1986

The Effects of Trace Organic Carbon on Aluminum Solubility

Fernand J. Tiblier
University of Central Florida

STARS Citation

Tiblier, Fernand J., "The Effects of Trace Organic Carbon on Aluminum Solubility" (1986). *Retrospective Theses and Dissertations*. 4985.
https://stars.library.ucf.edu/rtd/4985

THE EFFECTS OF TRACE ORGANIC CARBON ON ALUMINUM SOLUBILITY

BY

FERNAND J. TIBLIER, JR.
B.A., Drury College, 1982

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Graduate Studies Program of the College of Engineering
University of Central Florida
Orlando, Florida

Summer Term
1986

ABSTRACT

Alum jar tests were performed on raw potable waters of varying TOC. Parameters monitored included alum dose, pH and mixing conditions. Finished waters were analyzed for residual aluminum, residual TOC and hardness in order to investigate the effects of TOC on aluminum residual as would be encountered by alum coagulation and lime softening processes in practice.

Three-dimensional graphs of residual aluminum, residual TOC and pH were constructed to illustrate the relationship among these measured parameters for the different sources. Statistical analyses were conducted to verify aluminum-organic complexation at reduced alum dosages for varying TOCs; initial TOC, reaction pH and dose were investigated for variability of TOC and aluminum data sets. Actual pC versus pH diagrams were also developed for all source waters for comparison with theoretical aluminum equilibrium profiles.

Ad Majoriam Dei Gloriam. This work is dedicated "to the Greater Glory of God" and to His instruments, my loving and supportive parents, Dr. and Mrs. Fernand J. Tiblier, Sr.

ACKNOWLEDGEMENTS

Special thanks are due to the members of my committee, Drs. John D. Dietz and Yousef A. Yousef, for their kindly efforts in reviewing this research. Especially, I would like to thank my advisor and committee chairman, Dr. James S. Taylor, whose commitment to excellence in education and potable water research has been an inspiration to me.

I would also like to express my appreciation to Ms. Sharon Darling and Ms. Regina Terick for the preparation of this manuscript, and to Mr. Bruce Snyder for laboratory assistance with the Caloosahatchee River water.

TABLE OF CONTENTS

Appendices

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Statement of the Problem

A review of the literature has demonstrated that no suitable models of aluminum solubility exist which take into account trace organics removal processes of alum coagulation and lime softening.

Purpose

As the primary goal of this investigation, an effort has been undertaken to provide such an aluminum solubility profile which reflects the intricacies and variability of alum coagulation and lime softening encountered in practice. The mode of inquiry selected was the alum jar test tailored to meet the following goals:

1. To investigate the effect of natural organic carbon on aluminum residuals remaining after alum coagulation or lime softening.

2. To provide insights into the relationship between aluminum and trace organic residuals.

3. To explore alternate means of aluminum precipitation outside of the operational pH range (pH 5-8) of aluminum hydroxide.

4. To determine the effects of initial organic content on the alum dose to remove organic matter.

CHAPTER II

BACKGROUND AND RELATED RESEARCH

Background on Water Quality Standards

Aluminum salts have long been used as an effective coagulant for removal of color and turbidity from potable waters. In recent years, alum coagulation has been applied in the specific removal of trace organic contaminants. The presence of trace organic matter in drinking water is undesirable from an aesthetic point of view due to coloration, and from a health standpoint due to the potential for reaction with disinfection chlorine to form carcinogenic by-products. The by-products most often identified as carcinogenic are trihalomethanes, which are known to cause cancer in laboratory animals. Based on an arithmetic sum of the four most common trihalomethanes, namely chloroform, bromodichloromethane, dibromochloromethane and bromoform, the U.S. government has set a maximum contamination level of 100 ppb for drinking water. The American Water Works Association (AWWA) has set its goal to completely eliminate trihalomethanes from potable water supplies (AWWA 1986).

While there is presently no maximum contamination level for aluminum in potable waters set by the U.S. Environmental Protection Agency (EPA), reasons exist for its control. Post precipitation of aluminum in distribution systems along with other trace contaminants may hamper proper flow. In the presence of trace iron contaminants, residual aluminum has been known to cause water discoloration (World Health Organization (WHO) 1984). Qureshi and Malmberg (1985) have reported consumer complaints in the Minneapolis, Minnesota, area of "red water" associated with peak alum dosages which become aggressive to the city mains. Based on health considerations, control of residual aluminum in drinking water is not critical; however, research is ongoing. The aluminum in drinking water is small compared to the average dietary intake of 88 mg per person per day. Based on an arbitrarily high figure of 1.5 mg of aluminum per liter of water, two liters of water consumption would constitute less than 4% of the average daily intake (WHO 1984). Recent concern has arisen based on a cumulative deposition of aluminum in the brains of Alzheimer's disease victims. It is not known whether this condition is a cause in itself or merely an indicator of other factors (AWWA 1986). At any rate, residual aluminum on the average is elevated in alum coagulated waters with respect to other surface and groundwaters. An EPA survey conducted in 1983 found the median aluminum residual in alum coagulated waters to be 0.11 mg/l (0.01 to 2.7 mg/l range) and in non-coagulated waters, 0.05 mg/l (0.01 to 1.2 mg/l range). Based on the considerations stated, the WHO (1984) has established a guideline value of 0.2 mg/l for aluminum in drinking water, and the AWWA (1986) has stated its goal as 0.05 mg/l, as established in 1968.

Basic Jar Test Theory

The jar test is a laboratory technique employed to determine the coagulability of a particular water. The most important parameters relating to alum jar tests are alum dose and pH. In this test, raw water samples are poured into a series of beakers, treated with varying alum dosages and monitored for pH. The contents are first rapidly stirred to simulate rapid mixing, then slowly stirred to simulate flocculation, followed by a period of settling. The information provided by such tests may be applied at a treatment plant. A detailed outline of the physical and chemical reactions involved follows (Reynolds 1982).

Coagulation

Coagulation refers to the particulate aggregation of a colloidal suspension. Organic contaminants in water exist in soluble and suspended or colloidal forms. Soluble organic contaminants are removed by precipitation or coprecipitation, but cannot be truly coagulated (Liao and Randtke 1985). The coagulation process consists of two distinct steps, namely: (1) particle transport to provide interparticle contacts and (2) particle destabilization to permit attachment upon contact. Particle transport theories arise from fluid mechanics and particle destabilization theories are based on colloid and interfacial chemistry (O'Melia 1969).

Colloid Destabilization. Colloidal particles remain in stable solution by virtue of their electric charge. According to the

Electric Double Layer Theory, each primary charge (which may be positive or negative) on a colloidal particle is balanced by a counter ion of opposite charge which accumulates in the water near the particle surface. This region in which the counter ions accumulate is called the diffuse layer because the concentration of counter ions decreases with increasing distance from the surface of the colloidal particle. The origination of the surface charge on the colloidal particle may be due to: (1) imperfection of the particle crystal by manner of isomorphic replacement of atoms by others of dissimilar charge, (2) ionization of chemical groups present on the particle surface or (3) the preferential adsorption of ions from the solution onto the particle (O'Melia 1969). A net repulsive force is then operable between diffuse layers of like charge which surround these particles. An attractive force, known as van der Waals' force, attracts all colloidal particles regardless of charge to each other; in stable colloidal dispersions, this force is too weak to overcome the net repulsion and allow aggregation. Four methods of colloidal destabilization are applicable: (1) zeta potential reduction, (2) adsorption and charge neutralization, (3) precipitate enmeshment and (4) adsorption with interparticle bridging.

Zeta Potential Reduction. The net repulsive force between colloidal particles is due to zeta potential (ζ) which is given by (Reynolds 1982):

$$\zeta = \frac{4\pi qd}{D}$$

where:

q = charge per unit area

d = a distance from the shear plane (which encloses the water that moves with the particle) over which charge is effective

D = the dielectric constant of the liquid

Upon addition of alum, aluminum undergoes hydrolysis creating first, polyvalent metallic ion complexes of high positive charge and then the insoluble metal hydroxide. The degree to which the $Al(OH)_3$ is formed as an end product is pH-dependent. The destabilization of the colloid suspension is accomplished by the positively charged complex intermediates which concentrate in the diffuse layer. This results in the effective compression of the diffuse layer as the zeta potential is reduced. This destabilization mechanism allows the colloidal particles to aggregate due to the van der Waals' attractive forces and possibly some adsorption of the complexes onto their (i.e., the particle) surfaces (Reynolds 1982).

Adsorption and Charge Neutralization. Destabilization of colloidal particles may be the direct result of instantaneous adsorption of the positively charged aluminum complexes. The monohydroxocomplex, $Al(OH)^{2+}$, is readily adsorbed at the solid liquid interface. Highly charged species such as $Al_{13}(OH)_{34}{}^{5+}$ and $Al_7(OH)_{17}{}^{4+}$ may also be adsorbed by virtue of their electrostatic attraction to negatively charged colloids, but it should be noted that such species are characteristically highly soluble at low pH (less than pH 5). Efficient application of this theory requires that the coagulation reaction with hydrolyzed aluminum be carried out at low pHs, for which cationic aluminum species dominate. Adsorption of cationic aluminum onto the colloidal particle surfaces results in a decrease in the surface potential. The suspension is thus effectively destabilized. The suspension is considered completely destabilized when the surface charge on the colloidal particles is reduced to zero, bridging of polymeric aluminum between colloids is negligible and adsorbed species do not prevent the close interparticle arrangement required for the effectiveness of van der Waals' force. Colloids may become restabilized if the progressive adsorption of cationic aluminum results in a positive surface charge. The rate of particle destabilization is dependent on the transport of the aluminum cations to the negatively charged colloids. The rate of particle agglomeration from suspension is a function of orthokinetic rate constants which may be obtained as the slope of a semi-logarithmic plot of the particle fraction remaining versus time (Hahn and Stumm 1968).

Precipitate Enmeshment. Rapid precipitation of $Al(OH)_3$ from alum addition, or $Mg(OH)_2$ and $CaCO_3$ from softening processes may result in the enmeshment of colloidal particles which are carried out with the floc. Rapid precipitation is accomplished at a rate which is dependent on the degree of oversaturation of amorphous $Al(OH)_3$ with respect to its equilibrium solubility level. In some instances, the colloidal particles function as nucleation sites for the formation of a precipitate. In such cases, an indirect relationship between the amount of colloidal matter present in the water and optimum coagulant dosage may exist; which is to say a greater quantity of coagulant would be required to remove a lesser concentration of colloidal matter (Weber 1972).

Adsorption and Interparticle Bridging. Optimum destabilization of colloidal suspensions may be achieved with polymers having a charge similar to the colloidal surface. This observation is most common for the cases in which anionic polymers destabilize negatively charged colloids. At a pH above that in which $Al(OH)_3$ precipitation is decidedly dominant, aluminum exists as an anion, $Al(OH)_4^-$, with the ability to function as such an anionic polymer. Optimum destabilization occurs when only a fraction of the adsorption sites on colloidal particles is covered by the polymer which simultaneously adsorbs to the surfaces of adjacent particles. This phenomenon is referred to as interparticle bridging. Strong evidence suggests that divalent metal ions, such as Ca^{2+} and Mg^{2+}, are usually required to flocculate negative colloids with anionic polymers. The explanation given for this observation is threefold: (1) divalent ions compress the diffuse layers surrounding colloidal particles which are stable, (2) divalent ions reduce the inherent repulsive forces that would exist between like charges and, thereby, enhance adsorption and (3) divalent ions reduce the repulsive forces between adsorbed polymer molecules of similar charge and, thus, facilitates bridging. Other factors, in addition to the presence of divalent ions in solution, which promote adsorption and interparticle bridging include ion exchange, hydrogen bonding, complexation reactions, van der Waals' forces between coagulant and colloid, and the repulsion of the coagulant by the aqueous phase (O'Melia 1969).

Flocculation. While the term "coagulation" refers to the overall process of colloidal particle destabilization and transport, the term "flocculation" refers specifically to the particle transport step. Interparticle contacts may be accomplished in three main ways, namely: (1) by perikinetic flocculation characterized by random thermal molecular motion or Brownian movement, (2) by orthokinetic flocculation resulting in contacts due to mechanical agitation imparted to the fluid medium and (3) by differential settling in which varying sizes and densities of particles result in varying settling rates (Weber 1972).

Perikinetic Flocculation. Perikinetic flocculation is accomplished by random molecular motion. This mode of flocculation is not highly significant in the jar testing procedure which requires mechanical mixing. Perikinetic flocculation predominates in systems containing small particles and having low velocity gradients.

Orthokinetic Flocculation. The orthokinetic flocculation process is the dominant manner of particle transport in the jar testing procedure. This statement is valid if both the mechanical mixing imparted to the jar tests is of sufficient energy and/or the suspended particles are sufficiently large. The dependence of suspended particle size on the dominant mode of flocculation is best illustrated by example. For colloidal particles which are 0.1 micron in diameter, a velocity gradient of 1000 $\sec^{-1}$ is required for orthokinetic flocculation to be as significant as perikinetic flocculation. To further clarify this example, typical jar test paddle mixing speeds of 35 and 100 rpm correspond to approximate velocity gradients of 10 and 50 $\sec^{-1}$, respectively (Hudson 1965). The rate of orthokinetic flocculation is proportional to this mean velocity gradient ($\overline{G}$) which is dependent on the power dissipated within the water (O'Melia 1969). The orthokinetic flocculation process has been described by Hudson (1965) in the following relation:

$$\ln \frac{N_o}{N_t} = \frac{\phi A \overline{G} t}{\pi s}$$

where:

N_o = number of particles present initially

N_t = number of particles suspended at time, t

ϕ = a sticking ratio of particles which adhere upon collision

A = coagulant dose by weight per unit water volume

$\overline{G}$ = mean velocity gradient

s = the concentration of coagulant in the floc

This equation demonstrates that entrapment of suspended matter is related to the overall volume of floc produced rather than the size of floc particles. It is implicit in the relationship that suspended particles caught out on the "tentacles of a dragon-shaped floc particle" may be shaken off more easily than a particle entrapped in a voluminous precipitate (Hudson 1965). It should be noted that high values of $\overline{G}$ will tend to break up particle aggregates (O'Melia 1969). This critical $\overline{G}$ value varies with individual floc types (Hannah et al. 1967).

Differential Settling. Differential settling, known as class-2 clarification, describes the characteristics of flocculant particles undergoing sedimentation. In jar testing procedures, settling is generally conducted under quiescent conditions. Such conditions result in larger particles settling faster and overtaking finer particles in their descent. In practice, deep settling tanks and/or long detention times are advantageous in accommodating this mode of settling by providing greater particle contact opportunities (Weber 1972).

Coprecipitation

Coprecipitation is considered to be the most important manner of soluble organic contaminant removal in this study. Coprecipitation can be described as the process by which normally soluble impurities adsorb onto nuclei or crystals of parent precipitates and are removed in a single phase. Adsorption is a result of one or more of the following: (1) complexation between the precipitate and the impurity; (2) electrostatic interactions; (3) van der Waals' forces; or (4) dipole-dipole interactions. The adsorption attachment may remain surface oriented, become incorporated in the lattice of the crystalline precipitate, result in solid solution formation, or become surrounded by crystal growth as an imperfection (Liao and Randtke 1985). Such modifications of form are due to the rate of precipitation, agglomeration and mutual miscibility of parent precipitate and impurity (Walton 1967).

Aluminum Solubility Theory

The equations governing aluminum solubility theory include (Snoeyink and Jenkins 1980):

1. $Al^{3+} + H_2O \rightleftarrows Al(OH)^{2+} + H^+$; log K = -5

2. $7Al^{3+} + 17H_2O \rightleftarrows Al_7(OH)_{17}{}^{4+} + 17H^+$; log K = -48.8

3. $13Al^{3+} + 34H_2O \rightleftarrows Al_{13}(OH)_{34}{}^{5+} + 34H^+$; log K = -97.4

4. $Al(OH)_{3(s)} \rightleftarrows Al^{3+} + 3OH^-$; log K_{so} = -33
   (fresh
   precipitate)

5. $Al(OH)_{3(s)} + OH^- \rightleftarrows Al(OH)_4{}^-$; log K = 1.3

6. $2Al^{3+} + 2H_2O \rightleftarrows Al_2(OH)_2{}^{4+} + 2H^+$; log K = -6.3

7. $Al(OH)_{3(s)} \rightleftarrows Al^{3+} + 3OH^-$; $\log K_{so} = -36.3$
(gibbsite)

For purposes of solubility analysis and construction of the theoretical profiles, activities of the species cited are approximated by molar concentrations, thus neglecting the ionic strengths of the alum jars tested. As standard practice dictates, $[H_2O]$ and $[Al(OH)_{3(s)}]$ are defined as unit activity. The theoretical solubility data is calculated according to:

1. $$\frac{[Al(OH)^{2+}][H^+]}{[Al^{3+}][H_2O]} = 10^{-5} = \frac{[Al(OH)^{2+}][H^+]}{[Al^{3+}]}$$

2. $$\frac{[Al_7(OH)_{17}{}^{4+}][H^+]^{17}}{[Al^{3+}]^7[H_2O]^{17}} = 10^{-48.8} = \frac{[Al_7(OH)_{17}{}^{4+}][H^+]^{17}}{[Al^{3+}]^7}$$

3. $$\frac{[Al_{13}(OH)_{34}{}^{5+}][H^+]^{34}}{[Al^{3+}]^{13}[H_2O]^{34}} = 10^{-97.4} = \frac{[Al_{13}(OH)_{34}{}^{5+}][H^+]^{34}}{[Al^{3+}]^{13}}$$

4. $$\frac{[Al^{3+}][OH^-]^3}{[Al(OH)_{3(s)}]} = 10^{-33} = [Al^{3+}][OH^-]^3$$
(fresh
precipitate)

5. $$\frac{[Al(OH)_4{}^-]}{[Al(OH)_{3(s)}][OH^-]} = 10^{1.3} = \frac{[Al(OH)_4{}^-]}{[OH^-]}$$

6. $$\frac{[Al_2(OH)_2{}^{4+}][H^+]^2}{[Al^{3+}]^2[H_2O]^2} = 10^{-6.3} = \frac{[Al_2(OH)_2{}^{4+}][H^+]^2}{[Al^{3+}]^2}$$

7. $$\frac{[Al^{3+}][OH^-]^3}{[Al(OH)_{3(s)}]} = 10^{-36.3} = [Al^{3+}][OH^-]^3$$
(gibbsite)

Theoretical solubility data are calculated using equations 1 through 6 for fresh $Al(OH)_{3(s)}$ precipitate and using equations 1, 5, 6 and 7 for gibbsite precipitate. A summary of profile data is shown in tables 1 and 2. A discussion of specific factors which alter the equilibria described in tables 1 and 2 follows.

Factors Affecting Solubility Equilibria

The Zero Point of Charge (ZPC). In Stumm and Morgan (1970), a relation to describe the zero point of charge (ZPC) is given as:

$$\sigma_s = \frac{n_{OH^-} - n_{H^+} (F)}{s} = \text{numerically zero},$$

$$pH = pH_{ZPC}$$

This relationship describes the ZPC as that pH for which the surface charge (σ_s) on a solid (e.g., the $Al(OH)_3$ precipitate) is zero. Parameters involved include:

$n_{OH^-} - n_{H^+}$ = net number of OH^- moles bound to solid

F = Faraday's constant (electric charge of one mole of electrons)

s = surface charge of solid

TABLE 1

THEORETICAL FRESH $Al(OH)_{3(s)}$ PRECIPITATE EQUILIBRIA DATA

SPECIES	- LOG MOLAR ALUMINUM CONCENTRATION AS Al^{3+}, pC										
H^+ (pH)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	8.0	9.0	10.0	11.0
$Al(OH)^{2+}$	4	5	6	7	8	9	10	12	14	16	18
$Al_7(OH)_{17}^{4+}$	0.95	2.95	4.95	6.95	8.95	10.95	12.95	16.95	20.95	24.95	28.95
$Al_{13}(OH)_{34}^{3+}$	-.71	1.79	4.29	6.79	9.29	11.79	14.29	19.29	24.29	29.29	34.29
Al^{3+}	3	4.5	6	7.5	9	10.5	12	15	18	21	24
$Al(OH)_4^-$	8.7	8.2	7.7	7.2	6.7	6.2	5.7	4.7	3.7	2.7	1.7
$Al_2(OH)_2^{4+}$	4	6	8	10	12	14	16	20	24	28	32
$pC_{T\ Al}$	-0.72	1.76	4.18	6.33	6.68	6.20	5.70	4.70	3.70	2.70	1.70

TABLE 2

THEORETICAL GIBBSITE $Al(OH)_{3(s)}$ PRECIPITATE EQUILIBRIA DATA

SPECIES	- LOG MOLAR ALUMINUM CONCENTRATION AS Al^{3+}, pC										
H^+ (pH)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	8.0	9.0	10.0	11.0
$Al(OH)^{2+}$	7.3	8.3	9.3	10.3	11.3	12.3	13.3	15.3	17.3	19.3	21.3
Al^{3+}	6.3	7.8	9.3	10.8	12.3	13.8	15.3	18.3	21.3	24.3	27.3
$Al(OH)_4^-$	8.7	8.2	7.7	7.2	6.7	6.2	5.7	4.7	3.7	2.7	1.7
$Al_2(OH)_2^{4+}$	10.6	12.6	14.6	16.6	18.6	20.6	22.6	26.6	30.6	34.6	38.6
$pC_{T\ Al}$	6.26	7.57	7.68	7.20	6.70	6.20	5.70	4.70	3.70	2.70	1.70

It should be noted that the ZPC involves all ionic species bound to the solid, not just OH^- and H^+ ions used as a convenient subscript. The ZPC shifts in response to sorbable ionic species bound to the solid precipitate. Adsorption of cation impurities would shift pH_{ZPC} to more alkaline values; adsorption of anionic impurities would shift pH_{ZPC} to more acidic values. pH_{ZPC} usually corresponds to the pH of minimum solubility for a particular solid. The pH of optimum coagulation may be then considered an indirect indicator of pH_{ZPC}. The main point to be drawn from this discussion is that ionic impurities adsorbed to precipitates do, in fact, alter their solubility characteristics. Different raw waters exhibit varying coagulabilities.

<u>The Conditional Solubility Product</u>. The solubility product of $Al(OH)_3$ has been given as (for amorphous $Al(OH)_3$):

$$[Al^{3+}][OH^-]^3 = 10^{-33} = K_{so}$$

Under experimental conditions, instances may arise which alter this theory. For example, the cation and anion (i.e., Al^{3+} and OH^-) can form complexes with each other or with other species present, thus increasing solubility of the ions. The concept of the conditional solubility product affords an investigator a better means of predicting solubility under such conditions. The conditional solubility product (P_s) is defined by:

$$P_s = \frac{K_{so}}{(\alpha Al)(\alpha OH)^3}$$

where:

$$\alpha Al = \frac{[Al^{3+}]}{Al_{Total}}$$

$$\alpha OH = \frac{[OH^-]}{OH_{Total}}$$

For purposes of this study, the conditional solubility concept is presented in order to emphasize that $Al(OH)_3$ solubility is modified according to experimental conditions (Stumm and Morgan 1970).

Floc Characteristics. The characteristics of the flocs formed from alum addition are evaluated in terms of structure and stability in the following discussion. Such factors have effects on solubility equilibria.

Floc Structure. Aggregates of destabilized colloids with amorphous $Al(OH)_3$ have a four-level structure. The first level consists of primary particles **which together** form flocculi. Flocculi formation efficiency is directly related to the overall coagulability of a particular water. Flocculi formed at low shear rates are linear in shape; those formed at intermediate shear rates have a tortuous form; and those formed at high shear rates assume a spherical morphology. Flocculi combined with each other to form flocs. It is known that tortuous flocculi group themselves better. Flocs together form weak aggregates. Elastic bonds link individual particles and the different levels of organization (Francois and VanHaute 1985).

Floc Stability. The strength of a floc is one factor which affects its ability to remove suspended particles. A strong floc is formed rapidly when subjected to high velocity gradients; a weak floc or a less stable floc will break-up under such conditions. One quantifiable parameter of floc break-up is the reentrainment of aluminum into solution upon rapid mixing. In practice, a strong floc is desirable for its settling characteristics and its resistance to fragmentation by shear forces introduced by velocity gradients. Floc fragments which are larger are more susceptible to break-up. If a somewhat weakly bound floc is easily rearranged into a compact and dense structure with favorable settling conditions, it would then be more desirable than a stronger floc of less dense particles. In any case, the most desirable floc is one which displays optimum settling characteristics.

Hannah et al. (1967) reported on research which sought to measure floc strength. The indirect method of floc strength measurement consisted of first allowing a colloidal suspension treated with alum to undergo orthokinetic flocculation at a velocity gradient of 50 sec^{-1}, then next subjecting the emerging floc to a localized very high velocity gradient, and then counting and sizing the resulting fragments with a coulter counter. The size of the surviving fragments was considered an indicator of the floc strength. The significance of this research was that it provided a general criteria for floc strength based on: (1) rate of flocculation by which stronger flocs are formed; (2) the number of large floc particles surviving shear; and (3) the percentage of small particles remaining after flocculation. The most significant conclusion made with respect to the effects of organics removal processes on aluminum solubility is that alum floc alone is relatively weak and is strengthened by incorporating solids into the floc.

Trace Organic Matter

The background and related research concerning trace organic matter is presented on three levels relating to: (1) its nature ; (2) its propensity to form soluble complexes with aluminum ; and (3) processes for its removal.

The Nature of Trace Organic Matter

Trace organic compounds in soils and waters are grouped into two broad categories, non-humic and humic substances. Non-humic compounds include those such as carbohydrates, proteins, peptides, amino acids, fats, waxes and low molecular weight organic acids; all with definite physical and chemical characteristics. In general, such compounds are readily biodegradable by microorganisms. Of prime concern are humic substances which comprise the major class of organic matter in natural waters (Schnitzer 1971).

Humic Substances. Humic substances consist of a "mixture of poorly biodegradable decomposition products and by-products of natural organic matter produced by both plants and animals" (Snoeyink and Jenkins 1980). These materials are water soluble, amorphous, acidic, polydisperse substances, have molecular weights ranging from a few hundred to tens of thousands, and are responsible for the yellow-brown color typical of natural water (Schnitzer 1971). Humic substances also function as trihalomethane precursors, increase coagulant and chlorine requirements, foul exchange resins and membranes in nitrate and salt removal processes and have the potential to stabilize and transport metals (Weber and Jodellah 1985). Humic substances are often subdivided into three main fractions based on solubility: (1) fulvic acid - soluble in acids and bases with the lowest molecular weight, (2) humic acid - soluble in bases but not acids, and (3) humin - insoluble in acids and bases with the highest molecular weight (Schnitzer 1971). The fraction of greatest concern due to its predominance in nature is the fulvic acid constituent of humic substances.

Fulvic Acid. Fulvic acid accounts for up to 75% of the total organic matter in natural systems. The empirically derived formula for an average fulvic acid molecule is (Schnitzer 1971):

$$C_{20}H_{12}(COOH)_6(OH)_5(CO)_2$$

Note that at least 50 percent of this compound by weight is carbon. With a formula or molecular weight of 670 AMU, one mole of fulvic acid contains 341 grams of organic carbon.

Complexation Reactions

The nature of the association between humic substances and metals is not well-defined because the structure of humic substances varies from one water to another. Snoeyink and Jenkins (1980) have reported on research which demonstrated that waters of similar color (100 cpu) varied in dissolved organic carbon content from 10 to 30 mg/l. While it is well documented that trace organic matter does indeed combine with trace metals, the mode of binding varies. Binding is most commonly attributed to formation of complexes with metals reacting at the sites of functional groups, or to the stabilization of colloidal precipitate particles by adsorption of humic substances. Based on the molecular average formula for fulvic acid described by Schnitzer (1971), a stoichiometric relation of 1:1 on a molar basis is reported for soluble aluminum and fulvic acid. This ratio indicates that 100 mg of fulvic acid is capable of reacting with 4 mg/l of aluminum to form a soluble product. When the molar ratio of aluminum to fulvic acid increases, the product becomes decreasingly soluble; a molar ratio of aluminum to fulvic acid of 6:1 is considered to result in an insoluble complex.

The specific functional groups on the fulvic acid molecule that react with trace metals are not well known; however, investigators have shown that up to 86% of complexed aluminum could be linked to acidic carboxyl groups and phenolic groups associated with humic substances (Snoeyink and Jenkins 1980).

The Effects of Hardness Ions on Complexation Reactions. Ca^{2+} and Mg^{2+} ions are known to effect the stability of metal-organic complex reactions. This is shown to be the case in Stumm and Morgan (1970). In this example, the organic ligand EDTA is shown to undergo a complexation reaction with Fe^{3+} according to:

$$Fe^{3+} + EDTA^{4-} = (Fe\text{-}EDTA)^{-};\ \log K = 25.1$$

However, in the presence of Ca^{2+}, the reaction is altered according to:

$$(Ca\text{-}EDTA)^{2-} + Fe^{3+} = (Fe\text{-}EDTA)^{-} + Ca^{2+};\ \log K = 14.4$$

Based on this experimental observation, it may be generalized that the presence of hardness ions in solution may decrease the degree to which the metal-organic complexation reaction takes place. In natural waters, if and to what extent the hardness ions effect metal-organic complexation depends on the nature of the metal involved, the organic constituent involved and the environment in which the reactions occur. In other words, each case is unique and should be treated as such.

