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**SULFATE IN COLOURED WATERS.
II. EVALUATION OF APPROACHES FOR
CORRECTING HISTORICAL COLORIMETRIC DATA**

by

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ABSTRACT

The various approaches for correcting historical colorimetric sulfate data were discussed and evaluated. A simple and direct approach was found to be satisfactory. To correct historical colorimetric data, data sets are first categorized and grouped together based on geographical locations and seasonal variations of DOC (or colour) of a specific site, river, lake (or groups) which have similar amounts and nature of organic matter. For each group, the colorimetric and chromatographic SO_4 values are then obtained and related by an equation, which is used to convert the corresponding historical values to "true" SO_4 values.

EXECUTIVE SUMMARY

The ion chromatographic sulfate data generated from coloured waters have been found to be reliable, whereas their colorimetric counterparts were found to be biased high. The historical colorimetric SO_4 data need to be corrected to avoid biased interpretations and conclusions such as overestimation of SO_4 loadings.

The various approaches for correcting historical colorimetric data were evaluated. There is no simple and universal correction factor which readily corrects the colorimetric data. To correct historical colorimetric data, one simply obtains, case by case, the two types of SO_4 values, relates them by an equation and interpolates the corresponding historical values to obtain the true SO_4 values.

INTRODUCTION

The validity of sulfate measurements in organic-contaminated coloured waters has been of considerable concern to scientists studying acid rain due to the questionable quality of analytical data generated by colorimetric techniques. Up to about 1980, quantitative sulfate data were mostly generated by the colorimetric method using methylthymol blue (MTB). About this time, a new methodology, namely ion chromatography (IC), became available for routine SO_4 analysis. For coloured waters, the results by the two methods were different and many scientists suspected the MTB colorimetric data to be biased high, because coloured interferences could cause apparent higher SO_4 results. On the other hand, the IC data was relatively free of interferences (Kerekes et al. 1984, Pollock 1983, Underwood et al. 1983, Crowther and Wright 1980). However, there lacked concrete data to support the above view. Recently, Cheam et al. (1985) demonstrated that the IC methodology gives reliable results and confirmed that the MTB methodology gives biased high results.

The historical colorimetric data, if used uncorrected, can lead to unreliable interpretations and conclusions. For example, in calculating the historical acid loading, annually or spatially, the use of these raw data will yield substantial over-estimations of loading estimates. Depending on water types, the over-estimations can

easily range from ten to several hundred percent (Table 1). Naturally, this can lead to erroneous conclusions and decision making. Unless, there is some suitable means to know the degree of the bias and to correct the historical colorimetric data, they cannot be used as reliable SO_4 concentrations for scientific interpretation.

Several authors (Kerekes et al. 1984, Pollock 1983, Underwood et al. 1983) have attempted to find ways to correct the colorimetric data, but have met with only partial successes. Thus, in this paper, we wish to evaluate the various approaches and to find a satisfactory solution to render historical data useable.

EXPERIMENTAL

Fifteen coloured waters were used -- seven natural waters and eight humic acid fortified waters (Table 1). Each water was also spiked with SO_4 at three different levels equal to 0.5x, 1.0x and 2.0x the original SO_4 concentration in each of the waters as determined by IC (Table 1).

The ion chromatography (IC) analyses of SO_4 were carried out using an in-house automated system and a Dionex 2110 ion chromatograph. All samples were filtered before being introduced into a 50 μL sample loop. The eluent was prepared by dissolving 2.25 g of Na_2CO_3 and 2.25 g of NaHCO_3 in 10L of deionized distilled water. The eluent flow rate was 2.0 mL/minute. The sample passed through a guard column, a separator column, an anion fibre suppressor with dilute

H₂SO₄ as regenerant, and finally a conductivity detector. The detected signal was amplified and converted to concentration (C_{IC}) through a Hewlett Packard recorder/integrator.

The colorimetric SO₄ measurements were carried out using the automated methylthymol blue (MTB) method (Analytical Methods Manual, 1981). Using equimolar solution of BaCl₂ and MTB, the method allows Ba to react with SO₄ at low pH; on raising the pH, Ba reacts with MTB, leaving a grey uncomplexed MTB, which is measured and equated to SO₄ concentration (C_{MTB}) present in the sample.

Dissolved organic carbon (DOC in ppm) was analysed by the infrared Analyser Method (Analytical Methods Manual, 1981). Apparent colour, in Hazen Units, was determined by visual comparison using a Hellige Aqua Tester. Humic acid, HA, was purchased from Aldrich Chemical Co. Inc.; Na₂SO₄, Na₂CO₃ and NaHCO₃ from J.T. Baker Chemical Company. All containers were cleaned and stored in distilled water for at least one week before use (Cheam and Chau, 1982).

RESULTS AND DISCUSSION

Cheam et al. (1985) have validated the ion chromatography method for analysis of SO₄ using several organic-contaminated coloured waters. In their work, the IC sulfate values (C_{IC}) were demonstrated to be reliable and hence will be referred to as "true" SO₄ values in the text to facilitate the discussions. The colorimetric SO₄ values will be designated by C_{MTB} and the difference (C_{MTB} - C_{IC}) by ΔC.

Four of the waters prepared for this research had been previously used in an interlaboratory study (Aspila and Todd 1984), as part of the acid rain program, the Long Range Transport of Atmospheric Pollutants (LRTAP) program. The interlaboratory SO_4 results agree well with the in-house data and are plotted as L_4 points in Figures 1, 3, 5 and 10 for comparison purposes.

a. Colour - ΔC Approach

Kerekes et al. (1984) attempted to correct historical colorimetric data by relating the difference in SO_4 values, ΔC , versus water colour and found that when pooling all their data together, the relationship gave a poor fit. Repeating this approach with our own data, we likewise found that there was too much scattering to show any useful relationship. However, when we used the average ΔC values, some patterns began to show up, which are shown in Figure 1. In the Figure, each water is represented by two points connected by a vertical line. Each of the points represents the average ΔC value of six or more replicate analyses, and is tagged by the corresponding rounded C_{IC} value. As an example, for the water with 160 H.U. (Fig. 1), the vertical line connects the two points tagged with "2" and "6". The "2" (the lower number) means 2 ppm, the rounded C_{IC} value of the unspiked water, whereas the "6" (the higher number) means 6 ppm, the rounded C_{IC} value of the spiked water.

As seen in Figure 1, all the waters except two have their points with low C_{IC} values above the points with high C_{IC} values. (The exceptions are the two waters with colour 90 and 400 H.U.). To better see this general behaviour, a line is drawn to represent approximately the points with low C_{IC} values, and another line to represent the points with high C_{IC} values (Figure 1). One sees that the low C_{IC} line is distinct from, and higher than the high C_{IC} line. This suggests that the magnitude of C_{IC} has a certain function in data interpretation. This function could be hypothesized as follows: 1) for a given water colour, the higher the C_{IC} value the lower the ΔC ; and 2) for a given range of water colour, there must exist a series of similar ΔC curves, each being characterized by a specific C_{IC} value. The higher the C_{IC} value, the lower the curve.

To test the above hypothesis, we used and plotted in Fig. 2 the data from some 2500 observations on headwaters of the Atlantic region recently reported by Howell and Pollock (1985). This figure clearly shows that distinct least-squared curves can be drawn for the 2, 4, 6 and 8 ppm C_{IC} values, and that the 2 ppm curve is the highest followed gradually by the 4, 6 and 8 ppm curve (the lowest), which verifies the hypothesis.

