The effect of sulfate inputs on sulfide abundance and sulfur isotopic compositions of two constructed wetlands

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Abstract

Sulfate has been historically overlooked as a significant driver of the carbon cycle in freshwater systems. In this study, the effect of sulfate loading on sulfide production was examined in two constructed wetlands in suburban Maryland. Both sites receive sulfur from atmospheric sources, which has declined significantly since the 1980s. The two wetlands receive additional anthropogenic inputs: the golf course wetland receives stream runoff from a catchment that is fertilized, whereas the stormwater retention wetland receives highway runoff with high concentrations of road salt during winter months. The fertilizers used on the golf course yielded an average $\delta^{34}S$ value of ~5‰; the road salt had a value of ~10‰. Atmospheric sulfate given by the literature has a value of ~2‰.

Sediment cores were obtained from both wetlands, with one core from the stormwater retention wetland and two from the inlet and outlet sites of the golf course wetland. These cores were analyzed for organic content (total organic carbon [TOC] and bulk density), sulfur content (%S and mg S/cm^3), and isotopic composition ($\delta^{34}S$). All three cores contained sulfide, supporting the presence of microbial sulfate reduction at each site. The three cores exhibited distinct $\delta^{34}S$-depth profiles and displayed noticeable changes in data as the cores transitioned from clay-rich sediment to organic-rich soil. The inlet core displayed an increasingly positive $\delta^{34}S$ trend with decreasing depth, averaging 0‰ along its entire length. There was lower bulk density, higher TOC, and lower mg S/cm^3 present in the upper organic horizon of the core relative to the lower clay portion. The outlet core displayed a small range of $\delta^{34}S$ variation along its length, maintaining a consistent 4‰ signature. Its upper organic horizon recorded a slight increase in %S. The biogeochemical signatures exhibited by the inlet and outlet cores could record the transition of the golf course site from a pond to a wetland after a 2001 dam failure. The retention core experienced abrupt changes in bulk density, TOC, and mg S/cm^3 across its clay-organic transition, but exhibited a shift from a range of $\delta^{34}S$ values to a constant 4‰ in its organic horizon. This 4‰ value could represent the mixing of atmospheric and road salt sulfate inputs, although their respective isotopic contributions remain uncertain.

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Introduction

Statement of Problem

Organic carbon is an important source of energy. It is found in sugars, fats, and amino acids that heterotrophic organisms consume and metabolize to form ATP and assimilate the compound to form their own cells. When organisms decompose, the organic carbon in their cells can be converted to compounds such as CO_2 and CH_4, which can escape as gases, or be retained in water and sediments in the form of dissolved inorganic and organic carbon. All of these play a critical role for catabolic (energy yielding) and anabolic (biomass building) metabolism of microorganisms and provides strong connections to the biogeochemical cycles of other elements (Plugge et al., 2011; Baumgartner et al., 2006; Sim et al., 2012).

This thesis focuses on the links between the carbon and sulfur cycles in two wetlands at the University of Maryland, College Park. Sulfate, SO_4^{2-}, is delivered to watersheds by atmospheric deposition (acid rain), is commonly released by rock weathering, and is found in road salt, plaster/gypsum board, fertilizers, and other materials common to the urban environment (Serchan et al., 2009). Microbial sulfate reduction is driven by anaerobic prokaryotic organisms that oxidize organic compounds, using sulfate (SO_4^{2-}) as an electron acceptor (Lamers et al, 2013). Sulfate is reduced to sulfide, in the form of H_2S under acidic conditions and HS^- for basic conditions. Sulfate reduction occurs when environmental conditions are energetically favorable for sulfate reducers to gain energy by metabolizing sulfate. One example of a reduced environment is a wetland, where pore water sulfate is abundant and sulfate reduction can occur.

The ability of organisms to use sulfate for anaerobic respiration has been shown to be evolutionarily significant for bacteria, and archaea, as far back as 3.5 Ga (Shen et al., 2001). The ability to convert sulfate to sulfide, and with that the conversion of dissolved organic carbon to dissolved inorganic carbon, has had a profound effect on carbon cycling (Barton & Fauque, 2009). In this study, two constructed wetlands are examined to improve understanding of how sulfate inputs affect sulfide concentration, which in turn cycles organic carbon present.

Hypotheses

1. Sulfate concentrations and sufficiently reducing conditions exist in both wetlands to support microbial sulfate reduction. Sulfate enters into the system as atmospheric deposits, fertilizer, or road salt and is microbially transformed into sulfide. It is assumed that this takes place in-situ with no loss of sulfide. The null hypothesis is that sulfate reduction is not occurring in the wetlands, with any sulfide detected being primary sedimentary or rock sulfide.

2. Sulfate source influences sulfur concentration and isotopic composition. I hypothesize three possible scenarios of sulfur isotope profiles.

   <u>Case 1</u>: All three cores, two from the golf course wetland and one from the stormwater retention pond, exhibit similar $\delta^{34}S$ profiles. The similarity in core profiles would reflect a

lack of importance of the source of sulfate and would emphasize the importance of sub-surface microbial sulfate reduction on isotopic composition.

Case 2: there is a difference in $\delta^{34}S$ signature profiles between the golf course wetland and the stormwater retention wetland, but no noticeable difference between the two golf course cores. This would indicate that sulfate source is important in sulfur isotope fractionation.

Case 3: there is not only a difference in $\delta^{34}S$ signature profiles between the golf course wetland and the stormwater retention wetland, but there is also a noticeable difference between the profiles of the two golf course wetland cores. This would indicate that sulfate input *and* reduction environment are deciding factors in sulfur isotope fractionation.

Background

Sulfate Sources

It is important to consider the primary sources and the isotopic composition of sulfate delivered to the sites in order to interpret sulfur isotopic profiles in sediment cores of the study sites.

Atmospheric Sulfate Deposition

Both the golf course wetland and the stormwater retention wetlands receive atmospherically deposited sulfate. Anthropogenic sources of atmospheric sulfate are the combustion of fossil fuels, which accounts for the majority of sulfur in the atmosphere, and industrial byproducts, including cement, steel mill slag, and crushed limestone (Serchan & Jones, 2009). As Brimblecombe notes in his 2003 paper, the concentration of anthropogenic sulfur emitted to the atmosphere by industrial processes has decreased considerably since the mid-1980s due to smoke-stack scrubbers reducing the amount of SO_2 released from the burning of coal. The result is a decrease in sulfate in surficial waters and less H_2SO_4 being deposited with precipitation. Data from the National Atmospheric Deposition Program (NADP) indicate a stark contrast between atmospheric sulfate deposition via precipitation in 1985, the earliest year on record (*Figure 1a*), and 2013, the latest year (*Figure 1b*).

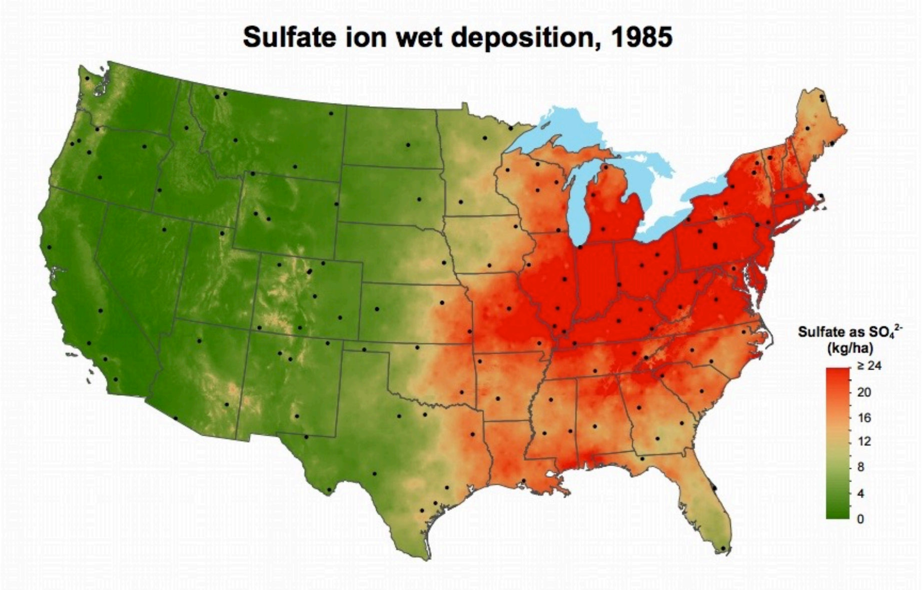
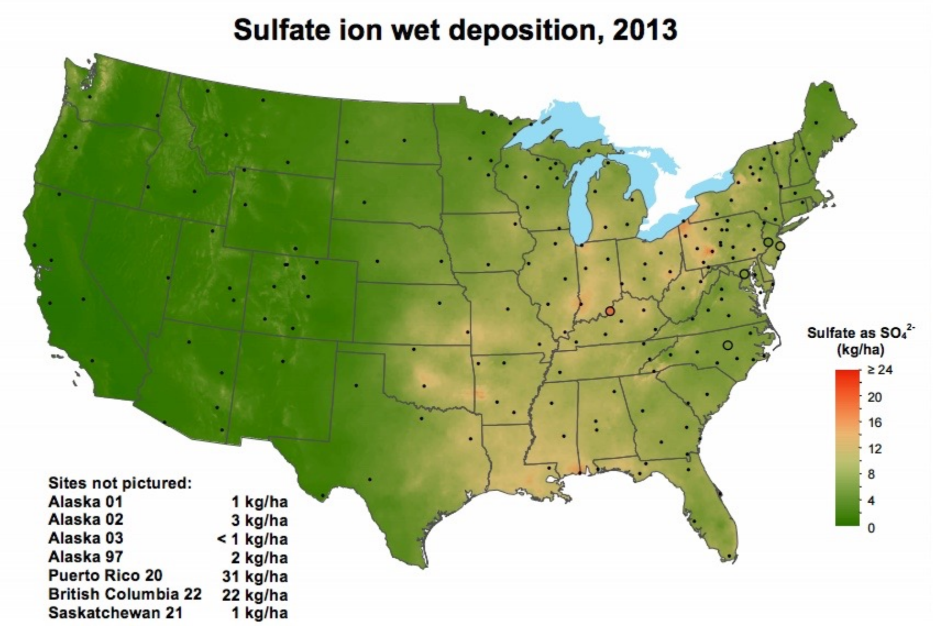


Figure 1a: MD [SO_4^{2-}] is ~22 mg/L [National Atmospheric Deposition Program (NADP)].



