

ORGANIC AND COLOR REMOVAL
FROM WATER SUPPLIES
BY SYNTHETIC RESINOUS ADSORBENTS



INSTITUTE OF WATER RESOURCES

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Fairbanks, Alaska 99701

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Organic and color removal from water supplies by synthetic resinous adsorbents
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Completion Report
by
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INTRODUCTION

Much of the surface and ground water found in North America contains organic matter to such an extent that it may not be acceptable for domestic or individual use without prior treatment. Additionally, iron and color are frequently found in conjunction with organic matter. The presence of iron and organics, as well as other compounds, can result in color which may be a serious problem even though it may not be harmful to human beings. For aesthetic reasons the consumer may turn to alternative water supplies which might be less safe. The US Public Health Service recommends a maximum limit of 15 units of color for drinking water in its *Drinking Water Standards*, (USDHEW, 1962).

It is believed that color is caused by organic matter and that the removal of organic matter from water generally results in color removal. Color in surface water is normally attributed to colloidal suspensions of organic chemical compounds which are referred to as humic or fulvic acids. Additionally, colored waters commonly contain iron which is complexed with organic matter (Oldham and Gloyna, 1969; Robinson, 1967; Christman and Ghassemi, 1966).

Conventional treatment processes such as flocculation and coagulation or aeration followed by sedimentation have been effectively used to remove organics and iron from water. Water containing iron can readily be converted into iron-free water by oxidation with air or chlorine with subsequent removal by sedimentation or filtration. In water containing iron complexed with organics, the removal of the iron is more difficult. Neither aeration nor chlorination will give totally satisfactory results (Alsentzer, 1963). The use of activated carbon, either granular or powder, applied to both water and wastewater to adsorb organic matter has been an effective treatment method.

Many natural organic compounds are believed to interact with iron to form heavily colored compounds which are not free to react in the inorganic form (Weickart, 1970). These complexed-iron compounds (organo-metallic complexes) present problems in water treatment due to difficulty of removal. Furthermore, these materials can result in color, taste, and odor problems in a distribution system.

The mechanism of color removal by adsorption on synthetic resins is similar to that observed with activated carbon. The mechanism of organic removal by resinous adsorbents is quite different from that of the ion exchange process in that adsorption involves no significant interchange of ions (Abrams, 1969). In removing organic matter, the resinous adsorbents exhibit several advantages over the conventional processes. Some of these advantages are low installation and maintenance costs and a capacity which can be almost fully restored by chemical regeneration.

OBJECTIVES

The objectives of this study as listed in the original project proposal were:

1. To evaluate the effectiveness of resinous adsorbents in removing organic matter from water.
2. To determine the amounts of iron, manganese, organic matter, and other materials removed.
3. To establish the economics of removing organics and minerals from natural waters by adsorption on synthetic resins.

Several synthetic resins were evaluated in comparison. A number of ancillary studies were performed to carry out the objectives and to aid in the predictive significance of the work. These included:

1. Determination of chemical and physical characteristics of the raw and treated waters. Where applicable, these included temperature, pH, color, conductivity, chemical oxygen demand (COD), turbidity, alkalinity, iron and hardness.
2. Definition of the operating parameters of the adsorption columns. These parameters included flow rate, capacity of resin to adsorb organics and minerals, strength and quantity of regenerant resin life, and the ratio of bed depth to bed area or volume.
3. Determination of the chemical and physical characteristics of the spent regenerant and the recovery of organic matter and the minerals from the adsorption columns.

PROCEDURES

A six-column test unit was constructed for the evaluation of the adsorbents which included a gravel pre-filter, constant head tank and distribution manifold, flow meter, and flow controller. The design of the columns was in accordance with the American Society for Testing and Materials (1966). A photograph and a schematic diagram of the columns are presented in Figures 1 and 2 respectively.

The design of the columns was based on a resin bed depth of 3 feet and a flow rate of 1 gallon per minute per cubic foot of bed volume. This flow rate was equivalent to 62 milliliters per minute through each column.

The following resins were used for this study: Amberite IRA 400 Anionic (Column 1), Duolite S-37 Resinous Adsorbent (Column 2), Dowex SA 1243.1 Anion Exchange Resin (Column 3), and Dowex 11 Anion Exchange Resin (Column 4). Additionally, activated carbon was used in parallel with the resins for comparative evaluation (Column 5).

The mobility of the unit enabled the study to be conducted *in situ* at three sites. The water sources included a small tiaga lake, a shallow domestic well and an extended aeration treatment plant effluent. The three sources tested were near Fairbanks, Alaska.

Chemical analyses were conducted at institute laboratories following methods outlined in *Standard Methods for the Examination of Water and Wastewater* (1965).

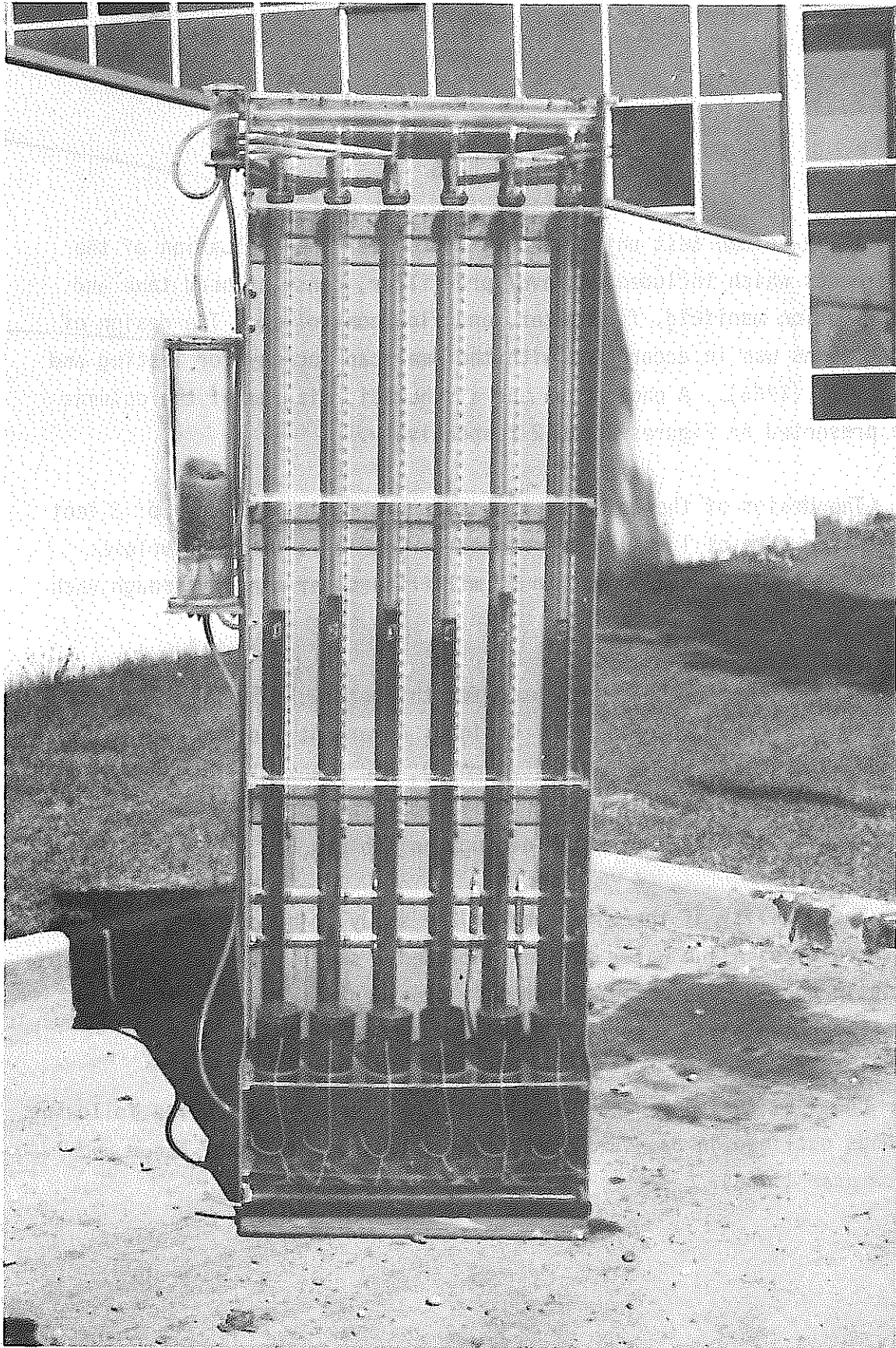


Figure 1: Experimental Apparatus: Synthetic Resin Adsorption Columns.

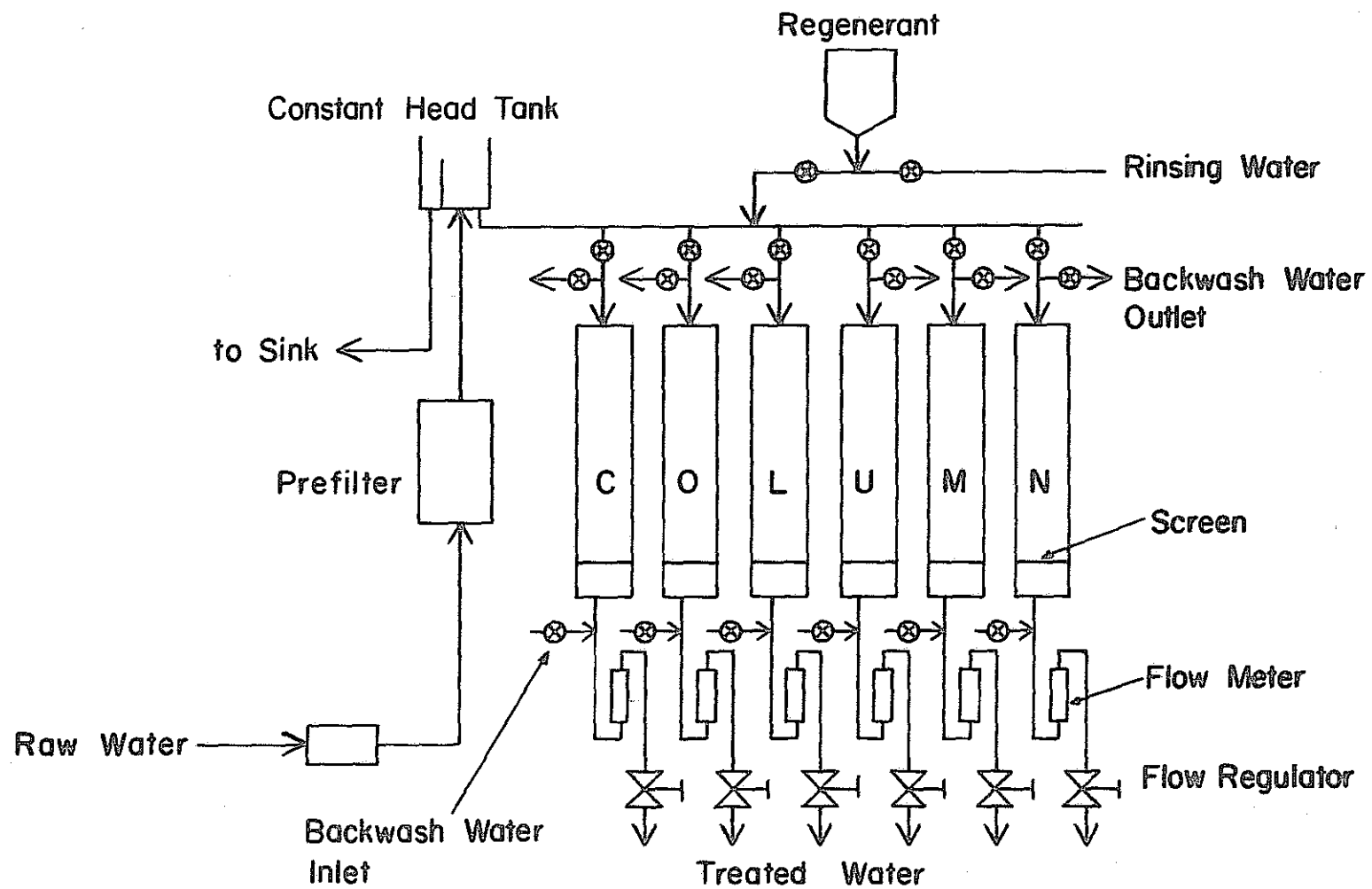


Figure 2: Schematic Diagram of the Experimental Apparatus.

