PALMERTON ZINC SUPERFUND SITE CONSTRUCTED WETLANDS[1]

by

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Abstract. Constructed wetlands were evaluated for removal of metals and nitrogen from industrial influent. Sixteen reactor cells (14 ft long x 7 ft wide x 4 ft deep) were arranged in four rows of four and filled with varied ratios of mixed mushroom compost, sphagnum peat, bog peat and two lime sources. Four additional cells (4' long x 4' wide x 4' deep) were filled with a high-calcium iron rich material to serve as either pre or post treatments for the wetlands. Tanks were planted with Typha latifolia sprigs and equilibrated with approximately 1 gal/min influent rates. Inorganic salts ($ZnSO_4$, $MnSO_4$, and NH_4NO_3) were injected to give influent concentrations of 300 mg/L Zn, 30 mg/L Mn, and 20 mg/L NO_3^--N respectively, 3 days per every other week. Flow meters monitored both inflow (0.5 gal/min) and outflow. Water was monitored weekly at fifteen *in-situ* points throughout the wetlands for pH, redox, temperature (air and water), dissolved oxygen, and chemical oxygen demand (COD). Other monthly sampling parameters included N, C, alkalinity, electrical conductivity, nutrients and metals.

The results indicate about 97% N removal (as TKN) efficiency during the six months evaluated. Removal of N and metals was directly related to substrate and to optimizing conditions at both the nitrification and denitrification stages. Ion adsorption and precipitation are thought to play important roles in removing approximately 94 and 86% of Zn and Mn, respectively, in the high peat aerobic (nitrification) and high mushroom compost anaerobic (denitrification) media.

Introduction

The constructed wetlands site is located at the Zinc Corporation of America (formerly New Jersey Zinc Co.) Superfund Site in Carbon County (Palmerton, PA) about 75 miles northwest of Philadelphia, PA. Primary zinc smelting occurred here from about the turn of the century until 1980. Emissions (SO_2, SO_x) from primarily zinc sulfide ores (sphalerite) contributed to the defoliation and destruction of several thousand acres of tree and plant communities on adjacent and company owned lands (Buchauer, 1971). In addition, air emissions of Zn, Cd, and Pb resulted in

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the oxide of that metallic species being redeposited predominately in the upper 0-2" of affected soils. Typical total soil Zn values in and around affected Blue Mountain soils have ranged from 26,000 mg/kg to 80,000 mg/kg Zn (Jordan, 1975). However, more recent surveys show total Zn soil levels ranging from about 5,000 mg/kg to 20,000 mg/kg (Wright, 1988).

Further complicating this issue is an estimated 33 million ton pile of spent residue from past smelting operations, portions of which are leaching heavy metals. The Cinder Bank runs essentially east to west and parallel to Blue Mountain. It is located between the Aquashicola Creek (town of Palmerton) and the base of Blue Mountain.

The remedial action for the Blue Mountain operable unit consists of soil pH management to keep soil metals out of solution, and revegetation to reduce wind or water erosion of suspended solids (Oyler, 1988). The revegetation program utilizes a synthetic soil-like material comprised of municipal sludge, powerplant flyash, limestone and potash. With the possibility of nitrogen and/or heavy metals being in the effluent from this unit, it was decided to conduct this research to devise a solution in anticipation of a problem.

In April 1989, the Zinc Corporation of America formally agreed to design and perform research necessary to evaluate the feasibility of using constructed wetlands for treatment of runoff and groundwater from the Blue Mountain and Cinder Bank prior to discharge.

Design of the constructed wetlands was completed by HRD and GAI Consultants, Inc. of Monroeville, PA, and actual construction was handled by local contractors during summer and fall of 1989.

