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THE EFFECTS OF ORGANIC ANIONS ON ALKALINITY MEASUREMENTS IN ORGANIC-RICH WATERS IN NOVA SCOTIA

by

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ABSTRACT

The impact of organic anions on both negative and positive alkalinity measurements in organic-rich waters in Nova Scotia has been evaluated and been found to be minimal, except in the uncommon situation of combined high DOC concentrations and 'high' pH.

Evaluation of the data suggests that SRA^-, not A^-, is the reactive organic species.

From this review of the data, the following recommendations are made:

1. Continue the established Gran alkalinity procedures.
2. In organic waters, continue the simultaneous analyses of sulfate by colorimetry and ion chromatography.
3. Make at least some direct measurements of dissolved CO_2 in some organic waters.

RÉSUMÉ

Les répercussions des anions organiques sur les mesures négatives et positives de l'alcalinité dans des eaux à forte teneur organique en Nouvelle-Écosse ont été évaluées et déclarées négligeables, sauf pour une situation inusitée où l'on retrouve à la fois des concentrations élevées de DOC et un pH élevé.

À la lumière de l'évaluation des données, on conclut que l'espèce organique réactive est SRA^- et non A^-.

Les recommandations suivantes ont été faites à la suite de l'examen des données :

1. continuer d'appliquer les modalités établies pour déterminer l'alcalinité de Gran;
2. dans les eaux organiques, continuer de faire simultanément des analyses des sulphates par colorimétrie et par chromatographie des ions;
3. faire quelques mesures directes du CO_2 dissous dans certaines des eaux organiques au moins.

EXECUTIVE SUMMARY

The realization of the presence of reactive and titratable organic anions in the strongly colored waters of Nova Scotia has called for reexamination of some of the analytical methods applied to such waters. This report discusses the effects of organic anions on the established Gran alkalinity titration procedures. The author concludes that the organic anion interference is in most cases minimal, and recommends that the alkalinity procedures be continued, that sulfate continue to be analyzed by both ion chromatographic and colorimetric methods, and that some direct measurements of dissolved carbon dioxide be made.

RÉSUMÉ EXÉCUTIF

La présence d'anions organiques réactifs et titrables dans des eaux fortement colorées de la Nouvelle-Écosse a justifié un examen de certaines des méthodes d'analyse de ces eaux. Le présent rapport porte sur les effets des anions organiques sur les modalités de titrage établies pour déterminer l'alcalinité de Gran. L'auteur conclut que l'interférence des anions organiques est, dans la plupart des cas, négligeable et il recommande qu'on continue d'appliquer les modalités établies pour déterminer l'alcalinité, qu'on continue d'analyser les sulphates tant par chromatographie des ions que par méthode colorimétrique et qu'on procède à des mesures directes du gaz carbonique dissous.

ABSTRACT

The impact of organic anions on both negative and positive alkalinity measurements in organic-rich waters in Nova Scotia has been evaluated and been found to be minimal, except in the uncommon situation of combined high DOC concentrations and 'high' pH.

Evaluation of the data suggests that SRA^-, not A^-, is the reactive organic species.

From this review of the data, the following recommendations are made:

1. Continue the established Gran alkalinity procedures.
2. In organic waters, continue the simultaneous analyses of sulfate by colorimetry and ion chromatography.
3. Make at least some direct measurements of dissolved CO_2 in some organic waters.

INTRODUCTION

Alkalinity measurements are made by titration of a water sample with an acid until some endpoint is reached. The amount of acid consumed is the measure of the amount of alkalinity present. Although not always explicitly stated, the assumption is usually made that in samples with higher pH the titratable species are CO_3^{--} and HCO_3^-, and this assumption hold true for many waters. In organic-rich waters, however, another titratable species, an organic anion, may be present. Following the nomenclature of Oliver _et_ _al_. (1983) the organic acid is indicated as HA, which dissociates:

$$HA = A^- + H^+.$$

The dissociation 'constant' for this reaction changes with pH. Figure 1 is a diagram showing the relative concentrations of species of interest as a function of pH. The figure is drawn for a dissolved organic carbon (DOC) concentration of 10 mg L^{-1}; the relative proportions of HA and A^- are calculated from pH and DOC by the method of Oliver _et_ _al_. (1983). HCO_3^- is calculated from pH, assuming a CO_2 pressure of $10^{-2.5}$. The diagram shows H^+ concentrations increasing much more rapidly than HA at pHs below 4. DOC concentrations in some waters are as high as 40 mg L^{-1}, however, so that at pHs between 3.7 and 4.0, there might be equal concentrations of H^+ and HA. Similarly, HCO_3^- concentrations increase rapidly at higher pHs.

Since 1980, in the Moncton Laboratory of Environment Canada's Water Quality Branch, alkalinity titrations in waters of low or negative alkalinity have been subjected to Gran analysis (Environment Canada 1985). The procedure is based upon the principle that added increments of mineral acid increase H^+ concentration linearly at low pH values (Stumm and Morgan, 1970). The procedure is applied to samples having an initial pH of 6.0 or lower.

