BIOTREATMENT AND CHEMICAL SPECIATION OF LEAD AND ZINC MINE/MILL WASTEWATER DISCHARGES IN MISSOURI, U.S.A.

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Abstract. Continued mining development in the world's largest lead producing area has generated and increased concern over effective mine water treatment in Missouri's New Lead Belt. A new type of mine/mill wastewater treatment system was constructed which consisted of a tailings pond followed by a series of artificially constructed meandering biotreatment channels and a polishing lagoon. This system provided additional retention time and distance for the removal of heavy metals by abundant aquatic plants and sedimentation. Seasonal field sampling and analytical testing that evaluated the present system confirmed that it provided good treatment for removal of heavy metals within the company property and produced a final effluent within the state and federal regulatory guidelines. On average, greater than 95% of zinc and manganese in the drainage water were removed by the biotreatment system, while lead and copper were 50 to 60%. A chemical equilibrium model, MINTEQ, was also used to identify various species of lead and zinc in the biotreatment system. The model predicted that the major species of carbonates and hydroxides would be the predominant complexes of lead and zinc for the pH and alkalinity values reported in the biotreatment system. These results were also supported by the literature.

Keywords: biotreatment, lead and zinc, mine wastewater, MINTEQ, speciation

1. Introduction

There are several lead mine/mill complexes which previously have operated or continue to operate in the 'Viburnum Trend' or New Lead Belt of Southeastern Missouri, U.S.A. Each operation has its own unique characteristics and waste treatment problems depending upon the size of the operation, amount of water that must be removed from underground to dewater the mine, types of concentrates processed, specific milling or benefaction procedures employed, and amount of wastewater generated. Each mill has at least one settling lagoon or tailings pond to settle and treat the large amounts of rock slurry created by modern hydrometallurgical procedures. Early studies (Bell, 1974; Wixson and Jennett, 1975) indicated that for some operations, a single tailings pond of appropriate size and residence time was sufficient to adequately remove suspended rock particles and residual milling reagents prior to discharge to a receiving stream. Some operations found it necessary to separate and recycle mill effluent while discharging excess water

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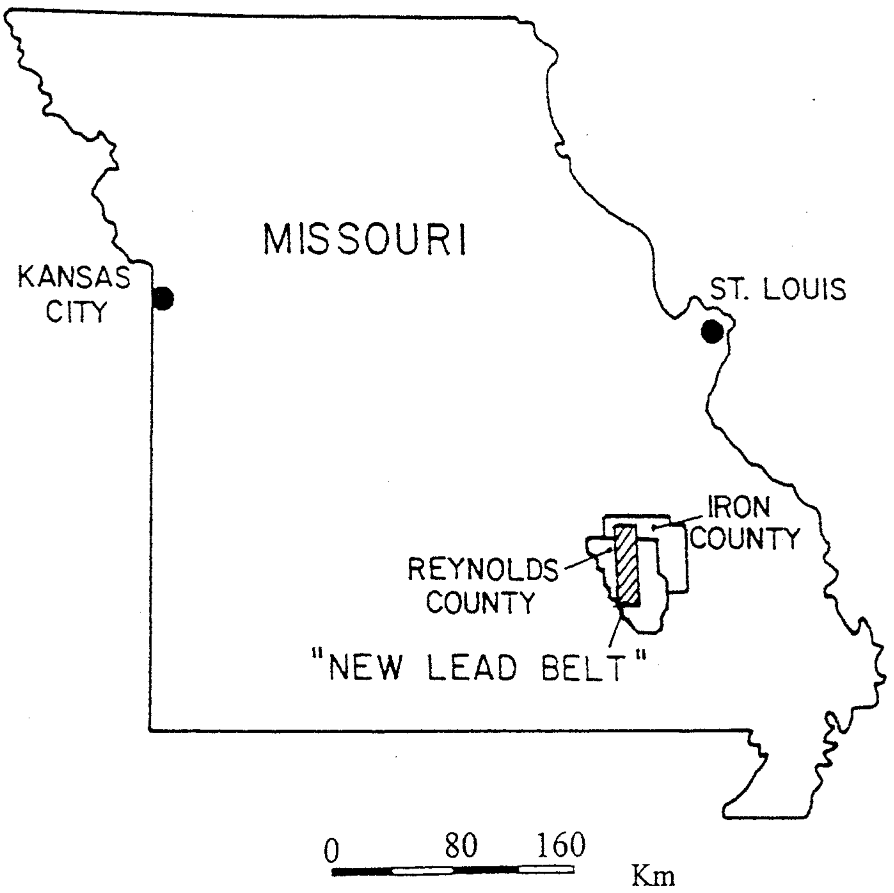


Figure 1. Location of the New Lead Belt in the United States.

pumped from the mine into entirely separate settling with ultimate discharge to a receiving stream.

One major mine/mill complex that is owned and operated by the Doe Run Buick Company in Southeast Missouri (Figure 1), has used a wastewater treatment system comprised of a primary tailings pond followed by a series of artificially constructed meandering biotreatment system, which is approximately 1 m in depth. This system empties into a final sedimentation pond with a baffled weir prior to treated water discharges into the nearby Strother Creek (Figure 2). Before construction of the biotreatment meanders and final sedimentation pond, many episodes of extensive algal blooms occurred in Strother Creek, often extending for several miles downstream. The two combined mine/mill wastewater treatment systems were found to be more cost effective than conventional mine/mill tailings pond treatment systems commonly used by the mining industry (Jennett and Wixson, 1975). This system can be applicable and advantageous when recycling is technically impossible

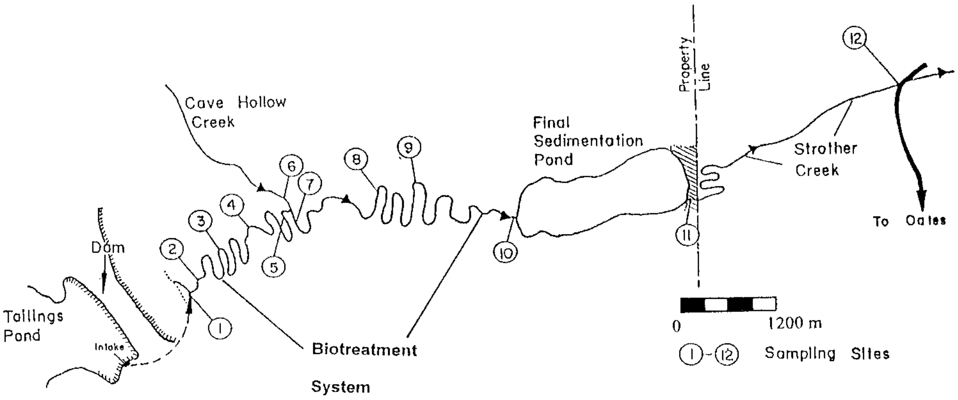


Figure 2. Schematic of Biotreatment Meander System at the Doe Run Buick Mine.

TABLE I

Laboratory methods used for sample analysis

Analysis	Method	APWA[a] method number
pH	Elecrometric method	4500-H
Conductivity	Platinum electrode	2510
Dissolved oxygen	Membrane electrode	4500-0G
Alkalinity	Titration	2320
Hardness	EDTA titration	2340-C
Total suspended solids	Gravimetric method	2540-D
Total dissolved solids	Gravimetric method	2540-C
Ammonia nitrogen	Ammonia selective electrode	4500 NH_3-D
Nitrate nitrogen	Spectrophotometric method	4500 NO_3-B
Nitrite nitrogen	Colorimetric method	4500 NO_3-B
Total Kjeldahl nitrogen	Macro-Kjeldahl method	4500-B
Total phosphorus	Acid digestion	4500 P-B
	Colorimetric	4500 P-E

[a] American Public Health Association, Inc. (1995).

or economically unfeasible in particular geographic areas for similar industries. Development of the biotreatment meanders permitted algal growth and sediment accumulation to occur within the artificial wastewater treatment system.

