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COLOR REMOVAL FROM SURFACE WATERS
BY HYPOCHLORITE

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ARCTIC AEROMEDICAL LABORATORY 23

AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
FORT WAINWRIGHT, ALASKA

Project 8246, Task 8246-1

(Prepared under Cross Service Agreement CSA 51-1 by
D. J. Baumgartner, Arctic Health Research Center
U. S. Public Health Service, Department of Health,
Education and Welfare, Anchorage, Alaska)

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ABSTRACT

Because of the unacceptably high color and chlorine demand in surface waters at some remote U. S. Air Force radar sites in Alaska, a method was sought to remove these objectionable characteristics. Carbon filters and chemical treatment have proved either ineffective or too expensive. Treatment with hypochlorite has been shown to be effective and acceptable in the laboratory, where samples showing from 40 to 70 units of color were successfully treated by chlorine doses ranging from 10 to 40 mg/l. The rate of color removal was faster at the higher doses; however, the chlorine residuals persisted for longer periods of time.

PUBLICATION REVIEW



HORACE F. DRURY
Director of Research

COLOR REMOVAL FROM SURFACE WATERS BY HYPOCHLORITE

SECTION I. INTRODUCTION

Many remote U. S. Air Force stations in Alaska use surface waters as their sources of supply. These waters generally contain large amounts of dissolved or colloidal organic material which, in addition to imparting an objectionable yellow color to the water, creates a large chlorine demand. An effective method was sought of treating the water primarily to remove the color and thus increase its potability, and also to eliminate or reduce the chlorine demand so that the disinfection would be more effective and a chlorine residual could be maintained in the water to provide protection throughout the system.

Several methods of removing color had been investigated. Raw water at the radar site on Middleton Island varied from 70 to 140 color units, but provision of a complete treatment plant succeeded in removing only 70 per cent of the color (Baumgartner, March 1963). At most of the radar sites which use surface waters the color is more commonly found to be about 70 color units. At the radar site at Kotzebue a small-scale carbon filter was investigated and was shown to provide about 50 per cent color removal at best (Baumgartner, October 1963). One batch of carbon used in this study was extracted with chloroform and yielded 180 parts per billion (ppb) (Middleton, personal communication). The alcohol extract amounted to 330 ppb. The infrared spectra indicated the raw extracts consisted of highly oxidized materials (extraction and infrared analysis performed by Organic Contaminants Unit, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio).

Since most of the radar sites are required to function as small independent communities with a population of 100 men, it was necessary to find an effective method of treatment which would be simple to operate and would require little maintenance and minimum supervision. These criteria were not met by the complete treatment plant at Middleton Island. The carbon filter met these criteria but its effectiveness was not determined. All of the radar sites utilized proportional pumps and hypochlorite solutions for chlorination as the only method of treatment for the water prior to distribution. If hypochlorite could be shown to be an effective color remover, all criteria would be met.

At the request of the Alaskan Air Command's Engineering Office, the U. S. Geological Survey (USGS) conducted a test on a sample of water obtained from the radar site at Kotzebue. This report showed that 20 mg/l of chlorine would reduce the color to zero in 25 days and provide a chlorine residual at that time of about 1 mg/l. Several larger doses of chlorine were shown to remove the color in a shorter period of time and provide larger residuals. With this background information available on the Kotzebue water supply, which was considered typical of existing supplies, further investigations were conducted on water samples from this site. The results of these investigations are described below. The objectives were to determine the variation in total available chlorine and free chlorine as a function of time of contact; to determine the change in pH which occurred during the contact period; and to record the temperature of the water continuously during the time of reaction.

