Development of a Liming Prediction Model for Llyn Brianne

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Abstract

This paper describes a model which was developed to simulate the effect of automated liming on the quality of a Welsh lake (Llyn Brianne) and its outflow river. The objective was to model the amount of lime required to dose the input streams under a variety of conditions. It was concluded that it would be feasible to install automatic-dosing equipment on the two input streams to deliver sufficient lime to ensure that the pH of the lake and water downstream was controlled at a pH value of 6.0 or greater, thus stabilizing water quality for fish and other aquatic biota.

Key words: **Acid waters remediation; liming; Llyn Brianne; modelling.**

Introduction

The Llyn Brianne project[1,2] identified the importance of the effects of acid deposition on streams in mid-Wales (Fig. 1) and demonstrated that the application of lime might be used to increase the in-stream alkalinity. The remediation of acidified waters is normally approached by (a) direct addition of lime to lakes, (b) catchment liming, and (c) direct dosing of input waters. Lake liming (the technique which is currently used in Llyn Brianne) has been shown to be effective since it commenced in 1991. An initial dose of 850 t of powdered limestone had been spread over the surface from a boat during February 1991. Further doses of 500 t were added in October 1991, March and October 1992.

Lake liming offers the advantages of a low manpower requirement and avoids potential damage to lakeside wetlands which might be caused by liming of the catchment; however, this approach may be of limited efficiency. The limestone may not dissolve and therefore will not affect water quality because, in suspension, it is lost through the lake outlet or, in shallow areas, it settles on the lake bed and is incorporated into sediments. A more important drawback of lake liming is that periodic treatment results in large and rapid changes in water quality, which can lead to the precipitation of trace metals and consequent effects on fish survival[3,4,5].

Catchment liming (an alternative remedial option) has the advantage that it neutralizes acidic inputs before they enter surface waters, thereby reducing mobilization of heavy metals and aluminium from soil and preventing the rapid changes in lake chemistry associated with direct addition to lakes. Using this approach, it has been shown that the rivers in the catchment might be suitable for fish spawning under most flow conditions for 5–10 years. The main disadvantages of application of the lime to land are that it is expensive and has a potentially detrimental effect on plant and animal ecology[6].

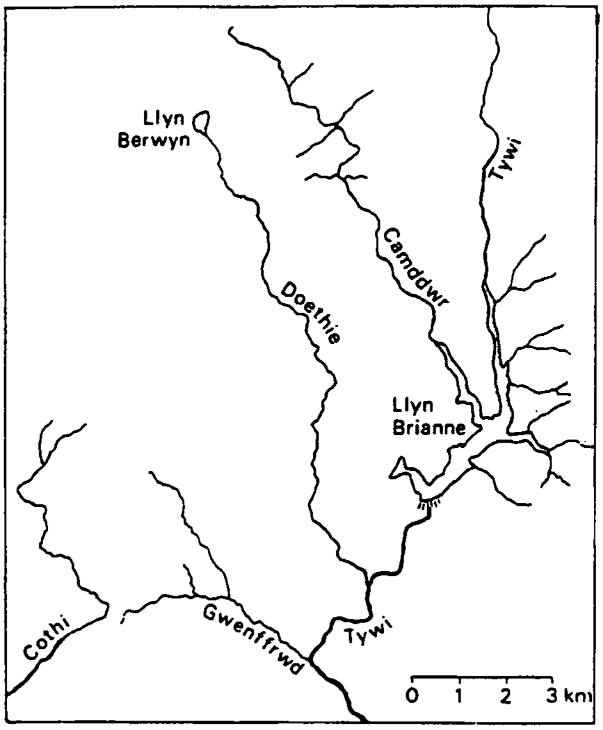

Fig. 1. Llyn Brianne catchment

A review which was undertaken by the Environment Agency indicated that direct dosing of the input streams to Llyn Brianne would be the most cost-effective and environmentally sensitive strategy for stabilizing lake chemistry and protecting biota in the outflow streams.

Dosing of lake input streams has been used successfully in Scandinavia where lime is dosed in proportion to the flow and pH of the water. Lime can be introduced either as a slurry (0–15 μm particles) where 90–100% of the solid material is dissolved within a few seconds, or as a dry powder (<0.2 mm) where approximately 50% dissolution occurs immediately – the remainder dissolving more slowly. Direct dosing to lake input streams has the advantages of (i) avoiding damage to wetlands and (ii) minimizing extreme changes in lake-water quality. Localized changes in stream chemistry near the dosing site are difficult to avoid, although sites can be chosen to minimize damage to the habitat of fish or other biota.

