

CHLORINATION OF SOLUBLE RESIDUAL ORGANICS
IN SEWAGE EFFLUENTS

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by

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A Project Report

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Engineering

McMaster University

October 1972

MASTER OF ENGINEERING
(Chemical Engineering)

McMaster University
Hamilton, Ontario

TITLE: Chlorination of Soluble Residual Organics in Sewage Effluents

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NUMBER OF PAGES: 131

ABSTRACT:

Filtered final effluent was chlorinated at various doses using calcium and sodium hypochlorite in order to study the effect of chlorination on the soluble organics present in final effluents. The biochemical oxygen demand (BOD) was measured over a period of five days and carbon analyses (TOC) were performed during the course of the reaction. Chemical oxygen demand tests (COD) on filtered chlorinated-dechlorinated and unchlorinated sewage at various doses were also performed. It was found that chlorination did not bring about a BOD₅ reduction nor rendered the soluble organics bioresistant or toxic to micro-organisms, owing to the presence of ammonia, as there was no significant difference in the extent of carbon degradation. The COD as well as TOC before and after chlorination remained unchanged indicating that there was no loss of organic content due to chlorination.

The pure compounds, glutamic acid, alanine, histidine, glycine, ammonia, phenol, n-butylamine, acetic acid and maleic acid were chlorinated at various chlorine doses in the presence and absence of ammonia and with chloramines. Glutamic acid and phenol were chlorinated at various pH

levels. The oxidation of glycine by sodium hypochlorite was also studied. It was found that pH influences the rate of reaction considerably and that the presence of ammonia, whether free or combined as chloramines, slowed down the rate and prevented the oxidation of glycine from occurring.

The effect of chlorine residuals on the seed micro-organisms was also investigated. Three levels of residuals, 0.2, 0.5 and 0.8 mg/l available chlorine, were employed. The chlorine demand of the sewage was satisfied prior to the addition of these residuals. The BOD was also monitored over a period of five days. The results indicated that longer lag phases resulted from the application of higher residuals and the lowest BOD was observed to occur at the highest residual. However, some micro-organisms survived chlorination as evidenced by the exertion of a BOD at the 0.8 mg/l available chlorine level.

The seeding technique employed by previous workers for measuring the BOD₅ of unfiltered chlorinated-dechlorinated sewage was also investigated. It was found that even when the unchlorinated sample was not seeded, it contained a higher microbial concentration as evidenced by plate counts performed on both chlorinated-dechlorinated seeded and unchlorinated unseeded samples at two dilutions commonly employed in BOD₅ determinations. Associated with these results was a BOD₄ reduction of about 2.2 mg/l/mg/l Cl absorbed. Seeding of the samples, at best, provides a uniformly mixed microbial population but not necessarily a uniform microbial concentration. These results could possibly explain the BOD₅ reductions observed on unfiltered chlorinated effluents.

ACKNOWLEDGEMENTS

I would like to extend my gratitude to Dr. K. L. Murphy for his help and guidance during this work.

My thanks are also extended to Mrs. Alina Latoszek for her microbiological work, to Mr. Tony Ho for his assistance in laboratory work, to Dr. M. Brownstein and Anna Addie for their help.

I also thank A. Neil for partly typing this manuscript.

The McMaster financial assistance is also appreciated.

LIST OF TABLES

		PAGE
TABLE 1	Break-Point Chlorination, Weber <u>et al</u> (1940).	7
TABLE 2	BOD ₅ Reductions with Chlorination, Baity and Bell (1929).	14
TABLE 3	Observed Bacterial and BOD ₅ Reductions in Receiving Streams, Baity <u>et al</u> (1933).	16
TABLE 4	Calculated First Order Parameters, Snow (1952).	18
TABLE 5	Effect of Seeding on BOD Curve, Thomas (1940).	23
TABLE 6	Calculated First Order Parameters, Thomas (1940).	24
TABLE 7	Toxicity of Selected Chlorinated Organics, the Manufacturing Chemist Association (1972).	26
TABLE 8	Chlorine Demand of Sewage After 30 Minutes Contact Time Using Calcium and Sodium Hypochlorite.	43
TABLE 9	COD of Chlorinated and Unchlorinated Sewage.	45
TABLE 10	Oxidation-Reduction Potentials of Chlorine Compounds, Handbook of Chemistry and Physics, 47th Edition.	46
TABLE 11	Effect of Ammonia on the Oxidation of Glycine.	74
TABLE 12	Chlorine Dosages Required for the Disinfection of Sewage, Sewage Treatment Plant Design Manual (1959).	74
TABLE 13	Chlorine Demand of Sewage, Runs 6, 7, and 8.	78
TABLE 14	Chlorine Residuals as a Function of Time in Seeded Filtered Effluents.	79

TABLE 15 Chlorine Demand of Unfiltered Sewage and Results
of Plate Counts.

86

LIST OF FIGURES

	PAGE
FIGURE 1 Biological Reactor.	30
FIGURE 2 BOD of Sewage Chlorinated with Calcium Hypochlorite, Run-1.	39
FIGURE 3 BOD of Sewage Chlorinated with Sodium Hypochlorite, Run-5.	40
FIGURE 4 Carbon Degradation of Chlorinated and Non-Chlorinated Sewage, Run-1.	41
FIGURE 5 Carbon Degradation of Chlorinated and Non-Chlorinated Sewage, Run-5.	42
FIGURE 6 Microbial Respiration Curve.	44
FIGURE 7 Chlorination of Glutamic Acid at Various pH Levels. Chloramination of Glutamic Acid at pH 7.2.	47
FIGURE 8 Chlorination of Phenol at Various pH Levels. Chloramination of Phenol at pH 7.2.	49
FIGURE 9 Chlorination and Chloramination of Glutamic Acid at Various Dosages.	52
FIGURE 10 Chlorination and Chloramination of Alanine at Various Dosages.	53
FIGURE 11 Chlorination and Chloramination of Histidine at Various Dosages.	54
FIGURE 12 Chlorination and Chloramination of Glycine at Various Doses.	56

FIGURE 13	Chlorination and Chloramination of Ammonia at Various Doses.	59
FIGURE 14	Chlorination of Phenol in the Presence and Absence of Ammonia.	61
FIGURE 15	Chlorination and Chloramination of n-Butyl- amine at Various Doses.	62
FIGURE 16	Chlorination of Acetic Acid at Various Dosages.	64
FIGURE 17	Chlorination of Maleic Acid in the Presence and Absence of Ammonia.	66
FIGURE 18	Chlorination of Histidine in the Presence of Ammonia.	68
FIGURE 19	Chlorination of Glycine in the Presence of Varying Amounts of Ammonia.	70
FIGURE 20	Extent of Chlorination and Oxidation of Glycine in the Absence of Ammonia.	72
FIGURE 21	Effect of Chlorine Residuals on the Seed, Run-6.	80
FIGURE 22	Effect of Chlorine Residuals on the Seed, Run-7.	81
FIGURE 23	Effect of Chlorine Residuals on the Seed, Run-8.	82
FIGURE 24	BOD Progression of Unfiltered Unchlorinated and Chlorinated-Dechlorinated and Seeded Sewage, Run-10	85

TABLE OF CONTENTS

	PAGE	
ABSTRACT	iii	
ACKNOWLEDGEMENTS	v	
LIST OF TABLES	vi	
LIST OF FIGURES	viii	
CHAPTER 1	Introduction.	1
CHAPTER 2	General.	3
2.1	History of Chlorination.	3
2.2	Chemistry of Chlorination.	4
2.3	Disinfection with Chlorine.	10
CHAPTER 3	Literature Review.	13
CHAPTER 4	Experimental Methods and Approaches.	28
4.1	Materials.	28
4.2	Apparatus.	29
4.3	Methods.	31
4.4	Determination of Chlorine Residuals.	33
4.5	Dechlorination with Sodium Sulfite.	35
4.6	COD Tests.	35
4.7	Standardization of Oxygen Probes.	35
CHAPTER 5	Discussion of Results.	37
5.1	Mixing and Chlorine Residuals.	37
5.2	Chlorination, the BOD of Sewage and Bio-degradability.	37

5.3	Chlorination and pH.	45
5.3.a	Glutamic acid.	45
5.3.b	Phenol.	48
5.4	Chlorine Concentration and Chlorination.	50
5.4.1	Glutamic acid.	50
5.4.2	Alanine.	51
5.4.3	Histidine.	52
5.4.4	Glycine.	55
5.4.5	Ammonia.	57
5.4.6	Phenol.	60
5.4.7	n-Butylamine.	60
5.4.8	Acetic acid.	63
5.4.9	Maleic acid.	65
5.4.10	Histidine.	65
5.5	Chlorination in the Presence of Ammonia.	67
5.6	Extent of Oxidation of Glycine in the Presence and Absence of Ammonia.	71
5.7	Chlorination and Viability of Seed Organisms.	77
5.8	Influence of the Seed on the BOD ₅ .	83
CHAPTER 6	Conclusions and Recommendations.	87
6.1	Conclusions.	87
6.2	Recommendations.	89
BIBLIOGRAPHY		91
APPENDIX		94

CHAPTER 1

INTRODUCTION

Chlorination as a treatment process has found wide application industrially and at the municipal level primarily as a disinfectant.

Chlorine and chlorine compounds used in water and wastewater treatment are potent oxidizing agents. They may often be dissipated in reactions with a number of chemical impurities before any significant disinfection occurs. The rate of these reactions may be fast or slow depending on the oxidation potential of chlorine and chlorine compounds formed in these reactions. Among the variable components of water that can affect disinfection the following are outstanding:

- 1) Alkalinity,
- 2) Inorganic reducing substances,
- 3) Ammonia and amines,
- 4) Oxidizable organic materials, and
- 5) Bacteria and other organisms.

Aside from its use as a disinfectant, chlorine found wide application in the control of odours, the prevention of septicity, and most important in reducing the BOD_5 of a waste. In spite of appearing to be a ubiquitous panacea of wastewater treatment, chlorination may in fact cause worse pollutional problems than it treats. The literature is replete with studies and reviews of the toxicological and coagulative properties of chlorine. Numerous studies have affirmed that chlorination reduces the BOD_5 loading and improves the physical characteristics of the receiving

streams. However, very few studies have been directed to the question of how chlorination brings about a BOD₅ reduction. In fact, the work presented in the literature is confined to studies on unfiltered effluents and on that basis it is virtually impossible to study the effects of chlorination as there are too many variables involved. Further, no consideration was given to the presence of ammonia and its behaviour with respect to the soluble organics present in sewage, and, in addition, no attention was given to the seed employed in BOD₅ determinations. There is no reported work in the literature on the chlorination of filtered sewage and its consequent effect on the BOD. Various investigators have attempted to explain what happens when sewage is chlorinated by chlorinating pure compounds and observing the resulting effect on the BOD₅. These studies have neglected the presence and role of ammonia during the reactions.

It is the intention of this study to examine the question of BOD₅ reduction and the effect of chlorination on sewage. The present work was divided into four sections. Section one considers the effect of chlorination on the BOD₅ and biodegradability of filtered sewage. Total organic carbon and chemical oxygen demand tests before and after chlorination were done in order to assess the extent to which the soluble organics in sewage can be oxidized to carbon dioxide at chlorine doses normally employed. Section two considers the effect and extent of chlorination on some selected pure compounds and the extent to which they can be oxidized to carbon dioxide. The role of ammonia in chlorination was studied in relation to the aforementioned objectives. Section three studies the toxicity of chlorine residuals towards micro-organisms, and section four, on the basis of the results found in the previous studies, attempts to explain why a BOD₅ reduction is observed when unfiltered sewage is chlorinated.

CHAPTER 2

GENERAL

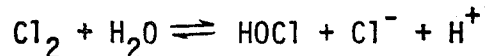
2.1 History of Chlorination:

Chlorination has been used for wastewater disinfection before it was used for water disinfection. Laubush (1962) reports that the earliest plant-scale adoption of sewage chlorination using lime occurred in 1854 by the Royal Sewage Commission in London for the purpose of deodorizing the waste. Application of chlorinated lime for disinfection was practiced in England in 1879 prior to discharge of infectious typhoid wastes into sewers. In 1894 experiments on sewage disinfection with hypochlorites were carried out in France and England. In 1907, Phelps made plant-scale studies on sewage disinfection at Red Bank, New Jersey, which marked the beginning of effective sewage chlorination practice in the United States. Liquid chlorine was first used in 1914 at Altoona, Pennsylvania. Tillman (1922) found that chlorination decreased the rate of decomposition of sewage. Baity and Bell (1929) were the first investigators to show the effect of chlorination on BOD_5 reduction and Baity et al (1933) investigated the effects of chlorination on receiving streams. Laubush (1962) reported that the use of chlorine for treating industrial wastes began about 1916 with the disinfection of tannery effluents. He also reported the use of chlorine in treating dairy wastes for odour control in 1928, for BOD_5 reduction of cannery wastes in 1929 and for BOD_5 reduction and coagulation in meat packing wastes also in 1929. Chlorine was used with textile wastes for coagulation

and colour reduction in 1933, for the chlor-oxidation of cyanide wastes in 1942, for the hypochlorination of wool-scouring wastes and recovery of wool grease in 1943 and plant-scale development of chlorine oxidation of phenolic wastes in 1950. In addition, the use of chlorine in the pulp and paper industry and at power stations to control slime growth in recirculation water had come into wide practice, Laubush (1962).

2.2 Chemistry of Chlorination:

When chlorine gas is added to water, the following equilibrium is established:

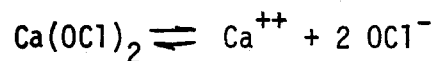


This reaction is essentially complete within seconds. Half of the chlorine is reduced to chloride ion (Cl^-) while the other half is oxidized to Cl^+ in the hypochlorous acid molecule (HOCl). Being a weak acid, hypochlorous dissociates according to:



Laubush (1962) reported that at 20°C the dissociation constant of HOCl is 2.8×10^{-8} moles/l. Accordingly, 97% of the chlorine is in the form of HOCl at $\text{pH} = 6.0$, about 75% at $\text{pH} = 7.0$, only 23% at $\text{pH} = 8.0$, and less than 3% at $\text{pH} = 9.0$. Chlorine existing in water as hypochlorous acid and hypochlorite ion (OCl^-) or both is defined as free available chlorine.

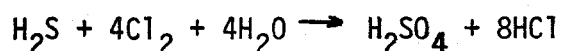
When sodium hypochlorite (Na(OCl)) or calcium hypochlorite (Ca(OCl)_2) is added to water, the hypochlorite ionizes to yield hypochlorite ion as follows:



The hypochlorite ions establish equilibrium with hydrogen ions depending

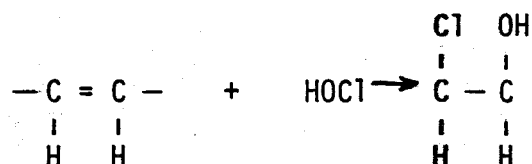
upon the pH. Thus the same equilibria are established in water regardless of whether elemental chlorine or hypochlorites (calcium or sodium) are employed.

Chlorine will react with a variety of impurities present in water. The reaction between hydrogen sulfide and chlorine is typical of the reactions which occur with other inorganic substances. Laubush (1962) gives the following reaction:



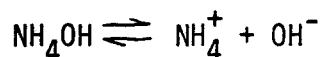
accordingly, one part of H_2S theoretically can be oxidized by about 8.0 parts of chlorine. Iron, manganese and nitrites will similarly be oxidized by chlorine.

Hypochlorous acid can also react with some organic compounds. Sawyer and McCarty (1967) stated that organic compounds that possess unsaturated linkages can add hypochlorous acid as follows:



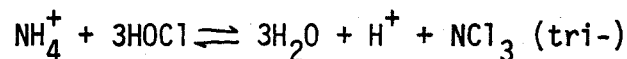
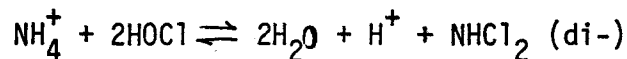
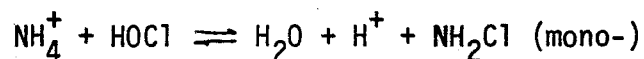
Phenols can also react with hypochlorous acid to give mono-, di-, or trichlorophenols depending on the reactant concentrations, pH, and temperature.

Most domestic sewages contain ammonia either in the form of ammonium ion, NH_4^+ , or ammonium hydroxide, NH_4OH , as controlled by the equilibrium:



McKee et al (1960) reported that the dissociation constant for this reaction at 25°C is 1.8×10^{-5} moles/l. Consequently, NH_4^+ will predominate at pH levels lower than 9.0. Hypochlorous acid or hypochlorite ion may react

with ammonium ions to form three types of chloramines:



The chloramine residuals thus formed are called combined available chlorine residuals. Total available chlorine is therefore the sum of the combined available chlorine and the free available chlorine residuals.

Theoretically, three moles of hypochlorous acid will be required to convert all the ammonia to nitrogen trichloride or tri-chloramine. However, according to Sawyer and McCarty (1967), in practice, these reactions are essentially complete when 2.0 moles of chlorine (Cl_2) have been added for each mole of ammonia. Laubush (1962) reported that chloramine residuals reach a maximum when one mole of chlorine has reacted with one mole of ammonia and then decline to a minimum value when two moles of chlorine have been added to each mole of ammonia. Further addition of chlorine will produce a free residual in proportion to the amount added. A slight combined residual (tri-chloramines) is observed to persist. The point of minimum residual is referred to as the break-point.

According to Sawyer and McCarty (1967) at equimolar ratios of chlorine and ammonia, monochloramines and dichloramines are formed, the relative amount of each is a function of pH. Greater proportions of dichloramines appear at low pH according to the relation:



and, that nitrous oxide, nitrogen, and nitrogen trichloride have been

identified among the gaseous products of the break-point reaction. The presence of nitrous oxide is accounted for according to the following relationship:



Weber et al (1940) have constructed a break-point curve from the data given in Table 1 in the presence of 10.0 mg/l of ammonia.

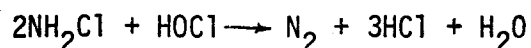
Table 1
Break-point Chlorination, Weber et al (1940)

mg/l NH ₃	Chlorine Applied mg/l Cl	Chlorine Residual mg/l Cl
10.0	25.0	23.3
10.0	50.0	38.6
10.0	60.0	27.8
10.0	62.5	21.6
10.0	65.0	14.4
10.0	75.0	7.1
10.0	85.0	16.2
10.0	100.0	29.0
10.0	125.0	50.6
10.0	150.0	73.0
10.0	200.0	119.6

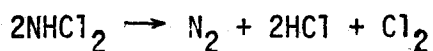
At the break, 67.9 mg/l available chlorine are consumed by 10.0 mg/l of ammonia or 6.8 mg/l Cl / mg/l NH₃. This corresponds to a molar ratio

1.63 moles of Cl_2 : 1.0 mole NH_3 or a molar ratio of 3.26 moles of HOCl : 1.0 mole of NH_3 which is in close agreement with the stoichiometric requirement of 3.0 moles of HOCl /mole NH_3 . It is only after the addition of 200.0 mg/l Cl that 1.92 moles of Cl_2 /mole NH_3 have been consumed and according to Sawyer and McCarty (1967) this would correspond approximately to the requirements for the final oxidation step of ammonia to nitrous oxide and other products. This is a molar ratio of 3.84 moles of HOCl /mole of NH_3 which is observed to occur far beyond the break-point.

Palin (1950) has investigated the products formed from ammonia and chlorine interacting at various pH levels. For the pH range 7 to 8, the initial Cl/N ratio required for the break-point in the chlorine-ammonia reactions is between 8.2/1 and 8.4/1 for a contact period of 1 day. Palin also observed that monochloramines are quite stable in the presence of excess ammonium ion and would decompose in excess chlorine according to the following relationship:



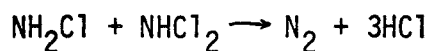
He also stated that systems which initially consisted almost exclusively of dichloramines are unstable and decomposition is accompanied by an increase in free chlorine, although the overall loss of available chlorine is considerable. He proposed the following relationship:



and the free chlorine hydrolyzing to HOCl . According to this reaction, 75% of the available chlorine would be lost. Palin also postulated that solutions which contain both mono- and dichloramines are unstable and decompose rapidly "with the disappearance of one or the other form depending on the relative concentrations at the start" and that the presence

of excess ammonium ion has a retarding influence on the decomposition.

He proposed the following reaction:



Furthermore, Palin stated that in the absence of chloramines, solutions containing both free chlorine and nitrogen trichloride are comparatively stable.

Audrieth and Rowe (1955) studied the stability of aqueous chloramine solutions and found that the decomposition of chloramines takes place more rapidly in solutions containing excess ammonia than in solutions prepared from stoichiometric amounts of hypochlorite and ammonia. Excess ammonia is desirable if the solution is to be used immediately, but undesirable if it is to be stored. In this work, it was found that when a solution of free available chlorine derived from hypochlorites was allowed to stand for several days both the pH and the strength of the solutions were weaker. This indicates that hydrogen ions and chloride ions are liberated when free chlorine solutions decompose. A break-point chlorination curve was also done by adding small increments of hypochlorite to a solution containing 1.0 mg/l of ammonia. It was observed that at the point of maximum residual the products of reaction in solution were a mixture of monochloramines and dichloramines. It was also observed that additional increments of hypochlorite converted the monochloramines to dichloramines. Nitrogen trichloride, as measured from the difference between the total available chlorine and the combined available residual, was found to form in increasing amounts as further additions of chlorine oxidized the residual dichloramines. It was only when 7.0 mg/l available chlorine were added that each additional increment of chlorine added was recovered such that the residual curve was parallel

to the theoretical 45° line. Beyond this point, the residual was composed entirely of free available chlorine and trichloramines. The trichloramines were observed to be stable and measured to be 1.0 mg/l available chlorine.

2.3 Disinfection with Chlorine:

Since ammonia is present in large quantities in domestic sewage it is pertinent to discuss the effect of chlorination on disinfection as it relates to the type of residual formed. The type of residual present in sewage is important as it determines the extent to which the waste will be disinfected. The type of residual is governed by such factors as pH, temperature and ammonia concentration. The extent of disinfection is governed by the contact time as well as by the aforementioned factors. Thus, pH will determine in the absence of ammonia the proportion in which hypochlorous acid and hypochlorite ion will be present. Laubush (1962) stated that the hypochlorite ion is a poorer disinfectant than is hypochlorous acid. When ammonia is present, Moore (1951) stated that 99% of the residual will be converted to chloramines at pH 8.3 within one minute. McKee et al (1960) stated that inorganic chloramines are much less effective killing agents than either forms of free available chlorine and Laubush (1962) maintained that organic chloramines are even less potent disinfectants than either free available or inorganic chloramine residuals. Weber et al (1940) have studied the effectiveness of chlorination in the presence of varying ammonia concentrations on B. metiens spores at pH 7.0. The time required to effect 99% kill, used as a measure of germicidal efficiency, was referred to as the killing time. They found that the killing time of the spore increased with increasing amounts of ammonia but was neither a function of the available chlorine

added nor of the residual chlorine. They also found that for residuals above the minimum break-point and below the point of maximum chloramine residual, it was possible to obtain the same residual for three different applied chlorine concentrations. They observed that 99% disinfection with free residual was achieved in less than three minutes whereas approximately 90 minutes were required for the same kill with chloramines. Thus longer contact times are required in the case of disinfection with chloramines than with free available chlorine.

In studying the effect of chlorine dosages on the extent of disinfection at the Pasadena, California, treatment plant, McKee et al (1960) found that 99% disinfection of coliform bacteria is accomplished with no measurable residual at 15.0 minutes contact time. They plotted the loss of coliform density against chlorine dosage and found that the data can be represented by two straight lines intersecting at about 12.4 mg/l available chlorine (0.35 me/l). They maintained that the rapid kill at doses less than 12.4 mg/l Cl may be related to the most susceptible coliforms, and the second straight line was attributed to the "hardier or protected" organisms. Sawyer (1957) claimed that Cl₂ gas in water (chlorine water) and hypochlorite should, theoretically, be equally effective in disinfection as they establish the same equilibria with water. However, experimentally, he found that hypochlorites were better disinfectants than was chlorine water. The chlorine demand of sewage was found to be greater when chlorine water is used than when hypochlorites are used. He claimed that when chlorine water was used the pH at the point of application was lowered and when mixing has been achieved the pH rose to a level near that of the original sewage. Similarly, when hypochlorites were used, there was a localized rise in the pH until

thorough mixing was achieved. On this basis, he contended that the chlorine demand of sewage chlorinated with chlorine water would be higher than when chlorinated with hypochlorites as low pH favoured the occurrence of undesirable side reactions.

CHAPTER 3

LITERATURE REVIEW

Chlorine has been used in water and treated waste waters primarily as a disinfectant. However, chlorination is also known to bring about a reduction of BOD₅, odour control, corrosion control and control of sludge bulking.

Tillman (1922) performed a series of experiments on sewage treated with amounts of chlorine gas ranging from 3.0 to 20.0 mg/l and showed that with the addition of small amounts of chlorine:

- 1) the rate of decomposition of sewage can be greatly decreased,
- 2) acid concentration may be held nearly constant,
- 3) nitrate decomposition takes place more slowly,
- 4) the formation of hydrogen sulfide takes place more slowly,
and
- 5) albuminous compounds are more slowly attacked.

Baity and Bell (1929) were the first investigators to show the effect of chlorination on BOD₅ reduction. They worked with a strictly domestic sewage from a primary treatment plant located at Chapel Hill, N.C. serving a population of 5,500 inhabitants. Their results are summarized in Table 2.

Table 2

BOD₅ Reduction with Chlorination, Baity & Bell (1929)

Chlorine Dose ppm	Chlorine Residual After 10 min. Contact ppm	BOD Unchlor. ppm	BOD Chlor. ppm	% Reduction
5 - 7.5	0	77	71	7.4
8 - 9	trace	94.3	79.6	15.5
10 - 15	0.2 - 0.5	85.2	48.9	42.7

When chlorine was applied in quantities insufficient to give a residual after 10 minutes, there seemed to be little effect on the BOD₅. In samples dosed with 5.0 - 6.0 ppm, or about one-half the dose required to give a 0.2 ppm residual, there was practically no decrease in BOD₅. With samples treated with a dose of about 9.0 ppm or about three-quarters the amount required for a residual of 0.2 ppm, they observed an appreciable "oxidation" effect. However, the maximum effect, of 42.7%, was found with an excess residual of 0.2 ppm. Furthermore, they observed that in samples heavily chlorinated and with residuals in excess of 0.2 ppm the results obtained were little, if any, better than those found with a 0.2 ppm excess. They concluded that chlorine treatment of sewage reduces the BOD₅ and retards biological activity.

Four years later, Baity, Merryfield and Uzzle (1933) conducted a series of experiments on the effluent from the Chapel Hill treatment plant in order to determine the effects of chlorination on the receiving stream. Nine sampling stations were established along a four mile stretch. Numerous observations were made at each station, such as appearance, odour,

dissolved oxygen, BOD₅, total bacteria and coliform counts.

They found the chlorination of sewage produced:

- 1) a remarkable improvement in the physical appearance of the receiving stream,
- 2) a marked reduction in obnoxious odours,
- 3) an improvement in the dissolved oxygen level at critical sections of the stream, and
- 4) a high degree of bacterial destruction in the receiving stream.

They also observed, as a result of chlorination, BOD₅ reductions as high as 25 to 40%. They concluded that the BOD₅ effects on the receiving stream "appear to be commensurated with this stabilization of non-settleable organic material".

