INTEGRATED PASSIVE TREATMENT TO REDUCE METAL AND NUTRIENT CONCENTRATIONS IN WATER[1]

by

Brian D. Bass and Robert F. Mueller[2]

Abstract. This study is part of a collaborative effort between Montana Tech and Atlantic Richfield Company to find solutions for treating metal-contaminated surface runoff from the surrounding city of Butte, Montana. The runoff flows into a storm drain, which transports the suspended and dissolved metals into nearby Silver Bow Creek, a tributary of the Clark Fork River. The study compared percent removal of metals and nutrients by treatments of (1) undiluted storm drain water, through a gravel bed amended with cow manure, supporting cattails, (2) storm drain water combined with water from the local sewage treatment plant, through a gravel-only bed, and (3) the same combined-source water, through a gravel-only bed supporting cattails. Nutrients essential for supporting plants and microbial populations were supplied by both influent and manure in the first case, and by the combined-source influent in the second and third cases. The three treatment cells were 1.5 cubic meter, non-recycling, pilot-scale wetlands systems. Metal and nutrient percent removals were examined over residence times of 15, 10, and 5 days. Three metals were reported: cadmium, copper, and zinc. For cadmium, the combined-source treatments achieved percent removals from diluted concentrations which were similar to those achieved by the manure-amended treatment receiving the undiluted source. Percent removals of copper and zinc were greatest in the manure-amended treatment. Percent removal of nitrate was greatest in the cells containing cattails. Percent removal of phosphorous was greatest in the gravel-only cell supporting cattails.

Additional Key words: constructed wetlands, metal removal, sulfate removal, nitrate removal.

Introduction

The ARCO/Montana Tech Wetlands Project, Integrated Treatment Study was initiated in January, 1996, to explore the feasibility and effectiveness of a wetlands treatment to treat a combined-source influent. The two sources are (1) nutrient-rich primary-treated water from the Butte Metro Sewage Treatment Plant (MSTP) clarifying pond, and (2) metal-contaminated storm-drain runoff from the surrounding Butte urban area (MSD). Currently, both of these sources eventually enter Silver Bow Creek, a tributary of the Clark Fork River.

For treatment purposes, MSTP water supplied nitrogen and phosphorous, nutrients necessary for plants and microbial growth. Microbial metabolic activity can reduce macro-nutrients which could contribute to river eutrophication (Reimold, 1994). Microbial activity in anaerobic environments can also be responsible for precipitation of dissolved metals to metal sulfides. A primary mechanism for this process is biotic reduction of sulfate to hydrogen sulfide, and the concurrent oxidation of organic nutrients to bicarbonate by sulfate reducing bacteria.

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$

$$S^{2-} + M^{2+} \rightarrow MS \quad (M = \text{metal})$$

[1] Paper presented at the 1997 National Meeting of the American Society for Surface Mining and Reclamation, Austin, Texas, May 10-16, 1997. Funding for this project was provided by the Atlantic Richfield Company (ARCO) and Butte/Silver Bow County, and is acknowledged.

[2] Brian D. Bass is a graduate student in Environmental Engineering, and Robert F. Mueller is Assistant Professor of Chemistry and Geochemistry, at Montana Tech of the University of Montana, 1300 West Park Street, Butte, Montana, 59701.

Proceedings America Society of Mining and Reclamation, 1997 pp 747-754
DOI: 10.21000/JASMR97010747

https://doi.org/10.21000/JASMR98010747

MSD water contains sulfate and dissolved metals which, considering the above equations, might be precipitated out as metal sulfides in an anaerobic reducing environment, with a carbon source present (Batal et al. 1994).

Two other abiotic mechanisms for metal retention which can occur are adsorption on exchange sites, and complexation with organic substrate. Few studies have quantitatively distinguished between these abiotic processes and biotic mechanisms, but in reduced environments, metal sulfide precipitation initiated by microbial sulfate reduction is the most effective retention mechanism because of metal insolubility (Faulkner et al. 1989). With that concept in mind, this study addressed retention of metals in the dissolved aqueous phase.