Samples with pH greater than 6.0 are analyzed by the two pH endpoint method, reaching a final pH of 4.2. Samples with pH in the range 4.1 to 6.0 are acidified to pH 4.1 or slightly lower, before the 'Gran' titration is performed. The final pH reached would be 3.8 or slightly lower. Samples with pH in the range 3.5 to 4.1 are titrated until the pH is lowered by 0.3 pH units. For these samples, the final pH could be as low as 3.2. There are, however, very few samples in this pH range.

Figure 2 shows the percentage of A^- that could be titrated to HA from the starting pH shown on the Y axis to the endpoint pHs of 4.2 and 3.8. These percentages were calculated from the equations given by Oliver et al. (1983), and show that for a sample initially at pH 6.0 and titrated ultimately to pH 3.8, that nearly 43% of the A^- present could be titrated, if the A^- reacts with H^+ rapidly enough. The automated alklinity procedure takes about one minute (T.L. Pollock, Water Quality Branch, Atlantic Region, personal communication, February, 1986).

In most samples at pH 6.0, however, DOC concentrations are low, so 43% of a small concentration of A^- would produce only a small amount of interference. Conversely, most samples with high DOC concentrations have low pHs; therefore, a smaller percentage of A^- could be titrated, so that, in this case too, the inference should be small. There are, however, some streams that have pH in the range 5.5 to 6.1, and also have high DOC concentrations (10.0 to 26.0 mg L^{-1}). In such samples, the organic anion interference can be shown only indirectly, by its influence upon apparent CO_2 pressure calculated from pH and from the assumption that all alkalinity is HCO_3^- alkalinity.

The analytical data to be discussed here were generated by the laboratory of Environment Canada's Water Quality Branch, Atlantic Region, in Moncton, New Brunswick. Alkalinity measurements by the procedure described above for samples at pH 6.0 or lower have been carried out there since mid-1980, and by now several thousands of such analyses have been performed. The data to be discussed here are for the LRTAP Monitor Rivers in Nova Scotia, and for some intensively sampled, highly organic streams in or near Kejimkujik National Park (KNP), Nova Scotia.

RESULTS

Negative Alkalinities

Negative alkalinities are reported for samples at pH 5.0 or lower, and are assumed merely to reflect the pH, or rather, the free H^+ concentration in the initial sample. This assumption is easily tested. The imprecision in the pH measurement is assumed to be of the order of 0.1 pH units, and plots were prepared of pH from 4.0 to 5.0 versus alkalinity from 0 to -5 mg L^{-1} $CaCO_3$, showing the alkalinity values to be expected from the measured pH ± 0.1 pH units. Then paired pH - alkalinity data can be entered on such plots, and the deviations from predicted alkalinity can be easily seen. Figure 3 shows such a plot of data for the Mersey River at George Lake, KNP. The samples are all at pH 4.8 or higher. The positive contribution of the organic anion to the alkalinity is evident, but the effect is small, of the order of 6 μeq L^{-1}. DOC for these samples ranges from 3 to 14 mg L^{-1}.

For Atkins Brook, KNP, a small highly organic headwater stream in which DOC ranges from 7 to 42 mg L^{-1} and pH ranges from 4.1 to 4.5, the data are shown in Figure 4. Because of the low pH values, the organic contribution to the alkalinity is not visible.

In Peskawa Lake, KNP, DOC ranges from 3 to 37 mg L^{-1} and pH ranges from 4.0 to 4.9. The pH and alkalinity data are shown in Figure 5. The plot shows, as does Figure 3, an obvious interference at higher pH and, as does Figure 4, no visibile interference at lower pH.

These three plots are typical of the results obtained for many such plots for streams or lakes in or near KNP and for the LRTAP Monitor Rivers in Nova Scotia. In general, the organic anion interference is noticeable only at the upper end of the pH range in which negative alkalinities can occur, and the effect is small, of the order of 6 to 14 μeq L^{-1}. These results are in accord with the consideration of the percent of organic anion that could be titrated from the starting pH of the sample to the endpoint pH of 3.8.

Positive Alkalinities

The evaluation of the organic contribution to positive alkalinity measurements can be established only indirectly, because the expected alkalinity cannot be predicted simply from pH. CO_2 pressure must be considered as well. HCO_3^- concentration is calculated from pH, an assumed CO_2 pressure, and the equilibrium constant for the reaction:

$$H_2O + CO_2 = H^+ + HCO_3^- ,$$

where $$K = [H^+][HCO_3^-]/P_{CO_2}$$

and, in log notation, $pK + pP_{CO_2} = pH + pHCO_3^-$, where p is used to denote negative logarithm of, and rearranging,

$$pHCO_3^- = pK + pP_{CO_2} - pH .$$

Most surface waters have a somewhat higher CO_2 pressure than that predicted by assuming equilibrium with atmospheric CO_2, because the reactions that generate CO_2, respiration and decay, are more rapid than those involving exchange of CO_2 between water and air. The degree of supersaturation is not usually very high, being of the order of 5 to 10 times atmospheric. In applying the CDR model to rivers in Newfoundland and Nova Scotia, Thompson (1982) used a mean CO_2 pressure of $10^{-2.5}$ or ten times atmospheric, because that was the pressure that best related measured pHs to measured alkalinities. To evaluate the organic anion interference to positive alkalinity measurements, the calculated CO_2 pressures must be considered. Regressions were run between calculated pP_{CO_2} and DOC for those rivers and streams in Nova Scotia that had enough positive alkalinities so that regressions could be run. The regressions varied considerably in significance, and the more significant ones were so apparently only because the number of data pairs was high, but the regressions were all of the same form:

