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16. ABSTRACT <p>Hundreds of organic byproducts of chlorination are now known to occur in drinking water along with the trihalomethanes. About twenty of these appear to be found with sufficient frequency and in sufficient concentration to attract consideration for regulations. These include chloral hydrate, chloropicrin, a trichloropropanone, haloacetonitriles, and haloacetic acids. Trihalomethane concentrations do not serve as good predictors of concentrations of these other byproducts because their conditions of formation vary widely. This is especially true when pH is changed.</p> <p>Treatment strategies for control of these byproducts including the trihalomethanes are:</p> <ol style="list-style-type: none"> <li>1. Remove the compounds after they are formed</li> <li>2. Remove precursors</li> <li>3. Use other disinfectants.</li> </ol> <p>The first option is not attractive because much of the formation occurs after the water enters the distribution system. Additionally, several of the compounds would be difficult to remove by established treatment processes. Current evidence supports the idea that precursor removal processes effective for trihalomethane control may be effective for the other byproducts as well.</p>					
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## FORMATION AND CONTROL OF NON-TRICHALOMETHANE BY-PRODUCTS

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Trihalomethanes (THMs) were first regulated in drinking water in 1979. The regulation of these compounds followed five years of work by this laboratory and others examining their formation on the bench-scale and control at the pilot- and full-scale.<sup>1</sup> At the same time, examination of the formation and control of other disinfection by-products (DBPs) (mainly resulting from chlorination) as measured by the surrogate parameter total organic halogen (TOX) was occurring.<sup>2,3</sup> TOX data presented in Fig. 1 suggested the formation of other DBPs whose summed concentrations likely equalled or exceeded those of the THMs.<sup>5</sup> Bench studies with chlorination of natural water and humic acid-spiked waters using extraction, capillary column chromatography and mass spectral analytical procedures detected over 500 DBPs.<sup>4</sup> Many of these were found at ug/L concentrations although most were probably much lower, and the majority were not identified. A survey of finished waters of ten U.S. cities confirmed the presence of ug/L concentrations of several of these.<sup>5</sup> The effort of placing rugged analytic procedures on-line for preservation and routine analyses of these DBPs that are listed in Table 1 was then taken, followed by studies of the formation, decay and stability of the non-THM DBPs. With the information gained from these studies regarding their formation dependency on pH, temperature, bromide concentration, oxidant concentration, etc., pilot-scale flow through studies to examine their control began.

Under the 1986 Amendments to the Safe Drinking Water Act (SDWA), allowable concentrations of THMs will be reconsidered for regulation in 1991. Parallel to this, a minimum of twenty-five new contaminants are to be regulated. These twenty-five likely will include several DBPs.

#### Pilot Plant Operation

For the studies reported herein pilot plant operation was utilized to produce water for bench-top chlorination studies. The pilot plant at EPA-Cincinnati treats Ohio River water and has been adequately described elsewhere.<sup>6</sup> Chlorination was not employed on the pilot plant, because results of continuous flow studies would be extremely difficult to interpret in the absence of the static bench-top-study information. In each study, chlorination of raw and undisinfected filtered water would produce terminal level DBP (analogous to term THM) concentrations, and consequently, a measure of the effect of pilot-scale treatment on DBP precursor.<sup>7</sup> The pilot plant was operated until steady-state operation was achieved (typically less than two days) before sampling.

Three studies were conducted with the EPA pilot plant treating Ohio River water. In each, the pH of the clarification process was different. The three studies were designed to provide a range of pH typical of the extremes occurring during water treatment.

In the first run (1A), low pH alum coagulation was employed. Early THM studies indicated that optimal removal of THM precursor material occurred during low pH coagulation and clarification. A previous pilot plant run predicted this, but did not include analyses of DBPs other than THMs. Water collected from run 1A was used to determine if other DBPs can similarly be controlled by low pH coagulation prior to chlorination. Low pH coagulation was achieved by feeding alum and adding an acid (HCl) to lower the pH to near 5.7. These were the conditions optimal for THM precursor control with alum in the previous pilot plant run.

During run 2A, pH was investigated at the other extreme during lime softening. Water was softened at a pH sufficient to precipitate  $Mg(OH)_2$ , near 10.8, so that the high pH effect on precursor control could be studied.

Ohio River water is not naturally a hard water, but, based on chemical analyses of the river water for calcium and hardness and alkalinity characteristics, sufficient chemicals were added to the water upon arrival at the EPA pilot facility to give the following attempted hard water quality (all as mg/L  $CaCO_3$ ):

total hardness = 240  
calcium = 150  
magnesium = 90  
P alkalinity = 0 (pH < 8.3)  
total alkalinity = 110

Chemicals were added as the pilot plant's raw water storage tank filled. Calcium was added as  $CaCl_2$ ; magnesium as  $MgSO_4$ ; and alkalinity as  $NaHCO_3$ . This water quality was then considered to be typical of hard waters.

Lime-soda ash softening occurred following the processes described by Sawyer & McCarty.<sup>8</sup> Iron was used as a coagulant in the form of technical-grade  $Fe_2(SO_4)_3 \cdot 3H_2O$ , which is approximately 68%  $Fe_2(SO_4)_3$ . Jar testing determined the proper dose of coagulant in addition to the calculated lime and soda ash doses. Jar testing also predicted the dose of NaOH required to reach  $pH\ 10.8 \pm 0.1$ , as required for precipitation of  $Mg(OH)_2$ .

Adjustment of pH after softening was not by the usual  $CO_2$  recarbonation, but was accomplished by the addition of an acid (HCl). The HCl dose was determined on the bench by an acid titration of the settled and softened water.

Finally, conventional pH (neutral) coagulation employing alum was studied in Run 3A.

#### Pilot Plant Operating Data

Tables 2, 3, and 4 present mean operational data representing these three pilot plant runs. The data indicate good turbidity control, softening where applicable, and achievement of the desired pH range.

## Procedures for Chlorination Experiments

Raw and filtered water samples were collected from the pilot plant runs 1A, 2A, and 3A in 30 to 40 liter quantities.

Aliquots of each sample were buffered to three different selected pH values (5, 7, and 9.4) by first placing 80 mL of a buffer solution (a combination of 0.25 M borate and 0.25 M phosphate) into a 10 L bottle, then filling to a 4 L mark with either raw water or filtered water. Either 1.0 N NaOH or 1.0 N H<sub>2</sub>SO<sub>4</sub> was added to the buffered sample, while stirring and monitoring with a pH meter, until the desired pH was reached. Each sample was then transferred to a 1 gallon bottle until needed for further work.