The study objectives were (1) to determine the effectiveness of a wetlands system in treating a combined-source influent of sewage treatment plant water and metal-contaminated water, and (2) compare the percent metal removal of the combined-source treatment to that of treating metal-contaminated water only, using manure as a supplemental nutrient source for cattails (*typha latifolia*) and bacteria. For purposes of this study, the term "removal" is used to represent the difference between influent and effluent concentrations or loadings, and may involve some or all of the retention mechanisms described above.

The effect on metal and nutrient removal by changes in residence time and the presence or absence of plants was also addressed. Residence times of 15, 10, and 5 days were tested.

Methods And Materials

The treatment cells were constructed of reinforced wood, lined with non-reactive, impermeable geotextile liners. The cells are 4 feet deep, 2 feet wide, and 8 feet in length. They were filled with bed material to a depth of approximately 36 inches. Gravel used for the bed material was washed ¾ inch smooth river gravel, mainly granite. Each cell has an influent and effluent port, and nested sampling wells at three depths (Figure 1). The nested sampling wells were located within each cell at positions that allow for broad sampling and analysis of water. The wells were made of $^{1}/_{4}$ inch polypropylene tubing, perforated at the inlet end.

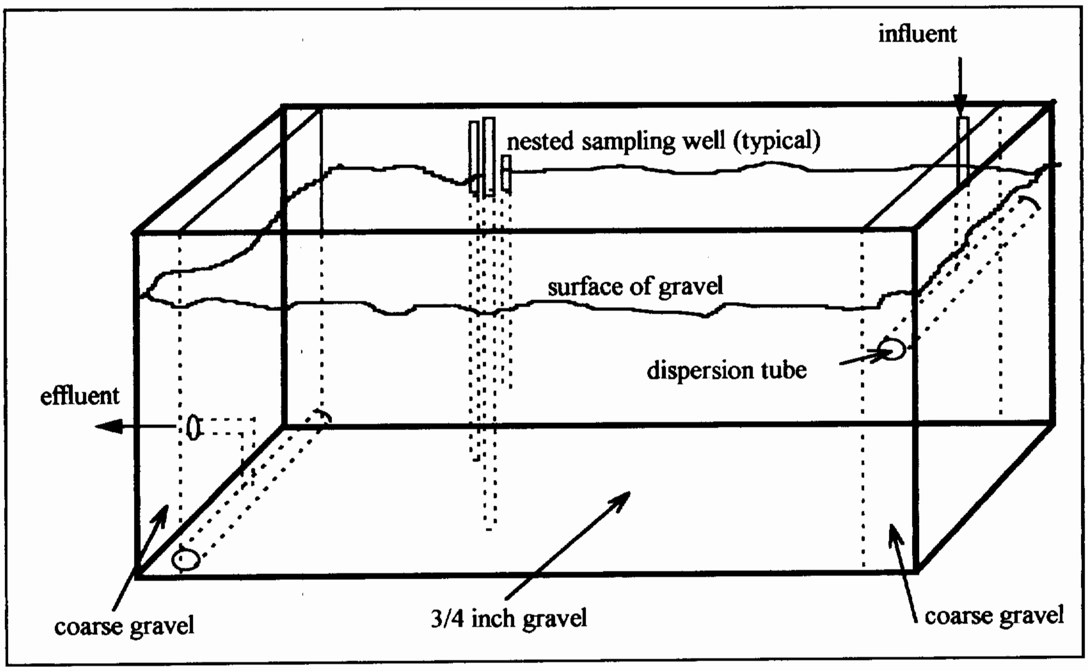

Figure 1. Typical Integrated Treatment Study cell

Cell "C-G" contains gravel only, cell "C-GP" contains gravel and plants only, and cell "S-GPM" contains gravel, plants, and manure:

