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Spheroidal Carbonaceous Particles in a Virginia Mill Pond Provide a Record of Local and Regional Coal Combustion

Kayla Cahoon

Spheroidal Carbonaceous Particles in a Virginia Mill Pond Provide a Record of

Local and Regional Coal Combustion

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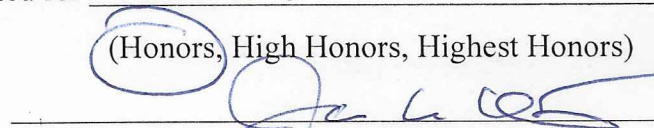
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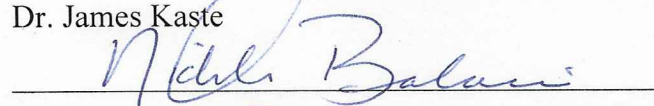
by

Kayla Michelle Cahoon

Accepted for _____Honors_____

(Honors, High Honors, Highest Honors)

_____

Dr. James Kaste

_____

Dr. Nicholas Balascio

_____

Dr. Rowan Lockwood

_____

Dr. Danielle Moretti-Langholtz

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we "suffered for fun." To the entire geology department faculty and staff, and to all the

geowallies for late nights and early mornings full of serious studying, and silly laughter. Finally,

thank you to my rock, my steady calm in a sea of chaos, my purveyor of a perfectly timed Diet

Coke, my biggest fan and critic, Jeff. I love you so much, thank you for all you have done to

make this a reality. Our lives will never be the same. Thank you.

Abstract

Spheroidal carbonaceous particles (SCP), a constituent of coal fly ash, are a sensitive indicator of local and regional coal combustion archived in lake sediments. Their unique morphology and chemical composition are not replicated by any naturally occurring substance on Earth. SCP accumulation in sediments has also been correlated to accumulation of heavy metals such as Mn, Fe, Ti, and Pb. We reconstructed SCP accumulation in a former mill pond in Williamsburg, VA, Lake Matoaka, and find a bimodal distribution with peaks c. 1790 and c. 1953. We believe that our study is the first to identify SCPs in sediments prior to the early 1800s, making this record unique. Grain size analysis shows a statistically significant difference in grains from the two peaks indicating different fly-ash provenance. The particles first appear in Lake Matoaka in 1734 and steadily increase from 15-300 SCP/gDM peaking in 1790. SCP concentration remains constant at ~100-200 SCP/gDM from c. 1800-1860, when a rapid increase in particle accumulation resumes, increasing abruptly from 500 SCP/gDM in 1860 to >8000 SCP/gDM in 1953. Modern accumulation rates have decreased in response to emission restricting legislation in 1970 but continue to accumulate 1000 SCP/gDM in surface sediments. Trends in SCP accumulation mirror major historical events including prominent socio-political wars and economic depressions.

Introduction

The consumption of coal and other fossil fuels has dramatically changed Earth's atmospheric and oceanic chemistry over the past 150 years (Crutzen and Stoermer, 2000; Crutzen, 2002). Global demand for fossil fuel energy has forced previously mineralized greenhouse gases (including CO_2, N_2, CH_4, SO_4, N_2O, and PO_4) and particulate pollutants into the atmosphere (Querol et al., 1996; Crutzen 2006; Canuel et al., 2012). Coal combustion releases mineralized metals that can be toxic in some environments such as Pb, Ar, Fe, Mg, Mn, Ti, Ni, and others (Rose, 1996; Stoffyn-Egli et al., 1997). Fossil fuels today are burned by large-scale industrial production and advanced technological systems. However, evidence of human fossil fuel consumption has been identified as early as 4800 yBP for use in agriculture (Li et al., 2012). Greenland ice core data show evidence of metal smelting (specifically copper and aluminum) as early as 2500 years ago, presumably by the Roman Empire (Hong et al., 1996. The primary difference between historical and modern coal consumption lies in scale and industry. Insufficient technology prior to the Industrial Revolution made coal difficult to mine so early civilization relied primarily on organic-based energy, such as wood and animal fat, until coal became more accessible circa 1800 (Fig. 1) (Allen, 2012). Post-IR global technology relied on coal leading to an economic and political dependence that continues to this day. Mohr and Evans (2009) predict, conservatively, that by 2050 global consumption of coal will reach 7.4 Gt/y.
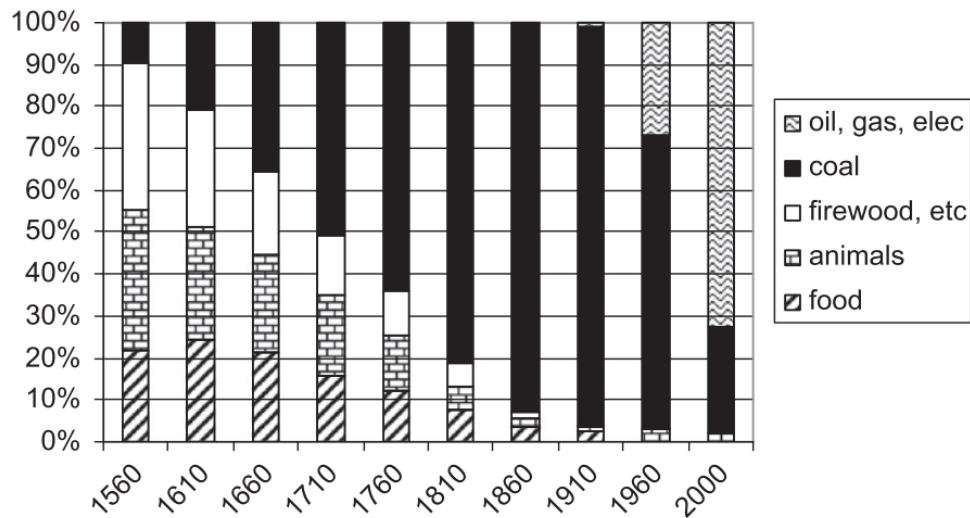
Figure 1: Material used for energy source in England 1560-2000 (Allen, 2012).

In British-Colonial America, coal was burned in small settlements, mostly as a heat source for metal works such as armory forges and metal foundries. In the mid-1700s, due to decreasing availability of trees for fire wood, Benjamin Franklin and Abraham Buzaglo introduced the three-tiered, coal-fired, external chimney Buzaglo stove for warming homes (Crowley, 2000). These stoves were an economic luxury and, therefore, only available to the wealthiest colonists. In the major political and cosmopolitan areas within colonial America, the stoves were in use circa 1750, ~50 years prior to IR (Crowley, 2000). Thus, coal consumption in this time-period is tied to urbanization and socio-political centers of wealth and controlled by economics and population density. Periods of high economic gain and larger population density will foster greater consumption of coal, while an economic depression would cause much lower consumption of coal (Graham, 1945; Hellier and Kelly, 1990).

In the past 50 years, researchers have argued the accumulation of pollutants, greenhouse gases, and synthetic chemicals released by coal dependence post-IR are ubiquitous globally and, therefore, these changes can be used as a marker for "The Anthropocene," an informal new

epoch of geologic time, occurring after The Holocene and characterized by human impacts on the Earth (Crutzen, 2006; Rose, 2008; Swindles et al., 2015; Yang and Rose, 2005). This has sparked global interest in the geochemistry and accumulation of coal ash and fly-ash particulate matter, and specifically, spheroidal carbonaceous particles (SCPs). These studies have focused on small remote lakes and peat bogs as catchments for regionally emitted SCPs and associated pollutants primarily in Europe to show a broad global impact detectable in sediments far from their source and industrial activities (Fig. 2). The primary focus of these studies is to identify four key points along a time-accumulation plot: the year or depth of the first occurrence, the period at which there is a large increase or "ramp up," a critical peak of accumulation marking a geologic time boundary ~1950, and a decline in surficial deposits due to recent pollutant-controlling regulations (Rose, 2001). However, a critical evaluation of previous work shows wide variation in both the accumulation peak between 1940 and 2000 (Hirakawa et al., 2011; Ruppel et al., 2013) and the first occurrence between 1835 and 1990 (Clark and Patterson, 1984; Rose et al., 2004). Furthermore, very few studies have been completed outside of Europe. This challenges the assumption that SCPs can be used as a global stratigraphic marker due to inconsistencies and incompleteness of global studies. In this study, we present the first study on the eastern coast of the US on SCPs and their accumulation in sediments since colonization. We also use the SCPs to complete a grain size analysis and a chemical composition analysis to evaluate changes to potential source and long range transport of fly-ash constituents over the past 300 years.
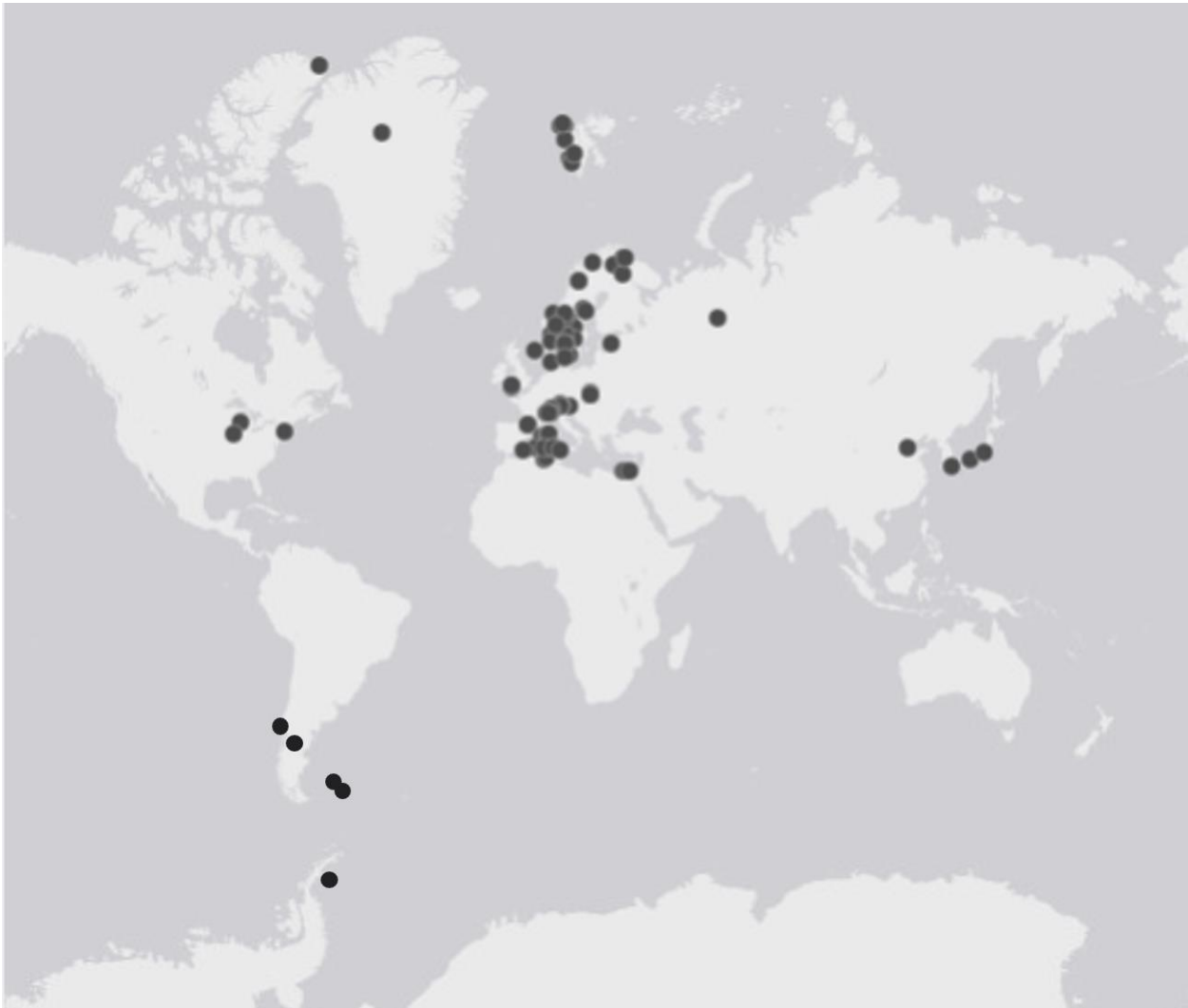
Figure 2:Global map of studies researching the accumulation of SCP in sediments. Notice the large proportion of the studies in Europe and three in the US. Map modified from Swindles et al. (2015).