Several studies indicated that the effluent from the mine/mill complex contains various amounts of lead, zinc and cadmium in a variety of site-specific forms (Davies *et al.*, 1976; Borgman, 1983; Bradley and Sprague, 1985). Several authors have stated the importance of the chemical form of the contaminant metals and the effects of chemical speciation such as; inorganic complexation, chelation, precipitation, and adsorption when assessing their bioavailability and toxicity (Biggins and Harrison, 1980; Khan and Frankland, 1983). For example, in areas where mining is the main activity that discharges metals, Pb is normally found as primary Pb minerals such as Galena (PbS), and secondary alteration products such as phosphates and oxides (Davis *et al*., 1992, 1993).

There are several computer models available that may offer considerable assistance in analysis of complex chemical behavior and speciation of heavy metals. One model, MINTEQA2 (MINTEQ) (Brown and Allison, 1987), which is a thermodynamic equilibrium computer model that computes aqueous speciation, adsorption, and precipitation/dissolution of solids, provides a useful guidance in predicting the major metallic species and transformations most likely to occur in the laboratory or in natural systems. Previous attempts have indicated useful application of MINTEQ, to characterize streams in the New Lead Belt (Schlachter, 1989; Erten *et al*., 1990a, b).

This study resulted from continuing investigations regarding environmental impacts of the lead mining wastewater and their treatment. The purpose of this study was twofold: (a) to evaluate the treatment performance of the Doe Run Buick mine biotreatment system and to determine if it was capable of removing the metal contaminants to levels established by the federal and state standards; (b) to identify various species of lead and zinc that may exist within the context of physical and chemical conditions present in the biotreatment system. To accomplish this, MINTEQA2 was utilized to predict which of the available ions will form insoluble mineral precipitates with lead and zinc measured in the biotreatment system.

2. Methods and Materials

To characterize water quality in the biotreatment system, five seasonal water quality samples were collected and analyzed from 12 locations (Figure 2). One major sampling effort targeted collection of data from five stations at the discharge of the tailings pond and along the meanders up to the confluence of Cave Hollow Creek, and one sampling station from the Cave Hallow Creek. Four additional sampling stations collected water before the final sedimentation pond and also two samples were collected after the pond; one within the property line and one from Strother Creek. Due to the fact that heavy metals and their characteristics are associated with the chemical and physical conditions of the water, 17 basic water quality parameters were measured. Water samples were collected in four different polyethylene sample bottles. All sample bottles were soaked in nitric acid and rinsed several times with distilled water. Before collection of each sample, bottles were rinsed several times with the stream water at the sampling point. After completion of the field measurement, the samples were taken at the approximate center of the stream flow. Water samples were prepared and preserved in accordance with the requirements stated in the Standard Methods (APWA, 1995) and by the Environmental Protection Agency guidelines (USEPA, 1985).

The parameters that were measured in the field included pH, dissolved oxygen, conductivity, temperature, and stream velocity. Other chemical analysis that were performed in the laboratory included total and calcium hardness, total alkalinity, chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), total nitrogen, and total phosphorus, following the procedures outlined in Standard Methods (APWA, 1995). A summary of laboratory methods used for analysis of major parameters (except metals) is shown in Table I. Samples were acidified with 1 + 1 HNO_3, and analyzed for unfiltered and filtered (through 0.45 μm membrane filter) metals including lead, zinc, cadmium, copper, and manganese in accordance with Standard Methods (APWA, 1995) by flame atomic adsorption spectrometry for all metals. Lead and cadmium were also analyzed by graphite furnace to obtain lower detection limits. In addition, inductively coupled argon plasma techniques were also used to analyze samples to check agreements with the flame method. Metals analyses were conducted by the Environmental Trace Substances Research Center of the University of Missouri in Columbia, Missouri.

The water quality data from three different sampling sites within the biotreatment meander system were then entered into the MINTEQ model. First sampling site was picked from the upstream of the biotreatment system before the confluence of the Cave Hollow Creek. The second site was selected from downstream before the sedimentation pond, and the third one after the sedimentation pond to observe if there was any difference in the speciation scheme. The input data included pH, cation and anion concentrations, alkalinity, and concentration of lead and zinc as heavy metals. MINTEQ computed the ionic strength and derived the activity coefficients. The cation and anion concentrations found in the biotreatment system were added to the input file. The total metal concentrations measured at three sampling stations of the biotreatment system were assumed to be completely dissolved when entered in the MINTEQ data files for both lead and zinc to represent the worst case conditions. Each data set for the metals were run twice; first without allowing precipitation, and second allowing precipitation to occur for those species with positive saturation indices at the end of the first run. The cadmium concentrations measured at all sampling stations along the treatment system were at or below detection limit of 0.002 mg L^{-1}, therefore, cadmium was not included in the chemical speciation calculations. The model output included different species of lead and zinc that should be formed under the specified water quality parameters at the designated sampling stations.

TABLE II

Concentration of major analytes measured in the biotreatment system

Station number		Temp (°C)	pH	Conductivity (dS m^{-1})	Dissolved oxygen (mg L^{-1})	Total dissolved solids (mg L^{-1})	Total suspended solids (mg L^{-1})	Total alkalinity (mg L^{-1})	Total hardness (mg L^{-1})	Calcium hardness (mg L^{-1})	Total nitrogen (mg L^{-1})	Total phosphorus (mg L^{-1})
1	Average	16.6	6.4	1322	3.86	1496	22	231	1450	698	2.287	0.024
	Maximum	17.5	7.1	1284	6.20	1581	50	238	1904	809	6.110	0.046
	Minimum	15.5	6.0	1279	1.10	1398	0	224	884	581	0.026	0.010
	Range	2.0	1.1	5	5.10	183	50	14	1020	228	6.084	0.036
2	Average	20.7	6.3	1284	4.68	1371	28	222	1248	488	1.945	0.025
	Maximum	25.0	6.9	1400	5.10	1528	78	227	1768	563	3.740	0.054
	Minimum	15.0	6.1	1180	3.90	1262	0	220	884	448	0.258	0.009
	Range	10.0	0.8	220	1.20	266	78	7	924	115	3.482	0.045
3	Average	19.0	6.7	1279	8.90	1356	30	218	1015	551	0.243	0.036
	Maximum	23.0	7.1	1320	9.60	1401	58	222	1086	664	0.826	0.038
	Minimum	12.0	6.7	1250	8.10	1316	1	214	952	452	0.130	0.034
	Range	11.0	0.4	70	1.50	85	57	8	134	212	0.696	0.004
4	Average	20.3	7.9	741	8.70	860	21	171	686	417	0.416	0.059
	Maximum	26.0	8.2	820	9.40	1510	29	192	952	548	0.853	0.082
	Minimum	11.0	7.0	650	8.00	409	7	147	382	268	0.029	0.033
	Range	15.0	1.2	170	1.40	1101	22	45	570	280	0.824	0.049

TABLE II

(continued)

