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Pilot Scale Limestone Bed Treatment of the Seep 1 Waste Rock Drainage

1990 Status Report

February 1998

Minnesota Department of Natural Resources
Division of Minerals

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0. Executive Summary

A pilot-scale bed was constructed in 1988 to assess the effectiveness of limestone for treating the mildly acidic Seep 1 stockpile drainage at the LTV Dunka mine. The cylindrical bed contained 2020 kg of high-calcium limestone (-1/4 inch = -6.4 mm), and was 1.3 m in diameter and 1.0 m deep. The objectives of this project were to:

1) elevate the pH and alkalinity while reducing the acidity and trace metal concentrations in the Seep 1 drainage;
2) describe the variation of treatment efficiency in terms of pH elevation and trace metal removal with the volume of drainage treated; and,
3) describe the variation of treatment efficiency as a function of detention time, or equivalently, flow rate.

In addition, the rate of alkalinity release (limestone dissolution) was quantified for extrapolation of results to other limestone bed treatment systems. This report presents data from May 5 to July 3, 1990. The bed received 3600 cubic meters of flow, at rates of 0.276 to 1.356 L/s, averaging 0.73 L/s or about 45 bed volumes per day. The bed was 100% efficient in neutralizing acidity in the seepage in 1990 (and throughout the study), raising the mean pH from 5.0 to 6.7 and the mean net alkalinity from -85 to +22 mg $CaCO_3$/L. Trace metal treatment efficiency was considerably lower. Copper concentrations were reduced by almost 68%, and zinc by about 42%, while nickel and cobalt concentrations were reduced by about 13%. Despite this removal, none of the effluent metal concentrations met discharge standards for the site. Treatment efficiencies for acid neutralization and trace metal removal were not influenced by the flow volume treated or the detention time.

The rate of acid neutralization by the Seep 1 limestone bed varied from 17 to 169 mg $CaCO_3$/s, with a mean value of 72 mg $CaCO_3$/s, and increased linearly with flow. Multiplying the average alkalinity release rate (or, equivalently, acid neutralization rate = [effluent alkalinity - influent acidity] x flow) by the 57 days of operation indicated that a limestone mass of 0.35 T was dissolved. Geochemical modeling indicated that a minimum of 0.10 T of limestone dissolved. The release rate was independent of the volume of treatment, indicating that the treatment capacity of the bed was not taxed.

The bed clogged persistently throughout the study and, consequently, the limestone (d < 6.4 mm) was replaced with a coarser-sized limestone July 12, 1990. The larger diameter limestone accepted 800 cubic meters of flow at an average 0.38 L/s from July 12 until August 6, 1990. Although this bed did not overflow, the effluent pH did not reach pH 6.0, the commonly required regulatory minimum. The bed was only able to raise pH from 4.7 to 4.9 and net alkalinity from -88 to -64 mg $CaCO_3$/L. Trace metal removal was very low. No more than 10% of copper, zinc, nickel or cobalt was removed from the drainage. Furthermore, the mean rate of acid neutralization was a nominal 10 mg $CaCO_3$/s. Clearly, the flow rates were far too high to allow an adequate detention time for the coarser limestone particles to improve Seep 1 drainage quality. For the larger particles to be effective, the limestone bed volume must be increased by at least a factor of two to four.

1. Objective

Limestone ($CaCO_3$) is an effective mineral for consuming acid (reactions 1 and 2). Reaction 1 is dominant above pH 6.3, while reaction 2 is dominant below this pH (Drever, 1997).

$$CaCO_3(s) + H^+(aq) = HCO_3^-(aq) + Ca^{2+}(aq) \tag{1}$$

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq) \tag{2}$$

As reaction 2 proceeds, the carbonic acid (H_2CO_3) generated will be converted to water and carbon dioxide, which is released to the atmosphere. At equilibrium with the atmosphere, the aqueous H_2CO_3 concentration represents an acidity of about 1 mg/L as $CaCO_3$.

Laboratory column experiments indicated that alkaline solids increased the pH and alkalinity of Seep 1 drainage, while reducing concentrations of acidity and trace metals (Lapakko and Antonson, 1989a, 1990b). The experiments further indicated that contact time and treatment capacity would be key variables in field treatment bed design. Based on these observations the following objectives were formulated for a pilot scale field study of Seep 1 drainage treatment by a limestone bed.

1) Elevate the pH and alkalinity while reducing the acidity and trace metal concentrations in the Seep 1 drainage.
2) Describe the variation of treatment efficiency of the limestone as a function of the cumulative volume of drainage treated. This may yield the treatment capacity for the limestone under field conditions.
3) Describe the variation of treatment efficiency as a function of detention time under field conditions.

In addition, the rate of alkalinity release (limestone dissolution) was to be quantified for extrapolation of results to other limestone bed treatment systems. This report presents results from May 5 to August 6, 1990. Results from 1988 and 1989 are presented in earlier reports (Lapakko and Antonson, 1989b; 1990a; 1990b).

2. Methods

2.1. Limestone bed

The limestone bed consisting of limestone chips, diameter <6.4 mm, (table 1), was housed in a polyethylene tank (d=132 cm, h=152 cm) that was placed into a steel tank to eliminate damage by freezing soil in the winter months. The bed was located 3.05 m down gradient from the Seep 1 weir at the Dunka mine. At this point the bedrock elevation is lowest and, therefore, allows the maximum bed depth.

2020 kg of limestone was added to form a bed 104 cm deep. This produced a bed volume of 1.4 cubic meters (1400 L) and a bulk density of 1.5 g/cu cm. Assuming a limestone density of 2.7 g/cu cm yields a porosity of 0.45 and a pore volume of 0.63 cubic meters. Laboratory tests on the finer particle size limestone indicated a hydraulic conductivity of 0.96 cm/s (STS Consultants LTD., 1988). The fine limestone bed was replaced by coarse limestone on July 12, 1990. The coarse limestone bed was also 104 cm deep, but the mass of the coarse limestone added was not determined.

At the inception of the study, 1987 flow and drainage quality data were used to estimate hydraulic and chemical loadings to the bed. For the average monthly Seep 1 flow in 1987, the detention times based on the overall bed volume and on the pore volume were 54 minutes and 22 minutes, respectively (Appendix 1). The estimated values for annual flow and acidity load were 4800 BV (5700 cubic meters) and 0.34 T as $CaCO_3$, respectively (Appendix 1).

2.2 Sampling and analysis

Water quality was examined by analyzing grab samples taken from the weir and the limestone bed discharge. Samples were analyzed for specific conductance, pH, alkalinity, and acidity. Selected samples were also analyzed for filtered copper, nickel, cobalt, zinc, iron, calcium, magnesium, and sulfate. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA 720 pH meter was used for pH analysis. Alkalinity and acidity were analyzed using standard techniques for endpoints of 4.5 and 8.3, respectively (AHPA et al., 1975). Metals were analyzed with a Perkin Elmer 603 atomic absorption spectrophotometer. Sulfate was analyzed using the barium sulfate turbidimetric technique (AHPA et al., 1975). Flow was measured by bucket gaging of the outflow and overflow from the bed. Flow was also metered using the recording gage (Stevens Type F, 68) at the Seep 1 weir.

2.3 Limestone dissolution calculations

The quality of effluent from the limestone beds was interpreted using two different models. First, the mass of limestone dissolved from each bed was calculated using a simple mathematical approach with geochemical considerations in conjunction with drainage quality. In this approach, the mass of limestone dissolved was calculated from the rate of alkalinity release and from the mass of calcium released. The rate of alkalinity release, in mg $CaCO_3$/s, multiplied by the total time of operation yielded the mass of alkalinity released from the bed due to limestone dissolution. Alternatively, the difference between the influent and effluent net alkalinities (in mg $CaCO_3$/L) multiplied by the cumulative effluent volume can be used to calculate the mass of alkalinity released due to limestone dissolution. Similarly, the difference between the influent and effluent cumulative calcium masses, in kg Ca, can be converted to tons of $CaCO_3$ assuming one mole of calcium was released for every mole of limestone that dissolved.

The second method employed the Geochemist's Workbench computer software (Bethke, 1994). Equilibrium effluent quality was modeled as a function of the mass of limestone dissolved. Flow weighted mean concentrations from 1990 were used to simulate Seep 1 drainage influent into the fine limestone bed. The mass of limestone used to represent the treatment bed in the model was calculated using the observed rate of alkalinity release for 1990. This mass was adjusted to reflect the model default setting of 1 kg of reactant, in this case, 1 kg of Seep 1 drainage.

3. Results and Discussion

3.1. Fine limestone treatment bed

3.1.1. Flow

The fine (-6.4 mm) limestone chips were retained in the bed from May 5 until July 3, 1990. Bucket gagings of the bed discharge indicated the flow through the bed ranged from 0.276 to 1.356 L/s (19 to 42 BV/d), with an average of 0.73 L/s, or about 45 BV/d. See Appendix 2 for detailed flow data. This represents detention times (t_d = V/Q = (1400 L/Q) min/ 60 s) of about 17 minutes to 85 minutes, with an average of 32 minutes. The average detention time was shorter than those in 1988 and 1989 (111 and 57, respectively).

Total flow through the bed over the 57 days was approximately 3600 cubic meters (3,600,000 L, 2600 BV, table 2). The total Seep 1 flow volume was estimated as 5300 cubic meters (Appendix 5); thus, about 1700 cubic meters exited the tank as overflow prior to contact with the limestone. The bed overflowed almost immediately after operation began in 1990. Twice, the water was pumped out of the bed through the central standpipe, in an attempt to eliminate solids which might have been plugging the bed. Nonetheless overflow recurred (see timeline, Appendix 3), as was the case in 1988 and 1989.

Several factors could contribute to plugging the bed, and evidence exists for the first two possibilities. First, solids could enter the bed with the inflow from Seep 1. The presence of such solids was indicated by observation of solids entrained in the Mirafi on top of the bed. It is possible that the Mirafi was not entirely effective and some solids passed through or around the mesh. A second source of fine solids is the limestone itself. Two percent of the 2020 kg limestone in the bed, was less than 1.7 mm in diameter (table 1). This represents about 40 kg of relatively fine material.

A third potential source of fines is precipitates which formed as a result of the contact between the drainage and the limestone. The primary precipitates would most likely be calcium sulfate and aluminum hydroxide (gibbsite), with some copper carbonate/hydroxides and iron oxyhydroxides. Sulfate concentrations decreased slightly after passing through the bed, which would be expected with calcium sulfate precipitation. However, this decrease was small and within the range of analytical error. Therefore, the contribution of fine calcium sulfate particles to plugging cannot be quantitatively verified. Furthermore, modeling results predicted that the drainage would remain undersaturated with respect to calcium sulfate minerals (gypsum, anhydrite, and bassanite). However, the model did predict gibbsite precipitation as a result of Seep 1 drainage reacting with the limestone. Fourth, the evolution of carbon dioxide gas may have contributed to the plugging. The gas is a product of the reaction of limestone and acid. Gas evolved may become trapped in the pores of the limestone bed and inhibit subsequent flow.

