been identified in brake dust according to a study by Adachi and Tainosho (2004) in which Ba was second to Fe in terms of abundance. Therefore multiple sources of barite exist but based on the amount of barium emitted by the HMEP, 270 lbs of Ba compounds in 2010, the barite is most likely coal derived (Envirofacts, HMEP, 2011).

Lead was a prominent but less common contaminant as compared to coal spherules and barium-rich particles. ICP-MS data indicates that average lead concentrations in the river sediment samples are higher than those observed in the reference sample set. References have an average of 15.3 ppm, bulk sediments averaged 23.2 ppm and fines contain the highest average lead with 28.6 ppm. All of these values are well below the standard set by the USEPA for bare soil which is 400 ppm in play areas and 1200 ppm in non-play areas (USEPA, 2001). According to the Committee on Environmental Health (1993) uncontaminated soil contains <50 ppm lead; all reference samples fall below this level however, 2 samples of the bulk and 1 sample in the fines are found to have concentrations above 50 ppm. Lead particles identified in the fine fraction of the sediment are typically less than 10 µm in size and show various weathering textures.

Multiple sources could have contributed to the Pb identified in the river sediment samples. Seventy years of leaded gasoline, 50 years as a common constituent in house paint, mining, pesticides and other industrial activities are potential sources of lead in the environment (Elless et al., 2007). In addition to historical sources of lead, in 2010 the HMEP released 20.6 lbs of lead by air emission (Envirofacts, HMEP, 2011). In an investigation by Davis et al. (2001) 79% of all lead in an urban environmental study was found to originate from building walls and the next largest source of lead originated from atmospheric deposition. One anhedral aggregate with a composition including Pb and P was also identified out of the river sediment (Figure 2.44). This particle potentially represents input from residential lawn fertilizer runoff. As lead paint on houses weathers and flakes off onto the ground those paint chips will continue to degrade and assimilate into the soil, with the possibility of Pb sorption onto clays (Elless et al., 2007). A prospective route for residential soil lead may be in combining with P from lawn fertilizer forming a particle with a composition similar to that of pyromorphite, Pb₅(PO₄)₃Cl (Elless et al., 2007). Lead phosphate found in the GMR sediment did exhibit a similar energy
dispersive spectra as that published in Elless et al. (2007) with peaks for Pb, P and Cl (Figure 2.44B).

Aside from discrete particles consisting of mainly lead, multiple masses of lead chromate (PbCrO₄) were identified. The particle in Figure 2.46 is a dull triangular mass that stands out from the background material with bright, randomly ordered imbedded crystals. The crystals are found to have a composition of PbCrO₄ while the dull background material is rich in Ca and organics (Figure 2.47 and 2.48 respectively). Additional PbCrO₄ crystals are identified within the samples, some still imbedded within a matrix and others without a matrix material. PbCrO₄ crystals are found to have similar dimensions with most crystals having a width of ~100 nm and lengths from 600 nm to ~300 nm. Due to the characteristic nature of these particular particles and the previous street sediment work completed by Detherage et al. (in review) these masses of PbCrO₄ have been sourced to yellow road paint applied to the streets of Hamilton, Ohio. Detherage et al. (in review) characterized the yellow road paint samples as containing dispersed euhedral to subhedral PbCrO₄ crystals within an organic polymer matrix rich in Ca and Si and crystal sizes ranging from 125 to 350 nm in length and 75 to 200 nm in width (Figure 1.12).

The masses of PbCrO₄ characterized in the GMR sediment are exceptionally similar in morphology to those of actual samples of yellow road paint studied by Detherage et al. (in review). However, the lead chromate characterized from the GMR sediments displays a significant rounding of the lead chromate crystals which is not observed in the majority of the crystals described by Detherage et al. (in review). This is especially visible in Figures 2.50 and 2.51 in which high magnification images of PbCrO₄ show rounding on the terminal ends of the crystals; this rounding is evidence of potential dissolution within the river environment. Even though PbCrO₄ has a low solubility it’s interaction with winter road treatments and the dynamic aqueous environment of the river may increase solubility. Mechanical abrasion of these particles along their entire route to the river has the potential to increase surface area, which could assist in the dissolution of the lead chromate crystals. In a study by Adachi and Tainosho (2004) lead chromate was identified as one of the pollutants found within samples of tire dust. These oval shaped particles were found in aggregates with particle size around 0.42 µm (Adachi et al., 2004). SEM images in the Adachi and Tainosho (2004) study of both a sample of yellow road paint and the Pb/Cr rich particle were found to be of similar morphology and these particles also seemed to display rounding similar to what was observed in the GMR.

Samples for the tire dust study by Adachi and Tainosho (2004) were collected in Japan; however, lead chromate is also a prevalent pigment for road paints in the United States. According to section 740 in the 2013 Specification Book released by the Ohio Department of Transportation (ODOT) in reference to pigment content “yellow material containing a minimum of 5% by weight of primary yellow (lead chromate) pigment (or a lead free pigment)” is to be furnished by the manufacturers of yellow road paint for use in the state of Ohio. Previously in section 740 of the 2010 Specification Book yellow material was still to contain a minimum of
5% by weight lead chromate but with no option of “a lead free pigment” (ODOT, 2010). This requirement by the state of Ohio for yellow paint manufacturers coupled with additional paint application requirements such as: painting a solid line at a thickness of 0.51 mm and a line width of 100 mm requires 50 liters of paint per every kilometer of line, at a lesser thickness of 0.38 mm a solid line requires 37 liters of paint per every kilometer of line (ODOT, 2013). The potential exists for a significant contribution of lead chromate to the environment from general wear and tear of yellow road paint off the highways of Ohio. Effort was made to contact the administrator of the Office of Materials Management at ODOT receiving the following reply (Lloyd Welker, personal communication, August 14, 2012) “ODOT does not establish the actual formulations for traffic markings. Our specifications are more performance based and the actual formulations are a manufacturer’s to define to meet our specifications. Our paint materials specifications are listed in the 740 section of the spec book.” As previously stated the Specification books both past and present do specify that lead chromate is to constitute a minimum of 5% by weight in yellow road paints, with the lead-free pigment option recently added to the 2013 Specification book.