Cell:	Influent / Composition	(% volume)
C-G:	combined source (95% MSTP + 5% MSD) / gravel only	
C-GP:	combined source (95% MSTP + 5% MSD) / gravel and plants	
S-GPM:	single source (100% MSD) / 90% gravel, plants, and 10% cow manure	

Sampling and analysis

Samples for nitrate, sulfate, and phosphate analyses were collected once per week, for all three cells. The samples were filtered through a 0.2 micron filter, and analyzed by a Dionex DX500 Ion Chromatograph (IC) with auto-sampler. Samples for metals analyses were collected every two weeks, filtered through a 0.45 micron filter, preserved with 2% (by volume) nitric acid, and refrigerated until being analyzed (APHA, 1990). The instrument used to analyze for metals was the Perkin-Elmer Optima 3000DV Inductively Coupled Plasma (ICP) Spectrophotometer with auto-sampler. Quality control standards were used during all analyses, and EPA protocol was followed (EPA Protocol SW846, Method 6010A, modified).

Results

Effluent concentrations neglect evaporation and transpiration. Evapo-transpiration was estimated using diurnal readings of influent flow and cumulative effluent volume. Effluent concentrations from analyses results were corrected using an evapo-transpiration factor:

$$C_{corr} = C_{anl} * f$$

where: $f = (Q_{eff}) / (Q_{eff} + Q_{evap})$

C_{corr} : corrected effluent concentration (ppm)
C_{anl} : analysis effluent concentration (ppm)
f : evapo-transpiration correction factor
Q_{eff} : average effluent flow (L/h)
Q_{evap} : average evapo-transpiration loss (L/h)

Cadmium

Average percent removal of cadmium ranged from 99.7% to 99.9% in all three cells during all three residence time periods, except for cell C-G during the 5-day residence time period, which achieved an average 93.5% removal (Figure 2). Cell S-GPM treated approximately 16 times the concentration of influent dissolved cadmium as cells C-G and C-GP, which accepted the diluted MSD water. Effluent concentrations for all treatments in all three cells were at or near instrument detection limit throughout most of the experiment. The average removal efficiency of combined-source treatment with cattails was approximately 6% greater than the combined-source treatment without plants, during the 5-day residence time period. No conclusive differences in removal efficiencies were observed among the tested residence times (Table 1).

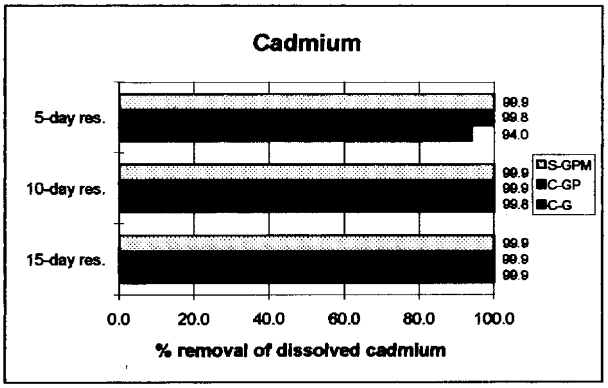

Figure 2. Percent removal of dissolved cadmium during 15, 10, and 5 day residence time periods. Cells C-G (gravel only), C-GP (gravel and plants), and S-GPM (gravel, plants, and manure).

Copper

Average percent removal for copper ranged between 96.5% and 99.1% for manure-amended treatment over all three residence time periods, with the highest percent removal occurring during the 15-day residence time period. The combined-source treatments achieved lower average percent removal, ranging from 50.8% to 71.2% over the three residence time periods. Highest combined-source percent removal was achieved by cell C-GP during the 15-day residence time period. Average percent removal by cells C-G and C-GP during the 5-day residence time period were 60.7% and 50.8% respectively, while cell S-GPM achieved 98.6% removal (Figure 3). Cells C-G and C-GP treated diluted influent concentrations of about one-fifth of the influent dissolved copper level entering cell S-GPM, yet yielded higher effluent concentrations of the element. No conclusive differences were observed between average percent removal of combined-source treatments with or without plants. There was no apparent correlation between percent removal and residence time (Table 1).

