

EFFECTS OF OZONATION ON THE APPARENT MOLECULAR  
WEIGHT OF NATURALLY OCCURRING ORGANICS  
IN THE WATERS OF KAW RESERVOIR

**E-004**

BY

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Naturally occurring organic compounds are present in the river and lake waters of the world. When surface waters are chlorinated so as to produce a free chlorine residual in the water, these naturally occurring organic compounds have been shown to be the precursors of several new organic compounds (1,2,3). Included in the group of newly formed compounds are the trihalomethanes (THM's). Four THM's that are usually formed are chloroform ( $\text{CHCl}_3$ ), dichlorobromomethane ( $\text{CHCl}_2\text{Br}$ ), chlorodibromomethane ( $\text{CHBr}_2\text{Cl}$ ) and bromoform ( $\text{CHBr}_3$ ). The highest concentration of THM's is usually in the form of chloroform, a known carcinogen. The other three THM's are suspected carcinogens.

Many investigators have published results of studies relative to the quantity and formation of THM's in the water treatment processes that are currently in use throughout the world. These results show large variations in the THM forming potential of the various water supply sources studied. In November, 1979, the U.S. Environmental Protection Agency set a maximum contaminant level of  $100 \mu\text{g}/\ell$  for THM's in certain public water systems.

Chlorination has been the most widely used method for disinfection of public drinking waters. Banning the use of chlorine for such purpose is not a practical solution to the problem of reducing the THM content in the public water systems. At the present time, the

most widely accepted technology for THM reduction in chlorinated waters is the use of granular activated carbon filters. It is recognized that the installation and operation of such filters will add greatly to capital and operating costs of most public water systems. Treatment alternatives that would replace pre-chlorination should reduce the formation of THM's. The use of ozone in lieu of chlorine is one such treatment alternative.

For this research project, water samples were taken from Kaw Lake which is located on the Arkansas River in northern Oklahoma. The dam for the lake was constructed by the U.S. Army Corps of Engineers and was completed in May, 1976. The Kaw Lake or Reservoir was developed for the purposes of (1) municipal water supply, (2) flood control, (3) water quality, (4) recreation and (5) fish and wildlife. The reservoir was designed to provide 860,000 acre-ft for water supply storage and a water supply yield of 230,700 acre-ft.

## OBJECTIVES

This research is aimed at studying one aspect of the formation of THM's in the water treatment processes by using water from Kaw Lake. The objectives of the research were:

1. Determination of the effects on the apparent molecular weight (AMW) distribution of naturally occurring organics where ozonation is used in lieu of chlorination as the pre-treatment process.
2. Comparison of the AMW distribution of the naturally occurring organics after ozonation with the AMW of the same organics

that were chlorinated, but not ozonated, in another research project.

The large water supply potential of Kaw Lake for cities in northern Oklahoma gives purpose to this research to evaluate the use of ozone as a pre-treatment disinfectant and its capability to inhibit or reduce the formation of THM's.

#### EXPERIMENTAL PROCEDURES

Samples of the water of Kaw Lake were collected by submerging 1 liter glass bottles, with plastic screw-on caps containing a PTFE sealing liner, below the water surface until filled. Upon arrival in the laboratory the samples were divided. One series of sub-samples were concentrated about 500 times by lyophilization. The other series of sub-samples were first subjected to ozone pretreatment and then concentrated about 500 times by lyophilization.

Following lyophilization of each sub-sample, the AMW fractionation of the sub-samples was accomplished with gel permeation chromatography using a calibrated Sephadex gel column. The resulting solution brought each sub-sample back to the original sub-sample concentration. The eluted sub-samples were collected and analyzed for total organic carbon (TOC). A chromatogram of TOC in mg/l versus elution volume in milliliters was prepared for each eluted sub-sample. A typical chromatogram is seen in Figure 1. The eluted fractions were then combined in six or seven AMW groups.

