

# TRIHALOMETHANE FORMATION POTENTIAL OF KENTUCKY RIVER WATER

By R.E. Rathbun, K.D. White, and R.D. Evaldi

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## CONVERSION FACTORS

Metric (International System) units used in this report may be converted to inch-pound units by using the following conversion factors:

<i>Multiply metric unit</i>	<i>By</i>	<i>To obtain inch-pound unit</i>
nanometer (nm)	$3.937 \times 10^{-8}$	inch (in.)
micrometer ( $\mu\text{m}$ )	$3.937 \times 10^{-5}$	inch (in.)
square kilometer ( $\text{km}^2$ )	$3.861 \times 10^{-1}$	square mile ( $\text{mi}^2$ )
microgram per liter ( $\mu\text{g/L}$ )	$6.243 \times 10^{-8}$	pound per cubic foot ( $\text{lb/ft}^3$ )
milligram per liter ( $\text{mg/L}$ )	$6.243 \times 10^{-5}$	pound per cubic foot ( $\text{lb/ft}^3$ )
milliliter (mL)	$3.531 \times 10^{-5}$	cubic foot ( $\text{ft}^3$ )
cubic meter per second ( $\text{m}^3/\text{s}$ )	$3.531 \times 10^1$	cubic foot per second ( $\text{ft}^3/\text{s}$ )

Temperature in degree Celsius ( $^{\circ}\text{C}$ ) may be converted to degree Fahrenheit ( $^{\circ}\text{F}$ ) using:

$$^{\circ}\text{F} = ^{\circ}\text{C}(1.8) + 32.0$$

## SYMBOLS AND DEFINITIONS

BR	Bromide concentration, in milligrams per liter
$\text{CHCl}_3$	Chloroform
$\text{CHCl}_2\text{Br}$	Dichlorobromomethane
$\text{CHClBr}_2$	Dibromochloromethane
$\text{CHBr}_3$	Bromoform
CL	Initial free-chlorine concentration, in milligrams per liter
DOC	Dissolved organic carbon, in milligrams per liter
EPA	Environmental Protection Agency
$\text{H}_2\text{SO}_4$	Sulfuric acid
MCL	Maximum contaminant level
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
$\text{Na}_2\text{S}_2\text{O}_3$	Sodium thiosulfate
NAWQA	National water-quality assessment program
pH	Hydrogen-ion concentration, in pH units
PH	pH in the prediction equations
SPCOND	Specific conductance, in microsiemens per centimeter at $25^{\circ}\text{C}$
TBR	Sum of the concentrations of the three brominated trihalomethane compounds, in micrograms per liter
THM	Trihalomethane
THMFP	Trihalomethane formation potential
USGS	United States Geological Survey
UV	Ultraviolet
UV254	Ultraviolet absorbance at 254 nanometers

# TRIHALOMETHANE FORMATION POTENTIAL OF KENTUCKY RIVER WATER

By R.E. Rathbun, K.D. White, and R.D. Evaldi

## ABSTRACT

The trihalomethane formation potential of water from the Kentucky River was determined as a function of pH and initial free-chlorine, dissolved organic carbon, and bromide concentrations for the period from July 1988 through March 1990. The formation potential ranged from 59.7 to 731 and averaged 240 micrograms per liter, compared with the U.S. Environmental Protection Agency standard of 100 micrograms per liter. The pH and the dissolved organic carbon were the most significant variables in determining the trihalomethane formation potential. An equation developed using multiple-linear regression analysis predicted the experimental trihalomethane formation potential with a standard error of estimate of 9.18 percent of the mean. The percentages by weight of the total trihalomethanes that were brominated ranged from 4.17 to 61.8 and averaged 20.6 percent. Formation of the brominated compounds was strongly dependent on the bromide concentration and the pH. An equation developed using multiple-linear regression analysis predicted the experimental brominated trihalomethane formation potential with a standard error of estimate of 12.5 percent of the mean.

The dissolved organic carbon concentration of the sample waters could be predicted from the ultraviolet absorbance at 254 nanometers with a standard error of estimate of 8.84 percent of the mean. Combining this relation with the multiple-linear regression analysis equation for trihalomethane formation potential eliminated the need for the dissolved organic carbon concentration. The resultant equation predicted the experimental trihalomethane

formation potential data with a standard error of estimate of 12.9 percent of the mean.

The bromide concentration of the sample waters could be predicted qualitatively from the specific conductance with a standard error of estimate of 33.7 percent of the mean. Combining this equation and the dissolved organic carbon-ultraviolet absorbance equation with the multiple-linear regression analysis equation for trihalomethane formation potential eliminated the need for dissolved organic carbon and bromide concentrations. The resultant equation predicted the experimental brominated trihalomethane formation potential with a standard error of estimate of 33.8 percent of the mean. Therefore, this equation is limited to qualitative estimates only.

The trihalomethane formation potential increased qualitatively as the water discharge increased. Conversely, the brominated trihalomethane formation potential decreased qualitatively as the water discharge increased, and previous flow conditions seemed to have some effect on the formation potential.