$$pP_{CO_2} = a + b[DOC] , \quad \text{where b is negative,}$$

showing that, in general, higher CO_2 pressures were calculated for samples with higher DOC concentrations. This is the result to be expected if the organic anion is contributing to the measured alkalinity. Table 1 lists some of the results of these regressions. Note that the mean pH and DOC are mean values for those samples that have positive alkalinities. The intercepts on the Y axis all indicate lower CO_2 pressures than the mean calculated CO_2 pressures, although all are higher than atmospheric ($pP_{CO_2} = 3.5$). The intercepts might be taken as the mean actual CO_2 pressures, except that the error estimates on the intercepts are high.

Roger Brook, KNP, is one of the streams in which high DOC concentrations occur in samples with pH in the range 5.5 to 6.1. For these data, A^- was calculated from pH and DOC by the method of Oliver et al. (1983), and SRA^- (soluble reactive A^-) was calculated as the difference between colorimetric and chromatographic sulfates. The concentration of each that could be titrated from the pH of the sample to a final pH of 3.8 was also calculated. A^- concentrations are too high, even when only the potentially titratable fraction of it is considered. In many cases the potentially titratable concentration of A^- was greater than the measured alkalinity. SRA^- concentrations, on the other hand, are of the same order of magnitude as measured alkalinities, and when only the potentially titratable concentrations of SRA^- are considered, they are lower than the alkalinities. Bicarbonate alkalinity was calculated from pH and an assumed CO_2 pressure of $10^{-2.5}$. The sum of titratable SRA^- and bicarbonate alkalinity was then compared with the measured alkalinity. The results of these calculations are shown in Table 2. As may be seen, in many cases, the sum of the titratable SRA^- and the bicarbonate alkalinity is very close to the measured alkalinities. If we accept that the calculated concentrations of HCO_3^- and titratable SRA^- are somewhere near correct, then we can compare their relative concentrations. The calculations show similar concentrations for HCO_3^- and titratable SRA^-, that is, the contribution of titratable SRA^- to the measured alkalinity is about half, and the amount ranges from 7 to 30 $\mu eq\ L^{-1}$. These data suggest that titratable SRA^- reacts completely with the titrant H^+, even though the elapsed time for each titration is very short.

The other example of a water body with pH 5.5 to 6.1 and DOC 7 to 13 mg L^{-1} is the Meteghan River in southwestern Nova Scotia. Some of the data for this river are shown in Table 3. SRA^- concentrations are lower in this river for similar values of pH and DOC than for Rogers Brook. It is likely that the organic matter in the river is more indurated than that in the headwater stream Rogers Brook. According to the calculations in Table 3, the organic contribution to the measured alkalinity ranges from 4 to 19 $\mu eq\ L^{-1}$. The greater part of the measured alkalinity in samples from the Meteghan River is apparently bicarbonate alkalinity.

DISCUSSION

The organic anion contribution to the alkalinity titrations is greatest for those samples with high DOC concentrations titrated over the widest pH range. In such samples, the organic anion can contribute to half or more of the measured alkalinity, or up to 30 μeq L^{-1} (Table 2). In the majority of samples, however, either the DOC concentrations are low or the sample pH is low, and the sample is titrated only over a narrow range of pH, thus minimizing the organic input. In these cases, the organic contribution to the measured alkalinity is small, of the order of 6 to 15 μeq L^{-1}. The effect of the organic anion upon samples at low pH, with so-called 'negative' alkalinities, is to make the measured alkalinity less negative than it would otherwise be, but only by a small amount, again because of the narrow pH range of the titration.

The term SRA^- was defined by Thompson (1985), and refers to that part of the organic anion that reacts with Ba^{++} in the colorimetric analysis for sulfate, and is calculated as the difference between colorimetric and ion chromatographic sulfates. In the evaluation of the impact of organic anions on positive alkalinity measurements, evidence was presented to show that in alkalinity titrations, SRA^- is apparently the reactive species, not A^- (Tables 2 and 3). This is a strong argument in favour of continuing the simultaneous analyses of sulfate by colorimetry and ion chromatography, because that is the only way of measuring SRA^-.

The Gran alkalinity titrations should be continued as well, because in most samples the organic interference is minimal, and because 'negative' alkalinities are one of the most convincing ways to show acidification of a water body.

The discussion of the relative amounts of organic and bicarbonate alkalinities depends to a large extent upon assumed CO_2 pressures. From measurements made elsewhere, it is known that CO_2 pressures in surface waters are likely to be higher than atmospheric, but direct measurements of dissolved CO_2 in organic waters in Nova Scotia would be very useful for supporting such calculations.

RECOMMENDATIONS

1. Continue the Gran alkalinity procedure as described in the Laboratory Operations Manual.
2. In organic waters, continue to measure sulfate colorimetrically (16304L) and by ion chromatography (16309L), because that is the only measure of the important species, SRA^-.
3. Make (some) direct measurements of dissolved CO_2. The procedure is simple, merely requiring measurement of pH and alkalinity, then equilibrating the sample with air, and re-measuring pH.