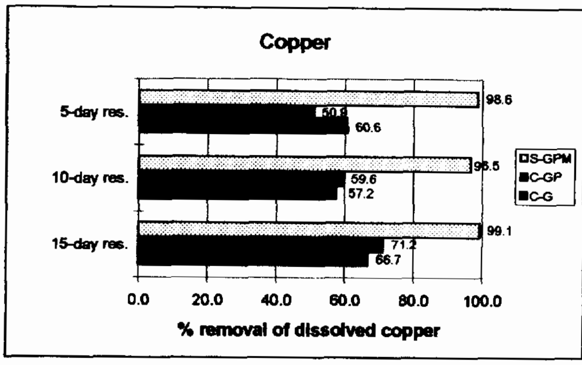

Figure 3. Percent removal of dissolved copper during 15, 10, and 5 day residence time periods. Cells C-G (gravel only), C-GP (gravel and plants), and S-GPM (gravel, plants, and manure).

Zinc

Manure-amended treatment in cell S-GPM achieved higher average percent removal for zinc over all three residence time periods, compared to the combined-source treatments. Cell S-GPM ranged from 99.8% to 99.9% average percent removal throughout the experiment. The average removal range for cells C-G and C-GP was 92.9% to 99.3%. The highest average percent removal for combined-source treatment was observed in cell C-GP during

Table 1. Average influent and effluent concentrations and percent removal of combined-source treatment relative to single source, manure-amended treatment, for cadmium, copper, and zinc. Concentrations in parts per billion (ppb).

		15-day res.time		**10-day res.time**		**5-day res.time**	
	avg.influent (+/- std. dev.)*	avg.effluent* (+/- std. dev)	avg % removal**	avg.effluent* (+/- std. dev)	avg % removal**	avg.effluent* (+/- std. dev.)	avg % removal**
Cadmium							
Cell C-G	*3.1 (+/- 1.3)*	bdl	99.9	bdl	99.9	0.20 (+/- 0.20)	93.5
Cell C-GP	*2.9 (+/- 1.4)*	bdl	99.9	bdl	99.9	0.01 (+/- 0.01)	99.7
Cell S-GPM	*49.6 (+/- 14.8)*	bdl	99.9	bdl	99.9	bdl	99.9
Copper							
Cell C-G	*28.51 (+/- 8.0)*	9.5 (+/- 2.9)	66.7	12.2 (+/- 3.1)	57.2	11.2 (+/- 1.4)	60.7
Cell C-GP	*26.00 (+/- 6.3)*	7.5 (+/- 5.4)	71.2	10.5 (+/- 6.5)	59.6	12.8 (+/- 4.1)	50.8
Cell S-GPM	*149.74 (+/- 45.7)*	1.4 (+/- 1.3)	99.1	5.3 (+/- 7.2)	96.5	2.1 (+/- 0.7)	98.6
Zinc							
Cell C-G	*948.3 (+/- 177.1)*	51.3 (+/- 11.5)	94.6	65.2 (+/- 26.5)	93.1	56.9 (+/- 7.3)	94.0
Cell C-GP	*962.8 (+/- 207.3*	53.4 (+/- 34.8)	94.5	6.6 (+/-6.6)	99.3	68.1 (+/- 43.4)	92.9
Cell S-GPM	*13842.4 (+/- 4346.2)*	32.2 (+/- 20.7)	99.8	3.0 (+/- 3.5)	99.9	18.6 (+/- 4.1)	99.9

bdl: below detection limit
* arithmetic average concentrations
** (avg. influent - avg. effluent) / avg. influent
C-G: (MSTP + MSD / gravel only)
C-GP: (MSTP + MSD / gravel + plants)
S-GPM: (MSD only / gravel + plants + manure)

the 10-day residence time period. Cell C-GP, with cattails, achieved approximately 6% greater average percent removal than cell C-G, without cattails, during the 10-day residence time period (Figure 4). Cell C-GP achieved greatest removal of zinc during the 10-day residence time period. The concentration of dissolved zinc entering cells C-G and C-GP was approximately 15 times less than the concentration in the undiluted influent entering the manure-amended cell S-GPM. There was no apparent correlation between percent removal and residence time for cells C-G and S-GPM (Table 1).