Station number		Temp (°C)	pH	Conductivity (dS m^{-1})	Dissolved oxygen (mg L^{-1})	Total dissolved solids (mg L^{-1})	Total suspended solids (mg L^{-1})	Total alkalinity (mg L^{-1})	Total hardness (mg L^{-1})	Calcium hardness (mg L^{-1})	Total nitrogen (mg L^{-1})	Total phosphorus (mg L^{-1})
5	Average	21.0	8.0	601	8.60	486	6	139	365	184	2.290	0.019
	Maximum	28.0	8.1	650	9.40	713	11	145	404	284	3.196	0.036
	Minimum	11.0	6.7	540	8.30	383	4	135	332	135	0.270	0.003
	Range	17.0	1.4	110	1.10	330	7	10	72	149	2.926	0.033
6	Average	18.6	8.0	289	8.84	204	7	175	227	116	1.090	0.019
	Maximum	24.0	8.3	310	9.10	409	12	208	258	188	3.530	0.039
	Minimum	12.0	7.2	260	8.40	90	1	145	190	86	0.074	0.005
	Range	12.0	1.1	50	0.70	389	11	63	68	102	3.456	0.034
7	Average	21.0	8.0	554	8.30	439	8	144	339	169	2.520	0.019
	Maximum	28.0	8.1	615	9.30	680	19	151	374	280	5.020	0.034
	Minimum	11.0	6.9	460	8.00	256	2	144	270	107	0.108	0.004
	Range	17.0	1.2	155	1.30	424	17	7	104	173	4.912	0.030
8	Average	21.1	8.1	8.05	8.60	424	7	148	336	170	2.089	0.020
	Maximum	27.5	8.1	8.1	9.20	577	14	155	394	276	5.690	0.038
	Minimum	12.5	7.9	7.9	6.90	249	4	145	278	114	0.076	0.004
	Range	15.0	0.2	0.2	2.30	328	10	10	116	162	5.614	0.034

TABLE II

(continued)

Station number		Temp (°C)	pH	Conductivity (dS m^{-1})	Dissolved oxygen (mg L^{-1})	Total dissolved solids (mg L^{-1})	Total suspended solids (mg L^{-1})	Total alkalinity (mg L^{-1})	Total hardness (mg L^{-1})	Calcium hardness (mg L^{-1})	Total nitrogen (mg L^{-1})	Total phosphorus (mg L^{-1})
9	Average	20.7	8.0	8.0	8.60	441	5	147	376	177	1.949	0.024
	Maximum	26.5	8.2	8.2	9.20	660	11	153	442	248	3.534	0.037
	Minimum	12.5	8.0	7.95	7.50	254	2	144	310	119	0.280	0.002
	Range	14.0	0.2	0.25	1.70	406	9	9	132	165	3.254	0.035
10	Average	17.4	8.1	8.1	9.00	499	5	150	305	208	1.762	0.027
	Maximum	24.5	8.4	8.4	9.30	623	10	154	400	268	2.975	0.054
	Minimum	10.0	8.0	8.0	8.60	270	0	147	320	114	0.632	0.004
	Range	14.2	0.4	0.4	0.70	353	10	7	80	154	2.343	0.050
11	Average	20.8	8.2	8.2	9.00	412	7	145	320	158	0.959	0.025
	Maximum	30.0	8.2	8.2	9.30	654	12	147	354	244	2.222	0.043
	Minimum	11.0	7.9	7.9	8.50	228	0	144	276	108	0.074	0.003
	Range	19.0	0.3	0.3	0.80	426	12	3	78	136	2.148	0.040
12	Average	21.5	8.2	8.2	9.02	450	8	128	345	255	1.768	0.020
	Maximum	30.0	8.4	8.4	9.60	596	11	147	406	294	3.713	0.035
	Minimum	11.0	8.0	7.98	8.60	362	0	74	270	132	0.016	0.007
	Range	19.0	0.4	0.42	1.00	234	11	73	136	162	3.697	0.028

TABLE III

Concentration of metals measured in the biotreatment system

Station		Copper		Lead		Zinc		Manganese	
number		Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved
		(mg L^{-1})							
1	Average	0.0048	0.0032	0.096	0.057	12.36	9.04	1.78	1.1
	Maximum	0.009	0.004	0.16	0.13	14.1	12.9	1.9	1.81
	Minimum	0.003	0.002	0.02	0.02	9.61	7.53	1.65	0.65
	Range	0.001	0.002	0.14	0.11	4.49	5.37	0.25	1.16
2	Average	0.0056	0.0034	0.062	0.039	8.49	5.95	1.444	0.942
	Maximum	0.01	0.005	0.11	0.08	9.53	8.07	1.85	1.2
	Minimum	0.003	0.003	0.02	0.02	7.44	5.82	1.28	0.8
	Range	0.007	0.002	0.09	0.06	2.09	2.25	0.57	0.4
3	Average	0.0045	0.0025	0.06	0.031	5.8	4.95	2.32	0.99
	Maximum	0.01	0.003	0.09	0.05	6.1	5.67	2.41	2
	Minimum	0.003	0.002	0.02	0.02	5.54	2.95	2.18	0.854
	Range	0.007	0.001	0.07	0.03	0.56	2.72	0.23	1.146
4	Average	0.004	0.003	0.079	0.036	2.977	0.98	1.378	0.75
	Maximum	0.008	0.004	0.11	0.05	3.85	3.25	1.79	1.62
	Minimum	0.002	0.002	0.03	0.025	0.528	0.353	0.162	0.692
	Range	0.006	0.002	0.08	0.025	3.322	2.897	1.628	0.928
5	Average	0.008	0.003	0.106	0.038	0.29	0.2	0.17	0.123
	Maximum	0.02	0.008	0.16	0.07	0.6	0.43	0.186	0.15
	Minimum	0.002	0.002	0.05	0.025	0.19	0.11	0.129	0.11
	Range	0.018	0.006	0.11	0.045	0.41	0.32	0.057	0.04
6	Average	0.004	0.003	0.045	0.02	0.16	0.003	0.013	0.003
	Maximum	0.008	0.003	0.086	0.04	0.062	0.004	0.026	0.006
	Minimum	0.002	0.002	0.02	0.02	0.003	0.003	0.002	0.002
	Range	0.006	0.001	0.066	0.02	0.059	0.001	0.024	0.004

TABLE III
(continued)

Station		Copper		Lead		Zinc		Manganese	
number		Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved
		(mg L^{-1})							
7	Average	0.0063	0.0028	0.118	0.032	0.251	0.166	0.162	0.099
	Maximum	0.013	0.004	0.17	0.15	0.555	0.33	0.186	0.145
	Minimum	0.002	0.002	0.03	0.02	0.17	0.117	0.088	0.01
	Range	0.011	0.002	0.14	0.13	0.385	0.213	0.098	0.135
8	Average	0.006	0.0025	0.076	0.026	0.154	0.1	0.136	0.099
	Maximum	0.01	0.005	0.1	0.03	0.2	0.12	0.164	0.145
	Minimum	0.002	0.002	0.04	0.02	0.13	0.08	0.094	0.01
	Range	0.008	0.003	0.06	0.01	0.07	0.04	0.07	0.135
9	Average	0.004	0.0025	0.108	0.03	0.245	0.116	0.126	0.085
	Maximum	0.01	0.005	0.16	0.04	0.412	0.19	0.13	0.11
	Minimum	0.002	0.002	0.04	0.03	0.12	0.07	0.119	0.065
	Range	0.008	0.003	0.12	0.01	0.292	0.12	0.011	0.045
10	Average	0.004	0.002	0.045	0.025	0.163	0.053	0.113	0.051
	Maximum	0.009	0.004	0.08	0.04	0.31	0.1	0.125	0.11
	Minimum	0.002	0.002	0.02	0.02	0.11	0.02	0.001	0.02
	Range	0.007	0.002	0.06	0.02	0.2	0.08	0.124	0.09
11	Average	0.003	0.002	0.034	0.024	0.081	0.03	0.081	0.04
	Maximum	0.009	0.004	0.07	0.035	0.23	0.04	0.151	0.07
	Minimum	0.002	0.002	0.02	0.02	0.036	0.022	0.001	0.03
	Range	0.007	0.002	0.05	0.015	0.194	0.018	0.15	0.04
12	Average	0.003	0.002	0.03	0.021	0.063	0.025	0.052	0.014
	Maximum	0.005	0.004	0.05	0.025	0.16	0.034	0.1	0.02
	Minimum	0.002	0.002	0.02	0.02	0.029	0.019	0.001	0.001
	Range	0.003	0.002	0.03	0.005	0.131	0.015	0.099	0.019