Other less common pollutant particulates identified in the SEM include: Sb, Cu sulfide, Co and As. These particular particles were recognized once or twice within the sample set studied and are thus not as abundant as the previously described contaminants, but nevertheless observable. Sb in particular displays relatively low concentrations according to the ICP-MS analysis which indicates that the highest concentration of Sb amongst all the fine samples is 1.22 ppm. In the sample with the highest ICP-MS concentration for Sb one ≤1 µm anhedral Sb particle was identified (Figure 2.53A). In addition to being rich in Sb the particle’s EDS also displays peaks for Pb and Fe with additional peaks for Si, Al and K representing the chemical composition of the surrounding material (Figure 2.53B).

In stark contrast to the anhedral particle another Sb-rich particle displays euhedral pseudocubic crystals free of Pb embedded in a Si, O and Al-rich matrix (Figure 2.52). This particular particle is in a sample that by ICP-MS contains 0.91 ppm Sb. Based on the morphology of the crystals ranging from 600-200 nm in size this particle is likely elemental antimony which is known to display pseudocubic crystals. A common alloying constituent, Sb was the fourth most prevalent metal identified in brake dust samples collected by Adachi and Tainosho (2004). As naturally occurring Sb is highly unlikely in this environment according to the geology, it is assumed that the majority of Sb present is anthropogenic. Stibnite (Sb₂S₃) is the most common Sb mineral along with sulfosalts, however, no S was present in the profiled particles. Thus, the particles identified in the SEM are interpreted to be anthropogenic as Sb rarely occurs naturally in its native form and is commonly used as an alloy particularly with lead for use in batteries (MEC, 2013).

One of the most texturally remarkable crystals identified within the sample set is in Figure 2.54. This mass of euhedral crystals is determined to be copper sulfide based on the EDS analysis which indicates high concentrations of both Cu and S. Also, since these are sediments in
direct contact with water, copper sulfide is relatively insoluble in comparison to copper sulfate. Cu is a comparatively common anthropogenic pollutant with the most common source being brake dust emissions (Davis et al., 2001). According to the study by Davis et al. (2001) 47% of copper is attributable to brake dust with another 21% attributable to building siding. Another study by Adachi and Tainosho (2004) reiterates this association with Cu being the third most abundant metal identified in brake dust.

The particle containing Co also includes a host of other metals such as: Cr, W, Pb and Fe. This particular tabular mass is buried beneath platy elementally light aggregates (Ca, K, Al and Si), making a clear analysis within the SEM difficult to obtain (Figure 2.55). However, the edges of the particle are visible and indicate potential mechanical abrasion. The close association of Co, Cr, W and Pb and the high concentrations of both Co and Cr make the case for specialty steel. The visibly jagged edges and thin tabular nature of this particle also bolster the argument for a thin specialty tooling steel. In terms of geographical origin such a determination cannot be made with the collected data.

Only one grain with a significant As peak is identified amongst platy particles rich in Si, O, Al, Ca and K. This particle appears <2 µm in size, subround, anhedral with EDS peaks for Fe and As (Figure 2.56). Arsenic concentrations within the fine sample set display an average of 7 ppm and a moderate correlation with Cu ($r^2=0.5673$). Due to the lack of distinctive characteristics of this particular grain an origin cannot be determined, only to say that this particle is most likely of anthropogenic genesis. This is due to the lack of natural sources for As in this environment and the ability of Fe-oxides to readily sorb As (Ritchie et al., 2013; Wang et al., 2011; Ying et al., 2012).

Identifying samples with high concentrations of anthropogenic metals (by ICP-MS) is an effective strategy to determine how particular elements occur within the sediment as observed with the SEM. Multiple particles are identified and characterized by this method and several correlations evident in the ICP-MS data are mirrored in the SEM/EDS analysis. In what is determined to be natural particulates strong correlations are observed between Fe and Ti (Figure 2.06A) along with Ti and Al (Figure 2.05) in the ICP-MS data. This relationship between Fe and Ti is then reflected in the SEM data with multiple particles similar to Figure 2.07 found within the sample set. The same relationship is found with Ce and La, which display a strong correlation and also appear frequently within the sediment imaged in the SEM (Figure 2.24 and 2.25).

Potential anthropogenic correlations are also observed in the data, a relatively strong relationship is observed between Co/Cr ($r^2=0.74$) and a weak relationship is present between Pb/Cr ($r^2=0.43$). In the SEM Co is found in a particle with Cr, and Pb is found in close association to Cr.

