ACIDIC PRECIPITATION IN ONTARIO STUDY

EXPERIMENTAL NEUTRALIZATION OF A SMALL, SEASONALLY ACIDIC STREAM USING CRUSHED LIMESTONE

APIOS 004/82

SUMMER 1982

Ontario

Ministry
of the
Environment

ACIDIC PRECIPITATION IN ONTARIO STUDY

EXPERIMENTAL NEUTRALIZATION OF A SMALL, SEASONALLY ACIDIC STREAM USING CRUSHED LIMESTONE

APIOS REPORT
No. 004/82

by
W. Keller
Ontario Ministry of the Environment
199 Larch Street
Sudbury, Ontario.
Canada, PH 5P9

and

J.M. Gunn
Ontario Ministry of Natural Resources
Box 3500, Station 'A'
Sudbury, Ontario
Canada, P3S 4S2

A.P.I.O.S. Coordination Office,
Ontario Ministry of Environment
6th floor, 40 St. Clair W.,
Toronto, Ontario,
Canada, M4V 1M2

Project Coordinator: E.W. Piché

SUMMARY

During July 1979, ~345 tonnes of crushed limestone were placed in the bed of a small, seasonally acidic stream. Addition of the limestone resulted in substantial alteration of water chemistry including significant elevations in pH, alkalinity, conductivity, Ca and Mg. During a one year period, contributions of buffering to the stream from the limestone were substantial with loading estimates indicating a decrease of ~65% (~3100 g) in. H^+ and an increase of ~145% (9000 kg) in alkalinity as $CaCO_3$.

Neutralization by the limestone was sufficient to protect incubating rainbow trout eggs during a period of moderate flow in late spring. However, during a previous period of very high flow, low pH and almost complete mortality of brook trout eggs were observed downstream of the limestone.

No influence by the limestone application on natural fish and macroinvertebrate communities or on introduced brook trout fingerlings was apparent.

INTRODUCTION

The acidification of freshwaters, and resultant adverse impacts on fish populations have become a major international concern in the last decade. Cases of fish population disappearance and/or depression, related to acidic inputs have been documented in many areas including Canada (Beamish and Harvey 1972; Conroy *et al.* 1978), the USA (Schofield 1976), Norway (Wright and Snekvik 1978) and Sweden (Almer *et al.* 1974).

Efforts to alleviate acidic conditions through base additions have been largely restricted to lakes (Dillon *et al.* 1979; Bengston *et al.* 1980; Blake 1980). Overall little attention has been devoted to experimental neutralization of acidic (from acidic precipitation) running waters even though streams and rivers may be a very important component of total fish habitat on a watershed basis, providing spawning and nursery areas as well as supporting resident populations.

Grahn and Hultberg (MS) indicated that attempts at stream neutralization by very simple means such as crushed limestone additions to streambeds have been largely ineffective due to insufficient quantities of material and/or problems with coatings of sediment, humic matter, and metal precipitates which may inactivate the limestone. Pearson and McDonnell (1975) working in acid mine drainage situations addressed these difficulties and developed guidelines for limestone barrier construction which cope with these problems through barrier design and quantity of material used.

This report outlines the results of an experiment in which crushed limestone was placed in the bed of a small, seasonally acidic stream. Resultant changes in stream chemistry and influences on aquatic biota were investigated.

THE STUDY AREA

The stream studied (designated Unnamed Creek for purposes of this report) originates at the base of the La Cloche Mountains in Rutherford Township near Killarney, Ontario (Fig. 1). The reach of the stream under study drains a watershed of 225 ha, of which approximately 68% is forested, 17% is wetland and 15% is exposed quartzite bedrock. During much of the year, flow in Unnamed Creek is very low (<10 L/sec) however, in fall, and particularly during spring flows are substantial (maximum recorded ~2100 L/sec). Depression of stream pH (to ~5.0) occurs mainly in association with springtime snowmelt. For most of the year ambient stream pH is generally >6.0.

MATERIALS AND METHODS

Limestone Application

Between July 23 and 28, 1979, 320 tonnes of crushed (2 cm diameter) limestone (source: Lacloche Island; 20% Ca; 1.6% Mg) were added to the bed of Unnamed Creek. An additional 25 tonnes of larger material (~15 cm diameter) were placed on the downstream face of the barrier to prevent movement of the smaller stone. The design criteria of Pearson and McDonnell (1975) were used as general guidelines for construction; however, because of site limitations (only a small reach of the stream was accessible) and a desire to keep the application simple and inexpensive (avoid the use of heavy equipment for re-channelization etc.) treatment was essentially restricted to manually filling in ~100 m of streambed with limestone to a depth of 0.5 - 1.0 m. Limestone was dumped on a road embankment adjacent to the stream and was distributed with wheelbarrows and shovels.