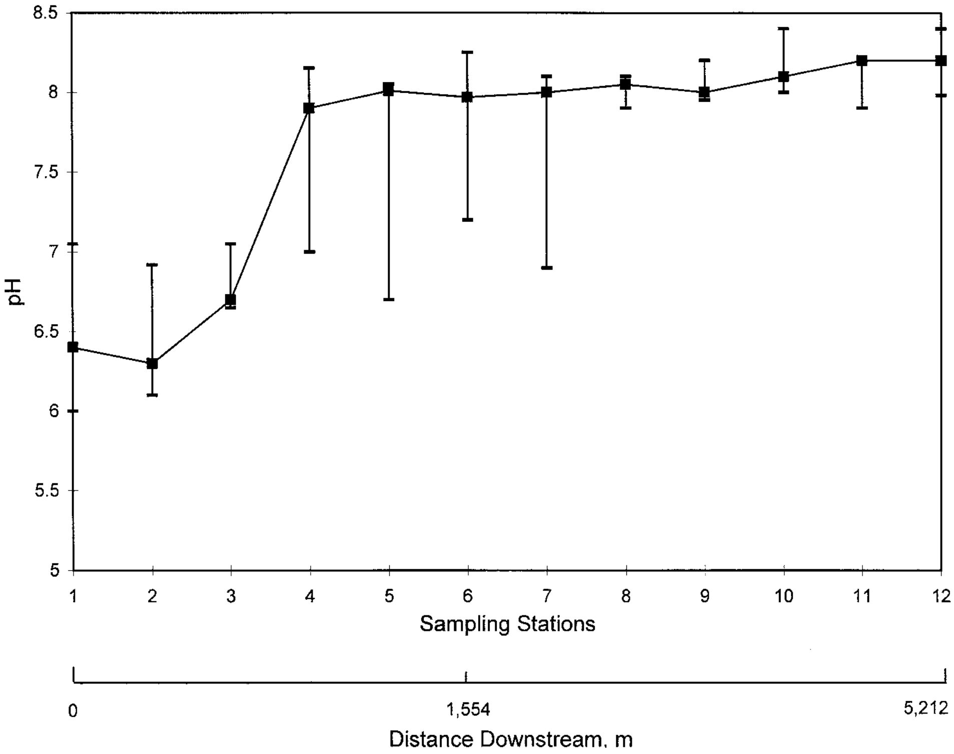


Figure 3. Median pH levels in biotreatment meanders.

3. Results and Discussion

3.1. TREATMENT SYSTEM AND PERFORMANCE

The wastewater treatment system (biotreatment system) of the Doe Run Buick Mine/Mill Complex has been the subject of several studies to characterize the industrial effluents in the New Lead Belt (Ernst, 1976). The biotreatment system was designed to accomodate approximately 18 900 m^3 day^{-1} (5 mgd) of water consisting of some 11 350 m^3 day^{-1} (3 mgd) mill waste mixed with 7500 m^3 day^{-1} (2 mgd) excess mine water. The first component of the combined wastewater treatment system consists of a 524 000 m^3 capacity (425 acre-ft) primary tailings pond. Effluent from the primary tailings pond is delivered into the biotreatment system which encourages growth of aquatic vegetation and removal of vagrant particulates (Figure 2). The biotreatment meanders have a detention time of 60 days and empties into a final sedimentation pond which has a volume of approximately 123 300 m^3 (100 acre-ft). The treated industrial effluent then comprises the majority of the water flow in he headwaters of Strother Creek.

Earlier studies indicated that the mine water is naturally hard (581 mg^{-1} $CaCO_3$) and alkaline (178 mg L^{-1} $CaCO_3$), and quite low in dissolved solids and organic

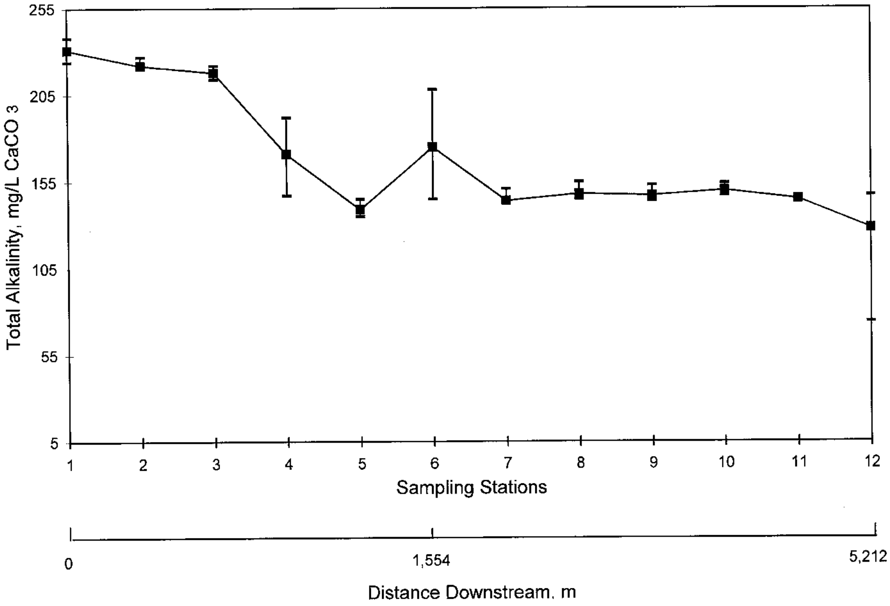


Figure 4a. Average alkalinity levels in biotreatment meanders.

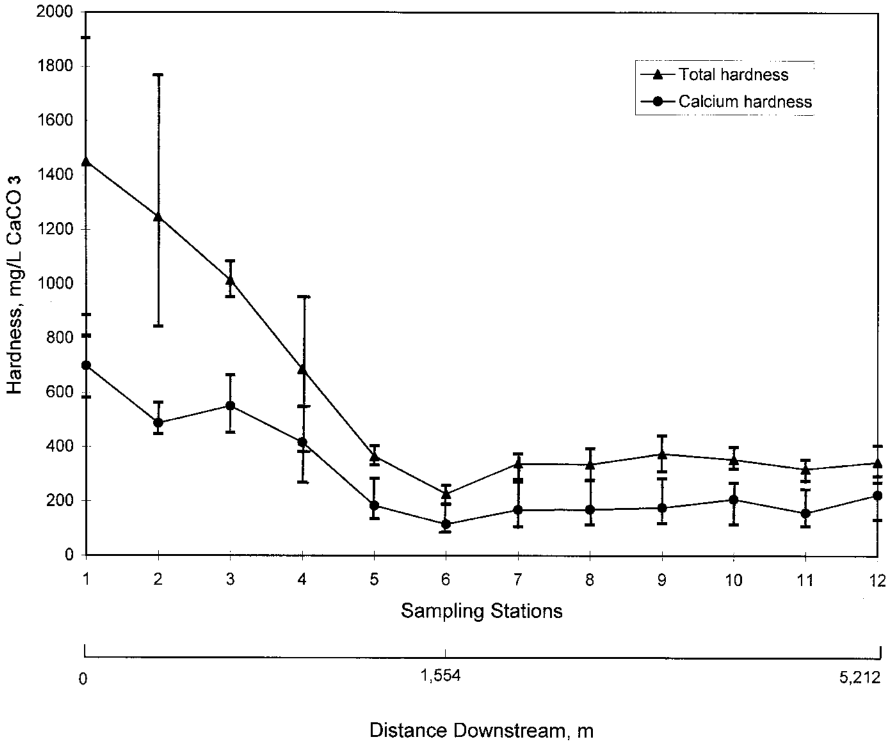


Figure 4b. Total hardness and calcium hardness levels in biotreatment meanders.

