TREATMENT OF METAL CONTAMINATED GROUNDWATER IN PASSIVE SYSTEMS: A DEMONSTRATION STUDY[1]

by
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Abstract. A pilot scale field test on passive treatment systems for metal and sulfate removal from ground water and surface runoff, is being conducted in Butte, Montana. This study is a collaborative effort between Montana Tech and the Atlantic Richfield Company (ARCO) to find solutions for treating metal contaminated water (e.g. Cu, Zn, Cd, and Fe). The field demonstration systems include anaerobic horizontal flow gravel bed wetlands with plants, horizontal flow gravel/organic substrate wetlands with plants, and vertical upflow gravel/organic substrate system without plants. The experimental design for sulfate and metal removal will be presented as well as the hydraulic design criteria used. Results from this test will be used to estimate system economics, long term performance and the life expectancy for these systems. Studies on mesoscale passive treatment systems such as 1.5 m high vertical upflow gravel/organic substrate columns are also presented. The parameters describing system performance are: hydraulic conductivity, volumetric sulfate-reduction rate, and metal immobilization rate.

Add. key words: Constructed wetlands, metal remediation, sulfate-reducing bacteria, field study.

Introduction

Acid mine drainage affects natural waters by decreasing water quality, stream aesthetics, and and the productivity of fisheries and other aquatic biota.

Natural and constructed wetlands have been used for many decades mainly in Europe, as a low cost, low maintenance waste water treatment system. In recent years constructed wetland systems have been adapted to treat AMD in the U.S. Passive anaerobic treatment of AMD was successful in immobilizing metals and increasing pH of the water (Wildeman, 1992).

One of the aims for the remediation effort in Butte, Montana (USA) is the emplacement of wetlands for the treatment of storm water runoff and near surface groundwater from the Metro Storm Drain (MSD) (Figure 1). Suspended and dissolved metals are being transported with the MSD water into Silver Bow Creek and eventually into the Clark Fork River. This research project is part of the ARCO remediation activities in the Clark Fork River Basin, in Southwestern Montana.

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[1] Paper presented at the 1996 National Meeting of the American Society for Surface mining and Reclamation, Knoxville, TN, May 19-25, 1996. Publications in this proceedings does not preclude authors from publishing their manuscripts, whole or in part, in other publication outlets. Funding for this project was provided by the Atlantic Richfield Company (ARCO) and is acknowledged.

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Proceedings America Society of Mining and Reclamation, 1996 pp 590-598

DOI: 10.21000/JASMR96010590

https://doi.org/10.21000/JASMR96010590

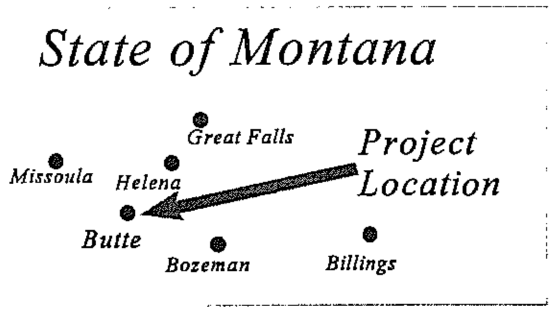


Figure 1. Location of the passive treatment demonstration site.

GOALS AND OBJECTIVES OF THE DEMONSTRATION STUDY

The overall goal of this demonstration study is to demonstrate the effectiveness of passive treatment systems for metal contaminated groundwater in Montana's alpine climate. Within this demonstration study the capabilities of three different passive treatment system designs are being evaluated based on hydraulic, chemical, microbial, and biological performance. An excessive monitoring system is in place to monitor hydraulic conductivity, water chemistry, and solids composition within the cells as well as in influent and effluent for each of the systems. Mechanistic and empirical models are being developed to increase our understanding of the fundamental processes occurring within these systems, including system performance, economy, and life expectancy. This information is essential for up scaling to a larger full scale operation.