The Pb and Cr correlation in the ICP-MS data is not particularly robust ($r^2=0.43$) and would not be a strong indicator for PbCrO$_4$ in the river sediment (Figure 2.45). However, the SEM study allowed for such subtle phases to be teased out from the overall bulk chemical data.
A visual microscopic scale investigation utilizing BSD and EDS revealed multiple organic masses with embedded PbCrO$_4$ crystals. Not only are these PbCrO$_4$ particles identified based on their characteristic size and shape but also by their chemistry. This ability to characterize the sediment visually and chemically allowed for detailed observations to be made of the GMR sediment, including the presence of lead chromate from yellow road paint applications. Based on the weaker correlation observed in the bulk ICP-MS data between Pb and Cr it would appear that the two would not be intimately associated. Not only did the SEM analysis allow for the identification of PbCrO$_4$ rich masses but multiple discrete particles of Pb-rich material are also characterized. These Pb-rich particles are potentially responsible for the weak correlation observed between Pb and Cr in the ICP-MS data. Within the river sediment there appear to be multiple sources of lead which overshadows the correlation between Pb and Cr of one particular source. If only ICP-MS data would have been analyzed, in respect to identifying potential contaminants, a definite conclusion regarding source would have been impossible to propose. However, the combination of ICP-MS elemental correlations and physical data obtained from the sediments with the SEM allow conclusions on relationships of contaminants and sources to be drawn. Although sediment is by EPA definition below the Pb standard (USEPA, 2001) the combined ICP-MS and SEM investigation proved beyond doubt that lead pollution is present. This data indicates that the GMR is a complex system with respect to Pb contaminants, most of which cannot be recognized by bulk chemical data alone.

Metal pollution has already been identified on the streets of Hamilton, Ohio by LeGalley and Krekeler (2013), however, establishing potential sources of metals observed in both the street sediment and the GMR sediment will require additional investigations. Due to the complex nature of urban sediment the most effective method of tracing sources is through the use of isotopes. LeGalley et al. (in press) utilized $^{208}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb to constrain potential sources of Pb, Cr, Cu and Zn contamination in Hamilton, Ohio street sediment. In LeGalley et al.’s (in press) study it was found that coal and fly ash from the nearby HMEP was not the main contributor of Pb observed in the street sediment. Instead, PbCrO$_4$ a component of yellow road paint was a significant source of Pb identified in the street sediment, even though discrete particles of PbCrO$_4$ were not identified in the SEM (LeGalley et al., in press; LeGalley and Krekeler, 2013). However, Pb isotopes were not successful in sourcing the elevated levels of Cu and Zn present in the street sediment and Pb isotopes were also unable to distinguish between different lead particles such as those derived from leaded-gasoline (LeGalley et al., in press). Isotopic studies such as LeGalley et al., (in press) will be essential in unraveling the story of anthropogenic pollution throughout time and attributing a source to categories of pollutants found. Investigations employing the use of other isotopic systems such as $^{66}$Zn may prove useful in further detailing the source of potential anthropogenic pollutants within an urban environment (Borrok et al., 2010).

In order to further characterize the sediment at a finer scale TEM and STEM were performed on selected samples which like the SEM samples contain high concentrations of
anthropogenic metals. The TEM results suggest that the most common clay particle present in
the GMR sediment fines is illite. Of the 10 paired SAED and bright field TEM images presented
8 contain illite in some form, whereas the other 2 are micrographs of calcite. This is consistent
with the expected mineralogy of the GMR sediment deduced from ICP-MS bulk chemical
analysis, XRD patterns and STEM. In addition to illite and calcite, Fe-oxide was plentiful and
noted to associate only with illite particles at the micrometer scale. Fe-oxides were found to exist
as discrete particles on illite or as cohesive mats. The micrograph in Figure 2.57B consists of two
mineral phases illite laths and Fe-oxide aggregates however, the accompanying EDS spectra has
a peak for Zn. Zn is not present naturally in either of these materials, thus it is suspected that the
Zn is sorbed onto the Fe-oxide aggregate as Fe-oxides have been found to be significant sinks of
metals in natural environments (eg., Xu et al., 2006 and Guo et al., 2006). STEM and elemental
map imaging further clarify the spatial elemental associations exhibited between natural
materials and suspected anthropogenic pollution.

Three representative maps illustrate the pollutant spatial distributions on the fine fraction
as identified in STEM. These maps contain the expected natural materials such as kaolinite,
dolomite and smectite but also contain additional anthropogenic elements such as Cu, Cr and Ni
(Figure 2.63). In Figure 2.63 there appears to be a close association with Cu, S, Fe and Mn, the
Cu and S likely representing a copper sulfide. Mn appears to be concentrated in three general
areas on the map and since Mn-oxides tend to accumulate heavy metals (eg., McKenzie, 1967;
Noor Azhar et al., 2003; Pampura, 1998; Tanji and Valoppi, 1989; Wang et al., 2012; Weaver
and Hochella, 2003), Cr and Ni are also associated with Mn (Weaver et al., 2002; Weaver and
Hochella, 2003). This relationship between Mn and heavy metals is also observed in Figure 2.64
with Fe and also in Figure 2.62 with Fe again and potentially Cu and S. Cu amongst the samples
was found to be associated with S as in Figure 2.62 but also disseminated such as in Figure 2.64.
Cu itself was found only in association with dolomite particles, from disseminated Cu to a Cu-
and S-rich mass both were found on dolomite and there appears to be no association with
kaolinite present within the particle. LeGalley and Krekeler (2013) noticed that Cu had a strong
tendency to sorb onto illite particles in samples of Hamilton street sediment. However, the
dominant particle identified in this study was dolomite with little illite and no chlorite identified,
contrary to the findings in LeGalley and Krekeler (2013). These observations suggest that the
behavior of Cu in the street sediment environment may be different than the behavior of Cu in
the subaqueous river environment. Another possibility is that dolomite may significantly out
compete illite for Cu-sorption in the river environment. These results suggest that dolomite
should be investigated as a potentially effective reactive media for Cu removal in this system.

