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The School of Public Health  
Department of  
Environmental Sciences and Engineering

The University of North Carolina at C  
Rosenau Hall 201 H  
Chapel Hill, N.C. 27514

April 18, 1980


Mr. Roger M. Fry  
Water and Sewer Division  
Department of Public Works  
PO Box 1810  
Wilmington, North Carolina 28402

Dear Roger:

Enclosed is some integrated information from our survey and experimental work on trihalomethanes in North Carolina. We thought you might find some of these preliminary results interesting.

Please let me know if you have any questions.

Sincerely,

  
Philip C. Singer  
Professor

PCS:pc

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CONTROL OF TRIHALOMETHANES IN NORTH CAROLINA  
DRINKING WATERS BY OXIDATION/COAGULATION

by

Alan E. Scrivner (Research Assistant), Philip C. Singer (Professor)  
and James J. Barry III (Research Assistant)

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Association for presentation at Paris  
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## ABSTRACT

In anticipation of the United States Environmental Protection Agency's establishment of a maximum contaminant level (MCL) of 100  $\mu\text{g/l}$  for trihalomethanes in drinking water, a survey was conducted at thirteen water treatment plants in North Carolina. The results of the survey showed a strong correlation between total organic carbon (TOC) concentrations in the raw water and instantaneous and terminal THM production in the finished water. In four plants, the instantaneous THM concentrations were observed to be in excess of the 100  $\mu\text{g/l}$  MCL. An experimental program was carried out to evaluate the feasibility of modifying plant operations at three of these utilities in order to bring the finished waters into compliance with the regulation.

The results show that alum coagulation and settling represents an effective means of removing THM precursors from drinking water. Reductions in the 7-day trihalomethane formation potential of approximately 60% were noted. Modification of prechlorination practices, by moving the point of chlorine application downstream of the settling tanks, appears to be an efficient mechanism for controlling THM formation at these utilities. In those plants where oxidative pretreatment of the water is required, ozonation or permanganate addition to the raw water can be substituted for prechlorination with little impact on subsequent alum coagulation and its capability for removing THM precursors.

## RESUME

En l'anticipation de l'établissement d'une norme fédérale pour le niveau maximum de contamination de 100  $\mu\text{g/l}$  du trihalométhane dans l'eau potable, des prélèvements d'eau ont été effectués sur treize stations d'épuration d'eau en Caroline du Nord. Les résultats de ces prélèvements ont démontré une forte corrélation entre la concentration COT de l'eau brut et la production instantanée et terminale du trihalométhane dans l'eau épurée. Dans quatre de ces stations d'épuration, les concentrations instantanées du trihalométhane ont été supérieures à 100  $\mu\text{g/l}$ . Un programme de recherche a été établi afin d'évaluer des possibilités de modification dans l'opération de trois des stations d'épurations afin de produire une qualité d'eau qui peut satisfaire les normes.

Ces résultats ont démontré que la coagulation avec alun suivie par la décantation est un moyen efficace d'enlever les précurseurs du trihalométhane de l'eau. Les réductions d'environ 60% sur le niveau de potentiel de formation du trihalométhane (7-jours) ont été constatées. Dans les stations qui pratiquent la préchloration, on pourrait éviter la formation du trihalométhane par l'application du chlore à l'aval du bassin de décantation. Dans les cas où un prétraitement oxydatif de l'eau est requis, l'addition d'ozone ou de permanganate à l'eau brut peut être substituée pour la préchloration sans impact sur la coagulation avec alun et sa capacité d'enlever les précurseurs de trihalométhane.

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# CONTROL OF TRIHALOMETHANES IN NORTH CAROLINA

## DRINKING WATERS BY OXIDATION/COAGULATION

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### Introduction

On November 29, 1979, the United States Environmental Protection Agency amended (1) the National Interim Primary Drinking Water Regulations, establishing a maximum contaminant level (MCL) of 0.1 mg/l (100 µg/l) for total trihalomethanes (TTHM's), including chloroform,  $\text{CHCl}_3$ . The effective date of the MCL is two years following promulgation of the regulation for community water systems serving 75,000 or more persons, and four years for community water systems serving 10,000 to 75,000 persons. In anticipation of this regulation, a research project sponsored by the Water Resources Research Institute of the University of North Carolina was initiated in September, 1978 to analyze raw and finished water quality at selected water treatment plants in North Carolina with respect to trihalomethane formation.

The data collected at each of the plants were analyzed by comparing the trihalomethane concentrations in the finished waters of each of the facilities with the 100 µg/l standard. In addition, the trihalomethane concentrations in the finished water were statistically compared to the raw water total organic carbon concentrations. More than 100 samples were collected during various times of the year from the water treatment plants at Asheville, Charlotte, Chapel Hill, Durham, Gastonia, Greensboro, Raleigh, Winston-Salem, and Wilmington, North Carolina. In all, thirteen treatment plants were sampled. The samples were analyzed for total organic carbon, and instantaneous and terminal THM concentrations at various locations throughout the plants. The results of these analyses were reviewed, along with other water quality data and pertinent operational characteristics of the plants in question, in an effort to ascertain trends associated with trihalomethane formation. The data collected included the nature (source) and quality of the raw water, time of collection (season), chlorine dose and point of application, coagulant additions, pH, temperature, use of other chemical oxidants or adsorbents, and detention times through various unit processes. All of the treatment plants surveyed, with the exception of the Durham plant, employed prechlorination of the raw water either as the water entered the plant or as it entered the pipeline carrying it from the source to the plant.

The results of this survey and analysis have previously been presented at the June, 1980 Annual Conference of the American Water Works Association (2). Examples of some of the correlations developed between raw water TOC and instantaneous THM production, and raw water TOC and terminal THM production in the finished water are shown in Figures 1 and 2, respectively. Despite the collective nature of the TOC parameter in that it is a measure of all organic substances in the water, it appears to be a good indicator of the trihalomethane formation potential of the water.

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Analysis of the data also showed that THM concentrations tended to be higher in the central and eastern parts of the State than in the western region. This may be due to the nature of the vegetation in the different watersheds, or due to the accumulation of humic materials in the surface waters as they flow toward the coast.

The data also showed that TOC concentrations were reduced an average of 35-40% as a result of coagulation and settling and that the terminal trihalomethane concentrations were reduced correspondingly, as suggested by the correlation in Figure 2. In fact, the percent reduction in TOC was strongly correlated to the percent reduction in terminal THM's ( $r = 0.80$ ).