SECTION 2. DESCRIPTION OF SYSTEM AND RAW WATER QUALITY AT KOTZEBUE

Kotzebue's water supply for the year is collected during the spring thaw period when the adjacent watershed produces runoff in a small creek. The water is pumped from a small impoundment into a 2,000,000 gallon heated storage tank. Pumping usually takes place during June and is completed in about 10 days. Chlorine is added to the system at frequent intervals in the pump house as the water is pumped into the 2,000,000 gallon tank. About 6,000 gallons of water per day are pumped from the 2,000,000 gallon tank to a 75,000 gallon tank. When water is required for use at the radar site, it is obtained from the 75,000 gallon tank. As the water is pumped from the 75,000 gallon tank into the distribution system, it is chlorinated. In the fall, shortly before freeze-up, the watershed usually produces sufficient flow in the creek from the fall rains to provide enough water to refill the 2,000,000 gallon storage tank. This water is then used throughout the winter. The water generally has a pH near neutrality, apparent color about 70 units, true color about 60 units, total iron less than 1 mg/l, and a temperature of less than 5 degrees Celsius ($^{\circ}$ C).

SECTION 3. LABORATORY PROCEDURES AND ANALYTICAL METHODS

At the time this investigation was initiated in February 1962, no samples of raw water were available since the creek and impounding reservoir were

covered with ice. Consequently, the samples used for analysis were obtained from the 75,000 gallon tank. When the water was collected and stored the previous summer an attempt had been made to reduce the color of the raw water by adding 15 mg/l of chlorine in the form of hypochlorite, using the method tried in the USGS study. As a result of this chlorination, the sample analyzed in the laboratory had a color of 40 units. This was a true color since there was no turbidity. The pH was 6.5, iron was 1 mg/l, and both the free and combined chlorine were measured as zero. A three-liter portion of the sample was distributed to each of five aspirator bottles which were painted on the outside and placed in a dark room. Two additional bottles were filled with distilled water (see Figure 1). All bottles contained 1 ml of 0.45 molar pH 7 buffer. Each sample was dosed with a predetermined volume of hypochlorite solution, and the bottle was well shaken before the zero time sample was withdrawn for the various analyses. Upon completion of the analyses the next succeeding bottle was dosed in the same manner. Some of the conditions of the experiment are shown in Table I.



FIGURE 1

Sample bottles in darkroom

TABLE I

COLOR REMOVAL COMPARISON

Bottle	Contents	Volume of water (ml)	Volume of stock chlorine (Sol, * ml)	Volume of 1/10 stock chlorine (Sol, ml)	Calculated chlorine concentration (mg/l)	Actual Cl concentration (mg/l)	
						Total	Free
1	Kotzebue Water	3000	0	0	0	0	0
2	Kotzebue Water	2970	30	0	10	9.5	8.0
3	Distilled Water	2970	30	0	10	10.0	8.8
4	Kotzebue Water	2940	60	0	20	19.4	17.6
5	Kotzebue Water	2991	0	9	30	28.8	25.3
6	Distilled Water	2991	0	9	30	29.0	25.5
7	Kotzebue Water	2988	0	12	40	39.3	35.0

* 1 ml contains 10 mg total available chlorine

Color was determined by comparison with standard color discs in glass tubes of 200 mm depth. A measure of color was obtained by determining the percent transmittance of light at a wave length of 350 mm through a 50 mm light path. For this determination it was necessary to compare the percent transmittance against a distilled water blank which contained a chlorine concentration approximately equivalent to the chlorine concentration in the sample, since at this wave length chlorine also absorbs some light (Figure 2).