Topical Trace Organic Removal Processes

Weber and Jodellah (1985) have researched the effectiveness of alum coagulation and lime softening processes for removal of TOC associated with humic substances. Three source waters were selected for study under jar testing conditions. The sources consisted of suspensions prepared from commercial humic acid added to a pretreated inorganic background matrix (IBM) of minimal organic content from the Huron River, from commercial fulvic acid added to the same IBM, and from raw Huron River water with no additions. The researchers reported that 80 percent TOC reduction was achieved in the humic and fulvic acid solutions prepared with the IBM by an alum dose of 50 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$ (7.7 mg/l as Al_2O_3). It was also found that only 30 percent and 50 percent TOC removal was accomplished by alum dosages of 50 and 150 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$ (7.7 and 23 mg/l as Al_2O_3), respectively, in the raw river water. For lime softening tests, a similar removal of TOC was observed. For all sources, an equivalent amount of TOC removal of under 50 percent was reported for a lime dosage of 150-160 mg/l as CaO. Higher lime dosages reduced the TOC from experimentally prepared source waters a total of about 80 percent, while no incremental reduction was reported beyond the 50 percent level for the raw river water. The researchers then subjected the alum and lime pretreated waters to activated carbon adsorption. Their findings revealed significant insights into the nature of the TOC removed and not removed by the alum and lime treatment. These findings are summarized as: (1) for the raw river water, neither lime nor alum pretreatment resulted in any change in non-adsorbable TOC levels, while the overall adsorbability of the adsorbable fraction remaining was enhanced by pretreatment; (2) for the humic acid solution, alum pretreatment improved the adsorbability of about half of the originally non-adsorbable TOC fraction, creating a new weakly adsorbable fraction; (3) for the fulvic acid solution, lime softening and alum coagulation removed the most absorbable TOC fraction. Pertinent to effects of organics removal processes is the researchers' conclusion that the effectiveness of alum and lime treatment varies according to differences in sources and types of TOC.

A follow-up report to Weber and Jodellah (1985) is included in Jodellah and Weber (1985). In this study, it was indicated that the least adsorbable TOC fraction is responsible for proportionately greater trihalomethane production. For alum and lime treatment, trihalomethane formation decreased generally at higher absolute levels of TOC removal. In economic terms, there is a point of diminishing marginal returns for control of trihalomethanes by simply removing TOC. The researchers concluded that control of trihalomethanes be optimized by trace organics removal processes rather than maximized for TOC removal.

Research by Liao and Randtke (1985) has dealt with the specific removal of fulvic acid extracted from groundwater by the lime softening process. Their report has addressed the mechanisms of organic removal by lime softening, the identification of organic contaminant characteristics which render lime softening suitable for TOC removal, and process modifications to facilitate contaminant removal. The aspects of this report considered topical are reviewed in the following summary.

The mechanisms of organic removal by lime softening identified by Liao and Randtke include coprecipitation, precipitation as calcium salts and coagulation or colloid destabilization. The coprecipitation mechanism is also suitable for the removal of metal ions such as $Al(OH)_4^-$ and was considered to be the primary means of TOC removal. The characteristics of fulvic acids (which make them suitable for coprecipitation with hardness) that were reported, clear up several apparent inconsistencies. Calcium carbonate is known to exhibit a negative surface charge as most colloidal particles and $Al(OH)_4^-$. This fact would indicate that a coprecipitation of the three substances is unlikely; however, calcium ions form surface-metal-ligand ternary complexes at interfaces to effect the adsorption of like-charged solute molecules. This ternary complex was explained to be a result of an accumulation of Ca^{2+} at the negatively charged surface, where Ca^{2+} acts as a coordinative link between the surface and the adsorbate. Complexation was reported to increase solute hydrophobicity by either neutralizing its negative functional groups or inducing a conformational arrangement of an anionic polymer.

These interactions are known to promote organics removal as trace organic matter binds to Ca^{2+} or adsorbs onto the $CaCO_3$ surface in the presence of Ca^{2+}. Modification to typical lime softening treatment processes was suggested by the authors to enhance trace organics removal. This two-stage process modification consists of first adding excess lime to elevate the pH and Ca^{2+} concentration, then adding carbonate alkalinity to promote $CaCO_3$ precipitation. The high pH was suggested for the benefits due to $Mg(OH)_2$ precipitation in the removal of fulvic acid; the high Ca^{2+} concentration was recommended for its properties described above.

CHAPTER III

MATERIALS AND METHODS

Raw Water Sources

Four raw source waters were collected for experimentation. These source waters were selected based on the range of trace organic matter represented. Laboratory prepared distilled water was included for its minimal trace organic content. A raw groundwater source from an inlet pipe to the Daytona Beach Water Treatment Plant (downtown Daytona Beach, Florida) provided an initial TOC content of about 10 mg/l. A river source from the Caloosahatchee River collected at an inlet to the Lee County Water Treatment Plant (near Ft. Meyers, Florida) represented an initial TOC of about 20 mg/l. Water collected at Lake Washington, the drinking water source of Melbourne, Florida, contained the highest TOC of about 30 mg/l. Samples were collected from each of these sources in five-gallon polyethylene containers for use in jar tests. Tests were conducted within several days of sampling to insure the integrity of the raw water.

Alum Jar Tests

A standard six-place paddle stirring apparatus (a product of Phipps and Bird, Inc.) was employed in the testing procedure. Alum dosages were applied to a total one-liter water volume, each contained in polyethylene beakers (a product of American Scientific Products). Alum dosages of 1, 5, 10, 20, 30 and 50 mg/l as Al_2O_3

were prepared from appropriate dilutions of a stock solution of 8.3% Al_2O_3 having a specific gravity of 1.33 (a product of Allied Chemical Co.). The alum dilution process was two-fold; first a dilute solution of 1 mg Al_2O_3/ml was prepared with distilled water, and this solution was then combined with the raw water to its final dilution. The chemically treated source waters were initially subjected to pH adjustment. Adjustments of pH were made with dilute solutions of $Ca(OH)_2$ (a slurry), H_2SO_4 and NaOH (above pH 10.3). The pH was varied from 4 to 11 over the course of the testing procedure. The measurement of pH was done with a calibrated Corning Model 12 Research pH meter. This instrument was calibrated with American Scientific brand pH buffer solutions of pHs 4, 7 and 10. Up to six beakers per mixing cycle were subjected to a one-minute period of rapid mixing, a fifteen-minute period of slow mixing and a thirty- to forty-minute period of settling. Rapid mixing was conducted at a paddle speed of 100 rpm; slow mixing at 35 rpm. Also, an alternate mixing sequence of slow mixing followed by rapid mixing was utilized on some jar tests with the goal of isolating the effects of floc shearing. In both sequences, pH was constantly monitored and accordingly adjusted during slow mixing.

Settled samples were decanted from the upper first centimeter into two separate containers to await laboratory analysis. Samples for trace metals analysis were held in 50 ml polystyrene beakers (a product of American Scientific Products) covered with laboratory film and sealed air tight. Samples for TOC analysis were contained in Wheaton brand opaque brown bottles, previously ashed at 300°C for a half-hour period, and covered with teflon-lined caps. Settled samples for metals analysis were stored at room temperature for no more than one month prior to analysis; those for TOC analysis were stored at 4°C for no more than two weeks prior to analysis.

Laboratory Analysis and Quality Control

All alum jar test samples were analyzed for residual aluminum and TOC; the jar tests conducted with no alum added were also analyzed for calcium and magnesium.

Metals Analysis

Analysis of aluminum, calcium and magnesium was performed with the Beckman SpectraSpan V. Special treatment of the performance of this instrument is in order because the most common technique for metals analysis of water is atomic absorption spectrophotometry.

The Beckman SpectraSpan V is an atomic emission spectrometer. It is employed at the Civil Engineering and Environmental Sciences Department of the University of Central Florida, for analysis of trace metal content in water, wastewater, stormwater and soil samples. Metals routinely analyzed for by means of a multi-element cassette included Al, Cd, Cr, Fe, Mn, Ni, P, Pb and Zn. The cassette is also engineered to analyze Ag, As, Ba, Ca, Hg, Mg and Se.

ICP System. Samples are introduced into a white-hot argon plasma (7000^{0}K in the excitation region) by means of a peristalic pump, a nebulizer and a spray chamber. The inductively coupled plasma (ICP) source is ignited by a telsa coil and is sustained by a radio frequency current. The emitted light, which is characteristic of the trace metals content of the sample, is then read by a computer.

Computer. The computer is programmed to identify a typical range for the analysis. This range is defined by the operator who introduces to the system a high and low standard of known metal content. For the current research, the high standards for analysis were prepared from American Scientific brand standards (containing 1 mg of metal/ml) diluted with distilled-deionized water to concentrations of 10, 25 and 100 mg/l of aluminum, magnesium and calcium, respectively. The low standards consisted of distilled-deionized water blanks. A linear calibration curve is then recognized by the computer according to the following illustration of the source program:

$$X = (Y - YL/YH - YL)(XH - XL) + XL$$

where:

XL = the low standard concentration

XH = the high standard concentration

X = the unknown sample concentration

YL = the measured value of the low standard

YH = the measured value of the high standard

Y = the measured value of the unknown sample

The computer is also equipped to measure each sample in replicate and to compute an average value with a corresponding standard deviation. The output for the analysis is recorded on hard copy by a Texas Instruments model printer. The hard copy data was also corrected in those instances for which drift of the standard span became significant. The drift correction relation, assuming a linear drift over time, was devised according to:

$$\text{AVADJ} = \text{AV}\left[\frac{\text{CONC}}{\text{STD}_1+(\text{STD}_2-\text{STD}_1)(\#/\text{TOT}\#)}\right] - [\text{BLK}_1+(\text{BLK}_2-\text{BLK}_1)(\#/\text{TOT}\#)]$$

where:

AVADJ = the adjusted average metal concentration

CONC = the high standard concentration

AV = the average sample output (unadjusted)

STD_1 = the average high standard measurement before sample unknowns

STD_2 = the average high standard measurement after sample unknowns

TOT# = the number of samples recorded between STD_1 and STD_2 outputs

\# = the number of samples recorded between STD_1 and AV outputs

BLK_1 = the average blank standard measurement before sample unknowns

BLK_2 = the average blank standard measurement after sample unknowns

The following is a sample of the hard copy output:

```
STANDARD 10PPM
TIME=10 REP= 3 CAS=1 SAMPLE=   1
14 AL 9.82 10.0 10.0 AV 9.96 SD .126

BLANK
TIME=10 REP= 3 CAS=1 SAMPLE=   2
14 AL .025 .002 .002 AV .009 SD .013

LW RAW
TIME=10 REP= 3 CAS=1 SAMPLE=   3
14 AL .333 .333 .333 AV .333 SD .000

LAKE WASHINGTON JARS
ALUM 0
PH=4.0
TIME=10 REP= 3 CAS=1 SAMPLE=   4
14 AL .397 .394 .394 AV .395 SD .002

PH=5.0
TIME=10 REP= 3 CAS=1 SAMPLE=   5
14 AL .346 .356 .348 AV .350 SD .005

PH=6.0
TIME=10 REP= 3 CAS=1 SAMPLE=   6
14 AL .348 .356 .360 AV .355 SD .006

PH=7.0
TIME=10 REP= 3 CAS=1 SAMPLE=   7
14 AL .364 .374 .362 AV .367 SD .006

PH=8.0
TIME=10 REP= 3 CAS=1 SAMPLE=   8
14 AL .417 .421 .417 AV .418 SD .002

PH=9.0
TIME=10 REP= 3 CAS=1 SAMPLE=   9
14 AL .474 .474 .480 AV .476 SD .003

PH=10.0
TIME=10 REP= 3 CAS=1 SAMPLE=  10
14 AL .495 .503 .501 AV .500 SD .004

PH=11.0
TIME=10 REP= 3 CAS=1 SAMPLE=  11
14 AL .586 .597 .590 AV .591 SD .006

STANDARD 10PPM
TIME=10 REP= 3 CAS=1 SAMPLE=  12
14 AL 9.99 9.98 9.91 AV 9.96 SD .043

BLANK
TIME=10 REP= 3 CAS=1 SAMPLE=  13
14 AL .015 .007 .015 AV .013 SD .004
```

Precision and Accuracy. Precision and accuracy data for the Beckman SpectraSpan V with ICP source is included in Appendix A.

TOC Analysis

Total organic carbon (TOC) was measured with a Dohrmann Model DC-54 Analyzer. Organic carbon is oxidized to CO_2 by means of ultraviolet light and an acidic persulfate solution. The CO_2 is then catalytically reduced to methane and measured with a flame ionization detector. Samples for analysis were run against a 10 ppm standard for TOC and a blank of reagent grade water. The 10 mg/l solution was prepared in the following manner: (1) a TOC stock solution of 1000 mg/l organic carbon was prepared by dissolving 0.2125 g of potassium acid phthalate in 90 ml of reagent grade water, acidifying with 1 ml of concentrated phosphoric acid, and diluting to 100 ml; (2) the stock solution was then diluted by a factor of 100 with reagent grade water (i.e., 1 ml stock solution diluted to 100 ml). This standard was analyzed and the instrument output was calibrated to 10.000 mg/l plus the output of a blank solution.

Samples for analysis were diluted to a concentration below 10 mg/l TOC if the undiluted concentration was greater than 10 mg/l. Each sample was treated with a persulfate reagent at a ratio of 50 ml sample to 1 ml reagent. Each sample was run a minimum of two times in order to guarantee a reproducibility of ± 0.1 mg/l. All results are reported as averages of replicates considered reproducible. The correction for organic carbon in the dilution water was to subtract the value of the blank from the analyzed value.

CHAPTER IV

RESULTS AND DISCUSSION

Brief Review of Procedure

A series of 323 alum jar tests were performed on potable waters from a distilled water source, a groundwater source (Daytona Beach, Florida), a freshwater lake (Lake Washington, Melbourne, Florida) and a river (Caloosahatchee River, Ft. Myers, Florida). Parameters monitored included alum dosage, pH and mixing sequence in addition to source. Alum dosages of 1, 5, 10, 20, 30 and 50 mg/l as Al_2O_3 were measured volumetrically from appropriate dilutions of a stock solution of 8.3% Al_2O_3 with a specific gravity of 1.33. pH adjustments were carried out with dilute solutions of H_2SO_4, $Ca(OH)_2$ (a slurry) and NaOH (above pH 10.3). pH was varied from 4 to 11 and measured with a pH meter. Mixing was conducted with a standard six place laboratory mixing apparatus in the following manner: (1) an appropriate alum dose was combined with a one liter source water sample; (2) this sample was contained in a plastic beaker in which preliminary pH adjustments were made; (3) the chemically treated source water was then subjected to rapid mix (one minute at 100 rpm), slow mix (15 minutes at 35 rpm) and settling (30-40 minutes); and (4) additionally the effect on floc subject to shearing was isolated by means of reversing the conventional rapid mix/slow mix sequence for some samples. pH was constantly monitored and accordingly adjusted during slow mix. The settled sample was decanted (from the top one centimeter) and analyzed instrumentally for soluble organic carbon and aluminum. The jar test control samples with no alum added were also analyzed for calcium and magnesium hardness in order to isolate the removal of trace organics by the water softening process.

Theoretical Aluminum Solubility

Figures 1 and 2 are pC (- logarithmic residual molar aluminum as Al^{3+} concentration) versus pH diagrams constructed by employing the equations pertaining to soluble aluminum in equilibrium with the $Al(OH)_3$ precipitate as presented in Chapter II. Figure 1 defines the theoretical equilibria relating to freshly precipitating $Al(OH)_3$. This equilibria is characterized by the dominance of the polynuclear cationic species. Figure 2 pictures aged or crystalline $Al(OH)_3$ in equilibrium with soluble aluminum. In this case, Al^{3+} is the dominant cationic species (below pH 5). Crystalline $Al(OH)_3$, known as gibbsite, predominates over a larger area than freshly precipitating or amorphous $Al(OH)_3$. All subsequent discussion of theoretical aluminum solubility is made in reference to the contents of figures 1 and 2; note that an appropriate model for purposes of this analysis would bear some semblance to both. The majority of the discussion on aluminum solubility deals with three specific pH ranges as follows: (1) below pH 5 - a range of soluble cationic species domination; (2)

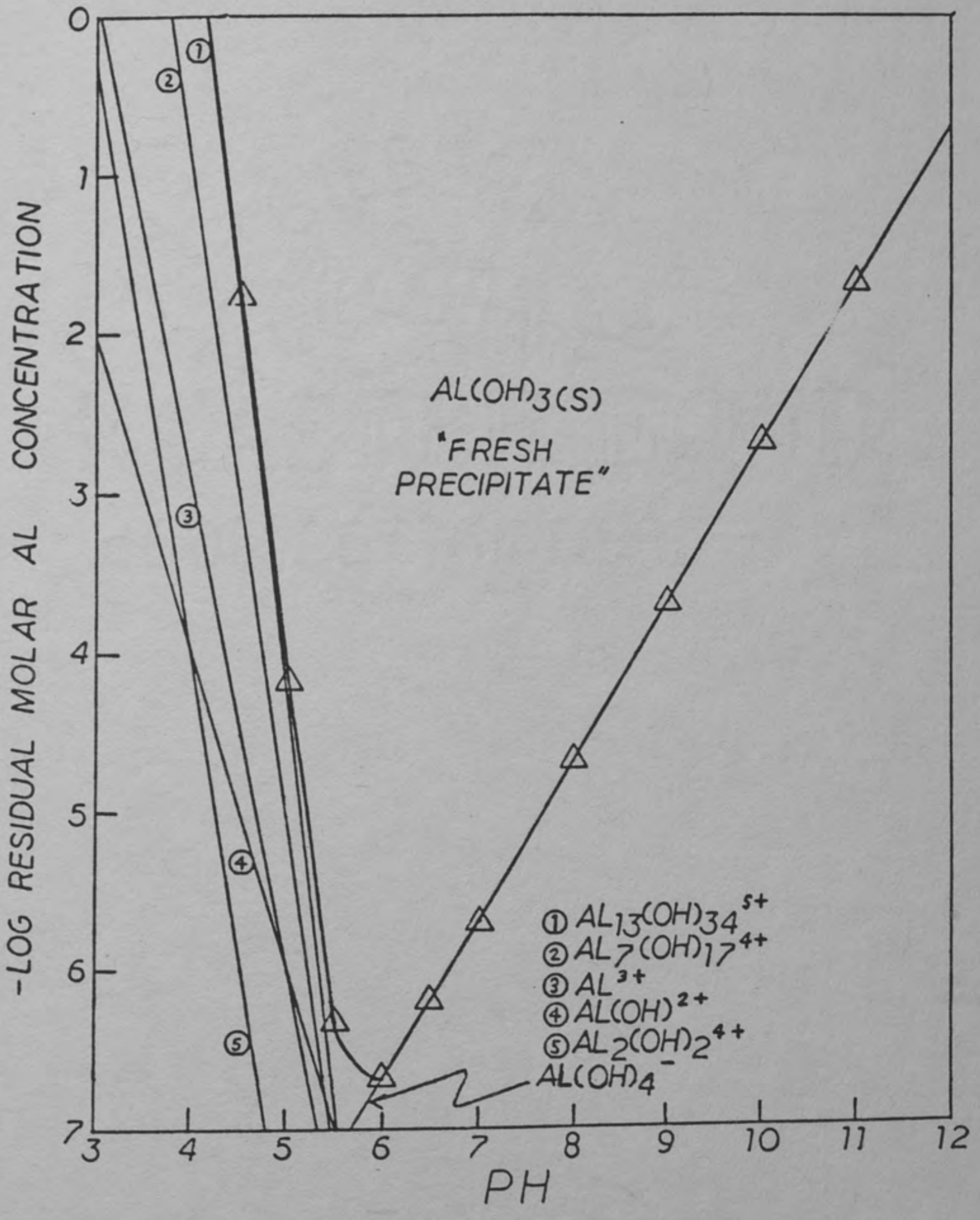

Figure 1. pC Versus pH for Aluminum Solubility Theory.

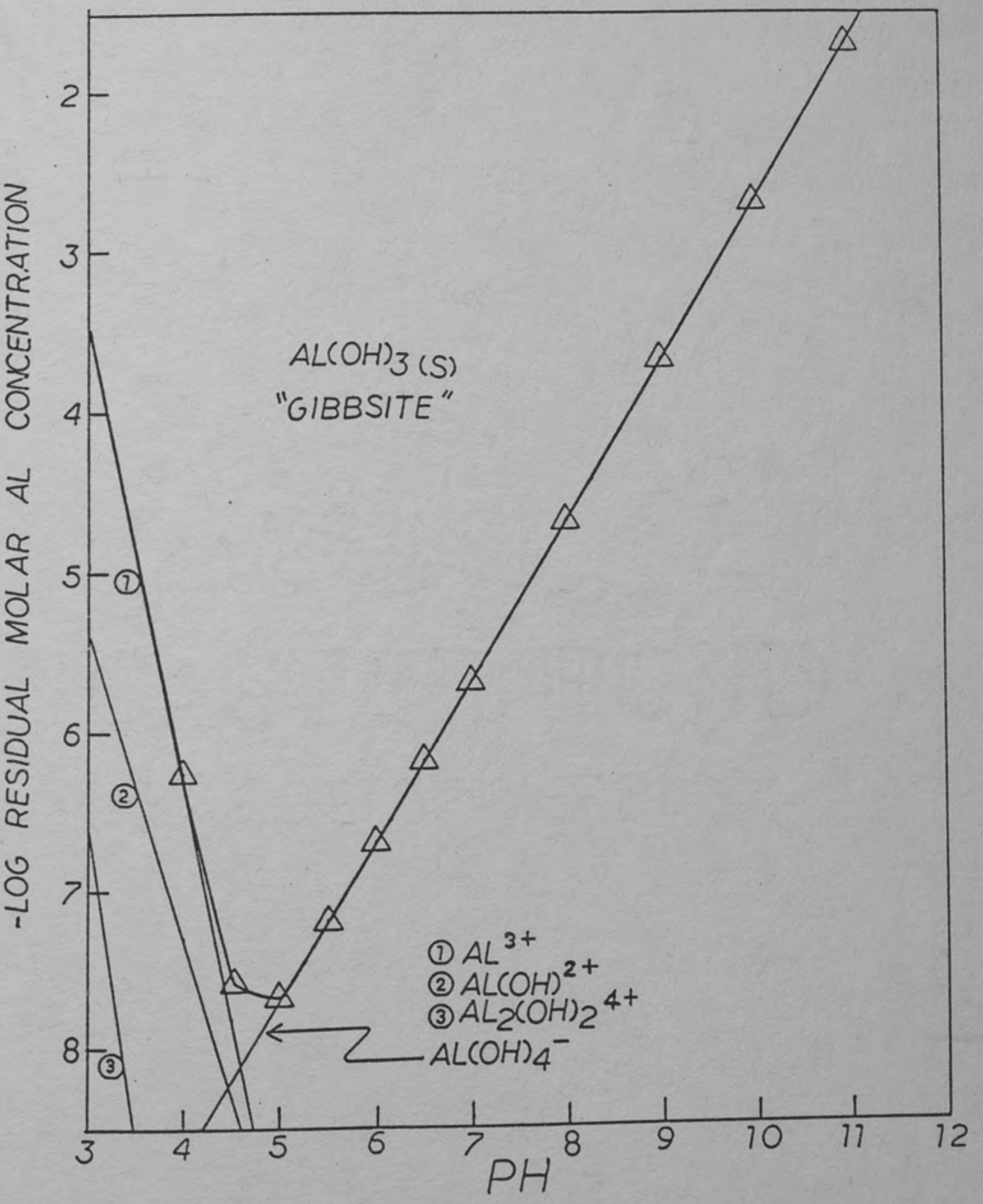

Figure 2. pC Versus pH for Aluminum Solubility Theory.

pH 5-8 - a range of minimum soluble aluminum; and (3) above pH 8 - a range of anionic dominance (i.e., $Al(OH)_4^-$ species).

Aluminum Solubility Range: Below pH 5

Below pH 5, aluminum solubility is characterized by the increasing solubility of cationic species with decreasing pH. In the presence of amorphous or freshly precipitating $Al(OH)_3$, the most prevalent cationic species are $Al_{13}(OH)_{34}^{5+}$ and $Al_7(OH)_{17}^{4+}$, with contributions by Al^{3+}, $Al(OH)^{2+}$ and $Al_2(OH)_2^{4+}$. Aluminum solubility theory predicts the formation of $Al(OH)^{2+}$ as an intermediate species in the formation of the more soluble polynuclear cationic species. For the special case in which sufficient agitation (i.e., rapid mixing) is applied to an aluminum treated system containing fine negatively charged colloids (e.g., organic color), $Al(OH)^{2+}$ may adsorb onto the negatively charged surfaces and, thus, function as a cationic polymer. In such a case, the effect of rapid mixing inhibits the formation of the polynuclear species as the $Al(OH)^{2+}$ precipitates with the negatively charged colloids (Weber 1972).

In the presence of crystalline $Al(OH)_3$ or gibbsite, the dominant cationic species is Al^{3+}, with contributions by $Al(OH)^{2+}$ and $Al_2(OH)_2^{4+}$ below pH 4.

Aluminum Solubility Range: pH 5-8

The most important role of alum is its function as a coagulant in which $Al(OH)_3$ precipitation is accompanied by the most significant levels of trace organics reduction. Theory predicts that $Al(OH)_3$

precipitation or minimum dissolved aluminum concentration is optimal at pH 5-6 and predominates over a range of pH 5-8. In the process of the precipitation of $Al(OH)_3$, trace organic matter becomes enmeshed in the "sweep floc." Minimum solubility in this pH range is not the case if aluminum is held in soluble complexed form with trace organic matter. Schnitzer (1971) describes that 100 mg/l of fulvic acid (51 mg/l TOC), the most abundant naturally occurring organic in aquatic systems, can maintain up to 4 mg/l Al^{3+} in stable solution from the practically insoluble hydroxide (i.e., $Al(OH)_3$).

Aluminum Solubility Range: Above pH 8

Above pH 8, the dominant aluminum species is the anionic $Al(OH)_4^-$. Aluminum solubility theory predicts that $Al(OH)_4^-$ is geometrically increasingly soluble with increasing pH. In practice, alum may be applied to water softening processes as a coagulant aid. The theory behind this practice is that $Al(OH)_4^-$ also functions as an anionic polymer, adsorbing onto the surfaces of positively charged floc constituents and precipitating. The effects of $Al(OH)_4^-$ functioning as a polymer are a heavier, faster settling floc and a reduced level of predictably soluble anion.

A Presentation of the Alum Jar Test Data

Raw Water Quality of Source Waters

Table 3 is provided as a presentation of the raw water quality of the source waters on which the alum jar tests were performed.

TABLE 3

RAW WATER QUALITY OF SOURCE WATERS

SOURCE	DISTILLED WATER	DAYTONA BEACH	LAKE WASHINGTON	CALOOSAHATCHEE RIVER
pH	-	6.7	7.2	7.8
Al^{3+} (mg/l)	0.002	0.47	0.33	0.20
Ca^{2+} (mg/l)	BDL	100	41.4	-
Mg^{2+} (mg/l)	BDL	9.65	7.64	-
TOC (mg/l)	0.049	10.15	31.40	22.28

* BDL - Below detectable limit of 0.001 mg/l

Alum Jar Test Results

In this section, alum jar test results for the four source waters are reported as a function of alum dose and pH by TOC remaining (mg/l), Al remaining (mg/l as Al^{3+}) and percent TOC remaining. These results are for those jar tests conducted in the conventional manner of mixing, rapid mix (destabilization) followed by slow mix (flocculation), referred to in the text as the "non-sheared condition." In Appendix D, alum jar test results for the reversed sequence, slow mix followed by rapid mix, are presented and referred to in the text as the "sheared floc condition."

Figure 3 provides a summary of TOC remaining (mg/l) for the jar tests conducted on the distilled water source. These results are sufficiently low (ranging from 0.01 to 0.45 mg/l) as to challenge the detection limit of the analytical instrument. TOC levels reported are thus quite significantly affected by artifacts of the testing procedure; for this reason, the distilled water TOC results have not been reported as a "percent remaining." The significance of the distilled water tests is that an experimental aluminum solubility profile is provided without the competing effects due to organic content and organic reduction present in the other sources. Figure 4 is a presentation of the aluminum remaining (mg/l) for the distilled water jar tests. The data contained within is reflective of several trends which include most notably: (1) at pH 4, aluminum residual increases with increasing dose due to the solubility of cationic species; (2) minimum levels of aluminum residual are accomplished at pH 5, though not related to alum dose; and (3) above pH 8, increasing aluminum residual with increasing pH suggests the presence of soluble anions.

Figure 5 contains the TOC remaining (mg/l) results for the Daytona Beach jar tests. Optimum TOC reduction is achieved at pH 5 and pH 11. At pH 5, TOC reduction is clearly dependent on alum dose or (more correctly) on the quantity of $Al(OH)_3$ precipitate as evidenced by decreasing organic content with increasing dose. At pH 11, TOC reduction is accomplished together with the water softening process and bears little relationship to the alum dose applied. The detailed role of the water softening process as it applies to the jar test data is discussed later in this chapter. Figure 6 provides the aluminum residual (mg/l) data for the Daytona Beach jar tests. Trends evident in this data set suggest: (1) the presence of soluble cationic

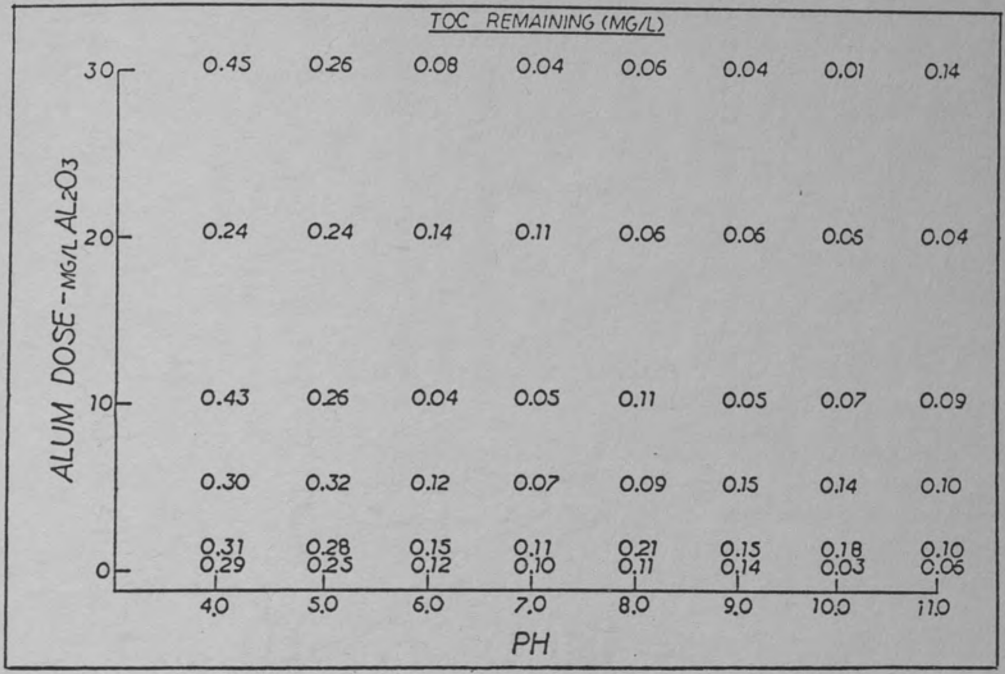

Figure 3. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Distilled Water.