In three cities, Chapel Hill, Raleigh, and Wilmington, the instantaneous THM concentrations in the finished water leaving the plants were observed to be in excess of the 100  $\mu\text{g/l}$  MCL. For these utilities, an experimental program was carried out in order to evaluate the feasibility of modifying plant operations in order to bring the finished waters into compliance with the regulation. In particular, the feasibility of altering the prechlorination practices at these plants, by moving the point of chlorine application downstream of the settling tanks, was investigated. Such a modification was previously found to be effective at Durham, NC (3). In conjunction with this relocation of the point of chlorine addition, the impact of adding ozone or potassium permanganate as alternative pretreatment chemicals, in place of chlorine, was also evaluated. This paper presents the results of this experimental program.

#### Procedures

The experimental studies were performed on a bench-scale in the laboratory, using conventional jar test procedures. Raw water samples were collected from Raleigh, Wilmington, and Chapel Hill, North Carolina and analyzed for total organic carbon (Beckman 915A Carbon Analyzer), turbidity (Hach Model 2100A Turbidimeter), and UV absorbance (254 nm wavelength, 1 cm cell). Samples of the different raw waters were dosed with alum at the same concentrations as those employed at the respective treatment plants. The treated samples were gently mixed at 40 RPM for 30 minutes on a paddle stirrer. Following 60 minutes of settling, aliquots of the settled water were removed and analyzed for residual TOC, turbidity, and UV absorbance. Samples of the coagulated and settled water and the raw untreated water were then dosed with chlorine to determine the trihalomethane formation potential (THMFP) and chlorine demand of the water. All chlorinations were accomplished by adding a known amount of chlorine (15-20 mg/l), and buffering the solutions at pH 6.7 using a phosphate buffer. The chlorinated solutions were stored at room temperature, in the dark, in headspace-free sealed bottles, for seven days. After this time period, an aliquot was removed for the measurement of residual chlorine, using the DPD procedure (4). In all cases, residual chlorine was present after the seven-day storage period. The remainder of the solution was quenched with excess sodium sulfite and sealed, headspace-free, prior to the analysis for trihalomethanes. The concentrations of the THM species were subsequently determined using the purge and trap procedure (5), employing a Tenax trap, Tracor MT-220 Gas Chromatograph with a Chromasorb 101 column, and a Hall Electrolytic Conductivity Detector. In all cases,  $\text{CHCl}_3$  was the predominant THM specie present, with only small traces of  $\text{CHBrCl}_2$  observed on occasion.

To evaluate the impact of ozone and potassium permanganate on the THMFP of the raw water and on the behavior of alum during the course of subsequent coagulation and settling, parallel samples of the raw water were dosed with 1-5 mg/l of ozone, and 1-3 mg/l of  $\text{KMnO}_4$ . Concentrated solutions of ozone

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(up to 50 mg/l) were generated by ozonating dilute sulfuric acid solutions (pH 4), prepared from organic-free deionized water. Ozone was generated from oxygen, using a Union Carbide Model No. SG4060 laboratory ozone generator. The concentration of ozone in the stock solution was determined iodometrically (4). In the case of potassium permanganate, stock solutions of reagent-grade  $\text{KMnO}_4$  were prepared and standardized amperometrically, by titration with standard phenylarsine oxide (PAO) (4). Various dilutions of the ozone or  $\text{KMnO}_4$  stock solutions were added to samples of the different raw waters, and the pH was adjusted, if necessary, to a value near its original pH. The waters were held for 45 min. to 2 hours, until no residual  $\text{O}_3$  or  $\text{MnO}_4^-$  could be detected. Aliquots of the treated water were analyzed for residual TOC, turbidity, and UV absorbance, and then chlorinated, under the same conditions as described above, for the measurement of THMFP and chlorine demand.

Parallel samples of the ozonated or permanganate-treated water were coagulated with alum, using the jar test procedures described above, and settled. The settled water was analyzed for residual TOC, turbidity, and UV absorbance, and then chlorinated to determine the residual THMFP and chlorine demand. A flow sheet outlining the treatment procedures is shown in Figure 3. In all cases, the THMFP refers to the 7-day trihalomethane formation potential, at pH 6.7, in the presence of excess  $\text{Cl}_2$ .

### Results and Discussion

Table 1 shows the characteristics of the raw water at the three utilities investigated. With the exception of the second Chapel Hill sample, the waters have a relatively moderate turbidity and a rather substantial organic carbon content, as reflected by the high TOC concentrations and UV absorbance values. Accordingly, the raw waters are also seen to have an appreciable 7-day trihalomethane formation potential.

The results of the alum treatment and subsequent settling are summarized in Table 2. It is apparent that alum is capable of reducing the 7-day trihalomethane formation potential of the waters by an average of approximately 60%. These results suggest that modifying chlorination practices at Chapel Hill, Raleigh Northside, and Wilmington, by moving the point of chlorine application downstream of the settling tanks, may bring these treatment plants into compliance with the new THM standard.

Table 3 summarizes the results of the ozonation and coagulation treatments on the Raleigh Northside water. The ozonated waters show noticeable reductions in the 7-day THMFP and UV absorbance values compared to the raw water, along with minor reductions in turbidity, 7-day  $\text{Cl}_2$  demand, and TOC (discounting the aberrant 8.1 value). The ozonated and coagulated samples, however, except for some minor variations, show little apparent difference in resultant quality when compared to the sample which was only coagulated. Hence, ozonation, while it does alter the nature of the organics in the water to some degree, seems to have little impact on the capability of alum for coagulating and removing organic precursors of trihalomethanes.

The results illustrating the effect of permanganate oxidation and coagulation on Wilmington water are shown in Table 4. Permanganate oxidation appears to reduce the 7-day THMFP to some extent, in much the same way as previously reported for Durham and Chapel Hill (6). There appears to be a slight increase in TOC and UV absorbance following the permanganate treatment, but this cannot be explained other than by possible analytical shortcomings of the respective measurements. The samples treated by permanganate and alum again, as in the case of ozone, show little difference compared to the sample treated by alum alone.