Chemical and Hydrological Monitoring

Commencing March 15, 1979, routine water sampling (usually weekly) was conducted upstream and downstream of the limestone addition site (stations U1 and U2 respectively; Fig. 1). Containerization was: 500-ml polystyrene for pH, alkalinity (total inflection point), conductivity; 500-ml acid washed polyethylene for trace metals (HNO_3 preserved); 1-L glass for major ions. Alkalinity, pH and conductivity determinations were completed either in the field or at the Sudbury MOE laboratory. Analyses of trace metals and major ions were conducted at the Toronto MOE laboratory.

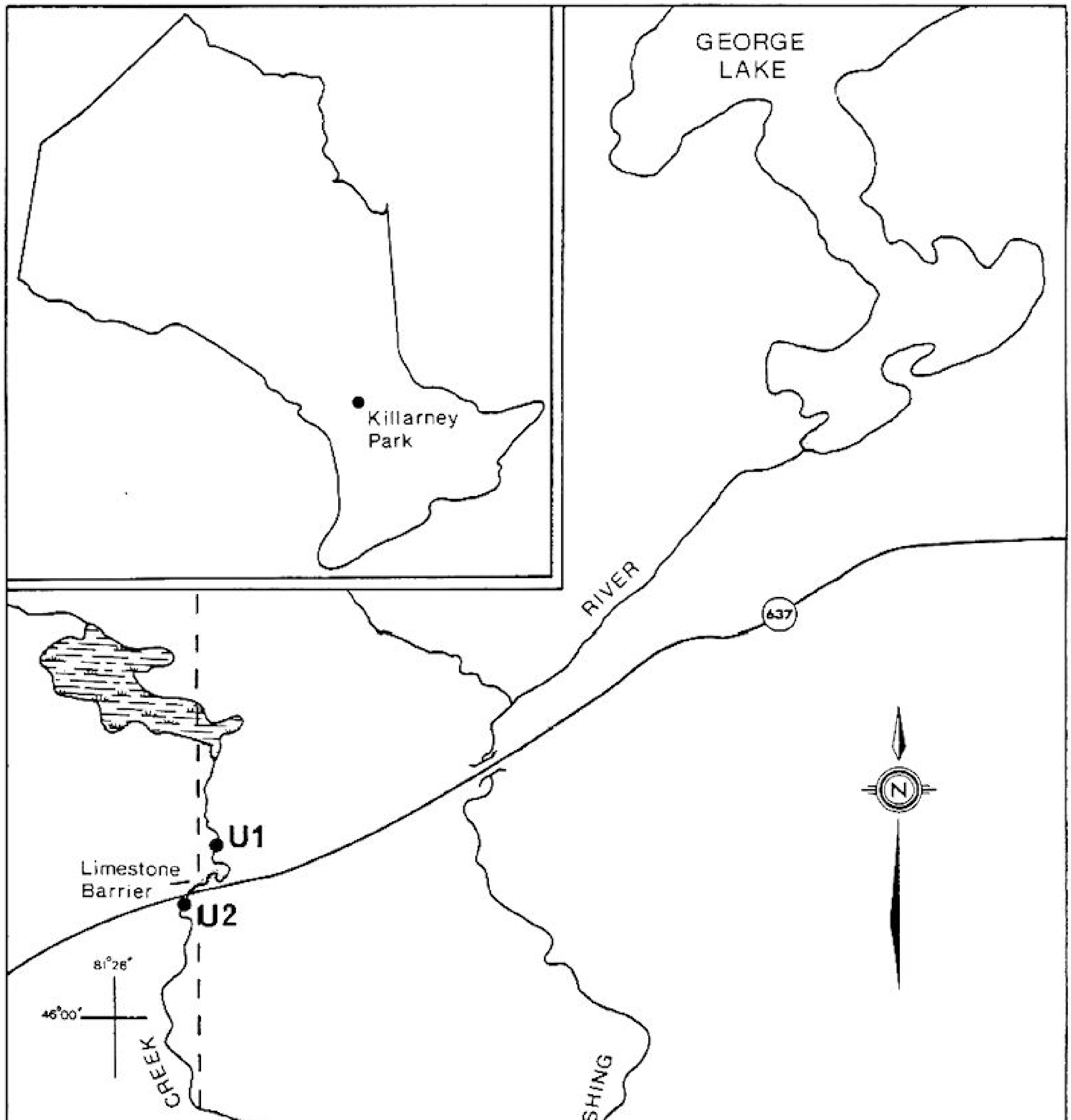

Figure 1. Location of Unnamed Creek and the sampling stations.