2.0 Background

2.1 Coal and Coal Consumption

Coal is a sedimentary rock that forms from the compaction of organic-rich, oxygen-deprived, and saturated environments including swamps, marshes, and peat bogs. These oxygen-poor environments also become traps for organically generated sulfur, nitrogen, and iron, leading to a buildup of arsenic and other toxic trace metals (Hower, 2012a). For coal to be efficient upon

combustion, and economically viable, it must have a minimum of 65% pure carbon. The remaining portion of coal is comprised of other mineral inclusions, such as pyrite, cerussite, and siderite (Mohr and Evans, 2009). Coal beds are classified by carbon purity into four subdivisions: anthracite, bituminous, sub-bituminous (or brown), and lignite. Anthracite is the cleanest, with 90–95% pure carbon, but also the rarest and, thus, most expensive. This makes anthracite a higher cost / same benefit resource for power supply companies today, as such it is not widely used. Most coal used today is bituminous (85–90% C) or sub-bituminous (80–85% C) (Hower, 2012b).

Producing energy from coal requires very specific conditions not found in natural Earth systems. According to the article *How Energy Works*, published by Duke Energy, coal is combusted by flash ignition in a dry furnace generating extreme heat that produces steam from liquid water. That steam then activates a turbine and generator creating an electrical current. The coal bed is kept burning until all the carbon bonds have been broken, a process lasting 18-24 hours. The water then cools and is recycled; however, new coal is required to repeat the procedure thereby continually generating electricity (www.duke-energy.com). In the furnace, coal experiences temperatures up to 1750°C at rates of 10^4°Cs^{-1}: maximum temperatures are sustained for a maximum of 18 hours before quenching (Rose, 2001). There are no known natural environments that simulate these same conditions, making some byproducts of coal combustion a proxy of human activity (Wik and Renberg, 1996; Rose, 2001).

In the furnace, coal breaks down into coal ash and fly ash: coal ash is the remnant material in the bottom of the furnace, and fly ash is the smaller, finer particles ejected from the furnace through the flu or chimney (Rose, 1996, 2001; Wik and Renberg, 1996, Kapička et al., 1999; Kapička et al., 2000). Coal ash is collected and disposed of in various ways, usually in

sealed landfills, and is comprised of slag or molten metals, devolatilized coal, and indiscriminate remnant ash. Fly ash particulate matter is released into the atmosphere alongside acidic and/or volatile material and gases (Wik and Renberg, 1996, Rose, 2001). These gases and acids create significant changes to atmospheric chemistry and pH of precipitation but are chemically similar to natural Earth emissions from volcanoes and divergent plate boundaries, such as the mid-ocean ridge (Crutzen, 2006).

2.2 Particulate Fly Ash Summary

Extensive studies have used fly-ash particulate matter as pollution tracers because, until 1970, nearly 100% of the particles and their associated pollutants were emitted into the atmosphere and later deposited by natural processes (Gustafsson et. al., 2001). Fly-ash particles are subdivided into three categories: charcoal, inorganic ash spheres (IASs), and spheroidal carbonaceous particles (SCPs) (Rose, 1994, 1996, 2001, 2008; Rose et al., 1999). Rose (2001) defines coal-combusted charcoal as a complete chemical alteration of carbon after combustion. Charcoal is pure carbon with no distinct chemical signature or morphology. IAS are the non-combustible fragments of the coal bed, primarily metals. They have a nearly perfectly spherical morphology (1.05% > aspect ratio > 95%) and represent 90-95% of all fly ash (Rose, 1994, 1996, 1999, 2001). Their morphology is defined by gravitational convection during upwelling in chimney stacks or flues (Hower, 2012a). Charcoal and IAS can both be found in natural Earth systems such as volcanoes and forest fire residues, among others, and include minerals such as mullite, spinel, pyrrhotite, and quartz glass (Rose, 2001; Hower, 2012a). The final constituent, SCP, however, are not formed by any natural process, and are not seen in the sedimentary record prior to the discovery and usage of coal for energy production, thereby directly correlating SCP

to human activity (Griffin and Goldberg, 1975; Rose, 1994, 1996, 2001, 2008; Wik and Renberg, 1996; Watt, 1998).

2.3 IAS

IAS have been identified in paleolimnological studies recently correlated with volcanic emissions and bolide impacts (Rose, 2001; Firestone et al., 2007). Recall IAS are formed due to partial melting of non-combustible mineral material in the coal bed, mainly metals. During volcanic eruptions, ejected molten lava has the heat capacity to generate spheres of heterogeneous molten metals sourced from magma chemistry, surface rocks, and sediments (Firestone et al., 2007). Additionally, IAS may form due to intense flash pressure melting of surface minerals upon bolide impact (Glass, 1990; Rose, 2001; Firestone et al., 2007). The force of impact causes the particles to eject into the atmosphere and rotate, a process very similar to upward convection in power plant chimneys (Rose, 2001). The resulting particles, called micro-meteorites or tektites, have a spheroidal to elongated morphology and have not undergone any devolatilization (Glass, 1990).

2.4 Charcoal

Charcoal is fully combusted carbon material (Rose, 2001). Formed by the complete chemical alteration of organic and/or inorganic carbon after intense and prolonged heat energy, charcoal exists in any environment after burning (Griffin and Goldberg, 1981; Rose, 2001; Turner et al., 2010). Charcoal particles in the sedimentary record have been used as a paleo proxy for early human activity including Neolithic agriculture and ancient to medieval agriculture and industry (Turner et al., 2010; Allen, 2012; Li et al., 2012; Hong et al., 1996). While used as an indicator of human activity, charcoal is also generated by natural forest fires, bolide impacts, and tectonic activity (Turner et al., 2010). Due to a variety of anthropogenic and

natural forces generating charcoal, these particles cannot be used exclusively as a proxy for human coal consumption.

2.5 SCP

SCP are formed when remnant, unburned carbon particles break off from the coal bed during combustion and fuse with present molten metals. Temperatures in the furnace are high enough to evaporate volatile materials, and partially melt minerals, releasing small droplets of heterogeneous metals. These elements, unburned coal microparticles, and partially molten mineral inclusions, fuse while in suspension (Wik and Renberg, 1996). The fused particles are then forced upwards due to heat energy where gravitational convection forces them into spheroidal particles. Volatiles expand and escape from the inner reaches of the particles leaving behind pores on the surface, and an overall spheroidal morphology with aspect ratios between 0.75 and 1.15 (Fig. 3) (Rose, 2001).
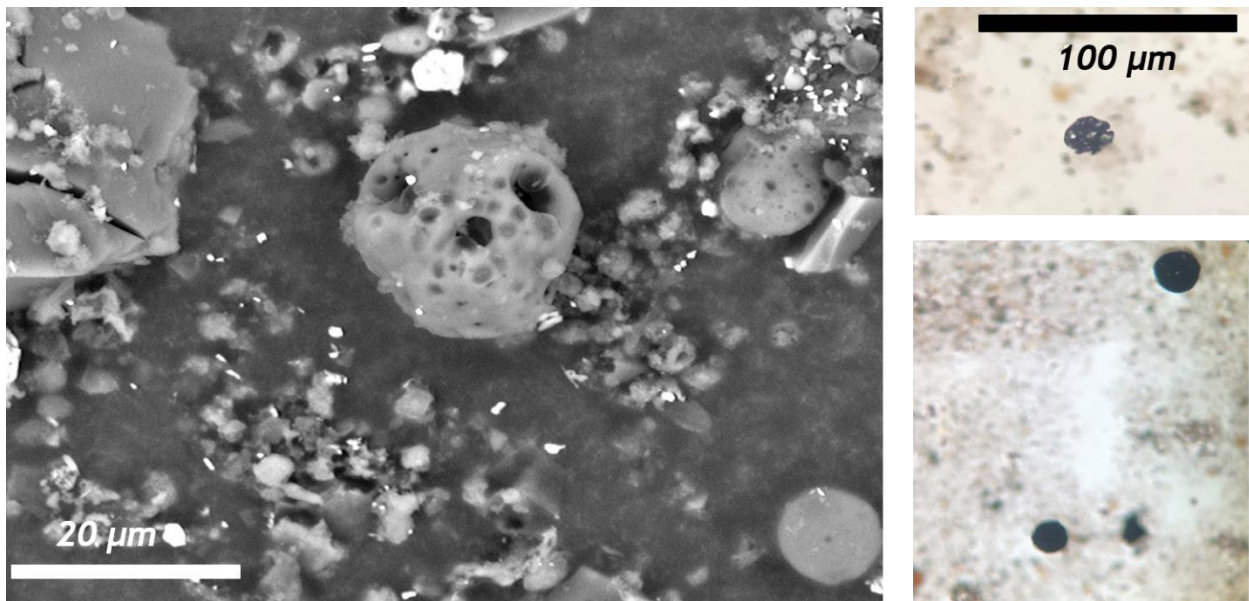
Figure 3: SCP particles isolated from sediment core. Left: SCP as they appear under scanning electron microscope, right: as they appear in standard reflective light microscope.

Due to the heterogeneous nature of the particles, very little is known about the physical properties of SCP. Their density, atmospheric residence time, and conductivity is poorly documented; however, physical characteristics and morphology have been well studied. SCPs range in size from submicron to ~200 µm, averaging between 5 and 50 µm. SCPs exist as cenospheres (single spheroidal particles) or pleiospheres (several smaller spherules housed inside a single larger spherule), are chemically inert and resistant to acid attack due to carbon enrichment, and are physically fragile (Rose, 1994, 2001, 2008; Wik and Renberg, 1996; Watt, 1998; Kapička, 1999, 2000; Rose et al., 1999; Hower, 2012a). Often, SCP are reported to have magnetic properties due to enriched iron bearing minerals in the source coal bed, but this is not universally true for all SCP (Kapička, 1999, 2000; Kukier et al., 2003; Grimley et. al., 2017).