The chlorine demand of each sample, as originally collected, was determined by a proposed Standard Method<sup>9</sup> for the determination of THM formation potential. The required amounts of chlorine, as determined above, were then measured into 1 liter bottles, using one bottle per experimental time period. Three experimental chlorination time periods were chosen for most of this work: 4 hours, 2 to 4 days (dictated by convenience), and 6 to 7 days. This required a total of 6 bottles per time period: three bottles containing buffered raw water, chlorinated at three different pH values, and three more corresponding bottles for filtered water. Chlorination reactions were allowed to proceed at 25°C until the reaction was quenched at the end of the given time periods.

Two procedures were used for stopping the chlorination reaction at the various time periods: (1) samples to be analyzed for dihaloacetonitriles (DHAN), chloropicrin (CP), 1,1,1-trichloropropanone (111-TCP), and trichloroacetonitrile (TCAN) were each poured into a 40 mL glass vial that already contained about 3 drops of ammonium chloride solution (5 g NH<sub>4</sub>Cl/100 mL); the vial was filled with sample, shaken, and then neutralized to pH 7 by adding either 1.0 N H<sub>2</sub>SO<sub>4</sub> or 1.0 N NaOH. (2) For samples to be analyzed for TOX and the other DBPs, the chlorine residual remaining in the 1L bottle was determined and was then destroyed by adding a slight excess of sodium sulfite; the pH was then adjusted to between 5 and 6. Samples for trihalomethanes (THM) and chloral hydrate (CH) were then taken in separate vials; samples for TOX and haloacetic acids (HAA) were also poured into separate 250 mL bottles, and the pH of the TOX sample was further reduced to 2 by adding nitric acid. All samples are stored at 4 to 6°C until ready for analysis.

## Results of Experiments on Effects of pH and Time

For the sake of brevity, only the data from run 1A are presented. The same trends were observed and general conclusions apply to the other two runs. These conclusions can be made as follow.

Total Organic Halogen (TOX) (Fig. 2) TOX concentrations were reasonably independent of pH in the range of 5 to 9.4; the TOX concentrations increased with time, although the 4 hour reaction produced approximately 60% of the TOX that was produced during 7 days reaction. This is consistent with historical data.<sup>2,3,10</sup>

Total Trihalomethanes (TTHM) (Fig. 3) The concentration of TTHM increased with time for each pH value; the TTHM concentrations after 144 hours reaction in raw water, were, for the pH values of 5, 7, and 9.4; 65, 183, and 252 ug/L (as CHCl<sub>3</sub>), respectively.

This trend for trihalomethane formation with pH and time is also well known<sup>1</sup> and is presented here for reference. From this trend for THM formation and that noted above for TOX, one can conclude that the non-THM portion of TOX decreases with increasing pH of chlorination in these experiments, also as reported previously (Fig. 1).<sup>2,3,10</sup>

Trichloroacetic Acid (TCAA) (Fig. 4) TCAA concentrations produced at pH values of 5 and 7 were about equal at any given reaction time (about 50 ug/L at 4 hours and 130 ug/L after 7 days reaction with raw water), but the TCAA concentrations were always significantly lower at a reaction pH of 9.4.

This trend is parallel to that mentioned with regard to nonpurgeable organic halogen and may partially account for it. Note that the absolute concentrations of TCAA are in the range normally expected for the TTHMs and, indeed exceed them in some cases.

Dichloroacetic Acid (DCAA) (Fig. 5) DCAA concentrations were essentially independent of the reaction pH at all time periods, but an increase with time was also always observed. Initial thinking is that this compound is formed by a different mechanism than is TCAA in spite of the obvious relationship by chemical class. Even if DCAA was an intermediate in the formation of TCAA, the high pH data could only support this contention if DCAA was stable and unlikely of further reaction at pH 9.4. Note that concentrations of DCAA, like TCAA, also rivals THM concentrations in some cases.

Chloral Hydrate (CH) (Fig. 6) The concentration of CH increased with time for the pH values of 5 and 7, and were in about equal concentrations for both pH values (about 5 ug/L at 4 hours and 25 ug/L after 7 days); CH was, however, initially formed most rapidly at a pH of 9.4 (10 ug/L produced at this pH in the 4 hours period or twice the amount produced at the lower pH values), but the rate of hydrolysis (decomposition) of CH at a pH of 9.4 quickly exceeded the rate of formation, and, consequently, the concentration of CH at the 9.4 pH value decreased with time (10 ug/L at 4 hours down to less than 2 ug/L after 7 days). Importantly, CH hydrolyzes (as does 111-TCP) to form chloroform which has enhanced formation at high pH (Figs. 1,3).

The competing formation and decay reactions of CH are the most clear demonstration of the difficulty of predicting the outcome of application of treatment strategies involving these chemically complex systems. Even minor pH adjustments in the range of 7 to 9 can dramatically affect product distribution.

Dichloroacetonitrile (DCAN) (Fig. 7) DCAN was stable only at pH 5, and its concentration steadily increased with time at that pH. At pH 7, the DCAN concentration decreased with time after the first sampling time of four hours (6 ug/L at 4 hours to 2 ug/L after 144 hours) and hardly formed at all at pH 9.4. At pH 7, a formation-decay competing reaction phenomenon is occurring much like CH at pH 9.4. For DCAN at pH 9.4, this effect is less clear. Nevertheless, DCAN concentrations are the lowest at high pH, again consistent with historical data.<sup>11</sup>

#### Treatment Studies

DBPs may be controlled by changing the oxidant or its application point, controlling the precursor material that the oxidant reacts with,

removing the formed DBPs, or a combination of these.<sup>1</sup> This has long been stated for THM control, although, because of their formation during the distribution of water, only the first two options are usually considered. The complexity of the mixture of other DBPs, their differing physical/chemical characteristics, and differing chemistries of formation cause this perceived restriction to only two viable treatment approaches to be reinforced.

#### Precursor Removal in Pilot Studies

In any discussion of precursors, especially in the case of experiments reported on herein, where the formation and, in some cases, decay, depends on several factors, the term precursor concentration has an uncertain meaning. This is the reason that, even for the relatively simple case of THMs, precursor has been defined as a "formation potential" that always must be accompanied by a stated specific set of reaction conditions, especially time, temperature, and pH value. Any significant differences between these important reaction conditions for separate samples make comparisons of absolute "precursor concentrations" meaningless. Further, one might wonder the value of precursor measurements at all at high pH for CH and DCAN, conditions where decay overtakes the formation reactions. Nevertheless, these reactions can both be thought of as taking place both at a slower rate and to a lesser extent at lowered precursor concentrations (such as resulting from treatment) just as with a stable DBP's formation. Thusly, the formation potential concept is used here to define precursor. The results of formation of DBP from whatever precursor is present in a sample under the stated reaction conditions are compared in a relative sense in the following section in a way that leads to some surprising and encouraging conclusions.