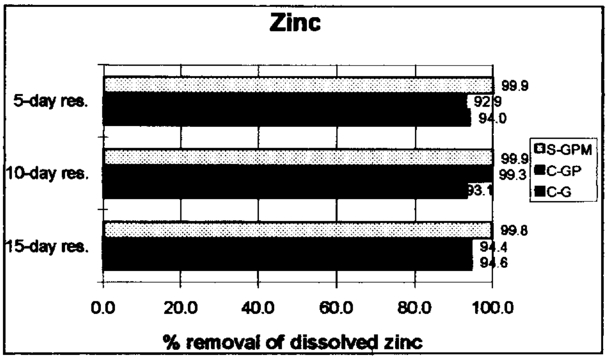

Figure 4. Percent removal of dissolved zinc during 15, 10, and 5 day residence time periods. Cells C-G (gravel only), C-GP (gravel and plants), and S-GPM (gravel, plants, and manure).

Nitrate

Concentrations of nitrate (recorded as ppm nitrogen) were removed by an average 81.2% to 98.3% in the manure-amended cell S-GPM, and by an average 80.4% to 99.9% in the combined-source cell C-GP, with cattails. The highest average percent removal for the combined-source treatments occurred during the 10-day residence time period. Cell C-G, without cattails, achieved lower average percent removal than the other two cells, ranging from 9.6% to 66.7%, the highest removal occurring during the 15-day residence period. (Figure 5). Overall, the three cells experienced a decline in percent removal as residence time decreased, with the single exception of cell C-GP which removed about 5% more nitrate during the 10-day residence time period than during the 15-day residence time period. Cell C-GP treated approximately 7 times the concentration of influent nitrate entering cell S-GPM (Table 2).

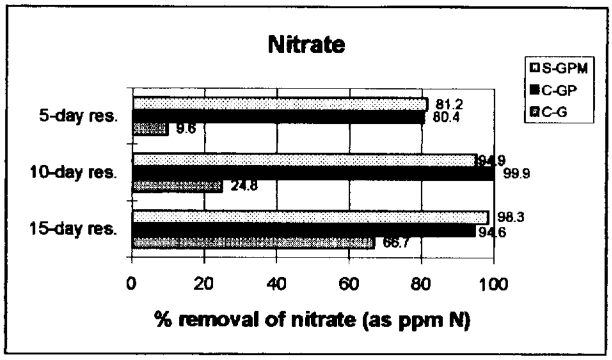

Figure 5. Percent removal of nitrate (as ppm N) during 15, 10, and 5 day residence time periods. Cells C-G (gravel only), C-GP (gravel and plants), and S-GPM (gravel, plants, and manure).

Phosphate

No observable phosphate removal occurred in the manure-amended cell S-GPM during the experiment. Average percent removal of phosphate (recorded as ppm phosphorous) in the combined-source cell C-GP ranged from 91.9% to 97.5% over the three residence time periods, the highest percent removal occurring during the 10-day residence time period. Cell C-G average percent removal ranged from 40.3% to 60.6%, the highest occurring during the 10-day residence time period (Figure 6). No apparent correlation between residence time and percent removal was observed (Table 2).