Several studies have completed energy dispersive x-ray spectroscopy (EDS) analysis to evaluate the chemical composition of SCP (Rose et. al., 1999; Watt, 1998; Gustafsson et. al. 2001; Kukier et al., 2003; Murakami-Kitase et al., 2010). These studies report differences in elemental trace metals and in stoichiometric proportions among those metals. Presently no studies have been performed comparing the petrology of source coal and chemical constituents of resulting fly ash. To track environmental impacts of SCP, a more thorough examination of particle chemistry must be performed with the goal of associating source coal petrology to fly-ash chemistry and establishing a fingerprint for the fly ash. In doing so, environmental impacts can be more readily predicted based on the amount and chemistry of the coal used and emitted in energy production.

2.6 SCPs Emissions and Atmospheric Circulation

Minimum regulation for power plant stack height requires them to be 2.5x the size of the power house. By today's standards, average power plant stack height is 600-800 feet high or

0.18-0.25 km tall (Thomas et al., 1963). This is relatively low in the atmosphere, but high enough such that emissions can be carried by prevailing wind currents and subjected to wet and dry deposition (Thomas et al., 1963; Griffin and Goldberg, 1981; Rose, 2001). Larger, denser particles are predicted to fall out first, followed by smaller and lighter particles. Studies have shown acidic gas emissions from the same source as SCP can be transported distances of several thousand kilometers from the source if atmospheric conditions are favorable (Thomas et al., 1963). Assuming smaller particles have low density, SCP are capable of being transported comparable distances through primary global wind patterns. This is distinct from pre-IR SCP which would have been emitted much lower to the ground. Cooler burns in open air coal pits, usually located within a home or building, were typical in the 17th and 18th centuries (Crowley, 2000; Mokyr, 2009). These particles were emitted through crude brick chimneys 3-10 meters into the atmosphere, significantly lower than their modern day counterparts (Crowley, 2000). Particles and pollutants emitted at this level are immediately deposited and transported along the ground into local watersheds as they are not high enough in the atmosphere to be transported long distances by climate and weather patterns (Mokyr, 2009; Makonese et al., 2014). This has implications for global modern deposition of SCPs compared to early depositions.

3.0 Literature Review and Summary of Previous Work

SCPs were first identified by Griffin and Goldberg (1975) after vague language in the Clean Air Act of 1970 regarding "particulate pollutants" and "fine particulates" led to scientific investigation into particulate pollution from coal combustion (Griffin and Goldberg, 1975). The Clean Air Act of 1970 called for major changes to national energy production and industry by implementing industrial emission standards, air quality standards, and performance standards for new and existing energy production facilities to include coal and oil-fired power stations. The

primary goal of the Clean Air Act was to reduce acidic gaseous emissions and toxic metal pollution (Pb, As, and Fe). Early SCP studies focused on identifying and characterizing coal combustion-derived particulate matter in the sedimentary record (Griffin and Goldberg, 1975, 1979). Clean air legislation continued to evolve, growing global attention; by the 1990s SCP studies were a focal research topic in Europe.

Today, SCPs are known to be a constituent of fly ash and one of two different spheroidal particles, however, this terminology was not well established until the early 1990s (Rose, 1990, 1994). Other terms used to discuss fly-ash microparticles include soot, soot balls, soot spheres, soot particles, soot spherules, carbon particles, elemental carbon particles, carbonaceous particles, charcoal particles, and spheroidal fly-ash particles (Wik and Renberg, 1996; Rose, 2001). The scientifically adopted term "spheroidal carbonaceous particles" first appears in the literature in 1994 by Neil Rose, the leading global SCP researcher.

3.1 SCP as a Geochronological Tool

The identification of fly-ash particles in catchments, and their strong correlation to fossil fuel consumption led to their immediate use in paleolimnology as a date tracer. Renberg and Wik (1985) pioneered this technique by isolating and quantifying particle accumulation in the sedimentary record normalized to local fossil fuel consumption rates. The application of this has been used to date sediment cores in central China (Boyle et al. 1999), Ferroscandinavia and the Kola Peninsula (Korhola et al., 1999), Svalbard (Rose et al., 2004), Ireland (Swindles and Roe, 2006), Estonia (Alliksaar and Renberg, 1998; Allikssar and Heinsalu, 2012), and Russia (Flower et al., 1995, 1997). These studies generally assign a concentration peak in sediments dating at 1950 $\pm$10 years.

There are three critical points in the SCP concentration curve to identify in order to use the accumulation as a dating tool: the first occurrence of the particles, a large ramp up or exponential increase in concentration leading to a sharp peak, and a modern decline (Fig. 4) (Renberg and Wik, 1985; Rose, 1990, 1994).
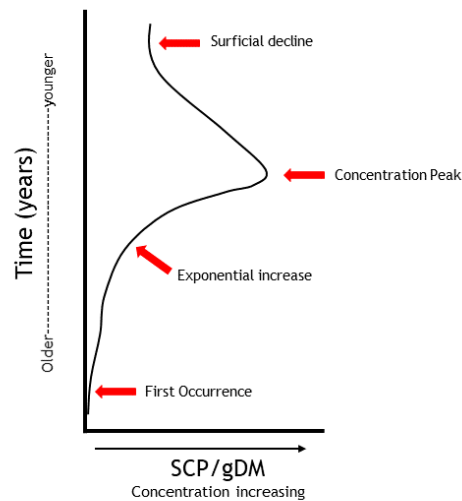
Figure 4: Idealized SCP concentration curve. Critical points to identify in an SCP study: the first occurrence of particles, the ramp up or exponential increase in particle accumulation, sharp peak representing the height of fossil fuel consumption, and a surficial decline (not observed in all studies).

Using the accumulation curve as a sedimentary geochronological tool then requires a study of local fossil fuel burning sources. The first occurrence is time correlated to the opening of the most proximal coal consuming facilities and normalized to the rate of coal consumption from that facility. The exponential increase is interpreted as the pre-legislation period in which all particulates were emitted directly into the atmosphere (Renberg and Wik, 1985). This peak is also regulated by the level of production within the facility itself; many coal-fired plants were opened and quickly closed, or saw a large increase in energy production, between 1940 and 1950 due to industrial demands during World War II (Nelson and Wright, 1992). The sharp decline represents the timing and implementation of emission collection technology, mainly scrubbers,

in chimney stacks and flues due to the 1970 and 1977 Clean Air Act and amendments (Renberg and Wik, 1985). These same critical points are used today in more detailed analyses of SCP accumulation and to demonstrate broader implications of SCP distribution and accumulation.

The method Renberg and Wik (1985) suggest, using SCP as a dating tool, is predicated on the assumption that SCPs are present in all catchments and first occurrence and peak concentrations can be normalized to the same date globally. This assumption has been challenged by Parry et al. (2013) who compared the normalized SCP concentration curve to proven dating techniques (counting varves, radionuclide geochronology, and ^{210}Pb accumulation) in a core taken from Dartmoor National Park in southwest England. They found statistically significant variance in dates assigned by SCP concentration curve and radionuclide data. This was attributed to a flux of regional SCPs that was unaccounted for. Ruppel et al. (2013) found similar results in their study of particle accumulation around power plants. This study demonstrates that within one kilometer of a power plant, the Renberg and Wik (1985) dating technique works, but at further distances, SCP accumulation is inconsistent with assumed normalized data: particle accumulation is greater than expected if only local sources are accounted for. Thomas et al. (1963) performed a case study on the atmospheric circulation of gaseous emissions from power plants. Their study shows, under specific atmospheric conditions and emission greater than 0.15 km above ground, particulate and gaseous by-products can be transported hundreds to thousands of km from their source. This signature in catchments overprints the local signature of particle accumulation in a fully industrialized world, making the use of SCP as a geochronological tool unreliable.

3.2 SCP and the Anthropocene

Crutzen and Stoermer's (2000) historic article "The Anthropocene" gave a renewed focus to SCP research. In the scientific search for a global stratotype and section point (GSSP) to mark the boundary of the Anthropocene, SCP seemed an obvious choice. SCPs carry a geochemical signature that is unique to the burning of coal, they have a clear accumulation, and are easily extracted and identified (Rose, 2008; Swindles et al, 2015). This spurred a flurry of research to quantify the SCP record in as many environments as possible. Preliminary work had established SCP presence in rural lakes, but little research had been conducted in remote lakes and environments. Some of the regions studied include eastern Japan (Murakami-Kitase et al., 2004; Nagafuchi et al., 2009; Hirakawa et al., 2011), the arctic circle at Ellesemere Island (Doubleday et al., 1995), remote Andes lakes in Chile (Chirinos et al., 2006), isolated lakes in Svalbard (Rose et al., 2004), dry river beds in the Australian outback (Cameron et al., 1993), Scottish peat bogs (Yang et al., 2001), Egypt (Appleby et al., 2001) and Antarctica (Martins et al., 2010; Rose et al., 2012). Most studies have occurred in remote regions of Europe including the Pyrenees Mountains in Spain, the Tatra Mountains in Poland and Slovakia, the eastern and western Alps in Slovenia, Austria, France, and Italy, the Iberian Peninsula in Portugal, and northern African countries Morocco, and Tunisia (Rose et al., 1995; Rose et al., 1999, Rose et al., 2003, Rose et al., 2004). These studies all focused on defining an accumulation curve for SCPs in very remote settings. Locations were specifically chosen to maximize distance from coal-fired power plants and urban towns or cities to show global deposition of SCPs. Particles were identified in all study locations except one lake in Chile (Chirinos et al., 2006). The investigation of two high Andes mountain lakes show an SCP profile in the first location, Laguna Chica San Pedro; however, no particles were recovered from Lake Galletue. This is the only published article

referencing SCP accumulation in any research setting with a complete absence of particles. Further, Chirinos et al. (2006) is the only published SCP research in South America to date. This shows a need for more research in the southern hemisphere to explain the presence or absence of SCP.

The results from these studies also varies significantly in the date of first occurrence, date of concentration peak, and actual concentrations. The date of the first occurrence of SCP ranges from 1835 (Clark and Patterson, 1984) to 1990 (Rose et al., 2004). While the concentration peak shifts from 1940 (Hirakawa et al., 2011) to modern surficial sediments (Ruppel et al., 2013). The number of particles accumulated also varies from 125 SCP / gram of dry mass (gDM) (Rose et al., 2012) to more than 100,000 SCP/gDM (Wik and Renberg, 1996). This shows an incomplete understanding of global SCP sources and mechanisms of dispersal that must be further researched before validating SCPs as a GSSP for the Anthropocene.

3.3 SCPs as tracers of Human Activity and Pollution

The scientific community agrees that SCPs are a proxy of human activity and act as a fossil fuel consumption tracer. In the literature, this is demonstrated by a strong agreement of SCP deposition and other fossil fuel related toxins, mainly Pb (Griffin and Goldberg, 1975, 1979; Doubleday et al., 1995; Boyle et al., 1999; Korhola et al., 1999; Lan and Breslin, 1999; Kapička, et al., 1999; Rose et al., 2003; Chirinos et al., 2006; Parry et al., 2013; Grimley et al., 2017). This is a logical association as coal beds are often Pb rich, and upon combustion, mineralized Pb will be released in soluble forms by the same means as fly-ash fine particulate matter (Chirinos et al., 2006; Parry et al., 2013; Grimley et al., 2017). In high resolution lake deposits, the relationship between SCP and Pb is highlighted and, when analyzed together, records decadal scale changes in agriculture and industry locally and regionally. Previous work

to date agrees there are no reported SCPs prior to 1800, they are an indicator of human activity in remote, rural, and urban settings, and are a fine particulate pollutant in every environment. They have a concentration record consistent with Pb concentration, and their physical properties make them easy to study and identify in the sedimentary record.