Each sub-sample was then chlorinated, detained for 48 hours and

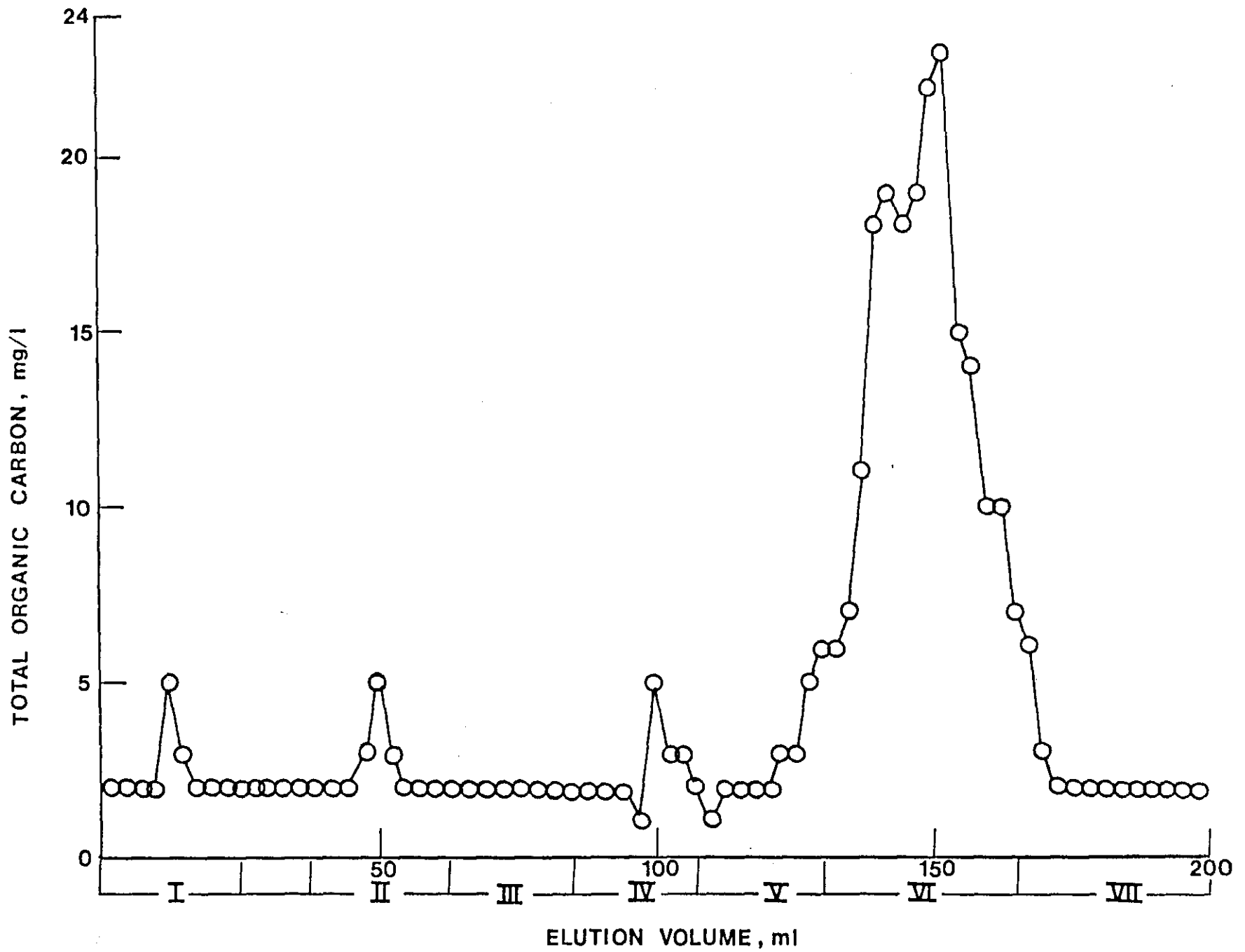


Figure 1. Chromatogram showing fractions for May 27, 1981. Ozonated sample. G-75 column.

analyzed for THM's by an electron capture gas chromatograph (GC) using a liquid-liquid extraction method. Elution water blanks were identically chlorinated to serve as a control.

## RESULTS AND DISCUSSION

The TOC chromatograms, as illustrated in Figure 1, for all samples show the predominance of one peak. This peak, over the study period, encompasses TOC having an apparent molecular weight of  $\approx 5000$  to  $\approx 1000$ . This would place the naturally occurring organics mostly in the molecular weight range of fulvic acids which tend to be the dominant form of naturally occurring organics in an aquatic environment (4).