Beginning October 4, 1979, staff gauge readings at station U2 were added to the sampling regimen. Streamflow was estimated from staff gauge readings by calibration against flows calculated from OTT and Gurley current meter measurements and stream cross section. From June 10 to October 28, 1980 additional flow measurements were obtained from a calibrated Parshall Flume installed near station U2.

Fish and Invertebrate Studies

The natural fish community of Unnamed Creek was qualitatively investigated before and after the limestone addition by various methods including seine nets, electrofishing and visual observation. To assess the direct effects of the addition, prior to "liming", 200 hatchery reared fingerling brook trout (*Salvelinus fontinalis*) were liberated above and below the limestone addition site for observation. After the limestone addition, eyed eggs of brook trout and rainbow trout (*Salmo gairdneri*) were incubated *in situ* (November 28, 1979 - April 18, 1980 for brook trout; April 17 - May 16, 1980 for rainbow trout) in screen substrate baskets (Gunn and Keller 1980) filled with non-calcareous gravel.

Stream macrobenthos were sampled before (May 22-23, 1979) and after (May 27-28, 1980) the limestone addition. Pre-neutralization sampling consisted of six-929 cm^2 Surber samples and 1 hour of qualitative collection with a hand sieve in the vicinity of station U2. Post-neutralization sampling consisted of the same effort (6 Surber samplers; 1 hour qualitative inspection) both upstream and downstream of the limestone addition site. Invertebrates were picked and preserved in 70% ethanol for subsequent identification and enumeration at the Sudbury MOE laboratory. After identification, Surber samples were oven dried (105°C for 4 hours) and weighed.

RESULTS AND DISCUSSION

Water Chemistry

Addition of limestone to the bed of Unnamed Creek resulted in substantial alteration of ambient water chemistry (Table 1). On a yearly (November 1979 to October 1980 inclusive) basis, significant ($P<0.05$ based on a paired t-test of monthly means) increases in pH, alkalinity, conductivity, Ca and Mg, related to reaction with limestone, were observed downstream of the barrier. Water chemistry above and below the barrier showed wide temporal variation (Table 1) with pH, conductivity, alkalinity and major ion minima associated with high spring flows and maxima associated with low summer flows.

During most periods, pH increases due to the limestone barrier were in the order of 0.5 unit (Fig. 2). Poorest pH adjustment occurred during high flows in combination with ice cover during which much of the runoff water had no contact with limestone. For example, on March 24, 1980, under ice cover at a flow of ~1500 L/sec, pH increased from 5.57 to only 5.69. On April 9, 1980 at even higher flow (2100 L/sec) but after disappearance of ice cover pH increased from 5.28 to 5.72. It should be noted that pH measurements are not a complete reflection of barrier performance since even small pH increases during low pH, high flow spring conditions represent a substantial H^+ decrease. On a quantitative basis contributions of buffering to Unnamed Creek from the barrier were substantial, with annual loading estimates indicating a ~ 65% reduction in H^+ and a ~ 145% increase in alkalinity as $CaCO_3$ (Table 2). Approximately 75% of the yearly H^+ decrease and ~ 35% of the alkalinity increase occurred during the high flow months of March and April.

Table 1: Yearly averages and ranges in concentration of chemical parameters in Unnamed Creek, upstream (U1) and downstream (U2) of a crushed limestone barrier. Data are from November 1979 to October 1980 inclusive.

Parameter	Upstream (U1)		Downstream (U2)		n
	Range	Avg.[a]	Range	Avg.[a]	
pH	5.26 - 6.54	5.90	5.57 - 7.70	6.47	51
TIA[b] (mg/L)	0.27 - 22.22	8.83	1.82 - 68.21	26.05	48
Conductivity (µs/cm)	27 - 62	44	28 - 153	75	51
Ca (mg/L)	2.4 - 7.4	4.7	3.0 - 26.0	11.1	45
Mg (mg/L)	0.50 - 2.45	1.42	0.70 - 3.05	1.62	45
Na (mg/L)	0.6 - 1.8	1.1	0.6 - 1.9	1.2	45
K (mg/L)	0.20 - 0.85	0.49	0.20 - 0.80	0.51	45
SO_4 (mg/L)	6.5 - 15.5	10.5	7.0 - 15.5	10.7	45
Cl (mg/L)	0.10 - 1.20	0.54	0.09 - 1.95	0.69	45
Colour (Hazen Units)	37 - 220	99	36 - 180	88	45
Total Al (µg/L)	90 - 450	230	30 - 590	180	42
Total Mn (µg/L)	30 - 350	139	12 - 350	117	42
Total Fe (µg/L)	270 - 3300	1460	240 - 2300	1030	42
Total Cu (µg/L)	<1 - 10	<2	<1 - 4	<2	41
Total Ni (µg/L)	<2 - 9	<5	<2 - 20	<5	42
Total Zn (µg/L)	<2 - 20	<8	<2 - 20	<8	42