Sites not pictured:	
Alaska 01	1 kg/ha
Alaska 02	3 kg/ha
Alaska 03	< 1 kg/ha
Alaska 97	2 kg/ha
Puerto Rico 20	31 kg/ha
British Columbia 22	22 kg/ha
Saskatchewan 21	1 kg/ha

Figure 1b: MD [SO_4^{2-}] is ~6 mg/L [NADP].

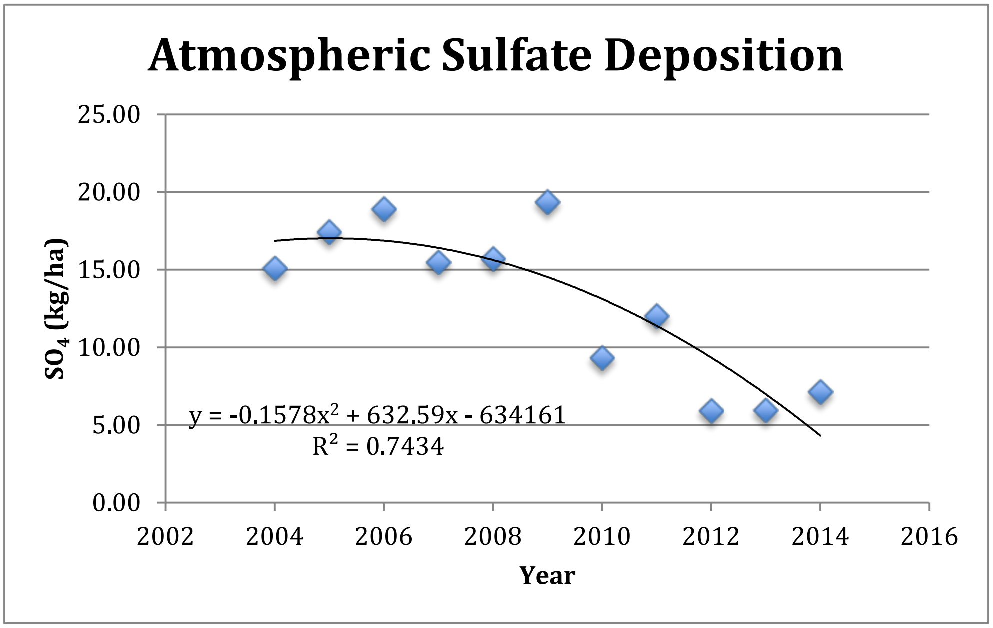


Figure 2: Atmospheric sulfate data from the Beltsville, MD, station for 2002-2014 [NADP].

With annual atmospheric sulfate deposition data provided by NADP (*Figure 2*) and approximated areas of the two wetland sites, a rough calculation can be made of the amount of atmospheric sulfate deposited on the sites. For the ~2 ha (20,000 m^2) golf course wetland, approximately 14 kg of sulfate were deposited in 2014. For the ~1 ha (9,800 m^2) stormwater retention wetland, approximately 7 kg of sulfate were deposited.

Jacqueline Mann, 2005, found that the average total global emission of sulfur to the atmosphere, excluding sea spray, ranges from 78 to 95 Tg of sulfur per year. The most significant fraction of this total was anthropogenic sources, contributing 65 to 73 Tg of sulfur as SO_2. Roughly 2 Tg of sulfur per year were globally emitted to the atmosphere directly as sulfate. Mann found that atmospheric sulfate has a $\delta^{34}S$ value of ~2‰

Fertilizer

Sulfur is a nutrient for a variety of plants and animals because it is a component of amino acids, proteins, and fats (Jasinski et al., 1999). These compounds serve a variety of functions, including aiding chlorophyll formation in plants (International Plant Nutrition Institute, 2010). A dominance of nitrogen and phosphorus-rich fertilizers coupled with a lowering of industrial sulfur emissions within the last two decades has led to a sulfur deficiency in some soils (Stewart, 2010). Mineral sulfates are highly soluble, making them ideal sulfur fertilizers. Fertilizers were then examined as sources of sulfate for the golf course wetland. A list of five fertilizers used on the golf course was provided by UMD golf course groundskeeper Brendan Rapp (*Table 1*).

Table 1: Golf Course Fertilizer Composition and Usage

Fertilizer Name	**Composition**	**Frequency of Use**	**Quantity Used**
0-0-50	fine polyon-coated fertilizer	applied to putting greens 1-2x annually	~4.5lbs/ 1000 ft^2
00-00-50	coarse K_2SO_4	1-2x annually	1.5 lbs/ 1000 ft^2
30-00-15	K_2O polymer encapsulated: 30% urea N, 15%	1x annually	4.5 lbs/ 1000 ft^2
25-00-10	*XCU Slow Release: 25% N, 10% K_2O	1x annually	NA
00-00-08	8% K_2SO_4, 15% S, 16.1% Ca, 5.4% Mg	2x annually	4.5 lbs/ 1000 ft^2

Table 1: Information for the five fertilizers used on the golf course, as provided by golf course groundskeeper Brendan Rapp. As defined by Koch Turf & Ornamental fertilizer company, “XCU Slow-Release Fertilizer” is a polymer-coated, sulfur-coated urea (PCSCU) fertilizer, with 43% nitrogen and 4% sulfur, which is designed to break down gradually throughout a plant’s growth cycle over a period of weeks to months.

The type of fertilizer, the frequency with which it is used, and the quantity that is used depends on the type of grounds on which the fertilizer is being applied (Rapp, 2015, Pers. Comm.). Fairways have different types of topsoil and vegetation than the greens, which requires the use of different fertilizers. The 2014 fertilizer records provided by the current golf course groundskeeper reveal that fertilizer amount and distribution varies depending on the overall appearance and health of the golf course. A lack of geographic distribution necessitates the assumption that all five types of fertilizers equally infiltrate the golf course wetland in roughly equal concentrations. This assumption will be discussed further in Discussion of Results.

Road Salt

The stormwater retention wetland, adjacent to the Clarice Smith Performing Arts Center, receives road runoff containing road salt. Salt is applied to roads to lower the melting temperature of ice and snow and prevent their buildup during periods of colder weather, commonly used because of its wide availability and relatively low cost. In 2011, the U.S. used

19.6 megatons of salt to de-ice roads, constituting 41% of total salt usage in the U.S. for that year (Kostick, 2011). According to the USGS, surface runoff, wind, and vehicular spraying of salt can affect soil, roadside vegetation, surface water, and groundwater (Corsi et al., 2010).

According to German salt corporation K + S Aktiengesellschaft, ~70% of global rock salt is mined from ancient deposits, whereas ~30% is obtained from modern marine sources (K + S Aktiengesellschaft, 2016). Modern marine sulfate has a $\delta^{34}S$ value of ~21‰ (*Figure 3*, Hoefs, 2004), although a range of 10‰ (~250 Ma) to 30‰ (~540 Ma) has been observed (Thode, 1991). The age of the rock salt used in road de-icing will determine the isotopic composition of the sulfate introduced to the affected urban surficial environment. A road salt sample was obtained from the Baltimore Harbor salt piles and analyzed to determine its sulfur isotope composition in an attempt to ascertain the age of the rock salt deposit from which the road salt was mined.

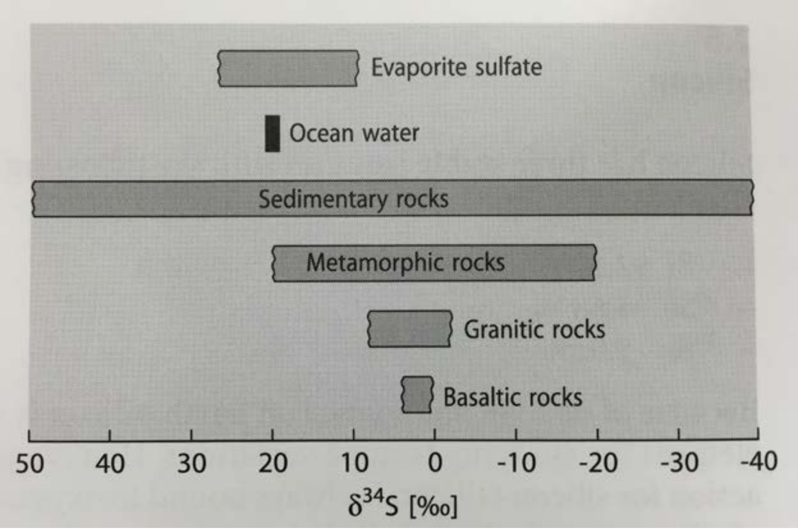


Figure 3: Sulfur isotope variations in naturally occurring sulfur reservoirs, with ocean water having a $\delta^{34}S$ of ~21‰ [Hoefs, 2004].

A Maryland State Highway Administration employee was able to provide further information regarding the origin of Maryland road salt. Scott Simons reported that the road salt used in eastern Maryland is shipped from Chile rather than coming from local seawater evaporation (Simons, 2016, Pers. Comm.). According to Morton Salt representative Bob George, this salt is mined in a location around two hours north of Santiago, Chile, in the Atacama Desert (George, 2016, Pers. Comm.). The area appears to be an interior drainage basin, the salt possibly the product of the weathering of surrounding volcanic rocks. Without knowing the exact area in which the rock salt is mined, the sulfate sulfur composition cannot be determined.

Description of Sites

The two constructed wetlands are located approximately 0.4 km apart in Prince George's County, Maryland. They are separated by Route 193, a multilane roadway (*Figure 4*). These two wetlands were chosen for this study because they are within the same small watershed, are underlain by similar geological units, receive similar atmospheric inputs, and were both relatively recently constructed. Road runoff is diverted towards the stormwater retention wetland and through the concrete spillway connecting the two wetlands beneath the highway. The land use of the Campus Creek sub-watershed is 45% grass/turf, 30.2% urban, 23.3% forested, and 0.5% open water (Olsen, 2015, GIS land coverage data).