For each chromatogram of the ozonated and non-ozonated (raw) subsamples, a graph of AMW versus cumulative percent TOC less than the AMW was prepared. A typical graph is shown in Figure 2. Figure 2 contains both the raw and ozonated samples for January 21, 1981, to illustrate any effects of ozonation. From these plots it was found that on the average about 51 percent of the TOC, in the raw water samples, had a molecular weight of  $\leq 4000$ . While in the ozonated samples, approximately 58 percent of the TOC was in the sub-4000 molecular weight group. There were shifts in the TOC pattern with time. In January the sub-4000 molecular weight group contained 30-40 percent of the TOC, by March 40-50 percent of the TOC was in this group. Finally by the end of May about 60 percent of the TOC was in the sub-4000 molecular weight group. The less than 1000 molecular weight on the average, for the raw and ozonated samples, contained about 8 percent and 7 percent of the TOC, respectively.

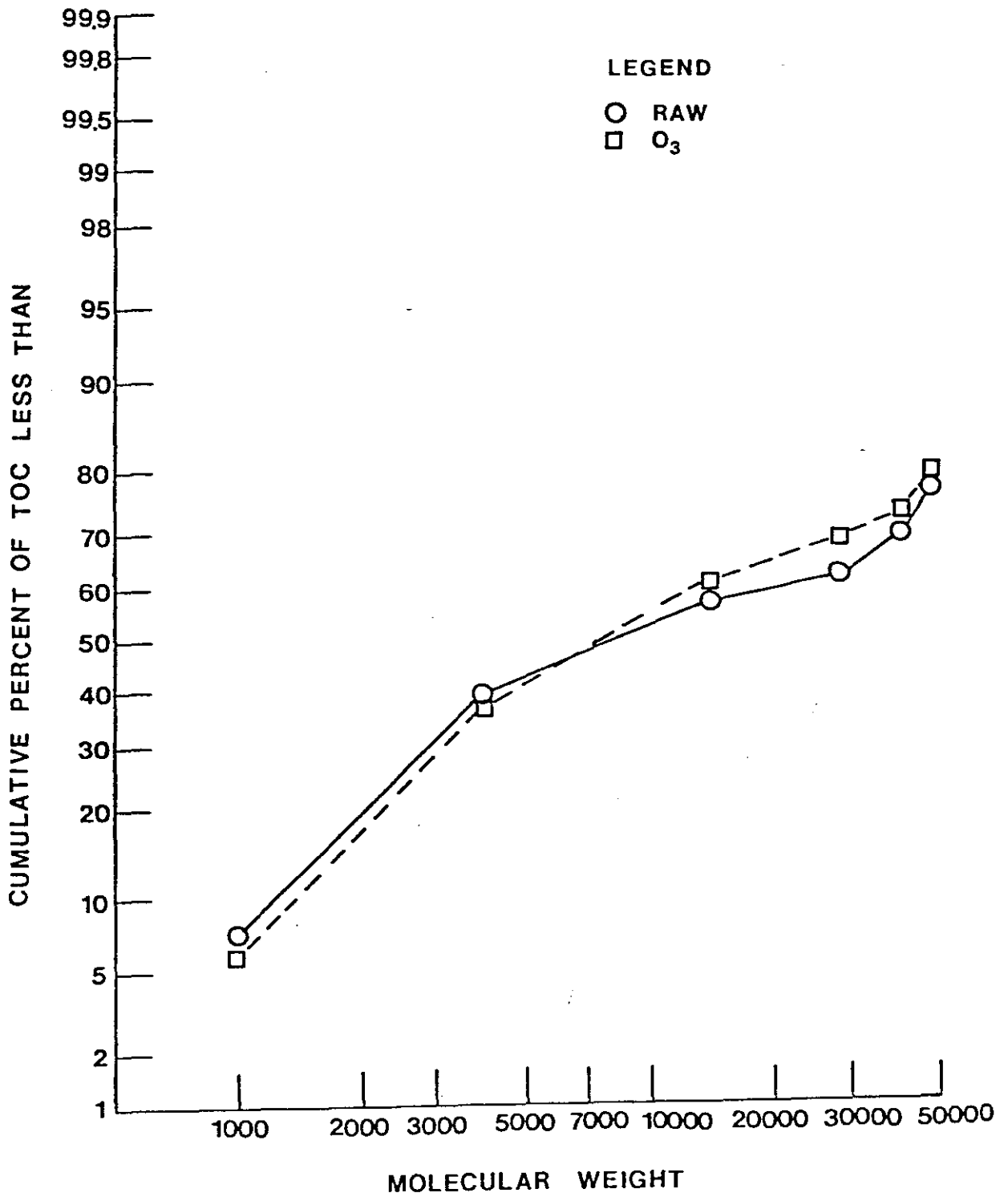


Figure 2. Cumulative percent of TOC less than apparent precursor molecular weight, Jan. 21, 1981 sample.