3.1.2. Water quality

Acid Neutralization

The bed of fine limestone particles elevated the pH, calcium concentrations, and net alkalinity of the acidic Seep 1 influent during the two months of operation in 1990 (see Appendix 2 for detailed water quality data). Influent pH ranged from 4.6 to 5.2 as compared to an effluent pH range of 6.4 to 7.1 (figure 1). The mean pH was raised from 5.0 to 6.7. Flow weighted mean calcium concentrations increased from 123 to 149 mg/L as the flow passed through the bed. Similarly, the mean net alkalinity for the seepage was raised from -85 to +22 mg $CaCO_3$/L (net alkalinity = alkalinity - acidity) due to contact with the limestone (figure 2). The range of effluent net alkalinity was -36 to 45 mg $CaCO_3$/L.

Two measurements of the effluent net alkalinity were considerably lower (-36 and -18 mg $CaCO_3$/L) compared to the range (0 to 45 mg $CaCO_3$/L) of the remaining values. These two values may be erroneous for two reasons. First, both of the alkalinity and acidity values are inconsistent with samples taken prior to and after these two measurements. In fact, the alkalinity data are more consistent with the acidity data from other samples and vice versa, implying a possible transposition of the data. Second, the flow rate through the bed had reached a minimum at this time. In general, as flow decreases, treatment (in this case, effluent net alkalinity) should improve. However, lower flow rates may have temporarily increased dissolved CO_2 (present as H_2CO_3) within the bed, resulting in elevated acidity. With the exception of the two anomalous net alkalinity values, the bed was 100% efficient in removing acidity.

The fairly constant effluent pH and net alkalinity suggest that the treatment efficiency was not highly dependent on the volume of flow treated or the detention time. Acid neutralization by the bed in 1990 was similar to the neutralization observed in 1988 and 1989. Throughout the study pH was elevated above pH 6.0, and net alkalinity to values near or above zero. Although effluent pH and alkalinity decreased over the course of the study, this was also the case for influent values of these parameters (table 3). The rate of alkalinity release increased over the course of the study. This was probably influenced by both the pH decrease (limestone dissolving more rapidly at low pH) and the increase in flow through the bed (see equation 4). Overall, there was no apparent substantial difference in treatment by the limestone over the course of the study.

Metals Removal

The flow weighted mean influent concentrations of filtered copper, nickel, cobalt, and zinc were 1.01, 14.3, 1.28, and 2.73 mg/L as compared to mean effluent concentrations of 0.33, 12.6, 1.12, and 1.66 mg/L, respectively. None of the metals met discharge standards for the site (table 4). The treatment efficiency was highest for copper, 68% of which was removed from the flow. The percent of zinc removed was at 42%. Removals for the remaining two trace metals were both about 13%. The trace metal removal was the result of pH elevation, and the greater degree of copper removal reflects a greater pH dependence of copper solubility for the range over which pH was elevated.

Influent iron concentrations averaged about 0.14 mg/L, 87% of which was removed as flow passed through the bed. Iron concentrations are highly pH dependent. The Seep 1 drainage pH was lower in 1989 and 1990 than in 1988 and the iron concentrations increased in response. Despite the increased influent concentrations, the bed was effective in reducing the effluent level to 0.02 mg/L in 1990. During the 1989 field season, iron removal was observed as rust stains on some of the limestone in the bed (Lapakko and Antonson, 1990a). This staining was limited to a fairly small fraction, and estimated as less than five percent of the particles observed in the top 0.5 m of the bed.

Flow weighted mean calcium concentrations increased from 123 to 149 mg/L as the flow passed through the bed. This was a reflection of limestone dissolution, as was the increase in net alkalinity (equations 1 and 2). There was little change in the concentrations of magnesium and sulfate. The slight apparent decrease in sulfate may have been due to calcium sulfate precipitation, however, this small change (less than 1%) was beyond the limits of analytical resolution.

Trace metal removal was similar throughout the study, showing some improvement over time (table 4). More copper, zinc, and iron appeared to be removed by the bed over time. The bed was unable to effectively remove iron in 1988. There is no apparent reason for the lower removal in the first year. No significant differences were observed for nickel, cobalt, calcium, magnesium or sulfate.

3.1.3. Rate of acid neutralization

The rate of acid neutralization, produced by limestone dissolution, was calculated as the difference between effluent and influent net alkalinity multiplied by the rate of flow:

$$dNalk/dt = ([Nalk]_{eff} - [Nalk]_{in})*Q \qquad (3)$$

where, dNalk/dt = rate of alkalinity release (mg $CaCO_3$/s), [Nalk] = net alkalinity of effluent or influent (mg/L), and Q = flow (L/s). The rate of alkalinity release varied from 17 to 169 mg $CaCO_3$/s, with a mean value of 72 mg $CaCO_3$/s.

To determine the dependence of the alkalinity release rate on cumulative volume of drainage treated and flow, linear regression analyses were conducted. The volume of flow treated was 3600 cubic meters or 2600 BV. There was little correlation between the release rate and cumulative flow volume (r^2=0.202). This indicates that over the 57 days of operation, treatment at the end of the season was not significantly different than at the beginning of the season (figure 3). This suggests that the treatment capacity of the bed was not greatly taxed.

The rate of alkalinity release was dependent on the flow rate, increasing as flow increased (figure 4). The two data points of anomalous effluent alkalinity were included in this analysis. The relationship was defined by the linear equation:

$$dNalk/dt = 133.7*Q - 20.87 \quad (r^2 = 0.86, n = 10) \tag{4}$$

This equation implies that for an average flow of 0.73 L/s, 77 mg of alkalinity was released to every liter of flow. This is fairly consistent with the observed difference of 95 mg $CaCO_3$/L net alkalinity between the mean influent and effluent concentrations. Furthermore, in conjunction with the fairly constant effluent pH and net alkalinity, this indicates the limestone reacted relatively rapidly with the influent water to produce the concentration ranges observed in the effluent. That is, the longer contact times at slower flows observed did not yield substantial additional reaction. Clogging of the bed may have decreased alkalinity release rate by eliminating flow through portions of the bed, but this hypothesis is difficult to evaluate.

3.1.4. Mass of limestone dissolved

The mass of limestone dissolved was calculated using a simple mathematical approach and by employing the Geochemist's Workbench (Bethke, 1994) computer software. Using a mathematical approach and multiplying the average net alkalinity release rate by the 57 days of operation indicated that a limestone mass of 0.35 T was dissolved. If the anomalous effluent net alkalinity values (see second paragraph under Acid Neutralization) are ignored, 0.41 T of limestone was dissolved. This calculation can also be based on cumulative calcium mass release (equation 5), which resulted in only 0.23 T of dissolved limestone.

$$\Delta CaCO_3 = (Ca_{eff} - Ca_{in}) \times Q \times \Delta t \tag{5}$$

For the second method, the amount of limestone that would be dissolved in the drainage was assumed to be 0.35 T as calculated from the drainage quality data. However, this mass was scaled down to 97 mg $CaCO_3$ to match the model default setting of 1 kg of water reactant ([1 kg/3,600,000 kg total volume] x 0.35 T $CaCO_3$ x 10^9 mg/T).

The model predicted that after 1 kg of Seep 1 drainage reacted with 97 mg of $CaCO_3$, the pH of the effluent would be 7.53, which was almost a full unit higher than the observed average effluent pH of 6.7. Based on the model, the pH would reach the observed effluent pH when 15 to 20% (approximately 0.10 T) of the limestone had dissolved. However, these results assume that no other variables affect the system, and it is not indicative of what actually occurs in the field. The simulated value of 0.10 T of limestone dissolved accounts only for neutralization of carbonate acidity. Therefore, it represents a lower limit to the amount of limestone dissolution required to achieve the observed neutralization.

The predicted mass of limestone dissolved (0.10 T) probably underestimated the amount of limestone dissolution required to achieve the observed effluent pH. The model calculated values for the influent and effluent acidity, alkalinity, and net alkalinity, and these values deviated from those observed for the limestone bed. The model predicted that the influent acidity would be approximately 70 mg $CaCO_3$/kg lower than the measured acidity, probably as a result of incomplete metals analyses used as input for the model or the presence of humic acids in the Seep 1 drainage. Furthermore, the modeled effluent alkalinity was 13 mg $CaCO_3$/kg lower than the measured alkalinity. This may have been due to the presence of organic matter in the drainage that could not be accounted for by the model. Previous data suggest that dissolved organic carbon in the Seep 1 drainage could be in the range of 12 to 27 mg/L, which may contribute to the observed alkalinity in the effluent.

3.2. Coarse limestone treatment bed

3.2.1. Flow

The fine limestone chips were replaced with coarser (-38.1 mm) limestone chips on July 12, 1990, in an attempt to prevent the bed from overflowing. This bed was operational until August 6, 1990. Flow through the coarse limestone bed ranged from 0.3 to 0.568 L/s, averaging 0.38 L/s or about 24 BV/d. These flows correspond to detention times ranging from 42 to 80 minutes and averaging 61 minutes (table 2). This detention time is roughly twice as long as the average detention time observed for the fine limestone bed in 1989 and 1990. No clogging occurred with the larger limestone particles.

3.2.2. Water quality

The coarse limestone did not raise the drainage pH or net alkalinity appreciably. The influent pH ranged from 4.4 to 4.9, while the effluent pH was slightly higher range of 4.8 to 5.1 (figure 5). Similarly, the mean values for the influent and effluent net alkalinity were -88 and -64 mg $CaCO_3$/L, respectively (figure 6). Thus, the treatment efficiency for acidity removal was only about 25 percent ([-87 - (-65)] 100/-87).

Influent flow weighted mean concentrations for copper, nickel, cobalt, zinc, and iron were similar to those observed for the finer particles. However, no more than 10% of any metal was removed from the drainage (table 4). In fact, any difference between influent and effluent concentrations was often at the boundary of analytical resolution. The flow weighted mean concentration of calcium only rose from 274 to 286 mg/L as the drainage passed through the bed. This indicates that very little of the limestone dissolved, and consequently, very little alkalinity released. This is consistent with the slight pH increase observed in the effluent from the coarse limestone bed. Both magnesium and sulfate concentrations appeared to increase slightly as flow passed through the bed. Whereas it is possible that some magnesium was released from the larger limestone, the difference between influent and effluent sulfate was beyond the limits of analytical resolution.

3.2.3. Rate of acid neutralization

The rate of alkalinity release was quantified as described above. The maximum rate was only 17 mg $CaCO_3$/s ranging all the way down to 5 mg $CaCO_3$/s, averaging one seventh of the values observed for the fine particles in 1990. Furthermore, there was little correlation between the alkalinity release rate and cumulative flow volume ($r^2 = 0.378$, figure 7). The lack of correlation with flow volume indicates the treatment capacity of the coarse limestone particles had not been reached. A slight dependence of alkalinity release rate on flow rate (r^2=0.682) was observed (figure 8). Thus, for an average flow rate of 0.38 L/s, 9 mg of alkalinity was released to every liter of flow.

$$dNalk/dt = 39.4*Q - 6.08 \qquad (r^2 = 0.68, n = 7) \qquad (6)$$

The poor treatment by the coarse limestone can be attributed to inadequate detention time to allow sufficient dissolution of the coarse particles. Dissolution rate is directly proportional to surface area of the particles. The calculated surface area of the fine limestone particles was 8 cm^2/g, or seven times larger than the surface area of the coarse limestone (1.15 cm^2/g). The 7-fold decrease in available limestone surface area had a significant affect on the dissolution rate per unit mass limestone, and consequently, the effectiveness of the bed. In order to allow adequate contact time between the Seep 1 drainage and the larger limestone, a detention time roughly seven times that used previously would be required.