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Figures 4 and 5 summarize the more significant results of treating the five different raw waters by ozone or permanganate oxidation, alum coagulation, and settling. Figure 4 shows that in all five cases, while alum alone reduces the TOC by 44-62%, oxidative pretreatment reduces the effectiveness of alum for removing organic carbon. This impact of the oxidants is more striking when the combined data for all five waters is examined than when the individual data for any one water is considered. The reduced efficiency of alum for coagulating the organics remaining in the oxidant-treated water probably arises from the increased solubility and decreased molecular weight of the resultant organics comprising the total organic carbon. Nevertheless, despite this increased presence of TOC arising from the oxidative pretreatment, Figure 5 shows that the oxidants have essentially no effect on the efficiency of alum for removing THM precursors.

### Conclusions

Alum coagulation and settling represents an effective means of removing trihalomethane precursors from drinking water. Modification of prechlorination practices, by moving the point of chlorine application downstream of the settling tanks, is an efficient mechanism for controlling trihalomethane formation in those facilities where the finished water exceeds the maximum contaminant level of 100 µg/l for trihalomethanes. In those plants where oxidative pretreatment of the water for controlling taste and odor and iron and manganese problems is required, ozonation or permanganate addition to the raw water can be substituted for prechlorination with little impact on subsequent alum coagulation and its capability for removing trihalomethane precursors.

### Acknowledgements

The authors would like to thank Glenn Palen for his assistance in this project, and the operators and managers of the Chapel Hill, Raleigh, and Wilmington water utilities for their cooperation. The authors are also appreciative of the Water Resources Research Institute of the University of North Carolina and the Office of Water Research and Technology of the United States Department of the Interior for their financial support of this project.

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1. "National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water; Final Rule", Federal Register, November 29, 1979.
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3. Young, JS and PC Singer, "Chloroform Formation in Public Water Supplies: A Case Study", Journal of the American Water Works Association, 71(2): 87-95 (1979).
4. Standard Methods for the Examination of Water and Wastewater, 14th edition, American Public Health Association, Washington, DC (1976).
5. "The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method", Environmental Monitoring and Support Laboratory, US Environmental Protection Agency, Cincinnati, Ohio, September, 1977.
6. Singer, PC, JH Borchardt, and JM Colthurst, "Effects of Permanganate Pretreatment on Trihalomethane Formation in Drinking Waters", accepted for publication by Journal of the American Water Works Association (in press).

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Table 1. RAW WATER CHARACTERISTICS

<u>Sample</u>	<u>Water Source</u>	<u>Turbidity, NTU</u>	<u>TOC, mg/l</u>	<u>UV Absorbance*</u>	<u>THMFP,** µg/l</u>	<u>Chlorine Demand,*** mg/l</u>
Chapel Hill	Lake	15	6.1	170	288	10.9
Chapel Hill	Lake	6.1	3.4	116	294	8.6
Raleigh Northside	River	15	6.6	160	341	12.0
Wilmington	River	15	6.7	190	411	14.8
Wilmington	River	14	5.9	190	376	13.4

\* Measured at 254 nm, 1 cm cell, on filtered raw water sample.

\*\* Trihalomethane formation potential after 7-days storage in pH 6.7 phosphate-buffered solution, in the presence of excess chlorine.

\*\*\* 7-day chlorine demand in pH 6.7 phosphate-buffered solution.

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Table 2. EFFECT OF ALUM COAGULATION AND SETTLING

Sample	Alum Dose, mg/l*	PERCENT REDUCTION				
		Turbidity	TOC	UV Absorbance	THMFP	Chlorine Demand
Chapel Hill	50	62	62	68	63	69
Chapel Hill	30	77	44	76	50	49
Raleigh Northside	40	77	52	78	57	50
Wilmington	30	77	54	81	66	51
Wilmington	30	86	49	81	67	64
AVERAGE	--	76	52	77	61	57

\*  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (MW = 666). NOTE: 1 mg  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  is equivalent to 0.081 mg Al.

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Table 3. RESULTS OF OZONATION/COAGULATION OF RALEIGH NORTHSIDE WATER

<u>Type of Treatment</u>	<u>Turbidity, NTU</u>	<u>TOC, mg/l</u>	<u>UV Absorbance</u>	<u>THMFP, µg/l</u>	<u>Chlorine Demand, mg/l</u>
none	15	6.6	160	341	12.0
40 mg/l Alum	3.5	3.2	40	147	6.0
1.3 mg/l O <sub>3</sub>	15	8.1	165	299	11.1
2.5 mg/l O <sub>3</sub>	14	5.9	136	291	11.4
4.4 mg/l O <sub>3</sub>	12	5.7	88	250	10.5
1.3 mg/l O <sub>3</sub> plus 40 mg/l Alum	2.6	3.1	35	148	5.3
2.5 mg/l O <sub>3</sub> plus 40 mg/l Alum	1.4	3.2	35	135	6.6
4.4 mg/l O <sub>3</sub> plus 40 mg/l Alum	2.5	4.6	32	140	6.3

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Table 4. RESULTS OF PERMANGANATE OXIDATION/COAGULATION OF WILMINGTON WATER

<u>Type of Treatment</u>	<u>Turbidity, NTU</u>	<u>TOC, mg/l</u>	<u>UV Absorbance</u>	<u>THMFP, <math>\mu</math>g/l</u>	<u>Chlorine Demand, mg/l</u>
none	14	5.9	190	376	13.4
30 mg/l Alum	1.9	3.0	37	123	4.8
1.0 mg/l $\text{KMnO}_4$	12	7.0	216	343	11.9
2.0 mg/l $\text{KMnO}_4$	12	7.1	196	320	12.4
3.0 mg/l $\text{KMnO}_4$	11	6.5	220	308	11.8
1.0 mg/l $\text{KMnO}_4$ plus 30 mg/l Alum	2.0	3.3	35	123	6.9
2.0 mg/l $\text{KMnO}_4$ plus 30 mg/l Alum	3.0	3.3	45	134	6.8
3.0 mg/l $\text{KMnO}_4$ plus 30 mg/l Alum	1.2	3.7	37	134	8.1

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CONCENTRATION IN RAW WATER AND INSTANTANEOUS THM  
CONCENTRATION IN FINISHED WATER