Our understanding of wetlands for treating metal contaminated waters is that vegetation (e.g.: T. latifolia) serve only a minor role in metals removal. Although the exact mechanisms are not yet fully understood, it seems likely that the greatest contributions of vegetation are: to anchor the substrate, fix atmospheric CO_2 for eventual CH_2O release in the rhizosphere, and to provide an oxygenated environment for chemical precipitation to occur in the substrate. Hence, design criteria for the wetlands focused on maximizing influent contact with the media to promote adsorption/ion exchange reactions and minimizing short circuiting or overland flow.

Objectives

The overall objectives for this research are to determine wetlands removal efficacy for N, Zn, Mn, Pb, and Cd. The research is being conducted in two Phases, with Phase 1 demonstrating removal of N, Zn, and Mn. Lead and cadmium will not be added until phase 2 after a level of confidence is developed using N, Zn, and Mn.

Specific objectives of phase 1 are:

1. to reduce metals concentrations in water from levels simulating Blue Mountain/Cinder Bank runoff and groundwater to acceptable NPDES quality standards for effluent.

2. to reduce dissolved nitrogen concentrations to acceptable NPDES limits by: a) promoting nitrification with the use of high peat: mushroom compost ratios, aeration, and high dissolved O_2 levels in water, and b) enhancing denitrification with the use of high mushroom compost: peat ratios, anaerobic conditions, and low dissolved O_2 levels in water.

TABLE 1. - Weekly (in situ) and monthly parameters.

Weekly

- Air temperature (°F)
- Water Flow (gal/min)
- pH
- Water temperature (°F)
- Redox (mV)
- Dissolved oxygen (mg/L)
- Chemical Oxygen Demand (mg/L)

Monthly

- pH
- EC (μmhos/cm)
- TSS (mg/L)
- Acidity (mg $CaCO_3$/L)
- Alkalinity (mg $CaCO_3$/L)
- Ammonia (mg/L)
- Chloride (mg/L)
- Nitrate nitrogen (mg NO_3/L)
- Phosphate (mg/L)
- Sulfate (mg/L)
- Aluminum (mg/L)
- Barium (mg/L)
- Cadmium (mg/L)
- Calcium (mg/L)
- Chromium (mg/L)
- Copper (mg/L)
- Iron (mg/L)
- Lead (mg/L)
- Magnesium (mg/L)
- Manganese (mg/L)
- Nickel (mg/L)
- Potassium (mg/L)
- Silver (mg/L)
- Sodium (mg/L)
- Zinc (mg/L)
- Kjeldahl nitrogen (mg/L)
- Total organic carbon (mg/L)

3. to assess the efficiency and longevity of metals removal by iron rich material (IRM), a product of HRD's current high-temperature metal recovery business, for both pre and post-wetlands treatment.

Materials and Methods

For three days every other week, a chemical injection system added 300 mg/L Zn solution as $ZnSO_4$, 30 mg/L Mn solution as $MnSO_4$, and a 20 mg/L NO_3^--N plus 6 mg/L NH_3^+ solution as NH_4NO_3.

Phase 1 involved monitoring and sampling over a six month period beginning in August 1991 and ending in February of 1992.

Weekly *in-situ* testing and monthly sampling for all parameters except metals commenced in August 1991. Monthly sampling for metals and analysis began in September 1991. Table 1 shows all parameters measured during the six month duration.

Water samples were collected by HRD technicians using teflon bailers (1.75" o.d. x 1') at 15 sampling points shown in Fig. 1.