It is clear from the above that C_{IC} is an important variable in data interpretation, and that if one attempts to derive a universal correlation between ΔC and colour alone, one will mask the effect of C_{IC} magnitude.

b. Organic Carbon - Δ C Approach

Another approach to correct historical data was attempted by Pollock (1983), who related Δ C and DOC but could not derive a satisfactory solution. Using our data to plot Δ C vs. DOC (Fig. 3), we also could not obtain a useful relationship, however, we observed two distinct behaviours: one for natural waters and one for HA fortified waters. Two different types of organic matter resulted in two distinct sets of curves. Obviously, the nature of organic matter, in addition to its amount, plays an important role in determining the amount of Δ C. Furthermore, for each type of organic matter, two lines could be drawn -- one for low C_{IC} values above the one for high C_{IC} values (as was observed in the last section). This again indicates that C_{IC} is an important variable in data interpretation.

In Figure 3, the solid circles used to represent the high C_{IC} values for natural waters were omitted in order to clearly show the four circles situated near the abscissa line. The latter circles represent the coordinates of water no. 2, which has a very high C_{IC} value (Table 1). This high value effectively minimizes Δ C the same way we observed in the last section, i.e., the higher the C_{IC} value, the lower the Δ C curves.

In short, Δ C depends not only on DOC concentration, but also on the nature of organic carbon and the magnitude of true SO_4 value. Therefore, if these two parameters are ignored, a universal Δ C-DOC

relationship cannot be satisfactorily derived. The nature of organic matter involves the types of chelating sites or complexing capacity of the organic matter (Cheam and Gamble 1974, Cheam et al. 1976) and should determine the extent of chemical reaction competing for Ba against MTB at pH -13.

c. The Importance of the True SO_4 Magnitude

We have shown in the last two sections that the SO_4 magnitude plays an important role in data interpretation. To best appreciate this importance, we plotted the SO_4 ratio, defined as C_{MTB}/C_{IC} against C_{IC} for both types of waters (Figs. 4-5). The plots readily reveal the ratio decreasing and approaching "1" (that is C_{MTB} approaches C_{IC}) as C_{IC} increases. Likewise, when we plotted the data reported by Howell and Pollock (1985), as shown in Figure 6, one clearly sees the rapid decrease of the ratio as C_{IC} increases. Furthermore, when we replotted these data as ΔC vs C_{IC} in Fig. 7, it was evident that ΔC rapidly decreases as C_{IC} increases for each of the 5 distinct curves pertinent to 5 different colour ranges.

d. Existence of Distinct $C_{MTB}-C_{IC}$ Curves

Since C_{IC} has been established to be an important variable in data analysis, and since the colorimetric SO_4 is the parameter that needs correction and is available as C_{MTB} , it seems quite relevant

to relate the two amounts directly rather than relating the calculated AC versus another variable. Figure 8, relating C_{MTB} vs. C_{IC} for HA fortified waters, shows well defined curves, each being characterized by a specific amount of DOC of 7.2, 3.9, 1.25 and 0.7 ppm (or specific colour of 440, 225, 90 and 50 H.U., respectively). Likewise, for natural waters, there are three distinct curves for three different DOC amounts -- 20, 14 and 9-11 ppm.

Figure 9, illustrating both the HA water curves and natural water curves, clearly shows existence of distinct curves depending on the nature and amount of DOC. For each type of water, as DOC increases the curve becomes higher with a general pattern that the natural water curves in spite of their high DOC content are relatively lower than the HA water curves. This suggests that for a given nature of DOC (or colour), at a small concentration range, there exists a relationship between its measured C_{MTB} and C_{IC} . This relationship can be described by a distinct curve describing C_{MTB} as a function of C_{IC} . Cheam et al. (1984) first referred to these curves in their 1984 internal report as "isocarbons" (meaning curves with the same amount and nature of dissolved organic carbon). In this report they showed the successful applicability of the "isocarbon" concept to correct the colorimetric SO_4 data. This concept has also been successfully applied by Howell and Pollock (1985) to establish the colour threshold using several hundred pieces of historical data. In view of the successes in the application of this concept, the detailed development of the "isocarbon" curves is described below.

Given a case where the nature of organic matter and a small range of its concentration is known, an "isocarbon" curve is described by a polynomial equation as follows.

$$C_{MTB} = a + b (C_{IC}) + c(C_{IC})^2 + \dots \quad (1)$$

The coefficients a, b, c, ... are derived from the curve plotting the measured C_{MTB} 's and C_{IC} 's. Depending on the case, equation (1) may be best described by a first order equation or by a higher order equation taking into account the realistic curvature of the "isocarbon". Considering a specific case illustrated in Figure 10 for a set of several natural waters with DOC of 10 ± 1 ppm, a second order was found to give a better fit than the first order and to give a realistic C_{MTB} - C_{IC} curve; the relationship was represented by the equation [$C_{MTB} = 3.05 + 0.66 (C_{IC}) + 0.009 (C_{IC})^2$].

e. The Approach for Correcting Historical Data

Based on the previous discussions, while it is clear there is no simple and universal correction factor for correcting colorimetric data, the "isocarbon" concept is a suitable approach. To correct historical colorimetric data, one first groups the data case by case based on the nature and concentration range of organic carbon in the

waters, obtains both C_{MTB} and C_{IC} values for each case and relates them by a representative equation as discussed above. One then interpolates the corresponding historical values to obtain the true SO_4 values. The data grouping refers to geographical locations such as a specific site, river, lake, or a group which has similar amount and nature of organic matter or colour. For example, the headwaters which Howell and Pollock (1985) grouped into five different colour ranges gave five distinct "isocarbons", having colour values of 0-20, 20-40, 45-60, 65-80 and 80-90 H.U. For illustration, only the two extremes of these "isocarbons" (i.e. colours 0-20 and 80-90) are shown in Figure 11 with their respective derived equations.

The data grouping also encompasses seasonal variations of DOC and colour. The DOC and colour in the Atlantic regional waters, according to Kerekes (personal communication), are linearly related; in this case, DOC and colour can be used interchangeably. On the other hand, if we deal with different types of organic matter, the two parameters may not be linearly dependent. In such instances, it is necessary to first identify the types of DOC (or ultimately the types of complexing sites) before the "isocarbon" approach can be properly applied.

Different types of DOC fractions have been identified in the same streams. For example, Bourbonniere (1986) found in his detailed work on organic matter fractionation that fulvic fraction predominates the DOC content leaving the bogs or headwaters (upstream), whereas further downstream, the humic fraction contributes greatly to the DOC

content. In these cases, it would be necessary to treat the data in terms of site-specific DOC, one site at a time, then extend to combine the sites having similar nature and amount of DOC.

In the cases where the range of the true SO_4 content (C_{IC}) is small, say 1-2 ppm or 5-6 ppm, the "isocarbon" approach may not be effective as it requires a significant range of C_{IC} for adequate derivation of an equation. A standard addition technique may be needed to help build an appropriate "isocarbon".

f. Conclusion

The "isocarbon" concept is a suitable approach for correcting historical colorimetric sulfate data. Table 2 compares the corrected results using this approach with the expected results for some of the water samples used.