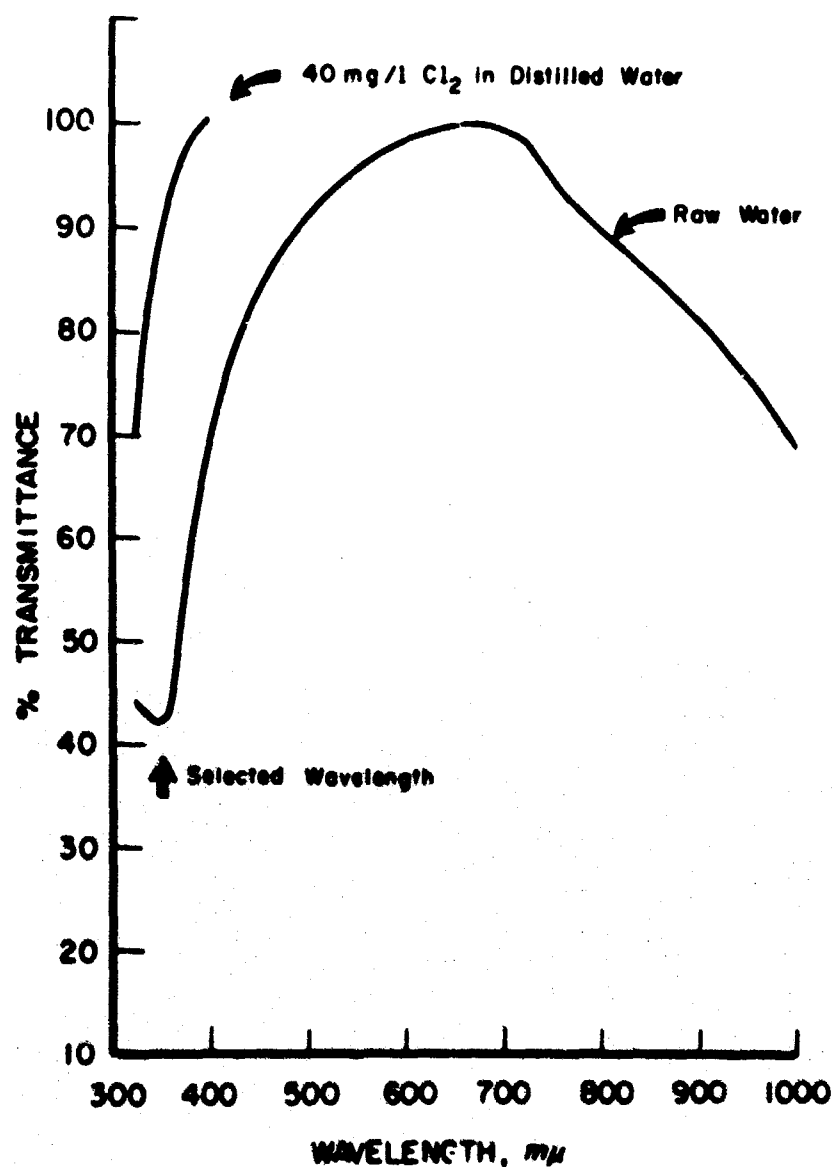


FIGURE 2

Spectral transmittance characteristics
50 mm light path

The pH was measured with an electronic pH meter which was standardized daily.

The temperature of the water was continuously recorded using a sensing element suspended in the sample blank.

The chlorine residual was measured with amperometric titrator, using the procedure outlined in Standard Methods (APHA, 1960) with the following exceptions:

1. In determining the combined available residual chlorine, with the sample previously used to determine the free-residual chlorine, 1 ml of pH 4 buffer was added followed by the addition of 1 ml of potassium iodide solution, as recommended by the manufacturer of the amperometric titrator. (Standard Methods specifies additions of the chemicals in the reverse order.)

2. In order to reduce the amount of phenylarsenoxide titrating solution required, appropriate sample dilutions were made with chloride demand free and chlorine free, buffered, distilled water. Dilutions were made in volumetric flasks which were coated on the outside with an opaque paint.

Early observations showed that various chlorine concentrations influenced the pH and, in addition, that the pH changed with time. In order to determine if this variable had any effect on the results of the experiments, the data shown in Figure 3 were obtained.

Thirteen determinations were made of each parameter, with daily measurements made initially and at less frequent intervals toward the end of the test. After the determination at zero time, samples were withdrawn from the tube at the bottom of the bottle without shaking.