As illustrated in Figure 2, the ozonated samples tend to plot above the raw samples for the same AMW. This indicates a shift in the TOC occupying the various AMW fractions. This shift shows that the ozonated samples have a greater percentage of their TOC in the lower molecular weight groups. The modified apparent molecular weight distribution of the organic water constituents, with smaller proportions of the higher molecular weight fractions and the shift towards somewhat lower molecular weight substances, is to be expected by powerful oxidation treatment such as ozone. Similar shifts in molecular weight distribution following ozone treatment have been seen by other investigators (5).

Since complete oxidation, to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , would be impossible to achieve we must settle for partial removal of organics. These organics are the precursors substance to trihalomethanes (THM's) which are formed during the water chlorination process. The amount of precursor reduction achieved by ozonation in this study is shown in Figure 3. From Figure 3 the precursor reduction is seen to range from -12.2 percent to 46.4 percent, with most of the values being under 20 percent. This agrees very well with data presented by Trussell and Umphres (6). Their precursor reduction values ranged from -15 percent to 80 percent, again with most of the reduction being less than 20 percent. Both sets of results presented here were considering data points with ozone doses of 6 mg/l or less.

The pattern of TTHM production, over the period of investigation, varied from 194  $\mu\text{g}/\text{l}$  to 617  $\mu\text{g}/\text{l}$  for the raw water samples and from 256  $\mu\text{g}/\text{l}$  to 521  $\mu\text{g}/\text{l}$  for the ozonated samples. This pattern is shown in