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The objectives of this project were to develop a liming model (based on existing data for pH, flow and major ion concentrations) to predict pH values of the lake and downstream rivers after lime addition to the input streams. It was assumed that direct dosing would commence immediately after a lake-liming exercise, with the aim of maintaining the pH of the lake and downstream rivers at or above a value of 6.0.

Modelling Methodology

For the Llyn Brianne catchment it was necessary to calculate the effect of dosing the Rivers Tywi and Camddwr on Llyn Brianne[7,8]. The effect of acid inputs from the River Doethie (joining downstream from the lake outlet) also had to be calculated. A stream/lake model was required to simulate the key water-quality variables; accordingly, a PC-based model[9] ('lime acid systems for environmental restoration', LASER) was developed to incorporate variables including alkalinity, pH, carbonate, sulphate, nitrate, chloride, aluminium, calcium, magnesium, sodium, potassium and ammonium, and organic acids. Output from the model included (a) water chemistry of Llyn Brianne and the River Tywi downstream on a weekly basis, in response to dosing at a specified rate and (b) the effects of interruption of dosing (for a specified period of time) on pH. Although the pH of the input rivers can vary over hours rather than days, the retention time of water in the lake (71–775 d depending on low or high input flows) has a damping effect on pH change. This means that the model time-steps of one week are adequate to simulate pH changes in the lake.

Fig. 2 illustrates the modelling approach. The lake is assumed to be a single well-mixed system, with the retention time determined by the following equation:

$$T = \frac{V}{Q_{lb}} \qquad (1)$$

where T is the retention time (s)
V is the volume of the lake (6.1×10^7 m^3)
Q_{lb} is the flow at the lake outlet (m^3/s)

The chemistry of the inputs to the lake is computed using the following mass-balance and equilibrium equations:

Approximate mass balance:

$$Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ + H^+ + Al^{3+} = Cl^- + SO_4^{2-} + NO_3^- + \text{organic acids} + HCO_3^- \qquad (2)$$

Hence:

$$\text{Alkalinity} = [HCO_3] - [H] \qquad (3)$$

$$[HCO_3] = \frac{k_1}{[H]} \qquad (4)$$

where concentrations are in micro-equivalents per litre and k_1 is the acid dissociation constant for carbonic acid.

Equations (3) and (4) can be solved as a quadratic equation to give the hydrogen-ion concentration, and equation (4) solved for the concentration of bicarbonate.

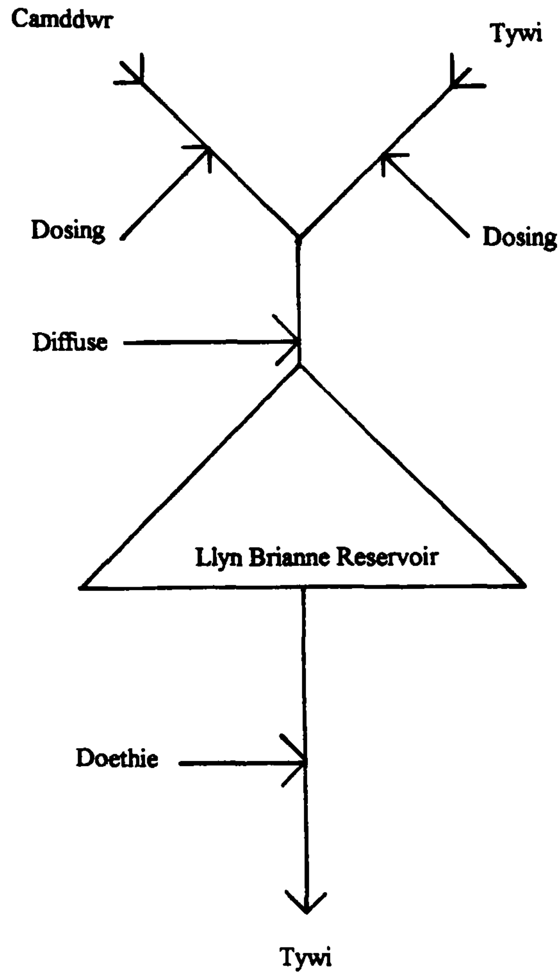

Fig. 2. Diagram of LASER modelling

The organic-acid term in equation (2) is relatively small and is estimated to be 3 micro-equivalents per litre.

Aluminium is estimated in the streams and lake using the following relationship which is based on Environment Agency survey data from the Llyn Brianne input streams (Fig. 3):

$$[Al] = 4.7 + k_2[H]$$

where units of H and Al are micro-equivalents per litre. The parameter k_2 (calculated as 1.9) is determined from regression analysis of filtrable aluminium and pH.