LITERATURE REVIEW

Literature on the subject of color and organic removal from water supplies is not extensive. The important aspects of color and organic removal from water by synthetic resins are reviewed in this section. Additionally, theoretical relationships of color and organic removal to the process of ion exchange are discussed.

EFFECTS OF COLOR AND ORGANICS ON HEALTH IN WATER SUPPLY

There is no direct evidence of the harmfulness of large amounts of organic matter in water. Excessive odors and tastes along with unpleasant appearance, however, may render the water unfit for both industrial and domestic use (Oldham and Gloyna, 1969; Fair and Geyer, 1954; Sawyer and McCarty, 1967). For these reasons the *Public Health Service Drinking Water Standards (USDHEW)* recommends a maximum limit for drinking water of 15 color units on a platinum-cobalt scale (Oldham and Gloyna, 1969; Black and Christman, 1963; Abrams, 1969). The standards do not recommend limits for either taste or odor. They do, however, suggest limits on specific organic materials.

COLOR AND ORGANIC RELATIONSHIP

The removal of organic matter from water is generally associated with color removal. Nonetheless, little attention has been directed to the fundamental nature of the organic materials that are responsible for color in water (Christman and Ghassemi, 1966; Fair and Geyer, 1954). Organic matter in water originates primarily from plants and animals. The subsequent color produced is a result of the water's coming into contact with decaying vegetation. Organic compounds found in water are so highly varied and in such minute quantities that they cannot be isolated directly (Sawyer and McCarty, 1967; Fair and Geyer, 1954).

Color-producing properties of organic material are variable in different waters (Abrams, 1969). This could be accounted for by corresponding variations in the chemical structure of various organic molecules. In 1917, Saville proposed that color in surface waters was due to a colloidal suspension of colored chemicals. It was suggested by Miller in 1925 that humic acids were the source of these chemicals that were soluble in alkali and precipitated in hydrochloric acid (Oldham and Gloyna, 1969). He further stated that the colored particles involved were negative colloids and not truly dissolved species. Stumm and Morgan (1970) indicated that "humic acid" is a general term used for a number of different high-molecular compounds of complex nature consisting largely of condensation products of phenols, quinones, and amino compounds. They further explained that these classes of compounds tend to form complexes with ferric iron. Research by Shapiro did not conclusively determine whether the colored entities were dissolved species or colloidal in nature (Oldham and Gloyna, 1969).

Christman and Ghassemi (1966) classified structural compounds of organic colored molecules and concluded that the organics were aromatic in nature. Additionally, they indicated that the organic compounds contained many carboxylic groups (Oldham and Gloyna, 1969). Wilson (1965) stated that colored organic materials in water are fulvic acids (soluble in alkali and not precipitated by hydrochloric acid) which are a part of natural soil humus (insoluble in alkali). This indicates that colored molecules have acidic properties. Shapiro (1964) believed that the organics causing color are primarily aliphatic polyhydroxy carboxylic acids. This was evidenced by the method of their extraction from water and by their pronounced solubility in alkali (Oldham and Gloyna, 1969). Furthermore, the extent of color extraction has been shown to depend on pH and water temperature.

Naturally colored water tends to show variations between color intensity and pH. Color intensity increases upon the addition of base

and decreases with the addition of acid although there is no linear relationship between pH and color (Oldham and Gloyna, 1969; Black and Christman, 1963). Because of this pH-color variation, it is necessary, when reporting color values, to specify the pH at which color is determined (APHA, 1965). There is little doubt that some of the color is due to the presence of the anionic form of weak organic acids. Evidence indicates, however, that at least part of the color remains unaltered by change in pH. This may be due to nonionic, chromophoric constituents in the organic compounds (Kunin, 1958). Colored water caused by organic matter, in general, appears yellowish-brown but shows little to no absorption in the 450-550 millimicron range. This suggests the color is not due to molecular absorption but rather to light-scattering.

Color caused by suspended matter is referred to as apparent color and color due to vegetable or organic extractions is called true color. Suspended matter must be removed to enable determination of true color. Filtration can remove suspended matter but this technique is not recommended because of possible adsorption of color on the filtering media. The determination of true color can be accomplished by removing suspended solids through centrifugation (APHA, 1965; Sawyer and McCarty, 1967).

IRON RELATIONSHIP IN WATER

Although present in relatively small quantities compared to many other minerals (Oldham and Gloyna, 1969; APHA, 1965), iron in water is one of the most troublesome water-carried materials. Iron problems are most severe with groundwater. However, difficulties can be encountered seasonally in surface waters. The most common form in which iron compounds are found in groundwater is in the bicarbonate form. Their solubilities are increased by the presence of free carbon dioxide in the water. The iron problem in impounded surface water supplies has been correlated with stratified reservoirs but occurs only in those in which

anaerobic conditions have developed in the hypolimnion (APHA, 1965). The solubility of ferric iron is 10^{-8} M in a pH range of 6 to 9. Solubilities of iron in natural waters have exceeded the theoretical value from 10^8 to 10^9 times but it is suggested that the higher concentrations are due to iron-organic complexes.

Unless iron is held in solution by chelation or in suspension by colloidal dispersion (peptization) within a normal pH range and dissolved oxygen level, conventional iron removal plants should be capable of reducing the iron content of a water to a satisfactory level: less than 0.3 mg/l (Oldham and Gloyna, 1969).

Scientists investigating colored water are divided on whether iron remains in solution due to its complexing or peptizing of the small metal colloids attached to organics (Oldham and Gloyna, 1969). One researcher concluded that peptization outweighs chelation in ferric iron stabilization. He contended that the primary mechanism by which the iron is stabilized is that the ferric hydroxide precipitate is dispersed as a result of adsorption of the organic acids onto the surface of the particles. According to Oldham and Gloyna, complexes of ferric iron have a tendency to be more stable than those of ferrous iron. They find a higher degree of complexation occurs in the ferric system and, when either ferrous or ferric iron is added to humic acid, a shift in the infrared peak occurs. It remains difficult, however, to distinguish analytically dissolved iron from suspended iron (Stumm and Morgan, 1970).

Iron bacteria can utilize iron and eventually deposit it in the form of hydrated ferric hydroxide or as a mucilaginous secretion (APHA, 1965). Organism decomposition is accompanied by taste and odor production and may result in a pH shift which can cause corrosion of metal in water distribution systems. Furthermore, the products of decomposition furnish additional nutrient material and increase the rate of decomposition.

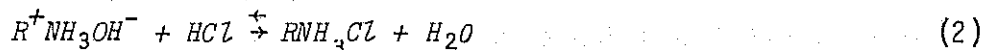
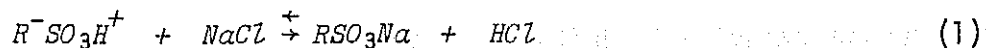
ION EXCHANGE AND SYNTHETIC RESINS

While there have been extensive studies conducted on the cationic ion exchange for removal of hardness from water, little work has been conducted on the anionic resins except for laboratory demineralizers of water in the field of chemistry. Recently attempts to remove color and organics by using the anionic resins have been made.

Industrial sugar liquor treatment by ion exchange normally yields satisfactory decolorization. Anion exchange resins have been shown to be more effective than cation exchange resins in color removal. This suggests that the chromophoric constituents are present in the anionic fraction of the organic molecules (Abrams and Dickenson, 1949). The so-called synthetic resinous adsorbents are porous anionic resins which readily facilitate diffusion of high molecular weight compounds into and out of the resin matrix (Abrams, 1969). The mechanism of organic removal by synthetic resinous adsorbents is quite different from that of the ion exchange principle. Ion exchange as defined by *Encyclopaedia Britannica* (1971) is:

a process in which ions (electrically charged atoms or group of atoms) attached to or incorporated within the molecular structure of insoluble substances, called the ion exchanger, exchange with ions present in a surrounding solution.

The ion exchange process is shown in Equations 1 and 2:



Ion exchange may undergo exchange either with positively charged ions (cations) as shown in (1) or negatively charged ions (anions) as shown in (2). In the former case, the process is referred to as cation exchange and in the latter as anion exchange.

The mechanism of organic removal by resinous adsorbents is similar to that observed with activated carbon (Coogan, *et al.*, 1968). Adsorption involves no significant interchange of ions between the liquid and solid phases (Abrams, 1969). The removal of organic matter occurs by non-ion exchange adsorption or perhaps by dissolution in the body of a hydrophilic polymer. In addition to having a high degree of porosity like activated carbon but unlike early resins, the synthetic resinous adsorbents have a chemically active group which gives them hydrophilic characteristics and electropositive charges. These charges result in an attraction for negatively charged molecules such as humic and fulvic acids (Coogan, *et al.*, 1968). Both capillarity and electropositivity are at work, giving rise to surface sorption and chemisorption (Abrams, 1969; Coogan, *et al.*, 1968). The term "adsorption" is confined to changes occurring at an interface or surface and "absorption" to those processes involving solids engulfing substances throughout their entire structure. Considerable confusion exists in the usage of these two terms. The ion exchange process involves both surface exchange and absorption and, therefore, it is suggested that the term "sorption" best defines it (Kunin, 1958).

The effluent quality from anion exchange units depends primarily on the factors of regeneration level, regenerant type, flow rate, temperature, nature of influent, and particle size. Breakthrough capacity of anion-exchange columns is greatly increased as the size of the particle is diminished.

Breakthrough capacity is defined as the amount of the ion which can be taken up quantitatively by the column under the condition in question, *i.e.*, the number of milliequivalents which can be retained without any leakage occurring (Kunin, 1958; Samuelson, 1953). Therefore, it is obviously of importance to use relatively fine particles. However, head loss increases greatly as particle size diminishes. Elevated temperatures

result in increased rates for the breakthrough curves but at the same time, allow an increase in breakthrough capacity (Samuelson, 1953).

It has been observed by researchers that the resinous adsorbent is also able to remove iron in the water. It may be postulated (Abrams, 1969):

1. that the iron in the filtrate is complexed with organic acids and thus adsorbed on the weak base resin;
2. that the iron precipitates when exposed to the higher alkalinity in the resin;
3. that it forms a chelate with the phenolic groups of the resin.

Another striking phenomenon, frequently observed with some anion exchangers, is that a resin which is completely exhausted by the organic acid groups can still effectively decolorize a solution percolated through it (Oldham and Gloyna, 1969).

The fouling of anionic exchange resins is generally attributed to the irreversible sorption of organic acids of vegetable origin of high molecular weight. Large organic molecules, such as the tannic, humic, and fulvic acids in water, enter the pores of the anion resin and are retained because they have a high affinity for the ion exchange sites and thus the rate of diffusion within the resin is very slow. These effects are observed more frequently with surface water than with groundwater. It has been reported that weak base resins have a limited exchange capacity for humic acids and are subject to fouling. Regeneration processes do not allow sufficient time for complete removal of the organic substance. The concentration of these substances builds up, resulting in what is known as organic fouling or poisoning of the resin (Abrams, 1969; Fresch and Kunin, 1960).

The mechanism of organic removal by synthetic resinous adsorbents exhibits several advantages over conventional processes. Some of these advantages are low installation and maintenance costs, high flow rate, and a capacity which can be fully restored by chemical regeneration. The effectiveness of resinous adsorbents is dependent not only upon the type of resin used but also the water to which the adsorbents are applied (Coogan, *et al.* 1968).

RESULTS

The complete data and results are published in a thesis by Kim (1973). This data and results are summarized in the following pages.

TEMPERATURE

The average and extreme water temperatures for the three water sources are presented in Table 1.

TABLE 1: WATER TEMPERATURE DATA

Source	Temperature (°C)			Average Temperature (°C) After Treatment
	Avg.	Low	High	
Lake	15.2	3.6	23.5	15.6
Well	5.4	4.3	6.5	10.1
STP	8.9	4.3	11.8	8.9

The lake source exhibited an average 0.4°C increase in temperature after treatment. The well water temperature increased by an average of 4.7°C while the sewage treatment plant effluent (STP) remained the same as that of the influent. Since the columns were operated in a warmer environment, the temperature increases were expected. Maintenance of temperature for the STP was due to a one-day holding period prior to column treatment.

The effect of temperature is evident from an examination of hydraulic and chemical relationships, important effects being drag coefficient and

ionic activity. Head loss decreases as temperature increases. Kettle and Boyd (Samuelson, 1953) have demonstrated that temperature increase results in a sharpening of the breakthrough capacity in ion exchange.

The variability of temperature exhibited by the respective sources inhibits any quantitative description of its effects in this study.