BOD₅ tests were performed on effluents immediately before and after the treatment with chlorine. The major improvement on the BOD₅ occurred 1,600 feet below the outfall. Below this station, the effect of chlorination on the BOD₅ diminished. It is interesting to note that BOD₅ reductions at various points along the stream were accompanied by a reduction in total bacteria and Bacterium coli. Table 3 summarizes this evidence.

Groff and Ridenour (1943) investigated the effects of varied chlorine doses on the BOD₅ of sewage. The effluents used were settled and trickling filters effluents and were strictly domestic in nature. The chlorine dosages used were such as to include the break-point. These authors concluded that chlorination at the break-point did not result in an increased 5-day BOD reduction over that obtained by the low dosages of chlorine commonly used, but that this reduction was permanent.

Table 3

Observed Bacterial and BOD₅ Reductions in Receiving Streams, Baity et al (1933)

Station	BOD		Bacterial Count per ml.	
	Unchlor.	ppm Chlor.	Unchlor.	Chlor.
Effluent Sewage	86.70	52.00	391,000	31,600
200 ft. above outfall	1.08	-	104.0	-
stream 600 ft. below outfall	23.60	14.00	65,000	6,400
stream 1,600 ft below outfall	16.80	6.37	85,000	2,950
stream 2,500 ft below outfall	12.20	9.25	-	-
stream 4 miles below outfall	3.53	2.95	1,200	750

The BOD₅ reduction obtained with low dosages of chlorine, in amounts sufficient to give a slight residual, was not permanent but lasted only until shortly after the beginning of the second stage of deoxygenation. Further effects of heavy doses of chlorine in sewage were investigated by Griffin and Chamberlin (1945). Their study differed from Groff and Ridenour (1943) in that they used dosages well beyond the break-point, up to 400 ppm. The authors recognized that below the break-point, the residuals

were of the chloramine type while if sufficient chlorine was added to obtain a break-point the residual would be predominantly free chlorine. In this study they considered sewage taken from four points within the same plant, namely, raw screened sewage, settled sewage, a combination of aerated mixed liquor from the aeration tank (95%) and activated sludge process effluent (5%), and activated sludge effluent alone.

Commenting on the effect of chlorine on the 5-day BOD of raw screened sewage, the authors indicated that the greatest BOD₅ reduction can be expected following the first appearance of a residual. Although at chlorine dosages beyond the break-point there seemed to be a tendency towards further reductions, the amounts were relatively insignificant. The same conclusion applied to combined plant effluent.

BOD₅ reductions in the case of highly purified effluents were somewhat different than in raw or settled sewage.

"The BOD reductions seemed to be a straight line function up to the break-point where the maximum reduction was obtained and beyond this, little or no further reduction appeared to take place; in fact, in none of the cases studied was there evidence of a noticeable change in the BOD₅ beyond the break-point."

Snow (1952) theorized that a reduction in the 5-day BOD of sewage as a result of chlorination in terms of a postulated first order removal equation may result in one of three ways as a reduction in:

- 1) the reaction velocity constant, k ,
- 2) the ultimate first stage demand, L , and
- 3) both of these parameters.

According to Snow, a reduction of " k " would imply that as a result of chlorination, a

"qualitative change in the character of the sewage constituents had taken place, so that they had become less readily decomposable by aerobic organisms."

A reduction of "L" would imply that as a result of chlorination, a

"quantitative change had taken place in the decomposable fraction of sewage."

A reduction of both "k" and "L" by chlorination would imply "quantitative" and "qualitative" changes in the decomposable organic matter in sewage.

Snow applied chlorine dosages varying from 0 to 320 mg/l. Table 4 summarizes his findings:

Table 4
Calculated First Order Parameters, Snow (1952)

Applied Chlorine (30 min. contact)	k day ⁻¹	L mg/l	kL mg/l/day
0	0.243	121	29.4
3.2	0.210	109	22.9
10	0.234	96	22.5
32	0.275	87	23.9
100	0.246	75	18.5
320	0.128	87	11.1

On the basis of this data, Snow concluded that

"there are both "qualitative" and "quantitative" changes in the decomposable materials in sewage as a result of chlorination."

He stated that he had confirmed previous findings that the greatest reduction increment resulted from applied chlorine doses sufficient to produce a slight 15 minute residual. However, no chlorine residuals were given.

Snow did not produce any further evidence demonstrating actual changes in the composition of the sewage due to chlorination. His conclusions are entirely based on calculated empirical parameters. Furthermore, the erratic decrease observed in the k values would not appear to indicate a qualitative change in the constituents of sewage.

In an attempt to evaluate the importance of specific compounds whose chlorination can bring about BOD reduction in sewage, Ingols and Jacobs (1957) considered the compounds; alanine, glycine, aspartic acid, valine, methionine, tyrosine and phenol. For the amino acids, BOD₂₀ reductions of 67.6%, 51%, 17.2%, 14.8%, 4.2% and 46.3% respectively, were reported when compared to the unchlorinated samples using the dilution method. In a 1:1 molar mixture of phenol and commercial grade trichlorophenol, a 50% reduction in the BOD₂₀ was observed and in pure trichlorophenol, the seed exerted less BOD than was exerted by the control, thus indicating a toxic effect by trichlorophenol on the seed micro-organism.

By analogy, these authors reasoned that chlorination of the phenol ring of the tyrosine could explain the large reduction of the tyrosine upon chlorination. No explanation was offered for the observed BOD reductions of the chlorinated amino acids. Unfortunately, these authors did not conduct such experiments in the presence of ammonia commonly found in sewage.

In the chlorination of the amino acids, Ingols and Jacobs (1957) used a molar ratio of 2.8:1 of chlorine to the amino acid. After a 24 hour

reaction period the excess chlorine was removed by exposing the solution to intense ultraviolet radiation. This dechlorination method was also employed for phenolic compounds.

Meiners et al (1968) have investigated the potential of UV catalyzed chlorine oxidation of highly nitrified waste waters. They found that UV radiation will significantly increase the rate of reaction between organics and chlorine and the extent of oxidation which can be achieved by chlorine with UV radiation is much greater than that which can be achieved by chlorine alone. They also investigated the effect of UV radiation during the chlorination of pure compounds and of particular interests are their results concerning glycine and phenol. These authors found that the TOC of glycine decreased by 61% in 4 minutes and by 78% in 30 minutes of irradiation and the TOC of phenol was decreased by 61% in 8 minutes. They have also investigated the effect of ammonia at concentrations usually encountered in sewage on UV catalyzed chlorine oxidation and found that the rate and extent of the UV catalyzed chlorine oxidation of organic matter is reduced by more than 10 fold.

These findings could largely explain the high BOD₂₀ reductions observed by Ingols and Jacobs (1957).

It is interesting to note that previously, Norman (1936) found that with the chlorination of one mole of glycine with 10.5 moles of hypochlorite in aqueous solutions containing excess hypochlorite, the glycine was completely oxidized. This implies the total conversion of the organic carbon in glycine, to inorganic carbon as evidenced by the evolution of carbon dioxide at pH 7.0.

Further work on the chlorination of phenol was done by Burttschell et al (1959). These workers covered weight ratios of phenol to chlorine

ranging from 0.5:1 to 4:1, for a pH range of 6.0 to 10.0. Their findings revealed that negligible chlorination occurred at pH 6.0. At pH 8.0 and higher the reaction products and taste thresholds were virtually identical. However, the higher chlorine residuals at pH 9.0 and 10.0 indicated that the maximum rate of chlorination occurs at pH 8.0.

Furthermore, when 10.0 mg/l of phenol, and 13.0 mg/l of ammonia were allowed to react with 30.0 mg/l of chlorine at pH 8.0; the solution consisted almost entirely of unreacted phenol after 18 hours of contact time. After 5-1/2 days, the presence of significant amounts of 2,4- and 2,6-dichlorophenol was noted. The combined effect of ammonia and pH on the rate of chlorination was studied using the appearance of 2,6-dichlorophenol on paper chromatograms as a measure of phenol chlorination. Phenol was present in all cases but 2,6-DCP formed slowly at pH 9.0, slightly faster at pH 8.0 and not at all at pH 6.0. In all cases the residual chlorine was still present after 5 days. In these experiments, the concentrations of phenol, ammonia and chlorine were 1.0 ppm, 3.0 ppm and 7.0 ppm, respectively.

Accordingly, the chlorination of phenol is influenced by such factors as concentration of reactants, temperature, pH and ammonia. Certain combinations of these factors may prevent or retard the detectable onset of the chlorination reaction.

Susag (1965) investigated the effect of chlorination on waste waters of "all degrees of stabilization" ranging from raw waste water to effluents of primary and secondary treatment process. The secondary treatment process effluents employed were effluents of pilot plants. Susag showed that the chlorination of waste waters resulted in a retardation in the rate of deoxygenation as expressed in terms of a reduction in the

deoxygenation constant. Although his data showed a reduction in the rate constant, k , with increasing chlorine dosage, such trend is not followed by the ultimate demand, L . The ultimate demand of the chlorinated samples was in most cases equal to or greater than the corresponding non-chlorinated samples. Furthermore, the chemical oxygen demand performed on non-chlorinated and chlorinated raw waste water samples were the same, indicating that "no decrease in organic content resulted from chlorination".

BOD_5 reductions of approximately 2.0 ppm per ppm of chlorine absorbed were obtained at chlorine dosages resulting in a low residual. This value of BOD_5 reduction decreased with increasing chlorine dosage. The effect of the type of chlorine dosing solution, chlorine gas or hypochlorite, on the BOD_5 reduction was also investigated. Both types of chlorine solutions brought about the same reduction in the BOD_5 , namely, about 1.0 ppm per ppm of chlorine absorbed. These latter tests were performed on primary effluents.

Although the work done by various investigators since 1922 was carried out with great care, little or no consideration was given to the seed, even though Thomas (1940) had performed a series of investigations in order to ascertain the effect of seeding upon the oxygen demand. BOD curves were obtained for influent waste seeded and unseeded as well as effluent waste seeded and unseeded from a New England activated sludge plant. Table 5 summarizes his data.

Table 5

Effect of Seeding on BOD Curve, Thomas (1940)

Time Days	Group A Influent Unseeded ppm	Group B Influent Seeded ppm	Group C Effluent Unseeded	Group D Effluent Seeded
0	0	0	0.0	0.0
1	32	38	-	-
2	57	64	-	2.3
4	84	94	0.8	4.0
6	106	104	3.0	9.2
8	111	109	-	-
9	112	112	7.6	14.0
10.2	119	172	-	30.0
12	152	231	10.0	54.0
14.2	183	275	18.0	72.0
16	-	-	43.0	-
17	199	326	-	-
18	-	-	59.0	-
20.2	260	364	68.0	81.0
26	290	392	82.0	85.0
30	307	398	85.0	86.0

From these observations Thomas made the following comments:

- 1) Seeding increases the rate of demand and this effect is apparent in the increase in k ,
- 2) Seeding brings about a reduction in the lag period in the BOD of the effluent and a decrease in the time of the beginning of the second stage in the BOD of the influent, and
- 3) In all groups the seeding produced no significant change in the value of the ultimate demand L .

The calculated values of k , L , and the lag phase, as given by Thomas, are summarized below:

Table 6
Calculated First Order Parameters, Thomas (1940)

1st Stage Influent Seeded	1st Stage Influent Unseeded	2nd Stage Effluent Seeded	2nd Stage Effluent Unseeded
$L = 115.5$	$L = 121.4$	$L = 91$	$L = 99.8$
$k = 0.178$	$k = 0.140$	$k = .106$	$k = 0.06$
$t_o = 16 \text{ min.}$	$t_o = 52 \text{ min.}$	$t_o = 8.4 \text{ days}$	$t_o = 11.84 \text{ days}$

The k and L values for the 1st stage of the effluent test were not calculated since the data did not follow the mono-molecular curve.

As chlorination has been praised for its various effects on effluents and their receiving streams, it has also been condemned for its induced toxicity. Recently, Esvelt et al (1971), in an extensive study

on toxicity removal from municipal waste waters at the San Francisco Bay delta waters claimed that the chlorination of treated municipal waste waters increased their toxicity to fish. They found that the 96 hr TL₅₀ was in the order of 0.2 mg/l chlorine. Furthermore, chlorine residuals were not completely dissipated from waste waters following contact up to 3 days, although the residual chlorine toxicity was somewhat reduced. They also found that the design of the chlorine contact chamber did not seem to influence the toxicity of chlorinated effluents towards fish, nor did extending the contact time from 30 minutes to 3 hrs; however, improved disinfection resulted. Dechlorination of chlorinated waste waters with sodium bisulfite added in slight excess removed the chlorine induced toxicity and resulted in a net toxicity reduction.

In a separate study, Krock and Mason (1971) conducted a series of experiments in order to determine the effect of chlorination on supporting trophic levels in the Bay. These experiments showed that the presence of a chlorine residual inhibited all of the functions measured, namely, respiration, photosynthesis and in situ growth. Residuals as low as 0.03 mg/l were found to have significant effects. The toxic effect of the chlorine residuals, present as chloramines, increased with increasing levels of residuals, and dechlorination with sodium bisulfite appeared to remove this chlorine induced toxicity.

Zillich (1972) discussed recent studies conducted by the Michigan water resources and summarized other studies on the toxicity of combined residual chlorine. Zillich reports that exceedingly small amounts of chlorine, less than that required to obtain any measurable residual chlorine, added to non toxic effluents containing thiocyanate produces a very toxic solution. The resultant cyanogen chloride is toxic at concentrations as low

as 0.08 mg/l to rainbow trout. Chloramine concentrations of a few tenths of a milligram per litre are lethal to warm-water fish such as sunfish, bullheads and minnows. Chloramine concentrations of 0.06 to 0.08 mg/l are lethal to trout. Life cycle studies have shown that chloramine concentrations of 0.085 mg/l nearly eliminated the spawning of the fathead minnows, and that concentrations of 0.043 mg/l significantly reduced reproduction.

On site continuous-flow bio assay at the Michigan treatment plants showed that average concentrations of 0.16 to 0.21 mg/l residual chlorine caused complete kill of fathead minnows; as low as 0.07 mg/l caused partial kill of the fish and 0.04 to 0.05 mg/l were the threshold concentrations of these waters. However, dechlorination with sodium thiosulfate rendered the effluents non toxic.

Recently, the Manufacturing Chemists Association (1972) investigated the effect of chlorination on selected organics.

The authors selected chlorinated compounds in order to examine the possible inhibition or toxicity of these compounds to an operative biological system. Table 7 summarizes their findings.

Table 7
Toxicity of Selected Chlorinated Organics -
The Manufacturing Chemists Association (1972)

Compound	No Inhibition	Mildly Inhibitory mg/l	Strongly Inhibitory mg/l	Toxic mg/l
2, 4, 6-Trichloro-phenol (TCP)	1 - 10	-	50 - 100	-
4-Chloro-3 methyl phenol	-	10	50	100
Chloranil	-	10	-	-
2, 4, 6-trichloranil	10	-	-	-

Five chlorinated compounds were tested for toxicity to fathead minnows. They found that the 96 hour TL_m range in mg/l for 2, 4, 6-TCP was 1.0 - 0.10, for 2, 4, 6-trichlor-aniline the range was 10 to 1, for 4-chloro-3-methyl phenol 0.1 to 0.01 and for chloranil, from 1 to 0.01. For p-benzoquinone, the probable toxic concentration level was determined to be less than 0.1 mg/l.

CHAPTER 4

EXPERIMENTAL METHODS AND APPROACHES

4.1 Materials:

Sewage Effluent

The final effluents used in the experiments were obtained from the Dundas activated sludge treatment plant. The effluent was collected by grab samples from the effluent channel of the final settling tank prior to the chlorination chamber.

Immediately after collection, the effluent was brought to the laboratory and filtered through 0.45 micron Sartorius filters and stored at 4°C. Prior to filtration the filter paper was rinsed with distilled water to remove organic material normally present on the filters.

Primary effluent was used as seed. The primary effluent was collected by grab samples from the exit channel of the primary sedimentation tank. The seed was always obtained on the day after the final effluent was collected and used immediately. The effluent was allowed to settle at $20 \pm 0.5^\circ\text{C}$ and the supernatant drawn off.

Pure Compounds

The pure compounds studied were as follows: glutamic acid, alanine, histidine, glycine, phenol, ammonia, n-butylamine, acetic acid and maleic acid. Stock solutions containing 2.0 m-mole/l of each compound were prepared when required. The molarity of each solution was verified on a Beckman total carbon analyzer (Model 915B). Definite volumes

were pipetted and placed in square jars and diluted with distilled water such that the final volume of the mixture of distilled water, phosphate buffer, pure compound and hypochlorite was one litre and the final concentration of the pure compound in the reaction mixture was 0.2 m-mole/l.

Dilution Water

In all experiments, 1.3 mls of seed/litre of dilution water were used. "Standard Methods" (1971) recommends 1-2 mls of seed per litre of dilution water. Ten litres of distilled water were allowed to stand at $20 \pm 0.5^{\circ}\text{C}$ for 24 hours. Seed, minerals and phosphate buffer (pH 7.2) were then added. The dilution water was aerated to saturation.

4.2 Apparatus:

Biological Reactors

A modification of the method proposed by Orford et al (1953) for BOD measurement was employed. The biological reactors consisted of two three-necked round-bottom flasks as illustrated in Figure 1. Through a rubber stopper in one neck of the bottom flask, a glass tubing sealed with a serum cap was inserted. This neck was used for sampling purposes using a hypodermic needle long enough to reach the bulk of the fluid. The middle neck was fitted with a Precision Scientific oxygen probe. This neck was sealed with 1/16 of an inch thick flexible neoprene rubber. The third neck was connected with glass tubing to the top flask. All flasks were covered with aluminum foil to prevent light penetration. All bottom flasks were gently stirred using a teflon coated bar and a magnetic mixer. The top flask was kept quiescent and used as a reservoir whenever a sample was taken so that the bottom flask would, at all times, be completely full.

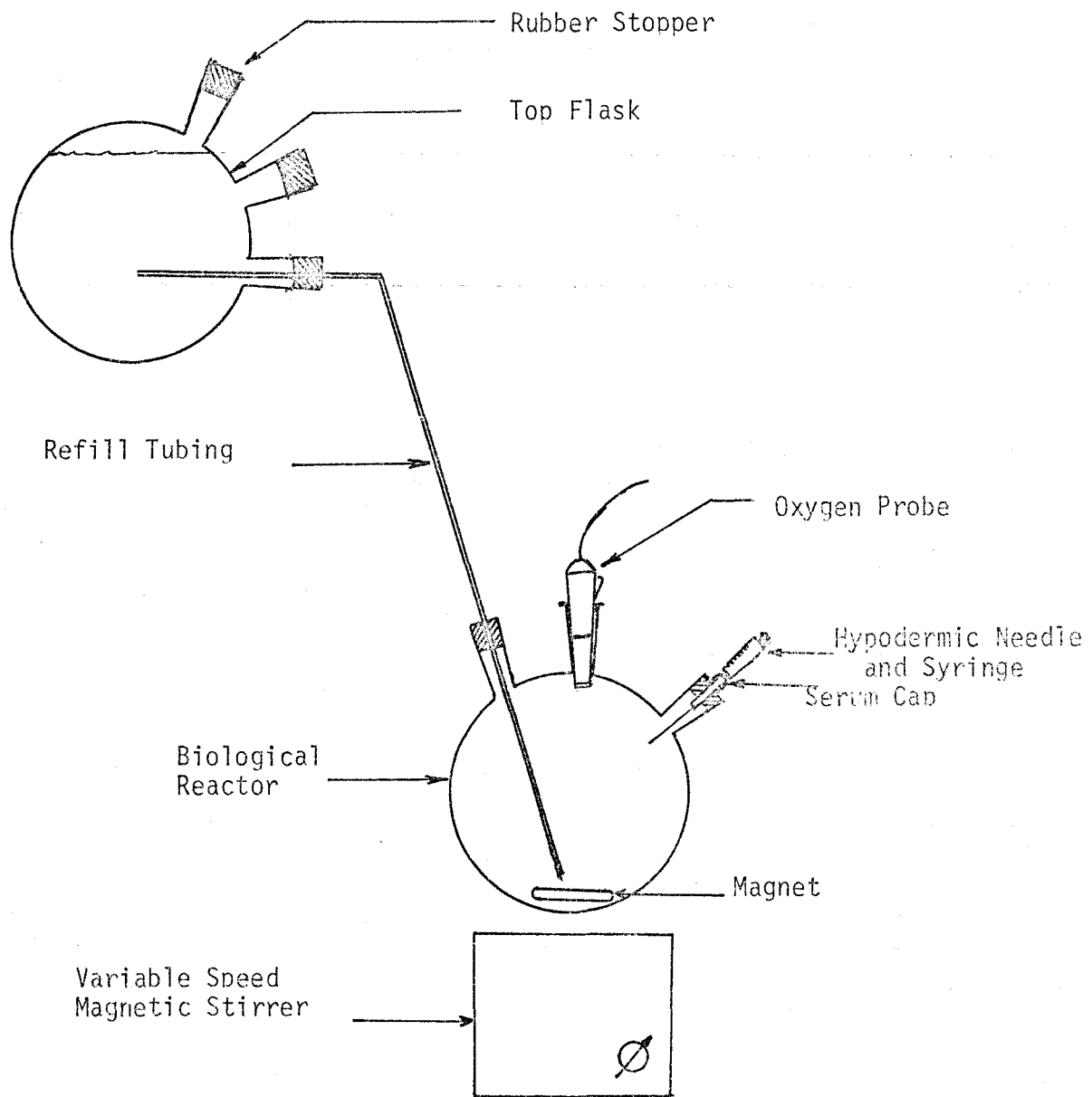


Figure 1 Biological Reactor

The tubing connecting the top and bottom flasks ensured immediate mixing of the refill liquid with the bulk of the fluid. The tip of the tubing was extended and directed just above the magnet. The refill tube in the top flask was placed such that the liquid would be removed from a point one half to one third of the height up from the bottom of the top flask.

Approximately three-quarters of an inch air gap was allowed between the reactors and the laboratory variable speed mixer. The mixers were insulated so as to minimize temperature disturbances.

Chlorination Apparatus

A jar test apparatus operating at 100 rpm was used for the chlorination of sewage and pure compounds. One litre square jars open to the atmosphere were used in all runs. The mixer blades were 3" by 1".

4.3 Methods:

Two hypochlorite solutions were used. Calcium hypochlorite containing approximately 440 mg/l available chlorine was used on the first two runs with sewage and in studying the effect of pH on phenol and glutamic acid. Sodium hypochlorite containing approximately 3,600 and 1,560 mg/l available chlorine was used in subsequent runs. The strength of the chlorine solution is indicated on the data. All solutions, hypochlorite as well as titrant, were standardized prior to use.

Calcium hypochlorite was prepared in the laboratory according to the procedure described by Kolthoff and Sandell (1952). Sodium hypochlorite was purchased from Fisher Scientific.

The chlorination of sewage was carried out at the pH of the effluent and was not buffered. It was felt that this procedure would

conform to plant operation. However, the chlorination of pure compounds was buffered to 7.2 using a phosphate buffer as prescribed in "Standard Methods" (1971).

Before chlorination of the sewage, the filtered effluent was allowed to come to thermal equilibrium at $20 \pm 0.5^{\circ}\text{C}$. Part of this effluent was chlorinated with a known quantity of hypochlorite for 30 minutes. Following this contact period, sodium sulfite, from a 0.05 M stock solution, was used as a dechlorinating agent. This solution, being unstable, was always prepared just prior to chlorination. Small increments of sodium sulfite were added and the residual checked on a Wallace and Tiernan amperometric titrator (A554003). This procedure was followed until no residual was detectable. A sample of each filtered chlorinated-dechlorinated and unchlorinated effluent was stored at 4°C for carbon analysis. The chlorinated-dechlorinated and unchlorinated filtered effluents were then aerated, partly to destroy any excess sodium sulfite present in the chlorinated-dechlorinated samples, and partly to satisfy any initial oxygen demand in both samples. A further sample of each was then stored at 4°C for carbon analyses in order to determine any effect of aeration on the organic carbon content. It was found that the aeration step did not result in a loss of organic carbon due to volatilization.

Following chlorination and dechlorination, the chlorinated sewage was mixed with dilution water in a four litre flask to give the desired mixture. The mixture was then poured in the reactors which were then sealed as previously described. The same procedure was followed for the unchlorinated filtered effluent. Both chlorinated-dechlorinated and unchlorinated filtered effluents were diluted using the same seeded dilution water.

A duplicate set of reactors, exactly as described above, was set up using the same sewage-dilution water mixture for the purpose of obtaining replicate samples for carbon analyses. The mixtures were reaerated whenever the dissolved oxygen level fell to about 2.0 mg/l. The compressed air was prefiltered through cotton. Oxygen uptake was monitored continuously using a two channel Phillips recorder (PM8010).

Three types of chlorination experiments were done with pure compounds varying the applied chlorine dose:

- 1) Free residual chlorination,
- 2) Chlorination using a solution of inorganic chloramines, and
- 3) Free residual chlorination in the presence of ammonia.

The chloramine solution was prepared by combining equimolar amounts of ammonia and hypochlorous acid. 482 mg of ammonium chloride (9.0 m-moles NH_4Cl) were dissolved in 20 mls of distilled water; 106 mg available chlorine (3.0 m-mole HOCl) were added. The mixture was then diluted to give the desired strength of chloramine solution. The mixture was allowed to stand in the dark at $20 \pm 0.5^\circ\text{C}$ for two hours to allow the reaction to go to completion. The solution was standardized using the starch-iodide test and the absence of free residual was verified on the amperometric titrator. The ammonia concentration derived from ammonium chloride was 9.0 m-moles.

4.4 Determination of Chlorine Residuals:

The residual chlorine after a given contact time was identified by the starch-iodide test and by amperometric titration for the pure compound studies whereas with sewage, the amperometric titrator alone was used.

These methods are essentially the same but differ in the end point detection. The amperometric titrator measures the current produced during the neutralization reaction with sodium thiosulfate (0.00564N) whereas in the starch-iodide method, the end point is detected by a colour change from blue to colourless.

"Standard Methods" (1971) recommends acidification with acetic acid. This procedure was modified so that acidification was achieved with 2.0 N sulfuric acid. Kolthoff and Sandell (1952) recommend such a procedure when hypochlorite is used to eliminate interferences from chlorates. Furthermore, it was found that potassium iodide dissolved too slowly in acetic acid and could cause serious timing problems. The starch-iodide test was not used for sewage because colour and turbidity interferences made the end point detection difficult and uncertain. The amperometric titrator was used in conjunction with pure compounds in order to identify the nature of the residual, free or combined, and, on certain cases, distinguish between monochloramines and dichloramines. The ammonia concentration in the chlorination of glycine in the presence of various amounts of ammonia, was monitored with an Orion ammonia electrode (Model 95-10) connected to a Fisher (Accumet Model 120) pH meter. The electrode was standardized according to the instructions given in the manual. Samples of chlorinated pure compounds analyzed for residual chlorine at contact time exceeding two hours were stored in BOD bottles covered with aluminum foil and gently stirred at $20 \pm 0.5^{\circ}\text{C}$. According to the instruction manual the error in end point detection using the amperometric titrator is within 0.01 mg/l available chlorine when a 200.0 ml sample is used.