4.0 Geologic Setting

4.1 Lake Matoaka

Southeastern Virginia lies on the coastal plain geologic province, a passive margin coast characterized by transgressive and regressive sequences through the Pliocene and Pleistocene. The sedimentary deposits in the region are broad and shallow terraces dipping gently to the southeast. The region has been largely dissected by four large rivers flowing from the Appalachian Mountains, approximately 200 km to the west: the Potomac, Rappahannock, York, and James. Sediments in the region are predominantly well sorted, sub rounded, fine to very fine quartz sands with 15-20% heavy minerals. Transgressive sequences of sea level high stand left behind multiple fossil rich sequences including the Yorktown Formation, rich with several species of *Chesapecten* and several other shallow marine mollusks (Goodwin et al., 1986). At 35° N latitude, the region is subtropical, with moderate seasonal climate shifts. The area experiences high annual precipitation of 1.1 m/yr (Kaste et al., 2016). High annual precipitation in a largely unconsolidated sedimentary bed, allows for high sedimentation rates throughout the year in all local catchments (Balascio et al., 2019).

Lake Matoaka (Fig. 5) is a former mill pond formed by damming College Creek, a tributary of the James River, in 1701. Today, Lake Matoaka is fed by four perennial streams: Crim Dell, College Creek, Berkeley/Pogonia Stream, and Strawberry Creek. Tributary streams down cut Quaternary sands from the Bacon's Castle and Yorktown Formations depositing

calcium and silica ions into the lake body (Pensa and Chambers, 2004). The lake rests at

35°15'49" N, 76°43'21" W in a heavily wooded area owned by the College of William & Mary

(WM). To the east lies the WM campus and Colonial Williamsburg, and to the northeast lies a

modern urban city. To the west and south, Lake Matoaka is surround by the College Woods, a

predominantly hickory, oak, birch, and tulip poplar forest, in a private and protected area also

owned by WM. The watershed land cover today includes 63% forest cover, 12% low population

density (residential), and 22% high population density (residential), and includes academic and

housing complexes (Packard and Evans, 2006). However, the region has seen three episodes of

land cover change since damming.
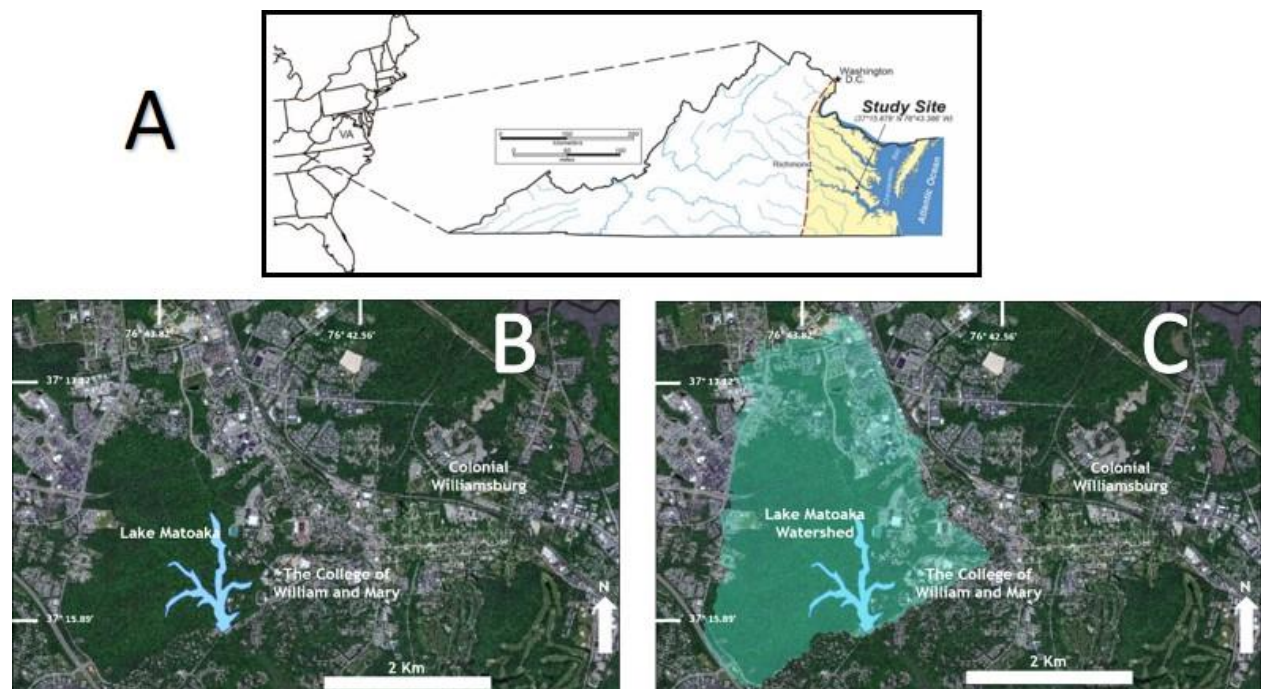
Figure 5: (A) Locator map showing the general location of Lake Matoaka in the southeastern Virginia coastal plain. The yellow area on the map indicates the coastal plain region and passive margin modified from Balascio et al. (2019). (B) Displays proximity of Lake Matoaka to the WM and Colonial Williamsburg. (C) Shaded area indicates Lake Matoaka watershed area including portions of the WM campus, a heavily populated area to the north and east, and pristine forested area to the west.

4.2 Colonial Williamsburg

The city of Williamsburg was founded in 1638, 34 years after the first English colonists arrived in Jamestown. In 1699, due to poor living conditions and several fires, the Virginia colonial capital was moved from Jamestown to Williamsburg making the city an urban center of commerce, agriculture, and industry (http://www.history.org/Foundation/cwhistory.cfm). As the capital, Williamsburg played host to many of the wealthiest families in Virginia and Britain invested heavily in impressive architecture to support governmental infrastructure which put significant strain on the local forest area. As the British forces encroached in 1780, the Virginia capital was moved from Williamsburg to its current location in Richmond. Williamsburg then experienced an economic depression with the removal of wealth and industry to the new capital (Handler and Gable, 1997), but this allowed the area to be largely reforested. In 1920, as part of a restorative project funded by John D. Rockefeller, Lake Matoaka was purchased by WM with several acres of surrounding land (Goodwin, 1937; Pensa and Chambers, 2004). The area to the north and east was repopulated and continues to grow today (Pensa and Chambers, 2004).

4.3 Local Coal Combustion Facilities

Lake Matoaka also lies 24 kms northwest of the Yorktown Power Station (YPS), a local coal-fired power plant (Fig. 6). In 1957, YPS began operations with two active emission chimneys, and opened a third in 1974. Today, YPS burns 20,000 barrels of oil and 2,200 tons of coal daily (www.dominionenergy.com, 2018). While very little information is available to the public regarding YPS emission rates and scrubbing technology, based on industry standards, a power station of this magnitude releases an average of 10 tons of fly ash daily with 5% SCP, or ~1.2 x 10^4 SCP/day (Rose, 2001).
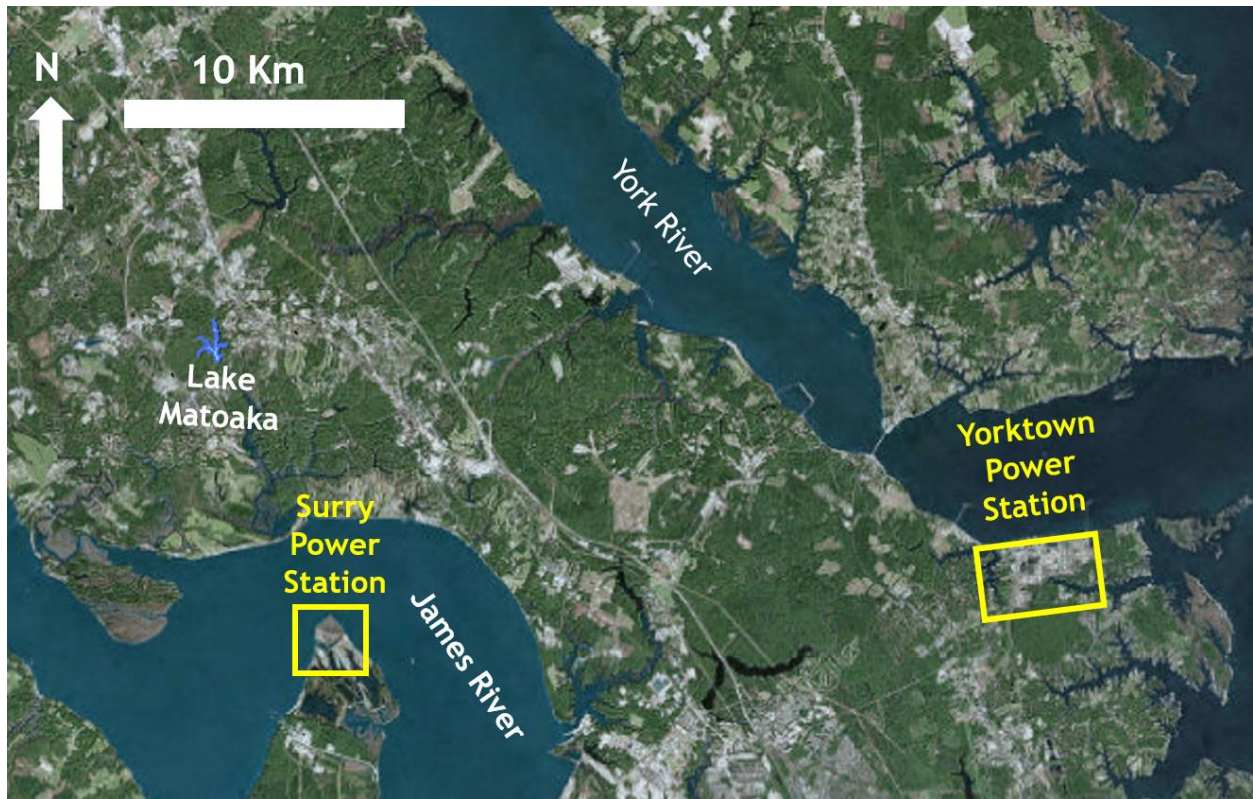
Figure 6: Lake Matoaka near two major power stations: Yorktown Power Station and Surry Power Station. The Surry power plant was only operational between 1940 and 1952 when it was decommissioned. See text for rate of emissions.

High sedimentation rates coupled with proximity to colonial and modern industry make Lake Matoaka an ideal location to study SCP and correlative pollution in southeastern Virginia. Southwesterly winds have potential to deliver pollutants from more than 100 coal-fired power plants in southern and southwestern US, with further deposition from power plants and industry in Japan and China.

