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SURVEY AND CONTROL OF SYNTHETIC ORGANICS IN TEXAS WATER SUPPLIES

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ABSTRACT

Four Texas water supplies (Lake Somerville, Lake Livingston, Neches River, and Sabine River) were surveyed to determine their tendency to form trihalomethanes when chlorinated. The ability of conventional and innovative treatment processes to reduce the level of trihalomethane formation potential (THMFP) in these waters was also investigated. Conventional alum coagulation was studied in a series of jar tests in which the effect of pH and alum dose on removal of THMFP, ultraviolet absorbance (UVA), total organic carbon (TOC), and visible absorbance (VA) was determined. Removal patterns for the more easily measured parameters (UVA, TOC, and VA) were analyzed to determine if they could be used to predict the removal patterns for THMFP. Visible absorbance was used as a surrogate for turbidity. Modification of conventional alum coagulation by addition of acid or base for pH control or by addition of secondary coagulants was studied. A medium molecular weight cationic polymer and activated silica were used in conjunction with alum and as sole coagulants. An innovative treatment process for removal of THMFP was also investigated. In these studies, batch and continuous flow experiments were conducted to evaluate the potential of activated alumina adsorption to remove organics from drinking water.

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INTRODUCTION

A major new problem in production of safe, healthy drinking water has been identified in the last few years. Toxic organic chemicals have been found to be widely distributed in potable water systems throughout the United States. Two groups of toxic organics can be identified. One group encompasses those compounds present in the raw water supplies. Over 700 of these specific organic compounds have been found in drinking waters. However, they represent only about 10 percent of the total organic carbon measured.[1] Although the effect of long term ingestion of low levels of these compounds is not known for certain, some laboratory and epidemiological data indicate that measureable adverse effects on public health are possible. Conventional water treatment systems are not designed to remove organics, so most of the compounds present in the raw water pass though the plant unchanged.

It is believed that most of the synthetic organics present in raw water supplies are the result of discharges from industrial or agricultural operations.[2] Many of these compounds do not appear normally in nature, so they tend to be slowly degraded by natural processes in aquatic environments. Chlorinated compounds appear to be particularly resistant to degradation. Recognition of the problem of chlorinated pesticides in drinking water is reflected in the primary drinking water standards for the United States in which six pesticides are regulated.[3] The trend toward increasing concern over toxic organics is also evidenced in amendments to the Federal Water Pollution Control Act,[4] which emphasizes removal of toxic compounds, rather than additional removal of conventional contaminants.

The second group of toxic organics found in drinking water are not found in the raw water, but are produced by chemical reactions that occur during treatment. Chlorine, which is added to disinfect the water, can react with natural organic material (humic and fulvic acids) to produce chlorinated organic compounds.[5-10] The major identified products of this reaction are members of a group of chemicals called trihalomethanes (THM). This group includes chloroform (trichloromethane), bromodichloromethane, dibromochloromethane, and bromoform (tribromomethane). Several national surveys have shown that these compounds are found in most all drinking waters which are treated with chlorine, and that there is a relationship between the total amount of THM produced and the TOC concentration in the raw water.[11,12] Trihalomethanes are believed to represent only a fraction of the total chlorinated products formed.[1]

Concern over the health effects of trihalomethanes and other halogenated by-products has resulted in a national interim primary drinking water standard being set for total trihalomethanes.[13] The USEPA made clear in promulgating this regulation that it was the first step in controlling toxic organics in drinking water, and that total trihalomethanes was being used as a surrogate for other halogenated compounds in addition to representing the combined effect of trihalomethane contamination. This standard applies to all water supplies which serve over 10,000 persons and add a disinfectant to their water. These regulations will have a significant effect on some Texas water supplies, particularly surface water supplies in East Texas. Some of these water systems have been found to have total trihalomethanes at concentrations nine times the maximum contaminant level set by the regulations.[14]

This project addresses the problem of increasing contamination of Texas water supplies by first surveying the problem, then addressing mechanisms for controlling contamination of drinking water by synthetic organics. The project focuses on the group of synthetic organics which are produced during conventional treatment. This approach was taken because of the widespread nature of the problem, national drinking water standards, and simple analytical procedures.

The primary objective of this project was to evaluate the significance of synthetic compounds produced during treatment in selected water supplies, and to investigate the effectiveness of conventional and non-conventional treatment technology for their control. To achieve this primary objective, the following subordinate objectives were pursued:

1) Develop and test analytical procedures to characterize contamination by synthetic organics;
2) Identify water supplies with specific problems of organic contamination;
3) Conduct laboratory treatability studies to determine the effectiveness of various treatment processes in removing synthetic organics or their precursors.

BACKGROUND

Formation of Halogenated Organics

In 1974, two independent reports showed that a group of halogenated chemicals called trihalomethanes were being produced in drinking water treatment plants.[5,6] It was shown that they were being produced by a reaction between natural organic matter and chlorine. The trihalomethanes are a group which consists of compounds containing one carbon (C), one hydrogen (H), and three halogens (Cl, Br, I, F). Chlorine containing trihalomethanes are most often produced by chlorination, but brominated compounds are also widespread.[11,12] Iodinated THMs have also been detected but fluorinated THMs have not been found. The most common THMs are chloroform ($CHCl_3$, also called trichloromethane), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$, also called tribromomethane). The combined effect of trihalomethanes in water is often expressed in terms of the total trihalomethane (TTHM) concentration. This is the sum of the concentrations of all trihalomethanes expressed in terms of mass-to-volume concentration units.

In 1974, following the discovery of organic chemicals in New Orleans water, the EPA initiated the National Organics Reconnaissance Survey (NORS).[12] NORS was created to study chlorination by-products that were formed in 80 water supplies across the country. The main objectives of the survey were to determine the amount of trihalomethanes in finished drinking water and to find out how water treatment practices and raw water sources affect the formation of trihalomethanes. Another objective was to determine the amounts and types of trihalomethanes produced from the different types of raw water sources.

The results of the survey showed that the four trihalomethanes are widespread in finished drinking waters which use chlorination. It was determined that the TTHM concentration was related to the organic matter in the water as measured by TOC. The results also indicated that higher concentrations of THM are found when surface waters rather than groundwaters are the source for water supply.

In late 1975, the EPA created the National Organics Monitoring Survey (NOMS). This survey further carried out the work of NORS. In it, 113 water utilities were tested for THM concentrations at the plant and after the water had been distributed through the system. The most significant conclusion of this report was that THM concentrations increased with time and would thus be greater at the consumers tap than at the plant.[11] Other reports have confirmed the findings of these national surveys.[14-21]

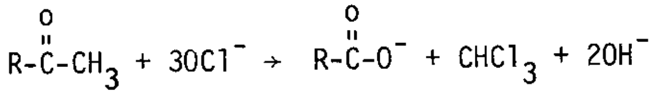
A survey of East Texas water supplies showed extremely high TTHM levels.[14,22] TTHM concentrations over 900 μg/l were measured at consumers taps. Poor removal of THM precursors was found at six water treatment plants studied. None of the plants removed more than 20 percent of the TTHM formation potential of the raw water and one plant showed no removal. These poor removals were probably due to the practice of adding chlorine before other treatment processes. This would allow THMs to form before the natural organic precursors could be removed.

The exact method by which THMs are formed during chlorination of natural water is difficult to describe because of the difficulty in characterizing the organic precursors. These precursors are part of the natural organic matter (NOM) which is found in natural aquatic systems. Natural organic matter in surface and ground waters is usually described as humic or fulvic acids. These terms were originally developed to characterize soil organic matter.[23] Most aquatic NOM is similar to soil fulvic acids,[24,25] but the size distribution of this material is disputed. Some reports conclude that NOM consists almost entirely of material of molecular weight greater than 10,000[26-28] while other reports show significant amounts of NOM with molecular weight below 10,000.[29-32] Much of this variation can probably be attributed to different analysis techniques while some undoubtedly is due to different types of natural organic matter. In general, natural organic matter of soil or aquatic origin can be described as flexible, linear, synthetic polyelectrolytes.[33]

The reaction of NOM with chlorine can be expressed in general terms by:

$$\text{organic precursors} + \text{chlorine} \rightarrow \text{trihalomethanes} + \text{other halogenated organics} + \text{chloride} \qquad (1)$$

The reaction which forms THMs has been described in terms of the haloform reaction between hypochlorite and ketones:[34]



$$R\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}CH_3 + 3OCl^- \rightarrow R\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}O^- + CHCl_3 + 2OH^- \qquad (2)$$

Others believe the reaction occurs between hypochlorite and the meta-hydroxy position of an aromatic ring of the humic/fulvic compounds.[8]

Other halogenated products are produced in addition to the trihalomethanes. They are not as well characterized as the trihalomethanes because most of them are non-volatile and cannot be analyzed by gas chromatography. However, some analyses of total organic halogens (TOX) for chlorinated waters show levels almost nine times as high as TTHM.[35]

The source of brominated organics is generally believed to be bromide present in the raw water.[6,10,21,36,37] Under conditions normally encountered in drinking water treatment, hypochlorous acid will oxidize bromide to hypobromous acid.

$$HOCl + Br^- \rightarrow Cl^- + HOBr \qquad (3)$$

Hypobromous acid can then react to form trihalomethanes. The relative distribution of different trihalomethanes, and the total amount produced, has been shown to be dependent on the bromide concentration.[37] Hypobromous acid tends to substitute more readily than hypochlorous acid so more stable halogenated products will be observed in water with high bromide levels. Trihalomethanes containing iodine can also be formed when water containing iodine is chlorinated.[37]

pH exerts a strong effect on formation of trihalomethanes. Increased rate and extent of THM production have been observed with increasing pH.[8,9] This is similar to the behavior of the haloform reaction with simple ketones.

The effect of chlorine concentration on production of trihalomethanes depends on the relative amount of organic precursors present. If sufficient chlorine is present to maintain a free chlorine residual, adding additional chlorine will result in only marginally more production of THM.[10,21,38] However, if sufficient chlorine is not present to maintain a free residual, it will stoichiometrically limit the reaction and the production of THMs will be linearly related to chlorine dose.

The exact health significance of halogenated organics in drinking water is difficult to determine since they are taken into the body for long periods of time at low doses. However, both laboratory studies with animals and the epidemiological studies of human populations have indicated that the synthetic organics in drinking water are potentially harmful to humans. Chloroform has been determined to be a carcinogen in laboratory rats,[39] and other trihalomethanes are considered to be equally as toxic.[40]

Concentrated tap water samples have been shown to be mutagenic in the Ames bioassay procedure,[41] and unconcentrated samples show an increase in mutations, but not to the extent to be positive in the test.[42] Positive results in this procedure have been correlated with human carcinogenicity.

Several epidemiological studies in Louisiana concluded that higher death rates for some forms of cancer occur in areas that obtain drinking water from more polluted sources.[43,44] A study in Ohio indicated higher death rates from some forms of cancer in residents who drank surface water compared to groundwater.[45] A study of New York water supplies which did not chlorinate their water showed that their users had lower cancer death rates.[46]

Analysis of Halogenated Organics

Trihalomethanes: All methods for measuring trihalomethane concentration in drinking water rely on gas chromatography (GC).[47] The trihalomethanes can be concentrated prior to measurement by purging them from the water sample and trapping them on a porous adsorbent,[15] or by extracting them with a non-polar solvent.[1,48-51] Direct injection of water samples has also been used,[52] but higher THM levels are obtained by this technique because the high temperature of the GC decomposes some non-volatile halogenated compounds to THMs.[53] The Hall Electrolytic Conductivity Detector is used with the purge-and-trap procedure while the other techniques use an electron capture detector. The USEPA has adopted both the purge-and-trap and liquid-liquid extraction procedures as approved techniques for monitoring THM in conjunction with requirements of the Safe Drinking Water Act.[13]

Total Organic Halogen: The analysis of total organic halogens is more difficult. Much of the halogenated organic matter in drinking water is non-volatile, so a pyrolysis step must be included to convert the halogenated organics to volatile products. These non-volatile halogenated compounds are poorly defined and may consist of a wide variety of different types of compounds. This fact makes it difficult to develop a repeatable, accurate measurement technique.

The first TOX procedure was developed in Germany, and consisted of adsorption of the halogenated compounds on activated carbon, pyrohydrolysis with steam and oxygen, and measurement of the resultant chloride.[54,55] This procedure has been modified by researchers in the U. S. who use a more sensitive technique for chloride analysis (microcoulometry) and reduce interference by inorganic halogens with a nitrate wash.[56] Other modifications of the technique include using activated carbon in mini-columns,[57] and using filtration rather than coagulation to remove the activated carbon after adsorption.[58] A resin adsorption, solvent elution procedure has also been used to concentrate organic halogens before pyrolysis and microcoulometric analysis.[59]

The need clearly exists for a rapid, reliable analysis technique to measure the total amount of halogenated organic matter in a water sample. It would be particularly desirable if the technique used equipment required for other trace organic analyses so that more labs would be able to conduct the analyses at lower costs.

Formation Potential for Halogenated Organics: In addition to measuring concentrations of THMs and TOX, it is desirable to measure the amount of organic precursors present in a water sample that has the potential to form THM or TOX when chlorine is added. National surveys showed a correlation between total organic carbon (TOC) levels and TTHM concentration.[11,12] However, the correlation was not good enough to use as a predictive tool.

Other surrogate measurements for TTHM, such as ultraviolet absorbance (UVA), fluorescence, and carbon chloroform extract showed less significant correlations with TTHM.

Although ultraviolet absorbance was not able to accurately predict TTHM concentration when data from a large number of water supplies was used, it is an attractive surrogate that may provide reliable information when applied to an individual water system. The use of ultraviolet absorbance as a THMFP surrogate is based on the fact that humic substances absorb in the ultraviolet range[33] due to their aromatic building blocks. The spectra is featureless without maxima or minima, and absorbance generally decreases as wavelength increases. The major advantage of using UVA as a surrogate is its ease of measurement. It has been used to characterize water quality in natural water systems[35,60,61] and wastewaters,[60,62,63] and to monitor water and wastewater treatment processes.[63,64]

The best way to measure precursors of THM in water is to chlorinate the water samples under controlled conditions and measure the resultant TTHM after a standard incubation time.[13] This procedure can be used to measure the potential of forming THM or TOX. The test can be conducted under conditions expected in the distribution system to provide an estimate for the concentration expected at the users tap.

A modification of the basic THMFP test offers the potential for easier analysis. This modification is based on the fact that iodine tends to form halogenated compounds more readily then chlorine, and that iodoform (triiodomethane) can be measured spectrophotometrically.[65] This test could be conducted similarly to the initial incubation step of the THMFP procedure, with the exception of adding iodine rather than chlorine. After incubation, the iodoform produced could be extracted with hexane, or other non-polar solvent, and measured spectrophotometrically at a wavelength near 349 nm. The reaction between iodine and precursors is not necessarily the same as that between chlorine and precursors. However, the similarities should be sufficient to allow the procedure to be used as an operational tool at water treatment plants that do not have extensive laboratory facilities. Since bromoform absorbs in the ultraviolet near 224 nm,[66] a simplified bromoform formation potential test may also be possible.

Options for Control of Halogenated Organics

Three approaches can be used to control halogenated organics that are formed during conventional water treatment.[67] First, an alternative disinfectant which does not form halogenated organics can be used in place of chlorine. Second, halogenated organics may be removed after formation. Third, precursors of halogenated compounds may be removed before chlorine is added. Because a maximum contaminant level has now been set for TTHM in the National Interim Primary Drinking Water Regulations,[13] major emphasis is expected to be directed toward removal of TTHM rather than TOX.

Several alternative disinfectants exist which can be used to reduce production of TTHM and TOX. The disinfectants which will probably find widest application are chloramines. This group of chemicals is attractive because it has been previously used in the U. S. It also can be adapted to systems which are presently using chlorine by the addition of an ammonia feed system. The reaction of chlorine with ammonia produces chloramines. Despite these attractive characteristics, application of chloramines as primary disinfectants should be done with caution. Chloramines are substantially weaker disinfectants than free chlorine.[68] This might lead to reduced microbial water quality if chloramines are used instead of free chlorine for disinfection. This is especially true for raw water with low microbial quality.

An alternative disinfectant, which is generally considered as effective as chlorine, is ozone. However, it is more costly than chlorine and does not maintain a residual concentration in the distribution system. The latter disadvantage may be ameliorated by addition of a small amount of chlorine before distribution of the treated water.

Chlorine dioxide is another alternative disinfectant with strength comparable to chlorine. However, chlorine dioxide and/or its by-products formed upon addition to water, appear to be toxic.[13] Sufficient data was not available to support a limitation on the amount of chlorine dioxide that can be added to potable water, but monitoring requirements were imposed.[13]

In summary, alternative disinfectants offer an effective means of reducing TTHM levels; however, the health effects of their reaction products are even less well understood than those of chlorine. Furthermore, some alternative disinfectants have weaker bacteriocidal and virucidal properties than chlorine. Substitution of these disinfectants for chlorine should be done with caution.

The second approach to reducing TTHM levels is to remove them after their formation. Air stripping and adsorption are two processes proposed for TTHM removal. Air stripping can be costly and energy intensive[69] and it can also introduce airborne microbial contamination. Furthermore, it does not reduce the level of non-volatile halogenated organics which may also produce adverse health effects. Adsorption with activated carbon or synthetic adsorbents, such as XE-340, can remove THM.[70] However, the capacity of activated carbon for THMs is relatively low and is reduced by competition for adsorption sites by natural organic matter. Some synthetic adsorbents have higher capacity for THM but are more costly. Another disadvantage of any process which only removes THM is that more halogenated compounds can form in the distribution system after leaving the treatment plant.

The third approach is to remove the precursors of THM and TOX before addition of a disinfectant. This approach not only reduces THM levels but also lowers TOX concentrations. It also allows the water treatment plant to continue to use chlorine for disinfection. Many years of experience in using chlorine have shown it to be an effective disinfectant with the ability to maintain a residual concentration in the distribution system. Furthermore, removal of precursors before chlorination is also attractive because many water treatment plants can apply it with minimal change in normal treatment procedures. Conventional treatment processes of coagulation and filtration can remove some of the trihalomethane precursors. Therefore, addition of chlorine after coagulation and filtration will result in at least partial reduction of TTHM and TOX.

Modification of the coagulation process offers the potential for additional removal of precursors. Since most water treatment plants are operated to minimize turbidity in the treated water, it may be possible to reduce THM levels by altering coagulant dose or other operating conditions. Other coagulants or coagulant aids such as synthetic polyelectrolytes or activated silica could be added to improve THMFP removal. Furthermore, innovative treatment processes such as adsorption or oxidation could also be applied in cases where additional treatment is required.

In summary, three approaches exist for control of halogenated organics in drinking waters. An alternative disinfectant can be used, the halogenated compounds can be removed by an additional treatment process, or the precursors of halogenated organics can be removed before addition of chlorine. The latter approach has the advantages of retaining an effective and widely used disinfectant, avoiding in many cases major changes in operating procedures at the treatment plants, and bringing about reductions in levels of both THM and other halogenated organics. The simplest and perhaps most economical way to apply this approach is to modify conventional coagulation processes to improve removal of precursors of halogenated organics.

Coagulation

Basic Alum Coagulation: Coagulation with salts of aluminum or iron, followed by filtration, is the conventional treatment process for removal of turbidity and color. Both of these coagulants use the same coagulation mechanisms but differ in the pH ranges for best removal. Because of the similarity, a review of coagulation will be presented in terms of aluminum sulfate or alum. However, in most cases the same conclusions can be drawn for coagulation with iron salts.

When alum is added to water, the aluminum ion quickly hydrolyzes to a variety of aluminum hydroxide species. These include mononuclear species ($AlOH^{+2}$, $Al(OH)_2^+$, $Al(OH)_4^-$, and multinuclear species ($Al_x(OH)_y^{3x-y}$).[71] The exact formula for multinuclear species is difficult to determine. Formulas such as $Al_8(OH)_{20}^{+4}$,[72,73] and $Al_{13}(OH)_{34}^{+5}$ have been proposed. Formation of larger multinuclear species results eventually in the production of a solid precipitate of aluminum hydroxide ($Al(OH)_3$), if sufficient alum is added and pH is in the proper range. The relative distribution of aluminum hydroxide species at equilibrium depends on pH.[71] Under conditions where equilibrium may not be achieved, the relative distribution of hydroxide products may also depend on the total amount of aluminum present.[74]

Four basic mechanisms have been identified by which coagulation can be accomplished.[75] First, the positively charged aluminum ion can compress the electrical double layer surrounding the colloidal particle. This decreases the repulsive force between colloids and can lead to their agglomeration, if colloid concentration is high enough to result in a sufficient opportunity for particle-particle contact. This mechanism is believed to be relatively unimportant in alum coagulation at typical water treatment plants because optimum coagulation usually occurs at pH values in which the aluminum ion is at relatively low concentrations.

The second coagulation mechanism results from the fact that positively charged aluminum hydroxide species can adsorb onto the surface of the colloid and neutralize its negative charge. Aluminum hydroxide species show an affinity for adsorption while the aluminum ion does not. Charge neutralization removes the repulsive force between like charged colloids and allows them to agglomerate.

A third mechanism occurs when high molecular weight polymers adsorb on the surface of colloids and "bridge" to another colloid. This destabilization mechanism is probably not important in alum coagulation because molecular weights of near a million are required to effectively bridge between particles. Aluminum hydroxide species are not believed to be stable at such sizes.

The fourth mechanism by which colloidal particles can be removed from solutions is by being trapped or enmeshed within a precipitate formed by the coagulant. This is an important mechanism in alum coagulation since in the pH range normally found in water treatment applications, the alum doses which are applied exceed the solubility of aluminum hydroxide. Since soluble aluminum hydroxide species are well adsorbed onto surfaces, formation of solid aluminum hydroxide tends to occur around those surfaces. Formation of aluminum hydroxide precipitates provides another explanation for removal of soluble organics since they can adsorb onto the surface of the solid.

This knowledge of the basic chemistry of aluminum in water and the mechanisms of coagulation can be applied to explain the effects of pH and coagulant dose on removal efficiency. The effects of alum dose and pH will be interrelated because the aluminum ion acts as an acid by withdrawing hydroxide from solution. As alum dose increases, the pH will decrease, unless a base is also added. This behavior makes it difficult to discern the independent effects of pH and dose.

The two predominant mechanisms of coagulation by alum are affected by dose in different ways because they are brought about by different aluminum species. As the alum dose is increased, the amount of aluminum hydroxide precipitate will increase, resulting in more efficient removal by the enmeshment mechanism. If an equilibrium model is used to describe the speciation of soluble aluminum hydroxide compounds, increasing the amount of alum added will have no effect on the concentration of soluble hydroxides present at equilibrium. However, experiments conducted under non-equilibrium conditions indicate that alum dose may have some effect on the concentration of soluble aluminum hydroxide species actually observed.[74] This is probably the case, since increased alum dose has been observed to lead to restabilization of some colloids.[75] This behavior is caused by adsorption of positively charged aluminum hydroxide species to the extent that the colloid becomes positively charged. The positive charge restabilizes the colloid through electrostatic repulsive forces. This overdosing effect is not observed when an enmeshment mechanism is predominant. Another phenomenon that is important when adsorption/charge neutralization is the dominant coagulation mechanism is the existence of a linear relationship between optimum coagulant dose and colloid concentration. This is called stoichiometric coagulation and is not observed unless adsorption is important to colloid removal.[75]

The effect of pH on coagulation efficiency is difficult to precisely describe because pH affects both the coagulant and the colloid. The distribution of aluminum species is primarily determined by pH. At pH below four, the aluminum ion (Al^{+3}) is the predominant species.[71,74] If optimal coagulation were observed to occur in this pH range, it could be attributed primarily to double layer compression by Al^{+3}. Soluble aluminum hydroxide species such as $AlOH^{+2}$ and $Al(OH)_2^+$ reach their highest concentrations in the pH range of 4-6.[71,74] However, the predominant specie in the pH range 5-8 in most water treatment applications is aluminum hydroxide solid. At pH values above eight the soluble hydroxide $Al(OH)_4^-$ becomes most prevalent.[71,74]

If pH had no effect on the colloid, the effect of pH on coagulation efficiency could be easily described in terms of aluminum speciation. However, pH does have an effect on most of the colloidal material found in natural waters. Most natural colloids are negatively charged. As pH decreases, a larger fraction of the groups responsible for the negative charge react with hydrogen ions. This results in a decrease in the net negative charge of the colloid, and therefore, its stability. It also results in effective coagulation with lower concentrations of soluble aluminum hydroxides if adsorption/charge neutralization is the dominant coagulation mechanism.

Coagulant aids are sometimes added in conjunction with alum.[75] Clays are used with low turbidity waters to increase the rate of flocculation by providing more opportunities for particle-particle collisions. Synthetic high molecular weight organic polymers are sometimes added to help coagulate particles destabilized by alum. Activated silica is also used for this purpose. This compound is prepared by producing an oversaturated silica solution by acidifying and diluting a concentrated solution of sodium silicate. The resultant compound is a high molecular weight anionic polymer or a negatively charged micro-colloid, depending on preparation conditions. These coagulant aids are believed to work by an adsorption/bridging mechanism.[76,77]

Coagulation for Removal of Color and Humic Substances: Coagulation with alum or iron salts has been used for sometime to remove color which is due to natural organic matter. Removal of color is motivated primarily for aesthetic reasons, but the organic matter associated with color has been shown to be able to solubilize and transport toxic metals and organics.[33,78] The natural aquatic organics which are responsible for color are similar to components of soil organic matter. They are normally classified as humic or fulvic acids depending on their solubility at a pH value of 1.0. A recent review is available on the characterization of aquatic organic matter and its removal by coagulation.[79]

Much of the research on color removal by coagulation has been done in laboratories with humic or fulvic acid solutions, sometimes with the addition of a well-defined clay to provide turbidity. All reports show the strong effect of pH on removal of natural organic matter (NOM). Maximum NOM removal by alum coagulation is normally observed in the pH range of 4.5-6.0.[78-87]

The width of the optimum pH range has been observed to increase with higher alum doses. These data indicate that positively charged soluble aluminum hydroxide species are probably the important agent of coagulation since they predominate in this pH range.

Stoichiometric coagulation is usually observed for NOM.[82,84,87,88] This further supports the belief that the important removal mechanism is one of adsorption/charge neutralization. Overdosing is not observed unless polymers are added with alum.[77] This observation indicates that an enmeshment mechanism may also be important for coagulation.

A complete stability diagram for a humic acid-alum system has been reported.[89] Six stability regions were found over a range of alum doses and pH values. At low pH and dose, the humic acid was stable. A region of instability was observed in the pH range of 3.5-5.0. Destabilization in this region was attributed to soluble aluminum hydroxide compounds. Another region of instability was observed in the pH range of 5-8 when aluminum hydroxide precipitate was present. Two regions of stability were observed at high pH and a region of coagulated, but stable humic acid, was observed at medium values of pH and alum dose. This region was attributed to charge reversal caused by adsorption of an excess of positively charged soluble aluminum hydroxides.

Magnesium, calcium, and sodium have been reported to improve removal of NOM by alum while chloride had no effect and sulfate hindered coagulation.[90] The effect of calcium has been confirmed in another report, but sulfate was observed to improve coagulation at the concentration tested.[89]

The relationship between removals of natural organic matter and turbidity by alum coagulation is important because most water treatment plants are operated to optimize turbidity removal. It has been observed that the optimum pH for NOM removal is usually several pH units below that for turbidity removal when separate tests are conducted either on humic or fulvic acid solutions or on clay suspensions.[82,84] When the tests are conducted with mixtures of NOM and clay together, the optimum pH for removal of NOM remains nearly the same and the optimum for turbidity removal is lowered to within about one pH unit of the NOM optimum. The alum dose required to remove NOM in mixed systems is very nearly the same as that needed for systems without clay.[84] However, the dose required for turbidity removal in mixed systems is greater than that required in clay-only systems. This is because the coagulant reacts first with the NOM present before destabilizing the clay.[91] For Mississippi River water, the optimum pH range for organic removal is more narrow than that for turbidity removal but is centered close to the same pH for most alum doses.[86] This behavior still leaves the possibility that conditions which result in good turbidity removal can result in poor organic removal.

The fact that optimum removal of NOM occurs in the pH range in which soluble aluminum hydroxide species are maximized indicates that they are important to coagulation. The importance of a reaction between negatively charged humic material and positively charged aluminum hydroxides is also supported by observations that optimum removal occurs when the electrophoretic mobility is near zero. This implies that the charge on the particles is near zero. Whether the reaction is between soluble hydroxide and soluble organic matter to produce insoluble precipitates, or between soluble hydroxides and micro-colloids is difficult to determine. In practice, the distinction makes little difference.

Removals of NOM by alum coagulation have been reported as high as 85 percent,[82,92] 90 percent,[83] 94 percent,[77] and 93 percent.[78] However, removal of TOC is usually significantly less than color removal. Color removal of 90 percent has been reported for fulvic acid solutions, but only about 30 percent removal of the total organic carbon (TOC) was observed.[83] In another case, removals were reported to be 93 percent and 50 percent for color and TOC, respectively.[78]

Coagulation for Removal of Precursors of Halogenated Organics: Fewer reports are available on the efficiency of alum coagulation for removal of trihalomethane precursors. A study of thirteen Canadian surface waters found removal of trihalomethane formation potential (THMFP) to range from 32 to 82 percent with the average value being 63 percent.[93] Another Canadian report found that 92 percent of THMFP could be removed by coagulation with alum and activated silica.[94] A laboratory study found that 70 percent of THMFP and 22 percent of TOC could be removed by alum coagulation of a fulvic acid solution.[83] Coagulation of humic acid resulted in 70 percent removal of THMFP and 86 percent removal of TOC.[83] Coagulation of Ohio River water has resulted in 46 percent removal of THMFP and 58 percent removal of TOC.[95] THMFP removal of 45 percent and TOC removal of 17 percent have been reported for a European surface water, but these experiments were conducted at relatively high pH so they may represent lower than optimal removal.[8] Lime softening of a groundwater with high organic levels has been reported to remove 29 percent of the initial THMFP and 31 percent of the initial TOC.[96]

Only one study has investigated the independent effect of pH and dose on removal of THMFP and TOC from a natural water.[97] This study found that better THMFP removal was generally observed at low pH in the range studied. However, the formation potential test was not conducted at a constant pH; therefore, the higher THMFP reported at higher pH could be the result of poor removal of precursor or more efficient production of THM at the higher incubation pH. The optimum pH region for removal of THMFP and turbidity was found to be similar, but not equivalent. These results are questionable also due to the manner in which the formation potential test was conducted. The optimum pH for TOC removal was observed to be slightly lower than the optimum for turbidity removal. This study found no evidence of an overdose effect on THMFP removal but did indicate that turbidity could be restabilized by overdosing.

Another study did find an overdose effect on removal of chloroform formation potential.[93] A minimum formation potential was found at an alum dose of approximately 12 mg/l with higher values at higher doses. The pH of this system was not reported. Therefore, the possibility exists that the overdose effect was caused by higher alum doses decreasing the pH to below the optimum range.

In summary, alum coagulation has been found in some cases to be an efficient means of removing precursors of halogenated organics. In other cases, removals are poor. There have been no systematic studies on the independent effects of pH and coagulant dose on removal of precursors from a variety of water supplies. Optimization of coagulation conditions for removal of precursors of halogenated compounds appears to be a most promising method for economically reducing levels of halogenated compounds in public drinking waters.

Activated Alumina Adsorption

Adsorption is a treatment process that can be applied to remove organic precursors of halogenated organics from public water supplies. Activated carbon is the adsorbent which is almost exclusively used for removal of organics from water or wastewater. However, activated carbon is primarily a non-polar adsorbent and has a low capacity for polar natural organics. Its low capacity for these compounds makes it somewhat inefficient and costly.

An attractive alternative to activated carbon treatment is adsorption using activated alumina. Little work has been reported on applying activated alumina adsorption to drinking water treatment, although a good deal of information is available on the general characteristics of activated alumina. This information indicates that activated alumina is particularly suited to removing natural organic precursors and has several advantages over activated carbon.

Activated alumina is a microporous crystaline solid with the general formula $Al_2O_3 - x\ H_2O$ where x typically is in the range 0-0.6.[98] It is formed by high temperature (300-900°C) dehydration of a variety of aluminum hydrates.[98] The final properties of activated alumina depend on the type of aluminum mineral used and on the activation conditions. Typical properties for activated alumina are shown in Table 1.[99-102]

In comparison to activated carbon, activated alumina generally has lower specific surface areas but is more dense and less expensive. Therefore, when activated alumina and activated carbon have comparable adsorption capacities, activated alumina will be the adsorbent of choice since it will require less adsorber volume and will cost less.

TABLE 1

Average Properties of Activated Alumina

Specific Surface Area	300 m^2/g
Bulk Density	0.8 g/cm^3
Specific Pore Volume	0.35 cm^3/g
Average Pore Diameter	4-5 nm
Cost	0.27 $/lb.

Activated alumina has certain properties which make it particularly well suited for adsorbing natural humic substances. The surface of activated alumina is polar and positively charged at pH values below 9,[103] so it is well suited for the removal of polar, negatively charged molecules such as humic substances.[104] Furthermore, activated alumina generally has a larger average pore size than carbon. This makes it better able to adsorb large molecules found in drinking water. The average pore size for activated alumina is in the range 4-5 nm,[100,101] while over 95 percent of the pore area in highly activated carbons is associated with pores less than 2 nm.[105]

Although activated alumina has been used as a chromatographic adsorbent for some time,[106] its use as an adsorbent for humic substances has been relatively recent.[107-116] However, theoretical arguments lead to the conclusion that activated alumina should readily adsorb humic compounds. Normally, mineral oxides display good adsorption of those compounds with which a component of the crystal lattice can form complexes.[117] Soluble aluminum can form complexes with natural humic/fulvic compounds.[31,104,118] Therefore, activated alumina would be expected to adsorb these compounds well. This is found to be the case since removal of humic substances from water by activated alumina has been shown to be as high as 99 percent,[110] 98.5 percent,[111] and 98 percent.[112] One study reported data from which a complete isotherm could be calculated for humic acid adsorption by activated alumina.[116] The Freundlich form of this isotherm is the following:

$$q = 13\ C^{0.16} \qquad (4)$$

q = solid phase concentration (mg/g)
c = liquid phase concentration (mg/l)

For comparison, a study of adsorption of humic acid on four activated carbons found that solid phase concentrations of between 10 to 20 mg/g were obtained at humic acid concentrations of 3 mg/l in the liquid phase.[119] The corresponding solid phase concentration on activated alumina can be calculated as 15 mg/g using Equation 4. Because of its lower price and higher density, these data indicate that activated alumina is the superior adsorbent for removal of humic substances from water. Comparison of results of different studies using different types of "humic acid" must be made with care because of differences in chemical composition of compounds labelled "humic acid." However, these comparisons do indicate the potential of the activated alumina adsorption process in water treatment.

Removal of natural humic/fulvic compounds by activated alumina is strongly affected by pH.[107] Maximum adsorption occurs in the pH range 4-6 and decreases as pH is raised. At pH values above 10, very little adsorption occurs. This characteristic makes activated alumina adsorption particularly well suited to treatment of low alkalinity, high organic surface waters such as those found in East Texas.[120]

Another component of natural organic matter found in water supplies, ligninsulfonic acid, has been shown to be well removed by activated alumina.[116,121,122] Other compounds such as surfactants,[123,124] substituted benzoates,[125] poly (vinyl) alcohol,[126] phenolic compounds,[116] napthalenesulfonic acids,[116] substituted pyridines,[116] and dyes[106,116] have also been reported as being adsorbable on activated alumina. In addition, activated alumina has been found capable of removing mixtures of unidentified organics from a variety of municipal and industrial wastewaters.[127-132]

A major advantage of activated alumina adsorption is the potential for regenerating the adsorbent by chemical rather than thermal means. Humic substances have previously been removed from activated alumina by phosphate at pH = 7,[112] and pH > 12,[111] sodium hydroxide,[133] sulfuric acid,[133] and ammonium hydroxide.[134] For water treatment applications, regeneration by extreme pH and/or high ionic strength appears to be the most promising. Regeneration occurs at high pH since adsorption of negatively charged molecules is inhibited by competition from hydroxide ions and/or changes in the surface of the adsorbent. Low pH regeneration is accomplished by protonating the humic molecules so that they become uncharged, less polar and less strongly adsorbed by activated alumina. Regeneration at high ionic strength can be considered analogous to regeneration of ion exchange resins. The most promising regenerants for water treatment applications appear to be lime (if carbonate precipitation can be avoided), sodium hydroxide, sodium chloride, and sodium hydroxide/sodium chloride mixtures.