MECHANISMS FOR METAL REMOVAL IN ANAEROBIC WETLANDS

Abiotic Processes

A pH increase in the aqueous phase due to the acid neutralizing capacity of the substrate can cause a consequent precipitation of dissolved metals and nonmetals. These pH induced precipitations can also indirectly cause other dissolved species to be removed from the aqueous phase. All of these pH initiated processes depend upon the acid neutralizing capacity, i.e. the alkalinity, of the substrate. If the alkalinity of the substrate will not be sustained, pH induced processes are short term.

Biotic Processes

Biotic initiated processes in anaerobic wetlands are the only long term self sustaining processes that will have a significant effect upon the effectiveness of the wetlands in treating acid metal and sulfate containing waters (Bolis *et al.* 1992). Sulfate reducing bacteria (SRB) will become active and produce hydrogen sulfide when exposed to a low redox potential (<-100 mV) and the presence of other required nutrients, such as short chain organic carbon compounds, nitrogen, phosphorous, and other required trace elements (Widdel, 1988). The presence of sulfide in anaerobic environments results in the formation of the corresponding metal sulfides which are extremely insoluble (Table 1) (Lawrence and McCarty, 1965). Many free metal ions can be inhibiting or toxic to the microbial consortium, whereas precipitated metal sulfides do not have a negative effect on microbial and acivity (Mueller and Steiner, 1992). These metal sulfide precipitates remain stable in anaerobic environments.

In most constructed wetlands for AMD a temperature between 4 and 20 °C is expected. Hence, the rate of microbial conversion will be slow and hydraulic residence times should be in the order of days to achieve sufficient microbial sulfate reduction from a complex substrate.

The microbial processes occurring in a natural or a constructed wetland are summarized in Figure 2. Complex organic carbon sources such as composts, or wood waste products are inexpensive and common energy sources. The carbon and energy inputs into the wetland system are present either from an external source (e.g., compost) or from plants within the system. This complex organic carbon is decomposed and converted microbially into suitable carbohydrates for fermentative organisms. Fermentative organisms

Table 1. Solubility of Heavy Metal Sulfides at 18 °C (Lawrence and McCarty, 1965).

Sulfide Salt	Solubility prod.	Solubility (mg/l)
CuS	$8.5\ 10^{-45}$	$9\ 10^{-18}$
Cu_2S	$2.0\ 10^{-47}$	$3\ 10^{-11}$
PbS	$3.4\ 10^{-28}$	$4\ 10^{-9}$
ZnS	$1.2\ 10^{-23}$	$3\ 10^{-7}$
FeS	$3.7\ 10^{-19}$	$5\ 10^{-5}$

further degrade these compounds into shorter chain volatile fatty acids and hydrogen that can be utilized by sulfate reducing bacteria. In the absence of sulfate or in the presence of inhibitors specific for sulfate reduction, methane could be produced (Loveley *et al.* 1982). Hence, a high sulfate concentration is desired to effectively suppress methane production.

System Design

Surge pond

The following is descibing design of systems presented in Figure 3 which is currently under construction. For most applications a surge pond or equalization pond is required to equalize water flow and water chemistry in the inlet water to the treatment systems. Another important function of the surge pond is solid settling. Since only minor fluctuations in water chemistry were observed for the MSD water and only a fraction of the total water flow is being treated, the main design criteria for the surge pond were its settling characteristics and its solid accumulation rate. Additionally the pond must hold a sufficient supply of MSD water to supply water to the treatment systems during a dry period.

Sediment settling tests in a 1.2 m high settling column were performed. After 30 hours a total suspended solids (TSS) reduction of 90% was observed. Multiplying by a safety factor of 3 and adjusting to a temperature of 2°C for increased water viscosity the resulting hydraulic retention time was 6.4 days.