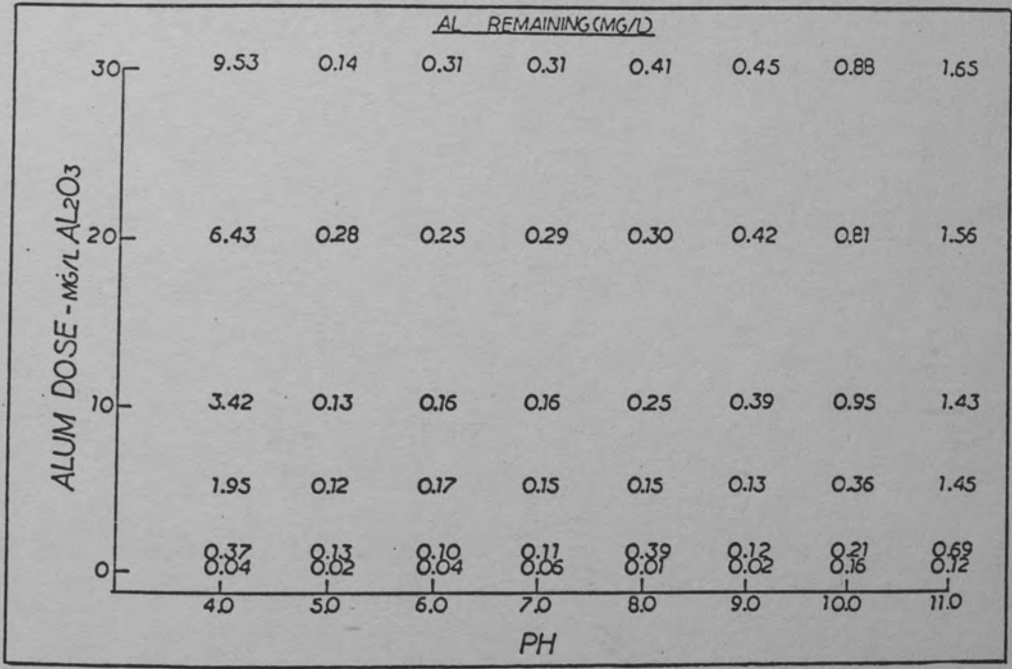

Figure 4. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Distilled Water.

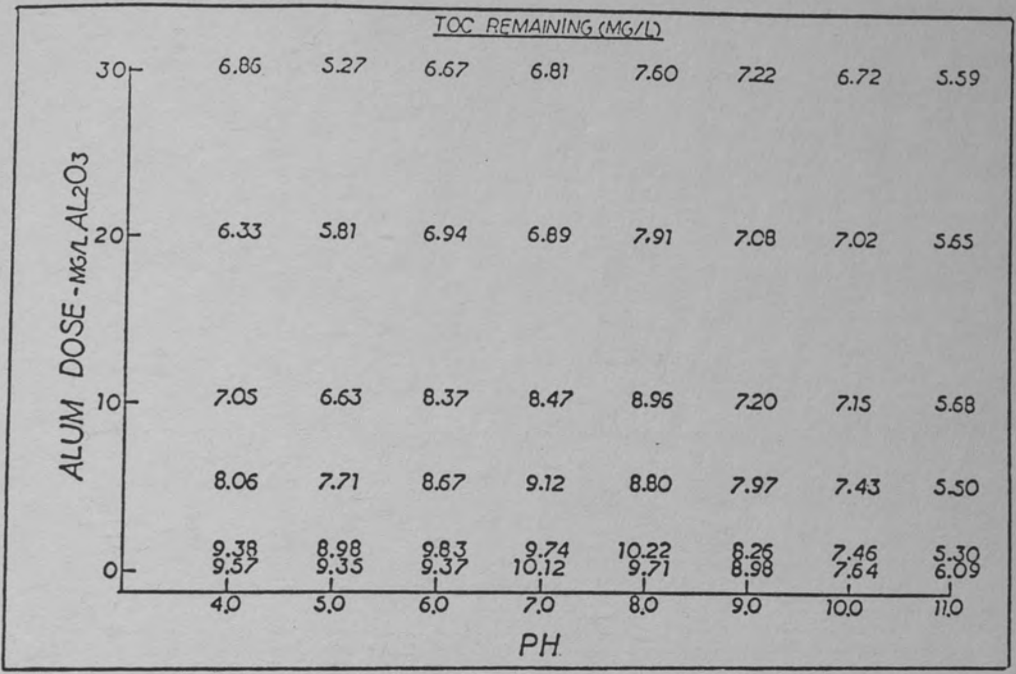

Figure 5. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Daytona Beach.

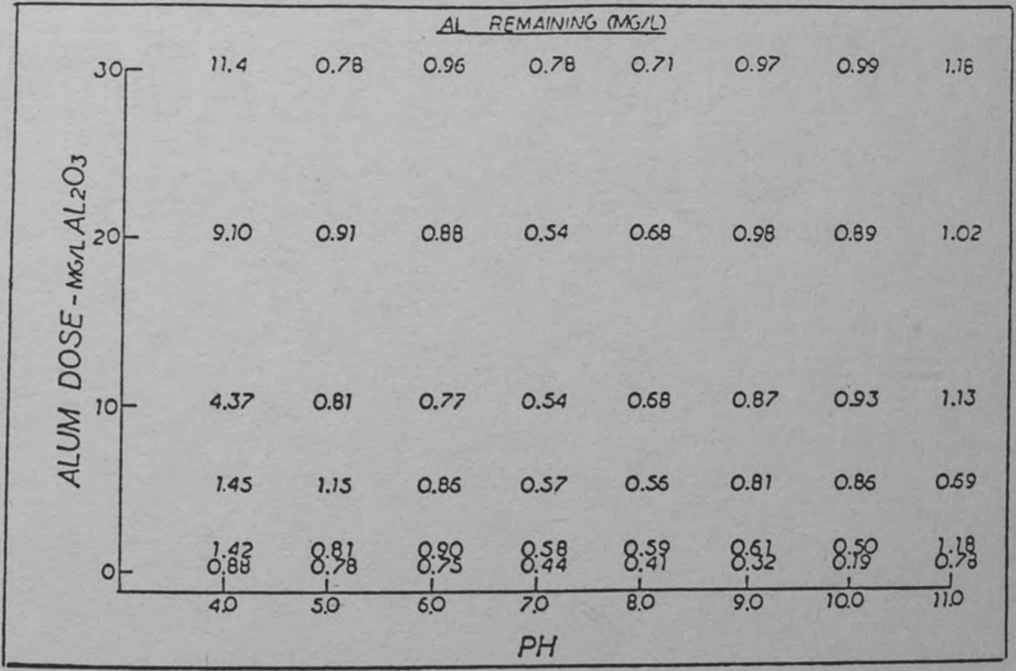

Figure 6. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Daytona Beach.

species at pH 4; (2) a tendency of greater aluminum residual relative to the results for the distilled water tests in the pH range of 5-8; and (3) a tendency of lessened aluminum residual at pH 11 relative to the distilled water tests. Figure 7 is an equivalent representation of the data displayed in Figure 5 (i.e., Daytona Beach TOC residuals) expressed as a percent of the raw water TOC. The minimum level of TOC residual achieved is 52%.

In Figure 8, TOC remaining (mg/l) is reported for the Lake Washington jar tests. Residual TOC is consistently high for alum dosages of 10 mg/l as Al_2O_3 and under. In Figure 9, aluminum residual (mg/l) results are provided for the Lake Washington jar tests. Likewise, as in the case of residual TOC, aluminum remaining is uncharacteristically high for alum dosages of 10 mg/l as Al_2O_3 and under in the pH range of 5-8. For alum dosages in excess of 10 mg/l as Al_2O_3, aluminum solubility theory in action is recognizable in that: (1) aluminum residual is highest at pH 4, (2) a minimum level of aluminum residual is achieved in the pH range of minimum aluminum solubility, and (3) elevated aluminum residuals are reported above pH 8. Figure 10 shows the percent TOC remaining for the finished Lake Washington samples. Note that a minimum level of residual TOC (as low as 24%) is accomplished with an alum dose of 30 mg/l as Al_2O_3.

Figure 11 is a presentation of the TOC residual (mg/l) results for the Caloosahatchee River jar tests. Note that these jar tests were conducted in a different manner from the other sets in that

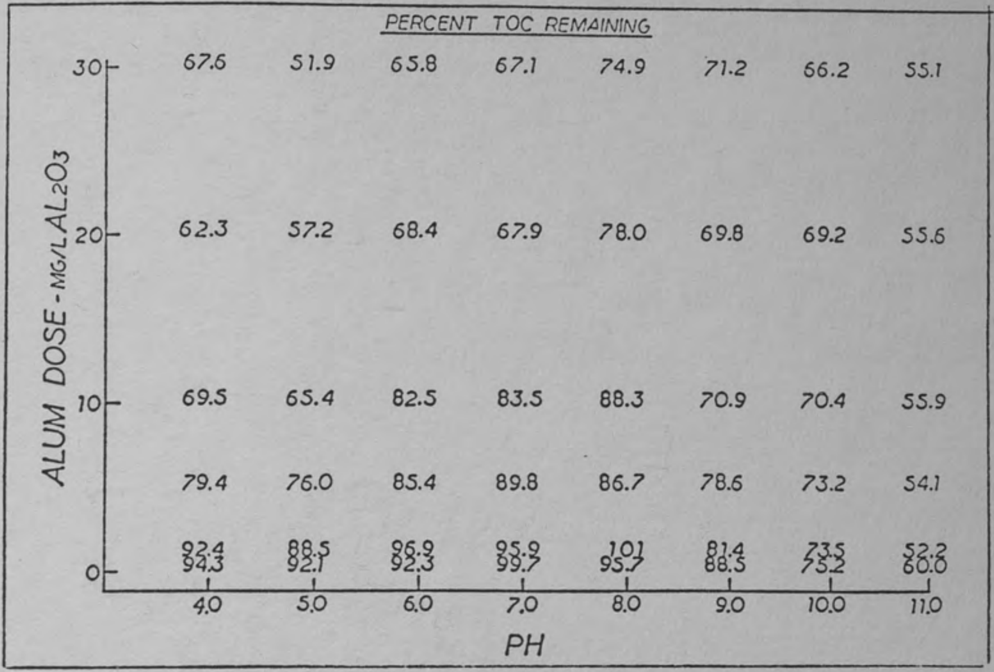

Figure 7. Alum Jar Test Results - Percent TOC Residual as a Function of Alum Dose and pH for Daytona Beach.

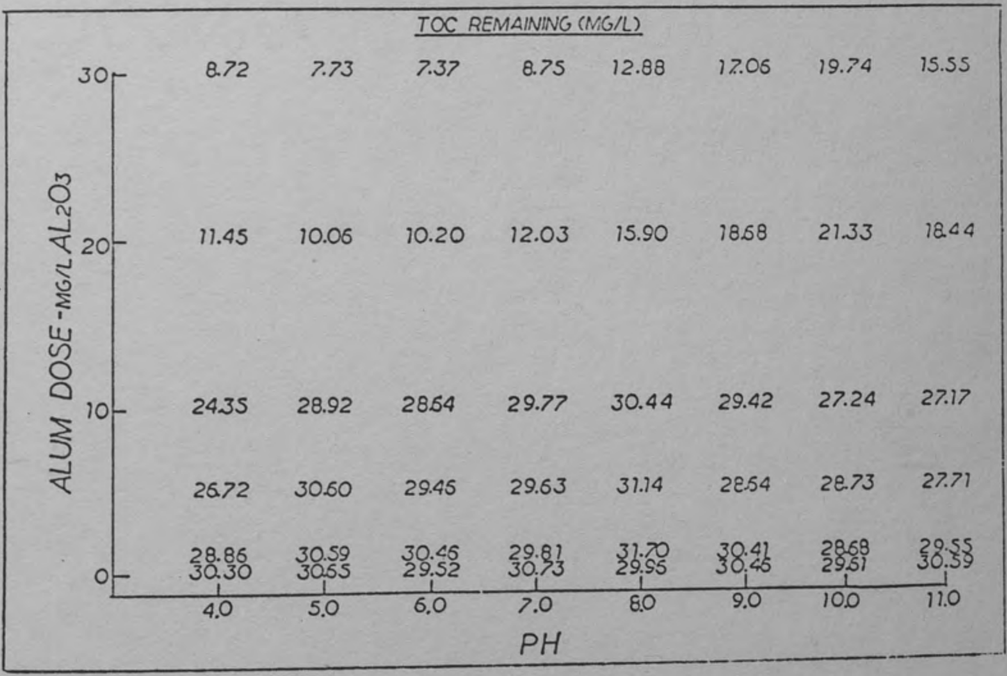

Figure 8. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Lake Washington.

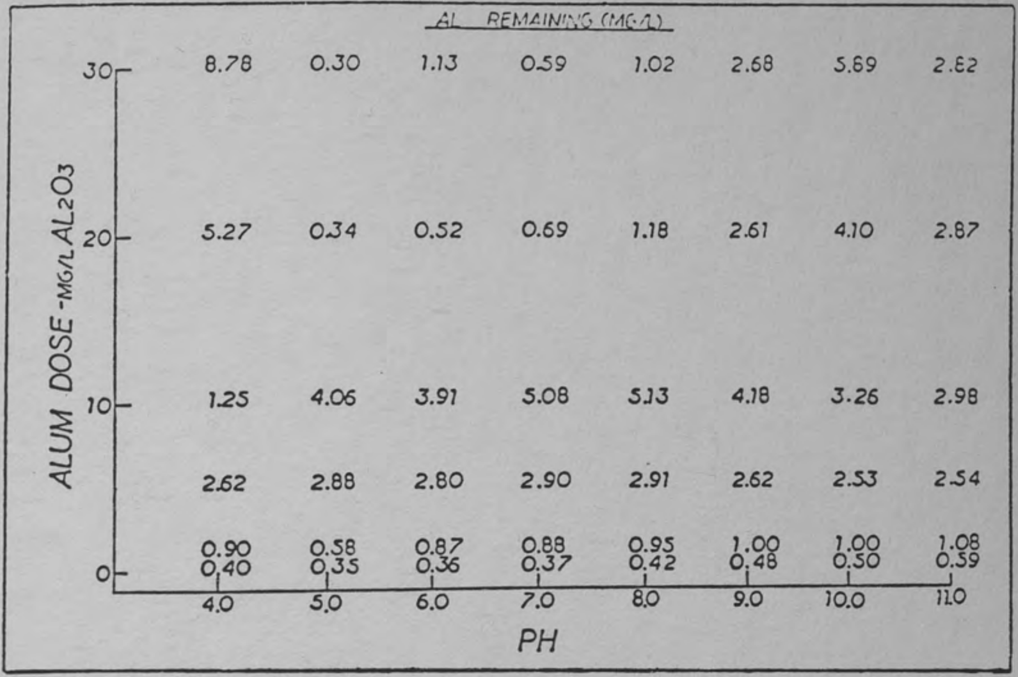

Figure 9. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Lake Washington.

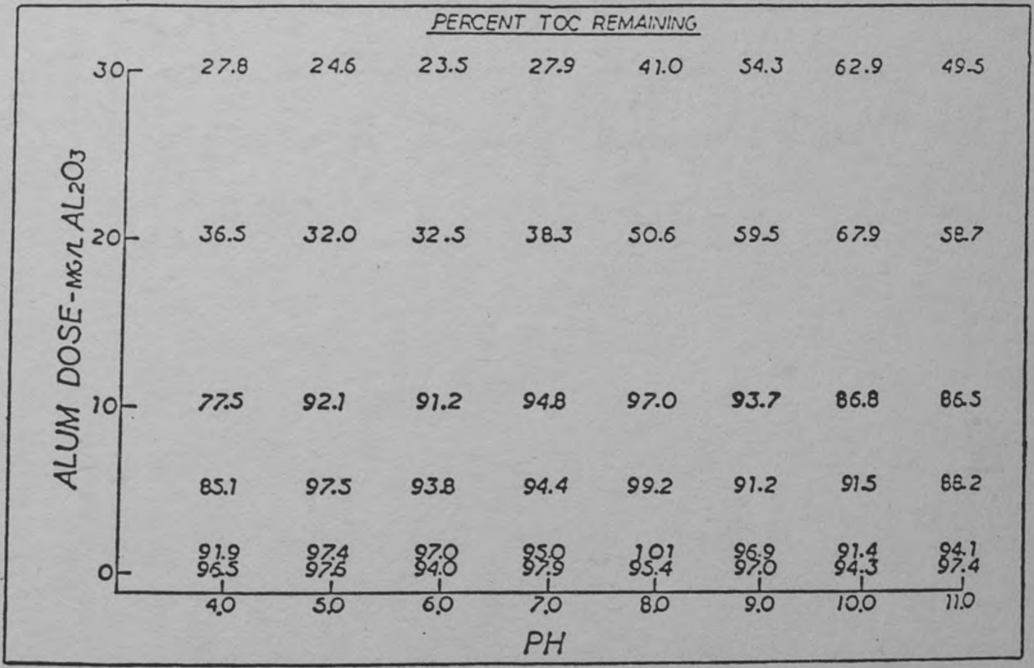

Figure 10. Alum Jar Test Results - Percent TOC Residual as a Function of Alum Dose and pH for Lake Washington.

alum dosage was varied from 5 to 50 mg/l as Al_2O_3, and pH was controlled from 4.5-8.0. The optimum pH for TOC removal for this source is 5 or 5.5. Figure 12 contains the aluminum residual (mg/l) results for the Caloosahatchee River jar tests. This data demonstrates: (1) the presence of soluble cationic species at pH 4.5; (2) a superior achievement of minimal residual aluminum; and (3) a tendency toward increased aluminum solubility at pH 8. Elevated levels of residual aluminum are indicated for an alum dose of 5 mg/l as Al_2O_3. Figure 13 is a report of the TOC remaining on a percent basis for the Caloosahatchee River jar tests. A minimum TOC residual of 21% was accomplished by an alum dose of 50 mg/l as Al_2O_3 for this source.

For all sources, the optimum jar test conditions provided were in the pH range of 5-8, a range for $Al(OH)_3$ precipitation dominance. Table 4 summarizes the optimum jar test conditions by source.

TABLE 4

OPTIMUM JAR TEST CONDITIONS BY SOURCE

SOURCE	OPTIMUM TOC REDUCTION CONDITION		MINIMUM Al^{3+} RESIDUAL
	pH	ALUM DOSE (mg/l AS Al_2O_3)	pH
Distilled Water	-	--	5
Daytona Beach	5	30	7
Lake Washington	6	30	5*
Caloosahatchee River	5.5	50	5-7*

* Denotes evidence of aluminum held in complex for lower alum dosages.

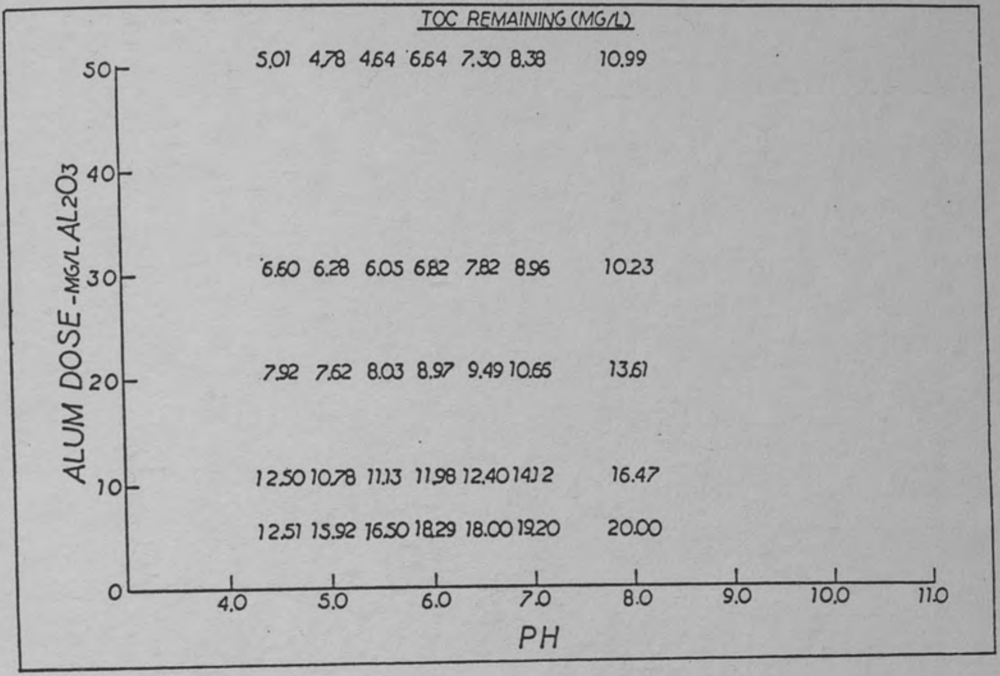

Figure 11. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Caloosahatchee River.

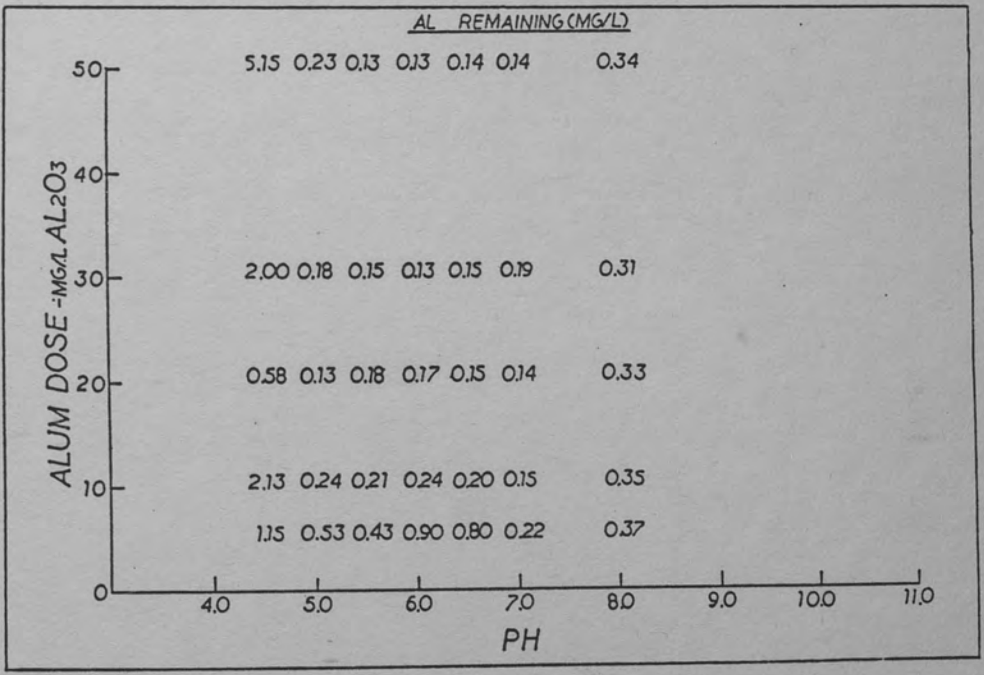

Figure 12. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Caloosahatchee River.

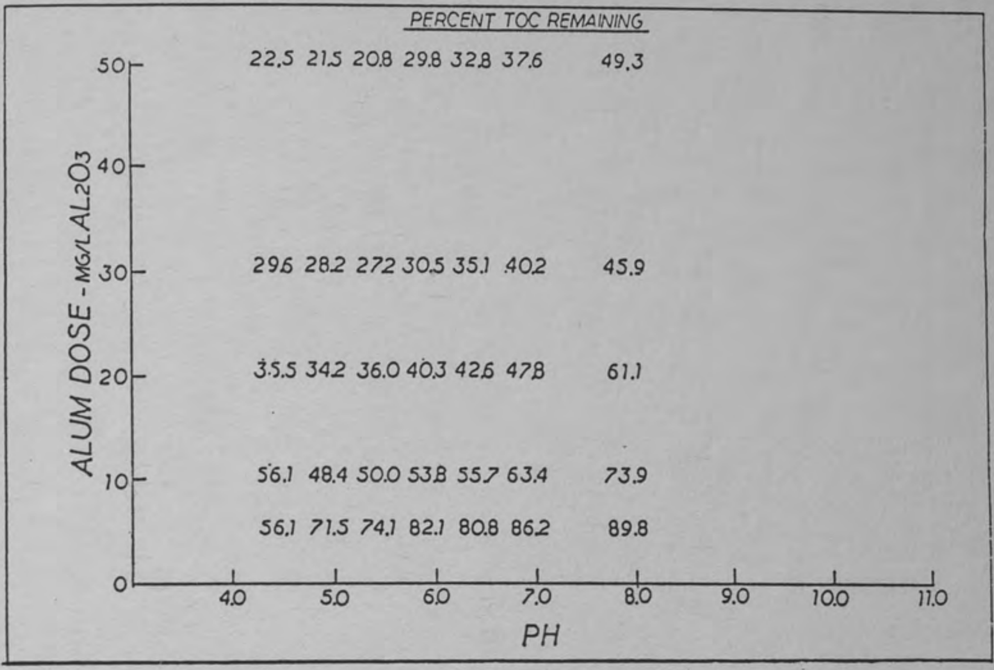

Figure 13. Alum Jar Test Results - Percent TOC Residual as a Function of Alum Dose and pH for Caloosahatchee River.

Deviation from Aluminum Solubility Models

The jar test residual aluminum data (as presented in figures 4, 6, 9 and 12) are at variance with the theoretical models for predicting aluminum solubility. The levels of soluble aluminum (in mg/l as Al^{3+}) predicted by the models presented in figures 1 and 2 are summarized in Table 5.

It has already been stated that an appropriate model for the aluminum residual data reported for the alum jar tests would bear some semblance to both solubility profiles (i.e., the fresh $Al(OH)_3$ equilibria model and the gibbsite equilibria model). This statement is defended by the following points: (1) the fresh precipitate equilibria model predicts minimum aluminum solubility at pH 6;

TABLE 5

SOLUBLE ALUMINUM PREDICTED BY SOLUBILITY MODELS

EQUILIBRIA MODEL	SOLUBLE ALUMINUM (mg/l AS Al^{3+}) PREDICTED										
	pH										
	4.0	4.5	5.0	5.5	6.0	6.5	7.0	8.0	9.0	10.0	11.0
Fresh $Al(OH)_3$	MDL*	MDL	1.78	0.01	<0.01	0.02	0.05	0.54	5.38	MDL	MDL
Gibbsite	0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.05	0.54	5.38	MDL	MDL

* MDL: denotes "maximum dose limited," whereas 30 mg/l as $Al_2O_3 \equiv 15.9$ mg/l as Al^{3+} and 50 mg/l as $Al_2O_3 \equiv 26.5$ mg/l as Al^{3+} represent the maximum alum dosages applied to the jar tests.

(2) the gibbsite equilibria model predicts minimum aluminum solubility at pH 5; (3) the experimental data supports both of the preceding statements; (4) the fresh precipitate equilibria model predicts nearly complete solubility of the aluminum supplied to the jar tests at pH 4; (5) the gibbsite equilibria model predicts 0.01 mg/l as Al^{3+} to be soluble at pH 4; and (6) the experimental data falls in between the range defined by the two preceding statements at pH 4. It has also been shown that for all four sources, trends suggest: (1) cationic solubility below pH 5; (2) minimum solubility in the range of 5-8; and (3) increasing anionic solubility with increasing pH above pH 8. Beyond this point, the equilibria models fail insofar as their propensity to account for the high residual values reported in the pH range of 5-8, and the low residual values reported at pH 8 and above.

The minimum aluminum solubility levels reported in the pH range of 5-8 for the jar tests are in most instances elevated with respect to the minimum levels predicted by theory. This observation is due to inefficiencies of the coagulation process or in specific instances, to the formation of aluminum-organic complexes. Both factors are shown to be linked to the source water itself in the succeeding discussion of Aluminum Solubility versus Trace Organics.

Above pH 8, aluminum solubility theory predicts a level of soluble aluminum much higher than the levels reported for the alum jar tests. The predicted aluminum solubility levels for pH 10 and pH 11 are limited only by the alum dosage applied to the jar tests.

The level of predictably soluble aluminum at pH 9 is 5.38 mg/l as Al^{3+}, an amount that is limited by an alum dose of 10 mg/l as Al_2O_3 (i.e., 5.3 mg/l as Al^{3+}) and under. The fact that aluminum has precipitated from the source waters to a greater extent than predicted for $Al(OH)_3$ at the higher pHs can be explained by the function of $Al(OH)_4^-$ as a polymer. As a polymer, $Al(OH)_4^-$ reacts with or adsorbs onto other precipitates (e.g., $CaCO_3$ or $Mg(OH)_2$) and is also effectively precipitated. Interestingly enough, this would also seem to be the case for the distilled water jar tests in which $Al(OH)_4^-$ would be associated with the calcium carbonate floc from the calcium supplied by the lime added for pH control. At this point, the question might arise, "Where does the alkalinity come from for $CaCO_3$ to precipitate?" The answer to this question is that atmospheric CO_2 is readily soluble in water at high pHs for open systems and exists in solution as CO_3^{2-} (Snoeyink and Jenkins 1980).