The shortest detention time observed for the fine particles was 18 minutes, and at this detention time the influent pH was elevated to an adequate level. A detention time of (7 x 18 =) 126 minutes would be expected to provide adequate acid neutralization by the coarse particles. The observed detention times for the coarse particles ranged from 42 to 80 minutes. Clearly, the detention times for the coarse limestone bed were not long enough for adequate drainage treatment. In order to increase the detention time for the coarse limestone bed, a larger bed volume is required. Using an average observed flow rate of 0.4 L/s and the detention time calculated above, the volume of the coarse limestone bed must be increased to at least 3024 L for adequate treatment of Seep 1 drainage. However, based on the fact that only 25% of the influent acidity was neutralized, a bed volume four times that presently used would be estimated (4 x 1400 = 5600 L). Additional experimentation would be required to accurately determine the bed volume required for the larger particles.

3.2.4. Mass of limestone dissolved

The mean rate was 10 mg $CaCO_3$/s which indicates that over 24 days of operation, only 0.02 T of limestone was dissolved. The mass of limestone dissolved was the same regardless of whether it was calculated using rate of alkalinity release or cumulative calcium mass release.

4. Summary

The flow through the finer limestone particle bed in 1990 averaged 45 BV/d, which is 1.8 times that in 1989 (table 2), and about nine times greater than the rate used in laboratory tests on Seep 1 drainage (Lapakko and Antonson, 1989a). Despite the elevated flow rate, the bed elevated the drainage pH at least 6.4 and typically above 6.7. The pH elevation was apparently the major cause of the reductions in trace metal concentrations. Concentrations of copper were reduced by about 68% as compared to 48% in 1989. Similarly, zinc was reduced significantly in 1990, 42% instead of 11% observed in 1989. The concentrations of nickel and cobalt were reduced by approximately 13%, which was approximately the same as seen in 1989.

The mean rate of alkalinity release from the Seep 1 bed was 72 mg $CaCO_3$/s, implying that a maximum limestone mass of 0.35 T was dissolved (compared to 0.52 T in 1989). The alkalinity release rate in 1990 was over twice that in 1989. However, the volume of drainage was only about half that in the previous year, resulting in approximately the same amount of limestone dissolution. Geochemical modeling calculated minimum limestone dissolution of 0.10 T in 1990.

The alkalinity release rate was independent of the volume of treatment, indicating that the treatment capacity of the bed was not taxed. The release rate did increase with flow, indicating that for the range of flows observed, the initial reaction of the flow with the limestone was relatively rapid. Although the bed provided acceptable elevation of pH and net alkalinity, as well as some reduction in trace metal concentrations, the observed flow impedance is a problem which must be addressed.

Larger limestone particles were tested, and although no overflow occurred, treatment efficiency decreased below acceptable levels. Their ineffectiveness was most likely due to inadequate detention time. Preliminary estimates indicated the bed volume must be increased by at least a factor of two to four for effective acid neutralization.

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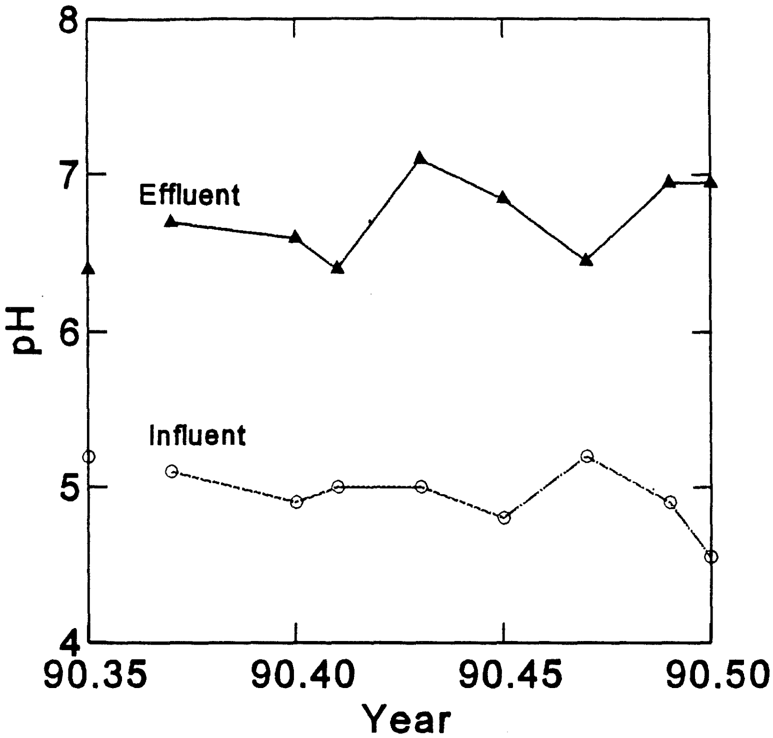


Figure 1. From May 6 to July 3, 1990, the fine limestone bed elevated the pH of the Seep 1 drainage above 6.0, the minimum effluent water quality standard for the site.

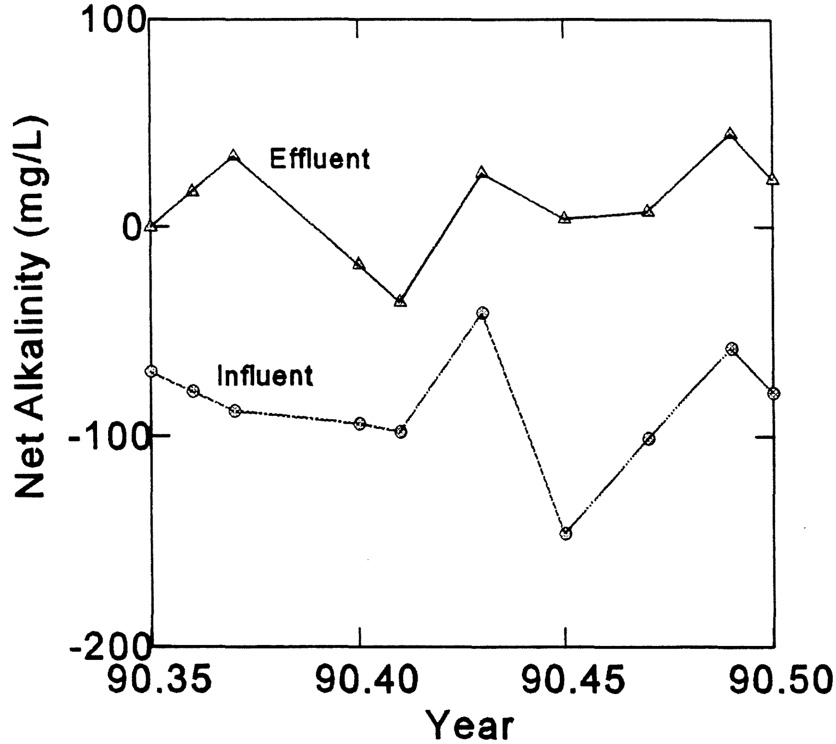


Figure 2. From May 6 to July 3, 1990, the fine limestone bed increased the net alkalinity (as mg $CaCO_3$/L) of Seep 1 drainage to values greater than zero. The two exceptions, which occurred on May 25 and 30, 1990, are assumed to be anomalous (see section 3.1.2, Acid Neutralization).

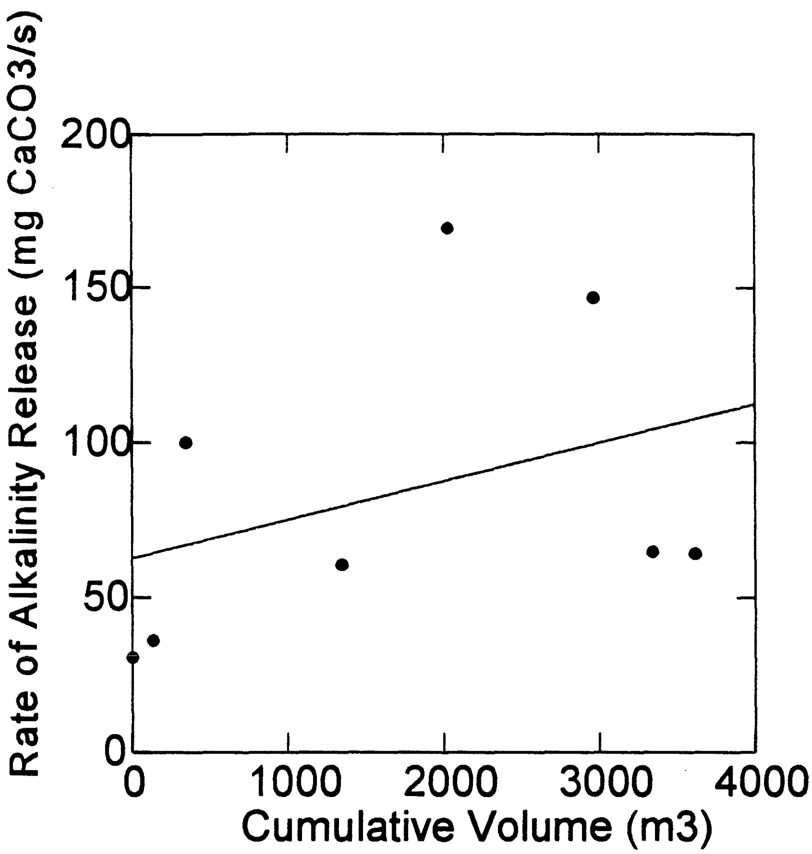


Figure 3. The low dependence (R^2 = 0.131) of the rate of alkalinity release on cumulative volume indicated that the capacity of the fine limestone bed was not taxed from May 5 to July 3, 1990. This plot excludes the two anomalous net alkalinity values (see section 3.2.1, Acid Neutralization).

