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QUANTIFYING SOLAR-POWERED REMOVAL OF AQUEOUS AND GASEOUS SULFIDE IN A MINE WATER PASSIVE TREATMENT SYSTEM

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QUANTIFYING SOLAR-POWERED REMOVAL OF AQUEOUS AND GASEOUS SULFIDE IN A MINE WATER PASSIVE TREATMENT SYSTEM

A THESIS APPROVED FOR THE SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

BY

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Abstract

Passive treatment systems can improve water quality for mine water discharges. However, some process units, like vertical flow bioreactors (VFBRs), may produce excess sulfide, which can be a source of nuisance odors and toxicity. Aqueous sulfide concentrations greater than 0.002 mg/L are considered chronically toxic to aquatic life, and prolonged human exposure to gaseous concentrations greater than 20 ppmv may lead to fatigue, poor memory and dizziness. In this study, a novel sulfide removal approach using a custom-designed solar-driven system and activated carbon filter (ACF) was evaluated. The study site, the Southeast Commerce passive treatment system (SECPTS) at the Tar Creek Superfund Site in Oklahoma, addresses 380 L/min of net alkaline lead-zinc mine waters in a four process unit passive treatment system. VFBR effluent enters a closed odor control structure (OCS) from which the sulfide-rich atmosphere is pulled into the ACF using a solar-powered exhaust blower. The ACF includes 180 kg of GC Sulfursorb activated carbon media. Aqueous sulfide concentrations were determined by laboratory analyses of surface grab water samples and gaseous sulfide concentrations were measured using a handheld gas detector and Draeger hydrogen sulfide gas detection tubes. Throughout the sampling period (December 2017-October 2018) maximum aqueous sulfide concentrations in the VFBR effluent were 83,750 µg/L, and gaseous sulfide concentrations in the OCS atmosphere were 950 ppmv, although values were typically lower. In addition to the sulfide removal system, solar-powered blowers re-aerate the water column in the post-VFBR final polishing unit (FPU). FPU effluent aqueous sulfide concentrations measured 131 ± 279 µg/L. ACF exhaust gaseous sulfide concentrations measured 41± 56 ppmv. Over the study period, approximately 14,000 kg S were retained by SECPTS, presumably mainly via bacterial sulfate reduction in the VFBR. Additionally, 100 kg gaseous S entered the ACF with 30 kg retained in the ACF media, 20 kg leaving the ACF as exhaust to the open atmosphere and 40 kg leaving the ACF in liquid form as sulfuric acid. Evaluation of the off-the-grid renewable energy-powered sulfide-removal and aeration systems indicates that they enhance water quality improvement effectiveness, efficiently remove gaseous sulfide and may be especially attractive for use in remote locations and/or at sites where operation and maintenance budgets are limited.

1.0 Introduction

Environmental contamination issues can arise from the mining process itself, material processing operations, dewatering, tailings leachate, flooding of abandoned mine workings, and the discharge of untreated mine water. These processes can cause land surface disturbances as well as ground and surface water contamination due to elevated trace metals and/or acidification (Younger et al., 2002). Perhaps the most severe of these impacts is the contamination and subsequent upwelling of water from underground mining sites. Mine drainage occurs because of activities that expose sulfide minerals to the weathering action of air and water (Hiibel et al., 2008). Mine drainage is typically characterized by elevated concentrations of trace metals and sulfate.

Most active mine drainage treatment facilities are modeled similarly to municipal wastewater treatment plants, as typical practice in the industry is to use conventional treatment methods for water contaminated during the mining process. Conventional mine drainage treatment aims to precipitate metals as hydroxides through the addition of lime or other alkaline materials, then flocculate and settle metal hydroxide sludge within a treatment plant (Akcil et al., 2004). Younger et al. (2002) discusses the most common method of active mine drainage treatment, ODAS (oxidation, dosing with alkali and sedimentation). Other treatment techniques include sulfidization (the process of reducing sulfate present in mine water to sulfide), sorption, filtration and ion exchange. However, these processes are chemical-dependent and very energy-intensive (Kalin, 2004).

More recently, passive treatment technologies have gained interest as a practical and more sustainable way to treat mine water. Passive treatment technologies use natural chemical, physical and biological processes to improve water quality. The ideal passive treatment system is not dependent on the input of chemicals and requires limited operation and maintenance (Hedin et al., 1994). These treatment systems can be particularly advantageous for use in remote locations and in cases where operation and maintenance budgets are limited. They are an application of ecological engineering, the design of sustainable ecosystems that integrate human society with its natural environment for the benefit of both (Mitsch and Jorgenson, 2004). Although passive treatment systems can improve water quality for untreated mine water discharges, some process units, like vertical flow bioreactors (VFBRs), may produce nuisance constituents, including excess sulfide (Kiran et al., 2017). Elevated sulfide concentrations are sources of nuisance odors and may lead to direct ecotoxicity. However, little research has been done addressing the issue of excess sulfide produced in the context of passive treatment, which is the focus of this research.

2.0 Literature Review

2.1 Mining Practices

Anthropogenic activities, including mining, redistribute metals within and between ecosystems (Allan, 1997). In general, mining is the extraction of minerals from geological formations. One major drawback associated with large-scale mining operations is the vast amount of waste generated. These wastes are produced in the form of water, waste rock (non-mineralized rock) and tailings (the remaining material left over from the extraction process). Allan (1997) reports

that a typical metal mine uses more water by weight during production than the weight of the ore grade material itself. Additionally, Hartman (2004) estimates that approximately 70% of all material excavated in surface mining is waste.

Mining processes can cause long-term contamination to the land itself, as well as to groundwater and surface water. The most common form of groundwater and surface water contamination caused by mining is the production of mine drainage. Most mined materials are chemically stable *in situ*. However, when excavated and exposed during the mining process these materials can become chemically unstable. Mine drainage is typically formed when rocks containing metal sulfides (e.g., FeS_2, PbS and ZnS) are exposed to the weathering actions of oxygen and water. Acid mine drainage (AMD) is characterized by low pH and trace metal contamination. However, mine drainage chemistry differs on a site-by-site basis because of its dependence on mineralogy and other geologic and hydrologic variables. In some areas with carbonate geology, mine drainage can be considered net alkaline in that carbonate dissolution produces alkalinity at a faster rate than pyrite oxidation produces acidity (Younger et al., 2002).

2.2 Typical Passive Treatment Techniques

The treatment of mine water typically requires the coupling of oxidative and reductive conditions, removal of trace metals, pH adjustment and retention of solids. “Active” treatment techniques are conventional practices that improve water quality using methods that require ongoing inputs of energy and/or chemical reagents (Younger et al., 2002). “Passive” treatment techniques aim to improve water quality using natural chemical, physical and biological processes that require no chemical inputs and limited operation and maintenance costs (Hedin et

al., 1994). Costello (2003) performed a comprehensive review and comparison of active and passive treatments for mine water discharges and found that, given the seriousness and extent of mine drainage and associated contamination, the results of passive treatment are encouraging.

It is well documented within the literature that passive treatment process units can successfully improve water quality (Hedin et al., 1994; Younger et al., 2002; Cravotta, 2007; Strosnider and Nairn, 2010; Amezaga et al., 2011; LaBar and Nairn, 2018). However, passive treatment systems differ from conventional treatment systems in that they require more land area and longer detention times to make up for the lack of chemical additives. Passive treatment techniques may be particularly advantageous at abandoned mining sites, which are often in remote locations. Although the treatment units in each system are site-specific and dependent on the type of water chemistry and mass loadings present, the typical components of a passive treatment system include oxidation ponds (which promote iron oxidation and trace metal sorption), treatment wetlands (which settle and retain precipitated iron), vertical flow bioreactors (VFBRs) (which promote bacterial sulfate reduction and metal sulfide formation) and final polishing units or ponds. A typical VFBR cross-section is shown in Figure 2.1.

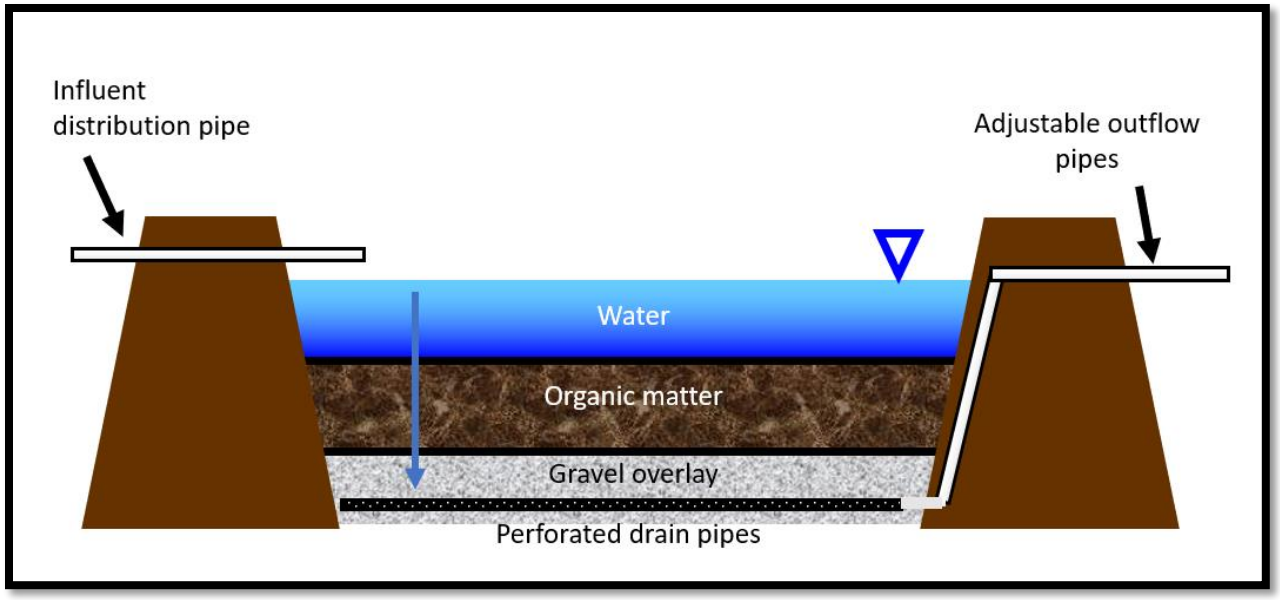

Figure 2.1. *Typical VFBR cross-section*

2.3 Production of Sulfide in VFBRs

VFBRs may be used in passive treatment to produce bicarbonate alkalinity and remove trace metals and sulfate from mine water (Watzlaf et al., 2004; Nairn et al., 2009). These bioreactors contain an organic carbon substrate that supports anaerobic sulfate reducing bacteria (Hiibel et al., 2008). During bacterial sulfate reduction, bacteria oxidize the organic carbon substrate and reduce the sulfate in the mine water to sulfide, resulting in the precipitation of metal sulfides. The reactions describing this process are written as follows:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad (1)$$

$$H_2S + M^{2+} + 2HCO_3^- \rightarrow \ MS(s) + 2H_2O + 2CO_2 \qquad (2)$$

where "CH_2O" represents a generic organic carbon substrate and M^{2+} represents a divalent metal, commonly Zn, Fe, Pb, Ni, or Cd. It is important to note that the reactions are net neutral with regards to alkalinity if all sulfide is used in metal sulfide precipitation.

Sulfate reducing bacteria that participate in these processes have been previously studied (Dvorak et al., 1992; Kaksonen et al., 2004; Neculita et al., 2011; Kiran et al., 2017). During sulfate reduction, the sulfate reducing bacteria in VFBRs often produce *excess* sulfide, or more than that needed for metal sulfide formation. For net acidic mine waters, VFBRs are primarily used to neutralize acidity through the production of bicarbonate, in which case the production of excess sulfide is necessary (LaBar and Nairn, 2018). However, for net alkaline mine waters the primary use for VFBRs is to remove trace metals through the precipitation of metal sulfides, where although production of excess sulfide is not desired, it often occurs and leads to nuisance concerns.