Activated alumina can also be regenerated by conventional thermal techniques. Its stablility at high temperature and resistance to abrasion indicate that it may be regenerated without the costly attrition losses associated with regeneration of activated carbon. Activated alumina regenerated eighty-three times showed little to no loss in adsorptive capacity.[132]

To date, only one reference has been found on using activated alumina adsorption for removing organics from drinking water.[116] This work measured the adsorption capacity of several activated aluminas for a wide range of organic compounds, including humic acid and ligninsulfonic acid. The latter are important in drinking water treatment since they constitute a large fraction of the organics found in natural water. Humic substances, ligninsulfonic acid, and other compounds with disassociable hydrogen ions were well adsorbed. They observed that large molecules tended to be better adsorbed up to a molecular weight of 20,000-40,000. Most compounds were found to be poorly adsorbed at high pH. For ligninsulfonic acid, a pH increase from 8 to 10 resulted in a decrease in adsorption of about 40 percent. There was also some evidence that adsorption of some compounds was reduced at low pH, although no experiments were reported below a pH value of 3. It was generally observed that adsorption of smaller molecules was best on activated alumina with high specific surface areas. However, the reverse was true for adsorption of large molecules such as ligninsulfonic acid. This behavior was believed to be due to the fact that adsorbents with large specific surface areas generally tend to have smaller average pore diameters. Hence, much of the surface area in adsorbents with high specific surface areas is not accessible to large ligninsulfonic acid molecules.

Laboratory scale adsorption studies were conducted with activated alumina in small (2 cm x 30 cm) columns. A constant TOC removal of 55 percent was maintained for two months (1,500 bed volumes) using a feed containing natural organic matter at a concentration of 7 mg/l as TOC.

Other tests were run with pilot scale columns (5.2 x 100 cm) using activated alumina and activated carbon in series. Feed to the columns was gravel-filtered groundwater. The two columns in series were able to remove 90-100 percent of the influent TOC for the experimental period of four weeks (1,000 bed volumes). No regeneration tests were reported. Although tentative, these results show the capability of activated alumina to remove a large fraction of the organic matter in drinking water and to be combined with GAC in an effective, well matched treatment system.

In summary, the literature indicates that activated alumina has physical and chemical characteristics which make it particularly well suited to remove organics from drinking water. Its ability to be regenerated by chemical means will reduce treatment costs. It can be used alone to remove organics which can form toxic compounds or it can also be used in conjunction with granular activated carbon to extend the capacity of GAC for toxic chemicals. Limited research in Germany has shown that activated alumina can be effectively used to remove organics from drinking water. However, the efficiency of the process for removal of natural organic precursors of halogenated compounds was not studied.

EXPERIMENTAL METHODS

Experimental Plan

The experimental plan was developed to achieve the subordinate objectives listed previously. First, analytical procedures were developed to characterize the organic chemical water quality of drinking water supplies. These included modifications of conventional analytical procedures for total organic carbon, trihalomethanes, trihalomethane formation potential, and ultraviolet absorbance. A novel, rapid procedure for total organic halogen was conceptualized and initial steps taken toward its development. Specific water supplies in Texas were then chosen for study. Samples from these water supplies were obtained and various conventional and innovative treatment techniques studied in laboratory tests. The independent effects of pH and alum dose on removal of total organic carbon (TOC), and trihalomethane formation potential (THMFP) were investigated. These experiments also examined the ability of ultraviolet absorbance (UVA) to act as a surrogate for THMFP and the relationship between THMFP removal and turbidity removal. A series of experiments were conducted to evaluate alternative coagulation procedures using synthetic organic polymers and activated silica. Finally, activated alumina adsorption was evaluated as an alternative treatment process in batch and continuous flow experiments.

Analytical Procedures

Trihalomethanes: Trihalomethanes were analyzed using a modification of the liquid-liquid extraction procedure of Glaze.[51] This procedure was conducted by taking a 5 ml sample, adding 5 ml of pentane, shaking, and injecting 1 μl of pentane into a Tracor MT-220 gas chromatograph with Ni-63 electron capture detector. The complete procedure is given in Appendix A-1.

Trihalomethane Formation Potential: Samples were collected for THMFP analysis and placed without headspace in 14 ml vials with teflon lined septa. These samples were chlorinated with enough 5 percent sodium hypochlorite solution to provide a residual. Potassium phosphate was added to each vial to buffer at pH 7, and the samples were stored at 25°C for seven days. After this incubation period, a chlorine spot check was run on the duplicate samples with a DPD reagent to assure a residual. The remaining samples were quenched with sodium thiosulfate to remove residual chlorine. The trihalomethane concentration was determined using the method previously discussed, and this concentration was reported as the formation potential of THMs. A detailed procedure for THMFP analysis is given in Appendix A-2.

Total Organic Carbon: The ampule method was used with the Oceanographic International Carbon Analyzer to measure total organic carbon. Sample volumes of 5 ml were transferred to an ampule along with approximately 0.2 gm potassium persulfate. The sample was acidified with 0.25 ml of 6 percent phosphoric acid solution and purged with nitrogen gas to remove carbon dioxide. The ampules were then sealed and placed in a autoclave at 130°C for at least four hours. A calibration curve was prepared by injecting known volumes of sodium carbonate solution. This calibration procedure was checked for accuracy by comparison with a series of organic carbon standards analyzed by the ampule method.

Ultraviolet Absorbance: Ultraviolet absorbance measurements were conducted with a Spectronic 710 spectrophotometer (Bausch and Lomb), using 1.0 or 10.0 cm silica cells. Absorbance of the sample was measured at 254 nm (E_{254}) amd at 665 nm (E_{665}). The measurement at 665 nm was used to correct for turbidity. Both absorbance measurements were made after zeroing the spectrophotometer with distilled water. The ultraviolet absorbance (UVA) was calculated as:

$$UVA = (E_{254} - E_{665})/L \tag{5}$$

L = path length of cell, (m).

Visible Absorbance: Visible absorbance (VA) was used as surrogate measurement for turbidity. It was measured along with UVA, and was calculated in a similar manner.

$$VA = E_{665}/L \tag{6}$$

Total Organic Halogen: The concept of a rapid TOX procedure was developed and equipment for the procedure was obtained. The analytical equipment consisted of a Varian model 400 A hot-wire pyrolysis unit attached through an injection needle to the inlet of a Tracor MT-220 gas chromatograph with Hall electrolytic conductivity detector. Interference by inorganic chlorides, represented by sodium chloride, was found to be negligible. Unfortunately, sensitivity of the procedure was not sufficient to measure total organic halogen in the concentration range of interest, i.e. below 1 mg/l.

Experimental Procedures

Jar Test: The coagulation jar tests were conducted using an alum solution of 10 g/l $Al_2(SO_4)_3 \cdot 18\ H_2O$ (Fisher Scientific Co.) and 0.1 N solution of sulfuric acid and lime for pH control. Alum dose and pH were controlled independently by adding acid or base to acheive the desired pH for each alum dose. The amount of acid or base required was calculated using data from an acidometric titration of the raw water sample. This procedure is described in Appendix B. Chemical additions were made to 1.0 liter samples contained in 2 liter beakers. A laboratory stirrer (Phipps and Bird, Inc.) was used to provide a 1 minute rapid mix (100 rpm), which was followed by a 20 minute slow mix (30 rpm). The samples were allowed to settle for 30 minutes at which time the pH was measured and samples taken for analysis. All filtered samples were filtered through glass fiber filters (Reeve Angel Grade 934 AH).

Sampling and Storage: Four Texas water supplies were chosen for study. They were selected based on the fact that they were sources of water for public water supplies and had high levels of organic matter. Therefore, they were likely to have a problem with halogenated organics. Many experiments were conducted with water from Lake Somerville, because of its proximity to Texas A&M University. Surface samples at Lake Somerville were taken near the Brenham water intake located at the dam. Other surface samples were obtained from Lake Livingston on the west shore near the Highway 190 bridge, from the Neches River near Highway 96, and from the Sabine River near Highway 259. Samples were collected in 5 gallon glass bottles and refrigerated if experiments could not be conducted within 24 hours.

Adsorption Equilibria: Adsorption equilibrium tests were conducted using 120 ml glass bottles with teflon lined caps. A weighed amount of adsorbent would be added to the bottle along with 100 ml of sample and placed in a laboratory shaker at low speed. After the specified contact time (usually seven days), the solution would be decanted and analyzed. Adsorbents used for these tests were either activated carbon (Hydrodarco 3000, 8/30 mesh, ICI Americas, Inc.) or activated alumina (F-1, 14/28 mesh, Alcoa Chemicals; A-2, 14/28 mesh, Kaiser Chemicals; RA-1, 0.25/0.125 inch, Reynolds Metals Co.; 2/5 mm, Rhone Poulenc, Inc.). All activated aluminas were acid washed with 1.0 N H_2SO_4, rinsed with distilled water, dried at 103°C, and stored in a desiccator before use.

Adsorption Columns: Continuous flow adsorption experiments were conducted with a set of four identical glass columns (11.0 mm ID x 630 mm) connected in series. The effluent from each column and the feed could be sampled. Gravity flow was maintained by setting a valve leading from a raised storage tank to the first column. The outlet of each column was set at a height above the adsorbent to insure that the adsorbent remained wetted. Each column was packed with 8 g of acid-washed activated alumina (Alcoa F-1), which filled a volume of approximately 10 ml.

RESULTS AND DISCUSSION

Conventional Alum Coagulation

Introduction: Coagulation with alum or iron salts is a common method of treating surface water supplies. The efficiency of this process for removal of trihalomethane formation potential (THMFP) was investigated using samples from four surface water supplies in Texas: Lake Somerville, Lake Livingston, Neches River, and Sabine River. Jar tests were conducted to determine the independent effect of pH and alum dose on removal of THMFP. The procedures followed during these tests are described in the section on experimental methods.

Results of these experiments were analyzed by constructing contour plots. These plots show concentration contours as a function of pH and alum dose. They were constructed with a computer subroutine developed by the Data Processing Center at Texas A&M University.[135] This subroutine places contour lines by linearly interpolating between data points and shapes the contour lines by performing a spline under tension interpolation.

Contour plots of trihalomethane formation potential (THMFP), ultraviolet absorbance (UVA), total organic carbon (TOC), and visible absorbance (VA) (as a surrogate for turbidity) were produced for each water supply. The contour plots for UVA, TOC, and VA can be compared to the plot for THMFP to determine how well these parameters predict removal of THMFP. Correlation plots of THMFP versus UVA and TOC, and TOC versus UVA, were also constructed to show the ability of these parameters to predict THMFP concentration.

Lake Somerville: The effect of pH and alum dose on removal of trihalomethane formation potential by conventional coagulation is shown in Figure 1. The THMFP for this water before coagulation was 930 μg/l. The data for individual trihalomethanes can be found in Appendix C-1. The strong effect of pH on removal at the higher doses is indicated by nearly vertical contour lines in this region. Dramatically improved removals occur at pH levels below pH 5.0. At lower alum doses, the effect of pH is less pronounced, but still apparent. This behavior is similar to the reported pH effect on removal by coagulation of the natural organic matter that causes color.[78-87]

Two patterns can usually be used to describe the effect of coagulant dose on removal. A breakpoint pattern occurs when doses above a level called the breakpoint dose result in little or no increased removal. Two types of overdose patterns can be described. In what will be called a "true overdose," the concentration of the compound under consideration increases with increasing coagulant dose at a constant pH. Since most water treatment plants do not independently control pH, another type of overdose pattern will be considered. This pattern will be called an "observed overdose." It will occur when increased coagulant dose results in increased concentration of the compound under consideration. This type of overdose occurs while pH is changing due to the acidity of the coagulant.

A region exhibiting a true overdose effect can be seen in Figure 1 in the pH range 5.5 to 6.5. For example, as alum dose increases at pH 6.0, THMFP contours of 800, 800, 700, 600, 500, 500, 600, 700, and 800 μg/l are crossed. The minimum THMFP is observed at an alum dose of approximately 50 mg/l.

The solid line containing asterisks represents the pH - alum dose

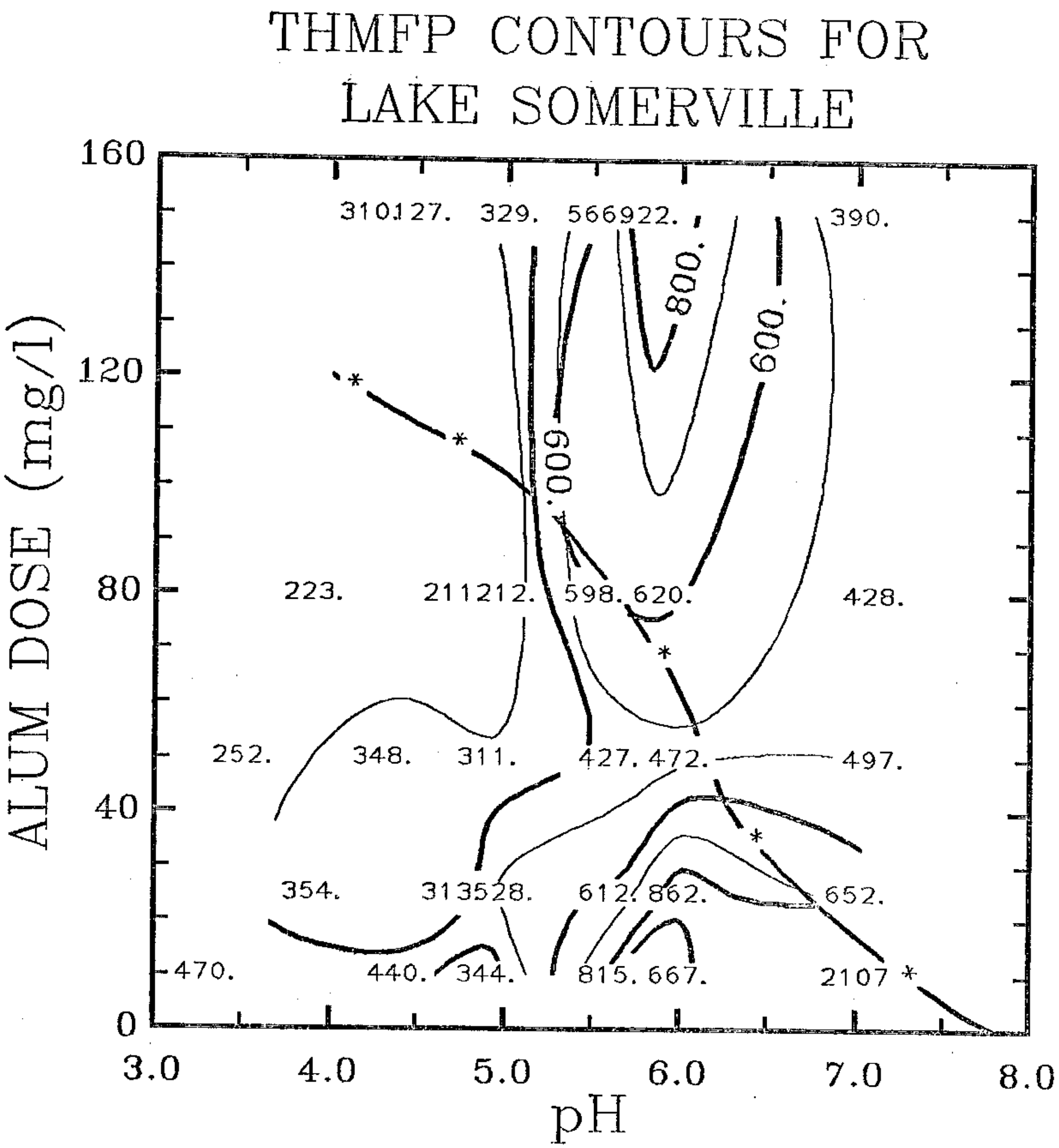
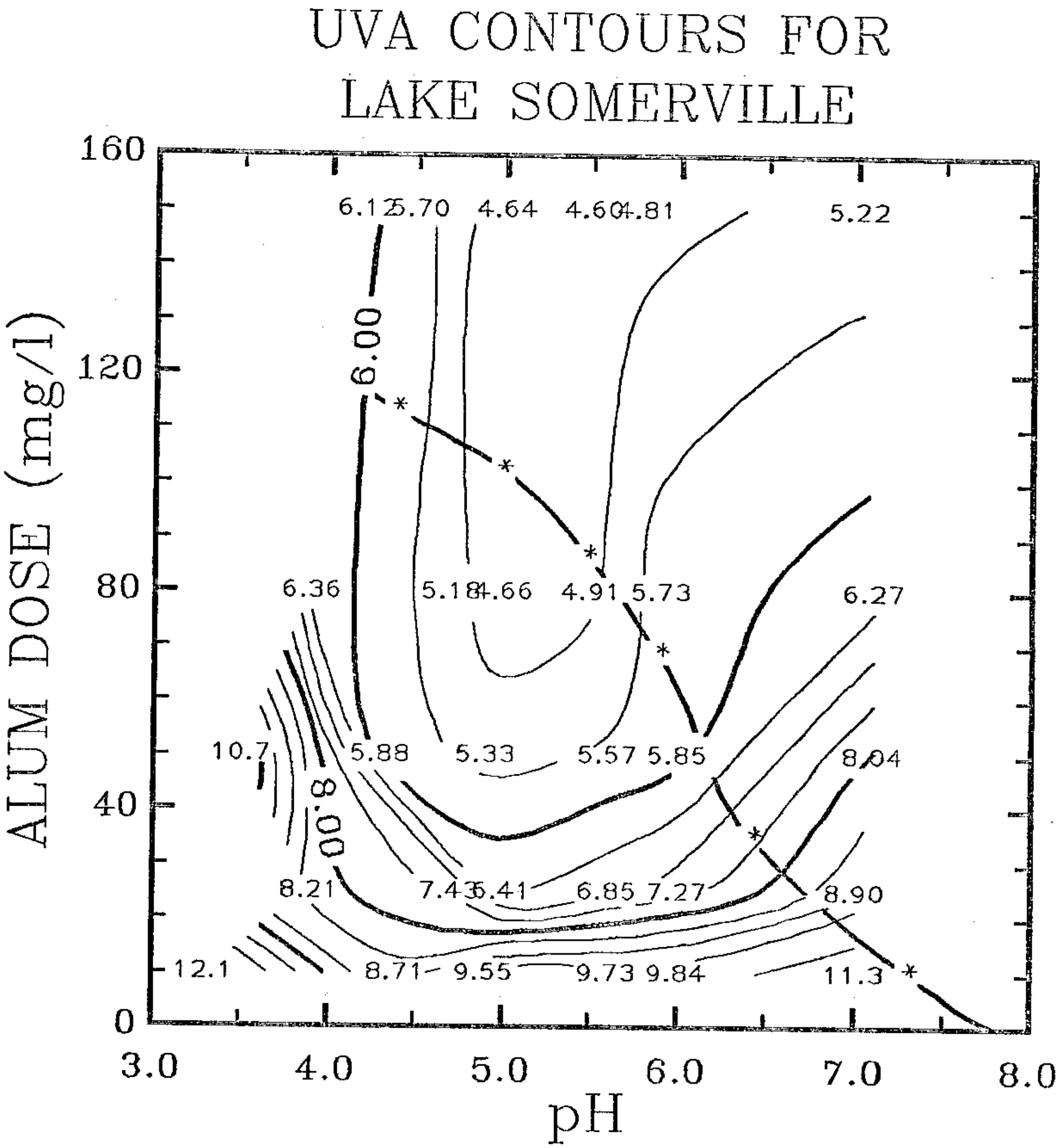


Figure 1. Trihalomethane Formation Potential Contours as a Function of pH and Alum Dose for Lake Somerville.

relationship that would be expected if alum is the only chemical added. This curve was constructed using titration data obtained on the raw water sample and assuming an equivalent weight of 222 for alum. This is equivalent to assuming that an aluminum hydroxide compound of the general form $Al_2(OH)_3^{+3}$ is produced. The titration data can be found in Appendix C-2. This curve can be used to predict the THMFP concentration to be expected if pH control is not employed.

The curve with asterisks in Figure 1 shows a slight observed overdose effect. As alum dose is increased the curve intersects contour lines representing THMFP concentration of 800, 700, 600, 500, 500, 600, 600, 500, 400, and 300 μg/l. This curve can also be used to determine if pH control by addition of strong acid or base along with the coagulant would be economically advantageous. Addition of an acid would shift the curve by an amount that can be calculated by converting the acid dose to an equivalent dose of alum using an equivalent weight of 222 g/eq for alum. This was done for an acid dose of 0.46 meq/l which is sufficient to reduce the initial pH (zero alum dose) to pH 5.0. Under these conditions, an alum dose of 10 mg/l would reduce the THMFP concentration to 400 μg/l compared to a required alum dose of 100 mg/l to reach the same level without acid addition. Using an alum cost of $146/ton and a sulfuric acid cost of $51.50/ton[136], total chemical costs of $\$0.0028/m^3$ and $\$0.0146/m^3$ can be calculated for the case of acid addition and no acid addition, respectively. For this water supply, addition of a strong acid in conjunction with alum coagulation appears to offer a significant economic advantage.

Figure 2 shows the effect of pH and alum dose on removal of ultraviolet adsorbance for Lake Somerville. The initial unfiltered UVA for this sample was 16.0 m^{-1} and the data used to produce this plot can be found in



UVA CONTOURS FOR LAKE SOMERVILLE

Figure 2. Ultraviolet Absorbance Contours as a Function of pH and Alum Dose for Lake Somerville.

Appendix C-3. Figure 2 indicates that ultraviolet absorbing materials are removed in a manner similar but not identical to THMFP. At alum doses of about 50 mg/l, the vertical contour again shows the strong effect of pH. However, in Figure 2 a trough of low UVA is observed to be centered near pH 5.0 while in Figure 1 THMFP is reduced rapidly as pH drops from 6.0 to 5.0 without increasing at pH values below 5.0. The trough broadens at lower alum doses indicating a weaker effect of pH. UVA contours also appear in a more orderly pattern with no true overdose effect observed. However, the asterisked curve indicates that an observed overdose effect would occur beginning at an alum dose of approximately 100 mg/l.

Figure 3 shows a slight positive correlation between THMFP and ultraviolet absorbance, but the correlation coefficient is very low ($R^2 = 0.15$).

The effect of pH and alum dose on removal of total organic carbon is presented in Figure 4. The raw water TOC was 7.0 mg/l. Appendix C-4 contains the data used to produce this figure. The effect of pH on TOC removal is similar to that observed for UVA removal. However, the minimum is observed near pH 6.0 rather than 5.0, and less effect of pH is observed at lower doses. The effect of alum dose is more important to TOC removal than pH. Most of the TOC is removed at a dose of 40 mg/l with slight improvement at higher doses. No true overdose effect is apparent, but observed overdose effects can be seen at alum doses of approximately 60 mg/l and 110 mg/l. However, the magnitude of change in TOC levels at these points is small.

A correlation plot of THMFP and TOC is presented in Figure 5. A very poor, but slightly positive correlation is observed ($R^2 = 0.12$). Figure 6 shows a better correlation between TOC and UVA ($R^2 = 0.69$). This indicates that it is likely a large amount of the scatter observed in the

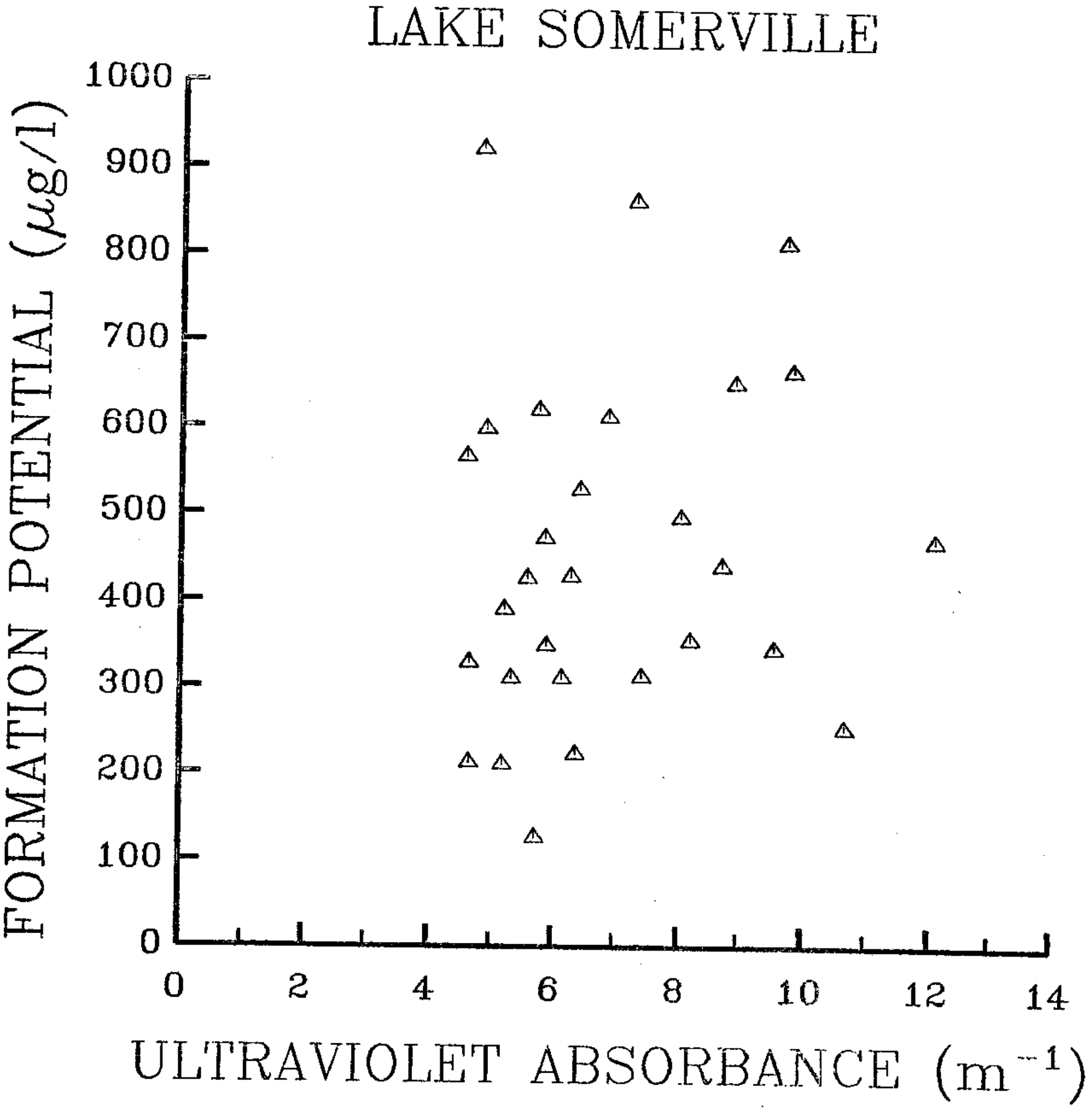


Figure 3. Correlation Plot of Trihalomethane Formation Potential and Ultraviolet Absorbance for Lake Somerville.

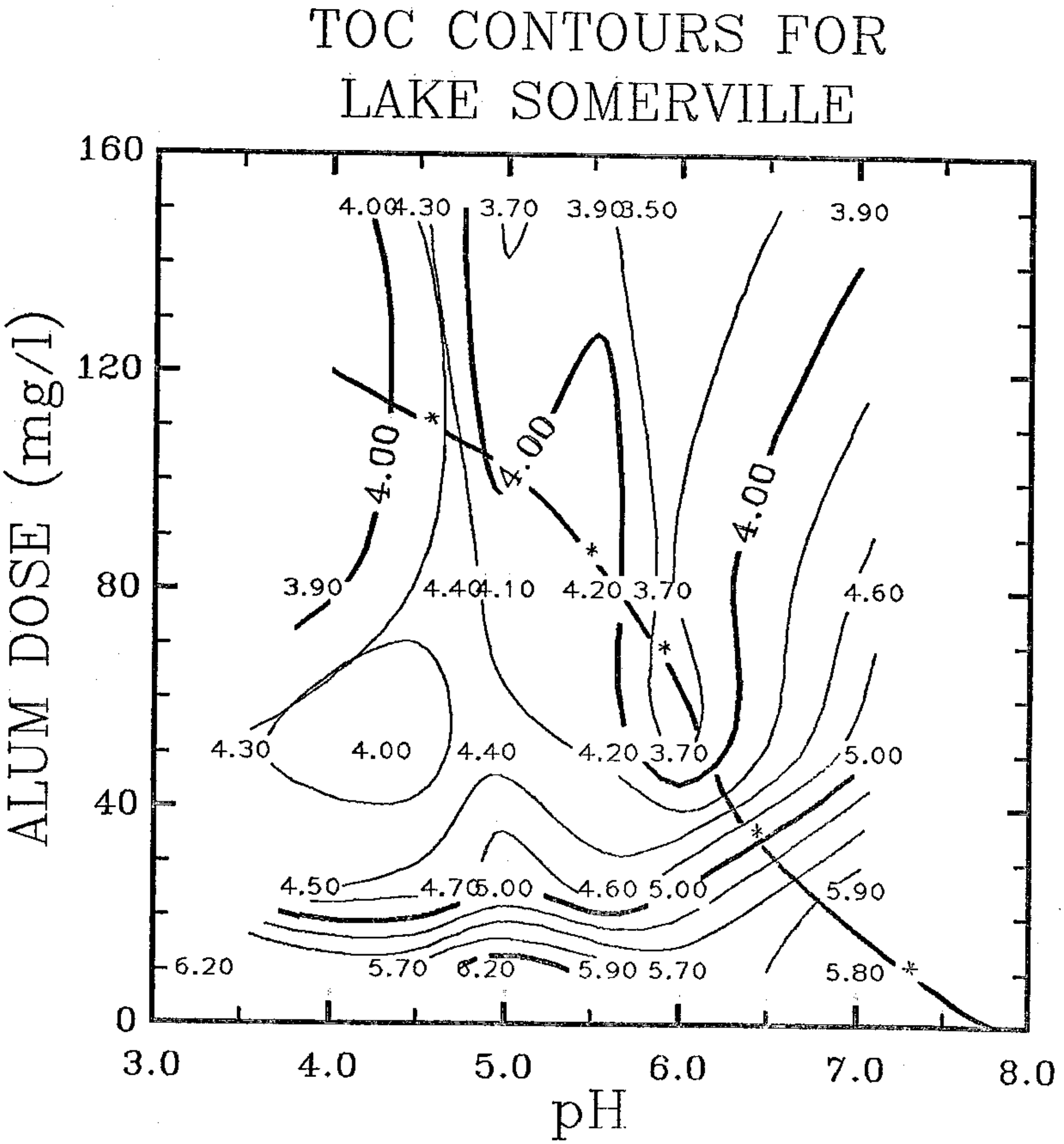


Figure 4. Total Organic Carbon Contours as a Function of pH and Alum Dose for Lake Somerville.

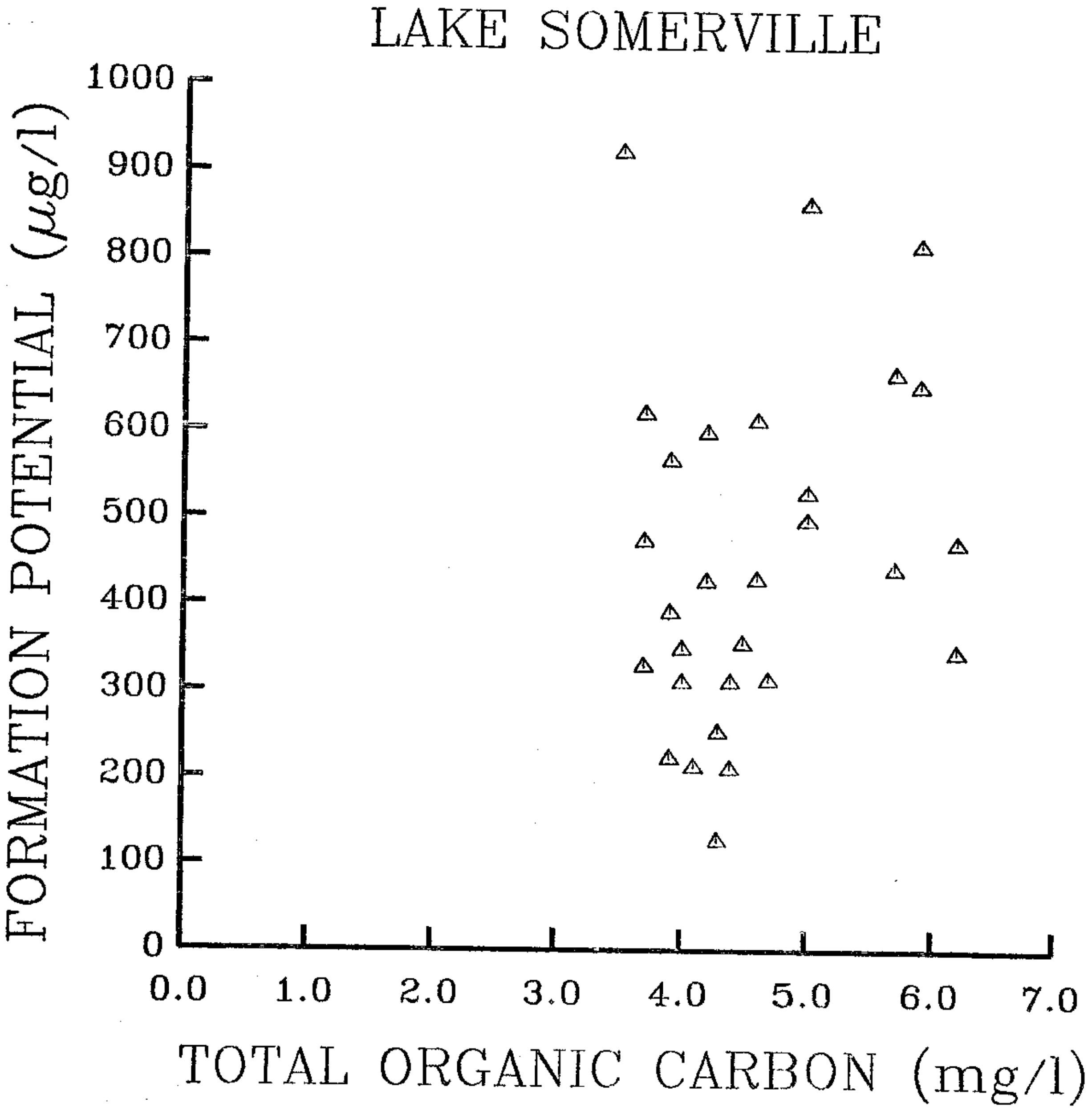


Figure 5. Correlation Plot of Trihalomethane Formation Potential and Total Organic Carbon for Lake Somerville.