Equipment:

Tank of compressed air, gas washing bottle, sealed reaction vessel, tubing, fritted disk, magnetic stirrer, pH electrodes and meter. Optional: Strip chart recorder.

Procedure:

1. Measure pH and (positive) alkalinity.
2. Place some of the sample in the sealed reaction vessel, stir vigorously,

3. Pass air through distilled water in the gas washing bottle, then into the reaction vessel via the fritted disk, for about 20 minutes. The air and sample water should be very well mixed.
4. Remeasure pH.

Alternatively, attach a strip chart recorder to the pH meter, and record pH during aeration until it no longer changes.

The change in pH is a direct measure of the excess CO_2 in the sample in log units.

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Environment Canada. 1985. Operational Methods Manual, 'Alkalinity and pH'. Water Quality Branch, Atlantic Region.

Oliver, B.G., Thurman, E.M., and Malcolm, R.L. 1983. The contribution of humic substances to the acidity of coloured natural waters. Geoch. Cosmoch. Acta 47, 2031-2035.

Stumm, W. and Morgan, J.J. 1970. Aquatic Chemistry. Wiley-Interscience, New York, p. 144.

Thompson, M.E. 1982. The cation denudation rate as a quantitative index of sensitivity of eastern Canadian rivers to acidic atmospheric precipitation. Water, Air and Soil Pollution, 18: 215-226.

Thompson, M.E. 1985. Cation denudation rates of rivers in Nova Scotia, 1971-1974 and 1977-1982. NWRI Contribution #85-28.

TABLE 1. Summary of regression data for rivers and streams in Nova Scotia, where $pP_{CO_2} = a + b[DOC]$.

River or Stream	n	a	b	$\overline{DOC}$	$\overline{pH}$	$\overline{pP_{CO_2}}$
Meteghan	29	3.12	-0.06	9.5	5.8	2.56
Kelley	27	2.89	-0.03	7.0	6.1	2.70
Wallace	32	2.86	-0.02	3.7	6.7	2.78
Mersey GL	29	3.30	-0.06	6.5	5.3	2.93
Mersey MF	206	2.86	-0.03	10.1	5.2	2.56
Medway	34	3.13	-0.06	6.3	5.5	2.77
La Have	36	3.06	-0.05	7.0	6.0	2.74
Liscomb	16	3.44	-0.08	8.9	5.2	2.69
St. Marys	29	2.80	-0.03	4.3	6.2	2.69
Clam Harbour	24	2.95	-0.03	6.0	6.4	2.75
Little	10	3.17	-0.06	10.4	5.0	2.53
Beaverskin LO	75	3.15	-0.02	1.8	5.4	3.10
Grafton Brook	119	2.98	-0.06	5.0	5.7	2.67
Mt. Tom Brook	6	3.12	-0.04	12.6	5.0	2.59
Rogers Brook	162	2.85	-0.03	11.9	5.4	2.44
Moose Pit Brook	13	2.64	-0.02	19.4	5.0	2.33
Pollock LO	123	2.81	-0.04	6.8	5.8	2.55

TABLE 2. Some data for Rogers Brook, KNP.

Sample Date	pH	DOC mg L^{-1}	SRA$^-$ μeq L^{-1}	A Titratable SRA$^-$ μeq L^{-1}	B Predicted Alkalinity μeq L^{-1}	A + B	Measured Alkalinity μeq L^{-1}
<u>1983</u>							
06-23	5.8	12.0	60	24	32	56	58
07-12	5.9	12.0	63	26	40	66	66
07-14	5.9	9.6	56	23	40	63	60
07-31	5.7	14.0	69	27	25	52	52
08-02	5.6	12.0	56	21	20	41	44
08-08	5.7	12.0	67	26	25	51	58
08-24	5.7	10.0	35	14	25	39	56
10-07	5.7	14.0	54	21	25	46	46
<u>1984</u>							
06-18	5.7	12.0	46	18	25	43	50
06-21	5.6	15.0	58	22	20	42	44
06-25	5.8	11.0	46	19	32	51	46
07-02	5.6	16.0	67	25	20	45	40
07-18	5.6	18.0	71	27	20	47	42
07-19	5.5	18.0	69	25	16	41	48
07-23	6.0	19.0	69	29	50	79	72
07-30	5.9	13.0	52	22	40	62	72
08-06	5.8	10.0	17	7	32	39	42
08-20	5.5	22.0	83	30	16	46	50
09-03	5.8	21.0	75	30	32	62	64
09-10	5.9	12.0	48	20	40	60	66
09-24	5.5	16.0	67	24	16	40	28
10-01	6.1	12.0	38	17	63	80	46

TABLE 3. Some data for Meteghan River, southwestern Nova Scotia.