[a] calculated from monthly averages; average H^+ for pH

[b] total inflection point alkalinity as $CaCO_3$

Average concentrations of Na, K, SO_4 and Cl were slightly higher and color was slightly lower downstream of the barrier (Table 1) but upstream/downstream differences were not significant ($P>0.05$). The crossing of Hwy 637 between stations U1 and U2 slightly influenced concentrations of Cl, and Na, however no effect on pH, alkalinity or concentrations of Ca and Mg could be determined. Sampling on four occasions prior to limestone addition showed no significant differences ($P>0.1$) in pH, alkalinity (total fixed endpoint), Ca or Mg between sites U1 and U2. Sampling on 5 occasions after barrier installation showed no significant differences ($P>0.1$) in pH or alkalinity (total inflection point) between station U2 and a point immediately downstream of the limestone but upstream of the road crossing.

Concentrations of Cu, Ni and Zn were not significantly different ($P>0.1$) upstream and downstream of the barrier, however, average concentrations of total Al, Fe and Mn were significantly lower ($P<0.05$) downstream (Table 1) reflecting precipitation on or within the limestone barrier during most sampling periods. Observations of a heavy late summer deposit of reddish floc (predominantly iron hydroxides and algae as identified by electron microscopy) extending ~ 50 m downstream from station U2 indicated that the precipitation process was not completed, within the limestone.

Changes, due to the barrier in waterborne concentrations of total Al and Fe showed a temporal pattern. The greatest upstream/downstream reductions in Al and Fe concentrations occurred during low flow periods in winter and summer (Fig. 3) when pH and alkalinity increases were greatest. With the onset of increased streamflow in fall and spring, downstream concentrations of Al and Fe exceeded upstream concentrations for short periods indicating flushing of precipitates from the limestone. Loading estimates for Al and Fe agree to within ~5% at stations U1 and U2, suggesting no long term accumulation in the barrier.