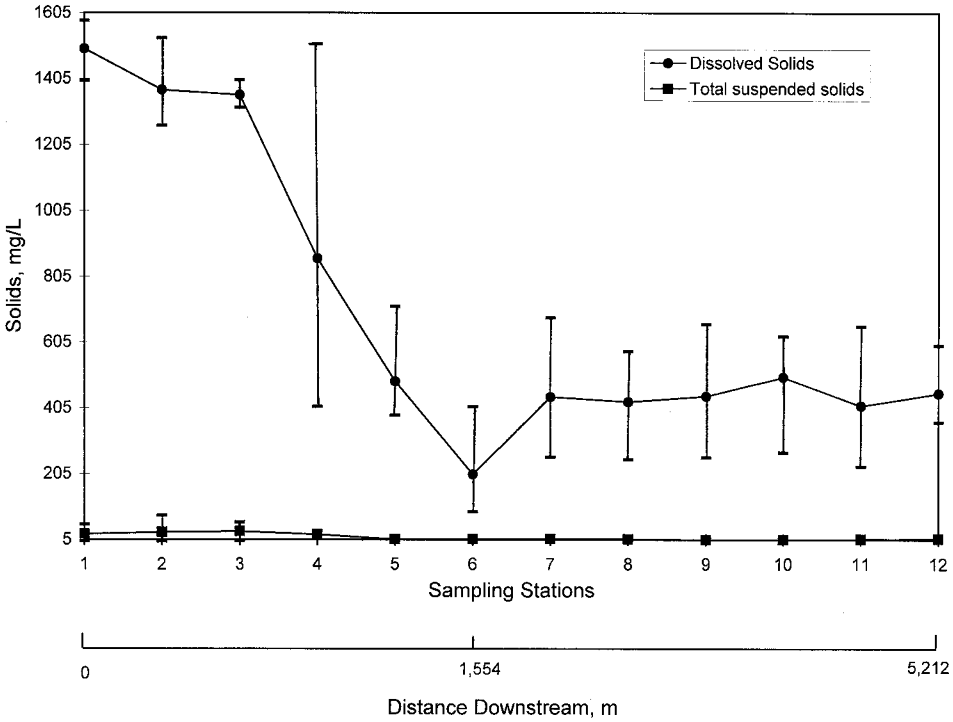


Figure 5. Total dissolved solids and total suspended solids values in biotreatment meanders.

matter (Jennett and Callier, 1977). However, the mill wastewaters were extremely high in turbidity and residual organics (8700 mg L^{-1} COD) created by the hydrometallurgical separation processes involving finely ground dolomitic ores and a variety of flotation reagent. Most of the trace organics removal occurred in the primary tailings pond (62%) followed by additional (26%) removal in the biotreatment system and the final sedimentation pond. The average refractory organic concentration discharged into Strother Creek was 0.54 mg L^{-1}. Dissolved organic complexing agents were generally lower in abundance than inorganic ligands especially bicarbonates and carbonates. In addition, abundant aquatic plant life within streams that were exposed to mine/mill effluents had been shown to bind lead, zinc, copper and manganese (Gale and Wixson, 1979). A comparison of the filtered versus unfiltered biotreatment water samples showed that considerable quantities of heavy metals were present in these waters in a finely divided suspended particulate state (Gale *et al.*, 1973; Jennet and Foil, 1979).

The different seasonal sampling results of this study showed that the primary tailings lagoon followed by the biotreatment system which has been in operation since 1971 continues to provide adequate treatment of the combined mine-mill wastewaters produced at this industrial site. A summary of the mean, minimum, maximum, and range for eleven major analytes are exhibited in Table II.

In the headwaters of the biotreatment system, observed pH values ranged from 6.0 to 6.5, increasing to levels near 8.0 at and beyond the confluence of a tributary, Cave Hollow Creek (Figure 3) as expected from the moderately hard, alkaline surface waters in this region. The dissolved oxygen (DO) levels, regardless of time of sampling, were lower (4.0 to 4.5 mg L^{-1}) at the beginning of the biotreatment meanders. The DO content, rose to constant levels near saturation (8.8 to 9.0 mg L^{-1}) within 600 m downstream. The initial low dissolved oxygen levels were attributed to the presence of some frothers used in the milling process which exerted considerable oxygen demand (Erten *et al.*, 1990a). Conductivity levels were high (1280 to 1320 dS m^{-1}) at the beginning of the biotreatment system. Increases in stream conductivity are normally expected below an industrial discharge however, the reduction in conductivity due to dilution with Cave Hollow Creek was evident.

Mean alkalinity (Figure 4a), calcium hardness and total hardness (Figure 4b) were initially high, decreasing to lower values approaching those of moderately hard waters throughout the middle and lower meander system. Levels of total dissolved and suspended solids were found to be very similar to those shown for total hardness (Figure 5). Total suspended solids were fairly low which was in agreement with low turbidity measurements and low velocities that would allow settling of the solids in the sediments. The low values also gave evidence to the effectiveness of solids removal in the primary tailings pond. The average nutrient concentrations such as total nitrogen and total phosphorus were above the generally expected levels that would produce an algal bloom. Even though the meandering biotreatment stream water contained enough nutrients for algal growth, very little growth was observed before the confluence of the small tributary Cave Hollow Creek. The aquatic vegetation was scarce at the upper meanders of the biotreatment system, however with dilution and precipitation of metal species and solids, productivity of the stream and biota usually increased with distance downstream beyond the confluence with Cave Hollow Creek.

Figures 6a through 6d show the average concentrations of heavy metals found in filtered (through 0.45 μm membrane filter) and unfiltered wastewater samples taken from the treatment system. A summary of the mean, maximum, minimum and range of the total and dissolved metal concentrations are also shown in Table III. Concentrations of zinc (Zn) and manganese (Mn) dropped dramatically within the first 1500 m (5000 ft) of the treatment system (Figures 6a and 6b). Copper (Cu) and lead (Pb) concentrations appeared to increase slightly within the first 1500 m, then subsequently dropped off gradually with increasing distance downstream (Figures 6c and 6d). These variations of heavy metal concentrations should be considered in context with concomitant decreases in hardness, dissolved and suspended solids, together with increasing pH and alkalinity levels. Moreover, stream flow velocity was not constant throughout the meanders and would be expected to have an effect on sedimentation or resuspension of metal-laden particulates. Highest concentrations of lead and copper occurred in a region where flow velocity was also greatest. This may also suggest the presence of metal-