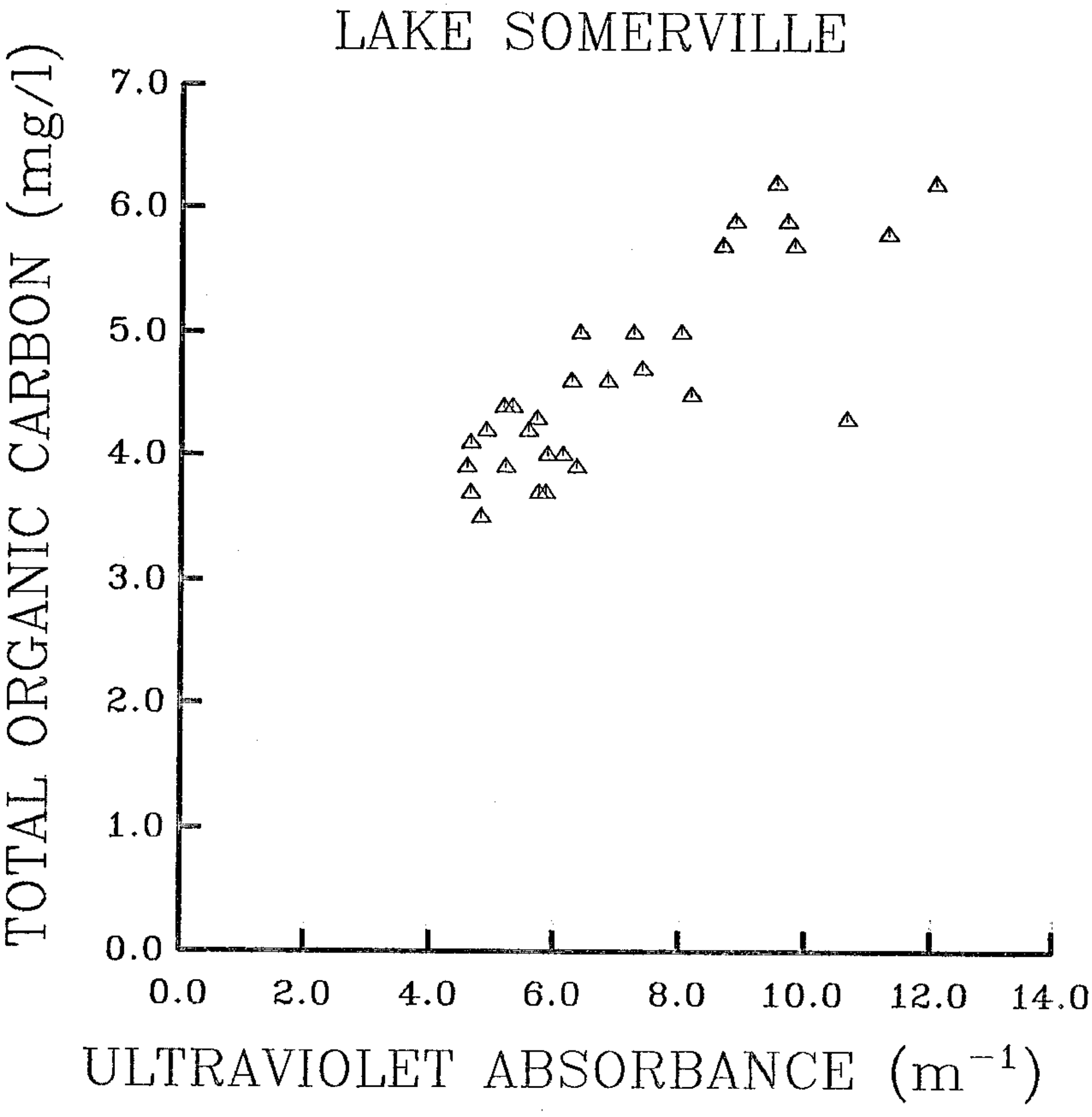


Figure 6. Correlation Plot of Total Organic Carbon and Ultraviolet Absorbance for Lake Somerville.

THMFP correlation plots is due to imprecision of the analytical technique for THMFP.

Figure 7 shows the contour lines for visible absorbance as a function of pH and alum dose. Visible absorbance was used during the study as a surrogate for turbidity. The initial VA for this sample was 1.8 m^{-1}; the entire set of data can be found in Appendix C-3. Figure 7 shows a very minor effect of pH on removal. Alum dose is the determing factor in predicting VA removal. A strong breakpoint effect is observed with little additional removal of VA observed at doses above 20 mg/l. Because of this behavior, a water treatment plant operated to remove only turbidity could show poor THMFP removal. A dose of 20-40 mg/l would be sufficient for good turbidity removal but would result in less than optimal THMFP removal.

In summary, removal of THMFP by alum coagulation is strongly affected by pH with best removals occuring below pH 5.0. Overdosing is observed both when pH is held constant and when it is allowed to decrease due to higher alum doses. Significant savings in chemical costs can be achieved by adding a strong base to reduce pH to the more favorable range below pH 5.0. None of the parameters studied (UVA, TOC, VA) was able to accurately predict the effect of pH and alum dose on THMFP removal. UVA did the best job because it showed a pH optimum near 5.0 and predicted an overdose effect. However, the overdose effect was observed at an alum dose significantly higher than that which caused a THMFP overdose. TOC indicated some effect of pH on removal at high alum doses but showed an optimum near pH 6.0 rather than below pH 5.0. Visible absorbance was unable to predict any of the characteristics of THMFP removal. A water treatment plant operated to maximize turbidity or VA removal would likely not remove as much THMFP as possible.

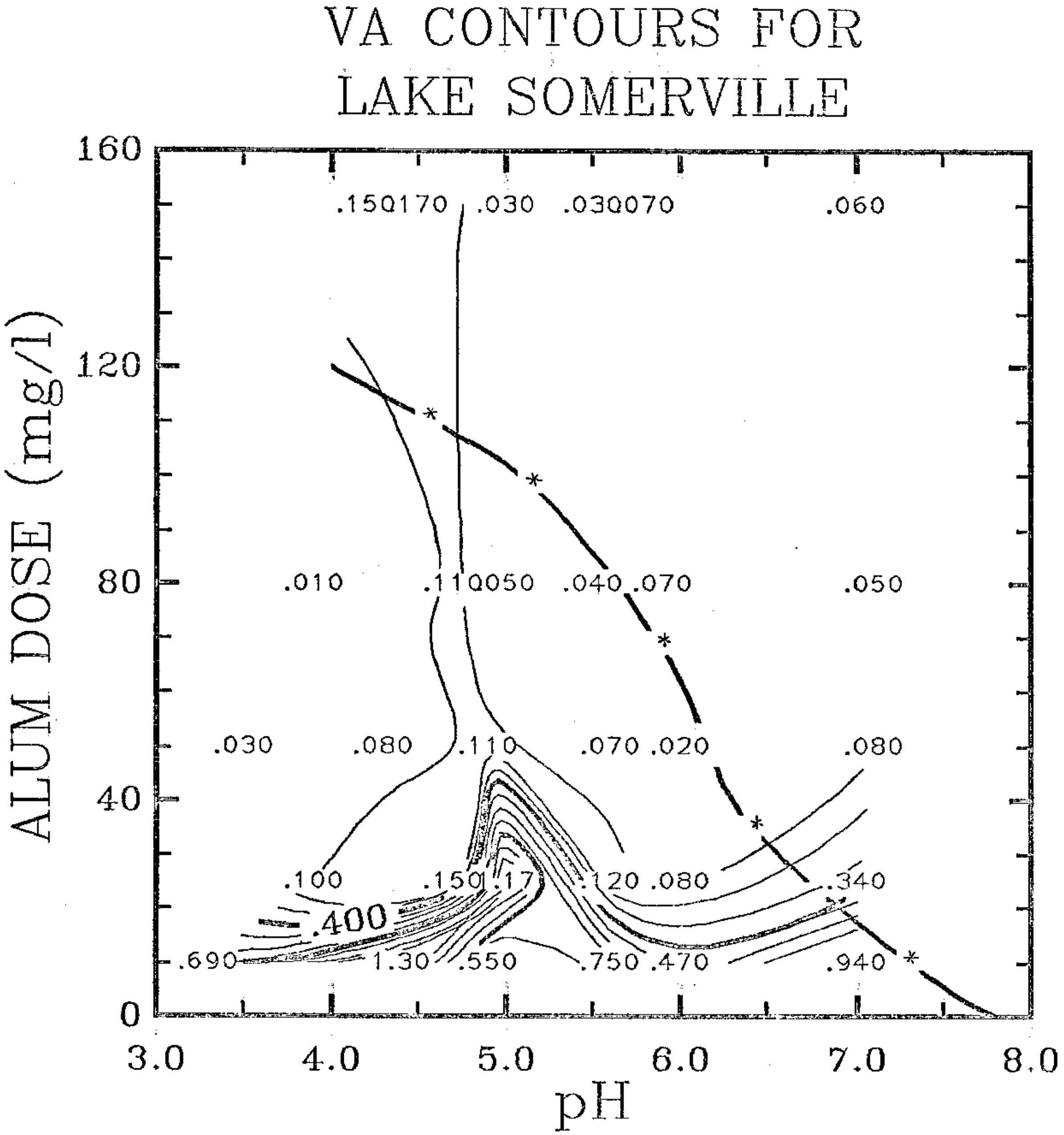


Figure 7. Visible Absorbance Contours as a Function of pH and Alum Dose for Lake Somerville.

Lake Livingston: The effect of pH and alum dose on removal of THMFP for Lake Livingston is shown in Figure 8, and the data can be found in Appendix C-5. The raw water THMFP for Lake Livingston was 825 μg/l. The nearly vertical contours in Figure 8 show that pH exerts a strong effect on THMFP removal in a similar way to that observed for Lake Somerville. However, in this case a trough of low THMFP is observed centered near pH 5.0 and at alum doses above 50 mg/l. As shown in Figure 1, THMFP removal for Lake Somerville did not have a trough since increased THMFP was not observed at lower pH. In Figure 8, another trough of low THMFP is observed centered at pH 6.0 and at alum doses above 100 mg/l. At low alum doses, Lake Livingston water shows the same effect that was observed for Lake Somerville water. Contours become more horizontal in this region indicating a stronger effect of alum dose on THMFP removal. At low doses, poor removals are observed around pH 5.5. Results for Lake Somerville showed similar behavior with higher THMFP concentrations observed near pH 6.0.

Figure 8 shows some indication of the possibility of a true overdose at pH 5.5 and at pH 7.0. The asterisked line, which predicts removals to be observed if coagulation is conducted without pH control, does not cross consecutive increasing THMFP contours. Hence, no observed overdose effect occurs. The data used to construct the asterisked line can be found in Appendix C-6.

Because of the low THMFP trough at pH 5.0, significant savings in chemical costs are possible if acid is added to reduce pH. If 0.81 meq/l sulfuric acid is added, the initial pH would be reduced to 5.75 and the alum dose required to reach the 400 μg/l contour would be reduced from 120 mg/l to 46 mg/l. This would result in a chemical cost for acid and alum of $\$0.0090/m^3$ compared to $\$0.0175/m^3$ for alum alone. However, if it

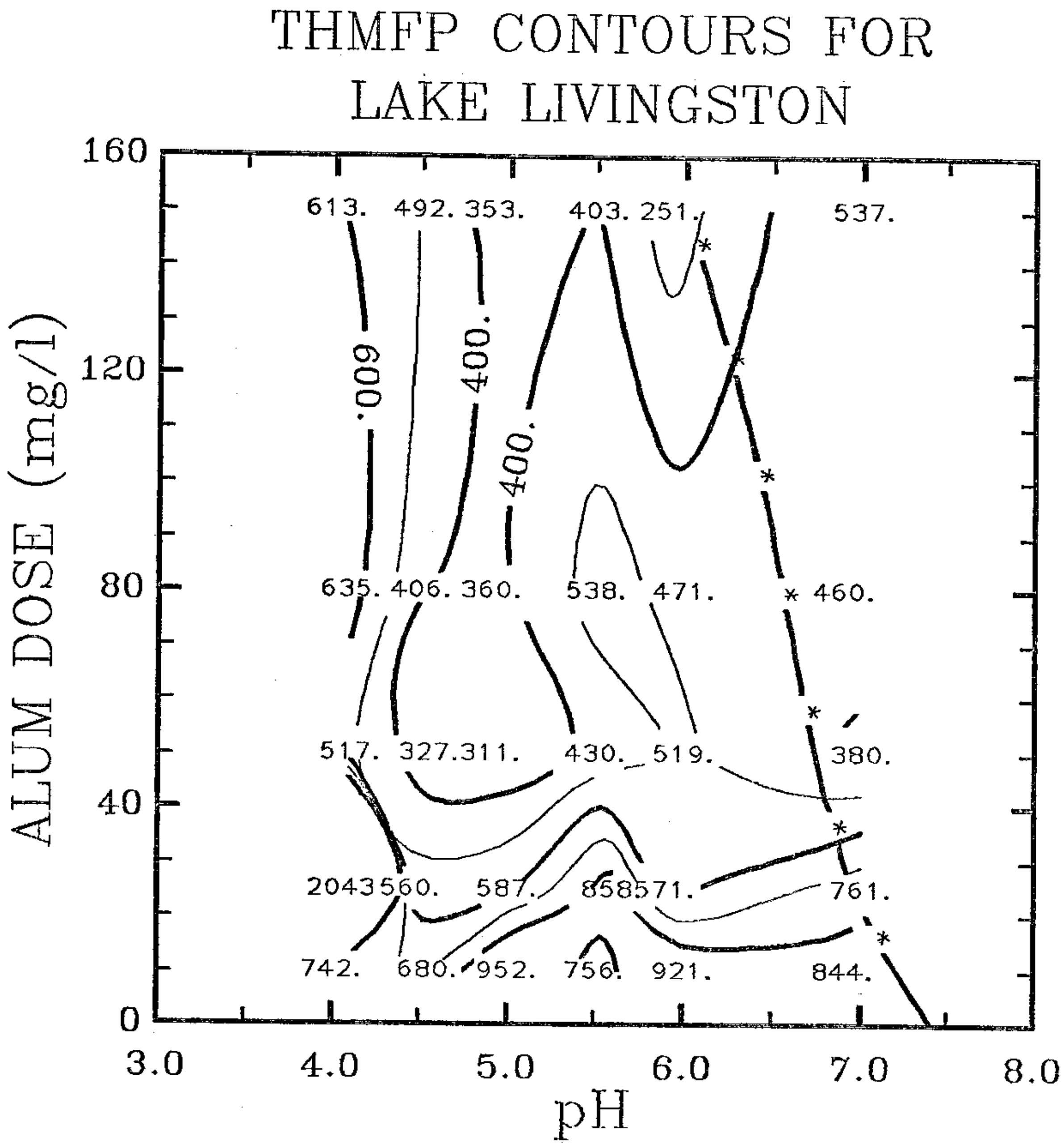


Figure 8. Trihalomethane Formation Potential Contours as a Function of pH and Alum Dose for Lake Livingston.

is only required to reduce THMFP concentration to 500 μg/l then it is cheaper to use alum alone.

The contour plot for ultraviolet absorbance is presented in Figure 9; the data is available in Appendix C-7. The unfiltered raw water UVA for Lake Livingston was 39.4 m^{-1}. The pattern of UVA removal for Lake Livingston (Figure 9) is similar to that for Lake Somerville (Figure 2). A strong effect of pH is noted at higher doses in Figure 9. A low UVA trough is observed to be centered near pH 5.5 and at alum doses above 50 mg/l. The contours flatten at lower doses showing that pH becomes a less important factor in UVA removal. For Lake Livingston, the pattern of UVA removal is very similar to that for THMFP removal. A trough is observed at high doses and flat contours are found at low doses. The UVA trough is centered near pH 5.5 while the major THMFP trough is centered near pH 5.0. The additional trough observed for THMFP removal at pH 6.0 is not seen in the pattern of UVA removal. Overdosing is not observed for UVA removal in Lake Livingston, and the tightly spaced contour lines below an alum dose of 40 mg/l show that most of the UVA removal occurs in this region.

The correlation plot of THMFP and UVA presented as Figure 10 shows that UVA is a much better predictor of THMFP than seen for Lake Somerville (Figure 3). However, a good deal of scatter is still observed (R^2 = 0.30). There is some indication of a non-linear relationship at higher values of THMFP and UVA. This could be caused by analytical errors which underestimate high concentrations of THMFP, or by the existence of ultraviolet absorbing materials which do not significantly form trihalomethanes and are removed easily by alum coagulation.

Figure 11 shows the dependency of TOC on pH and alum dose for Lake Livingston. The raw water TOC was 7.1 mg/l; the entire set of TOC data

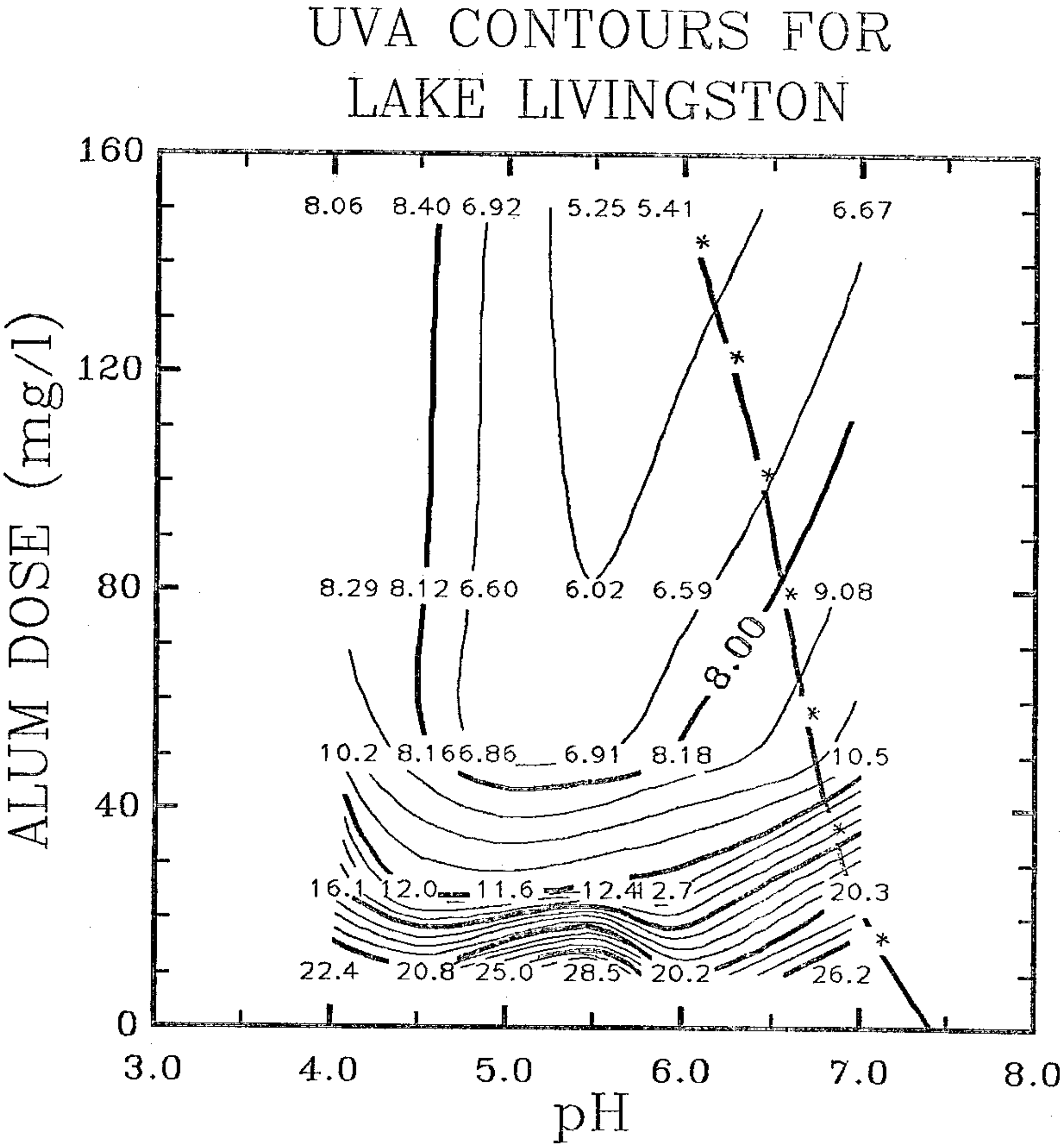


Figure 9. Ultraviolet Absorbance Contours as a Function of pH and Alum Dose for Lake Livingston.

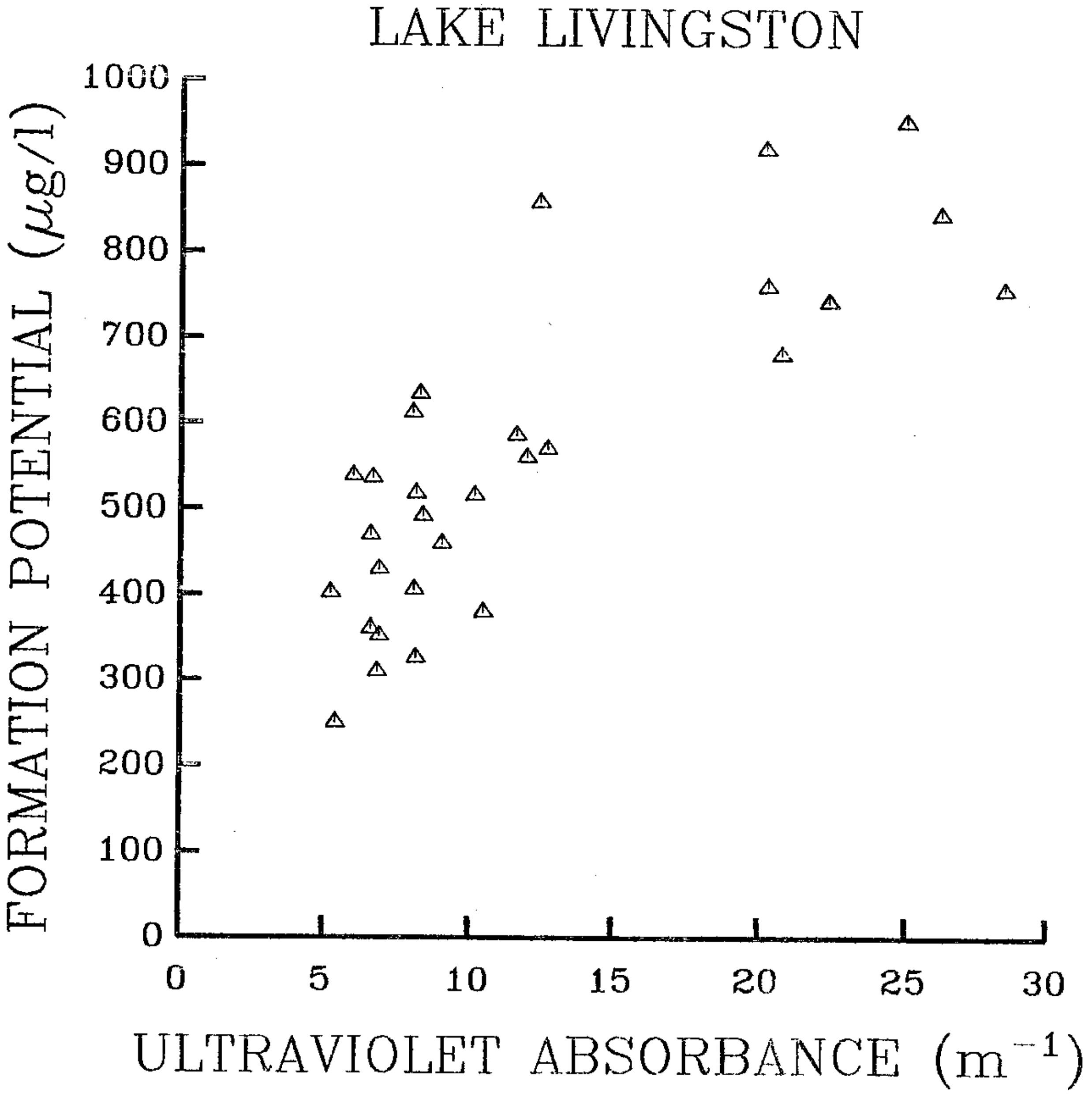


Figure 10. Correlation Plot of Trihalomethane Formation Potential and Ultraviolet Absorbance for Lake Livingston.

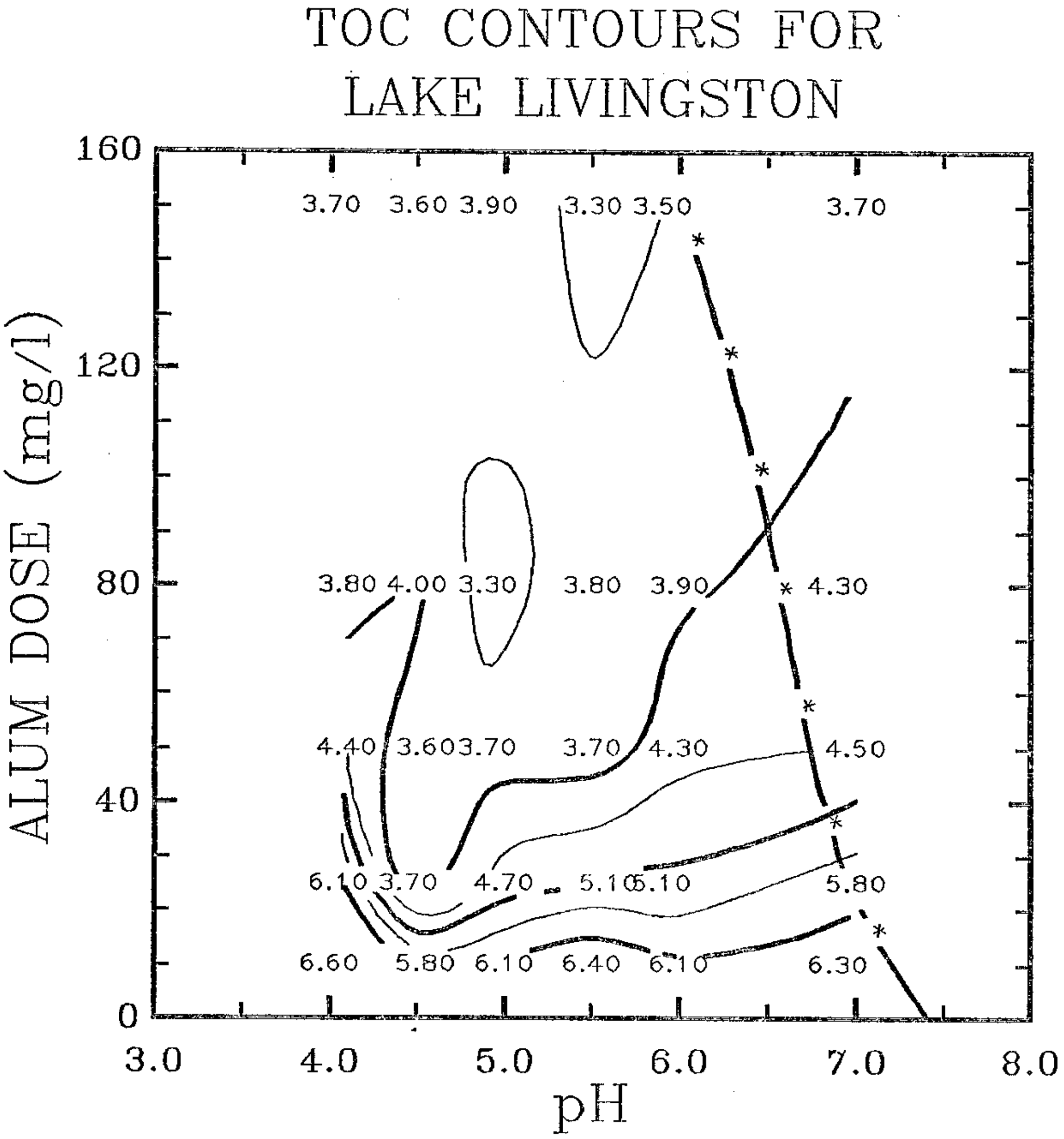


Figure 11. Total Organic Carbon Contours as a Function of pH and Alum Dose for Lake Livingston.

is given in Appendix C-8. TOC removal shows some of the same patterns exhibited for THMFP removal (Figure 8). A trough of low values for both parameters is centered near pH 4.5 at alum dose above 30-40 mg/l. In both cases, contour lines at doses below 30 mg/l are relatively flat, which indicates that alum dose is the primary determinant of removal and that pH has little effect. However, TOC removal does not show a region of improved removal at high dose near pH 6.0 as was found in the contour plot for THMFP removal (Figure 8). A slight tendency toward a true overdose effect can be seen in Figure 11 in the pH range 4.5-5.0 and at medium and high alum doses. No observed overdose effect is evident by examination of the asterisked line.

Figure 12 and 13 are correlation plots for THMFP with TOC, and TOC with UVA, respectively. Both of these figures show a positive correlation between the variables with less variability in the relationship between TOC and UVA ($R^2 = 0.88$) than for THMFP and TOC ($R^2 = 0.45$). This is similar to the results observed for Lake Somerville and indicates that much of the variability in the correlation of THMFP with TOC or UVA is due to analytical variability of the THMFP procedure.

The effect of pH and alum dose on removal of visible absorbance is shown in Figure 14. The VA for unfiltered raw water was 4.2 m^{-1}. Other values of VA can be found in Appendix C-7. Figure 14 shows that pH has little to no effect on removal of VA. Therefore, pH control by acid addition would not be advantageous. No overdose effects are evident and a breakpoint effect of alum dose can be observed. Practically all the VA is removed at an alum dose of 25 mg/l. Comparison of Figure 14 with Figure 8 shows that a water treatment system operated only to maximize VA or turbidity removal would not achieve maximum THMFP removal.

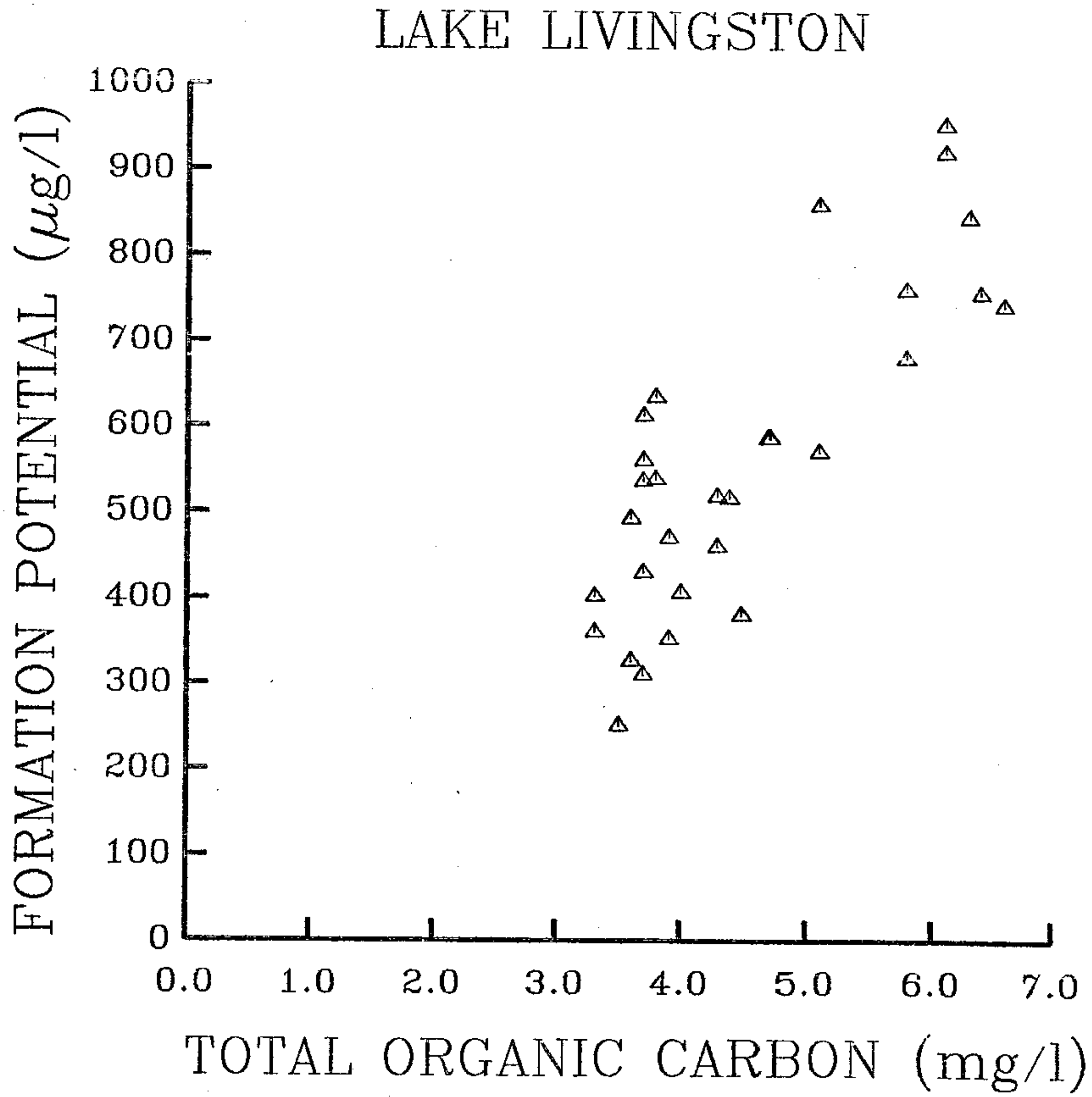


Figure 12. Correlation Plot of Trihalomethane Formation Potential and Total Organic Carbon for Lake Livingston.

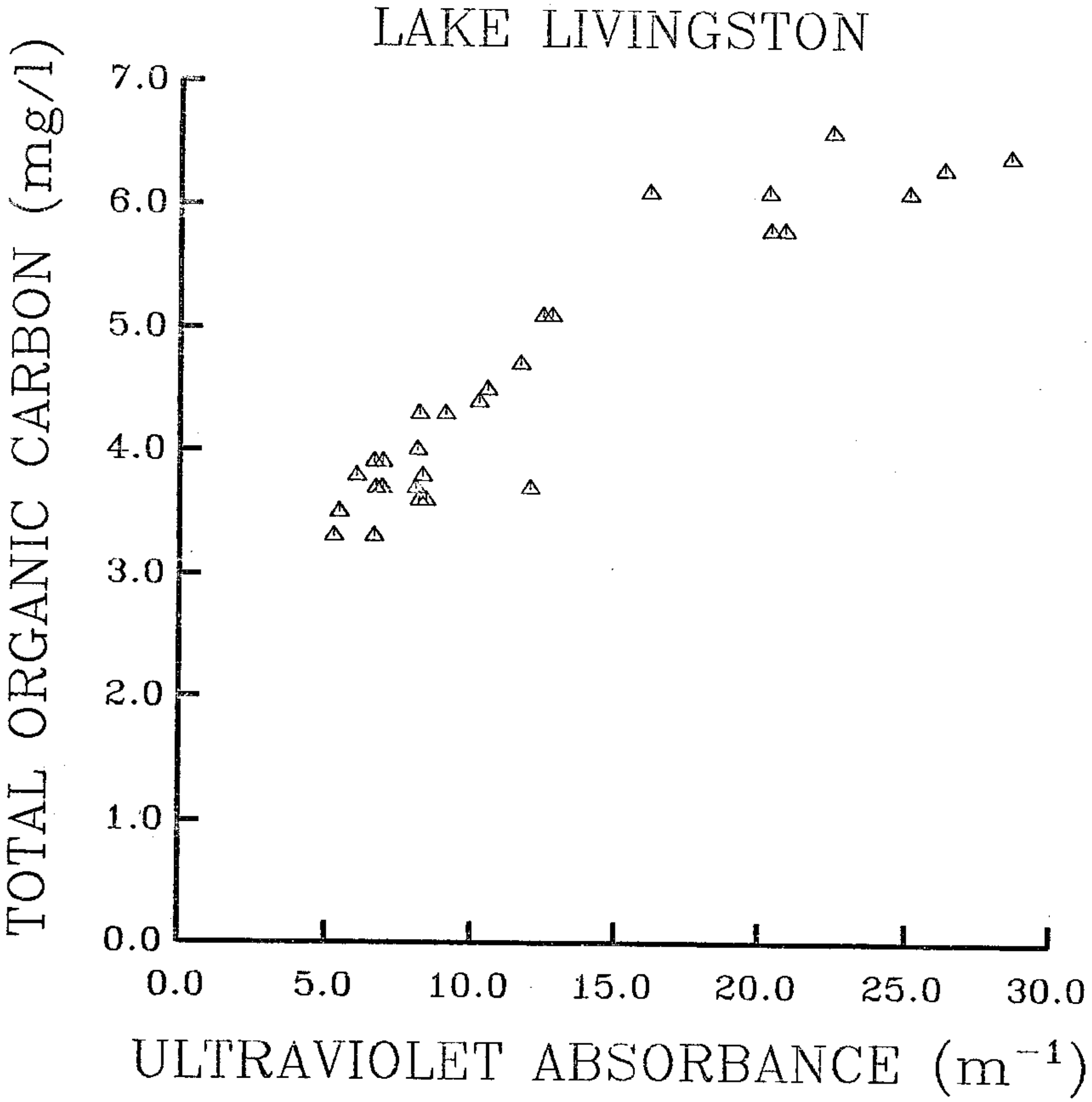


Figure 13. Correlation Plot of Total Organic Carbon and Ultraviolet Absorbance for Lake Livingston.