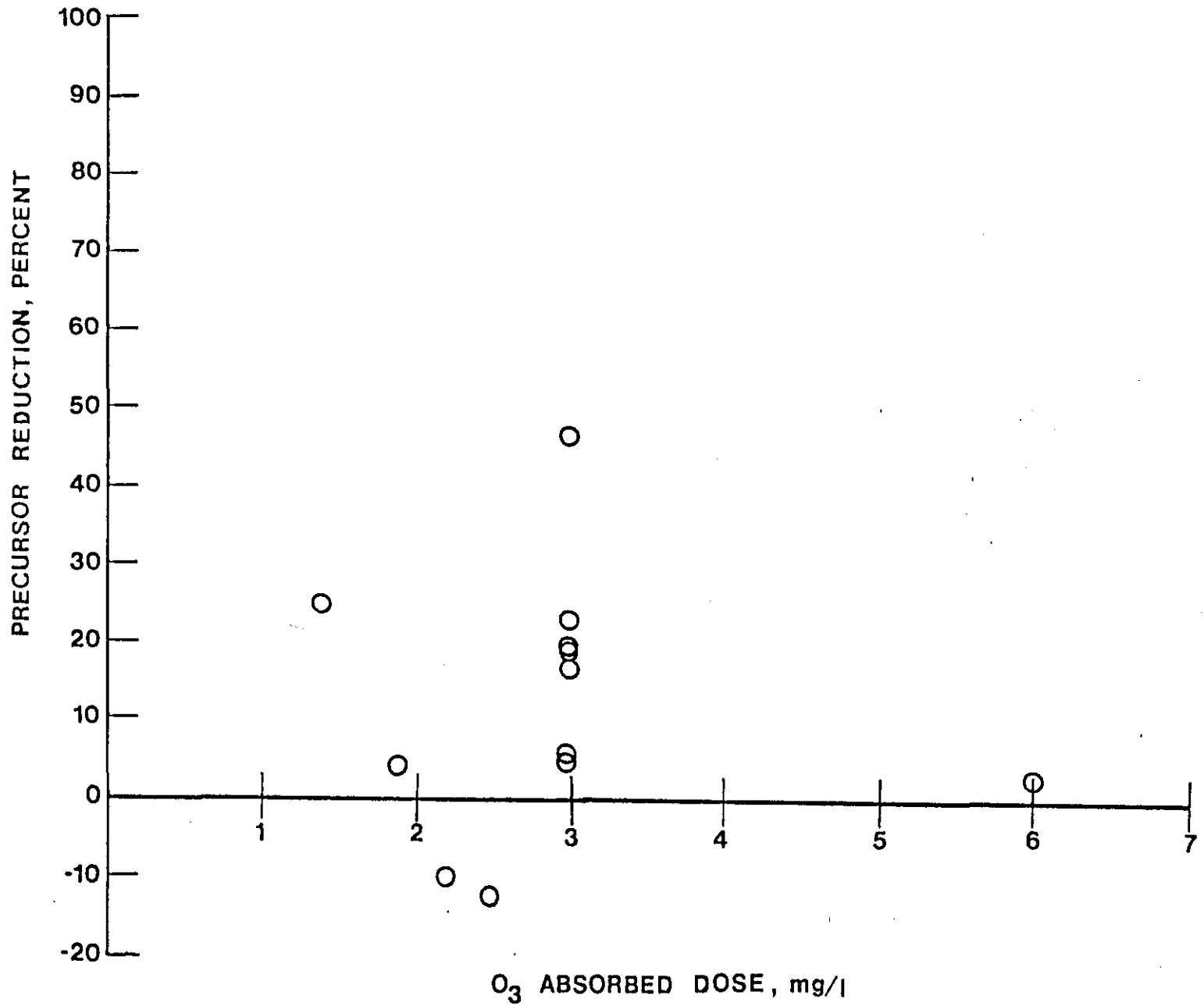


Figure 3. Precursor reduction achieved with ozone.

Figure 4. This figure indicates that the TTHM production of the ozonated samples is usually less than for the raw samples. The average percentage contribution of the four THM's to the total is shown in Table 1.

TABLE 1. AVERAGE PERCENT CONTRIBUTION OF THE FOUR THM'S TO THE TOTAL.

Compounds	Ozonated	Non-Ozonated
Chloroform	30%	33%
Bromodichloromethane	17%	18%
Dibromochloromethane	24%	25%
Bromoform	29%	24%

This data tends to agree with observations credited to Rook in an article by Trussell and Umphres (6). Rook noted preozonation resulted in a modest reduction in chloroform and dichlorobromomethane, a modest increase in chlorodibromomethane, and a substantial increase in bromoform.

Another way to check the effects of ozonation on precursor reduction, as shown in Figure 3, is to look at the effects on total trihalomethane (TTHM) production. In this study the reduction in the levels of TTHM's by ozonation varied from 31.1 percent to -100.5 percent. Considering values reported in the literature, this wide variation is to be expected. Rosen (7) and Umphres et al. (8) present TTHM reduction values of 70 percent to -62 percent and 90 percent to