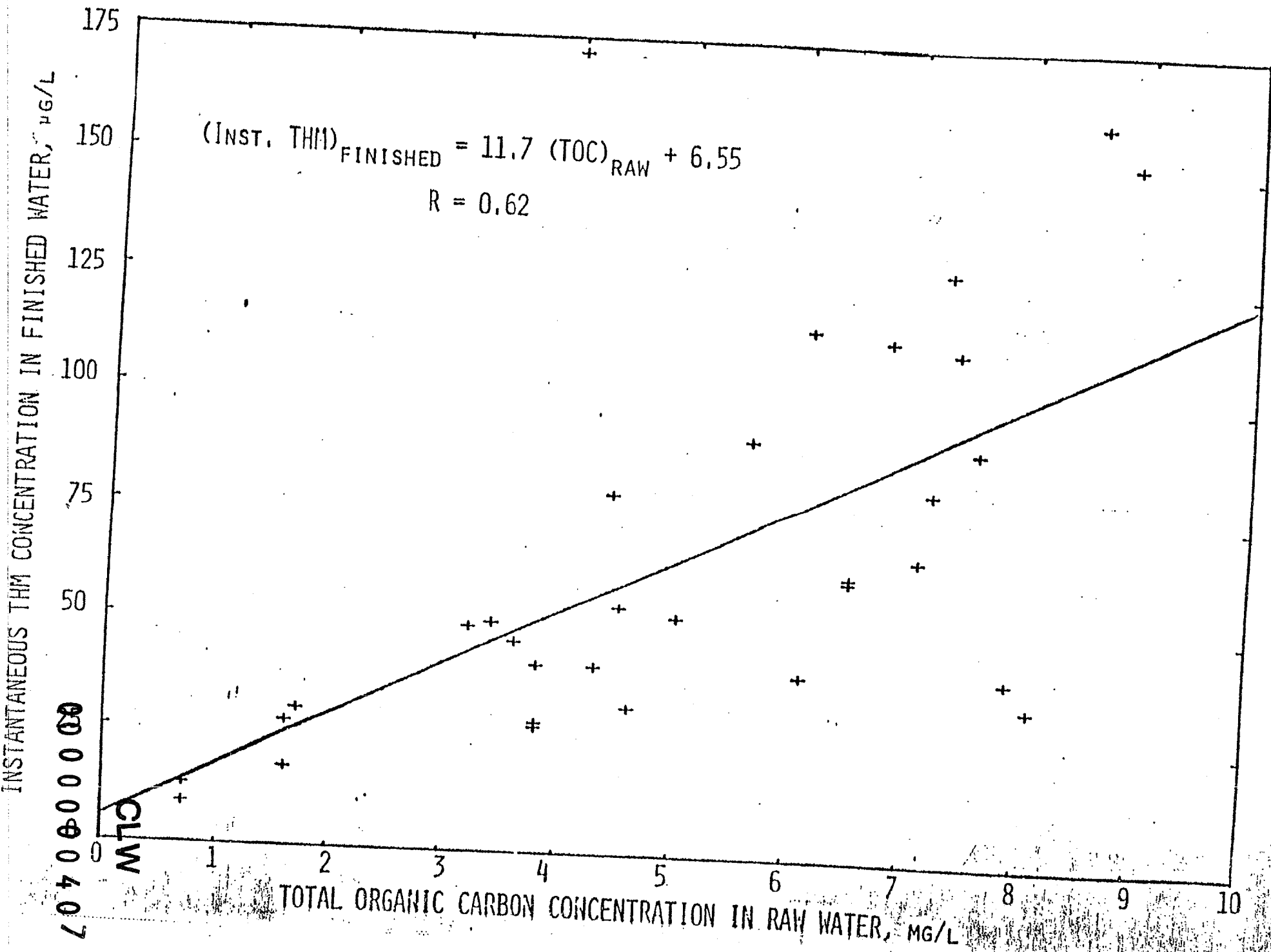


FIGURE 2. CORRELATION BETWEEN RAW WATER TOTAL ORGANIC CARBON AND TERMINAL TRIHALOMETHANES

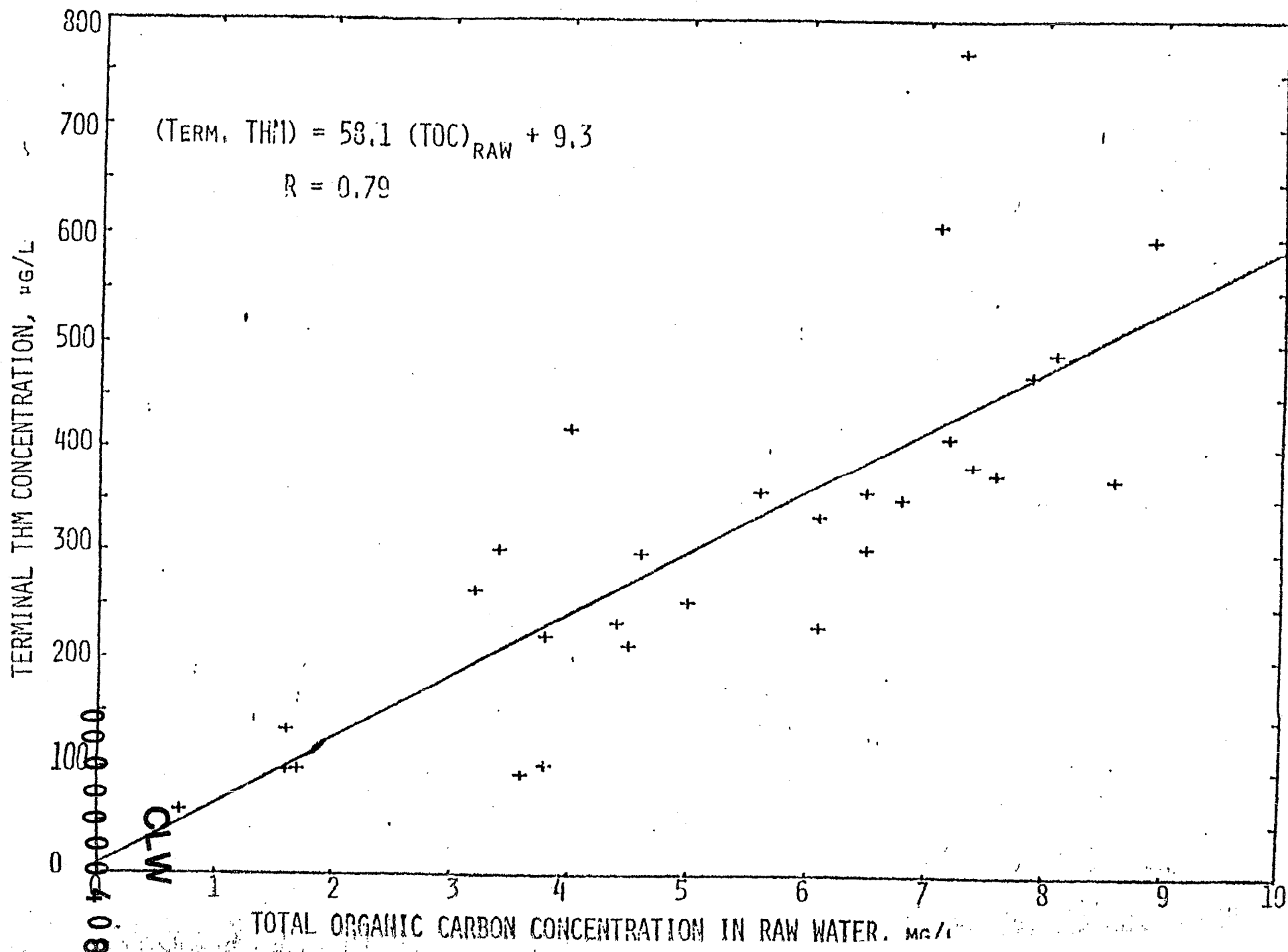
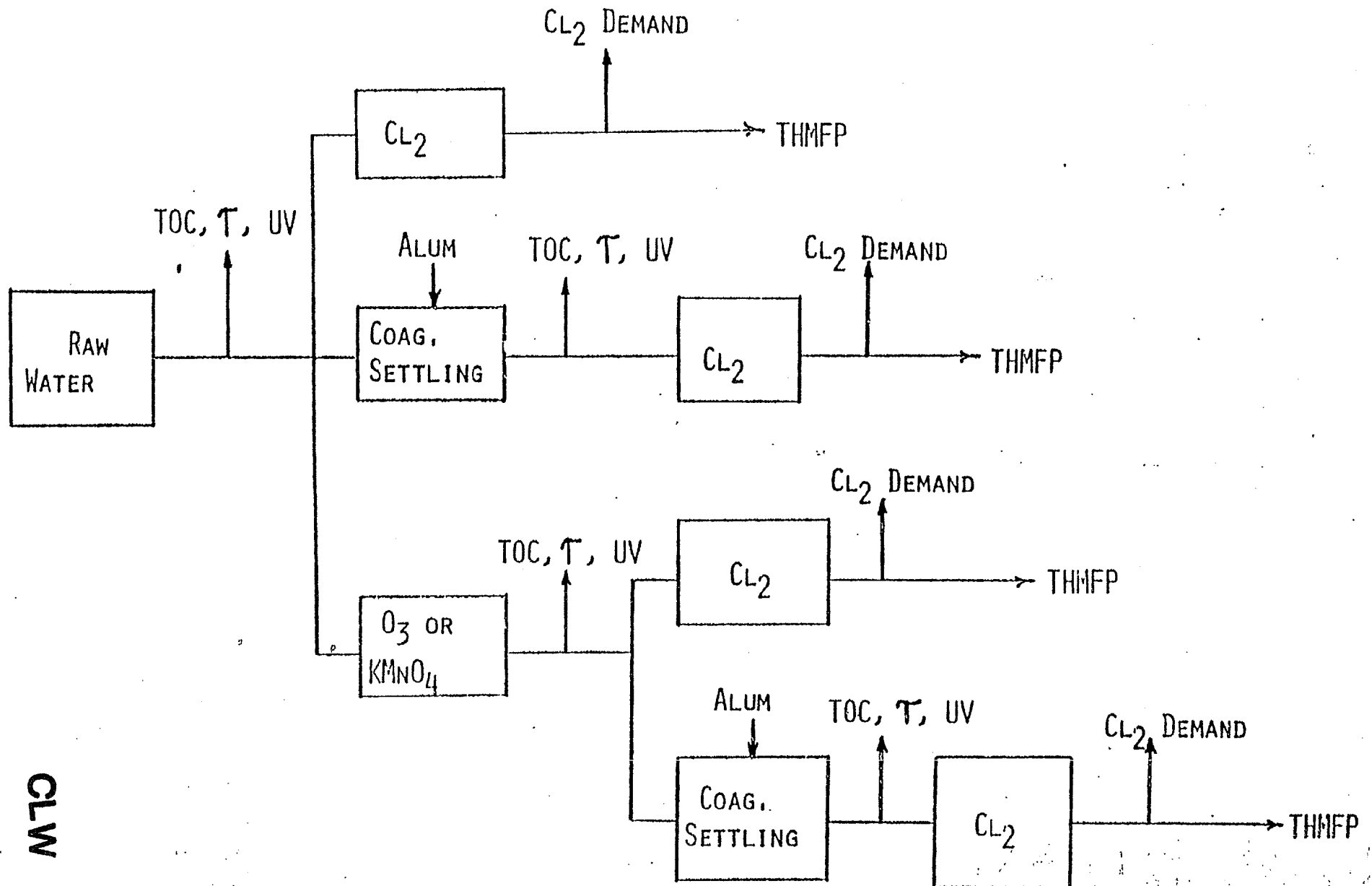




FIGURE 3. OUTLINE OF EXPERIMENTAL TREATMENT PROCEDURE



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FIGURE 4. INFLUENCE OF OZONE AND PERMANGANATE PRETREATMENT ON TOC REMOVAL BY ALUM COAGULATION