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TABLE 1 % Overestimation of SO₄ Loadings

	Type of Coloured Water	Colour H.U.	DOC ppm	SO ₄ (IC) ppm	SO ₄ (MTB) ppm	% Over-estimation*
1	Pebbleloggitch	100	10.3	2.86	5.5	92
2	Moose River	60	12.0	8.99	9.6	7
3	Dickie Lake	100	11.0	1.61	4.73	194
4	Atkins Brook	160	14.0	1.67	6.13	267
5	Upper Mercy River	90	9.0	5.10	6.44	26
6	Mount Tom Brook	100	10.7	2.08	5.17	149
7	Sand Pond	400	20.0	1.95	9.57	391
8	Humic Acid Fortified Water	60	0.9	2.17	3.07	41
9	Humic Acid Fortified Water	100	1.2	2.09	3.50	67
10	Humic Acid Fortified Water	250	3.4	2.20	5.82	165
11	Humic Acid Fortified Water	400	6.6	2.07	8.40	306
12	Humic Acid Fortified Water	60	0.8	5.68	6.75	19
13	Humic Acid Fortified Water	100	1.3	5.09	5.38	6
14	Humic Acid Fortified Water	250	3.8	5.16	7.63	48
15	Humic Acid Fortified Water	400	7.2	5.09	10.74	111

* % over-estimation = $\frac{SO_4(MTB) - SO_4(IC)}{SO_4(IC)} \times 100$

TABLE 2 Comparison between corrected MTB Results and Expected Results (C_{IC}) for Water Samples with DOC of 10±1 ppm

Uncorrected MTB Results	Corrected MTB Results	Expected Results	% Difference (Corrected- Expected)
4.63	2.32	1.98	+17
4.7	2.42	2.70	-10
4.9	2.70	2.08	+30
5.2	3.13	2.96	+6
5.3	3.27	3.22	+2
5.7	3.82	4.27	-11
6.3	4.63	5.04	- 8
6.7	5.17	5.72	-10
7.5	6.22	6.34	-2
8.1	6.99	6.98	+0
8.6	7.63	7.50	+2
9.3	8.50	8.95	-6
9.9	9.23	9.12	+1
10.9	10.43	10.49	-1
11.2	10.78	10.41	+4