## INTRODUCTION

The quality of the Nation's water is of great importance to the general health and well-being of the public. In 1986, the U.S. Geological Survey (USGS) initiated a National Water-Quality Assessment Program (NAWQA). The objectives of this program (Cohen and others, 1988) were to: (1) obtain a consistent evaluation of existing water-quality conditions for a large part of the Nation's water resources; (2) determine long-term trends or lack of trends in the water quality; and (3) define and explain

the principal processes affecting the water-quality conditions.

One of the initial surface-water study sites of the NAWQA program was the Kentucky River basin. This basin drains approximately 18,100 km<sup>2</sup> in east-central Kentucky. More than 95 percent of the population of this basin depends on surface water as a source for water (White and others, 1987). A water-quality problem of concern to these users is the potential for trihalomethane (THM) compound formation. Trihalomethane compounds are chlorinated and brominated derivatives of methane that are formed when a natural water is treated with free chlorine to produce drinking water.

## **PURPOSE AND SCOPE**

This report describes a study of the trihalomethane formation potential (THMFP) of water from the Kentucky River for the period from July 1988 through March 1990. The trihalomethane formation potential was determined as a function of natural variations in the dissolved organic carbon (DOC) and bromide concentrations and imposed variations in the pH and initial free chlorine concentration at a temperature of 25°C.

## **BACKGROUND INFORMATION**

The four THM compounds are chloroform (CHCl<sub>3</sub>), dichlorobromomethane (CHCl<sub>2</sub>Br), chlorodibromomethane (CHClBr<sub>2</sub>), and bromoform (CHBr<sub>3</sub>). THM's were first noted in finished drinking waters by Rook (1974) and Bellar and others (1974). Extensive research since that time has concluded that these THM's are formed when natural waters are disinfected with free chlorine to produce water safe for drinking. The chlorine reacts with humic substances naturally present in the water to produce CHCl<sub>3</sub>. If bromide ion is present in the water, then the bromide ion is oxidized by the chlorine to produce hypobromous acid.

This acid, in turn, reacts with the humic substances to produce the THM's containing bromine (Rook, 1974).

Reports by the U.S. Environmental Protection Agency (1975) and the National Academy of Sciences (1977) raised concern about the health effects of THM's in public drinking waters. Consequently, the U.S. Environmental Protection Agency (EPA) established a maximum contaminant level (MCL) in drinking water of 100 µg/L total of the four THM compounds (Federal Register, 1979a). This requirement resulted in considerable research directed toward understanding the THM formation process.

Results of this research were summarized by Culp (1984). This research indicated that the important factors in the THM formation process are pH, initial free-chlorine concentration, concentration of humic substances in the source water, temperature, and bromide concentration. Increasing pH, initial free-chlorine concentration, and temperature all resulted in increased THM formation. Humic substances in the source water are the precursors in the THM formation process. These substances result from the decay of organic matter, and the source, distribution, and characteristics of aquatic humic substances have been studied extensively (Thurman, 1985). The DOC frequently is used as a collective quantitative measure of the concentration of humic substances in water. The effect of bromide on the THM formation process has been reviewed by Cooper and others (1985). This review indicated that even trace amounts of bromide affected the distribution of the THM compounds formed, resulting in the formation of more of the brominated compounds and less of the chloroform.

The effect of the bromide concentration on the THMFP is of importance in the Kentucky River basin because of the presence of bromide in the river water. Most of the bromide originates from subsurface brines produced in connection with oil and gas production in the

upper part of the basin. Evaldi and Kipp (1990) studied the effects of this oil production on the water resources of the Kentucky River. They determined that the average annual yield of bromide from two subbasins having oil production was at least 10 times greater than the yield from a nearby control subbasin having no oil production. Also, the transport of the bromide was not uniform with time. Most of the bromide was transported during the first high flows following the low flows of summer and fall.

## EXPERIMENTAL PROCEDURE

Depth- and width-integrated samples of water were collected from the Kentucky River at Lock 10 near Winchester, Ky. (fig. 1) using either a DH-81 or a D-77 sampler. The water was transferred from the sampler, composited, and put in 1-gallon amber glass bottles with Teflon-lined caps. These bottles were placed in styrofoam cartons and shipped on ice in insulated coolers by overnight mail from the USGS District office in Louisville, Ky. to the project office in Arvada, Colo. The water was filtered through low-extractable 0.45- $\mu\text{m}$  membrane filters and stored in amber bottles at 4°C until the experiments were run. Each filter was pre-rinsed with one liter of high-purity water from a Barnstead<sup>1</sup> NANOPURE system. Water samples were collected in July and October of 1988 (7/88 and 10/88) and monthly from January 1989 (1/89) through March 1990 (3/90).

The THMFP of the various Kentucky River waters was determined as a function of the initial free-chlorine concentration and pH at 25°C for a time period of 7.0 days. Initial free-chlorine concentrations of 15, 30, and 50 mg/L and initial pH values of 6, 8, and 10 were used, resulting in nine THMFP values for each water.

