

	INFL		P1		P2		P3		EFFL
24-Sep-98	180	24-Sep-98	222	24-Sep-98	174	24-Sep-98	275	24-Sep-98	238
13-Oct-98	9	13-Oct-98	105	13-Oct-98	101	13-Oct-98	165	13-Oct-98	170
28-Oct-98	161	28-Oct-98	180	28-Oct-98	130	28-Oct-98	130	28-Oct-98	260
11-Nov-98	145	11-Nov-98	155	11-Nov-98	110	11-Nov-98	186	11-Nov-98	191
2-Dec-98	51	2-Dec-98	42	2-Dec-98	97	2-Dec-98	215	2-Dec-98	190
23-Feb-99	55	23-Feb-99	91	23-Feb-99	85	23-Feb-99	76	23-Feb-99	75
9-Mar-99	92	9-Mar-99	210	9-Mar-99	138	9-Mar-99	165	9-Mar-99	121
24-Mar-99	80	24-Mar-99	155	24-Mar-99	180	24-Mar-99	130	24-Mar-99	100
12-Apr-99	111	12-Apr-99	160	12-Apr-99	160	12-Apr-99	220	12-Apr-99	165
15-Sep-99	130	15-Sep-99	170	15-Sep-99	155	15-Sep-99	175	15-Sep-99	75
22-Sep-99	57	22-Sep-99	29	22-Sep-99	188	22-Sep-99	163	22-Sep-99	43
30-Sep-99	21	30-Sep-99	54	30-Sep-99	87	30-Sep-99	51	30-Sep-99	72
7-Oct-99	78	7-Oct-99	33	7-Oct-99	56	7-Oct-99	115	7-Oct-99	65
11-Oct-99	4	11-Oct-99	91	11-Oct-99	113	11-Oct-99	121	11-Oct-99	100
20-Oct-99	13	20-Oct-99	65	20-Oct-99	53	20-Oct-99	180	20-Oct-99	201
27-Oct-99	3	27-Oct-99	16	27-Oct-99	22	27-Oct-99	55	27-Oct-99	35
4-Nov-99	39	4-Nov-99	36	4-Nov-99	95	4-Nov-99	135	4-Nov-99	45
11-Nov-99	4	11-Nov-99	8	11-Nov-99	42	11-Nov-99	58	11-Nov-99	64

	W1		W2		WE
24-Sep-98	227	24-Sep-98	235	24-Sep-98	295
13-Oct-98	193	13-Oct-98	195	13-Oct-98	230
28-Oct-98	275	28-Oct-98	300	28-Oct-98	310
11-Nov-98	172	11-Nov-98	215	11-Nov-98	150
2-Dec-98	245	2-Dec-98	265	2-Dec-98	270
23-Feb-99	190	23-Feb-99	255	23-Feb-99	205
9-Mar-99	0	9-Mar-99	0	9-Mar-99	0
24-Mar-99	225	24-Mar-99	255	24-Mar-99	0
12-Apr-99	0	12-Apr-99	0	12-Apr-99	0
15-Sep-99	0	15-Sep-99	185	15-Sep-99	220
22-Sep-99	0	22-Sep-99	320	22-Sep-99	325
30-Sep-99	0	30-Sep-99	310	30-Sep-99	415
7-Oct-99	0	7-Oct-99	155	7-Oct-99	260
11-Oct-99	0	11-Oct-99	136	11-Oct-99	150
20-Oct-99	0	20-Oct-99	122	20-Oct-99	105
27-Oct-99	0	27-Oct-99	115	27-Oct-99	145
4-Nov-99	185	4-Nov-99	200	4-Nov-99	290
11-Nov-99	195	11-Nov-99	140	11-Nov-99	340

**SLIPPERY ROCK CREEK  
AN  
INTEGRATED APPROACH TO WATERSHED RESTORATION**

**FRED J. BRENNER<sup>1</sup>**

**ABSTRACT:** In 1994, the Slippery Rock Watershed Coalition, a public-private partnership, was organized to restore the Slippery Rock Creek Watershed. The project area encompasses a 70 km<sup>2</sup> portion of the headwaters of the Slippery Rock Creek Watershed in Butler and Venango Counties in Northwest Pennsylvania. To date, the coalition has developed a pilot demonstration project at an Environmental Education Center operated by the Pennsylvania Department of Conservation and Natural Resources. In 1996, the Coalition coordinated the reclamation of an abandoned coal storage and processing area (tipple) and two passive treatment systems have been installed on Pennsylvania Game Commission lands. The impact of these systems on receiving streams are being monitored by three local colleges. A series of seminars and publications are being prepared to educate the general public and community leaders on the formation and treatment of acid mine drainage.

**Key Terms:** Acid Mine Drainage, Education, Passive Treatment Systems, Restoration, Watershed

**INTRODUCTION**

Drainage resulting from abandoned underground and surface mines is the major cause for the deterioration of rivers and streams in Pennsylvania, as well as throughout the eastern coal fields (Brenner et al. 1993). Coal mine drainage may be characterized as net acidic or net alkaline. Net acidic mine discharges, commonly referred to as acid mine drainage (AMD), lack adequate buffering capacity to neutralize the entire complement of protons produced by the oxidation and hydrolysis of iron. Net alkaline mine drainage contains sufficient neutralizing potential, generally as bicarbonate (HCO<sub>3</sub>), to accept any proton acidity generated by the described reactions. Manganese and aluminum are also common mineral-acidity-producing components of coal mine drainage and require consideration in the balancing of net acidic versus net alkaline discharges. During the last decade, there has been a major effort to develop passive treatment systems to abate the adverse impacts of AMD on fresh water ecosystems. Early wetlands constructed for AMD treatment mimicked natural *Sphagnum* dominated wetlands that were receiving acid drainage (Burriss et al. 1984, Gerber et al. 1985) (Fig. 1). Previous studies on *Sphagnum* wetlands demonstrated that they were generally effective at iron removal, but only for a short period of time (Weider 1988, Weider et al. 1985, Hedin 1989). Weider (1988) indicated that, although the potential of *Sphagnum* uptake is great, as the amount of loading (rate of metal inflow) increases, these peatlands became saturated in a short period of time. Numerous other emergent species have been used in constructed AMD treatment wetlands, but currently, most constructed AMD wetlands are *Typha* dominated due to the adaptability of this species to acidic environments accompanied by high metal concentrations (Brenner et al. 1995).

In addition to wetland systems, anoxic limestone drains (ALDs) have been constructed to treat acid mine drainage in Appalachia (Turner and McCoy 1990, Hedin and Watzlaf 1994) (Fig. 1). These systems function to promote the contact of acid mine drainage with limestone under anoxic conditions, thereby, limiting the oxidation of ferrous iron which reduces the armorization (coating) of limestone with ferric hydroxide. Anoxic limestone drains are generally used to treat acid mine drainage prior to discharge into a constructed wetland. In theory, the ALDs raise the pH of the discharge to circumneutral levels (pH 6 and 7), along with introducing bicarbonate alkalinity. Upon exiting the ALD, the circumneutral pH level promotes metal precipitation and the bicarbonate alkalinity neutralizes the acidity produced by metal hydrolysis (Hedin and Nairn 1993). Broodie (1991) reported that ALDs enhanced the performance of existing constructed wetlands, thereby, reducing the cost of chemical treatment. However, in the presence of aluminum as the pH increases, a gel-like compound of aluminum oxides forms which plug the ALD resulting in a failure of the systems. Sev-

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eral studies have suggested using open limestone drains to treat AMD with elevated metal concentrations and, although these drains will armorize over time, they continue to function in reducing acidity, iron, and manganese concentrations (Ziemkiewicz et al. 1996).

However, both constructed wetlands and ALDs have limitations in the treatment of acidic mine discharges, primarily due to the insufficient alkalinity-producing or acidity - neutralizing capabilities of the systems. Anoxic limestone drains will generally treat approximately 300 mg/l of net acidic drainage, but current designs precludes using ALDs to generate alkalinity in excess of 300 mg/l because of concerns with dissolved oxygen. Wetlands essentially provide a substrate for sulfate reducing bacteria (Brenner et al. 1994); anoxic conditions resulting from the inherent oxygen demand of the organic substrate, and quasi-circumneutral pH values resulting from the dissolution of the carbonate fraction of the compost (Kepler and McCleary 1994). Kepler and McCleary (1994) suggest that limitations of wetland and ALDs systems may be addressed by combining existing treatment mechanisms into a system that will treat acidic waters ad infinitum. These successive alkalinity-producing systems (SAPS) combine ALD technology with sulfate reduction mechanisms. SAPS are a vertical flow systems in which AMD flows through an organic wetland substrate into a limestone bed with the final discharge either into a constructed wetland or receiving stream (Fig. 1). SAPS allow for the sizing of wetland treatment systems as a function of pH and alkalinity and associated contaminant loading. SAPS potentially decrease wetland area requirements and at the same time generate alkalinity in excess of acidity, regardless of acidity concentrations.

The causes and potential adverse impacts of mine discharges on aquatic ecosystems and the technologies available to treat these discharges is generally not available in a format that can be understood by persons outside of the mining and reclamation community. The program described in the current paper outline the various passive treatment systems being installed within the Slippery Rock Watershed located in Butler and Venango Counties in northwestern Pennsylvania, along with the development of demonstration projects at an environmental education center operated by The Pennsylvania Department of Natural Resources and Conservation. Another important component of the overall reclamation program is the involvement of college and university students in the planning, installation and monitoring of the effectiveness of all aspects of the reclamation efforts.

## STUDY AREA

The designated project area is the 70 km<sup>2</sup> drainage basin comprising the headwaters of Slippery Rock Creek, and is located in the Glaciated Plateau Providence in northwest Pennsylvania. The Brookville and Kittaning coal seams within the drainage basin have been extensively mined since the early 1900's. At present, there are over 260 known underground mine openings and over 15,000 acres affected by surface mining. Discharges from these mines have adversely impacted all streams within the watershed. for over 5 decades, and currently the pH of the receiving streams range from 2.5 to 6.0, with acidity exceeding alkalinity and iron and manganese concentrations varying from 2.0 to over 100 mg/L. In addition, many of these discharges have aluminum concentrations in excess of 100 mg/l. Based on an assessment of degradation relating to nonpoint source pollution within Pennsylvania, the Slippery Rock Creek was ranked as a medium priority by the Pennsylvania Department of Environmental Protection with acid mine drainage being the predominant source of pollution. In September 1994, the 27 square mile drainage basin was included in the Comprehensive Mine Reclamation Strategy (CMRS) developed by the Pennsylvania Department of Environmental Protection.

## SLIPPERY ROCK WATER QUALITY COALITION

Since its inception in 1994, the Slippery Rock Water Quality Coalition has been working in a collaborative manner to develop, evaluate, and implement passive treatment systems in the watershed, as well as to promote technology transfer to students, researchers, and the public at large. One of the major strengths of this on-going effort is the cooperation among the following participating governmental agencies, consultants, private industry, and faculty from surrounding educational institutions: State and Federal Agencies - Pennsylvania Department of Conservation and Natural Resources, Bureau of State Parks, Pennsylvania Department of Environmental Protection, Bureau of Mining Operations, United States Department of Energy, Pittsburgh Technology Center, Pennsylvania Game Commission, Pennsylvania Fish Commission; Consultants - Brenner's Ecological Service, C D S Associates, Inc, Chester Engineering, Hedin Environmental, Inc; Private Industry - AmKohl, Jesteadt Excavating, RECMIX of Pennsylvania, Waste Management Inc.; Educational institutions- - Butler County Community College, Grove City College, Slippery Rock State University, Youngstown State University; Nonprofit Organizations - Stream Restoration Incorporated, Trout Unlimited.

## JENNINGS ENVIRONMENTAL EDUCATION CENTER ACID MINE DEMONSTRATION PROJECT

### Historical Perspective

In 1943, a 70 acre commercial underground mine on the Middle Kittaning Coal Seam closed, resulting in an acidic discharge into Big Run, a tributary to Slippery Rock Creek. Between 1965 and 1970, an extensive water monitoring program was initiated documenting the impact of acidic and heavy metal loading on Big Run. The combined discharges were 144 L/min, with an average acidity of 300 mg/L and metal concentrations of 65 mg/L total iron, and 20 mg/L of dissolved aluminum. The total loading rates of acidic discharges into Big Run averaged 49.2 kg/day for total acidity and 10.7 kg/day and 3.3 kg/day for total iron and aluminum, respectively. As part of a comprehensive abandoned mine reclamation project, termed Operation Scarlift, mine seals were installed in 1973 creating a mine pool, and the coal refuse piles were partially removed and the area revegetated. In 1985, the mine seals failed, flooding the Jennings Environmental Education Center with acid mine drainage, and the failure of the revegetative effort generated additional acid discharges. During 1988, wetlands were constructed as passive treatment systems resulting, in a 40% improvement in water quality (Dietz et al 1994). These wetlands were undersized and their effectiveness decreased over time (Dietz et al. 1994). Between 1992 and 1993, an anoxic limestone drain was installed and the site was revegetated. As a result of these activities, there was a dramatic improvement in water quality until the drain became plugged by aluminum oxides within 18 months (Hedin and Watzlaf 1994). After the failure of the anoxic limestone drains, a pilot-scale vertical flow compost system was installed resulting in a temporary water quality improvement but the difficulties in flow regulation and the alkalinity generation capacity of the system was depleted after 13 months (C D S Associates, personal communication).

### Acid Mine Drainage Abatement Demonstration Project

Based on the results of a laboratory-scale vertical flow compost system at the U. S. Department of Energy, Pittsburgh Environmental Technology Center (Watzlaf and Pappas 1996), a pilot-scale vertical flow limestone fortified mushroom compost vertical flow system was installed in 1996 with the resultant improvement in water quality and operational efficiency being currently monitored at monthly intervals. In December of 1996, a full-scale vertical flow wetland systems using a mixture of 135 kg of mushroom compost and 171 kg of number 9 limestone was installed which will be monitored on a quarterly basis. In addition, a series of pilot - scale vertical flow systems utilizing different types of compost and combinations of limestone will be installed and monitored by college students as classroom and/or independent research projects. The combination of these passive treatment systems are designed to reduce the acidic loading rate to Big Run by 92% (45 kg/day) and the loading rates of iron and aluminum by 96% (10.3) and 97% for total iron aluminum, respectively. In addition to the expected improvements in water quality, these systems will provide an opportunity to acquaint the general public on causes, impact and treatment of acid mine drainage as well as providing research opportunity for college and university students. The Jennings Environmental Center provides environmental education opportunities for over 160,000 visitors annually. The interpretative naturalists, augmented by reclamation specialists will provide tours of the demonstration projects and seminars on the environmental impacts of acid mine drainage and watershed restoration. In addition, a 25 minute video has been prepared that documents all phases of the construction of these passive acid mine drainage systems which, along with color coded construction plans, will be available for public viewing at the Jennings Environmental Center.

### Reclamation Handbook

Although numerous articles have been published in professional journals and conference proceedings describing the formation and treatment of mine drainage, the general public is largely uninformed as to the formation of acid mine drainage and passive treatment technologies. The Slippery Rock Water Quality Improvement Coalition is currently developing a handbook designed to acquaint local government officials and landowners, as well as the public at large, on passive treatment technologies. The authors of the handbook will include reclamation scientists working with Grove City and Slippery Rock University students. The format will include: (1) the formation of acid mine drainage, (2) its impact on fresh water ecosystems, (3) passive treatment technologies, (4) how to choose the correct technology, and (5) governmental and private funding sources. The development of a guide to passive treatment technology to augment the demonstration of every type of passive treatment technology at a public Environmental Center will provide a unique opportunity for information transfer to the general public.

## WATERSHED MONITORING AND RECLAMATION EFFORTS

Since the incorporation of the Slippery Rock Watershed into the Comprehensive Mine Reclamation Strategy (CMRS) by the Pennsylvania Department of Environmental Protection, monthly water samples have been collected and analyzed from 129 locations throughout the project area. The results of the water quality survey have been used to establish reclamation priorities throughout the watershed. During 1996, a 6 ha abandoned coal tippie has been reclaimed and two passive treatment systems have been installed on Pennsylvania Game Lands No. 95. The reclamation of the tippie site included the removal and transportation of remaining coal to a local power generation plant, and the incorporation of the coal fines with fly ash from the local power plant. Once that had been completed, the site was regraded with top soil and revegetated. The reclamation of this abandoned tippie eliminated a major acidic discharge which had been a major source of contamination of the Slippery Rock Creek for over 5 decades. The acidic discharges on Game lands No. 97 are a combination of underground and surface mining, along with a coal tippie that existed on the site from the early 1900s' and remained in operation until the late 1970s'. These treatment systems consist of two anoxic limestone drains, one of which is the largest currently operating in Pennsylvania, two ponds which over the years have evolved into wetlands and a settling pond. These passive treatment systems are currently successfully treating acidic discharges by the addition of 129 Kg/ day of alkalinity and the removal of 23 kg/day of iron. The treatment of this discharge resulted in an increase in alkalinity from 4.2 to 5.7 mg/L along with a reduction in iron concentrations in the receiving stream by 54.1 percent (3.7-1.7 mg/l) 600 m downstream from the discharge. The effectiveness and impact of these discharges of the receiving streams is currently being monitored by the Pennsylvania Department of Environmental Resources and students from Slippery Rock University.

Students from Grove City College are currently in the second year of water quality monitoring program on Seaton Creek, a major tributary of Slippery Rock Creek. Seaton Creek is the most severely impacted of the subwatersheds within the Slippery Rock Creek Drainage Basin, with total acidity exceeding alkalinity at all sampling stations and total iron, manganese, and aluminum varying from 10 to 100 mg/L among the different sampling stations. Throughout the watershed, the pH of the stream varies from 2.5 to 6.0 and the stream is devoid of macroinvertebrate communities. Studies are currently underway to determine the affect of different substrates on recolonization by macroinvertebrate communities. These studies are providing background data base to determine the success of future reclamation efforts within the watershed. At present, a series of reclamation strategies are under consideration including the reclamation of an abandoned strip mine and re-mining portions of the watershed to eliminate acidic discharges, along with the construction of passive treatment systems in conjunction with the re-mining efforts. To acquaint the public with the reclamation efforts within the watershed, the coalition conducts bi-annual tours of the different projects during the fall and spring.