Percent Removals -- One Treatment pH, Three Chlorination pH Values At any specific set of reaction conditions, the relative concentration of each constituent shown in Figures 2 to 7 was lowered to a similar extent (Fig. 8). Removal percentages from raw to low pH alum coagulated/filtered water were all within range of approximately 60 to 80%. If one accepts that the "wobble" of 60-80% removal of precursors is caused by the variation in formation potential measurements compounded by the complexities brought about by the differing formation/decay mechanisms, the percent removal of precursors for any single constituent can probably serve as a fairly accurate predictor for the percent removal of the remaining five.

Surprisingly, this generalization seems to hold regardless of the pH of chlorination even though the absolute values of concentration for each compound change dramatically with pH.

Pilot runs 2A and 3A resulted in different percent removals of precursor overall (approximately 50% in run 2A and 40% in run 3A) but exhibited the same trends as described in fig. 8.

These observations about precursor removal through physical removal processes are extremely important because this increases the probability that the vast experience we now have with THM precursor control by physical removal processes may be transferred to the control of these other byproducts as well. No such general conclusions, however, can be drawn about removals of the compounds themselves after they are formed, nor can we make general statements concerning precursor control by chemical processes such as ozone oxidation.

## Alternate Disinfectants

Figure 9 compares the TOX formation by chlorine dioxide and chloramines with that of chlorine. The THMs are completely controlled with chlorine dioxide and nearly so with chloramines as applied in this earlier study. Non-THM organic halogen is also greatly reduced for both disinfectants. This information and that from previous studies<sup>6</sup> would indicate that the Table 1 chlorination byproducts are probably not a problem when these other disinfectants are used.

## Phenol Study - List Modification

The current list (Table 1) of the target byproducts for regulation contains brominated and mixed bromine/chlorine species of trihalomethanes and haloacetonitriles. These are known to form in bromide containing waters when they are chlorinated. Logically, the analogous mixed halo- and bromoacetic acids might also form. As a test of this idea, phenol, which gives TCAA in high yield as percentage of TOX,<sup>10</sup> was chlorinated in the presence of bromide ion under typical formation potential reaction conditions. Given the qualifications that several standards were (and still are) not available and that some reference mass spectra were not available, interpretation of the data indicated bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), bromochloroacetic acid (BCAA), and tribromoacetic acid (TBAA) were all formed.<sup>12</sup> The same array of products has since been seen when humic acids were chlorinated under similar conditions. The data indicate that the bromo- and mixed haloacetic acids probably should merit regulatory consideration to remain consistent with THM and DHAN precedents. Further work might also result in finding analogous products for 111-TCP, CP and CH.

## Summary of Implications for Treatment Strategies

1. The most important chemical variable to consider in chlorination byproduct formation is pH. Yields of nearly all halogenated organics can usually be either maximized or minimized by controlling the pH at which the various reactions occur, although dichloroacetic acid (DCAA) seems to be an exception to this rule. Table 5 summarizes this formation in a qualitative way.

The most obvious implication for water treatment is the direct trade-off between THM control (low pH) and control of most of the other byproducts (high pH). While DCAN, 111-TCP and CH are not likely to be problems at pH above 8-9 and TCAA above pH 10, under these conditions THM would be maximized. In general, the reverse is true at the lower end of the normal pH range of drinking water treatment (pH 5).

2. Precursor control may prove to be similar for all of these chlorination byproducts through physical removal mechanisms. At least the current data support this for conventional treatment. Experiments with adsorptive and membrane process are underway or anticipated. No such conclusion about oxidative removal or modification processes can be drawn from these data.

3. Analytical methods for DBP and preservation or dechlorination agents for samples were not addressed in any detail. The analyses for several of the DBP, especially the haloacids, are not easily put on line in the laboratory. We experienced considerable difficulty with the current procedures, delaying this work. Now that procedures have



been worked out, things should be simpler, but we do expect that compliance monitoring might be somewhat of a problem.

The sample dechlorination procedures used for the DBP were different, depending on the compounds to be measured. Ammonium ion was used for CP and the DHANs because commonly used sulfite destroys these compounds. This raises the possibility that SO<sub>2</sub> application (a common water treatment process) may be used in some way to control CP and DHANs.

Likewise, the fact that NH<sub>4</sub>Cl stops the formation of these substances supports the contention that these compounds will not be formed by chloramination.

4. Temperature and chlorine dose were not investigated for their effects on formation of DBP. This must still be done. As the THMs, the conclusion that higher temperatures will lead to higher concentrations of DBP at a faster rate is logical. Alternatively, however, hydrolysis rates for CH, DHANs, and possibly CP and the haloacids are also likely to increase, possibly having the opposite effect on the presence of these species.

Chlorine dose may also be important. Although chlorine dose appears to have little impact on THM formation, it does affect TOX significantly (Fig. 1). This may be reflected in increased concentrations of non-THM DBP with increased chlorine dose.

5. Concern concurrent with an oxidant's potential to form or not to form DBPs is its potential to control microbiologic contaminants during water treatment. Strategies for the control of DBPs must also ensure control of regulated microbiologic entities as well as the compounds under regulatory consideration. Hence, any change in oxidant type, location, or dose should examine both DBP and microbiologic levels.

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Table 1

## DPBs for Analysis in Pilot Plant Studies

chloroform	chloroacetic acid
bromodichloromethane	dichloroacetic acid
dibromochloromethane	trichloroacetic acid
bromoform	chlotal hydrate
dichloroacetonitrile	chloropicrin
bromochloroacetonitrile	1,1,1-trichloropropanone
dibromoacetonitrile	
trichloroacetonitrile	

TABLE 2

## RUN 1A PILOT PLANT OPERATION: LOW pH ALUM COAGULATION

Parameter	Water Quality <sup>a</sup>				clear well
	raw <sup>b</sup>	flocculated	settled	filtered <sup>b</sup>	
temperature, °C	11.1-26.2	17.2	17.1		
pH, units	7.58	5.3-5.8	5.79	5.93	5.89
turbidity, ntu	35-55		2.77	0.13	0.18
alum dose, mg/L	40.5				
HCl dose, mg/L	16.3				