Using the above equations, the main parameters of lake chemistry can be estimated at points in the lake or output rivers. One key parameter is the buffering capacity of Llyn Brianne/River Tywi waters downstream from the River Doethie (Fig. 2). The dosing rate (tonnes-Ca per week)[10] for the liming stations on the Tywi and the Camddwr can be set using the model to any desired value; the downstream chemistry is then computed.

The input-data file requires the user to specify the following:

(i) Flow (m^3/s) and chemistry (concentrations of Ca, Mg, Na, K, NH_4, SO_4, Cl, NO_3) expressed in micro-equivalent per litre for the four input flows, i.e. the Rivers Tywi, Camddwr, and the Doethie;

(ii) The flow from Llyn Brianne (assumed to equal the input, unless stated) and the initial alkalinity and calcium concentrations for Llyn Brianne;
(iii) The dosing rate (in tonnes calcium/week) for the River Tywi;
(iv) The dosing rate (in tonnes calcium/week) for the River Camddwr;
(v) The percentage dissolution (based on previous research)[11]; and
(vi) The number of weeks of interruption to the dosing.

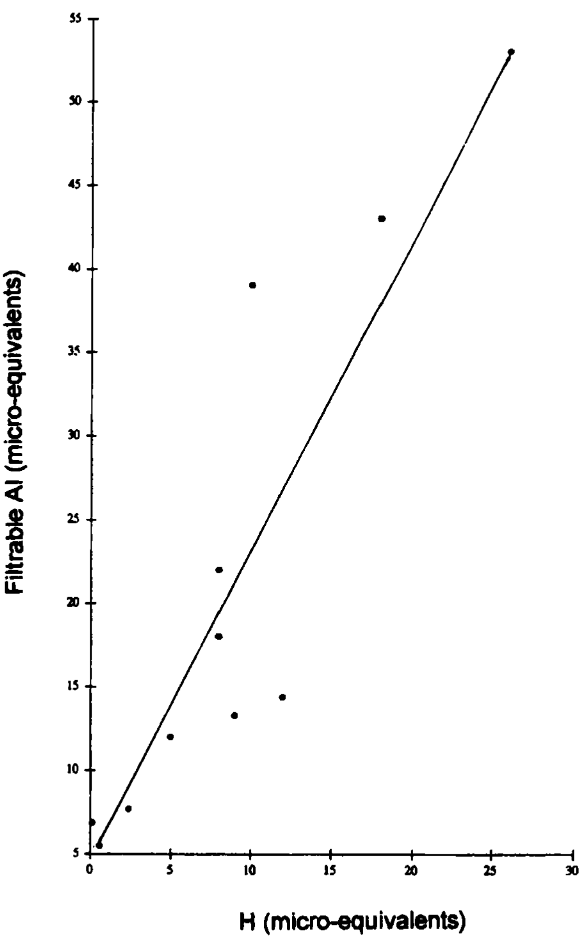

Fig. 3. Relationship between aluminium and hydrogen-ion concentration in Llyn Brianne's input streams

The output file generated by the model gives the predicted water quality downstream from the dosing points on the Rivers Tywi and Camddwr; thereafter the chemistry is calculated weekly for one year with outputs for both the lake and downstream from the River Doethie. After one year, the dosing is assumed to be interrupted for the number of weeks specified in the input file. This allows the rate of re-acidification of Llyn Brianne to be assessed.

Results and Discussion

Flow data (percentage of average daily flow exceeding a given volume per second) for three different flow conditions (high, medium and low) were run on the model to simulate the range of conditions in the Llyn Brianne catchment. A weighted mean (Table 1) of the top 20% of flows was chosen for the high flow conditions, the next 28% as medium flow, and the remainder (52%) as low flow conditions.

Table 1. Weighted mean flows for input streams (m^3/s)

Type of flow	River Tywi	River Camddwr	Diffuse streams	River Doethie
High	5.26	2.96	1.00	7.49
Medium	1.71	0.96	0.47	2.79
Low	0.44	0.25	0.10	0.72

As the flow of water running off the catchment increases, the pH value might be expected to decrease as a result of increased leaching of acid cations and organic acids from the peat catchment. Subsequently, it might be expected that the pH would begin to increase again because of washout of acidic ions from the catchment. However, monitoring data for the Llyn Brianne catchment indicate that, even at high flows, the tendency is for pH values to continue to decrease. This suggests that the acid-generating capacity of the catchment is not exceeded during most rainfall episodes.