Ni and Cr are good illustrations of the concept of scale within the STEM elemental maps
as they are visible only in Figure 2.63 which is a high magnification image of the upper right
hand corner of the particle imaged in Figure 2.62. There does not appear to be any association
between Cr and Ni as Cr has its highest concentrations in two areas at the bottom of the map and
Ni has 3 general areas of high concentration. However, both do seem to be spatially correlated
with the Fe and Mn present within the particle and to a lesser extent Cu and S. Cr and Ni are once again more closely correlated to the dolomite in the particle than the crystals of kaolinite adhered to the edges; elemental maps for Mn, Cr, Fe and Ni are sparse where Si and Al are rich. These patterns are similar to relationships observed in LeGalley and Krekeler (2013) in which Ni exhibited a correlation in the bulk chemical data to both Cr and Cu ($r^2=0.44$ and 0.65 respectively, Figure 1.10). In this study there does appear to be some weak spatial correlation of Ni to both Cr and Cu. Also, Ni appears to be more spatially correlated in Figure 2.63 than what was identified in LeGalley and Krekeler (2013) in which Ni was disseminated across multiple particles of illite and chlorite without clear spatial preference (Figure 1.13).

Finally, P is another element that can potentially be interpreted as anthropogenic due to the copious amounts of fertilizer used on agricultural fields and residential lawns which inevitably washes into local streams and rivers. Disseminated P was observed in Figure 2.64 and Figure 2.60 both of which may be anthropogenic in nature. For both particles there appears to be no association of P with the other elements present within the sample and no affinity to any particular area of the particle. LeGalley and Krekeler (2013) also observed P in street sediment from Hamilton, Ohio, however, P in the street sediment was found to preferentially sorb onto illite particles. In this study no preference in sorption was observed with P in the GMR sediment samples analyzed.

Two elements that display an excellent correlation in ICP-MS data are not explained well by the microscopy data, Zn and Cu with an $r^2=0.82$. This relationship in the ICP-MS data did not manifest itself in the SEM, TEM or STEM data. A few discrete particles of Cu sulfide were located within the samples (via SEM and STEM) and Zn was observed to potentially be in association with an Fe-oxide aggregate (TEM), however, no particles containing combinations of these elements were located. Cu and Zn are present in significant quantities, with Cu having a maximum concentration of 69.3 ppm and Zn having a maximum concentration of 170.9 ppm in the fine fraction of the sediment. Additionally Zn is a prevalent urban contaminant, Davis et al. (2001) found that the most prevalent source of Zn loading was from runoff of brick walls a total of 58%, with tire wear coming in second at 25% of the total Zn loading. STEM revealed associations of Cu and S identified in several of the particles mapped, however Zn was not identified in any elemental particle maps. Zn must be exceptionally disseminated within the sample material, very rarely achieving detectable quantities. In a single instance when Zn was located in Figure 2.57B the TEM was not in STEM mode capable of elemental mapping. The diffuse nature of Zn was also observed in LeGalley and Krekeler (2013) where strong correlations were present between illite, Cu and P, but Zn appears disseminated (Figure 1.13). Zn appears to redistribute or desorb in the river environment compared to the street sediment.

**Statistical Significance**

According to the statistical analysis provided in conjunction with Dr. Byran Smucker’s STA 475 class, 6 elements in the GMR sediment were determined to be significant in terms of
their deviation from reference materials. Zn, Sn, Sb, Cu, Pb and Sr were all found to have greater concentrations in the GMR fine sediment than in the reference fine sediment. Additionally, the GMR sediment samples were determined to each be independent samples even though samples were collected in close proximity of one another. Several of these elements have been identified through microscopy to determine the nature of the pollutant particulate: Sb, Cu, Pb and to a much lesser extent Zn. Continued study is necessary to determine the location of Zn within the sediment as the statistics and bulk chemistry point to Zn as a pollutant but significant examples of Zn in the microscopy are lacking (only one bright field TEM image).

The determination of higher concentrations of Sb in the GMR sediment as opposed to the reference material is remarkable considering the extremely low concentrations of Sb observed in the bulk chemistry (1.22 ppm maximum concentration in the GMR fines). As previously discussed two particles of Sb were identified in the SEM and assumed to be anthropogenic, this statistical analysis further confirms the presence of Sb as an anthropogenic pollutant within the GMR. Even though low concentrations of Sb were collected through the bulk chemical analysis SEM data and statistical significance has shown that even in low amounts Sb is a pollutant. This determination illustrates the sensitivity of this particular study that pollutants can be identified even if they are not prolific within the GMR environment. Additionally, multiple particles containing Pb and Cu have also been profiled with the microscopy with specific textures (such as PbCrO$_4$) which identified them as anthropogenic.

Sr is identified as being ~124 ppm greater in the GMR sediment than in the reference materials, which does potentially suggest either a natural or some anthropogenic enrichment (Appendix 7, Sr). Relative confidence is given to reference samples glacial till and Russell soil as representing the natural sediment in the GMR valley, thus seeing Sr concentrations exceed those samples by a significant margin requires investigation into potential sources. In air particulate studies there appears to be a potential source of Sr originating from brake and tire abrasion (Querol et al., 2012 and Minguillon et al., 2012) while other studies still associate Sr with being geogenic (Schleicher et al., 2012; Rahman and Ishiga, 2012). In a study by Adachi and Tainosho (2004) Sr was identified at low concentrations in brake dust and tire dust, with averages of 0.1 ± 0.1 wt% and 0.9 ± 0.3 wt% respectively. Additionally, the possibility exists that in the river environment source rocks are weathered and there is a concentration of Sr from the source rocks in the fines which is providing the increased Sr signal in the river sediment as opposed to the references. Sr isotopes may provide insights into Sr geochemistry and could potentially resolve whether elevated Sr levels are due to a natural or anthropogenic process.