<sup>a</sup>range as mean value<sup>b</sup>water sampled for organic analyses

TABLE 3

RUN 2A PILOT PLANT OPERATION: HIGH pH COAGULATION (LIME SOFTENING)

	Water Quality <sup>a</sup>					
	Ohio River <sup>d</sup>	raw <sup>b,e</sup>	flocculated	settled softened	pH adjusted	fil- tered <sup>b</sup>
temperature, °C			27.4	26.3	25.5	25.9
pH, units	8.2	7.96	10.6-10.8	10.72	8.6	8.45
turbidity, ntu	27	7-27		0.76		0.12
hardness <sup>c</sup>	103	235		67		64
calcium <sup>c</sup>	75	144		37		34
magnesium <sup>c</sup>	28	91		30		30
total alkalinity <sup>c</sup>	48	98		66		30
coagulant dose, mg/L		33.7				
lime dose, mg/L		186				
soda ash dose, mg/L		117				
NaOH dose, mg/L		66.2				
HCl dose, mg/L					24.2	

<sup>a</sup>range or mean value<sup>b</sup>water sampled for organic analyses<sup>c</sup>mg/L as CaCO<sub>3</sub><sup>d</sup>before spiking<sup>e</sup>following spiking

TABLE 4

RUN 3A PILOT PLANT OPERATION: CONVENTIONAL pH ALUM COAGULATION

	Water Quality <sup>a</sup>			
	raw <sup>b</sup>	flocculated	settled	filtered <sup>b</sup>
temperature, °C	28.1	28.0	26.7	26.9
pH, units	7.5	6.9	7.05	6.98
turbidity, ntu	5.4-11		0.75	0.09
alum dose, mg/L	25.5			

<sup>a</sup>range or mean value<sup>b</sup>water sampled for organic analyses

TABLE 5

## SUMMARY OF DBP FORMATION CONDITIONS

By-Product	pH of Chlorination		
	pH 5	pH 7	pH 9.4
TTHM	lower formation		higher formation
TCAA	similar formation		lower formation
DCAA	similar formation - perhaps slightly higher at pH 7		
MCAA	concentrations below 5 ug/L, trends not discernible		
DBAA	concentrations below 1 ug/L, trends not discernible		
CH	similar formation		forms within 4 hours; <u>decays</u> over time to less than 5 ug/L
CP	concentrations below 1 ug/L trends not discernible		
DCAN	higher formation	forms within 4 hours; then <u>decays</u> over time to less than 5 ug/L	concentrations below 2 ug/L trends not discernible
BCAN	concentrations below 2 ug/L trends not discernible		
DBAN	concentrations below 0.5 ug/L trends not discernible		
TCAN	not detected		
111-TCP	higher formation	concentrations below 2 ug/L trends not discernible	not detected

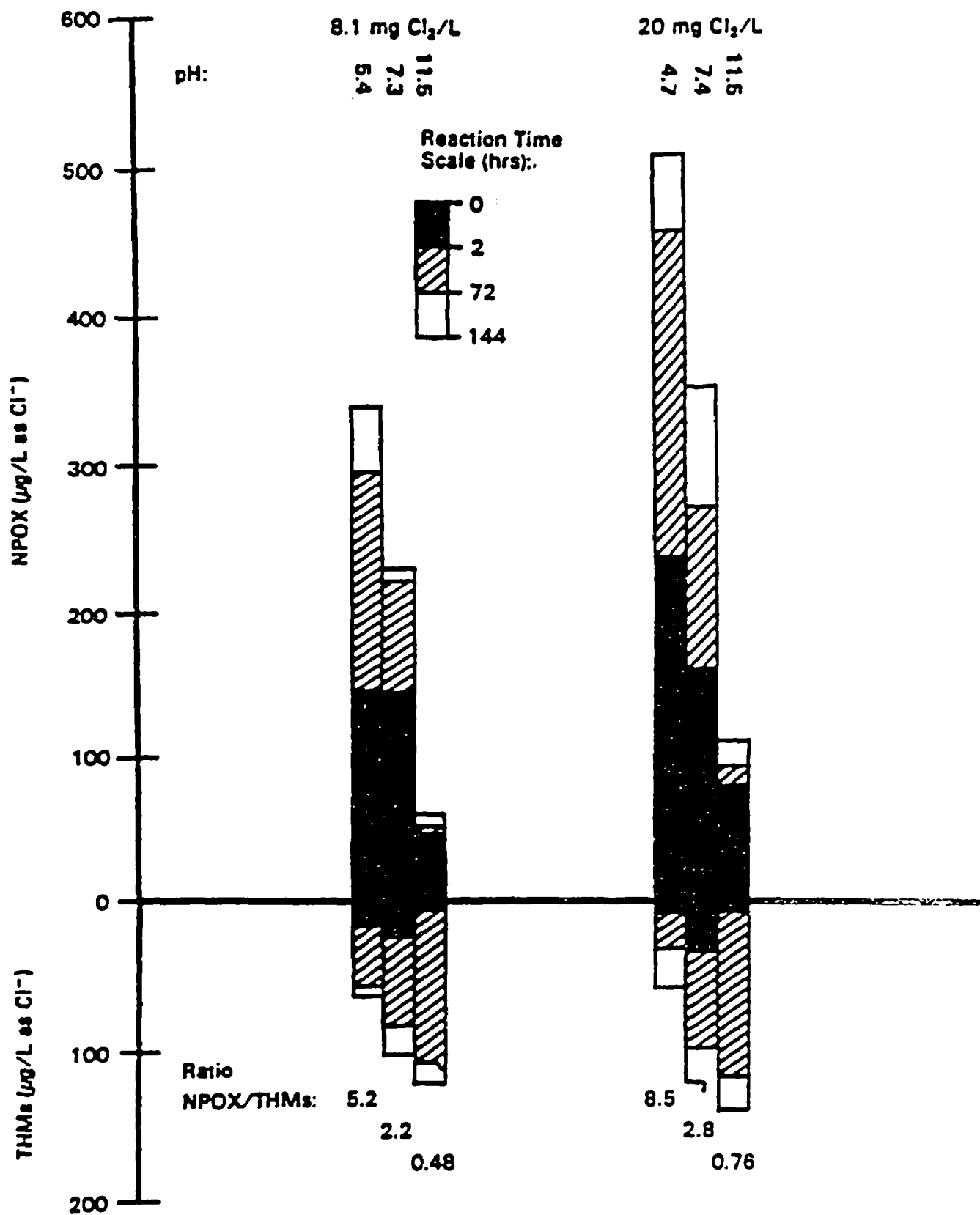


Figure 1. A comparison of the effects of pH and oxidant dose on the formation of NPOX and THMs (CHCl<sub>3</sub>) at 20°C (68°F) in distilled water solutions of 5 mg humic acid/L.