5.0 Methods

5.1 Sediment Core and Age-Depth Model

In March of 2016, a sediment core was taken from the deepest part of Lake Matoaka (Fig. 7) using a push coring system with a piston rig. The core was dated using ^{210}Pb, ^{137}Cs, and ^{206}Pb/^{207}Pb, developing a very fine scale age model across the 148 cm long core (Balascio et al.,

2019). The deepest layer of the core, 148-126 cm, shows cypress root fragments and poorly oxygenated black muds consistent with a swamp environment. For the purposes of this study, this portion of the core was excluded from sampling. Using stratigraphic markers and the age model (Fig. 8), sampling began at 126 cm. Sediments were sampled in four cm intervals from 126 cm to 55 cm, and 2.5 cm intervals from 55 cm to the surface water interface. Previous research shows, at 55 cm, correlated to 1910, the earthen dam was stabilized due to construction of Jamestown Road. This stabilized the lake levels and sedimentation rates, requiring a slightly different sampling interval to achieve higher quality resolution (Balascio et al., 2019). Sample conservation was paramount as this is an archived sediment core, therefore when extracting the sediments, only enough was removed such that dry mass was less than 0.2 g. Samples were dried in an oven at 80°C for 72 hours. All steps in the sampling, storage, and treatment of sediments were performed in a lab, under a fume hood and in closed containers to eliminate the possibility of contamination from atmospheric SCP particles. The accumulation record is then compared to accumulation of total Pb and normalized to sedimentation rates published in the literature.
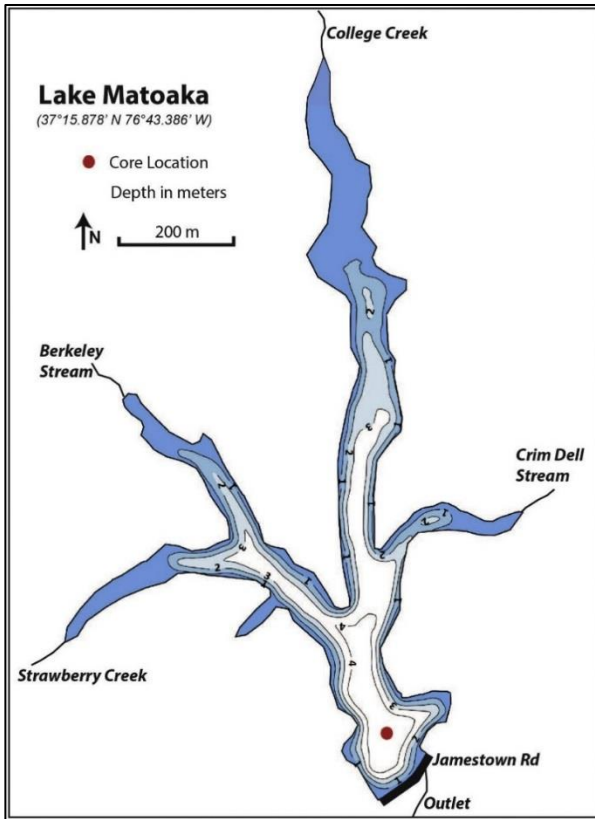
Figure 7: Bathymetric map of Lake Matoaka and tributary streams. Red point marks core location figure c/o Balascio et al. (2019).
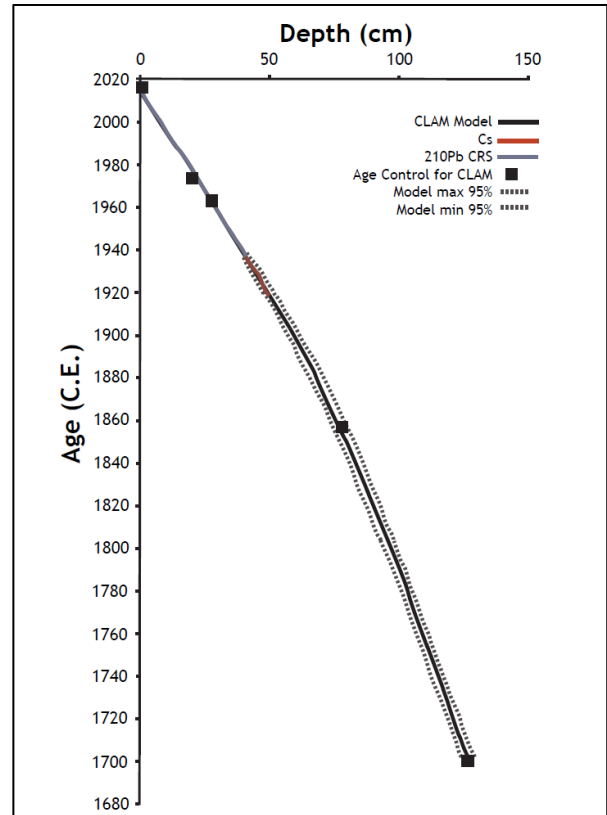
Figure 8:Lake Matoaka sediment core age depth plot. Anchor points based on known dates from historical records, ^{210}Pb, ^{137}Cs, and surface. Solid line indicates age plot, dotted lines represent 95% confidence interval margins. Figure modified from Balascio et al. (2019).

5.2 Acid Digestion and Point Counts

SCPs are isolated from sediment samples using a strong acid digest following the procedures defined by Rose (1994) with some modifications due to an increased amount of organic matter. 0.15 g of dry bulk sediment were placed in 15 ml polypropylene centrifuge tubes and submitted to sequential chemical attack followed by a 3-hour bath at 90°C, using 3 ml each of 30% concentrated H_2O_2, 70% HNO_3, 40% HF, and 6M HCl. These acids were chosen due to their properties of preferentially removing different types of material: H_2O_2 and HNO_3 attack organic matter, HF removes siliciclastic clays and rock fragments, and HCl attacks heavy metals such as iron and aluminum. Due to the more effusive reaction with H_2O_2 and HNO_3, these acids

were added in 0.75 ml aliquots while in an 80℃ hot water bath, so no sediment was lost. After

each digest, the centrifuge tubes were diluted with 12 ml deionized water and centrifuged at 3000

rpm for 5 minutes, except for the HF digest. For safety purposes, the HF digest was gravity

settled overnight, and pipetted off the next morning. The supernates were diluted and stored in

500 ml polypropylene containers for later testing. This digestion process reduced the amount of

sediment from 0.15g to 0.001g, eliminating 99% of original material (Rose, 2001). Remaining

particles were suspended in 500 µL deionized water and stored. 200 microliters of the digested

sediment in solution was then mounted on a microscope slide using a standard norland optical

adhesive diatom mount and cover slip. Point counts were completed using a standard reflective

light microscope with mechanical stage at 400x magnification. All particles that met the criteria

laid out in the literature were counted: intact or greater than half spheroidal particles that are

porous, dimensional, and opaque (Stoffyn-Egli, 1997; Rose, 2008). Any particle fragments less

than half were not counted.

5.3 SCP Grain Size Analysis

Grain size analysis was completed using a Leica ICC50 W light transmitted microscope

at 400x magnification and mechanical stage, with imaging technology and corresponding digital

Leica Application Software Suite (LAS). Particles were imaged, and the diameters of 212

individual grains from two depths were recorded. Grains were chosen based on noted peaks in

the results from the accumulation curve. This information was processed using a two-tailed t-test

to determine if early SCP accumulation is from a different source than later SCP accumulation.

5.4 SEM-EDS Chemical Analysis

Chemical analysis was completed using the PhenomWorld Desktop Scanning Electron

Microscope with Electron Dispersive Spectroscopy (SEM-EDS) Analyzer at WM. This tool

allows for high-resolution, three-dimensional images and measurements of particles, including

chemical analysis and stoichiometric proportions of elements within the fly-ash particles. Due to

carbon enrichment in the particle, C had to be disabled to obtain reliable results from the

instrument. This procedure scaled the proportions of trace metals after carbon was eliminated

from the analysis. Grains from five different depths were analyzed with results given in weight

percent after disabled elements. Elements analyzed include Fe, Mn, Ti, Ni, Pb, B, Tl, As, Hg, Zn,

Al, and Mg.

6.0 Results

6.1 SCP Temporal Reconstruction

First appearance of SCP in Lake Matoaka occurs in 1734 with 78 SCP/gDM. Generally,

temporal reconstruction shows a bimodal distribution with two peaks: the first in 1790 and the

second in 1953 (Fig. 9). The 1790 peak is preceded by generally increasing concentration up to

500 SCP/gDM for samples processed from 1775-1790. There is an immediate decrease and

constant concentration of particles through the early 1800s with 100-200 SCP/gDM found from

1790-1860. A rapid increase begins in 1870 with 500 SCP/gDM. Particle concentrations

continue to increase with a small local peak in 1919 of 1000 SCP/gDM and a larger peak in 1953

of 8300 SCP/gDM. Deposition decreases slightly but remains relatively elevated through the

1990s with 3000-4000 SCP/gDM. A sharp decrease occurs in 1998 with levels decreasing to

~1000 SCP/gDM remaining constant at the surface. A deep lake suspended sediment trap sample

was collected in fall 2018 and further analyzed to show concentration of particles in the

suspended sediment. Concentration counts from this sample show an accumulation of 1650

SCP/gDM, consistent with surface levels.
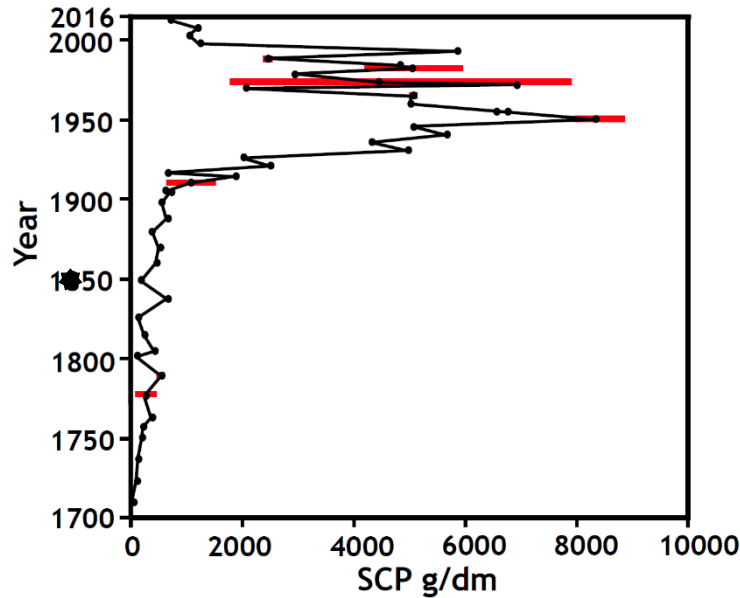
Figure 9: Temporal SCP curve constructed from Lake Matoaka core. Red bars indicate calculated standard error after repeat sampling and point counts. The graph shows a year by year increase in SCP beginning in 1730 continuing to increase through 1790, with an immediate decline after 1800. SCPs remain somewhat constant through the 1800s with another year-by-year increase beginning in 1860 and increasing over the next 100 years, peaking at 8300 particles in 1953, declining in modern and surficial sediments. Star plotted above the graph indicates SCP accumulation in suspended sediments.