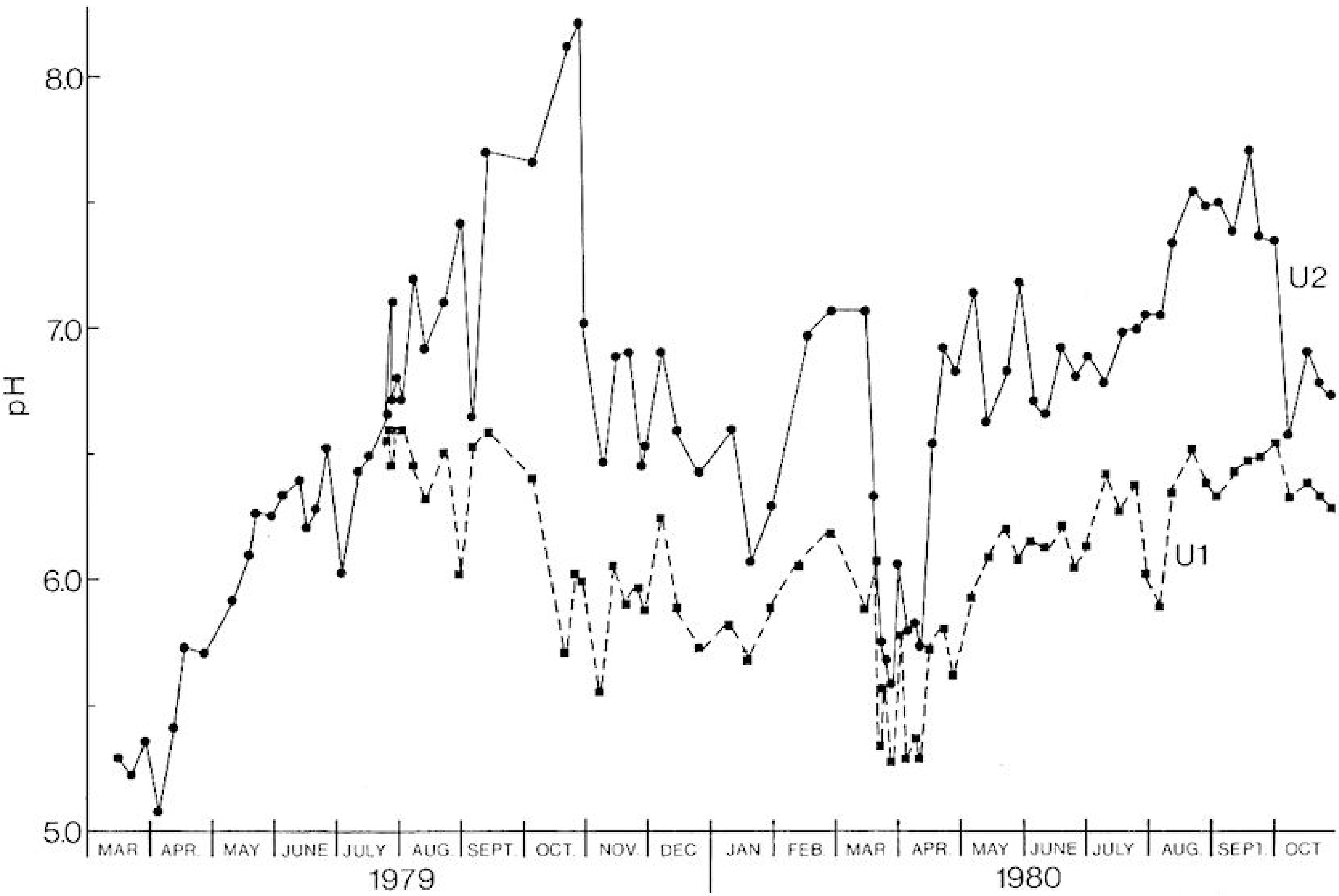

Figure 2: Temporal variation in the pH of Unnamed Creek, upstream (U1) and downstream (U2) of a crushed limestone barrier.

TABLE 2: Estimated monthly and yearly loadings of H^+, TIA, Fe, and Al upstream (U1) and downstream (U2) of a crushed limestone barrier (November 1979 to October 1980 inclusive).

	H^+ (g)		TIA as $CaCO_3$ (kg)		Tot. Fe (kg)		Tot. Al (kg)	
	U1	U2	U1	U2	U1	U2	U1	U2
Nov. 79	308.6	74.6	651.4	2308.4	74.4	80.6	34.8	47.0
Dec. 79	260.7	53.1	925.0	1803.1	105.6	88.4	25.4	26.5
Jan. 80	379.8	135.5	1462.0	3478.4	143.7	123.3	29.4	33.3
Feb. 80	18.4	2.3	270.2	748.4	45.5	32.0	8.3	4.1
Mar. 80	1085.4	587.2	1571.0	2892.4	154.7	246.5	89.5	87.8
Apr. 80	2714.7	876.4	518.6	2140.3	185.2	200.1	128.3	138.8
May 80	30.7	6.2	132.0	243.9	26.8	23.6	8.6	7.6
June 80	7.2	1.7	91.4	256.2	24.9	18.0	2.6	2.0
July 80	2.7	0.7	84.9	262.2	18.5	11.6	1.2	0.8
Aug. 80	2.5	0.2	67.6	242.4	9.9	4.6	0.4	0.3
Sept. 80	3.1	0.3	108.6	284.5	20.3	10.8	3.5	1.7
Oct. 80	35.5	15.3	349.7	611.7	44.5	35.5	11.4	10.9
Total	4849.3	1753.5	6232.4	15271.9	854.0	875.0	343.4	360.8