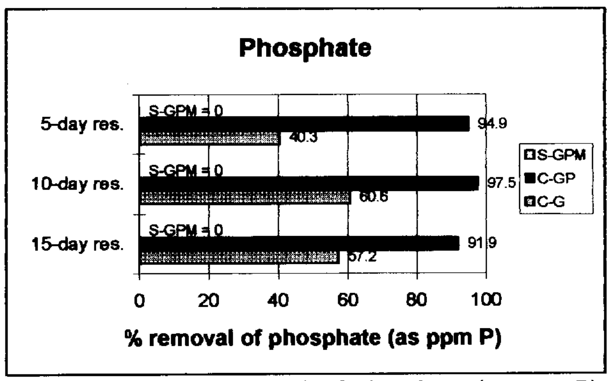

Figure 6. Percent removal of phosphate (as ppm P) during 15, 10, and 5 day residence time periods. Cells C-G (gravel only), C-GP (gravel and plants), and S-GPM (gravel, plants, and manure).

Table 2. Average influent and effluent concentrations and percent removal for nitrate, phosphate, and sulfate. Concentrations are in parts per million (ppm) of nitrogen, phosphorous, and sulfur, respectively.

		15-day res.time		10-day res.time		5-day res.time	
	avg.influent (+/- std. dev.)*	avg.effluent* (+/- std. dev)	avg % removal**	avg.effluent* (+/- std. dev)	avg % removal**	avg.effluent* (+/- std. dev.)	avg % removal**
Nitrate							
Cell C-G	*10.41 (+/- 2.80)*	3.47 (+/- 1.18)	66.7	7.83 (+/- 2.57)	24.8	9.41 (+/- 2.65)	9.6
Cell C-GP	*10.77 (+/- 2.50)*	0.58 (+/- 0.73)	94.6	bdl	99.9	2.11 (+/- 3.21)	80.4
Cell S-GPM	*1.56 (+/- 0.98)*	0.03 (+/- 0.08)	98.3	0.08 (+/- 0.18)	94.9	0.30 (+/- 0.43)	81.2
Phosphate							
Cell C-G	*1.34 (+/- 0.68)*	0.57 (+/- 0.21)	57.2	0.53 (+/- 0.44)	60.6	0.80 (+/- 0.19)	40.3
Cell C-GP	*1.49 (+/- 0.68)*	0.12 (+/- 0.11)	91.9	0.04 (+/- 0.09)	97.5	0.08 (+/- 0.21)	94.9
Cell S-GPM	*0.012 (+/- 0.04)*	0.65 (+/- 0.24)	0	0.65 (+/- 0.43)	0	0.20 (+/- 0.11)	0
Sulfate							
Cell C-G	*29.59 (+/- 3.44)*	23.86 (+/- 1.80)	19.4	30.52 (+/- 0.93)	0	28.86 (+/- 2.13)	2.5
Cell C-GP	*28.96 (+/- 3.67)*	77.54 (+/- 34.75)	0	35.21 (+/- 2.58)	0	36.21 (+/- 3.87)	0
Cell S-GPM	*178.95 (+/- 31.70)*	49.77 (+/- 13.01)	72.2	93.87 (+/- 39.24)	47.5	149.43 (+/- 19.65)	16.5

bdl: below detection limit
* arithmetic average concentrations
** (avg. influent - avg. effluent) / avg. influent
C-G: (MSTP + MSD / gravel only)
C-GP: (MSTP + MSD / gravel + plants)
S-GPM: (MSD only / gravel + plants + manure)

Sulfate

Significant removal of sulfate was observed only in the manure-amended cell S-GPM, ranging from an average percent removal of 16.5% to 72.2%, the highest occurring during the 15-day residence time period, and the lowest during the 5-day residence time period (Figure 7). The concentration of sulfate entering cell S-GPM was approximately 6 times the concentration of sulfate entering cells C-G and C-GP. Percent removal of sulfate in cells C-G and S-GPM decreased as residence time decreased (Table 2).