FIGURE 2. THE VARIATION OF TOX WITH pH AND TIME

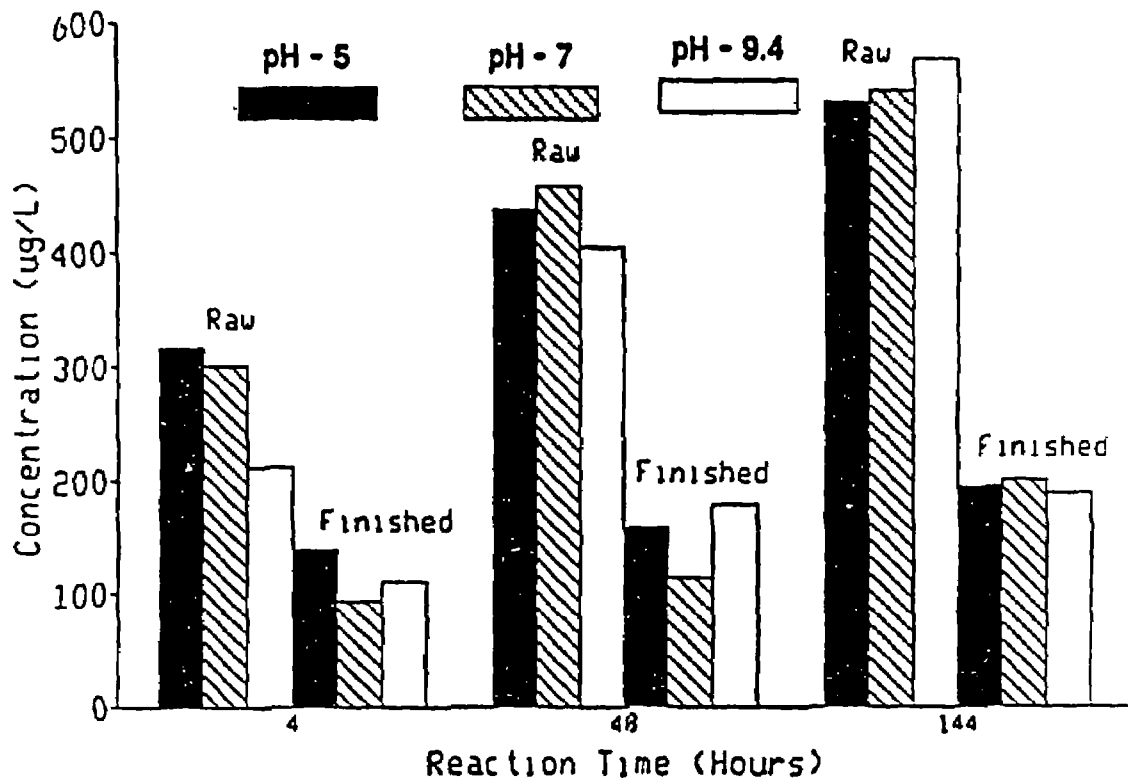


FIGURE 3. THE VARIATION OF TTHM WITH pH AND TIME

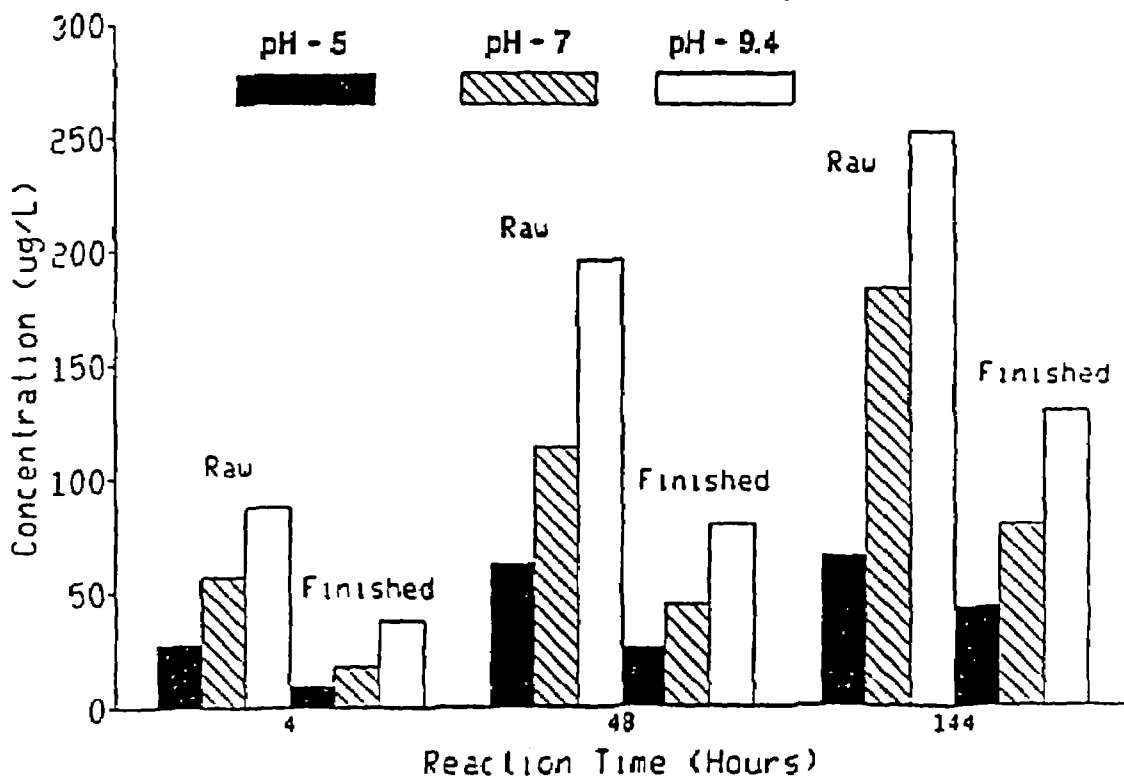