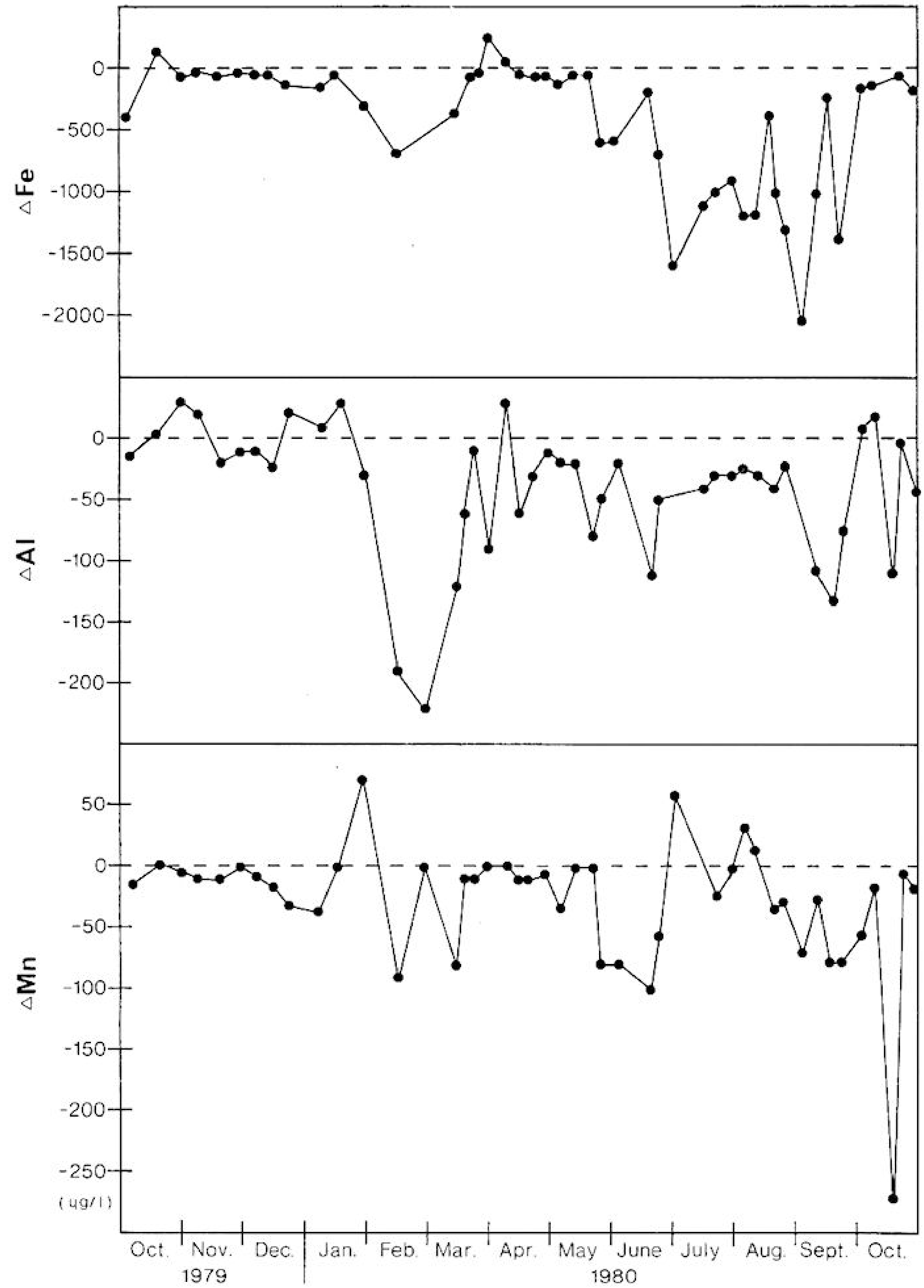

Figure 3. Differences (U2 - U1) in concentrations of Total Fe, Al, and Mn between sampling stations on Unnamed Creek.

Concentrations of total Mn generally followed the pattern observed for Al and Fe (Fig. 3); however, instances where downstream Mn concentrations exceeded upstream concentrations occurred in midwinter and midsummer and were not associated with increased flow.

Based on the above, total Al, Mn and Fe concentrations appeared to be actively reduced by the limestone during most periods, but flushing of precipitates during high flow conditions resulted in little if any long term Al and Fe accumulation within the limestone. The mechanism of periodic Mn losses from the barrier remains unclear.

Fish

Before the addition of limestone the natural fish community of Unnamed Creek included: white sucker (*Catostomus commersoni*), central mudminnow *(Umbra limi*), dace (*Chrosomus* sp.), brook stickleback (*Culaea inconstans*), brown bullhead (*Ictalurus nebulosus*), and common shiner (*Notropis cornutus*). No qualitative changes in the occurrence or abundance of these species were observed during or after neutralization.

Observations of brook trout fingerlings liberated upstream and downstream of the barrier showed no readily observable effects from turbidity and immediate chemical changes associated with barrier construction. No dead fish were observed and trout survived and grew through the season and were again observed both upstream and downstream of the barrier during the following summer (1980).

Eyed brook trout eggs incubated (November 29, 1979 - April 8, 1980) upstream and downstream of the limestone showed complete mortality when retrieved on April 8, 1980, although previous inspection (February 18, 1980) had shown eggs to be viable at Station U1. Between inspection and retrieval of the eggs, streamflow increased substantially due to rain and snow melt and pH was observed to decrease to 5.26 at station U1 and pH 5.57 at station U2.

Subsequent incubation of eyed rainbow trout eggs during a period of lower flow (April 17 - May 16, 1980) showed good hatching success (Table 3) downstream of the limestone (pH 6.25-6.71) and almost complete egg mortality upstream of the limestone (pH 5.70-5.99). Alevins hatched below the limestone showed good 13-d survival when held both upstream and downstream of the barrier (exposure pH 5.97-6.14 and 6.42-6.62 at U1 and U2 respectively).