The variations of color and chlorine residual in relation to time are shown graphically in Figures 4, 5 and 6. During the 28 days of observation the temperature varied from 22.9° C to 25.7° C and averaged about 24° C. The variations in pH in relation to time for the various samples are shown in Table II.

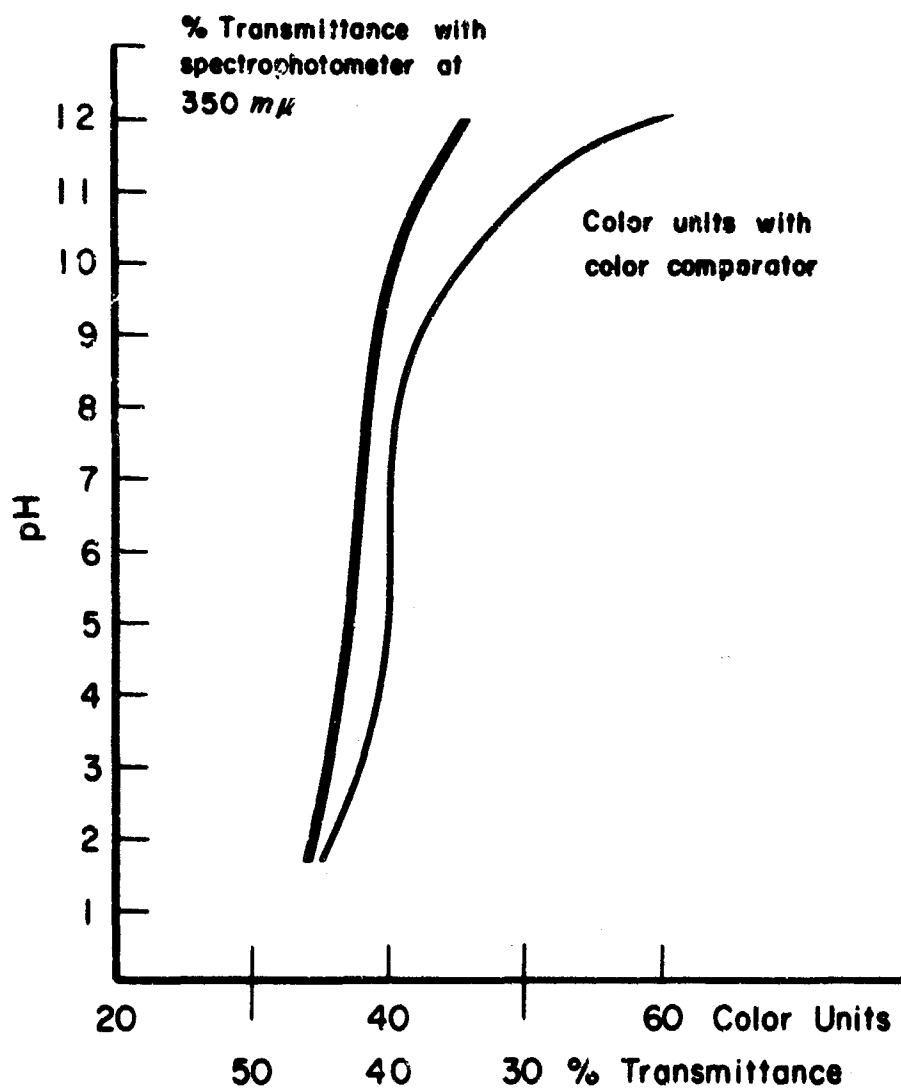


FIGURE 3

Variation of color with pH change

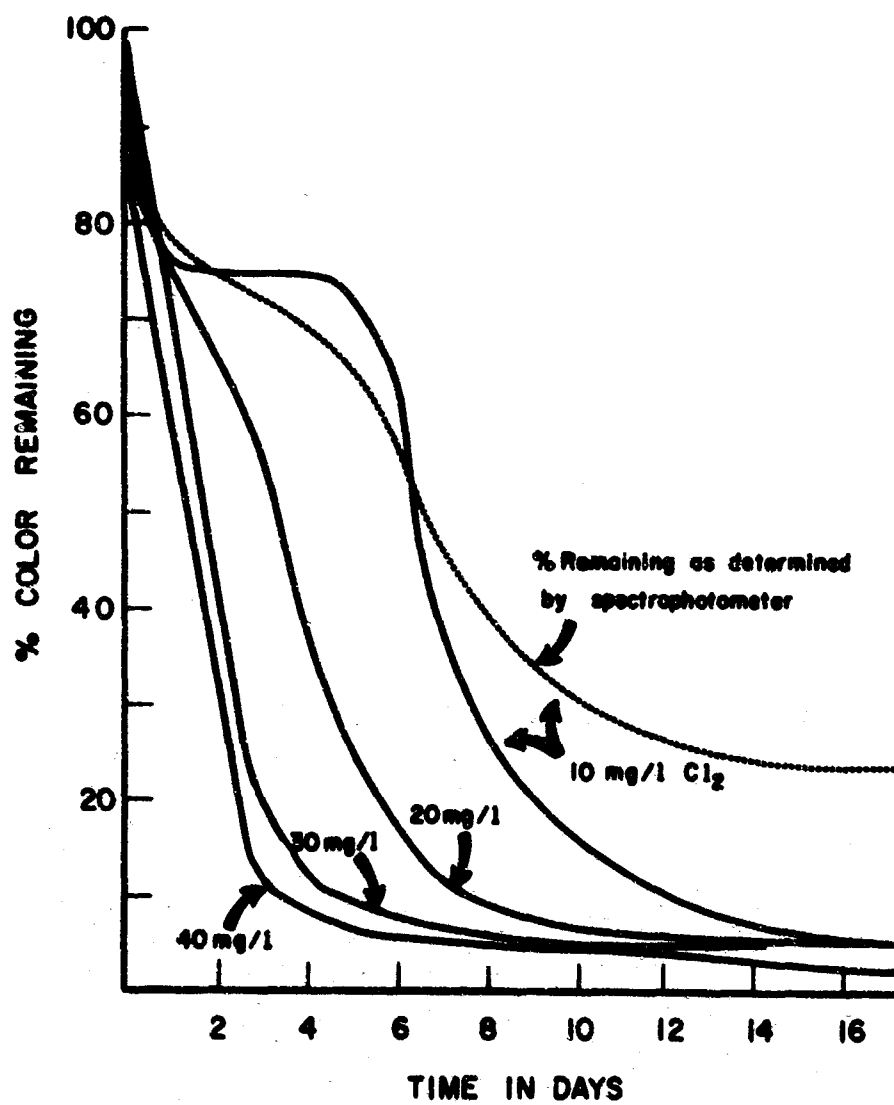


FIGURE 4

Effect of increased chlorine concentration
on rate of color removal

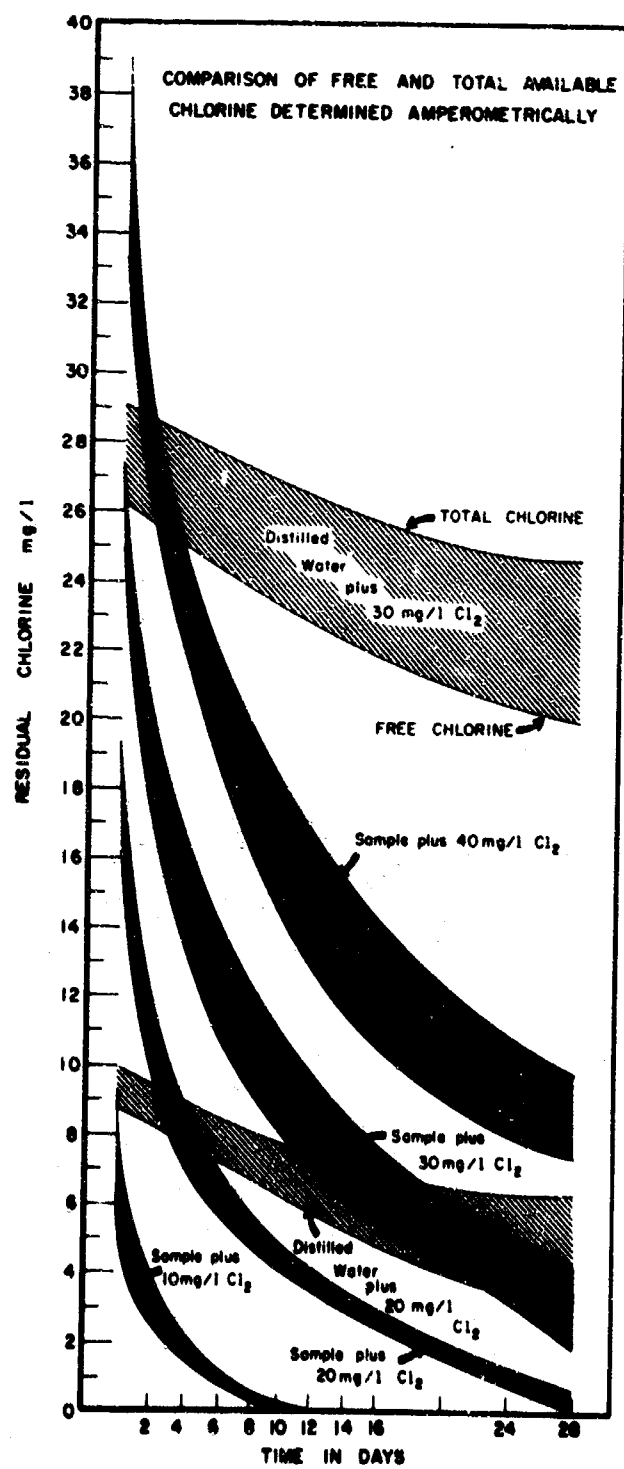


FIGURE 5

Comparison of free and total available chlorine determined amperometrically