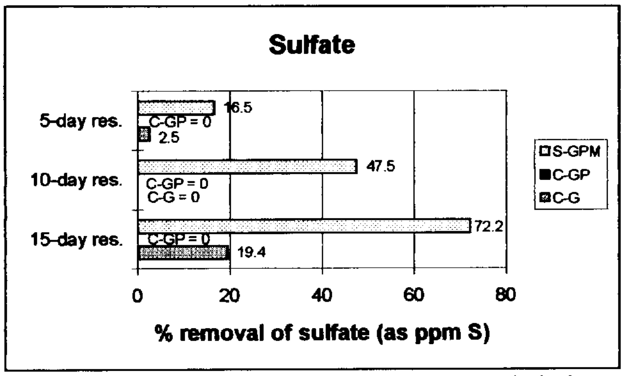

Figure 7. Percent removal of sulfate (as ppm S) during 15, 10, and 5 day residence time periods. Cells C-G (gravel only), C-GP (gravel and plants), and S-GPM (gravel, plants, and manure).

Discussion

Combined-source treatment appears to be capable of removing diluted, low concentrations of dissolved cadmium in metal-contaminated water, with percent removal similar to that achieved by treatment of single-source, undiluted influent, using manure supplement in the gravel bed matrix. During the experiment, the combined-source treatments were capable of immobilizing the diluted concentration of dissolved cadmium by an average 99.7% to 99.9%, compared to 99.9% removal in cell S-GPM, the manure-amended treatment of the higher, undiluted concentration. The single exception was 93.5% cadmium removal by cell C-G during the 5 day residence period. The results in cell S-GPM are similar to those achieved in another pilot wetland study using a 75% manure-amended treatment that reduced influent cadmium levels by more than 98% (EPA, 1993).

Percent removal of dissolved copper was greater by cell S-GPM, the single-source, manure-amended treatment, than by the combined-source cells. Combined source cells managed 50.8% to 71.2% average removal, while the manure-amended cell ranged from 96.5% to 99.1%. If the difference was a result of greater metal sulfide precipitation in cell S-GPM (sulfate removal was greater in this cell), this suggests that the addition of manure to the gravel bed may provide a better reducing environment than gravel or gravel and cattails alone. A bench scale experiment in central Norway recently explored the difference in removal efficiencies of copper from acid mine drainage, between a gravel/sand only reactor and a gravel/sand with cow manure reactor, finding removal efficiencies of 5-10% and 65-70%, respectively (Christensen et al. 1996).

Dissolved zinc was immobilized more effectively by the manure-amended cell S-GPM than by the combined-source cells, although the difference in percent removals was less than for copper. Cell S-GPM averaged over 99.8% removal throughout the experiment; the combined-source cells achieved average removals of 92.9% to 99.3%, in spite of insignificant sulfate removal. The EPA (1993) study achieved greater than 98% zinc removal with the 75% manure-amended treatment, and the study by Christensen et al (1996) found 5-15% zinc removal in both the gravel/sand only and manure-amended reactors.

Although effluent concentrations of dissolved metals indicated that the systems had reached steady-state before data averaging (concentrations of effluent metals had leveled out from initial high values after several weeks of operation), it is uncertain to what extent metals may have continued to adsorb onto the gravel or substrate. It has been proposed that abiotic chemical and physical processes, such as cation exchange, abiotic complexation, and filtering, can account for over 50% of metal retention in wetlands (Kleinmann 1991).

There was no apparent correlation between residence time and percent removal of cadmium or copper. Greater percent removal of zinc occurred during the 10 day residence time period than during the 15 day or 5 day residence time periods, but the reason for this is unclear. Compared with systems designed for nutrient removal, there is relatively little information or data available on metals removal versus loading rates and residence time for wetland systems (Watson et al. 1989). The apparent increase in sulfate (as ppm S) and nitrate (as ppm N) removal with an increase in residence time (decrease in influent flow and loading rate) is not unexpected, since water quality improvement for these nutrients usually follows first order kinetics, with higher removal efficiency directly related to increased contact time (Kadlec, 1989).