The egg incubation studies indicate that although the water quality changes produced by the limestone were sufficient to protect rainbow trout eggs during moderate flows, the limestone barrier could not cope with the high runoff, and ice conditions during the earlier period of brook trout egg incubation. Although the fish studies were very limited, they also suggest that in natural stream situations the fall-spawning brook trout may be highly susceptible to impacts via pH depression since the sensitive egg and sac fry stages are present in the gravel during periods of maximum snowmelt and minimum pH. The sensitive stages of spring-spawning gamefish such as walleye (*Stizostedion vitreum vitreum*) and rainbow trout may not be exposed to peak snowmelt, which normally occurs prior to spawning times.

Table 3: Hatching success of eyed rainbow trout eggs (April 17 - May 16, 1980) and 13-d survival of rainbow trout fry (May 19 - June 1, 1981) in Unnamed Creek upstream (U1) and downstream (U2) of a crushed limestone barrier. All fry for the survival experiment originated at site U2.

Hatching Success	Upstream (U1)	Downstream (U2)
Number of incubators	10	10
Egg number/incubator	200	200
Incubators with live alevins	1	10
% survival ($\bar{x}$ ± SD)	<0.1 ± 0.16	95.2 ± 1.89
Fry Survival		
Original number of fry	50	50
% survival (13-d)	98	100

Macrobenthos

Comparison of benthic invertebrate communities upstream and downstream of the barrier, and before and after barrier construction, showed no obvious effect on macrobenthos related to the limestone application (Table 4). Richness of taxa and biomass seemed slightly reduced downstream of the barrier but more variation in community composition, biomass and community richness occurred between sites sampled at the same time in the same reach of stream than between sites sampled at different locations and times.

Jaccard Coefficients of community ranged from 0.64 to 0.69 indicating that communities differed by about the same degree between locations.

Additional study of bottom fauna will be required to adequately assess any long term improvements related to stream neutralization or alternately, any adverse effects due to the deposition of metal precipitates downstream of the limestone.

Table 4: Results of benthic invertebrate collections, Unnamed Creek (numbers per m^2). P denotes presence in a qualitative sample (Q).

	May 22-23, 1979							May 27-28, 1980													
								Upstream (U1)							Downstream (U2)						
	1	2	3	4	5	6	Q	1	2	3	4	5	6	Q	1	2	3	4	5	6	Q
Diptera																					
Simulidae	86	11	183	253	237	721	P	226	-	-	140	54	22	P	-	-	-	97	-	97	P
Chironomidae	32	-	22	11	11	11	P	22	-	11	-	-	183	P	65	226	237	237	-	-	P
Rhagionidae	-	-	-	-	-	-	P	-	-	-	-	-	-		-	-	-	-	-	-	P
Trichoptera																					
Limnephilidae	11	-	-	-	54	11	P	-	22	-	11	-	-	P	-	-	-	-	-	-	P
Hydropsychidae	11	-	65	-	-	54	P	-	-	11	32	-	-	P							
Ephemeroptera																					
Ephemerellidae	-	-	-	-	-	-		-	22	-	-	-	22	P	11	22	-	-	-	-	P
Caenidae	-	-	-	-	-	-		-	-	-	11	-	-	P	-	-	-	-	-	-	
Siphlonuridae	-	-	-	-	-	-		-	-	-	-	-	-		-	-	-	-	-	-	P
Anisoptera																					
Cordulegasteridae	22	-	22	11	54	-	P	-	11	32	-	-	32	P	-	-	-	-	11	-	P
Coleoptera																					
Dytiscidae	-	-	-	-	-	-		11	11	-	-	11	11	P	11	-	-	11	11	-	P
Hemiptera																					
Corixidae	-	-	-	-	-	-									-	-	-	-	-	-	
Oligochaeta	11	-	-	-	-	-	P	-	-	11	22	-	54	P	22	-	-	-	11	-	P
Hirudinea	-	-	-	-	-	-		-	-	-	-	11	-	P	-	-	-	-	-	-	P
Gastropoda																					
Planorbidae	-	-	-	-	-	-	P	11	-	-	-	-	-	P	-	-	-	-	-	-	P
Pelecypoda	-	-	-	-	-	-	P	-	-	-	-	-	-	P	-	-	-	-	-	-	P
Number of taxa	6	1	4	3	4	4		4	4	4	5	3	6		4	2	1	3	3	1	
Biomass (mg/m^2)	139	4	121	7	110	370		3	94	66	12	25	11		24	24	<1	47	2	1	

Additional Observations

Several problems with the operation and maintenance of the barrier were encountered. A major difficulty, as previously noted, was ice cover during late winter/early spring which kept much of the runoff water out of contact with the limestone. Other difficulties related to siltation within the stone and clogging with debris, problems noted by previous investigators (Pearson and McDonnell 1975; Grahn and Hultberg MS). Although clean stone was purchased, grinding during transportation produced a large portion of fines which, through clogging, reduced the effective surface area of the limestone as applied in the stream.