FIGURE 4. THE VARIATION OF TCAA WITH pH AND TIME

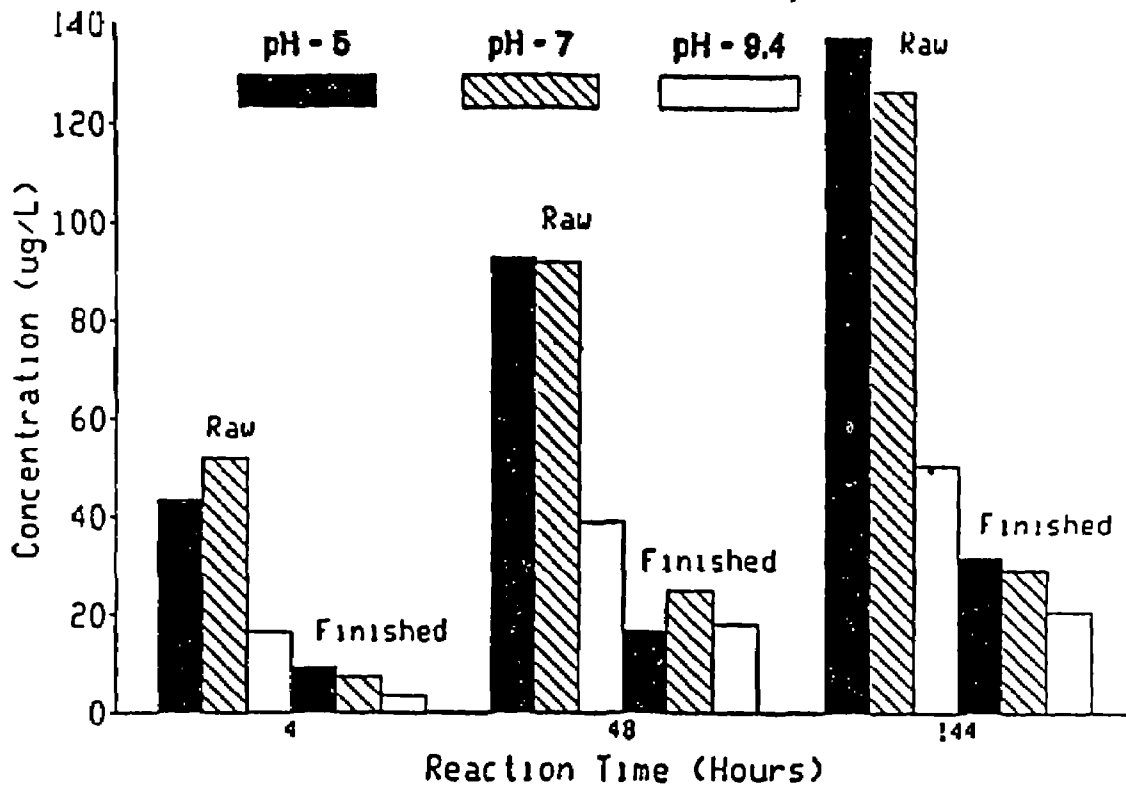


FIGURE 5. THE VARIATION OF DCAA WITH pH AND TIME

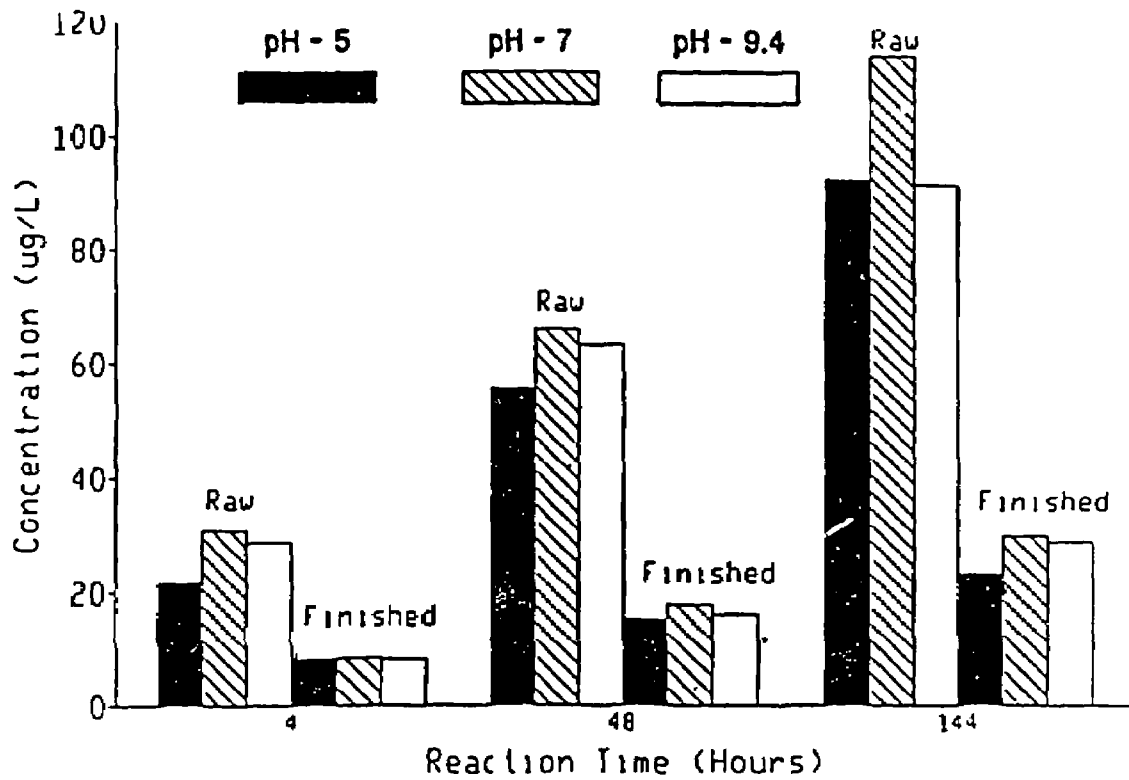




FIGURE 6. THE VARIATION OF CHLORAL HYDRATE WITH pH AND TIME