Sample Date	pH	DOC mg L^{-1}	SRA$^-$ μeq L^{-1}	A Titratable SRA$^-$ μeq L^{-1}	B Predicted Alkalinity μeq L^{-1}	A + B	Measured Alkalinity μeq L^{-1}
<u>1982</u>							
12-07	5.7	9.9	19	8	20	28	28
<u>1983</u>							
01-18	5.5	13.0	21	8	13	21	20
03-08	5.5	7.8	21	8	13	21	18
04-12	5.5	7.0	19	7	13	20	18
06-22	5.8	9.2	29	12	25	37	34
07-13	6.0	9.2	31	13	40	53	44
08-09	5.9	9.2	19	8	32	40	40
09-23	5.8	12.0	25	10	25	35	52
10-20	5.8	12.0	46	19	25	44	44
11-15	5.8	12.0	33	13	25	38	46
12-14	5.6	12.0	31	12	16	28	36
<u>1984</u>							
05-15	5.6	7.7	10	4	16	20	26
06-20	5.8	10.0	25	10	25	35	34
07-17	5.8	11.0	46	19	25	44	36
08-08	5.9	11.0	33	14	32	46	38
10-10	5.9	10.0	17	7	32	39	42
11-14	6.1	13.0	15	7	50	57	42

FIGURES

FIGURES

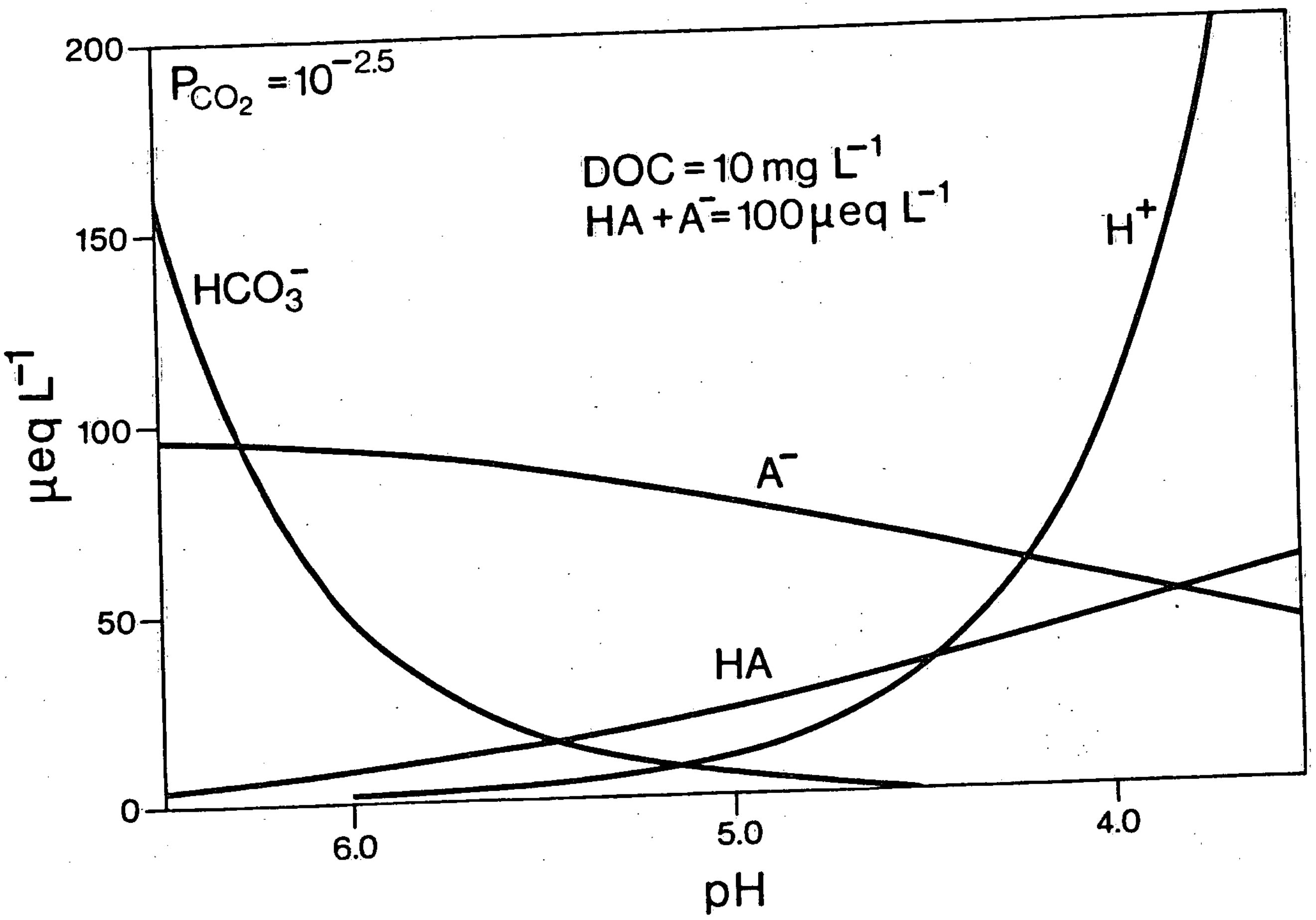

Figure 1. Plot showing the relative proportions of species of interest (HCO_3^-, HA, A^-, H^+) over the pH range 6.5 to 3.5.