### SUMMARY

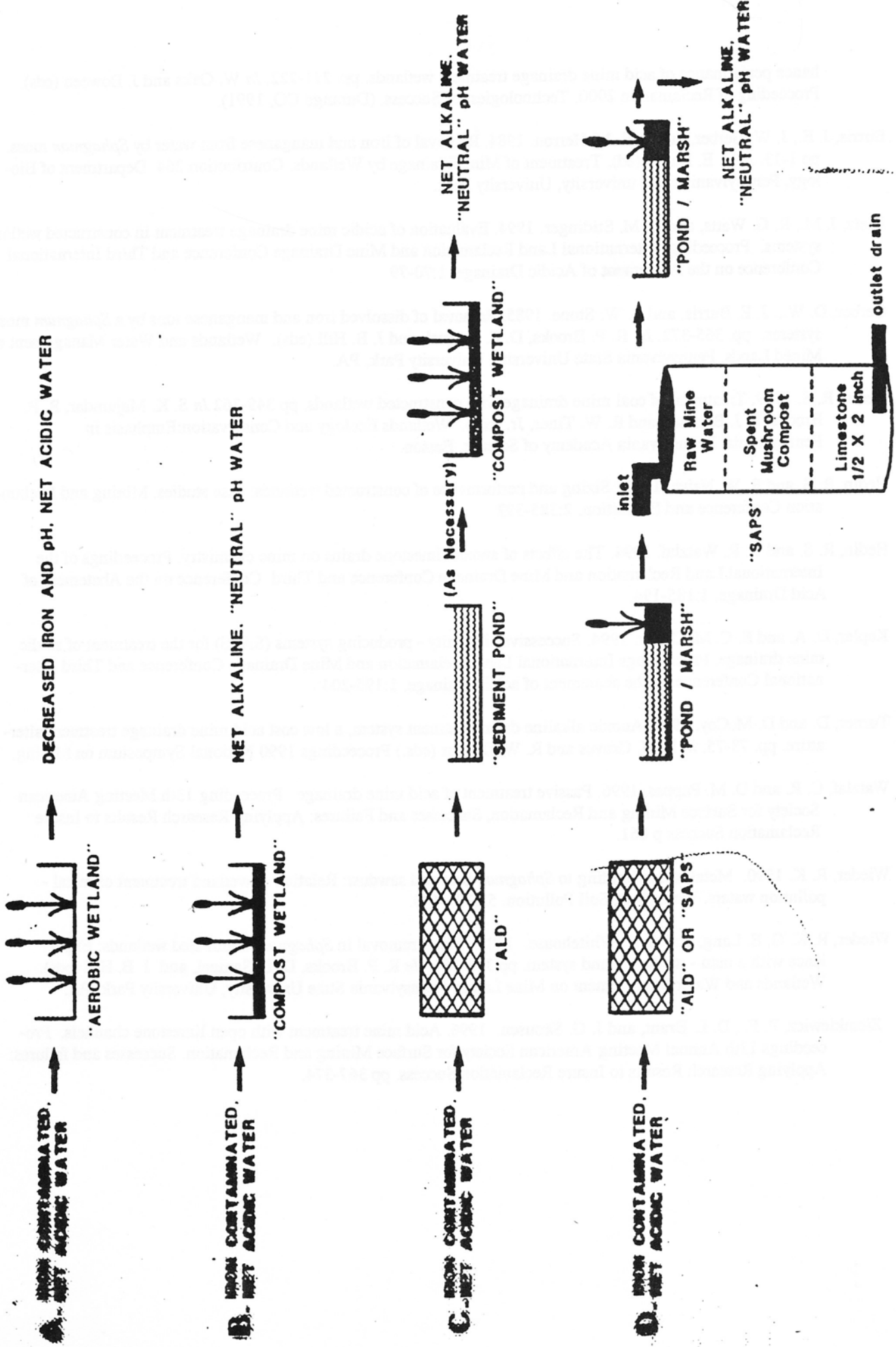
The Slippery Rock Watershed Coalition is a cooperative effort between the public and private segments of society to restore Slippery Rock Creek to a productive ecosystem, as well as to educate the general public and local governmental officials the formation, impact and treatment of acid mine drainage. This is being accomplished through a series of publications, demonstration projects and seminars where students and reclamation specialists discuss the results of their research on the watershed. In addition, the Coalition conducts bi-annual public tours of the different reclamation activities during the fall and spring. The Slippery Rock Creek Watershed Coalition is serving as a model of cooperation between the public and private sector for other watershed associations in Pennsylvania. Such cooperation can only improve water quality in degraded watersheds adversely impacted by mining or other sources of nonpoint source pollution.

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# FIGURE 1: Evolution of passive, wetland treatment technology

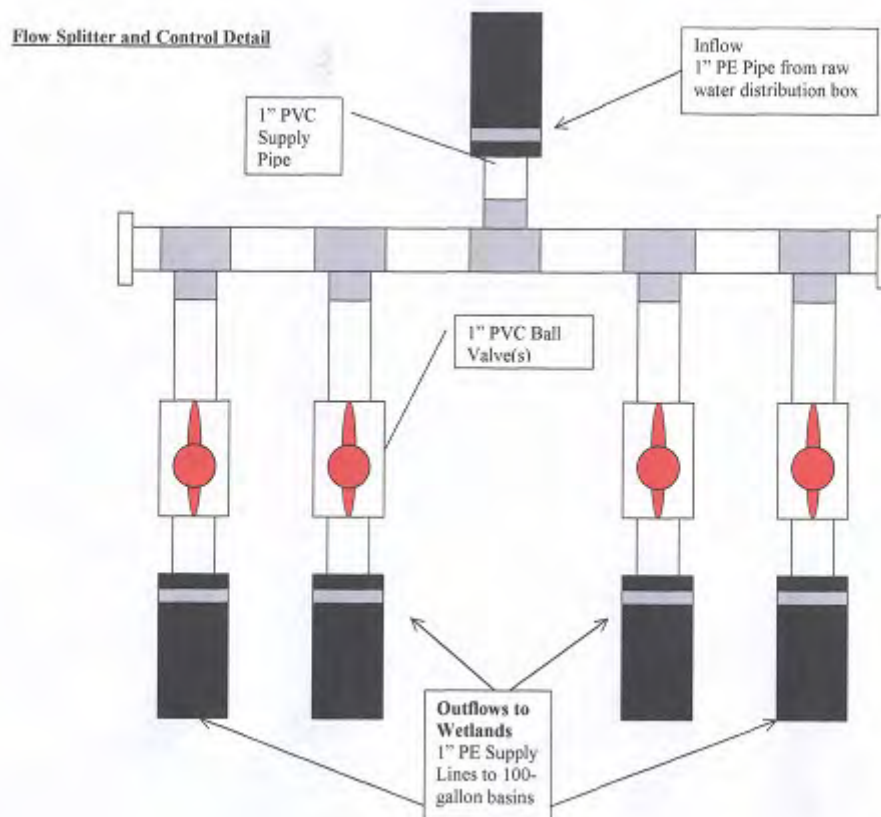


## **Westminster College: Pilot-Scale Systems**

### Description

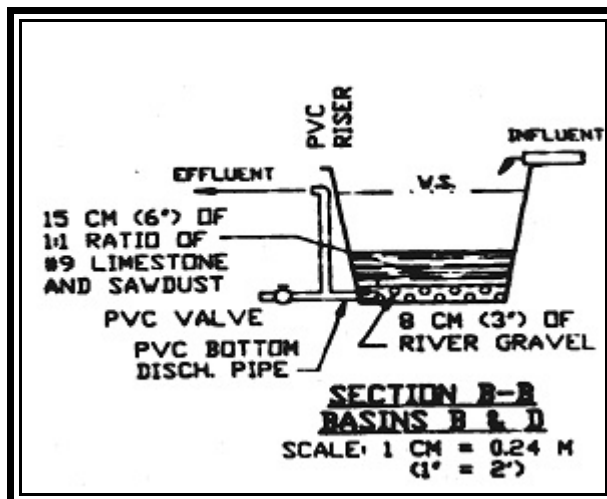
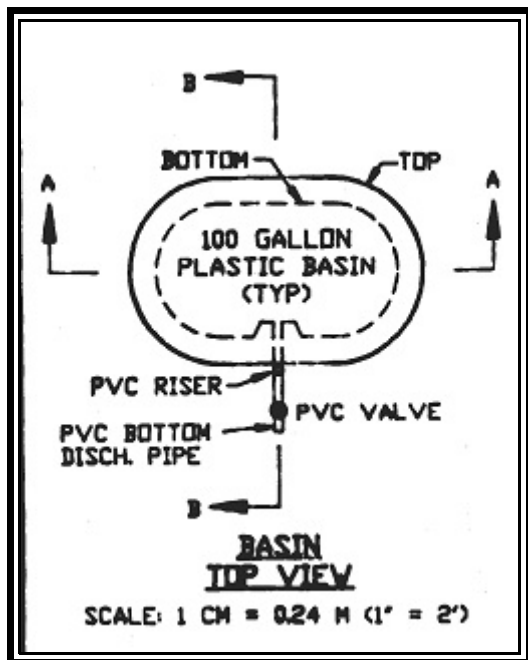
A research proposal was submitted by Westminster College students to the Slippery Rock Watershed Coalition and Jennings Water Quality Improvement Coalition to conduct a study to evaluate the effectiveness of two media in pilot-scale systems to treat abandoned mine drainage at the Jennings Environmental Education Center. (See attached proposal.)

As a Flow Splitter Box had been installed for just such pilot-scale demonstration projects, four tanks (two replicate) were placed on-line with assistance from C D S Associates, Inc. and BioMost, Inc.



The construction of these tanks were patterned after the existing full-scale Vertical Flow Pond and were identified as A, B, C, D. Basins A & C contained a mixture of #9 Special, 90% CCE, limestone aggregate with aquatic macrophyte compost. Basins B & D contained a mixture of the same limestone aggregate with sawdust. For more specifics, please see attached reports.



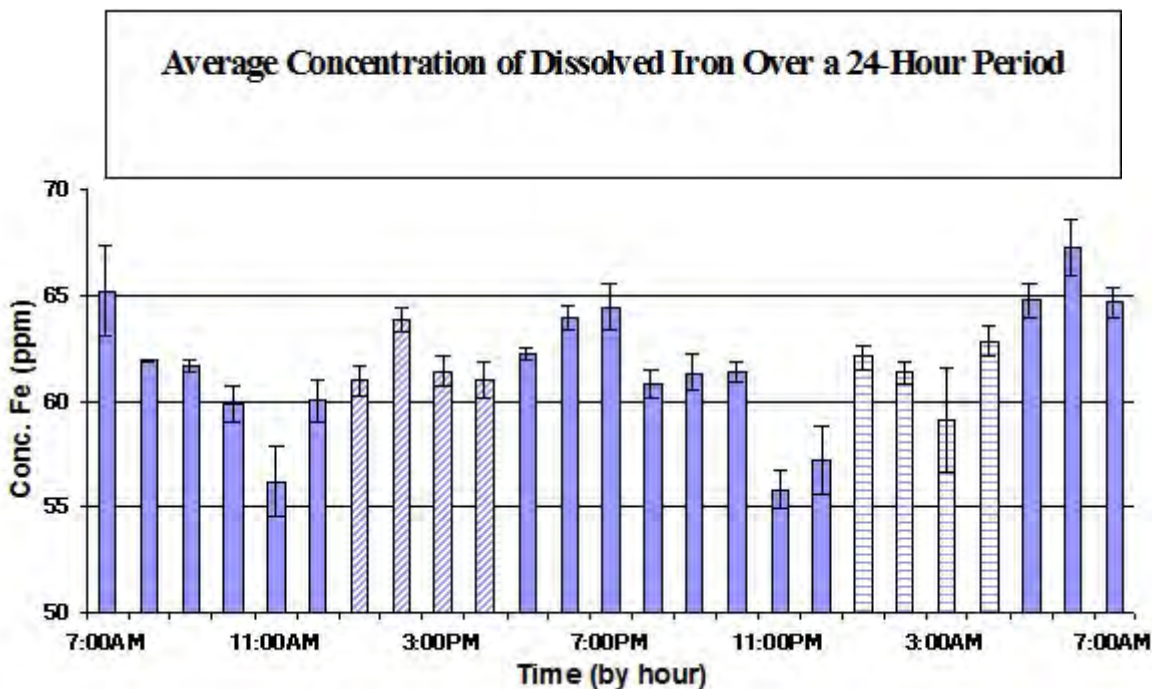


Eight samples (two for each tank) of the influent were collected hourly for 24 hours (actually 25 hours; 200 samples). In addition three times per week for two weeks, influent sampling was coordinated with sampling the effluent. During these six sampling events, five samples of each the four effluents were collected (120 samples). The students maintained a Quality Assurance and Quality Control Plan. The laboratory analyses with a statistical evaluation were conducted by the students. (See attached reports.)

Analyses included dissolved iron, dissolved aluminum, and dissolved nickel in both the influent and effluent. The average analyses were used to provide the most accurate representation of the concentrations.

### Findings

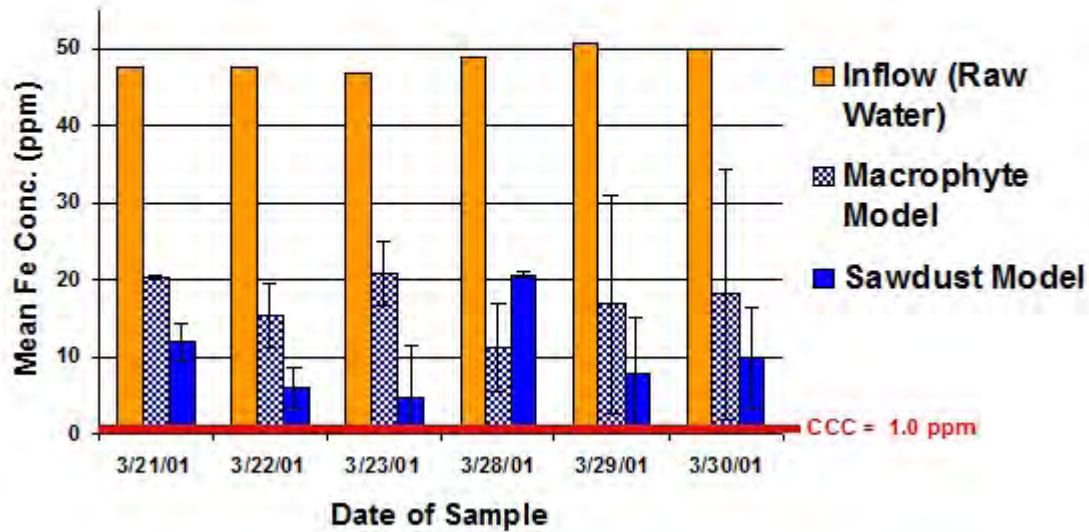
**Hourly average influent quality:** The average dissolved iron concentration ranged from 56 to 67 mg/l during the day and exhibited a pronounced cyclical 12-hour trend with the highest concentrations at 7AM and 7PM and the lowest at 11AM and 11PM. This suggests a biological component to the change in concentration.



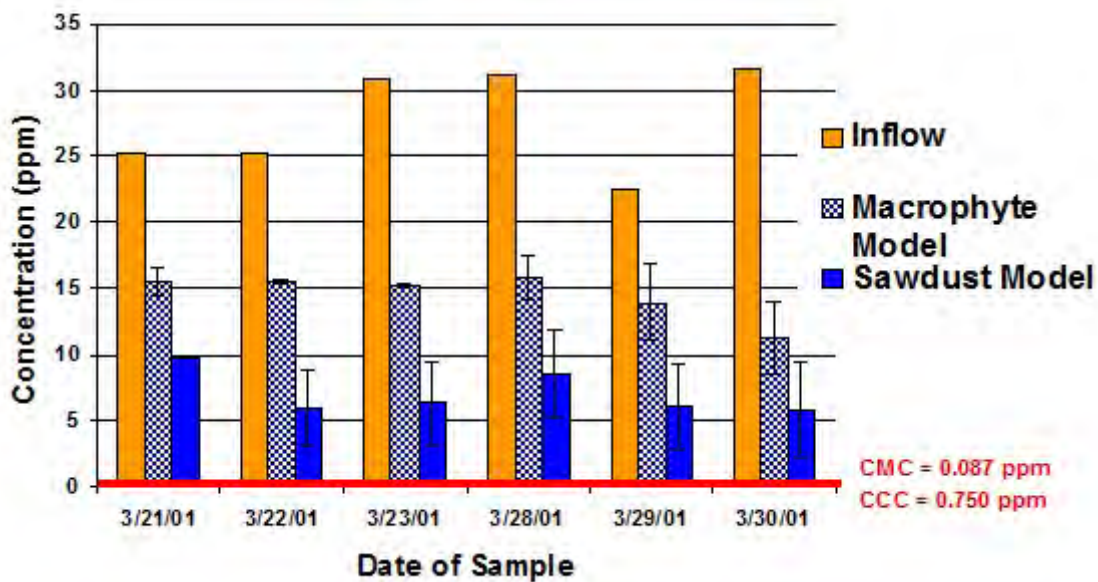
The average dissolved aluminum concentration ranged from 27 to 32 mg/l during the day and no cyclical trend was observed. The average absorbance values for nickel ranged from about 0.4600 to 0.7100 and a cyclical trend was not distinct; however, the highest values were recorded around 7AM and the lowest around 7PM. (For specific graphs, see attached reports.)

**Tri-weekly average influent and effluent quality:** Comparing the different treatment media (sawdust/limestone mix to the macrophyte/limestone mix), more iron and aluminum were retained in the sawdust model than in the macrophyte model. In other words, there were higher dissolved aluminum and iron concentrations in the discharge from the tank with the macrophyte media than from the tank with sawdust media. Neither media significantly retained nickel as over 90% remained in the discharge. Further research is needed to determine the mechanism(s) responsible.