Anaerobic treatment systems

The paradigm for successful treatment in a passive system includes three major components. The flow characteristics must be maintained within prescribed boundaries throughout the life of the system, the specific microbiological environment must be maintained, and heavy metals must be immobilized and permanently removed from the water phase. If any of these requirements are not met the system will be non functional with regard to effective metal removal.

The total required sulfate reduction may be calculated from the following based on metals and acid loading of the water (Eger, 1992):

$$M_{SO4}=\sum[Me^{2+}]+1.5\sum[Me^{3+}]+0.510^{-pH}$$

The volume of the constructed wetland has to provide sufficient sulfate removal to immobilize the metal loading and neutralize the acid loading. The required sulfate reduction rate (SRR) is dependent on flow rate and the total required sulfate reduction for metal removal in the contaminated ground water.

$$SRR = F\ x\ M_{SO4}$$

The volumetric sulfate reduction rate (VSSR) is driven by the organic fraction of the system and can be calculated after the sulfate reduction potential (SRP) for a chosen substrate has been experimentally determined.

$$VSRR = SRP\ x\ f_{co}$$

The total wetland volume (V_t) can then be calculated:

$$V_t = \frac{SRR}{VSRR}$$

Where:

F: flow rate [m^3/d];

f_{Co}: volumetric fraction of compost in the system [-];

SRP: sulfate reduction potential per volume substrate [$mole/m^3/d$];

M_{SO4}: stoichiometric amount of sulfate required to be reduced for complete metal immobilization and acid neutralization [mol/ m^3];
SRR: sulfate reduction rate for total metal immobilization and acid neutralization [mol/d];
VSRR: volumetric sulfate reduction rate per total system volume [mol/m3/d];
V_t: total wetland volume including inert gravel [m^3];

The effectiveness of the sequestering will impact the operational lifetime of the wetland. Information will be obtained by taking intact core samples and analysing the rate of metal accumulation in the systems, the form of the sequestered metals, and their stability.

Hydraulic considerations

The hydraulic residence time (HRT) of a gravel bed system can be calculated when the porosity (P) of the media is known:

$$HRT = \frac{V_t \times P}{F}$$

Hydraulic conductivity (K) is a critical parameter for a flow through a porous media and for the design of any wetland system. Most failures in the field have occurred because of inadequate knowledge of the short term and long term consequences of flow characteristics. K can be determined from Darcy's Law:

$$F = A_c \times K \times \frac{dh}{dl}$$

Where:
HRT: hydraulic residence time [d];
P: porosity [-]
A_c: crossectional area [m^2]
dh/dl: hydraulic gradient [-]
K: hydraulic conductivity [m/d]

There are several limits that will constrain the engineering choices that will be available. There will be a minimum allowable hydraulic conductivity, or alternatively for a fixed flow, there will be a maximum allowed hydraulic loading to the system to avoid fracturing, channeling, or short-circuiting around the wetland. As the fraction of organic material approaches zero (100 % gravel system) the fuel for the biological activity is eliminated, and this may adversely affect the microbial performance and the resulting metal removal efficiency.

Test Cell Dimensions and Layout

The tested passive treatment systems are two anaerobic gravel substrate wetlands sustaining horizontal flow of MSD water (Type 1 and 1A), an anaerobic organic compost - limestone gravel substrate wetland sustaining horizontal flow of MSD water (Type 2) and an anaerobic organic compost - limestone gravel substrate passive system sustaining upward flow of MSD water (Type 3) (Figure 3). The Type 1A wetland will have identical substrate as Type 1 but will be sized 50% smaller by volume. Each of the test systems are receiving MSD water from the surge pond. The effluent from each of these primary treatment systems passes through an aerobic wetland, designed to further, reoxidize and to remove iron and excess organic materials that have leached out from the compost systems. The surge pond effluent is distributed via underground pipes into each of the anaerobic test cells at a flow rate of 27.2 m^3d^{-1} to each unit. The effluents of cell 1 and 1A are combined and treated in an aerobic wetland. The effluents of cell 2 and 3 are combined and treated in a separate aerobic wetland. The effluents from the two aerobic wetlands are combined and discharged back into the MSD channel. Cell dimensions, hydraulic residence time, substrate/gravel composition, and the hydraulic conductivities are summarized in Table 2.