PRESSURE

Head loss for the columns tested on the lake and STP are plotted in Figures 3 and 4, respectively. Comparison of these two graphs indicates that the greatest rate of increase in head loss occurred in Column 1 (Amberite IRA 400 Anionic), Column 3 (Dowex SA 1243.1 Anion Exchange Resin) and Column 5 (Activated Carbon). Column 2 (Duolite S-37 Resinous Adsorbent) and Column 4 (Dowex 11 Anion Exchange Resin) had lesser head loss throughout the study than did the other columns.

Activated carbon (Column 5) had a major increase in pressure differential for the sewage treatment plant effluent as is shown in Figure 4. This was most likely due to the smaller void volume of carbon which has an irregular shape compared to the spherical resins and the relative sorption isotherms of the carbon and resins. Under both conditions retention is more favorable for carbon with resultant head loss across the filtration layer. Biological growth on the sorbed substrate could additionally result in increased head loss of the carbon (U.S. Environmental Protection Agency, 1971).

Increased rates of head loss in the resin columns was most likely related to the resin particle size in conjunction with the quality of water tested. Other explanations are discussed in the literature review.

Data for column head loss for the well source were not obtained due to plugging of the resins with iron.

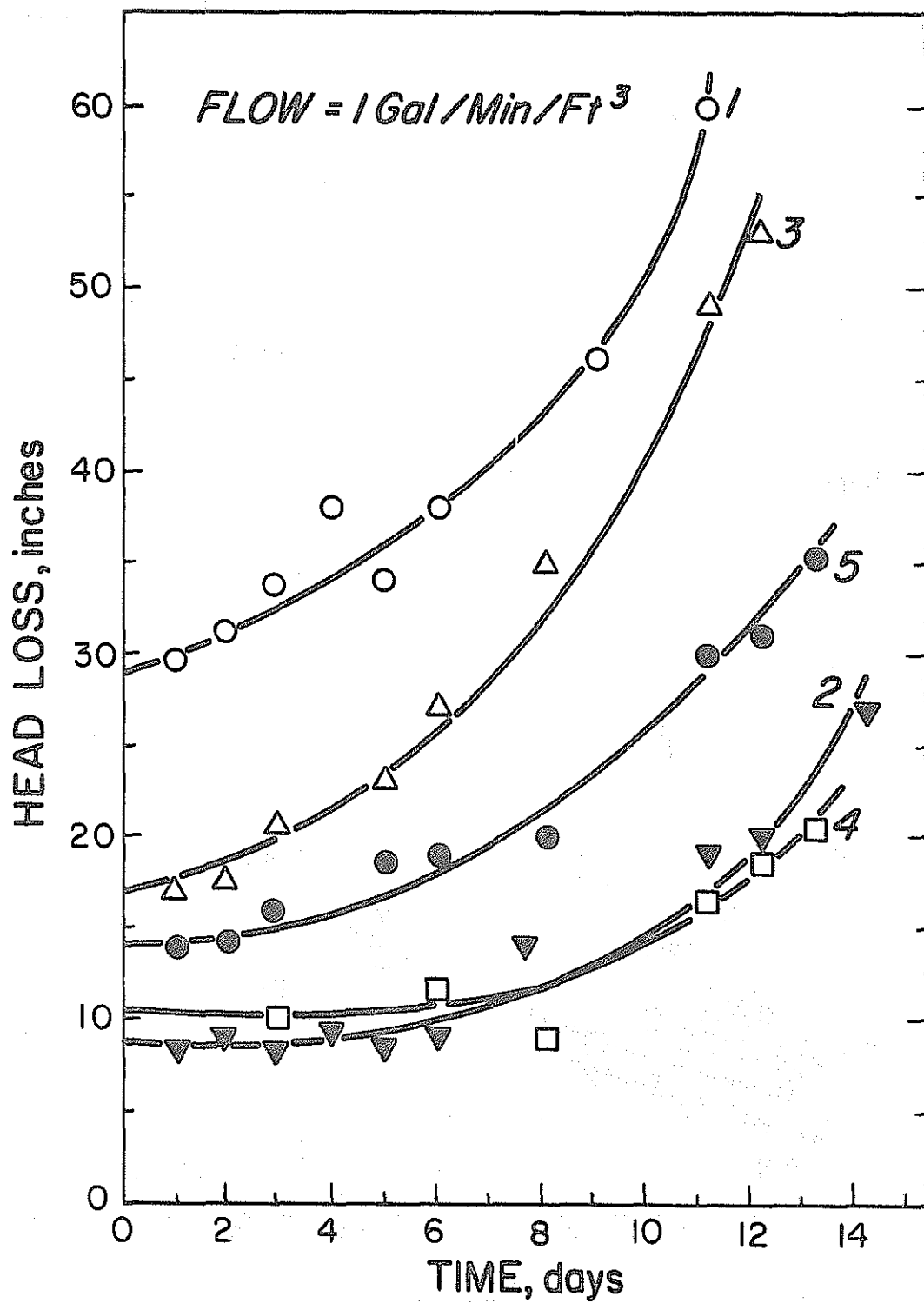


Figure 3: Head Loss versus Time of the Columns on the Lake Water, September 15 to 29, 1971.

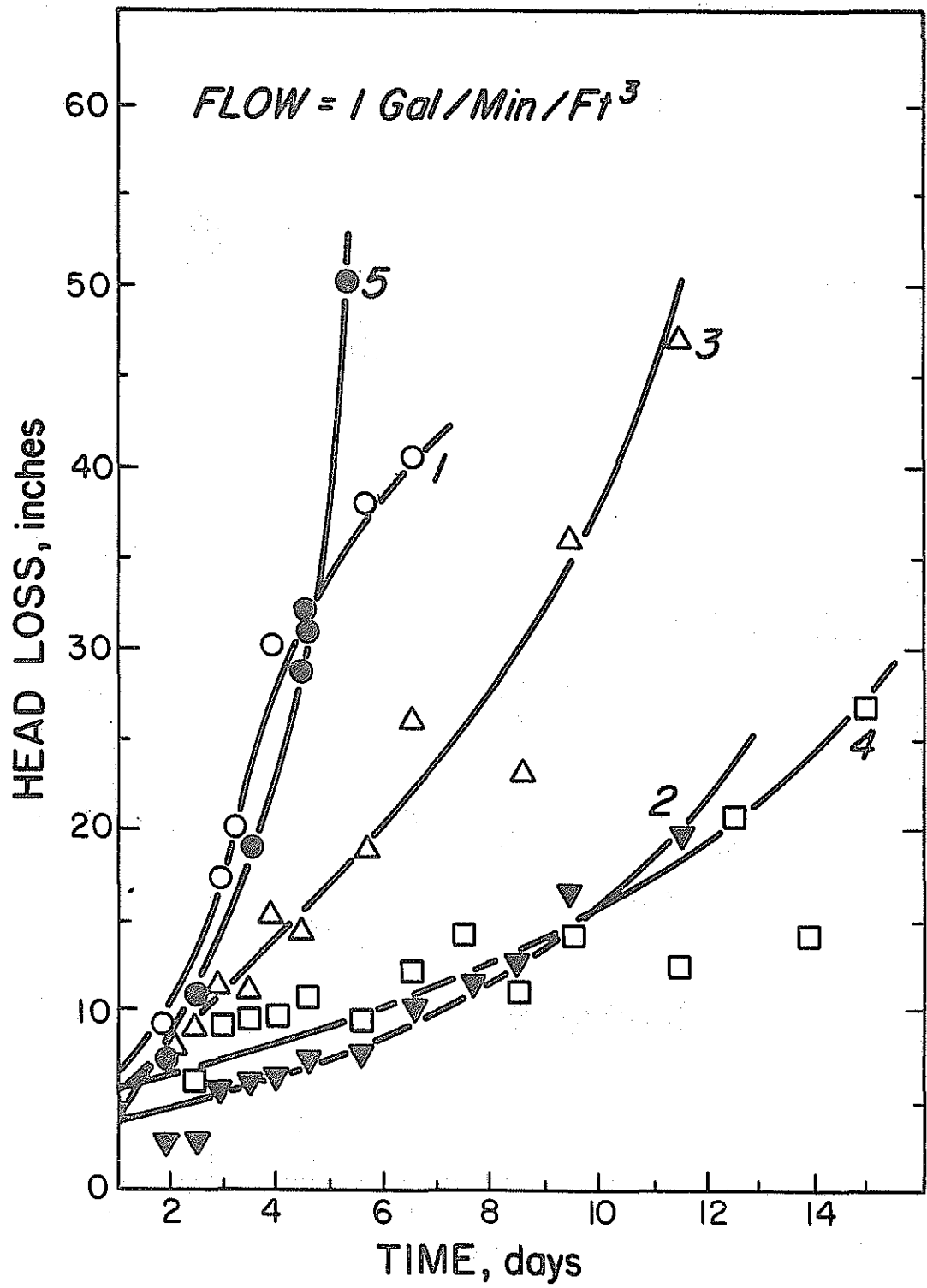


Figure 4: Head Loss versus Time of the Columns on the Sewage Treatment Plant Effluent, March 1 to 15, 1972.

pH

Column effluents exhibited high initial pH values for two to three days following caustic regeneration. The high values were probably due to hydroxy sorption by the resins. Duolite S-37 Resinous Adsorbent (Column 2) exhibited lower pH values following regeneration than did the other resins.

The STP and well sources had little pH change after resin contact. A slight pH reduction, on the order of 0.13 pH units, was noted for the lake water. In general, all column effluents were normally in the basic pH range. Literature dealing with synthetic resins indicates that adsorption of organics is improved with decreasing pH values (Weber, 1972; McGarvey and Kunin, 1957).

TURBIDITY

The average turbidity of the column influent and effluent for both the lake water and sewage treatment plant effluent are shown in Table 2. Data from the well are not included because of difficulties in measuring turbidity associated with high concentrations of hydrated ferric colloids.

TABLE 2: AVERAGE TURBIDITY, mg/l

	Lake	STP
Column Influent	0.75	4.64
Column Effluent		
No. 1	0.45	3.94
No. 2	0.45	4.00
No. 3	0.48	3.96
No. 4	0.49	4.01
No. 5	0.56	3.86

Column 5, activated carbon, exhibited the highest turbidity carryover. COD and TOC removal by column 5 was greater than columns 1, 3 and 4, the anionic resin columns. The anionic resins exhibited better turbidity removal. Since the nature of the colloidal material was quite different in the two sources, the mechanism can be hypothesized as follows. The treatment plant clarifier effluent turbidity was due primarily to small agglomerations and individual cells of the sludge organisms as well as polysaccharides from waste degradation. These particles, being fairly massive in relation to the pores of the resins and carbon, were effectively excluded with the small amount of turbidity removal being due to mechanical occlusion and some sorption. Turbidity of the lake water, a fairly static water body, was probably due to true colloidal particles and subsequently a commensurate degree of removal was achieved. The small differences in the lake water removals by the respective resins could be explained on the basis of adsorbent type, the non-ionics producing less turbidity removal and organic removal than the anionics which can effect charge stabilization. This explanation is strengthened by the high turbidity of the post-backwash effluent on the lake source, shown in Figure 5, which would follow from the highly ionic caustic regenerate. Figure 6, the sewage treatment plant effluent turbidity, shows a pattern similar to that of the lake water turbidity. No relationship for turbidity removal versus column backwash was evident.

CONDUCTIVITY

Conductivity of the lake water effluents showed some increase, particularly in the strong anion columns. The increase was especially pronounced after regeneration and exhibited nearly a twofold increase for the strong-anionic types. The increase was progressively smaller with time indicating depletion of exchange sites or reduction of regenerant carry-over.