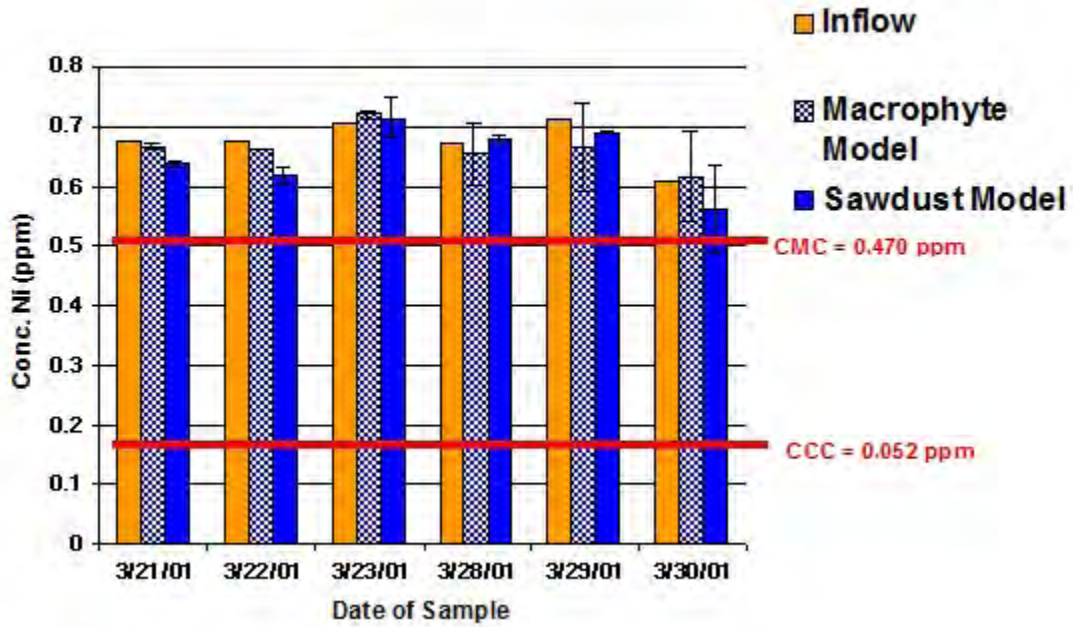
### Mean Concentration of Dissolved Iron in Outflow Samples



### Mean Concentration of Dissolved Aluminum in Outflow Samples



### Mean Concentration of Dissolved Nickel in Outflow Samples



## **PAPERS AND PRESENTATIONS**

### **Westminster College: Pilot-Scale Systems**

#### **Senior Paper**

BEHAM, Jessica; BENNETT, Jennifer; BORDEN, Katherine; HALL, Christopher; MARTIN, Joshua; RICE, Seth; ZAHNISER, Christina (2001) Investigation of Experimental Passive Treatment System Models for Acid Mine Drainage: Environmental Science Capstone 2001, Westminster College, Faculty: WOOSTER, Timothy, PhD; BALCZON, Joseph, PhD

#### **Oral Presentation**

BEHAM, Jessica; BENNETT, Jennifer; BORDEN, Katherine; HALL, Christopher; MARTIN, Joshua; RICE, Seth; ZAHNISER, Christina (2001) Investigation of Experimental Anoxic Passive Treatment Systems: Environmental Science Capstone 2001, Westminster College, Faculty: WOOSTER, Timothy, PhD; BALCZON, Joseph, PhD

#### **News Items**

"The Catalyst", Slippery Rock Watershed Coalition monthly newsletter (05/2001) "Westminster Students Conduct Research at Jennings"

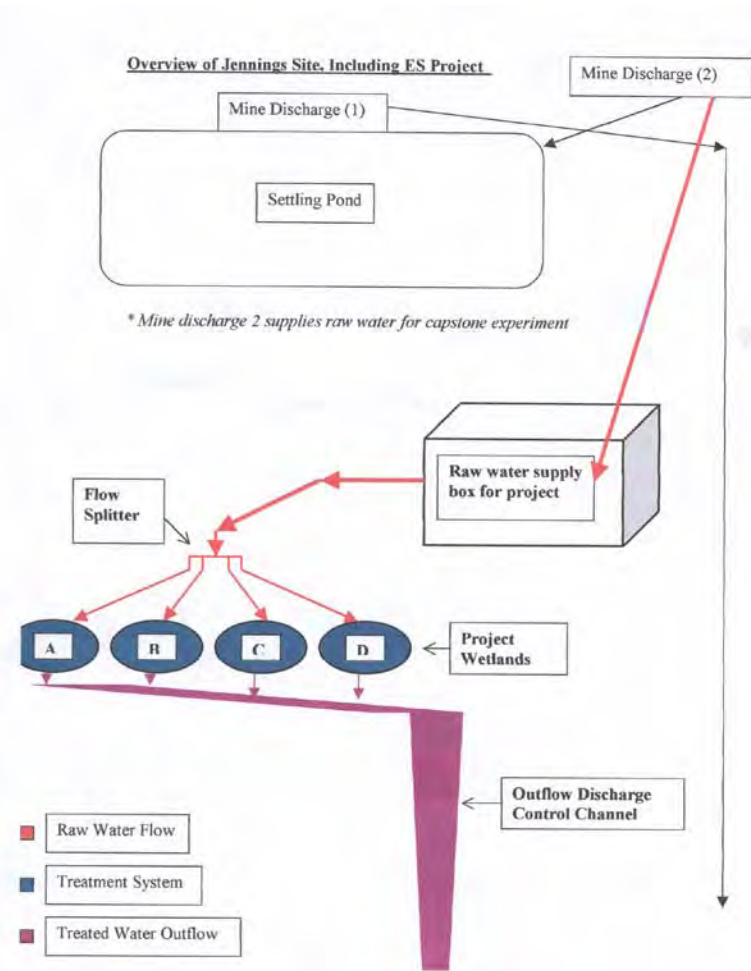


Diagram of the Westminster College students' project at Jennings Environmental Education Center for their senior capstone course.

**Flow Splitter and Control Detail**

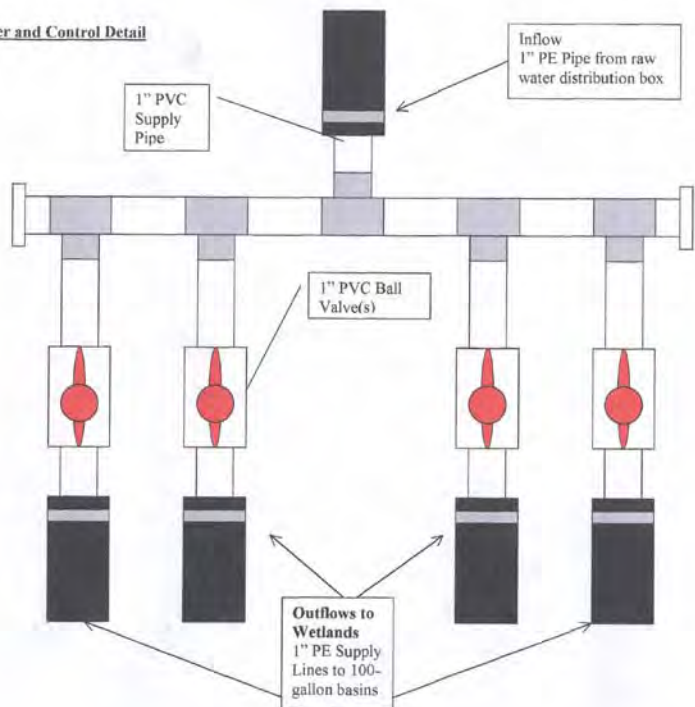
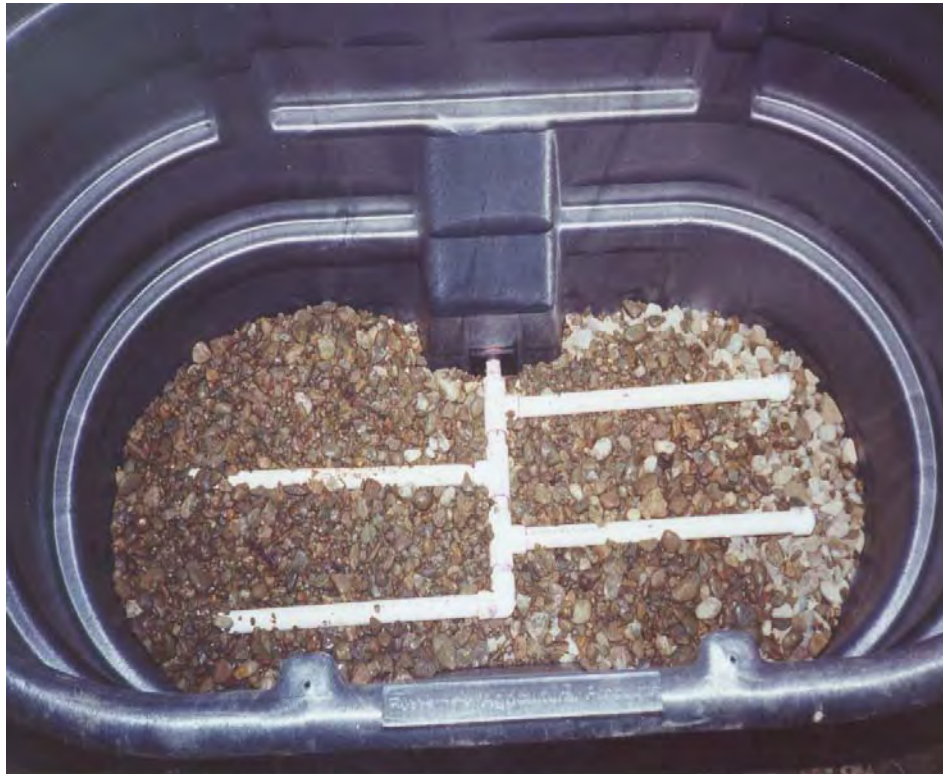


Diagram of the flow splitter box used by the Westminster College students for their capstone project to split the raw water between the different test tanks.



**Above:** Westminster students setting up their small-scale vertical flow pond tanks that they used for their experiment on the effectiveness of different treatment media.

**Below:** Birds eye view of one of the small-scale vertical flow ponds. Note the pipe system embedded within the media.





**Left:** Westminster College students setting up the small-scale vertical flow pond test tanks.  
**Right:** Westminster College students performing their initial 24-hour sampling period.



A Westminster student conducting weekly water monitoring and sampling.





**Above:** Westminster College student prepping to perform iron analyses.

**Below:** Westminster College student analyzing for metal concentrations on an Atomic Absorption Spectrophotometer.



# **Investigation of Experimental Passive Treatment System Models for Acid Mine Drainage**

**Environmental Science Capstone 2001  
Westminster College**

## **Researchers:**

Jessica Beham  
Jennifer Bennett  
Katherine Borden  
Christopher Hall  
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# Table of Contents

<b>I.</b>	<b>Background on the Environmental Science Capstone Study</b>	
❖	Background Information.....	3
❖	Acid Mine Drainage and Chemistry.....	3
❖	Remediation Techniques for Acid Mine Drainage.....	4
❖	Background on the Jennings Environmental Education Center.....	8
❖	Legislation and the Acid Mine Drainage Issue.....	11
<b>II.</b>	<b>Study Methods</b>	
❖	Design and Construction of the Model Systems.....	12
❖	Field Sample Collection Protocols.....	14
❖	Glassware and Equipment Cleaning Procedures.....	16
❖	Sample Preparation.....	16
❖	Analytical Technique for Iron Analysis.....	17
❖	Atomic Absorption Spectroscopy Methods for Aluminum and Nickel.....	20
<b>III.</b>	<b>Study Results</b>	
❖	Calibration Curve for Iron Analysis.....	22
❖	24-Hour Sample Results.....	22
❖	2-Week Sample Results.....	25
<b>IV.</b>	<b>Discussion.....</b>	<b>31</b>
<b>V.</b>	<b>Appendices.....</b>	<b>35</b>
❖	Appendix A: EPA Water Quality Standards	
❖	Appendix B: Chemistry of Acid Mine Drainage	
❖	Appendix C: Atomic Absorption Instrument Parameters	
❖	Appendix D: Statistical Analysis	
❖	Appendix E: Under-drain Diagram	
❖	Appendix F: Flow Splitter Diagram	
❖	Appendix G: Complete System Diagram	
❖	Appendix H: Diagram of Saw Dust Model	
❖	Appendix I: Diagram of Aquatic Macrophyte Model	
<b>VI.</b>	<b>Bibliography.....</b>	<b>33</b>
<b>VII.</b>	<b>Literature Cited.....</b>	<b>52</b>

## BACKGROUND INFORMATION

### Purpose

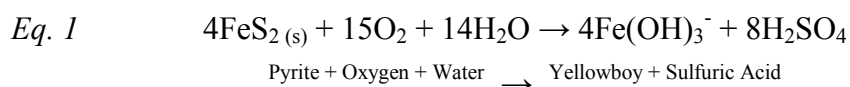
The primary water pollutants of concern in this investigation are metals contained in acid mine drainage on the Jennings Environmental Education Center site in Butler County, Pennsylvania. Natural waters impacted by acid mine drainage have an exceptionally low pH (app. 3-6) and generally high concentrations of heavy metals. The project detailed in this investigation sought to model the first stage of a passive treatment system, the alkalinity generation system. As such, the concentrations of the metals of concern (Iron, Aluminum, Nickel) were carefully monitored in the outflow water leaving the model systems so as facilitate comparison of the two treatment medias. The project is designed to bring the pH back up to a neutral level and to reduce the state of the dissolved metals iron, nickel, and aluminum, in the water.

### Acid Mine Drainage

Acid mine drainage (hereafter AMD) impairs over 8000 kilometers of streams in the Appalachian region of the Eastern United States. The pollutants introduced into these waterways causes the water quality to fall below the standards set by the Clean Water Act, *Table 1 of Appendix A*, to protect the aquatic communities (Skousen 1997). Acid mine drainage (AMD) is the toughest and most complex problem faced by the mining industry today (Smith 1997). Ninety-percent of AMD is from abandoned subsurface coal mines (Skousen 1997). Often, no one can be held financially responsible for the rehabilitation of the polluted water flowing from an abandoned mine (Skousen 1997).

### The Chemistry of Acid Mine Drainage

The exposed pyrite (sulfide) found in coalmines oxidizes and then reacts with water forming hydroxide, sulfate, and free hydrogen ions. The pyrite oxidizes when exposed to air, water, and the metabolic activities of some types of chemosynthetic bacteria (e.g., *Thiobacillus...*) that catalyze pyrite oxidation (Smith 1997), summarized in Equation 1:



Metals are released into the water either when the sulfide is oxidized or by simple leaching processes (Geller, *et al.* 1998). The implications for water quality as a result of this pollution includes impairment by a very low pH of 2 to 3, a high heavy-metal concentration, an increased sulfate concentration, and raised total dissolved solids levels. The contaminants of highest concern in AMD are acidity, iron (Fe), manganese (Mn), and aluminum (Al) (Smith 1997). These four factors are the primary focus of Pennsylvania's surface and subsurface mining effluent discharge permits.

## **Remediation Techniques for Acid Mine Drainage**

Acid mine drainage can be minimized and/or prevented through various methods. Organic wastes can be applied to the inside of the mine, therefore preventing pyrite oxidation and removing soluble iron from solution. Altering the mine's hydrology, disposing of the pyretic materials under water, and applying bactericides are other forms of AMD prevention. A newly developing prevention method is to seal the pyrite to prevent oxidation from occurring. Though effective in reducing the pollutants in the discharge from the mines, no one method fully prevents AMD from being discharged (Geller, *et al.* 1997).

Since 1968 when PA passed laws restricting discharge from mines, a variety of treatment methods have been developed to remediate the effects of AMD. The first type of treatment method to be used was chemical. Chemicals can be used to increase the pH and remove the metals, but this is an expensive and finite solution (Skousen 1997). Alkaline materials, such as limestone or fly ash mixed with soil and lime can be pumped into the mines. The limestone buffers the pH and causes metals to precipitate. Fly ash, soil, and lime have been found to significantly increase the pH and reduce the concentrations of iron, sulfate, and manganese. Though only temporarily effective, phosphate-based materials can also be used to treat AMD. This method prevents pyrite from being oxidized but only until iron armoring occurs (when iron coats the phosphate) (Geller, *et al.* 1997).

Passive treatment systems have been used since 1978 to treat AMD, and for the past 15 years, these systems have been used full-scale throughout the United States. Though not the first type of passive treatment to be utilized, anoxic limestone drains (ALDs) are used often to treat AMD. The acid mine drainage flows into the buried cells of limestone (the ALDs). The limestone dissolves in the water and produces bicarbonate, thus increasing the alkalinity and

allowing metals to precipitate out of the water when emptied into a settling pond where it becomes aerated. The effluent of an anoxic limestone drain should have a pH between 6 and 7. The ALDs are anoxic to prevent iron-armoring, the coating of surfaces with  $\text{Fe}(\text{OH})_2$ , and also to prevent the precipitation of metals from occurring inside the drain (Demchak, et al 1997). Though ALDs are relatively inexpensive (Skousen 1997), the problems with this method occur when the pH is too neutral (the limestone is not effective at higher pHs) and when the dissolution of limestone in the presence of oxygen forms a gel ( $\text{FeCO}_3$  or  $\text{MnCO}_3$ ) that can plug the drain or cause it to malfunction. Ideally, the limestone dissolves quickly in the inflowing low pH water, thus causing an increase in pH in the treated water (Geller, *et al.* 1997).

The first passive treatment method to be employed was the utilization of wetlands (Geller, *et al.* 1997), and specifically Sphagnum wetlands. These wetlands slow the flow of water promoting precipitation of metals from solution, as well as involve phytoremediation processes as a result of the aquatic macrophyte life living within the wetland system. Along with treating AMD, wetlands may perform many other functions for wildlife and humans, such as storing water, slowing the flow of water through an area, retaining excess nutrients, sediment and other pollutants suspended in the water, and wetlands also provide habitat for many species of plants and animals, including several endangered species (Tiner 1999). Wetlands also provide people with recreational and aesthetic enjoyment (Geller, *et al.* 1997).

There are two general categories of wetlands used as passive treatment systems: anaerobic and aerobic wetlands. The anaerobic wetlands contain a layer of organic-rich substrate and a layer of limestone. In some cases vegetation is transplanted into this organic substrate. These types of wetlands are generally used when the influent is predominantly acidic, such as AMD (Demchak et al 1997). As in the ALDs, the limestone decreases the acidic conditions, resulting in metals precipitation. Vertical flow systems, such as successive alkalinity producing systems (SAPS), are a combination of ALDs and anaerobic wetlands. In these types of wetlands, AMD flows into a settling pond, through organic matter, and then through limestone before flowing out of the system (Demchak et al 1997). Containing about 10% calcium carbonate, the organic matter, usually compost, serves to remove oxygen from the water, and the states of iron and aluminum are reduced chemically through exchange and filtering with the organic matter (Watzlaf, 1997). The anoxic conditions created by the bacteria in the compost increase the dissolution of the limestone, thus decreasing acidity.

The other type of wetland is the aerobic wetland, such as marshes and swamps. By aerating the water and slowing its flow to increase the residency time of the water (Demchak *et al* 1997), marshes and swamps can remove excess nutrients through plant uptake and thus prevent eutrophication of surrounding waters by acting as a buffer zone (Cole 1998). The vegetation (cattails, reeds, etc...) in these types of wetlands aid in the removal of metals, introduces fresh organic matter every season, and support uniform flow (Demchak *et al.* 1997). The metals are removed from the water through plant uptake (Williams 1991), the formation of ferric oxyhydroxides, complexation by organic substances, and by using bacteria in an anaerobic zone to precipitate the metals into insoluble oxides, oxyhydroxides, and sulfides. The precipitation is the only function that has any long-term potential. The other pathways of removal are insignificant or short-term (Geller, *et al.* 1997). These types of wetlands work best when the water is predominately alkaline (Demchak *et al.* 1997).

Aerobic wetlands were first used about 30 years ago to treat municipal waste discharge (Cole 1998). An example of a wetland treating sewage discharge is the Tinicum Marsh (Tiner 1999), a naturally occurring wetland located near Philadelphia (Cole 1998). Daily, the Tinicum Marsh receives discharge from three surrounding sewage-treatment plants, removing 4445kg of phosphorus, 3900kg of ammonia, and 162.60 kg of nitrate (Tiner 1999), and adding 18143 kg of oxygen to the system, thereby helping to offset the anoxia that occurs when heavy metals oxidize.