2.4 Sulfide Gaseous and Aquatic Toxicity

Aside from being malodorous as a waste gas, sulfide can also be hazardous to aquatic and human life at certain concentrations, as well as be corrosive to equipment (Williams and Miller, 1992; Yang and Allen, 1994). Both chronic and acute exposure to sulfide can be harmful. Aqueous sulfide concentrations greater than 0.002 mg/L are considered chronically toxic to aquatic life (United States Environmental Protection Agency, 1986). There have been several studies on aqueous sulfide toxicity to various organisms including the work of Affonso et al. (2004), Frawley et al. (2017) and Li et al. (2017). Gaseous hydrogen sulfide can be acute and chronically toxic to aquatic organisms as well. In 1976, the United States Environmental Protection Agency performed hydrogen sulfide acute and chronic toxicity tests on seven species of fish and eight invertebrates using continuous-flow bioassays. In 159 acute tests, lethal threshold concentrations for juvenile fish ranged from 0.0087 mg/L in rainbow trout (*Oncorhynchus mykiss*) to 0.0840 mg/L in goldfish (*Carassius auratus)*. In chronic exposure to hydrogen sulfide in 29 tests

running up to 825 days, the maximum no effect level ranged from 0.0004 mg/L in bluegill (*Lepomis macrochirus)* to 0.0100 mg/L in goldfish (*Carassius auratus)*. The 96-hour LC50 for invertebrates exposed to hydrogen sulfide ranged from 0.020 mg/L in mayflies (*Baetis)* to 1.070 mg/L in isopods (*Asellus)* (Smith et al., 1976).

Gaseous concentrations of hydrogen sulfide can adversely affect humans; concentrations above 10 ppm can cause damage to the human central nervous system (Rattapan et al., 2011). According to Guidotti (2010), the human odor threshold at concentrations of 0.01 to 0.3 ppm can detect hydrogen sulfide. Concentrations of 1-5 ppm may cause nausea, eye irritation, and headaches, and 10 ppm is the OHSA permissible exposure limit (Guidotti, 2010).

2.5 Sulfide Removal

Several studies on sulfide removal have been done and are reported in the literature; however, most are in the context of wastewater, industrial or petroleum processes. Rattapan et al. (2012) reviewed removal of hydrogen sulfide through various biofiltration techniques, specifically using *Thiobacillus* sp. as the sulfide oxidizing bacteria in the biofilm. Ben Jaber et al. (2016) studied the effects of several parameters, including pH and gas concentrations, on the removal of hydrogen sulfide under acidic conditions using biofilters packed with expanded schist. Activated carbon media has also been used as a promising approach to remove hydrogen sulfide and organic pollutants through adsorption (Nguyen-Tanh and Bandosz, 2005; Gupta and Saleh, 2013; Sitthikhankaew et al., 2014). Activated carbon media works well for the removal of hydrogen sulfide gas because of its unique properties including high surface area and pore volume (Bagreev and Bandosz, 2005). The presence of humidity in the gas stream facilitates the reaction

of hydrogen sulfide oxidation, and the pores in the activated carbon media can store oxidation products (elemental sulfur, sulfur dioxide and/or sulfuric acid) (Bagreev et al., 2005). Bagreev et al. (2005) found that while one of the most important factors influencing the lifetime of an activated carbon filter used to remove hydrogen sulfide is the influent hydrogen sulfide gas concentration, other factors including temperature, oxygen content and the presence of multiple constituents in the gas stream can also affect filter lifetime. However, activated carbon filters used to remove hydrogen sulfide from moist air streams can sometimes have disadvantages. Hydrogen sulfide is oxidized to either sulfur or SO_2, and in the presence of adsorbed water, SO_2 can be further oxidized to produce sulfuric acid (Bagreev and Bandosz, 2005), as presented in equations 3-4.

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \qquad (3)$$

$$2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4 \qquad (4)$$

Additionally, some caustic-impregnated carbon media can self-ignite due to low ignition temperatures during the exothermic reaction, which can result in additional costs to extinguish the fire and clean up the area (Bagreev et al., 2000).

2.6 Renewable Energy Used in Passive Treatment

Aeration in passive treatment systems is the driving force of iron oxidation and is important in treatment of the effluent of low DO-producing process units, like VFBRs. Typically, aeration in passive treatment systems is achieved by utilizing elevation changes or pressure head differences, or through entrainment of air by introducing turbulent flow (Nairn, 2015). Renewable energy can be particularly useful in the context of passive treatment when working in a relatively flat landscape where there is not enough difference in elevation or pressure head to

effectively aerate the water. Aeration systems typically use a renewable power source (usually wind- or solar-power) to build and store pressure in an air compressor. When the pressure is released through a submerged diffuser at the bottom of the pond, the air bubbles rise to the surface, causing a disturbance in the water column that helps to entrain oxygen (Nairn, 2015).

3.0 Hypotheses and Objectives

3.1 Hypotheses

The hypotheses for this research were:

1. Bacterial sulfate reduction in the VFBR produces excess sulfide beyond that needed for trace metal precipitation
2. Capture and removal of gaseous sulfide will decrease aqueous sulfide concentrations
3. The use of a solar-driven blowers and an ACF will effectively remove gaseous sulfide
4. The use of solar-driven float mix aerators (FMAs) will effectively remove aqueous sulfide in the final polishing unit (FPU)
5. Estimates of sulfur species in aqueous, gaseous and solid phases will account for a reasonable estimation of sulfur in a passive treatment system

3.2 Objectives

The objectives required to test the hypotheses for this research are:

1. Quantify aqueous sulfate and sulfide in successive process units from in a passive treatment system
2. Quantify gaseous sulfide within the odor control system atmosphere, granular activated carbon filter (ACF) exhaust and ambient air
3. Evaluate performance and quantify sulfide removal in ACF

4. Quantify changes in aqueous and gaseous phase sulfide caused by use of FMAs
5. Estimate a mass balance of all sulfur species in specific process units

4.0 Methods

4.1 Study Site

The Tri-State Lead-Zinc Mining District, (Figure 4.1), encompasses approximately 6,500 square kilometers of land in Oklahoma, Missouri and Kansas. This area was heavily mined for lead and zinc between 1885 and 1970, leaving behind approximately 500 million tons of mining waste including chat and mill tailings. The Oklahoma portion of the Tri-State Mining District is the Tar Creek Superfund site (ODEQ, 2017). The Tar Creek Superfund site was added to the National Priority List (NPL) in 1983 after it was found that there were elevated concentrations of iron, lead, zinc, and cadmium in water, chat, soils and biota.

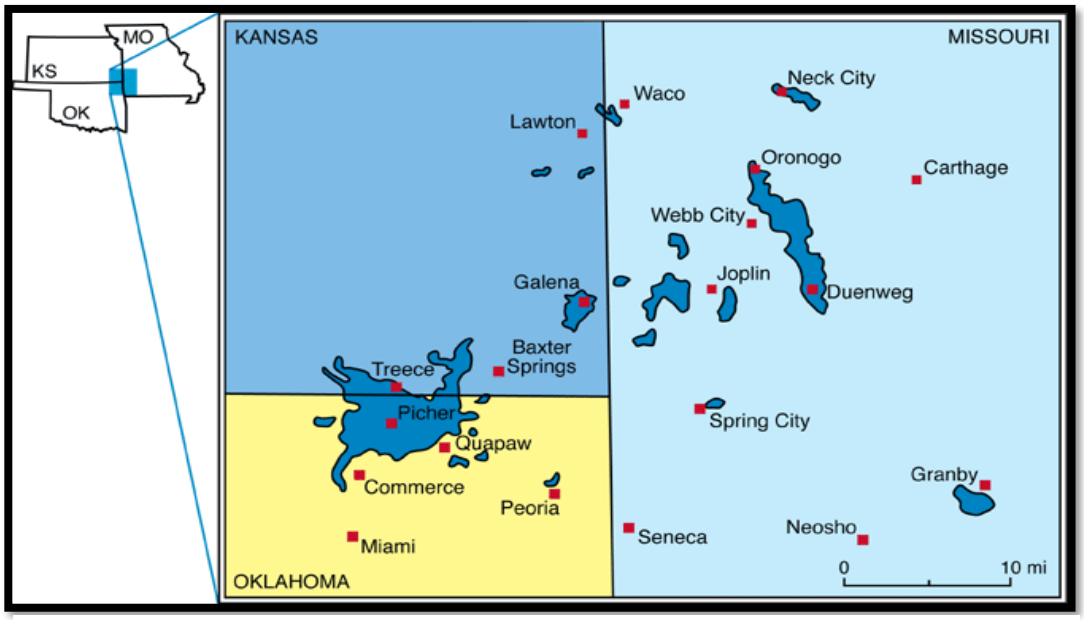

Figure 4.1. *Location of the Tri-State Mining District (Brosius and Sawin, 2001)*

4.1.1 Southeast Commerce Passive Treatment System

This study focuses on the Southeast Commerce passive treatment system (SECPTS), which is in the southwestern corner of the Tar Creek Superfund site, near Commerce, Oklahoma. At this site, an artesian discharge from an underground mine collapse feature began flowing in 1979. In 2006, the land was reclaimed, and a subsurface drainage structure installed which discharged polluted waters directly into an unnamed tributary to Tar Creek. In 2016-2017, SECPTS was constructed. SECPTS addresses approximately 380 L/min of net alkaline lead-zinc mine waters in four process units: oxidation pond (OP), wetland (WL), vertical flow bioreactor (VFBR) and final polishing unit (FPU), as seen in Figure 4.2. SECPTS utilizes a custom-designed solar-powered aeration and sulfide removal system. The system includes a 3,180-W photovoltaic module, combiner box, two charge controllers, a bank of eight 6V/400 AH/20HR batteries, 1500-W 24V DC inverter, two blowers with pressure kits and one blower with vacuum kit, some of which housed in a small shed located near the ACF. The solar-driven system is used to power a total of four float mix aerators and an odor control system. (Nairn et al., 2018). WL effluent water enters on the north side of the VFBR and flows down vertically to a four-cell drainage structure composed of perforated PVC pipes overlaid with river gravel, with each of the four cells having individual outlet discharge pipes. On top of the gravel layer sits the organic substrate needed for bacterial sulfate reduction. The substrate is composed of approximately 760 cubic meters of single-shredded wood chips (~80% by volume) and approximately 190 cubic meters of spent mushroom compost (~20% by volume). Water levels are controlled by four outlet risers from individual VFBR cells. Throughout the sampling period, all risers were at equal elevations (i.e., each cell draining approximately the same amount of water). VFBR effluent waters enter a closed odor control structure (OCS) from which the sulfide-rich atmosphere is pulled into an

activated carbon filter (ACF) using a solar-powered exhaust blower, as shown in Figure 4.3.

The OCS and ACF systems were custom-designed by BioMost, Inc. The ACF includes 180 kg of GC Sulfursorb Plus activated carbon media. GC Sulfursorb Plus is a non-impregnated activated carbon media made to remove hydrogen sulfide gas from air streams. This media has a minimum breakthrough capacity of 0.20 g H_2S/cc carbon (General Carbon 2018), and the ACF system has an approximate detention time of 47 seconds. Additional media specifications are presented in Table 4.1, and a detailed schematic of the ACF is presented in Figure 4.4. In addition to the sulfide removal system, solar-powered blowers re-aerate the water column using float mix aerators (FMAs) in the OP and post-VFBR FPU.