4.5 Dechlorination with Sodium Sulfite:

Sodium sulfite, 0.05 M, was used in all experiments as a dechlorinating agent. Susag (1965) investigated the use of sodium thiosulfate as a dechlorinating agent and found that the reaction product would exert a BOD, whereas sodium sulfite did not form by-products exerting a BOD. Sodium sulfite is quantitatively oxidized to sulfate by chlorine. The ability of sodium sulfite to react with both chloramines and free residual was investigated. The same quantity of sodium sulfite was required for both types of residuals.

4.6 COD Tests:

The COD tests were done in accordance with "Standard Methods" (1971).

4.7 Standardization of Oxygen Probes:

In the presence of a cobalt sulfate catalyst, the reaction of oxygen with sodium sulfite is very rapid. One litre of distilled water was allowed to stand for 24 hours at $20 \pm 0.5^{\circ}\text{C}$ in a square jar. Mixing was accomplished by using a variable laboratory speed mixer insulated so as to minimize temperature disturbances. A teflon coated magnetic bar was used. The distilled water was then saturated with oxygen using air. A few pellets of the catalyst were dissolved in the water.

A Yellow Springs oxygen probe fitted with a stirrer and connected to a Yellow Springs (Model 51) oxygen meter was used to determine the various levels of oxygen. This probe was standardized against tabulated oxygen concentration values. According to the specification in the instruction manual, the error with this direct calibration method is less than 0.5% saturation. The Precision Scientific oxygen probes used for measurements

of dissolved oxygen in the reactors, were calibrated against the Yellow Springs probe. They were all placed in a jar and small increments of freshly prepared 0.05 M sodium sulfite were added and the response observed. As the dissolved oxygen level in the sample was depressed, a definite deflection reaching steady state was observed on the recorder at which point the oxygen level was noted. At the end of this procedure, the water was brought back to saturation to ascertain the first point. A variable resistor was connected to the probe so that the output signal could be registered on a 10 millivolt recorder. The maximum resistance of these variable resistors was 1000 ohms. The resistance was set so as to read half of the full scale. The validity of calibrating the probes in distilled water was verified by calibrating the probes in filtered sewage. The two calibrations were the same and this latter procedure was discontinued.

CHAPTER 5

DISCUSSION OF RESULTS

5.1 Mixing and Chlorine Residuals:

The possibility of chlorine losses due to mixing was first investigated. A mixing level of 100 rpm as used in all experiments performed subsequently was selected. Chlorine was added from a stock solution to distilled water giving dosages of 10.4 and 27.7 mg/l available chlorine. At the lower dose the residual remained constant over one hour contact time; similarly the higher residual remained constant over that period of time but declined to 27.3 mg/l after 100 minutes. This corresponded to a loss of 0.4 mg/l available chlorine. The same loss was observed over a 100 minute contact time with chloramine solutions.

5.2 Chlorination, the BOD₅ of Sewage and Biodegradability

A series of five experiments was carried out in order to investigate the effect of chlorination on final effluents with respect to BOD₅ and organic carbon degradation. Although the literature stated that chlorination brings about a BOD₅ reduction ranging from 25 to 40% and that the greatest increment of BOD₅ reduction occurs at the appearance of a slight residual, no substantial evidence as to the cause of this BOD₅ reduction has been presented. Various investigators state that chlorine will oxidize organics in sewage and thus reduce the BOD₅ but no investigator substantiated such assertions on the basis of experimental evidence. All this reported work has been performed on unfiltered effluents.

In this work, the effluent was filtered in order to study the effect

of chlorination on the soluble organics present in sewage. It was felt that it would be the soluble organics that could be chlorinated and possibly rendered toxic, bioresistant, or oxidized to carbon dioxide. Thus the effect should be even more pronounced on an effluent that has been freed of interfering suspended solids and micro-organisms. On this basis the possible reactive substances in the effluent can be regarded as a composite of organics, reducing inorganic substances and ammonia. Since both chlorinated-dechlorinated and unchlorinated samples were diluted with the same seeded dilution water, then the same mixed microbial population should be present in both samples. If a BOD₅ reduction did result then it can only be attributed to one or more of the possible reactions between the chlorine and the dissolved organics. Furthermore, by making carbon analyses during the course of the reaction it was possible to associate the effect of chlorination on the BOD₅ with the effect on the soluble organics.

These experiments were conducted at chlorine doses ranging from 3.0 to 13.7 mg/l available chlorine using the two chlorinating solutions. Runs 1 and 2 were performed using calcium hypochlorite at chlorine dosages of 3.0 and 12.0 mg/l available chlorine. Runs 3 to 5 were done with sodium hypochlorite at chlorine doses of 3.0, 6.0 and 13.7 mg/l available chlorine. The results are given in Table 8. The chlorine demand of the filtered sewage is seen to increase as the chlorine dose is increased. Typical results of the BOD₅ and carbon analyses are illustrated in Figure 2 to Figure 5. Within the accuracy of the BOD₅ test, there appears to be no BOD₅ reduction due to chlorination as well as no delay in the exertion of the BOD in the chlorinated samples. Also, there seems to be no difference in the extent to which organics are degraded as no significant

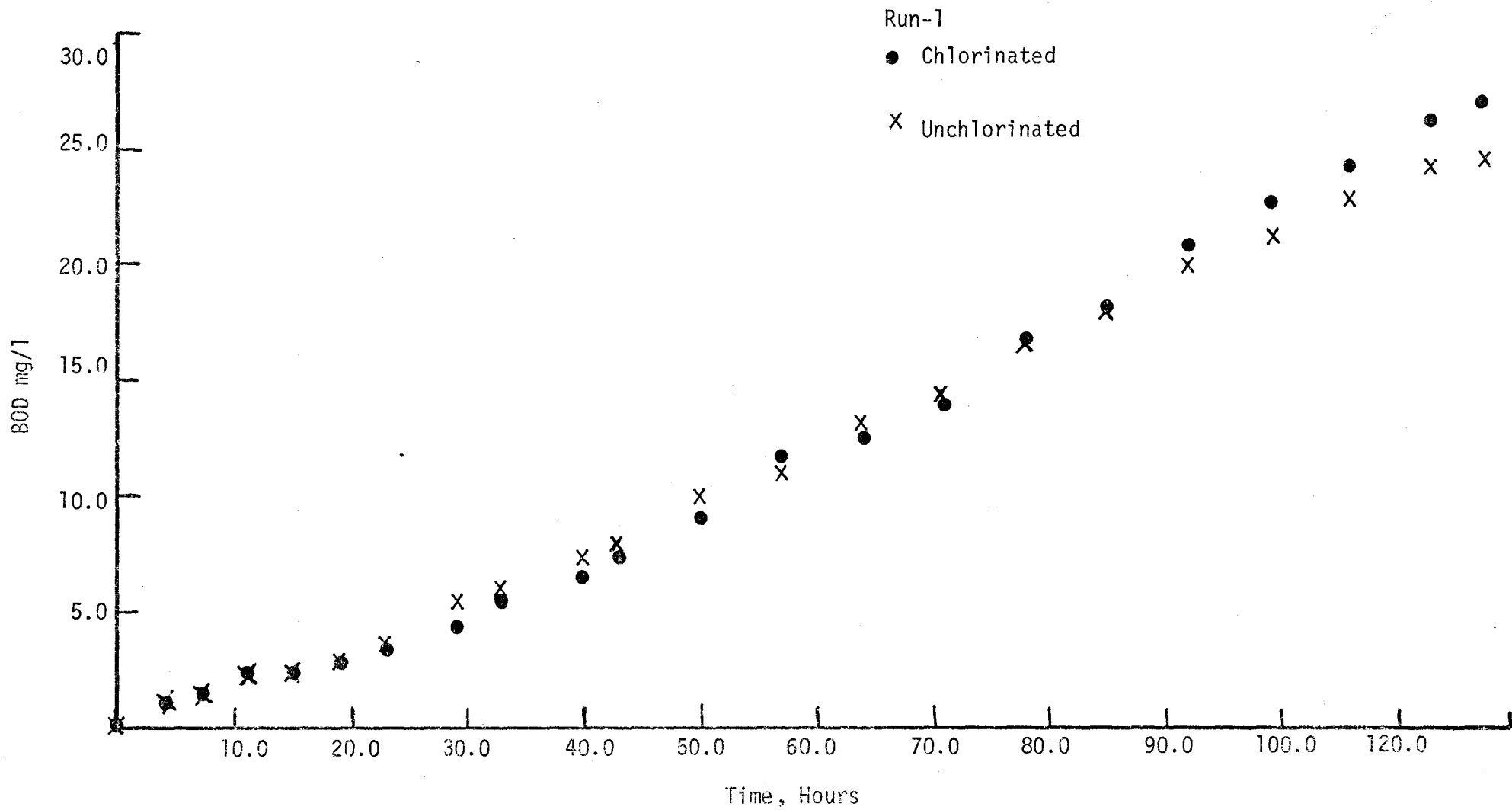


Figure 2 BOD of Sewage Chlorinated with Calcium Hypochlorite

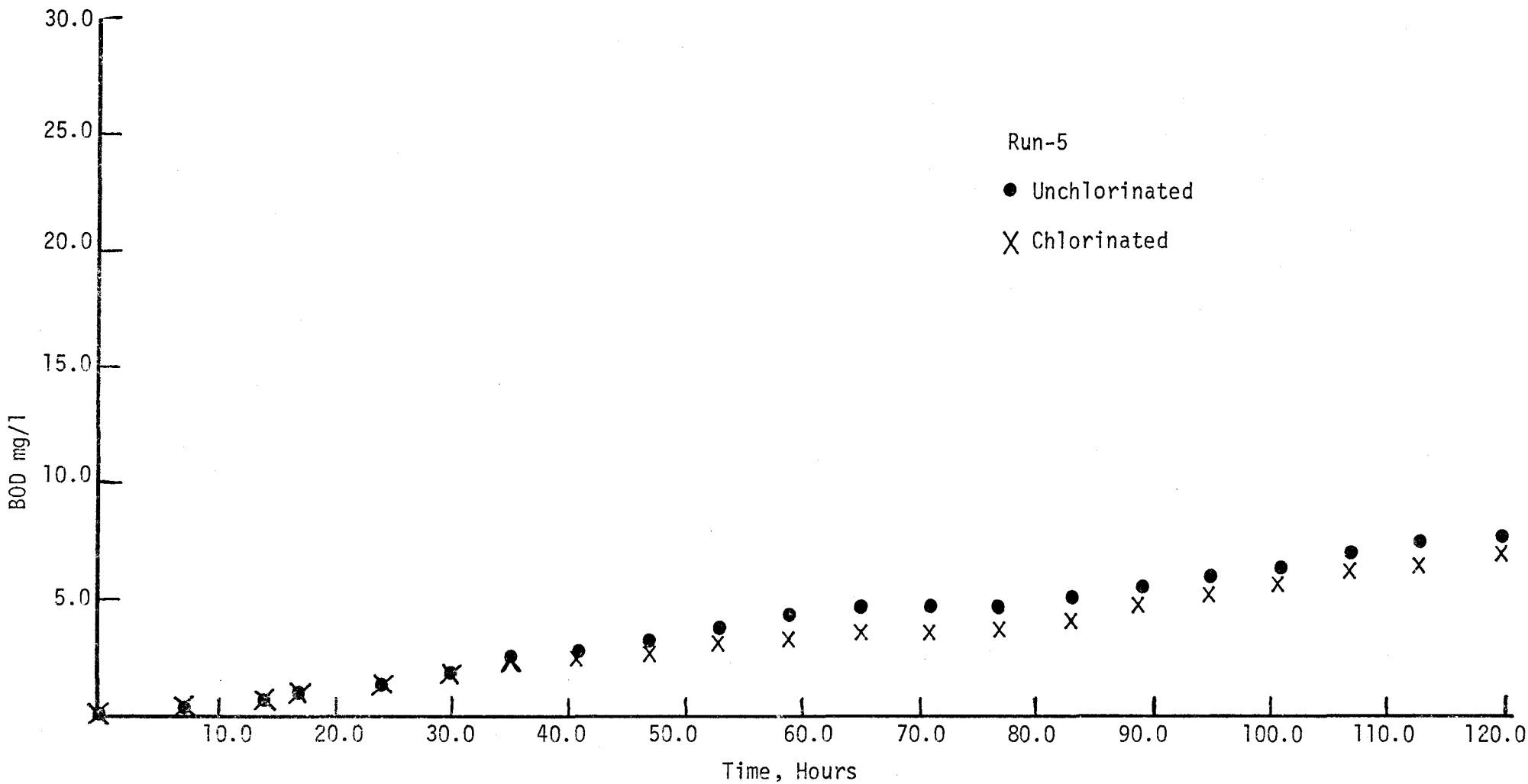


Figure 3 BOD of Sewage Chlorinated with Sodium Hypochlorite

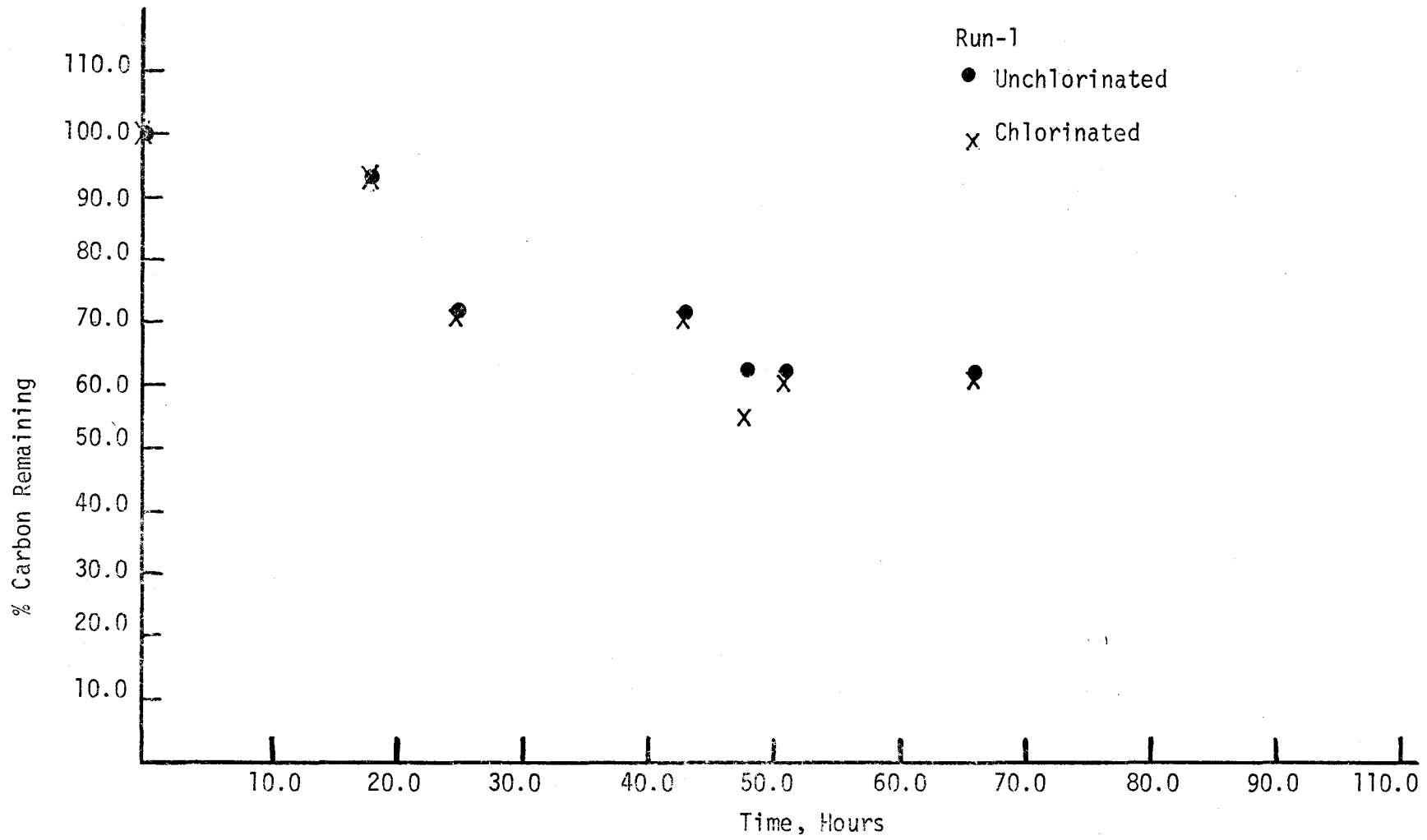


Figure 4 Carbon Degradation of Chlorinated and Non-Chlorinated Sewage

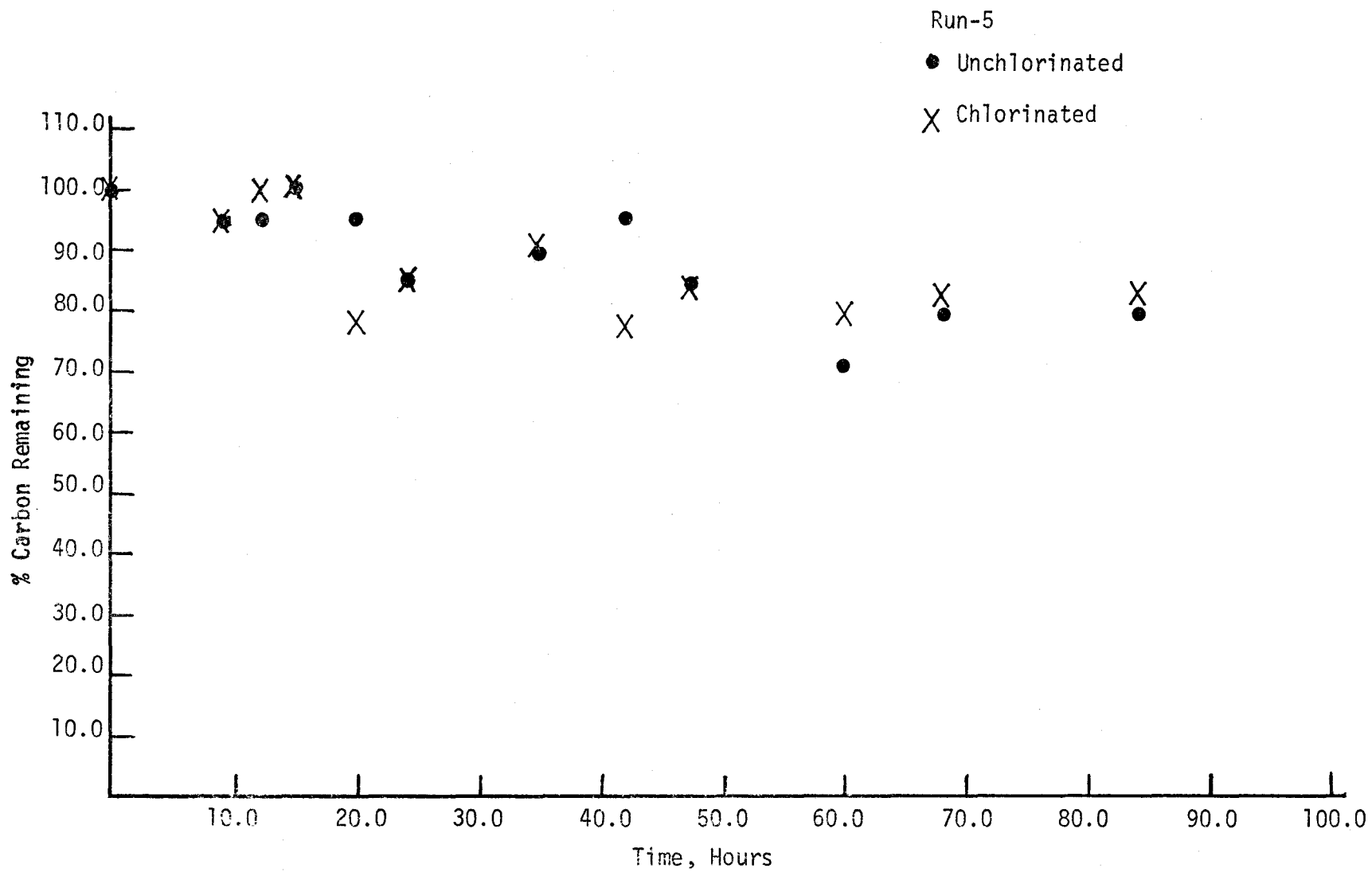


Figure 5 Carbon Degradation of Chlorinated and Non-Chlorinated Sewage

Table 8

Chlorine Demand of Sewage After 30 Minutes Contact Time
Using Calcium and Sodium Hypochlorite

Run	Chlorinating Solution	Applied Dose mg/l	Chlorine Residual mg/l	Chlorine Demand mg/l
1	calcium hypochlorite	3.0	2.1	0.9
2	calcium hypochlorite	12.0	9.8	2.2
3	sodium hypochlorite	3.0	2.6	0.4
4	sodium hypochlorite	6.0	5.0	1.0
5	sodium hypochlorite	13.7	12.2	1.5

difference in TOC was observed between chlorinated-dechlorinated and unchlorinated samples. As there was negligible carbon degradation in all runs except for run 1, it was felt that the measured BOD₅ were largely due to microbial respiration. Figure 6 illustrates the results obtained from two microbial respiration runs associated with runs 4 and 5.

The total organic carbon analyses before and after chlorination and dechlorination indicated that there was no reduction in the organic carbon of sewage thus no oxidation to CO₂ could have occurred. Furthermore, the chemical oxygen demand (COD) tests done on runs 2 and 3 on samples taken before and after chlorination and dechlorination indicate that the COD did not change, a further indication that no carbon loss occurred. The results are shown in Table 9.

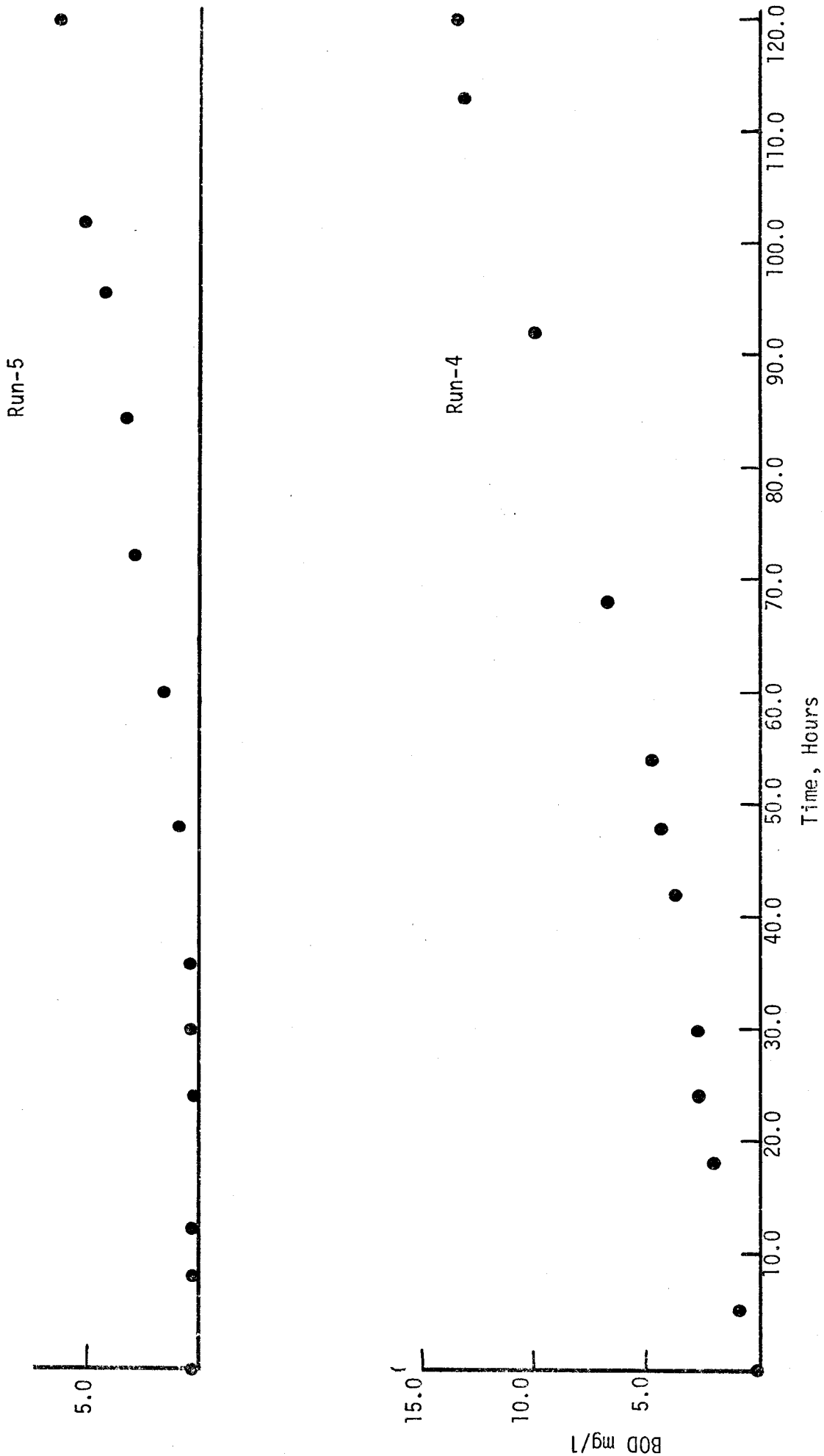


Figure 6 Microbial Respiration Curve

TABLE 9
COD of Chlorinated and Unchlorinated Sewage

Run	Chlorinating Solution	Chlorine Dose mg/l	COD mg/l
2	calcium hypochlorite	0.0	48.6
		6.0	48.6
		12.0	48.6
3	sodium hypochlorite	0.0	27.6
		12.0	27.6
		25.0	27.6

Susag (1965) similarly demonstrated that for unfiltered effluents the COD remained unchanged before and after chlorination. In all these experiments with sewage it was observed that the residual chlorine was of the chloramine type.

In order to examine possible reactions that could occur in sewage, a series of experiments were performed using pure compounds. The applied chlorine concentration ranged from 3.0 to 25.0 mg/l available chlorine. The pure compounds were selected as being representative of compounds that would be present in sewage.

5.3 Chlorination and pH:

a) Glutamic acid

When 71.5 mg/l of glutamic acid (0.5 m-mole/l) were chlorinated

with 27.1 mg/l available chlorine (0.76 m-mole/l as hypochlorous acid), (Figure 7), the rate of reaction was fastest at pH 4.2 and decreased as the pH increased to 9.2. These reactions were characterized by a rapid uptake of chlorine during the first 30 minutes followed by a declining rate. Laubush (1962) indicated that chlorine exists predominantly as hypochlorous acid (HOCl) at a pH of 4.2. At pH 7.2, a mixture of hypochlorous acid and hypochlorite ion (OCl⁻) would coexist, and at pH 9.2, the hypochlorite ion would predominate. On the basis of oxidation-reduction potentials it can be inferred that hypochlorous acid is a stronger oxidizing agent than the hypochlorite ion. Table 10 gives the Redox potentials of hypochlorous acid and hypochlorite ion.