Aluminum Solubility Versus Trace Organics

A three-dimensional presentation has been selected to demonstrate the complex inter-relation between residual aluminum and residual TOC already introduced as results of the alum jar testing procedure.

Figure 14 provides a picture of the experimental aluminum (as Al^{3+}) solubility profile as a function of alum dose and pH for distilled water in which trace organic content is minimal. Note that only at pH 4 does aluminum residual significantly increase with increasing alum dose. At pH 4, 60-74% of the aluminum supplied by alum remains

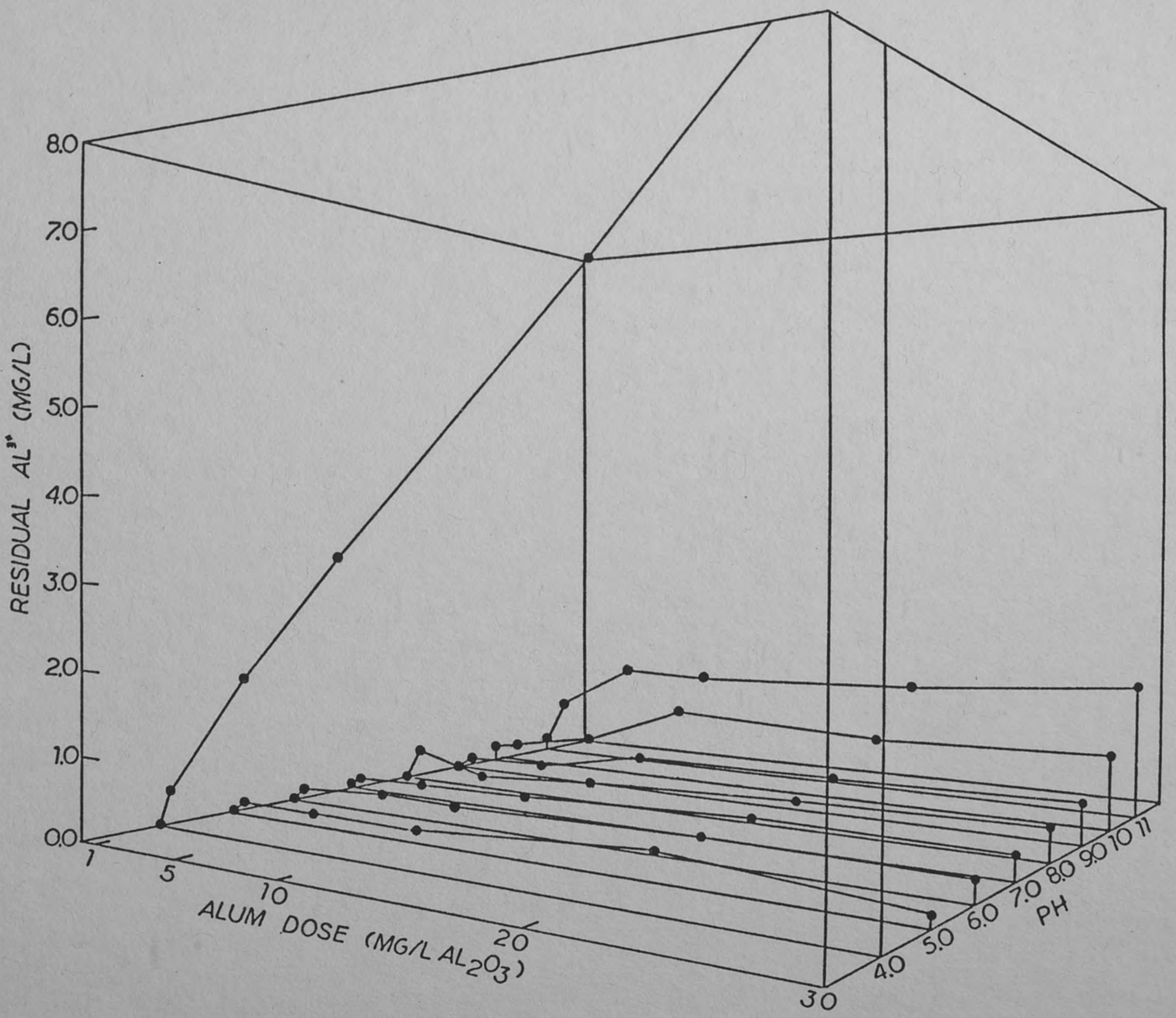

Figure 14. Distilled Water Al^{3+} Versus Dose Versus pH.

soluble. Minimum levels of aluminum residual are achieved in the pH range of 5-8 for which $Al(OH)_3$ precipitation dominance is predicted by theory, ranging from 0.10 to 0.41 mg/l as Al^{3+}. The logarithmic solubility relationship for aluminum with pH is aptly demonstrated above pH 8 in Figure 14.

Figure 15 is a graphical exhibition of aluminum residual (as Al^{3+}) for Daytona Beach jar tests as it relates to residual TOC and pH. Figures 16 and 17 are equivalent representations for the Lake Washington source and the Caloosahatchee River source, respectively. Several key items might aid in the interpretation of these figures: (1) each point on a graph represents four measured parameters; (2) the lines parallel to the TOC axis span the TOC residual concentrations (over the range of alum dose applied) for each pH at which the jar tests were conducted; and (3) lines connecting individual points for each pH can be followed through consecutively increasing alum dosages from the right ends to the left ends of the lines parallel to the TOC axis.

The Daytona Beach series of jar tests displayed the most complicated network of inter-relation (Figure 15). The residual aluminum increases with increasing alum dose as TOC is removed by increments to a level of 6.33 mg/l at pH 4. At pH 5, the level of residual aluminum remains nearly constant (ranging from 0.78 to 1.15 mg/l as Al^{3+}) with increasing alum dose, while TOC is gradually reduced to a global optimum level of 5.27 mg/l. This tendency of nearly constant residual aluminum coupled by a graduated reduction of

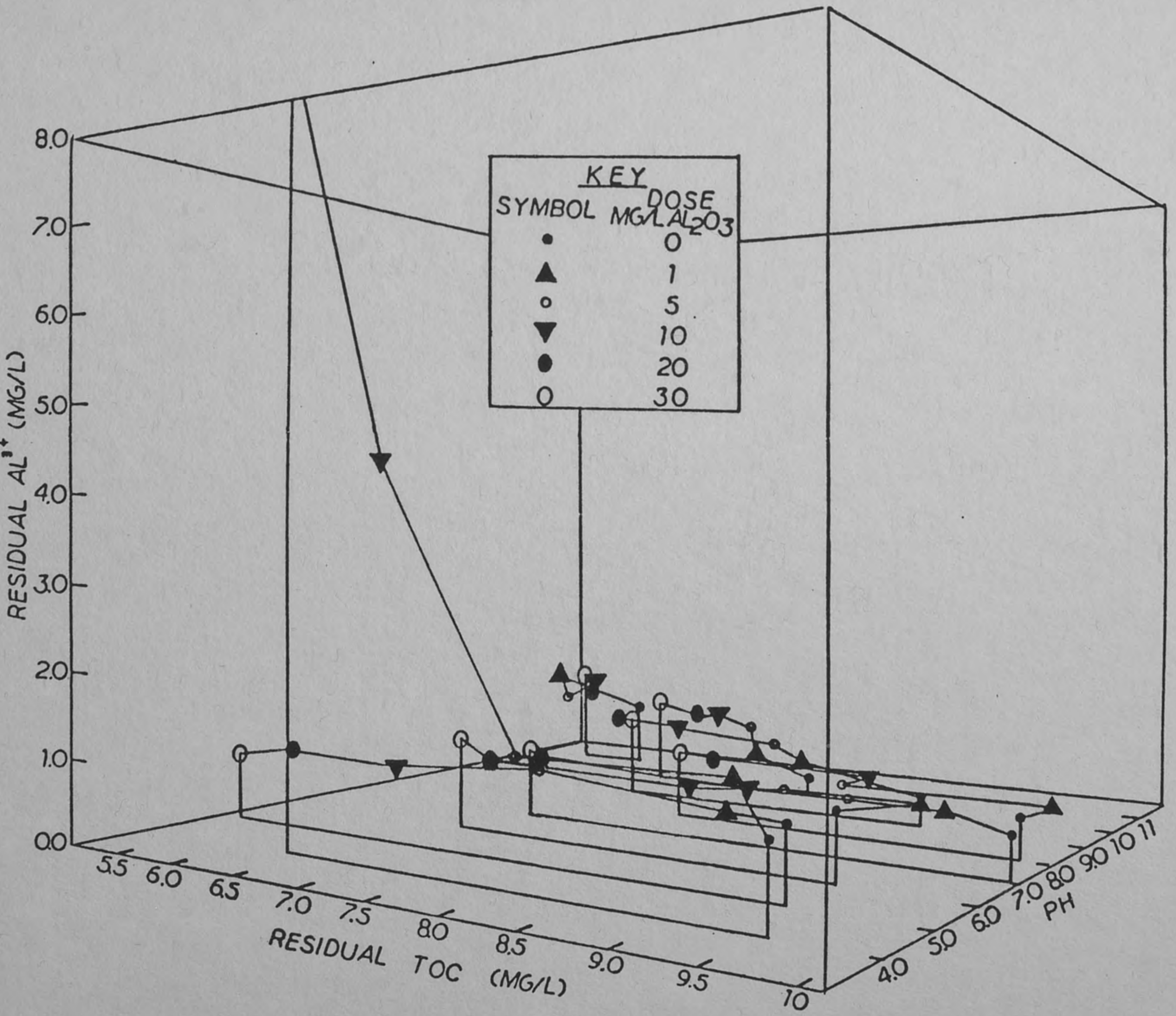

Figure 15. Daytona Beach Al^{3+} Versus TOC Versus pH.

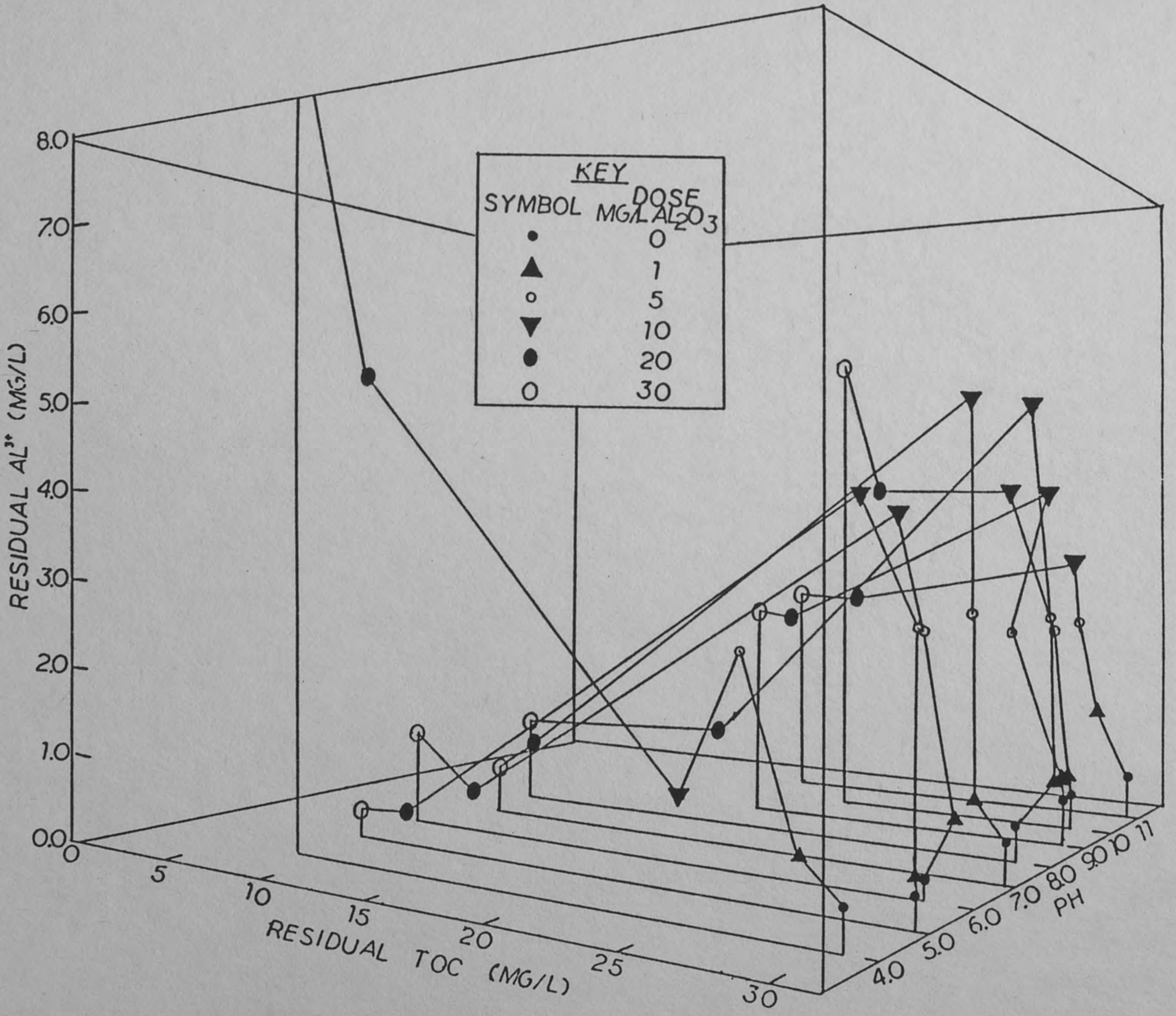

Figure 16. Lake Washington Al^{3+} Versus TOC Versus pH.

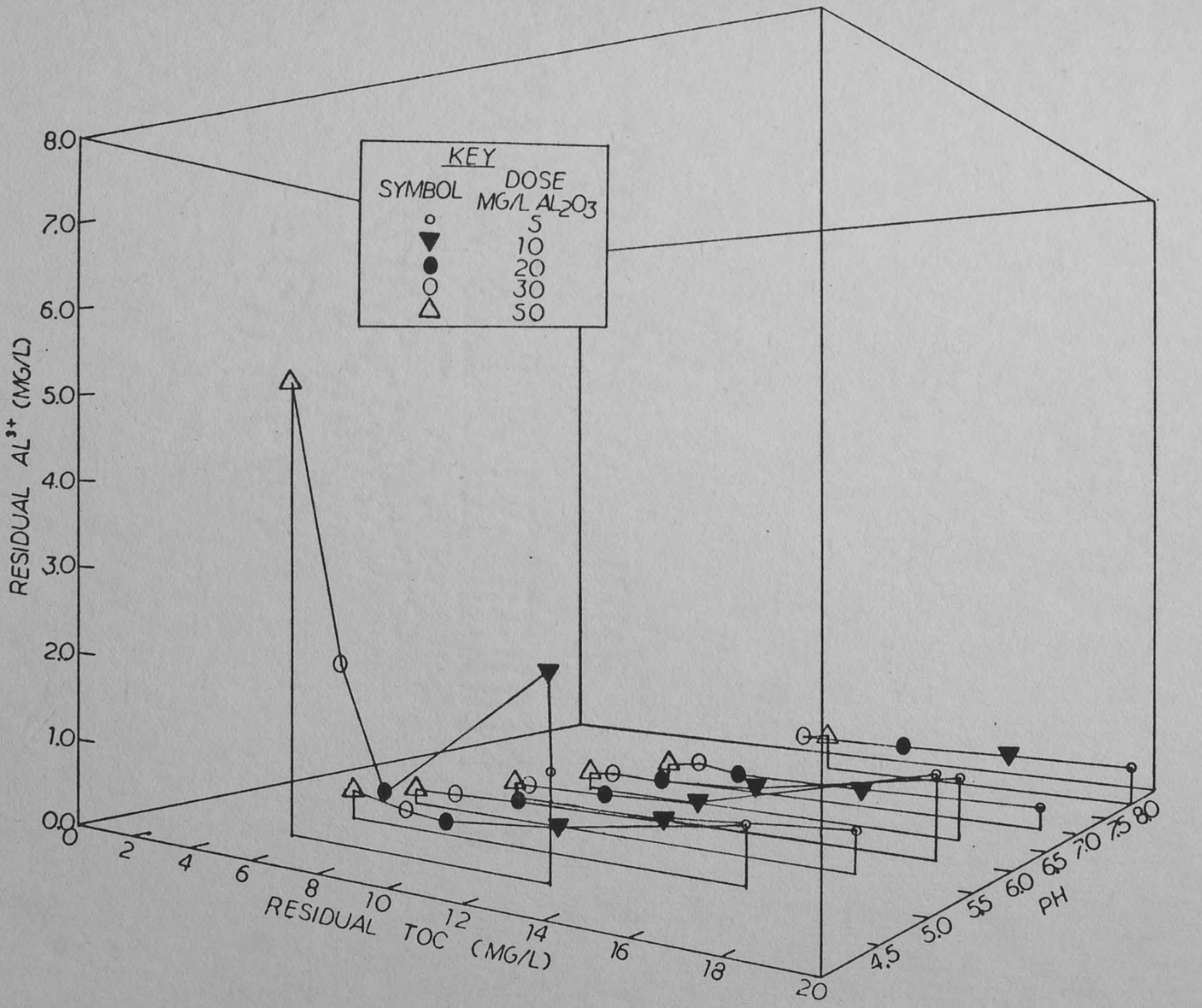

Figure 17. Caloosahatchee River Al^{3+} Versus TOC Versus pH.

TOC for increasing alum dosages is repeated for pHs 6, 7 and 8; however, the levels of TOC residual achieved increase with increasing pH in this range. Minimum TOC reduction (75-100% residual) is observed at pH 8. Above pH 8, the degree of dependence on alum dose to remove TOC is diminished with increasing pH. To illustrate this point, an examination of the range of TOC residual for all alum dosages at each pH 9, 10 and 11 is appropriate. At pH 9, the range of TOC residual is 7.08-8.98 mg/l; at pH 10, 6.72-7.64 mg/l; and at pH 11, 5.30-6.09 mg/l. This information reveals two facts: the span of TOC is shortened with increasing pH and an increasing level of TOC removal is accomplished with increasing pH. The logical conclusion is that TOC reduction in this range is achieved primarily by the water softening process, with a tapering degree of dependence on alum dose as pH increases. Residual aluminum in the pH range of 9-11 increases only slightly, suggesting a polymeric association of $Al(OH)_4^-$ with the hardness floc. In this pH range, incremental TOC removal beyond the levels obtained with no alum added can be attributed to the effects of $Al(OH)_4^-$ functioning as an anionic polymer. Note that minimum residual trace organic content is bimodal, occurring at both pH 5 and pH 11. Minimum TOC residual at pH 5 (5.27 mg/l) is dose-dependent, relying on the action of the $Al(OH)_3$ sweep floc. At pH 11, minimum TOC residual (5.30 mg/l) is slightly dose-dependent, requiring only 1 mg/l as Al_2O_3 to aid (as a polymer) in an additional 8 percent reduction of TOC.

The Lake Washington jar tests demonstrated the most significant deviation from aluminum solubility theory (Figure 16). The coexistence of elevated aluminum and TOC residuals for alum dosages of 10 mg/l as Al_2O_3 and under suggests the formation of aluminum-organic complexes. This trend is a complete one, effective at all pHs. For an alum dose of 1 mg/l as Al_2O_3 ($\equiv$ 0.53 mg/l as Al^{3+}), 67-100% of the total aluminum and 91-100% of the TOC remain in solution. Please note that the term "total aluminum" accounts for the aluminum present in the raw water. For an alum dose of 5 mg/l as Al_2O_3 ($\equiv$ 2.65 mg/l as Al^{3+}), 85-98% of the total aluminum and 85-99% of the TOC remain in solution. For an alum dose of 10 mg/l as Al_2O_3 ($\equiv$ 5.29 mg/l as Al^{3+}), up to 91% (or 5.13 mg/l as Al^{3+}) of the total aluminum and up to 97% of the TOC remain in solution. While soluble aluminum-organic complexation is speculated for alum dosages of 10 mg/l as Al_2O_3 or less, aluminum solubility theory predominates for alum dosages of 20 and 30 mg/l as Al_2O_3. At the higher alum dosages, optimum TOC reduction (24-51% residual) is coupled by minimal residual aluminum (0.30-1.18 mg/l as Al^{3+}) in the pH range of 5-8. Above pH 8, for the higher alum dosages, the relationship between TOC and aluminum residuals is summarized as follows: (1) TOC and aluminum residuals increase to maximum levels at pH 10, numerically 68% and 5.89 mg/l as Al^{3+}; (2) residual levels at pH 11 reflect a downward tendency with respect to the pH 10 levels, numerically as low as 50% TOC remaining and 2.82 mg/l as Al^{3+}. This information would seem to indicate a trend of increasingly soluble $Al(OH)_4^-$ with increasing pH is reversed by a polymeric association of $Al(OH)_4^-$ with the $Mg(OH)_2$ floc at pH 11. At pH 4, TOC reduction is accomplished to an appreciable degree (i.e., 28% TOC residual) and residual aluminum is attained to a maximum level of 8.78 mg/l as Al^{3+}, corresponding to the high alum dosage of 30 mg/l as Al_2O_3. At pH 4, TOC reduction may be associated with a polymeric affiliation of cationic aluminum and negatively charged organic colloidal color.

The Caloosahatchee River tests, carried out over a limited range of pH 4.5-8.0, exhibited limited variability (Figure 17). Over the entire spectrum of alum jar tests, trace organics reduction is shown to be related directly to the alum dose applied. The incremental trace organic reduction for an alum dose of 50 mg/l as Al_2O_3, as compared to 30 mg/l Al_2O_3 dose, is at best 1.6 mg TOC/l, even negative at pH 8. At pH 4.5, high residual aluminum (up to 5.15 mg/l as Al^{3+}) demonstrates an equilibrium relationship of soluble cationic species and $Al(OH)_3$ precipitate in which both exist in significant quantity. For an alum dose of 5 mg/l as Al_2O_3, the highest levels of residual aluminum exist in the pH range of 5-8, up to 0.90 mg/l as Al^{3+}. This observation is similar to that shown for the Lake Washington case for alum dosages of 10 mg/l as Al_2O_3 and under, although not to the same degree.

Aluminum-Organic Complexation

In all four source waters, a minimum level of soluble aluminum is attained at the pH values (5-8) for which $Al(OH)_3$ is predicted by theory. This level appears to be a characteristic of the source water. For those jar tests subjected to alum addition, a summary of the minimum levels of residual aluminum by source for pHs 5 through 8 is provided in Table 6.

TABLE 6

RESIDUAL ALUMINUM IN THE pH RANGE
OF $Al(OH)_3$ PRECIPITATION DOMINANCE

SOURCE	NUMBER OF SAMPLES	ALUMINUM RESIDUAL DATA FOR pH 5-8 (mg/l AS Al^{3+})		
		RANGE	MEAN	SAMPLE STANDARD DEVIATION
Distilled Water	20	0.10-0.41	0.22	0.10
Daytona Beach	20	0.54-1.15	0.75	0.16
Lake Washington	8*	0.30-1.18	0.72	0.35
Caloosahatchee River	24**	0.13-0.35	0.20	0.071

* Lake Washington samples do not include those to which an alum dose of 10 mg/l as Al_2O_3 or under was applied

** Caloosahatchee River samples do not include those to which an alum dose of 5 mg/l as Al_2O_3 was applied

Note that the data withheld (as asterisked) from the sample sets summarized in Table 6 correspond to those instances in which aluminum is presumed to be held in complex with trace organics. Tables 7A and 7B provide an insight into the extent of the link between elevated aluminum and TOC residuals, respectively, as evidence of the formation of aluminum-organic complexes.

TABLE 7

A SUMMARY OF THE EVIDENCE OF ALUMINUM-ORGANIC COMPLEXATION

A. Residual Aluminum Data

SOURCE	ALUM DOSE (mg/l AS Al_2O_3)	NUMBER OF SAMPLES	RESIDUAL ALUMINUM DATA FOR pH 5-8			
			MEAN (mg/l AS Al^{3+})	STANDARD DEVIATION (mg/l AS Al^{3+})	t STATISTIC RELATIVE TO TABLE 6 DATA	t STATISTIC 99% SIGNIFICANCE
Lake Washington	10	4	4.54	0.65	13.5	3.169
Caloosahatchee River	5	6	0.54	0.26	5.9	2.763

B. Residual TOC Data

SOURCE	DOSE SPAN (mg/l AS Al_2O_3)	Δ% TOC RESIDUAL FOR pH 5-8		
		RANGE	MEAN	STANDARD DEVIATION
Lake Washington	0- 5	0.8- 6.2	3.8	2.6
	5-10	-0.4- 5.4	2.4	2.4
	10-20	46.4-60.1	55.4	6.2
	20-30	7.4-10.4	9.1	1.3
Caloosahatchee River	0- 5	10.2-28.5	19.2	7.0
	5-10	15.9-28.3	23.2	4.1
	10-20	12.8-15.6	13.9	1.0

The information presented in Table 7A demonstrates that the aluminum residual data excluded from Table 4 represents uniquely independent sample sets by the t-test analysis. In other words, the t statistics obtained by analysis of the presumably complexed aluminum condition have exceeded the tabular t values corresponding to the 99% level of significance. For a brief summary of the t-test procedure, refer to Appendix B. Table 7B provides a summary of the incremental TOC reduction accomplished (as a percent) over a specified alum dose range. Note that for both the Lake Washington and Caloosahatchee River sources, the greatest incremental reduction of trace organics is achieved with the dose span contiguously below which aluminum complexation is apparent. Below this "threshold" dose span, incremental TOC reduction is limited by some soluble fraction that may be circumstantially associated with an aluminum complex. In the case of the Lake Washington source, this tendency is dramatic. For alum dosages in excess of the threshold dose for each case presented, trace organic reduction is directly related to the aluminum precipitated.

Aluminum Precipitation Versus TOC Removal

A suitable way to correlate the reduction of trace organics with aluminum solubility is to compare the aluminum precipitated with the TOC removed. Tables 8A, 8B and 8C provide a summary of this data for the Daytona Beach, Lake Washington and Caloosahatchee River sources, respectively.

TABLE 8A

ALUMINUM PRECIPITATED VERSUS TOC REMOVED FOR THE DAYTONA BEACH SOURCE, INITIAL: TOC = 10.15 mg/l; Al^{3+} = 0.47 mg/l

ALUM DOSE (mg/l AS Al_2O_3)	PRECIPITATE (mg/l)	pH							
		4	5	6	7	8	9	10	11
30	TOC	3.29	4.88	3.48	3.34	2.55	2.93	3.43	4.56
	Al^{3+}	4.95	15.57	15.39	15.57	15.64	15.38	15.36	15.17
20	TOC	3.82	4.34	3.21	3.26	2.24	3.07	3.13	4.50
	Al^{3+}	1.95	10.14	10.17	10.51	10.37	10.07	10.16	10.03
10	TOC	3.10	3.52	1.78	1.68	1.19	2.95	3.00	4.47
	Al^{3+}	1.39	4.95	4.99	5.22	5.08	4.89	4.83	4.63
5	TOC	2.09	2.44	1.48	1.03	1.35	2.18	2.72	4.65
	Al^{3+}	1.66	1.96	2.25	2.54	2.55	2.30	2.25	2.42
1	TOC	0.77	1.17	0.32	0.41	0.00	1.89	2.69	4.85
	Al^{3+}	0.00	0.19	0.10	0.42	0.41	0.39	0.50	0.00

TABLE 8B

ALUMINUM PRECIPITATED VERSUS TOC REMOVED FOR THE LAKE WASHINGTON SOURCE, INITIAL: TOC = 31.40 mg/l; Al^{3+} = 0.33 mg/l

ALUM DOSE (mg/l AS Al_2O_3)	PRECIPITATE (mg/l)	pH							
		4	5	6	7	8	9	10	11
30	TOC	22.68	23.67	24.03	22.65	18.52	14.34	11.66	15.85
	Al^{3+}	7.44	15.92	15.09	15.63	15.20	13.54	10.33	13.40
20	TOC	19.95	21.34	21.20	19.37	15.50	12.72	10.07	12.96
	Al^{3+}	5.65	10.58	10.40	10.23	9.74	8.31	6.82	8.05
10	TOC	7.05	2.48	2.76	1.63	0.96	1.98	4.16	4.26
	Al^{3+}	4.38	1.57	1.72	0.55	0.50	1.45	2.37	2.65
5	TOC	4.68	0.80	1.94	1.77	0.26	2.76	2.67	3.69
	Al^{3+}	0.36	0.10	0.18	0.08	0.07	0.36	0.45	0.44
1	TOC	2.54	0.81	0.94	1.59	0.00	0.99	2.72	1.85
	Al^{3+}	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00

TABLE 8C

ALUMINUM PRECIPITATED VERSUS TOC REMOVED FOR THE CALOOSAHATCHEE RIVER SOURCE, INITIAL: TOC = 22.28 mg/l; Al^{3+} = 0.20 mg/l

ALUM DOSE (mg/l AS Al_2O_3)	PRECIPITATE (mg/l)	pH						
		4.5	5.0	5.5	6.0	6.5	7.0	8.0
50	TOC	17.27	17.50	17.64	15.64	14.98	13.90	11.29
	Al^{3+}	21.57	26.44	26.54	26.54	26.53	26.53	26.33
30	TOC	15.68	16.00	16.23	15.46	14.46	13.32	12.05
	Al^{3+}	14.08	15.90	15.93	15.95	15.93	15.89	15.77
20	TOC	14.36	14.66	14.25	13.31	12.79	11.62	8.67
	Al^{3+}	10.21	10.66	10.61	10.62	10.64	10.65	10.46
10	TOC	9.78	11.50	11.15	10.30	9.88	8.16	5.81
	Al^{3+}	3.36	5.25	5.28	5.25	5.29	5.34	5.14
5	TOC	9.77	6.36	5.78	3.99	4.28	3.08	2.28
	Al^{3+}	1.70	2.32	2.42	1.95	2.05	2.63	2.48

Figures 18A through 18D have been constructed to illustrate the data presented in tables 8A through 8C for pHs 5, 6, 7 and 8 (the range in which $Al(OH)_3$ precipitation dominance is predicted by theory). Recall that in this range of pH the reduction of TOC is associated most closely with the aluminum hydroxide sweep floc. Other inherent factors play a major role in the organics reduction process at a lower pH (e.g., the adsorption of cationic aluminum onto negatively charged colloids) and at a higher pH (e.g., an association of TOC with precipitating hardness). The plots show that the relationship between aluminum precipitated and organics removed is a stoichiometric one (i.e., linear) within a certain range of alum dose applied. At the reduced alum dosages, a distinct curving trend in the Lake Washington and Caloosahatchee River plots is indicative of the phenomenon of aluminum-organic complexation which is summarized in Table 7. At the higher alum dosages, the incremental amount of TOC removed per aluminum precipitated tapers off. This observation is most demonstrable for the Daytona Beach source in which, at most, 0.54 mg/l of TOC was removed by an alum dose of 30 mg/l as Al_2O_3, in addition to that removed by an alum dose of 20 mg/l as Al_2O_3. Interestingly, though initial TOC for these three sources ranged from 10-31 mg/l, minimum TOC residuals ranged only from 5-7 mg/l. This information may indicate that a common baseline of stubbornly soluble TOC is shared by all three sources.