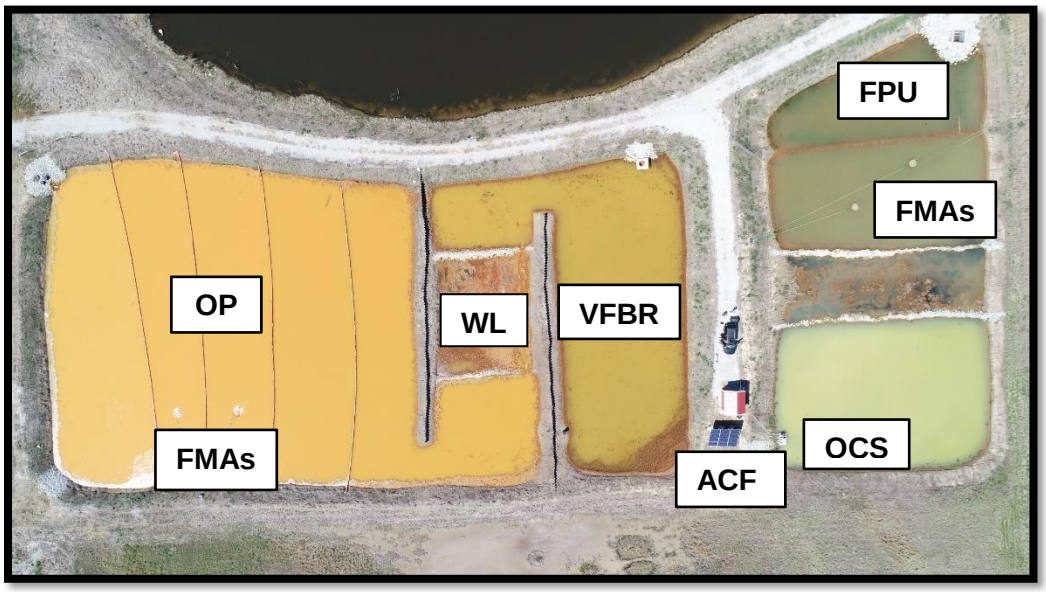

Figure 4.2. *Aerial view of SECPTS showing four process units (oxidation pond (OP), wetland (WL), vertical flow bioreactor (VFBR) and final polishing unit (FPU)) and locations of float mix aerators (FMAs), odor control structure (OCS) and activated carbon filter (ACF) captured with a DJI Phantom 4 Pro+ small unmanned aircraft system on September 15, 2018.*

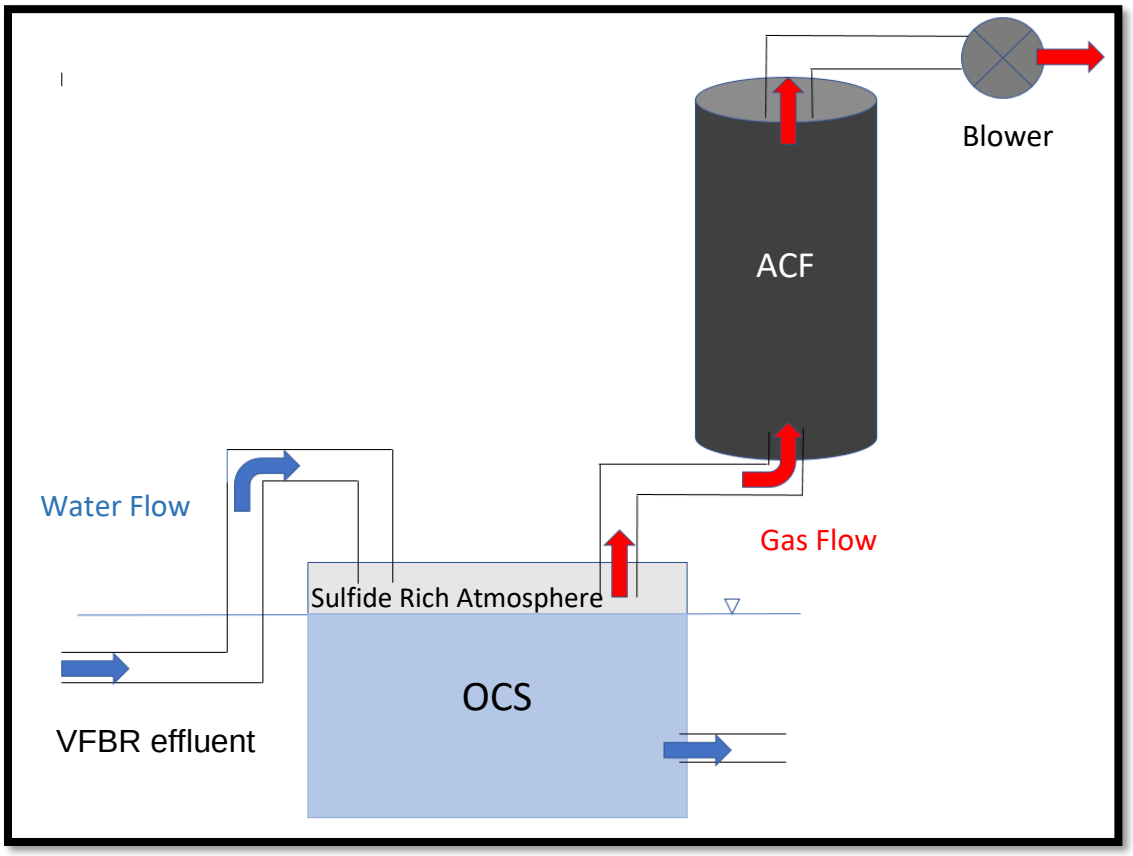

Figure 4.3. *Vertical flow bioreactor* **(***VFBR) effluent is captured by the Odor Control Structure (OCS) and pulled into the Activated Carbon Filter (ACF) by a solar driven exhaust blower (located inside shed)*

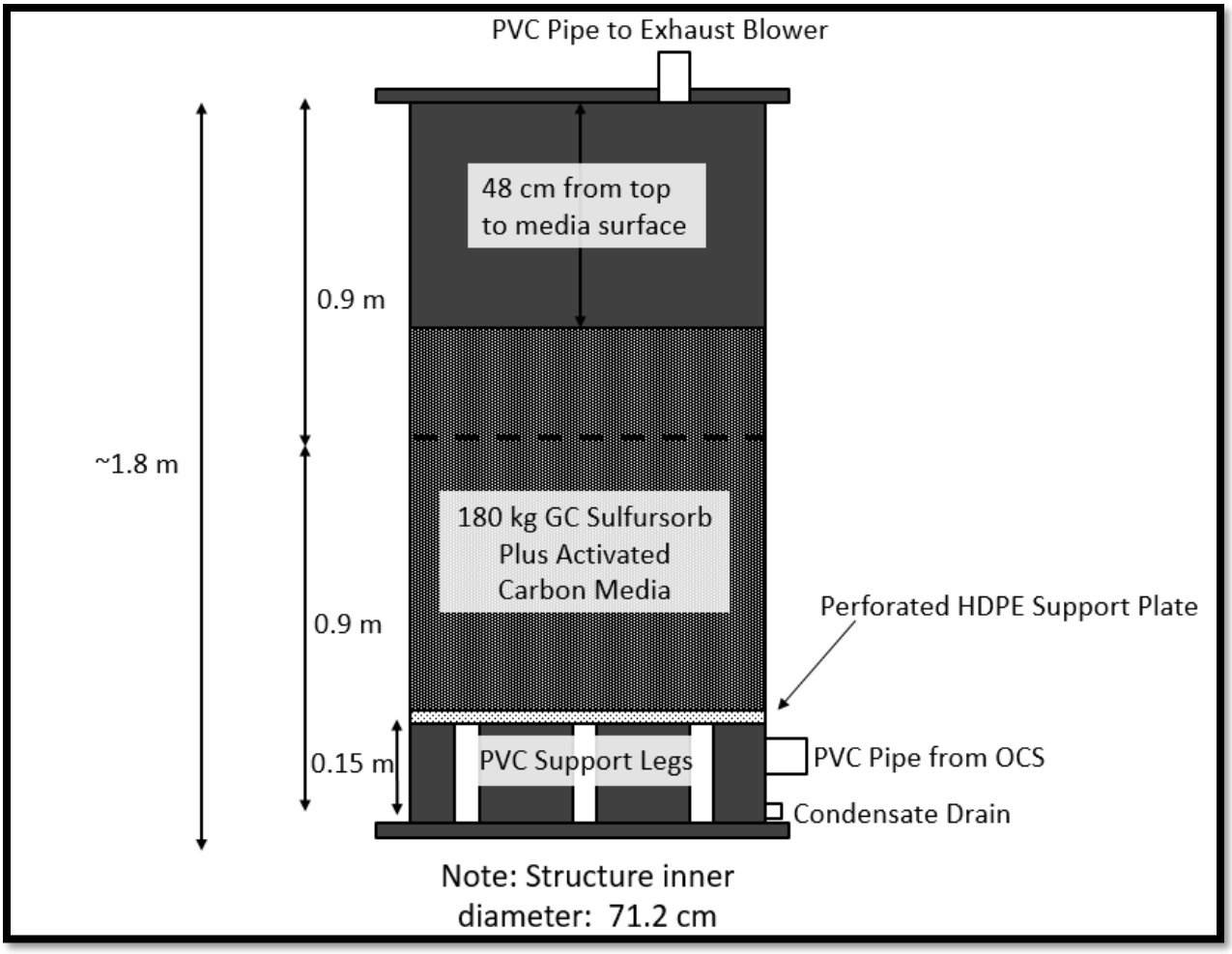

Figure 4.4. *Detailed schematic of Activated Carbon Filter (ACF)*

Table 4.1. *Activated Carbon Filter (ACF) media specifications as provided by General Carbon Corp. (2018)*

Media Specifications	
Mesh size	$\frac{1}{4}$"x$\frac{1}{8}$"
Less than No. 4 (%)	5 (maximum)
Greater than No. 8 (%)	10 (maximum)
Mean particle diameter (mm)	3.4
Moisture as packaged (%)	8 (maximum)
Typical density (g/cc)	0.40
Hydrogen sulfide breakthrough capacity (g H_2S/ cc carbon)	0.20 (minimum)
Hydrogen sulfide breakthrough capacity (weight on weight, %)	0.50 (minimum)

4.2 Water Quality Sampling

Samples for water quality analyses were taken from the system inflow, as well as outflows of the OP, WL, VFBR and FPU. Temperature, pH, dissolved oxygen, oxidation-reduction potential, total dissolved solids, conductivity and specific conductance were determined *in situ* with a YSI 600QS multiparameter data sonde and YSI 650MDS display. Total alkalinity and turbidity were measured immediately upon sample collection via titration with appropriate normality sulfuric acid using a Hach digital titrator (Method 8203) and via a Hach 2100P turbidimeter, respectively. Water samples for dissolved metals analyses were filtered on site through 0.45-µm disposable filters using a hand pump, and the filtered samples were collected in a 250-mL HDPE bottles and

preserved with trace metal grade HNO_3 to pH <1 until analyzed. Water samples for total metals analyses were collected unfiltered in 250-mL HDPE bottles and preserved with trace metal grade HNO_3 to pH <1. Sulfate samples were also collected in 250-mL HDPE bottles with zero headspace. All analyses were completed at the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma. Preserved samples for metals analyses were nitric acid digested in a CEM MARSXpress Digestion System following EPA Method 3015 (EPA 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) following EPA Method 6010b (EPA 2006) for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, S, and Zn.