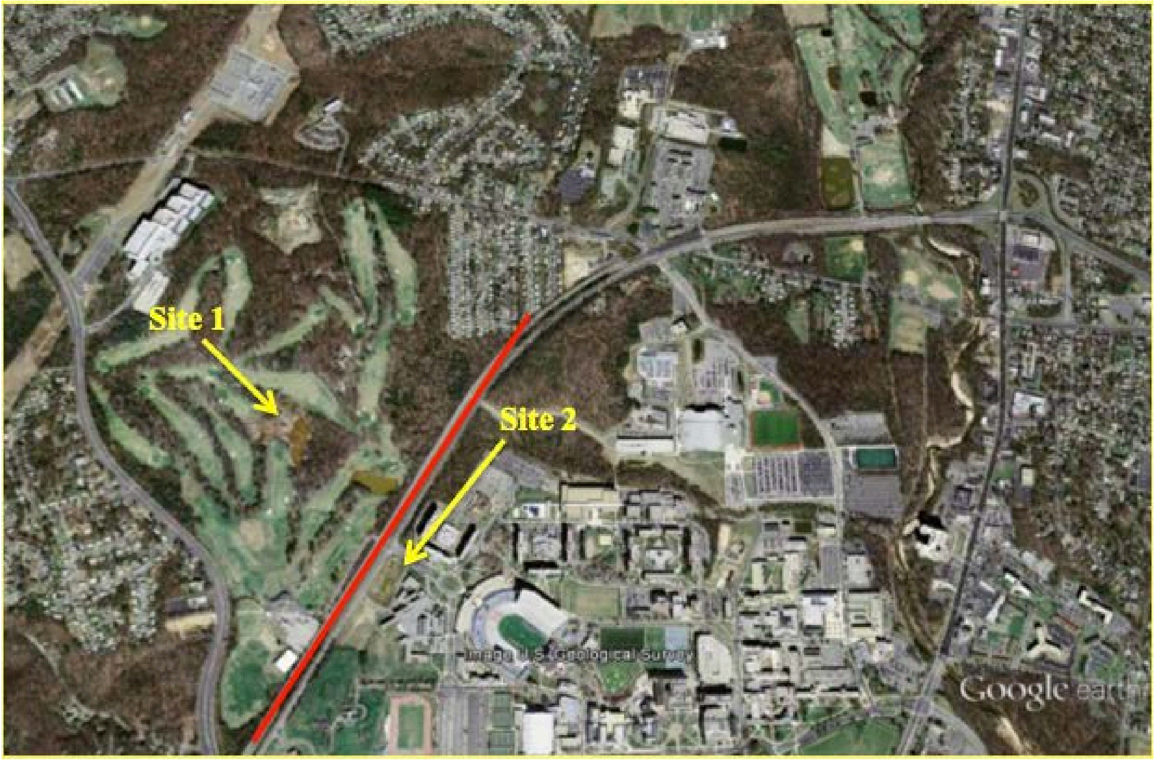


Figure 4: Campus Creek Watershed, with the two sites denoted in yellow and Route 193, forming the western border of UMD campus, denoted in red [U.S. Geological Survey].

Golf Course Wetland

The upstream wetland is located on the University of Maryland (UMD) Golf Course, a 150-acre area west of campus. The golf course was commissioned in November 1954 by then-UMD president Dr. Wilson H. Elkins (Starkey, 2008). At this time, University Boulevard was being constructed, forming the western boundary of campus. Part of the land the golf course was to be built on was being leased as a U.S. Army anti-aircraft site (Payette, 2012); the lease, which lasted from 1953-1957, was discontinued with the construction of the golf course, which was officially opened in May 1959.

The golf course wetland was formed when the earthen dam that contained a pond failed in 2001. The growth of wetland vegetation has modified the flow of water through the former pond, and the feature is now a flow-through wetland that conveys both surface and groundwater through the wetland. A chasm, formed by water seepage and the subsequent erosion of soil underneath a concrete sidewalk, is still visible (*Figure 5d*). The outflow of water from the failing of the dam led to the formation of the wetland (*Figures 5a-c*).

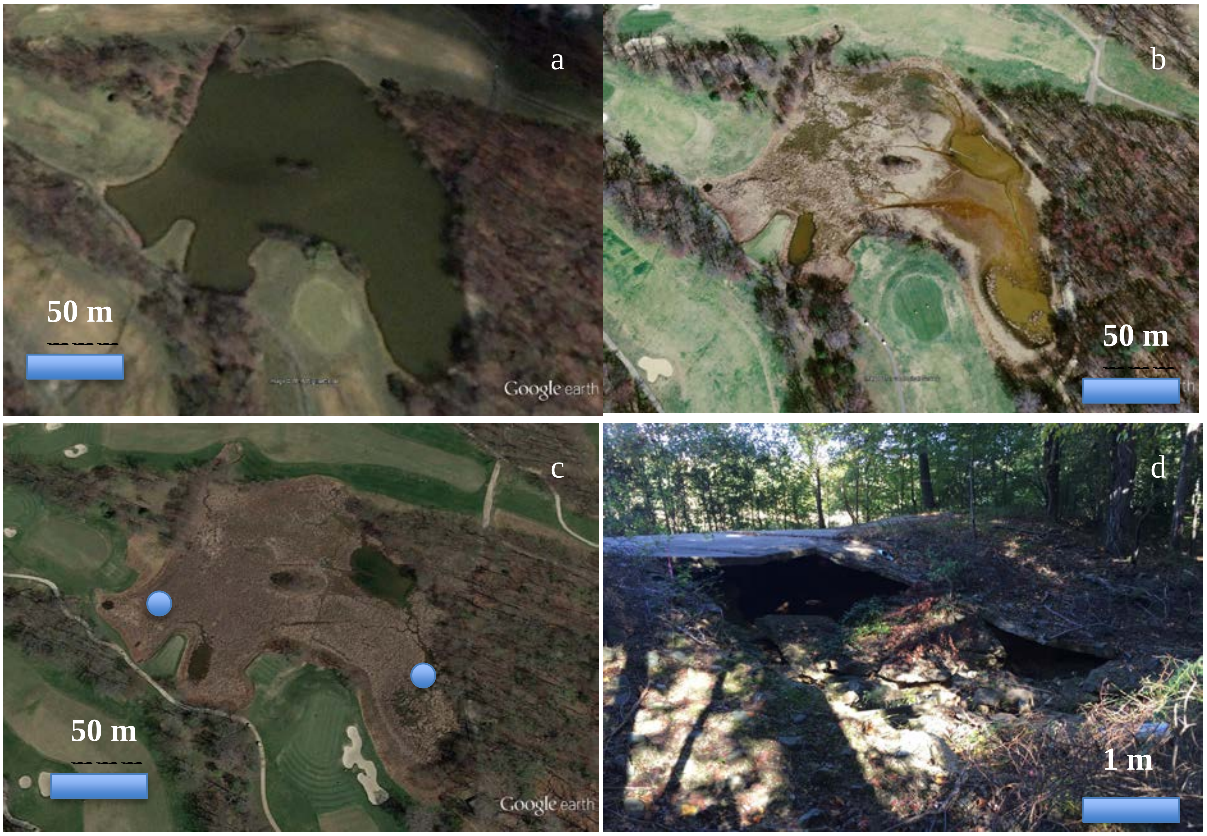


Figure 5a: The wetland shown in 2000, before the dam broke [Digital Globe]. Figure 5b: The wetland in 2006 after the dam broke, showing drainage [U.S. Geological Survey]. Figure 5c: The wetland in 2015, with more pronounced drainage and vegetation [Google Earth]. The blue dots indicate the two core sites. Figure 5d: A photo of the dam failure. The gap beneath the concrete sidewalk is approximately five meters wide.

Stormwater Retention Wetland

Figure 6a: The retention wetland in 2002, pre-construction [U.S. Geological Survey]. Figure 6b: Young vegetation present in 2006 [U.S. Geological Survey]. Figure 6c: The wetland in 2014, 9 years post-construction. Vegetation, including trees, is prominent [Google Earth]. The blue dot indicates the core site.

The second site is a stormwater retention wetland, constructed off the eastern boundary of University Boulevard. Although the highway itself was constructed in 1954, the retention wetland was built in 2003, during the construction of the Clarice Smith Performing Arts Center (*Figures 6a-c*). Because of its recent construction and the manner of construction, the substrate is only approximately 18 cm deep, in contrast to the golf course wetland, which is ~0.5-1 m of easily accessible sediment. This site was chosen because it receives stormwater runoff from the highway, with little chance for fertilizer runoff from the golf course.

Methods

Field methods

Sediment has been cored from the two sites using two main pieces of equipment: augers and coring tubes. An auger is a metal shaft used to penetrate the ground and extract a vertical column of soil. Coring tubes are plastic cylinders with two open ends, where one end has a screw-on lid and the other has a plug. 9-inch and 12-inch-long 2-inch diameter coring tubes were used in this study. In the field, the tube, with the screw-on lid at one end, is pushed into the ground. A spade or other shovel-like tool is used to dig the tube out, where the plug is then added to the other end.

For the feasibility sampling, an open face bucket auger, used for dryer soils and coring tubes, ideal for soft, wet soils, were used to extract cores. Due to concern that the coring tubes were compressing the upper part of cores and the difficulty of the bucket auger penetrating dense organic matter, a peat sampler was used for latter core collection (*Figure 7*). A peat sampler is an auger with a pivoting plate that cuts a half-cylinder core with minimal disturbance or compaction.

After extraction, core soil samples were placed in plastic bags. Intact cores remaining in coring tubes were stored and transported in plastic grocery bags or plastic 14-inch Ziploc bags. Cores that were subdivided into 2.5 cm segments for later analysis were stored in 6" x 3" and 7" x 9" Glad plastic bags. Soil samples collected from the field spent a transportation time of ~20-30 minutes from the field to a refrigeration unit.

Figure 7: The peat sampler used to collect sediment cores.