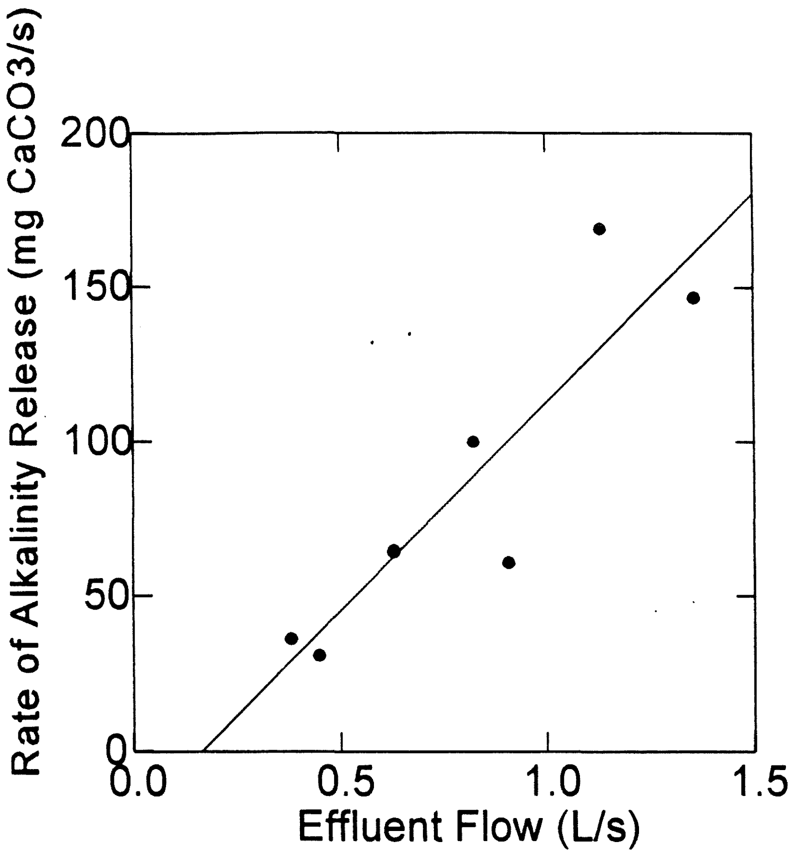


Figure 4. The rate of alkalinity release increased linearly ($R^2 = 0.805$) with increasing flow rate in the fine limestone bed from May 5 to July 3, 1990. This plot excludes the two anomalous net alkalinity values (see section 3.2.1, Acid Neutralization).

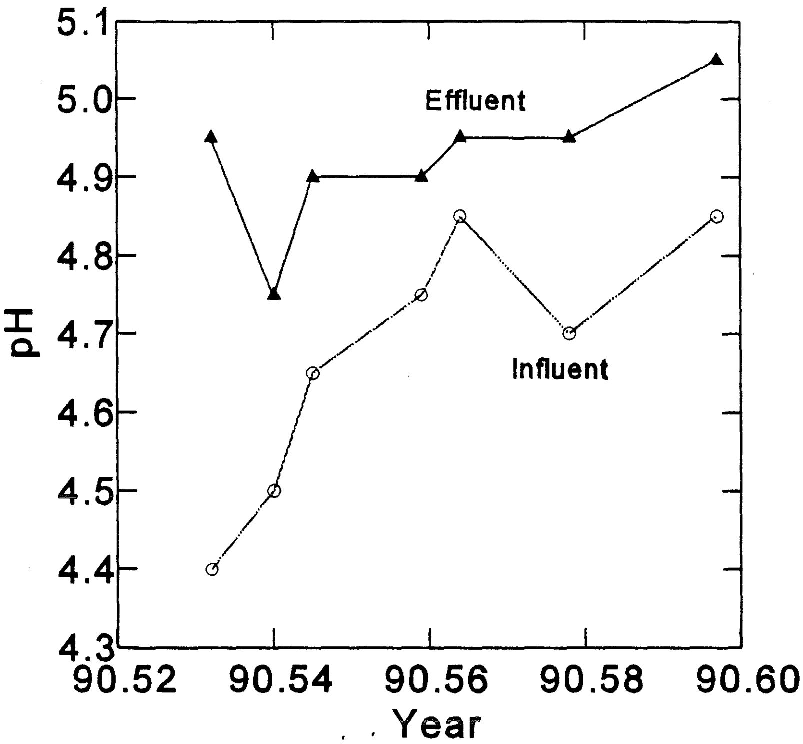


Figure 5. The coarse limestone bed was unable to increase the pH of Seep 1 drainage above 6.0 from July 12 to August 6, 1990.

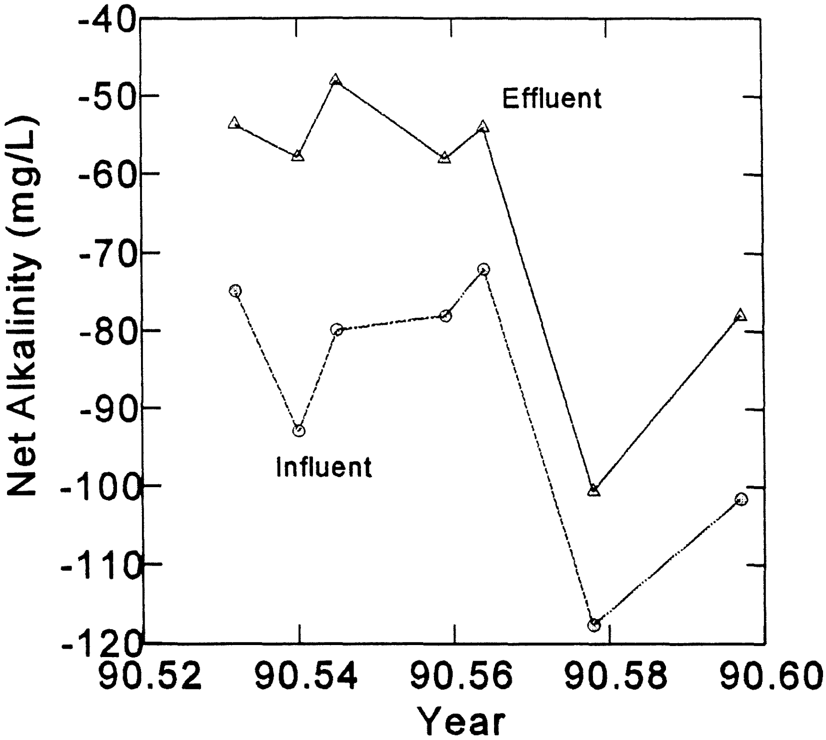


Figure 6. The coarse limestone bed did not increase the net alkalinity (mg $CaCO_3$/L) of Seep 1 drainage to values greater than zero from July 12 to August 6, 1990.

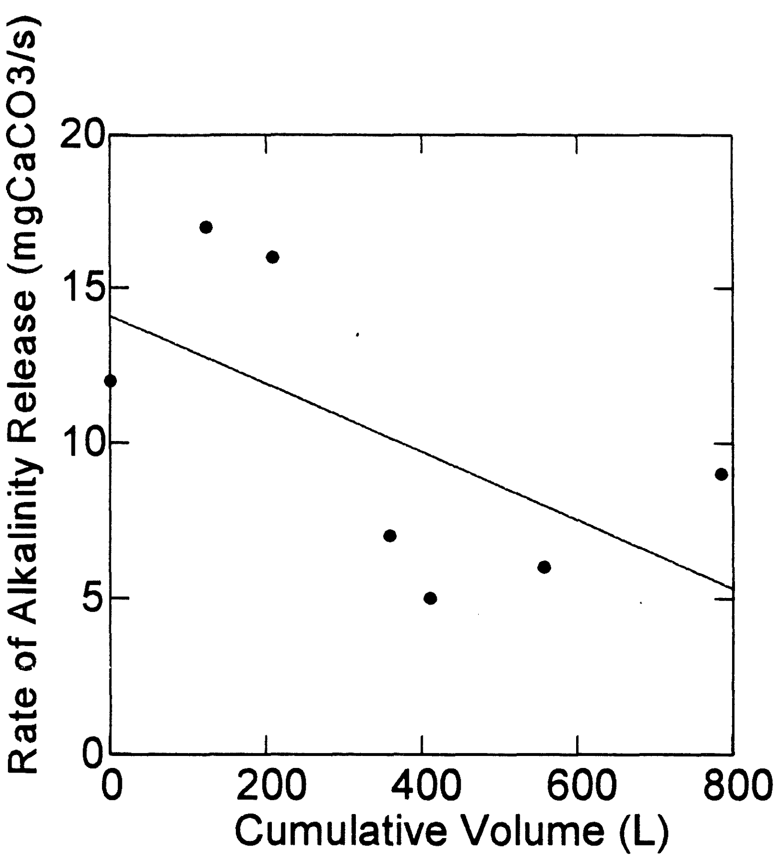


Figure 7. The low dependence (R^2 = 0.378) of the rate of alkalinity release on cumulative volume indicated that the capacity of the coarse limestone bed did not change substantially from July 12 to August 6, 1990.

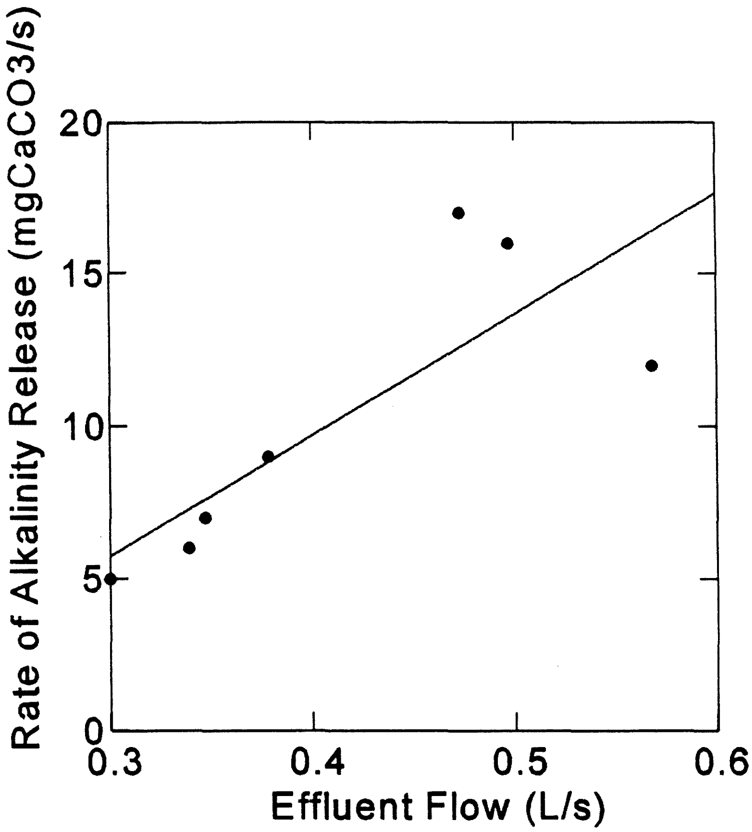


Figure 8. The rate of alkalinity release from the coarse limestone bed increased with effluent flow rate ($R^2 = 0.682$) from July 12 to August 6, 1990.

Table 1. (a) Screen and chemical analysis of fine calcium limestone chips from Hurlbut Calcium Chemicals.

SCREEN ANALYSIS		CHEMICAL ANALYSIS	
Diameter (mm)	% Pass	Component	Weight %
6.4	100	Silica	0.75
3.4	72	Alumina	0.19
1.7	2	$CaCO_3$	97.0
		CaO	54.39
		MgO	0.86

(b) Screen analysis of the large limestone particles conducted by MN DNR, Hibbing laboratory. Limestone obtained from Presque Isle Corp., Alpena, MI.