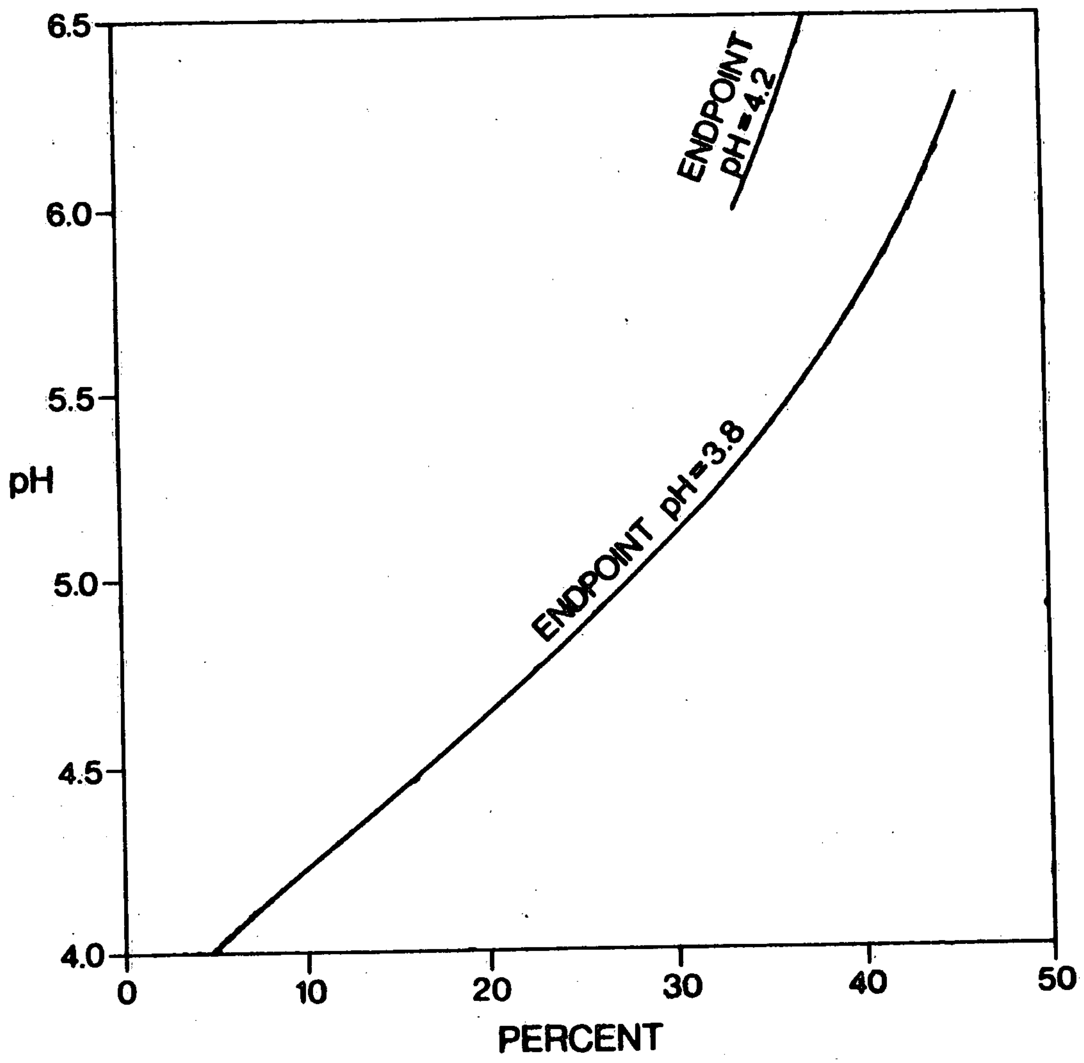

Figure 2. Graphical presentation of the percent of A^- or SRA^- that could be titrated from the initial pH as shown to the end point pH of 4.2 or 3.8.