Sample Preparation

Sulfate Sample Preparation

Sulfate precipitation was performed through the titration of an 8% solution of $BaCl_2$ with sulfate source samples (road salt and fertilizer) [verb-noun agreement] to precipitate $BaSO_4$, which could then be analyzed with a gas source mass spectrometer. The five fertilizer samples and the road salt sample were first dissolved in 18 MΩ Milli-Q water and mixed with 8% $BaCl_2$ solution. Five grams of the road salt and one gram of each fertilizer was weighed out and dissolved in ~100 mL of Milli-Q H_2O in separate 250 mL glass beakers for each sample. Each sample was stirred after first being added to the Milli-Q H_2O. After being left in the laboratory fume hood for around two days for maximum dissolution, the samples were stirred again and run through a filter apparatus. $BaCl_2$ titrated with the SO_4^{2-} sample to precipitate $BaSO_4$, a highly insoluble compound. Each solution was then filtered with a vacuum-assisted glass filter, with the $BaSO_4$ precipitate remaining on the 0.45 μm filter paper. The filter paper and precipitate were then placed in the oven for approximately one to two days. 0.10-0.12 mg of each dried sample were weighed out with the AT21 mass balance into tin cups, along with ~0.2-0.4 mg of combustion catalyst V_2O_5.

Sulfide Sample Preparation

To test the presence of sulfide in the golf course and the stormwater retention wetland, two cores were taken from a pond near the golf course wetland and the retention wetland. Aliquots were taken from the two cores and subjected to sulfide extraction, which was performed in a stable isotope laboratory. The two samples that underwent sulfide extraction were from the first field outing, retrieved for the purpose of demonstrating the presence of sulfide in the golf course wetland. One of the samples was taken from a hydrologic gauge site in western part of the golf course wetland. The other was taken from the bank of the pond located ~150 meters downstream of the wetland. Around 10 g of each sediment sample was centrifuged in an Eppendorf Centrifuge 5810 at ~3000 revolutions per minute for approximately two minutes. The resulting water from each soil sample was pipetted out into separate test tubes. An aliquot of this water was injected into glass holding flasks in the fume hood to undergo CRS (Chromium Reducible Sulfides) extraction.

CRS sulfide extraction took place in a glass "digestion vessel" and followed a method described by Canfield et al. (1985). The sample was placed in a lower digestion flask that was purged with nitrogen gas, which exited to a condenser. Past the condenser there is a water trap and another trap containing approximately 20 mL of a silver nitrate capture solution. The reaction was initiated by injecting 15 mL of a chromium (II) solution with 15 mL of 5 M HCl. The system was flushed with N_2 gas (at a rate of 2-3 bubbles per second). This extraction process was heated to approximately 90° C to facilitate a faster reaction. Sulfide in the sample was converted to volatile sulfide that then trapped the silver sulfide in the silver nitrate. The reaction took three hours. The silver nitrate precipitate was aged for two weeks, and then washed with six rinses of Milli-Q water. Each rinse was followed by centrifugation and decanting of the rinse. After the final rinse, centrifugation, and drying, the samples were dried at 80° C.

Upon sulfur isotope analysis of aliquots of the feasibility cores, direct combustion of soil samples was deemed possible and used for the two subsequent cores from the study sites, the last two samples listed in Table 2. The core segments were dried first in a low-temperature utility oven, each segment in an aluminum foil tray. The samples spent 2-3 days in the oven and were taken out when fully dried. Each sample was divided into two parts, one for sulfur isotopic analysis and one for combustion analysis. The halves used for sulfur isotopic analysis were crushed with a mortar and pestle. Visible woody debris was removed from each sample with tweezers. Approximately ~10 mg of each sulfide sample was then weighed out with the AT21 mass balance into tin cups, along with ~0.2-0.4 mg of combustion catalyst V_2O_5.

Data Analysis

Sulfur Isotopic Analysis

Sulfur isotopic analysis was performed by stable isotope co-laboratory manager Rebecca Plummer by using a Eurovector Elemental Analyzer (EA) and Isoprime Gas Source Isotope Ratio Mass Spectrometer (*Figure 8*). The tin capsules, at room temperature and pressure, were loaded into the EA's sample introduction chamber. The capsules were burned at 1,030°C and were then pushed into another chamber, where sulfur within the samples was converted to $SO_{2(g)}$. SO_2 was carried in a stream of He through a column of granulated copper, which absorbed excess O_2 from the system as it was reduced to CuO. Any H_2O produced was trapped in a magnesium perchlorate column. Thin tubes connect the EA to the mass spectrometer, where the SO_2 was separated from any other gases produced. SO_2 was transported via these thin stainless steel tubes at a rate of 90 mL per minute to the ion source of the mass spectrometer. A filament emitted electrons, which knocked electrons off SO_2 molecules and transformed them into positive ions. With a charge, these molecules could then be accelerated through an electromagnetic field. Molecular trajectories were bent to different degrees based on their relative mass, allowing Faraday cup collectors to receive SO_2 molecules of different masses. Each collection of ionized molecules generated a current, which was recorded in nano-amps (nA) by a computer connected to the mass spectrometer. These currents were measured against a standard tank of SO_2 gas and were normalized. The NBS-127 and NZ-S1 standards, as well as the standard SO_2 gas, produce data with an uncertainty of 0.2‰.

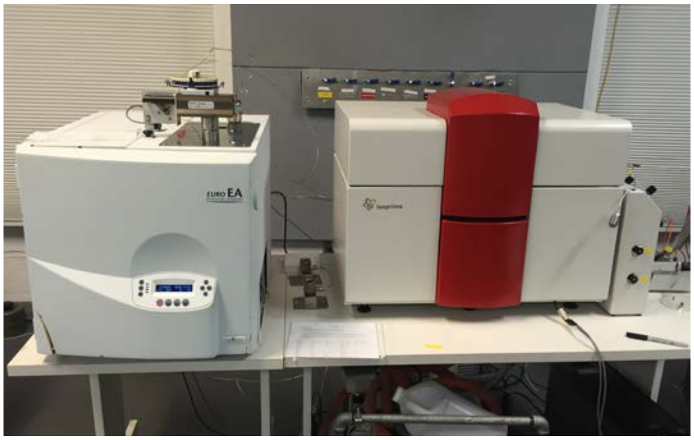


Figure 8: The Elemental Analyzer (left) and the Isoprime Mass Spectrometer (right).

Combustion Analysis

The other halves of the bulk samples were analyzed for their organic carbon content by loss on ignition (LOI). Around one gram of each sample was weighed out into ceramic crucibles, which were placed in a kiln. The optimal temperature for combusting the organic matter in the bulk samples is approximately 550°C (Hoogsteen et al., 2015). Samples spent around 5-6 hours in the kiln, then around 2-3 hours cooling. Once the samples had combusted, they were weighed again, with the difference in their original and post-combustion weights indicating the percentage of organic carbon in each core segment.

Analysis of Uncertainty

Analytical uncertainty for the sulfur isotopic analysis of the sulfate and sulfide samples is derived from the accuracy and precision of the mass spectrometer used to process the samples. Two standards were weighed out in addition to the samples for a basis of comparison for sulfur isotopic composition: NBS-127, barite, and NZ-S1, silver sulfide. These two standards are assumed to be pure, so they are run through the mass spectrometer to gauge the instrument's accuracy. The uncertainty routinely demonstrated through the running of these standards is ± 0.20‰. This uncertainty is then applied to the sulfate and sulfide core samples analyzed by the mass spectrometer.

There is additional uncertainty derived from the homogenization of the sulfide samples. After the grinding of each core segment by the mortar and pestle to a very fine powder, it is assumed that the sample is homogeneous. If the sample is not actually homogeneous, the weighing of ~10 mg of a tin cup sample could be unrepresentative of the whole sample, producing inaccurate %S data.

Results

Sulfur Source Composition

Before further testing could take place, the presence of sulfate in the identified sources and sulfide in the initial cores had to be determined. The road salt sample yielded a $\delta^{34}S$ value of ~10‰. Considering its origin in the Atacama Salt Flats, this value could indicate a possible mixing of generally lower volcanic sulfur signatures with the higher sulfur signatures (21‰) of sea salt (*Table 2*). The degree of sea salt mixing depends on how far inland the salt mine is; with the mine location uncertain, this degree of mixing cannot be determined. The five fertilizers yielded a range of $\delta^{34}S$ values, from ~-3.7 to 18.9‰. The percent sulfur detected in each sample was multiplied with that sample's respective $\delta^{34}S$ value, and all five fertilizer values summed, to produce a weighted $\delta^{34}S$ average of ~5‰. The four sediment cores taken to establish the presence of sulfide displayed a ~1.0 to 2.6% range of sulfur concentration. With the feasibility of sulfide sampling established, three sediment cores were taken from the study sites and analyzed for bulk density, % total organic carbon (TOC), %S, and $\delta^{34}S$.

Table 2: Sulfate Source and Sulfide Core Compositions

Sample	Sample Weight (mg)	%S	$\delta^{34}S$ (‰)
Atmospheric Sulfate			
Road Salt	0.10	10.58	10.17
Fertilizer 0-0-50	0.11	13.10	-3.66
Fertilizer 00-00-50	0.10	12.75	18.80
Fertilizer 30-00-15	0.12	10.65	18.85
Fertilizer 25-00-10	0.11	NA	NA
Fertilizer 00-00-08	0.10	13.49	5.93
Golf Course Pond Sulfide	0.13	2.62	-3.02
Golf Course Wetland Sulfide	0.11	2.17	1.04
Golf Course Wetland Soil	10.01	1.02	1.75
Stormwater Retention Wetland soil	10.10	2.02	-1.34

Table 2: %S and $\delta^{34}S$ values for the three sulfate endmembers, atmospheric sulfate, road salt, and fertilizer, and the four sediment samples taken to test for sulfide.

Table 3: Weighted and Unweighted Sulfur Averages of Fertilizers

Fertilizers	
Average S (%):	12.50
Average $\delta^{34}S$ (‰):	9.98
Weighted $\delta^{34}S$ Average (‰):	4.73

Table 3: Average values for %S and $\delta^{34}S$ for the five fertilizers. A weighted average was taken of the five fertilizers, using their %S and $\delta^{34}S$ values.

Sediment Cores

Core Sedimentological Features

Inlet Core

The upper 11 cm of the inlet core consists of loosely packed organic matter, ranging in color from medium to dark brown. Roots characteristic of the organic horizon of the retention wetland are visible in the picture of the core in Figure 9. Below a depth of ~11 cm, compacted clay replaces organic matter. This clay portion changes color around 23 cm depth from a light brown to alternating black, light gray, and yellow layers for the rest of the core. These distinct colors are characteristic of reduced sediment.