**Study Implications**

There are several implications of this pollution study. One of which is the impact of pollution on the quality of water in the GMRBVA on which 1.6 million people rely (Rowe, 1997). However, the GMRBVA is an extremely effective filter, which naturally removes the majority of particulate and biological contaminants before the water reaches the production wells
(Gollnitz et al., 2004; Mutiti and Levy, 2010; Levy et al., 2011). As water sampling was beyond the scope of this study, changes in water quality cannot be assessed. The water that is pumped from the aquifer and treated for human consumption does comply with all USEPA regulations for drinking water and is thus not of concern.

Conversely, the pollutants identified in this study were found to be mainly concentrated in the fine fraction of the sediment (≤40 µm) and in this size fraction complex aggregates of metals were identified along with other indicators of anthropogenic pollution. Since these anthropogenic metals are residing in the fine fraction of the sediment they are much more likely to become mobile when currents increase slightly or when sediments are disturbed. This mobility could potentially put anthropogenic metal laden fine sediments in direct contact with aqueous organisms. Potential contact risk is present for benthic organisms and those higher up in the food chain. Multiple studies have illustrated the presence of bioaccumulation in low trophic level organisms such as catfish and tilapia along with higher trophic level organisms (Alibabic et al., 2007; Burger et al., 2002; Klavins et al., 2009; Matsuo and Val, 2007; Nwani et al., 2010; Onwukeme and Mgbemena, 2012). In a study by Jabeen and Chaudhry (2009) which studied the tilapia O. mossambicus, Cr was found to bioaccumulate mainly in the muscle of the fish while the higher concentrations of Pb were found in the scales and fins. Gupta et al. (2008) also found a correlation between sediment metal concentration and maximum fish accumulation. In sediments the metal of highest concentration was Zn followed by: Pb, Cu, Cr and Cd; based on the results of studying the bioaccumulation of two catfish species the fish accumulated high concentrations of Zn followed by: Pb, Cr, Cu and Cd (Gupta et al., 2008).

In the fish studies, organisms at multiple trophic levels are studied including low trophic level organisms which have direct contact with riverbed sediments and regularly consume varying amounts of river sediment (Olowu et al., 2012). There exists the possibility that organisms higher in the trophic levels could acquire significant concentrations of anthropogenic metals as there are several different ways fish can accumulate pollutants (Burger et al., 2002). According to several studies (Burger et al., 2002; Jabeen and Chaudhry, 2009; Matsuo and Val, 2007; Nwani et al., 2010) pollutants in an aqueous environment can enter into a fish’s body by: consuming organic and inorganic material that contains a contaminant, from the water column through the gills or by being absorbed directly through the skin. Lower trophic level organisms are at risk for harboring contaminants observed in the sediments, however, even fish that are at a higher trophic level through either dissolved contaminants, sediment disturbance (releasing sediment contaminants into the water column) or by the consumption of lower level organisms.

Additionally, based on SEM and STEM data anthropogenic metals are mobile within the river sediment and dissolution of discrete particles occurs. In the case of PbCrO₄ identified within the river sediment distinctive rounding occurred on the terminal ends of the crystals which was a characteristic not observed in the chips of yellow road paint taken from the streets of Hamilton. This rounding indicates potential dissolution of PbCrO₄ into the river environment,
releasing not only Pb but Cr\textsuperscript{+6} into the water column. Once in the water column these metals could potentially combine with other metals, sorb onto clay particulate, persist in the water column or accumulate in an organism. Pb is a well known toxin and has a 0.015 mg/L maximum contaminant level (MCL) for drinking water according to the USEPA (USEPA, 2012). Cr is also a toxic metal that typically exists in one of two oxidation states (3\textsuperscript{+} or 6\textsuperscript{+}) and is an abundant element occurring naturally within some earth materials (Cheung and Gu, 2006; Ellis et al., 2002; Zahoor and Rehman, 2009). Cr (III) is a necessary element in maintaining normal carbohydrate metabolism in mammals and yeasts (Colin et al., 2012, Tziritis et al., 2012); however, high doses of Cr (III) can be detrimental to cell health. Cr (VI) is the carcinogenic form of Cr that is mobile and soluble within an aqueous environment (Cheung and Gu, 2006; Ellis et al., 2002; Zahoor & Rehman, 2008). In humans an accumulation of Cr (VI) in excess of 0.1 mg/g of body weight can be fatal and at lower doses nausea, skin ulcerations and lung cancer can result (Cheung and Gu, 2007; Costa, 2003; Tziritis et al., 2012). Due to Cr (VI)’s toxicity this element is considered to be an USEPA priority pollutant and studies have found that Cr (VI) is \sim100x more toxic and 1000x more mutagenic than Cr (III) (Colin et al., 2012; Costa, 2002). Even with all the potential health concerns the MCL of total Cr (III and IV) is 0.1 mg/L in drinking water (USEPA, 2012).