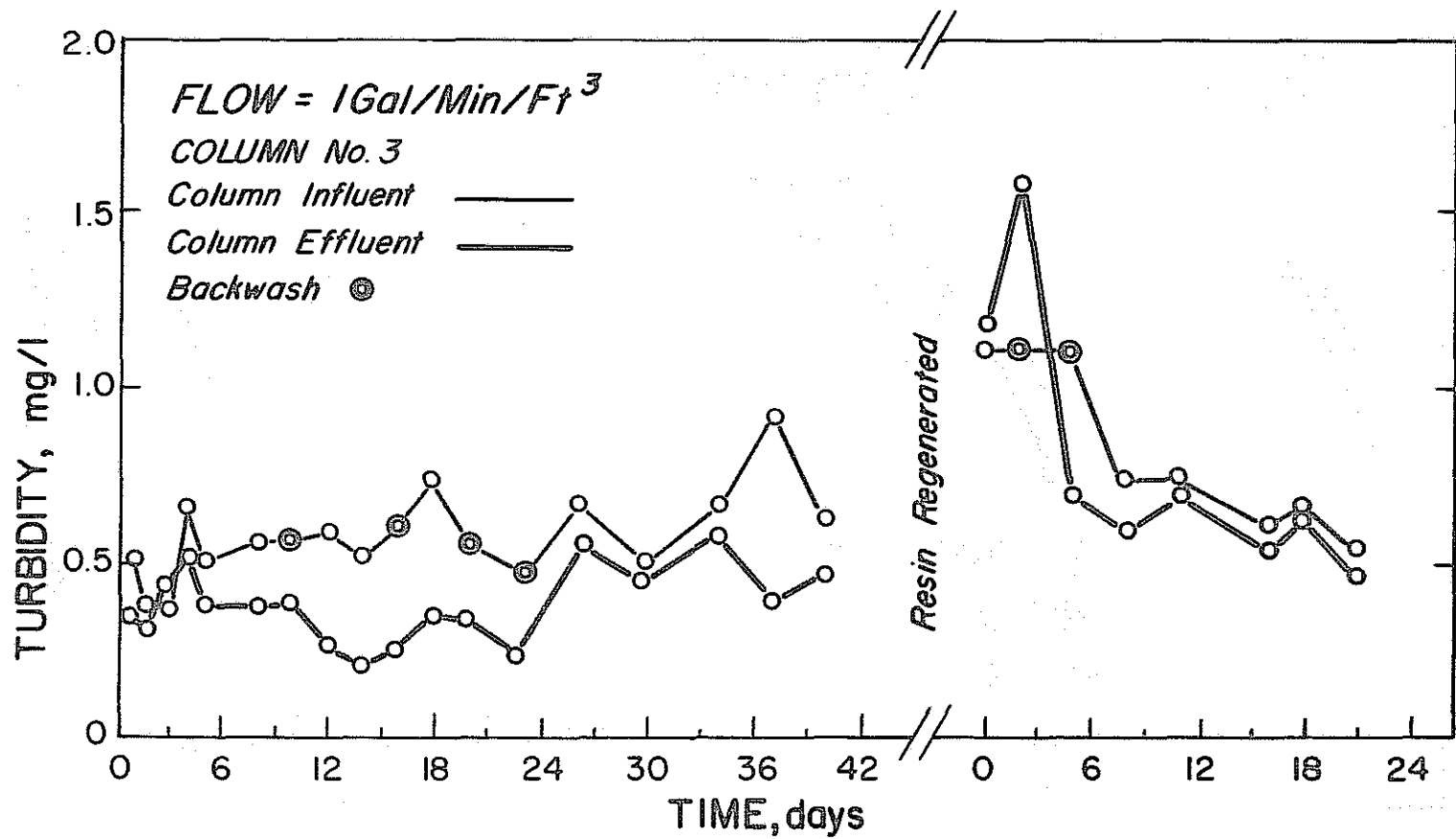


Figure 5: Turbidity of the Column Influent and Effluent for the Lake Water, August to October, 1971.

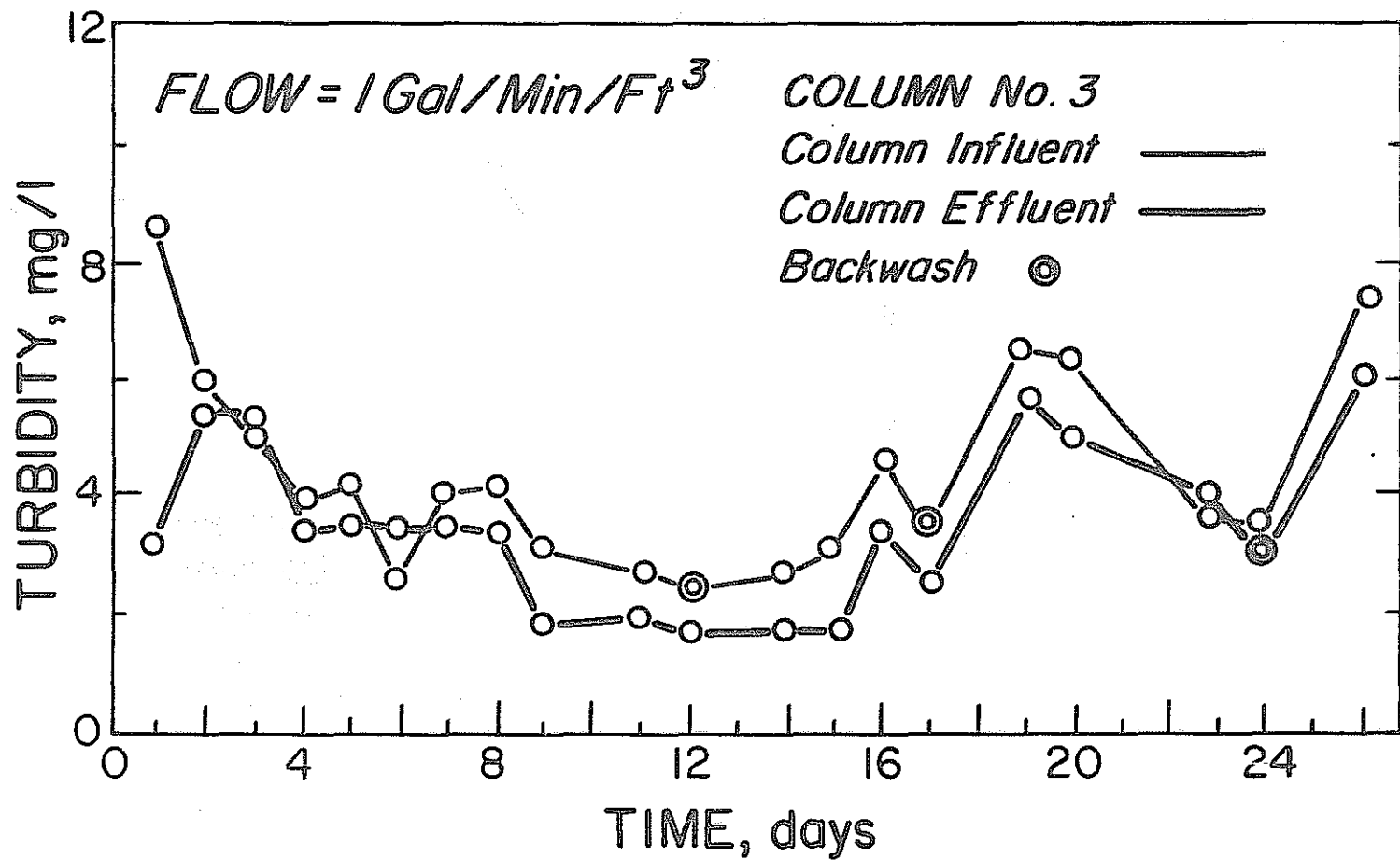


Figure 6: Turbidity of the Column Influent and Effluent for the Sewage Treatment Plant Effluent, March, 1972.

The STP samples showed a short initial increase in conductivity with subsequent values approximately equivalent to the influent.

IRON

The average iron concentrations for the three water sources were:

lake	- 0.05 mg/l;
well	- 30 mg/l;
treatment plant	- 1.3 mg/l.

The lake concentration was low due to the stability of the water body and the aerobic water at all levels. The high iron value of the well water is characteristic of the Fairbanks area. The treatment plant values are low in relation to the high iron content in the service area water supply which indicated removal at the source or during the treatment process.

Because of the low iron concentrations found in the lake influent iron removal was evident only with the well and treatment plant sources. The columns exhibited excellent removal of iron from the well source during the initial period following regeneration. This may have been due in large part to caustic precipitation of the iron at the high pH and subsequent filtration by the resin. Absence of pore blockage in the resin after regeneration may also have been significant.

Columns 2 and 4 exhibited the best iron removal from the STP effluents, with 45 and 37 per cent removal, respectively. Since the removal was independent of time, there is a question as to whether the process was simple filtration or resin-iron interaction.

Color and Organics

Inspection of influent and effluent data for the three sources revealed considerable variation of source quality in relation to time. Figures 7,

8 and 9 are graphs of concentration in relation to time for color, TOC and COD of the three sources evaluated. The greatest variation occurred in the color of the well water (Figure 8) which was due largely to the anoxic condition of the groundwater and the presence of ferrous iron whose subsequent oxidation presented problems in color analysis. Variations of the organic concentration were most pronounced for the STP effluent (Figure 9).

Graphs of per cent removal (color, TOC and COD) in relation to time for the column resins are presented in Figures 10, 11 and 12 for the respective sources (lake, shallow well and STP). These plots are very erratic, due, in part, to influent quality variation, and indicate a need for improved analytical control and sensitivity.

Of the three sources, the STP (Figure 12) most clearly shows a pattern of removal. The column effluent values closely follow influent variations with a constant, rather than proportional, removal. This constant removal results in considerable scattering when the data is plotted in terms of per cent removal since there is substantial variation in the influent values.

Organic removal was evaluated by measurement of TOC and COD. In general, the best TOC and COD removals were exhibited by activated carbon (Column 5) for all three sources. The largest degree of TOC and COD removal occurred on the shallow-well source (Figure 11). This was probably due to the relatively small organic concentrations and the removal of significant amounts of iron present in the well water.

Removal efficiencies for TOC and COD decreased with time (resin capacity or breakthrough) but increased immediately following regeneration of the resins. They did not, however, return to the maximum per cent removal initially observed which indicates some loss of resin effectiveness with time.

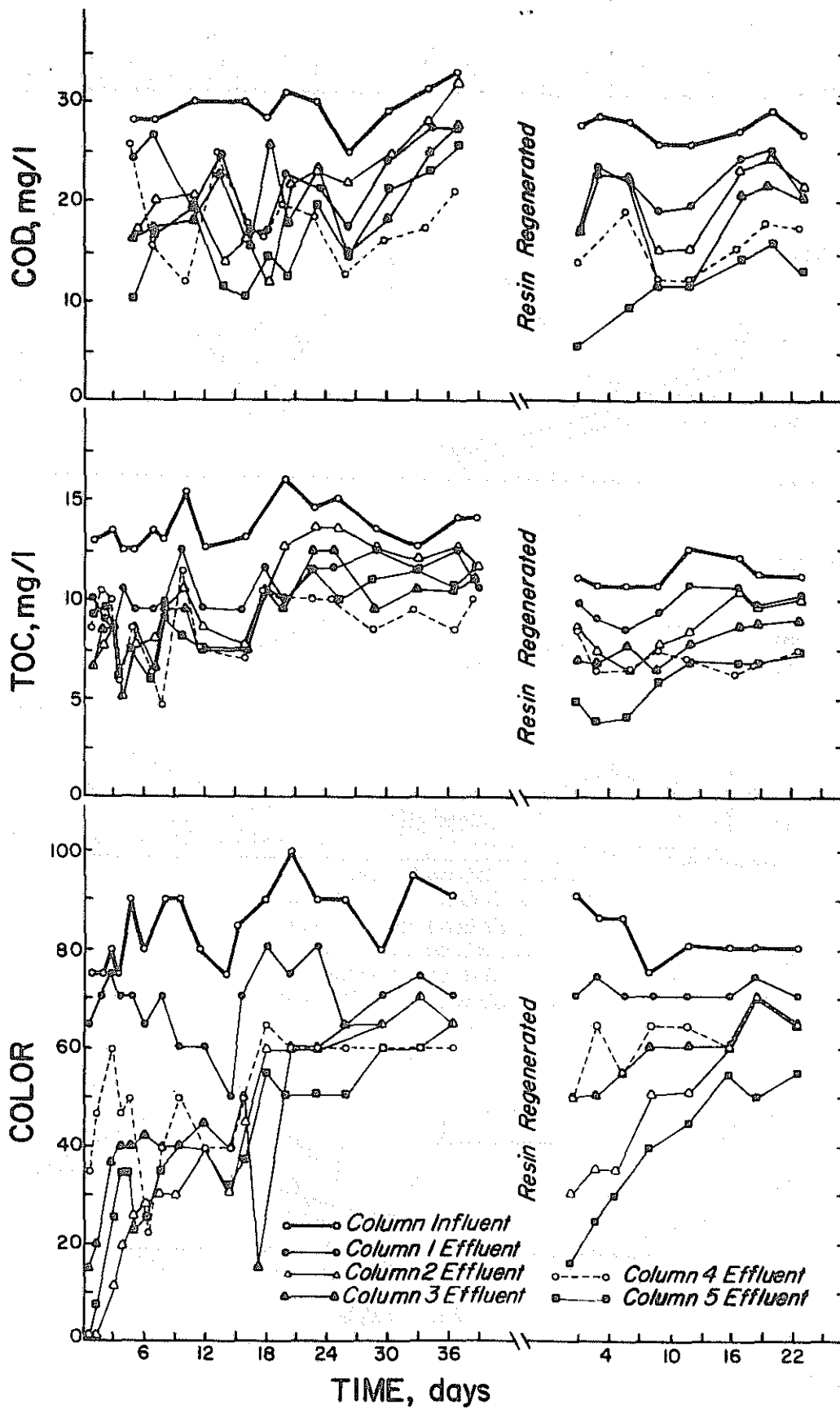


Figure 7: Concentration versus Time for Lake Water, July 11 to August 20 and September 11 to October 2, 1971.