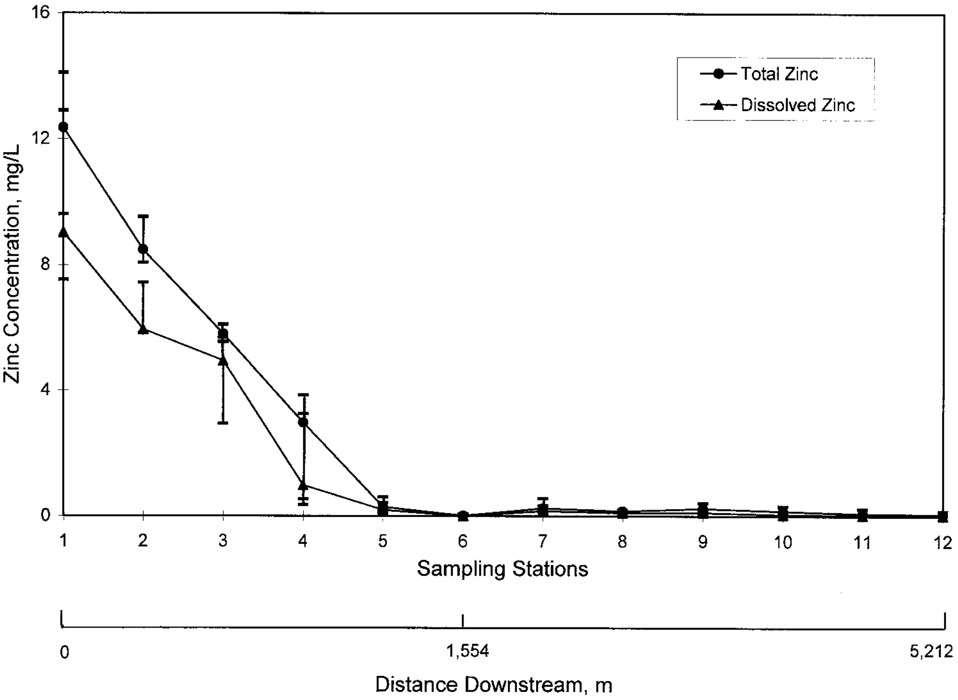


Figure 6a. Unfiltered and filtered zinc concentrations in biotreatment meanders.

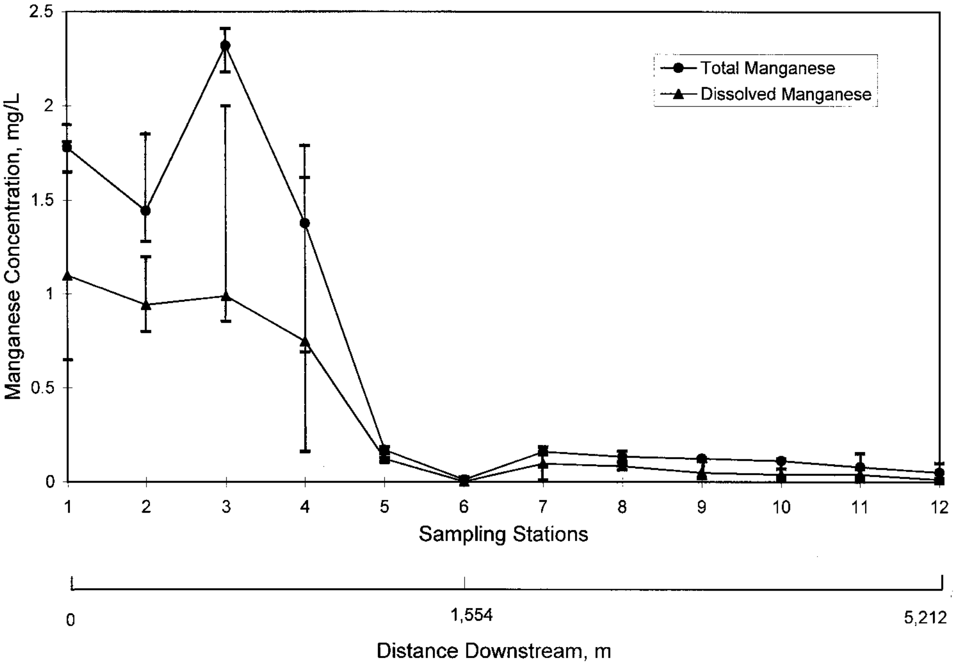


Figure 6b. Unfiltered and filtered manganese concentrations in biotreatment meanders.

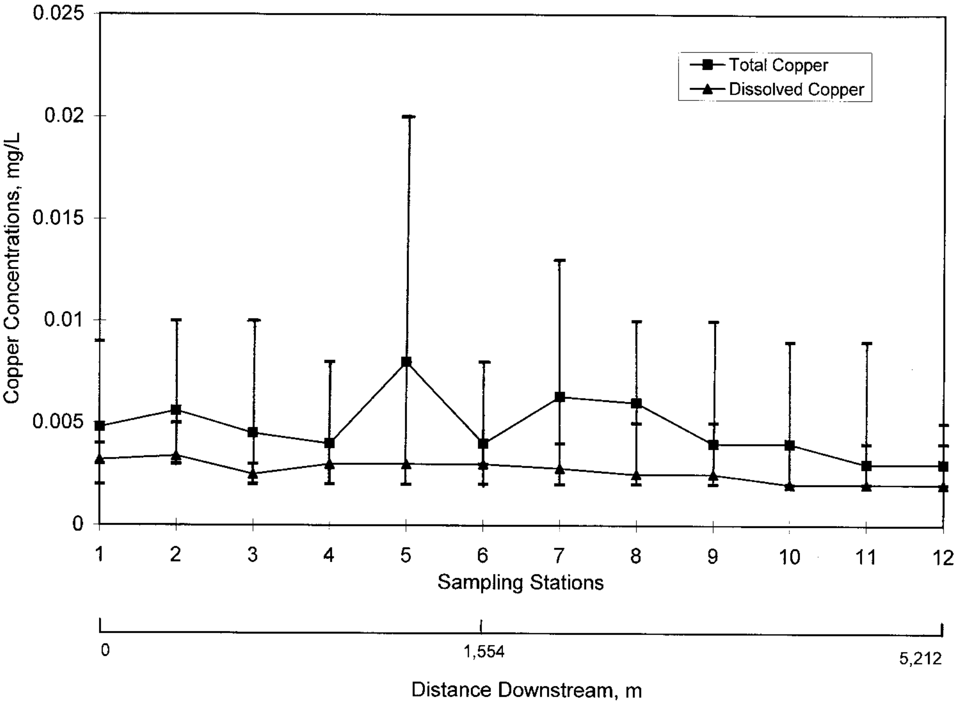


Figure 6c. Unfiltered and filtered copper concentrations in biotreatment meanders.

rich sediments that were subject to resuspension and horizontal transport within the system. The major portion of heavy metal removal occurred between stations three and eight, 0.6 to 2.5 km below the tailings pond. By the time the wastewater reached the lower meanders, most of the metals were removed. The transport of these metals can be described qualitatively as shown in Figure 7.

The dissolved heavy metal content of these wastewater was found to be lower because of the relatively high carbonate content and slightly basic pH conditions, a characteristic of streams and groundwater of this region. The average concentrations of total lead, zinc, copper and manganese were compared with permissible levels established in effluent guidelines. Actual lead concentrations at two sampling sites within the meandering biotreatment system (stations 7 and 9) exceeded permissible levels established in effluent guidelines. However, the effluent from the final sedimentation pond (Station 12), discharging to Strother Creek outside the company property consistently met the standards in all criteria examined.