Because this core was taken at the inlet of the golf course wetland, the clay-sized particles in the bottom half of the core are interspersed with sand particles from the sand-dominated delta of the inlet. Water entering the wetland decreases in velocity, losing the energy to move larger sand-sized particles, which fall out and deposit in a delta formation.

Outlet Core

The outlet core has an overall darker color than the inlet core (*Figure 10*). Although the top 15 cm contain bits of organic matter, only the top ~7 cm are almost entirely organic matter; the rest of the core is dark, reduced sediment. A compact, clay texture appears at a depth of ~20 cm. Like the inlet core, bands of black and yellow sulfide reduction are present towards the bottom of the core, particularly from 35-45 cm. The outlet core, and the surrounding sampling area, smelled strongly of sulfide; although hardly quantitative, the odor, coupled with the black and yellow layers, is another indicator of sulfide reduction taking place at the outlet site.

Stormwater Retention Core

The depth of the stormwater retention wetland only allowed for the extraction of a ~20 cm core. The upper part of the core consists of ~7 cm of loose, organic material, with leaf litter visible in the picture of the core (*Figure 11*). The rest of the core is compacted clay, with a redder brown color not seen in the inlet or outlet cores. Black and red stripes were present in the compacted bottom layer of the core, but were much thinner than the black and yellow reduced bands of sediment in the inlet and outlet cores.

Core Chemical Analyses

Inlet Core

The inlet core was analyzed for bulk density, %TOC, mg S/cm^3, and δ^{34}S (*Figure 9*). The inlet core displays a bulk density range from ~0.3 to 1.5 mg/cc, demonstrating a strong correlation between bulk density and depth. The top 10 cm of the core, which is dominated by organic matter, exhibited a roughly constant value of bulk density of ~0.3 g/cm^3, whereas bulk density had decreased steadily from the bottom of the core up to that depth. A similar trend is observed with TOC, where values steadily increase from 0% until the organic horizon, where values remain in a 20 -25% range.

An even more pronounced shift in data at the organic horizon is exhibited by mg S/cm^3. From the bottom of the core to ~30 cm, S values range from 0.4-0.5 mg S/cc. Moving up the core, 30 cm to ~13 cm displays a range from 1.2-1.6 mg S/cm^3. There is then a ~-0.8 mg/cc shift in values at the bottom limit of the organic horizon, where values remain fairly constant at ~0.4 mg S/cm^3 until the top of the core. Although mg S/cm^3 values do not shift in a linear matter like bulk density and TOC, there is a similarly noticeable distinction between values below the organic horizon and above.

δ^{34}S values generally decrease until the organic horizon, where they increase up the top of the core. From the bottom of the core to ~25 cm, δ^{34}S values range from -5 to 11‰. From ~30 to 15 cm, δ^{34}S steadily decreases, reaching a -5‰ minimum at the bottom of the organic horizon. Unlike bulk density, %TOC, and mg S/cm^3, however, δ^{34}S steadily increases by ~8‰ up to the top of the core instead of remaining constant.

Golf Course Wetland Inlet Core

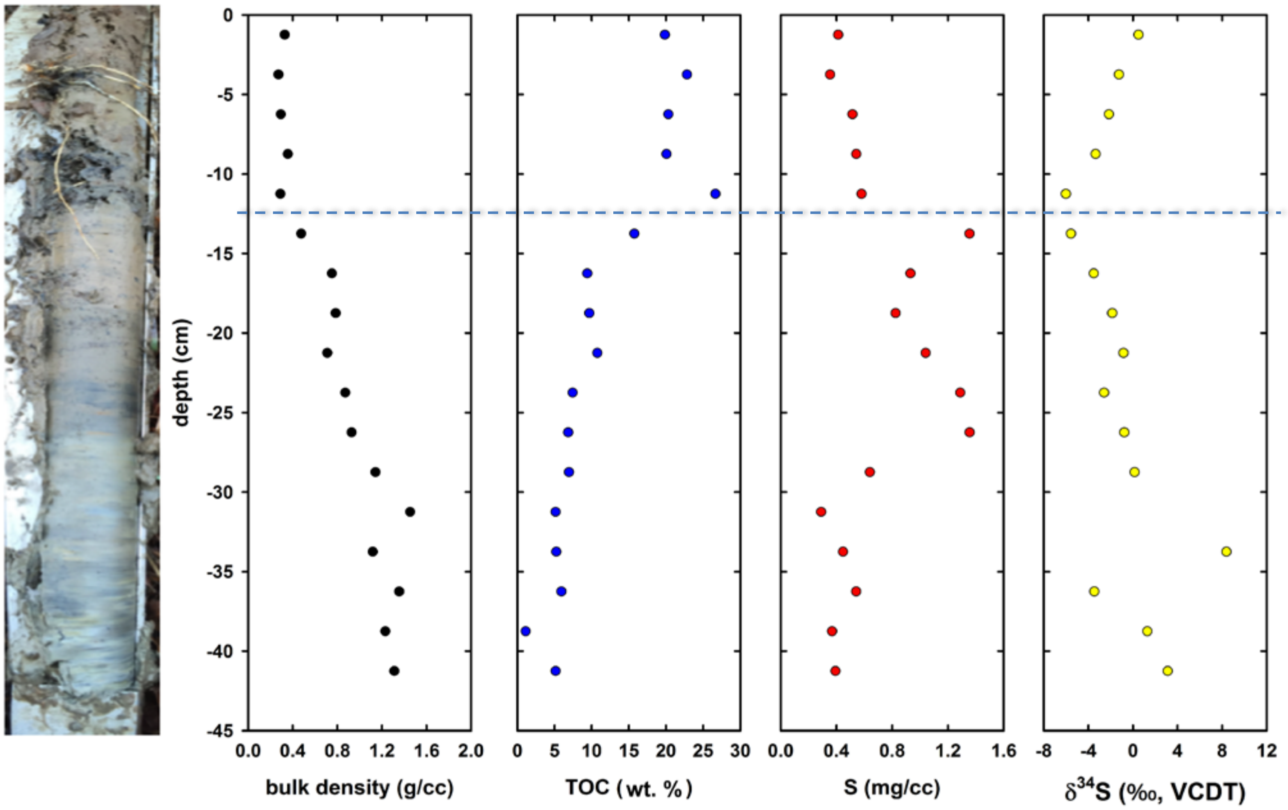


Figure 9: Bulk density, %TOC, sulfur weight per volume, and $\delta^{34}S$ values for the inlet core. The dotted line delineates the bottom of the organic horizon. Please note: “TOC” refers to “Total Organic Matter” in this thesis.

Outlet Core

The outlet core was analyzed for %S and $\delta^{34}S$ (*Figure 10*). %S varies throughout the core, increasing from 0.12 to ~0.24 from 45-40 cm, remaining a constant value of ~0.20 from 36-28 cm, and decreasing from 0.18 to 0.04% from 25-14 cm. It is difficult to interpret the %S trend in the organic horizon because sulfur content was below the limit of detection of the mass spectrometer, but the uppermost %S value obtained was 0.08, an increase from the 14 cm value.

The outlet core had the narrowest range of $\delta^{34}S$ values of all three cores, maintaining a 0-4‰ range for its entire length. From 45 to ~25 cm, $\delta^{34}S$ decreases slightly, but then increases to a value of 4‰ from ~20 cm to the top of the core.

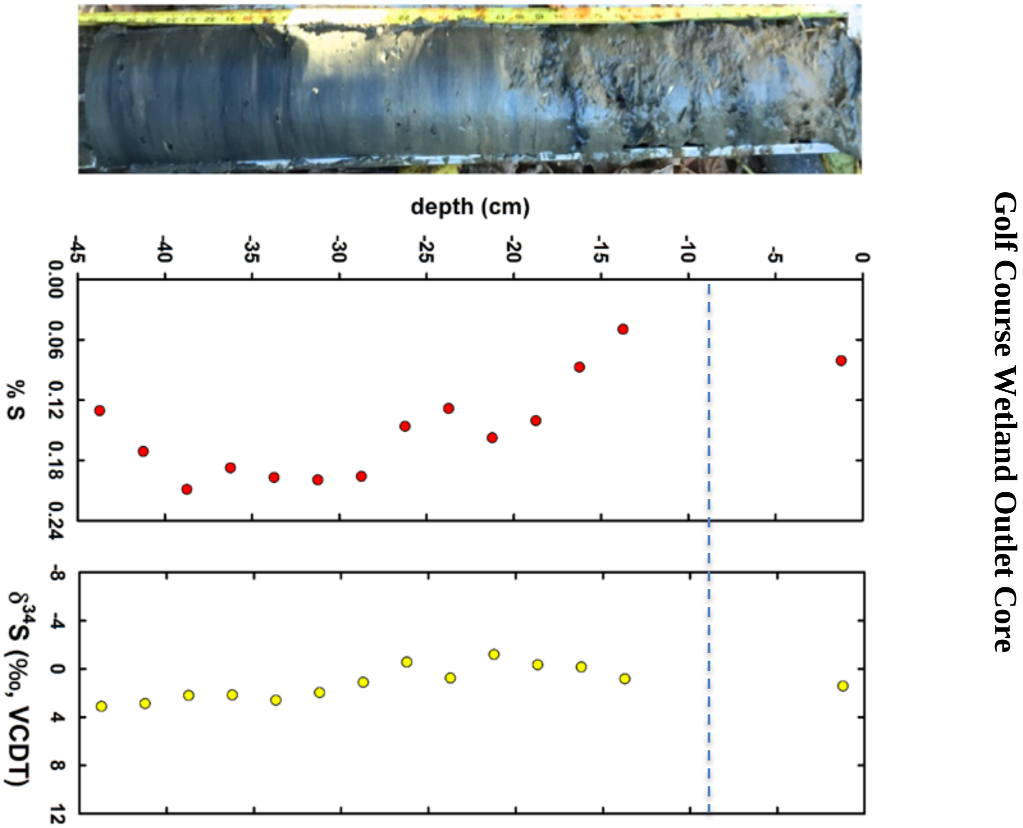


Figure 10: %S and d34S values for the outlet core. The dotted line delineates the bottom of the organic horizon.