Environment Agency monitoring data were used to match water quality with the chosen ranges of flow. Mean concentrations for data collected from upstream sites on the Rivers Tywi, Camddwr, and Doethie for January and February 1992–1994 were used to represent conditions of high flow. Values for March and April 1992–1994 were used for medium flows, and mean values from May and June 1992–1994 were used to correspond to low flow conditions. The pH values for these different river input flow conditions showed a smooth increase from high to low flows.

To obtain a single figure for the diffuse stream inputs, a flow-weighted average was derived for all eight stream inputs and used for the medium flow.

To validate the quality of the data used in the LASER model, each data set was input to the USEPA MINTEQA2 model[11] to ensure charge balance and that the pH value was within 0.2 units of that measured (Table 2). Equivalent doses of lime (tonnes-Ca per week) were then input to the two feeder streams in order to produce a pH value of at least 6.0, in both Llyn Brianne and the River Tywi downstream from the confluence with the River Doethie.

Under low flow conditions, the pH value of the input streams is approximately 6.0. Therefore, provided that the lake is limed prior to direct dosing, the model demonstrates that only minimal dosing would be needed. For high values of flow, with their accompanying poor water-quality conditions, 1.2 t of calcium per week in each input stream would be sufficient to give a pH value of over 6.0. For the medium flow-rates, 0.3 t of calcium per week was shown to be sufficient to achieve the desired water quality.

The required dose-rates for extreme values were also estimated. The input concentrations of sulphate were adjusted to give the lowest recorded pH values for each input river, and the model was then run at the high

Table 2. Input data for LASER model (all concentrations as micro-equivalents)

Flows	Ca	Mg	Na	K	NH_4	SO_4	Cl	NO_3	pH
Tywi									
High	80	76.5	240	4.9	1.5	119	281	4.4	5.3
Medium	60	68.3	220	4.6	1.5	107	241.5	2.7	5.4
Low	70	56.8	210	3.8	1.5	110.1	227.9	1.3	5.9
Camddwr									
High	68	69.1	195.6	5.1	1.5	108	223.7	3.8	5.7
Medium	57	63.3	191.3	3.8	1.5	100	241.5	3.3	6.0
Low	56	54.3	177.4	3.8	1.5	99.8	187.6	1.3	6.3
Doethie									
High	81	77.3	209.1	3.8	1.5	125	240	4.2	5.5
Medium	60	71.6	193.0	14	1.5	125	191.3	3.3	5.8
Low	70	72.4	201.3	3.8	1.5	112	214.7	1.2	6.2
Diffuse sources									
High	80	82.3	210	4.6	1.5	144	236.9	3.8	5
Medium	60	70	220	6.2	1.5	137	230.7	4.2	5.6
Low	70	80	204.3	6.4	1.5	125	250	3.8	6

flow-rates. The model showed that 3.0 t of lime per week would be required to increase the pH value in the lake and downstream to over 6.0. Using this water quality and allowing an increase of the flows of the inputs to an estimate of the upper 99 percentile (i.e. River Tywi 10 m^3/s), it was shown that a dose-rate of 10 t/week was required in each stream. Such a dose would only be necessary for 1–2% of the year. The predicted lime requirements are shown in Table 3.

Practical Application

The lime requirements (estimated above) apply to a specified set of flow regimes encountered during the course of a year. In practice the flows vary on an hourly basis; consequently, lime-dosing equipment is designed to respond to both water quality (pH value) and flow. Outputs from the LASER model have shown that under extreme conditions (encountered only a few days a year) a maximum total of 63 t/week (375 kg/h) of lime addition would be required (assuming 80% dissolution) in order to maintain the pH value of the lake at >6.0. Commercially available dosing equipment is capable of dosing up to 1600 kg/h and accommodating flows up to 65 m^3/s. This would be adequate to cope with the maximum flows encountered in the River Tywi. Such dosing equipment also has a capacity of, typically 90 t of lime, which would be more than sufficient to cover the very few days of extreme flows encountered in the Llyn Brianne catchment. A single doser on one of the lake inputs should therefore be capable of maintaining the pH value of the water at more than 6.0. This would result in substantial overdosing of the stream and the possibility of serious re-acidification if the doser failed. The doser would also have to be re-filled every two weeks during periods of very high flow. For these reasons, the use of two dosers (one on each input stream), each operating well within its capacity, was recommended.