Based on this research, the potential does exist for significant movement of anthropogenic metal contaminants up the trophic levels. Beginning with metals in the sediment they then move to benthic organisms, secondary consumers and finally to human consumers. The river is heavily utilized by residents along its banks and fishing appears to be a frequent activity of residents in Hamilton, Ohio. Impact to human health depends on many factors within the river and the fish consumed, thus this study cannot quantify a potential human risk; however, the bioaccumulation capability of anthropogenic metals such as Zn, Pb, Cr and Cu exists. This study provides a specific impetus to better understand subsistence fishing on the GMR in Hamilton, framed in the context of human health.

One potential method for reducing the amount of pollution within the GMR would be a stormwater filtration system. Currently in Hamilton, Ohio any water that ends up on the streets enters the city’s stormwater system which directs the water straight into the GMR without any filtration. Through this study it is shown that street sediment particulate such as lead chromate and likely some coal ash spherules do end up in the GMR through this process. Installing stormwater filtration systems could prove to be a relatively simple remedy to removing a significant percentage of anthropogenic pollutants entering the river system through the city’s stormwater system.

Stormwater filtration systems using soils have proven to be effective at reducing turbidity and removing metals (Hatt et al., 2008 and Madhukar et al. 2012). One of the main concerns of such filtration systems is maintenance as soil based filters tend to clog over time. Hatt et al. (2008) found that in a 1 m thick filter taking the top 2-5 cm off every two years would allow for
adequate performance. In addition, planting the surface of the filter could help in creating pore space within the sediment keeping the filter from becoming compacted and ultimately clogged (Hatt et al., 2008). For this location compost biofilters are another potential remedy for stormwater filtration. The humic substances present in compost are effective at not only absorbing anthropogenic metals but providing a habitat for microbes which can break down hydrocarbons present in the stormwater (Finney et al. 2010). These types of filters could be installed at an outflow point before the water empties into the GMR as they are simply filter bags filled with compost and stacked in the area requiring stormwater control. The biofilter studied by Finney et al., (2010) had an overall volume of ~7.4 m³ and 40% porosity. Over the two year study the biofilter was found to reduce anthropogenic metals such as Zn and Cu by 32 and 29% respectively and based on projections would remain a viable filter for at least 10 years (Finney et al., 2010). Since most atmospheric depositions have the propensity to end up in stormwater runoff a filtration system would be beneficial in reducing the pollutant load on the GMR in Hamilton.
Conclusion

Overall the combination of ICP-MS bulk and fine elemental analysis coupled with SEM and TEM characterization has provided a concise method of defining a mineralogically complex material. This analysis of sediments required the use of all three techniques in order to adequately assess the nature of pollution in the GMR. ICP-MS chemical data and correlations alone would not have determined metals to be indicative of anthropogenic pollution. Electron microscopy provides unprecedented detail regarding the processes of some pollutants such as PbCrO$_4$ and a comparative tool for Cu, Zn, Sb, P and coal ash. A comprehensive elemental analysis paired with detailed SEM/STEM/EDS data allowed for a more detailed analysis of the GMR sediment, identifying pollutants even at low concentrations (below regulatory action levels), and explaining causes of variation in bulk chemical data.

Statistical analysis performed on the fine fraction of the GMR sediment allowed for a more quantitative approach to identifying pollution. Through the comparison of reference material to GMR sediment 6 elements were determined to be significant in the river: Zn, Sn, Sb, Cu, Pb and Sr. This analysis, coupled with the microscopy and bulk chemical data, will provide a baseline for future studies in the GMR valley. As no detailed GMR sediment studies exist, this study, in conjunction with the investigations by LeGalley et al. (in press) and LeGally and Krekeler (2013), will provide a comprehensive analysis of environmental pollution in a post-industrial river town. This study has been able to draw connections between pollutant particulate observed in the street sediment in Hamilton, Ohio (LeGalley and Krekeler, 2013) and pollutant particulate present in the nearby GMR sediment.

This investigation has implications for environmental policy and long-term best management strategies. The potential does exist for bioaccumulation of anthropogenic metals by aquatic organisms which could then be caught and consumed by the residents of Hamilton. Additionally, this study provides a detailed description of the pollutants present in the GMR during the summer of 2012; thus, in the future comparisons could be made back to this investigation to study the impacts of pollutant control policies, new industries or environmental disasters.
References