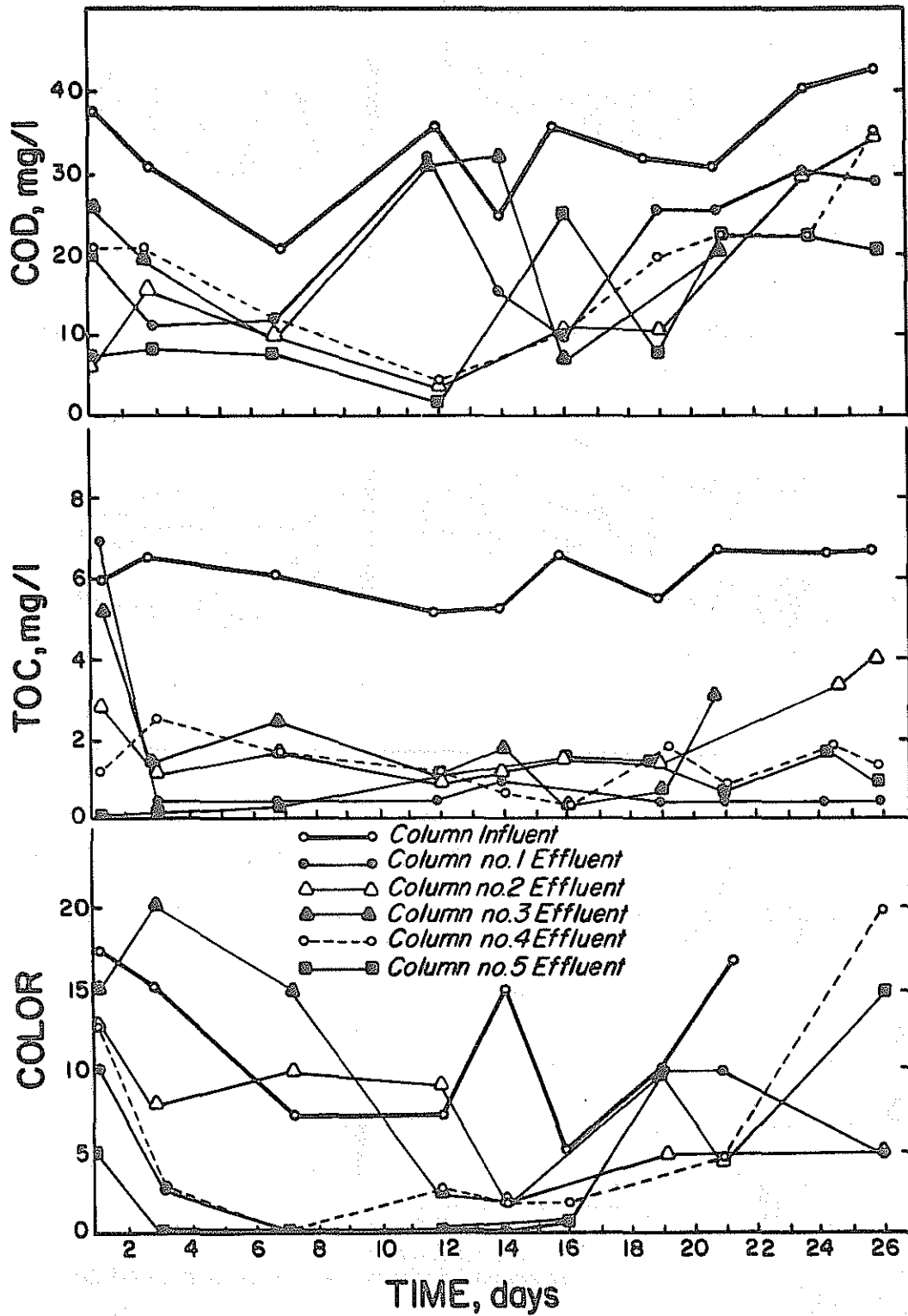


Figure 8: Concentration versus Time for Shallow Well, December 17, 1971, to January 11, 1972.

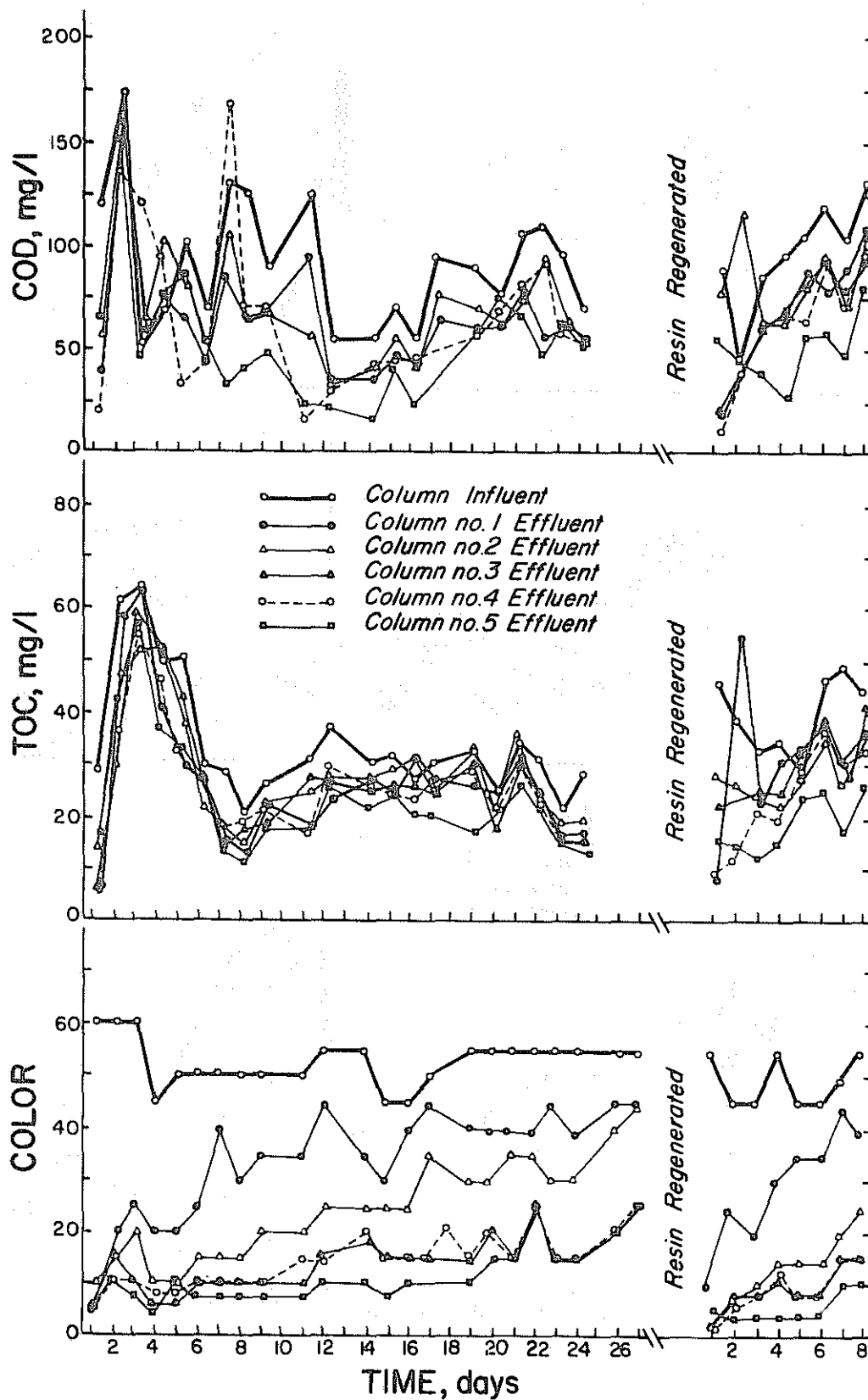


Figure 9: Concentration versus Time for Sewage Treatment Plant Effluent, March 1 to 28 and April 13 to 20, 1972.

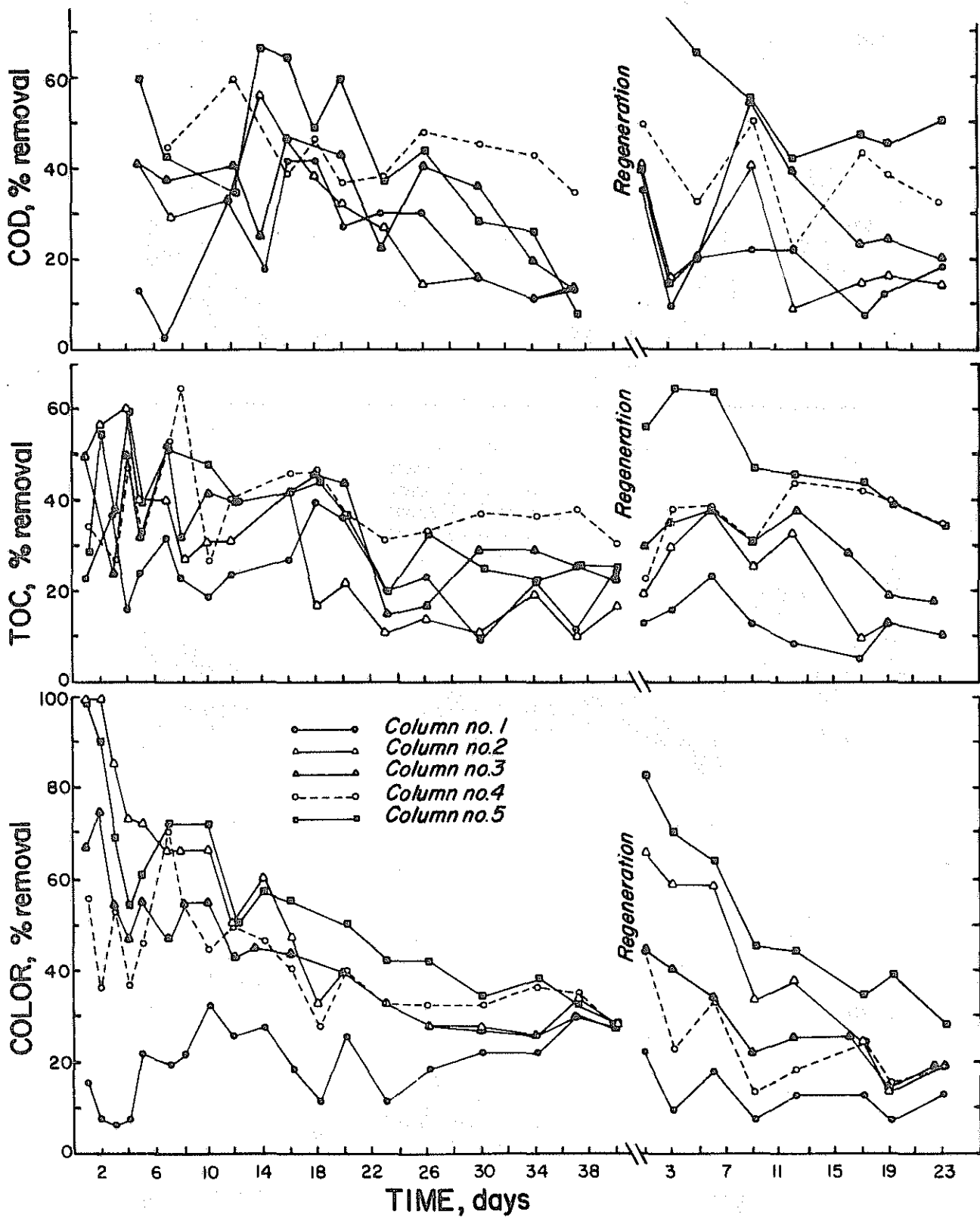


Figure 10: Removal versus Time for Lake Water, July 11 to August 20 and September 11 to October 2, 1971.