While natural wetlands, such as Tinicum Marsh, are still used to remedy pollution problems, it is now common to use constructed treatment wetlands. The use of constructed wetlands originated in Germany 30 years ago and has been found to be easier to manage and study. There are currently 500 treatment wetlands in Europe and over 600 in North America (Cole 1998). An example of a constructed wetland is the large Tres Rios Demonstration Wetlands project used to treat municipal wastewater in Phoenix, Arizona. This project includes 12 wetland cells constructed in former sludge beds. Along with treating sewage discharge water, wetlands also are constructed to treat industrial wastewater, acid mine drainage (AMD), agricultural runoff, and effluent from livestock farms (Cole 1998). In addition to aerobic wetlands, other types of constructed passive treatment systems include anaerobic wetlands, anoxic limestone drains, and vertical flow systems such as successive alkalinity producing

systems (SAPS) (Demchak et al 1997). These passive treatment systems have the advantage of being less expensive than most other types of treatments (Smith 1997).

Constructing wetlands has become popular because these wetlands can be made site-specific according to the particular pollutants of concern. When designing and constructing a wetland several variables or components should be considered. These include how the water will be retained, what type(s) of substrate (gravel, organic compost, etc...) will be used, and what, if any, vegetation will be added. If a wetland is built to promote biodiversity and wildlife recreation, a large diversity of wetland vegetation needs to be incorporated so that different species of animals and bacteria can flourish ([Waterwise](#) 1995). Alternatively, if the wetland is created to remediate polluted water, such as AMD, the system should contain material that encourages decreased acidity and metal concentrations. As with any treatment system, a leach-proof lining should be installed to prevent polluted water from escaping the system haphazardly ([Waterwise](#) 1995). The ability of the wetland to remove contaminants, such as AMD, can be improved by building a channel or settling pond upstream from the actual wetland (Xiu-Zehn and Xiang-Rong 1999).

There are two general types of constructed wetlands: low marshes and high marshes. Low marshes are considered to be horizontal flow wetlands because the wastewater moves across the substrate as it flows through plant roots, which are the main source of remediation. High marshes are the vertical flow wetlands, mentioned before, because the remediation of the polluted water takes place as it flows down through the treatment substrate and through plant roots (if present). In this type of system the treatment substrate plays a vital role in the remediation of the water ([Waterwise](#) 1995). Though much is known about wetlands remediating water, not all of the specific biological, chemical and/or physiological processes occurring within these systems are completely understood, so it is difficult for engineers to build predictive models (Cole, 1998).

## **Background on the Jennings Environmental Education Center**

In an attempt to improve the quality of water entering the Slippery Rock Creek watershed from an abandoned mine discharge point on the site vertical flow wetlands have been installed at Jennings Environmental Education Center, located in Butler County, Pennsylvania. This area, as well as the entire Slippery Rock Creek watershed, was subject to over 100 years of mining



activity, contributing to the significant deterioration in water quality of the Big Run Creek, a primary tributary to the Slippery Rock Creek (Danehy, 2000).

The Slippery Rock Creek watershed covers some 725 km<sup>2</sup> in Western Pennsylvania and was been severely impacted from surface and sub-surface mining. Local residents referred to the Slipper Rock Creek as “Sulfur Creek,” emphasizing the level of pollution present in the creek. Approximately 1618 hectares of the Slippery Rock watershed are underlain by abandoned deep mine workings with about 3237.5 hectares formerly permitted for surface mining (Danehy, 2000). The sub-surface mining activity within the watershed impacted 25% of the headwaters, while surface mining operations impacted 50% of the headwaters. In the recent past there has been only limited active mining; currently no mining operations are underway within the Jennings Environmental Education complex. The headwaters of the Slippery Rock Creek were first formally documented in 1970 during Operation Scarlift, a Pennsylvania state-funded mine reclamation program, and deemed a priority remediation site due to the impact of contaminated mine water on drinking water supplies and local fish stocks (Danehy, 2000).

In 1943, the commercial underground mine that under lays the Jennings Environmental Education Center was abandoned on the Middle Kittanning coal bed. After decommissioning, the sub-surface mine works were not properly sealed and reclaimed, resulting in the primary cause of the now 7.89 liters per second acid mine drainage raw flow. Between 1965 and 1967 extensive water sampling was undertaken in the Slippery Rock watershed, documenting the acidic mine drainage impact on the Big Run, a primary tributary to the Slippery Rock Creek. This study was the basis for future mine discharge investigations. In 1970 the quality and quantity of site water discharges was monitored monthly for one year. Through funding provided by Operation Scarlift, the pollution loading impact on Big Run was identified and the bases for the reclamation and remediation projects were established (Danehy: Mining History and Impact Abatement Initiatives 2001). Completed in 1973, the original reclamation design involved the installation of mine seals in an early attempt to significantly decrease the discharge of contaminated mine water. The design also included the partial removal of coal refuse piles and the revegetation of the area, though a significant portion of the site was left unreclaimed.

The mine seals remained in place until they failed in 1985, resulting in an acid mine drainage flood through the Jennings Environmental Education Center that caused a significant fish kill involving several thousand organisms in Big Run and the Slippery Rock Creek due to an

over loading of iron and aluminum into the water (Danhey, 2000). Furthermore, the 1973 attempt to re-vegetate the reclaimed area failed. These events subsequently lead to the basis for future abatement efforts (Danehy: Mining History and Impact Abatement Initiatives, 2001). In 1986, an unpublished overburden analysis was performed on the adjoining surface mining area by CDS Associates Inc. to determine the acid-producing potential of the refuse, as well as leachate characteristics. Between 1988 and 1994 constructed wetlands were installed. A monthly water quality monitoring protocol was established for that portion of the watershed for a three-year period. Primarily because of limited treatment areas and under-sized ponds, the installed wetlands were found to be only 40% effective in improving water quality (Watzlaf, 1997). Subsequent improvements were made to the treatment system, including the installation of an anoxic limestone drain (ALD) between 1992 and 1994, which resulted in a dramatic, though temporary, improvement of water. The system was quickly abandoned due to aluminum deposits that plugged the drain (Watzlaf, 1997).

The failure of the ALD system led to the construction (1994-1996) of a pilot-scale vertical flow compost system that was monitored monthly (Danehy, 2001). The system generated short-term water quality improvements until its failure 13 months after installation. Its failure was attributed to difficulties in regulating flow, as well as the tendency of the compost to reduce the alkalinity generation ability of the limestone (Danehy: Mining History and Impact Abatement Initiatives, 2001). To correct these problems, alternate media types were investigated. George Watzlaf of the United States Bureau of Mines performed lab-based studies of alternate media types (Watzlaf, 1997). His studies led to the installation of a second pilot-scale vertical flow system at the Jennings site, which utilized spent mushroom compost and limestone as the substrate. This system has been online since 1997 and is regularly monitored. The most recent activity at the Jennings site has involved the construction of a full-scale vertical flow system modeled after the second pilot-scale system (Danehy: Mining History and Impact Abatement Initiatives, 2001). The United States Environmental Protection Agency and the Pennsylvania Department of Environmental Protection Bureau of Land and Water Conservation provided funding for the installation of the system (Danehy, 2000).

Consisting of three parts, the overdrain, underdrain, and outlet, the vertical flow system project was completed in September 1997 (Danhey, 2000). The overdrain consists of a 5.08 centimeter PVC header pipe with 1.90 centimeter perforated laterals, 6.10 meters long, every

1.83 meters. Three 5.08 centimeter inlet pipes feed these from a flow splitter box, which is plumbed into the previously constructed anoxic collection system. Bedded in non-reactive river gravel, the underdrain consists of three sections of 5.08 centimeter PVC pipe, fed by 1.90 centimeter perforated laterals 4.57 meters long, every 1.83 meters. The outlet consists of a flexible 10.16-centimeter plastic pipe with a clear insert to allow observation; the outlet is adjustable to control the water level in the system (Danehy, 2000).

The vertical flow system, as a whole, is 45.72 meters long, 15.24m wide and 1.83m deep. The system contains  $2.72 \times 10^5$  kilograms of spent mushroom compost mixed with  $3.44 \times 10^5$ kg of #9 special limestone aggregate (Danehy, 2000). The purpose of this pond is to reduce the state of the metals, which prevents armoring and plugging, while increasing the alkalinity (**DEP**).

The vertical flow system is the first and primary means of improving water quality at the Jennings site, however two other important systems follow this initial treatment process. These include a channel wetland, which acts as a settling pond for the vertical flow system, measuring 53.34 meters long, 2.44 meters wide and 15.24 centimeters. The channel wetland employs an upper section comprised of cattails and rushes and a lower settling pond section. Upon exiting the channel wetland, the water enters a lower wetland section measuring 30.48 meters long, 6.09 meters wide and 15.24 centimeters deep. This lower wetland is sectioned off as the water is 'stepped' down gradient toward its final discharge into Big Run. Half of the wetland contains traditional vegetation (cattails and rushes) while the other half is left open much like a pond (Danehy, 2000). Water quality monitoring of this system still continues today.

There is no one single solution to treating or preventing AMD. The most effective treatment systems normally involve more than one method, recognizing the complex chemical and biological variables at work (Geller, *et al.* 1997). Several treatment wetlands have been built to treat AMD and modifications to these designs continues today. The Tennessee Valley Authority (TVA) has built 19 systems since it started its program in 1985. The early TVA projects were mostly natural marshes, but the more recent projects are constructed passive treatment systems. The Electric Power Research Institute in California, in an attempt to better understand the technology, is doing extensive research on passive treatment systems. They have spent \$2.5 million since 1994 on constructed wetland projects (Cole 1998). Along with research being done to provide a better means of pollution control and remediation, federal, state, and

local governments have written laws to protect our water, the organisms that depend on that water for survival, and us.

## **Legislation and the Acid Mine Drainage Issue**

In 1972 the federal government enacted the Federal Water Pollution Control, also known as the Clean Water Act. Amended in 1977, the Clean Water Act was enacted to restore and maintain the quality of the nation's waters. The act also created the National Pollutant Discharge Elimination System (NPDES), which requires permits or licenses for the discharge of effluent into U.S. waters including wetlands. The NPDES regulates the amount of chemicals, heavy metals, and biological wastes that are discharged in wastewater, from industrial processes and sewage treatment facilities, to wetlands. The discharging party must comply with state and federal water quality standards (see *Appendix A, Table 1* for the criteria pertaining to the metals of interest). Funding can be provided by the CWA to help communities meet their needs (Cornell University, 2001).

In the Commonwealth of Pennsylvania the goals of the Clean Water Act are administered under the Pennsylvania Clean Streams Law. Applications for discharge permits can be refused if the discharge will result in unacceptable adverse effects on certain classes of aquatic resources such as wetlands. Endangered Species Protection controls all the agencies dealing with endangered species. Consideration of the effect of an activity on the endangered species in the area is taken. Protection against the killing, endangering, or habitat modification of organisms is also monitored. Before issuance of any permit for activity, adverse impacts must be considered and evaluated.

## **Study Methods**

### *Section A: Design and Construction of the Model Passive Treatment Systems*

#### Phase One: Site Preparation

The site chosen to conduct the research project was the Jennings Environmental Education Center in Butler County, Pennsylvania, USA. We chose this site because of ease of access to an existing and well-studied acid mine discharge seep. Site preparation was an essential part of the research design and afforded a suitable area to setup the scaled treatment systems.

A 10-meter by 2-meter area was cleared of sod and leveled using standard river gravel. This area served as a level pad for the placement and setup of the four model passive treatment systems. A trench originating at the head box (tap in point to raw water for project) and leading to the leveled area adjacent to the treatment systems was excavated using hand tools to a depth of 30 cm. The trench was designed to accept the 2.67 cm raw water (inflow) supply line that feeds the four treatment systems. The raw water (inflow) supply line originated in the Quonset hut where it was connected to the main head box (constructed previously) that was in place to reduce the water pressure from one up-hill acid mine drainage seeps. We excavated a second trench to a depth of 30 cm to accept the water discharged from the treatment systems and channel that water into an existing downgrade wetland.

#### Phase Two: Assembly of Passive Treatment System Plumbing

Four, 378.54 liter Rubbermaid ® agricultural watering basins were purchased and transported to Jennings Environmental Education Center (site of construction). The under-drain and outlet-drain details were assembled using 1.90-centimeter rigid PVC pipe and pipe fittings. The solvent fittings were connected and made watertight using PVC pipe adhesive, while the screw fittings were wrapped with plumbers tape and tightened firmly. See Appendix E for a diagram of the under-drain system. A similar process was used in the assembly of the flow splitter system, with the exception that all pipe and pipe fittings were 2.54 cm rigid PVC. The flow splitter system employed 4, 2.54 cm PVC ball valves as a means to control raw water

supply to the four treatment systems. See Appendix F for a diagram of the flow splitter. A 1-meter by 1-meter by 30 cm pad was excavated and leveled with river gravel to accept the installation of the flow splitter system and incoming raw water supply line.

A 2.54 cm PVC gate valve was installed on the head box inside the Quonset hut as a primary means to regulate flow into the raw water (inflow) supply line. A 30 cm trench was excavated inside the Quonset hut (continuation of the trench leading to the treatment systems) to accept the supply line and gate valve coming off the head box. A 15.24-meter coil of 2.54 cm polyethylene water supply pipe was purchased and bedded in the prepared 30 cm trench to serve as the raw water supply line. Two, 2.54 cm PVC stab fittings secured with metal pipe clamps were installed on each end of the raw water supply line and completed the connection between the head box gate valve and the inlet to the flow splitter system. Once connections were completed on the raw water supply line and a visual inspection of the system was performed to check for leaks, the trench was back-filled using the soil and sod previously excavated in Phase One. See Appendix G for a diagram of the complete system setup.

### Phase Three: Placement of Interior Treatment System Materials

Once the interior and exterior piping was completed the interior material constituents were added using a bucket of known volume so that the mass of materials used in construction could be calculated. The under drain system was bedded (mid-level) within a layer of unreactive river gravel taken from the Jennings site; 63.95 kg of river gravel was used to bed the under drain system in each treatment system for a total of 255.80 kg for the entire project. The purpose of the river gravel was to allow percolation of treated water to enter the under drain system while preventing clogging from the upper organic layers. The next homogeneous material that overlaid the river gravel under drain system was comprised of number nine limestone collected from Quality Aggregates in Boyers, Pennsylvania and either saw dust, from an Amish saw mill near Volant, Pennsylvania, or aquatic macrophyte compost, harvested from Lake Britain on the Westminster College campus, depending on the treatment system design. Treatment system design one (replicated) called for the mixing of 44.93 kg of number nine limestone and 9.043 kg of saw dust. Both materials were pre-measured and mixed in a wheelbarrow prior to being placed into two of the four treatment systems. See Appendix H for a diagram of the sawdust model. Treatment system design two (replicated) called for the mixing of 44.93 kg of number

nine limestone and 13.16 kg of aquatic macrophyte compost. Again, both materials were pre-measured and mixed in a wheelbarrow prior to being placed into the remaining two treatment systems. See Appendix I for diagrams of the aquatic macrophyte model. Each treatment system was clearly marked with a laminated sign according to contents. A total of 179.71 kg of number nine limestone, 18.09 kg of saw dust, and 26.31 kg of aquatic macrophyte compost was used in the construction of this project.

#### Phase Four: Adjusting Raw Water Supply to Treatment Systems

Once all the constituents of the treatment systems were placed according to the research design the raw water supply was turned on by partially opening the previously installed gate valve fitted to the head box. Initially, the flow splitter ball valves (used to fine tune actual flow to the systems) were left in the full open position until the systems had filled to the desired level; care was taken not to allow pressurized flow to dig into the substrate material. The gate valve and flow splitter ball valves were adjusted to achieve a 12-hour retention time of the water entering the systems once the appropriate water level was reached. Periodic adjustments of both valves were made throughout the course of the research project to maintain the desired 12-hour water retention time.

#### *Section B: Field Sample Collection Procedure*

(Reference: USEPA, 1996 Method 1669)

The study design entailed two phases of sample collection; Phase One: 24-hour inflow (raw water) sample protocol and Phase Two: 2-week sample protocol. An identical sample collection method was employed during both phases. A checklist was developed to ensure each collector was consistent in sample collection.

#### Phase One: 24-Hour Sampling Protocol

We collected the samples in 220 ml polypropylene containers with snap lids. The purpose of the 24-hour sampling regime was to establish a baseline of data that demonstrated consistency (concentration of metals of concern) within the raw inflowing water. One to two

students collected samples at the beginning of each hour for a period of 24-hours. We collected two samples at the raw water inflow of each treatment system, and labeled them 1 and 2, respectively, followed by the date, time, and pond number. Sample containers were filled to a volume of 200-ml (according to markings on the containers) and capped, then placed aside for transport back to the lab. Eight samples total were collected per hour for a total of 200 samples over the 24-hour period (from 7:00 a.m. Saturday morning to 7:00 a.m. Sunday morning, for actually 25 hours of sampling). Upon returning to the lab, we acidified all samples below pH 2 by adding 1-ml of trace-metal grade nitric acid using a calibrated pipette so as to keep metals in a dissolved state. Samples were then placed in a standard refrigerator (between 4°-5°C) to maximize preservation (USEPA, 1996 Method 1669).

### Phase Two: 2-Week Sampling Protocol

The 2-week sampling protocol also used 220-ml polyethylene containers, with snap lids in field collection of samples. Samples were collected between the dates of March 21, 2001 and March 30, 2001 three times weekly (Wednesday, Thursday, Friday) during the afternoon at 2:00 p.m. A total of five, 200-ml samples were collected from the outflow of each treatment system for a total of 20 outflow-water samples per daily visit. The samples were labeled with the pond number, date and series number (1 through 5). One inflow sample was collected for each treatment system, for a total of four raw water (inflow) samples collected per daily visit. To ensure that metal concentrations were consistent with that of the results of the 24-hour (Phase One) sample analysis, raw water (inflow) samples were collected. Upon returning to the lab, the outflow water samples were acidified below pH 2 with 1.00-ml of trace-metal grade nitric acid. Once the samples were acidified they were placed in a standard refrigerator to maximize preservation (USEPA, 1996 Method 1669).

### **Field Blanks**

The protocol also called for the utilization of four field blanks (ultra-pure water), one for each of the model treatment systems (labeled A, B, C, D). Field blanks were opened during filling of the outflow water samples so as to determine whether contamination was entering the sample stream during collection. These blanks were then acidified (with 2.60-ml of trace-metal grade nitric acid) and filtered in the same manner as the other samples.



### *Section C: Glassware and Equipment Cleaning Procedure*

(Reference: USEPA, 1996 Method 1669)

A strict acid washing procedure was established to prevent extraneous metals contamination of field collected samples (USEPA, 1996 Method 1669). All glassware and related equipment (including plastics) was rinsed thoroughly with ultra-pure water, then 20% trace-metal grade nitric acid, followed by another rinse with ultra-pure water.

The filter funnel apparatus used in the preparation of samples was cleaned by rinsing with ultra-pure water, then 20% trace-metal grade nitric acid, then a second rinse with ultra-pure water. The filter apparatus was vacuum dried (the vacuum was turned on with no water or sample in the filter apparatus) following the cleaning procedure. The cleaning procedure was performed between each filtering to prevent cross contamination.