TABLE 10
Oxidation-Reduction Potentials of Chlorine Compounds
Handbook of Chemistry and Physics, 47th Edition

Reaction	Potential Volts
$\text{HClO} + \text{H}^+ + 2e = \text{Cl}^- + \text{H}_2\text{O}$	+ 1.49 ^a
$\text{ClO}^- + \text{H}_2\text{O} + 2e = \text{Cl}^- + 2\text{OH}^-$ <p>a=acid, b=base</p>	+ 0.9 ^b

The chloramination of glutamic acid in aqueous solutions at pH 7.2 was characterized by a slow depletion of the residual. About 20.0 mg/l Cl were consumed in 130 minutes. Laubush (1962) stated that chlorine reacts with free ammonia to form chloramines that have a lower oxidation potential

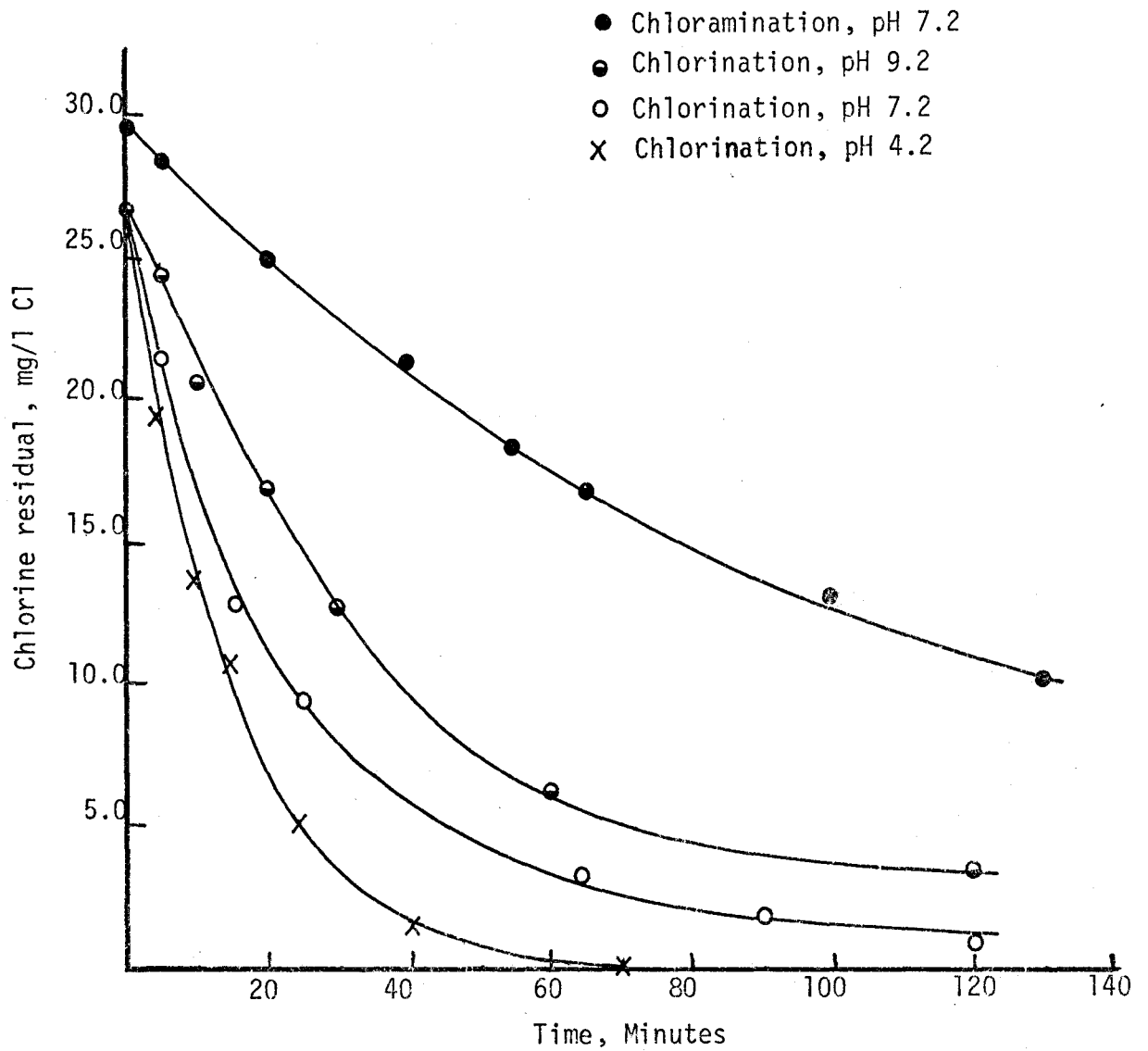


Figure 7 Chlorination of Glutamic Acid at Various pH Levels.
Chloramination of Glutamic Acid at pH 7.2.

than free available chlorine forms even though the chlorine is still available for chemical reaction. Furthermore, the oxidation potential and disinfecting power of organic chloramines is substantially lower than that for inorganic chloramines and free available chlorine forms.

b) Phenol

The chlorination of phenol exhibited a different trend. At pH 7.2, the reaction proceeded very fast, 86% of the applied chlorine dose being consumed in the first 10 minutes by phenol followed by a declining rate. At pH 9.2, the residual left after one hour decreased very slowly and was much higher than at pH 4.2. The residual at pH 4.2 was intermediate between the residual at pH 7.2 and the residual at pH 9.2. The applied chlorine dose was 27.5 mg/l available chlorine (0.77 m-mole/l as HOCl) and the phenol concentration was 10.0 mg/l (0.1 m-mole/l). These observations are in general agreement with the findings of Burttschell et al (1959). When a chloramine solution was added to phenol only a negligible change in the residual occurred. After one hour, 0.5 mg/l were depleted. This is almost identical to the loss of residual incurred due to mixing. Burttschell et al (1959) found that in the presence of ammonia, the reaction can be retarded considerably and even prevented. The extent is dependent on the ammonia level, the concentration of chlorine and phenol as well as the pH of the solution. Figure 8 illustrates the results.

In these experiments, although no attempt was made to identify the residuals, in the reaction between the pure compounds and chloramines, the residual would be a chloramine. Redox potentials cannot entirely explain the extent of chlorination of pure compounds as the pH is varied

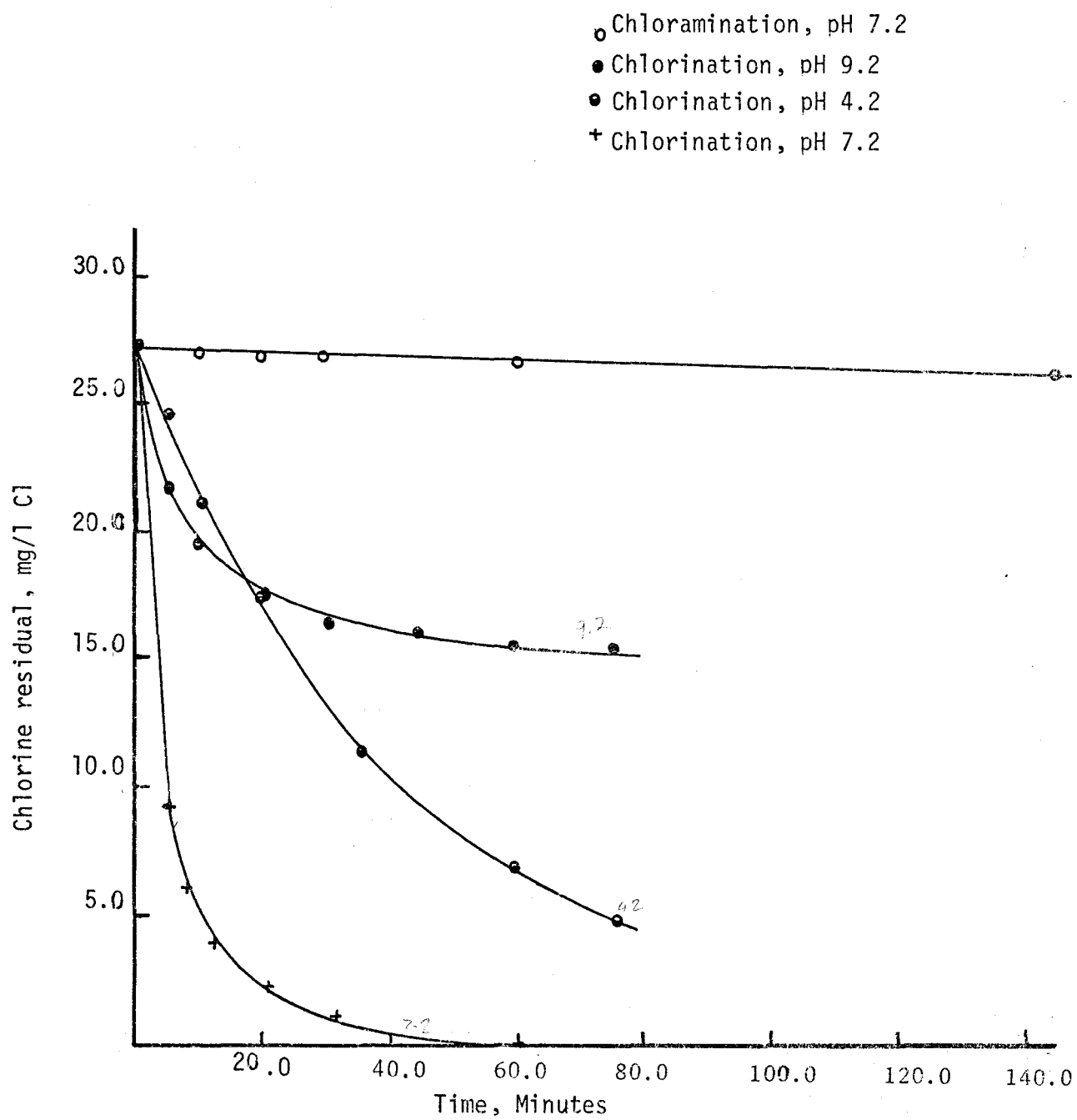


Figure 8 Chlorination of Phenol at Various pH Levels. Chloramination of Phenol at pH 7.2

as evidenced by the anomalies exhibited by phenol. Further knowledge of the effect of pH on the state in which a pure compound exists in solution and its effect on chlorination is needed in order to completely characterize the system.

5.4 Chlorine Concentration and Chlorination:

1. Glutamic acid

The reaction between 25.0 mg/l available chlorine (0.70 m-mole/l as HOCl) and glutamic acid (0.20 m-mole/l) differed widely from that occurring at lower dosages. It was observed that at the higher chlorine dose, the free residual was entirely depleted in the first 10 minutes at which time the rate of reaction was markedly depressed and a combined residual was left. After one hour contact time, 21.7 mg/l Cl were consumed. The residual was predominantly monochloramines and persisted for 27 hours from the beginning of the reaction.

At the lower chlorine dosage, 12.0 (0.34 m-mole/l as HOCl), 6.0 (0.17 m-mole/l as HOCl) and 3.0 mg/l (0.09 m-mole/l as HOCl), the residual depleted at a much slower rate and was found to be predominantly monochloramine. The residual remaining from the application of 12.0 mg/l Cl persisted for 27 hours whereas that resulting from the lower dosages, was depleted after 3 hours.

When chlorine was applied as a chloramine, the rates of depletion were slower. This is evident at the 25.0 mg/l Cl (0.70 m-mole/l as NH_2Cl) dose where it was noted that after 25 hours contact time, the residual was about 5.9 mg/l Cl whereas the same residual was observed after 20 minutes from the application of free chlorine. Furthermore, the residual remaining from the application of the chloramine solution, persisted and

was measurable at 3.9 mg/l Cl after 5 days. The residuals resulting from the application of 3.0, 6.0 and 12.0 mg/l Cl (0.09, 0.17, 0.34 m-mole/l as NH_2Cl , respectively) as chloramine was depleted after 2 hours in the lowest concentration, but within 25 hours at the higher concentration. Figure 9 illustrates the results.

2. Alanine

The reaction between alanine and chlorine both applied as free chlorine and chloramine was observed to be similar to that of glutamic acid. Figure 10 illustrates the results.

3. Histidine

Histidine differs from the other amino acids considered in that it has an aromatic ring, and exhibited very different chlorination characteristics than the other amino acids.

At the 25.0 mg/l (0.70 m-mole/l as HOCl) applied chlorine, the free residual is rapidly and entirely depleted in the first fifteen minutes during which time monochloramine and dichloramines were observed to form in increasing amounts. Beyond this initial fast rate, the rate began to slow down, giving a combined residual. About 23.8 mg/l Cl were consumed in 2 hours and within 6 hours the residual was as low as 0.3 mg/l. No residual was observed after 24 hours.

When 12.0 mg/l (0.34 m-mole/l as HOCl) were applied, the rate was as fast in the first 10 minutes as when 25.0 mg/l were applied. At this lower dose, 9.8 mg/l of available chlorine were consumed as compared to 10.3 mg/l Cl at the higher dose during the same contact time. The residual was zero after 15 minutes contact time. Similarly the residual was depleted much faster at 6.0 and 3.0 mg/l Cl (0.17 and 0.09 m-mole/l as

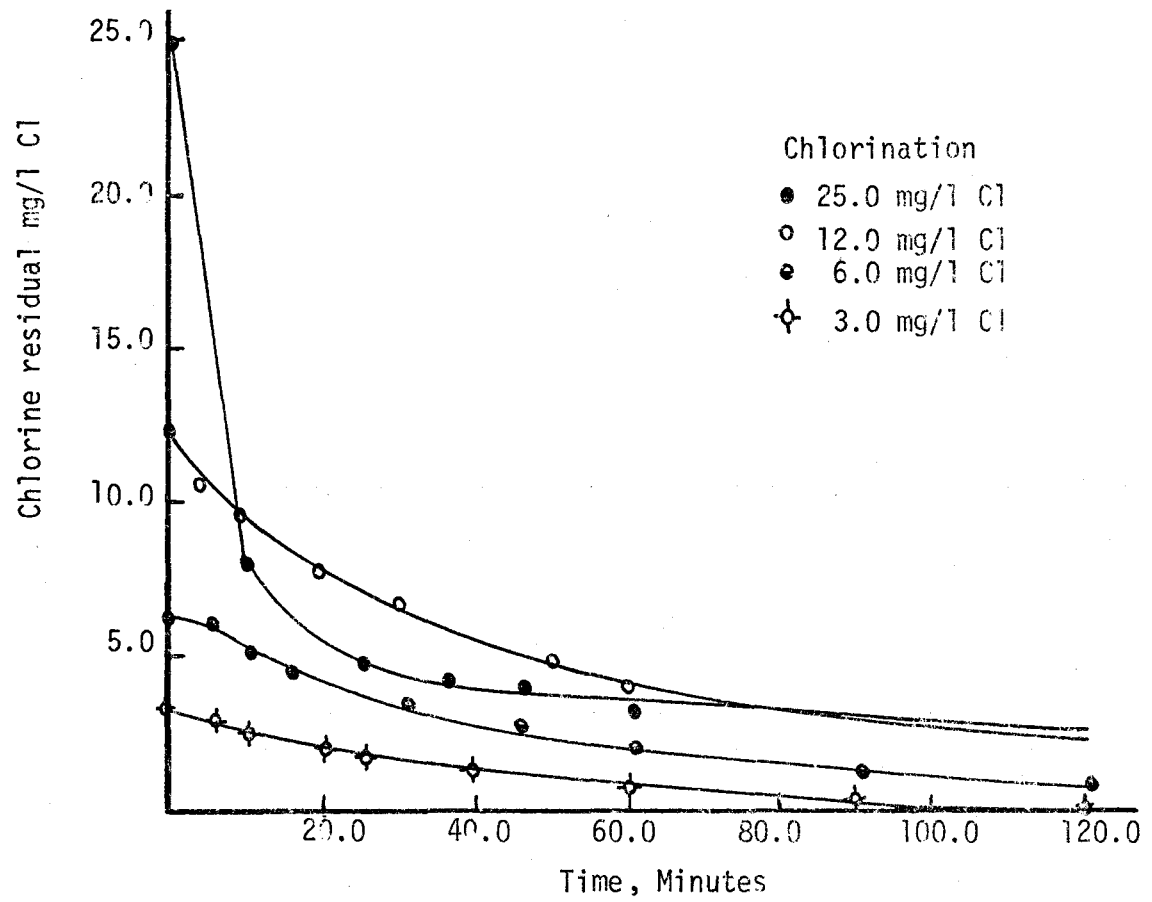
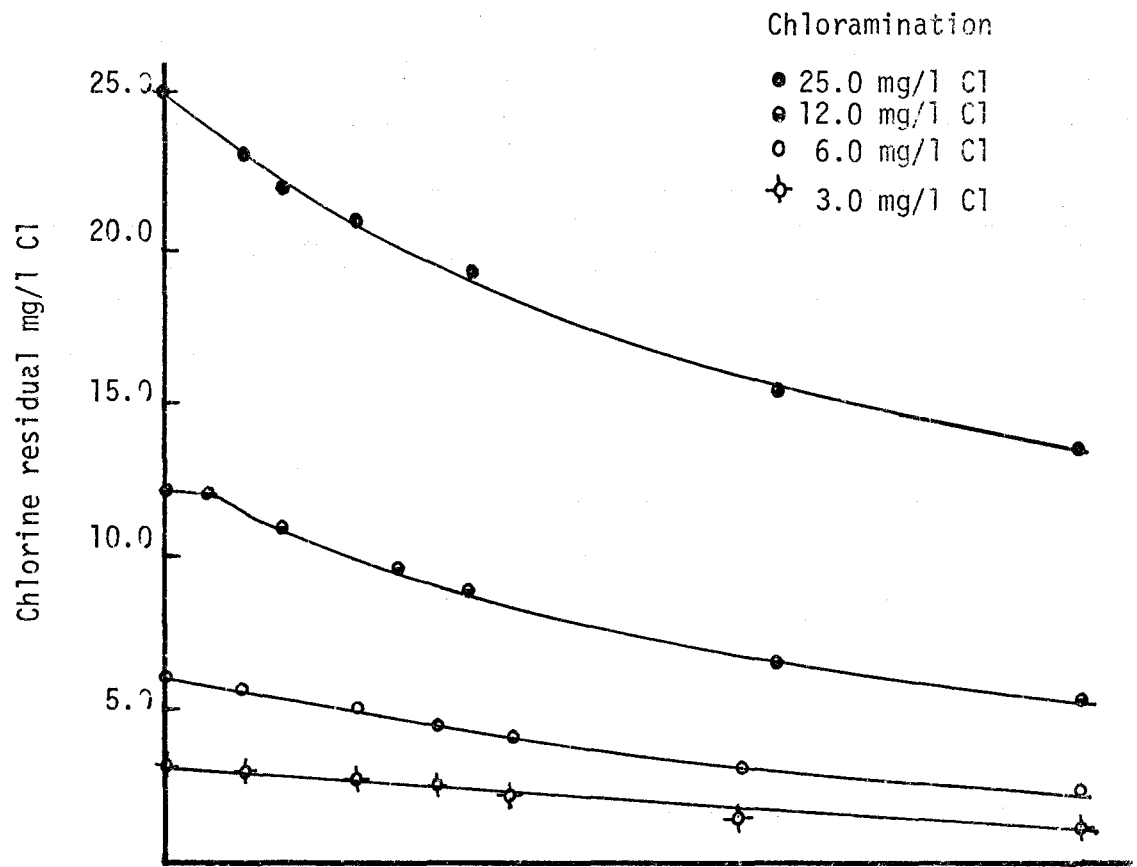


Figure 9 Chlorination and Chloramination of Glutamic Acid at Various Dosages.

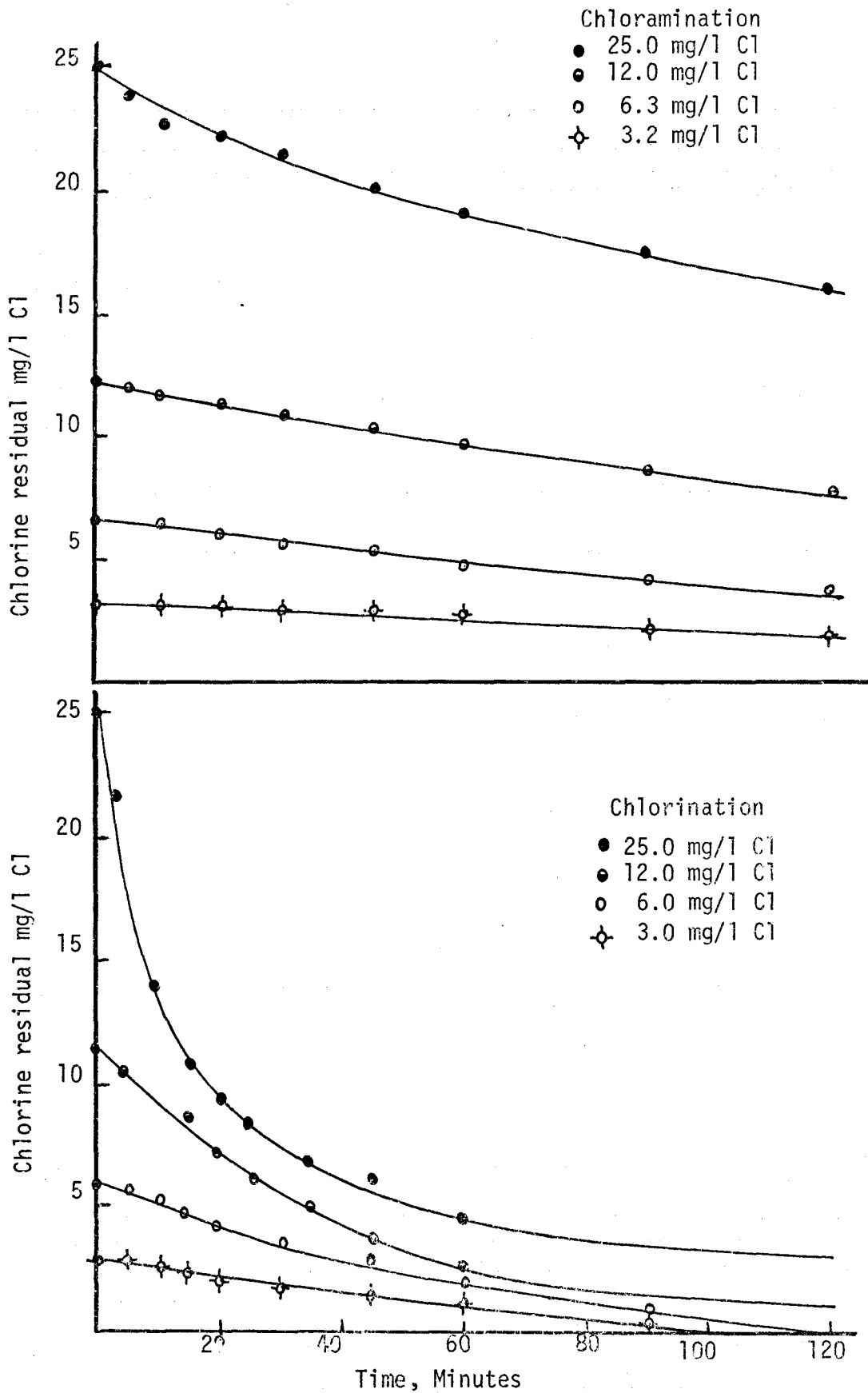


Figure 10 Chlorination and Chloramination of Alanine at Various Dosages.

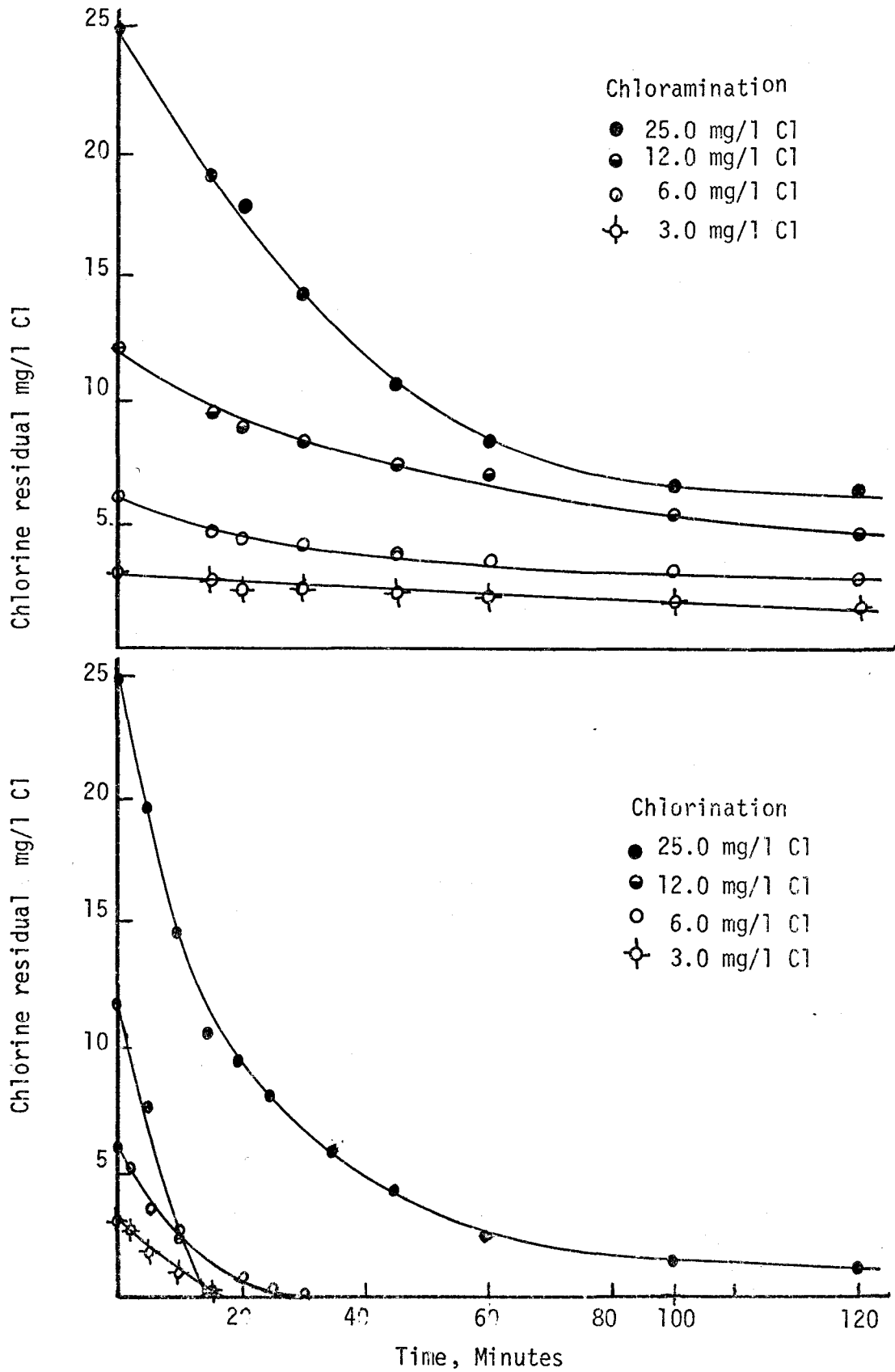


Figure 11 Chlorination and Chloramination of Histidine at Various Dosages.

HOCl) in the case of histidine than in the case of glutamic acid and alanine, and was of the chloramine form. The residual was 0.0 mg/l Cl after 30 and 15 minutes, respectively.

When histidine was chlorinated with chloramine at a dose of 25.0 mg/l available chlorine, (0.70 m-mole/l as NH_2Cl) the residual depleted much slower than in the case of free residual chlorination but much faster and to a larger extent than in the case of glutamic acid and alanine. In the case of histidine the residual persisted up to about 66 hours at the higher dose, slightly over 22 hours at 12.0 mg/l Cl (0.34 m-mole/l as NH_2Cl), and less than 22 hours but longer than 2 hours at doses of 6.0 and 3.0 mg/l Cl (0.17 and 0.09 m-mole/l as NH_2Cl respectively). In all cases the residual was of the combined form.