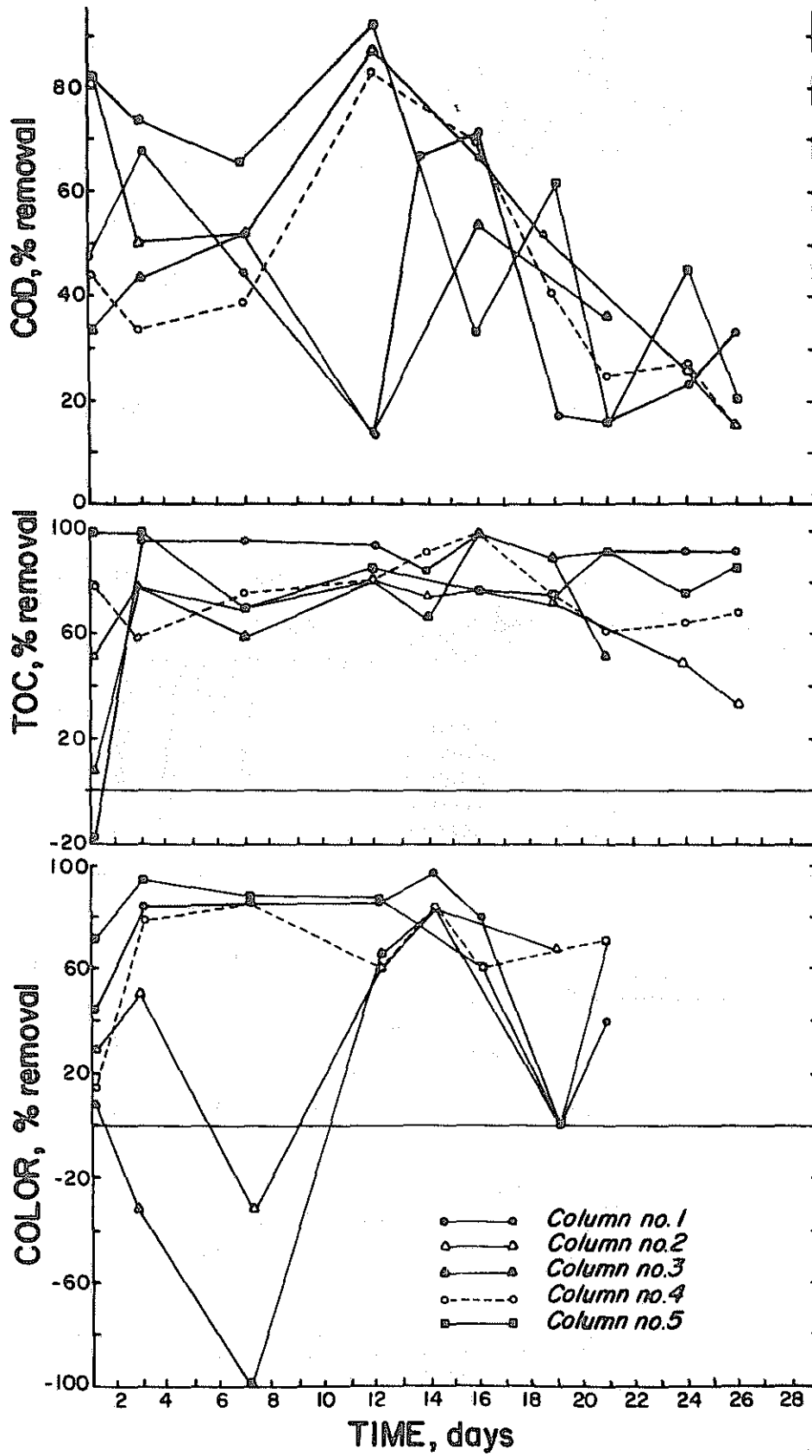


Figure 11: Removal versus Time for Shallow Well, December 17, 1971, to January 11, 1972.

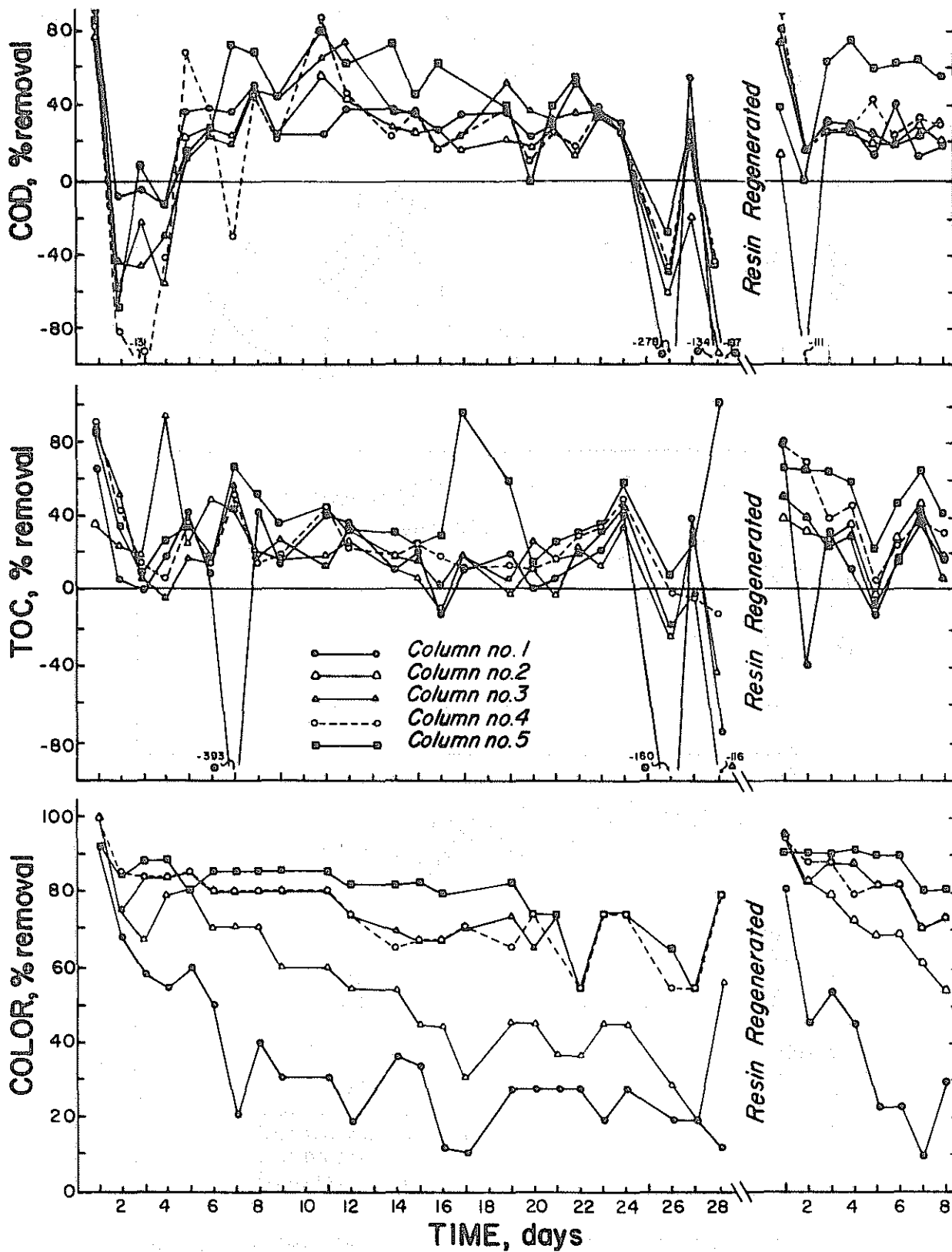


Figure 12: Removal versus Time for Sewage Treatment Plant Effluent, March 1 to 28 and April 13 to 20, 1972.

The TOC removal for all three sources was in the range of 5 to 10 mg/l regardless of the column influent value. Maximum TOC per cent removal, which is dependent upon the influent concentration, ranged from a high near 100 per cent for the shallow-well source to 70 per cent for the lake source.

COD values are more difficult to characterize due to greater scattering. Again, the effluent values follow the trends of the influent in all three sources. Removal appears to be more constant than proportional but there is some variation in absolute removal between the sources in the range of 20 to 40 mg/l (Figures 7 and 8). Since COD is highly dependent upon the degree of oxidation of the organics and the presence of reduced inorganic species, it is difficult to make a strict comparison of TOC and COD removal.

Negative per cent removals (TOC and COD) were encountered for the STP (Figure 12) and were apparently due to concentration breakthrough or exhaustion of the resin bed.

Only about a half of a second cycle (following regeneration) was run on the STP and lake samples. Future studies of such resins should include several cycles to determine reductions in cycle time, decrease in removal efficiency and changes in comparative efficiencies which may occur from irreversible destruction of sorption sites on the resin.

Figure 13 is a plot of the adsorption pattern for a fixed-bed unsteady-state adsorber under ideal conditions. C_0 is the highest influent concentration level and C is the effluent concentration at the time measured. For most adsorptive resins, a typical S-type curve will be obtained, however, the steepness of the curve and the breakpoint position will vary. Weber (1972) notes several factors affecting the curve shape including solute concentration, pH, particle size, depth of the column, velocity of flow

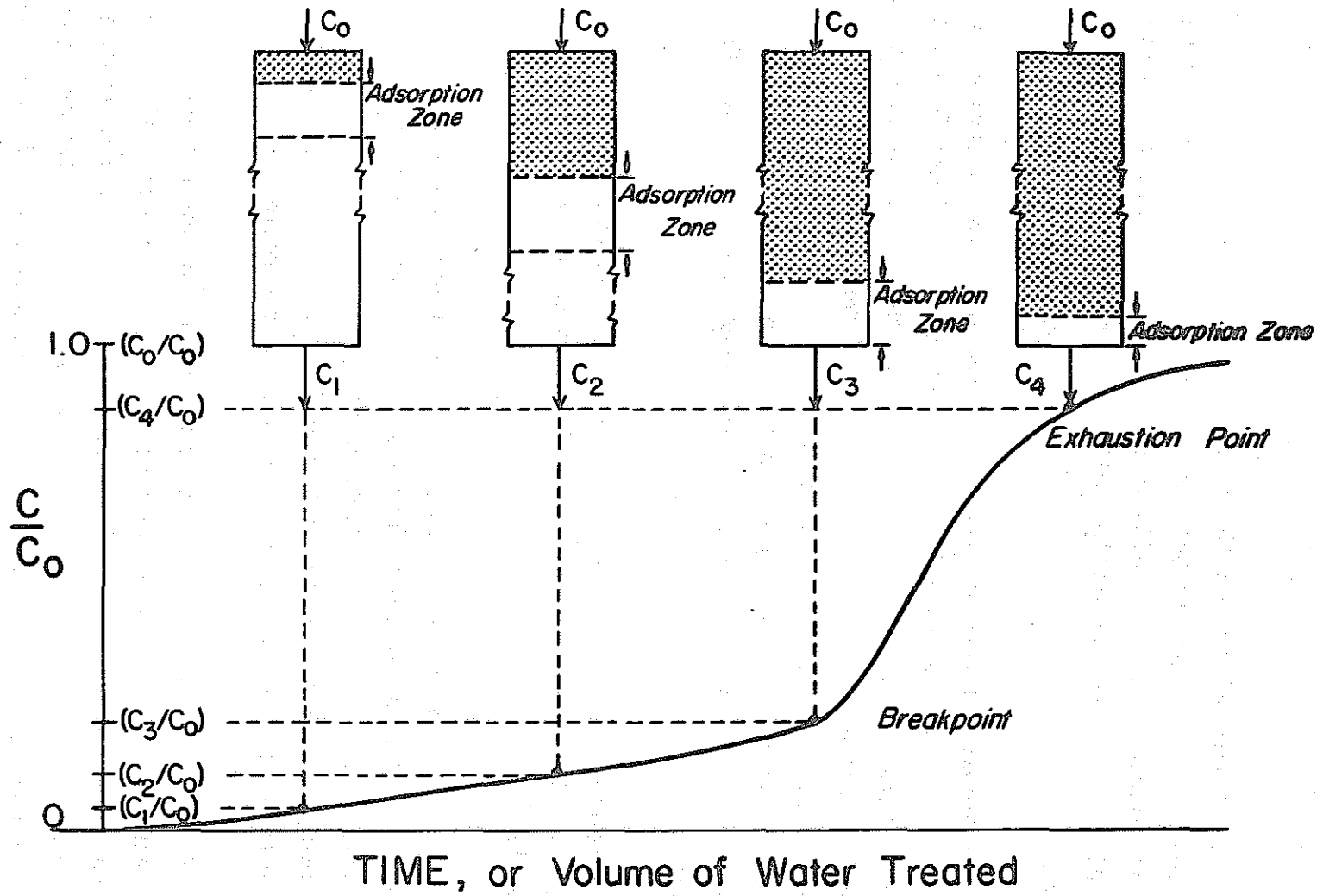


Figure 13: Breakthrough Curve, Adsorption Pattern for a Fixed-Bed Unsteady-State Adsorber.

and adsorptive mechanisms. The time to reach the breakpoint will be decreased through increased particle size, solute concentration, pH and temperature and decreased bed depth.