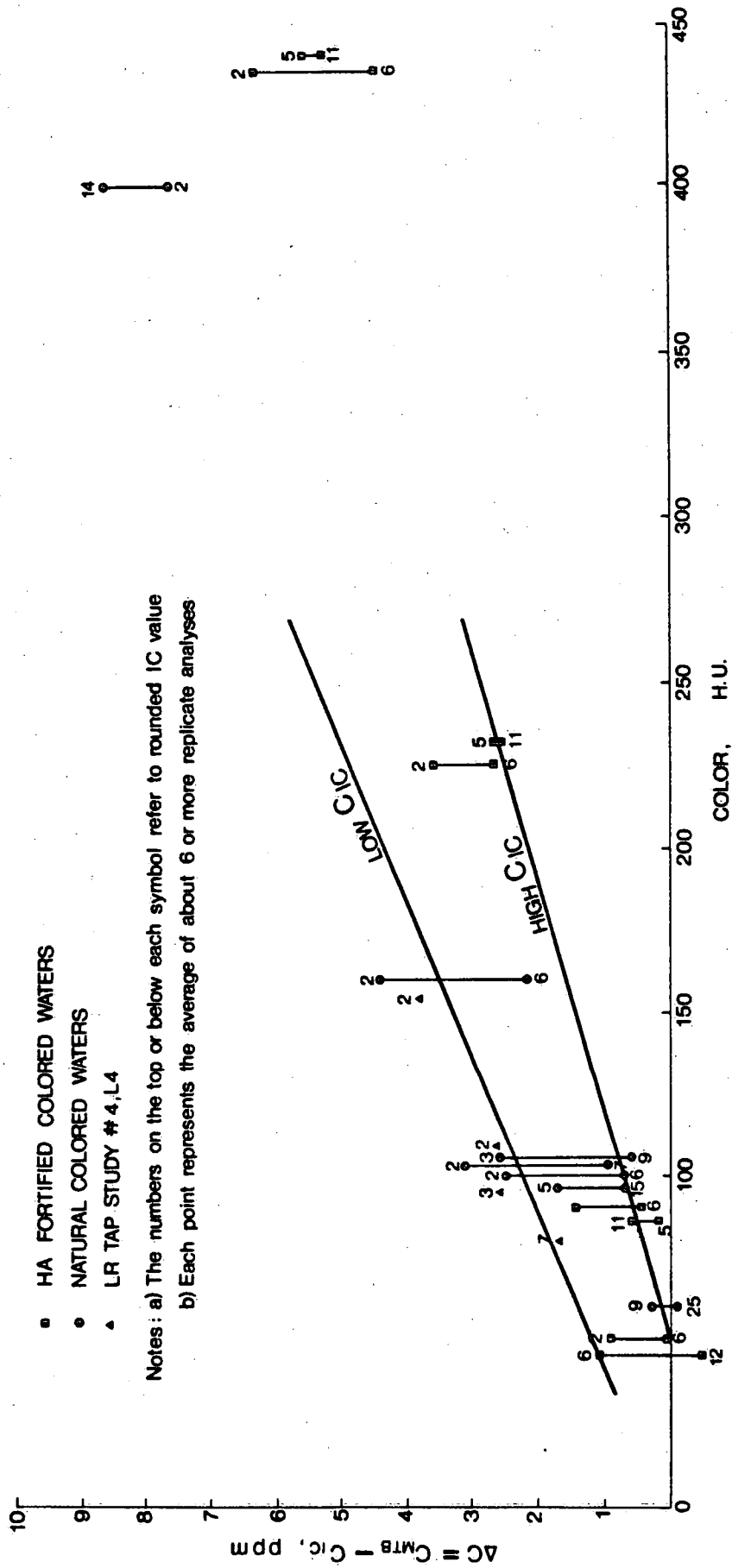


Fig. 1 RELATIONSHIP OF ΔC AND COLOR

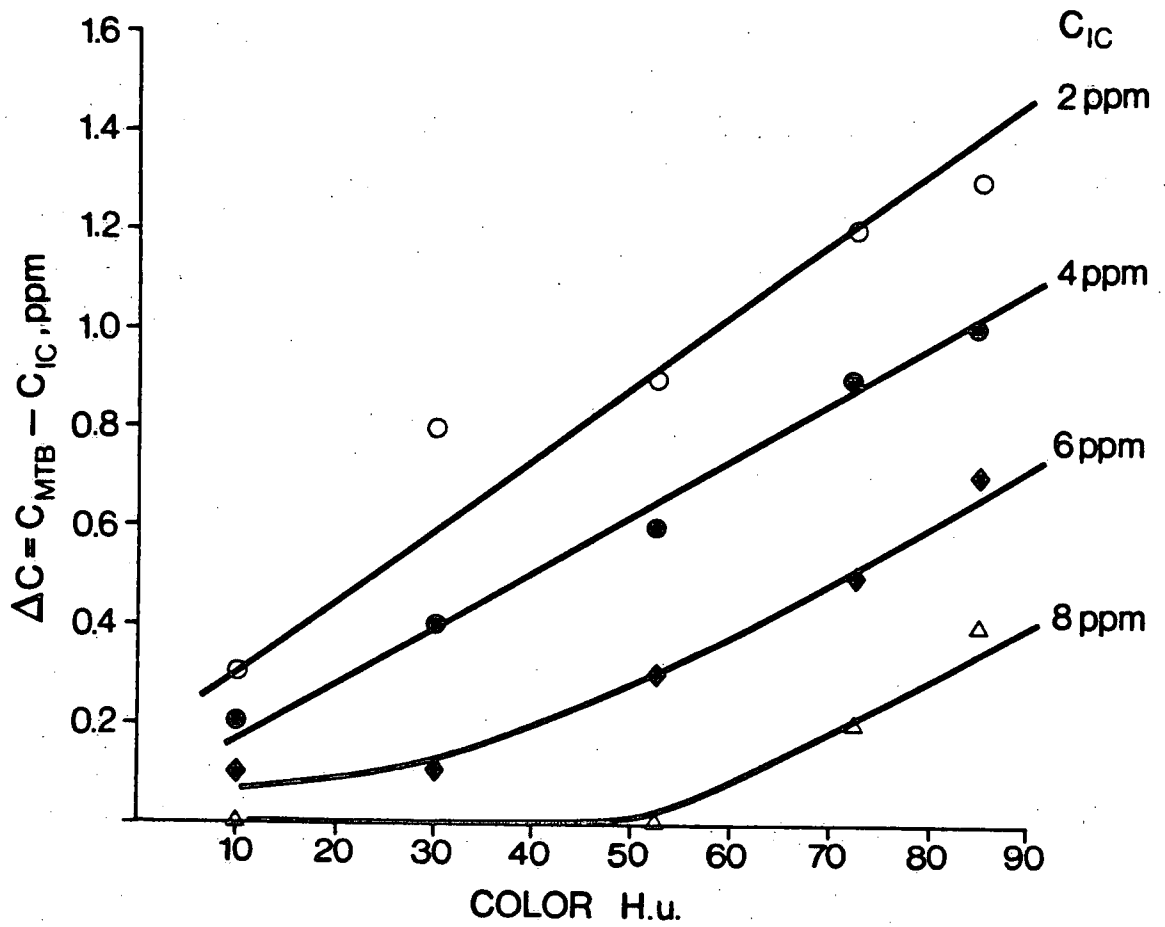


Fig. 2 Relationship of ΔC and Color

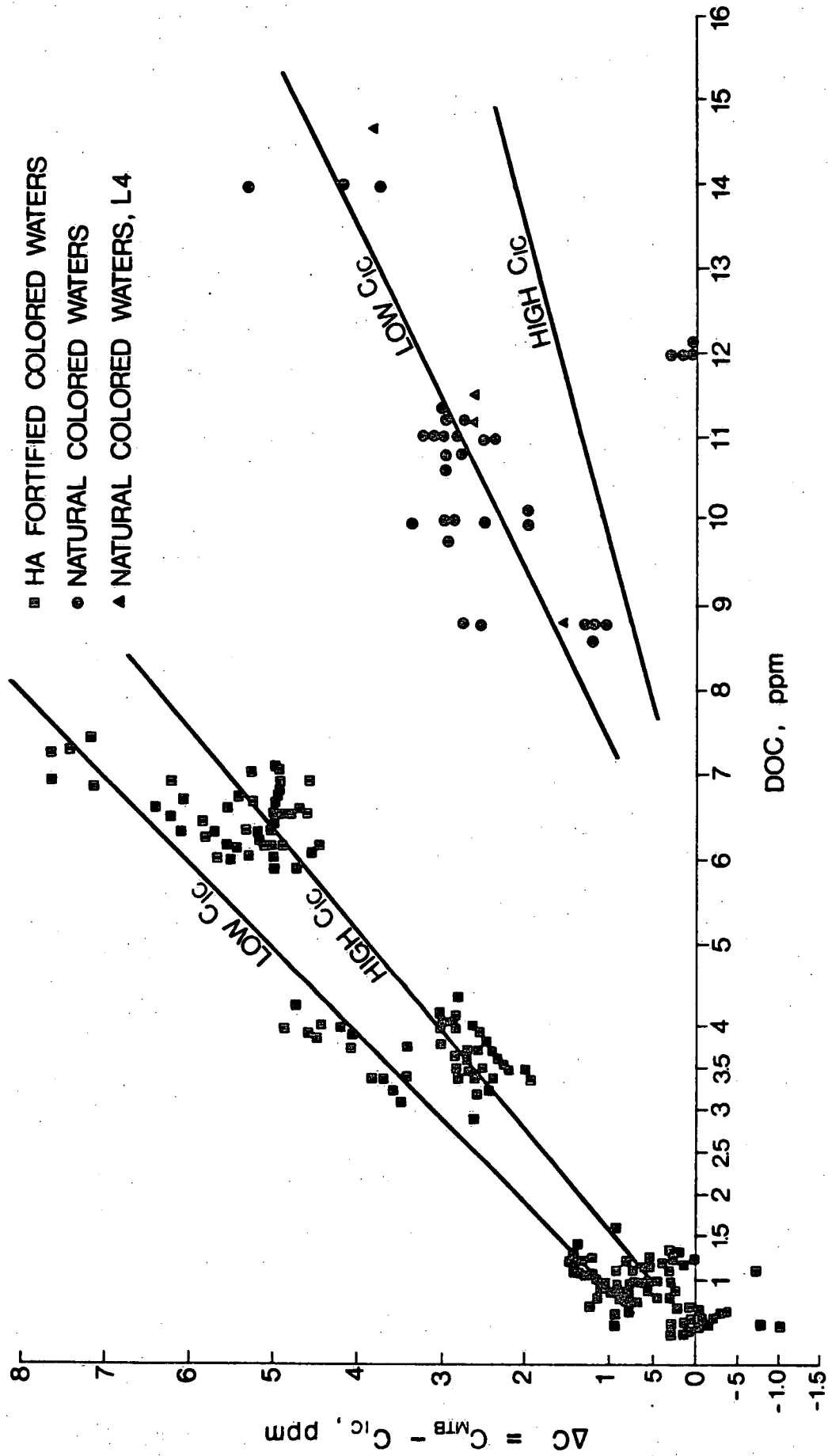


Fig. 3 RELATIONSHIP OF ΔC AND DOC