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## Appendix

### Appendix 1: Fine GMR Sediment ICP-MS Results

*ICP-OES Trace **ICP-OES Majors Calculated from Oxides

| Sample | Be ppm | V ppm | Cr ppm | Co ppm | Ni ppm | Cu ppm | Zn ppm | As ppm | Rb ppm | Sr ppm | Zr ppm | Nb ppm | Mo ppm | Cd ppm | Sn ppm | Sb ppm | Cs ppm | Ba ppm |
|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| JT 1 Fines | 0.86 | 45.81 | 44.00 | 6.59 | 26.32 | 17.99 | 115.26 | 5.96 | 47.09 | 473.22 | 21.60 | 117.05 | 4.26 | 1.21 | 0.07 | 1.21 | 0.69 | 2.89 | 309.94 |
| JT 2 Fines | 0.41 | 44.60 | 50.29 | 6.42 | 28.17 | 63.92 | 109.52 | 5.20 | 38.05 | 392.81 | 27.09 | 463.11 | 4.36 | 0.72 | 0.26 | 5.39 | 0.64 | 2.28 | 335.74 |
| JT 3 Fines | 1.54 | 53.40 | 48.84 | 8.44 | 26.77 | 29.14 | 139.79 | 6.39 | 52.80 | 305.78 | 25.31 | 319.42 | 4.87 | 1.94 | 0.15 | 1.89 | 0.86 | 3.21 | 323.02 |
| JT4 Fines | 1.58 | 69.42 | 52.16 | 10.60 | 42.83 | 27.39 | 131.41 | 5.91 | 72.05 | 216.17 | 24.83 | 174.51 | 7.27 | 2.48 | 0.08 | 2.72 | 1.08 | 4.10 | 352.03 |
| JT5 Fines | 1.07 | 51.72 | 54.44 | 8.59 | 26.62 | 28.06 | 157.91 | 7.43 | 52.34 | 278.33 | 26.73 | 387.56 | 7.88 | 1.56 | 0.16 | 3.96 | 0.86 | 3.13 | 313.74 |
| JT 6 Fines | 0.87 | 56.72 | 54.48 | 8.33 | 28.12 | 29.19 | 111.65 | 6.17 | 53.52 | 273.22 | 28.44 | 499.03 | 7.72 | 1.83 | 0.21 | 2.98 | 0.83 | 3.27 | 308.41 |
| JT7 Fines | 0.95 | 45.86 | 42.92 | 7.09 | 30.20 | 81.18 | 67.62 | 41.48 | 25.91 | 67.62 | 23.68 | 122.57 | 5.12 | 1.58 | 0.14 | 1.58 | 0.76 | 1.31 | 296.06 |
| JT 8 Fines | 1.32 | 48.90 | 45.93 | 6.96 | 23.23 | 21.37 | 101.10 | 7.16 | 49.30 | 218.99 | 25.48 | 199.63 | 4.14 | 1.65 | 0.09 | 1.02 | 0.84 | 2.61 | 296.57 |
| JT9 Fines | 0.99 | 56.39 | 46.62 | 7.96 | 28.94 | 25.29 | 125.20 | 7.43 | 59.87 | 338.89 | 21.99 | 97.15 | 3.75 | 1.60 | 0.04 | 0.78 | 0.72 | 3.60 | 329.06 |
| JT 10 Fines | 0.92 | 46.45 | 42.47 | 7.05 | 25.73 | 34.40 | 132.14 | 6.37 | 49.50 | 270.00 | 22.78 | 189.12 | 4.55 | 1.53 | 0.08 | 2.54 | 0.94 | 2.59 | 288.44 |
| JT 13 Fines | 0.95 | 57.05 | 53.53 | 8.73 | 29.66 | 30.23 | 139.57 | 8.39 | 58.29 | 266.13 | 25.21 | 308.40 | 9.30 | 1.67 | 0.15 | 3.09 | 1.05 | 3.42 | 345.60 |
| JT 14 Fines | 0.98 | 57.34 | 54.06 | 8.17 | 29.40 | 99.20 | 141.33 | 7.39 | 57.98 | 272.48 | 60.28 | 231.00 | 4.93 | 0.20 | 0.10 | 2.07 | 0.86 | 3.21 | 345.65 |
| JT 15 Fines | 0.83 | 53.18 | 48.89 | 8.15 | 29.00 | 27.70 | 110.28 | 7.37 | 55.32 | 282.72 | 22.90 | 138.94 | 3.92 | 1.80 | 0.05 | 1.66 | 0.76 | 3.02 | 342.11 |
| JT 16 Fines | 1.02 | 61.06 | 56.72 | 9.25 | 30.68 | 29.14 | 141.82 | 8.62 | 64.32 | 264.94 | 25.98 | 221.81 | 6.09 | 2.29 | 0.11 | 2.01 | 0.90 | 3.62 | 326.53 |
| JT 17 Fines | 1.01 | 60.18 | 50.35 | 9.09 | 31.18 | 30.03 | 121.05 | 7.31 | 62.64 | 266.40 | 24.61 | 193.58 | 4.73 | 1.74 | 0.07 | 0.91 | 0.70 | 3.43 | 319.58 |
| JT 18 Fines | 1.05 | 63.63 | 50.71 | 9.12 | 28.43 | 28.22 | 133.34 | 8.27 | 66.38 | 275.78 | 25.24 | 229.36 | 6.89 | 1.79 | 0.11 | 2.71 | 0.94 | 3.90 | 325.02 |
| JT 19 Fines | 0.72 | 47.81 | 45.77 | 7.13 | 24.28 | 23.23 | 106.66 | 7.07 | 48.91 | 219.45 | 23.70 | 155.65 | 3.60 | 1.43 | 0.06 | 1.01 | 0.62 | 2.26 | 284.16 |
| JT 18 Fines | 0.87 | 56.86 | 54.62 | 8.45 | 30.61 | 31.90 | 170.89 | 8.01 | 59.20 | 292.88 | 25.14 | 174.83 | 4.73 | 1.98 | 0.08 | 1.67 | 0.91 | 3.37 | 321.61 |
| JT 19 Fines | 0.85 | 57.70 | 64.81 | 8.79 | 34.21 | 31.63 | 158.79 | 7.83 | 58.76 | 265.77 | 26.06 | 443.89 | 7.47 | 2.01 | 0.22 | 3.87 | 1.22 | 3.33 | 315.53 |