SCREEN ANALYSIS	
Diameter (mm)	% Pass
38.1	99.2
25.4	75.2
19.1	25.5
12.7	2.5
6.4	0.7

Table 2. Flow data summary

	1988	1989	1990 fine	1990 coarse
Period of operation	26 Sept-28 Oct	23 April-31Oct	5 May-3 July	12 July-6 Aug
Days of operation	32	188	57	24
Q min (L/s)	0.039	0.032	0.276	0.300
Q max (L/s)	0.591	1.514	1.356	0.568
Q avg (L/s)	0.21	0.41	0.73	0.38
t_d min (min.)	40	13	17	41
t_d max (min)	600	600	85	78
t_d avg (min)	111	57	32	61
Effluent V (m^3)	580	6636	3612	785
Effluent V (BV)	410	4740	2580	561
Influent V (m^3)	247[1]	10,000	5335	1316

[1]1988 influent volume was calculated from the sum of effluent and overflow volume which were estimated from effluent flow and overflow rates.

Table 3. Neutralization and treatment efficiency summary

	1988	1989	1990 fine	1990 coarse
Period of operation (days)	32	188	57	24
Average pH in	5.4	5.0	5.0	4.7
Average pH out	7.5	6.9	6.7	4.9
Avg net influent alkalinity (mg $CaCO_3$/L)	-30	-51	-85	-88
Avg net effluent alkalinity (mg $CaCO_3$/L)	38	24	22	-64
Treatment efficiency (%acid neutralized)	100	100	100	25
Rate of alkalinity release (mg $CaCO_3$/s)	14	32	72	10
Total alkalinity release (kg as $CaCO_3$)	39	520	355	21
Ca mass release (kg as $CaCO_3$)	22	670	226	24

Table 4. Chemical input and removal summary

	Limit[2] mg/L	1988			1989			1990 fine			1990 coarse		
		C_i (mg/L)[1]	C_e (mg/L)[1]	Reduction (%)	C_i (mg/L)[1]	C_e (mg/L)[1]	Reduction (%)	C_i (mg/L)[1]	C_e (mg/L)[1]	Reduction (%)	C_i (mg/L)[1]	C_e (mg/L)[1]	Reduction (%)
Cu	0.023	0.32	0.22	34	0.97	0.50	48	1.01	0.33	68	1.76	1.58	10
Ni	0.213	14	13	8	15.6	14.2	9	14.3	12.6	13	20.2	19.5	4
Co	0.050	0.9	0.8	11	1.2	1.1	10	1.29	1.12	13	1.56	1.54	1
Zn	0.343	1.8	1.5	14	2.8	2.5	11	2.73	1.66	42	4.65	4.51	3
Fe	1.0	0.1	0.1	0	0.14	0.035	77	0.17	0.02	87	0.10	0.12	-19
Ca	NR	174	190	-9	241	282	-17	123	149	-22	274	286	-4
Mg	NR	185	188	-2	181	184	-1.7	153	152	1	223	240	-8
SO_4	NR	1170	1220	-4	1160	1140	1.7	1107	1059	5	1684	1691	-0

[1]Flow weighted mean concentration for influent and effluent
[2]Monthly average discharge limitation from LTV 1991 NPDES permit MN0042579, NR=not regulated.

APPENDIX 1

Features of Treatment Bed and Seep 1 Drainage

A1.1. Flow from seep 1 during 1987 and associated detention times
A1.2. Water quality at seep 1 in 1987.
A1.3. Additional features of treatment bed and seep 1 drainage

Table A1.1. Flow from Seep 1 during 1987 and associated detention times.

	Flow			Detention Time	
	cfs	gpm	L/s	t_d[1]	t_{dp}[2]
Assumed maximum	0.22	100	6.3	3.2	1.3
1987 maximum	0.15	68	4.3	4.7	1.9
1987 average	0.013	5.7	0.36	54	22
1987 monthly minimum[3]	0.0049	2.2	0.14	143	57

[1]Calculated using entire bed volume
[2]Calculated using pore volume
[3]October 1987 flow

Table A1.2. Water quality at Seep 1 in 1987. Summary data for 8 samples.

	Minimum	Median	Maximum
pH	5.05	5.5	6.35
Cu (mg/L)	0.10	0.38	1.0
Ni	3.1	13.5	26
Co	0.3	1.25	1.9
Zn	0.38	1.0	2.0
SO_4	790	1490	2175
SC (uS)	1462	2288	2550

Table A1.3. Additional features of treatment bed and Seep 1 drainage.

Bed volume:

Using actual bed dimensions

$BV = 3.14\ [(26/12)^2 - (2.125/12)^2]ft^2 \times 3.41ft \times 0.3048m^3/ft^3$
$= 1.4\ m^3$

Using a cross sectional area of 13 ft^2

$BV = 3.41 \times 13 = 44.36\ ft^3 = 322\ gal = 1.26\ m^3$

Estimated annual flow:

Using the average 1987 flow of 0.013 ft^3/s

$V = (0.013ft^3/s \times 86400s/d \times 180d)/42.25ft^3 = 4800\ BV$
$= 12{,}000$ pore volumes
$= 200{,}000\ ft^3$
$= 5700\ m^3$

The average of estimated and measured annual flow volume from 1978 through 1987 was 10,000 m^3.

Total solids required:

$M = 1.51t/m^3 \times 3.14 \times 1.4m^3$
$= 2.2$ metric tons

Estimated annual acidity (assuming 60 mg/L acidity):

$ACY = 60g/m^3 \times 5700m^3 = 342{,}000\ g/yr = 0.34\ T/yr$

$ACY = 60g/m^3 \times 10{,}000m^3 = 0.60\ T/yr$

APPENDIX 2

Treatment Bed Influent and Effluent Water Quality and Flow: 1990

Table A2.1. Influent water quality and flow data for the Seep 1 limestone bed (1989-90).

Date	Gage Height (m)	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
4 26 89	1.110	0.489	610.0	5.75	6.6	23.0	-16.4	0.08	1.53	0.21	0.44	0.10	40.0	48.0	276.0	1021
4 27 89	1.120	0.516	590.0	5.80	7.2	20.0	-12.8	0.06	1.54	0.21	0.43	0.10	52.0	50.0	310.0	1023
4 28 89	1.150	0.457	600.0	5.83	7.7	24.0	-16.3	.	.	.	.	.	.	.	.	
5 1 89	1.220	0.600	650.0	5.80	8.3	14.0	-5.7	0.04	1.65	0.21	0.39	0.00	54.0	56.0	310.0	1025
5 2 89	1.190	0.457	650.0	5.80	7.7	21.0	-13.3	.	.	.	.	.	.	.	.	
5 4 89	1.200	0.376	690.0	5.80	4.4	17.0	-12.6	0.04	1.98	0.22	0.55	0.00	58.0	56.0	326.0	1027
5 5 89	1.290	1.170	610.0	5.85	1.5	23.0	-21.5	.	.	.	.	.	.	.	.	
5 8 89	1.180	0.315	800.0	5.85	10.0	23.0	-13.0	0.06	1.80	0.19	0.45	0.00	68.0	66.0	370.0	1029
5 9 89	1.180	0.363	775.0	5.85	8.8	29.0	-20.2	.	.	.	.	.	.	.	.	
5 10 89	1.180	0.363	825.0	5.71	7.7	29.0	-21.3	.	.	.	.	.	.	.	.	
5 11 89	1.180	0.309	800.0	5.85	11.0	9.8	1.2	0.06	1.95	0.22	0.47	0.00	72.0	70.0	390.0	1031
5 12 89	1.180	0.284	820.0	5.85	8.8	16.0	-7.2	.	.	.	.	.	.	.	.	
5 15 89	1.200	0.363	1190.0	5.88	11.0	28.0	-17.0	0.07	3.57	0.33	0.66	0.00	112.0	98.0	775.0	1033
5 16 89	1.200	0.435	1490.0	5.74	11.0	31.0	-20.0	.	.	.	.	.	.	.	.	
5 17 89	1.220	0.473	1650.0	5.40	6.6	36.0	-29.4	.	.	.	.	.	.	.	.	
5 18 89	1.240	0.599	1720.0	5.15	4.4	41.0	-36.6	0.74	20.40	1.74	2.75	0.00	170.0	160.0	1075.0	1035
5 19 89	1.240	0.599	1650.0	5.05	6.6	59.0	-52.4	.	.	.	.	.	.	.	.	
5 22 89	1.220	0.457	1820.0	4.93	4.4	66.0	-61.6	1.20	21.60	1.84	3.31	0.00	192.0	168.0	1275.0	1037
5 24 89	1.210	0.930	2000.0	4.96	5.7	93.0	-87.3	.	.	.	.	.	.	.	.	
6 5 89	1.220	0.852	2400.0	4.85	3.3	107.0	-103.7	1.77	36.00	2.04	4.13	0.10	196.0	266.0	1630.0	1039
6 7 89	1.250	0.820	2290.0	4.80	4.4	104.0	-99.6	.	.	.	.	.	.	.	.	
6 9 89	1.220	0.489	2075.0	4.85	1.1	103.0	-101.9	1.44	31.00	1.66	3.30	0.00	178.0	232.0	1440.0	1041
6 12 89	1.260	0.851	2600.0	4.80	2.6	90.0	-87.4	1.70	37.00	2.00	4.04	0.10	212.0	280.0	1700.0	1043
6 13 89	1.360	1.198	.	.	.	.	.	.	.	.	.	.	.	.	.	
6 16 89	1.260	0.884	.	.	.	.	.	.	.	.	.	.	.	.	.	
6 20 89	1.230	1.136	2250.0	4.75	0.5	108.0	-107.5	1.63	23.60	1.70	3.70	0.11	140.0	242.0	1640.0	1045
6 23 89	1.270	1.073	.	.	.	.	.	.	.	.	.	.	.	.	.	
6 26 89	1.260	0.922	1900.0	4.82	2.2	90.0	-87.8	1.10	17.20	1.21	2.89	0.12	212.0	172.0	1320.0	1047
6 30 89	1.320	1.514	1650.0	4.85	3.3	69.0	-65.7	0.99	14.50	1.02	2.63	0.16	166.0	148.0	1200.0	1049
7 6 89	1.250	1.325	2100.0	4.72	2.4	95.0	-92.6	1.51	20.80	1.45	3.70	0.12	230.0	206.0	1550.0	1051
7 18 89	1.200	0.363	1920.0	4.92	4.4	73.0	-68.6	.	.	.	.	.	.	.	.	
7 21 89	1.190	0.315	2220.0	4.90	3.3	84.0	-80.7	1.32	20.10	1.39	3.65	0.13	236.0	218.0	1880.0	1053
7 24 89	1.180	0.284	2325.0	4.90	5.5	98.0	-92.5	1.33	21.20	1.48	3.83	0.16	252.0	230.0	1700.0	1055
7 26 89	1.180	0.276	.	.	.	.	.	.	.	.	.	.	.	.	.	
7 27 89	1.180	0.284	.	.	.	.	.	.	.	.	.	.	.	.	.	
7 31 89	1.180	0.237	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 1 89	1.180	0.237	2300.0	4.65	2.1	88.0	-85.9	1.42	22.00	1.59	3.94	0.15	256.0	236.0	2050.0	1057
8 3 89	1.310	1.451	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 4 89	1.220	0.520	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 7 89	1.180	0.229	2300.0	4.90	4.2	58.0	-53.8	1.20	19.50	1.78	4.36	0.13	302.0	226.0	1800.0	1059
8 8 89	1.170	0.205	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 9 89	1.170	0.284	2500.0	4.95	4.2	71.0	-66.8	1.48	20.50	1.85	4.68	0.09	324.0	232.0	1870.0	1061

Table A2.1. Influent water quality and flow data for the Seep 1 limestone bed (1989-90), continued.