Retention Core

The retention core was analyzed for bulk density, %TOC, (mg/cc) S, and $\delta^{34}S$ (*Figure 11*). Of all three cores, the retention core displays the most pronounced changes in values across the lower limit of its organic horizon. With bulk density and mg S/cc, there are notable decreases in values, whereas there is a notable increase in TOC. Bulk density exhibits a ~2 g/cc decrease, in contrast to a ~15 % increase in TOC, demonstrating the expected correlation of bulk density with TOC. The organic matter observed in the three cores is more loosely compacted than the clayey bottom horizons, which would indicate a lower bulk density for the organic layers. Organic layers presumably have higher carbon content than the clay horizons, and would be expected to negatively correlate with bulk density. This is demonstrated by both inlet and retention cores, although the retention core exhibits a more pronounced correlation than the inlet core.

S in mg/cc was at a constant value of ~0.7 from 20 to ~14 cm, but increased to ~ 1.2 around a depth of 8 cm. Upon reaching the organic horizon, mg S/cc decreased to ~4. The uppermost value obtained was ~0.5, just 0.2 mg/cc away from the lowermost value of 0.7 in the core. $\delta^{34}S$ is the only chemical characteristic of the retention core, or any of the cores, to maintain a constant value for an interval of roughly 13 cm. From ~20-18 cm, $\delta^{34}S$ is ~-2‰, which then increases to ~5 and then ~8‰ in the next 5 cm. $\delta^{34}S$ then decreases to and remains at an average of ~4‰ for the upper 13 cm of the core.

Stormwater Retention Wetland Core

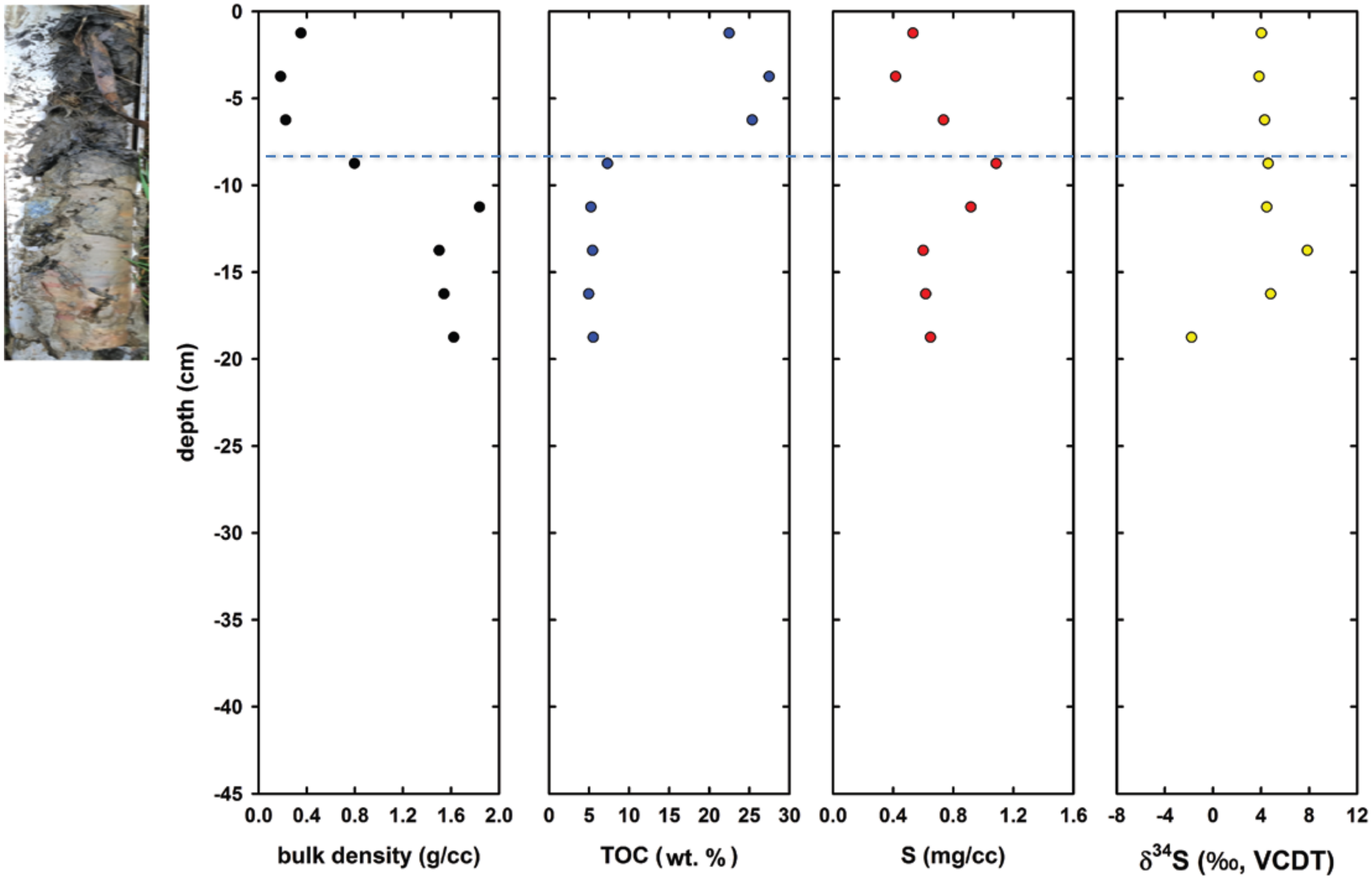


Figure 11: Bulk density, %TOC, %S, sulfur weight per volume, and d34S values for the retention core. The dotted line delineates the bottom of the organic horizon.

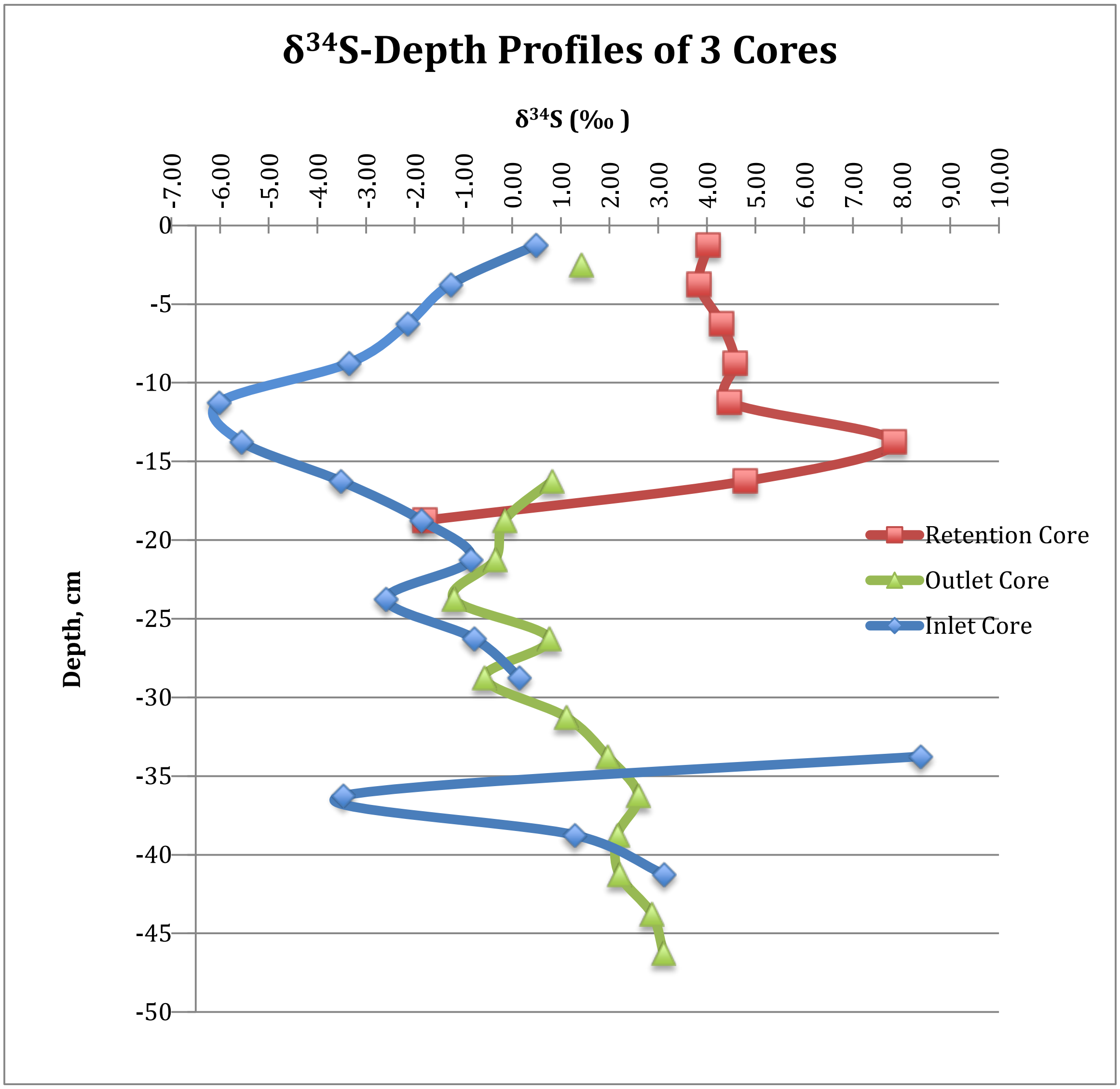


Figure 12: δ^{34}S-depth profiles for the inlet, outlet, and retention cores.

Discussion of Results

Effect of Depositional Environment on Organic Accumulation and Sulfur Fractionation

Several interpretations can be made from the chemical analyses performed on the three cores regarding the larger biogeochemical processes occurring in the golf course and retention wetlands. One interpretation is that the two golf course cores have recorded the pond-to-wetland transition of the current golf course wetland.