3.2. MINTEQ RESULTS

The data that was available through analytical measurements from Sampling Stations 10, 11, and 12 were used in the MINTEQ input file. The model determined different types of metal species that would form under the existing water quality

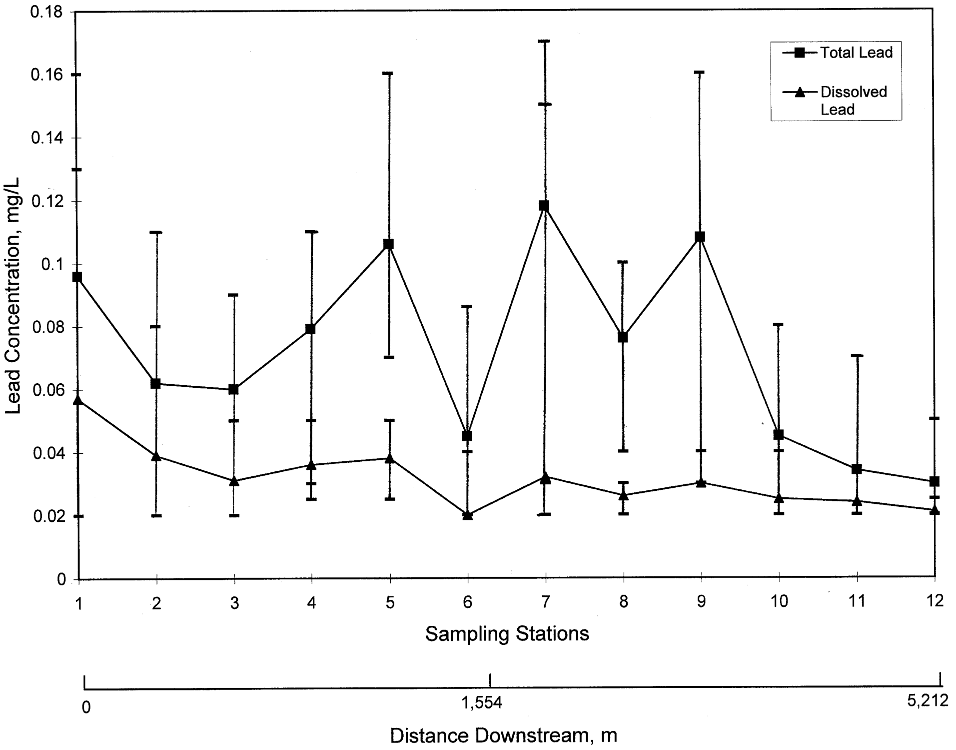


Figure 6d. Unfiltered and filtered lead concentrations in biotreatment meanders.

characteristics. These stations included the locations before and after the final sedimentation pond and the sampling location in the receiving stream Strother Creek, which is outside of the company property. Table IV exhibits the available data that was used as an input to the model. Tables V and VI show the different chemical species that MINTEQ predicted for both lead and zinc.

The model predicted that the major species of dissolved lead that would form in the biotreatment system was aqueous lead carbonate (66 to 85%) and other major species included ionic lead and lead hydroxide (Table V). Literature reports also indicated lead carbonate and lead hydroxy carbonate as the predominant species of lead within the pH ranges of 6.0 to 9.7 (Richard and Nriagu, 1978). The metals data and MINTEQ results also suggest that the complexation of the ion is primarily dependent upon the type and concentration of the anionic species in solution as well as on the existing pH values. Previous acute toxicity studies conducted with lead salts in moderately hard stream water also showed no acute toxicity to fathead minnows most probably due to the high alkaline conditions that induced carbonate speciation of lead in the biotreatment system and nearby streams (Erten *et al.*, 1990a). Minute quantities of aqueous lead carbonate ($PbCO_3$) which may exist at

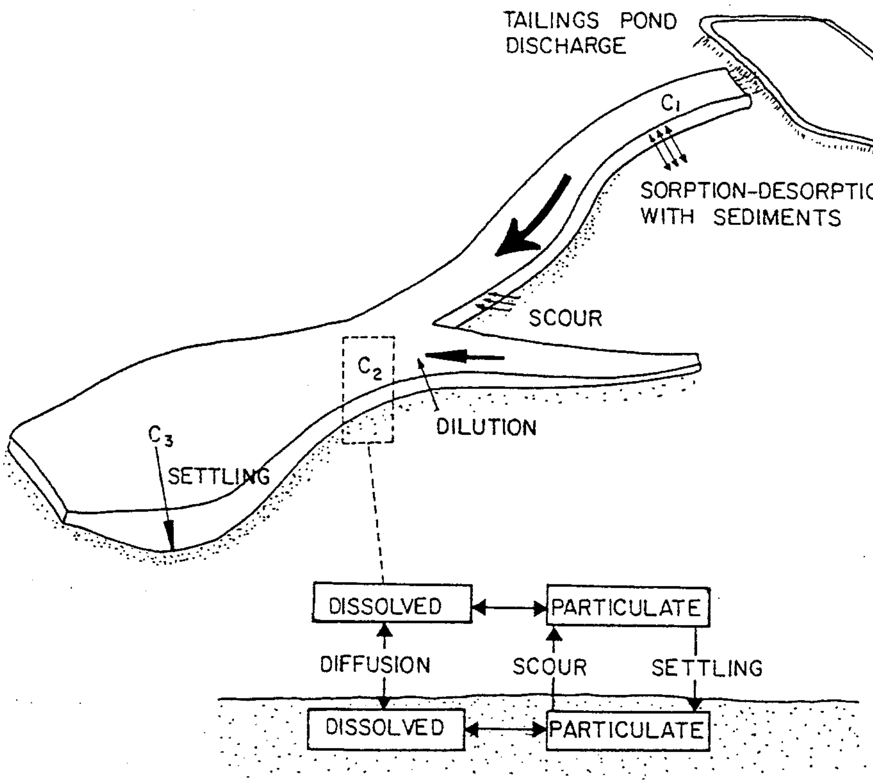


Figure 7. Mechanisms of heavy metal transport in the biotreatment meander system.

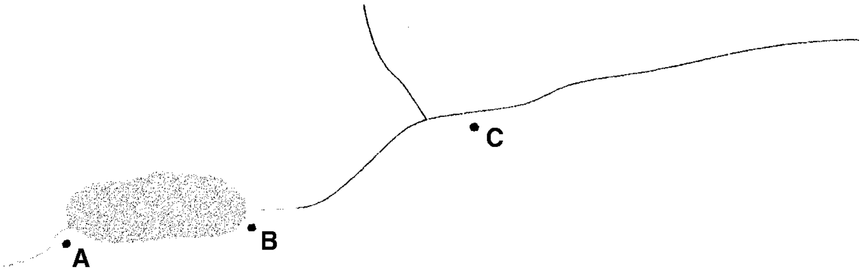
physiological pH do not tend to dissociate into free Pb^{2+}, which is a significant factor in lead bioavailability.

MINTEQ predicted that the major portion of dissolved zinc would exist as zinc carbonate (70 to 80%) complexes under the given water quality parameters. Other zinc species that were predicted include zinc hydroxide (6 to 12.6%) and zinc sulfate (4 to 7.8%) complexes in the biotreatment system (Table VI). At the pH levels of the biotreatment system, the stability diagrams also show that the predominant form of zinc would exist as carbonate and hydroxide species which concur with the model predictions (Erten *et al.*, 1990).