4. Glycine

Glycine is the simplest of all amino acids. The chlorination of glycine (0.2 m-mole/l) also exhibited different characteristics from glutamic acid, alanine and histidine in that it formed extremely stable chloramines. However, its chlorination at 25.0 mg/l available chlorine (0.70 m-mole/l as HOCl) did not show any difference. At this higher dose, it was found that the free residual which predominated at the beginning of the reaction, depleted rapidly during the first 10 minutes. In fact, after 10 minutes contact time, the free residual was zero. During this period of time, a combined residual formed and beyond this initial depletion period the residual was entirely of the chloramine form. About 21.5 mg/l available chlorine were consumed in 2 hours after which time the residual was found to be 3.5 mg/l Cl. This residual chloramine depleted very slowly and after 48 hours, it fell down to 2.6 mg/l and after 96 hours, it was still quite measurable at 1.8 mg/l.

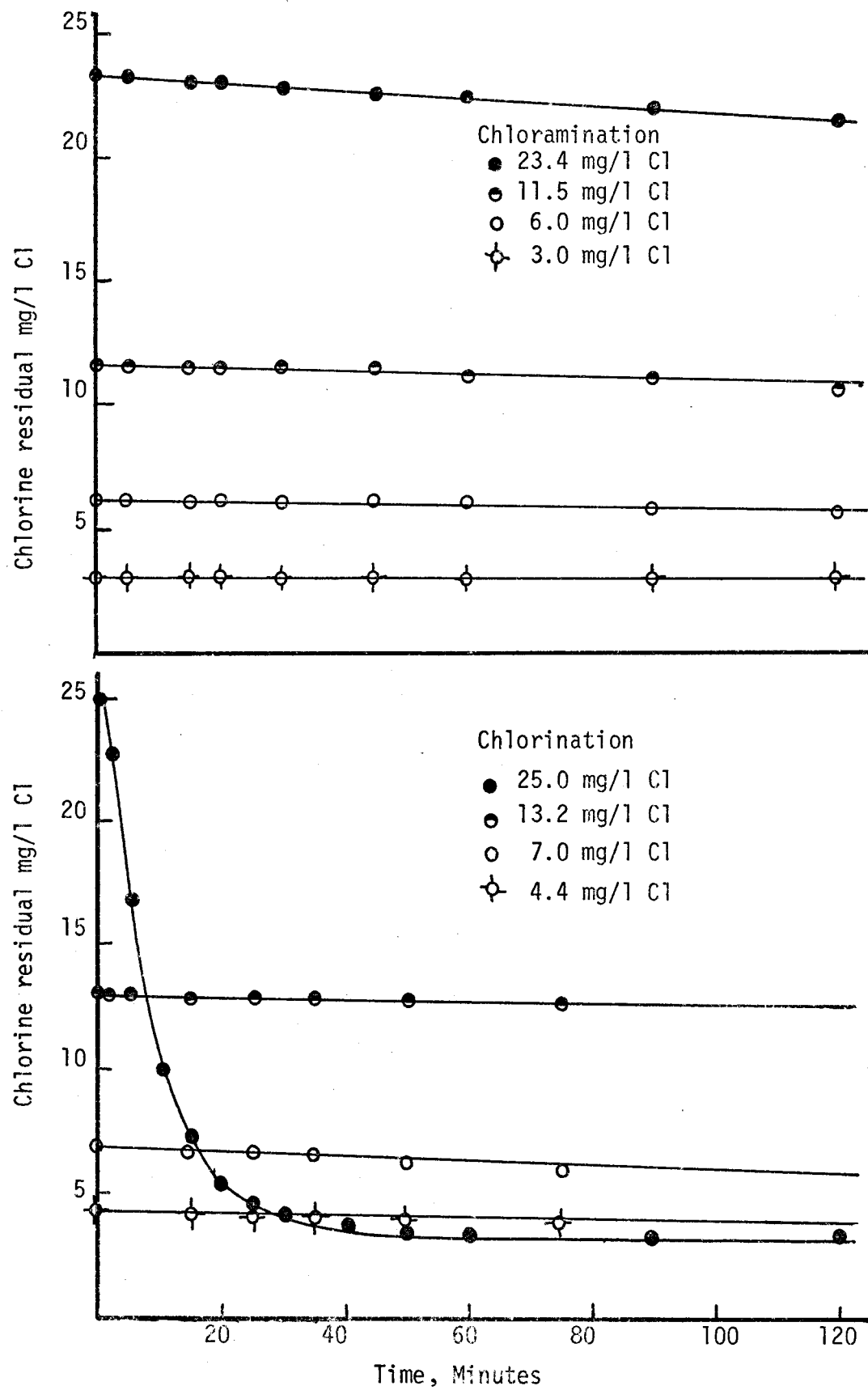


Figure 12 Chlorination and Chloramination of Glycine at Various Doses.

Contrary to the other amino acids considered, the residual chloramine at an applied dose of 13.2 mg/l available chlorine (0.37 m-mole/l as HOCl), was found to persist. This residual seemed to be extremely stable. At this dose, 0.8 mg/l Cl depleted in 150 minutes, 2.2 mg/l Cl disappeared in 12 hours, 5.4 mg/l Cl depleted in 48 hours and after 96 hours the residual was still 1.9 mg/l. Similar comments can be made at the lower dosages of 7.0 and 4.4 mg/l Cl (0.2 and 0.12 m-mole/l as HOCl, respectively).

The chloramination of glycine at 23.4, 11.5, 6.0 and 3.0 mg/l available chlorine (0.66, 0.32, 0.17 and 0.09 m-mole/l as NH_2Cl) also exhibited different characteristics than the other amino acids in that the residuals remained virtually unchanged. After 2 hours contact time, 2.1, 1.1, 0.4 and 0.1 mg/l Cl were depleted at doses of 23.4, 11.5, 6.0 and 3.0 mg/l available chlorine, respectively.

After 72 hours the residuals left at these four concentrations was quite high, much higher than encountered with the other amino acids. Approximately 50% of the applied dosage persisted. The residual was of the combined form. Figure 12 illustrates these results.

5. Ammonia

Ammonia was chlorinated at two chlorine dosages, 25.0 mg/l (0.71 m-mole/l as HOCl) and 13.0 mg/l (0.37 m-mole/l) available chlorine. The concentration of ammonia before the addition of hypchlorite was 4.3 mg/l (0.25 m-mole/l) as NH_3 as measured with the ammonia electrode.

The reaction was found to proceed extremely rapidly. Within 1.5 minutes, 15.0 mg/l available chlorine were depleted. Within 5 minutes from the beginning of the reaction, 21.5 mg/l Cl were consumed. This

same quantity of chlorine is depleted by the amino acids in more than one hour. The rate of reaction between ammonia and chlorine appears to be faster than the rate of reaction between amino acids and chlorine. The ammonia concentration after 120 minutes contact time was measured and found to be 0.34 mg/l after dechlorination with sodium sulfite. This corresponds to a loss of ammonia of 3.96 mg/l. Accordingly, 6.16 parts of chlorine as available chlorine were consumed per part of ammonia as NH_3 . This is in close agreement with the stoichiometric requirement of 6.26 parts of Cl/part of NH_3 for the oxidation of ammonia. The residual after two hours contact time titrated as free. After 30 minutes contact time the residual was predominantly free with small amounts of dichloramines formed. There was no monochloramine residual detected at this point.

When ammonia was chlorinated with 13.0 mg/l available chlorine, the residual was found to be predominantly monochloramines and quite stable. After two hours of contact, 1.4 mg/l available chlorine were depleted. The chloramination of ammonia at doses of 24.0 mg/l (0.68 m-mole/l as NH_2Cl) and 12.0 mg/l (0.34 m-mole/l NH_2Cl) available chlorine was observed to form very stable chloramine residuals. The depletion of the residual at the higher dose was 1.7 mg/l and 0.8 mg/l available chlorine at the lower dose after 90 minute contact time. After 18 hours, the residual had dropped to 20.2 and 10.8 mg/l Cl at 24.0 and 12.0 mg/l applied chlorine, or a depletion of 3.8 and 1.2 mg/l Cl respectively. The residuals persisted and were high after 5 days contact time. The residuals were 15.3 and 8.9 mg/l available chlorine for the higher and lower doses, respectively. Figure 13 illustrates the results.

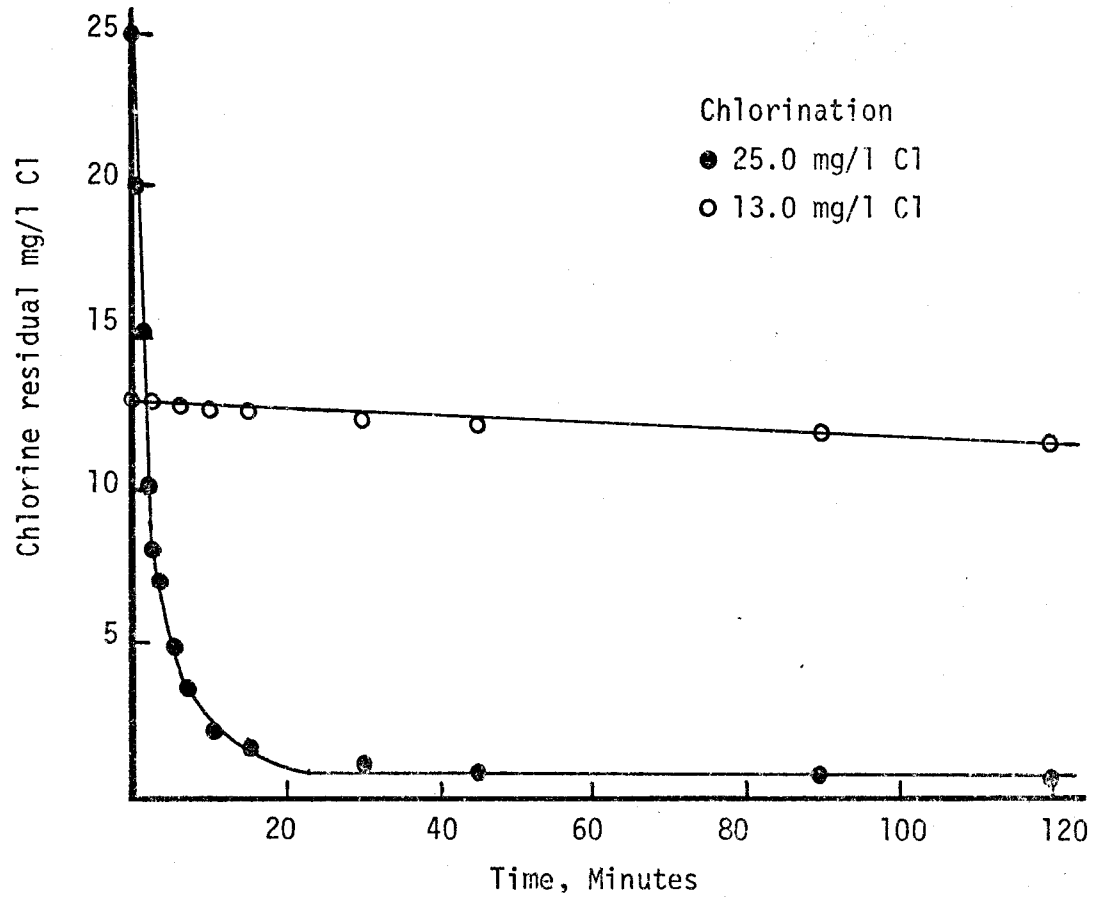
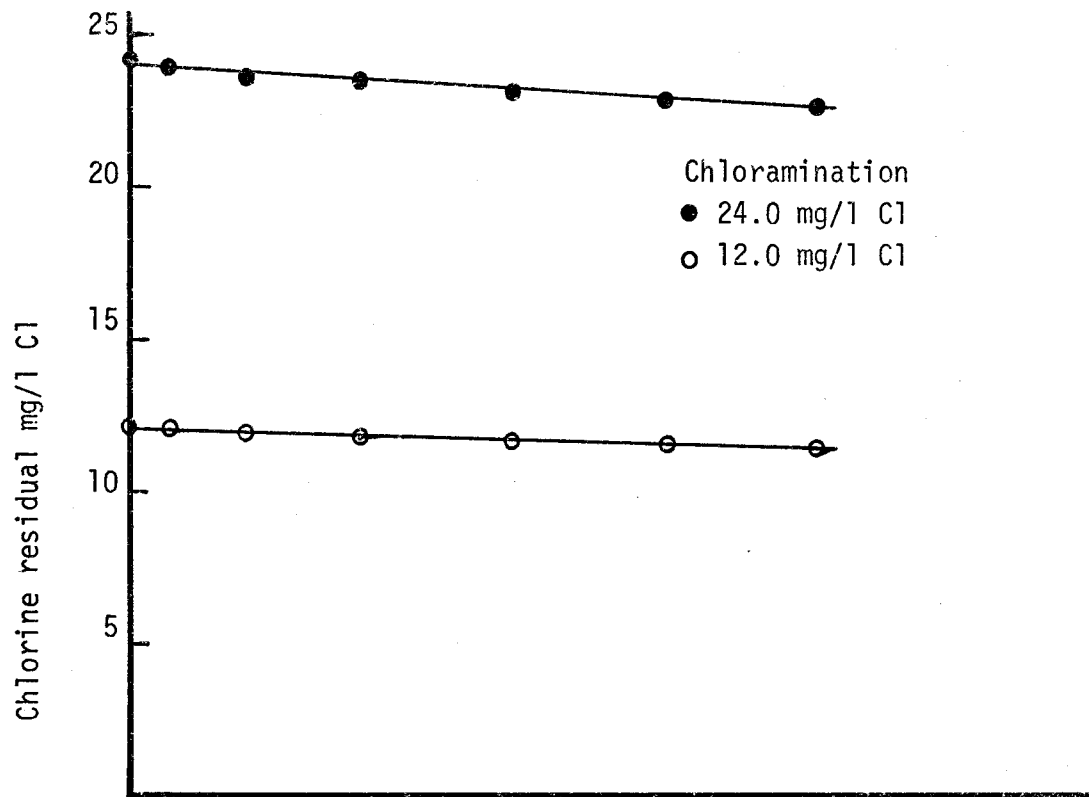


Figure 13 Chlorination and Chloramination of Ammonia at Various Doses.

6. Phenol

Phenol (0.2 m-mole/l) was chlorinated with 13.0 mg/l available chlorine (0.37 m-mole/l as HOCl) in the presence of 3.4 mg/l NH₃ (0.2 m-mole/l) ammonia. After 18 hours contact, the residual had fallen to 10.6 mg/l, or a depletion of 2.4 mg/l. After 5 days, the residual still persisted and was 8.8 mg/l available chlorine, or a depletion of 4.2 mg/l Cl. In the absence of ammonia, and for the same applied chlorine dose, the residual was completely depleted within 15 minutes. Figure 14 shows these results.

It appears, therefore, that ammonia inhibits strongly the reaction between chlorine and phenol. Furthermore, the similarity in the magnitude of the residuals remaining after 90 minutes of contact in the reaction between ammonia and chlorine, and the reaction between phenol and chlorine in the presence of ammonia indicate that ammonia is preferentially chlorinated. Such results are confirmed by the work of Burttschell et al (1959) referred to earlier.

7. n-Butylamine

n-Butylamine was chlorinated at two doses with free residual chlorine. (Figure 15). At the higher dose of 24.2 mg/l available chlorine (0.68 m-mole/l as HOCl), a stable chloramine residual formed during the first 15 minutes and depleted beyond that time to about 13.8 mg/l in 60 minutes after which the rate of depletion began to slow down. After two hours the residual fell to 8.0 mg/l and only by a further 0.7 mg/l in 24 hours. The residual persisted for 5 days and was measured to be 5.9 mg/l Cl. The residual was a mixture of monochloramines and dichloramines.

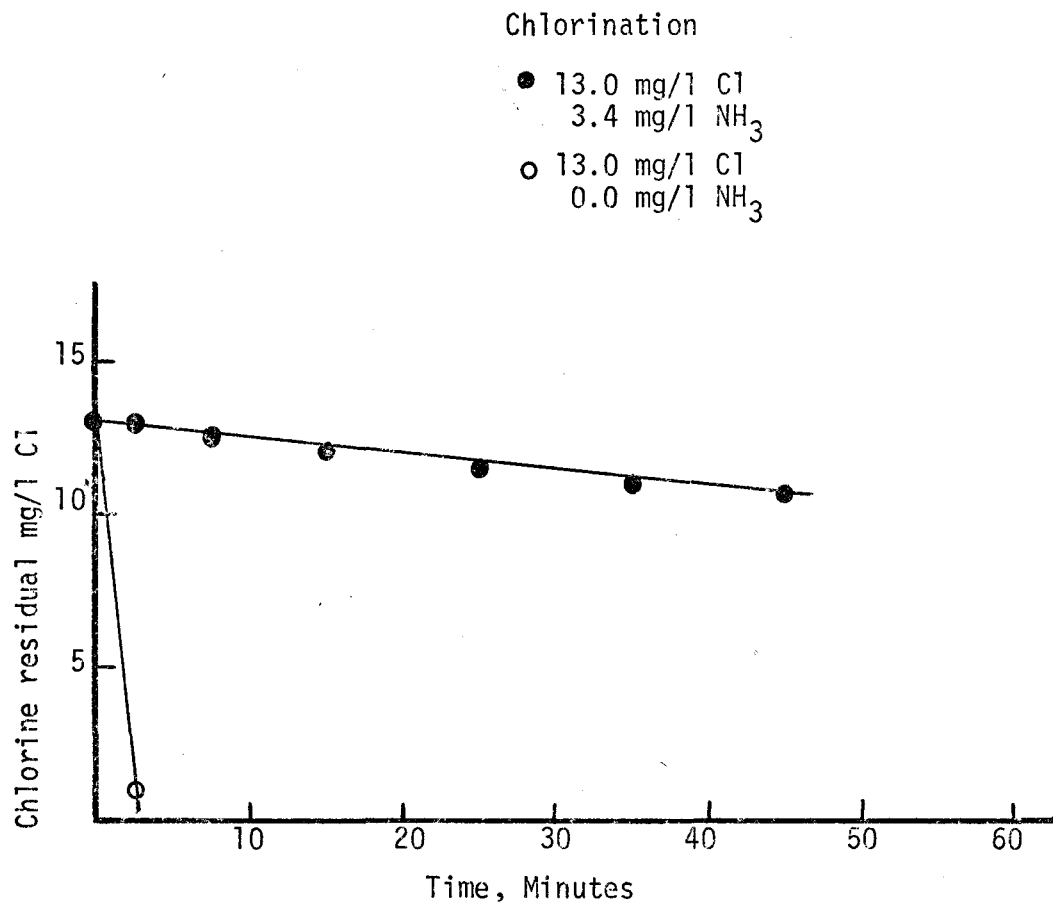


Figure 14 Chlorination of Phenol in the Presence and Absence of Ammonia.

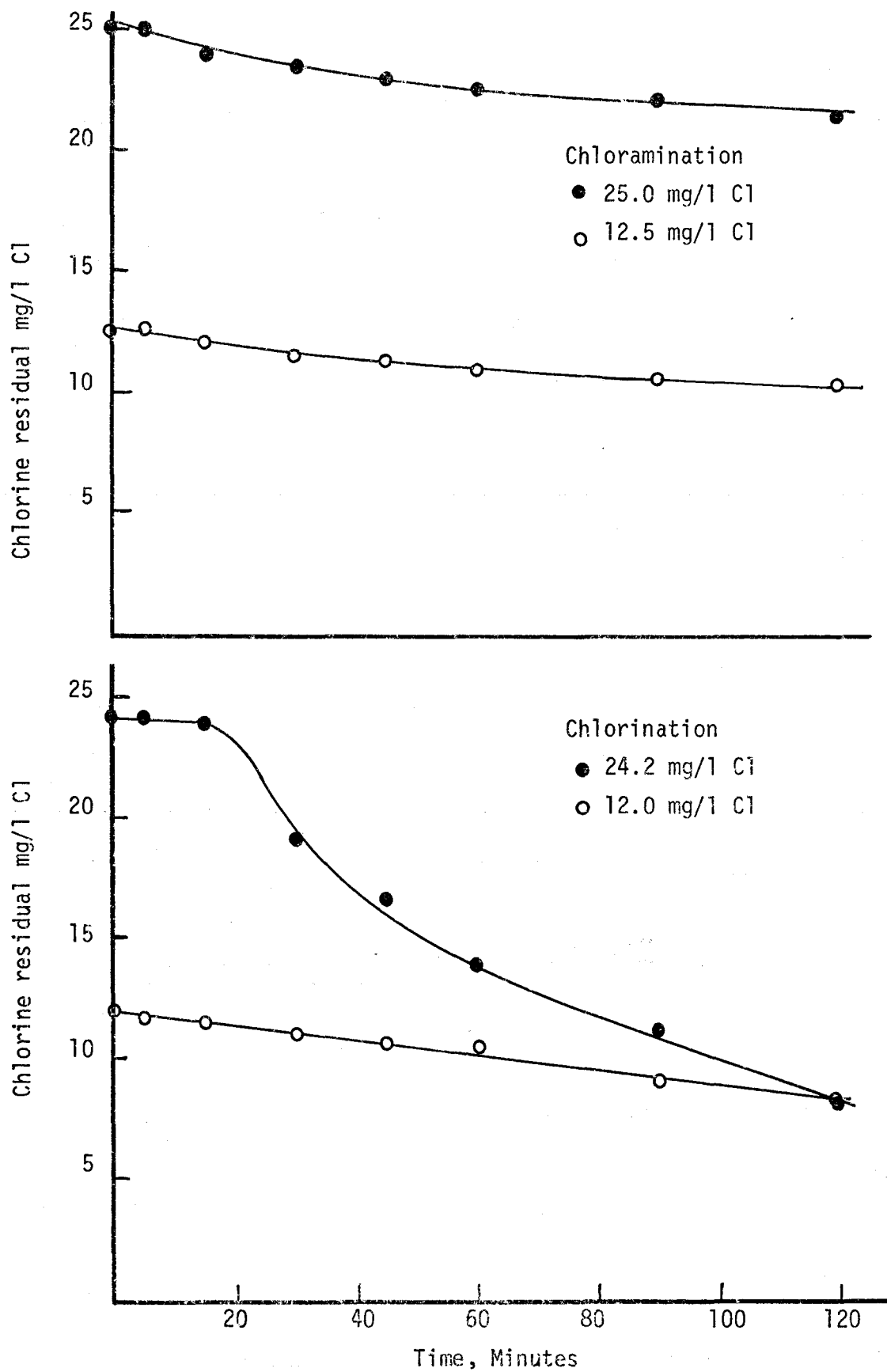


Figure 15 Chlorination and Chloramination of n-Butylamine at Various Doses.

At the lower dose, 12.0 mg/l Cl (0.34 m-mole/l as HOCl), 1.4 mg/l Cl depleted in 1 hour and about 3.9 mg/l in 2 hours. After 24 hours the residual had fallen to 7.8 mg/l and persisted for 5 days at which time it was measured to be 6.8 mg/l. The residual was of the combined form.

When n-butylamine was chlorinated at 25.0 and 12.5 mg/l available chlorine (0.70 and 0.35 m-moles/l as NHCl_2), the rates of reaction were considerably slowed down. At the higher applied dose, 3.7 mg/l were depleted in two hours as compared to 16.2 mg/l for the same period with free residual chlorination. Similarly, the residual was much higher after 5 days than in the previous case, and was measured to be 14.4 mg/l Cl or a depletion of 10.6 mg/l. The same trend is observed at the lower dose. 2.3 mg/l available chlorine were depleted in 2 hours as compared to 3.9 mg/l when free available chlorine was applied. The residual after 5 days, however, was not significantly higher.

8. Acetic acid

The chlorination of acetic acid was expected. After two hours contact time, the residual depleted only by 0.2 mg/l available chlorine at the two levels, namely, 24.7 and 12.0 mg/l available chlorine (0.70 and 0.34 m-mole/l as HOCl), Figure 18. The residual after 72 hours was high, 2.3 and 1.5 mg/l being lost at the higher and lower levels respectively. It is felt that these losses are due to decomposition of the hypochlorous acid and not due to a chemical reaction. The residual was free in nature. Similar conclusions are reached concerning doses of 6.1 and 3.1 mg/l available chlorine.

Acetic acid was not chloraminated.

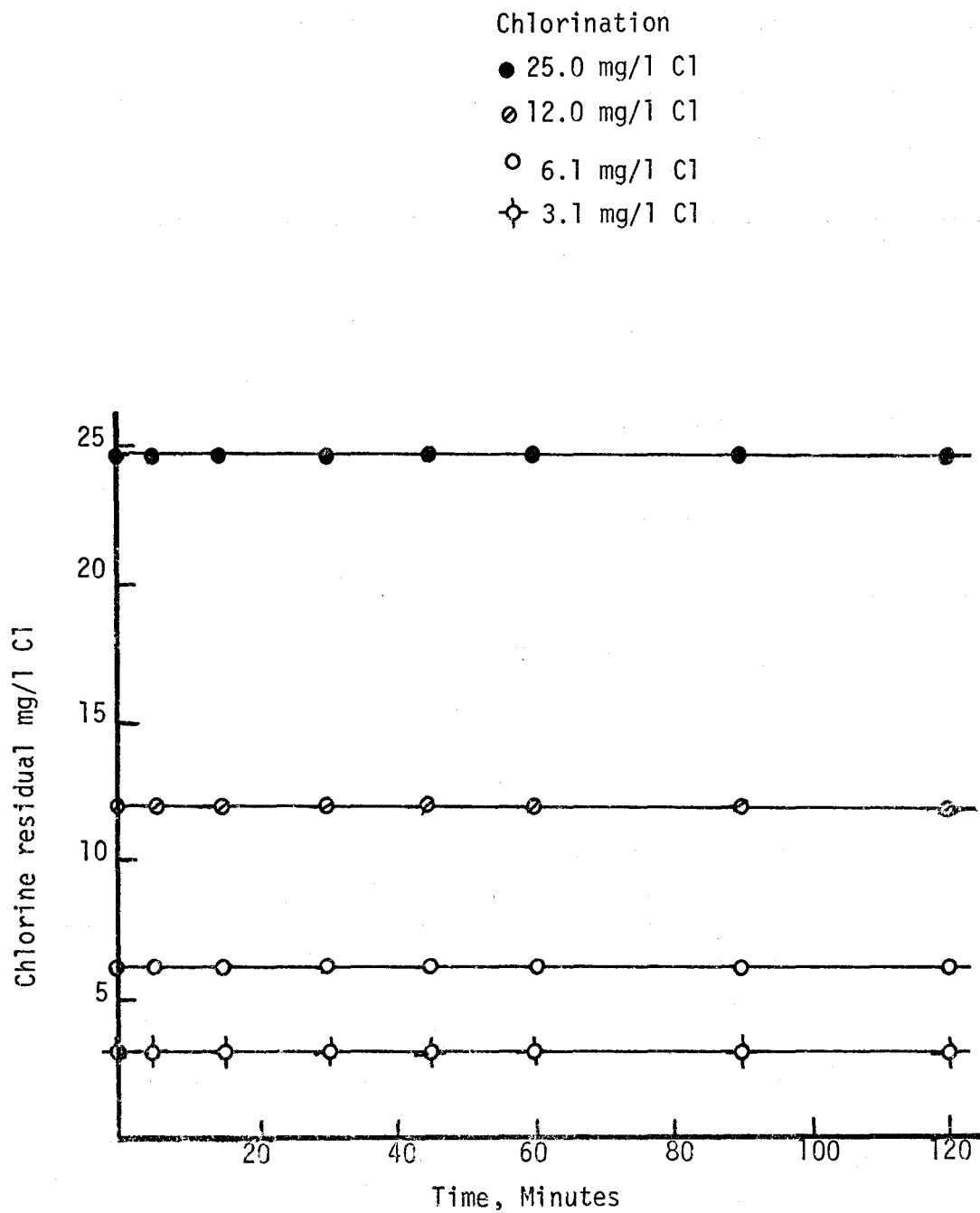


Figure 16 Chlorination of Acetic Acid at Various Dosages.