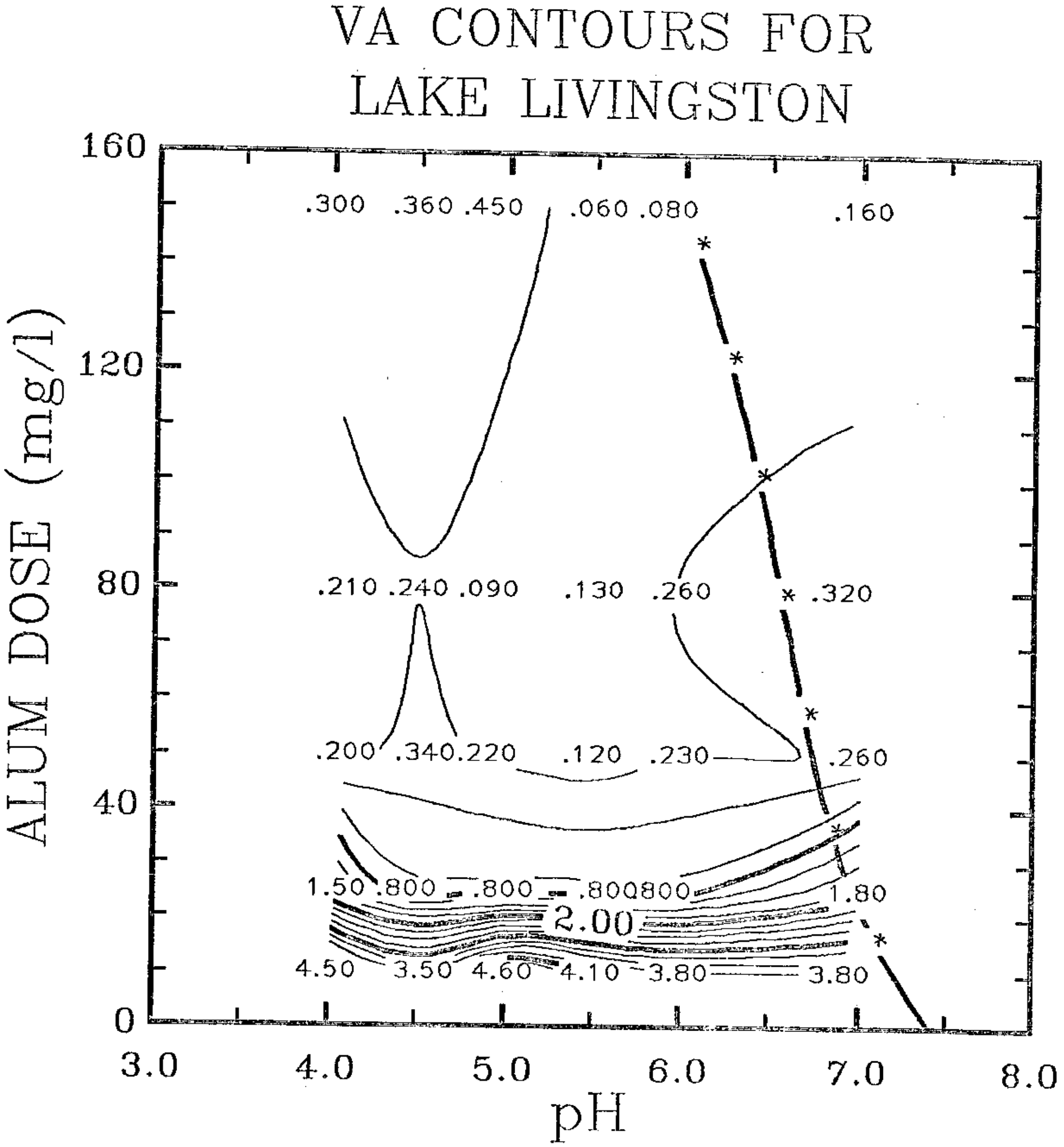


Figure 14. Visible Absorbance Contours as a Function of pH and Alum Dose for Lake Livingston.

The results of these coagulation experiments using Lake Livingston water shows that pH exerts a strong effect on THMFP removal. Minimum THMFP concentrations were observed near pH 5.0 at alum doses above 50 mg/l, and near pH 6.0 at alum doses above 100 mg/l. Only slight evidence of overdosing is observed for Lake Livingston. Acid addition could result in significant reduction of chemical costs by reducing the pH to more advantageous values. Total chemical costs to reach the 400 µg/l THMFP contour were estimated to be $\$0.0090/m^3$ and $\$0.0175/m^3$ for the case of acid addition and no acid addition, respectively. UVA was found to be a reasonably good predictor of THMFP removal. The region of optimum UVA removal was located in roughly the same region of pH and alum dose as the major area of optimum THMFP removal. Another region that was observed to result in good THMFP removal was not found to give good UVA removal. THMFP and UVA showed a positive correlation, but a large amount of scatter was observed. TOC also did a reasonably good job of predicting the pattern of THMFP removal. The optimum pH for TOC removal agreed fairly well with the pH of the major region of low THMFP. A slight tendency toward a true overdose effect was observed. Correlation of THMFP with UVA, THMFP with TOC, and TOC with UVA were all positive with the least scatter observed for the TOC-UVA correlation. Visible absorbance was removed in a manner decidedly different from that for THMFP, UVA, or TOC. Alum dose was the primary determinant of VA removal with little effect of pH observed. A breakpoint alum dose of 25 mg/l was observed beyond which little additional removal was evident. Use of UVA or TOC as surrogate parameters would result in some ability to predict THMFP removal. VA or turbidity removal shows no relationship to THMFP removal.

<u>Neches River</u>: The effect of pH and alum dose on removal of

trihalomethane formation potential is presented in Figure 15. The data used for this figure is given in Appendix C-9. The raw water THMFP for the Neches River was 795 μg/l. Figure 15 shows a distinctly different pattern of THMFP removal than observed for the other water supplies. A THMFP maximum is centered at pH 5.0 and an alum dose of 55 mg/l. This is near the pH of best removal observed for other water supplies. The best removal of THMFP from Neches River water occurs near pH 6.0 and at alum doses above 80 mg/l. Another minimum THMFP region is observed near pH 4.5 at alum doses above 130 mg/l. The nearly vertical contours at alum doses above 50 mg/l show again the strong effect that pH exerts on THMFP removal.

A true overdose effect can be seen at pH 5.0 and the asterisked curve indicates that an observed overdose effect also exists. The titration data used to construct the asterisked curve, which predicts the removals that would be observed if pH were not controlled, is given in Appendix C-10.

Because the asterisked curve in Figure 15 passes below the 400 μg/l THMFP contour, it is possible that addition of base along with alum would result in improved THMFP removal. Base addition would raise the asterisked curve and cause it to enter the region of low THMFP. The amount of base required and the cost of extra chemical additions could not be calculated, since data was obtained only for an acid titration.

Figure 16 shows the ultraviolet absorbance contours as a function of pH and alum dose for the Neches River. The unfiltered raw water UVA was 48.5 m^{-1}. The other data used to construct Figure 16 is presented in Appendix C-11. Figure 16 shows a pattern of UVA removal which is similar to the other water supplies. At higher alum doses, the effect of pH becomes important with best removals observed in the pH range 4.5-5.5.

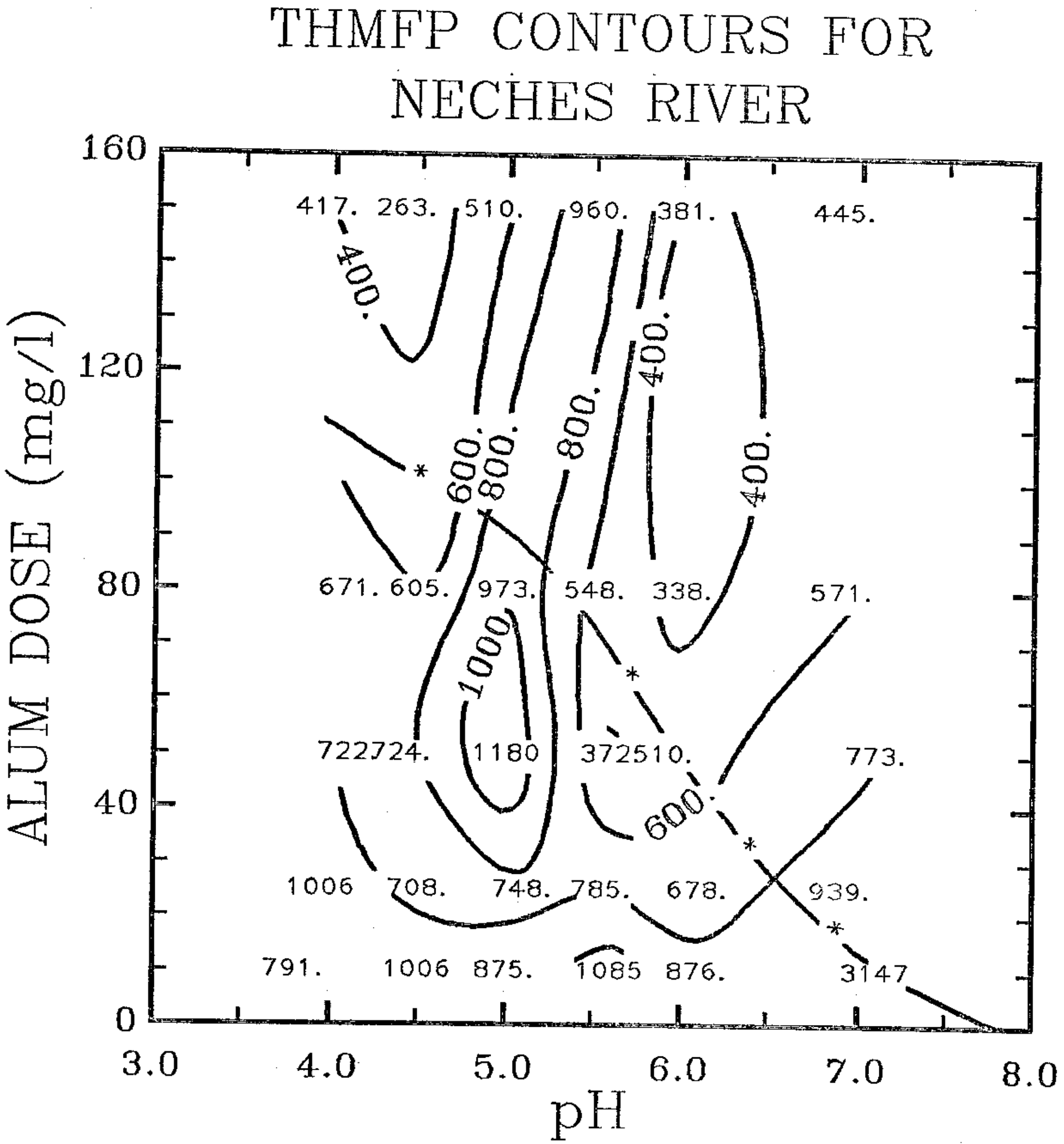


Figure 15. Trihalomethane Formation Potential Contours as a Function of pH and Alum Dose for the Neches River.

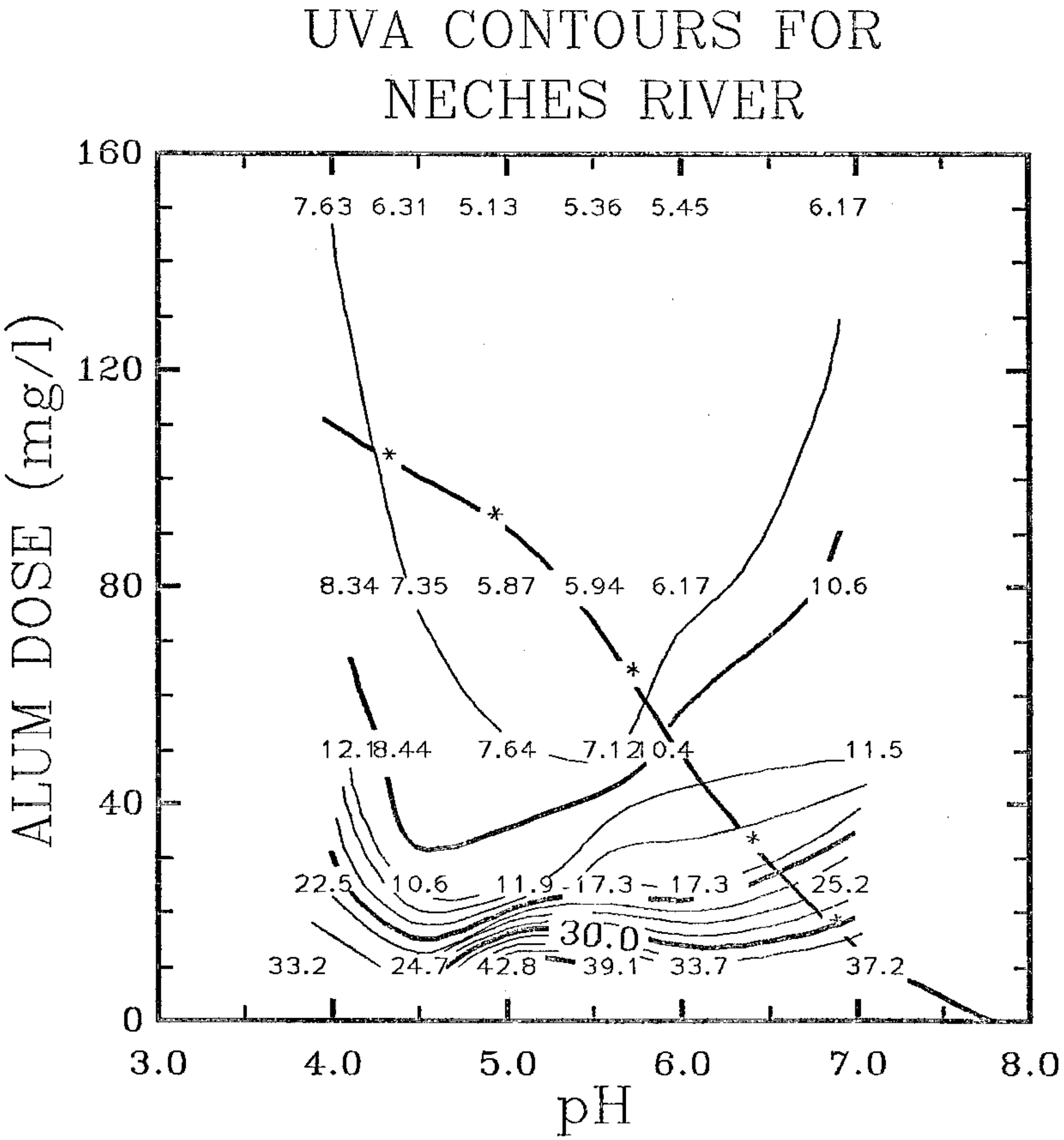


Figure 16. Ultraviolet Absorbance Contours as a Function of pH and Alum Dose for the Neches River.

The optimum pH tends to rise as alum dose increases. At lower alum doses the effect of pH is less important as it results in flat contours. No overdose effect is seen and most of the UVA removal occurs at alum doses below a breakpoint dose of approximately 50 mg/l. The pattern of UVA removal is a poor predictor of THMFP removal patterns. The regions of maximum and minimum THMFP are not evident in the UVA contours. In fact, using UVA removal to predict THMFP removal might result in operation that maximizes THMFP concentration.

The relationship between THMFP and UVA is shown in Figure 17. A positive correlation is observed but a good deal of scatter exists ($R^2 = 0.31$). The pattern observed in this plot is similar to that observed for Lake Livingston (Figure 10). In both plots, a tendency for THMFP to level off at higher values is observed.

The effect of pH and alum dose on TOC is shown in Figure 18. The data used to construct this plot can be found in Appendix C-12. The raw water TOC was 6.7 mg/l. The pattern of TOC removal is similar to that observed for UVA removal. Optimum TOC removal occurs in the pH range 5.0-6.0 at alum doses above 50 mg/l. At lower doses, pH has little effect with a very broad optimum pH range of 4.5-6.5. No overdose effects are observed. Most of the TOC removal is observed to occur below a breakpoint dose of approximately 50 mg/l. As with UVA, TOC is unable to predict the pattern observed for removal of THMFP.

Figures 19 and 20 show the correlation of THMFP with TOC, and TOC with UVA, respectively. Both show positive correlation, but the correlation of TOC with UVA shows much less scatter ($R^2 = 0.90$) than that for THMFP with TOC ($R^2 = 0.30$).

Figure 20 shows some evidence of a non-linear relationship between

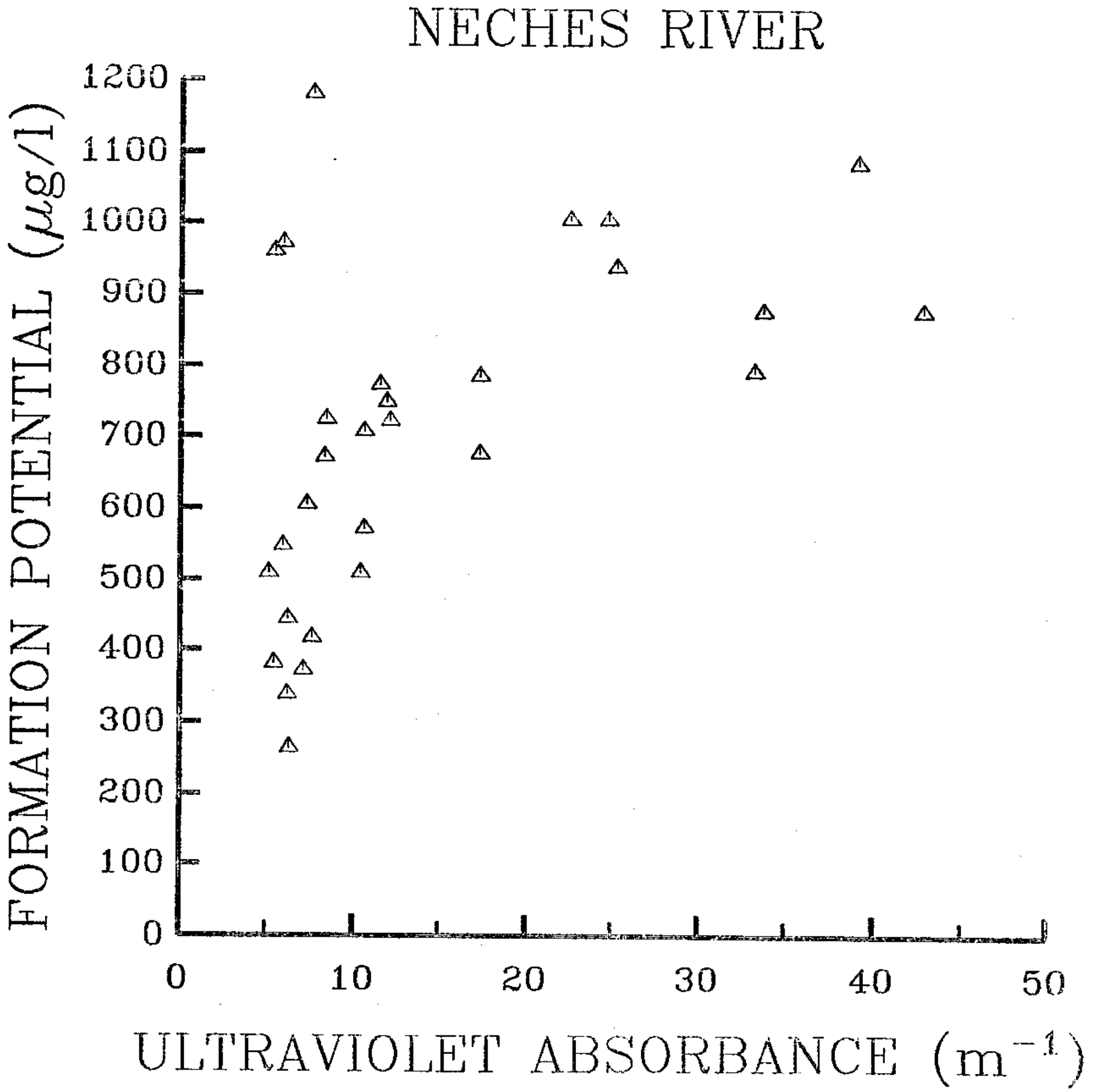


Figure 17. Correlation Plot of Trihalomethane Formation Potential and Ultraviolet Absorbance for the Neches River.

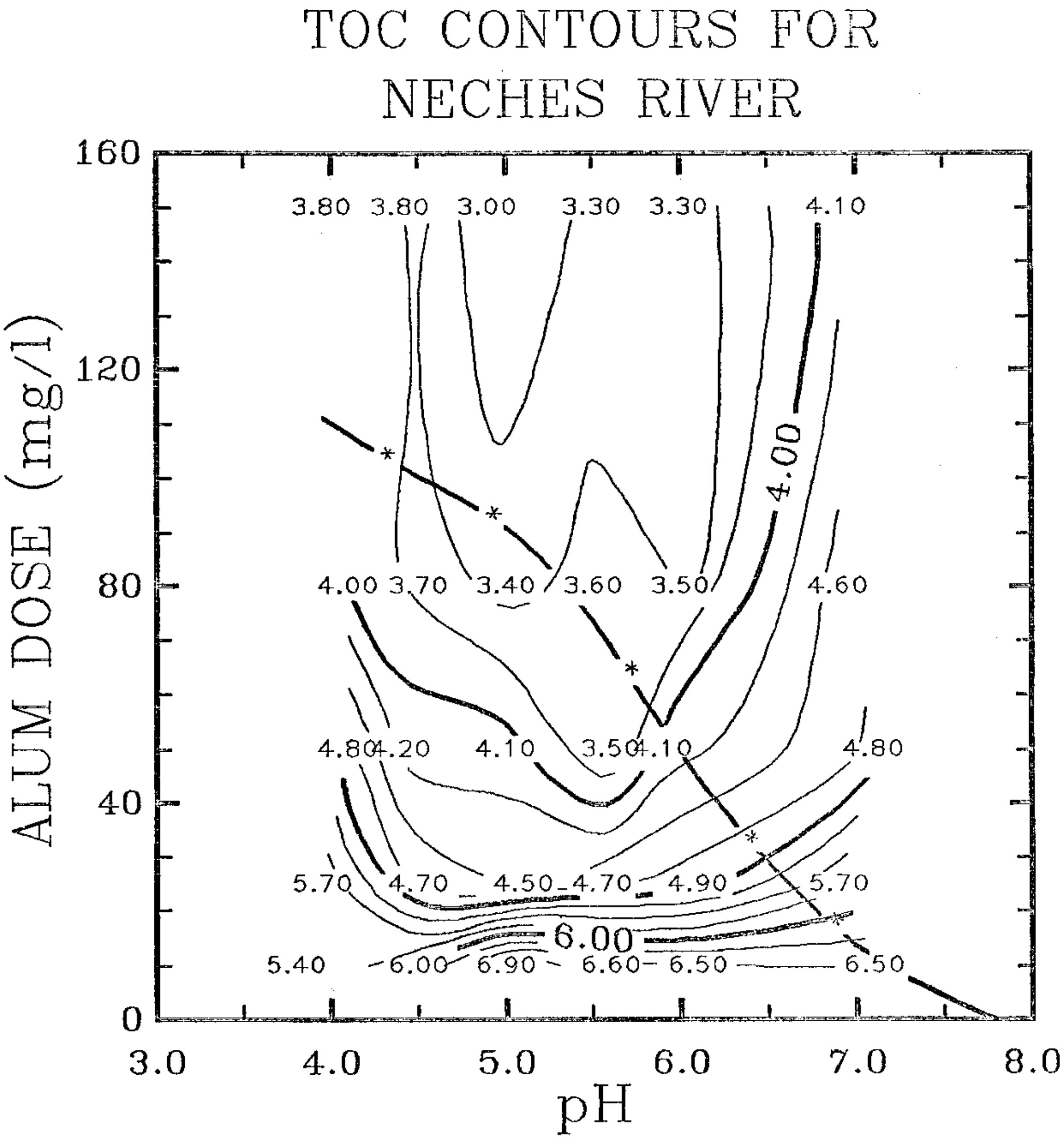


Figure 18. Total Organic Carbon Contours as a Function of pH and Alum Dose for the Neches River.

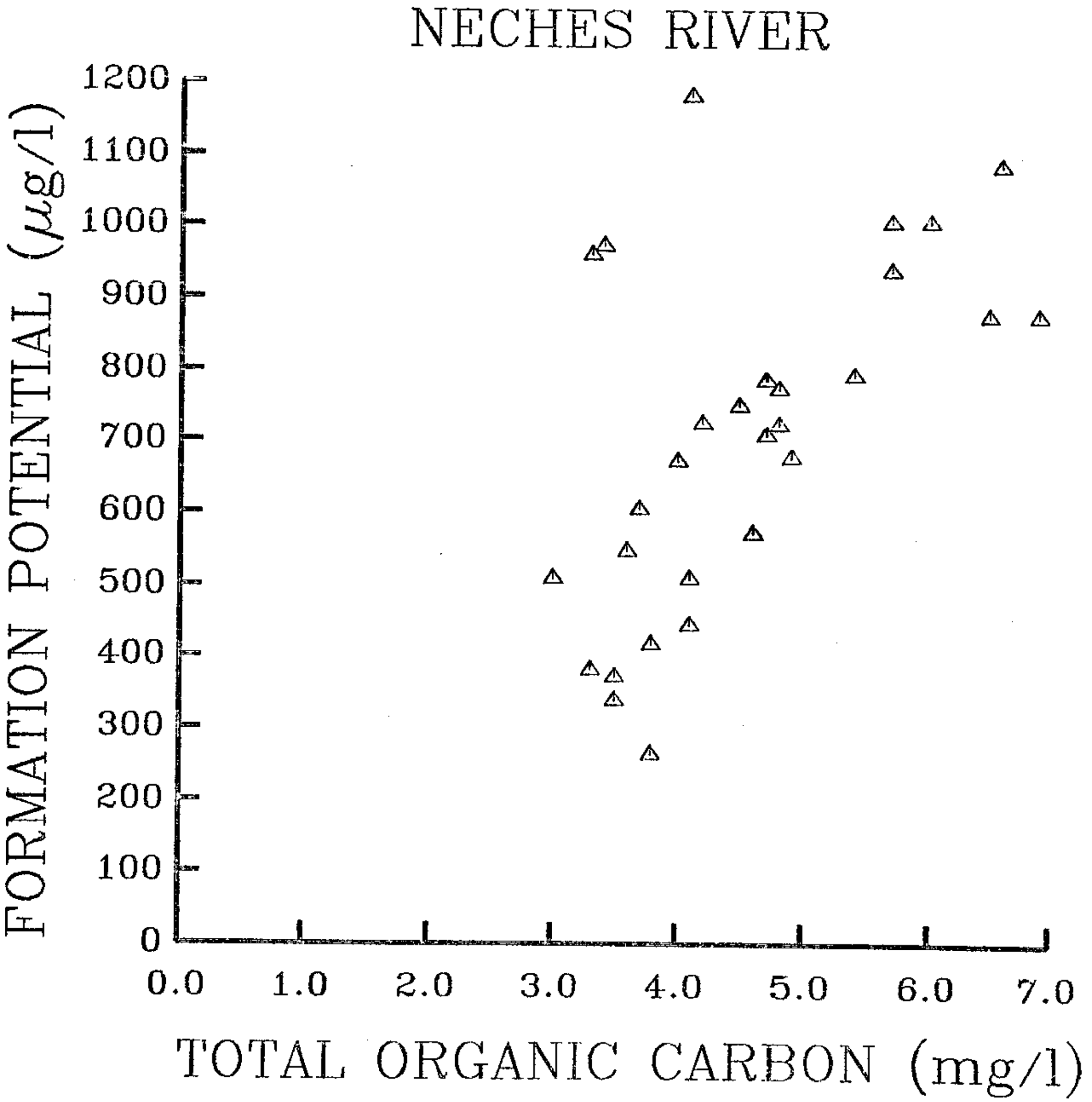


Figure 19. Correlation Plot of Trihalomethane Formation Potential and Total Organic Carbon for the Neches River.

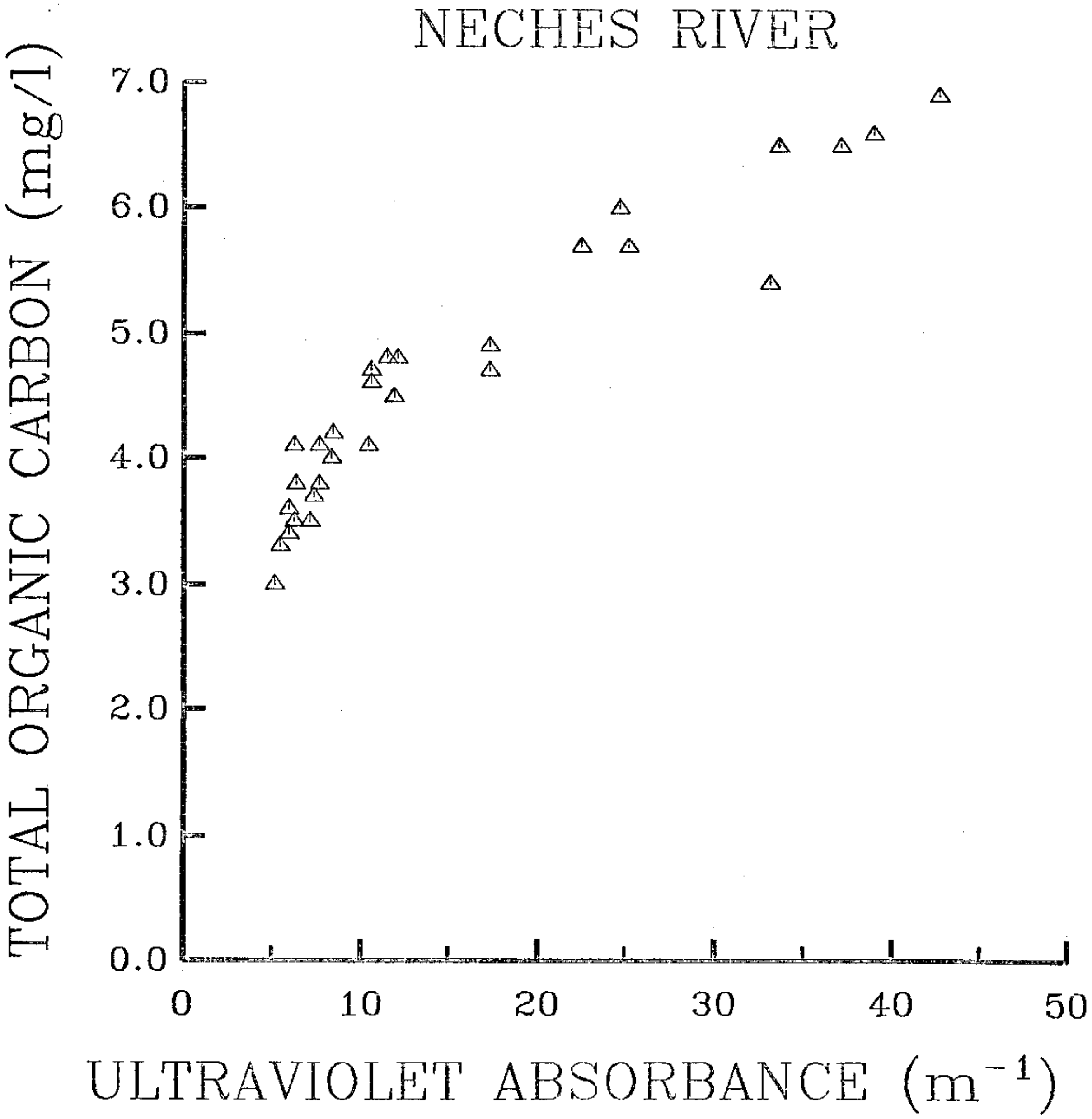


Figure 20. Correlation Plot of Total Organic Carbon and Ultraviolet Absorbance for the Neches River.

TOC and UVA. A much steeper slope is seen at lower values of TOC and UVA. This would indicate that those organic molecules that absorb ultraviolet light are preferentially removed by alum coagulation.

The effect of pH and alum dose on removal of visible absorbance is shown in Figure 21. The pattern shown in this figure is similar to that observed for other water supplies. Almost all the VA is removed at a breakpoint dose of 30 mg/l with no overdose effects observed. Removal of VA is unaffected by pH. Operation of a water treatment plant for the sole purpose of VA or turbidity removal would not result in optimum THMFP removal.

In summary, the results for the Neches River show that pH exerts a strong effect on THMFP removal with maximum concentrations observed at pH 5.0, and minimum concentrations at pH 6.0 and pH 4.5. Overdose effects were observed for THMFP, and the addition of a base for pH control appears to offer the possibility of reduced chemical costs. The patterns of UVA and TOC removal were similar with best removal near pH 5.0. Little effect of pH was noted at alum doses below the breakpoint dose of about 50 mg/l. Removal of visible absorbance showed little dependence on pH. Almost all of the VA removal occured at a breakpoint dose of 30 mg/l with no overdose effect observed. TOC, UVA, and VA were all unable to predict the pattern of THMFP removal. Use of any of these parameters to choose operating conditions could result in less than optimal THMFP removal or little to no THMFP removal.