Association of lead and zinc with OH^-, HCO_3^-, and CO_3^- have been determined at high and low pH levels (Stumm and Bilinski 1973; Bilinski *et al.*, 1976). In fresh water, bicarbonate and sulfate complexes were found to predominate below pH 6.5. At pH greater than 6.5, complexes allowable were those of carbonates, bicarbonates, and hydroxides. At the pH values reported in the treatment system (pH 8.2), the carbonate and hydroxide species were the predominant forms of lead and zinc expected in the biotreatment system. Both heavy metal data and MINTEQ results demonstrated that the conditions under which lead and zinc were likely to be removed may be due to complexation, precipitation/coprecipitation, entrapment

TABLE IV

Available data used as input to MINTEQA2



A		B		C	
Temp	= 16 °C	Temp	= 17 °C	Temp	= 20 °C
pH	= 8.1	pH	= 8.2	pH	= 8.2
Ca^{2+}	= 43 mg L^{-1}	Ca^{2+}	= 39 mg L^{-1}	Ca^{2+}	= 36 mg L^{-1}
Mg^{2+}	= 25 mg L^{-1}	Mg^{2+}	= 24 mg L^{-1}	Mg^{2+}	= 22 mg L^{-1}
Alk.	= 150 mg L^{-1}	Alk.	= 145 mg L^{-1}	Alk.	= 128 mg L^{-1}
SO_4^{2-}	= 115 mg L^{-1}	SO_4^{2-}	= 115 mg L^{-1}	SO_4^{2-}	= 77 mg L^{-1}
NO_3^-	= 1.05 mg L^{-1}	NO_3^-	= 0.64 mg L^{-1}	NO_3^-	= 1.03 mg L^{-1}
Ion. Str.	= 0.007	Ion. Str.	= 0.008	Ion. Str.	= 0.007
Pb^{2+}	= 0.049 mg L^{-1}	Pb^{2+}	= 0.028 mg L^{-1}	Pb^{2+}	= 0.020 mg L^{-1}
Zn^{2+}	= 0.145 mg L^{-1}	Zn^{2+}	= 0.083 mg L^{-1}	Zn^{2+}	= 0.047 mg L^{-1}

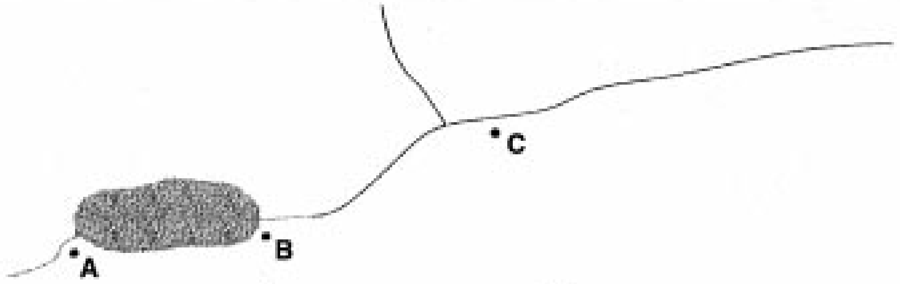
of the particulate metals within densely growing aquatic vegetation, or adsorption of soluble metals within the sediments.

4. Summary and Conclusions

The meandering biotreatment system that had been in operation at the Doe Run Buick Mine-Mill Complex since 1970 continues to provide adequate removal of the combined lead and zinc mine-mill wastewater produced at this industrial site. This low cost, low maintenance system routinely produces a final effluent which meets or surpasses the stringent guidelines established by state and federal regulatory agencies. It achieves this through application of biological and physical processes which efffectively trap, bind and retain heavy metal-containing particulate matter as well as other potential pollutants. The release of lead and zinc mine-mill related

TABLE V

MINTEQA2 model predictions for lead species



A		B		C	
Total Pb	$= 2 \times 10^{-7}$ M	Total Pb	$= 2 \times 10^{-7}$ M	Total Pb[a]	$= 1.1 \times 10^{-7}$ M
(Dissolved Pb = 100%)		(Dissolved Pb = 100%)		(Dissolved Pb = 100%)	
Pb^{2+}	= 16.9%	Pb^{2+}	= 5.6%	Pb^{2+}	= 12%
$PbOH^-$	= 10.1%	$PbOH^-$	= 6.5%		
$PbSO_4AQ$	= 4.8%	$PbSO_4AQ$	= 1.5%	$PbSO_4AQ$	= 2.3%
$PbCO_3AQ$	= 66.2%	$PbCO_3AQ$	= 84.8%	$PbCO_3AQ$	= 75.0%
$PbHCO_3^-$	= 1.7%	$PbHCO_3^-$	= 1.7%	$PbHCO_3^-$	= 1.5%

[a] 1.9:1 dilution.

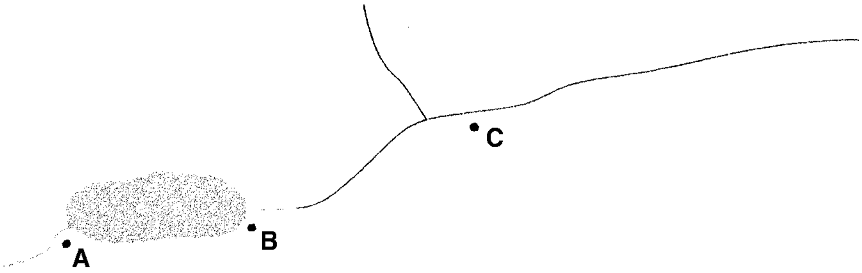
pollutants from the primary tailings pond is retained on the company property through employment of this biological treatment system before discharging into area streams. Overall, future biotreatment schemes offer additional versatility and economy to wastewater treatment with biological systems.

The high pH and alkalinity of regional ground and surface waters assure limited solubility and lowered toxicity of lead and zinc, the principal metallic industrial wastes of this industrial complex, by forming carbonate species. This was supported by literature as well as MINTEQ predictions.

Revised guidelines recently proposed by the USEPA and Missouri Department of Natural Resources require Whole Effluent Toxicity (WET) Tests using the arthropod *Ceriodaphnia dubia*. Even through these new guidelines are not actually enforced at the present time, recent studies (unpublished data) have shown that, due to the extreme sensitivity of the test organisms to dissolved zinc at very low concentrations, Doe Run Buick mine-mill complex may have difficulty in passing the WET test with dissolved zinc levels observed in the biotreatment meanders. The company recently installed a toedam at the base of the first tailings dam at the

TABLE VI

MINTEQA2 model predictions for zinc species



A		B		C	
Total Zn	$= 2 \times 10^{-6}$ M	Total Zn	$= 2 \times 10^{-6}$ M	Total Zn[a]	$= 5 \times 10^{-7}$ M
(Dissolved Zn = 100%)		(Dissolved Zn = 100%)		(Dissolved Zn = 100%)	
Zn^{2+}	= 1.2%	Zn^{2+}	= 3.9%	Zn^{2+}	= 1.8%
$ZnOH^-$	= 1.4%	$ZnOH^-$	= 2.5%	$ZnOH^-$	= 2.4%
$Zn(OH)_2AQ$	= 9.3%	$Zn(OH)_2AQ$	= 12.6%	$Zn(OH)_2AQ$	= 6.0%
$ZnSO_4AQ$	= 3.8%	$ZnSO_4AQ$	= 7.8%	$ZnSO_4AQ$	= 6.4%
$ZnHCO_3^+$	= 1.3%	$ZnHCO_3^+$	= 2.2%	$ZnHCO_3^+$	= 1.6%
$ZnCO_3AQ$	= 82.9%	$ZnCO_3AQ$	= 70.4%	$ZnCO_3AQ$	= 81.6%

[a] 1.9:1 dilution.

head of the biotreatment meander system to collect zinc rich seepage and pump it back into the first tailings pond. The company stated that this has significantly lowered the observed concentrations of zinc entering the biotreatment meander system, especially during the winter months when zinc concentrations exceeded acceptable numerical limits in a few episodes.

Acknowledgements

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