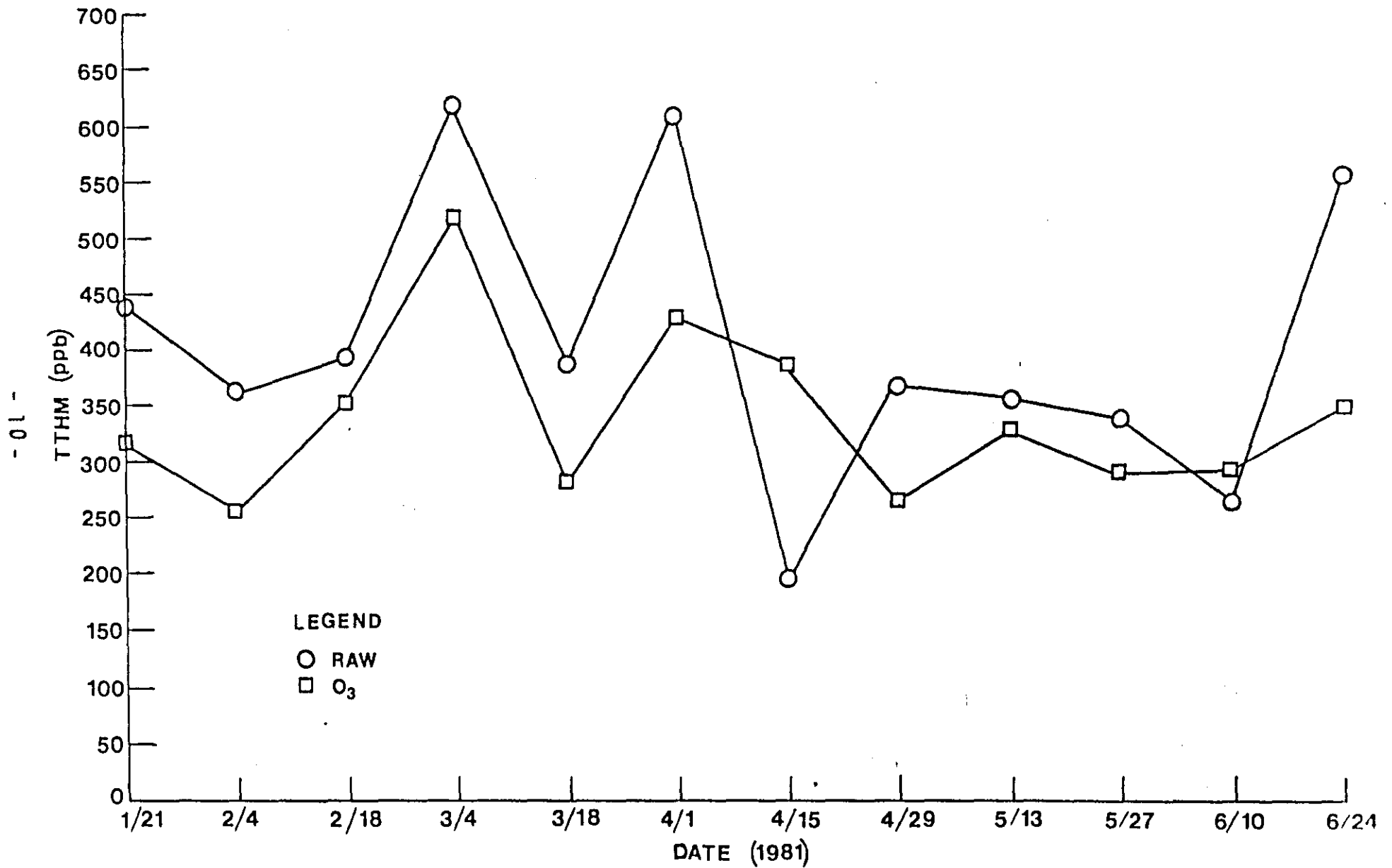


Figure 4. TTHM production versus time of year.

-29 percent respectively. This seems to point to the fact that since each water studied has its own unique characteristics, its reaction to ozonation in the form of maximum TTHM reduction will also be unique.

For each TOC chromatogram of the ozonated and raw sub-samples, a graph of AMW versus cumulative percentage TTHM's less than the AMW was prepared. Figure 5 is a typical graph showing this distribution. From this type of diagram it was found that on the average 46 percent of the ozonated and 48 percent of the raw samples TTHM's were produced in the sub-4000 AMW group. This corresponds to molecular weight group which contain the highest TOC values.

A comparison of percentage yield data for chloroform ( $\text{mg CHCl}_3$  as  $\text{C/mg TOC} \times 100$ ) with literature values as assembled by Veenstra and Schnoor (9) indicates that the values of .05 to .19 are in line with those found in the literature. This is especially true for those dealing with fractionated river water.

#### SUMMARY

From the data assembled in this study, it appears that pretreatment of the raw water with ozone causes a modification in the molecular weight distribution of naturally occurring organics. This modification takes the form of a reduction in the amount of natural organics along with a shift causing a larger percentage of the TOC to be found in the lower AMW groups.