Before the dam failure, when the golf course wetland was still a pond, water was relatively well-mixed. Sediment was deposited and reduced, with little disruption from plant life. When the dam failed in 2001, the pond gradually drained from the western side of the wetland (the inlet site) to the eastern side of the wetland (the outlet site). The inlet site therefore transitioned to a wetland before the outlet site. When the inlet became drier and exposed to the atmosphere, plant life increased, with roots taking up nutrients from the substrate. When these organisms died, their remains accumulated into a loose, organic horizon seen in the sediment cores taken. This could explain why there was a larger organic horizon in the inlet core than the outlet core, as well as the outlet core's darker color and distinct sulfidic odor. The inlet core had more time to accumulate organic matter, at the same time that the outlet core was experiencing reduction. If the transition from reduced, clay-rich sediments to organic matter represents this pond-to-wetland transition, it may be possible to approximate the date of that transition to 2002, about a year after the dam failure. The outlet core will have transitioned at a later date; differences in rates of deposition and microbial sulfate reduction complicate dating of this core.

Another chemical signature the pond-to-wetland transition could explain is the $\delta^{34}S$ depth profiles for the two cores. The larger magnitude of fractionation observed in the inlet core could be attributed to a lower rate of sulfate reduction, whereas a higher rate could explain the relatively constrained fractionation observed in the outlet core. When there is an abundance of sulfate, both ^{32}S and ^{34}S are taken up in relatively equal amounts (Bradley et al., 2016), resulting in a small magnitude of fractionation. This could be what was happening in the outlet site, where significant sulfide reduction appears to have taken place. With lower sulfate concentrations, sulfate-reducing microbes tend to preferentially take up ^{32}S, resulting in a greater magnitude of fractionation.

There are several factors that could contribute to the greater amount of sulfate reduction in the outlet core. Reduction could be affected by the degree of anoxia in the substrate or the remineralization of organic matter. In addition to the possibility of an uneven geographic distribution of golf course fertilizers, the rate of microbial sulfate reduction is also a key uncertainty. The number of microbes present in the soil substrate of the two golf wetland sites and their behavior with regards to factors like temperature could be affecting the rate of reduction, although this is merely speculative without further testing.

Effect of Sulfate Source on $\delta^{34}S$ Signature

The $\delta^{34}S$-depth profiles (*Figure 12*) allow for interpretation regarding sulfate source input and possible source mixing for the three sites examined. The sulfate sources identified for the two wetlands were atmospheric sulfate, with a $\delta^{34}S$ value of ~2‰ (Mann, 2015), fertilizer, with a weighted average of ~5‰ (*Table 3*), and road salt, with a value of ~10‰ (*Table 2*). The inlet core exhibited a general decrease in $\delta^{34}S$ in its lower portion, whereas its organic upper portion displayed an increase. The core as a whole maintained a $\delta^{34}S$ average of ~0‰. Considering that the organic horizon could represent post-dam failure drainage, it is possible that paludal sulfide reduction was responsible for the decrease in $\delta^{34}S$. When the dam broke and the inlet drained to become a wetland, less sulfate reduction occurred, and the positive sulfate signatures contributed by 2‰ atmospheric deposition and ~ 5‰ from fertilizers could have supported the increasing $\delta^{34}S$ trend.

The outlet core has only experienced drainage in the last couple of years (Figures 5a-c), and has thus been a more reducing environment than the inlet. With presumably similar positive atmospheric and fertilizer sulfate inputs as the inlet, its reducing environment perhaps contributed to a greater consumption of sulfate and, therefore, a smaller magnitude of fractionation. The outlet core maintained a relatively steady average of 4‰ compared to the -6 to 8‰ range of the inlet core. However, the increasing $\delta^{34}S$ trend demonstrated by the inlet core could indicate a return to a more positive $\delta^{34}S$ average, indicating that the depositional environment of the sites controls the microbial sulfate reduction occurring at the sites. The drainage of the two sites has resulted in increases in $\delta^{34}S$, although differing rates of increase appear to depend on the time of site drainage.

The retention wetland demonstrates a more visible difference in $\delta^{34}S$ over time. The red compacted clay in the lower half of the core probably represents the original material of the substrate pre-construction, although the construction could have compacted this material even further. After construction took place, plant life could develop, thus creating an organic horizon. The rather abrupt transition from a 0-12‰ $\delta^{34}S$ range to a very consistent value of ~4‰ across the lower limit of organic matter could indicate a transition from reduction in the pre-construction soil to less-reducing conditions. The ~10‰ road salt and ~2‰ atmospheric deposition entering the retention site could be driving the more positive $\delta^{34}S$ signature, although relative contributions of the two respective sources remain uncertain.

Conclusions

Three sediment cores were taken from the two main sites in this study to examine the effect of sulfate inputs on sulfide production via microbial sulfate reduction. Two cores were taken from the golf course wetland, one from its inlet on the western side of the wetland and one from its outlet on the eastern side of the wetland. A third core was taken from the stormwater retention wetland across highway Route 193. These cores have been analyzed for their sulfur and organic carbon content, including %S, $\delta^{34}S$, TOC, and bulk density.

Two of the three endmembers identified as possibly significant sulfate sources to the two wetlands were tested, and displayed sulfate content. The five fertilizers provided by the UMD golf course groundskeeper had a weighted average of ~5‰ $\delta^{34}S$, whereas the road salt sample had a value of ~10‰. Jacqueline Mann, 2015, provided a 2‰ value for atmospheric deposition. After establishing the input of sulfate into the two wetlands, the presence of sulfide, the product of microbial sulfate reduction, needed to be established. Cores were taken across transects of the golf course and retention wetlands and tested, revealing the presence of sulfide and failing to disprove the first hypothesis of this thesis that microbial sulfate reduction is occurring at the two wetlands.

Three cores were then taken from the two wetlands and analyzed. The inlet core displayed an increasingly positive $\delta^{34}S$ trend with decreasing depth, with lower bulk density, higher TOC, and lower mg S/cc present in the upper organic horizon of the core relative to the lower clay portion. The outlet core displayed a small range of $\delta^{34}S$ variation along its length, with the upper organic horizon recording a slight increase in %S. These chemical analyses, combined with the sedimentological characteristics of the cores themselves, suggest that as the golf course pond drained and gradually became a wetland, the inlet core became a less reducing environment and has been more affected by the positive sulfate sulfur isotopic inputs of atmospheric deposition and fertilizer. The outlet core has only recently been drained and reflects a more reducing environment, which constrains its magnitude of $\delta^{34}S$ fractionation.

The retention core demonstrated a very different $\delta^{34}S$-depth profile than the two golf course cores, disproving the first case of the second hypothesis that all three cores would exhibit similar $\delta^{34}S$ profiles. The retention core experienced an abrupt change in $\delta^{34}S$ values across its clay-organic transition, having a constant $\delta^{34}S$ value of ~4‰ for its entire upper half. This may be attributed to the recent development of a wetland at the retention site, allowing for an organic horizon to develop and lessen the effect of sulfate reduction. The constant 4‰ value could reflect a mixing of the 2‰ $\delta^{34}S$ atmospheric deposition and 10‰ road salt inputs to the retention site, although the degree of mixing was not able to be determined. Because each of the three sites exhibited unique $\delta^{34}S$-depth profiles, the second case of the second hypothesis is disproven and the third case fails to be disproven, meaning sulfate input and reduction environment are both possible factors in sulfur isotope fractionation. For all three of the cores, it is important to note that the rates of microbial sulfate reduction, organic matter accumulation, and reduced sediment deposition are unknown, so the mineralogical and chemical observations for each core allow for qualitative, rather than quantitative, inferences about underlying biogeochemical processes at the two wetlands.

Broader Implications

Examining how different sulfate inputs affect sulfur isotope fractionation broadens understanding on the anthropogenic impacts on surficial environments. Although atmospheric sulfate deposition has declined significantly over the last three decades (Brimblecombe, 2003, NADP, 2015), road salt production and the use of fertilizers has increased (Kostick, 2011). Every winter season renews salting efforts in the face of heavier inclement weather-induced litigation. The amount and frequency of distribution of fertilizers used on the university golf course is largely based on the aesthetic conditions of the greens and fairways instead of comprising a fixed regimen. These influxes of sulfate produce variation in sulfide production throughout these two wetlands, yielding visible geochemical signatures at each of the three sites. Increased sulfate loading has been linked to other pollutants, such as methylmercury, a bioaccumulating neurotoxin, which has been directly linked to sulfate contamination in the Everglades because the increased sulfate-reducing bacteria are also responsible for its production. On the other side of the reaction, sulfide can act as a potent soil phytotoxin (Lamers et al., 2013) at sufficient concentrations from increasing SO_4^{2-} levels. With greater understanding of sulfate loading and the subsequent production of sulfide, the processes responsible for the propagation of such detrimental environmental issues can perhaps be better understood.

Future Work

A deeper understanding of the biogeochemical processes examined in this thesis can be attained through additional sampling of the golf course and stormwater retention wetlands. Although sediment cores were only extracted from three sites, a transect along the two wetlands consisting of multiple cores could provide a greater abundance of data. For the golf course wetland, the western (inlet) and eastern (outlet) margins of the wetland were sampled, but an additional core in the middle of the wetland could allow further investigation into the $\delta^{34}S$, bulk density, and mg S/cm^3 signatures observed in the two cores. A greater number of samples would reduce the likelihood of sedimentological heterogeneity in extracted cores and would be more representational of the entire wetland. An additional core from the outlet site would allow for bulk density and TOC analysis, which would provide data for comparison to the inlet and retention core values.

Only one core was taken from the retention wetland, serving as a comparison for the two golf course wetland sites. Sampling along a transect in the retention wetland could reveal any bulk density, %TOC, %S, or d $\delta^{34}S$ trends within the retention wetland previously unobserved through lack of sampling.

In addition to collecting a greater number of cores, the depths of cores extracted could be increased for further investigation of geochemical trends. Cores ~45 cm were extracted from the golf course wetland. Although I am constrained with depth for the retention wetland, it is possible for 0.3-0.6 m cores to be taken from the golf course wetland with the peat sampler.

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References

Please note: All pictures were taken by Elizabeth Lee unless otherwise noted.

Barton, L. L. & Fauque, G. D. (2009). Biochemistry, Physiology and Biotechnology of Sulfate-Reducing Bacteria. *Advances in Applied Microbiology, 68,* 41-98.