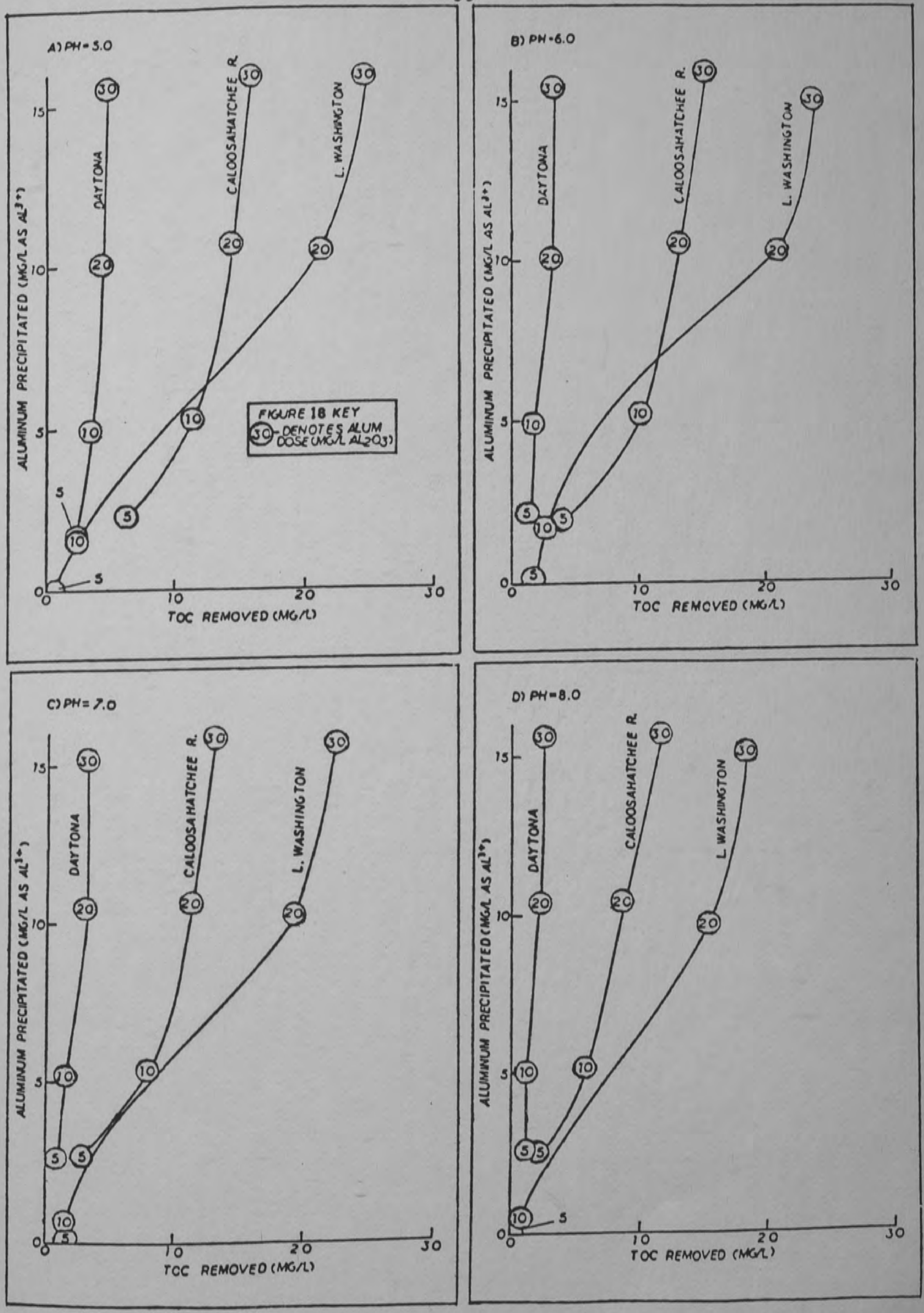

Figure 18. Aluminum Precipitated Versus TOC Removed: (a) pH = 5, (b) pH = 6, (c) pH = 7 and (d) pH = 8.

Identifying Sources of Variation

The following section is devoted to answering several questions pertaining to the alum coagulation process and aluminum solubility vis-a-vis trace organic content and organics reduction. An analysis of variance method (Miller and Freund 1977) has been employed. The goal of this investigation is to identify the root causes of variation in selected data sets. The analysis of variance method, in general, consists of calculating an F statistic for a parameter that is a possible source of variation in a given data set and then comparing it to the tabulated F values. If the calculated F statistic exceeds the tabular F statistic at a given level of significance, the conclusion of the analysis is that the parameter represented by the calculated F statistic is a source of variation for the data set at that stated level of significance. If the calculated F statistic falls below the tabular F value, the null hypothesis cannot be rejected. The null hypothesis suggests that a given parameter is not a source of variation in a data set. A complete description of the method as well as a thorough listing of all data sets for the analyses are given in Appendix C. The format of this presentation may be summarized as follows: (1) a specific topic of investigation is stated as a sub-heading; (2) a brief introduction and statement of purpose follows; (3) the conclusions of the analysis of variance is then presented in tabular form, (4) analysis of variance tables containing pertinent statistical information from which conclusions were drawn follow; and (5) a brief discussion summarizes the results.

The Effects of Initial TOC and pH on Aluminum Residuals. It is understandable that the effects of initial TOC on a given parameter would be difficult to pinpoint. For purposes of this analysis, the effect of the raw water source on aluminum residual is investigated as an indicator of the effects of initial TOC. Recall that the four source waters represent a broad spectrum of TOC content, numerically: 0.05 mg/l in distilled water, 10.2 mg/l in the Daytona Beach water, 22.3 mg/l in the Caloosahatchee River water and 31.4 mg/l in the Lake Washington water. Two ranges of pH (5-8 and 4-11) are examined with respect to this analysis in order to focus in on effects on both the minimum levels of aluminum residuals and the overall experimental aluminum solubility profiles. The goal of this analysis is to demonstrate statistically those experimental conditions in which the raw water source and/or pH is a source of variability in the residual aluminum data. Keep in mind that the raw water source is an indicator of a particular quantity and quality of TOC. The conclusions of this investigation are presented in Table 9, with the analyses of variance for each data set presented in tables 10 through 17. The corresponding data sets for tables 10 through 17 are listed in Appendix C.

The information contained in tables 9 through 17 may be summarized as follows:

1. Over the limited range of pH 5-8, source and not pH is a prime cause of variability of residual aluminum. The calculated F values of 150 and 160 for alum dosages of 10 and 5 mg/l as Al_2O_3, respectively, testify to the high degree of dependence of residual

TABLE 9

CONCLUSIONS OF INVESTIGATIONS INTO THE EFFECTS OF INITIAL TOC AND pH ON RESIDUAL ALUMINUM

ALUM DOSE (mg/l AS Al_2O_3)	pH RANGE	LINKED TO VARIABILITY		REFER TO TABLE #
		SOURCE	pH	
30	5- 8	yes	no	10
30	4-11	no	yes	11
20	5- 8	yes	no	12
20	4-11	no	yes	13
10	5- 8	yes	no	14
10	4-11	yes	no	15
5	5- 8	yes	no	16
5	4-11	yes	no	17

TABLE 10

ANALYSIS OF VARIANCE OF ALUMINUM
RESIDUALS BY SOURCE AND pH
Alum Dose: 30 mg/l as Al_2O_3; pH Range: 5-8

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	3	1.17	0.39	11	6.99	3.86
pH	3	0.22	0.073	2.0	6.99	3.86
Error	9	0.32	0.036			
Total	15	1.71				

TABLE 11

ANALYSIS OF VARIANCE OF ALUMINUM
RESIDUALS BY SOURCE AND pH
Alum Dose: 30 mg/l as Al_2O_3; pH Range: 4-11

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	5.71	2.86	3.0	6.51	3.74
pH	7	210.94	20.13	32	4.28	2.76
Error	14	13.18	0.94			
Total	23	229.83				

TABLE 12

ANALYSIS OF VARIANCE OF ALUMINUM RESIDUALS BY SOURCE AND pH

Alum Dose: 20 mg/l as Al_2O_3; pH Range: 5-8

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	0.95	0.32	7.4	6.99	3.86
pH	3	0.12	0.040	0.93	6.99	3.86
Error	9	0.39	0.043			
Total	15	1.46				

TABLE 13

ANALYSIS OF VARIANCE OF ALUMINUM RESIDUALS BY SOURCE AND pH

Alum Dose: 20 mg/l as Al_2O_3; pH Range: 4-11

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	3.36	1.68	1.4	6.51	3.74
pH	7	97.94	13.99	12	4.28	2.76
Error	14	16.71	1.19			
Total	23	118.01				

TABLE 14

ANALYSIS OF VARIANCE OF ALUMINUM RESIDUALS BY SOURCE AND pH

Alum Dose: 10 mg/l as Al_2O_3; pH Range: 5-8

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	3	52.86	17.62	150	6.99	3.86
pH	3	0.29	0.097	0.83	6.99	3.86
Error	9	1.05	0.12			
Total	15	54.20				

TABLE 15

ANALYSIS OF VARIANCE OF ALUMINUM RESIDUALS BY SOURCE AND pH

Alum Dose: 10 mg/l as Al_2O_3; pH Range: 4-11

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	38.64	19.32	10	6.51	3.74
pH	7	4.24	0.61	0.32	4.28	2.76
Error	14	27.06	1.93			
Total	23	69.94				

TABLE 16

ANALYSIS OF VARIANCE OF ALUMINUM RESIDUALS BY SOURCE AND pH

Alum Dose: 5 mg/l as Al_2O_3; pH Range: 5-8

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	3	18.00	6.00	160	6.99	3.86
pH	3	0.16	0.053	1.4	6.99	3.86
Error	9	0.34	0.038			
Total	15	18.50				

TABLE 17

ANALYSIS OF VARIANCE OF ALUMINUM RESIDUALS BY SOURCE AND pH

Alum Dose: 5 mg/l as Al_2O_3; pH Range: 4-11

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	21.94	10.97	55	6.51	3.74
pH	7	1.65	0.24	1.2	4.28	2.76
Error	14	2.80	0.20			
Total	23	26.39				

aluminum on the coagulability of the initial TOC. Recall that the coagulation efficiency of the Lake Washington and Caloosahatchee River raw waters is limited by complex formation at reduced alum dosages. For the alum dosages of 20 mg/l as Al_2O_3 and above, overall coagulation efficiency is greater for all source waters, yet the residual aluminum levels are nonetheless affected by the source water. These minimum levels of residual aluminum might well also be indicative of a particular quantity and coagulability of initial TOC.

2. Over the broader range of pH (4-11), and alum dosages of 20 mg/l as Al_2O_3 and above, the aluminum residual data is less distinguishable by source as it begins to approximate the theoretical aluminum solubility models characterized by a high degree of pH dependency.

3. Over the broader range of pH (4-11), and reduced alum dosages, the aluminum residual data is heavily weighted by the Lake Washington case in which aluminum is held in soluble complex form. For this reason, the variation by pH evident in the other sources is less significant.

The Effects of Alum Dose and pH on TOC Residuals. The goal of this analysis is to demonstrate statistically by raw water source whether or not alum dose and/or pH is a factor in the variability of TOC residual data. The conclusions of this investigation are presented in Table 18, with the analyses of variance for each data set presented in tables 19 through 21. The corresponding data sets for tables 19 through 21 are listed in Appendix C.

TABLE 18

CONCLUSIONS OF INVESTIGATIONS INTO THE EFFECTS OF ALUM DOSE AND pH ON RESIDUAL TOC

SOURCE	LINKED TO VARIABILITY		REFER TO TABLE #
	ALUM DOSE	pH	
Daytona Beach	yes	yes	19
Lake Washington	yes	no	20
Caloosahatchee River	yes	yes	21

TABLE 19

ANALYSIS OF VARIANCE OF TOC RESIDUALS BY ALUM DOSE AND pH

Source: Daytona Beach

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Dose	5	36.45	7.29	19	3.61	2.49
pH	7	42.57	6.08	16	3.21	2.29
Error	35	13.76	0.39			
Total	47	92.78				

TABLE 20

ANALYSIS OF VARIANCE OF TOC RESIDUALS BY ALUM DOSE AND pH
Source: Lake Washington

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Dose	5	2741.05	548.21	80	3.61	2.49
pH	7	104.07	14.87	2.2	3.21	2.29
Error	35	239.78	6.85			
Total	47	3084.90				

TABLE 21

ANALYSIS OF VARIANCE OF TOC RESIDUALS BY ALUM DOSE AND pH
Source: Caloosahatchee River

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Dose	4	511.81	127.95	160	4.22	2.78
pH	6	115.52	19.25	25	3.67	2.51
Error	24	18.78	0.78			
Total	34	646.11				

The information contained in tables 18 through 21 may be summarized as follows:

1. TOC residual is strongly dose-dependent, but not equally so for each source. This dependence is strongest in the Caloosahatchee River case and weakest in the Daytona Beach case (which was limited in organic content initially).

2. The TOC residual dependence on pH for the Lake Washington case has not been confirmed by the analysis of variance due to the reduced alum dosages which resulted in complexation. The F value in this case is quite near the tabular F for the 95% level of significance.

3. In general, TOC reduction is very pH-dependent, particularly for dosages of 20 and 30 mg/l as Al_2O_3.

<u>The Effects of Initial TOC and Alum Dose on Percent TOC Removal</u>. As in a previous discussion, the effects of initial TOC are here considered to be isolated by source, an indicator. The goal of this investigation is to determine whether the raw water source has a statistically verifiable effect on the alum dose to remove TOC on a percent basis. The conclusions of this investigation are presented in Table 22, with the analyses of variance for each data set presented in tables 23 through 26. The corresponding sets for tables 23 through 26 are listed in Appendix C.

TABLE 22

CONCLUSIONS OF INVESTIGATIONS INTO THE EFFECTS OF INITIAL TOC AND ALUM DOSE ON PERCENT TOC REMOVAL

pH	LINKED TO VARIABILITY		REFER TO TABLE #
	SOURCE	ALUM DOSE	
5	no	yes	23
6	no	yes	24
7	no	yes	25
8	no	yes	26

TABLE 23

ANALYSIS OF VARIANCE OF PERCENT TOC REMOVAL BY SOURCE AND ALUM DOSE pH: 5.0

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	729	364	1.5	10.90	5.14
Dose	3	4450	1483	6.1	9.78	4.76
Error	6	1457	243			
Total	11	6636				

TABLE 24

ANALYSIS OF VARIANCE OF PERCENT TOC REMOVAL BY SOURCE AND ALUM DOSE

pH: 6.0

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	1168	584	2.5	10.90	5.14
Dose	3	4591	1530	6.5	9.78	4.76
Error	6	1412	235.3			
Total	11	7171				

TABLE 25

ANALYSIS OF VARIANCE OF PERCENT TOC REMOVAL BY SOURCE AND ALUM DOSE

pH: 7.0

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	676	338	1.8	10.90	5.14
Dose	3	4336	1445	7.7	9.78	4.76
Error	6	1125	188			
Total	11	6137				

TABLE 26

ANALYSIS OF VARIANCE OF PERCENT
TOC REMOVAL BY SOURCE AND ALUM DOSE
pH: 8.0

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F VALUE	TABULAR F (99%)	TABULAR F (95%)
Source	2	431	216	1.3	10.90	5.14
Dose	3	2978	993	6.1	9.78	4.76
Error	6	980	163			
Total	11	4389				

The information contained in tables 22 through 26 may be summarized as follows:

1. Percent TOC removal is shown to be statistically linked to alum dose at the 95% level of significance for the pH range of 5-8. As already demonstrated, TOC removal is more correctly related to the quantity of aluminum precipitated in this pH range.

2. Percent TOC removal cannot be statistically linked to the initial TOC of the raw water. In other words, initial TOC does not demonstrate a conclusive effect on the alum dose to remove TOC on a percent basis.

3. For the range of pH under consideration (5-8), there is little difference in the level of significance at which percent TOC removal is dependent on alum dose.

The Effects of the Softening Process

The role of the softening process in trace organics reduction and as a vehicle for $Al(OH)_4^-$ adsorption has been documented throughout. Table 27 provides a summary of the hardness parameters measured in the distilled water, Daytona Beach and Lake Washington sources for the jar tests conducted with no alum addition under non-sheared mixing conditions.

TABLE 27

HARDNESS ANALYSIS SUMMARY
Alum Dose: Zero

pH	RESIDUAL HARDNESS (mg Me^{++}/l)					
	DISTILLED WATER		DAYTONA BEACH		LAKE WASHINGTON	
	Ca^{++}	Mg^{++}	Ca^{++}	Mg^{++}	Ca^{++}	Mg^{++}
6.0	3.59	BDL	100	9.51	47.4	7.82
7.0	7.44	0.01	99.9	9.53	69.9	7.79
8.0	1.95	BDL	99.9	9.47	99.8	7.88
9.0	2.70	BDL	99.3	9.27	99.9	7.81
10.0	23.7	0.04	28.6	8.84	99.9	7.92
11.0	17.1	0.02	99.9	3.54	99.8	7.73

The data presented in Table 27 is indicative of several points of interest. In the Daytona Beach source, calcium precipitation is achieved at pH 10 to a level of 28.6 mg/l as Ca^{++}. Similarly, magnesium precipitation is achieved to a minimum residual level of

3.54 mg/l as Mg^{++} at pH 11. In contrast, the Lake Washington source demonstrates a strong tendency to retain hardness ions in soluble form. In both the Daytona Beach and Lake Washington sources, the available hardness should be considered sufficient to provide ample adsorption sites for $Al(OH)_4^-$ in its function as an anionic polymer. The Daytona Beach hardness data is consistent with previous statements linking trace organics removal to the softening process at pHs 10 and 11. Trace organics reduction in the Lake Washington source at pHs 10 and 11 may also be linked to the softening process, but is alum dose-dependent. The fact that aluminum is predictably anionic at the high pHs suggests that, in the Lake Washington source, $Al(OH)_4^-$ is instrumental as a polymer in the water softening and TOC removal processes.

Aluminum Solubility by Source

In order to sum up the net effects of trace organics content and trace organics reduction processes on aluminum solubility, a pC versus pH analysis of residual aluminum by raw water source is presented for each alum dose. The goal of this presentation is to provide a practical working model of aluminum solubility by source which accentuates the logarithmic relationship of soluble aluminum with pH. To assess the extent of the departure of the following models from the theoretical models for aluminum solubility, the reader may want to refer back to figures 1 and 2, the theoretical models.

Figure 19 provides an insight into the background levels of soluble aluminum at each pH for the distilled water, Daytona Beach and Lake Washington sources. In the Lake Washington source, this background level is steady over the entire pH range. In the Daytona Beach source, background levels vary somewhat with pH, reaching a minimum level at pH 10, at which calcium precipitation has been demonstrated. This would tend to suggest a polymeric affiliation of residual aluminum with the $CaCO_3$ precipitate. In the distilled water source, the background levels of aluminum reflect no more than an inherent source of error for the jar test procedure.

In Figure 20, the levels of soluble aluminum present upon an alum dose of 1 mg/l as Al_2O_3 are shown. The morphology of these solubility profiles is similar to that of the background profiles except for the fact that aluminum residual is greater in every instance.

For the net effects of organic content and organic reduction on aluminum solubility resulting from an alum dose of 5 mg/l, see Figure 21. In this figure, all four source waters are represented. Note the broad range of variation in soluble aluminum by source. The near complete solubilization of the complexed aluminum in the Lake Washington source is aptly depicted. Contrast this to the distilled water source which exhibits a well-defined pH range of minimum aluminum solubility. The Daytona Beach source demonstrates the beginnings of an aluminum solubility profile characterized by a minimum residual at pHs 7 and 8. Again, the decidedly downward trend

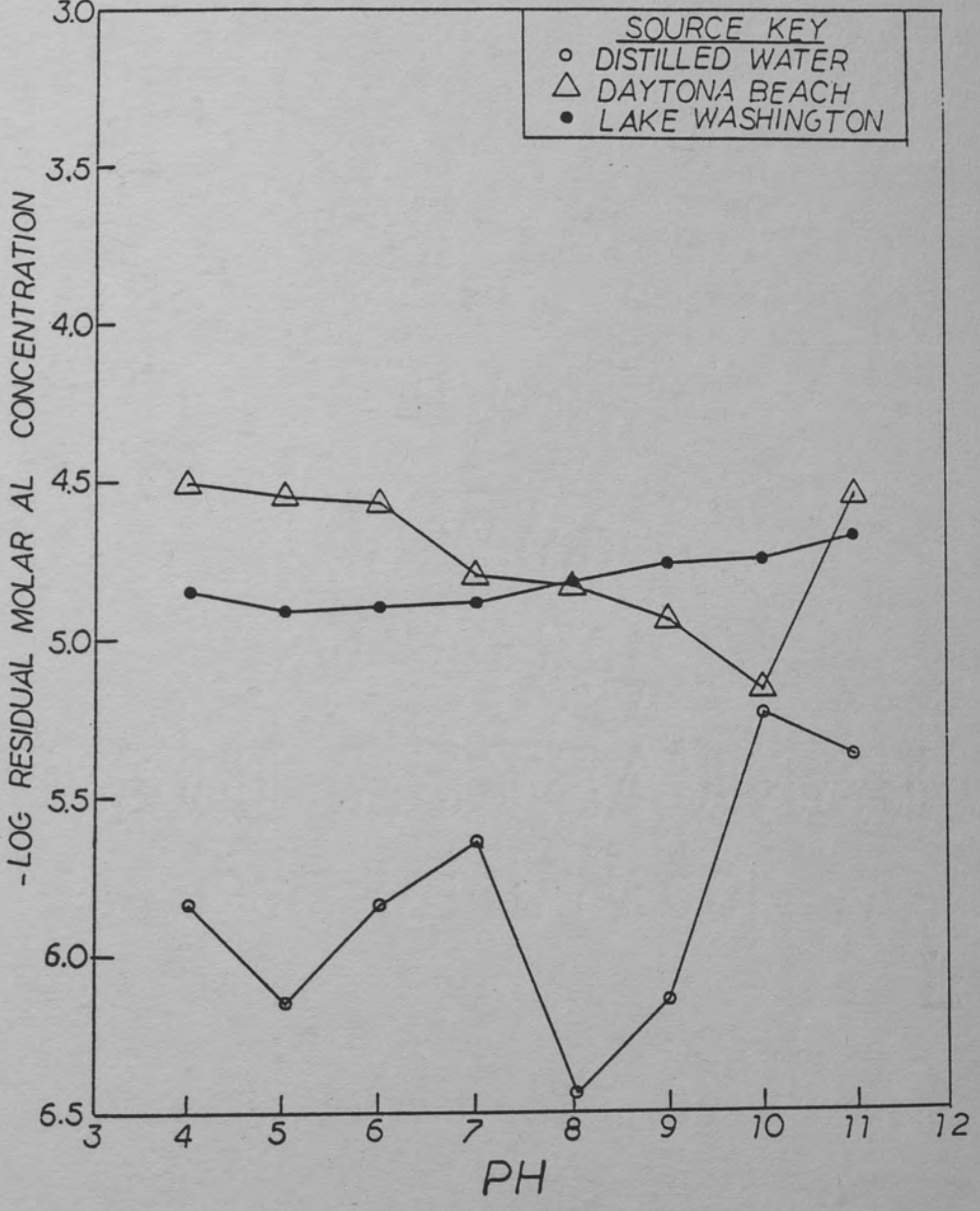

Figure 19. pC Versus pH for Alum Jars: Dose = 0 mg/l Al_2O_3 (Non-Sheared Condition).

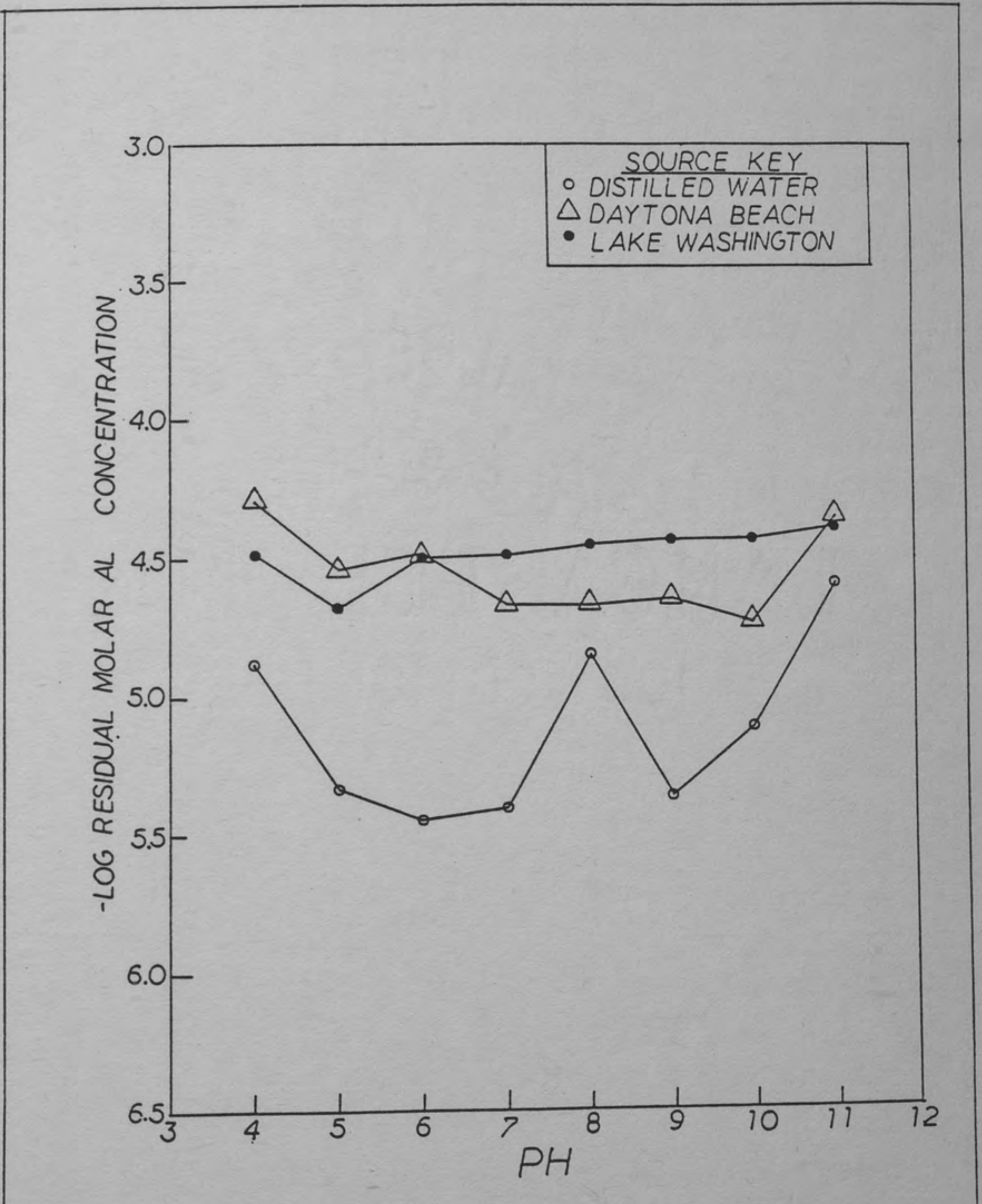

Figure 20. pC Versus pH for Alum Jars: Dose = 1 mg/l Al_2O_3 (Non-Sheared Condition).