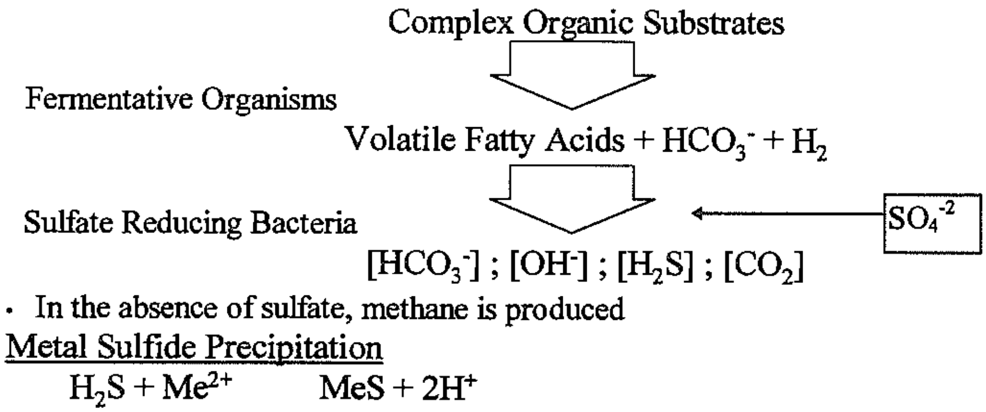


Figure 2. *Metabolic Pathways in anaerobic wetland systems.*

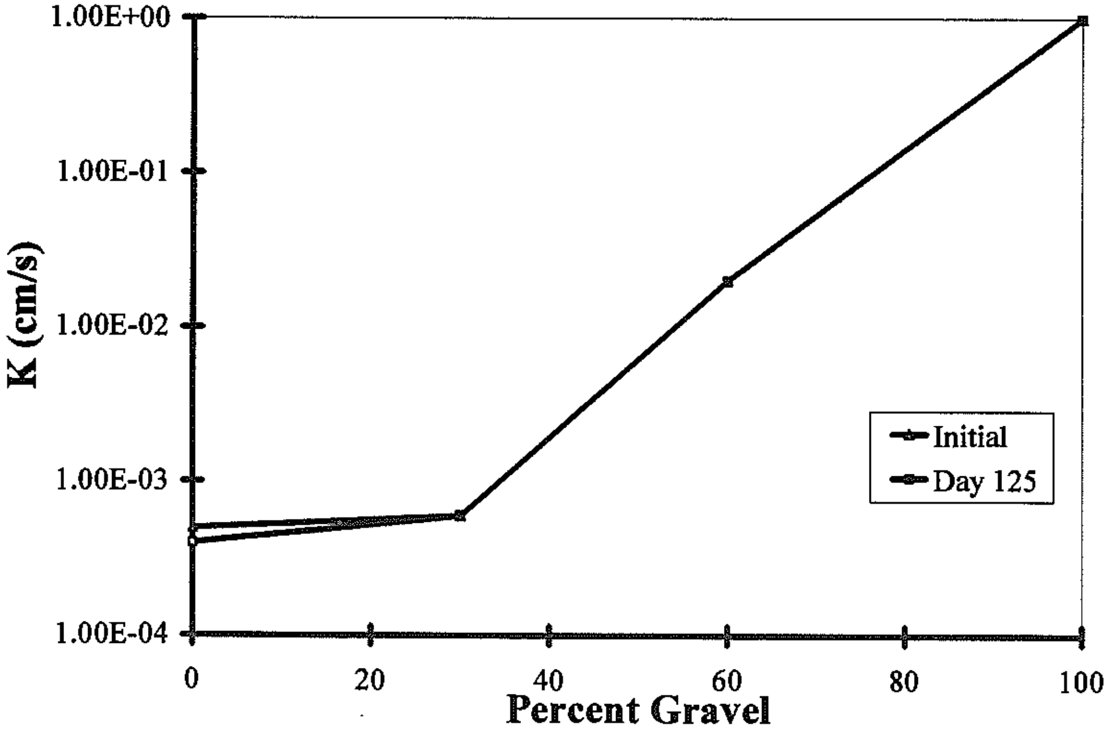


Figure 4. *Changes in hydraulic conductivity over time.*

Table 2. Design parameters for the anaerobic and aerobic test cells.

Unit Cell#	HRT [d]	flow [m³/d]	lxwxd [mxmxm]	vol m³	porosity [-]	compost/gravel [%/%]	hydraulic conductivity [cm/s]
Pond	7.0	154	20x36x1.5	1080	-	-	-
An 1	10.0	27.2	31x31x0.75	721	0.38	0/100	1-10
An 1a	5.0	27.2	22x22x0.75	370	0.38	0/100	1-10
An 2	6.0	27.2	14x27x1.2	453	0.36	20/80	0.1-0.5
An 3	1.5	27.2	9x9x1.5	122	0.34	50/50	0.01-0.06
A 1	2.8	54.5	28x8x0.7	157	NT	soil mix	NT
A 2	8.0	54.5	49x13x0.7	446	NT	soil mix	NT

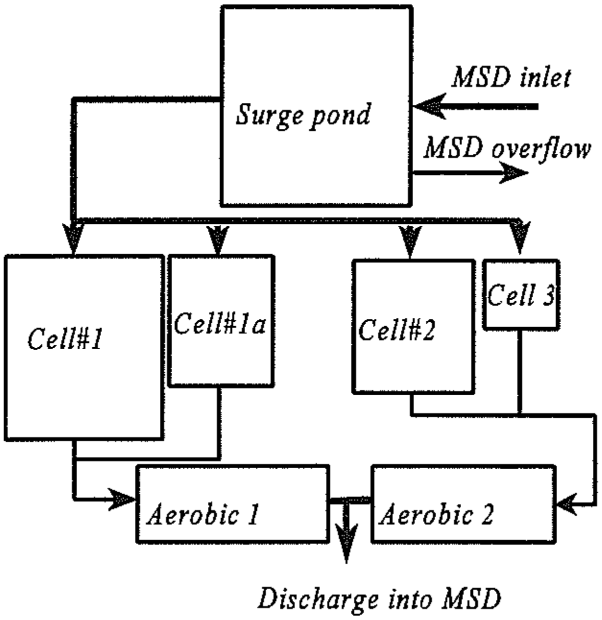


Figure 3. Schematic layout of the demonstration system.

Laboratory Results with Anaerobic Upflow Columns

Hydraulic Performance

Four 1.5 m high and 25 cm diameter upflow columns were operated over 6 months to test for hydraulic performance, sulfate reduction capacity, and metal removal efficiency. These tests columns were identical in height to the actual field system. Different ratios of compost to gravel were placed in each of the columns (Table 3). The hydraulic residence time was set at 1.5 days in all four columns. The hydraulic conductivity decreased significantly with a higher compost content in the columns. Table 3 indicates the dependence of hydraulic conductivity on substrate composition. The hydraulic conductivity was a function of substrate composition ranging from 100% compost to 100% gravel. A higher gravel fraction increased the hydraulic conductivity, causing the hydraulic conductivity value to asymptotically approach the performance of a pure gravel system as the pore size created by the gravel dominated the flow regime. Changes in hydraulic conductivity during 4 months of operation were not statistically significant for any of the tested

Table 3. Hydraulic conductivity values (K) measured in various gravel/compost mixt substrate.