<u>Sabine River</u>: The effect of pH and alum dose on THMFP removal for the Sabine River is shown in Figure 22. The data used to construct this figure is presented in Appendix C-13. The raw water THMFP for the Sabine River was 1780 μg/l. The vertical contours in Figure 22 show once again the strong effect of pH on THMFP removal. Lowest THMFP concentrations are

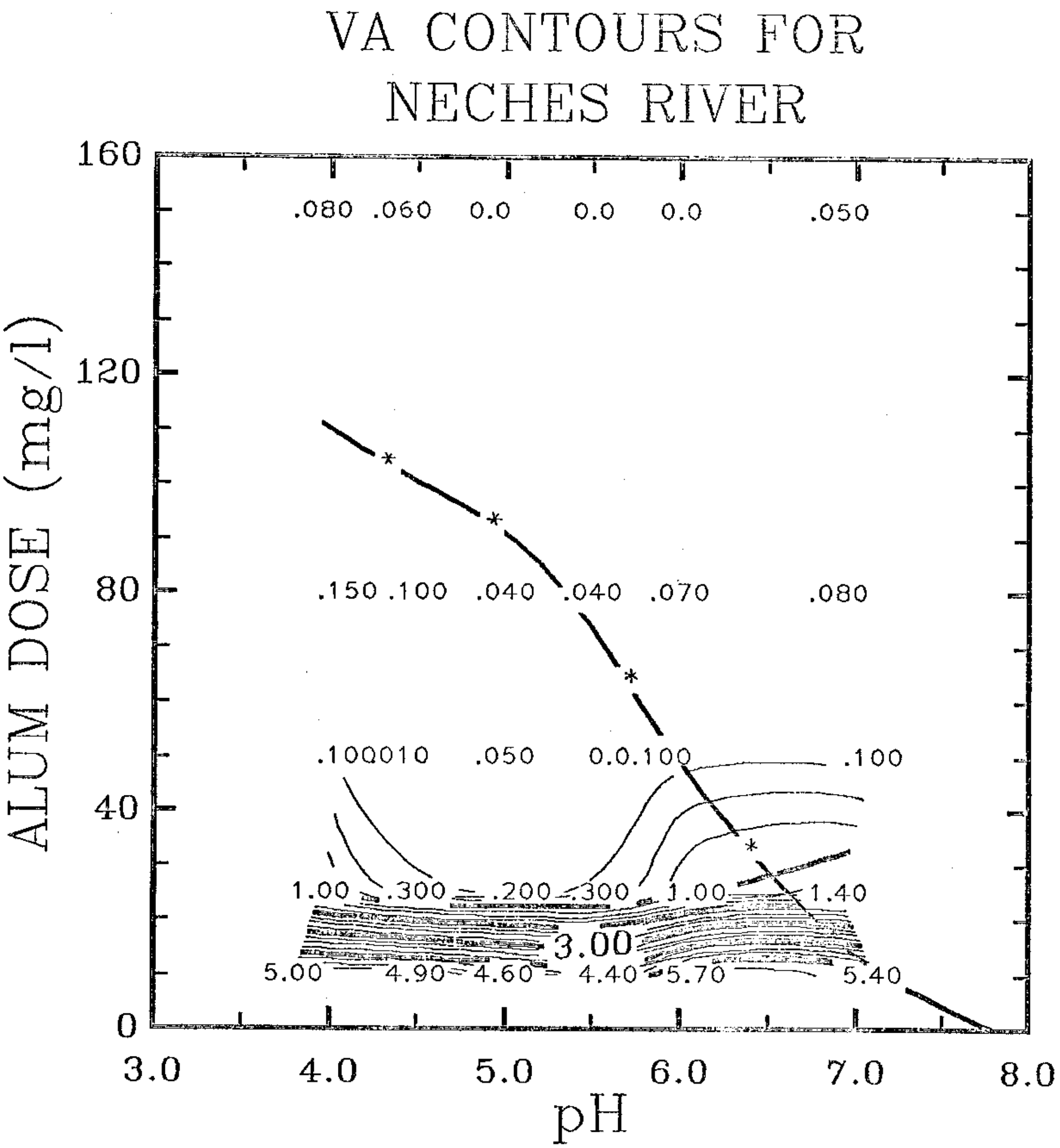


Figure 21. Visible Absorbance Contours as a Function of pH and Alum Dose for the Neches River.

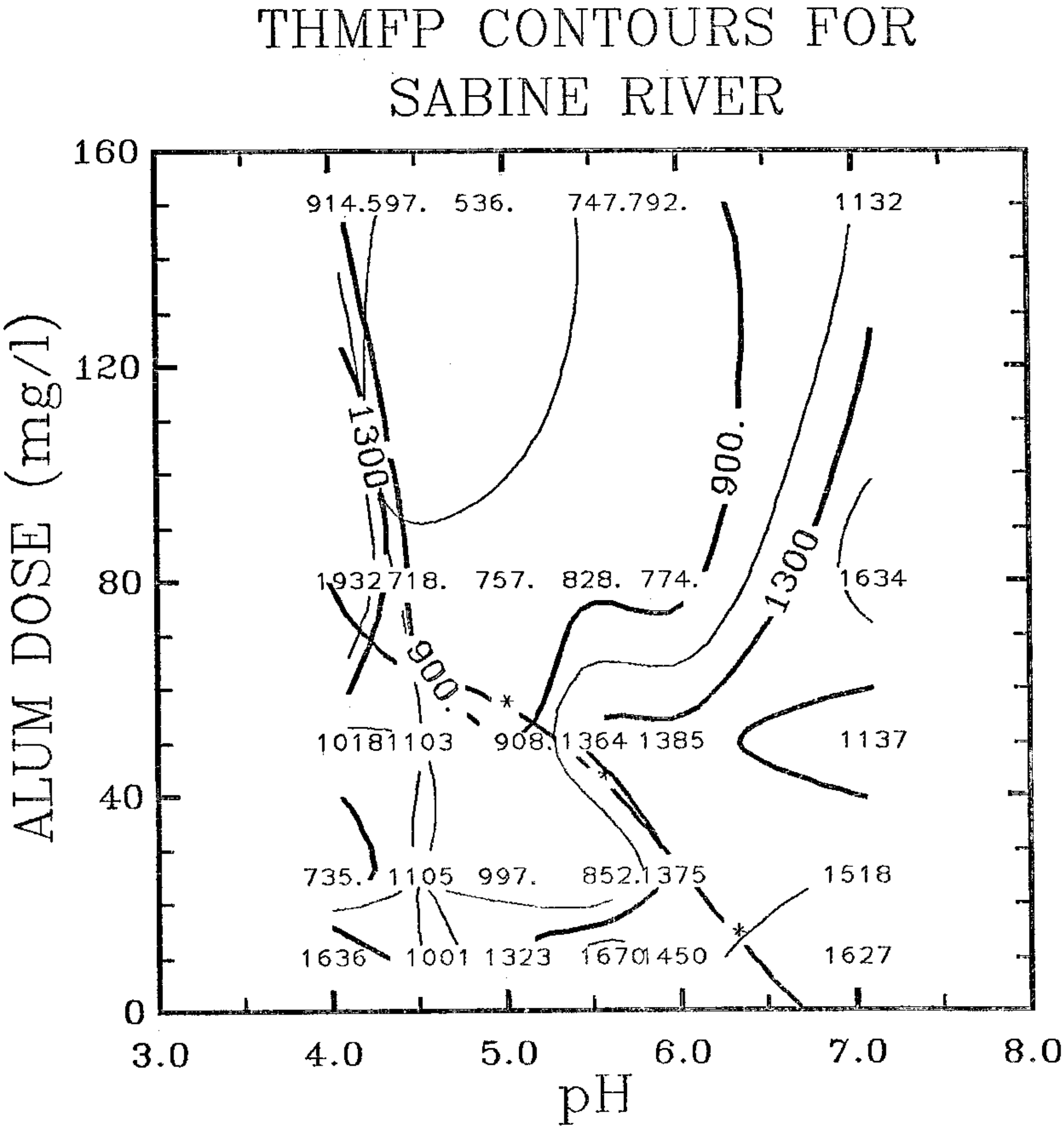


Figure 22. Trihalomethane Formation Potential Contours as a Function of pH and Alum Dose for the Sabine River.

observed in the pH range 4.5-5.5. Some evidence of a true overdose effect can be seen in the pH range 5.5-7.0, but the variability of the data makes it difficult to make a firm conclusion on this point. The asterisked line in Figure 22 shows that an observed overdose effect is found at alum doses above 60 mg/l. The titration data used to construct the asterisked line can be found in Appendix C-14. Using this titration data along with chemical costs presented previously, the cost of adding supplemental acid can be estimated. Addition of 0.045 meq/l strong acid to reduce initial pH to 6.4 will result in reducing the alum dose required to meet the 1100 μg/l THMFP contour from 50 mg/l to 25 mg/l. This results in a reduction of overall chemical costs from $\$0.0075/m^3$ to $\$0.0036/m^3$. However, this effect could be the result of data scatter rather than actual coagulation characteristics. Further examination of Figure 22 shows that supplemental acid addition will not reduce the alum dose required to meet the 900 μg/l THMFP contour. However, it would be possible to reach the 700 μg/l contour by adding a base. This contour would not be encountered if alum were the only chemical added.

Figure 23 shows that the pattern of removal of ultraviolet absorbing substances from Sabine River water is similar to that observed for other water supplies. The data used to construct Figure 23 can be found in Appendix C-15. The unfiltered raw water UVA was 52.0 m^{-1}. Figure 23 shows that at higher alum doses pH becomes an important determinant of UVA removal with best removals occurring in the range pH 5.0-5.5. At lower doses, pH becomes less important and flat contours are observed with a broad minimum in the pH range 4.0-6.0. The tightly spaced contours at low doses indicate a breakpoint dose effect, i.e. the bulk of UVA removal occurs at alum doses below 50 mg/l. Comparison of Figures 22 and 23 shows that

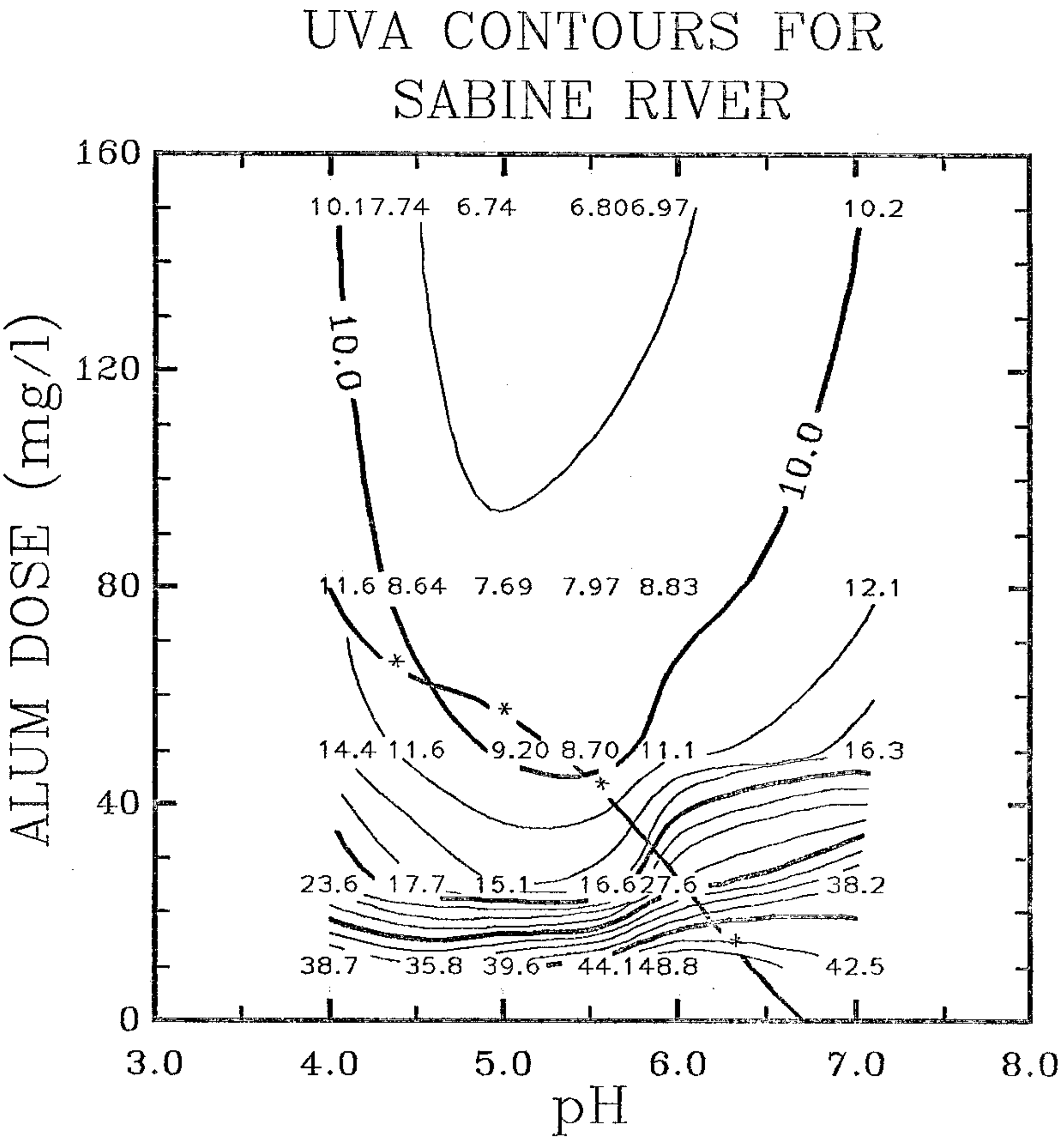


Figure 23. Ultraviolet Absorbance Contours as a Function of pH and Alum Dose for the Sabine River.

the pattern of UVA removal is similar to that of THMFP removal, especially at higher doses. The best pH for removal of UVA coincides with that for removal of THMFP. However, the breakpoint effect noted for UVA removal is not found for THMFP removal. More THMFP can be removed with alum doses above 50 mg/l.

A correlation plot for THMFP and UVA is shown in Figure 24. As found previously for other water supplies, a positive correlation is present, but a good deal of scatter exists in the data (R^2 = .34).

The effect of pH and alum dose on removal of TOC from Sabine River water is shown in Figure 25. The raw water TOC was 8.0 mg/l. The data used to construct this figure is presented in Appendix C-16. The pattern of TOC removal shown in Figure 25 is very much the same as that observed for UVA removal (Figure 23). A strong effect of pH is noted at higher alum doses with flatter contours at lower doses. Best removals are observed in the pH range 4.5-5.5. The contours became more closely spaced at lower alum doses which indicates a breakpoint effect. Most of the TOC is removed at alum doses below 50 mg/l. TOC removal is as good a predictor of THMFP removal as is UVA removal. The pH effect on THMFP removal is similar to that observed for TOC removal. However, the breakpoint effect that is seen in the pattern of TOC removal is not observed in the pattern of THMFP removal.

A correlation plot of THMFP with TOC is presented in Figure 26. As observed before, a positive correlation is found, but the amount of scatter is high (R^2 = 0.35). Figure 27 shows the correlation of TOC with UVA for the Sabine River. A much better positive correlation is observed (R^2 = 0.90) indicating that either TOC and UVA do not accurately measure compounds which form trihalomethanes, or that the THMFP test procedure introduces a

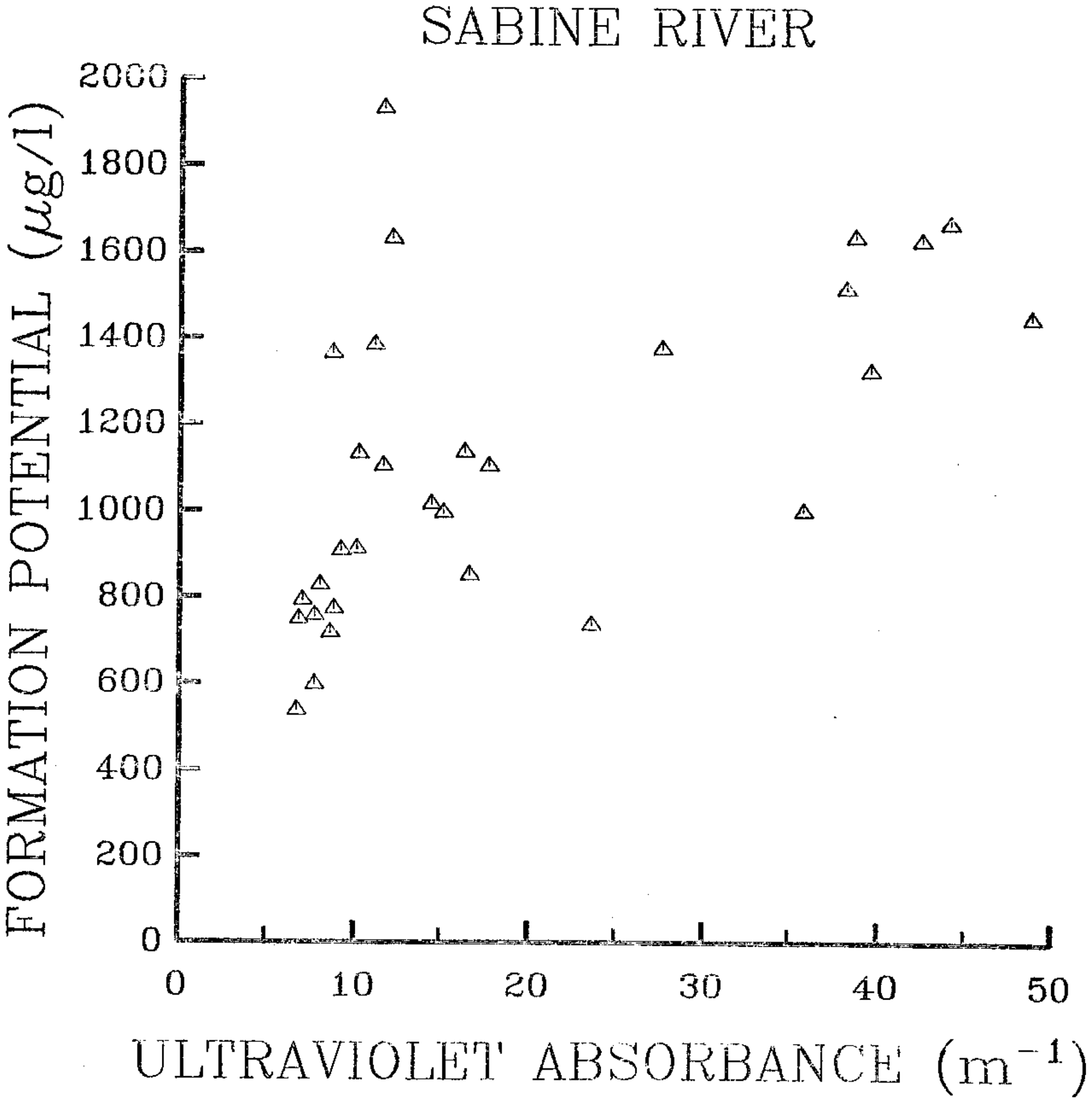


Figure 24. Correlation Plot of Trihalomethane Formation Potential and Ultraviolet Absorbance for the Sabine River.

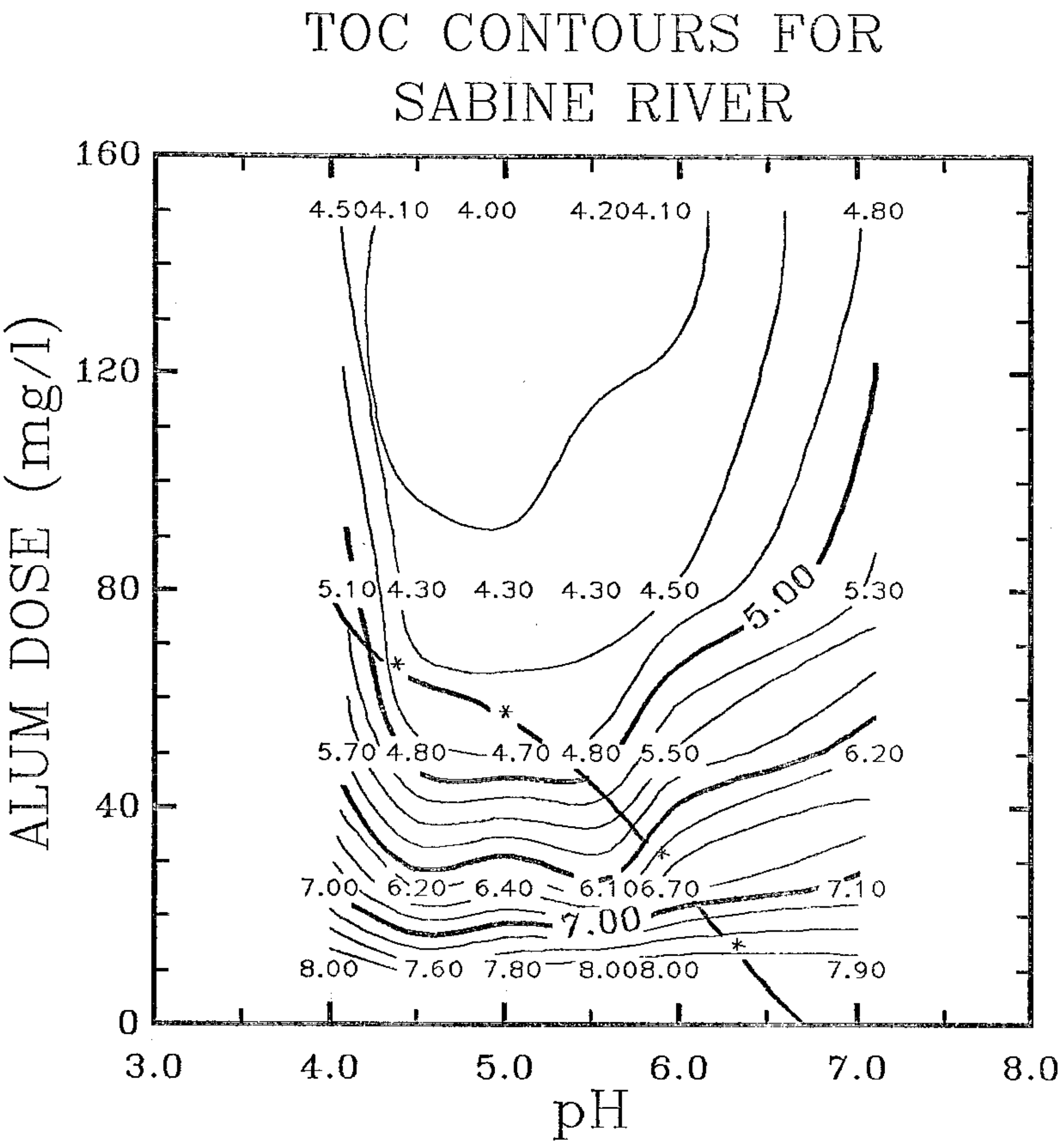


Figure 25. Total Organic Carbon Contours as a Function of pH and Alum Dose for the Sabine River.

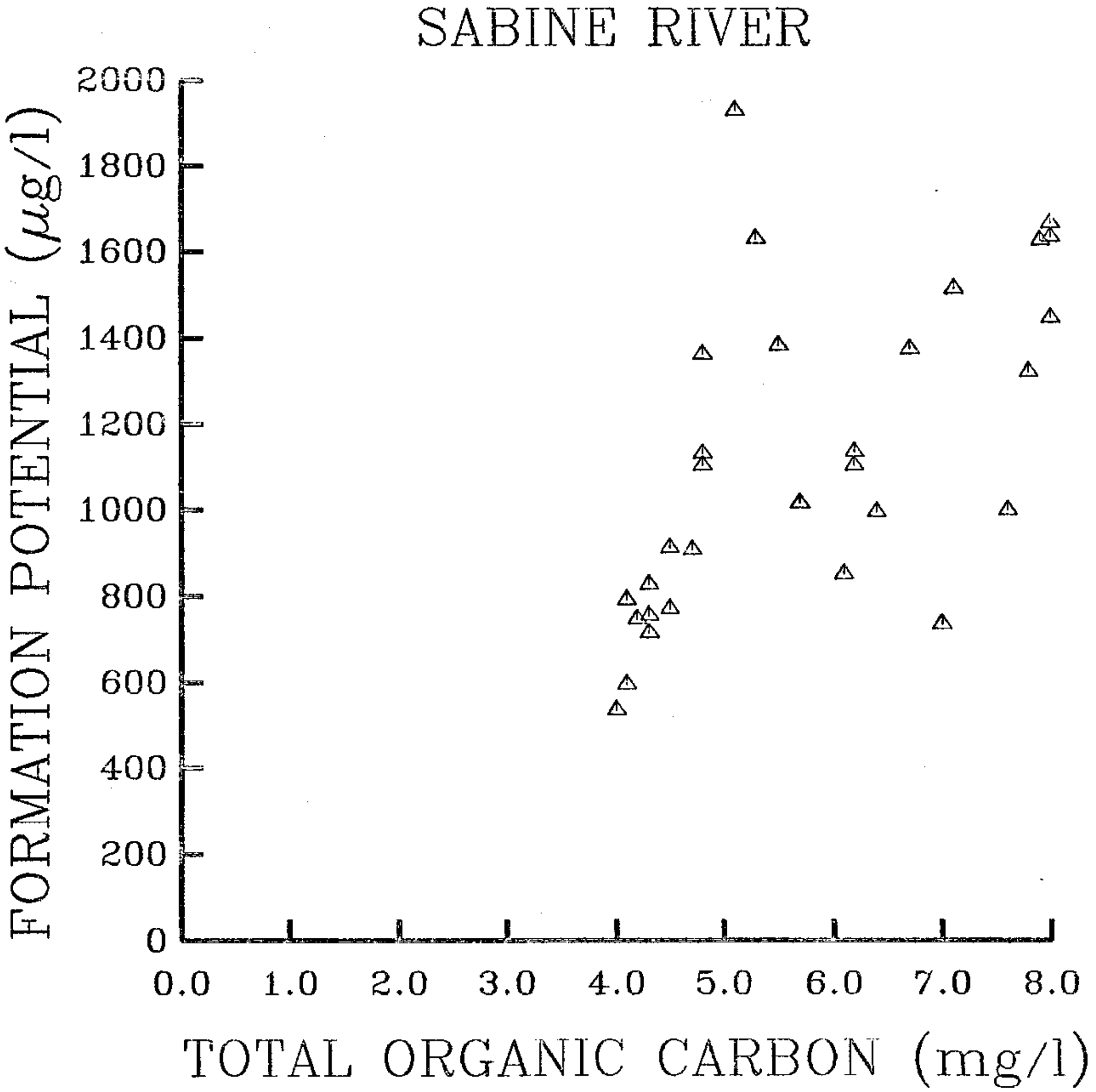


Figure 26. Correlation Plot of Trihalomethane Formation Potential and Total Organic Carbon for the Sabine River.

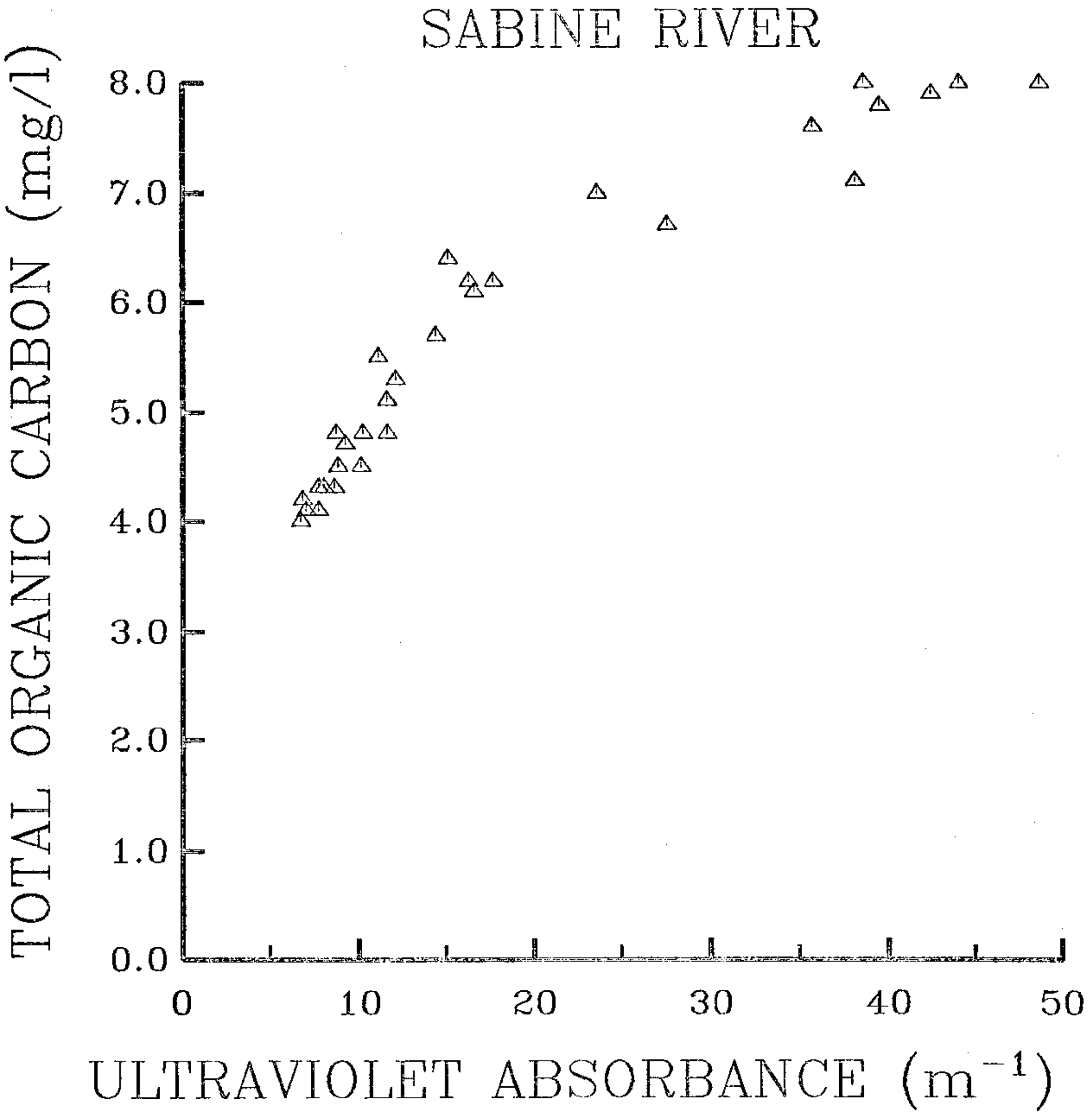


Figure 27. Correlation Plot of Total Organic Carbon and Ultraviolet Absorbance for the Sabine River.

significant amount of error into the correlation.

Figure 28 shows the pattern of removal of visible absorbance by alum coagulation. The unfiltered raw water VA was 3.3 m^{-1}. The set of data to construct Figure 28 can be found in Appendix C-15. The pattern of removal of VA from the Sabine River water is similar to that observed for TOC and UVA removals. However, the breakpoint effect is more pronounced with little additional removal of VA observed at alum doses above 40 mg/l. A pH optimum in the range 4.5-5.5 is evident at low alum doses. To some extent a stronger effect of pH at higher doses can be seen in the data, but contours were not drawn at higher doses due to the relatively low values of VA found in that region.

In summary, these experiments show that pH exerts a strong effect on THMFP removal with best removal observed near pH 5.0. Some evidence of true and observed overdose effects exists. Reduction in chemical costs and/or improved THMFP removal appears to be possible by addition of acid or base along with alum. Removal of UVA, TOC, and VA all occur with the same general pattern. Removal at higher doses is more strongly affected by pH with the optimum pH agreeing with that observed for THMFP removal. At lower doses, pH becomes less important than alum dose in determining removal. Breakpoint doses of 40-50 mg/l were observed for removal of UVA, TOC, and VA. All of these parameters describe the pH dependency of THMFP removal, but fail to adequately describe the effect of alum dose.

All Sources: Correlation plots for THMFP with UVA, THMFP with TOC, and TOC with UVA using data from all sources are presented in Figures 29, 30, and 31, respectively. These plots show the same trends exhibited for the individual water supplies. Correlation of TOC with UVA shows much less scatter than the correlation of these variables with THMFP. The correlation

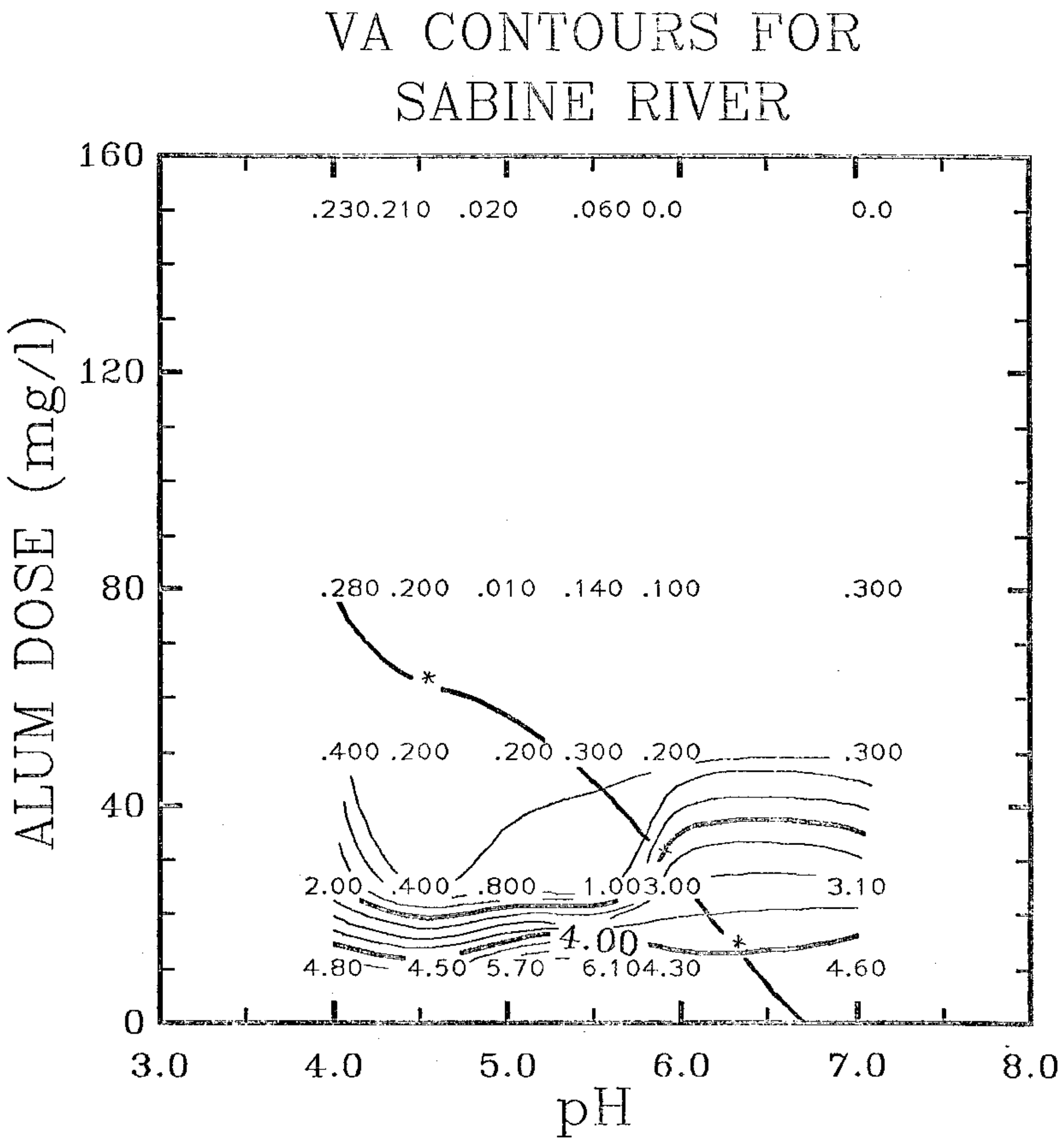


Figure 28. Visible Absorbance Contours as a Function of pH and Alum Dose for the Sabine River.