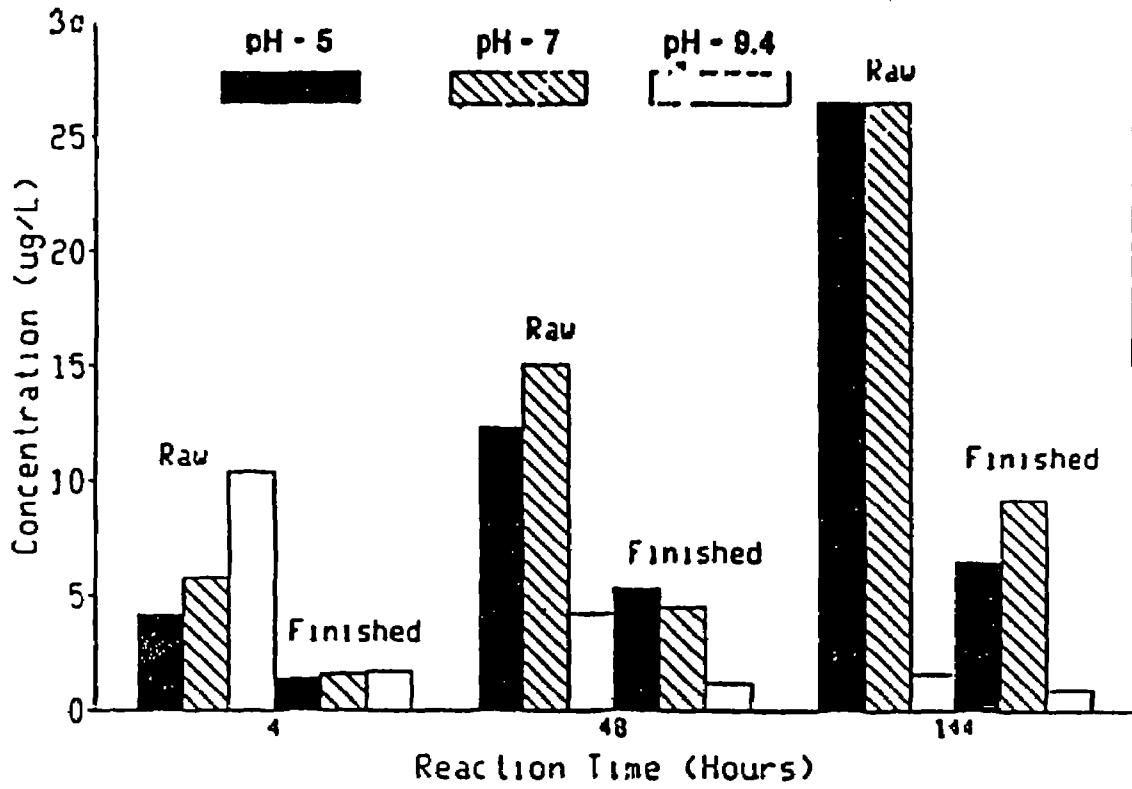


FIGURE 7. THE VARIATION OF DCAN WITH pH AND TIME

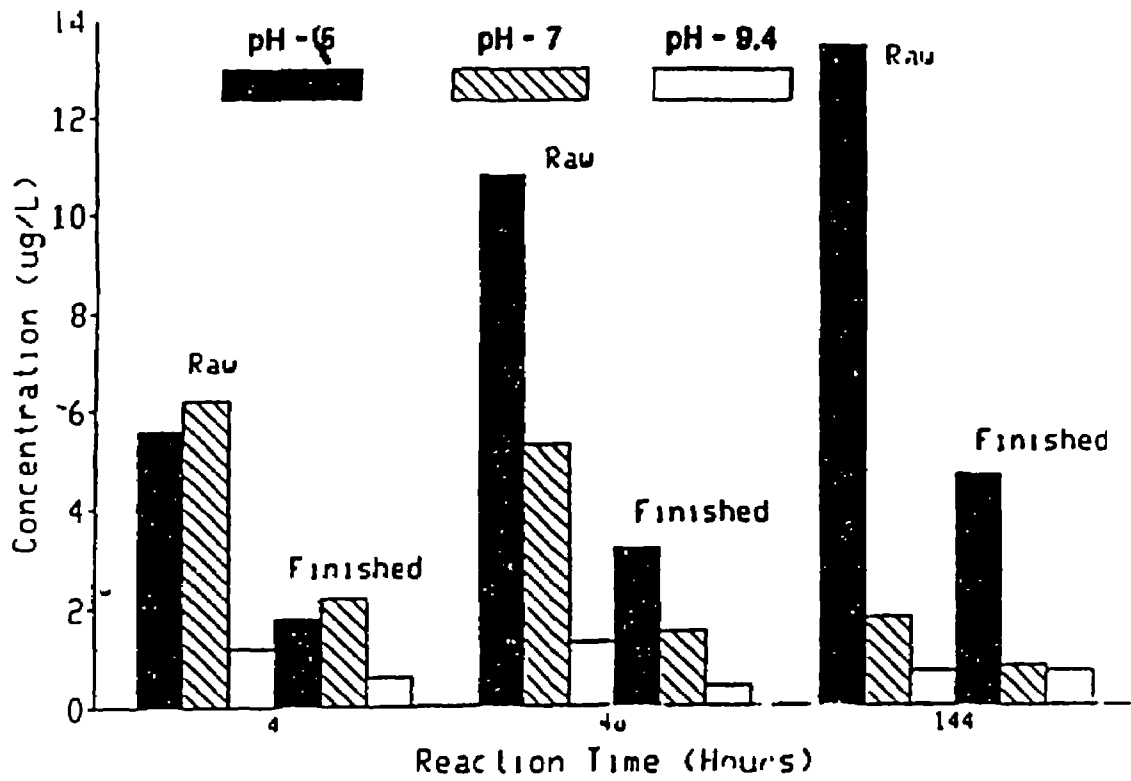
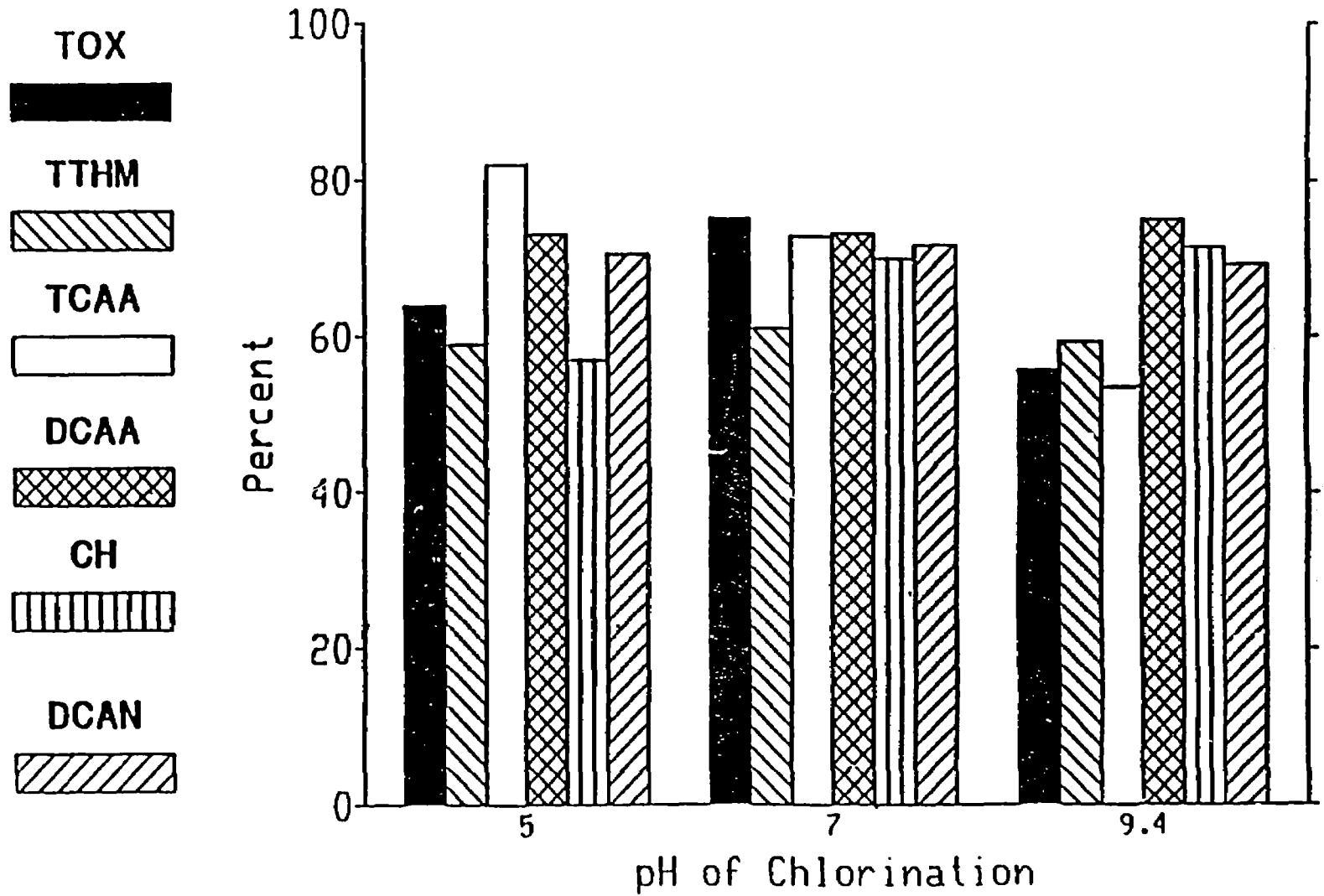