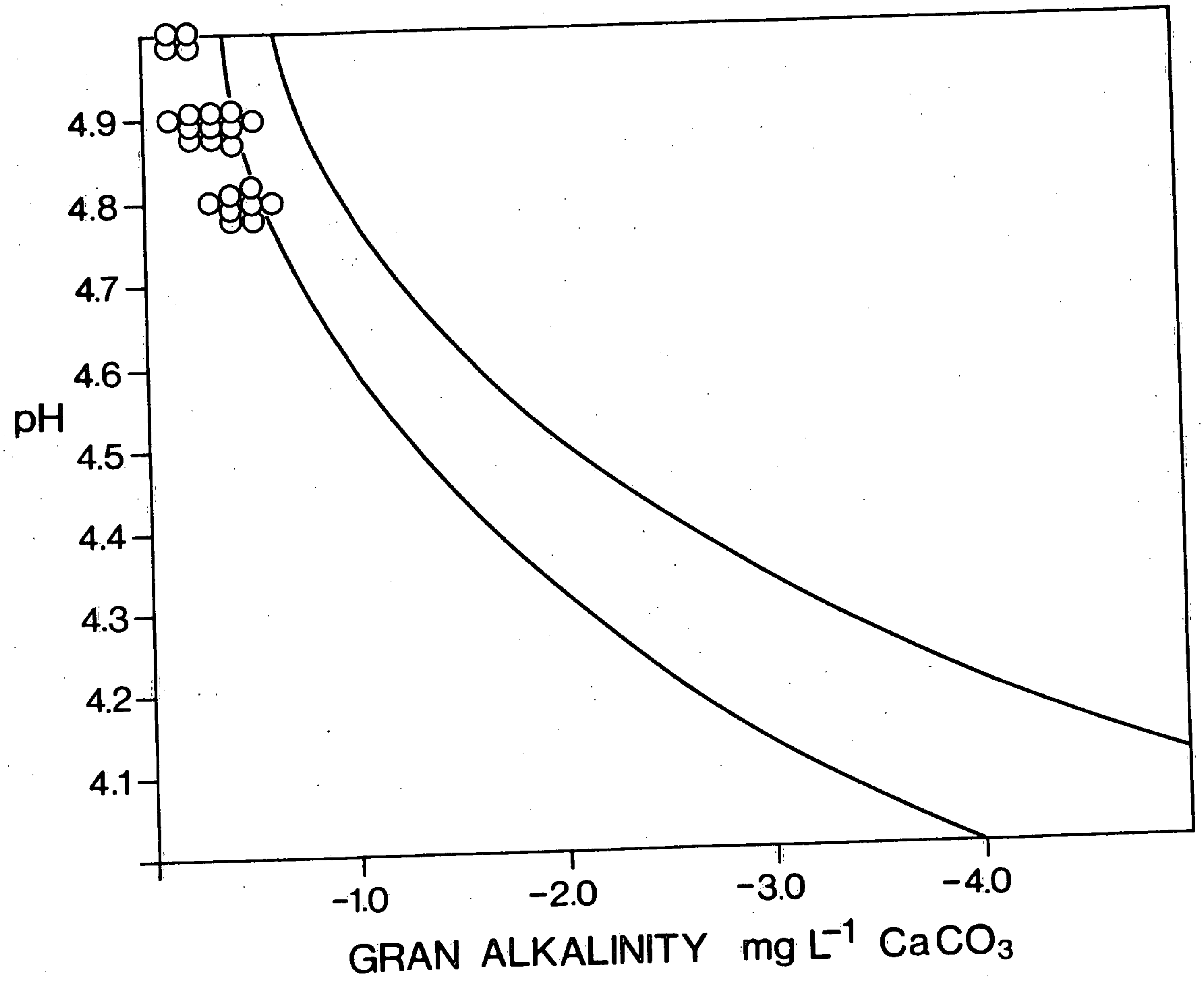

Figure 3. Plot of negative alkalinity data for the Mersey River at George Lake, KNP.