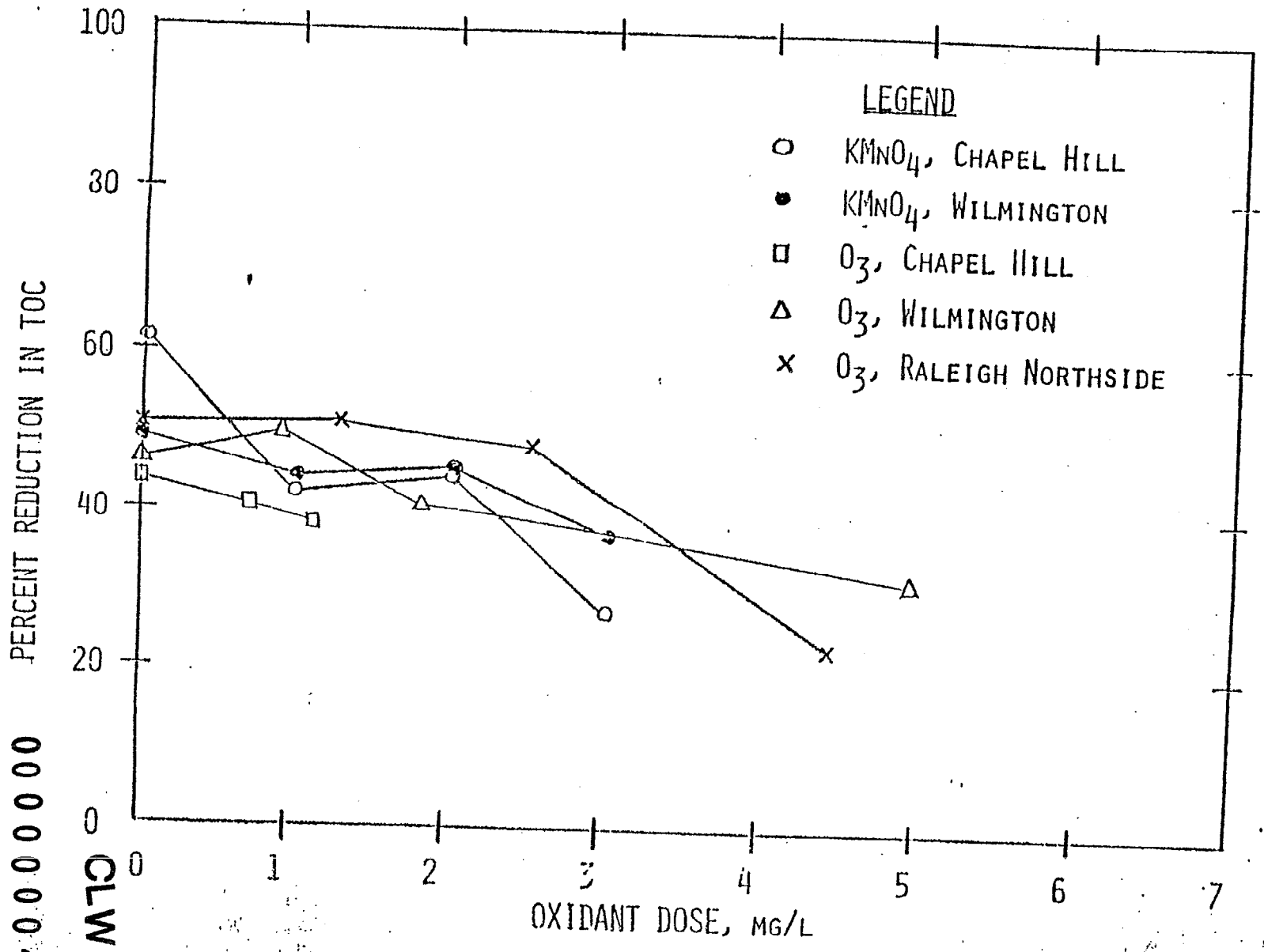
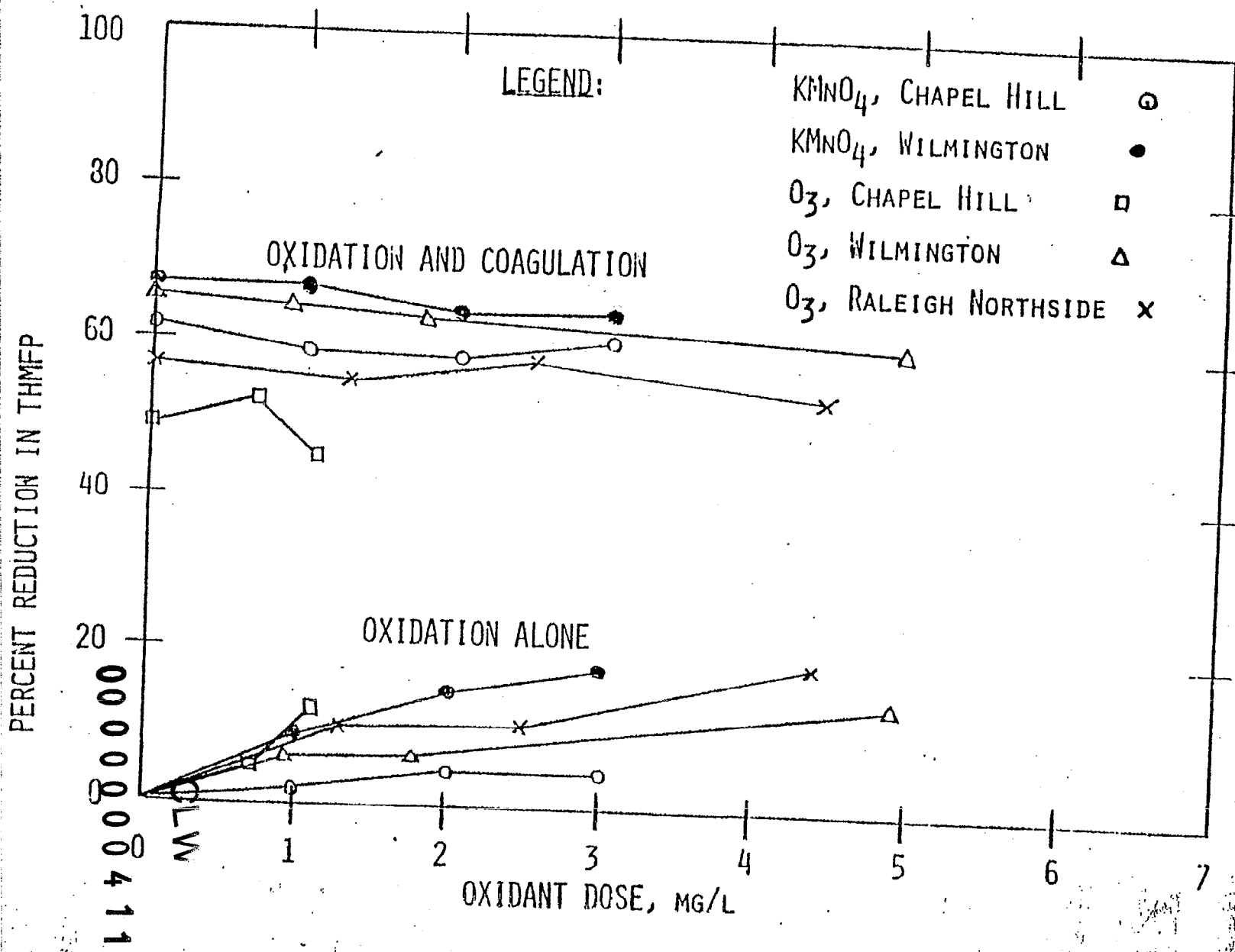