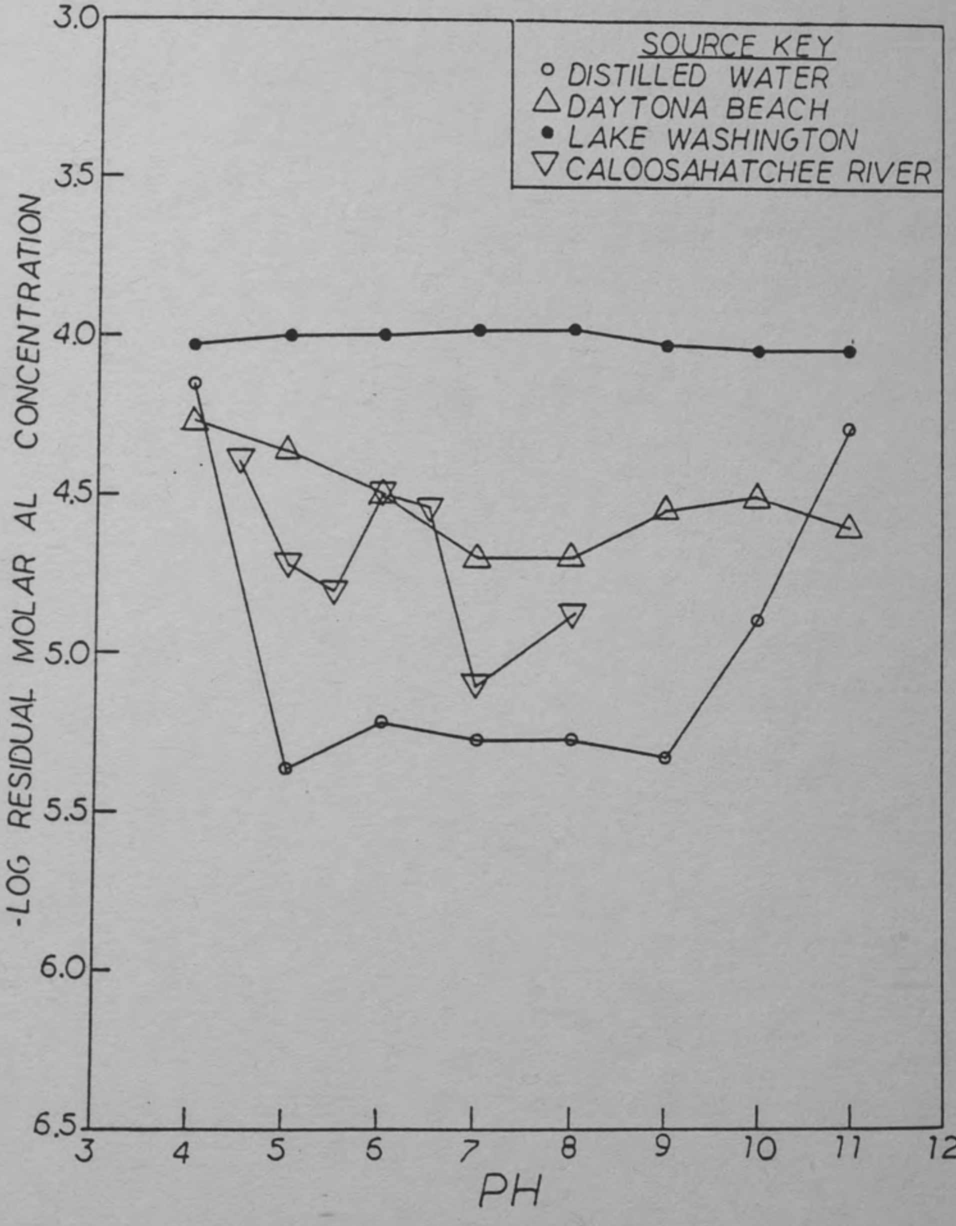

Figure 21. pC Versus pH for Alum Jars: Dose = 5 mg/l Al_2O_3 (Non-Sheared Condition).

of soluble aluminum at pHs 10 and 11 for this source reflects some measure to adsorption of $Al(OH)_4^-$ onto hardness precipitates. Recall that the Caloosahatchee River water tests conducted at this alum dose (i.e., 5 mg/l as Al_2O_3) produced a statistically verifiable difference which has been attributed to soluble complexed aluminum. The effects of the aluminum complexation are obviously contrary to solubility theory, but are not consistent over the entire pH range for this source.

In Figure 22, the experimental aluminum solubility conditions resulting from an alum dose of 10 mg/l as Al_2O_3 is characterized by more pronounced solubility profiles with the exception of the Lake Washington source. An identifiable minimum level of residual aluminum in the pH range of 5-8 is shown for the distilled water, Daytona Beach and Caloosahatchee River sources, while the Lake Washington source again appears to retain aluminum in soluble complexed form over the entire range of pH.

Figures 23 and 24 show the experimental aluminum solubility profiles related to alum dosages of 20 and 30 mg/l as Al_2O_3, respectively. These two figures demonstrate sufficient similarities to warrant a common discussion. In both instances, the F test analysis has shown that residual aluminum cannot be conclusively linked to source over the entire pH range, but can be over the pH range of 5-8. While the tendency of the aluminum solubility profile is to conform to some common theory, the raw water TOC quality, TOC quantity, coagulability and characteristic hardness work together

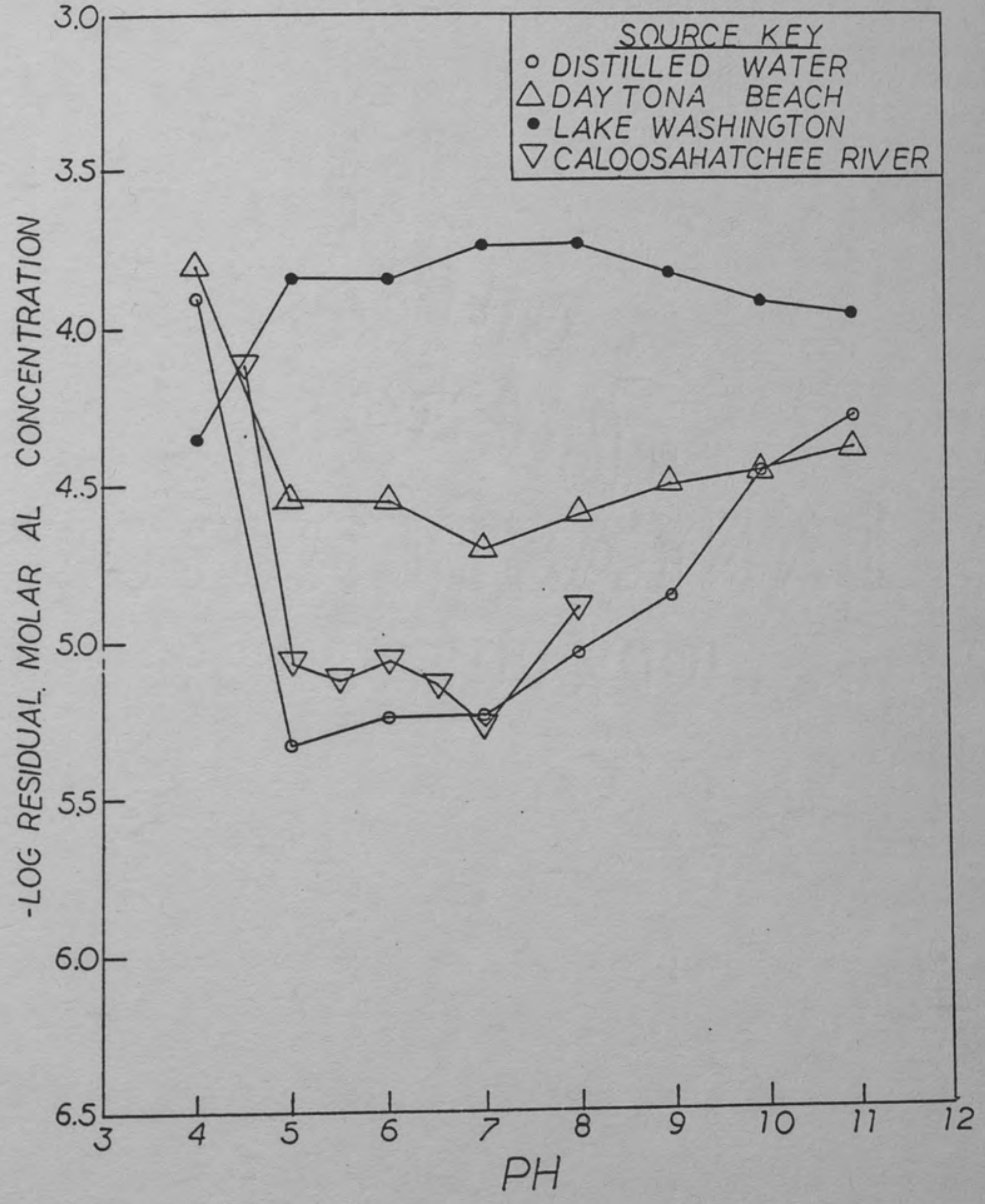

Figure 22. pC Versus pH for Alum Jars: Dose = 10 mg/l Al_2O_3 (Non-Sheared Condition).

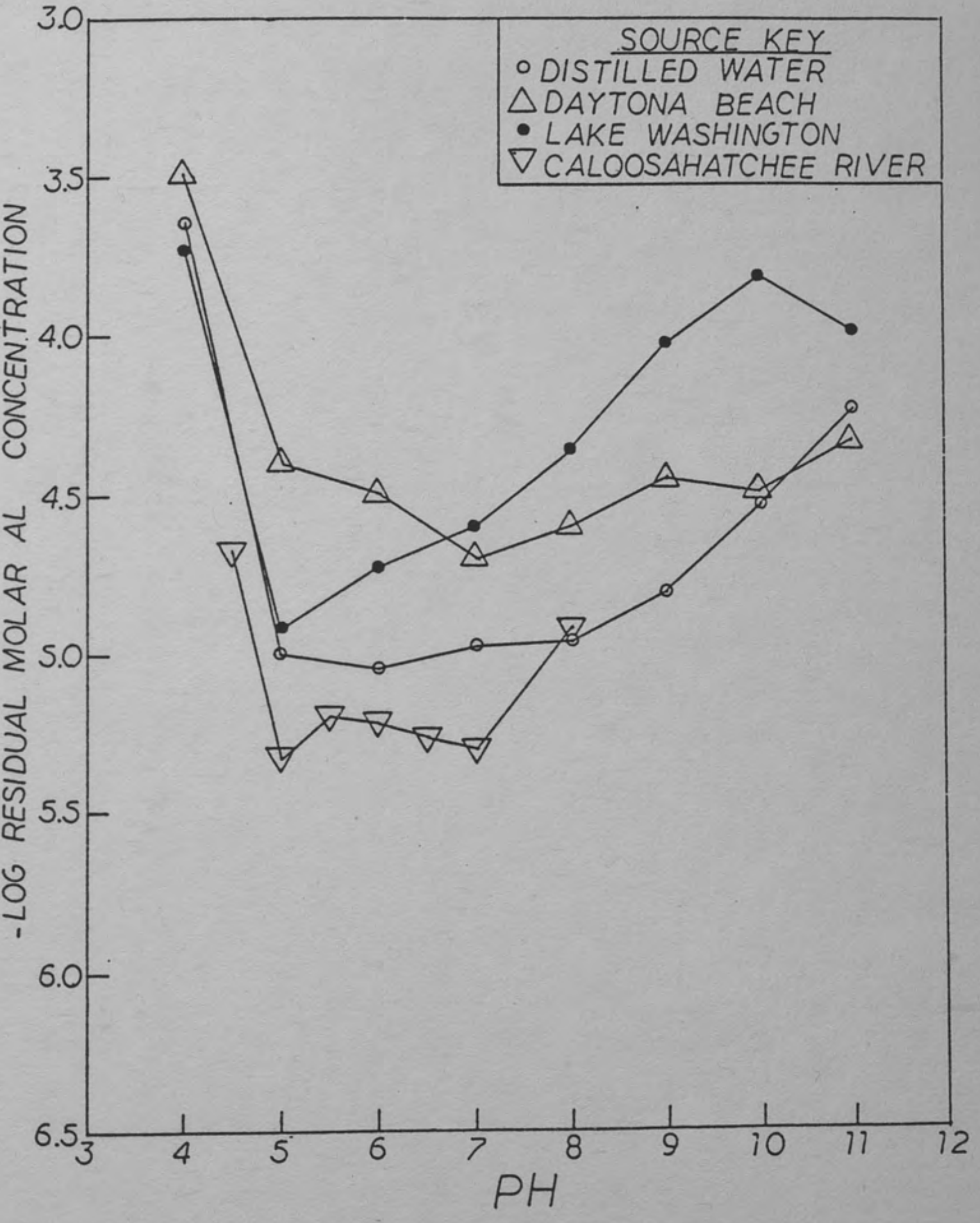

Figure 23. pC Versus pH for Alum Jars: Dose = 20 mg/l Al_2O_3 (Non-Sheared Condition).

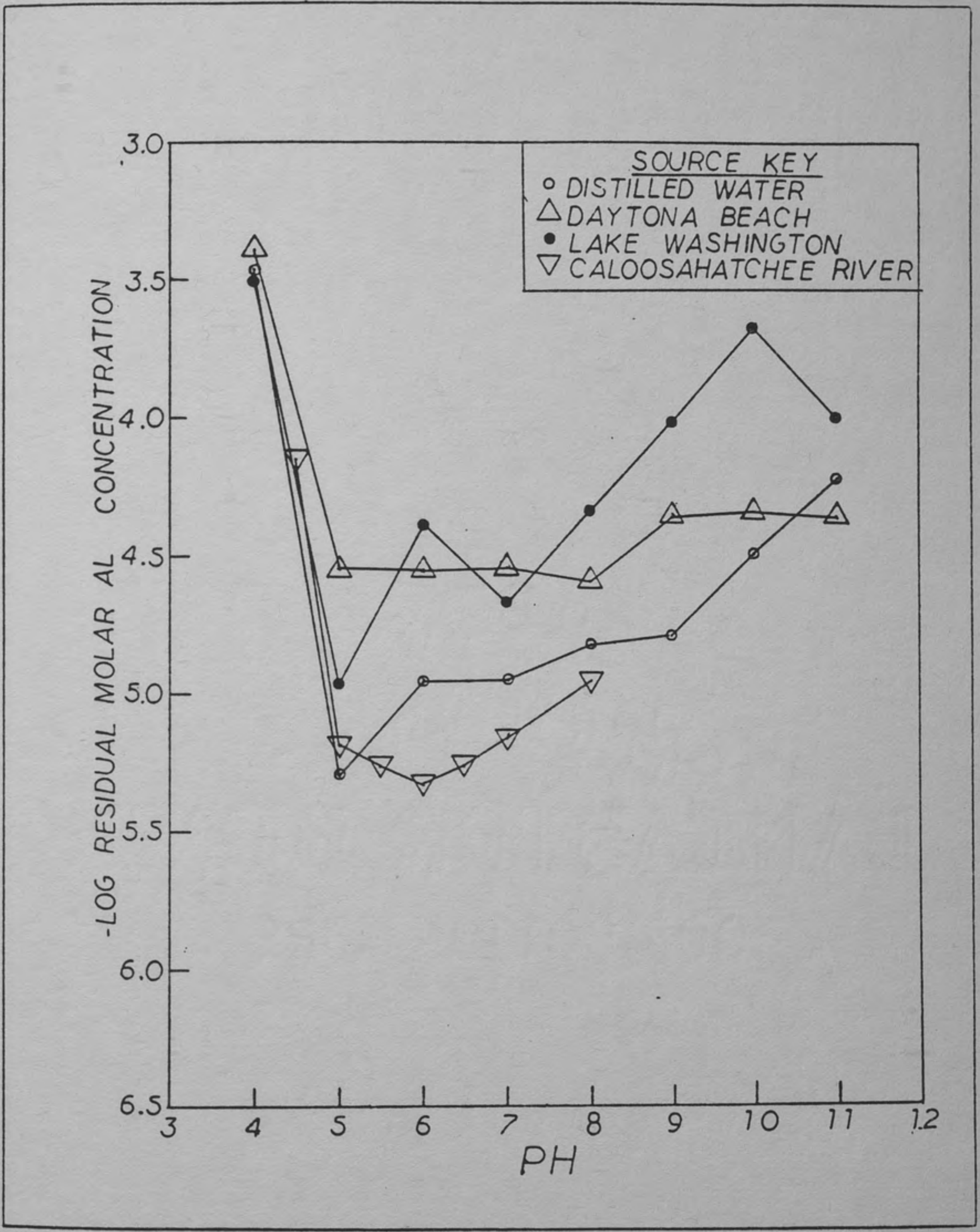

Figure 24. pC Versus pH for Alum Jars: Dose = 30 mg/l Al_2O_3 (Non-Sheared Condition).

to render each source unique with respect to aluminum solubility. In the pH range of 5-8, the Caloosahatchee River water and the distilled water provide the best conditions for minimizing residual aluminum. The Daytona Beach source is unique in that residual aluminum in this pH range is elevated at a consistent level, while the other sources demonstrated a well-defined pH of minimum residual aluminum. Above pH 8, aluminum solubility theory would predict much higher levels of soluble aluminum as $Al(OH)_4^-$; however, residual aluminum levels from each source exhibit a unique departure from theory. In all sources, reduced levels of soluble aluminum at the high pHs may be explained by a polymeric affiliation of $Al(OH)_4^-$ with hardness precipitates. (Note: In distilled water, calcium is supplied by the lime added for pH control, and alkalinity is supplied by atmospheric CO_2.) The Daytona Beach source exhibits the most dramatic tendency of reduced aluminum residuals at the high pHs; note the "flattening" of the solubility profile above pH 8 for this source. The Lake Washington source displays a downward trend of soluble aluminum at pH 11, suggesting an association of $Al(OH)_4^-$ with magnesium hydroxide floc. Below pH 5, cationic solubility is dominant for each experimental solubility profile.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Founded on the results of this study into the effects of trace organic removal processes on aluminum solubility, the following conclusions were drawn:

1. Theoretical aluminum solubility models are not suitable for predicting precise solubility levels resulting from alum coagulation and lime softening treatment processes. They do, however, provide a starting point for predicting relative high and low solubility levels with varying pH. This statement is accurate if the aluminum to organic substance ratio is sufficiently high as to result in the predominance of insoluble constituents and/or complexes.

2. Over the pH range of 4-11 and in the absence of soluble aluminum-organic complexation, aluminum solubility exhibits a predictably strong pH dependence with only a weak degree of variability due to the initial TOC of the raw water.

3. Minimum aluminum residual levels in the pH range of 5-8 are linked to the coagulability of the raw water, but are not related to pH.

4. Aluminum-organic complex formation is believed to be dependent on both the quantity and source of organic matter present.

Over the pH 5-8 range, pH is not considered to be a statistically significant source of variation.

5. TOC reduction is strongly alum-dependent, but not equally so for each source; again, this is reflective of a particular quantity and source of TOC. The nature of this relationship differs in the alum coagulation and lime softening processes.

6. Initial TOC source does not demonstrate a conclusive effect on the alum dose to remove TOC on a percent basis.

7. A stoichiometric relationship between TOC removed and aluminum precipitated exists in the pH range (5-8) of minimum aluminum solubility up to a characteristic TOC residual level (of 5-7 mg/l for this study) which remains stubbornly soluble.

Recommendations

Future studies into the effects of organics removal processes on aluminum solubility should include a comparison of waters of similar TOC content to isolate the residual aluminum variability due to type of TOC.

Under the threshold ratio of aluminum to organic matter at which these contaminants are soluble, experimental aluminum solubility must be treated on a case-by-case basis; above this level, aluminum solubility as affected by alum coagulation and lime softening would likely fall within a range defined by figures 23 and 24, recommended as practical models.

APPENDICES

APPENDIX A

BECKMAN SPECTRASPAN V PRECISION AND ACCURACY

Precision and accuracy data for the Beckman SpectraSpan V with ICP source is summarized in tables 28 (accuracy data) and 29 (precision data). This data is based on fifteen "spiked" samples of known aluminum content run against a high standard of 10 mg/l and a low standard of 0 mg/l. The results demonstrate accuracy in the range of 95-100% of the known value, and precision within ± 2% of the mean value for possible combinations of sample replicates.

TABLE 28

ACCURACY DATA

SAMPLE NO.	1.00 mg/l Al		2.50 mg/l Al		5.00 mg/l Al	
	OUTPUT	% ACCURACY	OUTPUT	% ACCURACY	OUTPUT	% ACCURACY
1	1.04	96.0	2.43	97.2	5.04	99.2
2	1.01	99.0	2.41	96.4	5.09	98.2
3	1.03	97.0	2.41	96.4	4.97	99.4
4	1.00	100	2.39	95.6	4.99	99.8
5	1.02	98.0	2.38	95.2	5.00	100

TABLE 29

PRECISION DATA

SAMPLE NO. COMBINATIONS	± % ABOUT COMBINATION MEAN		
	1.00 mg/l Al	2.50 mg/l Al	5.00 mg/l Al
1 and 2	1.46	0.41	0.49
1 and 3	0.48	0.41	0.70
1 and 4	1.96	0.83	0.50
1 and 5	0.97	1.04	0.40
2 and 3	0.98	0.00	1.19
2 and 4	0.50	0.42	0.99
2 and 5	0.49	0.63	0.89
3 and 4	1.48	0.42	0.20
3 and 5	0.49	0.63	0.30
4 and 5	0.99	0.21	0.10

APPENDIX B

STATISTICAL ANALYSES

t-Test Method (from Miller and Freund 1977)

$$t = \frac{(\overline{X}_1 - \overline{X}_2)}{\sqrt{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}} \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}}$$

where:

X_1 = mean sample set "1"

X_2 = mean sample set "2"

n_1 = number of samples in set "1"

n_2 = number of samples in set "2"

S_1 = standard deviation of sample set "1"

S_2 = standard deviation of sample set "2"

Significance: If calculated t value is less than tabulated t value (corresponding to a predetermined level of significance), the null hypothesis cannot be rejected at that level of significance. If calculated t value is greater than or equal to the tabulated t value, the null hypothesis can be rejected at that level of significance. The null hypothesis is that the two sample sets are from the same population.

APPENDIX C

STATISTICAL ANALYSIS RELATING TO TABLES 9-26

Analysis of Variance
Method (from Miller and Freund 1977)

$$C = \frac{T_{..}^{2}}{ab}$$

$$SST = \sum_{i=1}^{a} \sum_{j=1}^{b} y^{2}_{ij} - C$$

$$SS(Tr) = \frac{\sum_{i=1}^{a} T^{2}_{i.}}{b} - C$$

$$SS(Bl) = \frac{\sum_{i=1}^{b} T^{2}_{.j}}{a} - C$$

$$SSE = SST - SS(Tr) - SS(Bl)$$

where:

y = observation "y"

$T_{i.}$ = sum of b observations for ith treatment

$T_{.j}$ = sum of a observations in the jth block

$T_{..}$ = the grand total of all observations

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	F
Treatments	a-1	SS(Tr)	$MS(Tr) = \frac{SS(Tr)}{a-1}$	$\frac{MS(Tr)}{MSE}$
Blocks	b-1	SS(Bl)	$MS(Bl) = \frac{SS(Bl)}{b-1}$	$\frac{MS(Bl)}{MSE}$
Error	(a-1)(b-1)	SSE	$\frac{SSE}{(a-1)(b-1)}$	
Total	ab-1	SST		

Data Set for Table 10: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 30 mg/l as Al_2O_3				
	5.0	6.0	7.0	8.0	TOTALS
Distilled Water	0.14	0.31	0.31	0.41	1.17
Daytona Beach	0.78	0.96	0.78	0.71	3.23
Lake Washington	0.30	1.13	0.59	1.02	3.04
Caloosahatchee River	0.18	0.13	0.19	0.31	0.81
Totals	1.40	2.53	1.87	2.45	8.25

Data Set for Table 11: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 30 mg/l as Al_2O_3								
	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	TOTALS
Distilled Water	9.53	0.14	0.31	0.31	0.41	0.45	0.88	1.65	13.68
Daytona Beach	11.4	0.78	0.96	0.78	0.71	0.98	0.99	1.18	17.77
Lake Washington	8.78	0.30	1.13	0.59	1.02	2.68	5.89	2.82	23.21
Totals	29.71	1.22	2.40	1.68	2.14	4.10	7.76	5.65	54.66

Dat Set for Table 12: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 20 mg/l as Al_2O_3)				
	5.0	6.0	7.0	8.0	TOTALS
Distilled Water	0.28	0.25	0.29	0.30	1.12
Daytona Beach	0.91	0.88	0.54	0.68	3.01
Lake Washington	0.34	0.52	0.69	1.18	2.73
Caloosahatchee River	0.13	0.17	0.14	0.33	0.77
Totals	1.66	1.82	1.66	2.49	7.63

Data Set for Table 13: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 20 mg/l as Al_2O_3								
	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	TOTALS
Distilled Water	6.43	0.28	0.25	0.29	0.30	0.42	0.81	1.56	10.34
Daytona Beach	9.10	0.91	0.88	0.54	0.68	0.98	0.89	1.02	15.00
Lake Washington	5.27	0.34	0.52	0.69	1.18	2.61	4.10	2.87	17.58
Totals	20.80	1.53	1.65	1.52	2.16	4.01	5.80	5.45	42.92

Data Set for Table 14: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 10 mg/l as Al_2O_3				
	5.0	6.0	7.0	8.0	TOTALS
Distilled Water	0.13	0.16	0.16	0.25	0.70
Daytona Beach	0.81	0.77	0.54	0.68	2.80
Lake Washington	4.06	3.91	5.08	5.13	18.18
Caloosahatchee River	0.24	0.24	0.15	0.35	0.98
Totals	5.24	5.08	5.93	6.41	22.66

Data Set for Table 15: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 10 mg/l as Al$_2$O$_3$								
	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	TOTALS
Distilled Water	3.42	0.13	0.16	0.16	0.25	0.39	0.95	1.43	6.89
Daytona Beach	4.37	0.81	0.77	0.54	0.68	0.87	0.93	1.13	10.10
Lake Washington	1.25	4.06	3.91	5.08	5.13	4.18	3.26	2.98	29.85
Totals	9.04	5.00	4.84	5.78	6.06	5.44	5.14	5.54	46.84

Data Set for Table 16: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 5 mg/l as Al$_2$O$_3$				
	5.0	6.0	7.0	8.0	TOTALS
Distilled Water	0.12	0.17	0.15	0.15	0.59
Daytona Beach	1.15	0.86	0.57	0.56	3.14
Lake Washington	2.88	2.80	2.90	2.91	11.49
Caloosahatchee River	0.53	0.90	0.22	0.37	2.02
Totals	4.68	4.73	3.84	3.99	17.24

Data Set for Table 17: Aluminum Residuals (mg/l as Al^{3+})

BLOCKS (SOURCE)	TREATMENTS (pH) FOR ALUM DOSE = 5 mg/l as Al_2O_3								
	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	TOTALS
Distilled Water	1.95	0.12	0.17	0.15	0.15	0.13	0.36	1.45	4.48
Daytona Beach	1.45	1.15	0.86	0.57	0.56	0.81	0.86	0.69	6.95
Lake Washington	2.62	2.88	2.80	2.90	2.91	2.62	2.53	2.54	21.80
Totals	6.02	4.15	3.83	3.62	3.62	3.56	3.75	4.68	33.23

Data Set for Table 19: TOC Residuals (mg/l)

BLOCKS (ALUM DOSE) (mg/l as Al_2O_3)	TREATMENTS (pH) FOR DAYTONA BEACH SOURCE								
	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	TOTALS
30	6.86	5.27	6.67	6.81	7.60	7.22	6.72	5.59	52.74
20	6.33	5.81	6.94	6.89	7.91	7.08	7.02	5.65	53.63
10	7.05	6.63	8.37	8.47	8.96	7.20	7.15	5.68	59.51
5	8.06	7.71	8.67	9.12	8.80	7.97	7.43	5.50	63.26
1	9.38	8.98	9.83	9.74	10.22	8.26	7.46	5.30	69.17
0	9.57	9.35	9.37	10.12	9.71	8.98	7.64	6.09	70.83
Totals	47.25	43.75	49.85	51.15	53.20	46.71	43.42	33.81	369.14

Data Set for Table 20: TOC Residuals (mg/l)

BLOCKS (ALUM DOSE) (mg/l as Al_2O_3)	TREATMENTS (pH) FOR LAKE WASHINGTON SOURCE								
	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	TOTALS
30	8.72	7.73	7.37	8.75	12.88	17.06	19.74	15.55	97.80
20	11.45	10.06	10.20	12.03	15.90	18.68	21.33	18.44	118.09
10	24.35	28.92	28.64	29.77	30.44	29.42	27.24	27.17	225.95
5	26.72	30.60	29.46	29.63	31.14	28.64	28.73	27.71	232.63
1	28.86	30.59	30.46	29.81	31.70	30.41	28.68	29.55	240.06
0	30.30	30.65	29.52	30.73	29.96	30.46	29.61	30.59	241.82
Totals	130.40	138.55	135.65	140.72	152.02	154.67	155.33	149.01	1156.35

Data Set for Table 21: TOC Residuals (mg/l)

BLOCKS (ALUM DOSE) (mg/l as Al_2O_3)	TREATMENTS (pH) FOR CALOOSAHATCHEE RIVER SOURCE							
	4.5	5.0	5.5	6.0	6.5	7.0	8.0	TOTALS
50	5.01	4.78	4.64	6.64	7.30	8.38	10.99	47.74
30	6.60	6.28	6.05	6.82	7.82	8.96	10.23	52.76
20	7.92	7.62	8.03	8.97	9.49	10.66	13.61	66.30
10	12.50	10.78	11.13	11.98	12.40	14.12	16.47	89.38
5	12.51	15.92	16.50	18.29	18.00	19.20	20.00	120.42
Totals	44.54	45.38	46.35	52.70	55.01	61.32	71.30	376.60

Data Set for Table 23: Percent TOC Removed

BLOCKS (SOURCE)	TREATMENTS (ALUM DOSE, mg/l as Al_2O_3) FOR pH = 5.0				
	5	10	20	30	TOTALS
Daytona Beach	24.0	34.6	42.8	48.1	149.5
Lake Washington	2.5	7.9	68.0	75.4	153.8
Caloosahatchee River	28.5	51.6	65.8	71.8	217.7
Totals	55.0	94.1	176.6	195.3	521.0

Data Set for Table 24: Percent TOC Removed

BLOCKS (SOURCE)	TREATMENTS (ALUM DOSE, mg/l as Al_2O_3) FOR pH = 6.0				
	5	10	20	30	TOTALS
Daytona Beach	14.6	17.5	31.6	34.2	97.9
Lake Washington	6.2	8.8	67.5	76.5	159.0
Caloosahatchee River	17.9	46.2	59.7	69.5	193.3
Totals	38.7	72.0	158.8	180.2	450.2

Data Set for Table 25: Percent TOC Removed

BLOCKS (SOURCE)	TREATMENTS (ALUM DOSE, mg/l as Al_2O_3) FOR pH = 7.0				
	5	10	20	30	TOTALS
Daytona Beach	10.2	16.5	32.1	32.9	91.7
Lake Washington	5.6	5.2	61.7	72.1	144.6
Caloosahatchee River	13.8	36.6	52.2	59.8	162.4
Totals	29.6	58.3	146.0	164.8	398.7

Data Set for Table 26: Percent TOC Removed

BLOCKS (SOURCE)	TREATMENTS (ALUM DOSE, mg/l as Al_2O_3) FOR pH = 8.0				
	5	10	20	30	TOTALS
Daytona Beach	13.3	11.7	22.0	25.1	72.1
Lake Washington	0.8	3.0	49.4	59.0	112.2
Caloosahatchee River	10.2	26.1	38.9	54.1	129.3
Totals	24.3	40.8	110.3	138.2	313.6

APPENDIX D

FLOC STABILITY - THE EFFECTS OF A SHEARED FLOC MIXING SEQUENCE

Floc stability, characteristic of the source water quality, is a factor which has required a special effort to qualify. The following discussion concerns a set of alum jar tests in which the conventional rapid mix/slow mix mixing sequence is reversed. This altered mixing sequence is referred to as the sheared floc condition.