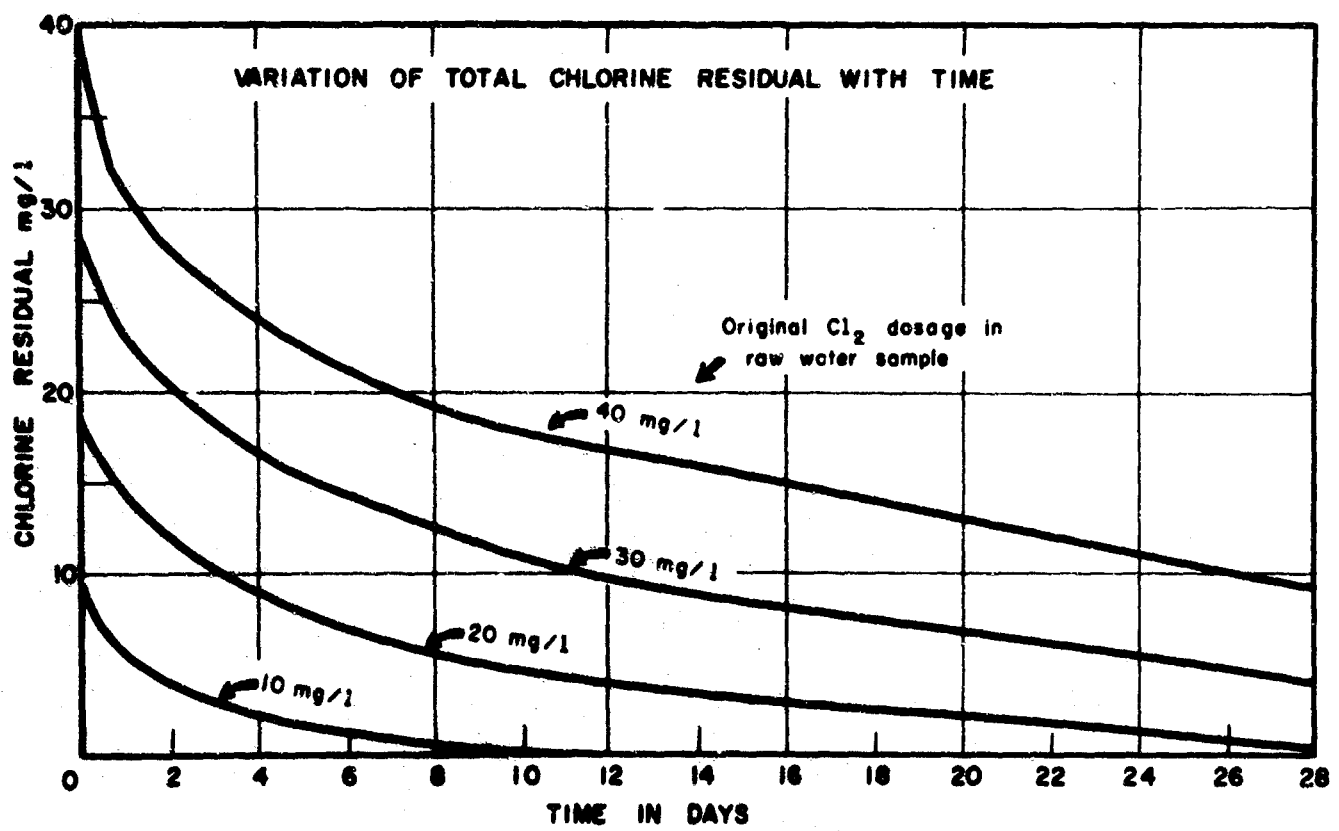


FIGURE 6

Variation of total chlorine residual with time

TABLE II
pH COMPARISONS OF RAW WATER AND TREATED WATER

Time days	Sample blank	Sample plus 10 mg/l Cl ₂	Sample plus 10 mg/l Cl ₂	Dist. H ₂ O plus 10 mg/l Cl ₂	Sample plus 20 mg/l Cl ₂	Sample plus 30 mg/l Cl ₂	Dist. H ₂ O plus 30 mg/l Cl ₂	Sample plus 40 mg/l Cl ₂
0	6.9	7.3	6.8	7.4	7.6	7.6	7.7	7.7
1	6.9	7.0	6.4	7.1	7.3	7.4	7.4	7.4
3	7.0	7.0	6.4	7.1	7.2	7.5	7.3	7.3
4	7.0	7.0	6.4	7.1	7.2	7.5	7.3	7.3
5	7.1	6.9	6.4	7.0	7.1	7.5	7.3	7.3
6	7.2	7.0	6.4	7.1	7.2	7.5	7.3	7.3
7	7.1	6.9	6.5	7.0	7.1	7.5	7.2	7.2