Additional surface grab samples were taken at VFBR and FPU outflows and, from June 2018 to October 2018, and at three additional sites within FPU (FPU Cell #1, FPU Cell #2 and FPU Cell #3 as shown in Figure 4.5). For these samples, analytes included chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), and aqueous sulfide. Sulfate, sulfide and COD samples were collected in 250-mL HDPE sample bottles and BOD_5 samples were collected in 1-L HDPE sample bottles. Sulfide samples were preserved with 2.5 mL of 2N zinc acetate and 2.5 mL of 1 N sodium hydroxide. All samples were preserved as appropriate and stored in a cooler at 4°C until analyzed in the laboratory.

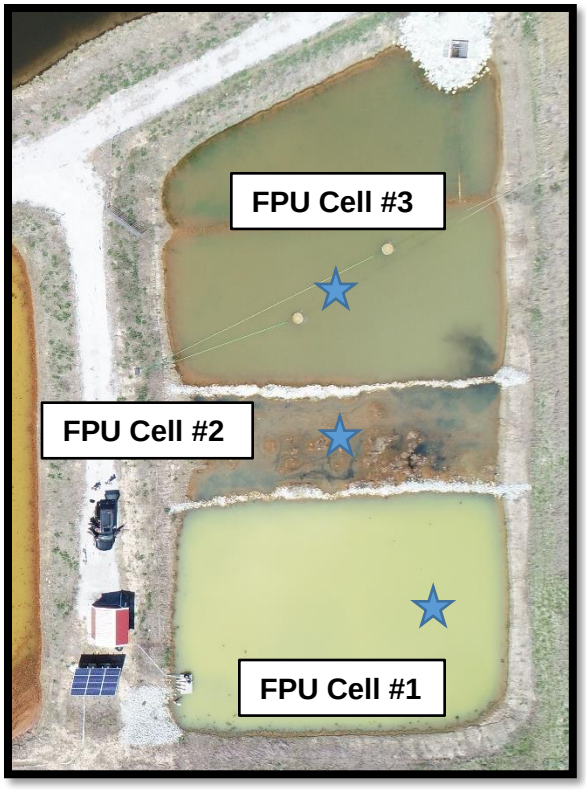

Figure 4.5. *Additional Final Polishing Unit (FPU) sampling locations, with sampling location indicated by star*

4.3 Volumetric Discharge Rate Measurements

Volumetric flow rates were measured at the effluent of the VFBR and the effluent of the FPU. Flow rates at the VFBR effluent were measured using a 20-L calibrated bucket and stop watch and recorded. VFBR effluent was captured by four open-flow pipes. Flows were taken five times at each of the four pipes, averaged and summed to account for the total effluent discharge rate. Water elevations in the FPU effluent outflow structure were gathered using a Solinst LevelLogger pressure transducer deployed within the outflow structure and adjusted for barometric pressure. Additionally, water elevations determined by the pressure transducer were checked with a staff gauge located inside the outflow structure. Flow rates at the FPU effluent were calculated using the 90-degree sharp-crested weir equation and water depths collected by

the pressure transducer.

4.4 Air Quality Sampling

An Industrial Scientific GasBadge Pro personal single gas monitor was used to measure gaseous H_2S concentrations in parts per million by volume (ppmv). H_2S measurements were taken in ambient air, in the open atmosphere on top of the OCS, inside the closed atmosphere of the OCS, from the ACF exhaust and in the atmosphere directly above the four open-flow VFBR effluent pipes. The GasBadge Pro was positioned in each of the sampling locations and allowed to stabilize for two minutes. After stabilization, an average measurement was recorded. For H_2S concentrations above the detection limits of the GasBadge Pro (500 ppmv), H_2S Draeger tubes and a Draeger Accuro handheld pump were used to measure gaseous concentrations in the range of 100 to 2000 ppmv. Additionally, H_2S Draeger tubes with a detection limit of 2-200 ppm were used to check the accuracy of the GasBadge Pro.

4.5 Air Flow Measurements

A Kanomax Climomaster Anemometer was used to measure air flow rates, temperature, and relative humidity. Air flow rate measurements were taken in-line at the blowers (housed inside the shed) pushing air to the FMAs located in the OP and FPU, at the OCS effluent pipe, and from the ACF exhaust. The instrument automatically calculated the maximum, minimum and mean of each constituent while running in “Calculation mode” with a sampling time of 10 seconds and a trial number (n) of 3.

4.6 Water Quality Laboratory Analyses

The information in Table 4.2 summarizes the water quality analytes and respective analytical methods.

Table 4.2. *Laboratory Water Quality Analytes and Corresponding Methods*

Parameter	Method
COD	APHA 5220D
BOD_5	EPA 5120B
Trace Metals	EPA 3015A; EPA 6010C
Sulfide	EPA 8131
Sulfate	EPA 300.1
Turbidity	EPA 180.1
Alkalinity	EPA 310.1

4.7 VFBR Substrate Analyses

Five substrate samples were collected from the VFBR using a three-inch diameter closed bucket auger and core tubes at the approximate sampling locations shown in Figure 4.6. Substrate core samples were collected and immediately placed in Ziploc bags and evacuated and sealed with a handheld vacuum system. All substrate samples were stored in a cooler on ice until analyzed. The samples were analyzed for acid-volatile sulfide (AVS) according to Leonard et al. (1996) and Brouwer and Murphy (1994) and EPA 8131, and moisture content according to ASTM Method D4531-86 (2008). Additionally, these samples were nitric acid digested in a CEM MARSXpress Digestion System following EPA Method 3051 (EPA, 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer for metals and total sulfur content.

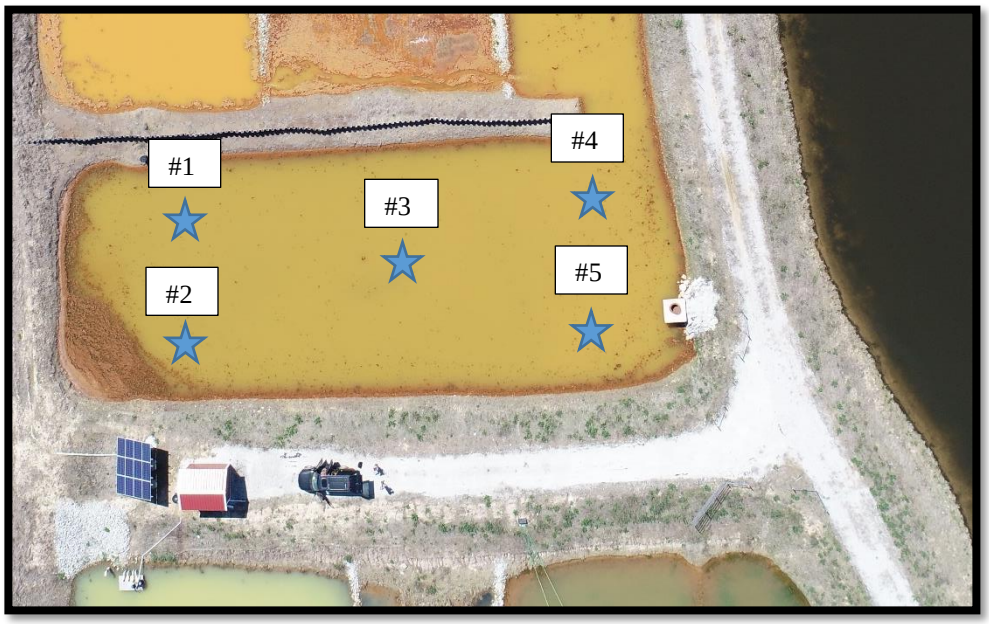

Figure 4.6. *Vertical Flow Bioreactor (VFBR) substrate sampling locations, indicated by star*

4.8 ACF Media Analyses

On October 12, 2018, the ACF was taken offline and the activated carbon media was sampled. Activated carbon media was sampled from the surface and composited from three cores at depths of 20 to 25 centimeters, 46 to 51 centimeters, 71 to 76 centimeters, 97 to 102 centimeters and 114 to 119 centimeters. Locations of the three cores and respective depths are shown in Figures 4.7 and 4.8. Additional samples were collected of the surface media and what appeared to be deposits of elemental sulfur along the rim of the HDPE container housing the media. Approximately 100 grams of activated carbon media was collected from each of three cores at depth and immediately placed in vacuum-sealed Ziploc bags. The samples were analyzed for acid volatile sulfide (AVS) following a method by Leonard et al. (1996) modified from Brouwer and Murphy (1994) and EPA 8131 in triplicate. The activated carbon media was also nitric acid digested in a CEM MARSXpress Digestion System following EPA Method 3051 (EPA, 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively

Coupled Plasma-Optical Emission Spectrometer for metals and total sulfur content. Additionally, activated carbon media samples were also analyzed for moisture content according to ASTM Method D4531-86 (2008).

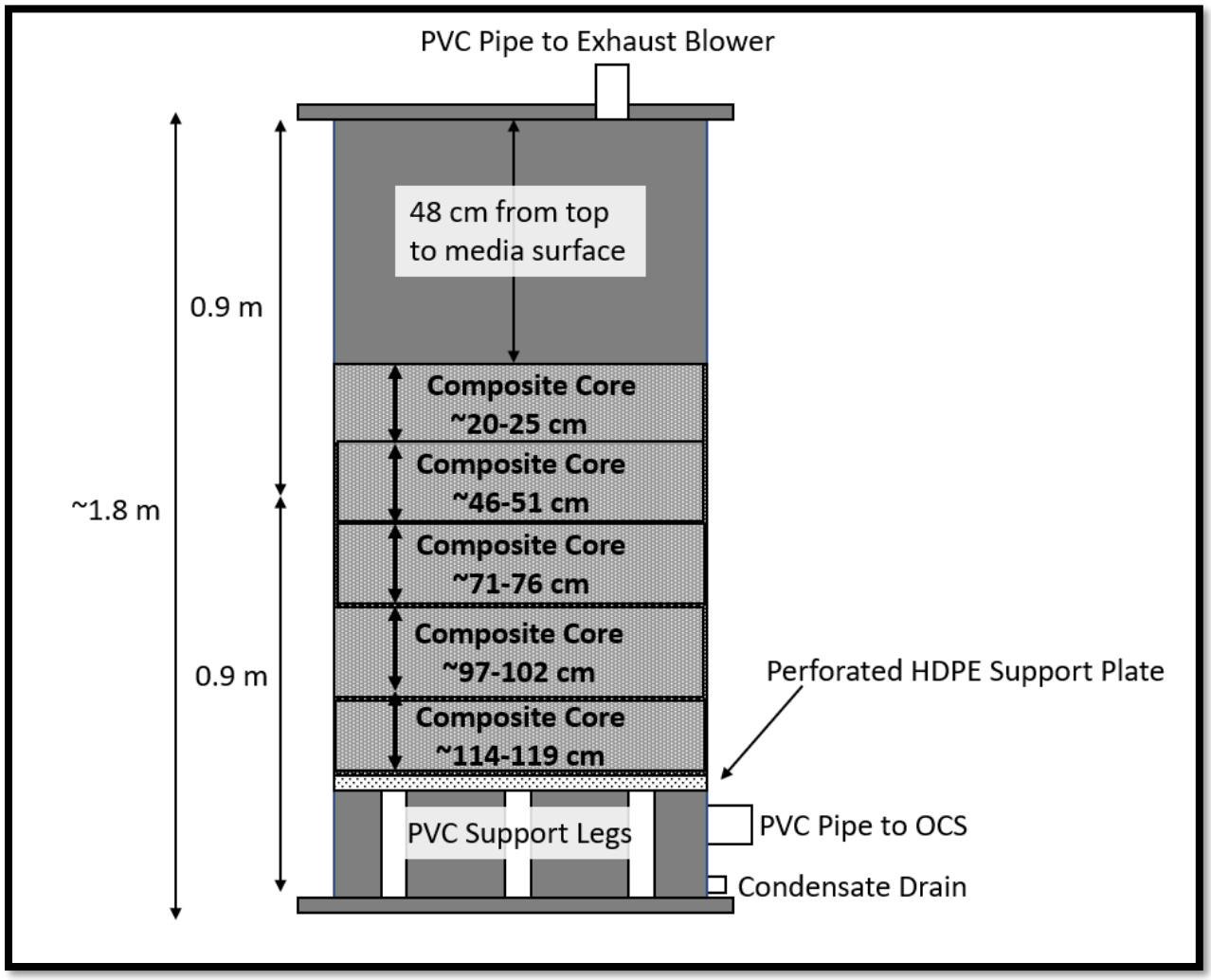

Figure 4.7. *Schematic of Activated Carbon Filter (ACF) including composite core sampling locations/depths*



Figure 4.8. *Activated carbon media core samples at depth 20-25 centimeters*

4.9 Data Quality Assurance, Quality Control and Statistical Analyses

To ensure statistically valid results and conclusions, several statistical analyses of the collected data were performed. For the comparison of H_2S measurements entering and exiting the ACF, VFBR influent and effluent water quality and FPU influent and effluent water quality, a means comparison was performed via Student's t-test. Additionally, CREW standard operating procedures for sample collection and data analyses were followed to ensure scientifically valid data and results. Standard quality assurance/quality control protocols were performed to test

precision, accuracy and representativeness. Sample collection included a laboratory blank, field blank, duplicate sample and spike sample.