Floc Stability Criteria

Aluminum added to the jar test may be precipitated as $Al(OH)_3$ (pH 5-8); it may become enmeshed in precipitating hardness (above pH 8) by virtue of its anionic character in the $Al(OH)_4^-$ species, or it may precipitate as a cationic polymer (below pH 5). For aluminum to function as an ionic polymer, the raw water TOC, $CaCO_3$, or $Mg(OH)_2$ floc must contain sufficient sites onto which the ionic aluminum may adsorb. A fragile floc then can be described as one which is contained in an environment deficient in such sites. Reentrainment of aluminum into solution upon belated rapid mixing (observed at the higher and lower pHs) has been accepted as evidence of a fragile floc. On the other hand, an increase in aluminum precipitate upon belated rapid mixing would then constitute a stable floc. In this analysis of the sheared floc mixing condition, the primary goal has been to qualify the stability of those flocs in which aluminum functions as an anionic polymer or a cationic polymer.

A Presentation of the Sheared Floc Condition Jar Test Data

Raw Water Quality of Source Waters

The raw water quality of the source waters on which the sheared floc condition jar tests were performed is presented in Table 30.

TABLE 30

RAW WATER QUALITY OF SOURCE WATERS
(SHEARED FLOC JAR TESTS)

SOURCE	DISTILLED WATER	DAYTONA BEACH	LAKE WASHINGTON
pH	-	6.0	6.2
Al^{3+} (mg/l)	0.001	0.22	0.15
Ca^{++} (mg/l)	BDL*	108	58.9
Mg^{++} (mg/l)	0.007	9.14	13.1
TOC (mg/l)	0.32	10.80	24.13

* BDL - Below detection limits of 0.001 mg/l

Sheared Floc Jar Test Results

With the following discussion, the alum jar test results for the sheared floc condition are presented as a function of alum dose and pH. The reader should understand from the outset that the inferences made in this discussion may be strictly academic without practical application. This concern is expressed based on the settling time allocated in the jar testing procedure. Recall that 30 to 40 minutes of settling time had been allowed before the top one centimeter of sample was drawn for analysis; this is equivalent to an overflow rate of 8.8-11.8 gal/day-ft^2. This overflow rate is very small compared to the typical overflow range of 500-800 gal/day-ft^2 employed in alum coagulation treatment processes (Reynolds 1982).

In Figure 25, the TOC residual results (mg/l) for the sheared floc condition jar tests performed on the distilled water source are presented. As in the non-sheared condition tests, the TOC residuals for the distilled water tests are minimal (0.09-0.78 mg/l), with consequently minimal effects on residual aluminum presented in Figure 26. These residual aluminum results, expressed as mg/l Al^{3+}, conform best to the theoretical aluminum solubility models. At pHs 10 and 11, aluminum solubility is limited only by the aluminum supplied as theory dictates. Minimum aluminum residual is reported for pHs 6 and 7, above and below which aluminum solubility is increasingly soluble with increasing and decreasing pH. A comparison between the aluminum residual data for the non-sheared jar tests (Figure 4) and the sheared floc tests (Figure 26) reveals that the distilled water source is suitable for the formation of a fragile floc with respect to aluminum below pH 6 and above pH 8. This inference is based on the reentrainment of soluble aluminum at the higher and lower pHs as a result of belated rapid mixing. At the higher pHs, this phenomenon is most profound in that as much as 15 mg/l as Al^{3+} remains soluble for the sheared floc condition compared to 1.6 mg/l as Al^{3+}, the maximum solubility observed in the non-sheared condition. This

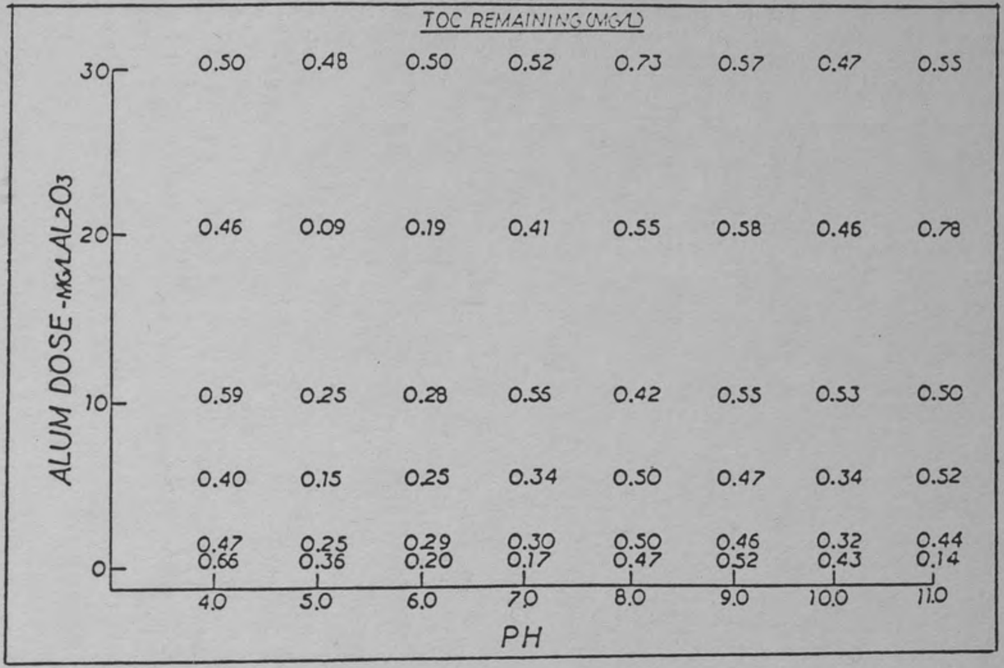

Figure 25. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Distilled Water (Sheared Floc Condition).

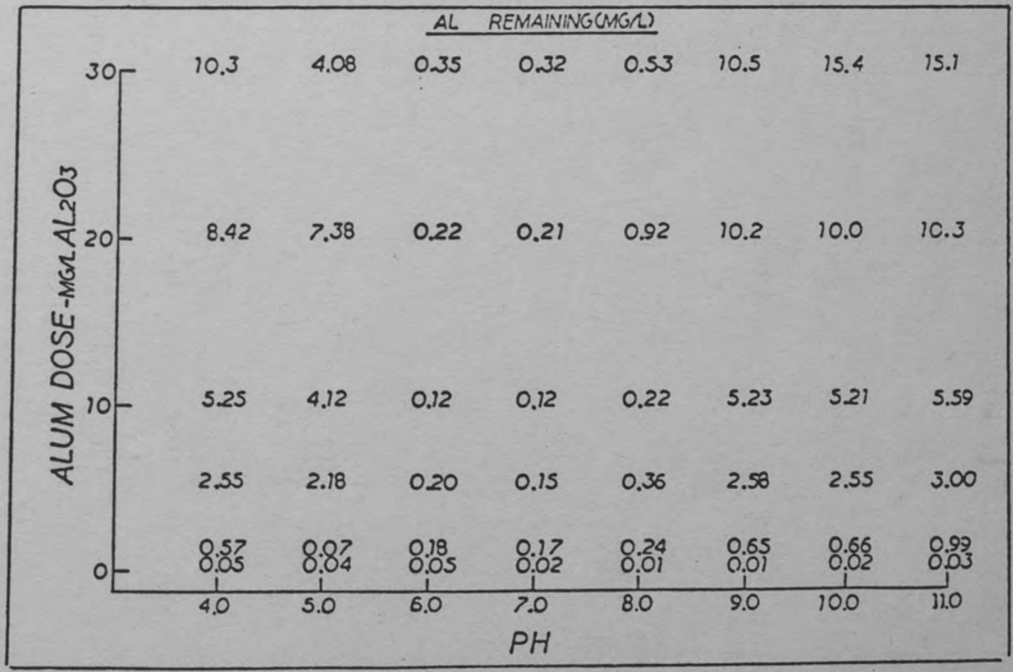

Figure 26. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Distilled Water (Sheared Floc Condition).

observation comes as no surprise since the only quantifiable adsorption sites in the distilled water source to accommodate $Al(OH)_4^-$ as a polymer are associated with the calcium carbonate floc formed from the calcium added as lime for pH control and atmospheric CO_2.

The TOC residuals (mg/l) for the sheared floc jar tests conducted with the Daytona Beach source are given in Figure 27. As shown in the non-sheared condition test results previously, TOC reduction optimization is bimodal, occurring simultaneously with both $Al(OH)_3$ and hardness precipitation. The most noteworthy difference between the non-sheared and sheared floc condition TOC residual data sets is a greater dose dependency for TOC reduction in the sheared floc case observed at pH 11, resulting in a 7.9% relative decrease in residual TOC. Figure 28 contains the aluminum residual results (mg/l) for the sheared floc Daytona Beach jar tests. In direct contrast to the fragile polymeric association of aluminum in the distilled water tests is the stable association of $Al(OH)_4^-$ with hardness precipitates from the Daytona Beach and Lake Washington source waters. The data even suggests that the action of belatedly rapid mixing the floc enhances the viability of $Al(OH)_4^-$ as an anionic polymer. It is believed that the physical act of rapidly mixing the floc effectively increases the surface area of the adsorption sites for $Al(OH)_4^-$, resulting in a floc which is very stable due to interparticle bridging by the polymer. This theory would also explain the increased efficiency of the TOC reduction process at pH

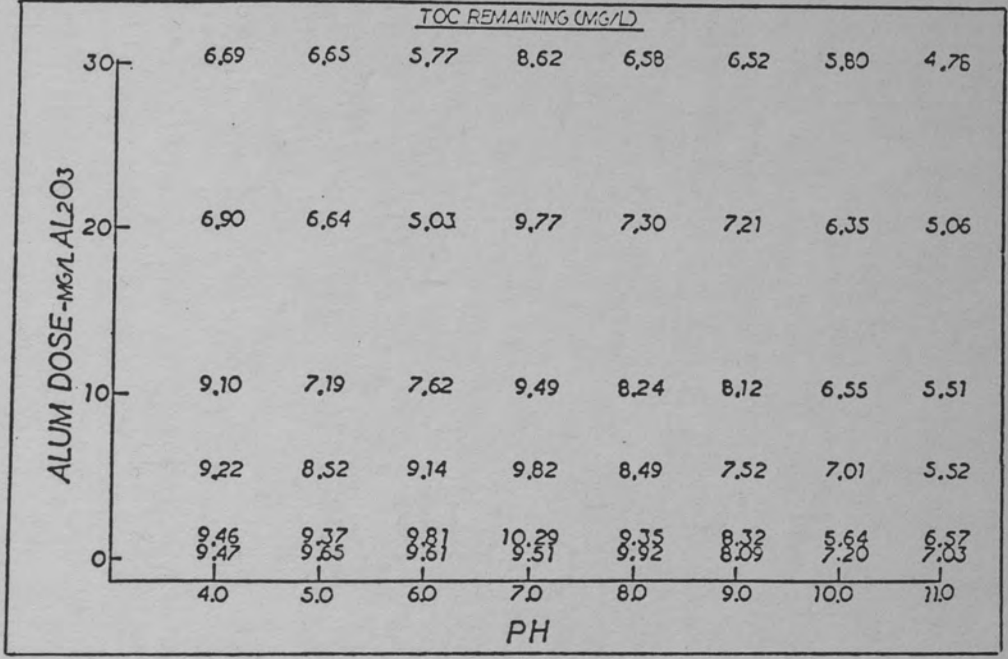

Figure 27. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Daytona Beach (Sheared Floc Condition).

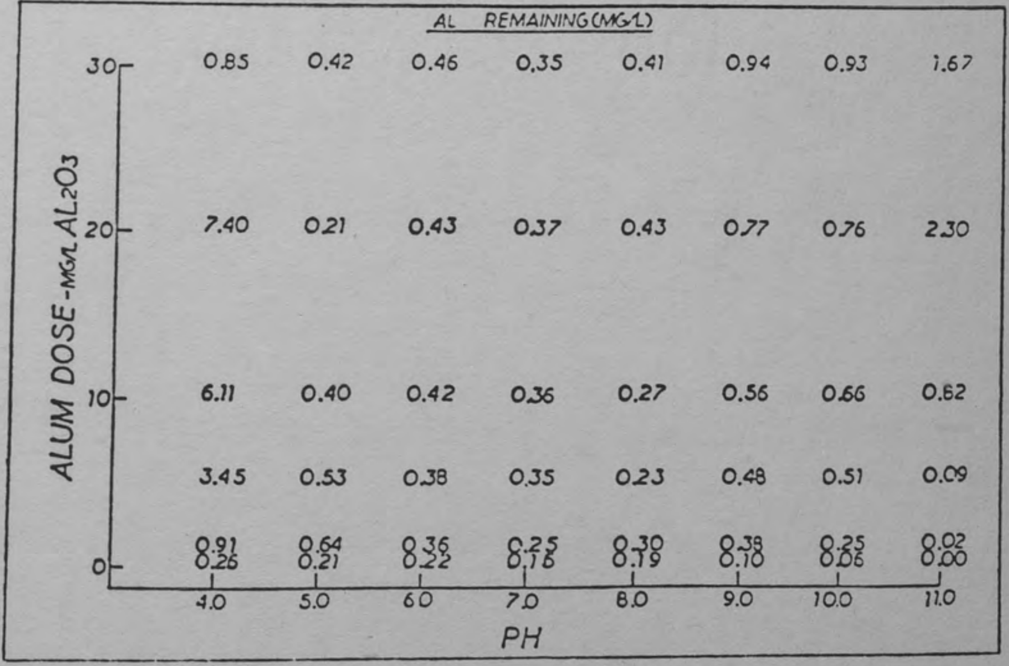

Figure 28. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Daytona Beach (Sheared Floc Condition).

11. Similarly, the sheared floc condition may also be instrumental in reducing aluminum residuals at pH 4 by enhancing the function of the cationic polymer, $Al(OH)^{2+}$. As previously shown in the theoretical solubility profiles, $Al(OH)^{2+}$ is not a dominant cationic species, but normally functions as an intermediate species for more soluble hydroxometal complexes such as $Al_{13}(OH)_{34}{}^{5+}$ and $Al_7(OH)_{17}{}^{4+}$. Rapid mixing allows $Al(OH)^{2+}$ to be adsorbed onto negatively charged colloids lest it differentiate into the more soluble species. The net effects of the sheared floc condition and coagulation on the Daytona Beach source residual aluminum levels may be summarized as follows: (1) almost complete precipitation (less than 0.1 mg/l as Al^{3+} residual) of aluminum at pH 11 for alum dosages of 5 mg/l as Al_2O_3 and under, probably due to $Al(OH)_4{}^-$ functioning as a polymer; (2) a level of soluble aluminum of 0.85 mg/l as Al^{3+} at pH 4 and alum dose of 30 mg/l as Al_2O_3 which suggests cationic polymer precipitation; and (3) a significantly reduced residual over pHs 5-8, numerically 0.15-0.64 mg/l as Al^{3+}, relative to the non-sheared condition. For ready reference, Figure 29 contains the TOC residual data for the Daytona Beach sheared floc jar tests expressed as a percent remaining.

In Figure 30, TOC remaining (mg/l) results are given for the Lake Washington sheared floc jar tests. Note that significant trace organics reduction is accomplished with an alum dose of 10 mg/l as Al_2O_3 and at pHs 10 and 11, resulting in ranges of TOC residual of 12.7-20.6 mg/l (52.6-85.2%) and 12.1-21.0 mg/l (50.3-87.2%),

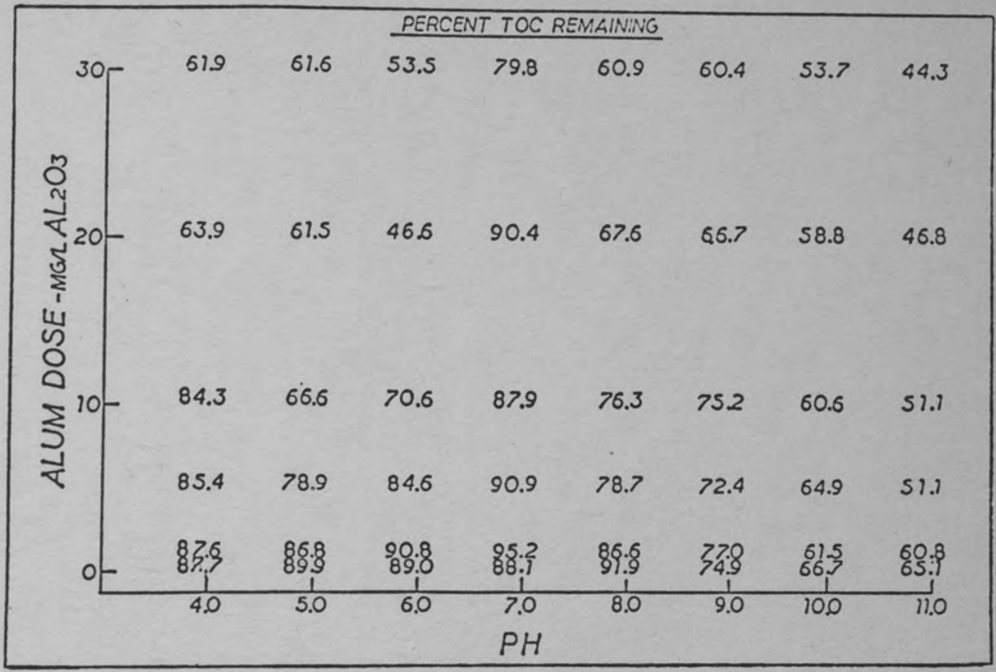

Figure 29. Alum Jar Test Results - Percent TOC Residual as a Function of Alum Dose and pH for Daytona Beach (Sheared Floc Condition).

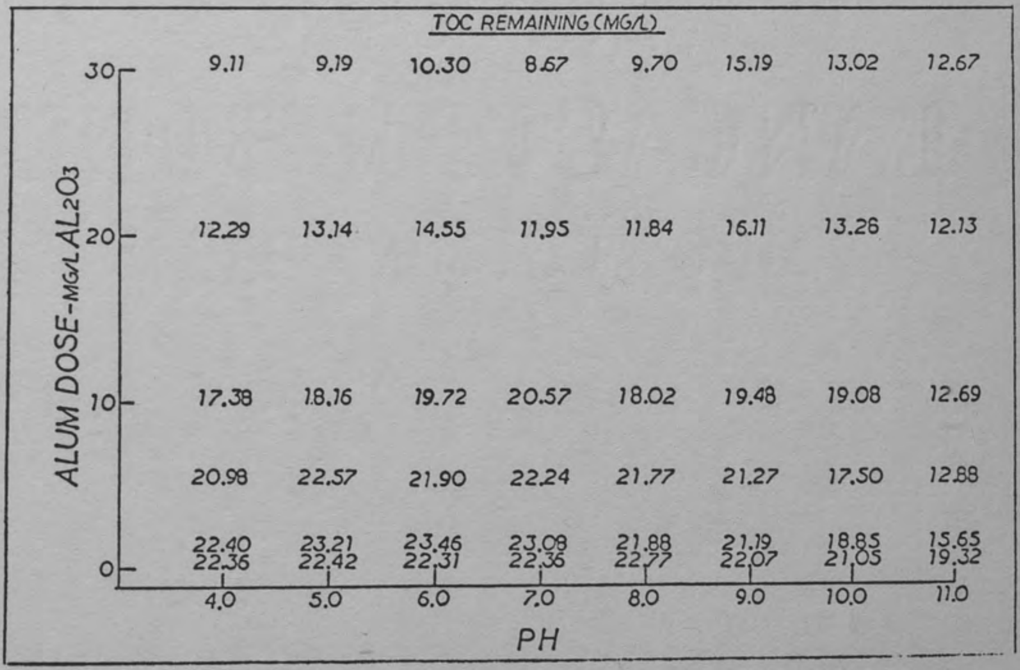

Figure 30. Alum Jar Test Results - TOC Residual as a Function of Alum Dose and pH for Lake Washington (Sheared Floc Condition).

respectively. In Figure 31, the aluminum residual results (mg/l as Al^{3+}) are reported for the Lake Washington sheared floc test series. This data confirms that the Lake Washington source is suitable for the formation of stable polymeric aluminum floc, as evidenced by the minimal levels of residual at pH 4 (0.17-1.34 mg/l as Al^{3+}) and pHs 10 and 11 (0.06-3.67 mg/l as Al^{3+}). Coincident with the reduction of TOC shown for an alum dose of 10 mg/l as Al_2O_3 is a level of residual aluminum of 0.51-3.05 mg/l as Al^{3+} which is significantly reduced with respect to the corresponding non-sheared test condition. For aluminum to precipitate as an anionic polymer, the optimum conditions provided by this series of tests are an alum dose of 5 mg/l as Al_2O_3 (2.65 mg/l as Al^{3+}), coupled by the sheared floc mixing sequence. These conditions resulted in a 17.5% TOC reduction at pH 11 in the Lake Washington source, relative to its zero alum dose counterpart as well as a residual aluminum level of 0.18 mg/l as Al^{3+}. This information is consistent with the work done by Ferraro (1981), who reported that an insignificant level of residual aluminum and an additional 20% TOC reduction was the result of adding 2 mg/l Al^{3+} to a lime coagulation treatment of Lake Washington at pH 11.5. Evidence of reduced aluminum solubility due to cationic polymerization is demonstrated in the Lake Washington test results for alum dosages in excess of 5 mg/l as Al_2O_3 in which only 0.17-0.51 mg/l as Al^{3+} remain soluble. See Figure 32 for a summary of the TOC residual data expressed as a percent remaining.

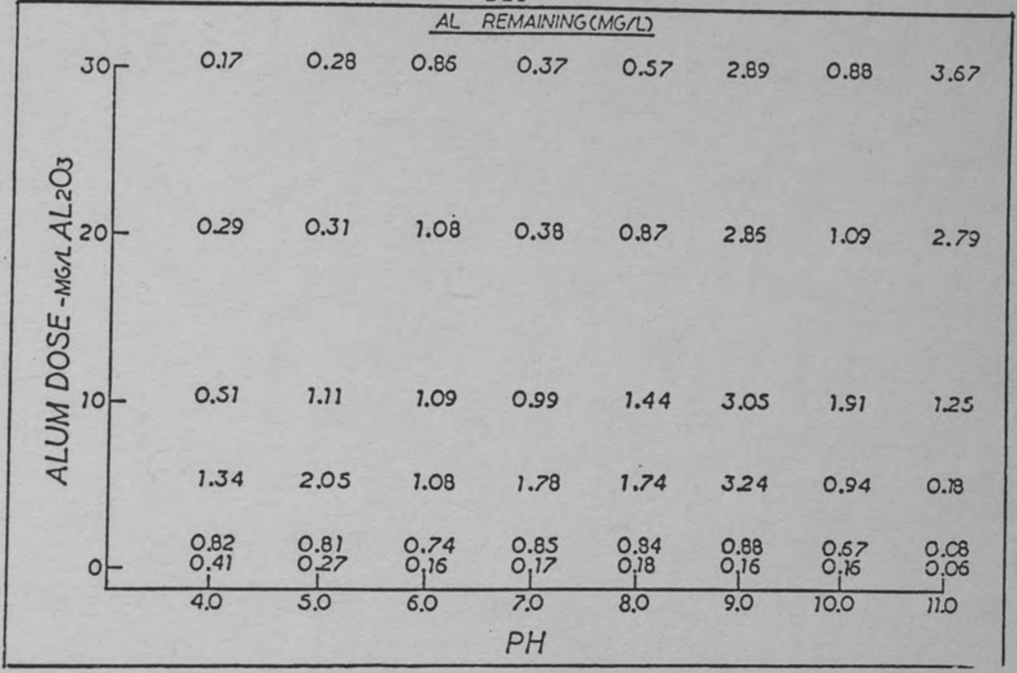

Figure 31. Alum Jar Test Results - Aluminum Residual as a Function of Alum Dose and pH for Lake Washington (Sheared Floc Condition).

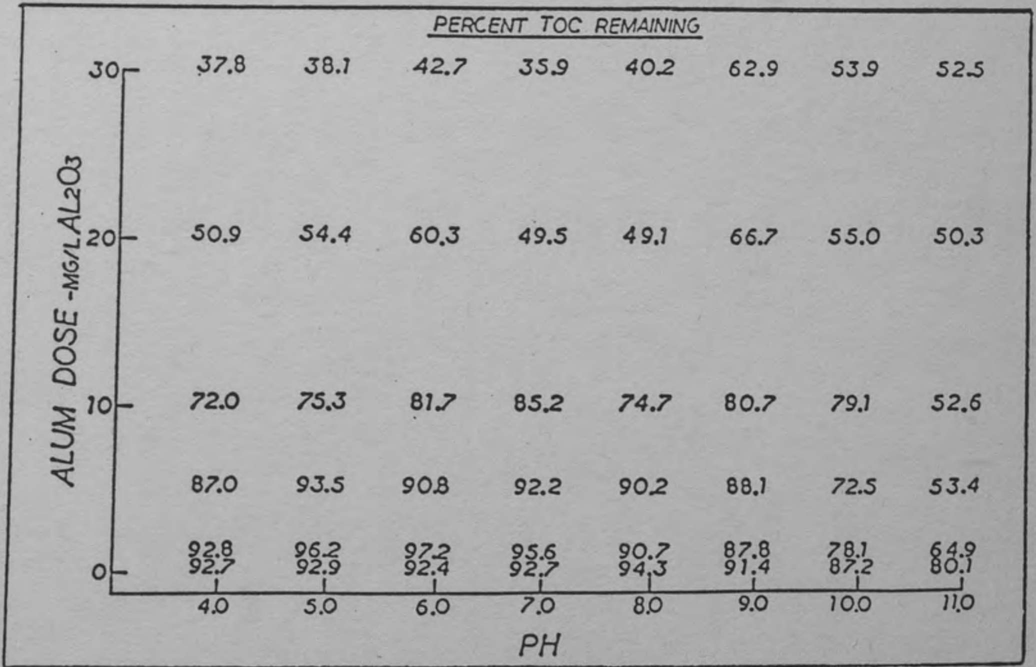

Figure 32. Alum Jar Test Results - Percent TOC Residual as a Function of Alum Dose and pH for Lake Washington (Sheared Floc Condition).

The Sheared Floc Condition and the Softening Process

Table 31 provides a summary of the hardness parameters measured in the distilled water, Daytona Beach and Lake Washington sources for the jar tests conducted with no alum addition under sheared floc mixing conditions.

TABLE 31

SHEARED FLOC CONDITION HARDNESS
Alum Dose: Zero

pH	RESIDUAL HARDNESS (mg Me^{++}/l)					
	DISTILLED WATER		DAYTONA BEACH		LAKE WASHINGTON	
	Ca^{++}	Mg^{++}	Ca^{++}	Mg^{++}	Ca^{++}	Mg^{++}
6.0	BDL	0.08	108	9.13	59.6	12.7
7.0	15.3	0.06	81.5	8.77	67.1	12.4
8.0	7.04	0.03	80.3	8.29	61.4	12.7
9.0	2.18	0.02	40.3	7.45	67.4	12.9
10.0	5.28	0.01	17.1	7.09	58.2	12.8
11.0	6.38	BDL	5.28	5.63	24.2	11.7

Several aspects of the hardness data presented in Table 31 are worthy of note. From the Daytona Beach source, calcium is precipitated in significant quantity at all pHs 7 through 11. This observation varies from that presented for the non-sheared condition by which calcium was precipitated at pH 10 only. In the Lake Washington case, $CaCO_3$ precipitation is achieved at pHs 10 and 11, resulting in a minimum Ca^{++} residual of 24.2 mg/l. Recall for the non-sheared condition Lake Washington tests, calcium was held in soluble form over the entire range of pH. The rapid mixing would seem to provide the energy for initial precipitation to occur (much analogous to priming a pump). Magnesium residual data is similar for both mixing sequences, characterized by significant levels of precipitation from the Lake Washington source. This information provides further evidence that $Al(OH)_4^-$ is instrumental in the TOC/hardness reduction process as a polymer, in the case of Lake Washington at pH 11, particularly.

Sheared Floc Aluminum Solubility by Source

In order to summarize the net effects of the sheared floc condition in addition to trace organic content and organic reduction processes on aluminum solubility, the following discussion is presented. The manner of presentation is the pC versus pH diagram for easy comparison, with the theoretical as well as the non-sheared condition aluminum solubility profiles.