6.2 Grain Size Analysis

A two-tailed T-test applied to 107 particles from the 1953 peak and 101 particles from the 1790 peak shows a statistically significant difference in grain size between these two sets. The 1790 peak particles had a mean diameter of 14.7 µm, and the 1953 particles showed mean diameter of 25.2 µm with $P = 2.3 \times 10^{-13}$, meaning there is a statistically significant difference between the two populations. Generally, the 1790 peak shows a smaller spread with standard deviation of 5.01, while the 1953 peak had a standard deviation of 8.9 (Fig. 10). 1790 data shows a unimodal distribution with 95% of the analyzed particles smaller than 20 µm in size. Further analysis of the 1953 peak shows two distinct SCP groups, with 73% of the particles between 10-25 µm, 25% 25-50 µm, and 2% larger than 60 µm in size.
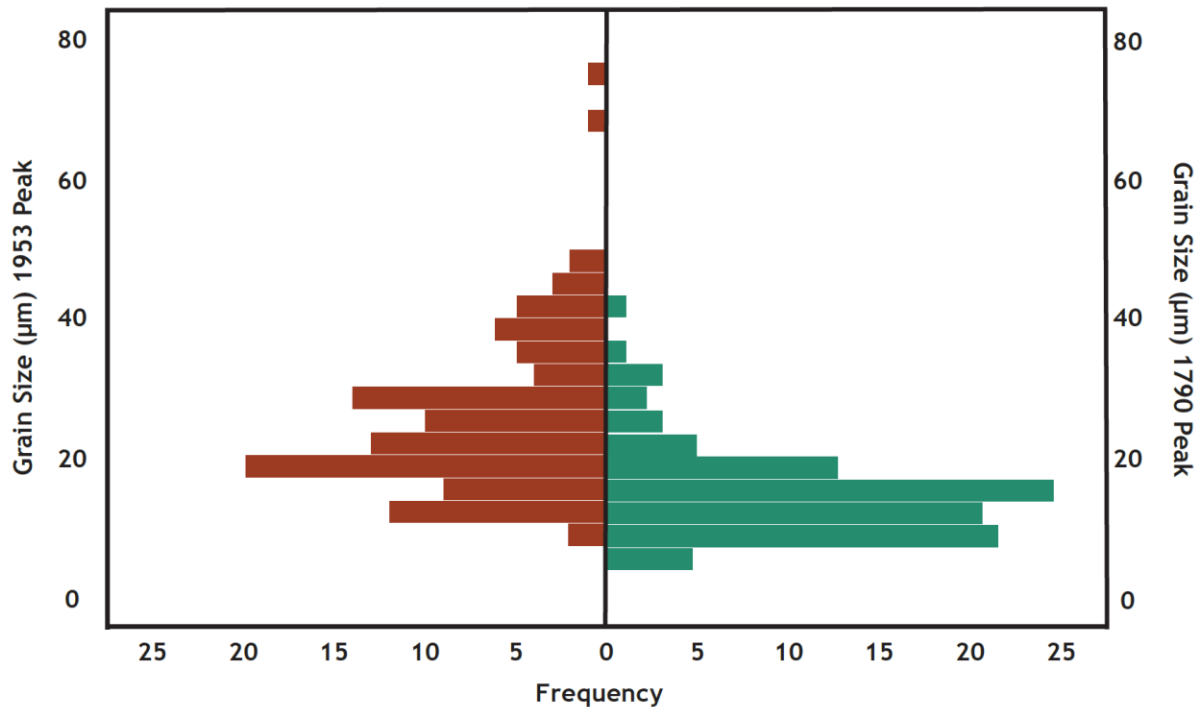
Figure 10: Grain size distribution for particles analyzed from the two concentration peaks: 1953 and 1790. The 1953 peak (n = 107) shows a bimodal distribution with broad size variance, while the 1790 peak (n = 101) shows a unimodal distribution with narrow size variance.

6.3 Chemical Composition

SEM-EDS analysis of SCP particles show significant carbon enrichment of 95-98% carbon and oxygen. Occasional interference of the chemical signature due to strong acid digest required the analysis to be restricted to Fe, Mn, Ti, Ni, Pb, B, Tl, As, Hg, Zn, Al, and Mg. Of these elements, Fe, Mn, and Ti are most abundant and represent 90-98% of the non-carbon portion of SCPs (Fig. 11). The five samples chosen and analyzed are the 1790 peak in SCP emissions, one from the era of legislation (1994), one sample from the uppermost section of the core (2004), one from the lowermost section of the core still containing SCP (1748), and a midpoint (1916).
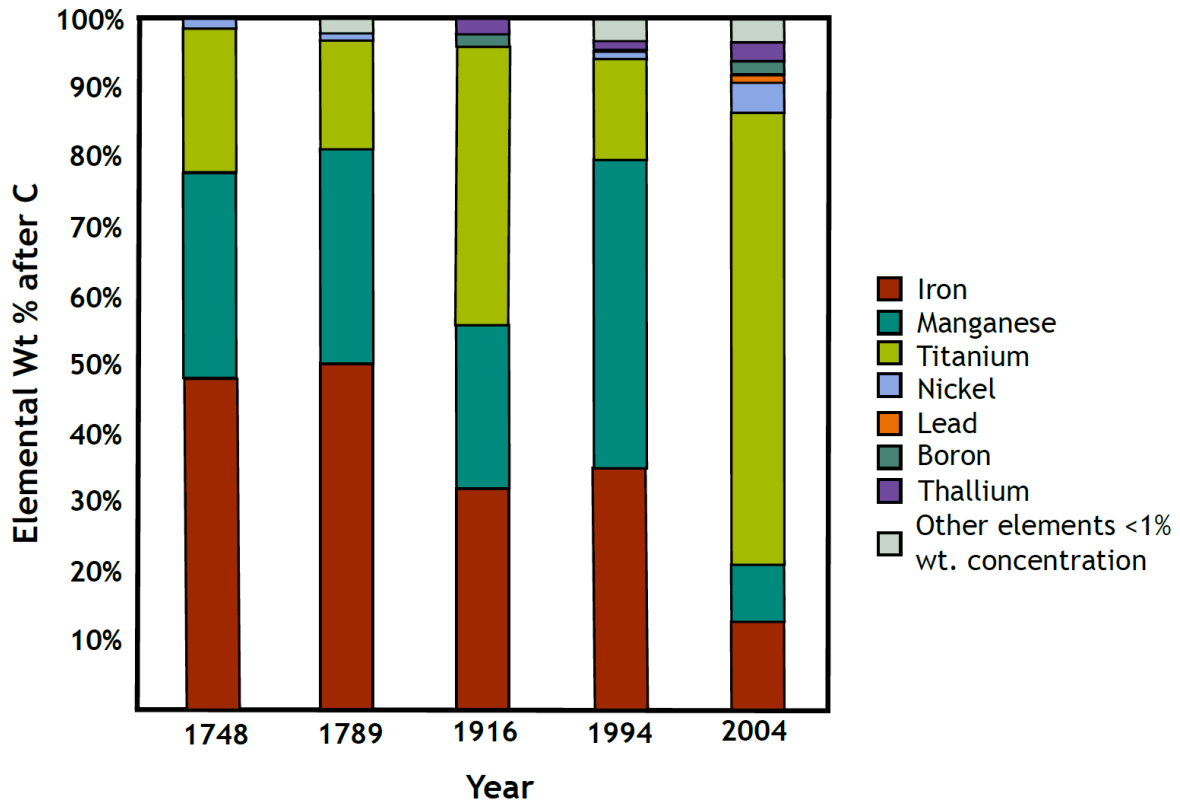
Figure 11: Concentration of primary elements by weight %.

Particles analyzed from 1748 and 1789 show similar elemental composition with 48% and 50% enrichment in iron, 29% and 30% enrichment in Mn, and 21% and 15% enrichment in Ti, respectively. This pattern shifts in 1916 with a reduction in Fe, and Ti becomes the most abundant element with 40% enrichment. 1994 data show primary enrichment of 40% Mn, and 2004 shows primary enrichment of 65% Ti. Moving from older to younger particles, the chemical composition is increasingly variable: particles from 1748 show enrichment by three main elements, Fe, Mn, and Ti, and the 2004 sample shows enrichment in 6 main elements Fe, Mn, Ti, Ni, Pb, and B in amounts >1%.

7.0 Interpretation and Discussion:

High sedimentation rates in Lake Matoaka allow decadal scale analysis of SCP accumulation from colonial to modern times. Broadly speaking, the SCP temporal distributions

measured here are similar to those reported elsewhere. However, I observe SCPs starting in 1734 (Fig. 9), which is 100 years prior to the earliest reported SCPs in the literature by Clark and Patterson (1984), and 70 years before IR, starting 1784. Further examination of the temporal distribution shows a strong correlation to local and regional human activities. These data are supported by total Pb concentrations in the core and onset of major historical events to be discussed below. Chemical composition changes down core suggest shifting SCP sources through time; this is supported by my grain size analysis showing different particle sizes between the two peaks and within the younger peak. EDS analysis of coal particles show strong enrichment in Fe, Mn, and Ti in varying proportions through time. I hypothesize this is a signature of the chemical composition of the source coal, and is controlled by combustion conditions. These data suggest chemical composition can be used as a further tool to identify different sources of grains. More broadly, chemical composition analysis has environmental implications: if we fully understand the relationship between the source coal petrology and the fly-ash chemical composition, civil services such as waste management and groundwater management are better able to implement effective remediation efforts.

7.1 SCP and Pb temporal accumulation and historical context

Coal is generally enriched in scavenged conservative elements that form minerals in oxygen deprived environments. Lead-bearing minerals in coal include cerussite ($PbCO_3$) and galena (PbS) (Querol et al., 1996; Hower, 2012a; Grimley et al., 2017). These elements each have melting points well below industrial furnace temperatures and open-pit coal fires (cerussite = 300°C, galena = 327°C) (Chang et al., 1998; Kapička et al., 1999, 2000). The presence of Pb and SCP in a catchment at the same time indicate coal combustion particles and associated pollutants are present in the atmosphere surrounding that catchment. After our SCP

temporal distribution curve is normalized to sedimentation rate and compared to total Pb concentration down core the pre-IR peak is confirmed, and the modern peak more prominent (Fig. 12).
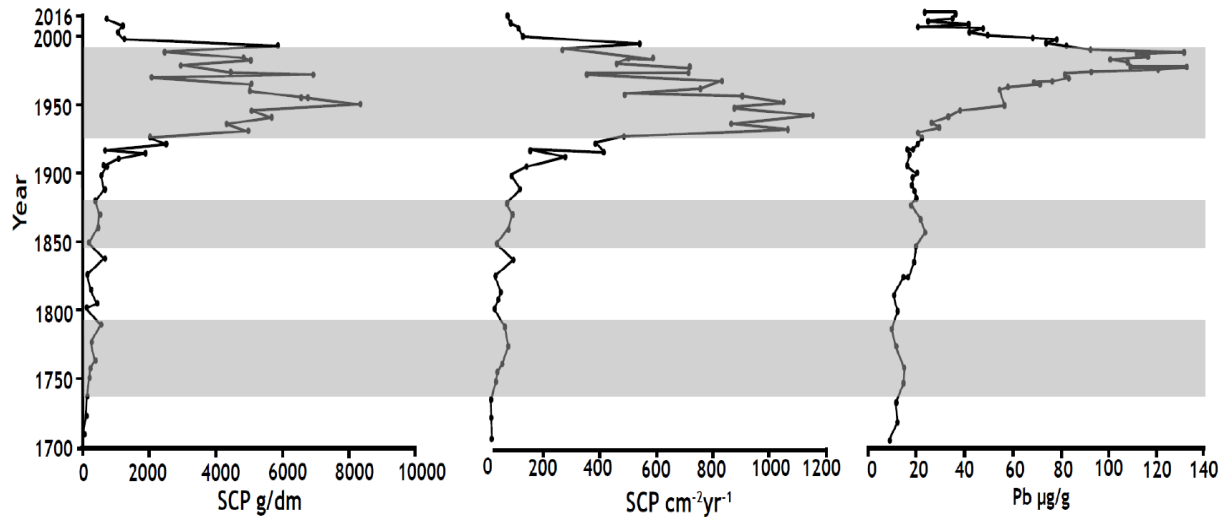
Figure 12: SCP temporal distribution results from this study. SCP normalized to known sedimentation rates over time and compared to total Pb concentration up-core. Sedimentation rate and total Pb data taken from the literature, c/o Balascio et al., (2019). All three plots show year by year concentration increase beginning in 1730, decreasing after 1800, increasing in 1860, with sharp rise and peak 1950. Lead data has a slightly younger peak due to restrictions on leaded gasoline in automobiles.