5.0 Results and Discussion

5.1 SECPTS Performance

Water enters the first process unit, the OP, from three distinct upwellings. In addition to the North and South inflows, there is a third upwelling in the OP that was discovered during SECPTS construction. This inflow is not captured in a pipe, but upwells in the southwestern corner of the OP, and is estimated to contribute an approximate flowrate of 3-4 L/sec based on calculation of differences from measured inflows and outflows. SECPTS influent water quality data are summarized in Table 5.1. These water quality characteristics are typical of net-alkaline mine water discharges, with a pH > 5.64 (Younger et al., 2002). System influent enters the OP where the focus is iron oxidation, hydrolysis and settling. The first set of FMAs are designed to provide additional oxygenation. Water flows from OP to WL, which focuses on trace metal sorption, and then from WL to VFBR where bacterial sulfate reduction occurs. Water flows from the VFBR to the final process unit, the FPU, where the focus is reaeration using FMAs and settling of solids.

Table 5.1. *Southeast Commerce Passive Treatment System (SECPTS) Influent Water Quality*

Parameter		Sample size (n)*
pH	5.8-6.6	54
Total Alkalinity (mg/L)	297-415	53
Turbidity (NTU)	0.710-11.8	53
Total Fe (mg/L)	110-180	54
Total Zn (mg/L)	5.4-8.3	42
Total Cd (µg/L)	<PQL-30	40
Total Pb (µg/L)	50-290	42
Total As (µg/L)	<PQL-430	37
SO_4^{2-} (mg/L)	1800-2300	52

*Sample size represented by number of analyses greater than practical quantitation limit.

Mean total and dissolved fractions of trace metals into and out of the VFBR are summarized in Table 5.2. Additionally, VFBR and FPU mean physical parameter data are presented in Table 5.3, along with BOD_5 and COD data in Table 5.4. These data show that conditions within the VFBR are ideal to support anaerobic sulfate reducing bacteria, by providing a low oxygen environment and reducing conditions (Hiibel et al., 2008; Younger et al., 2002).

Table 5.2. *Mean total and dissolved metals in the Wetland Outflow (WL-Out) and Vertical Flow Bioreactor Outflow (VFBR-Out)*

	Ca (mg/L)	Cd (mg/L)	Co (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)
WL-Out										
Total	627	0.002	0.042	5.25	149	2.51	77.1	0.517	0.054	5.32
Dissolved	624	0.002	0.044	1.13	146	2.54	74.6	0.519	0.060	5.15
VFBR-Out										
Total	631	0.001	0.009	1.05	150	2.63	79.7	0.072	0.051	0.171
Dissolved	639	0.001	0.008	0.984	147	2.68	77.1	0.082	0.047	0.025

Table 5.3. *Mean water quality physical parameters in the Vertical Flow Bioreactor outflow (VFBR-Out) and Final Polishing Unit outflow (FPU-Out) with standard error. Sample size (n)=19. ND = no data*

Parameter	VFBR-Out	FPU-Out
pH	6.47±0.06	6.89±0.07
Oxidation reduction potential (ORP) (mV)	-194.0±22	48.9±27
Dissolved oxygen (mg/L)	ND	6.77±0.73
Temp (degrees Celsius)	19.3±1.9	17.4±1.8

Table 5.4. *Mean Five-Day Biological Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) concentrations from Vertical Flow Bioreactor (VFBR) to Final Polishing Unit Outflow (FPU-Out) with standard error. Sample size (n=9)*

	BOD_5 (mg/L)	COD (mg/L)
VFBR-Out	5.37±0.47	64.8±22
FPU Cell #1	3.97±0.58	40.0±7.5
FPU Cell #2	4.36±0.50	35.4±6.3
FPU Cell #3	3.96±0.57	29.3±4.8
FPU-OUT	5.27±0.90	24.5±3.1

5.2 Aqueous Sulfate and Sulfide Results

Measurements of aqueous and gaseous sulfide throughout the sampling period suggest that bacterial sulfate reduction is occurring in the VFBR and producing more sulfide than needed for trace metal precipitation. Monthly aqueous sulfide data from VFBR-Out to FPU-Out are summarized in Table 5.5 and Figure 5.1 and mean aqueous sulfate and sulfide concentrations throughout SECPTS are shown in Figure 5.2. The large standard deviations seen in the mean aqueous sulfide data can be attributed to seasonal changes, since bacterial sulfate reduction is a biological process where production is generally increased with increased temperature (Lovell and Konopka, 1985).

Table 5.5. *Monthly aqueous sulfide data from the Vertical Flow Bioreactor (VFBR) outflow to the Final Polishing Unit (FPU) outflow. ND= no data*

Aqueous Sulfide (µg/L)					
	VFBR-Out	FPU Cell #1	FPU Cell #2	FPU Cell #3	FPU-Out
June 2017	147	123	85	22	15
July 2017	24	66	28	39	26
August 2017	9	11	22	28	12
September 2017	10	ND	ND	ND	2
October 2017	3270	ND	ND	ND	5
November 2017	2.5	ND	ND	ND	2.5
December 2017	ND	ND	ND	ND	ND
January 2018	2	ND	ND	ND	2.5
February 2018	2.5	ND	ND	ND	2.5
March 2018	1670	ND	ND	ND	5
April 2018	14800	ND	ND	ND	26
May 2018	36800	ND	ND	ND	3
June 2018	58700	4050	2800	1200	600
July 2018	78700	13200	7900	2700	500
August 2018	83750	19600	13000	3100	1000
September 2018	5293	250	250	40	20
October 2018	4700	100	35	17	8

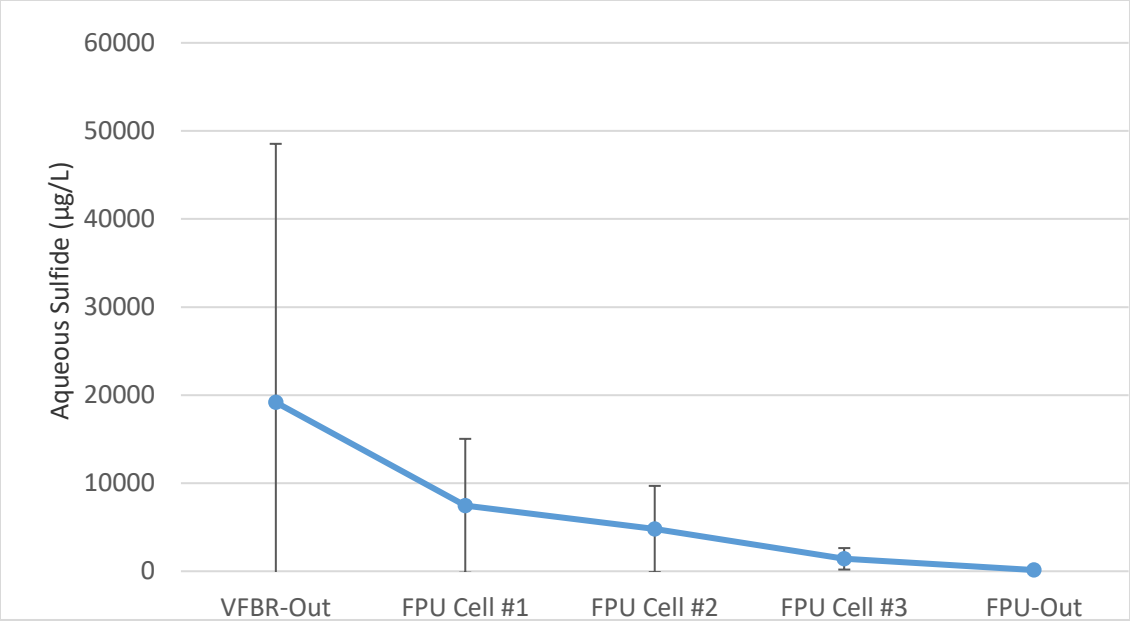

Figure 5.1. *Mean aqueous sulfide from the Vertical Flow Bioreactor (VFBR) outflow to the Final Polishing Unit (FPU) outflow. Sample size (n)= 17. Error bars show standard deviation*

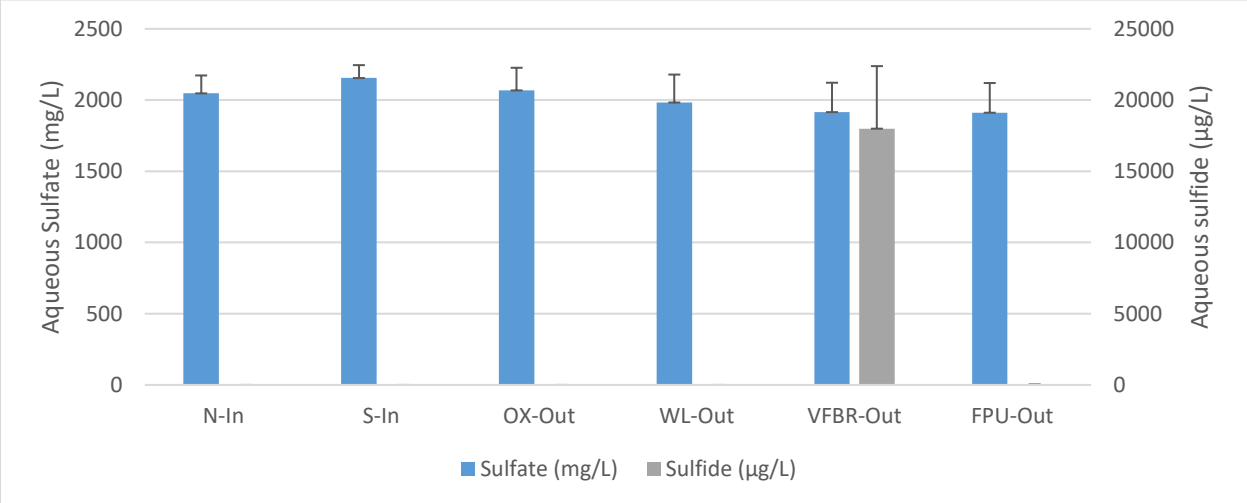

Figure 5.2. *Aqueous sulfate and sulfide data throughout the Southeast Commerce Passive Treatment System (SECPTS). Sample size for sulfate data (n)=17 and for sulfide data at Vertical Flow Bioreactor Outflow (VFBR-Out) and Final Polishing Unit Outflow (FPU-Out) sample size (n)=16. Error bars show standard deviation. Note sulfate concentrations are in mg/L and sulfide concentrations are in µg/L*

Additionally, the presence of anaerobic, photosynthetic sulfur oxidizing bacteria (e.g., *Chromatium* spp.) was noted in the FPU and in VFBR effluent pipes during the summer months of the sampling period, as shown in Figures 5.3 and 5.4. These phototrophic bacteria thrive in anaerobic, sulfur enriched environments and oxidize sulfide to sulfate or sulfur (Bharathi, 2008), another indication of excess aqueous sulfur compounds being produced in the VFBR.