Clogging problems were aggravated by eroding stream banks and autumn leaf litter, particularly when on several instances beavers constructed dams across the limestone and leaves and other debris settled in the ponded water before dams could be removed. Due to blockage of interstices within the stone and the relatively small (~ 2 cm diameter) stone used, the flow through capacity of the barrier was very low thus for most of the year (at flows greater than ~ 10 L/sec) flow was primarily over, not through the limestone thus the term barrier is technically a misnomer.

Although limestone reactivity increases with decreasing diameter (i.e.: increasing surface area), in field situations the easy clogging of small stone seems to negate this advantage. Larger stone (5-10 cm) would likely provide better neutralization performance and would also give less likelihood of material movement. During this experiment, some downstream movement of limestone occurred during particularly severe runoff events.

Coating of the stone by metal precipitates did not appear to be a major problem during the present study. Coatings were not apparent during high flow periods apparently due to flushing of most precipitates with the onset of increased flow. When present, metal coatings did not inactivate the limestone since substantial changes in pH (Fig. 2) and alkalinity remained evident during late summer and late winter when "iron staining" was most pronounced.

CONCLUSIONS

The results presented in this report must be regarded as preliminary since they largely represent only a single years data from a longer term study.

The present data indicate that despite problems encountered with ice-cover, siltation and blockage by litter, even a very simple addition of a large amount crushed limestone can contribute substantial additional buffering to a stream with estimated H^+ decreases of ~ 65% and alkalinity increases of ~ 145% observed during a one year period. The data further suggest that a limestone-treated stream could act as a conveyor of substantial amounts of alkalinity to downstream aquatic systems. More rigorous adherence, to design criteria such as provided by Pearson and McDonnell (1975) through stream re-channelization etc. and use of larger stone should substantially improve limestone barrier performance.

Although neutralization by the barrier appeared sufficient to protect incubating rainbow trout eggs during a period of moderate flow, the low pH observed downstream of the limestone during high runoff conditions, and related mortality of brook. trout eggs, indicate that some mechanism of flow regulation may have to be incorporated into stream neutralization schemes if pH criteria sufficient to protect sensitive aquatic biota are to be continuously met.

No alteration in natural fish or macroinvertebrate communities related to installation or operation of the limestone barrier was observed.

ACKNOWLEDGEMENTS

The list of persons involved during the course of this project is too long to provide here. We wish to thank all those who participated in the various phases of the study.

REFERENCES

Almer, B., W. Dickson, E. Ekstrom, E. Hornstrom and U. Miller. 1974. Effects of acidification on Swedish lakes. Ambio 3:30-36.

Beamish, R. J. and H. H. Harvey. 1972. Acidification of the Lacloche Mountain lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Board Can. 29: 1131-1143.

Bengston, B., W. Dickson and P. Nyberg. 1980. Liming acid lakes in Sweden. Ambio 9:34-36.

Blake, L. M. 1980. A review of acid pond liming in New York. New York State Dept. of Environmental Conservation Report.

Conroy, N. I., K. Hawley, and W. Keller. 1978. Extensive monitoring of lakes in the greater Sudbury area, 1974-76. Ontario Min. Environment Tech. Rept.

Dillon, P. J., N. D. Yan, W. A. Scheider, and N. Conroy 1979. Acidic lakes in Ontario, Canada: Characterization, extent and responses to base and nutrient additions. Arch. Hydrobiol. Beih., Ergebn. Limnol. 13:317-336.

Gunn, J. M. and W. Keller. 1980. Enhancement of the survival of rainbow trout (*Salmo gairdneri*) eggs and fry in an acid lake through incubation in limestone. Can. J. Fish. Aquat. Sci. 37:1522-1530.

Pearson, F. H. and A. J. McDonnell. 1975. Limestone barriers to neutralize acidic streams. J. Environ. Eng. Div. 101: 425-440.

Schofield, C. L. 1976. Acid precipitation: Effects on fish. Ambio 5:228-230.

Wright, R. F. and E. Snekvik. 1978. Acid precipitation: Chemistry and fish populations in 700 lakes in Southernmost Norway. Verh. Internat. Verein. Limnol. 20:765-775.