The high sedimentation rate in Lake Matoaka give this study excellent resolution. As such decadal scale observations of changes in population and industry, locally and regionally, over the past 315 years are observed clearly in the concentration and accumulation curves (Kaste et al., 2016; Balascio et al., 2019). This distinguishes our study from those published in the literature. Regionally, SCP and Pb accumulation rises during political conflict (war) and decrease during peacetime and legislation development. Locally, SCP and Pb accumulations show evidence of economic changes for 18th century Williamsburg and local coal mining.

In times of political conflict, industrial production and technological advancements increase as governments invest heavily in the production of new and better transportation, weapons, and armor (Crowley, 2000). In the 18th century, technological advances were made by

coal-fired metal works, blacksmith forges, and metal foundries, as demand for goods and arms increased (Mokyr, 2009). Later, 19th and 20th century warfare generated an increased demand for coal-fired electricity and large-scale production of metal works for goods such as battleships and planes (Jaworski, 2017). For this reason, Lake Matoaka trends in SCP concentration and accumulation show peaks during four major political conflicts: the Revolutionary War (1776-1783), the American Civil War (1861-1865), World War I (1914-1918 for the US), and World War II (1941-1945 for the US).

7.2 SCP in the 18th Century

As capital to the Virginia Colony, Williamsburg in the 1700s was a hub of industry and innovation (Goodwin, 1937; Crowley, 2000). Estimates from medical records indicate a population of ~750 people, not including enslaved Africans, in 1747, increasing to 1880 persons by 1775 (Hellier and Kelly, 1990). Early colonial industry was dominated by small, local artisans manufacturing handmade goods and selling their products to fellow community members. Local timber in the area was quickly consumed for building materials, so alternative heat sources in the form of coal-fired house warming stoves became standard in wealthier homes, public buildings like the Wren Building (home of WM), and the Governor's Palace (Goodwin, 1937; Handler, 1997, Crowley, 2000). Historical records show extensive house warming coal stoves in use at the Governor's Palace by 1770 in a household inventory list which includes 6 John Tazewell housewarming stoves, 1000 bushels (~6000 lbs) of Richmond coal, and associated tools (Graham, 1945).

Industrial production also required coal to operate blacksmith forges and metal foundries, which supplied daily use goods such as dishes, buttons, building materials, and weapons to the local community (Allen, 2012). The James Anderson Armory was opened in Williamsburg by

1765 (exact date unknown). James Anderson was asked to be the main armor to militia and troops under George Washington. Between 1774 and 1780, Anderson operated eight smithing forges up to 18 hours/day working to supply chainmail, bullets, and weapons to the colonial forces. While exact amounts of coal used are unknown, modern coal forges require ~20 lbs of coal / 8 hours of forging (Jaworski, 2017). Projecting this figure out, we can estimate the James Anderson Armory was burning ~130,000 lbs of coal per year between 1774 and 1780, and emitting SCP ~4 meters from the ground, two kilometers from Lake Matoaka (Fig. 13). With the threat of encroaching British forces in 1780, the James Anderson Armory was relocated to the new Virginia capital in Richmond, the Governor's Palace was closed and emptied, and many of the wealthiest families fled the area.
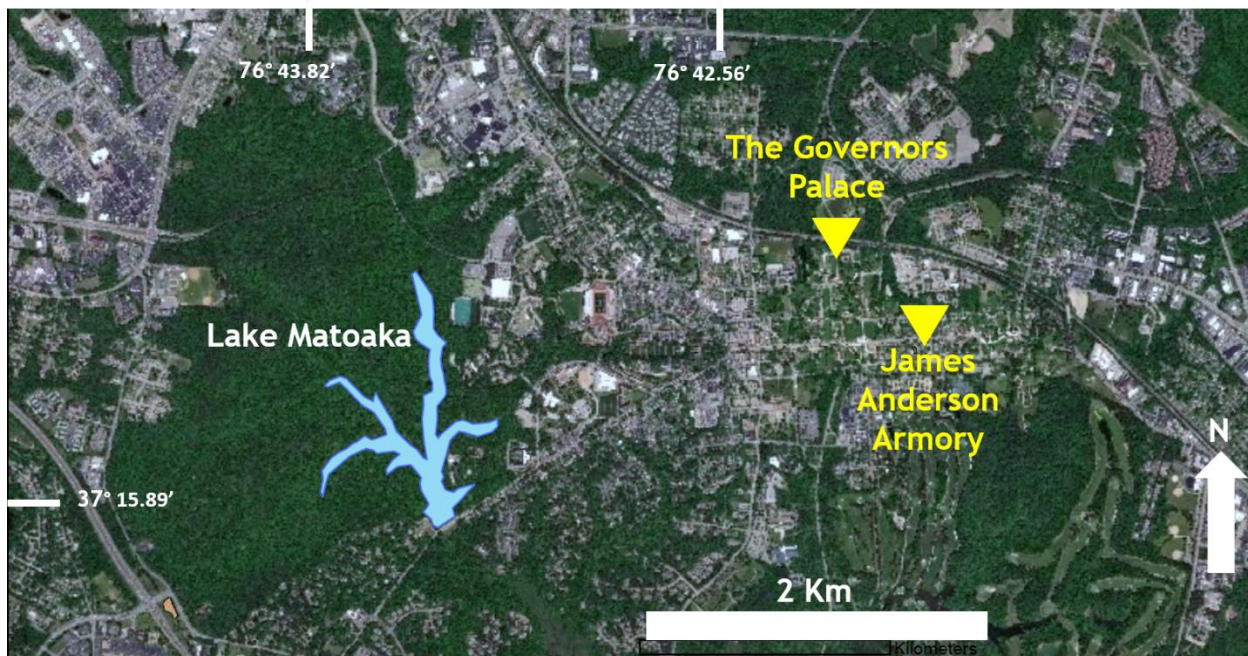
Figure 13: Lake Matoaka, James Anderson Armory, and the Governor's Palace. James Anderson Armory emit SCP through black smith forges between 1765 and 1780. The Governor's palace used coal-fired housewarming stoves throughout the 1700s. These are the local sources of SCP and Pb relative to Lake Matoaka.

Early coal combustion increased through the 18th century and deposited SCPs into Lake Matoaka at a rate of 100 SCP/cm^2/yr by 1790. This local activity led to significant particle

accumulation between 1700 and 1790, with evidence of an economic depression evident by a sharp decline in SCP accumulation rate in 1880, 12 SCP/cm^2/yr. The value of my study lies in the proximity of our study site to human activity. SCP studies focusing on remote catchments have preferentially eliminated pre-IR results from their studies. Under-representation of early SCP emission cause inaccuracies when trying to use them as a dating technique. Additionally, this complicates the understood accumulation record, discrediting SCP use as a GSSP for the Anthropocene. To completely understand SCP distribution over time, more studies need to be completed in catchments proximal to early industry. Understanding early local deposition, and the shift to more regional deposition will offer a more complete understanding of global pollution distribution and fossil fuel consumption pre-IR.

7.3 SCP in the 19th Century

The 19th century is known globally as a period of industrialization and saw the invention of the steam engine in 1784 which led to advancements in the transportation sector. In the US, this was a time of nation building, requiring a formal military with battleships, a functioning railway system, arms, and forts. All of which were powered by coal-fired energy and built using coal-fired industrial techniques (Mokyr, 2009). However, most of this technological advancement occurred in the northern states; the impact of slavery dependence in the south led to a lag in development over the successful agriculture regime already in place (Nelson and Wright, 1992). The Civil War (1861-1865) led to the development of two primary companies proximal to Lake Matoaka: Tredegar Ironworks, and the Shipbuilding Company (Hallerman, 1978).

After the Civil War, the American South underwent a period of social and economic shift from a plantation and agriculture driven model to a more industrial driven model. This generated a demand for infrastructure changes, specifically the development of a railroad (Nelson and

Wright, 1992). Trains at this time were coal-fired, depositing coal-fired pollutants, including

SCP, along the tracks while in motion (Liu et al., 2009). In 1881, the Chesapeake and Ohio

Railroad Company opened a station in Colonial Williamsburg. This station operated a coal-fired

train from 1881 until the mid-1960s when it switched to diesel (The Great American Stations,

2008). The rapid rise in SCP concentration seen in our analysis can be attributed to the

technological advancements locally (Tredegar Iron Works, the Shipbuilding Company, and the

Williamsburg Train Station).

7.4 SCP in the 20th century

SCP and Pb temporal accumulation post-IR is heavily dependent on global wind

circulation (Rose et al., 2012). As previously mentioned, long range atmospheric deposition is

only possible when particles are emitted at such an altitude that they enter global air circulation

patterns (Thomas et al., 1963). Fossil fuel combustion-derived acidic gases HNO_3 and H_2SO_4

have been shown to impact precipitation pH (Galloway et al., 1982). Modeled plume heights

predict that power stacks >1300 feet tall (0.4 km) will produce a plume 500-1000 feet tall (0.15-

0.3 km) persisting 100 km away from the source, or up to several thousand kilometers if

conditions are favorable (Thomas et al., 1963). SCPs have been found in locations well outside

any local source of coal burning (Renberg and Wik, 1985; Doubleday et al., 1995, 2004; Rose et

al., 2003, 2004; Chirinos et al., 2006). These studies generally show very low concentrations

with later peaks and later first occurrences than we observe in Lake Matoaka. Modern SCP and

Pb accumulation in Lake Matoaka is therefore a function of both local and regional deposition,

developing a stronger regional signal in the late 1800s and substantial increases in the early

1900s (160-950 SCP/cm^2/yr between 1905 and 1955, respectively). This is not due to local

industry, but rather an indicator of industrialization in the southern US after the Civil War in 1865 (Jaworski, 2017) and global industrialization after WWI (Nelson and Wright, 1992).