The containers (220-ml polyethylene plastic containers) used to field collect samples were purchased for original one-time usage in the study, eliminating the need to acid wash prior to filling. A fresh container and lid was used in the collection of each field sample. To verify that the containers were not inherently contaminated with metals, several containers were filled with ultra-pure water and allowed to set for 24-hours, then analyzed for the metals of concern using graphite furnace or flame atomic absorption spectroscopy. Similarly, method and field blanks were analyzed to verify that metals contamination did not pervade the sample collection and preparation process.

### *Section D: Sample Preparation Protocol* (Reference: USEPA, 1996 Method 1669)

The same method was utilized in the preparation of all samples and blanks analyzed during the study, based upon the guidelines set forth by EPA Method 1669. Method blanks were analyzed for the metals of concern to ensure the sample preparation procedure was not inherently contaminating our filtered samples. Prior and between filtering the cleaning regime detailed in Section A of the Methods portion of this paper was performed; a second 1000-ml vacuum flask was used exclusively during the cleaning step.

Previously acidified samples were filtered into 50-ml polyethylene centrifuge tubes with screw on lids using a standard vacuum apparatus employing an acid-resistant 0.45 $\mu$ m, 47 mm

filter paper. The 50-ml centrifuge tube was placed inside a 1000-ml vacuum flask that was partially filled with gravel so that the tube was properly oriented in an upright position in order to allow proper suction. The filter funnel apparatus was then placed on top of the vacuum flask containing the filter paper; the vacuum flask was connected to a sink aspirator using a rubber hose. Sample was then slowly poured by hand into the funnel, allowing the suction to pull sample through the filter paper and into the centrifuge tube. Approximately 40-ml of sample was filtered into the centrifuge tube. Once filtering was complete the centrifuge tube was removed from the vacuum flask and labeled with the analytic identification number that corresponded to the date, time and treatment system designation for that sample. Analytic identification numbers were based upon random numbers generated using a Microsoft Excel spreadsheet and assigned to the sample information (date, time, system designation). A master analytic identification spreadsheet was prepared for both the 24-hour and 2-week sampling protocol. The individuals performing the metals analysis on the samples were not privy to the master identification spreadsheets in the interest of eliminating bias (USEPA, 1996 Method 1669).

The filtered samples were placed in a standard refrigerator until analysis so as to maximize preservation. Prepared samples were analyzed in sequential order according to the analytic identification number written on the centrifuge tube (see Methods of Analysis section). The remaining unfiltered 'stock' samples were retained for potential future usage; these samples were frozen.

### *Section E: Analytical Technique for Iron Analysis*

A separate method of analysis was devised to examine iron concentrations in field samples due to the inability of the atomic absorption graphite furnace method to effectively distinguish the high concentrations of iron known to be present from the pilot study. An instrumental blank and series of dilution standards were prepared in advance of field sample analysis. The method is detailed in the subsequent paragraphs.

## **Instrumental Blank Preparation**

The method called for the preparation of an instrumental blank as follows. A 100ml volumetric flask was acid washed and rinsed with ultra-pure water. Constituents of the blank were added to the flask by mass as follows: 2ml of Hydroquinone, 3ml of o-phenanthroline, and 2.83ml of sodium citrate (pH 3.5). The required amount of sodium citrate to achieve proper acidification was determined using a calibrated pH meter. Once all reagents were added to the flask, the solution was diluted to the 100ml mark using ultra-pure water. The blank is to be analyzed each time the instrument is prepared to run a batch of samples. A fresh instrumental blank was prepared every two days so as to ensure the blank was not aging, potentially impacting the quality of field sample analysis.

## **Preparation of Stock Iron Solution**

A stock solution of iron standard was first prepared analytically and then used to generate the subsequent four dilution standards necessary to build a calibration curve. The stock iron solution was prepared analytically by combining 0.289 g of reagent-grade  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 1ml of 95%  $\text{H}_2\text{SO}_4$ , diluted to 1000ml with ultra-pure water in a volumetric flask. A range of dilution standards were prepared from the stock iron solution to elucidate a calibration curve, these comprised 10, 5, 2, and 1 ml of the stock iron solution. Preparation details are discussed in the following paragraph.

## **Preparation of Iron Dilution Standards (Calibration Curve)**

The field samples collected from the four model systems were prepared for analysis based upon the following method. Samples were prepared in acid-washed and ultra-pure water rinsed 100ml volumetric flasks.

Prior to preparing the dilution standards the proper proportion of sodium citrate for each standard was determined so that a pH of 3.5 was achieved. Similarly, calculations were completed to determine proper scaling of all other reagent constituents. The first dilution standard was prepared analytically by adding 10ml of stock iron solution to a 100ml volumetric flask by mass, followed by 2.83ml of sodium citrate, 2ml of hydroquinone and 3ml of o-phenanthroline (all volumes measured by mass). The second dilution standard was prepared in a similar fashion by adding 5ml of stock iron solution to a 100ml volumetric flask by mass,

followed by 1.42ml of sodium citrate, 2ml of hydroquinone, and 3ml of o-phenanthroline (all volumes measure by mass). The third dilution standard was prepared analytically by adding 2ml of stock iron solution to a 100ml volumetric flask, followed by 0.571ml of sodium citrate, 2ml of hydroquinone, and 3ml of o-phenanthroline (all volumes measured by mass). The fourth and final dilution standard was prepared by adding 1ml of stock iron solution analytically to a 100ml volumetric flask, followed by 0.238ml of sodium citrate, 2ml of hydroquinone, and 3ml of o-phenanthroline (all volumes measured by mass). Dilution standards were allowed to stand for 10-minutes to allow for prescribed color development prior to analysis. Each of the dilution standards was then analyzed on the spectrophotometer and these values were saved on the computer hard disk so that the calibration curve could be examined to determine iron concentrations in field samples.

### **Field Sample Preparation Prior to Analysis**

Prior to analysis all field samples were prepared as follows. A 100ml volumetric flask was acid washed and rinsed with ultra-pure water. Next, 3ml of field sample was added to the flask by mass, followed by 2ml of hydroquinone, 0.846ml of sodium citrate (pH 3.5) and 3ml of o-phenanthroline. Once all reagents were added, the solution was diluted to the 100ml mark on the flask using ultra-pure water. After a 10-minute period, the samples were placed in suprasil quartz cuvettes for spectrophotometric analysis.

The analysis of all blanks, standards and field samples was performed on a standard spectrophotometer connected to a computer interface (ChemStation by Agilent Technologies) set to a wavelength of 508nm. Prior to beginning analysis the instrument is turned on and allowed to warm-up for 10-minutes. A previously devised and saved computer method was utilized throughout the analysis to maintain consistency. A suprasil quartz cuvette was used in analysis of all samples. Prior to analyzing a sample, the suprasil quartz cuvette was rinsed with ultra-pure water and filled with 1ml of sample three times in order to thoroughly rinse all surfaces. Following cuvette cleaning, the spectrophotometer was blanked and a sample was placed in the instrument; data was saved on the computer hard disk for future use. The previously generated standard curve allowed for the field samples to be quantified for the respective iron concentration. Both sets of field samples (24-hour and 2-week) were analyzed according to the generalized method discussed in this paragraph.

*Section F: Atomic Absorption Spectroscopy Methods for Aluminum and Nickel*  
(Reference: USEPA, 1994 Method 200.9)

Atomic absorption spectroscopy was used to analyze all of the samples for nickel and aluminum (See appendix for instrument parameters). Graphite Furnace Atomic Absorption (GFAA) was used to analyze the nickel 24-hour samples. The remaining samples (24-hour aluminum and weekly samples) were analyzed using flame atomic absorption.

### **Graphite Furnace Atomic Absorption (GFAA)**

The 24-hour nickel sampling using GFAA was analyzed somewhat differently than the flame analysis. Since we were only trying to support the theory that all of the inflow water had approximately the same concentrations of heavy metals, we did not create a standard curve so as to quantify the results. We could use the absorbencies to calculate whether the concentrations were consistent throughout the day. Since the concentrations of nickel in the samples were large, the samples had to be diluted so that the graphite furnace would be able to accurately determine the absorbencies. For each sample, 1000 $\mu$ g of 5% nitric acid was added to 100 $\mu$ g of sample. This gave an absorbance in the middle range of about 0.5.

### **Flame Atomic Absorption**

Flame atomic absorption was used to analyze the 24-hour samples for aluminum and the weekly samples for both metals. Flame was used for this part of the analysis because it is not as sensitive as graphite furnace; it is able to read at higher concentrations (in the parts per million range).

### **Quality Control**

A calibration blank, consisting of 5% nitric acid, was analyzed every 10 samples as the quality control for the graphite furnace. The calibration blank was set up to ensure that there was no accumulation of nickel on the furnace tube. Other quality control parameters were put in place to make certain that there was no contamination in our sampling procedure or preparation of samples. These other quality control parameters, along with the calibration blank, were

utilized during our analyzing of the weekly samples. Field blanks ensured that our samples were not being contaminated in the field. One field blank for each tub was taken every sampling day. The field blank consisted of ultra-pure water and was taken through the same procedure as all of our other samples, including handling in the field, acidification, and filtration. The method blank, or laboratory reagent blank, is ultra-pure water that was acidified and filtered the same as our samples. Since the method blank was exposed to the same glassware as our samples, the data from these blanks was used to verify that our samples received no contamination from the filtering process. In addition, for the flame analysis, the standard curve was recalibrated every ten samples to ensure that the instrument was not drifting.

## Results

The results of the study will be presented in two parts, the first part being the 24-Hour inflow (raw water) data and the 2-Week outflow (discharged water) data. Additionally, the calibration curves used in the atomic absorption spectroscopy and spectrophotometric analysis are included.

### Calibration Curve for UV/vis

Figure 1 below shows the calibration curve for the UV/vis technique. The figure shows the absorbencies for four iron standards of differing concentrations. The points representing each standard are labeled with actual prepared concentrations. All UV/vis analysis was performed at a wavelength of 508 nm.

Figure 1: Iron Calibration Curve for UV/vis Analytical Technique

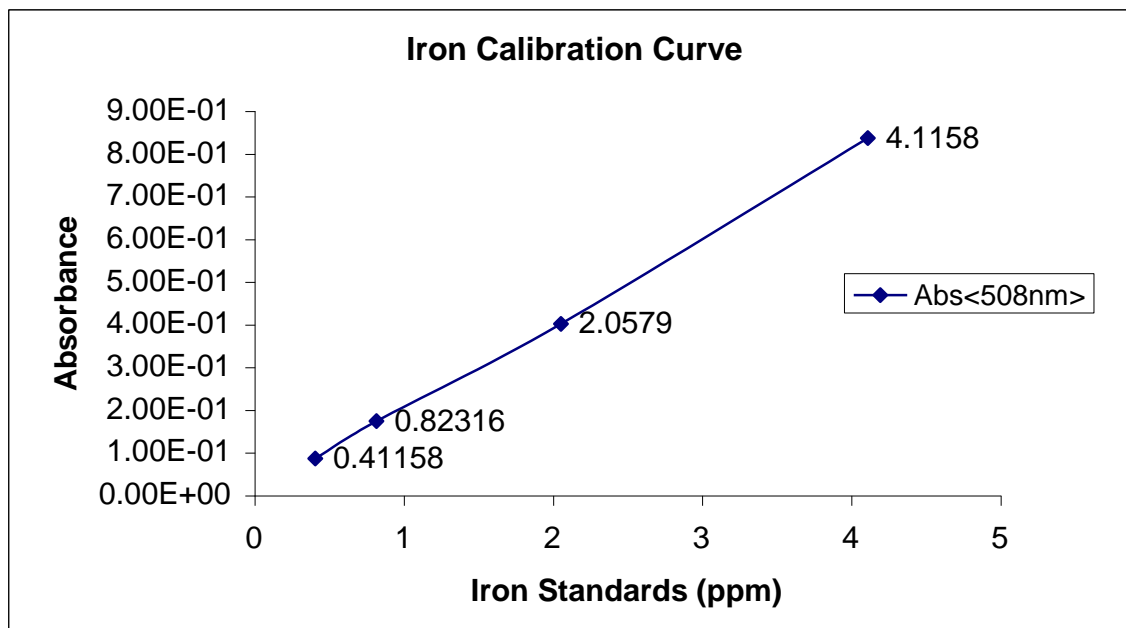


Figure 2: Aluminum Calibration curve

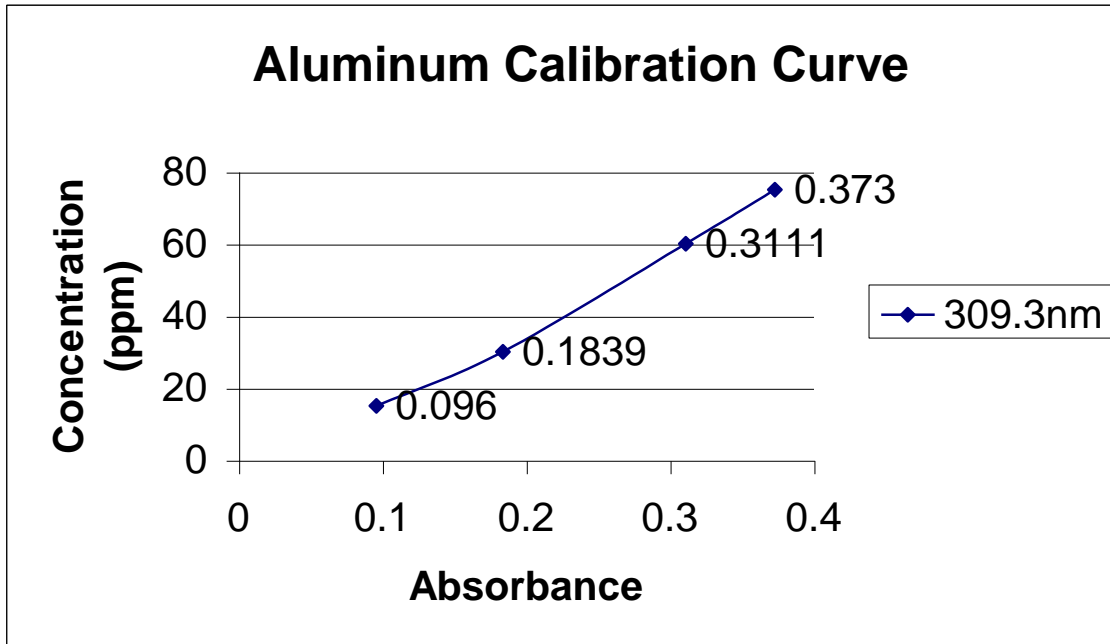
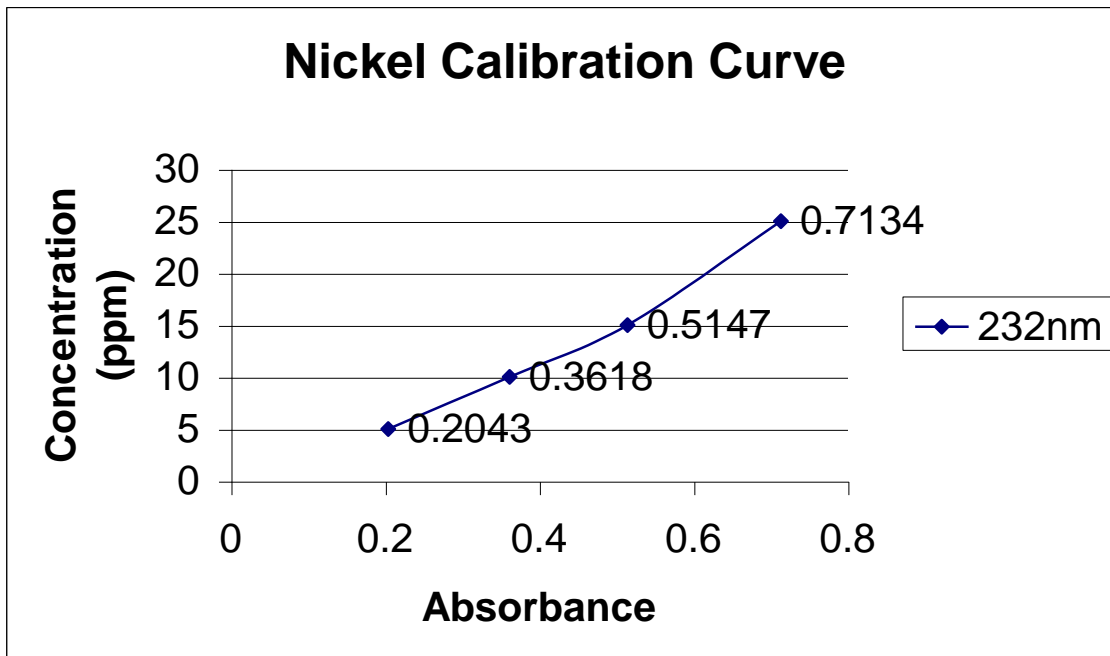


Figure 3: Nickel Calibration Curve



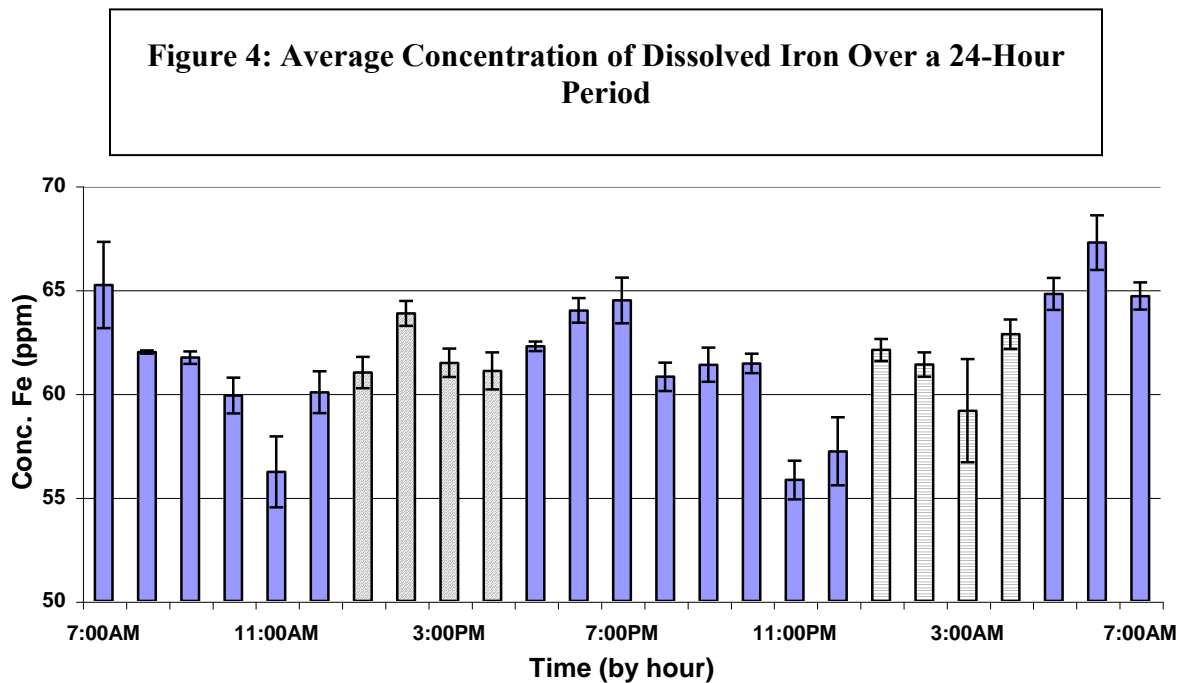


## 24-Hour Results by Metal

There was no statistical evaluation of the 24-Hour data because the samples in this case were not independent of one another, being that the water collected at the inflow to each model shared a common source, a single acid mine drainage seep.