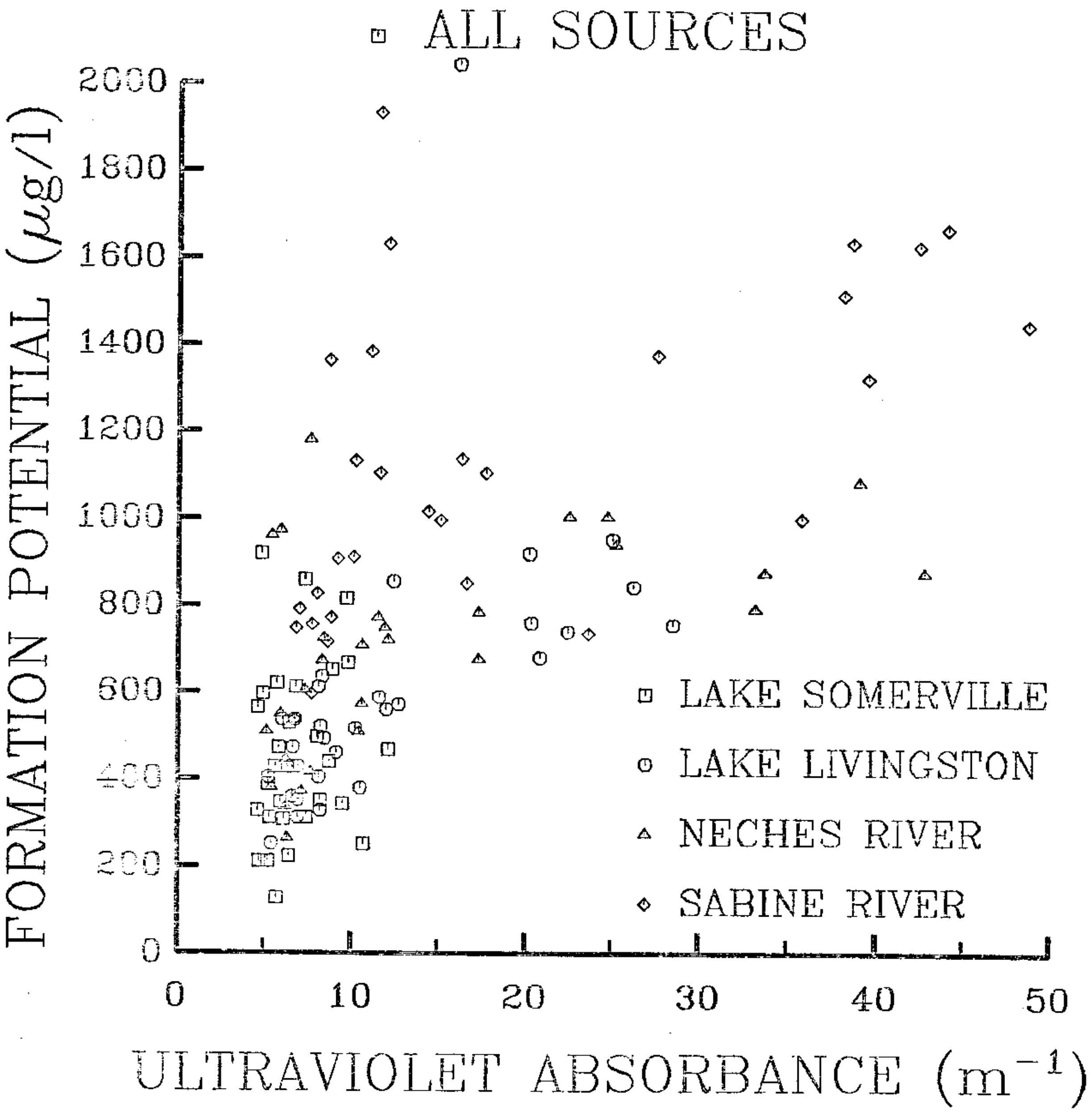


Figure 29. Correlation Plot of Trihalomethane Formation Potential and Ultraviolet Absorbance for All Sources.

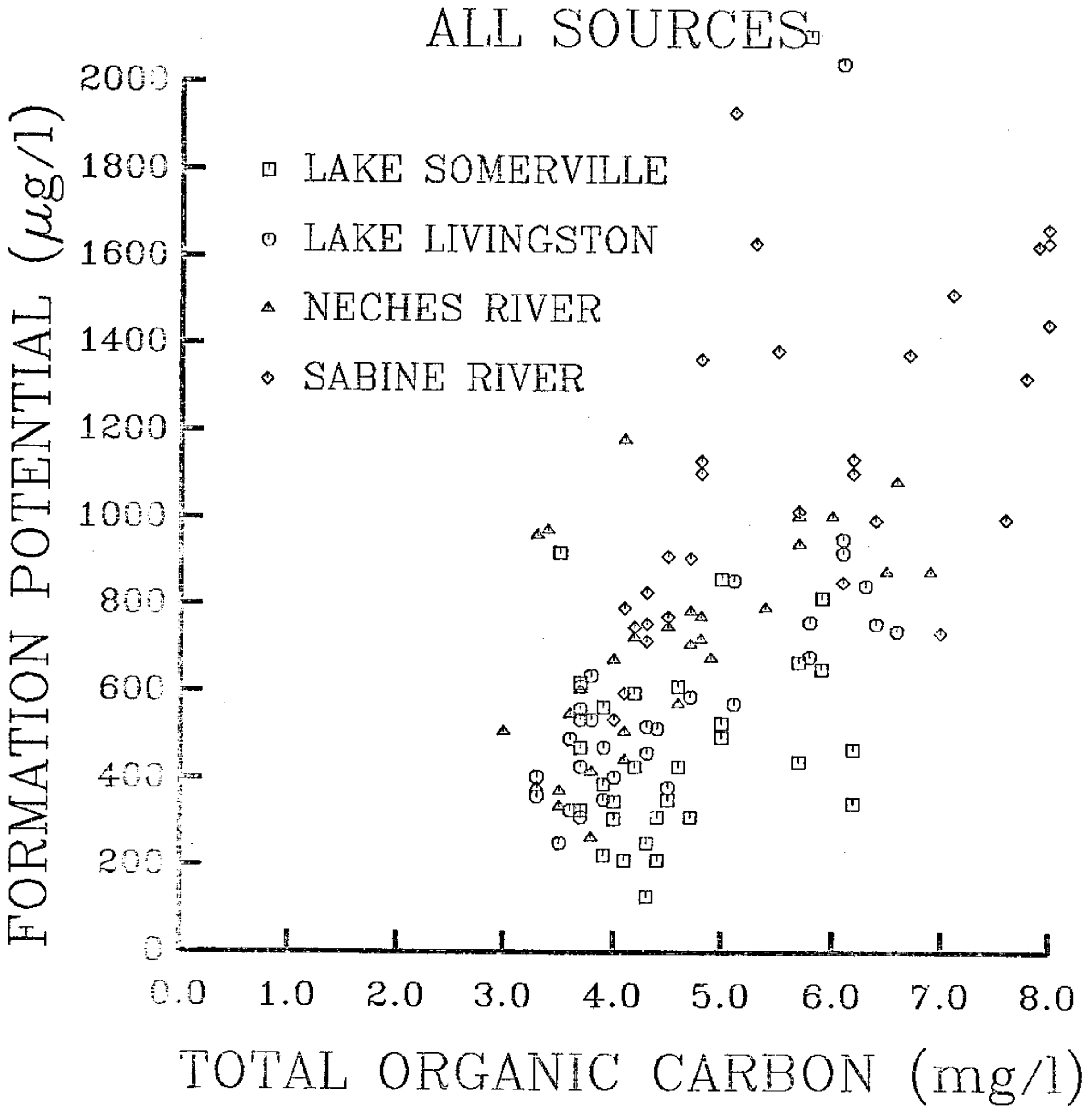


Figure 30. Correlation Plot of Trihalomethane Formation Potential and Total Organic Carbon for All Sources.

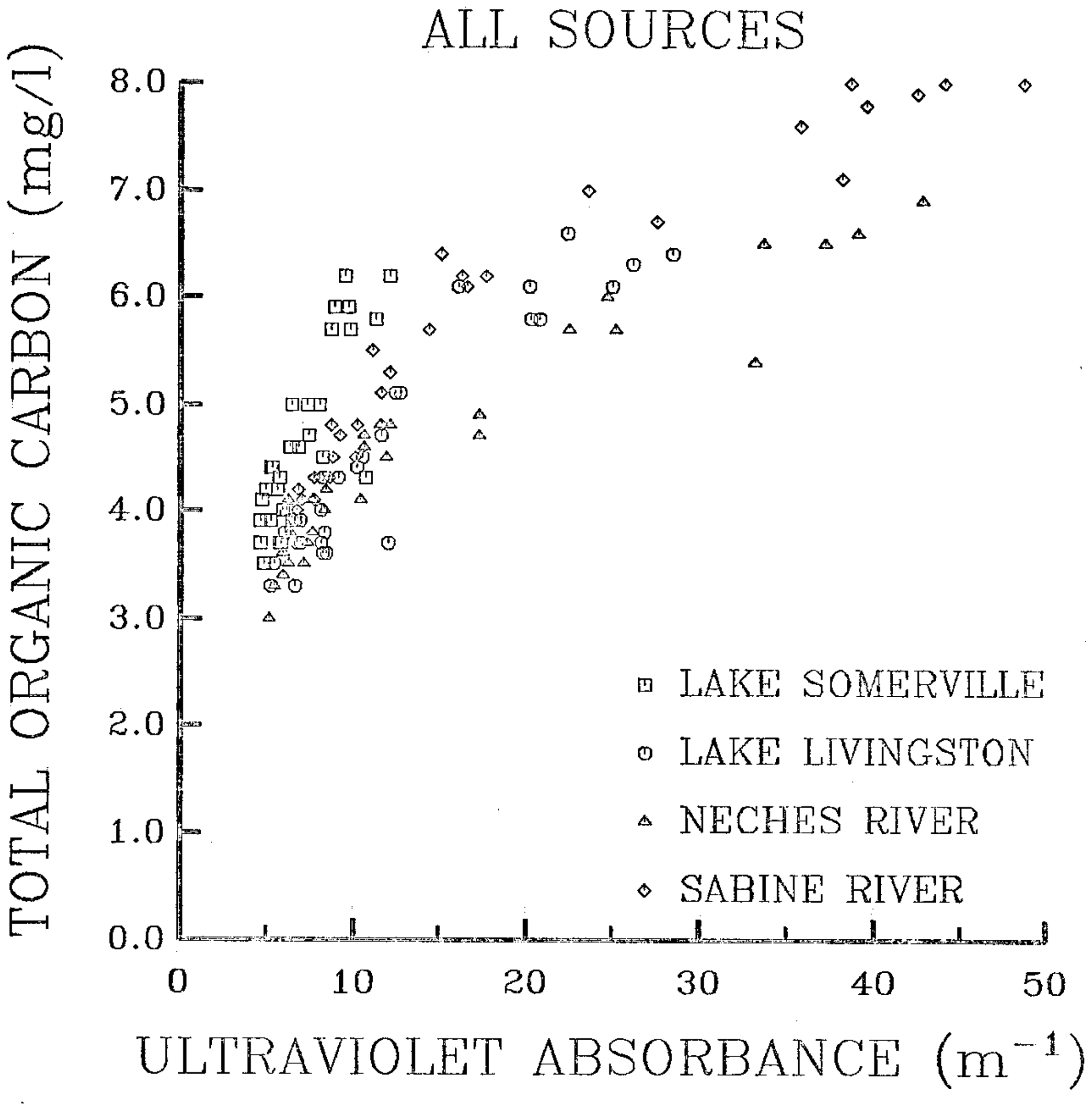


Figure 31. Correlation Plot of Total Organic Carbon and Ultraviolet Absorbance for All Sources.

of THMFP with UVA shows a tendency towards two regions which display two relationships between the variables. At high values of UVA, there is a tendency for THMFP to increase less rapidly as UVA increases. This could indicate that a large fraction of the ultraviolet absorbing materials is removed easily by coagulation and does not form trihalomethanes as readily as the fraction which is more resistant to coagulation. This behavior would be inconsistent with experimental reports that coagulation of humic and fulvic acids preferentially removes trihalomethane precursor materials.[83]

Another possible explanation is that the procedure used for measuring trihalomethanes was not able to accurately measure high values. This could be caused by a depletion of free chlorine during the incubation period. A spot test for chlorine was conducted at the end of the incubation period to check for the existence of a free chlorine residual. However, the possibility exists that a positive test could occur when the free chlorine residual was low enough to affect the rate of production of trihalomethanes. The plateau effect observed in Figure 29 is not evident in the correlation plot of THMFP with TOC in Figure 30. This tends to support the first hypothesis and reaffirm the reliability of the THMFP analysis procedure. Figure 30 shows that for all sources approximately 2-3 mg/l of residual TOC exists which does not form trihalomethanes. Figure 31 shows that approximately 2-3 mg/l of TOC exists which does not appreciably absorb ultraviolet light. However, Figure 29 shows that practically all ultraviolet absorbing materials do act as trihalomethane precursors. Hence, in the water supplies studied there appears to be about 2-3 mg/l of TOC that is resistant to coagulation, does not form trihalomethanes, and does not absorb ultraviolet light.

Figure 31 shows a remarkably good correlation between TOC and UVA considering that the data was taken from four different water supplies. With the exception of the data from Lake Somerville, the data from all sources are well intermixed.

The results of alum coagulation experiments on four water supplies show the strong effect of pH on THMFP removal. Each source exhibited vertical THMFP contours at medium to high alum doses. For three of the four water supplies the optimum pH was near 5.0. At the fourth, a maximum in THMFP concentration was observed at pH 5.0 and a minimum at pH 4.5 and 6.0. The strong effect of pH on THMFP removal results in the observation that independent pH control by acid or base addition can result in improved THMFP removal and/or reduced chemical costs. Acid addition allows the optimum pH range to be reached at lower alum doses,thus resulting in reduced chemical costs. Base addition leads to higher alum doses being achieved in the optimum pH range which can result in better THMFP removal.

Results for all water supplies showed some effect of overdosing. In some cases the effect was marginal, perhaps resulting from scatter in the data.

In general, ultraviolet absorbance did the best job of predicting the pattern of THMFP removal. In all cases except one, it was able to accurately predict the pH optimum for THMFP removal. The effect of pH on UVA removal tended to be most apparent at higher doses. However, UVA was unable to predict the effect of alum dose on THMFP removal. Removal of UVA was characterized by the appearance of a breakpoint dose. Most UVA removal occurred at doses below the breakpoint dose which was generally around 50 mg/l. A breakpoint dose was not observed for THMFP removal. UVA removal patterns did not exhibit the overdose effects observed in THMFP removal.

The pattern of TOC removal was usually similar to that of UVA removal. However, it was somewhat less accurate than UVA in predicting the optimum pH for THMFP removal.

Visible absorbance did the worst job of predicting THMFP removal. The effect of pH on VA removal was usually much weaker than the effect of pH on THMFP removal. VA removal exhibited a strong breakpoint dose pattern, therefore, it was unable to predict the effect of dose on THMFP removal. A plant operated to economically remove turbidity, or its surrogate VA, would very likely achieve substantially sub-optimum THMFP removal.

Modified Coagulation

The possibility of modifying conventional alum coagulation to improve THMFP removal was investigated in a series of jar tests. These experiments used Lake Somerville water without controlling pH. In one series of tests, a moderate molecular weight cationic polymer (Nalco 8101, Nalco Chemical Co.) was tested alone and in combination with alum. Coagulation with alum alone was also studied to provide a basis for comparison.

In another series of jar tests, the ability of activated silica to improve THMFP removal was studied. Tests were conducted using alum and activated silica separately and together. The activated silica solution was prepared by acidifying a 0.2 M solution of sodium silicate with sulfuric acid to pH 6.0, aging for 30 minutes, and diluting to 0.002 M. The results of the alum/polymer experiments are tabulated in Appendix C-17 and shown graphically in Figures 32 and 33.

Figure 32 shows the effect of alum dose on THMFP removal. An observed overdose effect exists as it was predicted by Figure 1. The THMFP at a dose of 80 mg/l was 520 μg/l. Figure 33 shows the effect of cationic

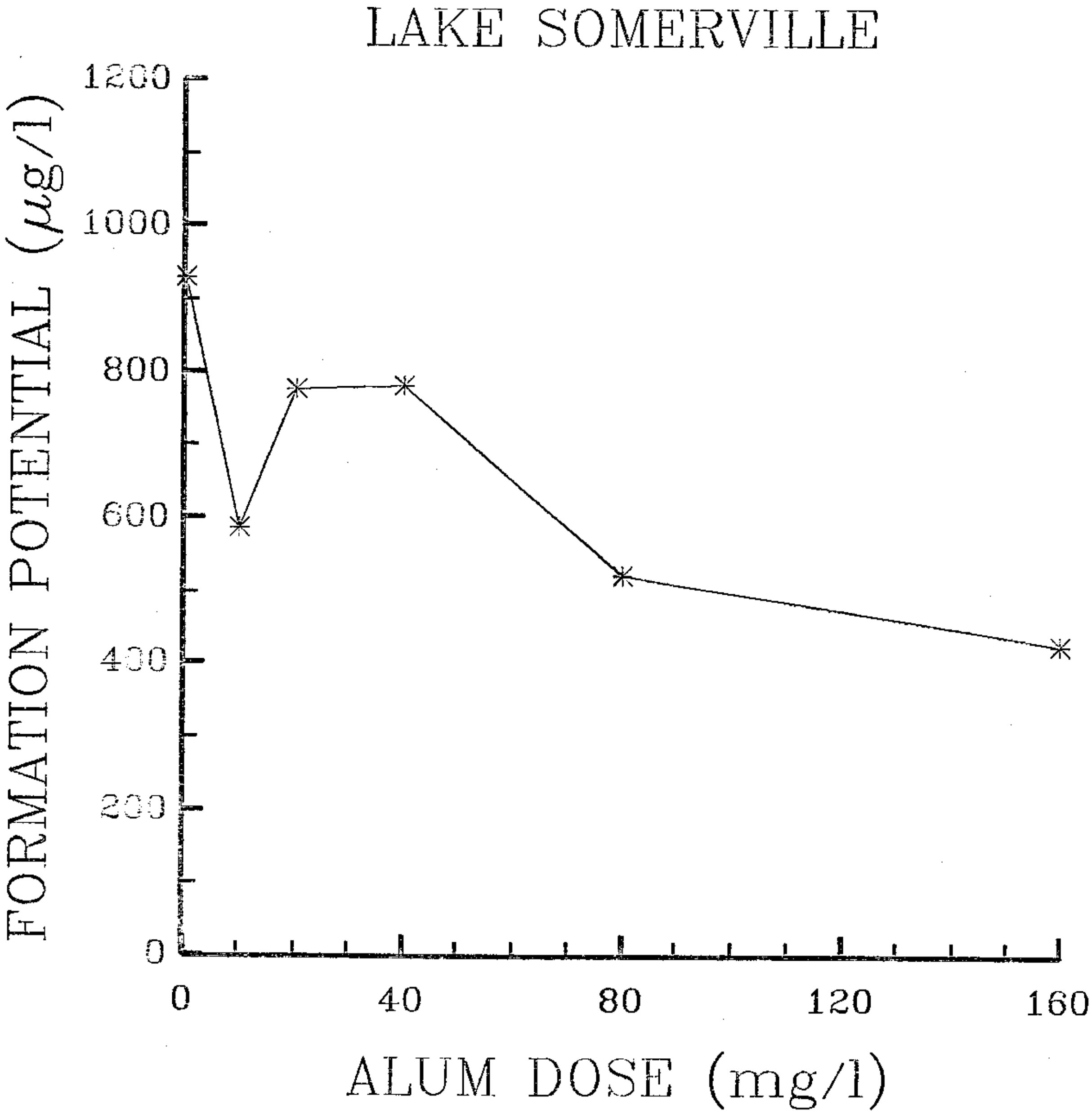


Figure 32. Effect of Alum Dose on Concentration of Trihalomethane Formation Potential for Lake Somerville.

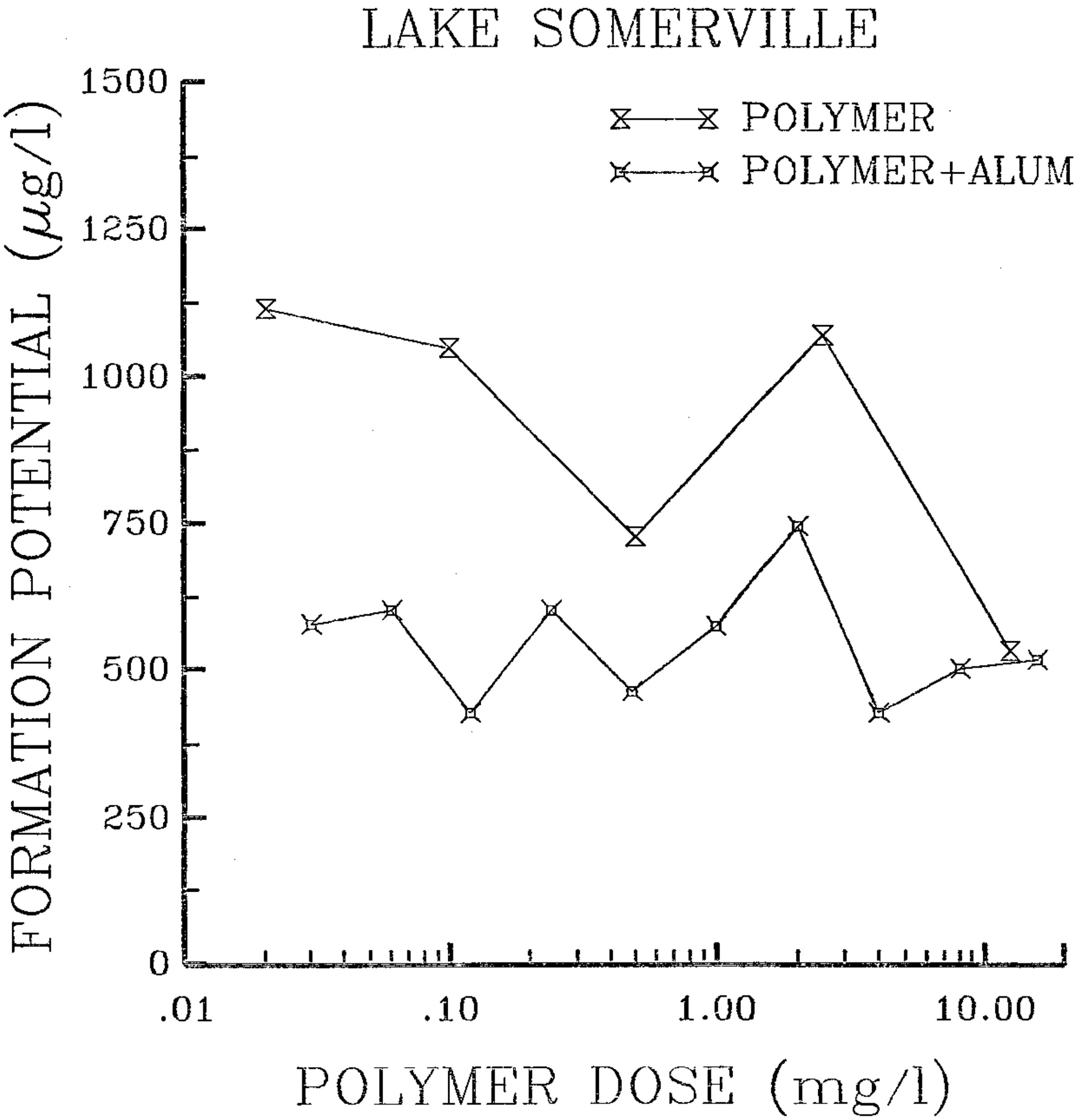


Figure 33. Effect of Cationic Polymer Dose on Concentration of Trihalomethane Formation Potential for Lake Somerville With and Without an Alum Dose of 80 mg/l.

polymer dose on THMFP removal with and without an alum dose of 80 mg/l. The polymer alone is ineffective as a coagulant for THMFP except at a dose above 12 mg/l. The possibility exists that a narrow region of good removal exists at polymer doses between the values studied. Alum + polymer coagulation showed little improvement over coagulation with alum only. In summary, the cationic polymer tested was either ineffective as a coagulant for removal of THMFP or was effective in a very narrow range of doses lying between the doses studied. This conclusion is valid for coagulation with the polymer alone or in conjunction with alum.

Figures 34 and 35 show the results of experiments conducted to determine the efficiency of activated silica as a coagulant for removal of THMFP. The data used to construct these figures can be found in Appendix C-18. Figure 34 shows that in tests with alum as the only coagulant, an overdose is observed in agreement with previous predictions (Figure 1). At an alum dose of 80 mg/l, the residual THMFP was 750 μg/l. Figure 35 shows the effect on THMFP removal of activated silica used alone and in conjunction with 80 mg/l alum. When used as the sole coagulant, activated silica showed excellent THMFP removal at a dose of 0.48 mg/l. At doses twice this level, THMFP concentration is dramatically increased and remains relatively constant at all higher doses.

Similar behavior is observed in the activated silica + alum system. Dramatically improved THMFP removal is evident at activated silica doses near 0.48 mg/l. The range of activated silica doses that result in improved removals appears to be broader when alum is also used as a coagulant. The similarity observed between removal by activated silica with and without alum indicates that the mechanism of activated silica coagulation primarily involves interaction between activated silica and the natural

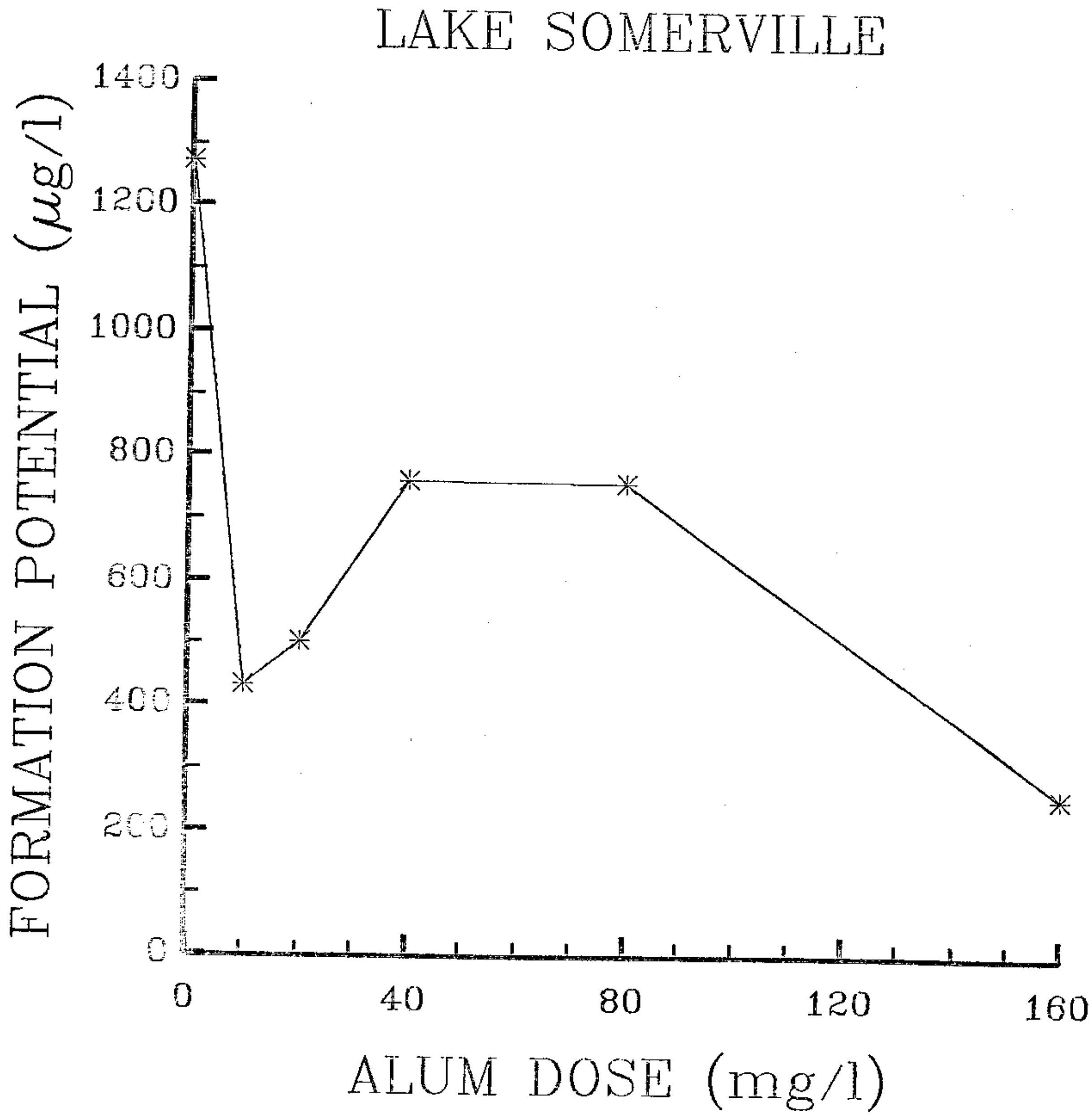


Figure 34. Effect of Alum Dose on Concentration of Trihalomethane Formation Potential for Lake Somerville.

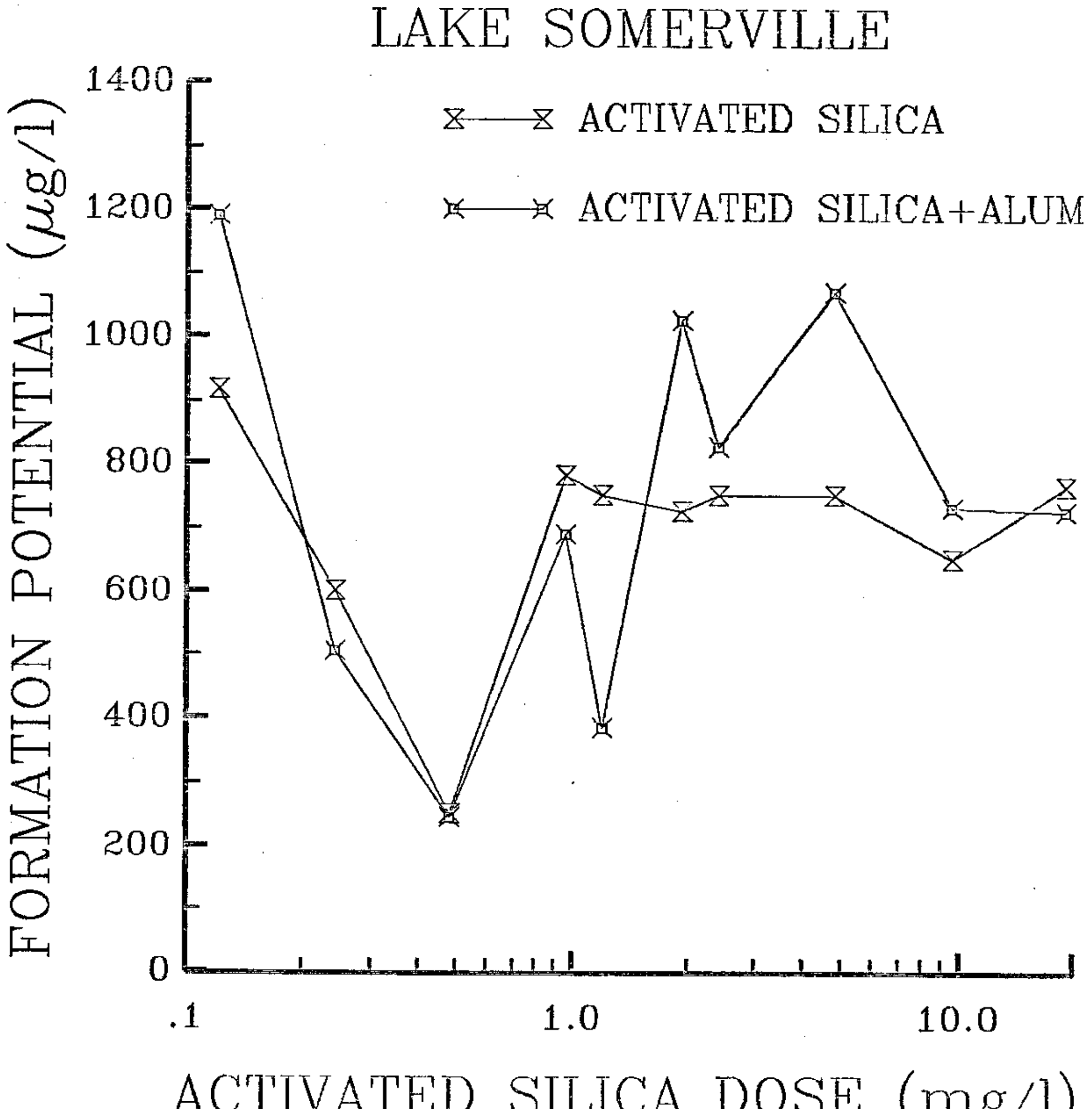


Figure 35. Effect of Activated Silica Dose on Concentration of Trihalomethane Formation Potential for Lake Somerville With and Without an Alum Dose of 80 mg/l.

organic material, rather than between activated silica and a complex of natural organic material and aluminum hydroxides.

In summary, these results indicate that modification of conventional alum coagulation can result in significant improvements in THMFP removal. For Lake Somerville, the most promising modification would be to use activated silica in conjunction with alum.

Activated Alumina Adsorption

Adsorption Equilibria: An innovative treatment process for removing trihalomethane formation potential was also studied. Activated alumina adsorption was chosen for study as an innovative treatment process because the chemical and physical properties of this chemical indicate that it would be well suited to removing the natural organic materials which are precursors to trihalomethanes. Both batch equilibrium experiments and continuous flow experiments were conducted to evaluate this process. A series of batch equilibrium adsorption experiments were conducted to screen a variety of commercially available adsorbents for their ability to remove natural organic matter, to determine the effect of adsorbent dose on removal, and to measure the maximum removal to be expected after coagulation.

Results of the experiment used to screen four commercially available activated alumina adsorbents can be found in Appendix C-19 and are summarized in Table 2. These results show little difference between the available adsorbents. Alcoa F-1 was chosen for further studies.

TABLE 2

Removal of TOC and UVA from Lake Somerville Water by Various Activated Alumina Adsorbents

	Percent Removal	
	UVA	TOC
RA-1 (Reynolds)	86	48
RP 2/5 (Rhone-Poulenec)	90	35
F-1 (Alcoa)	90	51
A-2 (Kaiser)	80	54

The effect of alumina dose on removal of TOC and UVA is shown in Figure 36 and the data is presented in Appendix C-20. The results show maximum removals of TOC and UVA of approximately 70 and 90 percent, respectively. These removals correspond to a residual TOC concentration of 3.2 mg/l and residual UVA of 1.03 m^{-1}. Significant removal of UVA and TOC were observed at all alumina doses tested (0.25-20 g/l). These results confirm expectations that activated alumina can remove natural organic material from surface waters.

Equilibrium tests of activated alumina adsorption of TOC were conducted in conjunction with the jar tests that were used to study the effect of pH and alum dose on THMFP removal. These tests were conducted with coagulated samples from four water supplies and are presented in Appendices C-4, C-8, C-12 and C-16. These results show an almost constant concentration of TOC remains after contact for seven days with 20 g/l activated alumina. The average TOC values for the various water supplies are presented in Table 3.