C#	RG [%]	CG [%]	compost [%]	K [cm/s]
1	0	0	100	$7.8\ 10^{-4}$
2	10	20	70	$7.4\ 10^{-4}$
3	40	20	40	3.210^{-2}
4	80	20	0	1.0

substrates (Figure 4).

Table 4. Chemical Composition of the Organic Compost Used in this Study

Constituent	value
pH (1:4 DI water)	6.7
alkalinity	23 mg $CaCO_3$/g dry weight
moisture	57 % by weight
organic content	80 % by dry weight
total organic carbon	46 % by dry weight
total Kjeldahl nitrogen	1.6 % by dry weight
SIN*	1713 ppm per dry weight
C/N - ratio	29.7
phosphate-P	276 ppm per dry weight
Cu	28 ppm per dry weight
Cd	<1 ppm per dry weight
Zn	114 ppm per dry weigh
Fe	272 ppm per dry compost

SIN: soluble inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$).

Chemical and microbial performance

Organic Substrate. To screen for a source of organic substrate to be used in an anaerobic passive treatment system for AMD the following criteria were applied: The total organic carbon content in the substrate should be high, the metal content should be low (most of the metals present will ultimately contribute to the overall metal load into the system), the buffering capacity should be high to raise the pH of the AMD, and other required nutrients for SRB growth and metabolism should be present at the required concentration ratios, e.g. carbon:nitrogen:phosphorous at approximately 100:10:1 by weight (Widdel, 1988). However, leaching of nutrients from the organic substrate should be relatively slow in order to avoid discharging nutrients and to supply a long lasting nutrient source for SRB and subsequent metal removal. The organic substrate used was a mixture of composted sewage sludge and wood chips.The chemical composition of this compost is presented in Table 4. Within approximately 10 residence times, the chemical oxygen demand (COD) dropped to a level of <100 ppm (eq. to a BOD of 40 ppm).

Sulfate reduction and Metal removal. A significant reduction in sulfate was observed after approximately 10 residence times in the upflow columns (Figure 5). On average a reduction rate of 100 to 200 mmol Sulfate per m^3 compost and day were observed. For comparison, a sulfate removal rate of 300 mmoles sulfate per cubic meter of compost per day by an active SRB consortium was observed by Wildeman (1993).

Metal removal was observed as soon as operation started. The initial removal of metals was most likely due to adsorption onto particulate organic matter (Angelidis and Gibbs, 1989). Metal concentrations in the effluent of the various gravel/compost columns were similar for all columns containing compost, and the metal removal efficiencies were on average 99 % for zinc, 90% for copper and 90% for cadmium (Table 5). Copper and cadmium were present at much smaller concentrations in the MSD water and the removal rate was defined by the analytical detection limit. Zinc concentration measurements

Table 5. MSD water chemistry before and after treatment in anaerobic vertical upflow columns

Constituent	MSD water (Influent)	Column effluent	Units	treatment efficiency %
Cu	80-900	10-70	µg/l	88-99
Cd	40-120	10-40	µg/l	75-92
Zn	8000-11000	90-250	µg/l	97-99
Mn	8500-9000	8000-9500	µg/l	0
Fe	40-100	900-1000	µg/l	0
pH	6.6-6.8	6.8-7.0	-	-
Sulfate	127-270	119-255	mg SO4-S/l	ND
TSS	5-2500	NT	mg/l	-