### 24-Hour Inflow Results for Iron:

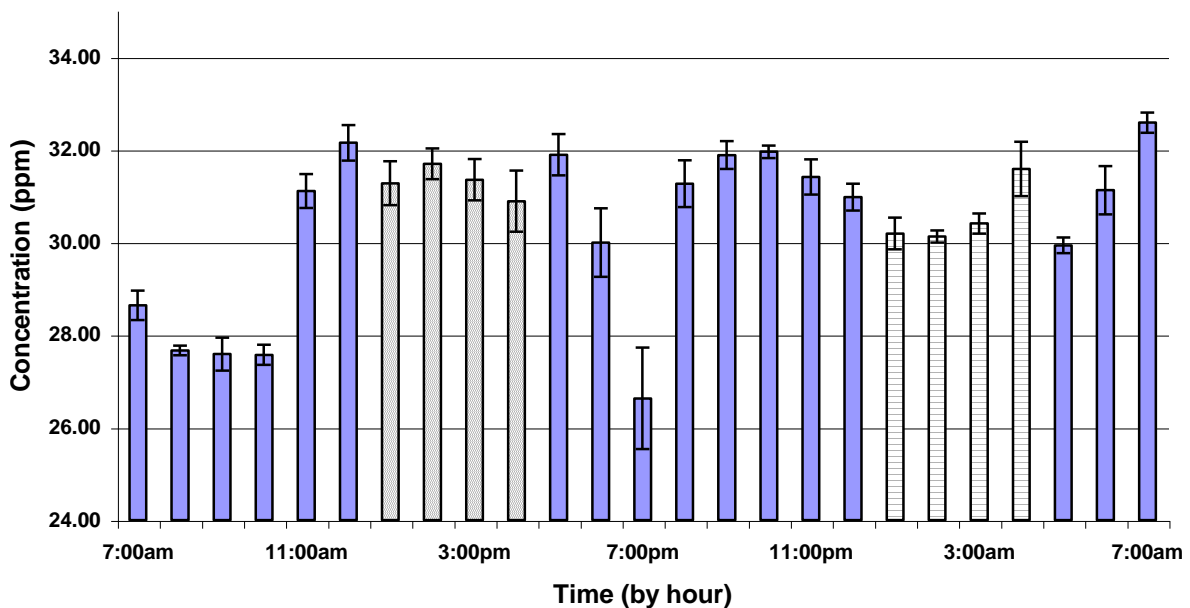
The data shown below in Figure 4 represents the average concentration trend of iron obtained during a 24-hour sampling process performed on the inflow water supply feeding the model passive treatment systems examined in the study. The figure indicates a trough in the data at 11:00 am and 11:00 pm; a peak in the data is indicated at 7:00 pm and 7:00 am. Figure 4 indicates the daylight hours (1:00 pm to 4:00 pm) corresponding to the times 2-Week sampling occurred, additionally, the iron concentrations 12 hours from that point are noted (1:00 am to 4:00 am). Standard error bars at the 95% confidence limit were calculated and are presented graphically in the figure below. The units for concentration are parts per million (ppm) and time are denoted by hour.



## 24-Hour Inflow Results for Aluminum:

The data shown below in Figure 5 represents the average concentration trend of aluminum obtained during a 24-hour sampling process performed on the inflow water supply feeding the model passive treatment systems examined in the study. The aluminum data collected over the 24-Hour sampling period did not indicate a distinguishable trend or cycle over a 24-Hour period like that of iron and nickel. Figure 5 indicates the daylight hours (1:00 pm to 4:00 pm) corresponding to the times 2-Week sampling occurred, additionally, the aluminum concentrations 12 hours from that point are noted (1:00 am to 4:00 am). Standard error bars at the 95% confidence limit were calculated and are presented graphically in the figure below. The units for concentration are parts per million (ppm) and time are denoted by hour.

**Figure 5: Average Concentration of Dissolved Aluminum Over a 24-Hour Period**

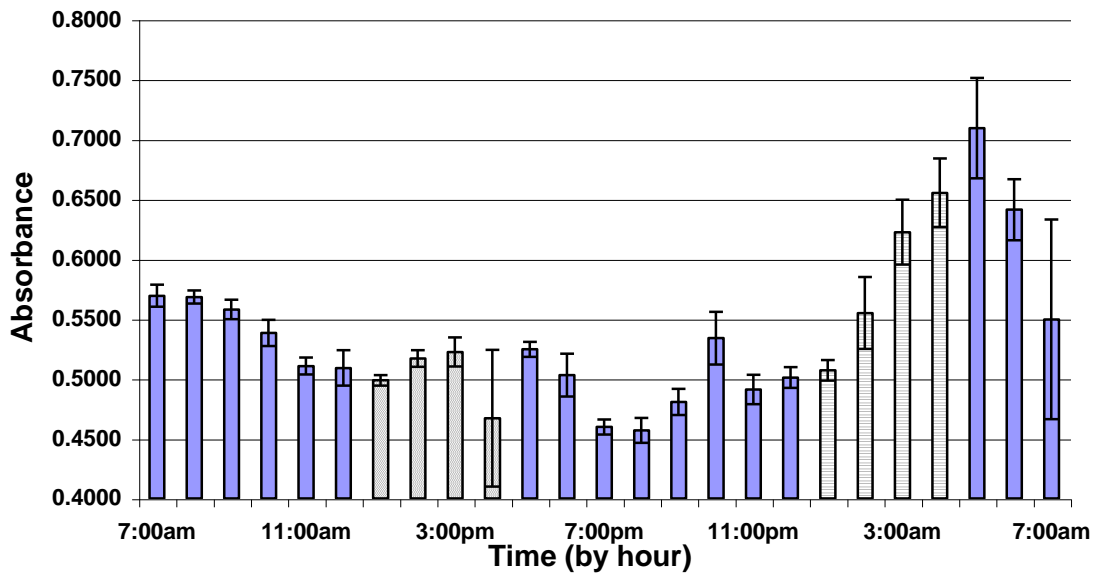


## 24-Hour Inflow Results for Nickel:

The data shown below in Figure 6 represents the average concentration trend of nickel obtained during a 24-hour sampling process performed on the inflow water supply feeding the

model passive treatment systems examined in the study. The nickel data collected during the 24-Hour sampling period did not present a very distinct trend or cycle, as was the indicated for iron. However, there did appear to be a peak at about 7:00 am and a trough at about 7:00 pm, although it is not clear this trend is realistic. Figure 6 indicates the daylight hours (1:00 pm to 4:00 pm) corresponding to the times 2-Week sampling occurred, additionally, the iron concentrations 12 hours from that point are noted (1:00 am to 4:00 am). Standard error bars at the 95% confidence limit were calculated and are presented graphically in the figure below. The units on the y-axis are absorbance and the units on the x-axis time are denoted by hour.

**Figure 6: Average Absorbance of Dissolved Nickel Over a 24-Hour Period**



## 2-Week Results by Metal

The 2-Week data is presented below. For each metal examined in this study a figure presenting the mean concentration/absorbance values was prepared, as well as a second figure with percentage of metal discharged in the outflow sample. Two statistical tests were used to evaluate whether or not differences existed between the two treatment medias (sawdust and macrophyte compost) of concern. The first statistical test was the parametric 2-sample t-test.

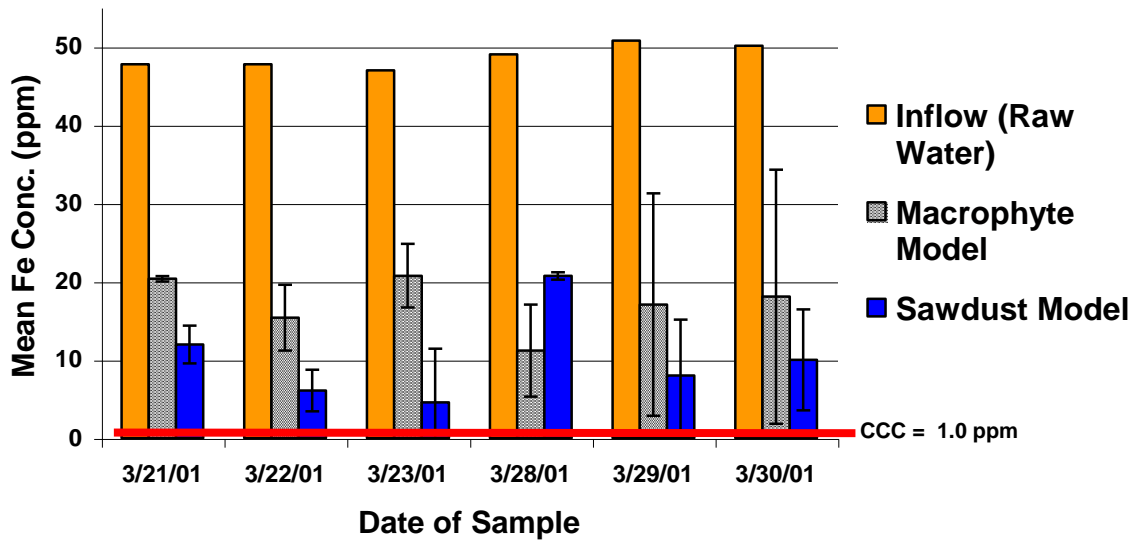
The second statistical test utilized was the non-parametric equivalent to the 2-sample t-test, the Mann-Whitney test. Both statistical tests indicate that the null hypothesis cannot be rejected, meaning that the two systems are not different. See Appendix D for specific statistical results, including p-values.

## 2-Week Results for Iron

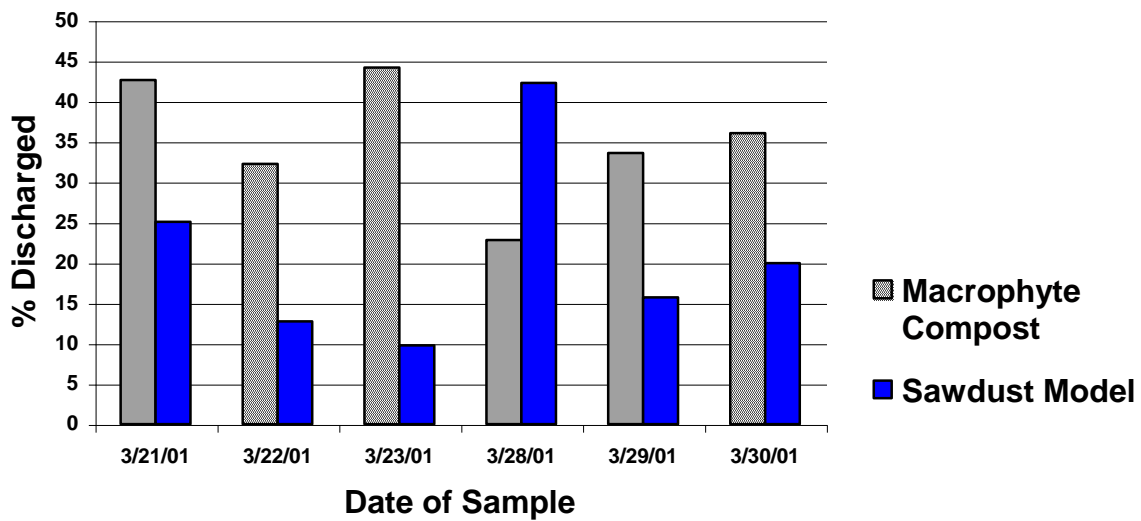
The data shown below in Figure 7 represents the mean concentration (ppm) of iron in outflow (discharged) water samples over a six-day sampling period. The inflow water sample data for each day is included for reference purposes, these samples are separate from the inflow data taken during the 24-Hour sampling and were collected at the same time the outflow water samples were collected. The red line labeled as 'CCC' (1.0 ppm) indicates the continuous exposure level for iron set forth by the Clean Water Act, indicating significant adverse biological effects above this threshold concentration. The results indicate a strong likelihood of significant adverse biological effects resulting from exposure to contaminated acid mine water.

Figure 8 represents the percent of iron discharged by the system of the original raw water inflow. Percentage of iron discharged relates to the percentage of metal discharged in a soluble form and not retained within the treatment media or system water column. This percentage is based upon the inflow data collected on the day the outflow samples were taken and not the 24-Hour data.

**Figure 7: Mean Concentration of Dissolved Iron in Outflow Samples**



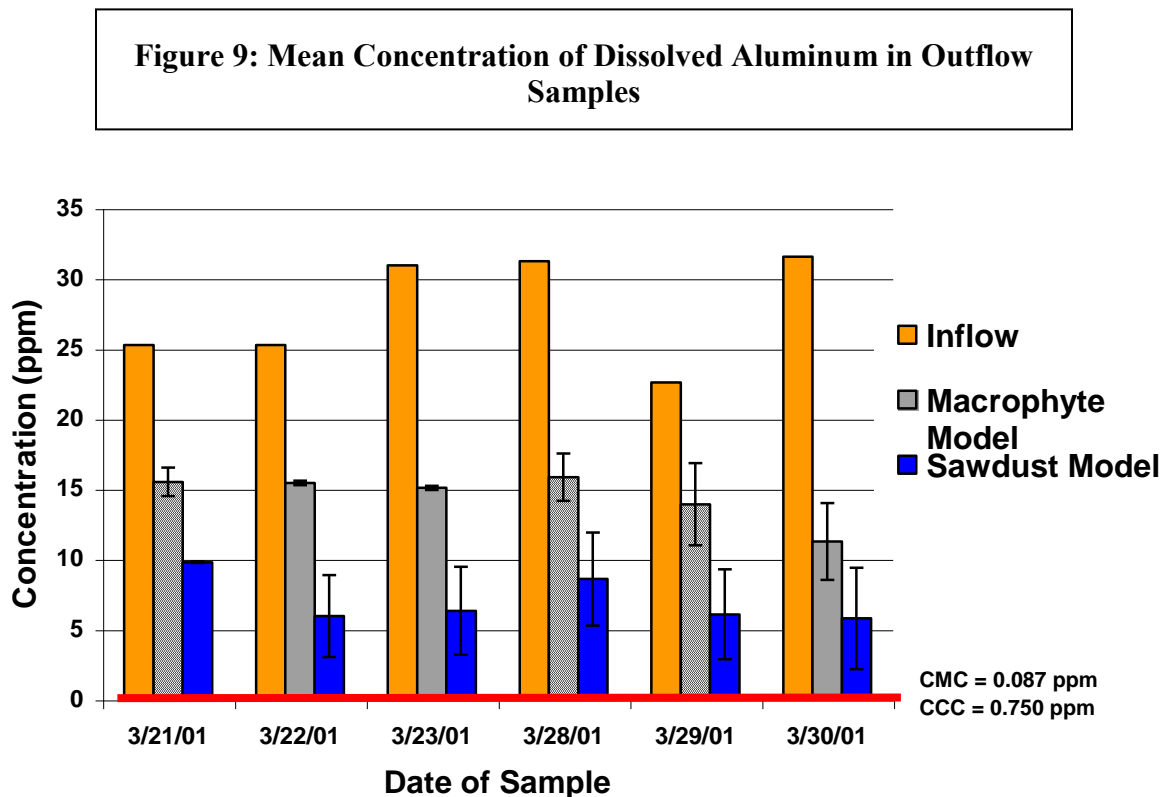
**Figure 8: Percentage of Dissolved Iron Discharged in Outflow**



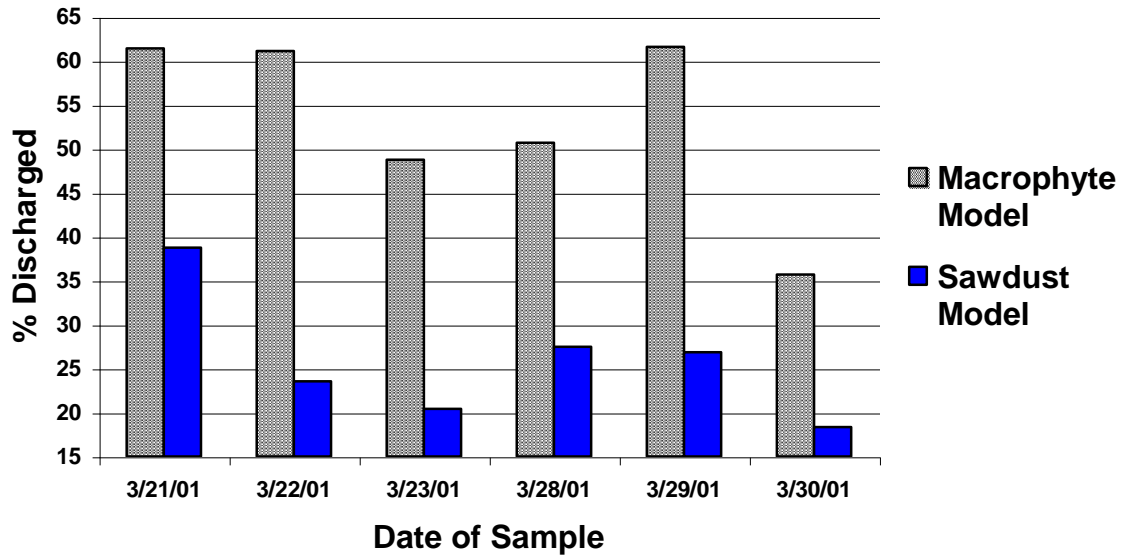
## 2-Week Results for Aluminum

The date shown below in Figure 9 represents the mean concentration (ppm) of aluminum in outflow (discharged) water samples over a six-day sampling period. The inflow water sample data for each day is included for reference purposes, these samples are separate from the inflow data taken during the 24-Hour sampling and were collected at the same time the outflow water samples were collected. The red line labeled as ‘CCC’ (0.750 ppm) indicates the continuous exposure level for iron set forth by the Clean Water Act. The line labeled as ‘CMC’ (0.087 ppm), set forth by the Clean Water Act, indicates a one-time maximum level of metal’s contamination, above which adverse impacts are likely. The results indicate a strong likelihood of significant adverse biological effects resulting from exposure to contaminated acid mine water.

Figure 10 represents the percent of aluminum discharged by the system of the original raw water inflow. Percentage of aluminum discharged relates to the percentage of metal discharged in a soluble form and not retained within the treatment media or system water column. This percentage is based upon the inflow data collected on the day the outflow samples were taken and not the 24-Hour data.