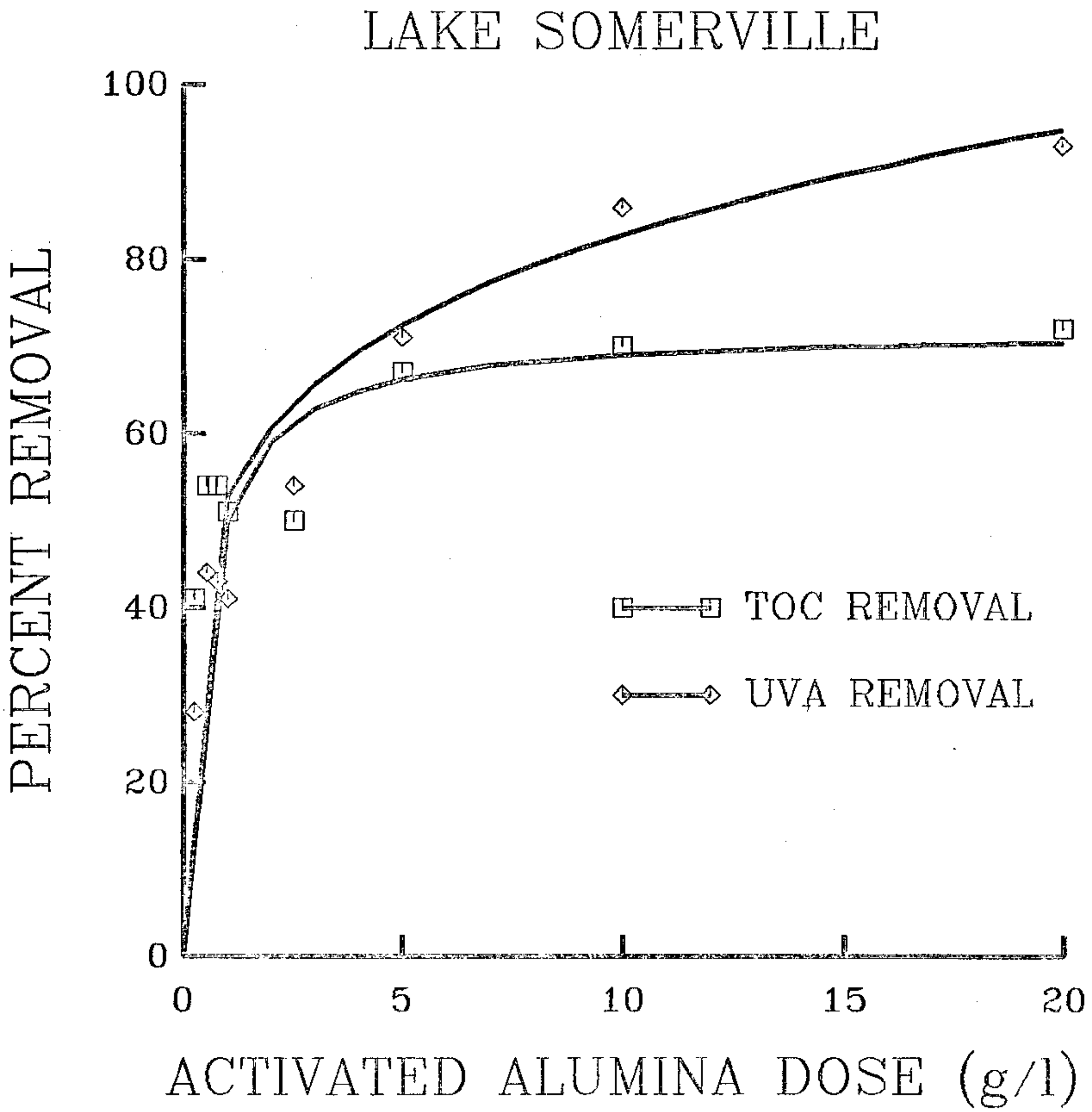


Figure 36. Removal of Total Organic Carbon and Ultraviolet Absorbance from Lake Somerville Water as a Function of Activated Alumina Dose.

TABLE 3

Average TOC After Activated Alumina Adsorption

Source Water	TOC (mg/l)	Standard Deviation (mg/l)
Lake Somerville	3.4	1.3
Lake Livingston	3.1	0.17
Neches River	3.2	0.24
Sabine River	3.3	0.21

The data for Lake Somerville contained one outlier of 10 mg/l. If this value is ignored, the average TOC becomes 3.1 mg/l (0.25). Estimates of residual THMFP concentrations can be made using a linear regression equation fitted to THMFP and TOC data obtained for each water supply. The following THMFP concentrations are obtained in this manner: Lake Somerville, 290 μg/l (± 225); Lake Livingston, 320 μg/l (± 128); Sabine River, 750 μg/l (± 187);and Neches River, 440 μg/l (± 217). The values in parentheses represent the 90 percent confidence interval. For most of the samples this would result in significant reduction of THMFP. However, THMFP levels approaching these values were obtained for most water supplies by optimal combination of pH and alum dose. The estimated THMFP concentration should be used with caution since use of the regression equations results in relatively poor predictions of THMFP concentration.

The ability of activated alumina to remove THMFP from alum coagulated water was studied in two series of jar tests using Lake Somerville water. Results of these experiments are shown in Figures 37 and 38 and the data is presented in Appendices C-21 and C-22. Each figure shows consistent removal of THMFP by activated alumina with the exception of one point in each experiment. Average reductions in THMFP of 270 and 220 μg/l were obtained. These concentrations correspond to average removals of 31 and 23

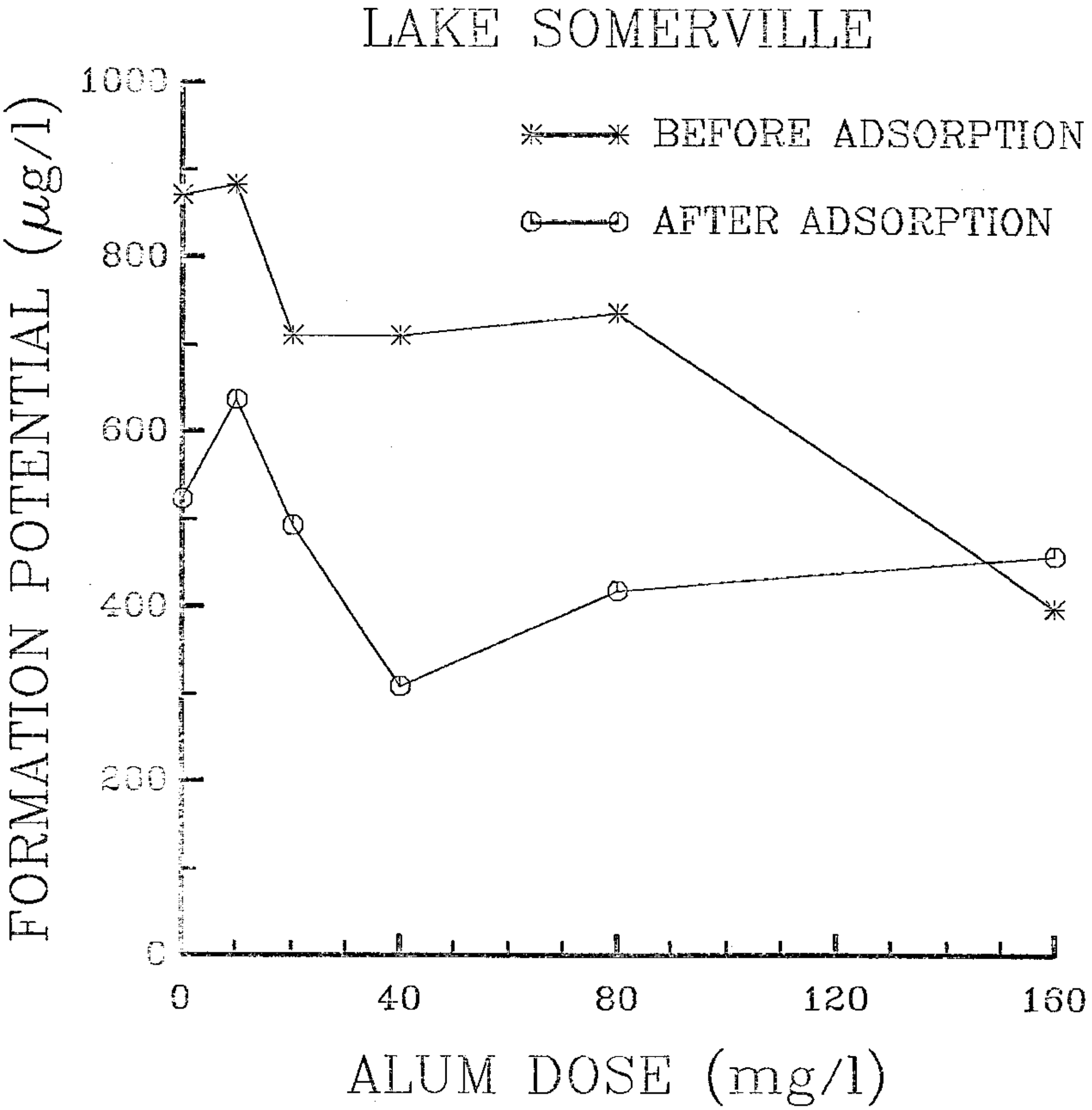


Figure 37. Trihalomethane Formation Potential for Coagulated Lake Somerville Water Before and After Contact with 20 g/l Activated Alumina as a Function of Alum Dose.

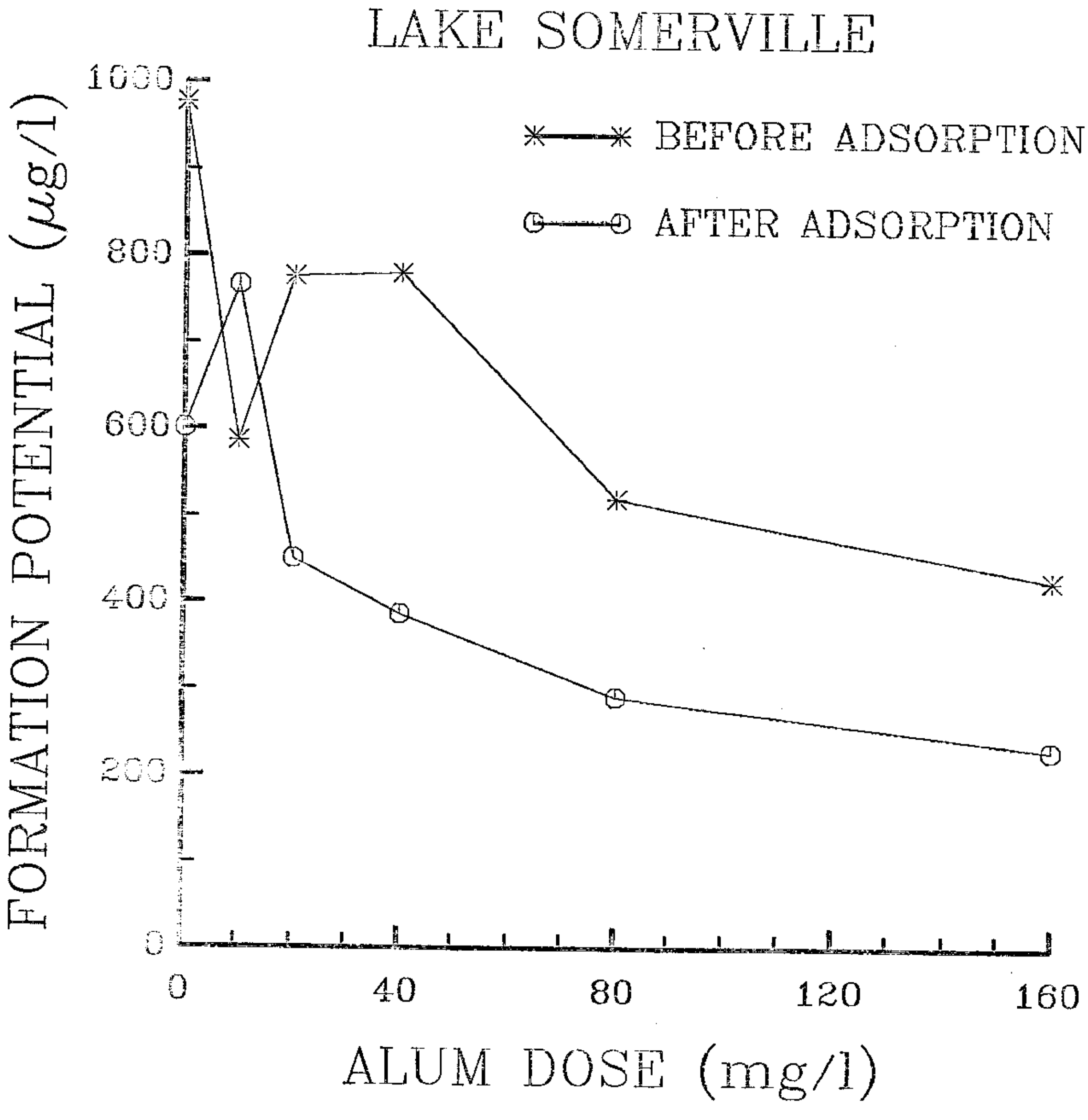


Figure 38. Trihalomethane Formation Potential for Coagulated Lake Somerville Water Before and After Contact with 20 g/l Activated Alumina as a Function of Alum Dose.

percent, respectively. The results show that substantial reduction in THMFP of alum coagulated water is possible with activated alumina adsorption.

Adsorption Columns: Two continuous flow adsorption column experiments were conducted to evaluate the ability of activated alumina to remove precursors of halogenated organics from drinking waters. The first experiment was conducted using Lake Somerville water that had been coagulated with 80 mg/l alum. Flow through the columns was maintained at approximately 15 ml/min for the first portion of the experiment (8 liters passed). The first column became progressively clogged and flow was reduced to about 8.5 ml/min for the duration of the experiment. These flows correspond to hydraulic loadings of 9.6 m/hr. (3.9 gpm/ft^2) and 5.4 m/hr. (2.2 gpm/ft^2), respectively. Because hydraulic interferences are to be expected in small columns, direct extrapolation of this data to full scale systems should be avoided. The results of this experiment are summarized in Table 4 and shown graphically in Figure 39. The data obtained during this experiment can be found in Appendix C-23.

TABLE 4

Results of Activated Alumina Column Experiment Using Coagulated Lake Somerville Water

	Flow-Weighted Average UVA (m^{-1})	Percent Removal (Incremental/ Overall)	Flow-Weighted Average THMFP (μg/l)	Percent Removal (Incremental/ Overall)
Feed	6.68	--	770	--
Column 1	5.86	12/12	670	13/13
Column 2	5.40	7/19	670	0/13
Column 3	5.07	5/24	540	17/30
Column 4	5.00	1/25	510	4/34

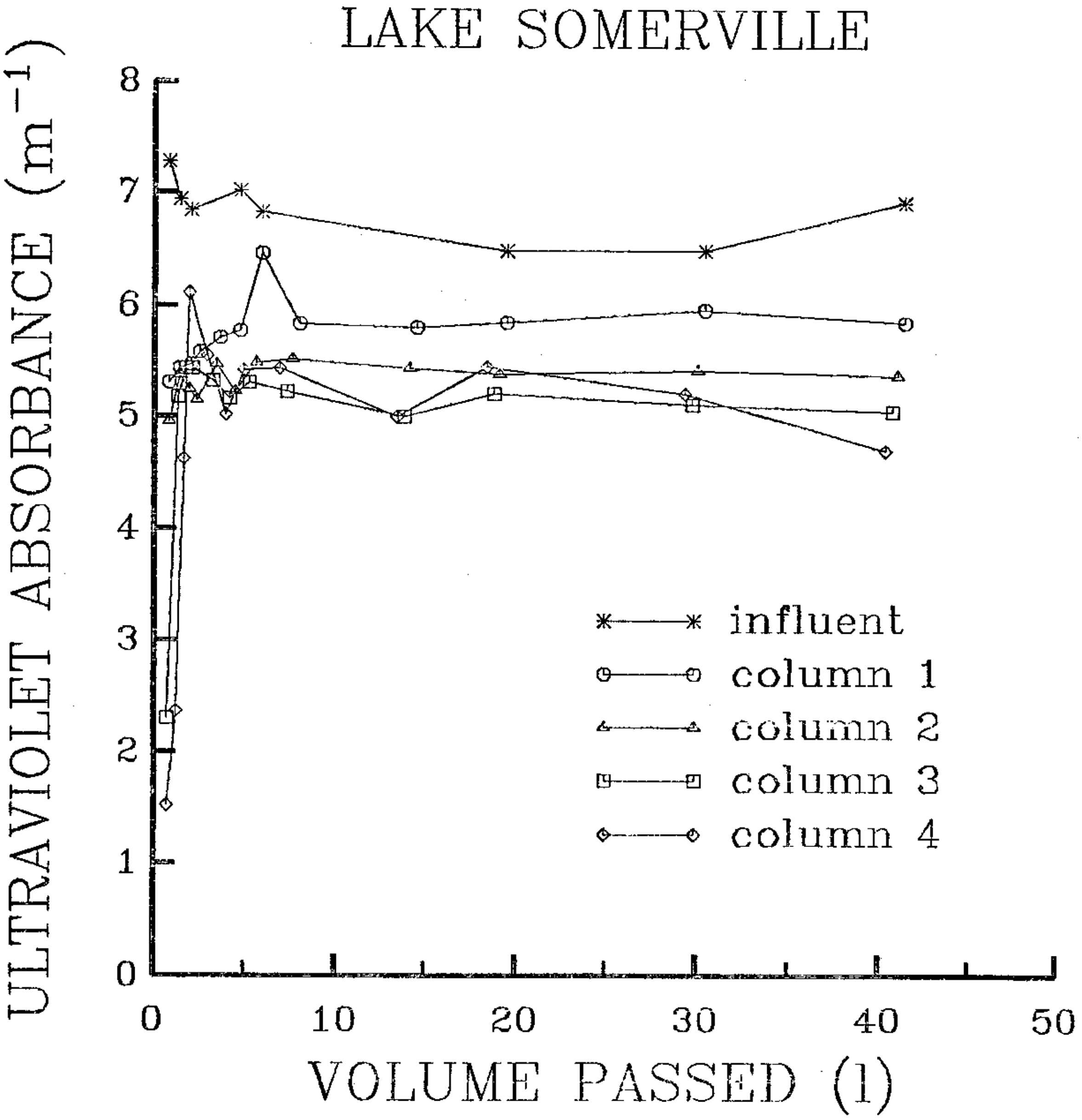


Figure 39. Ultraviolet Absorbance of Coagulated Lake Somerville Water as Influent to and Effluent from a Series of Activated Alumina Columns.

The overall removal of THMFP of 34 percent compares well with average removals of 31 and 23 percent achieved in batch equilibrium experiments. The variability in removals in each column is probably the result of variability in the THMFP analysis procedure. The removals of UVA are much more orderly. Incremental removals range smoothly from 12 percent in the first column to 1 percent in the last column. This indicates that significant adsorption capacity remained to be used at the end of the experiment. This conclusion is supported by the UVA breakthrough curves presented in Figure 39. After an initial period of superior removal, all columns approached a constant removal which was maintained for the duration of the experiment. The first column continued to remove ultraviolet absorbing substances after treating more than 40 l. This corresponds to more than 4,000 bed volumes. The initial breakthrough occurred in columns 3 and 4 at about 25 bed volumes.

Another column experiment was conducted with Sabine River water coagulated with 80 mg/l of alum. This experiment was conducted with an average flow rate of 10.7 ml/min which resulted in an average hydraulic loading of 6.8 m/hr (2.8 gpm/ft^2). The results of this experiment are summarized in Table 5 and shown graphically in Figure 40. The data gathered during the experiment is listed in Appendix C-24.

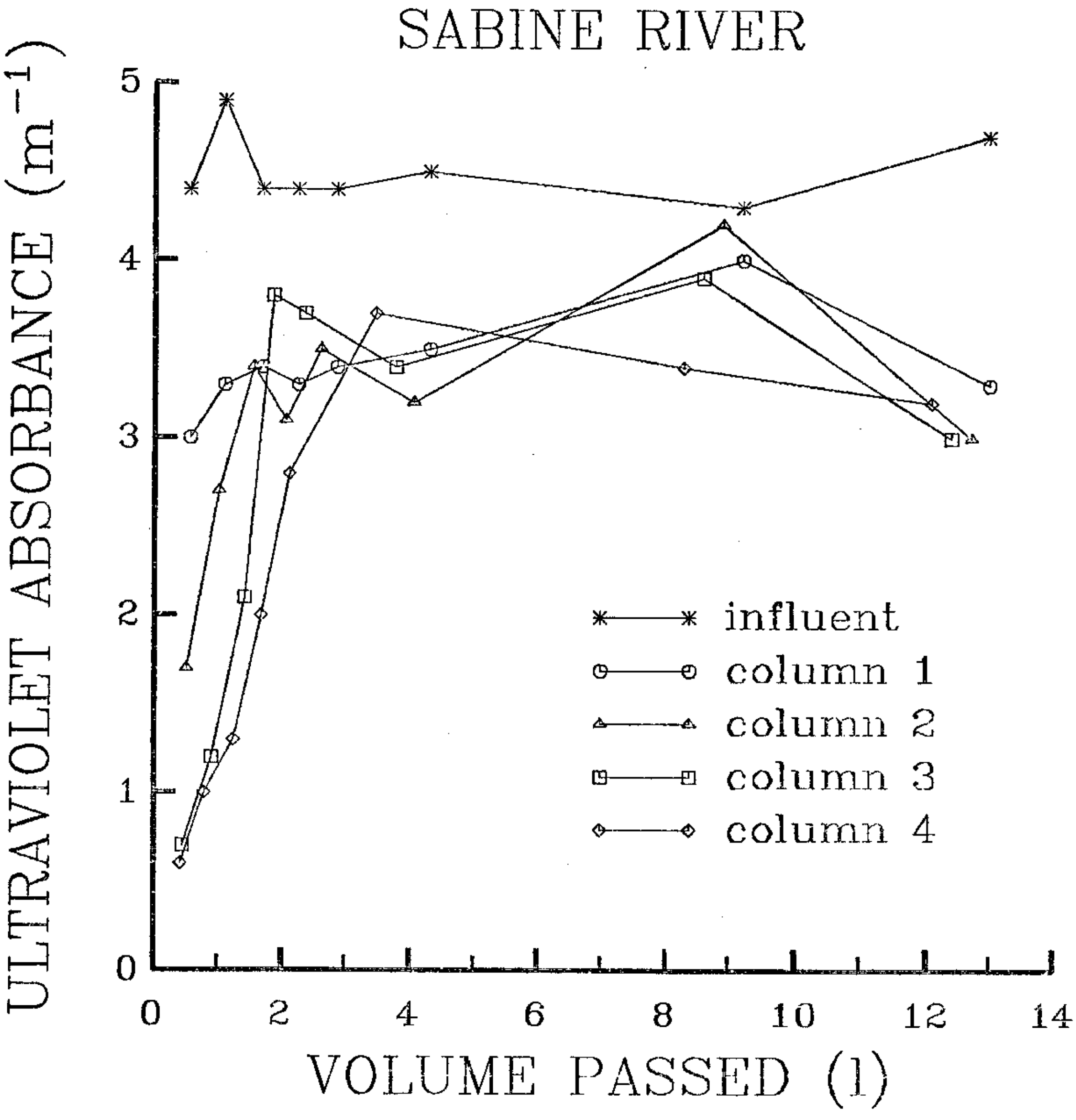


Figure 40. Ultraviolet Absorbance of Coagulated Sabine River Water as Influent to and Effluent from a Series of Activated Alumina Columns.

TABLE 5

Results of Activated Alumina Column Experiment

Using Coagulated Sabine River Water

	Flow-Weighted Average UVA (m^{-1})	Percent Removal (Incremental/ Overall)	Flow-Weighted Average THMFP (μg/l)	Percent Removal (Incremental/ Overall)
Feed	4.48	--	1050	--
Column 1	3.58	20/20	630	40/40
Column 2	3.47	2/22	770	-13/27
Column 3	3.27	5/27	640	13/40
Column 4	3.05	5/32	770	-13/27

The water used as feed for the continuous flow column experiments was also used in an equilibrium adsorption experiment. The results are shown in Figure 41. The data used to construct this graph is listed in Appendix C-25.

A similar pattern can be observed in the results of the experiment with Sabine River water as is seen in the results of the experiment with Lake Somerville water. An overall UVA removal of 32 percent was observed throughout the run (Table 5) which corresponds well with the maximum removal noted in the batch equilibrium experiment (Figure 41). The bulk of the UVA removal occurred in the first column indicating that significant adsorption capacity remained at the end of the experiment.

Overall removal of 27 percent of influent THMFP was observed. Once again the THMFP removal data is much more irregular than the UVA data. However, the bulk of THMFP removal also appears to have occurred in the first column; therefore, it is likely that significant capacity for removal

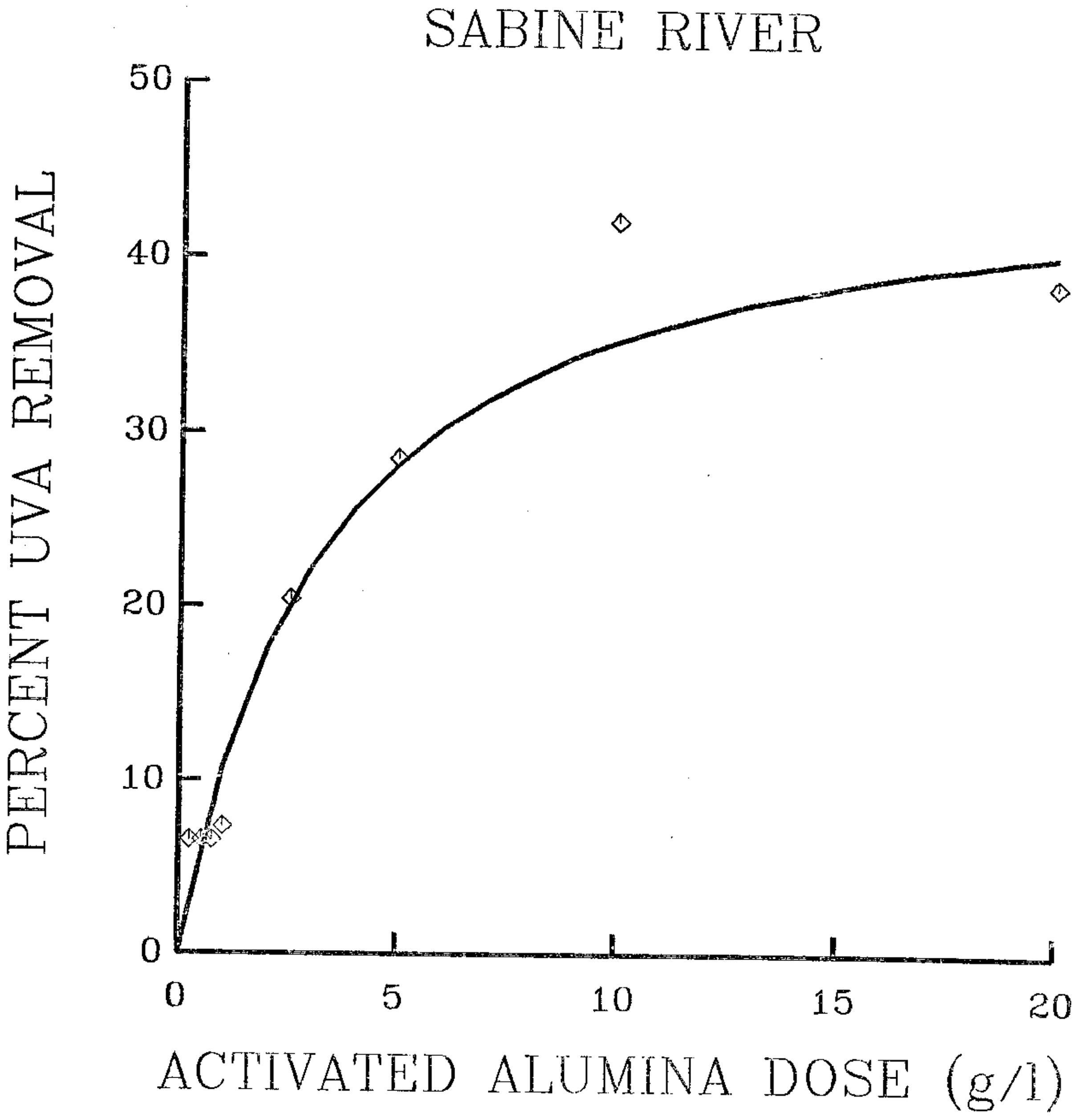


Figure 41. Removal of Ultraviolet Absorbance from Coagulated Sabine River Water as a Function of Activated Alumina Dose.

of THMFP was not used during this experiment.

The breakthrough curve for UVA presented in Figure 40 again indicates an initial period of superior removal followed by an extended period of constant removal. The initial breakthrough occurred in columns 2, 3, and 4 at approximately 43 bed volumes. This is longer than that observed in the Lake Somerville experiments which would be expected due to the lower UVA of the feed.

In summary, these preliminary experiments with activated alumina support the contention that this adsorbent has significant potential as a method for removing natural organic materials from water. Removals of 90 percent of the ultraviolet absorbing materials and 70 percent of the total organic carbon from untreated lake water was observed. Trihalomethane formation potential removals of 220 and 270 μg/l were observed after coagulation of lake water with alum. Continuous flow experiments with coagulated river waters showed consistent removals of UVA and THMFP in the range of 25-35 percent throughout the tests. More extensive removals may have occurred if the water had been coagulated with the minimum alum dose required for turbidity removal. Despite the potential of activated alumina adsorption much research remains to be done. Regeneration techniques need to be studied along with pretreatment methods to improve adsorption capacity and kinetics. Column experiments of a larger scale should also be conducted.

CONCLUSIONS

Based on experiments on samples of four water supplies in Texas, the following conclusions can be made concerning control of synthetic organics produced during conventional water treatment.

1. A high potential for production of trihalomethanes exists in all water sources tested (Lake Somerville, Lake Livingston, Neches River, Sabine River).
2. Conventional treatment by alum coagulation can be an effective means of reducing the level of trihalomethane formation potential (THMFP). Maximum removals in the range of 72 to 87 percent were observed at optimal conditions of pH and alum dose.
3. Removal of THMFP is strongly affected by pH, especially at alum doses above 40 mg/l. The optimum pH was observed to be near pH 5.0 in three of the water supplies tested, while a fourth had poor removals at this pH.
4. Near optimal THMFP removal in most cases could be achieved with alum doses in the range of 50 mg/l. However, the pH which is necessary for near optimal removal would often not be encountered unless supplemental acid or base were added in addition to alum.
5. Reduction in chemical costs to achieve a given level of THMFP removal or improved removal at constant chemical cost appear to be possible by addition of acid or base prior to alum addition to achieve a more favorable pH for coagulation.
6. Increased concentrations of THMFP are observed under some conditions when alum dose is increased. Overdosing was observed when pH was controlled at constant values or when it was allowed to decrease with increasing alum doses.

7. None of the variables tested (ultraviolet absorbance, total organic carbon, visible absorbance) was able to accurately predict the effects of both alum dose and pH on THMFP removal.

8. Ultraviolet absorbance (UVA) was usually able to predict the optimum pH for THMFP removal. However, the effect of alum dose on the pattern of UVA removal was not the same as that observed for THMFP removal. The patterns of UVA removal typically showed no overdosing, and little extra removal above a breakpoint dose which was in the neighborhood of 50 mg/l. THMFP removal patterns typically did show overdosing and only a slight tendency toward a breakpoint dose.

9. The removal pattern of total organic carbon (TOC) was similar to that for UVA. No overdosing was observed, and a slightly weaker breakpoint dose effect was seen. The ability of TOC removal patterns to predict optimum pH for THMFP removal was not as reliable as UVA removal patterns.

10. Visible absorbance (VA) was used as a surrogate for turbidity and showed little similarity to THMFP in its removal patterns. Little to no effect of pH was noted on VA removal, and a strong breakpoint dose was evident. Operation of a water treatment plant for the sole purpose of turbidity removal will likely result in significantly poorer removal of THMFP than is possible.

11. Modification of alum coagulation by addition of a medium molecular weight cationic polymer did not improve THMFP removals at the polymer doses studied.

12. Modification of conventional alum coagulation by addition of activated silica did improve THMFP removal. Activated silica was

equally effective for THMFP removal when used as the sole coagulant.

13. Activated alumina was capable of removing significant amounts of THMFP, UVA, and TOC in both batch and continuous flow systems.

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APPENDICES

Section A - Analytical Procedures

Appendix A-1: Analysis of Trihalomethanes by Liquid/Liquid Extraction

A. Reagents

1. Extraction solvent - Pentane (Fisher P-400)
2. Methyl alcohol - ACS Reagent Grade (Mallinckrodt 5106)
3. Chlorine reducing agent - Sodium thiosulfate
4. Chloroform, ACS Certified - (Fisher Scientific C-574)
5. Bromodichloromethane - (Aldrich Chem. Compounds 13.918-1)
6. Dibromochloromethane - (Columbia Org. Chemicals D-1843)
7. Bromoform - (Fisher B-386)
8. Internal Standard - Ethylene dibromide - (Aldrich D4, 075-2)

B. Make up of Stock Standards

1. Fill 10.0 ml volumetric flask with about 9.8 ml of methyl alcohol.
2. Weigh unstoppered flask to nearest 0.1 mg.
3. Add 1 to 2 drops of standard with 50 μl syringe and reweigh.
4. Dilute to 10.0 ml with alcohol and mix by inversion.
5. Store at 4°C. (Stable for 4 weeks)
6. Using a 1.0 ml syringe, add the quantity of each standard required to give a 1.0×10^4 μg/l concentration to a 25 ml volumetric flask. Dilute with methyl alcohol. Mix by inversion.
7. The resultant solution will contain a 1.0×10^4 μg/l

concentration of each THM compound.

8. Dilute standard with distilled blank water using volumetric pipettes, to concentrations 1, 10, 30, 50, 100, and 200 µg/l.
9. These standards are used to establish a calibration curve and are to be prepared daily.

C. Sample Glassware and Collection Preparation

1. Wash all sample bottles and septa in detergent and rinse with distilled water.
2. Place sample bottles in oven at 550°C for 1 hour to destroy any organic matter.
3. Clean flasks and pipettes with chromic acid. Rinse with distilled water.
4. Collect samples in 14 ml screw cap vials by Pierce.
5. Seal with Teflon faced septa without headspace.

D. Extraction and Analysis

1. Remove 5.0 ml of sample from sealed sample vial with 10 ml glass syringe and place in a clean, empty, sealed vial.
2. Put 0.5 ml of sample in another clean sealed vial. Dilute with distilled blank water to 5.0 ml. This yields a 1/10 dilution of sample.
3. Add 5.0 ml pentane to 5.0 ml sample.
4. Shake vial for 1 minute.
5. Let stand for 1 minute to allow separation of phases.
6. Analyze sample by injecting 1.0 µl of the upper phase (pentane).

E. Gas Chromatograph System

1. Segments

- a. Gas Chromatograph - Tracor MT-220 GC
- b. Detector - Tracor Ni-63 electron capture detector.
- c. Voltage Source - Tracor electron capture power supply
- d. Recorder - Westronics MT22
- e. Carrier Gas - prepurified nitrogen

2. Conditions
   - a. Temperatures
     - 1) Oven - 50°C
     - 2) Detector - 275°C
     - 3) Inlet - 110°C
   - b. Nitrogen Flows
     - 1) Regulator - 50 psi
     - 2) Purge - 20 cc/min
     - 3) Carrier - 2 (25cc/min @ 50 psi)
   - c. Electron Capture Power Supply - Voltage output set at amount required to give 90 percent of maximum response.
   - d. Column
     - 1) Glass column - No. 2-0475 from Supelco
     - 2) 6 ft length
     - 3) 2 mm inside diameter
     - 4) Packing - 3 percent SP-2100 on 80/100 Supelcoport

F. Calculation of TTHM

1. Locate each trihalomethane and the internal standard in the sample chromatogram and measure its peak height.
2. Determine ratio of peak heights of internal standard and each trihalomethane.

3. Determine THM concentration by comparing peak height ratio to calibration curve found for standards.
4. Calculate TTHM by summing the four individual trihalomethane compounds.