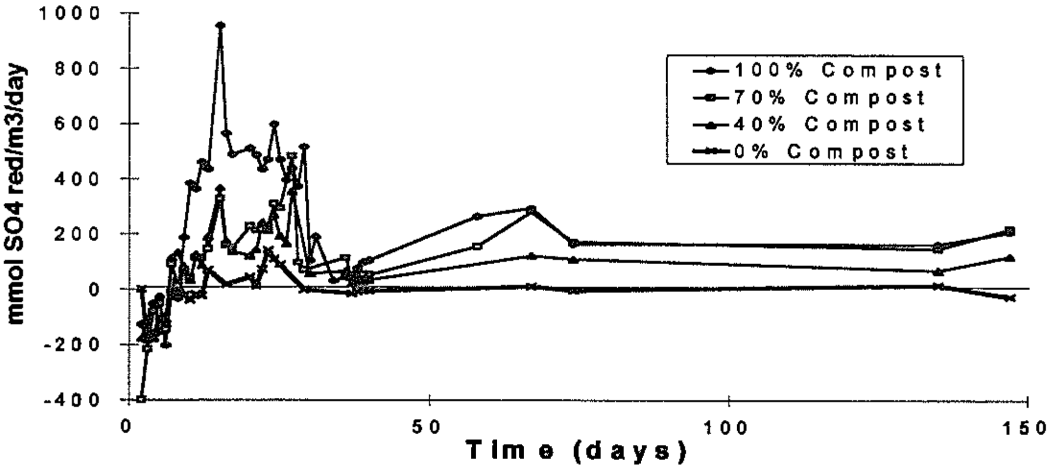
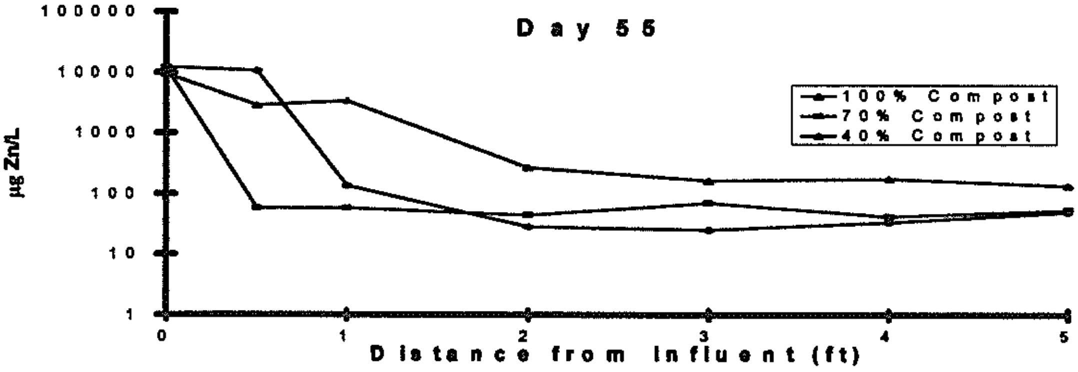
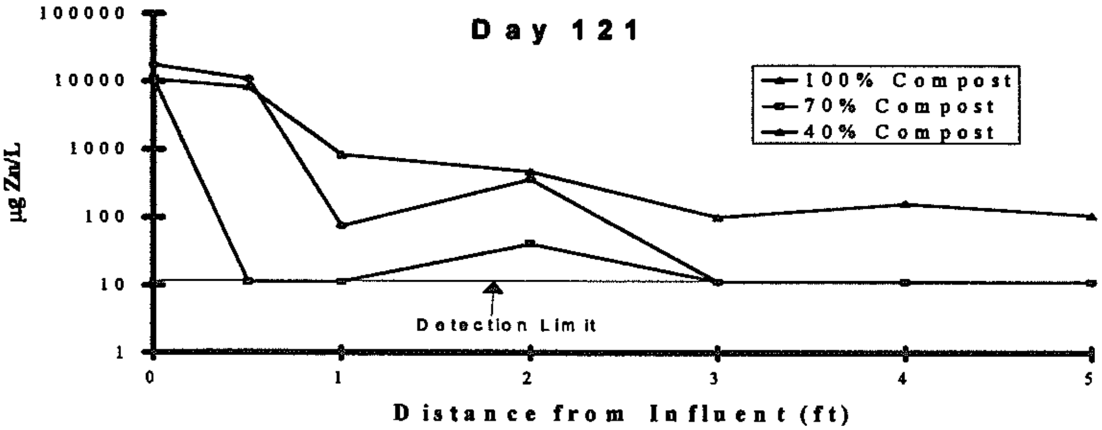


Figure 5. Sulfate removal rate was plotted over time. Significant sulfate reduction was observed in all columns with organic content.