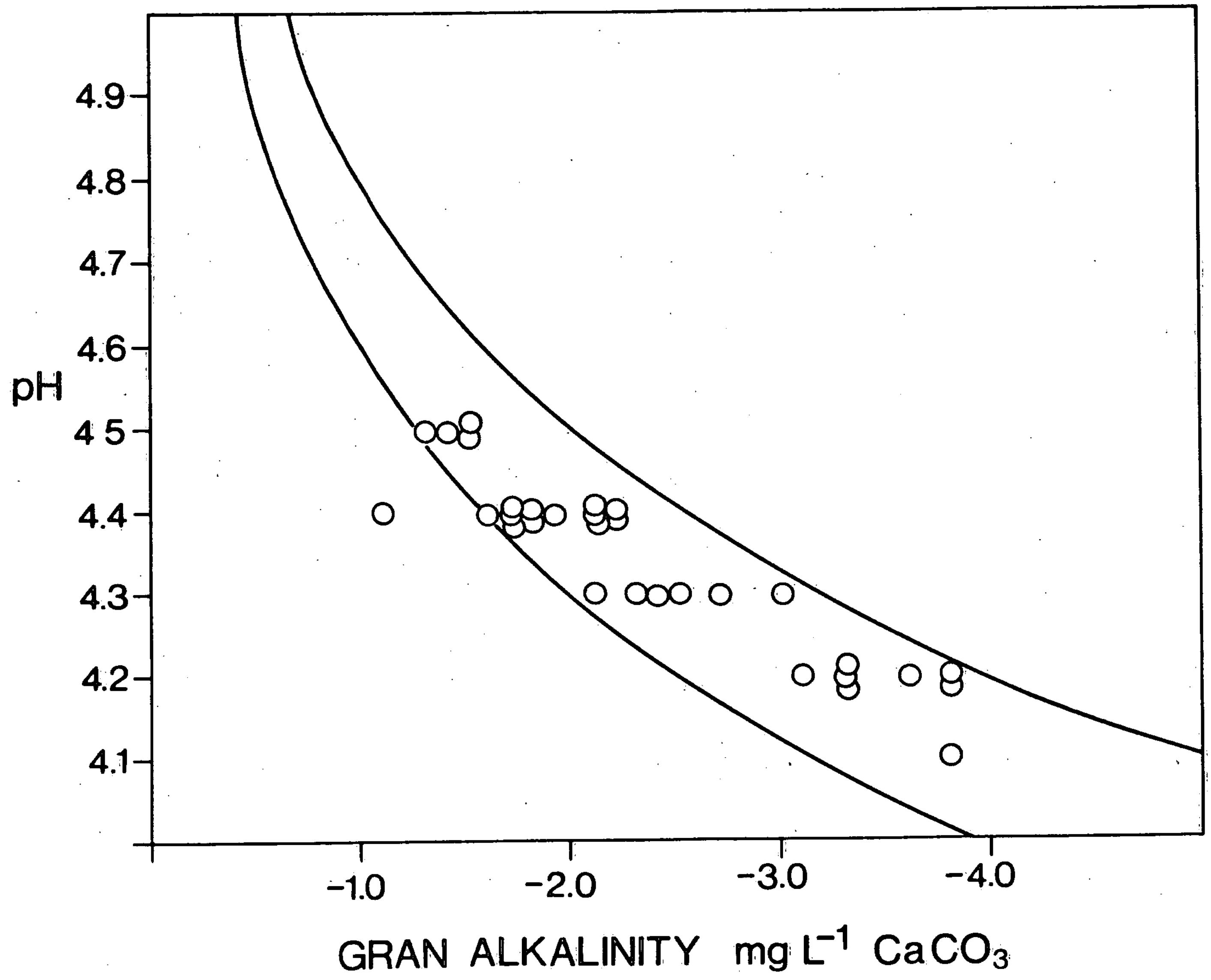

Figure 4. Plot of negative alkalinity data for Atkins Brook, KNP.

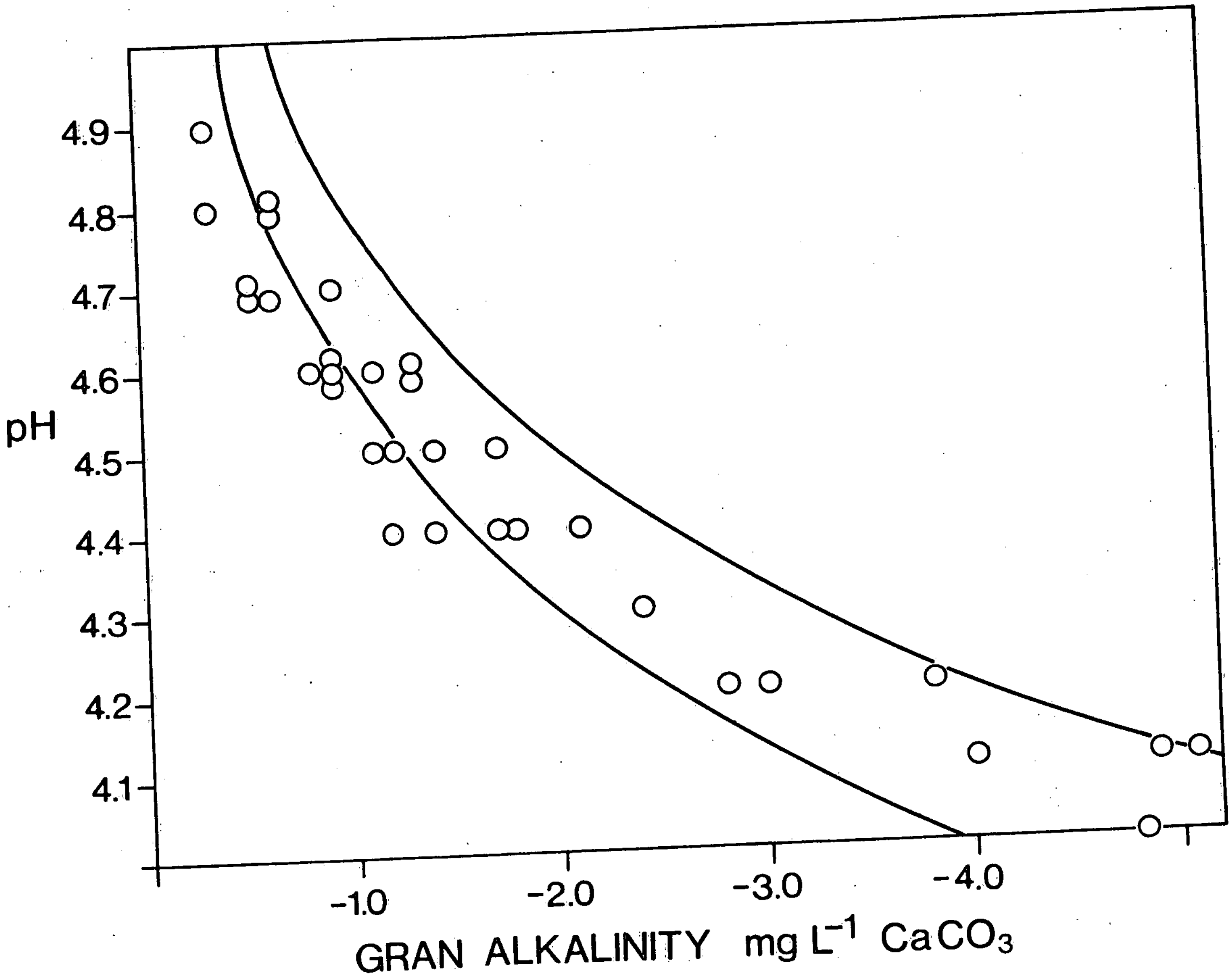

Figure 5. Plot of negative alkalinity data for Peskawa Lake, KNP.