Figure 33 displays the sheared floc aluminum solubility profiles for background aluminum. Noteworthy is the fact that even background levels of aluminum are precipitated at pHs 10 and 11 in the stable Daytona Beach and Lake Washington flocs. This striking observation is explainable in terms of the enhancement of $Al(OH)_4^-$ as an anionic polymer by the action of sheared floc mixing.

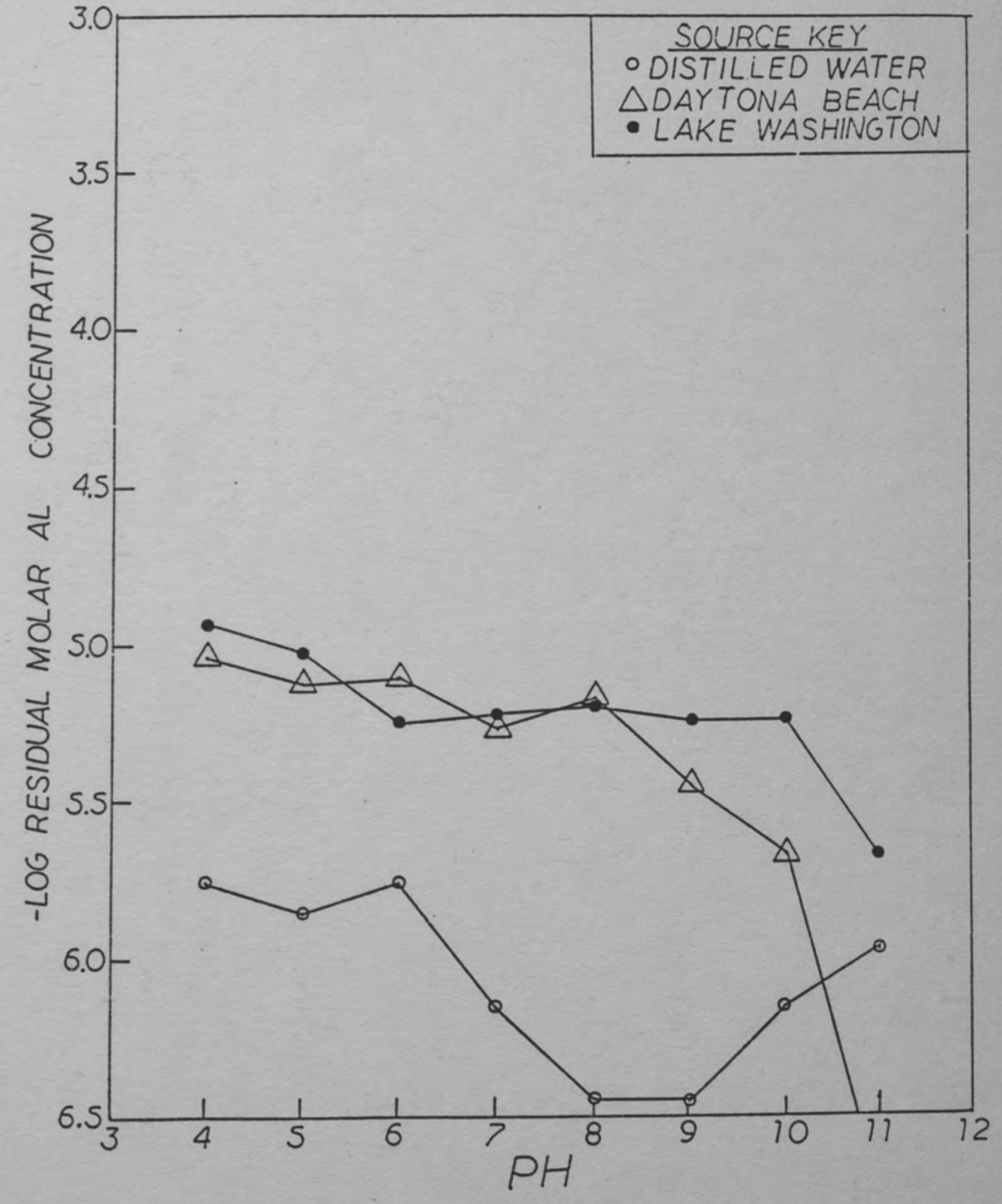

Figure 33. pC Versus pH for Alum Jars: Dose = 0 mg/l Al_2O_3 (Sheared Floc Condition).

In Figure 34, residual aluminum solubility for the source waters subjected to an alum dose of 1 mg/l as Al_2O_3 and sheared floc mixing is presented. In this figure, the dramatically reduced levels of soluble aluminum in the Daytona Beach and Lake Washington sources at pH 11 are in contrast with the elevated aluminum residuals in the distilled water source. The high incidence of soluble aluminum for pHs 4 through 9 in the Lake Washington source suggests the now familiar phenomenon of aluminum-organic complexation. The same trends are repeated in Figure 35, the experimental aluminum solubility profiles for an alum dose of 5 mg/l as Al_2O_3 coupled with sheared floc mixing. Additionally, the following factors may also be observed in Figure 35: (1) the distilled water aluminum solubility profile is in close agreement with aluminum solubility theory in that for pHs 4, 9, 10 and 11 soluble aluminum is limited only by the alum dose; (2) the Daytona Beach profile demonstrates an area of minimum $Al(OH)_3$ solubility over pHs 5-8; and (3) the Lake Washington source exhibits a decidedly reduced level of soluble aluminum at pH 4, probably due to cationic polymer precipitation.

In Figure 36, the experimental aluminum solubility profiles resulting from an alum dose of 10 mg/l as Al_2O_3 and sheared floc mixing are shown. This figure demonstrates the first conclusive evidence of the breaking up of the aluminum-organic complex formed in the Lake Washington source which shows an area of $Al(OH)_3$ precipitation. Again, the distilled water source demonstrates an aluminum solubility profile which is in close agreement with theory.

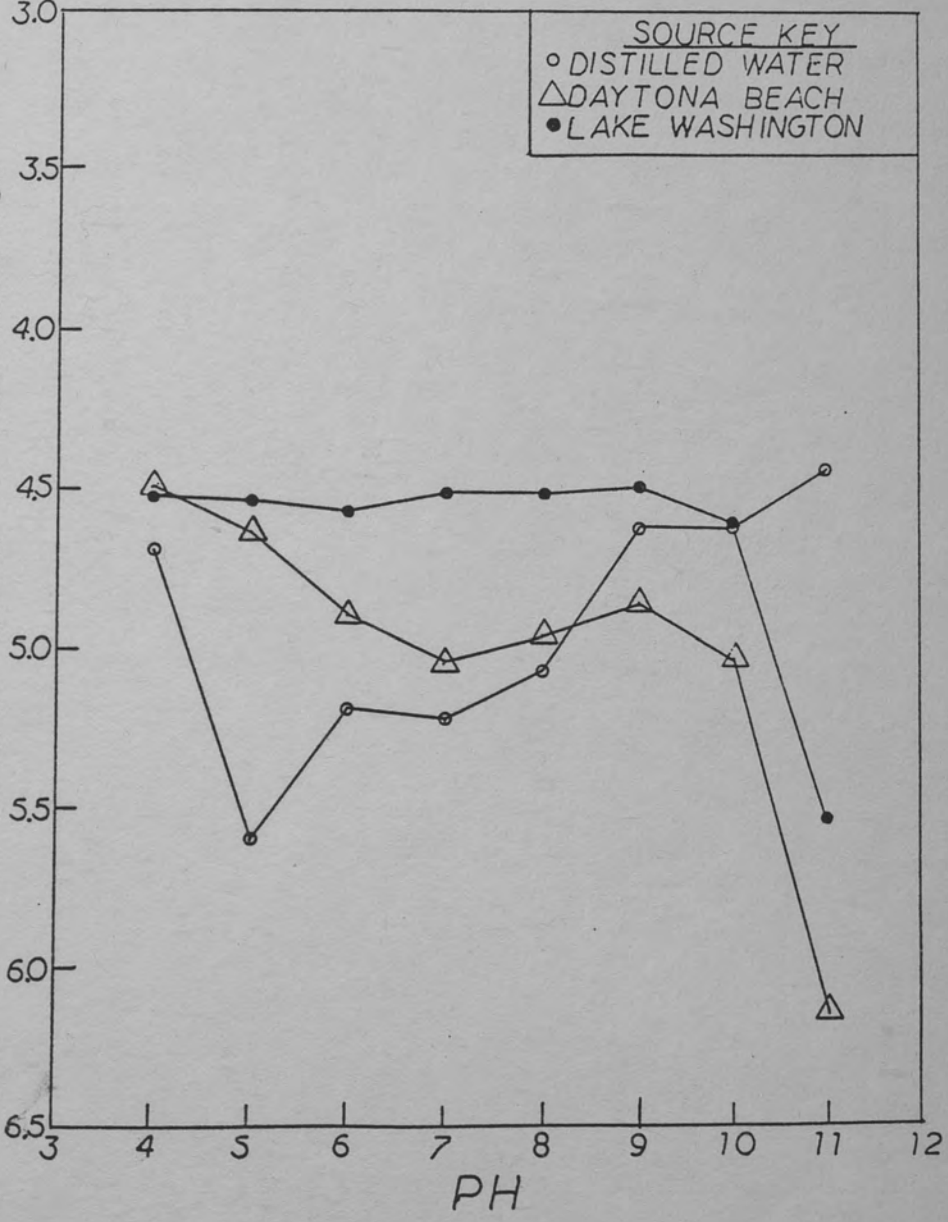

Figure 34. pC Versus pH for Alum Jars: Dose = 1 mg/l Al_2O_3 (Sheared Floc Condition).

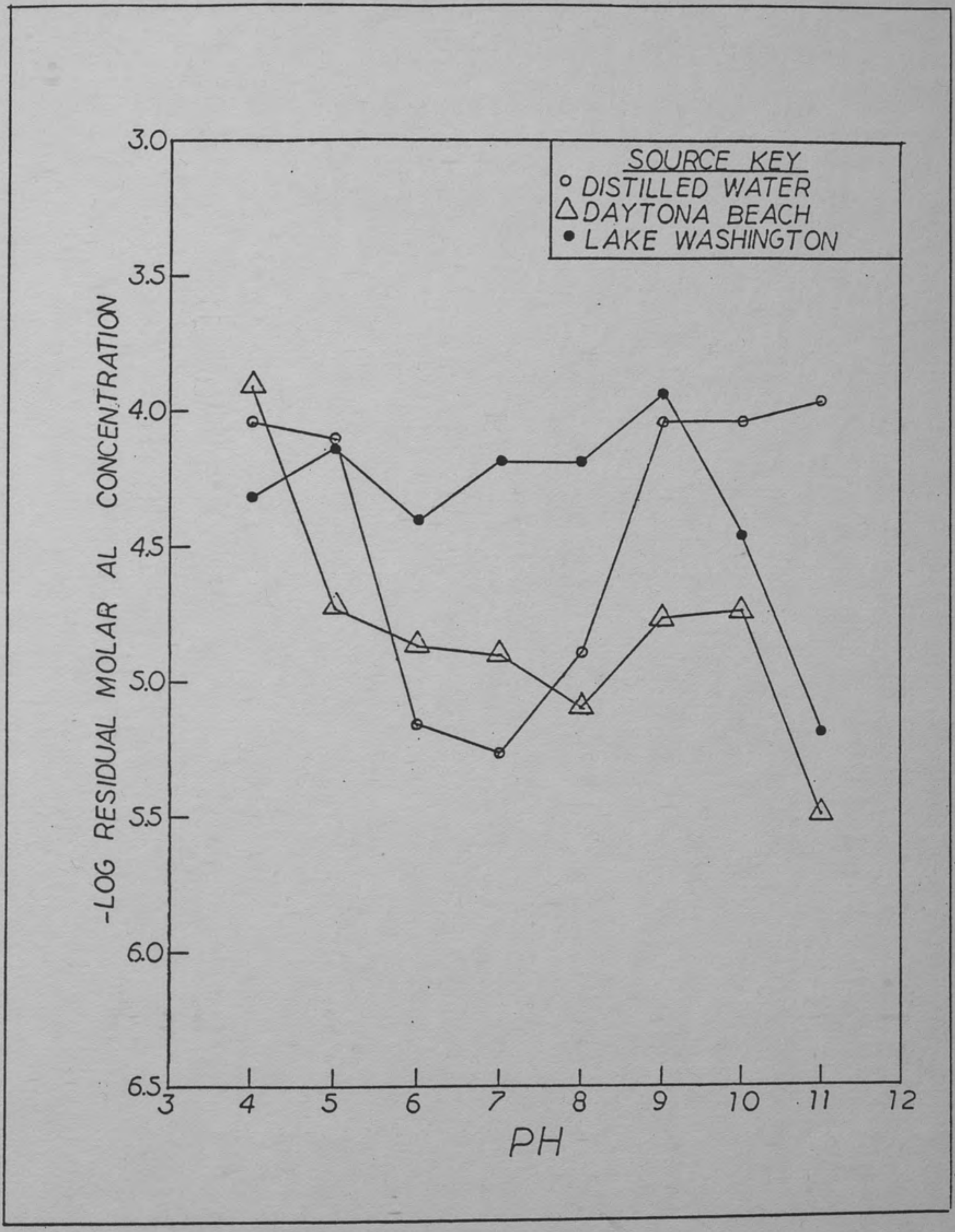

Figure 35. pC Versus pH for Alum Jars: Dose = 5 mg/l Al_2O_3 (Sheared Floc Condition).

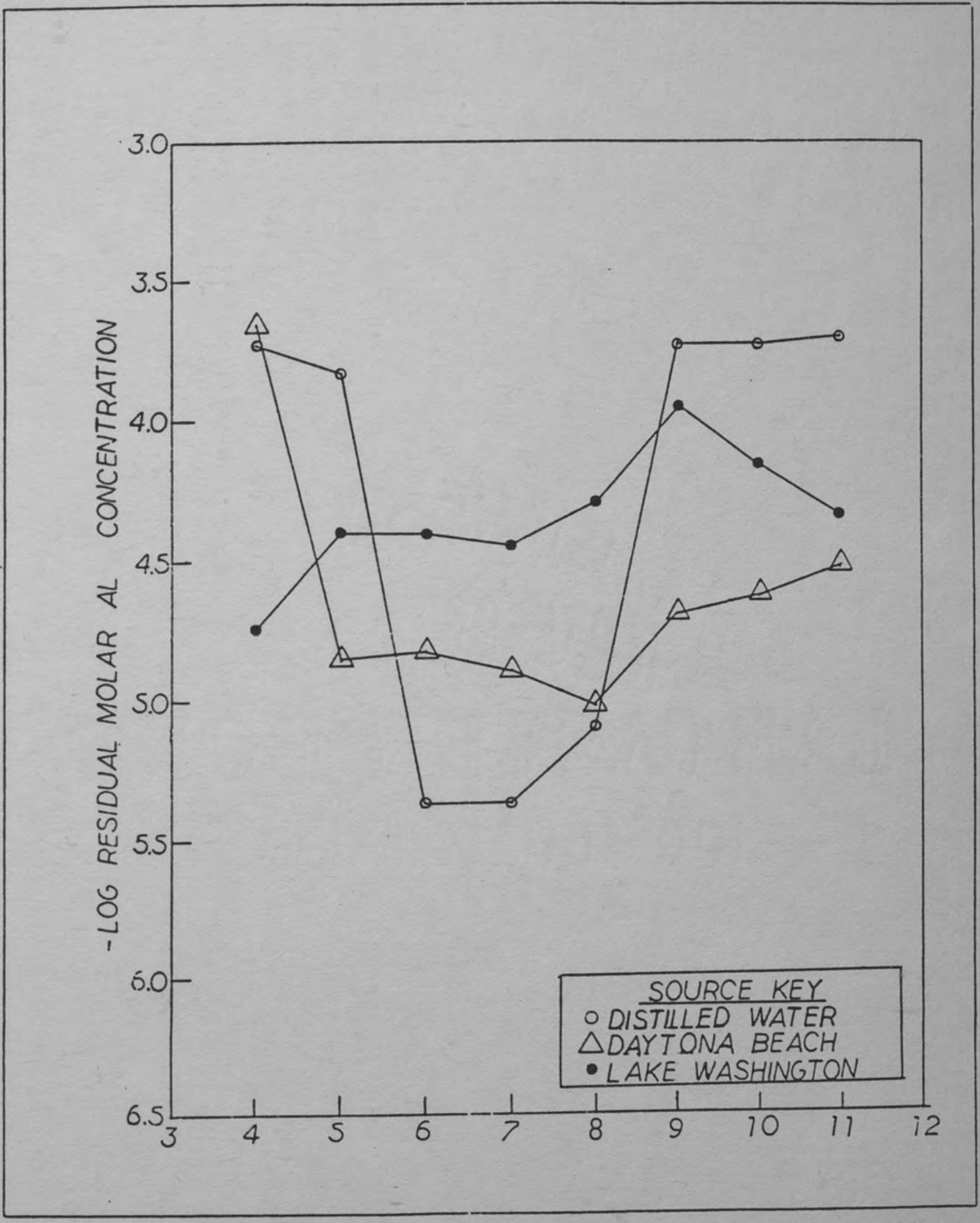

Figure 36. pC Versus pH for Alum Jars: Dose = 10 mg/l Al_2O_3 (Sheared Floc Condition).

The Daytona Beach source profile is much similar to its non-sheared counterpart with the exception that residual aluminum is reduced for the sheared floc condition for pHs 5 through 11. The instance of cationic polymer precipitation described for Lake Washington is better defined for this alum dose.

Figure 37 exhibits the experimental aluminum solubility conditions resulting from an alum dose of 20 mg/l as Al_2O_3 and sheared floc mixing. Note that at pH 11, the trend of minimum soluble aluminum is reversed; this is explainable by an exhaustion of adsorption sites on the pH 11 flocs (of the Daytona Beach and Lake Washington sources) for the $Al(OH)_4^-$ polymer. Aside from this, the aluminum solubility profiles are of a similar shape as already described.

In Figure 38, the aluminum solubility profiles for an alum dose of 30 mg/l as Al_2O_3 and sheared floc mixing are presented. Two factors render these profiles unique: (1) at pH 9, the distilled water aluminum solubility is clearly no longer limited by the alum dose applied as theory dictates; and (2) cationic polymer precipitation is also evident for the Daytona Beach source in addition to the Lake Washington source at pH 4.

Sheared Floc Conclusions

The following are conclusions drawn from the preceding "sheared-floc" discussion.

1. It is speculated that anionic aluminum exhibits a fragile association with $CaCO_3$ floc that is effectively strengthened by the

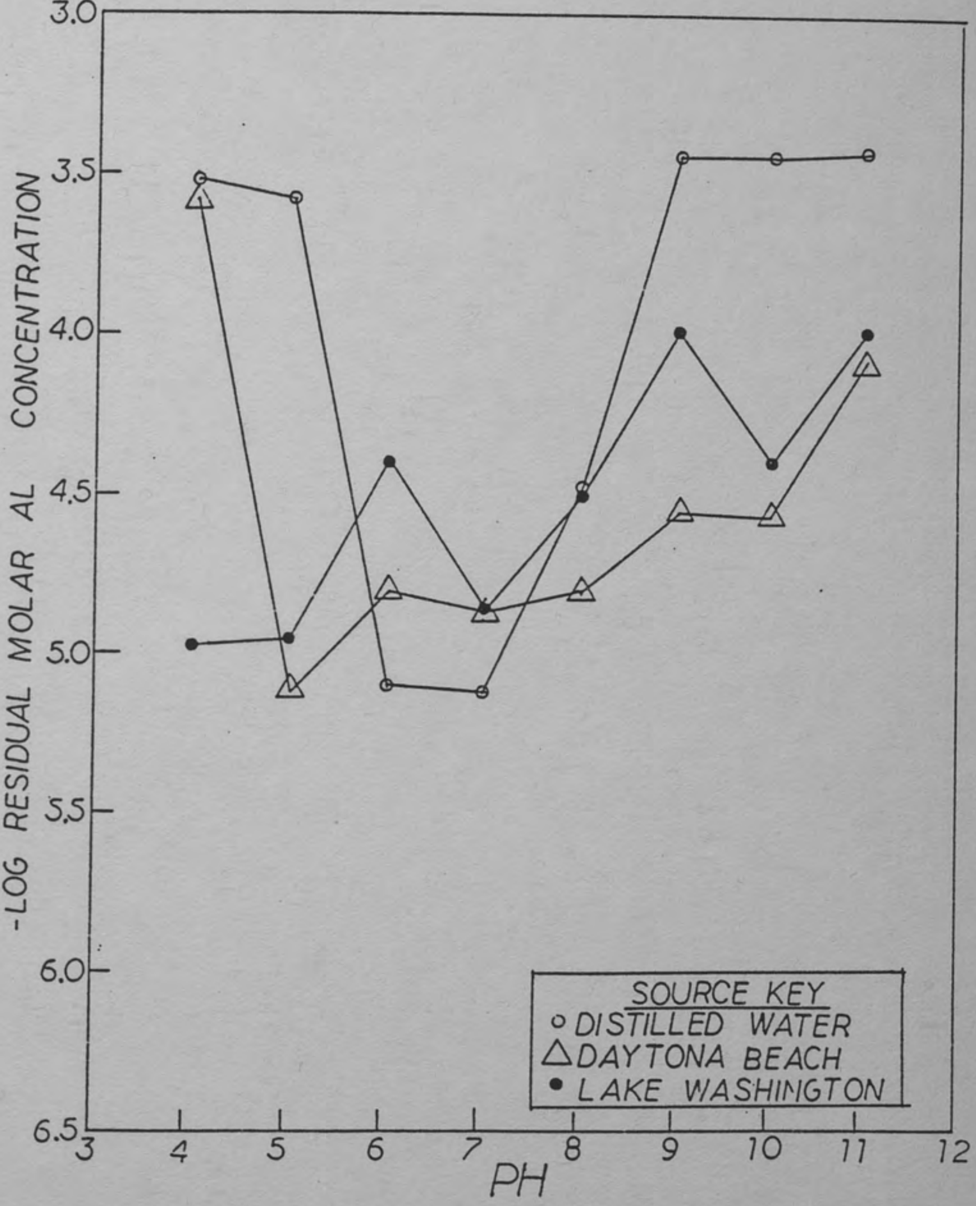

Figure 37. pC Versus pH for Alum Jars: Dose = 20 mg/l Al_2O_3 (Sheared Floc Condition).

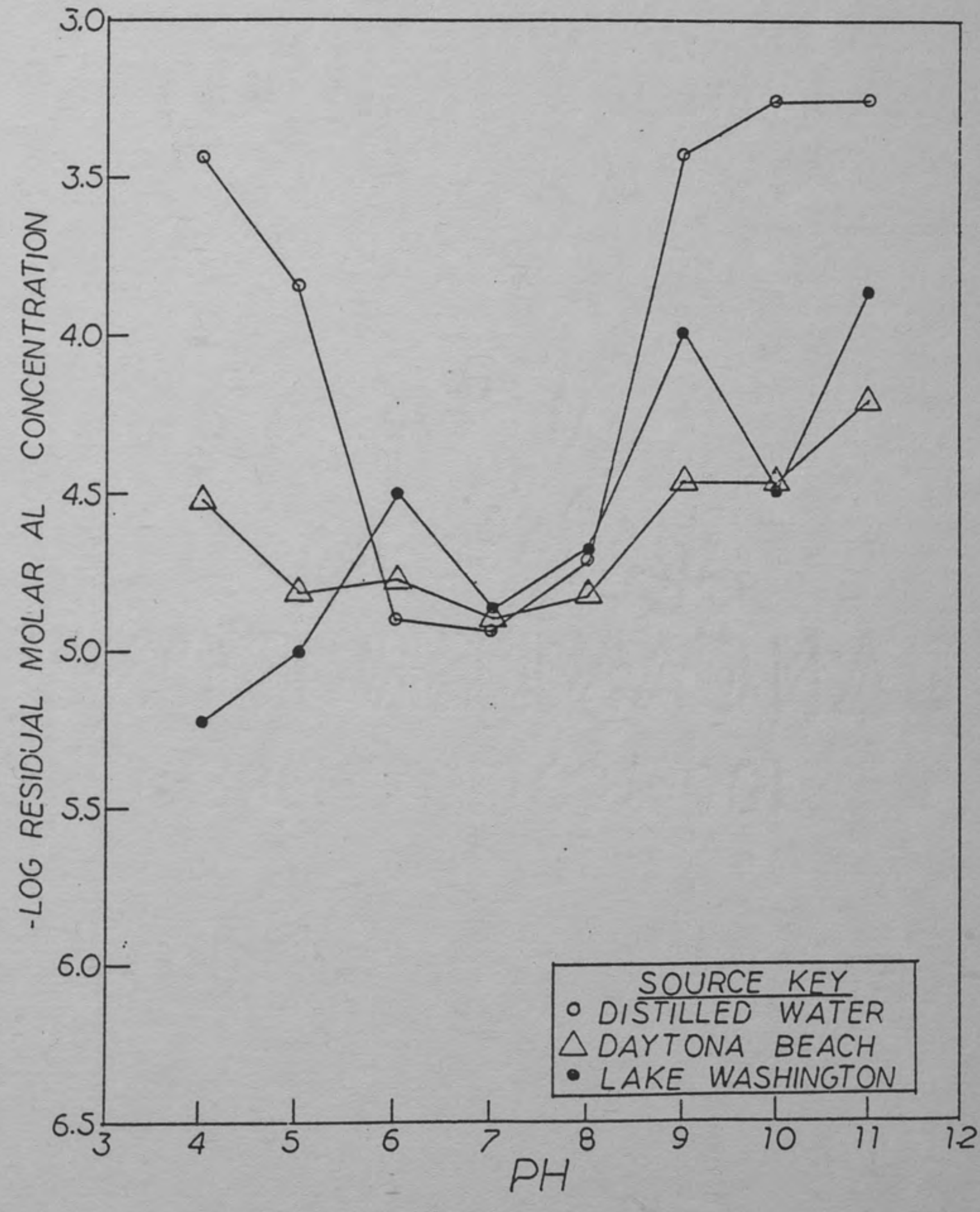

Figure 38. pC Versus pH for Alum Jars: Dose = 30 mg/1 Al_2O_3 (Sheared Floc Condition).

presence of trace organic and inorganic contaminants. Alum applied to function as an anionic polymer to enhance the efficiency of the lime softening/TOC removal process should be optimized with respect to residual aluminum. Preliminary evidence suggests dosages of 5 mg/l as Al_2O_3 and under are most effective.

2. Sheared floc mixing is seemingly advantageous for aluminum to function as an ionic polymer and for calcium precipitation.

3. Distilled water subjected to sheared floc mixing conforms best of all sample sets to the theoretical aluminum solubility models.

It is recommended that an effort should be made to determine the reproducibility and feasibility of the floc sheared advantage in ionic aluminum polymerization. It should be noted that these tests conducted at pH 11 resulted in residual aluminum levels near the AWWA goal of 0.05 mg/l as Al^{3+}. For this reason, the unconventional practice of floc shearing might be explored further in the future.

REFERENCES

American Water Works Association. AWWA Statement on Drinking Water Quality (draft). Denver, CO: AWWA, 1986.

Ferraro, C. "Trihalomethane Precursor Reduction Using Magnesium Coagulation." Master's Thesis, University of Central Florida, Orlando, 1981.

Francois, R.J., and Van Haute, A.A. "Structure of Hydroxide Flocs." Water Research 19 (October 1985): 1249-1254.

Hahn, H.H., and Stumm, W. "Kinetics of Coagulation with Hydrolyzed Al(III)." Journal Colloid and Interface Science 28 (September 1968): 134-143.

Hannah, S.A.; Cohen, H.M.; and Robeck, G.G. "Measurement of Floc Strength by Particle Counting." Journal of the American Water Works Association (July 1967): 843-858.

Hudson, H.E., Jr. "Physical Aspects of Flocculation." Journal of the American Water Works Association (July 1965): 885-892.

Jodellah, A.M., and Weber, W.J., Jr. "Controlling Trihalomethane Formation Potential by Chemical Treatment and Adsorption." Journal of the American Water Works Association (October 1985): 95-100.

Liao, M.Y., and Randtke, S.J. "Removing Fulvic Acid by Lime Softening." Journal of the American Water Works Association (August 1985): 78-88.

Miller, J., and Freund, J.E. Probability and Statistics for Engineers, 2nd ed. Englewood Cliffs, NJ: Prentice-Hall, Inc., 1977.

O'Melia, C.R. "A Review of the Coagulation Process." Public Works (May 1969): 87-98.

Qureshi, N., and Malmberg, R.H. "Reducing Aluminum Residuals in Finished Water." Journal of the American Water Works Association (October 1985): 101-108.

Reynolds, T.D. Unit Operations and Processes in Environmental Engineering. Belmont, CA: Wadsworth Publishers, Inc., 1982.

Schnitzer, M. "Metal-Organic Matter Interactions in Soils and Waters." In Organic Compounds in Aquatic Environments, pp. 297-315. Edited by S.D. Faust and J.V. Hunter. New York: Marcel-Dekker, Inc., 1971.

Snoeyink, V.L., and Jenkins, D. Water Chemistry. New York: John Wiley and Sons, Inc., 1980.

Stumm, W., and Morgan, J.J. Aquatic Chemistry. New York: Wiley Interscience, 1972.

Walton, A.G. The Formation and Properties of Precipitates. New York: Interscience Publishers, 1967.

Weber, W.J., Jr. Physicochemical Processes for Water Quality Control. New York: Wiley Interscience, 1972.

Weber, W.J., Jr., and Jodellah, A.M. "Removing Humic Substances by Chemical Treatment and Adsorption." Journal of the American Water Works Association (April 1985): 132-137.

World Health Organization. Guidelines for Drinking Water Quality, Volume 2. Geneva, Switzerland, World Health Organization, 1984.