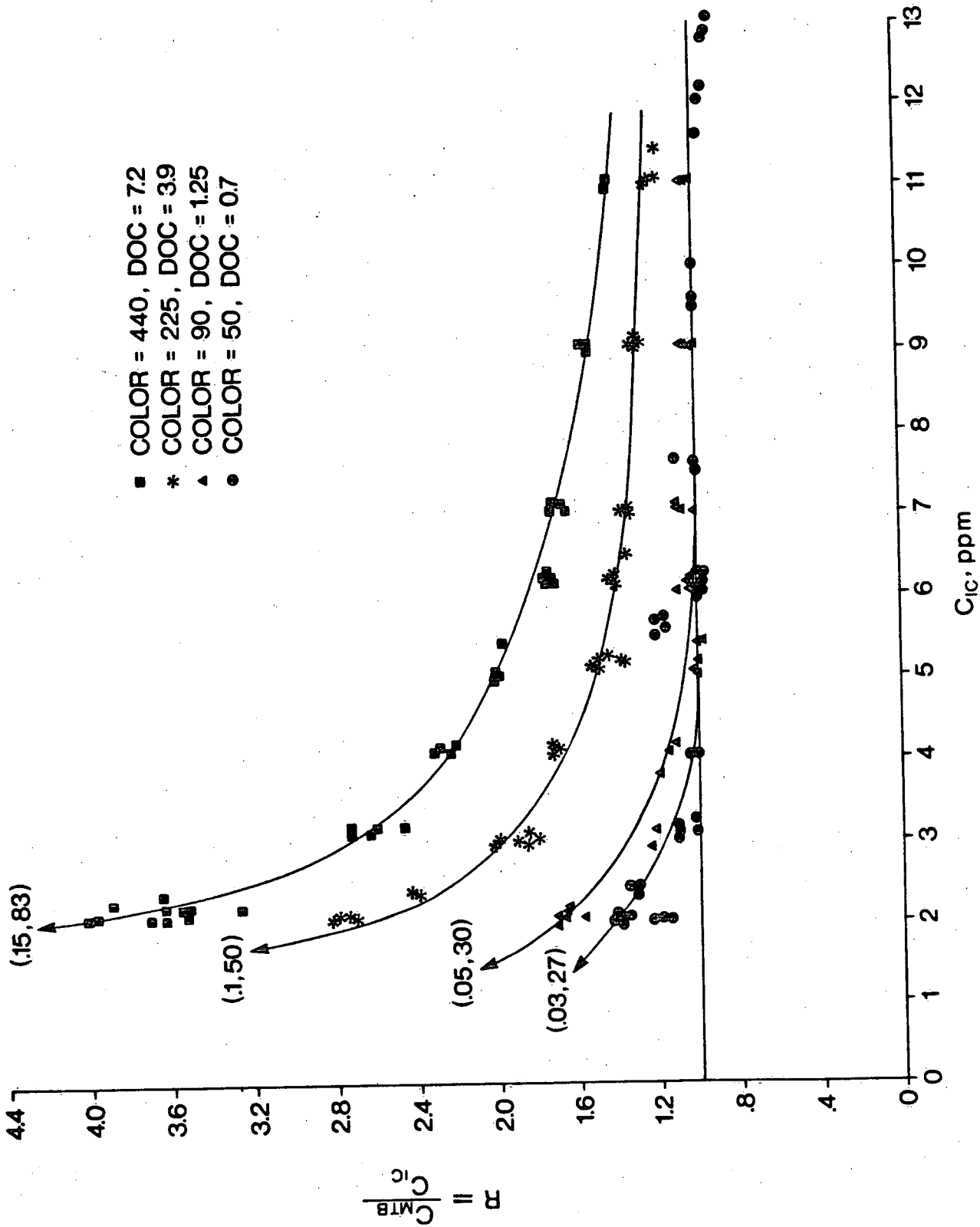


Fig. 4 RELATIONSHIP OF SO₄ RATIO, R, AND C_{IC} FOR HUMIC ACID FORTIFIED COLORED WATERS

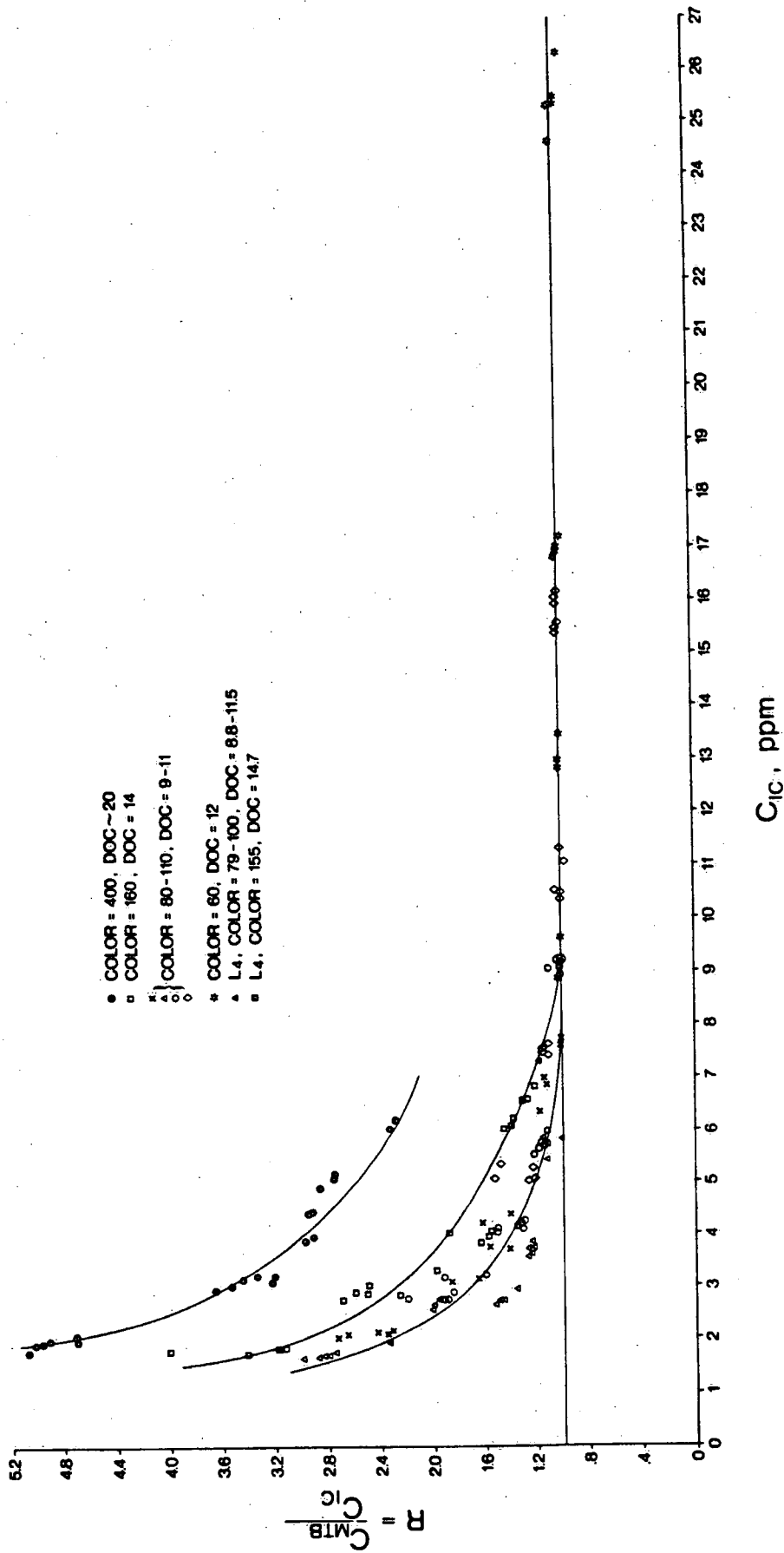


Fig. 5 RELATIONSHIP OF SO₄ RATIO, R, AND