This loss of organic material is portrayed in Figure 3 which shows precursor reduction versus absorbed ozone dose. This reduction is also

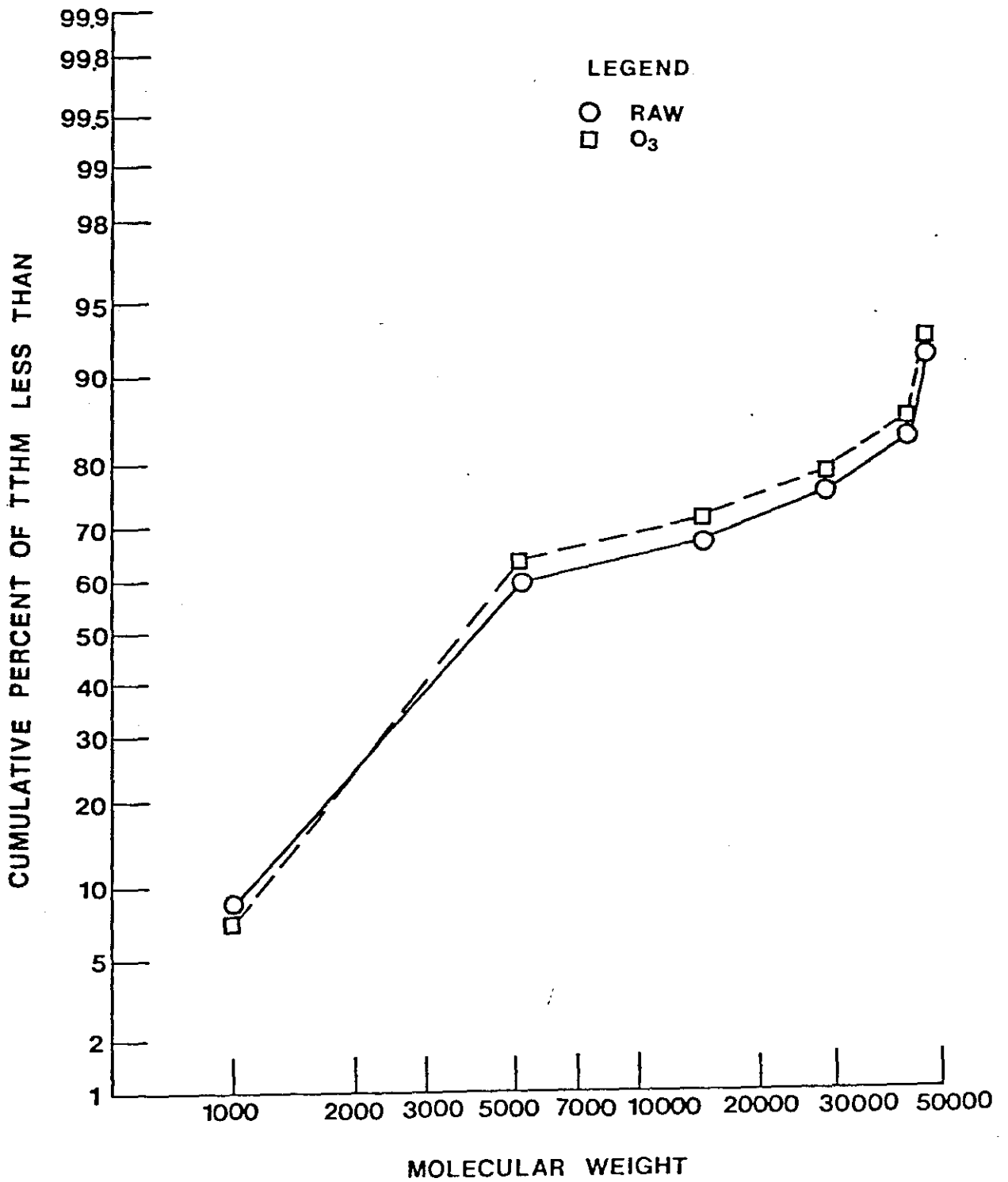


Figure 5. Cumulative percent of TTHM less than apparent precursor molecular weight, June 10, 1981 sample.

seen in the TTHM reduction levels which range from 31.1 percent to -100.5 percent.

Ozonation can effectively remove precursors. This conclusion is the same as that reached by other investigators (6). This removal seems to be variable in quantity depending on a large number of factors. These factors seem to include the nature of the organic material in the water and the ozone dosage. Since precursor reduction is not uniform, so neither is the reduction in TTHM levels. This poses a problem in that in order to be in compliance with EPA's current limit on TTHM's, the reduction must be sufficient enough so the TTHM level is consistently below 100  $\mu\text{g}/\ell$ . The results of this study indicate that ozone pretreatment of Kaw Lake water can be a supplement to any treatment process used to reduce the TTHM content below 100  $\mu\text{g}/\ell$ .

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