(a)



(b)

Figure 6. Zinc concentrations over the lengths of the columns at day 55 (a), and day 121 (b). Zinc was removed faster in the columns with higher organic compost fractions.

were taken at various location of the column after 3 month of continuous operation. A shorter column length was necessary to remove zinc for the columns with a higher organic compost fraction (Figure 6). Little or no metal removal was observed in the 100% gravel columns (data not presented).

Conclusions

Laboratory experiments were used to design field test systems for metal removal from contaminated ground and surface water in Butte, Montana. The design calculations were based on the metal and acidity load of the MSD water, the potential sulfate reduction rate, the hydraulic conductivity for the chosen substrate (as observed in laboratory experiments), and on the total flow rate. The field system is being brought on line in May of 1996.

Successful zinc, copper, and cadmium removal were achieved in 1.5 m high upflow mixed substrate columns. The long term removal of these metals were based on the microbial sulfate reduction within the column substrate.

The hydraulic conductivity of the substrates controlled the flow regime of the upflow columns. Hydraulic conductivity was increased successfully by increasing the gravel/compost ratio.

Literature Cited

Angelidis, M., R.J. Gibbs. 1989. Chemistry of Metals in Anaerobically Treated Sludges. Wat. Res. **23**:29-33. https://doi.org/10.1016/0043-1354(89)90057-2

Bolis, J.L., T.R. Wildeman, H.E. Dawson. 1992. Hydraulic Conductivity of substrates used for passive acid mine drainage treatment. In Proceedings of the 1992 National Meeting of the American Society of Surface Mining and Reclamation, Duluth, MN.
https://doi.org/10.21000/JASMR92010079

Eger, P. 1992. The use of sulfate reduction to remove metals from acid mine drainage. In Proc. American Society for Surface Mining and Reclamation Meeting. Duluth, MN. June 14-18, 1992. https://doi.org/10.21000/jasmr92010563

Girts, M.A., and R.L.P. Kleinman. 1986. Constructed wetland for treatment of acid mine drainage: A preliminary review. p. 165-171. In National Syposium on Mining, Hydrology, Sedimentology, and Reclamation. Univ. of Kentucky, Lexington, KY.

Lawrence, A.W. and P.L. McCarty. 1965. The Role of Sulfides in Preventing Heavy Metal Toxicity in Anaerobic Treatment. JWPCF. **37**:392-406.

Loveley, D.R., D.F. Dwyer, M.J.Klug. 1982. Kinetic Analysis of Competition Between Sulfate Reducers and Methanogens for Hydrogen in Sediments. Appl. Environ. Microbiol. 43:1373-1379.

Mueller, R.F., Steiner, A. 1992. Inhibition of Anaerobic Digestion Caused by Heavy Metals, Wat. Sci. Tech. **26**:835-846.

Skousen, J., A. Sexstone, K. Garbutt, J. Sencindiver. 1994. Acid mine drainage treatment with wetlands and anoxic limestone drains. p. 263-281. In Applied Wetland Sciences and Technology. (Ed. D.M. Kent), Lewis Publishers, Ann Arbor.

Whiting, K., R.J. Brunswick, R.L. Olsen, J.N. Cevaal. 1994. Treatment of acid mine drainage using a passive biological system design and preliminary results from a full scale system. In Proceedings of the 1994 annual Conference of Society of Mining, Metallurgy and Exploration. Albuquerque, New Mexico.

Wildeman,T. 1992. Constructed wetlands treatment for toxic metal contaminated waters. EPA Emerging Technology Bulletin. EPA/540/F-92/001.

Wildeman,T. 1993. Handbook for constructed wetlands receiving acid mine drainag. EPA Emerging Technology Summary. EPA/540/SR-93/523.