C_{IC} FOR NATURAL COLORED WATERS

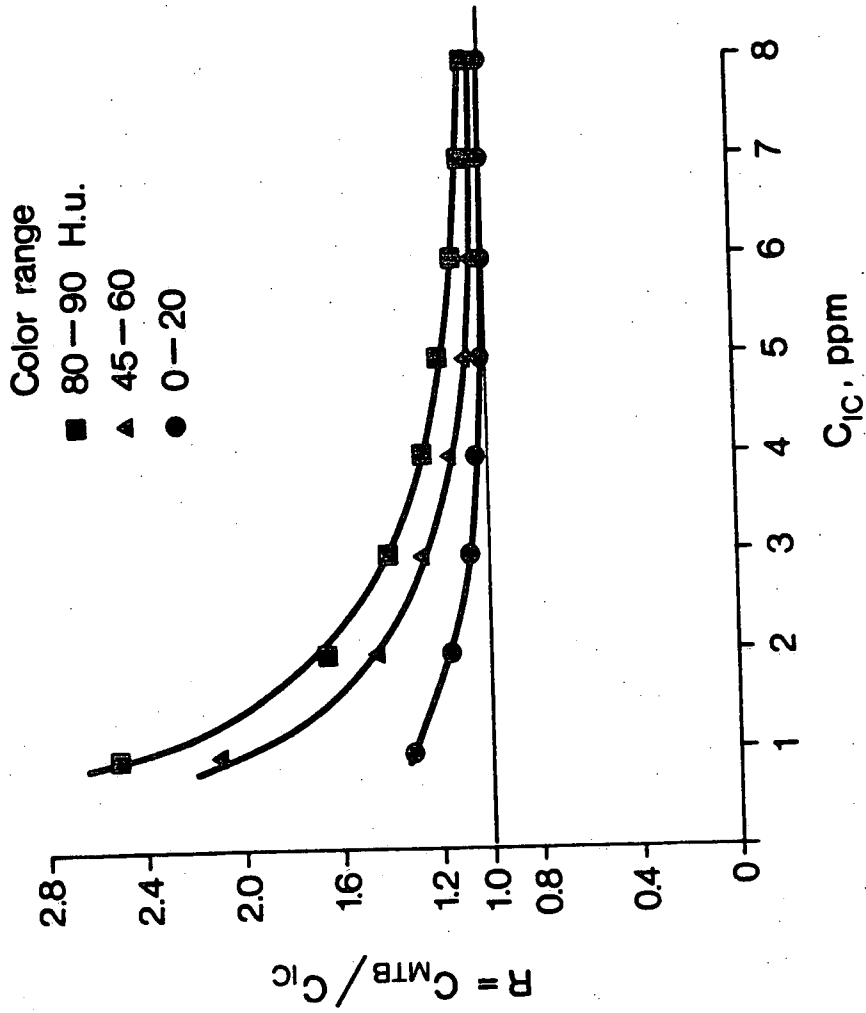


Fig. 6 Relationship of SO_4 ratio, R, and C_{IC}

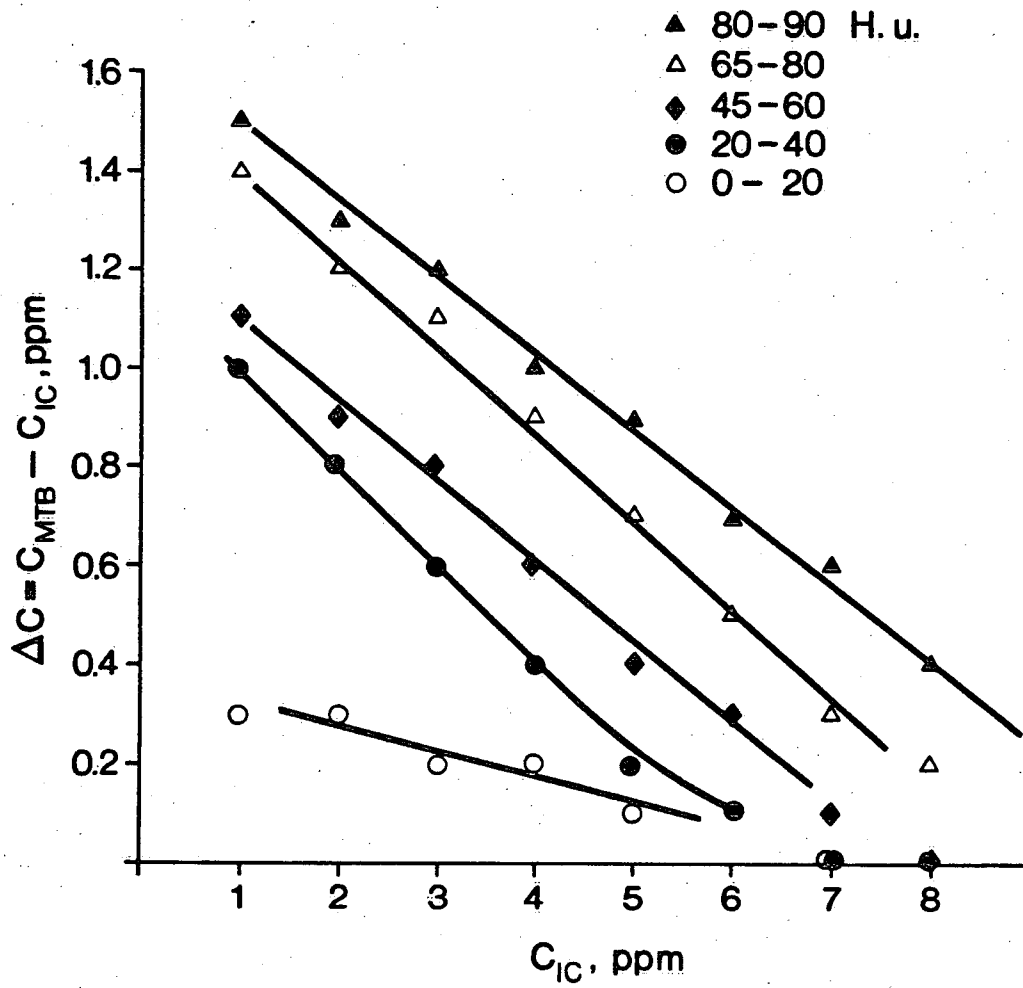


Fig. 7 Relationship of ΔC and C_{IC}