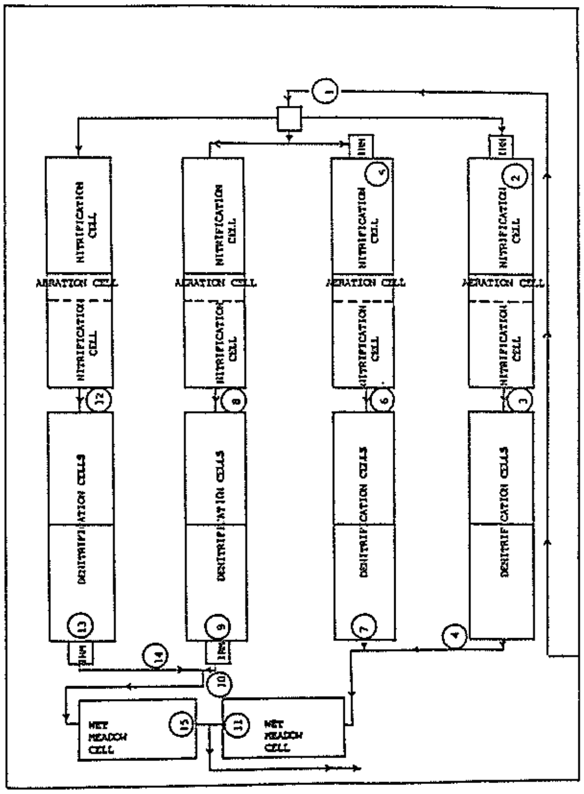

Figure 1. Water sampling points

For determinations done monthly, samples were filtered through 5.0 μm and .45 μm micropore filters and preserved with H_2SO_4 (for Total Kjeldahl N and total organic carbon) or with HNO_3 (for metals), filtered only (for phosphorus), or left unfiltered (for ammonia, nitrate, alkalinity, conductivity, pH, acidity, sulfate, and total suspended solids). All monthly samples were preserved with ice packs at 4°C in ice chests for immediate shipment to the lab in accordance with standard EPA analytical methods (SW-846).

Results and Discussion

In-situ measurements for pH, redox, temperature, oxygen, and COD.

Table 2. - Mean Values of Weekly *In-Situ* Parameters from 8/5/91 through 2/21/92

SAMPLE POINT #	WATER TEMP. (°F)	*AIR TEMP. (°F)	WATER FLOW (gal/min)	pH	REDOX (mV)	DISS. O_2 (mg/L)	COD (mg/L)
1	63.1	49.4	.45	6.72	+188.8	8.69	10.6
2	59.0	49.4	.44	6.31	+195.5	8.08	13.7
3	52.1	49.4	.48	6.63	+143.8	3.76	23.6
4	51.3	49.4	.43	6.88	+100.5	2.08	40.3
5	59.1	49.4		6.57	+182.7	4.74	37.3
6	52.4	49.4		6.80	+131.2	2.76	21.4
7	50.6	49.4		6.83	+123.5	2.26	78.3
8	52.0	49.4		6.73	+142.2	4.00	24.4
9	50.7	49.4		6.87	+109.8	2.10	39.8
10	50.7	49.4		6.84	+171.3	5.97	26.8
11	51.3	49.4		6.88	+169.2	5.43	22.3
12	52.3	49.4		6.72	+133.7	3.07	28.6
13	50.7	49.4		6.92	+126.3	2.78	177.6
14	51.1	49.4		6.87	+148.8	6.69	28.0
15	51.4	49.4		6.87	+165.0	6.81	20.1

Redox (Eh) and dissolved oxygen (DO):

Redox mean values, a measure of anaerobiosis, were positive (+). This was somewhat unexpected and may indicate more metals sorption by the compost than originally anticipated. According to Hedin et al. (1989), the lack of organic matter and dissolved SO_4^{2-} or porewater pH's consistently less than 5.0 are some of the most common factors limiting SO_4^{2-} reducing bacterium activity. These key factors have been provided or maintained. But, since anaerobic SO_4^{2-} reduction and metals removal occurs at redox values of less than about -220 mV, presumably little to no bacterial SO_4^{2-} reduction has occurred during the first six months. A trend toward ever increasing dissolved O_2 and more positive eH values since the three month evaluation suggests a similar conclusion with little recourse to an anaerobic state.

Monthly laboratory determinations for N, metals, and nutrients

All ammonia (Fig. 2), Total N (Fig. 3), and nitrate (Fig. 4) levels showed that at least 78% of the N in the influent can be removed by IRM pretreatment. Although NH_3^+ removal efficiency (Fig. 2) was less than TKN and NO_3^--N removals (Fig. 3 and 4) for pre IRM treatments, an ascending trend toward greater NH_3^+ removal occurred as effluent progressed to the final wet meadow cells. Table 3 gives the N quality of wetlands effluent.