FIGURE 5. INFLUENCE OF OZONE AND PERMANGANATE PRETREATMENT ON THMFP REDUCTION AND SUBSEQUENT THMFP REMOVAL BY ALUM COAGULATION



## TRIHALOMETHANES IN NORTH CAROLINA DRINKING WATERS

On November 29, 1979, the Environmental Protection Agency amended (1) the National Interim Primary Drinking Water Regulations, establishing a maximum contaminant level (MCL) of 0.1 mg/l for total trihalomethanes (TTHM's), including chloroform,  $\text{CHCl}_3$ . For community water systems serving 75,000 or more persons, the effective date of the MCL is two years following promulgation of the regulation. For community water systems serving 10,000 to 75,000 persons, the effective date of the MCL is four years from the date of promulgation.

In anticipation of this regulation, Dr. Philip C. Singer and graduate students James J. Barry, Alan E. Scrivner, and Glenn M. Palen have been conducting a research project, sponsored by the Water Resources Research Institute of the University of North Carolina, to analyze raw and finished water quality at selected water treatment plants in North Carolina with respect to trihalomethane formation. Additionally, plant operations are being reviewed and laboratory treatability studies are being performed to investigate alternative means of reducing and controlling trihalomethane formation at these facilities.

The data collected at each of the plants are being analyzed by comparing the trihalomethane concentrations in the finished waters of each of the facilities with the 100 ug/l standard, and by statistically comparing the final trihalomethane concentrations to the raw water total organic carbon concentrations. To date, more than 100 samples have been collected during various times of the year from the water treatment plants at Asheville,

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Charlotte, Chapel Hill, Durham, Gastonia, Greensboro, Raleigh, Winston-Salem, and Wilmington, North Carolina. The samples have been analyzed for total organic carbon, and instantaneous and terminal THM concentrations at various locations throughout the plants. The results of these analyses are being reviewed, along with other water quality data and pertinent operational characteristics of the plants in question, in an effort to ascertain trends associated with trihalomethane formation. The data being collected include the nature (source) and quality of the raw water, time of collection (season), chlorine dose and point of application, coagulant additions, pH, temperature, use of other chemical oxidants or adsorbents, and detention times through various unit processes. All of the treatment plants surveyed, with the exception of the Durham plant, employ prechlorination of the raw water either as the water enters the plant or as it enters the pipeline carrying it from the source to the plant.

Examples of some preliminary correlations between raw water TOC and terminal THM production, and raw water TOC and instantaneous THM production in the finished water are shown in Figures 1 and 2, respectively. Despite the collective nature of the TOC parameter in that it is a measure of all organic substances in the water, it appears to be a good indicator of the trihalomethane formation potential of the water.

Analysis of the data also shows that THM concentrations tend to be higher in the central and eastern parts of the State than in the western region. This may be due to the nature of the vegetation in the different watersheds, or due to the accumulation of humic materials in the surface waters as they flow toward the coast.

The data also show that TOC concentrations are reduced an average of 35-40% as a result of coagulation and settling and that the terminal trihalomethane concentrations are reduced correspondingly, as suggested by the

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correlation in Figure 2. In fact, the percent reduction in TOC is strongly correlated to the percent reduction in terminal THM's ( $r = 0.80$ ).

In three cases where the instantaneous THM concentrations in the finished water leaving the plant have been observed to be in excess of the 100 ug/l MCL, bench-scale experiments have shown that coagulation and settling of the water prior to the addition of chlorine reduces the 7-day trihalomethane formation potential of the water to concentrations below 150 ug/l. These results suggest that altering prechlorination practices by moving the point of chlorine application downstream of the settling tanks may bring these treatment plants which exceed the MCL into compliance with the regulation. This is in accordance with earlier studies conducted at Durham <sup>(2)</sup>. These studies have also shown that the use of ozone or potassium permanganate as alternative pretreatment chemicals to chlorine does not influence the behavior of alum with regard to its capability for removing THM precursors. It should be noted, however, that if such changes in chlorination practices are made, close attention should be paid to the biological monitoring program to ensure the adequacy of disinfection under the modified operating scheme.