Figure 5.3. *Purple sulfide oxidizing bacteria seen in Final Polishing Unit (FPU) in June 2018*



Figure 5.4. *Purple sulfide oxidizing bacteria seen in a cap on the Vertical Flow Bioreactor (VFBR) effluent pipes*

The VFBR contains approximately 790 total cubic meters of substrate. Based on this value and the mean values for WL-Out and VFBR-Out aqueous sulfate concentrations, the approximate aqueous sulfate removal rate was found to be about 488 mM sulfate per cubic meter of substrate per day. Typical sulfate removal rates in similar constructed treatment systems range from 300 millimoles sulfate per cubic meter of substrate per day to around 800 millimoles sulfate per cubic meter of substrate per day (mM/m^3d) (Younger et al., 2002). Therefore, it appears the VFBR is functioning as designed with regard to rates of bacterial sulfate reduction.

5.3 Gaseous Sulfide Results

Throughout the sampling period for gaseous sulfide (December 2017 to October 2018), ACF effluent hydrogen sulfide gas concentrations were significantly lower than ACF influent concentrations ($p=0.009$). Figure 5.5 shows gaseous hydrogen sulfide concentrations in the OCS

atmosphere (considered ACF influent) and exiting the filter in the ACF exhaust (considered effluent). During the May 2018 sampling, the hydrogen sulfide gaseous concentration within the OCS atmosphere was out of measuring range for the GasBadge Pro gas monitor (>500 ppm H_2S). These data are represented in Figure 5.5 with an unfilled data point, as the concentration of hydrogen sulfide was greater than 500 ppm, but the exact value was not able to be determined. All gaseous hydrogen sulfide values greater than 500 ppm were measured with H_2S Draeger tubes from June 2018 to the end of the sampling period.

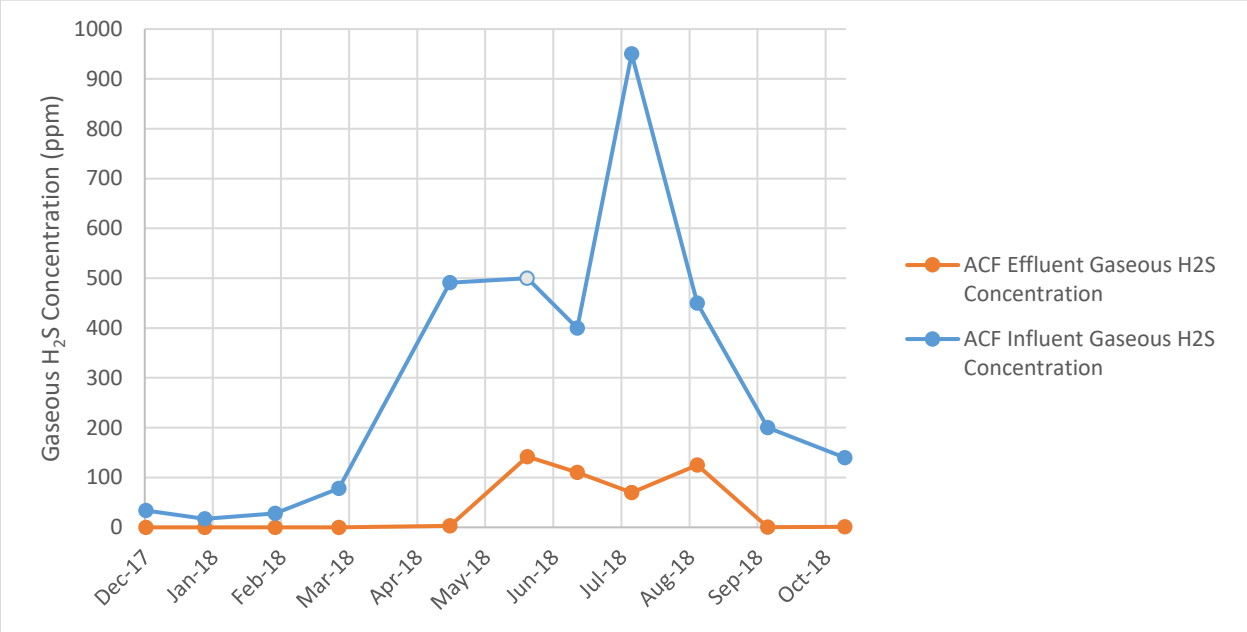

Figure 5.5.*Activated Carbon Filter (ACF) influent and effluent gaseous H_2S concentrations from December 2017 to October 2018*

Additionally, Figure 5.6 shows the temperature and percent relative humidity for the ACF influent and ACF effluent. Overall, the ACF increased temperature and decreased relative humidity of the treated air stream.

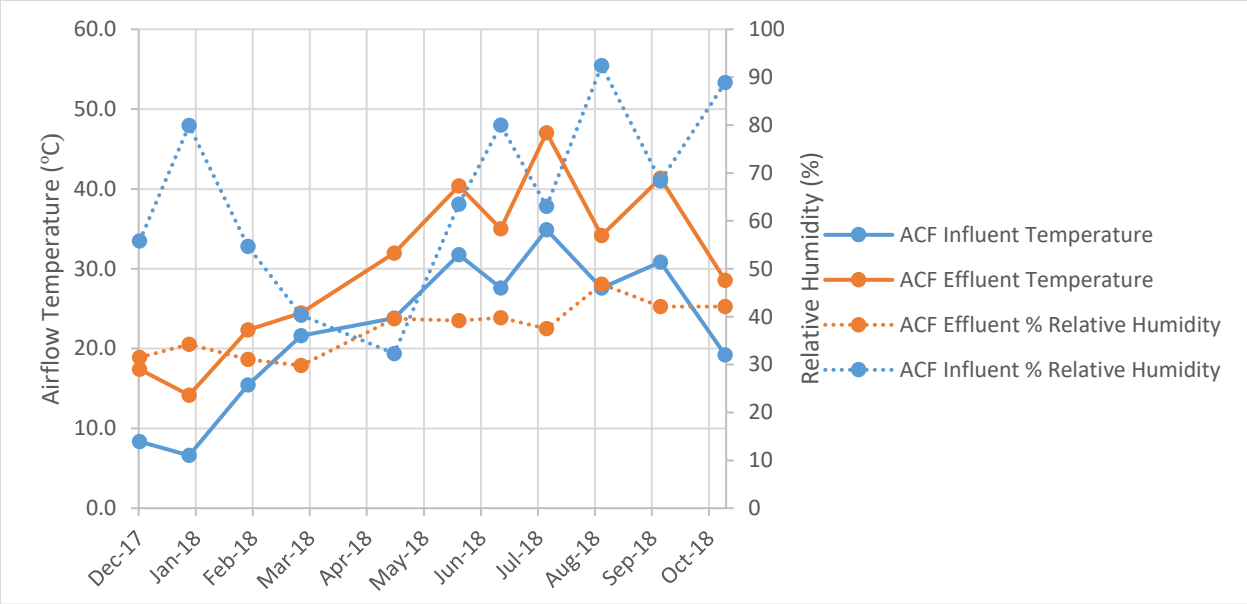

Figure 5.6. *Activated Carbon Filter (ACF) influent and effluent airflow temperatures and percent relative humidity from December 2017 to October 2018*

Additional gaseous hydrogen sulfide measurements were taken in ambient air on top of the berm where the shed is located. These measurements were consistently below 1 ppm H_2S throughout the entire sampling period.

5.4 ACF Performance

The ACF contained 180 kg of GC Sulfursorb Plus activated carbon media. Based on the minimum capacity of the media provided by the manufacturer (0.2 g H2S/ cc carbon media) and the typical bulk density of the media (0.4 g/ cc), it was estimated that the mass of activated carbon media used could sorb a minimum total of 90 kg H_2S. Table 5.6 shows the mean volumetric air flow, temperature and percent relative humidity passing through the ACF. Using the mean volumetric flow rate and concentrations of gaseous H_2S entering the filter, the total mass load of sulfur was estimated. Approximately 100 kg of sulfur entered the filter, and approximately 20 kg of sulfur exited the filter to open atmosphere from December 2017 through October 2018. Throughout the sampling period, the ACF had an average hydrogen sulfide gas

removal efficiency of ~90% based on an average ACF influent concentration of 300 ppmv and an average effluent concentration of 40 ppmv.

Table 5.6. *Mean volumetric air flow, temperature and percent relative humidity in solar-powered sulfide removal system with standard error. Sample size (n)=11*

	Air Flow (L/sec)	**Temperature (°C)**	**Relative Humidity (%)**
OCS Effluent	14±0.2	23±2.7	65±5.5
ACF Exhaust	15±0.1	31±9.1	38±1.5

When a gas stream containing hydrogen sulfide gas and oxygen is oxidized on the surface of activated carbon media, the following major reaction occurs:

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + \frac{1}{2}S_2 \qquad (5)$$

where water and elemental sulfur are the products. However, under certain conditions, other reactions can occur that generate products such as sulfate and sulfuric acid (Bansal and Goyal, 2005). In late May 2018, it was found that sulfuric acid being produced by the ACF. From May 2018 to September 2018, approximately 72 liters of sulfuric acid were collected from the outlet drain on the bottom of the ACF. Although production of sulfuric acid may be seen as a detrimental aspect of performance, the process may effectively prolong the life of the ACF because sulfur is being removed as a liquid.

When dealing with activated carbon filters, breakthrough is defined as the point where the effluent concentration (C) divided by the influent concentration (C_0) is equal to 0.1. Additionally, the point when $C/C_0 = 0.9$ is defined as exhaustion (Watts, 1998). As seen in Figure 5.5

throughout the entirety of the sampling period, the ACF was still removing gaseous H_2S and filter exhaustion had not yet been achieved, although the mass load of H_2S into the filter throughout the sampling period was greater than the estimated minimum capacity of the ACF media. However, approximately 43 kg of sulfur was removed in the form of sulfuric acid production (rather than being sorbed to the ACF media or leaving the ACF exhaust) over the sampling period, which, again, may have led to the prolonging of the ACF media lifetime.

5.5 Substrate Analyses

The VFBR substrate media was analyzed for AVS in duplicate. All samples measured below detection limits. Although no AVS was determined, these results could be because substrate samples were difficult to collect, and analyses were not performed under strictly anaerobic conditions leading to loss of sulfide to the atmosphere. During sample collection, approximately 1 kg (wet weight) of media was collected at each sampling location. VFBR substrate media consists of approximately 80% single-shredded woodchips and 20% spent mushroom compost. According to the AVS method by Leonard et al. (1996) modified from Brouwer and Murphy (1994), a subset of 5 g (wet weight) of sample is to be collected from the 1 kg sample to be analyzed for AVS. Collecting the labile carbon portion of this media while not including solid wood chips for analysis was very difficult, therefore for future studies this collection method may not be ideal for analyzing AVS of similarly composed substrates.