10	7.1	6.8	6.4	6.9	7.0	7.4	7.1	7.1
12	7.1	7.0	6.5	6.8	7.0	7.4	7.1	7.1
14	7.1	7.1	6.5	6.9	7.1	7.6	7.2	7.2
17	7.2	7.0	6.3	6.8	7.0	7.4	7.0	7.0
24	---	---	6.4	6.8	6.8	7.3	6.9	6.9
28	---	---	6.4	6.7	6.8	7.2	6.8	6.8

SECTION 4. DISCUSSION OF RESULTS

The USGS report showed that 20 mg/l reduced the color to zero in 25 days; however, although the Kotzebue water had been treated with 15 mg/l of chlorine, 40 color units still remained when this project began. Unfortunately, no information was available concerning the quality of the raw water when it was pumped into the 2,000,000 gallon storage tank during the previous summer. It could have contained significantly greater than 60 units of color, which was the point from which the USGS figure of 20 mg/l Cl_2 was estimated. Also, the fact that the water had been in the 2,000,000 gallon storage tank for at least five months (September until February) could be considered to have had some effect on the water quality. Thus, the deposit of sediment in the tank may have been due to the water added in September or, more likely, it may have been accumulated from the raw water over many years. This sediment may have intensified the color in the water by prolonged contact.