The presence or absence of plants in the systems appeared to have no significant effect on the removal of dissolved cadmium, copper, or zinc. There is some evidence, however, that the presence of plants may have promoted nutrient removal. Of the combined-source cells, cell C-GP, with plants, experienced greater than 80% average removal of nitrate and phosphate over the entire experiment, while cell C-G, without plants, removed only 9.6% to 66.7% nitrate and 40.3% to 60.6% phosphate, suggesting that nitrate and phosphate removal may be directly or indirectly facilitated by the presence of plants. A Mississippi study using wetlands to treat pulp mill effluent found that plant uptake was responsible for 45% of the total nitrogen removal and 80% of total phosphorous removal (Thut, 1988).

There was insignificant sulfate removal in the combined-source treatments, cells C-G and C-GP, relative to percent removal in the manure-amended cell S-GPM. This suggests that sulfate removal is independent of the presence of plants, but may be, in part, a function of the availability of substrate (in this case, manure) in the bed matrix.

Conclusions

A gravel bed, with no supplemental substrate, receiving a combined-source influent of metal-contaminated water and sewage treatment plant water, shows potential for achieving greater than 90% removal of diluted concentrations of dissolved cadmium and zinc, with percent removals ranging approximately 5% to 6% below those of a single-source, manure-amended bed which treats the undiluted source. Manure-amended gravel treatment, however, appears to achieve greater percent removal of undiluted concentrations of dissolved copper than combined-source treatment of diluted influent from the same source, possibly by creating a more reducing environment. The same holds true for removal of sulfate. The addition of cattails to the system appears to enhance removal of concentrations of nitrate and phosphate present in the influent. For a residence time of 5 to 15 days, percent removals of nitrate and sulfate increase with longer residence time.

References

APHA (American Public Health Association) 1990. Selected physical and chemical standard methods for the examination of water and wastewater, 17th ed. Methods 3030 A, B, C, D. APHA, Wash. D.C.

Batal, Wafa, Leslie S. Laudon, Thomas R. Wildeman,and Noorhanita Mohdnoordin. 1989. Bacteriological tests from the constructed wetland of the Big Five Tunnel, Idaho Springs, Colorado. In: Constructed wetlands for wastewater treatment. D.A. Hammer, ed. 1989. Lewis Publishers, Chelsea, Michigan.

Christensen, Bjorn, Morten Laake, and Torleiv Lien. 1996. Treatment of acid mine water by sulfate reducing bacteria; results from a bench scale experiment. Water Res., Vol. 30, No. 7, pp. 1617-1624.
https://doi.org/10.1016/0043-1354(96)00049-8

EPA, 1993. Handbook for constructed wetlands receiving acid mine drainage. United States Environmental Protection Agency Technology Report EPA/540/SR-93/523. U.S. Government Printing Office.

Faulkner, Stephen P. and Curtis J. Richardson. 1989. Physical and chemical characteristics of freshwater wetland soils. In: Constructed wetlands for wastewater treatment. D.A. Hammer, ed. 1989. Lewis Publishers, Chelsea, Michigan.

Kadlec, Robert H. 1989. Hydrologic factors in wetland water treatment. In: Constructed wetlands for wastewater treatment. D.A. Hammer, ed. 1989. Lewis Publishers, Chelsea, Michigan.

Kleinmann, R.L.P. 1991. Biological treatment of mine water: an overview. In: Applied wetlands science and technology. D.M. Kent. 1994. Lewis Publishers, Boca Raton, Florida.

Reimold, Robert J. 1994. Wetlands functions and values. In: Applied wetlands science and technology. D.M. Kent. 1994. Lewis Publishers, Boca Raton, Florida.

Thut, Rudolph N. 1988. Utilization of artificial marshes for treatment of pulp mill effluents. In: Constructed wetlands for wastewater treatment. D.A. Hammer, ed. 1989. Lewis Publishers, Chelsea, Michigan.

Watson, James T., Sherwood C. Reed, Robert H. Kadlec, Robert L. Knight, and Alfred E. Whitehouse. 1989. Performance expectations and loading rates for constructed wetlands. In: Constructed wetlands for wastewater treatment. D.A. Hammer, ed. 1989. Lewis Publishers, Chelsea, Michigan.