However, these samples were also digested and analyzed for total sulfur and metals content via ICP-OES. The results are presented in Tables 5.7 and 5.8. All samples showed elevated Ca concentration, likely due to the lime added to the mushroom substrate during the farming process. Trace metals concentrations were also elevated above median values determined for the

spent mushroom substrate by LaBar (2016) of 5500 mg/Kg Fe, 93 mg/Kg Zn, 1.14 mg/kg Cd, 313 mg/Kg Mn, 5.53 mg/Kg Ni, 14.1 mg/Kg Pb and < detection limit for Co. Additionally, sulfur concentrations in substrates containing spent mushroom compost may be elevated due to a temporary export of sulfate caused by the dissociation of gypsum (Stark and Williams, 1995).

Table 5.7. *Concentrations of divalent metals in Vertical Flow Bioreactor (VFBR) substrate samples*

	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Na (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Substrate Sample #1	17500	38.1	122	6040	1760	514	305	1160	244	27200
Substrate Sample #2	5660	7.32	13.3	1160	1490	229	96.2	118	94.1	1890
Substrate Sample #3	21700	38.9	128	6080	2600	803	634	1370	184	4640
Substrate Sample #4	26800	28.3	149	4750	2310	795	535	1620	178	28300
Substrate Sample #5	14800	40.9	142	10000	2010	231	525	1430	242	50800

Table 5.8. *Total Sulfur concentrations in Vertical Flow Bioreactor (VFBR) substrate samples*

	S (mg/kg)
Substrate Sample #1	24400
Substrate Sample #2	3240
Substrate Sample #3	42800
Substrate Sample #4	48600
Substrate Sample #5	46300

5.6 ACF Media Analyses

The composite core samples of the activated carbon media were analyzed for AVS and results are shown in Table 5.9. Most of the samples had no detectable AVS, except for the sample that appeared to have elemental sulfur deposits along the rim of the HDPE tubing. Again, because analyses were not performed under strictly anaerobic conditions, the loss of sulfide to the atmosphere likely contributed to these results.

Table 5.9. *Acid Volatile Sulfide (AVS) concentrations of Activated Carbon Filter (ACF) media*

	AVS (µg/g)						
	Surface Sample	**Sample with Appearance of Elemental Sulfur on HDPE rim**	**Composite 20-25 cm**	**Composite 46-51 cm**	**Composite 71-76 cm**	**Composite 97-102 cm**	**Composite 114-119 cm**
#1	BDL	0.018	BDL	BDL	BDL	BDL	BDL
#2	BDL	0.004	BDL	BDL	BDL	BDL	BDL
#3	BDL	0.002	BDL	BDL	BDL	0.004	0.004

The ACF media samples were also analyzed for moisture content according to ASTM Method D4531-86 (2008), and the moisture content by total mass was calculated and is presented in Table 5.10. During the ACF media sampling it was noticed that the media became moister and more compacted with depth, which is shown by the moisture content data.

Table 5.10. *Moisture content of Activated Carbon Filter (ACF) media samples*

	Moisture Content by Total Mass (%)
Surface Sample	29.3
Sample with Appearance of Elemental Sulfur on HDPE rim	43.9
Composite 20-25 cm	30.5
Composite 46-51 cm	31.0
Composite 71-76 cm	32.9
Composite 97-102 cm	37.2
Composite 114-119 cm	40.5

The results for metals and total sulfur content from ICP-OES analyses are presented in Tables 5.11 and 5.12. Sulfur concentrations in the ACF media generally increase with increasing depth from the media surface, which is to be expected given that the gas stream flows from the bottom of the ACF upwards.

Table 5.11. *Concentrations of divalent metals in activated carbon filter (ACF) media samples*

	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Na (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Surface	2770	0.356	1.48	4580	1120	63.7	204	3.77	11.4	2.38
Appearance of Elemental Sulfur on HDPE rim	8650	0.131		1400	803	26.7	108	3.92	10.1	6.89
Composite 20-25 cm	3030	0.423	1.88	5450	1390	86.3	242	4.54	11.2	8.17
Composite 46-51 cm	3190	0.323	1.57	4410	1120	70.3	194	3.89	10.7	2.14
Composite 71-76 cm	3000	0.245	1.92	3010	1320	61.3	239	4.44	8.03	2.72
Composite 97-102 cm	3740	0.174	1.70	2270	1010	36.8	145	4.68	8.09	3.84
Composite 114-119 cm	1060	0.152	1.21	2040	1100	40.6	105	3.69	6.26	3.67

Table 5.12. *Total sulfur concentrations in activated carbon filter (ACF) media samples*

	S (mg/kg)
Surface	129000
Sample with appearance of elemental sulfur on HDPE rim	81500
Composite 20-25 cm	136000
Composite 46-51 cm	138000
Composite 71-76 cm	132000
Composite 97-102 cm	155000
Composite 114-119 cm	248000

5.7 Sulfur Mass Balance

From December 2017 to October 2018, it was estimated that approximately 100,000 kg of S entered SECPTS through the inflows (North inflow, South inflow and OP upwelling), using the average influent sulfate concentration for North inflow and South inflow (2,113±16 mg/L) and assuming the average FPU-out flowrate of 4.7±0.04 L/s over the 335-day sampling period. Using the monthly aqueous sulfate and sulfide data for the respective process units and an average flowrate of 4.7±0.04 L/s, it was estimated that 96,000 kg S left the OP, 92,000 kg of S left the WL, 91,000 kg of S left the VFBR and 86,000 kg of S left the FPU.

Based on mean influent sulfate concentrations and effluent flow rates, and assuming no other forms of S in the mine water, it was estimated approximately 100,000 kg of S were loaded into

SECPTS during the study period. Accounting for S retention in the VFBR, conversion of sulfate to sulfide and subsequent losses to the atmosphere and using the system effluent aqueous sulfate and sulfide concentrations and flow rates, it was estimated approximately 86,000 kg of S were exported at FPU outflow. The lack of water quality data at the oxidation pond upwelling contributes to the uncertainty of the influent calculations. Additionally, formation of ferric hydroxysulfate minerals in the oxidation pond, wetland and on the surface of the VFBR substrate represents an S loss mechanism that was not examined.

Overall, based on changes in aqueous sulfate and sulfide changes in the VFBR, approximately 2800 kg of aqueous S were removed within the VFBR. Based on ICP-OES analyses of VFBR substrate samples, the average concentration of S in the substrate media was 32,900 mg S/kg. These analyses were performed on the spent mushroom compost portion of the VFBR substrate by selectively removing large chunks of wood chips, as this is a more labile carbon source. Based on this estimated S concentration in the substrate, an approximate volume of 190 cubic meters of spent mushroom compost and an approximate spent mushroom compost density of 177 kg/m^3 (LaBar and Nairn, 2016) it was estimated that approximately 1,100 kg of S were retained in the VFBR media. The value derived from the substrate samples may be an underestimate based on difficulties in sample collection.

VFBR effluent passes through the OCS and the sulfide rich atmosphere is pulled through the ACF. Throughout the sampling period, it was estimated that 100 kg S entered the ACF, and approximately 20 kg of gaseous S left the ACF as exhaust to the atmosphere. Although the sulfuric acid was an unforeseen product, it may have helped to prolong the life of the ACF

media. In total, approximately 43 kg of S was estimated to be removed through sulfuric acid production from the end of May through September. Approximately 30 kg of S was retained in the ACF media from the time the system went online in February 2017 to October 2018 based on ICP-OES analyses of ACF media. Estimated sulfur concentrations entering and exiting the OCS and ACF system are shown in Figure 5.7.

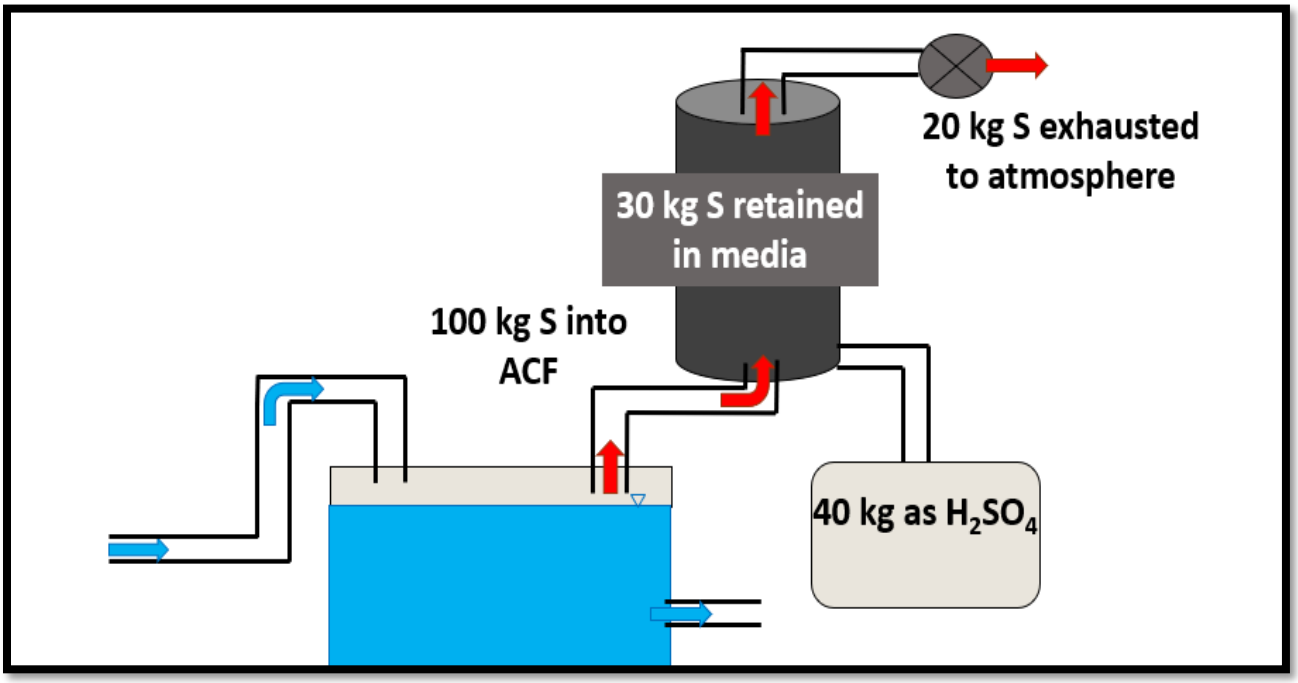

Figure 5.7. *Approximate sulfur concentrations passing through the odor control system (OCS) and activated carbon filter (ACF) from December 2017 to October 2018*

Concentrations of aqueous sulfate at VFBR-Out and FPU-Out were not significantly different ($p=0.68$) due to the great variability in concentrations, so the majority of the sulfur mass change in FPU is presumably due to removal of aqueous sulfide. Mean aqueous sulfide concentrations from VFBR-Out to FPU-Out are presented in Table 5.13.

Based on these average concentrations and the average flow rate of 4.7 L/s, the average S

removal rate was calculated for each cell within the FPU. These data are presented in Table 5.13. Using these removal rates over the 335-day period, it was estimated that approximately 3,800 kg of aqueous S^{2-} were removed in the FPU, likely due to operation of the FMAs.

Table 5.13. *Mean aqueous sulfide concentrations from December 2017 to October 2018 with standard deviation*

	Aqueous sulfide (µg/L)	S^{2-} removed/day (kg)
VFBR-Out	28095±31922	ND
FPU Cell #1	7440±7721	8.4
FPU Cell #2	4797±4985	1.1
FPU Cell #3	1411±1295	1.4
FPU-Out	217±338	0.48

6.0 Conclusions

In conclusion, SECPTS is a uniquely designed passive treatment system that is using natural chemical, physical and biological processes with off-the-grid renewable energy technology to effectively improve mine drainage water quality. During bacterial sulfate reduction within the VFBR, excess sulfide is being produced. VFBR effluent is captured in the OCS, and the gaseous sulfide-rich atmosphere is pulled through the ACF using solar-powered blowers. The ACF significantly ($p=0.009$) reduced gaseous sulfide concentrations throughout the duration of the sampling period. Although the ACF effectively removed gaseous sulfide, capture and removal of gaseous sulfide did not significantly lower aqueous concentrations from VFBR-Out to FPU Cell #1 ($p=0.06$).