Appendix A-2: Analysis of Trihalomethane Formation Potential

A. Reagents

1. Chlorine Solution - 5 percent sodium hypochlorite
2. Buffer Solution - 1.16 M K_2HPO_4
3. Quench Solution - 1.0 N sodium thiosulfate
4. Chlorine spot check - DPD reagent

B. Glassware Preparation and Sample Collection

1. Wash all sample bottles and septa in detergent and rinse with distilled water.
2. Place sample bottles in oven at 550°C for 1 hour to destroy any organic matter.
3. Clean flasks and pipettes with chromic acid. Rinse with distilled water.
4. Collect samples in 14 ml screw cap vials by Pierce.
5. Seal with Teflon faced septa without headspace.

C. Procedure

1. Chlorinate duplicate sealed samples with chlorine solution using a 50 μl syringe. Add enough solution to yield residual after seven days (25 to 100 μl).
2. Buffer sealed sample to pH 7 with buffer solution using a 50 μl syringe. Add an equal amount of buffer and chlorine.
3. Store samples at 25°C for 7 days.
4. From a duplicate sample remove approximately 2 ml. Add approximately 1 ml of DPD reagent. A pink color indicates a chlorine residual.
5. Remove residual chlorine from other sample by adding 20 μl

of quench solution with a 50 μl syringe.

6. Analyze for THMs using the procedure outlined in Appendix B. Resulting THM concentrations will be the trihalomethane formation potential.

Section B - Experimental Procedures

Appendix B: Procedure for pH Control During Coagulation

A. Determination of Alkalinity Titration Curve

1. Take 100 ml of raw sample and determine initial pH.
2. Titrate with .02 N H_2SO_4 and record ml of titrant used to reach pH values at intervals of about 0.5 pH units.
3. Multiply ml of titrant recorded for each case by 0.2 to yield meq/l.
4. Plot meq/l vs. pH to obtain alkalinity titration curve.

B. Acid-Lime Quantities

1. From the alkalinity titration curve determine meq/l needed for the pH value wanted.
2. Subtract the number of meq/l that will be added due to alum. (Assume 0.0045 meq/mg of Alum. This assumes that each aluminum ion reacts with 1.5 hydroxide ions. Based on experimental results, this appears to be the best assumption.)
3. The remaining meq/l is the amount of acid needed. (If remaining meq/l is negative, that quantity of lime is required.)
4. If 0.1 N H_2SO_4 and 0.1 N CaO is used, the meq/l required is multiplied by 10 to give ml of acid or lime needed.

Section C - Data

Appendix C-1: THMFP Results for Lake Somerville

pH	Alum (mg/l)	$CHCl_3$ (µg/l)	$CHBrCl_2$ (µg/l)	$CHBr_2Cl$ (µg/l)	$CHBr_3$ (µg/l)	THMFP (µg/l)
3.3	10	410	55	5	nd	470
3.9	25	300	45	9	nd	354
3.5	50	225	20	7	nd	252
3.9	80	185	30	8	nd	223
4.2	150	250	55	5	nd	310
4.4	10	355	80	5	nd	440
4.7	25	275	30	8	nd	313
4.3	50	285	55	8	nd	348
4.7	80	185	20	6	nd	211
4.5	150	120	0	7	nd	127
4.9	10	330	80	6	nd	344
5.0	25	390	130	8	nd	528
4.9	50	230	70	11	nd	311
5.0	80	150	55	7	nd	212
5.0	150	225	95	9	nd	329
5.6	10	650	155	10	nd	815
5.6	25	510	90	12	nd	612
5.6	50	380	35	12	nd	427
5.5	80	485	100	13	nd	598
5.5	150	485	75	6	nd	566
6.0	10	505	90	12	nd	667
6.0	25	695	155	12	nd	862
6.0	50	465	0	7	nd	472
5.9	80	565	50	5	nd	620
5.8	150	750	165	7	nd	922
7.0	10	1940	155	12	nd	2107
7.0	25	545	100	7	nd	652
7.1	50	395	90	12	nd	497
7.1	80	325	90	13	nd	428
7.0	150	290	100	0	nd	390
Raw THMFP		850	82	0	nd	932
Raw THM		0	0	0	nd	0

nd - none detected

Appendix C-2: Acidometric Titration Data for Raw Lake Somerville Water

Acid Added (meq/l)	pH
0.0	7.8
0.18	6.3
0.28	6.0
0.42	5.3
0.46	5.0
0.50	4.5
0.54	4.0

Appendix C-3: UVA and VA Results for Lake Somerville

pH	Alum (mg/l)	Unfiltered UVA (m^{-1})	Unfiltered VA (m^{-1})	Filtered UVA (m^{-1})	Filtered VA (m^{-1})
3.3	10	13.2	0.7	12.1	0.2
3.9	25	8.2	0.1	8.2	0.2
3.5	50	7.0	0.0	10.7	1.1
3.9	80	6.0	0.0	6.4	0.1
4.2	150	7.2	0.2	6.1	0.2
4.4	10	15.1	1.3	8.7	0.3
4.7	25	8.1	0.2	7.4	0.2
4.3	50	6.8	0.1	5.9	0.1
4.7	80	7.2	0.1	5.2	0.0
4.5	150	7.4	0.2	5.7	0.1
4.9	10	12.0	0.6	9.6	0.1
5.0	25	9.3	1.2	6.4	0.1
4.9	50	5.9	0.1	5.3	0.1
5.0	80	5.0	0.1	4.7	0.4
5.0	150	4.9	0.0	4.6	0.1
5.6	10	11.7	0.8	9.7	0.1
5.6	25	7.4	0.1	6.9	0.1
5.6	50	5.6	0.1	5.6	0.0
5.5	80	5.3	0.0	4.9	0.1
5.5	150	4.7	0.0	4.6	0.1
6.0	10	11.3	0.5	9.8	0.2
6.0	25	7.7	0.1	7.3	0.1
6.0	50	6.1	0.0	5.9	0.0
5.9	80	5.7	0.1	5.7	0.1
5.8	150	5.0	0.1	4.8	0.1
7.0	10	13.1	0.9	11.3	0.0
7.0	25	9.7	0.3	8.9	0.0
7.1	50	8.1	0.1	8.0	0.0
7.1	80	6.4	0.1	6.3	0.0
7.0	150	5.3	0.1	5.2	0.0
Raw		16.0	1.8	----	---

Appendix C-4: Total Organic Carbon of Coagulated Lake Somerville Water Before and After Contact with 20 g/l Acid-Washed Activated Alumina (Alcoa F-1)

pH	Alum (mg/l)	Total Organic Carbon (mg/l) Before	Total Organic Carbon (mg/l) After
7.8	0	7.0	3.4
3.3	10	6.2	3.1
3.9	25	4.5	3.9
3.5	50	4.3	3.4
3.9	80	3.9	3.2
4.2	150	4.0	10.0
4.4	10	5.7	3.2
4.7	25	4.7	3.5
4.3	50	4.0	3.3
4.7	80	4.4	3.1
4.5	150	4.3	(3.0)
4.9	10	6.2	3.2
5.0	25	5.0	3.1
4.9	50	4.4	3.1
5.0	80	4.1	3.0
5.0	150	3.7	2.9
5.6	10	5.9	3.4
5.6	25	4.6	(3.1)
5.6	50	4.2	3.0
5.5	80	4.2	2.8
5.5	150	3.9	3.0
6.0	10	5.7	3.2
6.0	25	5.0	3.1
6.0	50	3.7	3.0
5.9	80	3.7	(2.85)
5.8	150	3.5	2.7
7.0	10	5.8	3.2
7.0	25	5.9	3.1
7.1	50	5.0	3.3
7.1	80	4.6	2.9
7.0	150	3.9	2.8

NOTE: Values in parentheses are estimated values used to generate contour plots.

Appendix C-5: THMFP Results for Lake Livingston

pH	Alum (mg/l)	$CHCl_3$ (µg/l)	$CHBrCl_2$ (µg/l)	$CHBr_2Cl$ (µg/l)	$CHBr_3$ (µg/l)	THMFP (µg/l)
4.0	10	670	72	nd	nd	742
4.05	25	1980	63	nd	nd	2043
4.1	50	460	57	nd	nd	517
4.1	80	580	55	nd	nd	635
4.0	150	560	53	nd	nd	613
4.55	10	620	60	nd	nd	680
4.45	25	500	60	nd	nd	560
4.55	50	280	47	nd	nd	327
4.5	80	355	51	nd	nd	406
4.5	150	435	57	nd	nd	492
5.0	10	890	62	nd	nd	952
5.0	25	530	57	nd	nd	587
4.9	50	260	51	nd	nd	311
4.9	80	310	50	nd	nd	360
4.9	150	310	43	nd	nd	353
5.5	10	690	66	nd	nd	756
5.6	25	800	58	nd	nd	858
5.5	50	375	55	nd	nd	430
5.5	80	490	48	nd	nd	538
5.5	150	355	48	nd	nd	403
6.0	10	850	71	nd	nd	921
5.9	25	500	71	nd	nd	571
6.0	50	480	39	nd	nd	519
6.0	80	410	61	nd	nd	471
5.9	150	205	46	nd	nd	251
6.9	10	780	64	nd	nd	844
7.0	25	685	76	nd	nd	761
7.0	50	310	70	nd	nd	380
6.9	80	410	50	nd	nd	460
7.0	150	480	57	nd	nd	537
Raw THMFP		760	65	nd	nd	825
Raw THM		4	nd	nd	nd	4

nd - none detected

Appendix C-6: Acidometric Titration Data for Raw Lake Livingston Water

Acid Added (meq/l)	pH
0.0	7.4
0.1	7.0
0.47	6.4
0.68	6.0
0.94	5.5
1.08	4.9
1.15	4.2
1.18	4.0

Appendix C-7: UVA and VA Results for Lake Livingston

pH	Alum (mg/l)	Unfiltered UVA (m^{-1})	Unfiltered VA (m^{-1})	Filtered UVA (m^{-1})	Filtered VA (m^{-1})
4.0	10	36.3*	4.5	22.4*	1.2
4.05	25	24.3*	1.5	16.1	0.3
4.1	50	11.6	0.2	10.2	0.1
4.1	80	9.5	0.2	8.3	0.1
4.0	150	8.7	0.3	8.1	0.2
4.55	10	34.3*	3.5	29.8	0.9
4.45	25	16.0*	0.8	12.0	0.2
4.55	50	9.4	0.3	8.2	0.2
4.5	80	8.4	0.2	8.1	0.4
4.5	150	8.3	0.4	8.4	0.4
5.0	10	37.5*	4.6	25.0*	1.2
5.0	25	----	---	11.6	0.2
4.9	50	8.4	0.2	6.9	0.2
4.9	80	6.9	0.1	6.6	0.1
4.9	150	9.2	0.5	6.9	0.1
5.5	10	38.2*	4.1	28.5*	1.6
5.6	25	16.2*	0.8	12.5	0.2
5.5	50	7.8	0.1	6.9	0.1
5.5	80	6.7	0.1	6.0	0.1
5.5	150	5.3	0.1	5.3	0.1
6.0	10	37.6*	3.9	20.2*	0.8
5.9	25	17.5*	0.9	12.7	0.3
6.0	50	8.7	0.2	8.2	0.1
6.0	80	8.0	0.3	6.6	0.1
5.9	150	5.6	0.1	5.4	0.1
6.9	10	37.7*	3.8	26.2*	1.1
7.0	25	28.6*	1.8	20.3*	0.8
7.0	50	11.1	0.3	10.5	0.2
6.9	80	10.6	0.3	9.1	0.1
7.0	150	7.4	0.2	6.7	0.1
Raw		39.4*	4.2	----	---

* 0.01 m cell used, otherwise 0.10 m cell used.

Appendix C-8: Total Organic Carbon of Coagulated Lake Livingston Water Before and After Contact with 20 g/l Acid-Washed Activated Alumina (Alcoa F-1)

pH	Alum (mg/l)	Total Organic Carbon (mg/l)	
		Before	After
7.4	0	7.1	3.3
4.0	10	6.6	3.2
4.05	25	6.1	3.3
4.1	50	4.4	3.3
4.1	80	3.8	3.3
4.0	150	3.7	3.2
4.55	10	5.8	3.2
4.45	25	3.7	3.1
4.55	50	3.6	3.1
4.5	80	4.0	3.2
4.5	150	3.6	2.9
5.0	10	6.1	3.2
5.0	25	4.7	3.1
4.9	50	3.7	3.1
4.9	80	3.3	3.4
4.9	150	3.9	3.3
5.5	10	6.4	3.1
5.6	25	5.1	3.1
5.5	50	3.7	3.3
5.5	80	3.8	3.1
5.5	150	3.3	3.0
6.0	10	6.1	3.3
5.9	25	5.1	3.2
6.0	50	4.3	3.2
6.0	80	3.9	3.1
5.9	150	3.5	2.6
6.9	10	6.3	3.1
7.0	25	5.8	3.3
7.0	50	4.5	3.2
6.9	80	4.3	2.9
7.0	150	3.7	2.8

Appendix C-9: THMFP Results for the Neches River

pH	Alum (mg/l)	$CHCl_3$ (μg/l)	$CHBrCl_2$ (μg/l)	$CHBr_2Cl$ (μg/l)	$CHBr_3$ (μg/l)	THMFP (μg/l)
3.8	10	740	51	nd	nd	791
3.95	25	950	56	nd	nd	1006
4.1	50	675	47	nd	nd	722
4.1	80	626	45	nd	nd	671
3.95	150	378	39	nd	nd	417
4.5	10	950	56	nd	nd	1006
4.5	25	660	48	nd	nd	708
4.4	50	675	49	nd	nd	724
4.5	80	560	45	nd	nd	605
4.4	150	225	38	nd	nd	263
5.0	10	820	55	nd	nd	875
5.1	25	705	43	nd	nd	748
5.0	50	1155	25	nd	nd	1180
5.0	80	930	43	nd	nd	973
4.9	150	480	30	nd	nd	510
5.6	10	1030	55	nd	nd	1085
5.55	25	740	45	nd	nd	785
5.6	50	320	52	nd	nd	372
5.5	80	500	48	nd	nd	548
5.5	150	930	30	nd	nd	960
6.1	10	820	56	nd	nd	876
6.1	25	625	53	nd	nd	678
5.9	50	465	45	nd	nd	510
6.0	80	290	40	nd	nd	338
6.0	150	340	41	nd	nd	381
7.1	10	3090	57	nd	nd	3147
6.9	25	885	54	nd	nd	939
7.1	50	720	53	nd	nd	773
6.9	80	515	56	nd	nd	571
6.9	150	400	45	nd	nd	445
Raw THMFP		755	40	nd	nd	795
Raw THM		8	0	nd	nd	8

nd - none detected

Appendix C-10: Acidometric Titration Data for Raw Neches River Water

Acid Added (meq/l)	pH
0.0	7.8
0.06	7.0
0.13	6.5
0.22	6.0
0.33	5.5
0.41	5.0
0.41	4.4
0.50	3.95

Appendix C-11: UVA and VA Results for the Neches River

pH	Alum (mg/l)	Unfiltered UVA (m^{-1})	Unfiltered VA (m^{-1})	Filtered UVA (m^{-1})	Filtered VA (m^{-1})
3.8	10	45.7*	5.0	33.2*	1.7
3.95	25	25.8*	1.0	22.5*	0.5
4.1	50	14.3*	0.1	12.1*	0.0
4.1	80	9.4	0.2	8.3	0.0
3.95	150	8.0	0.1	7.6	0.0
4.5	10	46.2*	4.9	24.7*	0.9
4.5	25	13.9*	0.3	10.6*	0.0
4.4	50	9.3	0.0	8.4	0.1
4.5	80	7.9	0.1	7.4	0.1
4.4	150	6.4	0.1	6.3	0.1
5.0	10	47.6*	4.6	42.8*	2.6
5.1	25	13.9*	0.2	11.9*	0.4
5.0	50	6.3	0.1	7.6	0.2
5.0	80	6.1	0.0	5.9	0.1
4.9	150	4.9	0.0	5.1	0.1
5.6	10	47.6*	4.4	39.1*	1.9
5.55	25	14.8*	0.3	17.3*	1.0
5.6	50	7.3	0.0	7.1	0.0
5.5	80	6.0	0.0	5.9	0.0
5.5	150	5.4	0.0	5.4	0.0
6.1	10	50.4*	5.7	33.7*	1.6
6.1	25	20.9*	1.0	17.3*	0.4
5.9	50	7.3*	0.1	10.43	0.4
6.0	80	5.8	0.1	6.2	0.1
6.0	150	5.3	0.0	5.5	0.1
7.1	10	50.0*	5.4	37.2*	2.1
6.9	25	27.9*	1.4	25.2*	1.0
7.1	50	10.2*	1.0	11.5*	0.3
6.9	80	9.3	0.1	10.7*	0.2
6.9	150	6.1	0.1	6.2	0.1
Raw		48.5	4.1	----	---

* 0.01 m cell used, otherwise 0.10 m cell used.

Appendix C-12: Total Organic Carbon of Coagulated Neches River Water Before and After Contact with 20 g/l Acid-washed Activated Alumina (Alcoa F-1)

pH	Alum (mg/l)	Total Organic Carbon (mg/l) Before	Total Organic Carbon (mg/l) After
7.8	0	6.7	3.0
3.8	10	5.4	3.3
3.95	25	5.7	3.4
4.1	50	4.8	3.3
4.1	80	4.0	3.1
3.95	150	3.8	3.3
4.5	10	6.0	3.1
4.5	25	4.7	3.1
4.4	50	4.2	3.5
4.5	80	3.7	3.2
4.4	150	3.8	3.1
5.0	10	6.9	3.2
5.1	25	4.5	3.3
5.0	50	4.1	3.3
5.0	80	3.4	3.4
4.9	150	3.0	2.9
5.6	10	6.6	3.2
5.55	25	4.7	3.0
5.6	50	3.5	3.5
5.5	80	3.6	3.1
5.5	150	3.3	2.7
6.1	10	(6.5)	(3.2)
6.1	25	4.9	3.1
5.9	50	4.1	3.3
6.0	150	3.3	2.6
7.1	10	6.5	3.2
6.9	25	5.7	3.4
7.1	50	4.8	3.6
6.9	80	4.6	3.3
6.9	150	4.1	2.7

NOTE: Values in parentheses are estimated values used to generate contour plots.

Appendix C-13: THMFP Results for the Sabine River

pH	Alum (mg/l)	$CHCl_3$ (μg/l)	$CHBrCl_2$ (μg/l)	$CHBr_2Cl$ (μg/l)	$CHBr_3$ (μg/l)	THMFP (μg/l)
4.0	10	1570	66	nd	nd	1636
4.0	25	661	74	nd	nd	735
4.1	50	947	71	nd	nd	1018
4.1	80	1870	62	nd	nd	1932
4.05	150	858	56	nd	nd	914
4.6	10	929	72	nd	nd	1001
4.5	25	1036	69	nd	nd	1105
4.5	50	1036	67	nd	nd	1103
4.5	80	661	57	nd	nd	718
4.4	150	446	51	nd	nd	597
5.05	10	1251	72	nd	nd	1323
5.0	25	929	68	nd	nd	997
5.1	50	840	68	nd	nd	908
5.0	80	697	60	nd	nd	757
4.9	150	482	54	nd	nd	536
5.6	10	1600	70	nd	nd	1670
5.6	25	786	66	nd	nd	852
5.5	50	1300	64	nd	nd	1364
5.5	80	768	60	nd	nd	828
5.55	150	679	68	nd	nd	747
5.95	10	1380	70	nd	nd	1450
5.95	25	1300	75	nd	nd	1375
5.95	50	1320	65	nd	nd	1385
5.95	80	714	60	nd	nd	774
5.9	150	732	60	nd	nd	792
7.0	10	1550	77	nd	nd	1627
7.0	25	1440	78	nd	nd	1518
7.1	50	1072	65	nd	nd	1137
7.1	80	1570	64	nd	nd	1634
7.1	150	1072	60	nd	nd	1132
Raw THMFP		1720	63	nd	nd	1783
Raw THM		12	0	nd	nd	12

nd - none detected

Appendix C-14: Acidometric Titration Data for Raw Sabine River Water

Acid Added (meq/l)	pH
0.0	6.7
0.03	6.5
0.20	5.5
0.27	4.8
0.29	4.4
0.37	3.95

Appendix C-15: UVA and VA Results for the Sabine River

pH	Alum (mg/l)	Unfiltered UVA (m^{-1})	Unfiltered VA (m^{-1})	Filtered UVA (m^{-1})	Filtered VA (m^{-1})
4.0	10	50.4*	4.8	38.7*	1.5
4.0	25	36.0*	2.0	23.6*	0.3
4.1	50	16.8*	0.4	14.4*	0.2
4.1	80	13.1	0.3	11.6	0.3
4.05	150	10.6	0.2	10.1	0.2
4.6	10	51.3*	4.5	35.8*	1.4
4.5	25	20.3*	0.4	17.7*	0.3
4.5	50	13.0	0.2	11.6	0.1
4.5	80	8.9	0.2	8.6	0.2
4.4	150	8.2	0.2	7.7	0.2
5.05	10	50.5*	5.7	39.6*	1.5
5.0	25	23.3*	0.8	15.1*	0.1
5.1	50	9.3*	0.2	9.2*	0.2
5.0	80	7.7	0.0	7.7	0.1
4.9	150	6.8	0.0	6.7	0.0
5.6	10	52.6*	6.1	44.1*	2.2
5.6	25	24.1*	1.0	16.6*	0.4
5.5	50	10.8*	0.3	8.7*	0.0
5.5	80	7.9	0.1	8.0	0.0
5.55	150	6.7	0.1	6.8	0.0
5.95	10	52.9*	4.3	48.8*	2.8
5.95	25	42.7*	3.0	27.6*	1.2
5.95	50	11.8*	0.2	11.1*	0.2
5.95	80	9.1	0.1	8.8	0.1
5.9	150	6.8	0.0	7.0	0.0
7.0	10	53.8*	4.6	42.5*	1.6
7.0	25	47.2*	3.1	38.2*	1.7
7.1	50	16.8*	0.3	16.3*	0.5
7.1	80	12.9*	0.3	12.1	0.0
7.1	150	10.3*	0.0	10.2	0.1
Raw		52.0*	3.3	----	---

* 0.01 m cell used, otherwise 0.10 m cell used.

Appendix C-16: Total Organic Carbon of Coagulated Sabine River Water Before and After Contact with 20 g/l Acid-washed Activated Alumina (Alcoa F-1)

pH	Alum (mg/l)	Total Organic Carbon (mg/l)	
		Before	After
6.7	0	8.0	3.4
4.0	10	8.0	3.6
4.0	25	7.0	3.1
4.1	50	5.7	3.2
4.1	80	5.1	3.2
4.05	150	4.5	3.4
4.6	10	7.6	3.7
4.5	25	6.2	3.2
4.5	10	4.8	3.3
4.5	80	4.3	3.1
4.4	150	4.1	3.3
5.05	10	7.8	3.9
5.0	25	6.4	3.4
5.1	50	4.7	3.3
5.0	80	4.3	3.5
4.9	150	4.0	3.3
5.6	10	8.0	3.5
5.6	25	6.1	3.1
5.5	50	4.8	3.3
5.5	80	4.3	3.1
5.55	150	4.2	3.3
5.95	10	8.0	3.5
5.95	25	6.7	3.6
5.95	50	5.5	3.2
5.95	80	4.5	3.1
5.9	150	4.1	3.2
7.0	10	7.9	3.8
7.0	25	7.1	3.2
7.1	50	6.2	3.1
7.1	80	5.3	3.3
7.1	150	4.8	3.2

Appendix C-17: Removal of Formation Potential from Lake Somerville Water by Coagulation with Alum, Cationic Polymer, and Alum + Cationic Polymer

1. Alum Coagulation

Alum Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP ($\mu g/l$)
0(filtered)*	7.4	0.7	0.15	13.8	900
0*	7.4	3.4	1.5	14.4	710
10	7.2	0.49	0.11	12.11	585
20	7.2	0.35	0.07	9.81	775
40	6.9	0.24	0.07	7.38	780
80	6.7	0.23	0.02	5.90	520
160	4.55	0.4	0.03	4.94	425

* Data for this dose are averages of 3 analyses

2. Polymer Coagulation

Polymer Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP ($\mu g/l$)
0(filtered)*	7.4	0.7	0.15	13.8	900
0*	7.4	3.4	1.5	14.4	710
0.02	7.2	1.0	0.29	13.85	1110
0.10	7.5	0.54	0.17	14.17	1050
0.50	7.35	0.44	0.15	13.88	725
2.50	7.45	0.45	0.14	13.49	1070
12.5	7.05	0.35	0.11	11.82	530
62.5	7.6	0.23	0.02	12.52	870

* Data for this dose are averages of 3 analyses

3. Alum (80mg/l) + Polymer Coagulation

Polymer Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP (μg/l)
0	6.35	0.35	0.09	5.16	500
0.03	6.15	0.25	0.07	4.73	575
0.06	6.15	0.26	0.03	4.76	600
0.12	5.9	0.27	0.0	4.70	425
0.24	6.6	0.32	0.03	5.36	600
0.48	6.45	0.24	0.03	5.03	460
1.0	6.25	0.33	0.04	4.97	570
2.0	6.15	0.24	0.07	4.75	745
4.0	6.25	0.20	0.0	4.78	425
8.0	6.2	0.15	0.0	3.48	500
16.0	6.2	0.16	0.01	4.58	520

Appendix C-18: Removal of Formation Potential from Lake Somerville Water by Coagulation with Alum, Activated Silica, and Alum + Activated Silica

1. Alum Coagulation

Alum Dose (mg/l)	pH	Turbidity (m^{-1})	VA (m^{-1})	UVA (m^{-1})	THMFP (μg/l)
0(filtered)*	7.4	0.7	0.21	13.7	970
0*	7.4	3.4	1.7	12.9	1270
10	7.1	0.9	0.12	11.26	430
20	7.0	0.74	0.17	9.97	500
40	6.5	0.23	0.14	6.99	760
80	6.0	0.24	0.09	5.61	755
160	4.65	0.41	0.04	5.09	255

* Data for this dose are averages of 3 analyses

2. Activated Silica Coagulation

Activated Silica Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP (μg/l)
0(Filtered)*	7.4	0.7	0.21	13.7	970
0*	7.4	3.4	1.7	12.9	1270
0.12	7.6	3.1	0.30	13.46	915
0.24	7.65	3.0	0.20	13.59	600
0.48	7.6	3.0	0.32	14.20	250
0.96	7.65	3.0	0.20	13.84	780
1.2	7.6	3.6	0.22	13.80	750
1.92	7.6	2.9	0.19	14.16	725
2.4	7.6	2.95	0.18	13.74	750
4.8	7.35	2.8	0.3	13.86	750
9.6	7.6	2.8	0.35	13.74	650
19.2	7.65	2.8	0.26	13.80	765

* Data for this dose are averages of 3 analyses

3. Alum (80 mg/l) + Activated Silica Coagulation

Activated Silica Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP (μg/l)
0	6.0	0.24	0.09	5.61	755
0.12	5.9	0.3	0.34	6.07	1190
0.24	5.85	0.42	0.06	5.69	505
0.48	5.9	0.24	0.04	5.73	460
0.96	5.9	0.25	0.01	4.24	700
1.2	5.9	0.22	0.10	5.65	385
1.92	5.95	0.24	0.06	5.55	1025
2.4	5.9	0.26	0.05	5.40	825
4.8	5.9	0.18	0.08	5.68	1070
9.6	5.95	0.20	0.07	5.25	730
19.2	5.95	0.15	0.07	5.45	725

Appendix C-19: Equilibrium Adsorption Tests Using Various Acid-Treated Activated Aluminas and Lake Somerville Water

Sample	DAY 0 pH	DAY 0 UVA (m^{-1})	DAY 19 pH	DAY 19 UVA (m^{-1})	DAY 19 TOC (mg/l)
Blank	7.1	13.04	7.1	13.95	6.3
RA-1 (Reynolds)	6.9	---	6.4	1.92	3.3
RP 2/5 (Rhone-Poulenc)	6.8	---	5.2	1.33	4.1
F-1 (Alcoa)	6.9	---	5.5	1.38	3.1
A-2 (Kaiser)	7.0	---	5.9	2.74	2.9

Appendix C-20: Isotherm Data for Acid-Treated Activated Alumina F-1 and Lake Somerville Water (34 day contact)

Alumina Dose (g/l)	TOC (mg/l)	Percent Removal	UVA (m^{-1})	Percent Removal
0.0	11.4	--	14.05	--
0.25	6.7	41	10.07	28
0.50	5.3	54	7.86	44
0.75	5.3	54	8.00	43
1.00	5.6	51	8.23	41
2.50	5.7	50	6.41	54
5.00	3.8	67	4.07	71
10.00	3.4	70	2.00	86
20.00	3.2*	72	1.03	93

* Average of 4 data points

Appendix C-21: Removal of Formation Potential and UVA by Alum Coagulation and Activated Alumina Adsorption (20 g/l, 7 day contact) from Lake Somerville Water (sampled 6/27/80)

(After Coagulation/After Coagulation and Adsorption)

Alum Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP (μg/l)
0(filtered)	7.25/5.8	0.66/30	1.63/2.2	14.28/19.1	760/520
0	7.25/6.0	4.0 /29	0.08/1.8	14.58/15.2	870/430
10	7.35/5.9	0.58/29	0.65/1.8	11.63/15.5	880/635
20	7.2 /5.7	0.65/35	0.73/2.3	9.92/17.8	710/490
40	6.6 /5.1	0.2 /12	0.68/0.7	6.72/16.0	710/310
80	6.3 /5.4	0.15/160	0.56/7.5	4.57/52.5	735/420
160	4.25/5.0	0.25/145	0.62/6.5	4.46/44.3	400/460

NOTE: Turbidity, VA, and UVA measurements made after adsorption are high due to abrasion of the alumina caused by overagitation.

Appendix C-22: Removal of Formation Potential and UVA by Alum Coagulation and Activated Alumina Adsorption (20 g/l, 7 day contact) from Lake Somerville Water (sampled 7/2/80)

(After Coagulation/After Coagulation and Adsorption)

Alum Dose (mg/l)	pH	Turbidity	VA (m^{-1})	UVA (m^{-1})	THMFP (μg/l)
0(filtered)	7.55/7.0	3.0 /0.53	0.07/0.16	13.82/3.05	975/600
0	7.35/7.0	0.39/0/54	2.02/0.14	14.24/4.89	495/535
10	7.2 /7.0	0.49/0.33	0.11/0.07	12.11/2.67	585/765
20	7.2 /7.0	0.35/0.33	0.07/0.33	9.81/2.49	775/450
40	6.9 /6.9	0.24/0.33	0.07/0.12	7.38/2.29	780/385
80	6.7 /6.9	0.23/0.3	0.02/0.05	5.90/2.12	520/290
160	4.55/6.7	0.4 /0.31	0.03/0.03	4.94/1.89	425/230

Appendix C-23: Activated Alumina Column Experiment Using Coagulated Lake Somerville Water

Feed

Volume Passed (l)	pH	UVA (m^{-1})	THMFP (μg/l)
0.79	6.6	7.28	1250
1.43	6.6	6.94	1435
1.98	6.6	6.84	1015
4.68	6.6	7.03	--
5.87	6.35	6.83	730
19.5	6.3	6.50	650
30.5	6.3	6.50	1025
41.5	6.3	6.93	600

Column 1

Volume Passed (l)	pH	UVA (m^{-1})	THMFP (μg/l)
0.79	7.05	5.31	960
1.43	7.1	5.44	1010
1.98	6.95	5.48	915
2.48	7.0	5.59	965
3.64	6.9	5.71	810
4.68	6.9	5.78	1100
5.87	6.8	6.46	1110
8.00	6.5	5.84	725
14.5	6.9	5.81	535
19.5	6.4	5.85	575
30.5	6.3	5.97	715
41.5	6.3	5.86	575

Column 2

Volume Passed (1)	pH	UVA (m^{-1})	THMFP (µg/1)
0.75	7.2	4.96	1030
1.35	7.3	5.37	325
1.86	7.0	5.25	665
2.32	7.1	5.16	1425
3.41	7.1	5.47	835
4.41	7.15	5.24	675
5.55	7.05	5.49	755
7.64	6.9	5.52	100
14.1	7.1	5.44	900
19.1	6.45	5.40	--
30.1	6.4	5.42	600
41.1	6.4	5.37	675

Column 3

Volume Passed (1)	pH	UVA (m^{-1})	THMFP (µg/1)
0.71	5.8	2.30	500
1.26	7.1	5.18	550
1.73	7.3	5.44	635
2.15	7.3	5.44	1290
3.19	7.2	5.33	925
4.14	7.35	5.17	550
5.23	7.25	5.32	--
7.28	7.05	5.23	365
13.8	7.0	5.00	315
18.8	6.5	5.22	600
29.8	6.35	5.12	575
40.8	6.4	5.06	575

Column 4

Volume Passed (1)	pH	UVA (m^{-1})	THMFP (μg/1)
0.65	5.8	1.52	900
1.16	5.9	2.37	325
1.58	6.8	4.63	645
1.95	7.4	6.11	1050
2.95	7.3	5.55	750
3.89	7.3	5.03	900
4.94	7.6	5.42	--
6.94	7.2	5.44	--
13.4	7.0	5.00	410
18.4	6.6	5.45	390
29.4	6.3	5.21	425
40.4	6.8	4.71	640

Appendix C-24: Activated Alumina Column Experiment Using Coagulated Sabine River Water

Feed

Volume Passed (l)	pH	UVA (m^{-1})	THMFP (μg/l)
0.55	6.65	4.4	910
1.09	6.7	4.9	820
1.69	6.75	4.4	960
2.25	6.65	4.4	1030
2.85	6.7	4.4	1240
4.31	6.65	4.5	2720
9.2	6.65	4.3	810
13.0	6.65	4.7	800

Column 1

Volume Passed (l)	pH	UVA (m^{-1})	THMFP (μg/l)
0.55	6.65	3.0	1150
1.09	6.7	3.3	1150
1.69	6.75	3.4	820
2.25	6.65	3.3	990
2.85	6.7	3.4	1490
4.31	6.65	3.5	460
9.2	6.65	4.0	470
13.0	6.65	3.3	540

Column 2

Volume Passed (l)	pH	UVA (m^{-1})	THMFP ($\mu g/l$)
0.51	5.75	1.7	920
1.00	6.6	2.7	810
1.54	7.0	3.4	520
2.05	7.0	3.1	960
2.61	6.9	3.5	1200
4.07	6.95	3.2	510
8.9	6.85	4.2	930
12.7	6.8	3.0	600

Column 3

Volume Passed (l)	pH	UVA (m^{-1})	THMFP ($\mu g/l$)
0.46	5.6	0.7	1070
0.90	5.7	1.2	680
1.40	6.3	2.1	750
1.86	6.6	3.8	1080
2.36	6.4	3.7	1540
3.79	7.0	3.4	470
8.6	7.0	3.9	540
12.4	7.0	3.0	540

Column 4

Volume Passed (1)	pH	UVA (m^{-1})	THMFP (μg/1)
0.41	5.6	0.6	990
0.80	5.6	1.0	830
1.24	5.7	1.3	720
1.66	6.0	2.0	890
2.11	6.45	2.8	1910
3.48	7.0	3.7	410
8.3	7.05	3.4	870
12.1	7.05	3.2	610

Appendix C-25: Equilibrium Adsorption of Coagulated Sabine River Water by Acid-washed Activated Alumina (Alcoa F-1)

Alumina Dose (g/l)	pH	UVA (m^{-1})	Percent Removal	THMFP (µg/l)	Percent Removal
0	6.3	3.68	--	300	--
0.25	6.4	3.44	7	300	0
0.50	6.5	3.44	7	300	0
0.75	6.4	3.44	7	320	-7
1.00	6.4	3.41	7	270	10
2.50	6.3	2.93	20	230	23
5.00	6.35	2.63	29	210	30
10.00	6.3	2.13	42	200	33
20.00	6.3	2.26	39	80	73