9. Maleic acid

Maleic acid being an unsaturated acid was expected to chlorinate to some extent by addition of chlorine at the double bond.

This acid was chlorinated at 2 doses with free residual (27.0 and 13.8 mg/l) and one dose (27.2 mg/l) in the presence of 10.0 mg/l ammonia (Figure 17).

At the 27.0 mg/l available chlorine (0.76 m-mole/l as HOCl), the residual depleted by 1.5 mg/l in 90 minutes. 2.0 mg/l depleted when ammonia was present. 1.0 mg/l available chlorine depleted when 13.8 mg/l Cl (0.39 m-mole/l as HOCl) were applied to the ammonia free solution. Little or no difference is observed in the presence or absence of ammonia in this case, and no conclusions can be drawn as to whether or not maleic acid was chlorinated.

Identification of the product of reactions compared to the pure solution would determine any changes that may have occurred. It appears, however, on the basis of the large magnitude of the residuals, that negligible chlorination has occurred during this contact period and under the conditions used.

10. Histidine

Histidine was chlorinated again in the presence of ammonia. The ammonia concentrations employed were 3.4 and 10.3 mg/l as NH_3 (0.2 m-mole/l and 0.6 m-mole/l, respectively), and the applied chlorine dose was 13.0 and 12.0 mg/l available chlorine (0.37 and 0.34 m-mole/l as HOCl, respectively).

Increasing the concentration of ammonia to 0.6 m-mole/l did not seem to slow the rate of reaction more than when 0.2 m-mole/l were used.

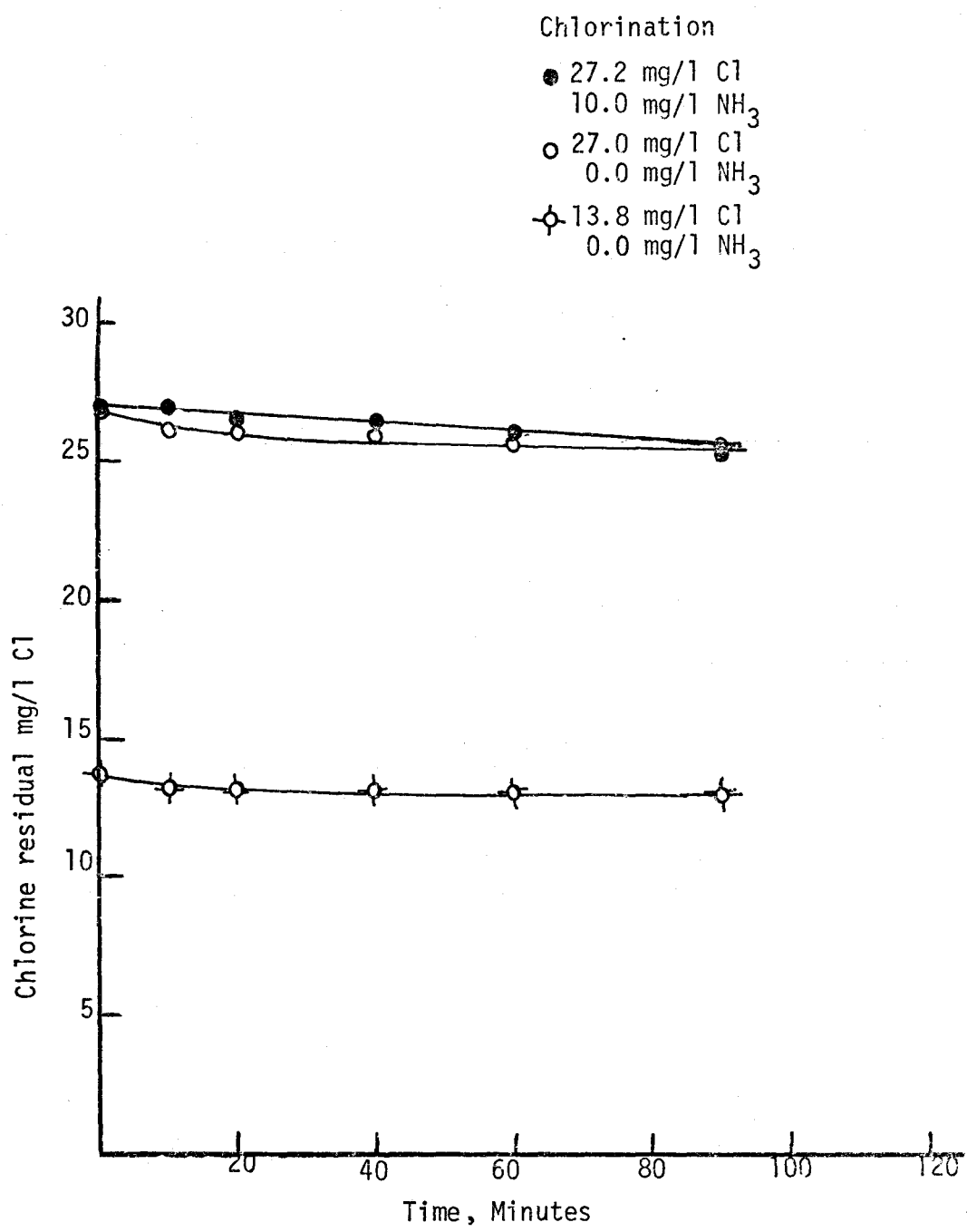


Figure 17 Chlorination of Maleic Acid in the Presence and Absence of Ammonia.

However, the residual was entirely chloramines. The residual chlorine in these reactions seemed to be substantially lower than the residuals observed when histidine was chloraminated at the same dose. However, it is obvious that the presence of ammonia, whether added as free ammonia or as a chloramine solution, substantially depresses the rate of reaction. It is felt that in the absence of ammonia, free or combined as chloramine, a dual reaction takes place, where the aromatic ring is attacked as well as the amino group. The similarity with the rate of depletion of the residual in the chlorination of phenol even at a 12.0 mg/l dose seems to substantiate this hypothesis. However, the presence of chloramines indicate that the amino group has also been attacked. By analogy to phenol, the presence of ammonia, free or combined, would tend to inhibit the attack of the ring as well as markedly depress the rate of depletion of the residual. Figure 18 illustrates these results.

5.5 Chlorination in the Presence of Ammonia:

A series of experiments was devoted to investigate the role of ammonia in the chlorination of amino acids. Glycine was selected because of the stability of its chloramines.

This series of experiments consisted of chlorinating 15.0 mg/l glycine (0.20 m-mole/l) with 26.4 mg/l available chlorine (0.74 m-mole/l as HOCl) at pH 7.2 and varying the ammonia concentration from 0.00 to 0.50 m-mole/l. The residual curves were obtained, the nature of the residual was identified, the level of ammonia in solution was determined at various times during the reaction and at the end of the reaction the residual was destroyed with sodium sulfite and the ammonia concentration was determined.

Glycine in the absence of ammonia and chlorinated at a dose of

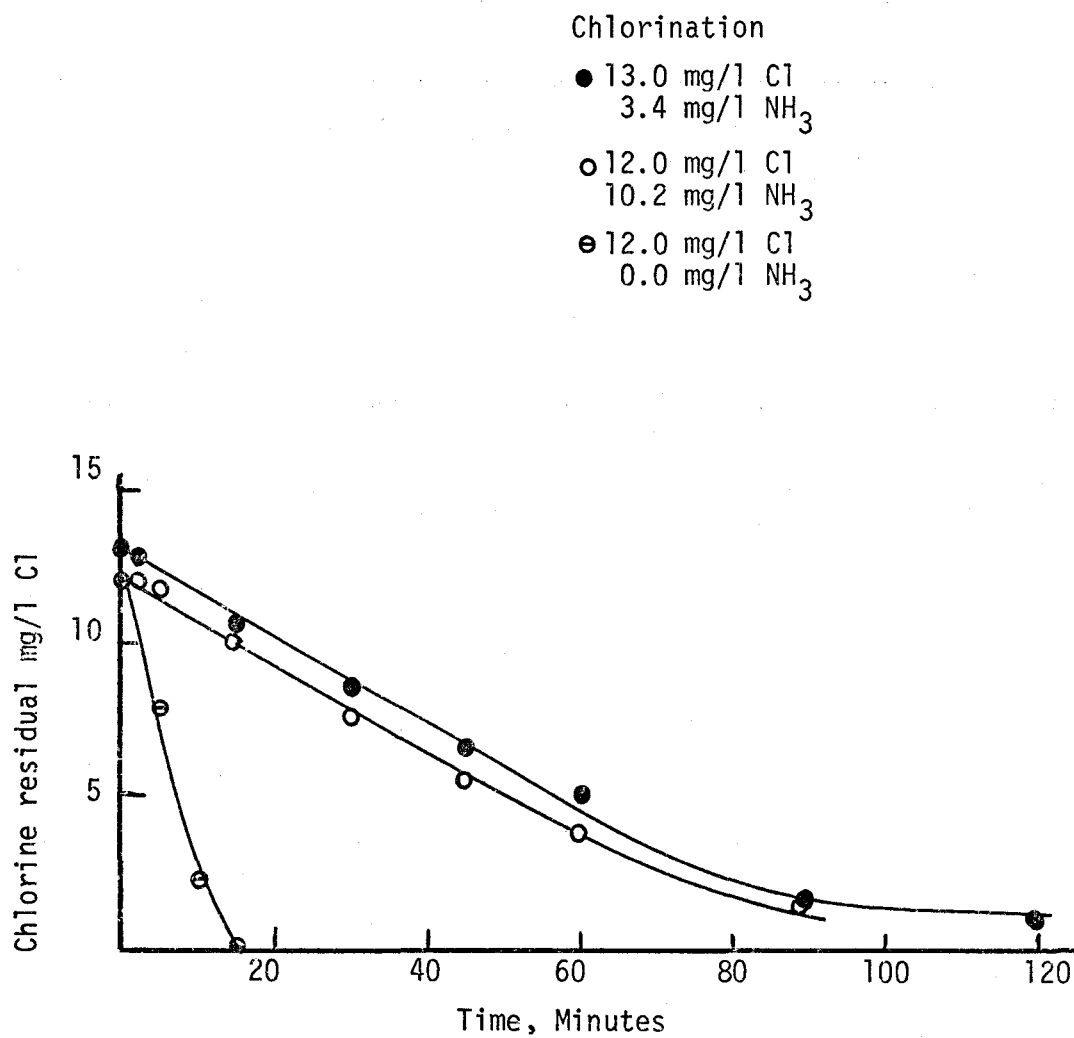


Figure 18 Chlorination of Histidine in the Presence of Ammonia.

26.4 mg/l available chlorine behaved in a similar manner as previously discussed. The level of ammonia before the addition of hypochlorite was zero and remained so during the reaction and at the end of the reaction when the residual was destroyed. However, as previously discussed, the residual was a mixture of monochloramines and dichloramines. When 1.9 mg/l NH_3 (0.11 m-mole/l) were added, the rate of reaction was markedly depressed. About 8.4 mg/l available chlorine disappeared after 2 hours contact, as compared to 23.8 mg/l when ammonia was absent. It was noted that the residual during the reaction was a mixture of mono and dichloramines but predominantly monochloramines. The ammonia level decreased from 1.9 mg/l to 0.54 mg/l or a decrease of 1.36 mg/l. However, when the residual was destroyed, all the ammonia was recovered.

When the added ammonia concentration was doubled from 1.9 to 3.81 mg/l (0.22 m-mole/l as NH_3), the residual remained very stable and decreased only by 1.0 mg/l in 2 hours. The residual was entirely monochloramine. The ammonia level during the course of the reaction had fallen from 3.81 to 1.26 mg/l or a decrease of 2.55 mg/l. However, it was all recovered once the residual was destroyed.

When 8.5 mg/l NH_3 (0.50 m-mole/l) were added, the residual chlorine was exactly the same as in the above case and the nature of the residual was monochloramines. The ammonia level had fallen from 8.5 to 5.61 mg/l or a decrease of 2.89 mg/l which was recovered entirely after dechlorination. Figure 19 illustrates the above results.

On the basis of the above result it appears that the chloramine residuals derived from chlorinating the amino acids are not of the same type as those derived from ammonia. Chloramines derived from ammonia liberate the bound ammonia upon dechlorination. No ammonia has been detected

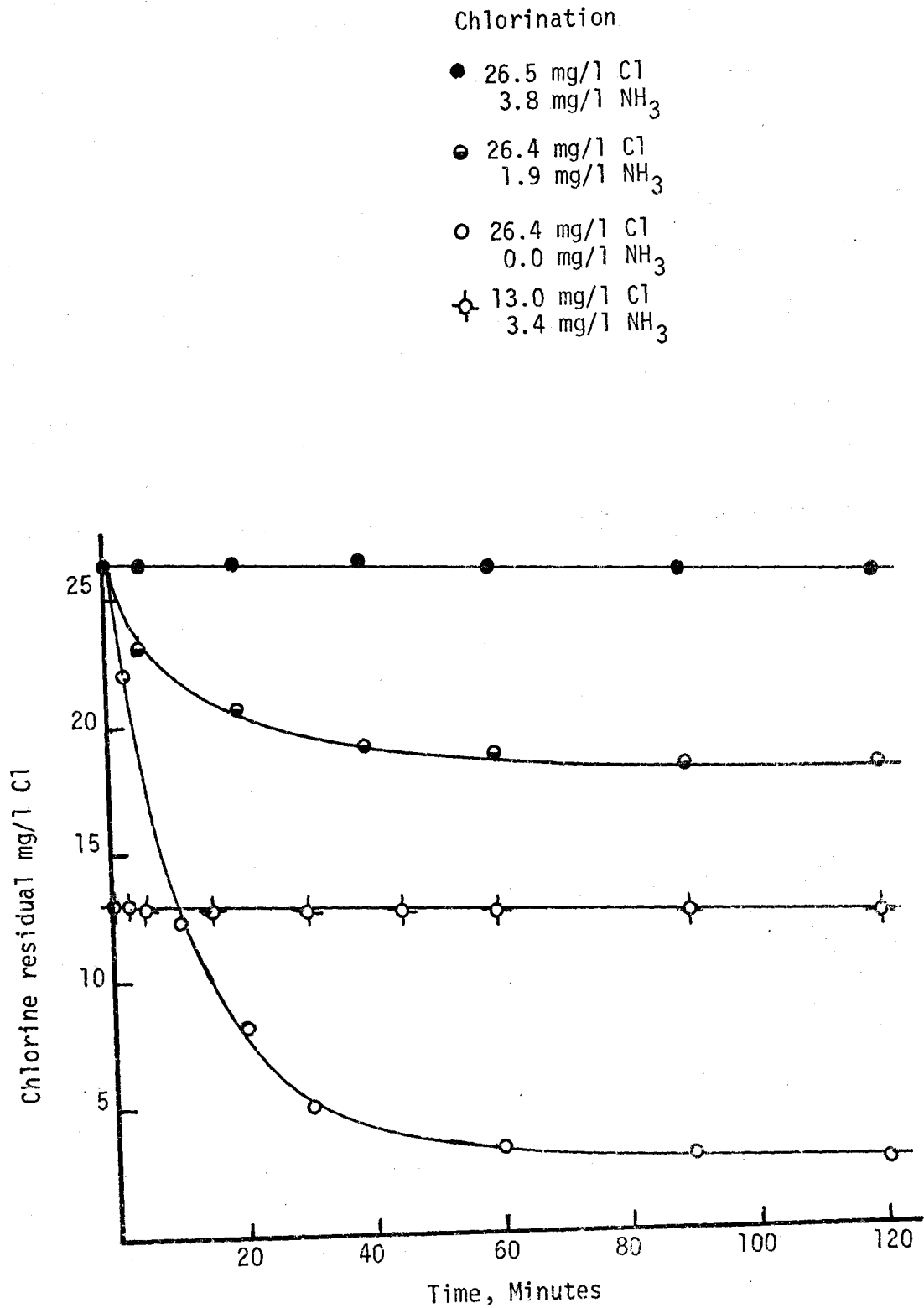


Figure 19 Chlorination of Glycine in the Presence of Varying Amounts of Ammonia.

when organic chloramines are dechlorinated.

The amount of ammonia used in the formation of chloramines does not seem to increase in proportion to the amount of ammonia added.

It appears that the presence of ammonia slows down the rate of reaction considerably such that when 2.55 mg/l NH_3 are used, the residual left is very stable and persistent. Increasing the ammonia level has little or no effect on the type of residual or its stability. When 0.2 m-mole/l NH_3 are added to glycine in the presence of 13.0 mg/l available chlorine, the residual remained virtually unchanged.

Norman (1936) had found that 10.0 mg of glycine (0.13 m-mole) could be completely oxidized to carbon dioxide by 50.0 mg available chlorine (1.41 m-mole). The volume of the solution was 100 ml. and the pH 7.0.

5.6 Extent of Oxidation of Glycine in the Presence and Absence of Ammonia:

A series of experiments was conducted to assess the extent to which glycine can be chlorinated and oxidized in the presence and absence of ammonia. The solutions were buffered to 7.2 and the volume of the solutions was 100 ml. The molar ratios of chlorine as hypochlorous acid to glycine were: 1.83:1 to 10.5:1. Residual chlorine and carbon measurements were made after two hours contact time. Figure 20 gives the percent chlorine and carbon remaining versus the molar ratio. At molar ratios less than 2.0 it had been previously determined that the residual was chloramines and was found to be quite stable. Since no carbon loss was observed it appears then that only chlorination of the amino group had happened. A molar ratio of 2:1 would be required to form dichloroaminoacetic acid. At molar ratios greater than 2.0 a sharp decrease in the organic content was observed such that 75% of the carbon was depleted and

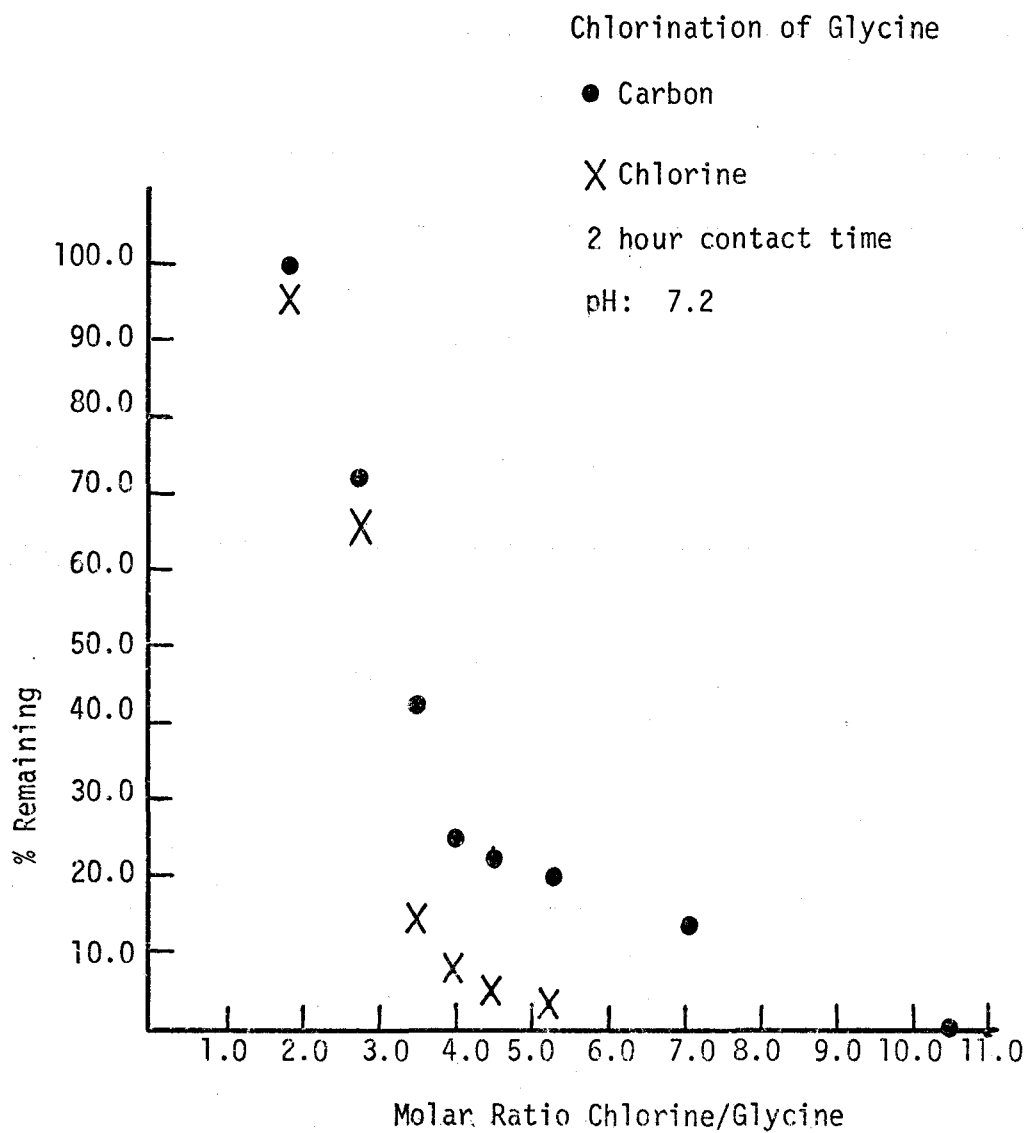


Figure 20 Extent of Chlorination and Oxidation of Glycine in the Absence of Ammonia.

only 7.4% of the chlorine residual persisted at a molar ratio of 4.0:1. Beyond this ratio, the increment carbon lost was small and an additional 6.5 moles of chlorine as HOCl were required to achieve 100% carbon depletion. Also beyond this molar ratio the percent residual chlorine remaining seems to decrease very slowly. The data above the molar ratio of 2.0 are characterized by two regions each of which can be represented by a straight line intersecting at a molar ratio of 4.0. The residual chlorine data is also characterized by two regions. Below the molar ratio of 4.0 and above 2.0, the percent residual remaining is observed to deplete rapidly and beyond the ratio of 4.0 the percent residual remaining falls off slowly. The two curves appear to bear the same shape. Thus 2 moles of hypochlorous acid would be required to form chloramines, a further two moles would be required to oxidize 75% of the carbon and an additional 6.5 moles would be needed to achieve 100% oxidation, or a total of 8.5 moles for oxidation.

When ammonia was added no carbon reduction was observed and the residual chlorine was very stable as previously discussed. Table II shows the effect of ammonia on the oxidation of glycine.

Wright (1926) had determined that 2 moles of chlorine as hypochlorous acid would be required to form dichloramines and 8 moles of hypochlorous acid to complete the oxidation of glycine. In the light of these results the high BOD₂₀ reductions of glycine as reported by Ingols and Jacobs (1957) can be due to partial oxidation of glycine to carbon dioxide and other products and to UV-catalyzed chlorine oxidation. Since Ingols and Jacobs have used a molar ratio of 2.8:1, then about 28% of the organic carbon would be converted to CO₂ and 66% of the applied chlorine would not be depleted in two hours.

TABLE 11

Effect of Ammonia on the Oxidation of Glycine

Molar Ratio: m-mole Chlorine to m-mole Glycine $\text{HOCl}:\text{CH}_2\text{NH}_2\text{COOH}$	Molar Ratio of Chlorine to Ammonia $\text{HOCl}:\text{NH}_3$	Weight Ratio of mg Chlorine to mg Ammonia $\text{Cl}:\text{NH}_3$	% Carbon Remaining After 2 Hours
1.83:1	1.83:1	3.8	100
3.5:1	1.20:1	2.5	100
7.05:1	0.49:1	1.0	100

It is interesting at this point to consider the levels of ammonia in sewage and the applied chlorine dosages to achieve disinfection. Meiners et al (1968) report levels of ammonia in sewage effluent ranging from 15.0 to 30.0 mg/l as N. The ammonia concentration in the Dundas activated sludge treatment plant was measured to be 10.0 mg/l as NH_3 . Connell and Forbes (1961) reported values ranging from 4.0 to 17.0 mg/l as N. The chlorine concentrations normally used in sewage disinfection as given in Table 12.

TABLE 12

Chlorine Dosages Required for the Disinfection of Sewage, Sewage Treatment Plant Design Manual (1959)	
	mg/l
Raw sewage	6.0 to 12.0
Settled sewage	5.0 to 10.0
Activated Sludge Effluent	2.0 to 8.0

These chlorine doses are such that the reaction with ammonia would give a chloramine residual. This has been verified in this study. Also it was demonstrated that the presence of ammonia completely inhibited the oxidation of glycine and it is felt that since glycine is the simplest of all the amino acids, the presence of ammonia should prevent the oxidation step from occurring with other amino acids. It has also been shown that in the presence of ammonia, a chloramine residual formed when phenol was chlorinated and that this residual was quite stable. This is supported by the work of Burttschell et al (1959) who had found that ammonia would inhibit and can even prevent the reaction between chlorine and phenol. Also it was shown in this study that acetic acid would not chlorinate as the residual was observed to remain virtually unchanged. At the same time the reaction between ammonia and chlorine was observed to be very fast at pH 7.2 and that 40% of the residual was depleted in 1 minute when 25.0 mg/l Cl (0.71 m-mole/l as HOCl) were applied. Moore (1951) had found that "a water of 25°C receiving 0.8 mg/l of chlorine and 0.32 mg/l of ammonia nitrogen will convert 99% of the chlorine to monochloramine in 1 minute at pH 8.3". McKee et al (1960) stated that

"at the considerably higher ammonia concentrations found in sewage, the reaction will be rapid enough so that HOCl and OCl⁻ will be present only momentarily in concentrations greater than those resulting from equilibrium with chloramine."

The pH of the sewage from the Dundas activated sludge treatment plant was found to vary from 7.5 to 7.9 during the course of this study. McKee et al (1960) have investigated the importance of pH changes resulting from the addition to settled Pasadena sewage of chlorinated water (pH = 2.0) and sodium hypochlorite (pH = 11.1). They concluded that at the concentrations

normally used in sewage the pH changes are not significant. They also found that the Pasadena sewage had a chlorine demand less than 3.0 mg/l and contains few reducing substances such as sulfides, sulfites and nitrites but that it contained 15.0 to 30.0 mg/l of ammonia nitrogen. These authors stated that the chlorine added was not

"consumed by a large inorganic chlorine demand but is taken up immediately by the ammonia to form monochloramines and organic chloramines, and in the form of chloramine, the residual is inactive toward other organic matter during the 15-minute contact."

In this present study it was also found that during the addition of hypochlorite the pH fluctuated between the pH of the sewage (7.5 to 7.9) and 9.2. However, at these doses and due to the buffering capacity of the sewage, the pH fell back to its original value. Sawyer (1959) arrived at the same conclusion concerning the addition of hypochlorite at a Boston sewage treatment plant and that the addition of 10.0 mg/l of chlorine water to the same sewage (alkalinity about 10.0 ppm) depressed the pH by insignificant amounts from 7.0 to 6.7 in one case and from 7.4 to 7.15 in another. Furthermore, Susag (1965) demonstrated that chlorine water or hypochlorites brought about the same BOD₅ reduction.