**Figure 10: Percentage of Dissolved Aluminum in Discharge Outflow**

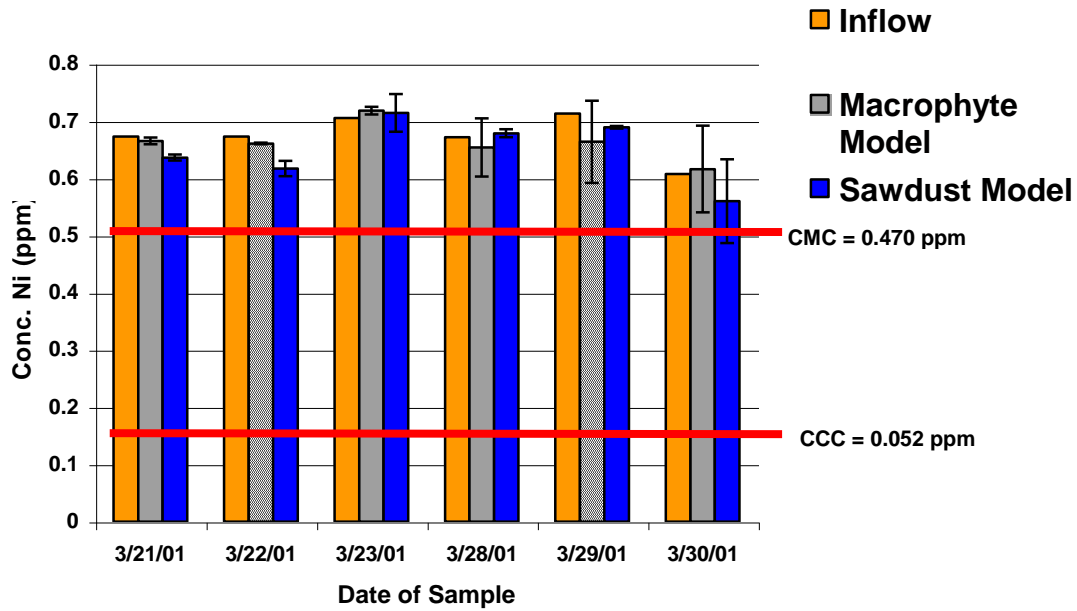


## 2-Week Results for Nickel

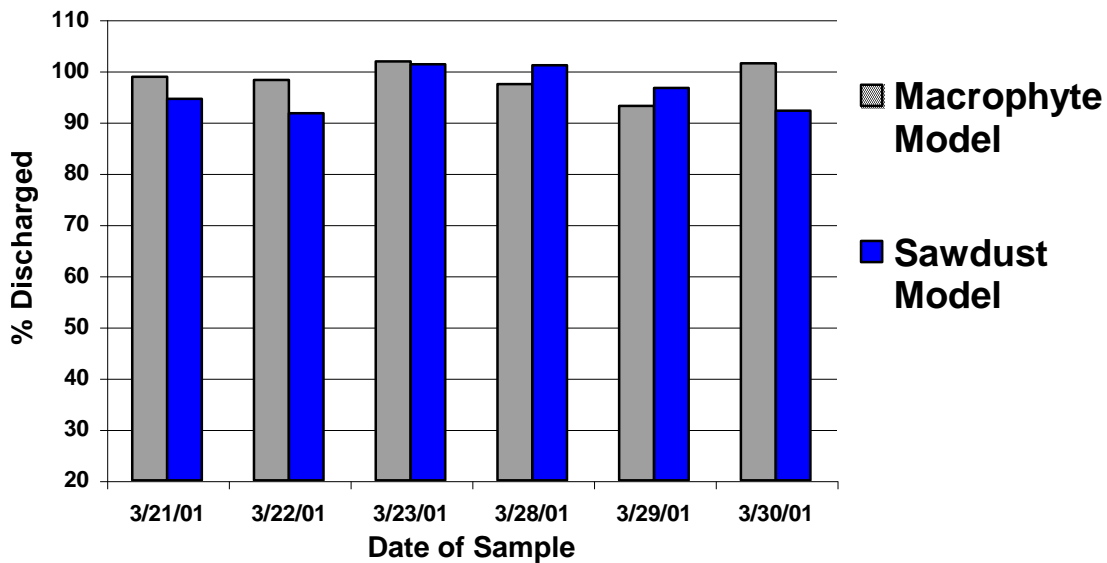
The date shown below in Figure 11 represents the mean concentration (ppm) of nickel in outflow (discharged) water samples over a six-day sampling period. The inflow water sample data for each day is included for reference purposes, these samples are separate from the inflow data taken during the 24-Hour sampling and were collected at the same time the outflow water samples were collected. The red line labeled as ‘CCC’ (0.052 ppm) indicates the continuous exposure level for iron set forth by the Clean Water Act. The line labeled as ‘CMC’ (0.047 ppm), set forth by the Clean Water Act, indicates a one-time maximum level of metal’s contamination, above which adverse impacts are likely. The results indicate a strong likelihood of significant adverse biological effects resulting from exposure to contaminated acid mine water.

Figure 12 represents the percent of nickel discharged by the system of the original raw water inflow. Percentage of nickel discharged relates to the percentage of metal discharged in a soluble form and not retained within the treatment media or system water column. This percentage is based upon the inflow data collected on the day the outflow samples were taken and not the 24-Hour data.

**Figure 11: Mean Concentration of Dissolved Nickel in Outflow Samples**



**Figure 12: Percentage of Dissolved Nickel Discharged**





## Discussion

Originally, we first investigated the use of the passive treatments systems to decrease the metal concentration from the water affected with AMD. However, after further research, we learned that passive treatment systems were not supposed to decrease the metal concentrations in the water. Instead, a successful system would have a higher metal concentration in the effluent because the organic substrate would be reducing the state of the metal ions.

In an attempt to remediate AMD, two different passive treatment systems were built for the purpose of comparing the effectiveness of the organic substrates. Organics reduce the oxygen concentration in the water, thus reducing the state of the metal ions, which prevents them from precipitating out and clogging the system.

The twenty-four hour sampling led us to believe that the concentrations of metals were not constant throughout the day. The dissolved iron showed a 12-hour pattern with peaks at 7am and 7pm, and troughs at 11am and 11pm (Figure 4). The dissolved aluminum showed no pattern throughout the sampling process (Figure 5). The dissolved nickel showed a 24-hour pattern with a peak at 7am and a trough at 7pm (Figure 6). Since the weekly samples were taken at approximately the same time each day (1pm-4pm), it was believed that there was little variation in the concentration of each metal in the samples taken.

The data from the weekly sampling provided information on the concentrations of metals that were removed from each of the two models (Figures 7, 9, and 11). The ocular analysis of the results would lead one to believe that the two types of substrates retained different concentrations of dissolved metals. When a statistical analysis was performed on the data, the p-values were greater than 0.05, indicating there was no significant difference between the two systems (Appendix D). It was believed that if the systems had more replicates of the differing substrates, then more statistical power would have been added and a difference would have been calculated. Adding another value in the range of values that we already had and performing the statistical analysis again confirmed this.

The system that contained the aquatic macrophyte substrate visibly retained more dissolved metals (only aluminum and iron) in its outflow (Figures 8 and 10). Our nickel data showed that its concentrations were not retained in the system (Figure 12). This may be due to nickel being a metal that is not easily oxidized. Since our data showed that the macrophyte

system retained more metals, we concluded that it was more effective. Originally the purpose of our system was to remove dissolved metals from water. This would lead to better water quality. After follow up research, it was realized that the system that was modeled had the purpose of raising alkalinity and keeping metals in solution. Problems have arisen with metals precipitating from the water in this stage of remediation and clogging the drainage system. This would lead to higher maintenance and decreased life of the vertical flow ponds.

Possible reasons that the macrophyte system retained more metals in the water could have been due to porosity and more microbial activity. Increased porosity would allow greater contact area, and microbes would better be able to come in contact with the water. Raised microbial activity and quantity would decrease the levels of oxygen bringing the system to a more anoxic state. As this occurs more metals are reduced and therefore are encouraged to remain in solution.

In the future it would be suggested that several things are changed within the study. First and foremost, levels of alkalinity will need to be monitored. Raised alkalinity is the major purpose of a vertical flow pond. Secondly, further replicates of the system should be implemented for greater statistical power. Thirdly, a longer outflow sampling period and additional 24-hour inflow sampling might have led to a better understanding of the patterns of retention through out temperature variances. Trying the experiment in the summer, when microbial activity would be higher, could also improve the experiment. Lastly, improved flow control could have equalized the systems better.

This project has allowed us to better understand wetlands and their use as a remediation tool. We were able to utilize the skills that we have learned throughout our four years at Westminster College, and apply them during the different phases of our study.

## Appendix A

### EPA Water Quality Standards (Clean Water Act)

*Table 1. EPA Water Quality Standards for Fresh Water (1998)*

<b>Metal</b>	<b>CMC (ppb)</b>	<b>CCC (ppb)</b>
Aluminum*	750	87
Iron	- - -	1000
Nickel	470	52

\* pH 6.5-9.0

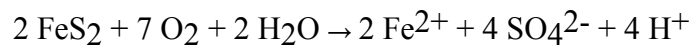
“Criteria Maximum Concentration (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect (EPA, 1998).”

“Criterion Continuous Concentration (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (EPA, 1998).”

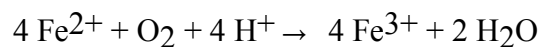
## Appendix B

### Chemical Formation of AMD

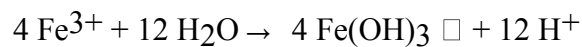
Eq. 1. **Step 1:**



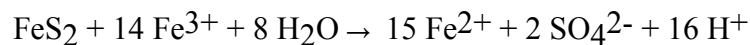
Eq. 2. **Step 2:**



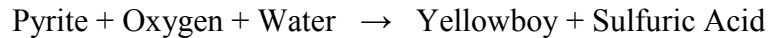
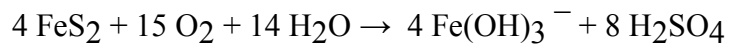
Eq. 3. **Step 3:**



Eq. 4. **Step 4:**



Eq. 5. **Summary Reaction:**



□

## Appendix C

### Atomic Absorption Instrument Parameters

**Element - Matrix:** Al -  
**Instrument Type:** Flame  
**Conc. Units:** mg/L  
**Instrument Mode:** Absorbance  
**Sampling Mode:** Manual  
**Calibration Mode:** Concentration  
**Measurement Mode:** Integrate  
**Replicates Standard:** 3  
**Replicates Sample:** 3

**Expansion Factor:** 1.0  
**Minimum Reading:** Disabled  
**Smoothing:** 5 point  
**Conc. Dec. Places:** 2

**Wavelength:** 309.3 nm  
**Slit Width:** 0.5 nm  
**EHT:** 37 Volts  
**Lamp Current:** 10.0 mA  
**Lamp Position:** 1  
**Background Correction:** BC Off

**STANDARD 1:** 15.00 mg/L  
**STANDARD 2:** 30.00 mg/L  
**STANDARD 3:** 40.00 mg/L  
**STANDARD 4:** 50.00 mg/L  
**Reslope Rate:** 50  
**Reslope Standard No.:** 2  
**Reslope Lower Limit:** 75.0 %  
**Reslope Upper Limit:** 125.0 %  
**Recalibration Rate:** 100  
**Calibration Algorithm:** New Rational  
**Cal. Lower Limit:** 20.0 %  
**Cal. Upper Limit:** 150.0 %  
**SIPS:** On  
**Neb. Uptake Rate:** 5.0 mL/min  
**Bulk Conc.:** 99.56 mg/L  
**Num SIPS Stds:** 3

**Measurement Time:** 5.0 s  
**Pre-Read Delay:** 10 s

**Flame Type:** N2O/Acetylene  
**N2O Flow:** 11.00 L/min  
**Acet. Flow:** 7.20 L/min  
**Burner Height:** 0.0 mm

**Element - Matrix:** Ni -  
**Instrument Type:** Flame  
**Conc. Units:** mg/L  
**Instrument Mode:** Absorbance  
**Sampling Mode:** Manual  
**Calibration Mode:** Concentration  
**Measurement Mode:** Integrate  
**Replicates Standard:** 3  
**Replicates Sample:** 3

**Expansion Factor:** 1.0  
**Minimum Reading:** Disabled  
**Smoothing:** 5 point  
**Conc. Dec. Places:** 3

**Wavelength:** 232.0 nm  
**Slit Width:** 0.2 nm  
**EHT:** 86 Volts  
**Lamp Current:** 4.0 mA  
**Lamp Position:** 1  
**Background Correction:** BC Off

**STANDARD 1:** 5.000 mg/L  
**STANDARD 2:** 10.000 mg/L  
**STANDARD 3:** 15.000 mg/L  
**STANDARD 4:** 25.000 mg/L  
**Reslope Rate:** 50  
**Reslope Standard No.:** 2  
**Reslope Lower Limit:** 75.0 %  
**Reslope Upper Limit:** 125.0 %  
**Recalibration Rate:** 100  
**Calibration Algorithm:** New Rational  
**Cal. Lower Limit:** 20.0 %  
**Cal. Upper Limit:** 150.0 %  
**SIPS:** On  
**Neb. Uptake Rate:** 5.0 mL/min  
**Bulk Conc.:** 98.183 mg/L  
**Num SIPS Stds:** 3

**Measurement Time:** 5.0 s

**Pre-Read Delay:** 10 s  
**Flame Type:** Air/Acetylene  
**Air Flow:** 13.50 L/min  
**Acetylene Flow:** 2.00 L/min  
**Burner Height:** 0.0 mm

**Element - Matrix:** Ni -  
**Instrument Type:** Furnace  
**Conc. Units:** µg/L

**Sampling Mode:** AutoMix  
**Calibration Mode:** Concentration  
**Measurement Mode:** Peak Height  
**Replicates Standard:** 1  
**Replicates Sample:** 1

**Expansion Factor:** 1.0  
**Minimum Reading:** Disabled  
**Smoothing:** 5 point  
**Conc. Dec. Places:** 2

**Wavelength:** 232.0 nm  
**Slit Width:** 0.2 nm  
**EHT:** 86 Volts  
**Lamp Current:** 4.0 mA  
**Lamp Position:** 3  
**Background Correction:** BC On

**STANDARD 1:** 20.99 µg/L  
**STANDARD 2:** 41.98 µg/L  
**STANDARD 3:** 83.96 µg/L  
**STANDARD 4:** 104.96 µg/L  
**Reslope Rate:** 0  
**Reslope Lower Limit:** 75.0 %  
**Reslope Upper Limit:** 125.0 %  
**Recalibration Rate:** 0  
**Calibration Algorithm:** New Rational  
**Cal. Lower Limit:** 20.0 %  
**Cal. Upper Limit:** 150.0 %

**Workhead Height:** 0.0 mm  
**Total Volume:** 20 µL  
**Sample Volume:** 10 µL  
**Vol. Reduction Factor:** 5  
**Bulk Conc.:** 104.96 µg/L

<b>Bulk Vial No.:</b>	51
<b>Makeup Vial No.:</b>	52
<b>Modifier 1 Mode:</b>	Co Inject
<b>Modifier 1 Vol.:</b>	2 uL
<b>Co Last Dry Step:</b>	2
<b>CCBPos:</b>	1



## Appendix D

### Statistical Analysis: 2-week data

2 sample T-test (parametric)			
Sample Date	p values- aluminum	p values- Iron	p values- nickel
21-Mar	0.112	0.179	0.169
22-Mar	0.19	0.313	0.191
23-Mar	0.219	0.278	0.929
28-Mar	0.301	0.353	0.716
29-Mar	0.322	0.670	0.784
30-Mar	0.44	0.724	0.689

**p values > .05 not significant**

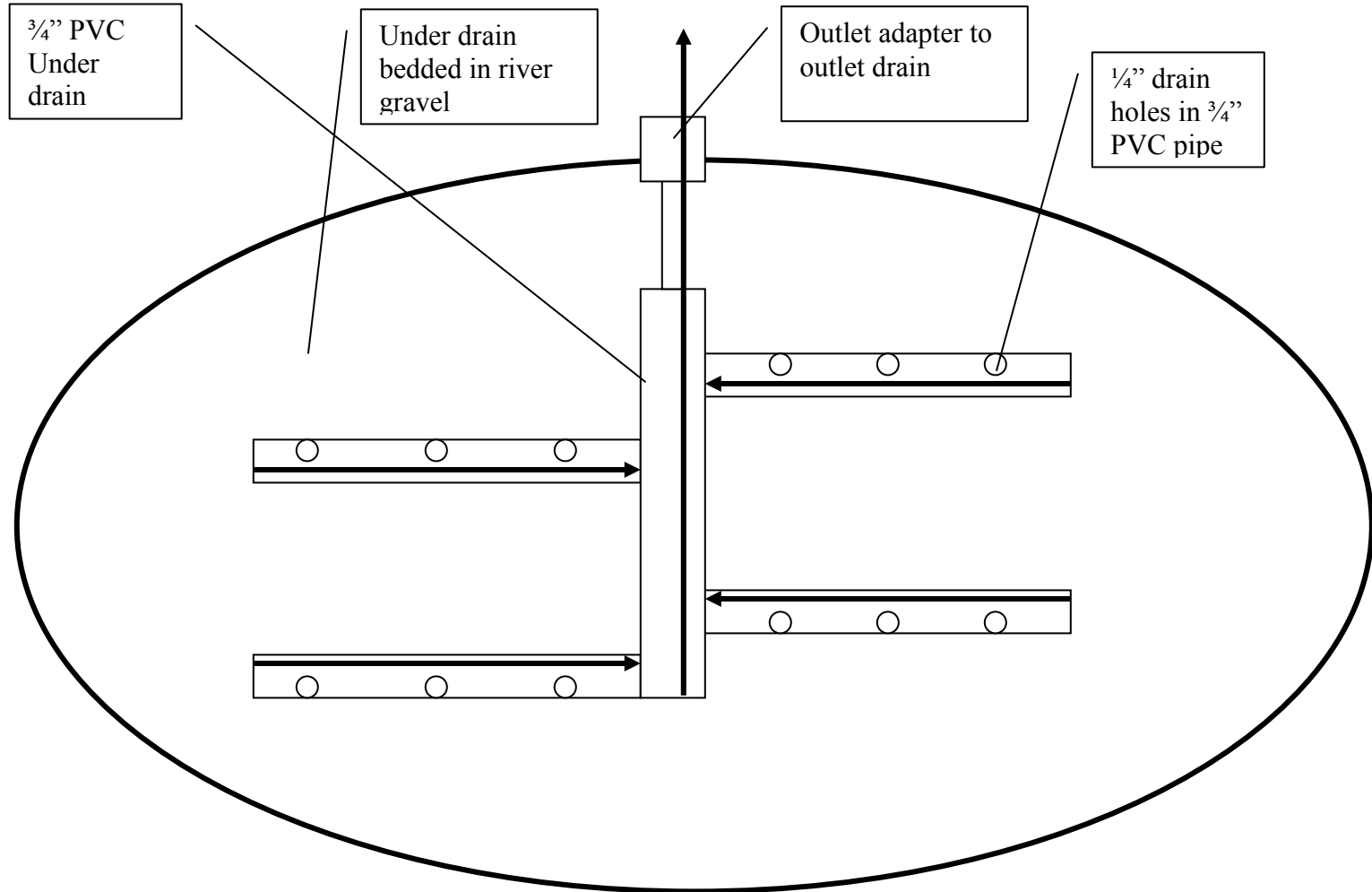
Mann-Whitney Test (non-parametric)		
Sample Date	Point estimate-aluminum	Confidence interval
21-Mar	5.719	(4.652,6.786)
22-Mar	9.494	(6.418,12.570)
23-Mar	8.764	(5.476,12.052)
28-Mar	7.250	(2.26,12.25)
29-Mar	7.850	(1.70,13.99)
30-Mar	5.480	(-0.87,11.84)