Date	Gage Height (m)	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
8 14 89	1.180	0.276	2225.0	4.75	3.2	71.0	-67.8	1.20	18.50	1.66	4.17	0.09	314.0	210.0	1700.0	1063
8 15 89	1.180	0.237	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 16 89	1.170	0.189	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 17 89	1.160	0.150	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 18 89	1.160	0.142	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 21 89	1.180	0.221	2050.0	4.90	4.2	69.0	-64.8	1.07	16.70	1.49	3.68	0.08	302.0	200.0	1700.0	1065
8 22 89	1.160	0.071	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 23 89	1.160	0.189	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 24 89	1.160	0.158	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 25 89	1.150	0.158	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 28 89	1.230	1.040	2190.0	4.90	5.9	64.0	-58.1	0.96	15.80	1.39	3.36	0.14	296.0	194.0	1590.0	1067
8 29 89	1.240	0.757	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 30 89	1.200	0.457	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 31 89	1.250	0.773	1625.0	5.20	4.2	39.0	-34.8	0.74	11.60	1.00	2.36	0.11	222.0	144.0	1180.0	1069
9 6 89	1.340	1.293	1600.0	5.00	4.2	51.0	-46.8	0.70	11.50	0.96	2.46	0.11	226.0	144.0	1100.0	1071
9 7 89	1.240	0.568	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 8 89	1.230	0.552	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 12 89	1.230	1.096	1950.0	4.90	4.2	58.0	-53.8	.	.	.	.	.	.	.	.	1073
9 14 89	1.190	0.327	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 18 89	1.180	0.250	2300.0	4.85	4.2	76.0	-71.8	.	.	.	.	.	.	.	.	1075
9 21 89	1.300	1.521	1820.0	5.00	4.2	74.0	-69.8	.	.	.	.	.	.	.	.	
9 22 89	1.260	0.844	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 25 89	1.190	0.579	1975.0	5.00	3.2	54.0	-50.8	.	.	.	.	.	.	.	.	1077
9 27 89	1.180	0.276	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 28 89	1.180	0.264	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 2 89	1.210	0.591	1950.0	5.10	4.2	53.0	-48.8	.	.	.	.	.	.	.	.	1079
10 4 89	1.180	0.379	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 5 89	1.180	0.315	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 6 89	1.190	0.331	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 9 89	1.160	0.221	2000.0	4.95	2.6	54.0	-51.4	.	.	.	.	.	.	.	.	1081
10 11 89	1.170	0.221	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 12 89	1.160	0.189	2000.0	5.25	4.2	41.0	-36.8	.	.	.	.	.	.	.	.	
10 13 89	1.160	0.189	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 16 89	1.160	0.158	2100.0	5.15	4.2	15.0	-10.8	0.72	11.80	0.93	2.48	0.04	360.0	244.0	1470.0	1083
10 17 89	1.150	0.173	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 19 89	1.150	0.158	2110.0	5.15	1.0	48.0	-47.0	0.62	10.80	0.86	2.36	0.03	340.0	234.0	1280.0	1085
10 20 89	1.150	0.158	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 23 89	1.140	0.130	1900.0	4.90	2.1	45.0	-42.9	.	.	.	.	.	.	.	.	1087
10 24 89	1.150	0.118	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 25 89	1.140	0.125	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 26 89	1.140	0.134	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 30 89	1.200	0.363	1900.0	5.10	3.0	28.0	-25.0	0.58	10.20	0.84	2.13	0.06	320.0	220.0	1150.0	1088
10 31 89	1.180	0.260	.	.	.	.	.	.	.	.	.	.	.	.	.	

Table A2.1. Influent water quality and flow data for the Seep 1 limestone bed (1989-90), continued.

Fine Limestone

Date	Gage Height (m)	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
5 7 90	1.320	1.31	1200.0	5.20	3.0	72.0	-69.0	.	.	.	.	.	.	.	.	1090
5 11 90	1.260	0.88	.	.	.	.	.	.	.	.	.	.	.	.	.	
5 14 90	1.300	1.16	1580.0	5.10	3.0	91.0	-88.0	1.02	16.10	1.50	2.64	0.21	114.0	156.0	1180.0	1092
5 25 90	1.220	0.59	2150.0	4.90	3.8	98.0	-94.2	1.21	18.50	1.67	3.50	0.32	156.0	204.0	1420.0	1094
5 30 90	1.210	0.53	2400.0	5.00	2.4	100.0	-97.6	1.40	21.50	1.95	4.32	0.26	188.0	240.0	1630.0	1096
6 6 90	1.300	1.16	1380.0	5.00	2.0	43.0	-41.0	0.82	10.60	0.89	2.17	0.12	114.0	126.0	900.0	1098
6 13 90	.	1.54	2225.0	4.80	2.4	148.0	-145.6	1.78	21.80	1.89	4.49	0.13	194.0	232.0	1670.0	1100
6 21 90	1.360	1.69	1650.0	5.20	4.7	.	.	0.91	10.60	0.85	2.41	0.11	112.0	124.0	900.0	1102
6 28 90	1.270	0.97	2100.0	4.90	4.7	63.0	-58.3	1.26	16.10	1.34	3.75	0.08	194.0	186.0	1380.0	1104
7 3 90	.	1.28	2200.0	4.55	.	84.0	-79.3	1.51	17.20	1.43	4.22	0.12	180.0	184.0	1440.0	1106

Coarse Limestone

Date	Gage Height (m)	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
7 13 90	1.280	1.03	2400.0	4.40	.	76.0	.	1.68	18.68	1.37	4.54	0.11	252.0	202.0	1640.0	1108
7 16 90	1.250	0.80	2650.0	4.50	.	94.0	.	1.76	20.10	1.52	4.75	0.11	277.0	220.0	1670.0	1110
7 18 90	1.260	0.88	2750.0	4.65	1.2	81.0	-79.8	.	.	.	.	.	.	.	.	
7 23 90	1.240	0.73	2580.0	4.75	4.0	82.0	-78.0	1.76	20.20	1.54	4.51	0.07	280.0	222.0	1670.0	1112
7 25 90	1.220	0.59	2775.0	4.85	2.0	74.0	-72.0	1.78	19.60	1.71	4.66	0.11	257.0	239.0	1750.0	1114
7 30 90	.	0.59	2900.0	4.70	2.4	120.0	-117.6	1.90	21.10	1.85	5.00	0.11	263.0	244.0	1830.0	1116
8 6 90	.	0.47	2400.0	4.85	-1.0	102.0	-103.0	1.43	20.30	1.49	3.96	0.14	241.0	218.0	1630.0	1118

Note: pH values are in standard units, specific conductance (S.C.) values are in microsiemens, flow values are in L/s, and all other values are mg/L.

Table A2.2. Effluent water quality and flow data for the Seep 1 limestone bed (1989-90).

Date	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
4 26 89	0.489	600.0	7.4	44.0	6.1	37.9	0.04	0.55	0.08	0.10	<0.01	56.0	40.0	256.0	1020
4 27 89	0.516	625.0	6.9	32.0	7.0	25.0	0.06	1.55	0.21	.	.	.	.	.	1022
4 28 89	0.457	650.0	7.3	35.0	6.1	28.9	.	.	.	.	.	.	.	.	
5 1 89	0.600	690.0	7.0	33.0	7.1	25.9	0.05	1.68	0.20	0.38	<0.01	62.0	54.0	316.0	1024
5 2 89	0.457	675.0	7.3	33.0	6.1	26.9	.	.	.	.	.	.	.	.	
5 4 89	0.376	700.0	7.3	37.0	6.1	30.9	0.04	1.80	0.21	0.34	<0.01	70.0	56.0	320.0	1026
5 5 89	1.170	620.0	6.6	24.0	9.8	14.2	.	.	.	.	.	.	.	.	
5 8 89	0.315	820.0	7.0	39.0	9.8	29.2	0.04	1.87	0.19	0.47	<0.01	80.0	64.0	370.0	1028
5 9 89	0.363	800.0	7.2	42.0	5.5	36.5	.	.	.	.	.	.	.	.	
5 10 89	0.363	800.0	7.1	42.0	6.7	35.3	.	.	.	.	.	.	.	.	
5 11 89	0.309	850.0	7.4	42.0	4.9	37.1	0.03	2.00	0.19	0.49	<0.01	86.0	66.0	390.0	1030
5 12 89	0.284	860.0	7.0	40.0	0.0	40.0	.	.	.	.	.	.	.	.	
5 15 89	0.363	1200.0	7.1	43.0	9.8	33.2	0.05	3.53	0.33	0.64	<0.01	126.0	94.0	725.0	1032
5 16 89	0.435	1500.0	7.1	39.0	12.0	27.0	.	.	.	.	.	.	.	.	
5 17 89	0.473	1620.0	6.7	39.0	17.0	22.0	.	.	.	.	.	.	.	.	
5 18 89	0.599	1800.0	6.6	37.0	17.0	20.0	0.43	19.90	1.68	2.59	<0.01	186.0	162.0	1100.0	1034
5 19 89	0.599	1700.0	6.9	35.0	22.0	13.0	.	.	.	.	.	.	.	.	
5 22 89	0.173	1870.0	6.7	48.0	12.0	36.0	0.62	20.20	1.65	2.98	<0.01	216.0	166.0	1125.0	1036
5 24 89	0.489	2080.0	6.8	61.0	17.0	44.0	.	.	.	.	.	.	.	.	
6 5 89	0.489	2500.0	6.6	55.0	24.0	31.0	0.74	29.00	1.58	2.91	0.10	234.0	276.0	1600.0	1038
6 7 89	0.710	2380.0	6.7	36.0	39.0	-3.0	.	.	.	.	.	.	.	.	
6 9 89	0.197	2125.0	6.9	44.0	24.0	20.0	0.87	26.00	1.31	2.40	<0.01	200.0	228.0	1430.0	1040
6 12 89	0.189	2750.0	6.5	51.0	44.0	7.0	1.11	32.00	1.67	3.28	0.10	250.0	286.0	1750.0	1042
6 13 89	0.252	.	.	.	.	.	.	.	.	.	.	.	.	.	
6 16 89	0.032	.	.	.	.	.	.	.	.	.	.	.	.	.	
6 20 89	0.568	2375.0	7.1	40.0	42.0	-2.0	0.63	20.70	1.44	3.17	0.03	248.0	242.0	1640.0	1044
6 23 89	0.442	.	.	.	.	.	.	.	.	.	.	.	.	.	
6 26 89	0.047	1930.0	6.8	59.0	22.0	37.0	0.27	13.70	0.97	1.63	0.06	212.0	174.0	1320.0	1046
6 30 89	1.514	1700.0	6.2	23.0	25.0	-2.0	0.48	13.60	0.91	2.60	0.08	178.0	152.0	1180.0	1048
7 6 89	0.694	2220.0	6.6	55.0	22.0	33.0	0.37	17.50	1.25	2.51	0.04	264.0	210.0	1580.0	1050
7 18 89	0.363	2000.0	6.3	38.0	24.0	14.0	.	.	.	.	.	.	.	.	
7 21 89	0.315	2250.0	6.4	39.0	26.0	13.0	0.91	17.30	1.17	2.89	0.05	208.0	220.0	1580.0	1052
7 24 89	0.284	2375.0	6.9	44.0	51.0	-7.0	0.91	18.40	1.20	3.01	0.06	276.0	234.0	1580.0	1054
7 26 89	0.276	.	.	.	.	.	.	.	.	.	.	.	.	.	
7 27 89	0.166	.	.	.	.	.	.	.	.	.	.	.	.	.	
7 31 89	0.071	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 1 89	0.237	.	6.8	35.0	26.0	9.0	1.01	19.00	1.30	3.11	0.07	280.0	236.0	1750.0	1056
8 3 89	0.994	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 4 89	0.520	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 7 89	0.229	2375.0	6.7	34.0	17.0	17.0	0.97	19.40	1.71	4.25	0.02	354.0	228.0	1930.0	1058
8 8 89	0.205	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 9 89	0.189	2550.0	6.6	47.0	25.0	22.0	0.97	19.60	1.76	4.62	0.02	354.0	228.0	1850.0	1060