It appears, therefore, on the basis of the above results and the findings of other workers, that the chlorine dosages normally encountered in the disinfection of sewage containing substantial amounts of ammonia are not sufficient to oxidize the soluble organics in the sewage. The work done on the pure compounds as well as the fact that the TOC and COD before and after chlorination remained unchanged even at doses as high as 25.0 mg/l available chlorine corroborates this hypothesis. The fact that there was no BOD₅ reduction and no significant difference between the extent of

carbon degradation of both chlorinated and unchlorinated filtered effluents indicate that at least no bioresistant or toxic organics have resulted from chlorination. It is felt that the organics were not attacked at all due to the presence of ammonia except possibly amino compounds if they are present. It was demonstrated that the chloramination of amino acids at chlorine doses employed in sewage would form chloramine products with greater stability than when free residual chlorine was added. However, the mechanisms and products of the breakdown of organic chloramines as well as the products of dechlorination with sulfites is not known. Whatever the products are, they do not have any adverse effect on the BOD₅ or the extent of carbon degradation.

5.7 Chlorination and Viability of Seed Organisms

A series of experiments was carried out in order to observe the effect of chlorination on the seed. Filtered final effluent was chlorinated to satisfy its chlorine demand, following which it was dechlorinated and diluted with the same dilution water employed for the unchlorinated filtered effluent. The reactors were as described earlier. The chlorine demands are tabulated in Table 13. In run 7, three chlorine residuals were applied and the depletion of the residual was monitored as a function of time (Table 14). The residuals employed were 0.2, 0.5 and 0.8 mg/l available chlorine. The depletion of the residuals would be solely attributed to the kill of micro-organisms introduced in the seed since the chlorine demand of the filtered sewage had been satisfied.

The data from runs 6, 7 and 8 presented in Figures 21, 22 and 23 indicated that increasing the available chlorine residual induced a longer

TABLE 13

Chlorine Demand of Sewage, Runs 6,7,8

Run	Chlorine Applied mg/l	Chlorine Residual mg/l	Chlorine Demand mg/l
6	12.5	10.5	2.0
7	13.2	11.3	1.9
8	13.4	11.8	1.6

lag phase. The data in run 7 indicated that a residual of 0.2 mg/l available chlorine induced a 16 hour lag, a residual of 0.5 mg/l available increased the lag to somewhat over 20 hours, and a residual of 0.8 mg/l available chlorine induced a lag of approximately 40 hours. In all cases the residual chlorine was found to be of the chloramine form. In run 8, no lag phase was observed. The BOD₅ of the samples injected with 0.8 mg/l available chlorine (runs 6, 7 and 8) was less or just equal to the BOD₅ of the unchlorinated samples, ranging from 35 to 100%. The BOD₅ of the samples treated with 0.2 or 0.5 mg/l available chlorine was approximately 30 to 86% higher than the BOD₅ of the corresponding unchlorinated samples. This deviation could indicate a selective kill as it indicates a deviation beyond the estimated inaccuracy of the test.

It is, therefore, apparent that even at the appearance of a slight residual, some micro-organisms will survive chlorination since a BOD was observed. However, reducing the concentration of micro-organisms has a

TABLE 14

Chlorine Residuals as a Function of Time in Seeded Filtered Effluents

Time - Minutes	Chlorine Residuals mg/l		
0.0	0.2	0.5	0.8
15.0	0.0	0.0	0.3
30.0	0.0	0.0	0.085
45.0	0.0	0.0	0.055

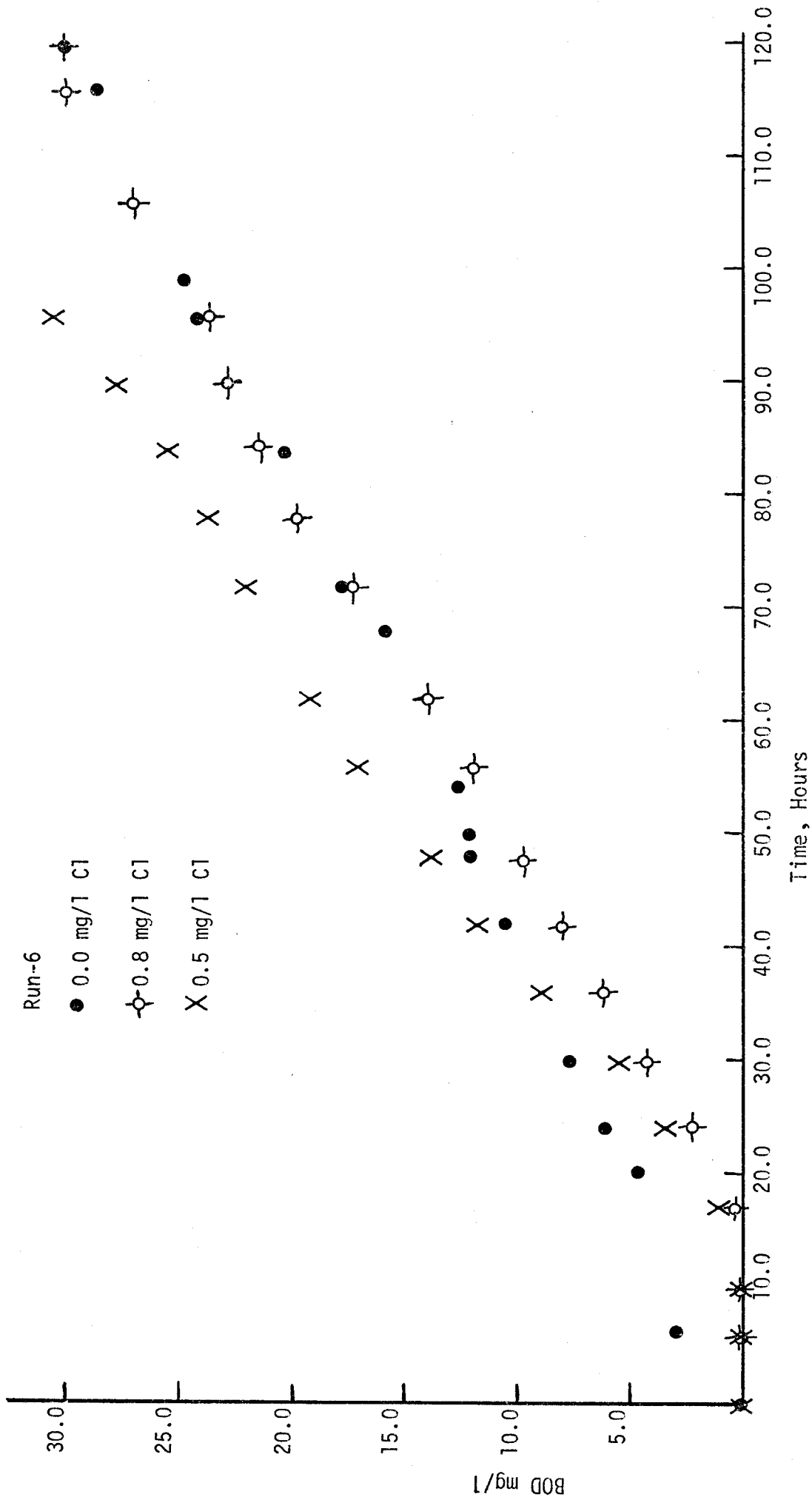


Figure 21 Effect of Chlorine Residuals on the Seed

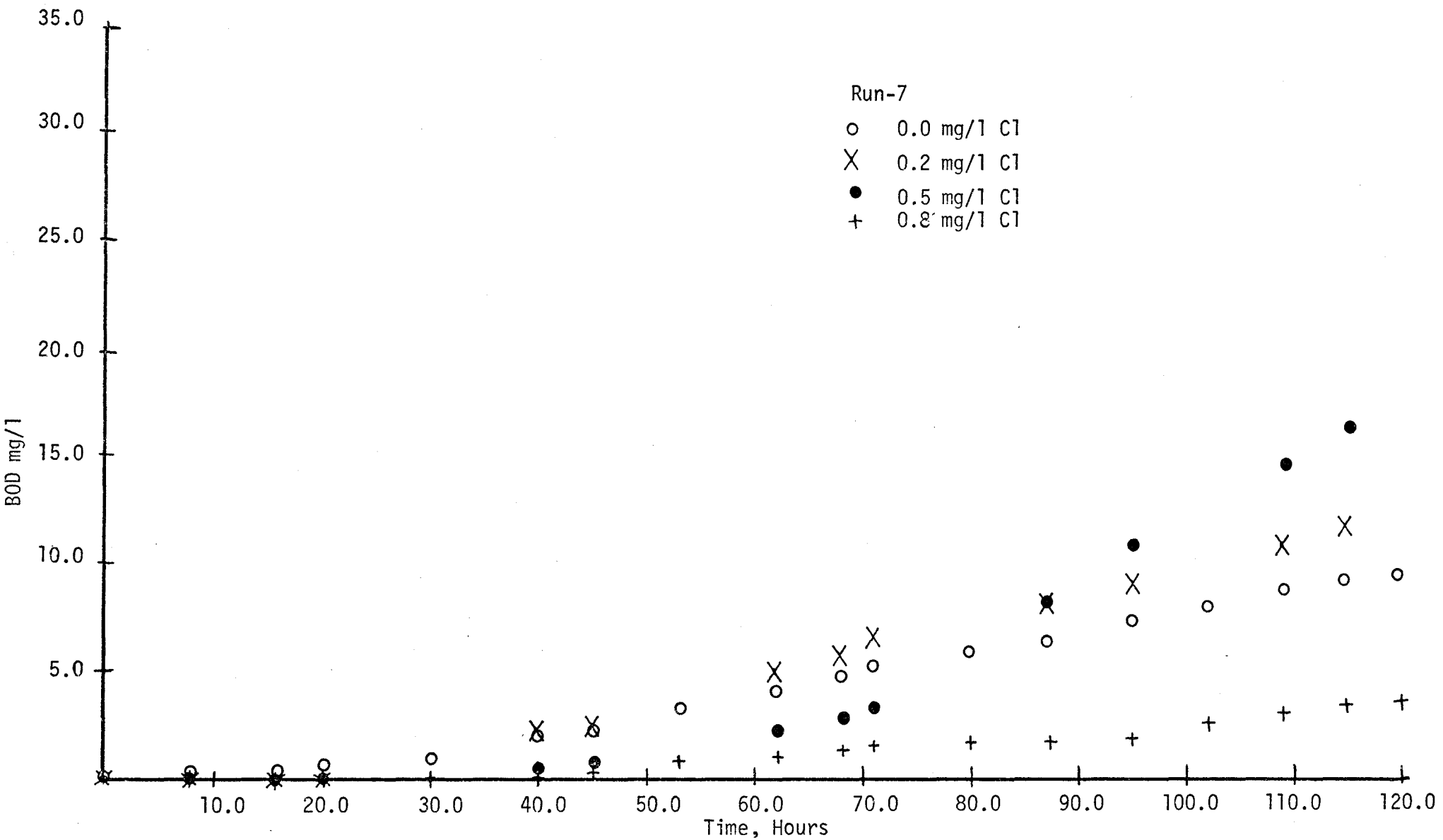


Figure 22 Effect of Chlorine Residuals on the Seed

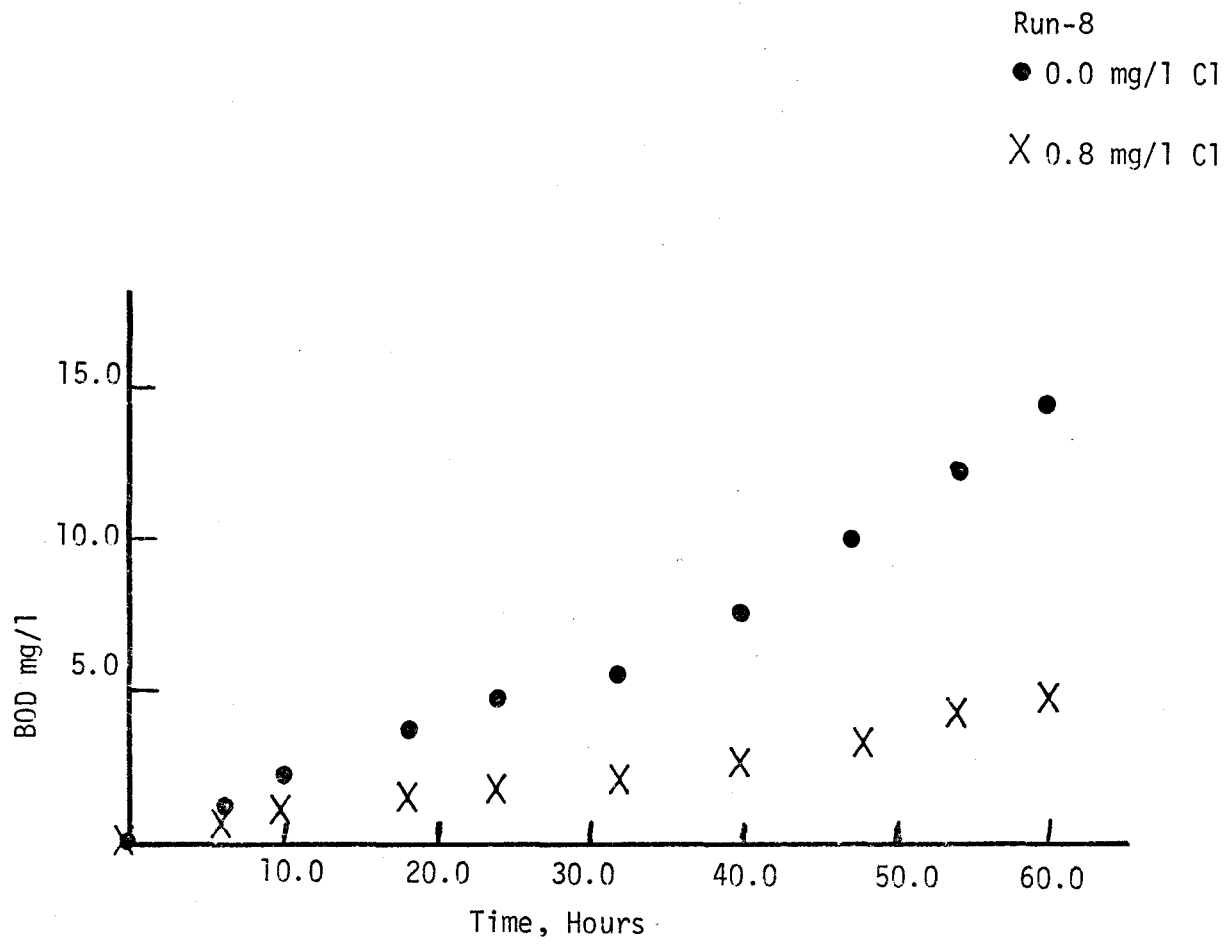


Figure 23 Effect of Chlorine Residuals on the Seed

net effect on the resulting BOD. Since it was observed that no BOD reduction occurred when sewage is filtered, chlorinated-dechlorinated and seeded with the same seeded dilution water as employed in unchlorinated samples, this series of experiments indicates distinctly that a BOD reduction can occur if a residual is left or if the samples do not contain the same concentration of seed.

5.8 Influence of the Seed on the BOD₅:

It is apparent that a closer investigation of the seeding procedure employed by previous investigators could explain the observed BOD reductions. "Standard Methods" (1971) recommends that if a waste, in particular sewage, is suspected to contain few micro-organisms as a result of chlorination, for example, then it must be seeded in order to provide a "uniform microbial population". However, if the effluent is suspected to be naturally seeded such as a final effluent, then it must not be reseeded. Two experiments were done following the procedure outlined in "Standard Methods". In the first experiment, run 9, unfiltered final effluent was chlorinated and dechlorinated and diluted to a ratio of 9:1 with seeded dilution water. The unchlorinated sample was diluted to the same ratio with the same dilution water but prior to seeding. Due to the high dilution ratio no appreciable depletion in dissolved oxygen occurred, however, a plate count at the beginning of the reaction indicated that the unchlorinated unseeded diluted sample contained 32,000 cells/ml whereas the chlorinated-dechlorinated seeded diluted sample gave a plate count of 1400 cells/ml. These results indicated a 20:1 higher ratio of bacteria in the unchlorinated sample.

In the second experiment, run 10, a lower dilution ratio was used such that the dissolved oxygen could be monitored. A ratio of 7:3 or 70% dilution was used and the same procedure employed. The plate counts at the beginning of the reaction indicated that the chlorinated-dechlorinated sample had 8,900 cells/ml whereas the unchlorinated sample had 47,000 cells/ml or approximately a 5:1 ratio. After 48 hours the chlorinated sample had 114,000 cells/ml and the unchlorinated sample 222,000 cells/ml or a ratio of about 2:1 in favour of the unchlorinated unseeded sample. Associated with these observations was a BOD reduction after four days of 5.8 mg/l. The chlorine absorbed in this run was 2.6 mg/l thus giving a BOD reduction after four days of 2.2 mg/l/mg/l of chlorine absorbed. The carbon analysis before and after chlorination and dechlorination on the original samples indicated that no carbon loss had occurred. Table 15 gives the chlorine demand observed in these runs and the plate counts, and Figure 23 illustrates the BOD data.

It appears that even though the chlorinated sample was seeded and the unchlorinated sample was not seeded, there was a significant difference in microbial concentration even after 48 hours between the two samples. Associated with this difference a BOD₄ reduction of 2.2 mg/l/mg/l Cl absorbed was observed. It is postulated that this BOD₄ reduction is the result of such unequal microbial concentration. Use of the BOD₅ test for such comparisons has led to erroneous conclusions. In such a procedure, there is absolutely no guarantee, even within the accuracy of the BOD₅ test, of obtaining the same microbial concentration. At best a uniform mixed population can be expected. Such efforts would be even more pronounced when both samples are seeded. The BOD₅ reductions observed by

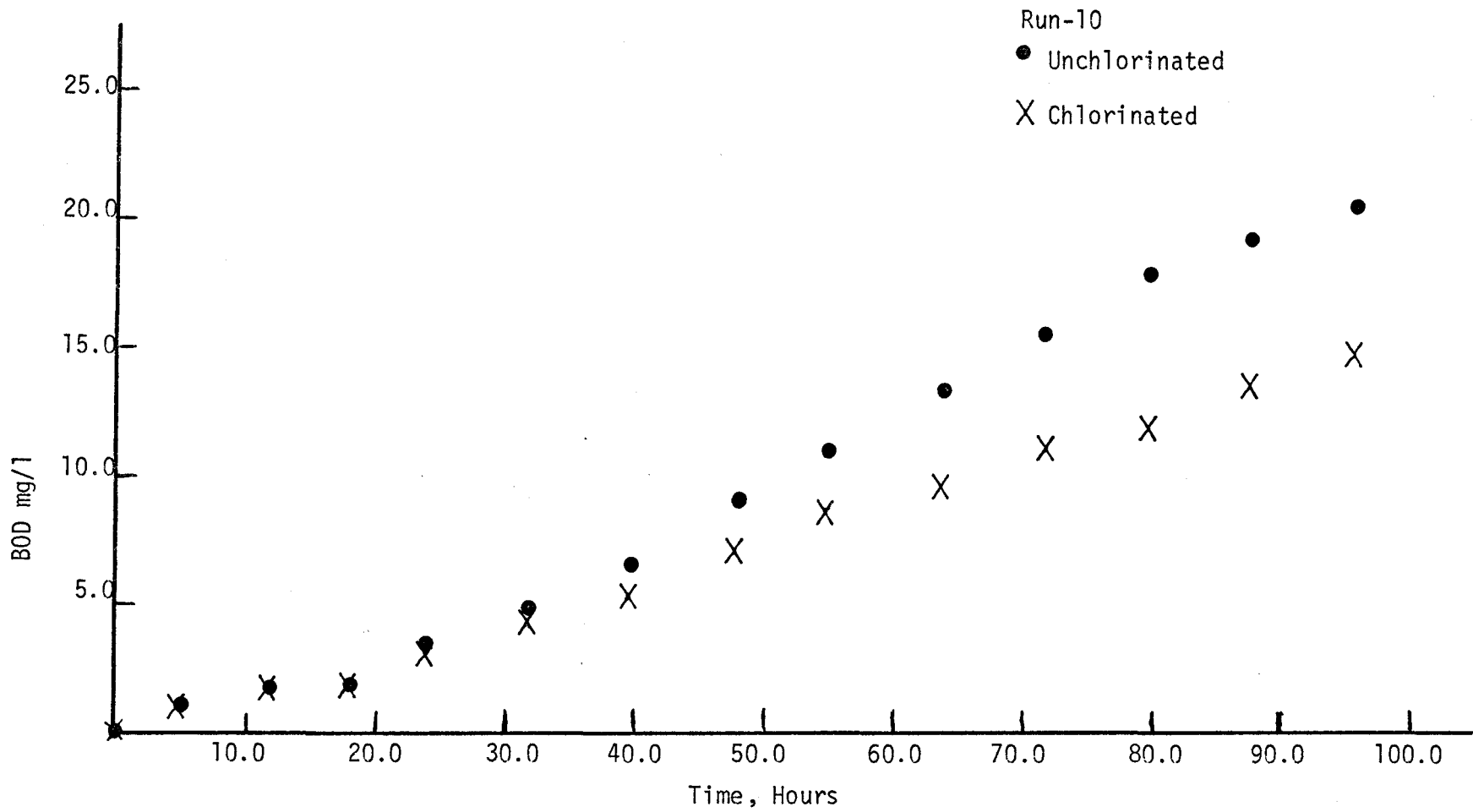


Figure 24 BOD progression of Unfiltered Unchlorinated and Chlorinated-Dechlorinated and Seeded Sewage

TABLE 15

Chlorine Demand of Unfiltered Sewage and Results of Plate Counts

% Dilution	Chlorine Dose mg/l Cl	Chlorine Residual mg/l Cl	Chlorine Demand mg/l Cl	Plate Counts	
				Unchlorinated cells/ml	Chlorinated cells/ml
9:1	12.5	10.0	2.5	32,000	1,400
7:3	13.6	11.0	2.6	47,000	8,900
			After 48 hours	222,000	114,000

various investigators, who worked exclusively with unfiltered effluents, could be the result of variations in seed and not to the "qualitative" and "quantitative" changes of the sewage caused by chlorination referred to in their work.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions:

1) The chlorination of filtered final effluents does not bring about a reduction of measured BOD_5 nor does it render the soluble organics bioresistant or toxic to micro-organisms as there was no significant difference in the extent of carbon degradation. Chlorination does not bring about a reduction in the organic carbon content of filtered sewage as evidenced by the unchanged values of the COD and TOC. In these studies, with the exception of one run, the BOD_5 does not seem to represent the carbonaceous demand of the filtered sewage as there was negligible carbon degradation and seems to be largely due to microbial respiration. Due to the presence of ammonia in sewage, chlorine in the form of chloramines, is not likely to oxidize the soluble organics present.

2) When chloramine solutions or chlorine added to solutions containing ammonia, are employed as chlorinating agents, the rate and extent of chlorination of pure compounds is considerably decreased. The rate and extent of chlorination of amino acids with chloramine solutions or with free available chlorine added to solutions containing ammonia, is intermediate between the rate and extent of chlorination of pure ammonia solution and solutions of the amino acids, indicating an interaction between chloramines and amino acids. Furthermore, the similarity in the rates and extent of chlorination of pure compounds with chloramines and chlorine added to solutions containing ammonia indicates that ammonia is preferentially chlorinated. Organic chloramines are not of the same

type as inorganic chloramines and do not liberate ammonia upon dechlorination as do inorganic chloramines.

3) The seeding procedure employed for the comparison of the BOD_5 of a chlorinated-dechlorinated and unchlorinated unfiltered sewage is inadequate and does not guarantee equal microbial concentrations even within the accuracy of the test. At least, a uniformly mixed population will be present. The BOD_5 reductions as well as the observed lag phases or delays in the exertion of the BOD reported by previous investigators could be due to this unequal microbial concentration and not to any "qualitative" and "quantitative" changes in the constituents of sewage as reported in their work.

4) The induced toxicity of chlorine, present as chloramines, increases as the applied chlorine concentration is increased. It is characterized by longer lag phases and reduced BOD_5 values. A residual of 0.5 mg/l available chlorine, added to seeded filtered effluent, seemed to induce a selective kill of micro-organisms as evidenced by an increase in the BOD_5 values which cannot be attributed to the inaccuracy of the test. A reduction in the BOD_5 will be observed if a residual chlorine is left in the sample or if an unequal microbial concentration is present as a result of chlorination. A lasting residual will bring about a maximum reduction. However, some micro-organisms will survive chlorination as evidenced by the exertion of a BOD at an applied residual of 0.8 mg/l Cl which lasted more than 45 minutes.

5) Amino acids will form monochloramines and dichloramines or both depending on the chlorine dose. The oxidation of glycine is characterized by two phases or regions, the first of which is easy and requires two moles of chlorine as hypochlorous acid and the second more

difficult and necessitates an additional 6.5 moles of chlorine as hypochlorous acid. The extent to which glycine is oxidized is closely followed by the extent to which the residual is depleted. The latter is also characterized by two phases in the two hour contact time allowed. The presence of ammonia inhibits completely the oxidation of glycine and probably of all other amino acids. The amount of ammonia used during the chlorination of glycine does not increase in proportion to the amount of ammonia added, and beyond a minimum concentration of ammonia, the stability of the residual is not affected. Glycine was found to form the most stable chloramines of the amino acids studied and histidine the least.

6) The extent of chlorination of pure compounds increases with increasing chlorine dose and the stability of the resulting chloramines decreases as the dose is increased. Acetic acid and maleic acid did not chlorinate to any appreciable extent.

7) The extent of chlorination of pure compounds is strongly dependent on pH. Phenol chlorinates fastest at pH 7.2, slower at pH 4.2, and slowest at pH 9.2 whereas glutamic acid chlorinates faster as the pH is lowered.

6.2 Recommendations:

1) Chlorination should not be used for the purpose of reducing the BOD₅ of sewage effluents as it does not reduce the organic load. Due to the induced toxicity of chlorine residuals, present as chloramines, towards the aquatic fauna, sewage effluents must be dechlorinated prior to discharge into the receiving waters. In order to achieve efficient disinfection, chlorination chambers must be designed to provide for contact times greater than thirty minutes and possibly as high as 90 minutes. Dechlorination of

the effluent can be achieved readily with sulfur dioxide by inserting a diffuser at the inlet of the effluent channel of the chlorination chamber. Alternative methods of disinfection should be considered such as ozonation or UV radiation and the effects on the soluble organics, BOD₅, ammonia, and micro-organisms as well as economics should be studied.

2) It is proposed that further work on the chlorination of pure compounds be undertaken. The following areas of studies are suggested:

- a) Identification of the products of chlorination as well as the products of dechlorination of pure compounds and in particular the amino acids.
- b) Identification of the products of chlorination of pure compounds in the presence of ammonia in order to assess the role of ammonia during the reaction.
- c) Identification of the products of oxidation by hypochlorites of glycine and other amino acids.
- d) The influence of pH on the ionization of amino acids and phenol and the extent to which chlorination is affected.

3) The effect and extent of chlorination on sewage effluents following nitrification and denitrification should be studied.

4) If the BOD of sewage should be compared after the addition of oxidizing agents or treatment with UV radiations, it is suggested that the samples be filtered prior to seeding so that the effect of such treatment on the organic constituents of the sewage can be evaluated. If such studies should be undertaken the presence of ammonia must be considered.