Baumgartner, L.K., Reid, R.P., Dupraz, C., Decho, A.W., Buckley, D.H., Spear, J.R., Przekop, K.M., & Visscher, P.T. (2006). Sulfate reducing bacteria in microbial mats: Changing paradigms, new discoveries. *Sedimentary Geology, 185,* 131-145.

Bradley, A.S., Leavitt, W.D., Schmidt, M., Knoll, A.H., Girguis, P.R., & Johnston, D.T. (2015). *Geobiology, 14,* 91-101.

Brenot, A., Calmels, D., Gaillardet, J., & France-Lanord, C. (2007). Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: Climatic perspectives. *Geology, 35,* 1003–1006.

Brimblecombe, P. (2003). The Global Sulfur Cycle. *Treatise on Geochemistry, 8,* 645-682.

Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., & Berner, R. A. (1985). "The Use of Chromium Reduction in the Analysis of Reduced Inorganic Sulfur in Sediments and Shales". *Chemical Geology, 54,* 149-155.

Corsi, S., Graczyk, G., Geis, S., Booth, N., & Richards, K. (2010). A Fresh Look at Road Salt: Aquatic Toxicity and Water-Quality Impacts on Local, Regional, and National Scales. *Environmental Science & Technology, 44,* 7376-7382.

Digital Globe. (2015-2016). Provider of images retrieved through Google Earth.

George, Bob. (2016). Personal communication: Morton Salt: representative: information on origin of Maryland road salt.

Google Earth. (2015-2016). Provider of satellite images of study sites.

Hoefs, J. (2004). Stable Isotope Geochemistry. Chapter 2: Isotope Fractionation Mechanisms of Selected Elements & Chapter 3: Variations of Stable Isotope Ratios in Nature. *SpringerLink.*

Hoogsteen, M. J., Lantinga, E. A., Bakker, E. J., Groot, J. C., & Tittonell, P. A. (2015). "Estimating soil organic carbon through loss on ignition: effects of ignition conditions and structural water loss". *European Journal of Soil Science*, 66, 320-328.

Holmer, M. & Storkholm, P. (2001). Sulphate reduction and sulphur cycling in lake sediments: a review. *Freshwater Biology*, 46, 431-451.

Jasinski, S. M., Kramer, D. A., Ober, J. A., & Searls, J. P. (1999). Fertilizers: Sustaining Global Food Supplies. *USGS Fact Sheet*, 1-4.

K + S Aktiengesellschaft. (2016). "Global Salt Deposits". http://www.k-plus s.com/en/wissen/rohstoffe/salzvorkommen.html

Koch Agronomic Services. (2015). Enhanced Efficiency Fertilizers. *Koch Turf & Ornamental*, http://kasturf.com/products/duration/ , http://kasturf.com/products/xcu/

Kostick, D. S. (2011). "USGS 2011 Minerals Yearbook: Salt". *USGS*, *63*, 1-6.

Lamers, L. P. M., Govers, L. L., Janssen, I. C. J. M., Geurts, J. J. M., Van der Welle, M. E. W., Van Katwijk, M. M., Van der Heide, T., Roelofs, J. G. M., & Smolders, A. J. P. (2013). Sulfide as a soil phytotoxin- a review. *Frontiers in Plant Science, 4,* 268-287.

Mann, J. L. (2005). Determination of sulfur isotope composition in sulfate from two high elevation snowpits by multi-collector thermal ionization mass spectrometry using a double strike. *Doctor of Philosophy thesis*, 7-12.

McArthur, J. M., Turner, J., Lyons, W. B., & Thirlwall, M. F. (1989). Salt sources and water-rock interaction on the Yilgarn Block, Australia: isotopic and major element tracers. *Applied Geochemistry, 4,* 79-92.

Meybeck, M., Green, P. A., Vorosmarty, C. J., Galloway, J. N., Peterson, B. J., & Boyer, E. W. (2004). "Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology." *Biogeochemistry, 68*, 71-105.

NADP. (2015). "Annual NTN Maps by Year: SO_4^{2-}". National Atmospheric Deposition Program/National Trends Network. http://nadp.isws.illinois.edu/maplib/pdf/2005/SO4_conc_05.pdf

NADP. (2016). "NTN Annual/Seasonal Depositions", SO_4^{2-}. National Atmospheric Deposition Program/National Trends Network. http://nadp.sws.uiuc.edu/nadpdata/depoRep

Olsen, Christopher. (2015). Land usage of Campus Creek Watershed via GIS.

Orem, William H. (2013). "Impacts of Sulfate Contamination on the Florida Everglades Ecosystem." *USGS*. http://pubs.usgs.gov/fs/fs109-03/fs109-03.html

Payette, Pete. (2012). "Washington's Cold War AAA Defenses". *American Forts Network.* www.northamericanforts.com/East/mdwest.html#cold

Plugge, C.M., Zhang, Weiwen, Scholten, J.C.M., & Stams, A.J.M. (2011). Metabolic Flexibility of Sulfate-Reducing Bacteria. *Frontiers in Microbiology*, *2*, 1-8.

Rapp, Brendan. (2015-2016). Personal communication: UMD Golf Course superintendent: information on fertilizers used on golf course and physical samples.

Serchan, S. & Jones, D. (2009). Sulfate. *Baltimore Ecosystem Study.*

Shen, Y., Buick, R., & Canfield, D. E. (2001). Isotopic evidence for microbial sulphate reduction in the early Archaean era. *Nature*, *410*, 77-81.

Sim, M.S., Ono, S., & Bosak, T. (2012). Effects of Iron and Nitrogen Limitation on Sulfur Isotope Fractionation during Microbial Sulfate Reduction. *Applied and Environmental Microbiology*, 78, 8368-8376.

Simons, Scott. (2016). Personal communication: Maryland State Highway Administration: information on the origin of Maryland road salt.

Starkey, N. B. (2008). The University of Maryland Golf Course. *Division of Student Affairs* & *University of Maryland Archives*. http://www.terpgolf.umd.edu/-golf-course-history

Stewart, W.M. (2010). Sulfur-The 4th Major Nutrient. *International Plant Nutrition Institute*, *No. 7*, www.ipni.net/pnt.

Thode, H.G. (1991). Sulphur Isotopes in Nature and the Environment: An Overview. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment. John Wiley & Sons Ltd.

U.S. Geological Survey. (2015-2016). Provider of images retrieved through Google Earth.

Appendix I: Raw Data

Inlet Core

Approximate GPS Coordinates: 38°59’44.71” N, 76°57’21.14” W

Depth	Bulk Density	%TOC	%S	S (mg/cm^3)	δ^{34}S
0-2.5	0.328	19.85	0.126	0.413	0.49
2.5-5.0	0.273	22.83	0.130	0.355	-1.26
5.0-7.5	0.294	20.32	0.175	0.515	-2.15
7.5-10.0	0.357	20.06	0.152	0.543	-3.35
10.0-12.5	0.290	26.66	0.200	0.580	-6.02
12.5-15.0	0.476	15.75	0.285	1.356	-5.56
15.0-17.5	0.751	9.41	0.124	0.931	-3.52
17.5-20.0	0.786	9.68	0.105	0.825	-1.86
20.0-22.5	0.711	10.76	0.146	1.040	-0.85
22.5-25.0	0.871	7.44	0.148	1.290	-2.59
25.0-27.5	0.928	6.85	0.146	1.356	-0.78
27.5-30.0	1.142	6.95	0.056	0.640	0.15
30.0-32.5	1.454	5.16	0.020	0.291	Below LOD
32.5-35.0	1.119	5.25	0.040	0.447	8.39
35.0-37.5	1.356	5.93	0.040	0.542	-3.47
37.5-40.0	1.232	1.12	0.030	0.370	1.29
40.0-42.5	1.312	5.15	0.030	0.394	3.12

Figure 13: Bulk density, %TOC, %S, mg S/cm^3, and δ^{34}S values for the inlet core. Depths are given as 2.5 cm-sections as the cores were sectioned in the field. LOD = Limit of Detection.

Outlet Core

Approximate GPS Coordinates: 38°59’41.36” N, 76°57’16.15” W

Depth	%S	δ^{34}S
0-2.5	0.081	1.42
2.5-5.0	Below LOD	Below LOD
5.0-7.5	Below LOD	Below LOD
7.5-10.0	Below LOD	Below LOD
10.0-12.5	Below LOD	Below LOD
12.5-15.0	0.050	0.82
15.0-17.5	0.087	-0.16

17.5-20.0	0.141	-0.35
20.0-22.5	0.158	-1.2
22.5-25.0	0.128	0.76
25.0-27.5	0.146	-0.57
27.5-30.0	0.196	1.11
30.0-32.5	0.199	1.96
32.5-35.0	0.197	2.59
35.0-37.5	0.187	2.16
37.5-40.0	0.209	2.2
40.0-42.5	0.171	2.87
42.5-45.0	0.131	3.11

Figure 14: %S and δ^{34}S values for the outlet core. Depths are given as 2.5 cm-sections as the cores were sectioned in the field.
LOD = Limit of Detection.

Retention Core

Approximate GPS Coordinates: 38°59’31.14” N, 76°57’04.50” W

Depth	Bulk Density	%TOC	%S	S (mg/cm^3)	δ^{34}S
0-2.5	0.352	22.48	0.151	0.532	4.03
2.5-5.0	0.183	27.47	0.228	0.418	3.84
5.0-7.5	0.225	25.36	0.327	0.736	4.3
7.5-10.0	0.797	7.29	0.136	1.086	4.59
10.0-12.5	1.837	5.24	0.050	0.918	4.47
12.5-15.0	1.502	5.44	0.040	0.601	7.85
15.0-17.5	1.542	4.96	0.040	0.617	4.8
17.5-20.0	1.623	5.53	0.040	0.649	-1.78

Figure 15: Bulk density, %TOC, %S, mg S/cm^3, and δ^{34}S values for the retention core. Depths are given as 2.5 cm-sections as the cores were sectioned in the field.

Appendix II: List of Instruments Used

- VWR Scientific Products Model 1305Y Utility Oven
- Vacuum-assisted glass filter
- AB104 Mass Balance
- AT21 Mass Balance
- Eurovector Elemental Analyzer
- Isoprime Gas Source Isotope Ratio Mass Spectrometer
- Paragon enameling kiln