The rate of color removal in the laboratory did compare favorably, however, with the rates recorded by the USGS. This would indicate that if the water did extract additional color from the sediment, the rate of extraction was probably much slower than the rate of removal by the chlorine. After the chlorine residual had dropped to zero, recoloring probably began to occur but at a slower rate.

In following the rate of color removal for the various chlorine concentrations it was observed that measurements by the spectrophotometer transmittance agreed with visual determinations; however, the ultimate percentage removal indicated by the spectrophotometer was not as great as that indicated by visual determination.

The rate of residual chlorine depletion in this study was also comparable to that obtained in the USGS study.

The rates of removal for both the free and the combined chlorine residuals were essentially the same, indicating that free chlorine was not converted into the combined forms. This had been expected since the total nitrogen content of the raw water was less than 0.5 mg/l. The portion of the residual chlorine which was in the combined form appeared to be a function of the original chlorine dosage and was almost uniform with time. This appears to be a characteristic of the hypochlorite solution used for the study rather than a characteristic of the amperometric method.

The changes in pH which occurred were not considered to have had any effect on the results; however, the average of 24° C is significantly higher than the temperature which would be associated with a similar test in the field.

The 2,000,000 gallon storage tank at Kotzebue is heated during the winter to prevent freezing but the temperature is very seldom above 10° C and is more commonly below 5° C. Consequently, reaction rates would be significantly slower. The rate of color removal would be reduced and the chlorine residuals would persist for longer periods at the lower temperatures. This is corroborated in part by the work of Nehlsen and Traffalis (1954).

SECTION 5. CONCLUSIONS

1. The color found in a sample of surface water from a remote Air Force station in Alaska was removed by chlorine treatment in the laboratory.

2. It was shown that 10 mg/l of total available chlorine reduced the color by 95 per cent in 14 days, whereas 40 mg/l reduced the color by 95 per cent in about 5 days.

3. Although higher chlorine doses reduced the color more rapidly, the persistence of the larger chlorine residuals resulting from the higher doses indicates that the smallest practical dose should be employed.

4. For color concentrations in the range normally expected, about 60 to 70 color units, it appears that about 30 mg/l of chlorine should be used to remove the color from solution and to partially satisfy the chlorine demands of the sediment. Preferably the sediment should be flushed out of the tank before this test.

5. It is expected that the unacceptably high chlorine residual would persist for at least 60 days due to the temperature conditions in the storage tank.

REFERENCES

1. American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 11th Ed., New York, 1960.
2. Baumgartner, D. J. Water supply and waste disposal problems at remote Air Force sites in Alaska. AAL-TN-62-1, Arctic Aeromedical Laboratory, Ft. Wainwright, Alaska, March 1963.
3. Baumgartner, D. J. Color removal from surface waters by carbon filter. AAL-TDR-62-37, Arctic Aeromedical Laboratory, Ft. Wainwright, Alaska, October 1963.
4. Middleton, F. M., Chief, Organic Contaminants Unit, R. A. Taft Sanitary Engineering Center, U. S. Public Health Service, Cincinnati, Ohio, personal communication.
5. Nehlsen, W. R. and J. J. Traffalis. Persistence of chlorine residuals in stored water and ice. TN-206, U. S. Naval Civil Engineering Research and Evaluation Laboratory, Port Hueneme, California, November 1954.