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APPENDIX

Mixing and chlorine residuals

Time Minutes	Chloramine Residuals mg/l	Free Available Residuals mg/l	
0.0	28.1	27.7	10.4
10.0	28.0	-	-
15.0	-	27.7	-
20.0	-	-	10.4
30.0	28.0	27.7	-
45.0	-	-	10.4
60.0	28.0	27.7	10.4
100.0	27.7	27.3	-

Chlorination of filtered sewage

Run Number	Chlorine Solution	Time Minutes						
		0.5	5.0	10.0	15.0	20.0	25.0	30.0
		Chlorine Residual mg/l						
1	calcium hypochlorite	3.0	2.3	-	2.2	2.1	-	2.1
2	calcium hypochlorite	12.0	10.8	10.3	10.0	9.9	-	9.8
2a*	calcium hypochlorite	6.0	5.1	4.6	-	4.5	4.5	4.5
3	sodium hypochlorite	3.0	3.0	2.9	2.8	2.6	-	2.6
4	sodium hypochlorite	6.0	5.6	5.3	5.1	5.0	-	5.0
5	sodium hypochlorite	13.7	13.3	12.7	12.3	12.2	12.2	12.2

* NO BOD OR CARBON MEASUREMENTS WERE MADE ON THIS RUN.

calcium hypochlorite solution: 440 mg/l Cl
sodium hypochlorite solution: 3600 mg/l Cl

BOD₅ and carbon analysis

Run-1

Time Hours	BOD mg/l	
	Chlorinated	Unchlorinated
0.0	0.0	0.0
4.0	1.2	1.0
7.0	1.5	1.2
11.0	2.4	2.0
15.0	2.4	2.0
19.0	2.8	3.1
23.0	3.4	3.8
29.0	4.4	5.4
33.0	5.4	6.0
40.0	6.4	7.2
43.0	7.4	8.0
50.0	9.0	10.0
57.0	11.6	11.0
64.0	12.4	13.2
71.0	13.8	14.6
78.0	16.6	16.6
85.0	18.2	18.0
92.0	20.6	19.8
99.0	22.6	21.0
106.0	24.6	22.6
113.0	26.2	24.0
117.0	26.9	24.5

Time Hours	% Carbon Remaining	
	Chlorinated	Unchlorinated
	ORGANIC CONTENT OF UNDILUTED SEWAGE: 30.0 mg/l	
0.0	100.0	100.0
18.0	93.4	93.6
25.0	70.0	71.9
43.0	70.0	71.9
48.0	53.4	62.5
51.0	60.0	62.5
66.0	60.0	62.5

Run-2

Time Hours	BOD mg/l	
	Chlorinated	Unchlorinated
0.0	0.0	0.0
6.0	0.0	0.0
14.0	0.3	0.8
19.0	1.2	0.8
25.0	2.5	1.6
31.0	4.6	3.2
38.0	6.2	4.5
45.0	8.0	7.0
52.0	9.6	8.5
59.0	11.0	9.6
66.0	12.3	10.8
75.0	12.3	10.8
82.0	13.3	12.6
89.0	14.3	13.8
96.0	15.7	15.2
103.0	16.7	16.2
107.0	17.1	16.6
120.0	17.6	17.4

Time Hours	% Carbon Remaining	
	Chlorinated	Unchlorinated
	ORGANIC CONTENT OF UNDILUTED SEWAGE: 21.0 mg/l	
0.0	100.0	100.0
6.5	117.0	100.0
10.0	94.5	88.0
21.0	106.0	109.0
24.0	103.0	111.0
27.0	100.0	93.0
30.0	111.0	103.0
33.0	109.0	106.0
48.0	111.0	107.0
72.0	100.0	89.0

Run-3

Time Hours	BOD mg/l	
	Chlorinated	Unchlorinated
0.0	0.0	0.0
8.0	1.0	0.4
14.0	2.1	1.0
22.0	3.1	1.8
32.0	4.6	3.4
40.6	5.9	4.5
48.0	7.6	6.1
54.0	8.5	7.4
63.0	12.1	10.4
71.0	16.1	14.0
78.0	19.2	17.0
85.0	23.7	21.0
92.0	26.1	24.0
100.0	29.6	26.0
112.0	34.6	29.4

Time Hours	% Carbon Remaining	
	Chlorinated	Unchlorinated
	ORGANIC CONTENT OF UNDILUTED SEWAGE: 11.0 mg/l	
0.0	100.0	100.0
12.0	89.5	102.0
20.0	83.6	91.2
24.0	90.6	81.4
36.0	90.6	81.4
42.0	92.0	92.5
48.0	84.3	92.5
60.0	97.8	91.2
72.0	83.0	81.4
84.0	93.0	92.5

Run-4

Time Hours	BOD mg/l	
	Chlorinated	Unchlorinated
0.0	0.0	0.0
6.0	0.4	0.5
12.0	1.1	1.5
18.0	1.5	2.1
24.0	2.0	2.9
30.0	2.6	3.8
36.0	3.4	4.9
42.0	3.9	5.5
48.0	4.5	6.1
54.0	5.2	6.8
60.0	6.0	7.5
66.0	6.6	8.0
72.0	7.7	8.0
78.0	8.5	9.1
84.0	9.4	9.9
90.0	10.3	10.4
96.0	11.3	11.1
102.0	12.5	11.6
108.0	13.9	12.3
114.0	15.3	12.8
120.0	16.5	13.3

Time Hours	% Carbon Remaining	
	Chlorinated	Unchlorinated
	ORGANIC CONTENT OF UNDILUTED SEWAGE: 10.5 mg/l	
0.0	100.0	100.0
12.0	96.0	101.0
18.0	101.0	99.0
24.0	88.5	88.0
36.0	96.0	75.0
42.0	93.6	100.0
48.0	90.0	95.0
60.0	97.5	89.0
72.0	86.0	91.5
84.0	80.0	92.6
96.0	71.0	78.0

Run-5

Time Hours	BOD mg/l	
	Chlorinated	Unchlorinated
0.0	0.0	0.0
7.0	0.4	0.2
14.0	0.7	0.6
17.0	1.1	1.0
24.0	1.4	1.4
30.0	1.8	1.8
35.0	2.1	2.4
41.0	2.3	2.8
48.0	2.7	3.4
53.0	3.1	3.9
59.0	3.4	4.4
65.0	3.7	4.9
71.0	3.7	4.9
77.0	3.8	4.9
83.0	4.1	5.1
89.0	4.8	5.6
95.0	5.1	5.9
101.0	5.6	6.4
107.0	6.2	7.2
113.0	6.5	7.6
120.0	7.1	7.9

Time Hours	% Carbon Remaining	
	Chlorinated	Unchlorinated
	ORGANIC CONTENT OF UNDILUTED SEWAGE: 12.0 mg/l	
0.0	100.0	100.0
12.0	100.0	95.0
15.0	100.0	100.0
20.0	78.0	95.0
24.0	85.5	84.0
35.0	91.0	89.5
42.0	77.0	95.0
48.0	83.0	84.0
60.0	79.0	70.5
68.0	83.0	79.0
84.0	83.0	79.0

COD RESULTS

Run Number	Chlorinating Solution	Chlorine Dose mg/l Cl	COD mg/l
2	calcium hypochlorite	0.0	48.6
		6.0	48.6
		12.0	48.6
3	sodium hypochlorite	0.0	27.6
		12.0	27.6
		25.0	27.6

MICROBIAL RESPIRATION

Run 4-A

Time Hours	BOD mg/l
0.0	0.0
5.0	0.8
18.0	2.0
24.0	2.8
30.0	2.8
42.0	3.8
48.0	4.5
54.0	4.8
68.0	6.8
92.0	10.0
113.0	13.4
120.0	13.6

Run 5-A

Time Hours	BOD mg/l
0.0	0.0
8.0	0.2
12.0	0.2
24.0	0.2
30.0	0.3
36.0	0.3
48.0	0.8
60.0	1.5

Run 5-A cont'd.

Time Hours	BOD mg/l
72.0	2.8
84.0	3.1
96.0	4.0
102.0	5.0
120.0	6.2

Chlorine Solution: calcium hypochlorite. 440.0 mg/l Cl
 Phenol: 0.1 m-mole/l (10.0 mg/l)

Time Minutes	Free Residual Chlorination mg/l Cl			Chloramination mg/l Cl pH = 7.2
	pH = 9.2	pH = 7.2	pH = 4.2	
0.0	27.4	27.5	27.4	27.1
5.0	21.6	8.8	24.7	-
8.0	-	5.6	-	-
10.0	19.5	-	21.1	27.0
11.0	-	3.8	-	-
20.0	17.6	2.1	17.1	26.8
30.0	16.4	0.8	-	26.8
35.0	-	-	11.5	-
45.0	16.0	-	-	-
60.0	15.6	0.0	7.0	26.6
75.0	15.4	-	4.8	-
145.0	-	-	-	26.2

Chlorination and pH Effects

Chlorine Solution: calcium hypochlorite. 440.0 mg/l Cl

Glutamic Acid: 0.5 m-mole/l (71.5 mg/l)

Time Minutes	Free Residual Chlorination mg/l Cl			Chloramination mg/l Cl pH = 7.2
	pH = 9.2	pH = 7.2	pH = 4.2	
0.0	27.1	27.1	27.1	30.2
2.0	-	24.7	-	30.2
5.0	24.3	21.6	19.5	28.7
10.0	20.6	-	13.7	-
15.0	-	13.1	11.1	-
20.0	16.9	-	-	25.5
25.0	-	9.6	5.2	-
30.0	12.8	-	-	-
40.0	-	-	1.3	21.6
55.0	-	-	-	18.5
60.0	6.1	-	-	-
65.0	-	3.3	-	17.1
70.0	-	-	0.0	-
90.0	-	1.8	-	-
100.0	-	-	-	13.3
120.0	3.7	0.8	-	-
130.0	-	-	-	10.2
17.0 hours	0.0			
41.0 hours	0.0			

Chlorine Concentration and Chlorination: glutamic acid: 0.2 m-mole/l
 Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l			
0.0	3.0	6.0	12.0	25.0
3.0	3.0	-	-	-
5.0	-	5.8	10.0	-
6.0	2.7	-	-	-
10.0	2.4	4.9	9.1	7.9
15.0	-	4.4	-	6.4
20.0	1.9	-	7.7	-
25.0	1.8	-	-	4.8
30.0	-	3.7	6.7	-
35.0	-	-	-	4.3
40.0	1.2	-	-	-
45.0	-	2.7	-	4.0
50.0	-	-	4.7	-
60.0	0.7	1.8	4.0	3.3
90.0	0.3	1.3	-	-
120.0	0.0	0.8	-	-
2.5 hours		0.4	-	-
3.0 hours		0.0	-	-
4.0 hours			0.4	1.2
27.0 hours			0.1	0.8

Glutamic Acid: 0.2 m-mole/l
 Chloramine Solution: 440 mg/l Cl

Chloramination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	3.0	6.0	12.0	25.0
5.0	-	-	12.0	-
10.0	2.8	5.6	-	23.2
15.0	-	-	10.8	22.3
25.0	2.6	5.0	-	21.1
30.0	-	-	9.7	-
35.0	2.3	4.4	-	-
40.0	-	-	8.8	19.4
45.0	2.0	4.0	-	-
75.0	1.4	2.9	-	-
80.0	-	-	6.6	15.4
120.0	1.2	2.1	5.2	13.4
4.0 hours	0.0	1.4	3.6	10.5
25.0 hours	0.0	0.0	0.0	5.9
120.0 hours	0.0	0.0	0.0	3.9

Alanine: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	3.0	6.0	12.0	25.0
3.0	-	-	-	22.1
5.0	3.0	5.8	10.7	-
10.0	2.6	5.4	-	14.0
15.0	2.4	4.7	8.8	11.0
20.0	2.2	4.3	7.3	9.3
25.0	-	-	6.2	8.4
30.0	1.7	3.7	-	-
35.0	-	-	5.1	7.1
45.0	1.6	3.1	4.0	6.2
60.0	1.0	2.2	2.6	4.8
90.0	0.4	1.2	-	-
4.0 hours	0.0	0.0	0.0	3.4
24.0 hours	0.0	0.0	0.0	-
54.0 hours	0.0	0.0	0.0	2.6
120.0 hours	0.0	0.0	0.0	2.5

Alanine: 0.2 m-mole/l
Chloramine Solution: 440 mg/l Cl

Chloramination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	3.2	6.3	12.0	25.0
5.0	-	-	11.9	23.9
10.0	3.2	6.3	11.6	22.7
20.0	3.1	5.7	11.3	22.4
30.0	2.9	5.5	10.8	21.5
45.0	2.8	5.4	10.3	20.3
60.0	2.3	4.7	9.6	19.1
90.0	2.0	4.1	8.5	17.5
120.0	1.6	3.6	7.7	16.0
4.0 hours	0.6	1.5	4.4	12.2
18.0 hours	0.0	0.0	0.8	8.5
24.0 hours	0.0	0.0	0.0	7.8

Histidine: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	3.0	6.0	12.0	25.0
2.0	2.6	5.3	-	-
5.0	1.8	3.6	7.7	19.8
10.0	0.9	2.7	2.2	14.7
15.0	0.0	1.3	0.0	10.6
20.0		0.6		9.5
25.0		0.2		8.2
30.0		0.0		-
35.0				5.9
45.0				4.2
60.0				2.5
90.0				1.5
120.0				1.3
6.0 hours				0.3
24.0 hours				0.0

Histidine: 0.2 m-mole/l
Chloramine Solution: 440 mg/l Cl

Chloramination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	3.0	6.0	12.0	25.0
15.0	2.8	4.6	9.5	19.2
20.0	2.4	4.4	9.0	17.9
30.0	2.3	4.2	8.6	14.3
45.0	2.2	3.7	7.6	10.7
60.0	2.1	3.5	7.0	8.6
90.0	2.0	3.1	5.3	6.7
120.0	1.7	2.7	4.7	6.5
22.0 hours	0.0	0.0	0.7	2.5
66.0 hours	0.0	0.0	0.0	0.7

Glycine: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	4.4	7.0	13.2	25.0
2.0	-	-	13.2	23.1
5.0	-	-	13.0	17.0
10.0	-	-	-	10.2
15.0	4.2	6.9	12.8	7.4
20.0	-	-	-	5.4
25.0	4.2	6.7	12.8	7.4
30.0	-	-	-	4.3
35.0	4.1	6.7	12.8	-
40.0	-	-	-	3.8
50.0	4.0	6.4	12.8	3.7
60.0	-	-	-	3.6
75.0	4.0	6.0	12.7	-
90.0	-	-	-	3.6
120.0	-	-	-	3.5
2.5 hours	3.9	5.5	12.4	-
12.0 hours	-	-	11.0	-
24.0 hours	2.7	1.8	-	-
48.0 hours	-	-	7.8	2.6
96.0 hours	-	-	1.9	1.8

Glycine: 0.2 m-mole/l
Chloramine Solution: 440 mg/l Cl

Chloramination

Time Minutes	Chlorine Residual mg/l Cl			
	0.0	3.0	6.0	11.5
5.0	3.0	6.0	11.4	23.1
15.0	3.0	6.0	11.4	22.9
20.0	3.0	6.0	11.4	22.8
30.0	3.0	6.0	11.3	22.7
45.0	3.0	6.0	11.3	22.5
60.0	3.0	6.0	11.0	22.3
90.0	3.0	5.8	11.0	21.8
120.0	2.9	5.6	10.4	21.3
24.0 hours	2.7	4.6	8.0	17.3
72.0 hours	1.4	3.0	5.6	11.7

Ammonia: 0.25 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l Cl		Ammonia mg/l
0.0	13.0	25.0	4.3
0.5	-	20.0	
1.0	-	15.2	
1.5	-	10.2	
2.0	12.8	8.1	
3.0	-	7.0	
5.0	-	4.9	
6.0	12.7	3.5	
10.0	12.7	2.2	
15.0	12.6	1.5	
30.0	12.3	1.0	
45.0	12.1	0.8	
90.0	11.9	0.7	
120.0	11.6	0.6	0.34

Ammonia: 0.25 m-mole/l
 Chloramine Solution: 440 mg/l Cl

Chloramination

Time Minutes	Chlorine Residual mg/l Cl	
	0.0	12.0
5.0	11.9	23.7
15.0	11.8	23.4
30.0	11.6	23.3
50.0	11.5	22.9
70.0	11.4	22.7
90.0	11.2	22.3
18.0 hours	10.8	20.2
120.0 hours	8.9	15.3

Phenol: 0.2 m-mole/l
 Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl
 Ammonia: 0.2 m-mole/l
 0.0 m-mole/l

Time Minutes	Chlorine Residual mg/l Cl	
	NH ₃ = 0.2 m-mole/l	NH ₃ = 0.0 m-mole/l
0.0	13.0	13.0
5.0	12.9	0.7
15.0	12.4	0.0
30.0	11.9	
50.0	11.5	
70.0	11.0	
90.0	10.6	

Phenol cont'd.

18.0 hours	10.6	
120.0 hours	8.8	

N-butyl-amine: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l Cl	
0.0	12.0	24.2
5.0	11.6	24.0
15.0	11.4	23.8
30.0	11.0	19.0
45.0	10.6	16.6
60.0	10.6	13.8
90.0	9.0	11.0
120.0	8.1	8.0
24.0 hours	7.8	7.3
120.0 hours	6.8	5.9

N-butyl-amine: 0.2 m-mole/l
Chloramine Solution: 440 mg/l Cl

Chloramination

Time Minutes	Chlorine Residual mg/l Cl	
0.0	12.5	25.0
5.0	12.5	25.0
15.0	12.0	24.0
30.0	11.4	23.4
45.0	11.2	23.0
60.0	10.8	22.6
90.0	10.4	22.0
120.0	10.2	21.3
24.0 hours	8.9	18.2
120.0 hours	7.4	14.4

Acetic Acid: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination

Time Minutes	Chlorine Residual mg/l Cl			
0.0	3.1	6.1	12.0	24.7
5.0	3.1	6.1	12.0	24.7
15.0	3.1	6.1	12.0	24.7
30.0	3.1	6.1	12.0	24.7
45.0	3.1	6.1	12.0	24.7
60.0	3.1	6.1	12.0	24.6
90.0	3.0	6.1	11.9	24.5
120.0	3.0	6.1	11.8	24.5
18.0 hours	2.6	5.7	11.1	24.4
72.0 hours	2.3	5.0	10.5	22.4

Maleic Acid: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination in Presence of Ammonia: 10.0 mg/l

Time Minutes	Chlorine Residual mg/l Cl		
	NH ₃ = 0.0 m-mole/l	NH ₃ = 0.0 m-mole/l	NH ₃ = 0.6 m-mole/l
0.0	13.8	27.0	27.2
10.0	13.3	26.2	27.0
20.0	13.2	26.1	26.5
40.0	13.2	25.8	26.1
60.0	13.1	25.7	25.8
90.0	12.9	25.5	25.2

Histidine: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination in the Presence of Ammonia

Time Minutes	Chlorine Residual mg/l Cl	
	NH ₃ = 0.2 m-mole (3.4 mg/l)	NH ₃ = 0.6 m- mole/l (10.0 mg/l)
0.0	13.0	12.0
2.0	12.7	12.0
5.0	11.9	11.7
15.0	10.5	10.0
30.0	8.5	7.6
45.0	6.5	5.5
60.0	5.0	3.8
90.0	1.8	1.5
120.0	0.9	

Glycine: 0.2 m-mole/l

Chlorine Solution: sodium hypochlorite: 3600 mg/l Cl

Free Residual Chlorination in the Presence of Ammonia

Time Min.	Chlorine Residual mg/l Cl	Ammonia Residual mg/l	Chlorine Residual mg/l Cl	Ammonia Residual mg/l	Chlorine Residual mg/l Cl	Ammonia Residual mg/l	Chlorine Residual mg/l Cl	Ammonia Residual mg/l	Chlorine Residual mg/l Cl	Ammonia Residual mg/l
0.0	26.4	0.0	26.4	1.90	26.5	3.81	26.5	8.50	13.0	3.4
2.0	22.0	-	-	-	-	-	-	-	13.0	
5.0	-	-	22.9	-	26.4	-	26.4	-	12.8	
10.0	12.3	-	-	-	-	-	-	-	-	
15.0	-	-	-	-	-	-	-	-	12.7	
20.0	8.2	-	20.5	-	26.3	-	26.3	-	-	
30.0	5.0	0.0	-	0.54	-	1.26	-	5.61	12.7	
40.0	-	-	19.0	-	26.2	-	26.2	-	-	
45.0	-	-	-	-	-	-	-	-	12.6	
60.0	3.2	-	18.6	-	25.8	-	25.8	-	12.5	
90.0	2.8	-	18.1	-	25.6	-	25.6	-	12.3	
120.0	2.6	0.0	18.0	0.54	25.4	1.26	25.4	5.61	12.2	
Dechlorinated:		0.0		1.90		3.81		8.50		

Oxidation of Glycine with Sodium Hypochlorite in two hour contact time, pH 7.2

Molar Ratio Chlorine to Glycine as HOCl : CH ₂ NH ₂ COOH	% Residual Chlorine Remaining after 2 hours	% Organic Carbon as TOC Remaining after 2 hours
1.83 : 1	95.0	100.0
2.82 : 1	66.0	72.0
3.50 : 1	14.0	42.0
4.00 : 1	7.5	25.0
4.50 : 1	4.5	22.0
5.25 : 1	3.0	20.0
7.10 : 1	-	14.0
10.50 : 1	-	0.0

Effect of Ammonia on the Oxidation of Glycine

Molar Ratio Chlorine to Glycine HOCl : CH ₂ NH ₂ COOH	Molar Ratio Chlorine to Ammonia HOCl : NH ₃	Weight Ratio to Chlorine to Ammonia HOCl : NH ₃	% Carbon Remaining after 2 hours
1.83 : 1	1.83 : 1	3.8 : 1	100.0
3.5 : 1	1.20 : 1	2.5 : 1	100.0
7.05 : 1	0.49 : 1	1.0 : 1	100.0

Chlorination and Viability of Seed Organism

Run-6: filtered sewage effluent

Chlorine Solution: sodium hypochlorite: 1560 mg/l Cl

Chlorine Dose: 12.5 mg/l Cl

Chlorine Residual after 30 Minutes: 10.5 mg/l Cl

Chlorine Demand: 2.0 mg/l Cl

Organic Content of Undiluted Sewage: 12.0 mg/l as TOC

Time Hours	BOD mg/l		
	0.0 mg/l Cl	0.5 mg/l Cl	0.8 mg/l Cl
0.0	0.0	0.0	0.0
6.0	2.9	0.0	0.0
10.0	-	0.0	0.0
17.0	-	1.0	0.4
20.0	4.7	-	-
24.0	6.1	3.4	2.4
30.0	7.6	5.4	4.2
36.0	-	8.9	6.2
42.0	10.5	11.8	8.0
48.0	12.0	14.4	9.8
50.0	12.0	-	-
54.0	12.7	-	-
56.0	-	17.0	12.0
62.0	-	19.0	13.8
68.0	15.8	-	-
72.0	17.8	22.0	17.8
78.0	-	-	-
84.0	20.2	25.5	21.4
90.0	-	27.6	22.8

Run-6 Cont'd.

96.0	24.3	30.5	23.8
99.0	24.8	-	-
106.0	-	35.5	27.0
116.0	28.8	39.6	30.0
120.0	30.0	41.2	30.3

Run-7: filtered sewage effluent

Chlorine Solution: sodium hypochlorite: 1560 mg/l Cl

Chlorine Dose: 13.4 mg/l Cl

Chlorine Residual after 30 Minutes: 11.8 mg/l Cl

Chlorine Demand: 1.6 mg/l Cl

Organic Content of Undiluted Sewage: 11.6 mg/l as TOC

Time Hours	BOD mg/l			
	0.0 mg/l Cl	0.2 mg/l Cl	0.5 mg/l Cl	0.8 mg/l Cl
0.0	0.0	0.0	0.0	0.0
8.0	0.3	0.0	0.0	0.0
16.0	0.4	0.0	0.0	0.0
20.0	0.6	0.3	0.0	0.0
30.0	0.9	-	-	0.0
40.0	1.6	2.3	0.4	0.0
46.0	2.3	2.5	0.6	0.3
53.0	3.3	-	-	0.8
62.0	4.0	5.1	2.3	0.9
68.0	4.8	5.9	2.7	1.2
71.0	5.2	6.6	3.4	1.3
80.0	5.9	-	-	1.6
87.0	6.4	8.3	8.3	1.6
95.0	7.4	9.2	10.6	1.8

Run-7 Cont'd.

102.0	8.0	-	-	2.5
109.0	8.8	10.7	14.7	2.9
115.0	9.3	11.6	16.3	3.4
120.0	9.6	-	-	3.6
123.0	9.9	12.7	18.2	3.6

Persistence of Residual Chlorine

Time Minutes	Chlorine Residual mg/l Cl			
	0.0	0.0	0.2	0.5
15.0	0.0	0.0	0.0	0.3
30.0	0.0	0.0	0.0	0.085
45.0	0.0	0.0	0.0	0.055

Run-8: filtered sewage effluent
 Chlorine Solution: sodium hypochlorite: 1560 mg/l Cl
 Chlorine Dose: 13.2 mg/l Cl
 Chlorine Residual after 30 Minutes: 11.3 mg/l Cl
 Organic Content of Undiluted Sewage: 12.0 mg/l as TOC

Time Hours	BOD mg/l	
	0.0 mg/l Cl	0.8 mg/l Cl
0.0	0.0	0.0
6.0	1.3	0.5
10.0	2.3	0.9
18.0	3.8	1.5
24.0	4.8	1.7
32.0	5.5	2.2
40.0	7.6	2.7
48.0	10.0	3.3
54.0	12.3	4.2
60.0	14.4	4.7

Influence of the Seed on the BOD

Run-9: unfiltered sewage effluent
 Chlorine Solution: sodium hypochlorite: 1560 mg/l Cl
 Chlorine Dose: 12.5 mg/l Cl
 Chlorine Residual after 30 Minutes: 10.0 mg/l Cl
 Chlorine Demand: 2.5 mg/l Cl
 Organic Content of Sewage: 12.5 mg/l as TOC
 Dilution Ratio: 9 : 1

Plate Count Results

Time Hours	cells/ml	
	Unchlorinated	Chlorinated-Seeded
0.0	32,000	1,400

Run-10: unfiltered sewage effluent
 Chlorine Solution: sodium hypochlorite: 1500 mg/l Cl
 Chlorine Dose: 13.6 mg/l Cl
 Chlorine Residual after 30 Minutes: 11.0 mg/l Cl
 Chlorine Demand: 2.6 mg/l Cl
 Organic Content of Sewage: 12.0 mg/l as TOC
 Dilution Ratio: 7 : 3

Plate Count Results

Time Hours	cells/ml	
	Unchlorinated	Chlorinated
0.0	47,000	8,900
48.0	222,000	114,000

BOD Result

Time Hours	BOD mg/l	
	Unchlorinated	Chlorinated
0.0	0.0	0.0
6.0	1.0	0.7
12.0	1.5	1.7
18.0	1.8	1.8
24.0	3.6	3.2
32.0	4.8	4.3
40.0	6.6	5.3
48.0	9.0	7.2
56.0	11.0	8.6
64.0	13.3	9.7
72.0	15.6	11.0
80.0	17.7	12.0
88.0	19.2	13.5
96.0	20.5	14.7