Sulfuric acid was an unforeseen product of the sulfide removal system. However, it may have led to the prolonging the life of the ACF media. Future operation of the sulfide removal system will require the capture and disposal of sulfuric acid, or potentially the installation of a desiccant to

strip the moisture from the gas stream before it enters the ACF, reducing sulfuric acid production.

In addition to the sulfide removal system, solar-powered exhaust blowers ran FMAs located in FPU Cell #3 to help re-aerate the water column and strip sulfide. Aqueous sulfide concentrations were significantly ($p=0.03$) decreased from VFBR-Out to FPU-Out. Although the FMAs presumably lower aqueous sulfide concentrations in the FPU, their effect may have been limited in comparison to the large surface area of the FPU where surface diffusion and wave-induced entrainment may have also helped in loss of sulfide.

Estimates of sulfur in the aqueous, gaseous and solid phases accounted for most of the mass of total sulfur throughout SECPTS. Approximately 100,000 kg of S entered the system and 86,000 kg of S left the FPU. It was estimated that a total of 100 kg of gaseous S entered the ACF, and approximately 90 kg of S was accounted for within the media, as exhaust to the atmosphere or as sulfuric acid. This innovative sulfide removal and aeration system may be a viable option to effectively improve air and water quality for passive treatment systems in remote locations and/or at sites with limited operation and maintenance budgets.

7.0 Literature Cited

Affonso, E., Polez, V., Corrêa, C., Mazon, A., Araújo, M., Moraes, G. and Rantin, F. 2004. "Physiological responses to sulfide toxicity by the air-breathing catfish, *Hoplosternum littorale* (Siluriformes, Callichthyidae)."Comparative Biochemistry & Physiology Part C: Toxicology and Pharmacology139, no. 4: 251-257.

Akcil, A. and Soner, K. 2004. "Acid Mine Drainage (AMD): causes, treatment and case studies." Journal of Cleaner Production. no. 14: 1139-1145.

Allan, R. 1997. Introduction: Mining and metals in the environment. Journal of Geochemical Exploration, vol. 58, no. 2: 95-100.

Amezaga, J.**,** Rötting, T., Younger, P., Nairn, R., Noles, A., Oyarzün, R., and Quintanilla, J. 2011. "A rich vein? Mining and the pursuit of sustainability," Environmental Science & Technology, vol. 45, no. 1: 21-26.

Bagreev, A. and Bandosz, T. 2005. "On the mechanism of hydrogen sulfide removal from moist air on catalytic carbonaceous adsorbents." Industrial and Engineering Chemistry Research, vol. 44, no. 3: 530-538.

Bagreev, A., Adib, F., and Bandosz, T. 2000. "pH of activated carbon surface as an indication of its suitability for H_2S removal from moist air streams." Carbon, vol. 39, no. 12: 1897-1905.

Bagreev, A., Katikaneni, S., Parab, S., and Bandosz, T. 2005. "Desulfurization of digester gas: prediction of activated carbon bed performance at low concentrations of hydrogen sulfide." Catalysis Today, vol. 99, no. 3: 329-337.

Bansal, R., Goyal, M. 2005. "Activated carbon adsorption." Boca Raton: CRC Press, 263-272.

Ben Jaber, M., Couvert, A., Amrane, A., Rouxel, F., Le Cloirec, P., and Dumont, E. 2016. "Biofiltration of high concentration of H_2S in waste air under extreme acidic conditions," New Biotechnology, vol. 33, no. 1: 136-143.

Bharathi, P.A. 2008. “Sulfur cycle.” Encyclopedia of Ecology, vol. 1: 3424-3431.

Brosius, L., and Sawin, R. 2001. “Lead and zinc mining in Kansas.” Kansas Geological Survey (KGS), http://www.kgs.ku.edu/Publications/pic17/pic17_1.html.

Costello, C. 2003. “Acid mine drainage: innovative treatment technologies.” US EPA Office of Solid Waste and Emergency Response Technology Innovation Office, Washington, D.C.

Cravotta, C., 2007. “Passive aerobic treatment of net-alkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA,” Mine Water and the Environment, vol. 26, no. 1: 128-149.

Dvorak, D., Hedin, R., Edenborn, H., and McIntire, P. 1992. “Treatment of metal-contaminated water using bacterial sulfate reduction: Results from pilot-scale reactors.” Biotechnology and Bioengineering, vol 40, no. 5: 609-616.

Frawley, K., Cronican, A., Pearce, L. and Peterson, J. 2017. "Sulfide toxicity and its modulation by nitric oxide in bovine pulmonary artery endothelial cells." Chemical Research in Toxicology 30, no. 12: 2100-2109.

General Carbon. 2018. “GC sulfursorb plus activated carbon for H_2S treatment.” http://www.generalcarbon.com/

Gupta, V. and Saleh, T. 2013. “Sorption of pollutants by porous carbon, carbon nanotubes and fullerene- An overview.” Environmental Science and Pollutant Research no. 20: 2828–2843.

Guidotti, T. 2010. "Hydrogen sulfide: advances in understanding human toxicity." International Journal of Toxicology (Sage) vol. 29, no. 6: 569-581.

Hartman, H. 2004. “Introductory mining engineering.” Mining Engineering, vol. 56, no. 3: S12-S13.

Hedin, R., Nairn, R. and Kleinmann, R. 1994. “Passive treatment of coal mine drainage.” Bureau of Land Mines Information Circular 9389. United States Department of the Interior, 2-4.

Hiibel, S., Pereyra, L., Inman, L., Tischer, A., Reisman, D., Reardon, K., and Pruden, A. 2008. “Microbial community analysis of two field-scale sulfate-reducing bioreactors treating mine drainage.” Environmental Microbiology, vol. 10, no. 8: 2087-2097.

Jones,J., Nadeau, T., Voytek, M. and Landa, E. 2006. “Role of microbial iron reduction in the dissolution of iron hydroxysulfate minerals.” Journal of Geophysical Research, vol. 111, no. G01012:1-8.

Kaksonen, A., Dopson, M., Karnachuk, O., Tuovinen, O. and Puhakka, J. 2008. “Biological iron oxidation and sulfate reduction in the treatment of acid mine drainage at low temperatures.” In: Margesin R., Schinner F., Marx J., Gerday C. (eds) Psychrophiles: from Biodiversity to Biotechnology, 429-454.

Kiran, M., Pakshirajan, K. and Das, G. 2017. “An overview of sulfidogenic biological reactors for the simultaneous treatment of sulfate and heavy metal rich wastewater.” Chemical Engineering Science, vol. 158, 606-620.

Kalin, M. 2004. "Passive mine water treatment: the correct approach?" Ecological Engineering vol. 22, no. 4/5: 299-304.

LaBar, J. 2016. “Determination and prediction of products of trace metal removal in laboratory and field scale vertical flow bioreactors.” PhD dissertation, The University of Oklahoma, 121.

LaBar, J. and Nairn, R. 2018. “Characterization of trace metal removal products in vertical flow bioreactor substrates at the Mayer Ranch Passive Treatment System in the Tar Creek Superfund Site.” Chemosphere, vol. 199, 107-113.

Li, T., Li, E., Suo, Y., Xu, Z., Jia, Y., Qin, J., Chen, L. and Gu, G. 2017. "Energy metabolism and metabolomics response of Pacific white shrimp *Litopenaeus vannamei* to sulfide toxicity." Aquatic Toxicology, vol. 183, 28-37.

Lovell, C. and Konopka, A. 1985. “The effects of temperature on bacterial production in a dimictic eutrophic lake.” FEMS Microbiology Ecology vol.31, 135-140.

Nairn, R., Beisel, T., Thomas R., LaBar, J., Strevett, K., Fuller, D., Strosnider, W., Andrews, W., Bays, J., and Knox, R. 2009. “Challenges in design and construction of a large multi-cell passive treatment dystem for ferruginous lead-zinc mine waters.” Proceedings of the 26th National Conference of the American Society of Mining and Reclamation, Billings, MT, 871-892.

Nairn, R. 2015. “Aerating off the grid: advancing passive treatment with solar and wind power.” Cooperative Agreement S11AC20000, Applied Science Program, Office of Surface Mining, Reclamation and Enforcement. Final Report to Sponsor, 8-9.

Nairn, R., Shepherd, N., Danehy, T. and Neely, C. 2018. “Aeration via renewable energies improves passive treatment system performance.” Proceedings of the 11th International Congress on Acid Rock Drainage/ International Mine Water Association/ WISA Mine Water Division Conference, Pretoria, South Africa, 151-156.

Neculita, C., Yim, G., Lee, G., Ji, S., Jung, J., Park, H., and Song, H. 2011. “Comparative effectiveness of mixed organic substrates to mushroom compost for treatment of mine drainage in passive bioreactors.” Chemosphere, vol. 83, no. 1: 76-82.

Nguyen-Tanh, D. and Bandosz, T. 2005. “Activated carbons with metal containing bentonite binders as adsorbents of hydrogen sulfide.” Carbon, vol. 43, no. 2: 359-367.

Oklahoma Department of Environmental Quality (ODEQ). 2017. Tar Creek Superfund Site. http://www.deq.state.ok.us/lpdnew/SF/Superfund%20Project/SF%20Site%20Summaries/TarCreek.html. Accessed 13 March 2018.

Rattapan, C. and Weerawat O. 2012. "Removal of hydrogen sulfide gas using biofiltration - a review." Walailak Journal of Science & Technology 9, no. 1: 9-18.

Sitthikhankaew, R., Chadwick, D., Assabumrungrat, S., and Laosiripojana, N. 2014. “Effects of humidity, O_2, and CO_2 on H_2S adsorption onto upgraded and KOH impregnated activated carbons.” Fuel Processing Technology, vol. 124(C), 249-257.

Smith, L., Oseid, D., Adelman, I., and Broderius, S. 1976. “Effect of hydrogen sulfide on fish and invertebrates Part 1- acute and chronic toxicity studies.” United States Environmental

Protection Agency; EPA-600/3-76-062a.

Stark, L. and Williams, F. 1995. “The roles of spent mushroom substrate for the mitigation of coal mine drainage.” Proceedings from the 1994 Spent Mushroom Substrate Symposium, Philadelphia, Pennsylvania, 80-81.

Strosnider, W. and Nairn, R. 2010. “Effective passive treatment of high-strength acid mine drainage and raw municipal wastewater in Potosí, Bolivia using simple mutual incubations and limestone.” *Journal of Geochemical Exploration*, vol. 105, no. 1: 34–42

United States Environmental Protection Agency. 1986. “National recommended aquatic life criteria.”

Watts, R. 1998. “*Hazardous wastes: Sources, pathways, receptors.”* New York: J. Wiley. 593.

Watzlaf, G., Schroeder, K., Kleinmann, R., Kairies, C., and Nairn, R. 2004. “The passive treatment of coal mine drainage.” DOE/NETL-2004/1202. National Technical Information Service, Springfield, VA, 72.

Williams, T. and Miller, F. 1992. “Odor control using biofilter.” Biocycle; vol. 33, 72-7.

Yang, Y. and Allen, E. 1994. “Biofiltration control of hydrogen sulphide, 1: design and operational parameters.” J. Air Waste Manage. Assoc.; vol. 44, 863-8.

Younger, P., Banwart, S. and Hedin, R. 2002. “Mine Water: Hydrology, Pollution, Remediation.” The Netherlands: Kluwer Academic Press, 311-394.