Primary wind currents over southeastern US are out of the southwest, and above the equator (Fig. 14). This strong jet stream delivers subtropical air from China, the southernmost portions of the US and into southeastern Virginia. (Cressman, 1981; Galloway et al., 1982). Given the potential for long range transport of fossil fuel emissions (Thomas et al., 1963; Galloway et al.; 1982), the propagation of industry through the American South beginning 1865 (Jaworski, 2017) and post WWI industrialization of China (Nelson and Wright, 1992; Allen, 2012), I can conclude that the primary source of SCP and Pb found in Lake Matoaka after 1800 are regional.
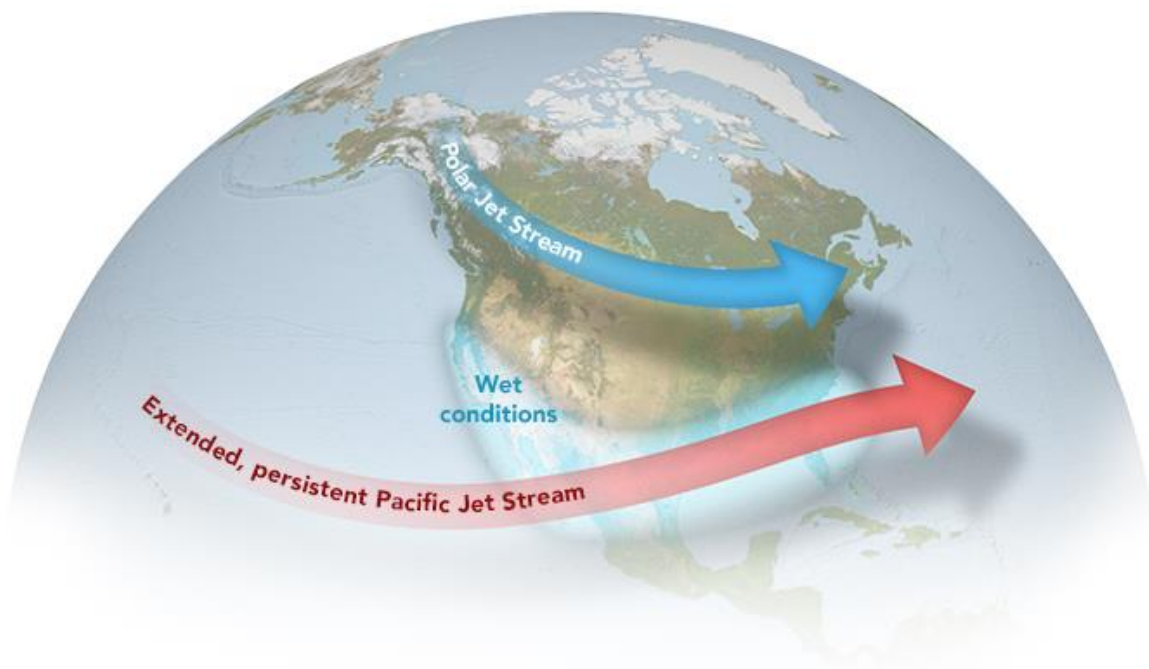

Figure 14: Primary wind directions over the US from the west and persistent over the Pacific Ocean. Image c/o NASA Earth Observatory data repository.

7.5 Grain size and Chemical Composition

      Grain size analyses completed as part of this study further support the idea that Lake Matoaka SCP come from both local and regional sources. SCP grain size is controlled by the temperature and duration of burn (Makonese et al., 2014). SCP require remnant elemental carbon to fuse with partially melted metals (Rose, 2001). This requires near complete ignition of all carbon bonds and temperatures that will cause metals to partially liquefy and form new compounds (Bond et al., 2002; Makonese et al., 2014). Extended high-temperature burns result in more complete carbon reduction and more molten metals, ultimately forming larger SCP particles (Bond et al., 2002). Modern blacksmith forges can reach temperatures up to 1500°C, but only under regulated airflow and contained fire pot conditions. Forges used in the 18th century could reach maximum temperatures closer to 700°C, although sustained burn temperature averages were between 350-500°C (Masekameni et al., 2018). This is in contrast to large scale industrial power plants where boiler temperatures reach an average 1200-1750°C (Lightman and Street, 1983; Rose, 2001). There is some variation in modern coal-fired power plant boiler temperatures, due primarily to capacity. Most standard power stations report sustained boiler temperatures of 1200-1500°C (Lightman and Street, 1983). Due to the differences in temperatures between 18th century blacksmith forge fires and modern power plants, SCPs from these sources will have different particle sizes (Makonese et al., 2014). Further, particles from different power plants will be distinct based on the boiler temperature from each plant. The grain sizes from the 1790 peak show a unimodal distribution with a mean particle diameter of 14.7 µm. This is distinct from the 1953 peak, which showed a bimodal distribution with two populations, 73% of the grains are 10-15µm, 25% are 25-50µm, and 2%

are larger than 60 µm. These data show a single source of SCP-generating particles in the 1700s, but by 1953, that had shifted to at least two sources distinct from the 1790 SCP source (Fig. 10).

Few studies have analyzed SCP chemical composition, and none of the studies in the literature compared chemical composition to known source coal petrology. This is because the source of any given SCP in sediments is unknown and difficult to determine. Due to the presence of pre-IR SCPs from a single known source, this analysis can be completed. The 1770 Governor's Palace household inventory, recovered by Graham (1945), specifically indicates the Richmond coal beds as the source.

In 1701, French Huguenot immigrants began to settle in Manakin-Town just south of modern Richmond, VA. Here they discovered a small bituminous coal deposit and began to mine (Brock, 1966). This mined coal was shipped to four primary ports of call: Philadelphia, Pennsylvania; Charlestown, South Carolina; New York Harbor, New York; and down the James River to Williamsburg, Virginia (Brock, 1966). English coal was of higher quality, but difficult and expensive to transport by ship. As often as possible, the American colonies relied on American sourced coal due to lower prices (Crowley, 2000).

Richmond coal basin petrology has been studied extensively and general chemistry is well known (Goodwin et al., 1986). Unfortunately, the results of those studies are proprietary and inaccessible for the purposes of this study. I do, however, know that Richmond coal is classified as bituminous (85-90% carbon) with interstratified coal and coke beds. Mining accidents and explosions were very common, implying the coal beds are unusually high in volatile elements such as methane and sulfur (Goodwin et al., 1986).

Our chemical composition analysis of particles selected from mid- to late-1700s show primary enrichment in Fe, Mn, and Ti in nearly identical proportions. This suggests the particles

are from the same source and supports other findings from this study. If the elemental composition of the Richmond coal basin were made public, these results could be correlated and a ratio could be developed, informing the scientific community, policy makers, and general public the extent of trace metal contamination in fly-ash storage pits.

Of the particles analyzed, all showed significant enrichment in Fe, Mn, and Ti in varying proportions. Fe shows a decreasing trend from older to younger particles with 50% in 1748 and 1789, 35% in 1916 and 1994, down to 10% in 2004. Some studies have suggested significant magnetic changes in sediments are a result of fly-ash iron contamination (Kapička et al., 1999, 2000). The results of this study suggest that magnetic enrichment in sediments due to the presence of SCP is not uniform due to variable concentrations of Fe within the particle. Before using this method to track environmental contamination a chemical analysis must first be completed to test for the presence of Fe within the particles.

7.6 The Modern Problem

Coal combustion continues to be the leading energy source in the US and China (Nelson and Wright, 1992; Querol et al., 1996; Kuckier et al., 2003; Jaworski, 2017). Today, clean air legislation requires coal-burning facilities to use scrubbers to reduce particulate and volatile emissions. While some pollutants are still released directly into the atmosphere, most fly ash is collected and disposed of in landfills or storage ponds; however, trace metal contamination has been recorded in the environment surrounding these storage areas (Kapička et al., 1999, 2000; Sushil and Batra, 2006). In January, 2019, Virginia legislation passed House Bill 2786 and Senate Bill 1355 requiring removal of fly-ash landfills, storage ponds, and surrounding contaminated areas in four EPA regulated sites due to toxic trace metal plumes. However, there

are at least three additional fly-ash landfills not addressed by this legislation, including the

storage ponds actively in use by the Yorktown Power Station (Fig. 6).

I hypothesize there is a relationship between the petrology of the source coal bed and

chemical composition of fly ash that can be predetermined based on a known set of parameters

including duration and temperature of the burn. If the relationship between source coal petrology

and fly-ash chemical composition can be established and a more complete understanding of the

mechanisms by which SCP and associated pollutants are distributed and deposited globally can

be ascertained, then we can mitigate ongoing pollution from coal combustion. This is an

excellent avenue for continued work in this field.

8.0 Conclusion

Fossil fuel dependence is a global phenomenon that fostered the Industrial Revolution

and remains the primary driver of global economic dominance (Rose, 1990, 1994, 2001; Allen,

2012). The invention of the coal-fired steam turbine engine impacted every aspect of daily life,

from transportation, building materials, electricity, manufacturing, and even the modern digital

movement (Crutzen and Stoermer, 2000; Crutzen, 2002, 2006). However, people have been

using coal as a heat and energy source for hundreds of years before the Industrial Revolution (Li

et al., 2012; Hong et al., 1996). Coal combustion particulate and chemical pollutants are evident

in the sedimentary record and are a sensitive proxy of human activity in the environment (Rose,

1999, 2008, 2012; Swindles et al., 2017)

This study presents the first SCP temporal accumulation in close proximity to both early

urban development (Colonial Williamsburg) and modern industry. Our study site also has

exceptionally high sedimentation rates, giving this study decadal scale resolution of

accumulating pollutants in the atmosphere (Kaste et al., 2016; Balascio et al., 2019). As such,

our results show a year by year increase in coal combustion beginning in 1734 and continuing today. This is the first SCP study to show particle accumulation prior to 1800 and continued SCP accumulation in modern sediments (active sediment trap), demonstrating the need for more studies in varied catchments.

The bimodal peaks in particle accumulation allowed this study to investigate early and modern coal-fired pollution and shifting sources of that pollution both pre- and post-IR. Strong correlations in the accumulation of Pb and SCP show that these pollutants are both derived from the burning of coal. SCP grain size and chemical composition data support our hypothesis that early coal combustion led to the local release of small SCPs, while modern large-scale coal combustion leads to regional release of large SCPs. These findings are consistent with those reported in the literature (Bond et al., 2002; Makonese et al., 2014). The potential particle distribution through atmospheric winds after high elevation emission have caused a global signature that has been extensively studied (Thomas et al., 1963; Galloway et al., 1982). SCP concentration in the sedimentary record has been argued to represent a GSSP for the Anthropocene and is actively being used as a dating tool for sediment cores (Renberg and Wik, 1985; Boyle et al., 1999; Korhola et al., 1999). However, the results from this study and an extensive literature review shows a wide variance in the temporal accumulation of SCPs in the areas in which they have been studied. Furthermore, there is a distinct lack of studies performed in the southern and western hemispheres, and catchments proximal to early urban environments.

Coal combustion leads to the release of fly ash, a suite of acidic gases, particulate matter, and radiant ions into the atmosphere (Thomas et al., 1963; Griffin and Goldberg, 1975, 1979; Galloway et al., 1982; Rose, 1990, 1994, 1999, 2001; Makonese et al., 2004). By studying and understanding the mechanisms by which SCP are distributed and accumulate in the environment,

I can also understand the distribution of other fly-ash pollutants such as Pb, a known environmental toxin. This study shows similar concentration trends between Pb and SCP demonstrating they are distributed by the same mechanisms. Applying our results to the global conversation reveals an incomplete understanding of early pollutants, their early and modern release into the atmosphere, and the mechanisms by which they are globally distributed. More research needs to be completed to understand these processes and to mitigate further pollution by ongoing industry. Understanding the SCP chemical composition and behavior in sediments is critical to developing proactive measures to reduce environmental contamination.

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