When the lake is being filled (it is used as a reservoir), the flow from Llyn Brianne is only one seventh that of the River Doethie. The model was therefore run assuming high flows (low water quality) for the river inputs and a flow leaving the lake (1.07 m^3/s) one-

Table 3. Typical liming requirement using two dosers on input stream dosing at same rate

Flow	% of year	Dose-rate of Ca for each of two dosers (t/week)	Tonnes-Ca per year (total input for both streams)	Tonnes of $CaCO_3$ per year	Tonnes of $CaCO_3$ per year assuming 80% dissolution	Tonnes of $CaCO_3$ per year assuming 50% dissolution
Extreme flow and worst water quality	1	10.0	10.4	26.0	32.5	52.0
High flow and poorest quality water	2	3.0	6.2	15.6	19.5	31.2
High flow and 'typical' poor-quality water	18	1.2	22.4	56.2	70.3	112.4
Medium flow and water quality	27	0.3	8.4	21.1	26.4	42.2
Low flow and good-quality water	52	0.1	2.7	6.8	8.5	13.6
Total	100	14.5	50.1	125.8	157.3	251.6

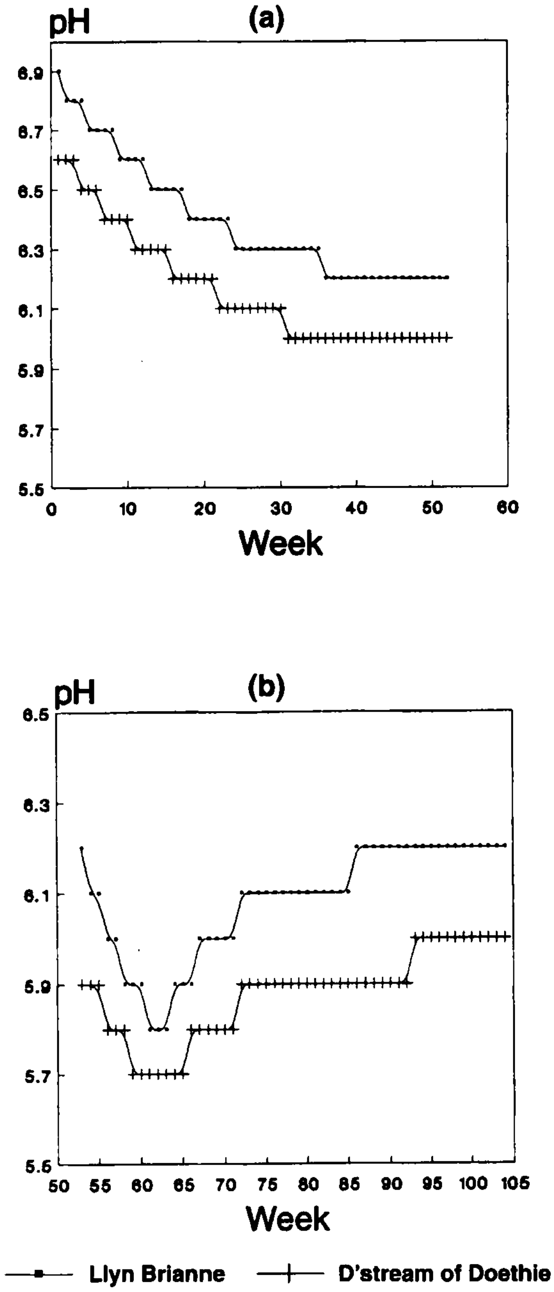

Fig. 4. Graph of model output showing effect of dosing input streams on pH in lake and River Tywi under high flow conditions (a) after lake liming and (b) after dosing interruption of ten weeks

seventh of that from the Doethie (7.49 m^3/s). Under these conditions the model predicted that 2.5 t of calcium per week from each doser (7.8 t of lime, assuming 80% dissolution)[10], would be required to maintain the pH of the Tywi below the Doethie/Tywi confluence above 6.0.

Using the dosing-rate appropriate to the high flow conditions (1.2 t Ca per week for each doser), the LASER model estimated that a dosing interruption of up to 5 weeks could be tolerated before the pH of the Tywi downstream from the Doethie input decreased below 6.0 (Fig. 4).

Conclusions

1. Under typical high flow conditions it is predicted that a dose-rate of 1.2 t Ca per week would be required from two dosers sited on the input streams.
2. Under extreme conditions, when very high flows (highest 2%) are combined with the poorest measured water quality, the dose-rate from each system would have to be increased to 10 t Ca per week.
3. Commercially available lime dosers are capable of delivering sufficient lime to neutralize acidic inputs even under extreme conditions. However, the actual amount of lime would depend upon the dissolution rate.
4. When the output is restricted in order to fill the lake, overdosing (1.2–4.0 t Ca per week from each doser at high flows) may be necessary to neutralize acidic waters entering the River Tywi from the River Doethie.

Acknowledgements

The authors wish to thank the Environment Agency for funding this work. The model (LASER) which has been established to simulate acidification and liming in streams and lakes can be obtained from Professor Paul Whitehead at the University of Reading.

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