### Analytical error ± 5% (Dr. John Morton)
### Appendix 2: Bulk GMR Sediment ICP-MS Results

**ICP-OES Trace**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Be ppm</th>
<th>V ppm</th>
<th>Cr ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Zn ppm</th>
<th>As ppm</th>
<th>Rb ppm</th>
<th>Sr ppm</th>
<th>Y ppm</th>
<th>Zr ppm</th>
<th>Nb ppm</th>
<th>Mo ppm</th>
<th>Cd ppm</th>
<th>Sn ppm</th>
<th>Sb ppm</th>
<th>Ti ppm</th>
<th><strong>Fe ppm</strong></th>
<th><strong>Al ppm</strong></th>
<th><strong>Ti ppm</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>JT 1 Bulk</td>
<td>1.24</td>
<td>10.32</td>
<td>13.94</td>
<td>3.60</td>
<td>3.50</td>
<td>2.20</td>
<td>1.15</td>
<td>0.06</td>
<td>1.15</td>
<td>1.94</td>
<td>2.48</td>
<td>1.95</td>
<td>0.85</td>
<td>0.65</td>
<td>2.93</td>
<td>1.46</td>
<td>2.61</td>
<td>382.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JT 2 Bulk</td>
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**Analytical error ± 5% (Dr. John Morton)**

99
Appendix 3: Reference Sample ICP-MS Results

*ICP-OES Trace  **ICP-OES Majors Calculated from Oxides

| Sample                     | Be ppm | V ppm | Cr ppm | Co ppm | Ni ppm | Cu ppm | Zn ppm | As ppm | Rb ppm | Sr ppm | Y ppm | Zr ppm | Nb ppm | Mo ppm | Cd ppm | Sn ppm | Sb ppm | Sb ppm | Cs ppm | Ba ppm | La ppm | Ce ppm |
|---------------------------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Russell Soil Fines        | 0.93   | 66.75 | 57.42  | 9.12   | 21.05  | 18.91  | 68.61  | 7.59   | 66.55  | 92.15  | 33.23 | 556.67 | 10.45  | 1.12   | 0.30   | 1.07   | 0.65   | 3.02   | 415.91 | 32.07  | 61.37  |
| Russell Soil Bulk         | 0.64   | 60.92 | 49.17  | 11.19  | 18.68  | 16.12  | 59.12  | 6.18   | 63.36  | 109.79 | 27.31 | 402.30 | 8.05   | 0.99   | 0.22   | 0.67   | 0.45   | 2.67   | 427.99 | 25.69  | 51.66  |
| Abandoned Stream Fines    | 0.58   | 51.69 | 46.01  | 7.09   | 23.19  | 18.20  | 69.26  | 5.21   | 42.85  | 194.59 | 27.75 | 376.43 | 3.67   | 1.49   | 0.20   | 1.08   | 0.57   | 1.86   | 306.94 | 26.17  | 52.50  |
| Abandoned Stream Bulk     | 0.46   | 50.71 | 28.96  | 6.08   | 16.51  | 8.60   | 39.10  | 4.97   | 30.33  | 221.94 | 19.82 | 120.97 | 2.46   | 0.53   | 0.05   | 0.50   | 0.26   | 0.77   | 272.99 | 16.87  | 34.08  |
| 4 Mile Creek Bulk         | 0.37   | 32.56 | 21.63  | 4.28   | 25.81  | 6.36   | 21.44  | 2.98   | 31.81  | 232.60 | 15.39 | 100.38 | 1.67   | 0.16   | 0.04   | 0.44   | 0.11   | 0.79   | 296.17 | 11.68  | 22.88  |
| 4 Mile Creek Fines        | 0.72   | 50.90 | 46.39  | 7.88   | 34.37  | 21.64  | 66.29  | 5.43   | 49.94  | 220.93 | 23.94 | 200.25 | 4.16   | 1.18   | 0.11   | 0.86   | 0.44   | 2.32   | 324.51 | 22.82  | 45.14  |
| Glacial Till Bulk         | 1.48   | 64.70 | 45.25  | 9.86   | 25.53  | 18.48  | 49.90  | 8.59   | 73.47  | 208.26 | 21.99 | 186.72 | 10.04  | 8.30   | 0.13   | 1.09   | 0.54   | 2.83   | 353.12 | 23.71  | 47.88  |
| Glacial Till Fines        | 1.23   | 73.61 | 51.68  | 11.83  | 31.07  | 24.08  | 64.08  | 6.34   | 80.84  | 172.24 | 25.01 | 159.01 | 6.12   | 2.56   | 0.08   | 1.05   | 0.45   | 4.12   | 339.45 | 26.70  | 51.89  |

Analytical error ± 5% (Dr. John Morton)
### Appendix 4: GPS Coordinates for Reference Samples and Unknown GMR Sediment Samples

#### Reference GPS Coordinates

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<td>Abandoned Stream</td>
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#### Sample GPS Coordinates

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Sediment Sample Map - created at GPSVisualizer.com

(A) Represents sample JT 5- JT 7  (B) Represents sample JT 1- JT 4  (C) Represents sample JT 14- JT 16
(D) Represents sample JT 17- JT 19  (E) Represents sample JT 8- JT 10  (F) Represents sample JT 11- JT 13
Appendix 5: XRD Powder Results
Reference Samples

Quartz

Russell Soil

Glacial Till

Feldspars

Calcite

Dolomite

101

100

104
Sediment Samples

- JT 18 Fines
- JT 10 Fines
- JT 2 Fines

Minerals:
- Quartz
- Calcite
- Dolomite
- Feldspars

Graphs showing intensity (counts) vs. two-theta (deg) for each sample.
Appendix 6: Boxplots indicating the differences observed between the fines and bulk for Cr and Cu. Adapted from Dr. Byran Smucker’s STA 475 class.
Appendix 7: Boxplots for the 6 significant elements in the GMR, adapted from Dr. Byran Smucker’s STA 475 class.