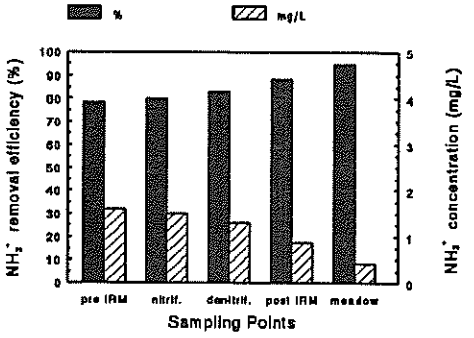

Figure 2. Mean NH_3^+ removal efficiency (%) and concentration (mg/L) in effluent from Aug. 1991 - Sept. 1992.

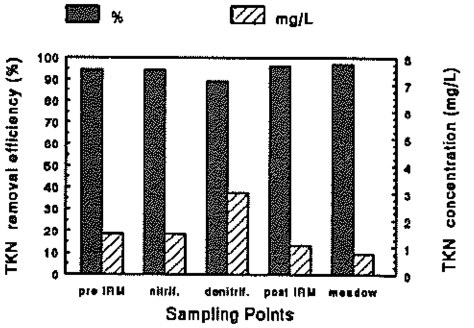

Figure 3. Mean TKN removal efficiency (%) and concentration (mg/L) in effluent from Aug. 1991 - Feb. 1992.

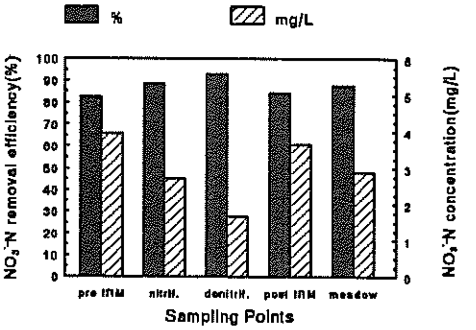

Figure 4. Mean NO_3^--N removal efficiency (%) and concentration (mg/L) in effluent from Aug. 1991 - Feb 1992.

Table 3. Nitrogen quality of constructed wetland effluent from August 1991 through February 1992.

	Concentrations, mg/L		
Sampling Point	NH_3^+	TKN	NO_3^--N
1	7.5	27.5	23.1
2	2.7	2.2	5.5
3	1.9	1.7	4.3
4	0.5	1.0	1.6
5	0.6	0.7	2.4
6	1.6	1.7	2.4
7	0.8	1.9	1.1
8	2.1	1.8	3.2
9	1.3	1.6	2.4
10	0.9	1.1	3.6
11	0.3	0.7	1.7
12	0.5	0.7	0.8
13	2.6	7.5	1.5
14	0.9	1.0	3.6
15	0.5	0.9	4.1

The 7.5 mg/L NH_3^+ at sampling point #1 versus the 27.5 mg/L TKN and 23.1 mg/L NO_3^--N lends some explanation to the lessened NH_3^+ removals experienced after pre IRM (sampling points #2 and #5) treatments.

Nitrification cells (sampling points #3, #6, #8, #12) removed at least 80% of ammonia, total N, or nitrate from water entering them. Denitrification cells (sampling points #4, #7, #9, #13) further reduced to 83% the concentrations of these same three parameters. A further % removal for all N parameters following denitrification would have been realized had sampling point #13 not consistently shown high N effluent values every month. Even though Table 1 shows a positive redox (+126.3 mV) for point #13, the depressed dissolved O_2 (2.8 mg/L) and higher COD 178 (mg/L) levels might indicate an inhibition of organic matter oxidation with more dissolved N remaining in solution.