Mann-Whitney Test (non-parametric)		
Sample Date	Point estimate-Iron	Confidence interval
21-Mar	8.393	(5.650,11.135)
22-Mar	9.320	(2.44,16.20)
23-Mar	15.030	(5.23,24.84)
28-Mar	-9.55	(-15.89,-3.21)
29-Mar	9.080	(-12.30,30.46)
30-Mar	8.070	(-14.60,30.74)

Mann-Whitney Test (non-parametric)		
Sample Date	Point estimate-nickel	Confidence interval
21-Mar	0.029	(0.01780,0.04000)
22-Mar	0.044	(0.02900,0.05820)
23-Mar	0.004	(-0.03597,0.04357)
28-Mar	-0.025	(-0.0828,0.0334)
29-Mar	-0.025	(-0.0992,0.0486)
30-Mar	0.056	(-0.0930,0.2052)

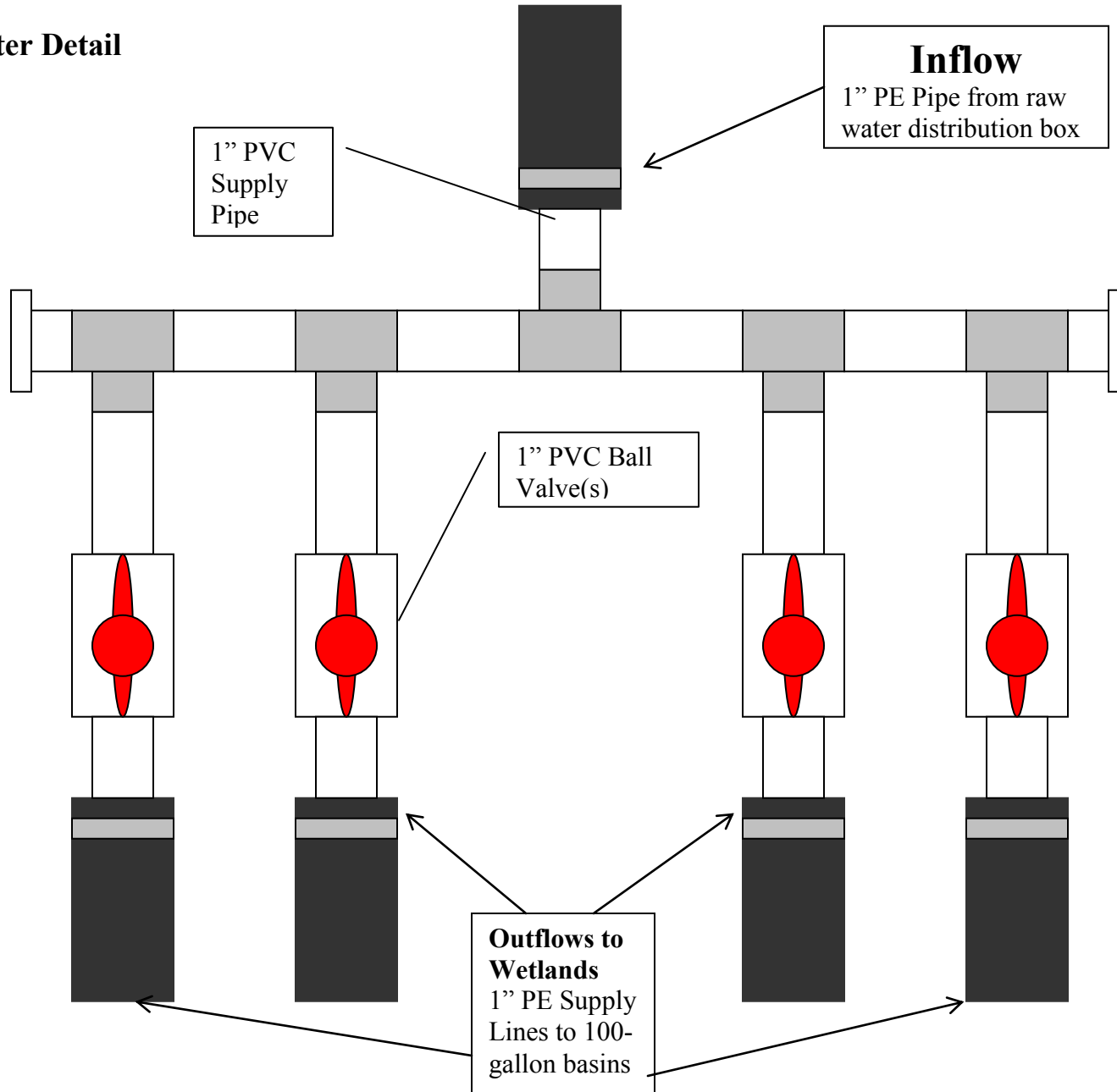
Appendix E

**Under Drain Detail**  
*(Arrow denotes normal flow of treated water)*



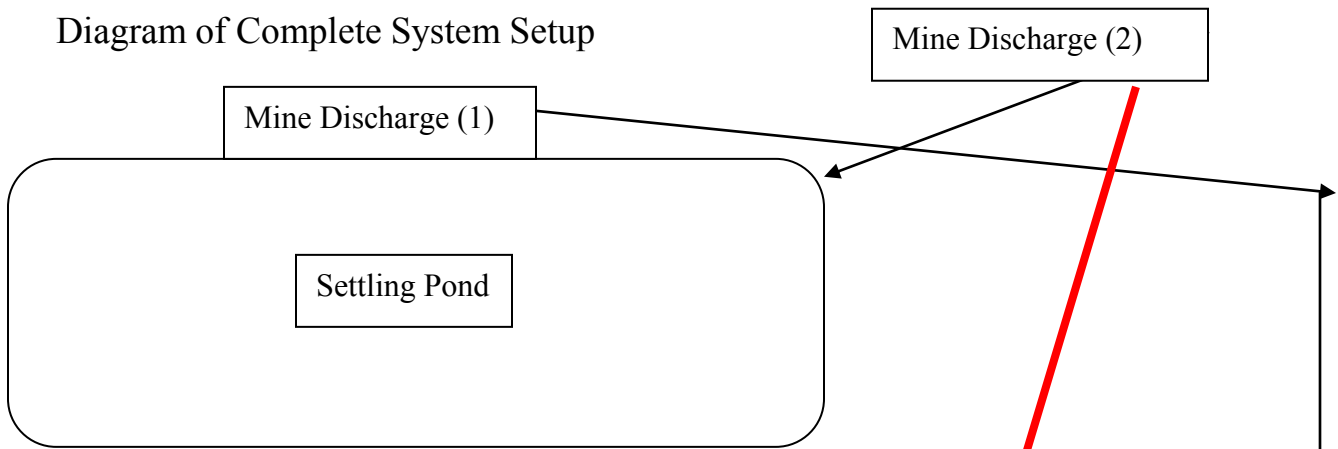
**Appendix F**

**Flow Splitter Detail**

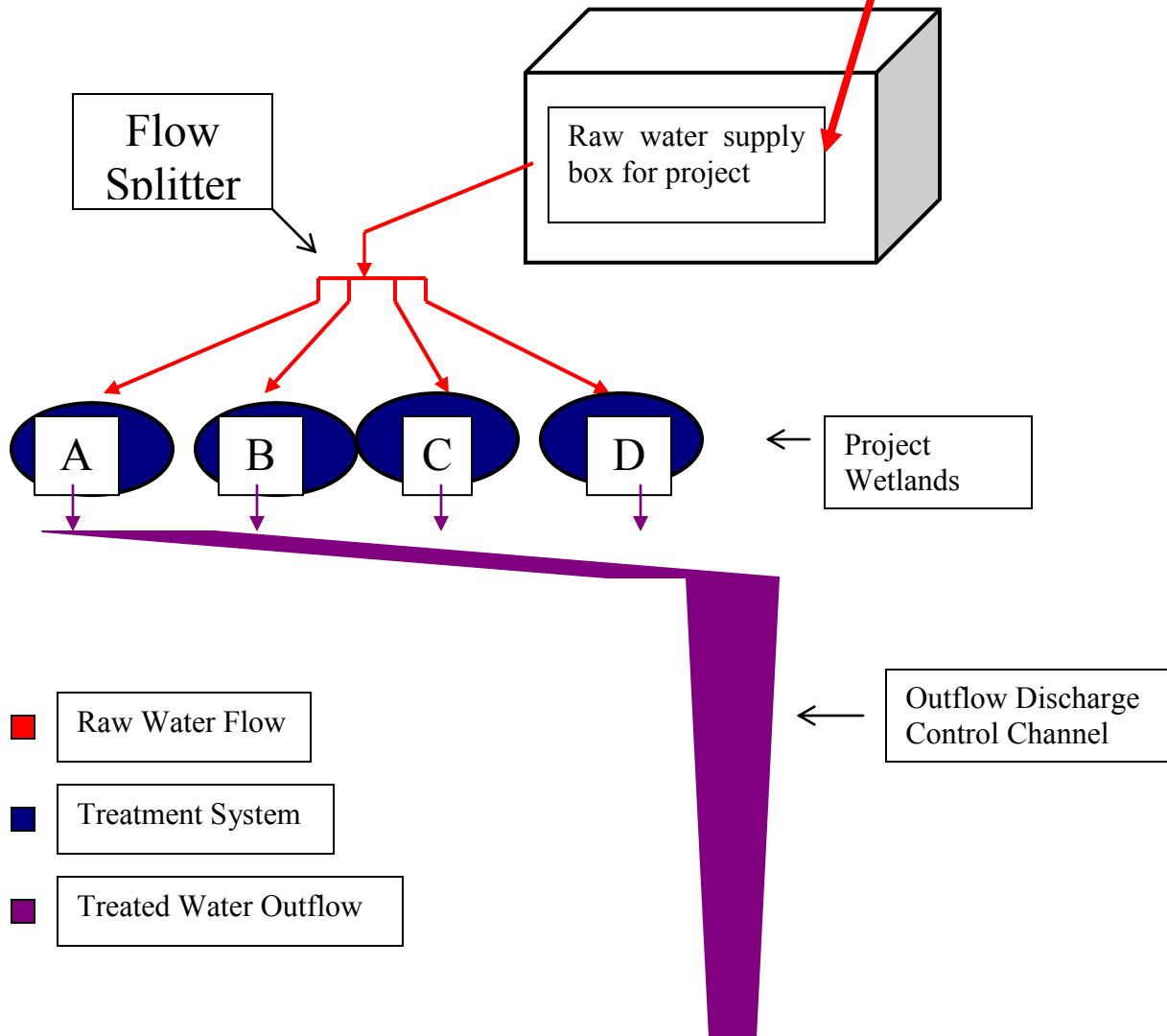


# Appendix G

## Diagram of Complete System Setup

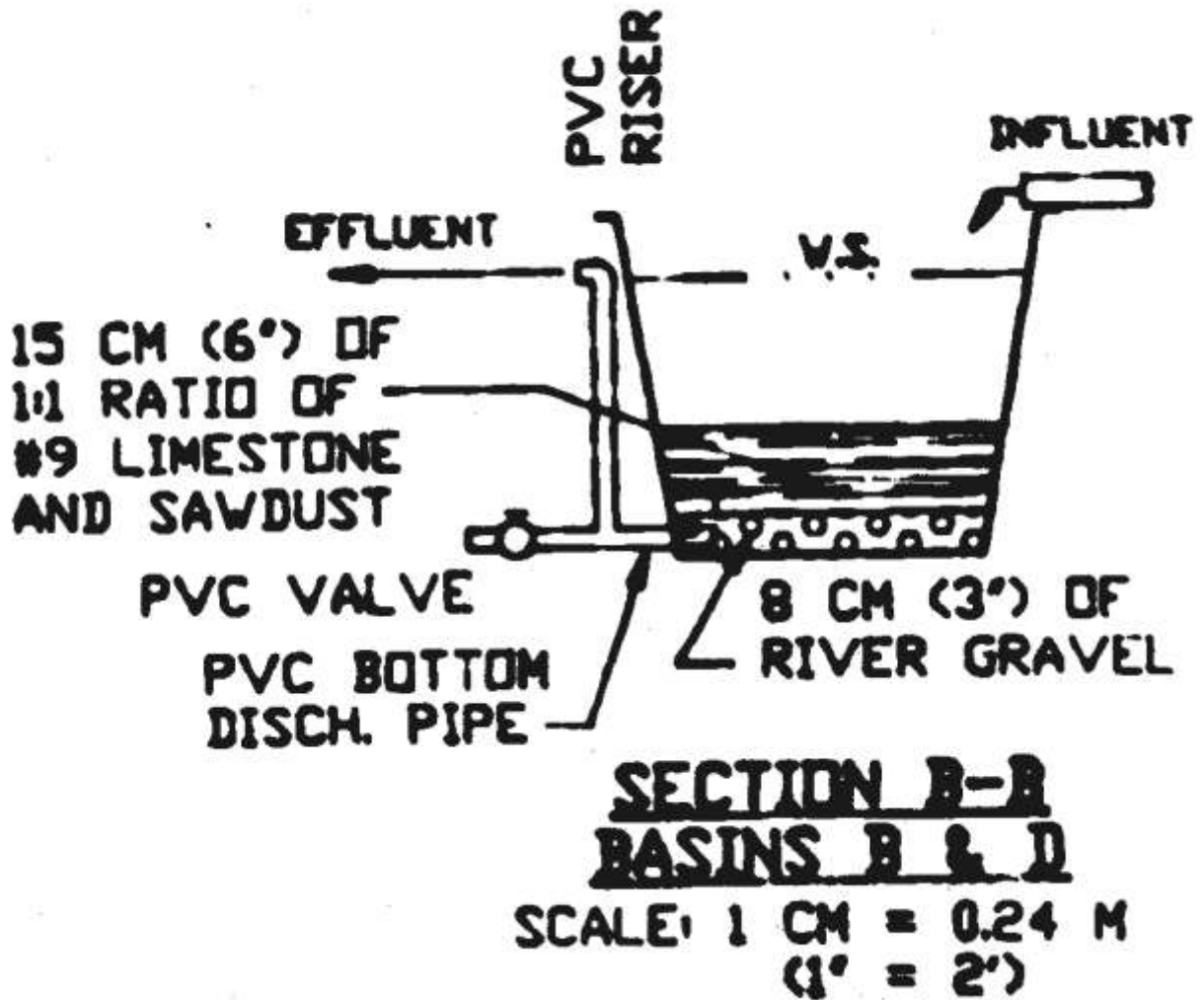


*\* Mine discharge 2 supplies raw water for capstone experiment*



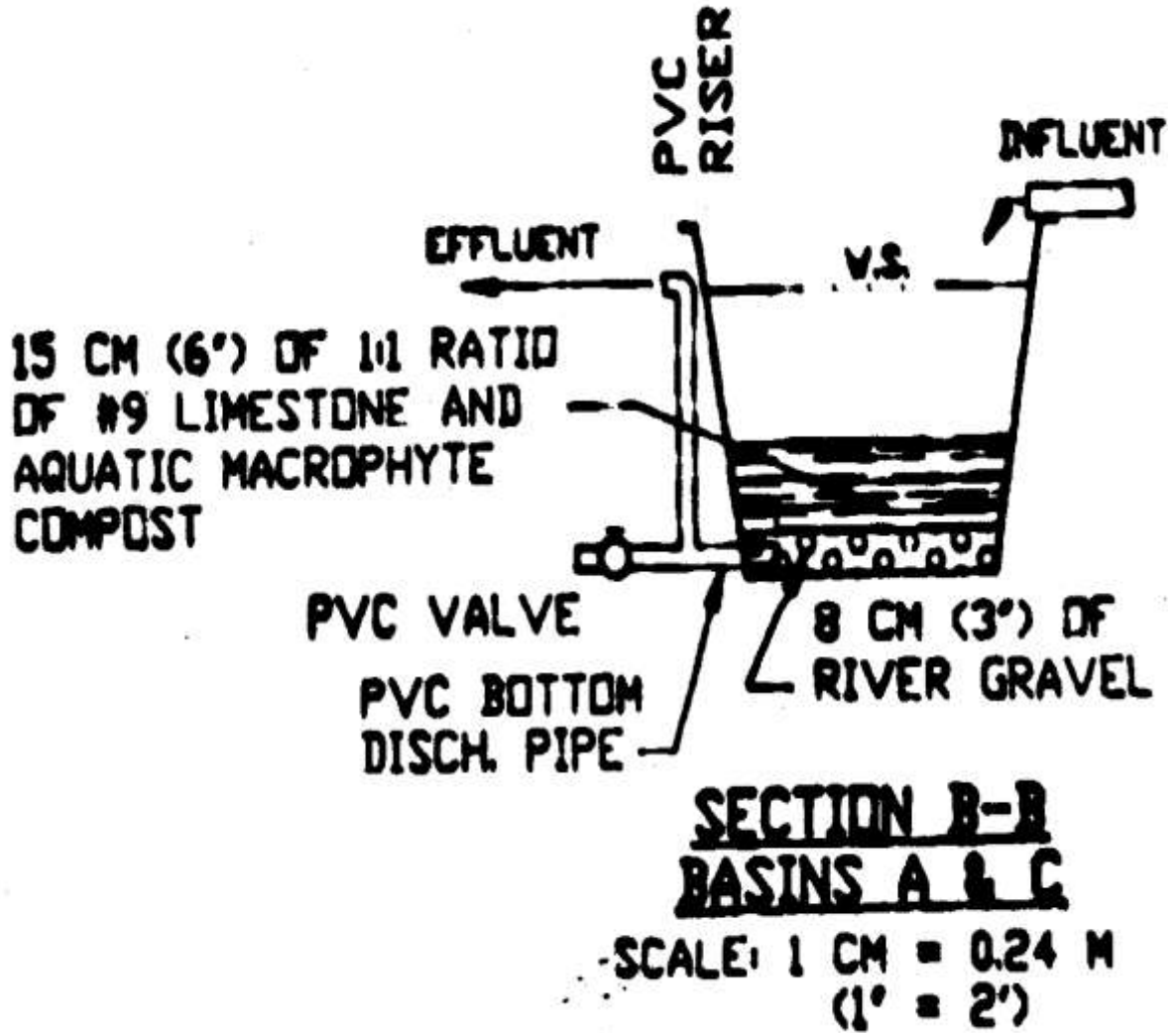
Appendix H

Diagram of Saw Dust Model



Appendix I

Diagram of Aquatic Macrophyte Model



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