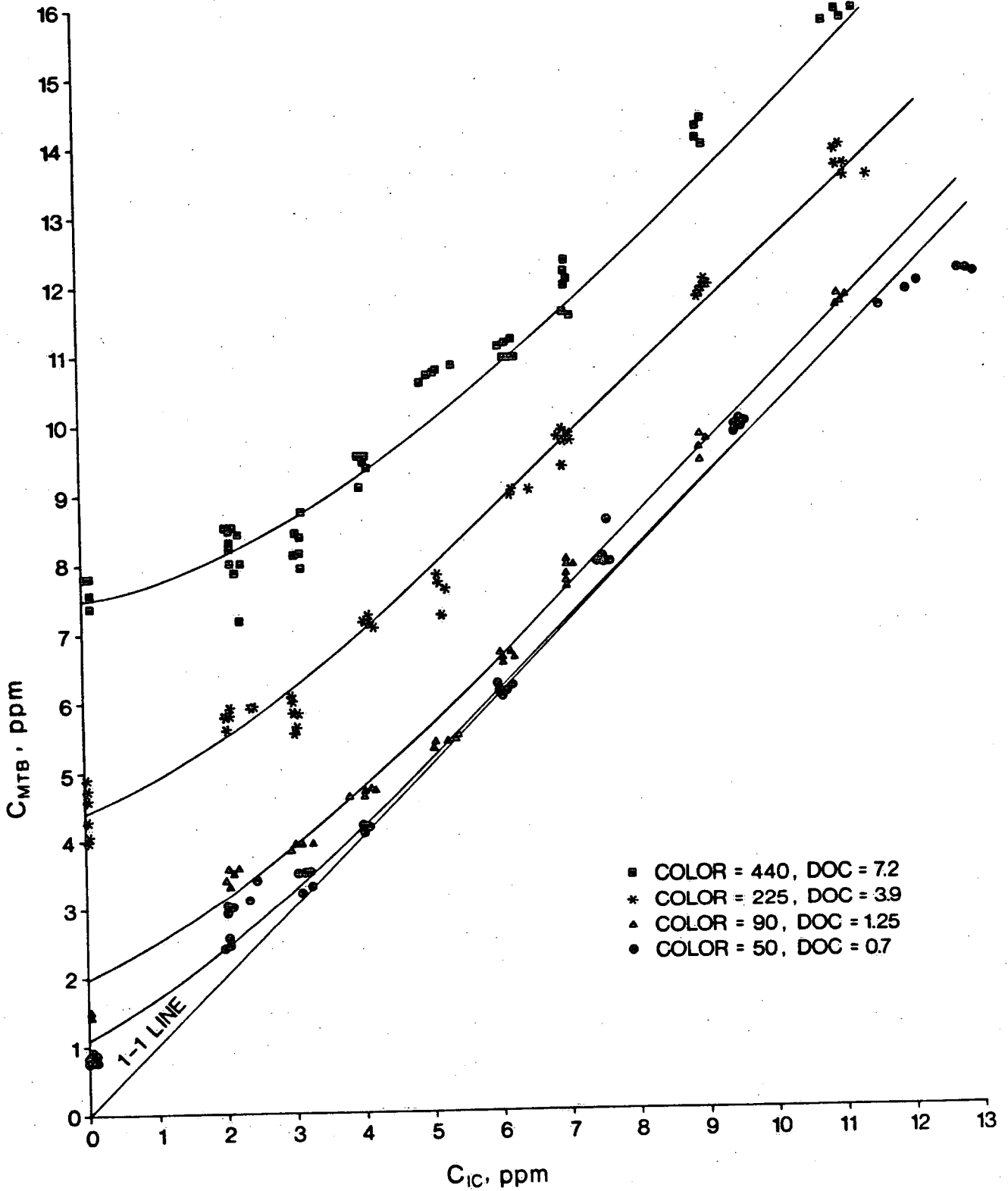


Fig. 8 THE $C_{MTB} - C_{IC}$ RELATIONSHIP FOR HUMIC ACID FORTIFIED COLORED WATERS

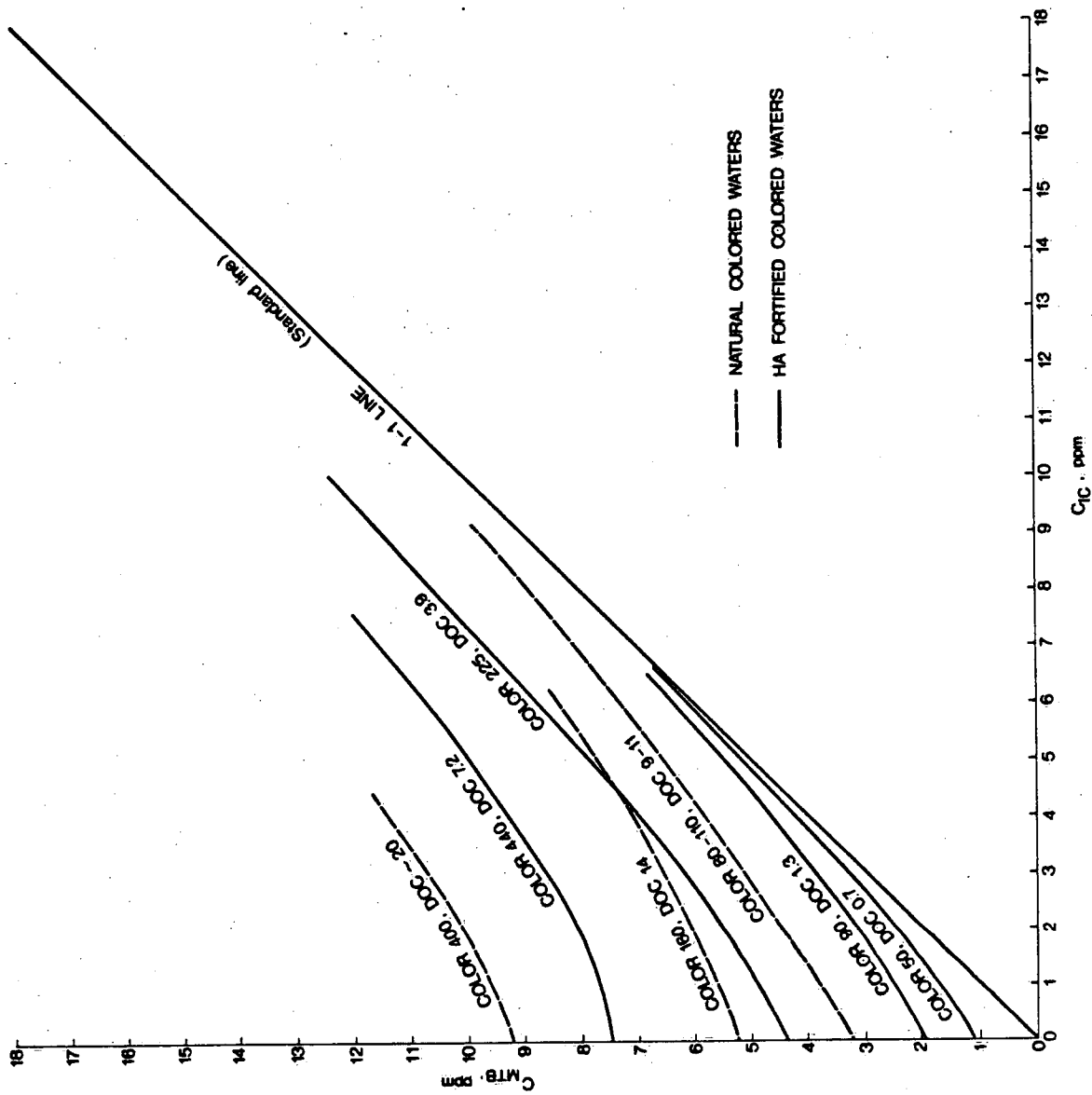


Fig. 9 The C_{MTB} - C_C relationship for HA fortified and natural waters.