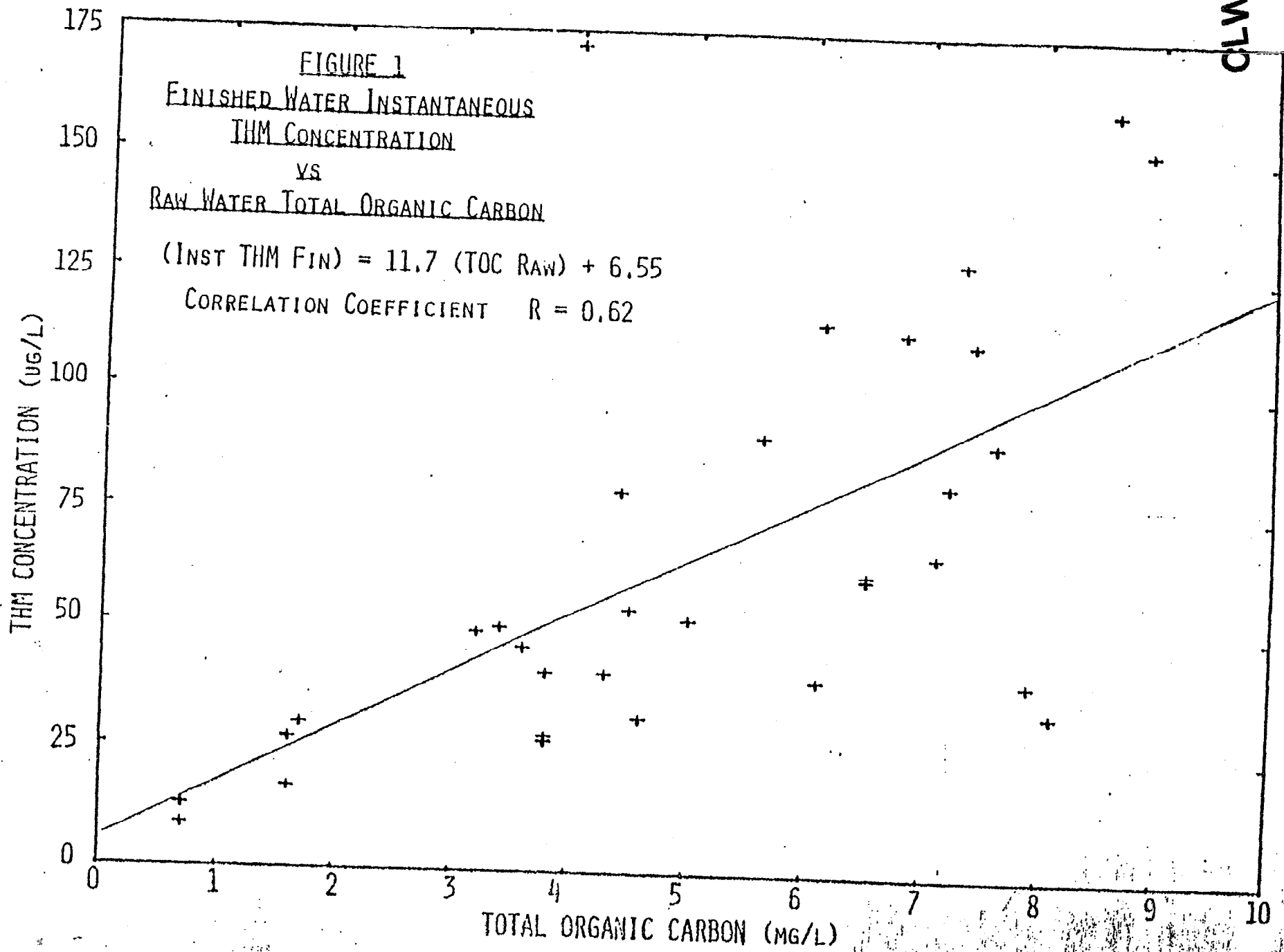
Editor's Note: The results of this research will be presented at the American Water Works Association Annual Conference in Atlanta in June.

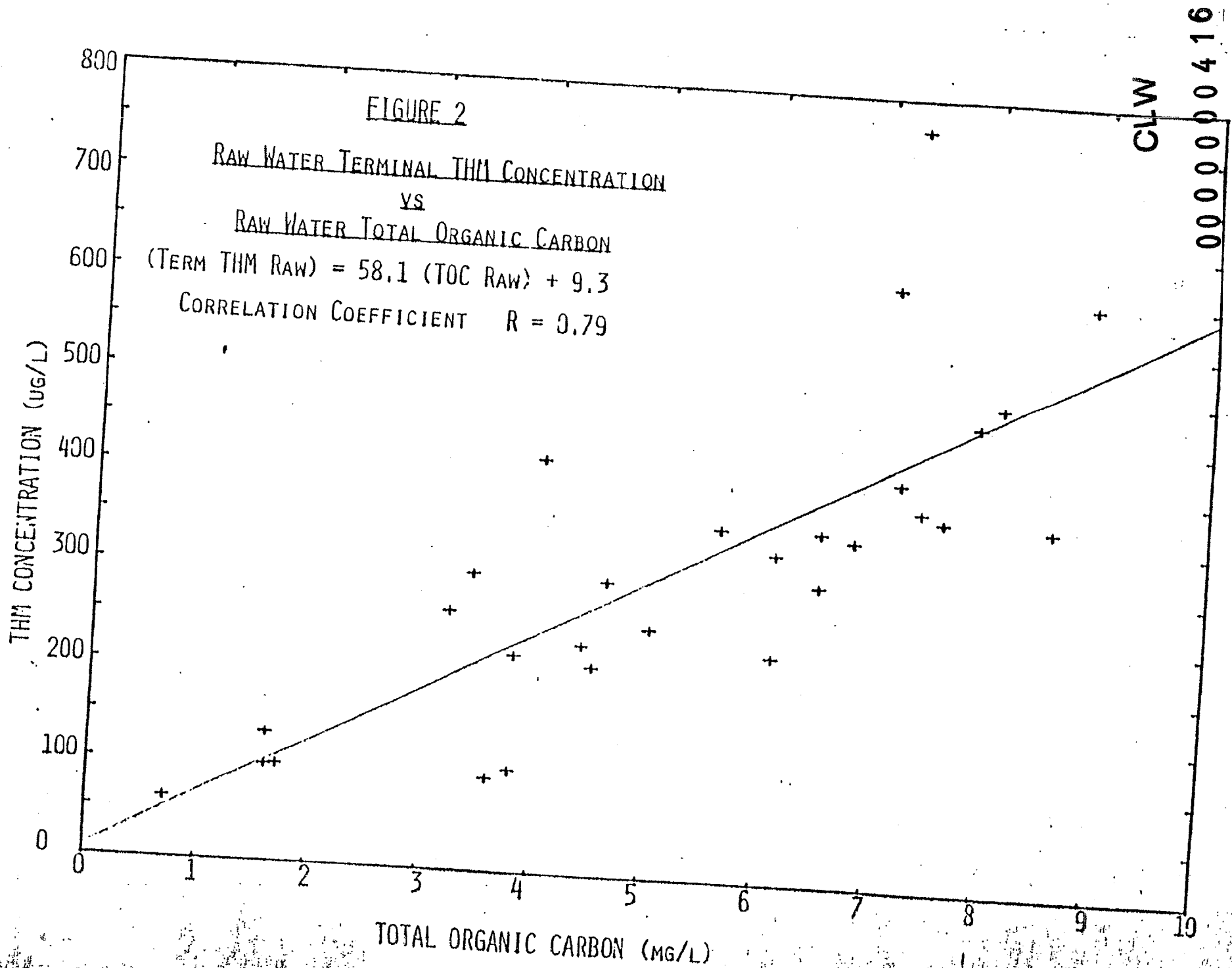
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