8 14 89	0.276	2300.0	6.8	38.0	20.0	18.0	0.78	18.10	1.59	3.93	0.03	332.0	232.0	1750.0	1062

Table A2.2. Effluent water quality and flow data for the Seep 1 limestone bed (1989-90), continued.

Date	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
8 15 89	0.237	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 16 89	0.189	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 17 89	0.150	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 18 89	0.142	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 21 89	0.221	2190.0	6.9	40.0	21.0	19.0	0.78	16.40	1.45	3.58	0.02	326.0	204.0	1630.0	1064
8 22 89	0.071	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 23 89	0.189	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 24 89	0.158	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 25 89	0.158	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 28 89	1.040	2190.0	6.2	21.0	25.0	-4.0	1.09	15.90	1.41	4.08	0.05	302.0	198.0	1600.0	1066
8 29 89	0.757	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 30 89	0.457	.	.	.	.	.	.	.	.	.	.	.	.	.	
8 31 89	0.773	1675.0	6.8	39.0	15.0	24.0	0.39	11.20	0.94	1.88	0.03	246.0	144.0	1230.0	1068
9 6 89	1.293	1600.0	7.1	42.0	17.0	25.0	0.27	11.20	0.89	2.02	0.03	246.0	142.0	1180.0	1070
9 7 89	0.363	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 8 89	0.237	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 12 89	0.591	2000.0	7.0	45.0	16.0	29.0	0.42	15.60	0.96	2.40	0.02	234.0	192.0	1500.0	1072
9 14 89	0.059	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 18 89	0.050	2300.0	7.1	55.0	21.0	34.0	0.41	19.30	1.16	2.83	0.01	282.0	222.0	1770.0	1074
9 21 89	1.470	1900.0	7.1	49.0	21.0	28.0	.	.	.	.	.	.	.	.	
9 22 89	0.063	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 25 89	0.311	2000.0	7.0	43.0	14.0	29.0	0.37	14.30	0.93	2.35	0.02	236.0	188.0	1430.0	1076
9 27 89	0.039	.	.	.	.	.	.	.	.	.	.	.	.	.	
9 28 89	0.043	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 2 89	0.591	1975.0	6.7	29.0	18.0	11.0	0.58	14.00	0.93	2.43	0.03	228.0	198.0	1500.0	1078
10 4 89	0.379	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 5 89	0.315	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 6 89	0.331	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 9 89	0.221	2050.0	6.8	34.0	17.0	17.0	0.57	13.10	0.82	2.35	0.03	224.0	198.0	1500.0	1080
10 11 89	0.221	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 12 89	0.189	2050.0	6.9	34.0	15.0	19.0	.	.	.	.	.	.	.	.	
10 13 89	0.189	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 16 89	0.158	2150.0	6.8	36.0	18.0	18.0	0.56	11.40	0.91	2.42	0.01	380.0	246.0	1340.0	1082
10 17 89	0.173	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 19 89	0.158	2200.0	6.7	40.0	21.0	19.0	0.52	10.55	0.83	2.40	0.01	380.0	236.0	1280.0	1084
10 20 89	0.158	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 23 89	0.130	1925.0	6.7	40.0	18.0	22.0	.	.	.	.	.	.	.	.	1086
10 24 89	0.118	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 25 89	0.125	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 26 89	0.134	.	.	.	.	.	.	.	.	.	.	.	.	.	
10 30 89	0.363	1900.0	6.7	39.0	11.5	27.5	0.35	9.76	0.80	1.68	0.01	360.0	222.0	1120.0	1089
10 31 89	0.260	.	.	.	.	.	.	.	.	.	.	.	.	.	

Table A2.2. Effluent water quality and flow data for the Seep 1 limestone bed (1989-90), continued.

Fine Limestone

Date	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
5 7 90	0.446	1250.0	6.4	30.0	30.0	0.0	.	.	.	.	.	.	.	.	1091
5 11 90	0.378	.	.	.	.	.	.	.	.	.	.	.	.	.	
5 14 90	0.820	1740.0	6.7	64.0	30.0	34.0	0.21	12.80	1.19	0.87	0.02	152.0	146.0	1020.0	1093
5 25 90	0.347	.	6.6	34.0	52.0	-18.0[1]	0.86	17.80	1.62	3.25	0.05	186.0	220.0	1450.0	1095
5 30 90	0.276	2500.0	6.4	26.0	62.0	-36.0[1]	0.36	19.70	1.81	2.84	0.04	210.0	242.0	1580.0	1097
6 6 90	0.906	1500.0	7.1	36.0	10.0	26.0	0.26	9.90	0.84	1.56	0.02	130.0	126.0	900.0	1099
6 13 90	.	2300.0	6.8	62.0	58.0	4.0	0.30	18.50	1.60	2.32	0.02	226.0	224.0	1630.0	1101
6 21 90	1.356	1700.0	6.4	47.0	.	.	0.24	9.80	0.79	1.63	0.01	134.0	120.0	900.0	1103
6 28 90	0.627	2200.0	6.9	66.0	21.0	45.0	0.29	15.20	1.25	2.54	0.04	208.0	182.0	1400.0	1105
7 3 90	.	2300.0	6.9	47.0	24.0	23.0	0.29	14.90	1.26	2.42	0.03	220.0	188.0	1440.0	1107

Coarse Limestone

Date	Flow (L/s)	S.C.	pH	Alk.	Acy.	Netalk.	Cu	Ni	Co	Zn	Fe	Ca	Mg	SO_4	#
7 13 90	0.563	2400.0	4.9	-1.0	54.0	-55.0	1.46	18.89	1.29	4.26	0.07	263.0	200.0	1530.0	1109
7 16 90	0.473	2700.0	4.7	.	60.0	.	1.59	19.10	1.51	4.61	0.12	291.0	221.0	1680.0	1111
7 18 90	0.497	2700.0	4.9	4.0	52.0	-48.0	.	.	.	.	.	.	.	.	
7 23 90	0.347	2500.0	4.9	4.0	62.0	-58.0	1.58	19.40	1.52	4.38	0.10	284.0	277.0	1670.0	1113
7 25 90	0.300	2825.0	4.9	5.0	59.0	-54.0	1.60	20.20	1.70	4.46	0.17	274.0	241.0	1820.0	1115
7 30 90	.	2950.0	4.9	-3.0	102.0	-105.0	1.65	21.20	1.82	4.76	0.16	297.0	246.0	1800.0	1117
8 6 90	.	2460.0	5.0	-1.0	78.0	-79.	1.37	20.10	1.48	3.93	0.08	244.0	213.0	1640.0	1119

Note: pH values are in standard units, specific conductance (S.C.) values are in microsiemens, flow values are in L/s, and all other values are mg/L.

[1]Effluent alkalinity and acidity values (and therefore net alkalinity values) are suspect (see section 3.2).

APPENDIX 3

Seep 1 Treatment Bed Timeline: 1990

A3.1. Seep 1 treatment bed timeline, 1990.

Table A3.1. Seep 1 Treatment Bed Timeline, 1990. Overflow rates are given in parentheses.

5/4	Started filling bed
5/7	Took first sample. Bed overflowing (3.1 L/s)
5/11	Bed overflowing (21.7 L/s)
5/14	Bed overflowing (48.5 L/s)
5/18	Bed overflowing (39.9 L/s)
5/23	Bed overflowing (20.0 L/s), cleaned bed by pumping from the center pipe and stirring the limestone during pumping. Checked bed two hours later and there was no overflow.
5/25	Bed overflowing (0.9 L/s)
5/30	Bed overflowing (14.3 L/s), pumped bed to clean out fines.
6/6	Bed overflowing (51/3 L/s)
6/21	Bed overflowing (79.8 L/s)
6/28	Bed overflowing (36.1 L/s)
7/3	Last sample from bed with small limestone, emptied bed.
7/12	Filled bed with larger particle size limestone.
7/16	Bed functioning properly (no overflow).
7/27	No overflow
7/30	Input line to the bed is leaking (no flow to the bed).
8/1	Bed is repaired and back on line.
8/6	Last sample, LTV dismantled the bed to construct pre-treatment system.