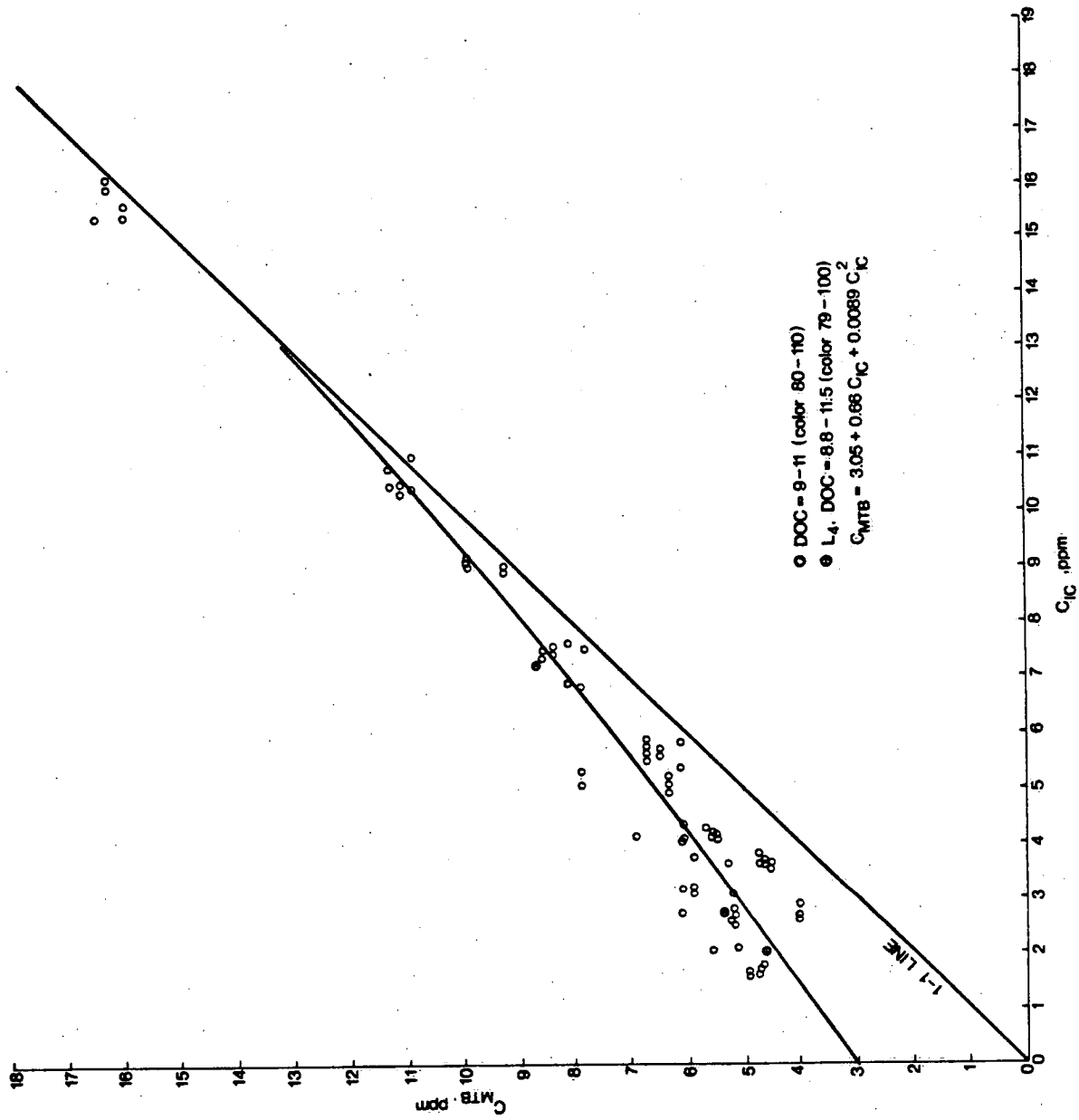


Fig. 10 The $C_{MTB} - C_{IC}$ relationship for the natural waters with DOC of 9-11 ppm (color 80-110 H.u.)

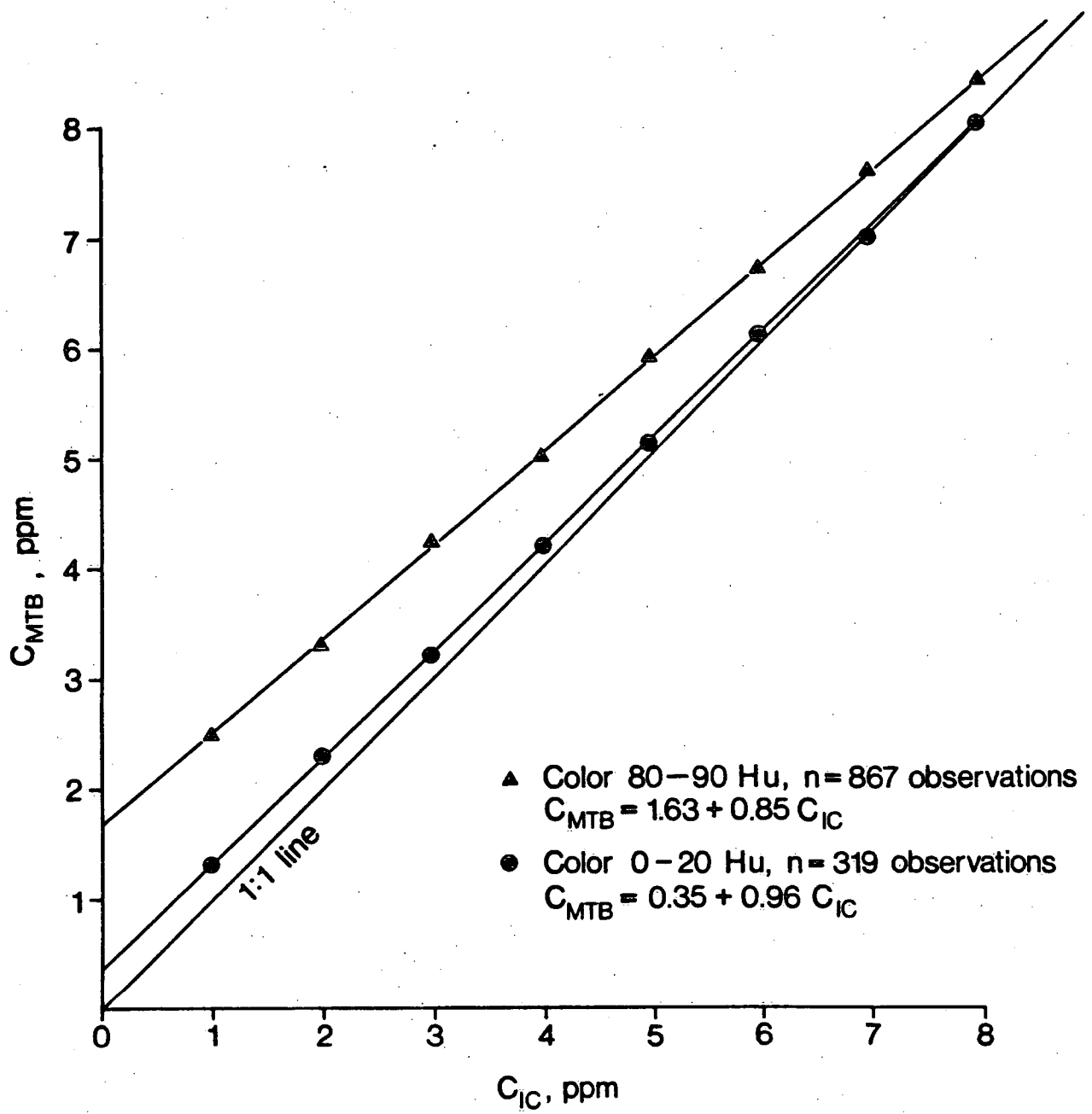


Fig. 11 The $C_{MTB} - C_{IC}$ relationship