Removal efficiencies (%) of N following a nitrification - denitrification sequence was consistent or better than other literature reports on N removal with constructed wetlands. For example, Davido and conway (1989) found a 95% overall reduction of TKN from a marsh influent to a meadow effluent at the Iselin Marsh/Pond/Meadow facility in western Pennsylvania. Conversely, McIntyre and Riha (1991) examined NO_3-N removals in an artificial wetlands greenhouse study and found a mean removal ranging from only 57%-63%.

Federal regulations require <10 mg/L NO_3^--N and the ZCA/HRD NPDES permit requires <0.5 mg/L NH_3^+ in effluent. The preliminary results above (Table 2, points #11 and #15 or meadow cell) suggest that these goals can probably be attained.

Manganese (Mn) and zinc (Zn) additions and effluent values for each sampling point are shown in Table 4. Figure 5 shows Mn and Zn removal efficiencies (%) and the concentration (mg/L) in effluent for both metals at all sampling points.

Table 4. - Manganese and Zinc quality of constructed wetland effluent from September 1991 through February 1992.

	Concentrations, mg/L	
Sampling Point	Mn	Zn
1	30.1	309.0
2	8.6	56.0
3	4.4	13.5
4	0.8	1.5
5	13.3	51.2
6	6.2	10.0
7	1.6	1.8
8	5.6	16.0
9	2.6	3.2
10	2.7	9.0
11	0.4	4.6
12	3.6	21.8
13	3.5	4.9
14	2.4	12.2
15	1.1	12.0

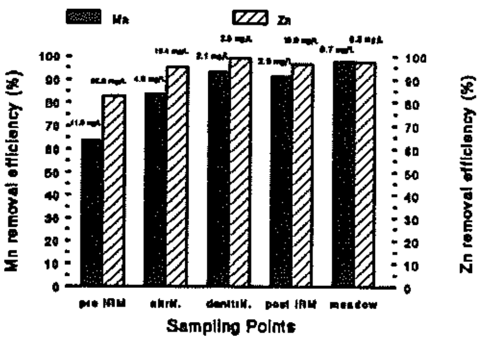

Figure 5. Mean Mn and Zn removal efficiency (%) and concentration (mg/L) in effluent from Sept. 1991 - Feb. 1992.

IRM pre-treatment removed 63% and 83% of the Mn and Zn respectively, from the 30.1 mg/L Mn and 309.0 mg/L Zn in the influent. The nitrification and denitrification cells increased total Mn removal to 84% (4.9 mg/L) and 93% (2.1 mg/L), respectively. By the time water had passed the final wet meadow cells, 97.6% (0.7 mg/L) of the Mn had been removed. Zinc, on the hand, showed a 95% removal (15.4 mg/L) following nitrification and a 99% removal (2.8 mg/L) following denitrification. Post-IRM and meadow cell removals for Zn declined somewhat to 96% and 97%, respectively. The experienced decline may be due to Zn release from IRM. The IRM may have approached its sorptive capacity and Zn breakthrough could be occurring at the post-IRM (points #4, #7, #9, #13) and meadow cell (points #11, #15) sampling points.

Conclusions

Excellent removal efficiencies were experienced for both nitrogen, Mn, and Zn during the first six full operating months. About 97% removal of total Kjeldahl N and approximately 97 and 98% removal of Zn and Mn, respectively, were attained by the whole system during the evaluation period.

IRM performed favorably over this period and preliminary results suggest that IRM is beneficial for metals removal before contact with wetlands media. However, a metals sorptive capacity or IRM longevity point may have been approached.

No attempt to date has been made to ascertain removal efficiency differences for the mushroom compost, sphagnum peat or bog peat.

After Phase I ends in February 1992, the following points will be addressed by Phase II studies in order to design a commercial scale constructed wetland:

- Evaluation of lead (Pb) and cadmium (Cd) removal efficiencies.
- Calculation of water residence times so that flow rates, land areas, and volumes of wetland media can be better correlated with metals loading rates and removal efficiencies.

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