APPENDIX 4

Seep 1 Water Quality Summary Statistics: 1976-1990

Table A4.1. Summary statistics of 1989 influent water quality and flow data from the Seep 1 Bed experiment. (I = influent)

TOTAL OBSERVATIONS: 85

	GAGEI	FLOWI	SCI	PHI	ALKI
N OF CASES	85	85	49	49	49
MINIMUM	1.110	0.071	590.000	4.650	0.500
MAXIMUM	1.360	1.521	2600.000	5.880	11.000
RANGE	0.250	1.450	2010.000	1.230	10.500
MEAN	1.200	0.493	1682.959	5.196	4.933
STANDARD DEV	0.048	0.367	623.146	0.417	2.674
MEDIAN	1.180	0.363	1900.000	5.000	4.200

	ACYI	NALKI	CUI	NII	COI
N OF CASES	49	49	29	29	29
MINIMUM	9.800	-107.500	0.040	1.530	0.190
MAXIMUM	108.000	1.200	1.770	37.000	2.040
RANGE	98.200	108.700	1.730	35.470	1.850
MEAN	54.710	-49.778	0.891	15.390	1.154
STANDARD DEV	29.234	30.910	0.572	10.004	0.625
MEDIAN	54.000	-50.800	0.990	16.700	1.390

	ZNI	FEI	CAI	MGI	SO4I
N OF CASES	29	29	29	29	29
MINIMUM	0.390	0.000	40.000	48.000	276.000
MAXIMUM	4.680	0.160	360.000	280.000	2050.000
RANGE	4.290	0.160	320.000	232.000	1774.000
MEAN	2.666	0.077	203.517	174.138	1243.345
STANDARD DEV	1.409	0.057	97.078	72.396	551.146
MEDIAN	2.890	0.100	212.000	200.000	1320.000

Table A4.2. Summary statistics of 1990 influent water quality and flow data from the Seep 1 Bed experiment. (I = influent)

TOTAL OBSERVATIONS: 17

	GAGEI	FLOWI	SCI	PHI	ALKI
N OF CASES	13	0	16	16	13
MINIMUM	1.210	.	1200.000	4.400	-1.000
MAXIMUM	1.360	.	2900.000	5.200	4.700
RANGE	0.150	.	1700.000	0.800	5.700
MEAN	1.268	.	2208.750	4.834	2.662
STANDARD DEV	0.043	.	513.889	0.237	1.534
MEDIAN	1.260	.	2312.500	4.850	2.400

	ACYI	NALKI	CUI	NII	COI
N OF CASES	15	0	14	14	14
MINIMUM	43.000	.	0.820	10.600	0.850
MAXIMUM	148.000	.	1.900	21.800	1.950
RANGE	105.000	.	1.080	11.200	1.100
MEAN	88.133	.	1.444	18.027	1.500
STANDARD DEV	24.065	.	0.355	3.632	0.327
MEDIAN	84.000	.	1.470	19.140	1.510

	ZNI	FEI	CAI	MGI	SO4I
N OF CASES	14	14	14	14	14
MINIMUM	2.170	0.070	112.000	124.000	900.000
MAXIMUM	5.000	0.320	280.000	244.000	1830.000
RANGE	2.830	0.250	168.000	120.000	930.000
MEAN	3.923	0.143	201.571	199.786	1479.286
STANDARD DEV	0.916	0.071	61.385	40.142	297.721
MEDIAN	4.270	0.115	194.000	211.000	1630.000

Table A4.3. Summary statistics of 1989 effluent water quality and flow data from the Seep 1 Bed experiment. (O=effluent or outflow)

TOTAL OBSERVATIONS: 85

	FLOWO	SCO	PHO	ALKO	ACYO
N OF CASES	85	48	49	49	49
MINIMUM	0.032	600.000	6.200	21.000	0.000
MAXIMUM	1.514	2750.000	7.450	61.000	51.000
RANGE	1.482	2150.000	1.250	40.000	51.000
MEAN	0.369	1716.563	6.880	40.184	17.990
STANDARD DEV	0.306	643.785	0.278	8.333	10.407
MEDIAN	0.284	1927.500	6.850	39.000	17.000

	NALKO	CUO	NIO	COO	ZNO
N OF CASES	49	34	34	34	33
MINIMUM	-7.000	0.030	0.550	0.080	0.100
MAXIMUM	44.000	1.110	32.000	1.760	4.620
RANGE	51.000	1.080	31.450	1.680	4.520
MEAN	22.194	0.520	14.120	1.019	2.385
STANDARD DEV	12.255	0.339	7.951	0.512	1.171
MEDIAN	24.000	0.500	14.950	0.965	2.430

	FEO	CAO	MGO	SO4O
N OF CASES	33	33	33	33
MINIMUM	0.000	56.000	40.000	256.000
MAXIMUM	0.100	380.000	286.000	1930.000
RANGE	0.100	324.000	246.000	1674.000
MEAN	0.028	233.818	182.970	1291.576
STANDARD DEV	0.029	92.109	67.019	484.133
MEDIAN	0.020	236.000	198.000	1430.000

Table A4.4. Summary statistics of 1990 effluent water quality and flow data from the Seep 1 Bed experiment. (O=effluent or outflow)

TOTAL OBSERVATIONS: 17

	FLOWO	SCO	PHO	ALKO	ACYO
N OF CASES	13	15	16	15	15
MINIMUM	0.276	1250.000	4.750	-3.000	10.000
MAXIMUM	1.356	2950.000	7.100	66.000	117.000
RANGE	1.080	1700.000	2.350	69.000	107.000
MEAN	0.564	2268.333	5.928	28.000	51.267
STANDARD DEV	0.306	503.189	0.939	25.425	26.353
MEDIAN	0.473	2400.000	6.400	30.000	54.000

	NALKO	CUO	NIO	COO	ZNO
N OF CASES	0	14	14	14	14
MINIMUM	.	0.210	9.800	0.790	0.870
MAXIMUM	.	1.650	21.200	1.820	4.760
RANGE	.	1.440	11.400	1.030	3.890
MEAN	.	0.861	16.964	1.406	3.131
STANDARD DEV	.	0.634	3.812	0.321	1.287
MEDIAN	.	0.610	18.695	1.495	3.045

	FEO	CAO	MGO	SO4O
N OF CASES	14	14	14	14
MINIMUM	0.010	130.000	120.000	900.000
MAXIMUM	0.170	297.000	277.000	1820.000
RANGE	0.160	167.000	157.000	920.000
MEAN	0.066	222.786	203.286	1461.429
STANDARD DEV	0.053	56.741	46.562	309.239
MEDIAN	0.045	223.000	216.500	1555.000

APPENDIX 5

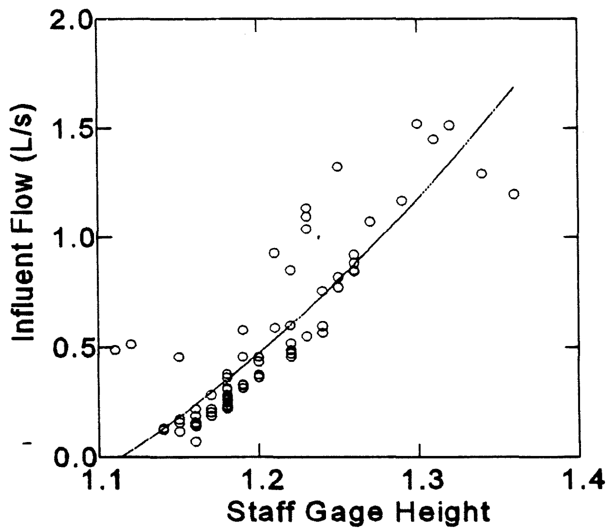
Summary of 1990 Calculation Methods

A5.1. Flow
A5.2. Neutralization
A5.3. Metal removal
A5.4. Volume of Treatment Bed Required for Coarse Limestone

A5.1. Flow

Effluent flow(Q): Reported effluent flow in L/s was used in all calculations. No averaging or weighting was used to normalize effluent flow.

Influent flow: Influent flow was measured from a staff gage in 1990. The standard equation used to convert staff gage readings to flow in L/s was no longer available. Therefore, 1990 influent flow rates were graphically estimated from the 1989 data. The 1989 influent flow rates were plotted against staff gage height for all of 1989 (figure A.5.1.). Systat was used to quadratically smooth the data. 1990 staff gage heights were then plotted on this graph, and the corresponding influent flow values were estimated using the best fit curve.



Seep 1 Limestone Bed: Influent Flow versus Staff Gage Height.

Figure A5.1. Best fit quadratic curve for Seep 1 limestone bed 1989: influent flow (L/s) versus staff gage height. This graph was used to estimate 1990 flow rates in L/s from the corresponding staff gage height readings.

A5.1. Flow cont.

Volume: $V\ (L) = Q * t * 86400(s/day)$
$V\ (m^3) = V\ (L)/1000$
$BV = V(m^3)/1.4$

Cumulative volume (L) (both influent and effluent):
$$\sum V = Q_1{*}t_1 + Q_2{*}t_2 + \ldots\ Q_n{*}t_n$$

Overflow volume (L) = $\sum V_{in} - \sum V_{eff}$

Average flow: Total volume (L) that flowed through the bed, divided by the total time of operation.

Detention time (t_d) = 1400/Q*60(s/min)

where, Q_n = measured flow rate (in L/s) for sample taken at t_n (assumed to be constant over the time period prior to the next sample)
V = volume in L or m^3
$\sum V$ = cumulative volume
BV = bed volume
1400 L (1.4 m^3) is the volume of the bed using actual dimensions
t_n = time in seconds for sample "n"

A5.2. Neutralization

Net alkalinity (Nalk) = alkalinity - acidity

Rate of alkalinity release = [Net alkalinity out - Net alkalinity in]*Q

Linear regression: Systat was used to run linear regression for the rate of alkalinity release versus $\sum V$ and Q at each point.

Mass of Limestone Dissolved:
Based on Ca release: $M= (\sum M_{Caout}-\sum M_{Cain}) * 100.09/40.08/10^3$
Based on net alkalinity release: $M = N_{avg}{*}t_d{*}86400/10^6/10^3$
or, $M= (N_{out}-N_{in}){*}\sum V/10^9$

The values of M and N can be estimated from the data or from modeling results.

where,
alkalinity and acidity are in $mgCaCO_3/L$
t_d=total time of operation in days
86400 s per day
10^6 mg per kg
10^3 kg per ton

$\sum M_{caout/in}$ = cumulative mass of Ca in the effluent and influent, respectively
100.09 = molecular weight of limestone
40.08 = molecular weight of calcium

A5.3. Metal Removal

Cumulative mass ($\sum M$) = $\sum C_n * V(L)$

Flow weighted mean concentration (mg/L) = $\sum M / \sum V(L)$

%Removal = $(\sum M_{in} - \sum M_{eff}) * 100\% / \sum M_{in}$

Linear regression:

% Removal for Cu and Zn at each point were calculated using the following method,

Mass (M) = $C * V(L)$
%Removed = $(M_{in} - M_{eff}) * 100\% / M_{in}$

Systat was used to run linear regressions for %Cu and %Zn versus CV and Q, respectively.

where,

C_n = concentration in mg/L for sample taken at time t_n (assumed to be constant over the time period prior to the next sample)
M = mass in mg or kg

A5.4. Volume of Treatment Bed Required for Coarse Limestone

Estimation 1:

d_{50} of fine limestone = 3mm
d_{50} of coarse limestone = 22mm
so, coarse = 7.3 * fine

SA $\propto$ 1/d so,
$SA_{fine} = 7 * SA_{coarse}$

surface reaction rate (r) $\propto$ SA so,
$r_{coarse} = 7 * r_{fine}$ and,

detention time $\propto$ r so,

$t_{dcoarse} = 7 * t_{dfine}$
$= 7*18=126$ minutes

where, 18 minutes is the slowest observed, effective detention time for the fine particle limestone flow rate (Q) is considered uncontrollable, or "constant" at approximately 0.4 L/s

$$V_{bed} = t_d{*}Q = (126\ \text{min})(60\text{s/min})(0.4\text{L/s}) = 3024\ \text{L}$$

Estimation 2:

A log-log relationship exists between particle diameter (d) and the cumulative percent of particles having a diameter less than d. Using linear regression, the slope and intercept of the equation describing this relationship can be determined. The surface area can be calculated using the determined slope and intercept, and a minimum diameter (1 um in this case). The surface area of the fine limestone was 8.00 cm/g, and the coarse limestone was 1.15 cm/g using this method. The ratio of the fine and coarse limestone surface area is 6.96, which is approximately equal to estimation 1.