Breakthrough curves for the three sources tested in this study are included in Figures 14, 15 and 16. As can be seen from these curves, the data was very erratic and therefore attempts to draw smooth lines for plotting C/C_0 versus time were not successful. The erratic plots resulted from influent quality variation, insufficient analytical control and, perhaps, a non-uniform removal rate for the respective adsorbents evaluated. A general pattern does exist for several of the curves in that they tend to consist primarily of the upper portion of the typical S curve.

Figure 14, a breakthrough curve for the lake water source, shows relatively good removal for color but the plots of COD and TOC are very erratic and inconsistent for removal with time. Column 1 (Amberlite IRA 400) had the poorest overall removal for the three parameters used. Following regeneration of the resins, retention of some adsorptive capacity occurred. They did not, however, regenerate to 100 per cent of initial capacity.

Figure 15, a breakthrough curve for the shallow well source, essentially gives no pattern for removal. This occurred primarily because of iron-fouling of the resins.

In both Figures 15 and 16, several values of C/C_0 in excess of 1.0 can be noted. These values are an indication of column leakage and may reflect improper resin preparation, particularly early in the time period evaluated. Values of $C/C_0 > 1.0$ which occurred late in the testing of the STP source were probably due to complete resin exhaustion (Figure 16).

Color analysis produced the clearest distinction between resin efficiencies. Ferrous iron gave erratic results in the color measurement

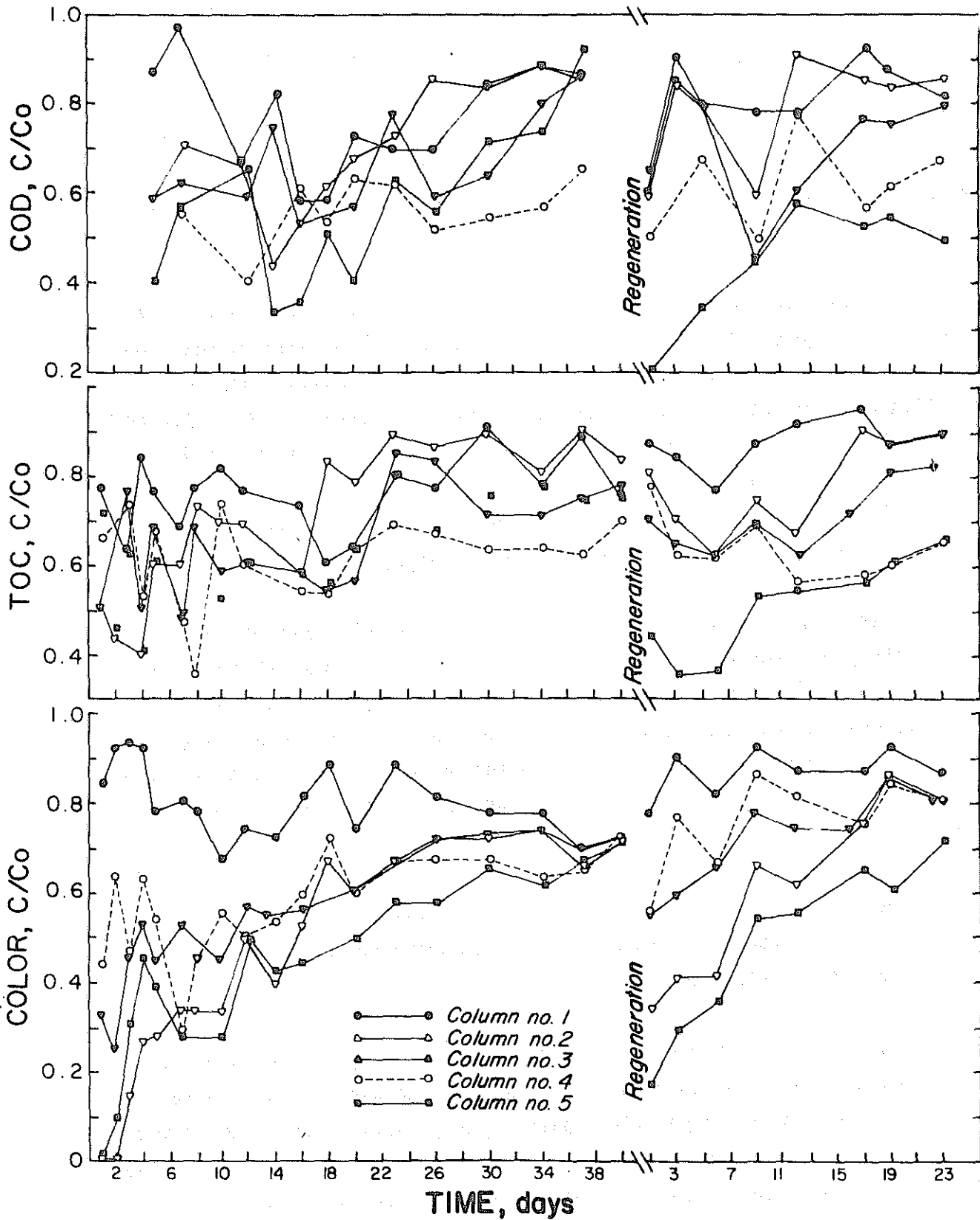


Figure 14: Breakthrough Curve for Lake Water, July 11 to August 20 and September 11 to October 2, 1971.

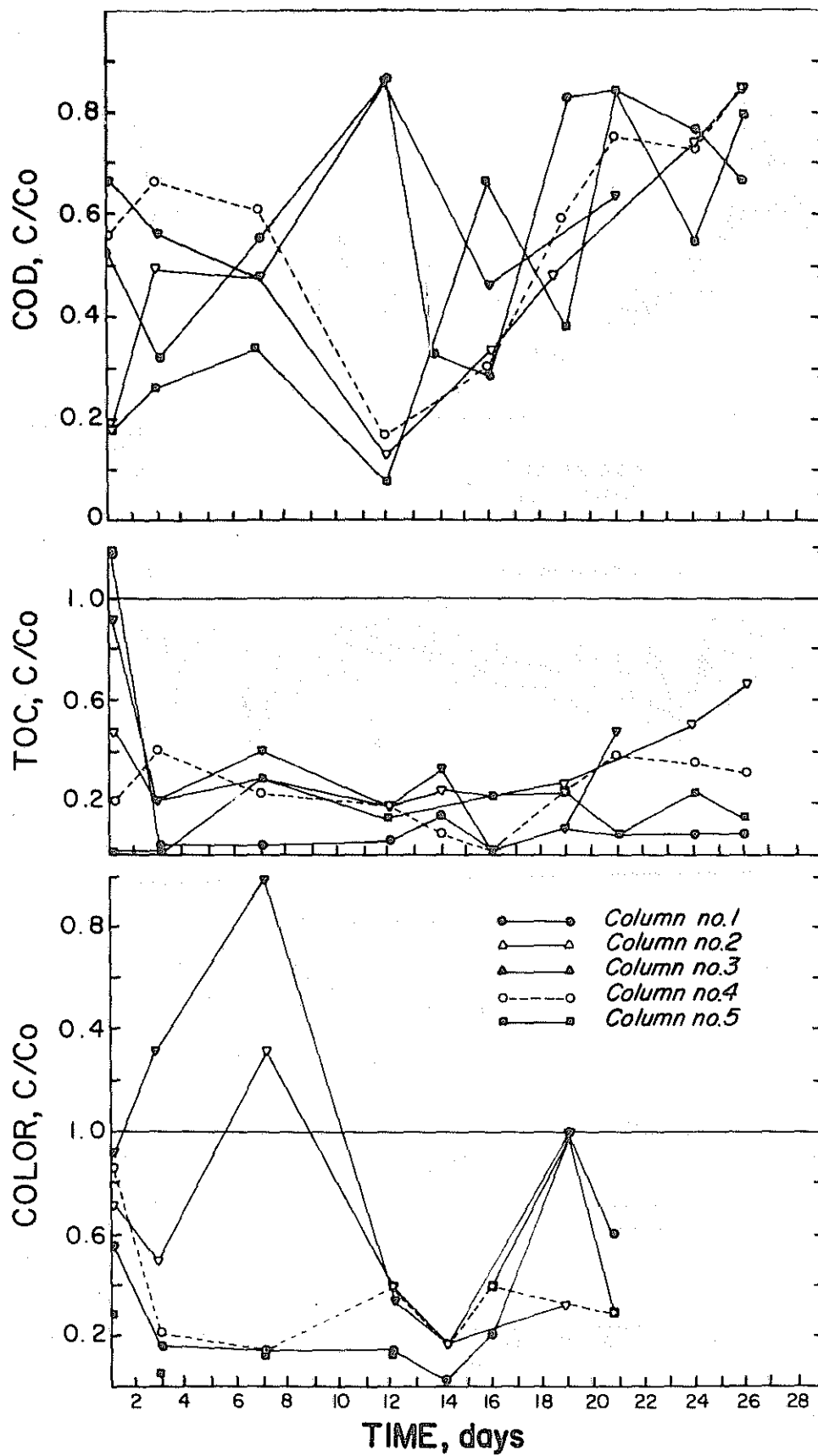


Figure 15: Breakthrough Curve for Shallow Well, December 17, 1971 to January 11, 1972.

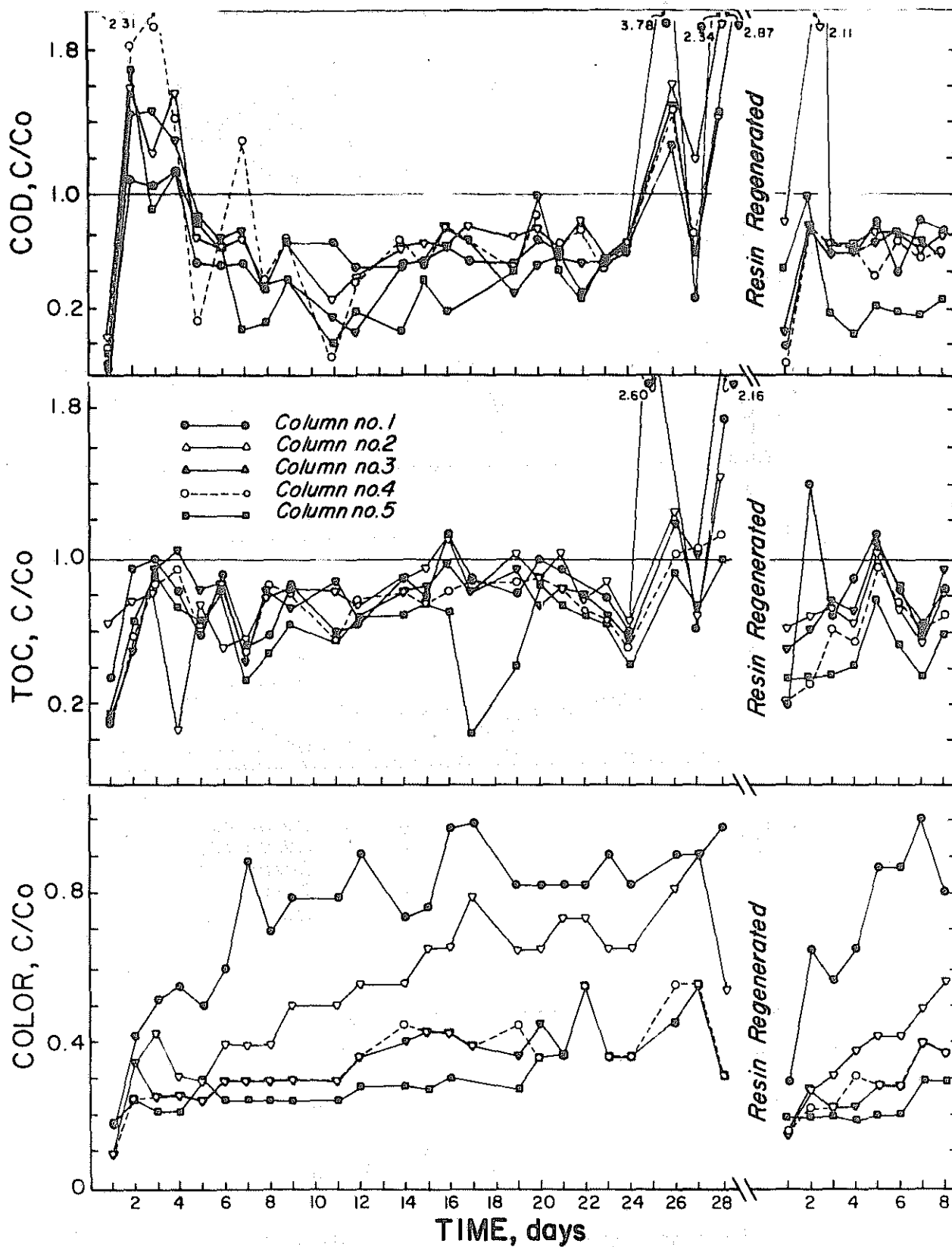


Figure 16: Breakthrough Curve for Sewage Treatment Plant Effluent, March 1 to 28 and April 13 to 20, 1972.