FIGURE 8. PERCENT FORMATION POTENTIAL REMOVAL FOR COMPOUNDS AFTER 48 HOURS CHLORINATION (RAW --> FILTERED)



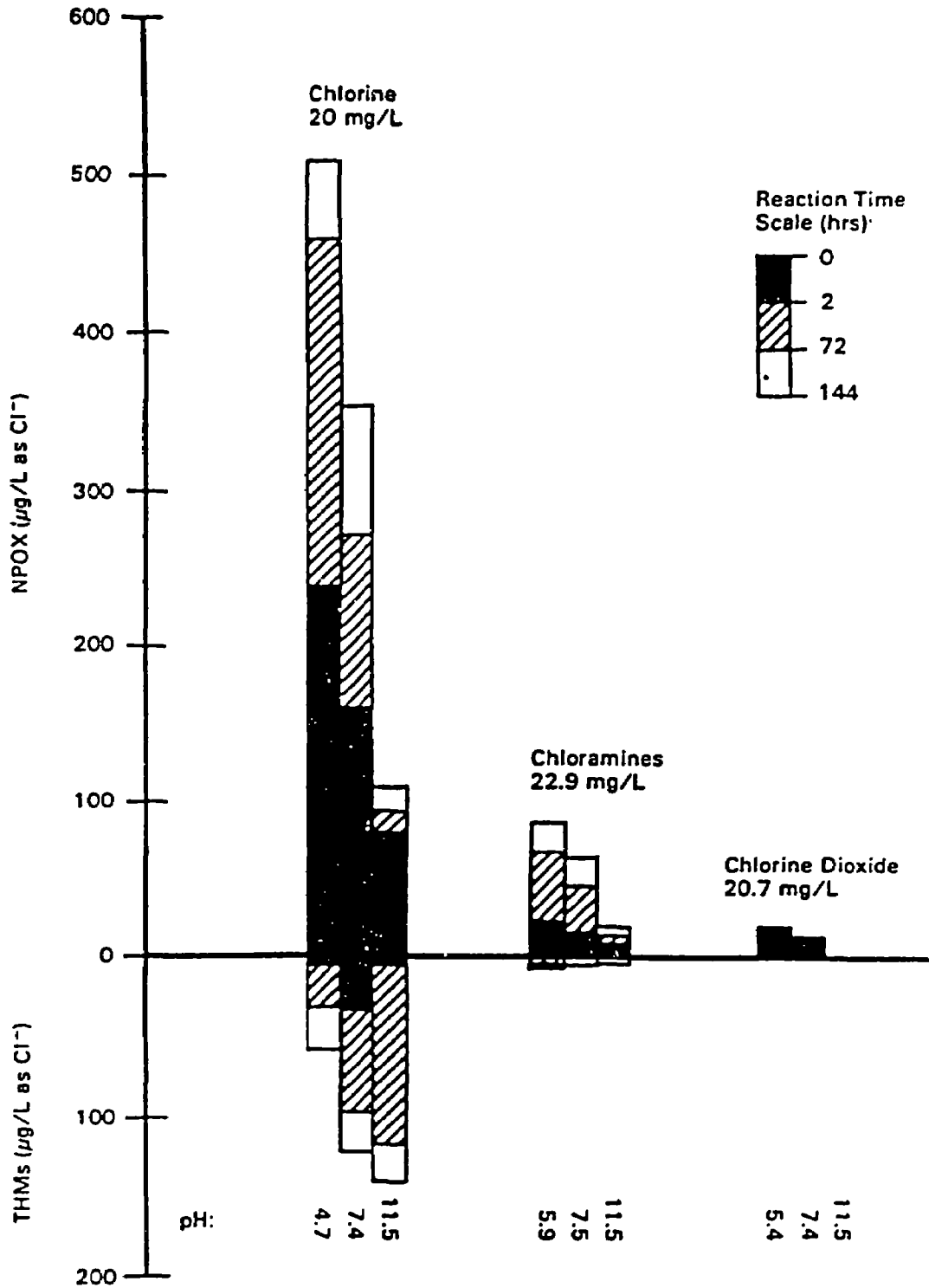


Figure 9. A comparison of the formation of NPOX and THMs ( $\text{CHCl}_3$ ) at  $20^\circ\text{C}$  ( $68^\circ\text{f}$ ) in distilled water solutions of 5 mg humic acid/L dosed with various disinfectants.