for the shallow well source. The STP (Figures 9 and 12) source clearly demonstrates the differing color removal capabilities of the resins. In both the lake and STP sources, the removal was highly dependent upon time with a significant reduction of efficiency prior to regeneration of the resin and this clearly indicates the onset of site exhaustion of the resin. It appears that removal of color tends to be more specific than for organics.

Color removal for the specific resins varied with the respective sources tested. Color removal for the STP source (Figure 12) runs from best to poorest: 5 > 4 > 3 > 2 > 1. However, on the lake water (Figure 10) the order is 2 > 5 > 3 > 4 > 1 and for the well (Figure 11), 5 > 1 > 4 > 2 > 3. It is evident then that color removal by a resin cannot be predicted easily. In general, activated carbon resulted in the best color removal percentage for all three sources. The color concentrations were reduced enough to be consistent with USPHS drinking water standards (15 color units) for the shallow well source only. This acceptable level was achieved because of low initial color concentration in the source.

Color-producing organics are complex and attempts to match a resin to a water source are difficult. Also, other objectionable qualities, which may be introduced into the water by dissolved organics, were not determined in this study. Odor and taste may follow a different removal order such that satisfactory water-conditioning is not achieved. It is apparent that the resins had little capacity under the restraints of column (resin) volume and flow rate used for this study. The capacity of a column could be increased to provide for a high concentration of influent of organics and color. Additionally, improved removal would result by using a reduced flow rate.

From the organic removal patterns of this study the following conclusions have been drawn:

1. In most cases, activated carbon was superior to resins in the removal of organic material.
2. In certain cases, the weak anionic resin gave superior removal to the strong anionic resins indicating that "exchange" is less important than "sorption".
3. The efficiency of a resin cannot be predicted easily.
Application of resins to domestic units requires:
 - a) a range of resin types and mixtures be evaluated in combination to determine the most feasible product, or
 - b) each resin must be tested in a wide range of sources to establish operation and application guidelines.

Economics of Synthetic Resinous Absorbent Units

Prior to the installation of a synthetic resin unit for domestic water treatment, the following should be determined:

1. Analysis of the water that is to be treated. This survey should include possible variations that may be encountered, such as seasonal fluctuations in temperature, concentration of organics, color, iron and others.
2. The volume of water to be treated.
3. The suitability of the synthetic resin for a particular water to be treated in relation to the desired effluent quality.

After obtaining the above information, the type of resin and size of the column best suited for the operation should be determined.

Generally, for household water units, operational costs are insignificant when compared with capital costs (Kunin, 1958). This, however, applied primarily to brine-regenerated cation exchange resins. Resin costs are five to eight times that of activated carbon on a volume basis. At present, resins which can be regenerated appear to be economically feasible. Coogan's studies on resin life found that Duolite A-7 after 200 cycles revealed a slight increase in resin requirement, moderated iron fouling, but no apparent decline in color-removing ability (Coogan, *et al.*, 1968). Even for municipal water supplies, resinous adsorption involves lower capital investment than activated carbon because costly thermal regenerations are not required (Abrams, 1969). For small household units, thermal regeneration of activated carbon is not practical because of the high installation cost and complicated operation. The disposal of the spent activated carbon may create a solid waste problem whereas the disposal of alkaline regenerant could result in

a wastewater treatment problem. Spent regenerant deserves careful attention as caution must be exercised because of the extreme alkaline conditions of the regenerant.

Estimated cost information for anion exchange resins, activated carbon, sodium hydroxide, and ion exchange units (resin housing) for use by a small household are listed below for reference.

Anion exchange resin	\$70 to \$110 per cu. ft.
Activated carbon	\$18 to \$25 per cu. ft.
Sodium hydroxide	\$0.36 to \$1.20 per pound
Ion exchange unit	\$270 to \$420 dollars

Specific cost information for particular resins should be obtained from manufacturers or their representatives.

A cost analysis example is presented below for a synthetic resinous adsorption unit for water with characteristics similar to those of the lake water used in this study. Water usage is estimated at 75 gallons per capita per day for a family of four. The water source is assumed to have a moderately high organic concentration, and it is desired that the finished water supply approach 50 per cent removal of color and 30 per cent removal of organics. Costs for the process do not include removal of hardness, iron, or elements other than color and organics.

Unit size	= family of four
Flow rate	= 75 gal/capita/day
	= 300 gal/day/family
	= 0.21 gal/min (gpm)
Specific flow rate	= 1 gal/cu. ft./min
Bed depth	= 3 feet

A minimum of 15 days is desired between regenerations for purposes of convenience. The following calculations are based on the above assumptions.

Bed volume, $V = 0.21 \text{ gpm/gal/cu.ft./min}$
 $= 0.21 \text{ cu.ft.}$

Surface area, $S = 0.21 \text{ cu.ft./3 ft. (bed depth)}$
 $= 0.07 \text{ cu. ft.}$

Diameter, $= \left(\frac{4 \times 0.07}{3.14}\right)^{1/2}$
 $= 0.30 \text{ ft.}$
 $= 3.60 \text{ inches}$
 Use diameter = 4 inches

Assuming that 0.84 gal/min (4 times average flow rate) is provided for peak consumption during a day, a column 8 inches in diameter would be required to obtain the desired water quality. The increased resin volume provided would reduce the frequency of regeneration by a factor of four.

For a flow rate of 1 gal/min/cu.ft., a column depth of 3 feet and a column diameter of 8 inches, the column design results in the following:

Resin volume = bed depth x surface area
 $= 3 \times (3.14/4) \times (8/12)^2$
 $= 1.05 \text{ cu.ft.}$

Resin cost = (\$100/cu.ft.) x 1.05 cu. ft.
 $= \$105$

Amount of regenerant for the bed volume of 1.05 cu.ft. is provided for 40 minutes at 0.5 gal/min/cu.ft. of bed volume. Using a 2 per cent caustic soda solution the amount of regenerant per column is:

$0.5 \text{ gal/min/cu.ft.} \times 40 \text{ min.} \times 1.05 \text{ cu.ft.} = 21 \text{ gal}$
 $21 \text{ gal} \times 8.34 \text{ lb/gal} = 175 \text{ gal of solution}$
 $175 \text{ gal} \times 0.02 \text{ (per cent solution)} = 3.5 \text{ lbs of caustic}$

Estimated number of regenerations = 6/yr
 Regenerant cost = \$1.00/lb x 3.5 x 6 = \$21/year

Capital cost (ion exchange unit) = \$400

Assuming that the purchase of an ion exchange unit is made by initial payment with no interest and the estimated life expectancies for the ion exchange unit and the resin in use are 10 and 5 years, respectively, the cost per year for the 300 gpd household unit is:

Unit	\$400/10 years
Resin	105/5 years
Regenerant	<u>21/year</u>
Total estimated annual operating cost	\$82

Water consumption per year is:

$$300 \text{ gallons} \times 365 \text{ days/year} = 109,500 \text{ gallons}$$

The cost per 1,000 gallon is, therefore:

$$\$81/109,500 \times 1,000 = \$0.74$$

Water can be treated approximately at the cost of \$0.74 per 1,000 gallons for small individual household use. The cost of \$0.74 per 1,000 gallons is relatively high when compared with \$0.17 to \$0.19 per 1,000 gallons which Eliassen and Bennet (1967) predicted for a 3-mgd plant. Nonetheless, small scale treatment is expected to cost more than municipal systems. Because of the experimental nature of this design, the economics of synthetic resinous treatment will need further evaluation.

Abram's study (1969) showed that estimated capital costs for a 1-mgd resin sorption plant for two flow rates, 2.5 and 5.0 gal/min/cu.ft., are \$128,000 and \$89,300, respectively, and that total operating costs vary from \$.085 to \$.165 cents per 1,000 gallons of treated water. A study on color removal was conducted at the Massachusetts Experiment Station on the Merrimack River at Lawrence and preliminary results indicate that satisfactory color removal could be achieved at a cost for materials of \$0.03 to \$0.04 per 1,000 gallons.

Cost information on the use of synthetic anion exchange resins is very limited and highly variable. Nonetheless, previous studies indicate that the use of these resins is promising and the economics for such use are favorable.

SUMMARY AND CONCLUSIONS

A totally satisfactory method of removing color and organics from water has not yet been developed. Activated carbon is the most common method used extensively for removing color and organics from water and wastewater. Recently much study has been conducted on the effectiveness of removing color and organics by using synthetic resinous adsorbents.

The mechanisms of color and organic removal by synthetic resinous adsorbents are not well established. Adsorption is the most prevalent and accepted theory.

CONCLUSIONS

1. In general, the synthetic resinous adsorbents were effective in removing color and organics at moderate concentrations found in most water supplies.
2. The degree of removal of color and organics by synthetic resins was highly variable. This variability, in part, could be due to different organic compounds contained in the water sources tested for this study. The degree of removal was dependent on the water quality and the characteristics of the specific resins.
3. Generally, activated carbon showed better organic and color removal than did the synthetic resinous adsorbents tested for this study.
4. Comparatively, synthetic resinous adsorbents removed color more effectively than organics from water. This phenomenon was much

more pronounced for the sewage treatment plant effluent than the surface water tested. This indicates that resinous adsorbents may be a good tool for removing color and organics from water containing moderately high color and relatively low organic concentrations.

5. High iron content in water did not necessarily lower the efficiency of resins for removing organics. Nonetheless, plugging of the resin beds occurred quite rapidly under these conditions. The mechanism underlying iron removal by resinous adsorbents was primarily due to the filtering effect on the resin bed.
6. Resinous adsorbents did not remove either alkalinity or hardness from water effectively. Carbonates and bicarbonates tended to precipitate on the alkaline resin beds.
7. Water containing color and organics can be treated at a cost of approximately \$0.74 per 1,000 gallons for small individual household water treatment through the use of synthetic resinous adsorbents.
8. Use of synthetic resinous adsorbents appears to be feasible for color and organic removal based on the analytical tests and economical evaluation of this study. The greatest use will probably occur for small water supplies typical of an individual household. Due to variations in the effectiveness of resinous adsorbents more, detailed study on removal mechanisms will be necessary prior to wide application and acceptance of this treatment process.

RECOMMENDATIONS FOR FURTHER RESEARCH

Areas needing further research on organic removal from water by using resinous adsorbents are many:

1. Investigation of the removal efficiencies for color and organics at increased flow rates and in various bed depths.
2. Investigation of the concentrations of color and organics in the regenerant solutions.
3. Evaluation of resin life to determine when the resin should be replaced.
4. Development of a technique to determine the resin capacity for regeneration purposes.
5. Analysis of column influent and effluent, qualitatively and quantitatively, for particular compounds or radicals producing color.
6. Evaluation of a more detailed economics study of the treatment process.
7. Evaluation of synthetic resins and their related effectiveness to specific types of organic compounds.
8. Evaluation of the economics of a prototype unit.

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