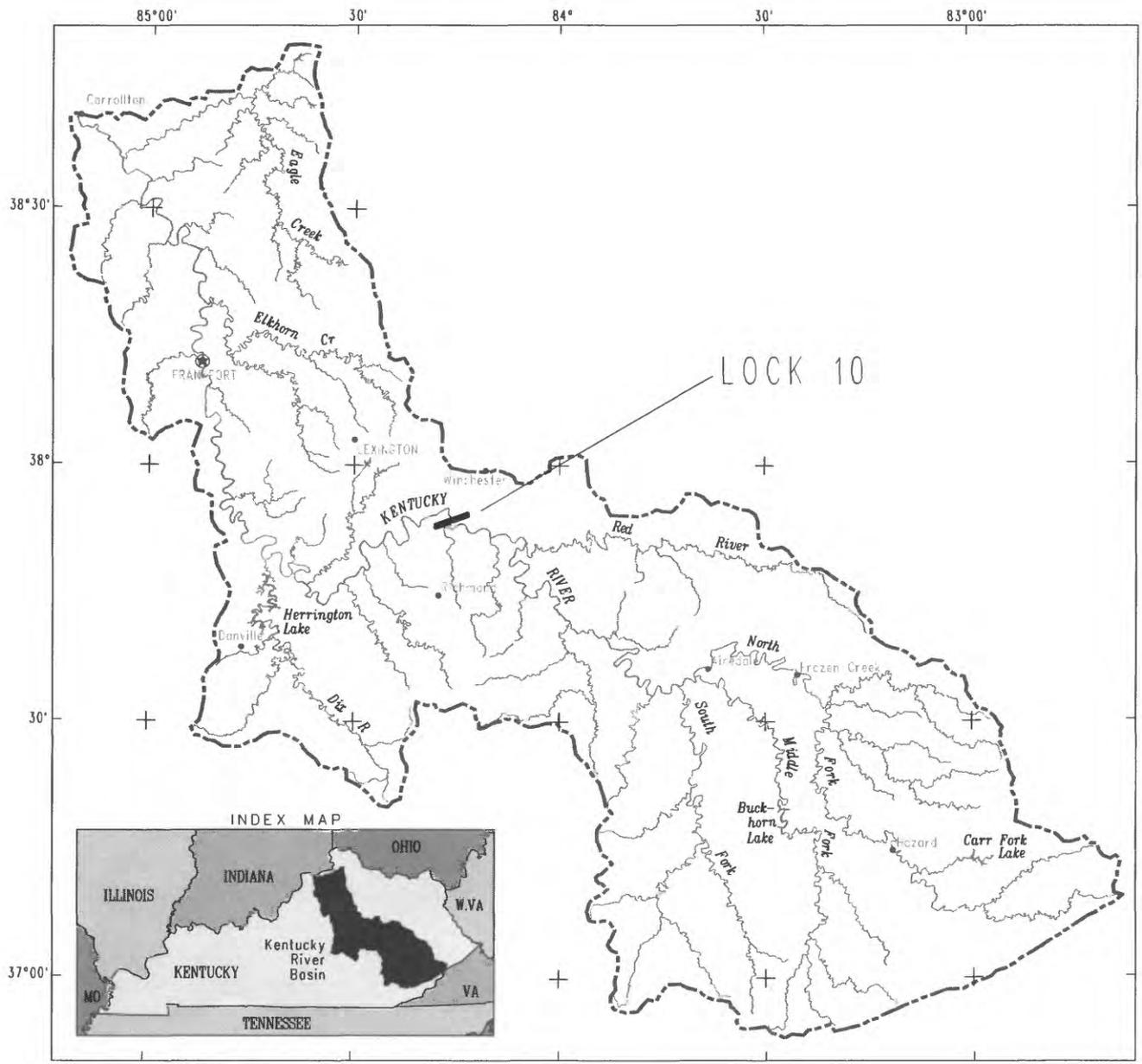
<sup>1</sup>Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The free chlorine was obtained from a reagent-grade solution of NaOCl. The free-chlorine concentration of this solution was determined before the start of each experiment using an amperometric titration procedure. The absence of THM's in the NaOCl solution was verified by adding aliquots of the solution to NANOPURE water containing sufficient Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to quench the free chlorine. Analysis of the resultant mixtures indicated no significant concentrations of the THM's.

Preparation for an experiment consisted of taking sufficient water for a blank plus two samples for each of the three free-chlorine concentrations and adding 2 percent by volume of the appropriate buffer. These buffers were prepared from dry-salt capsules and the high-purity NANOPURE water. Phosphate buffers were used for pH's of 6 and 8 and a bicarbonate-carbonate buffer was used for pH 10. The pH of the solutions then was adjusted to the desired initial pH using 0.1N H<sub>2</sub>SO<sub>4</sub> or 0.1N NaOH. These solutions were stored overnight in an incubator at 25°C.

The THMFP experiments were done in 40-mL glass vials with Teflon-faced septum caps. Initiation of an experiment consisted of filling the blank vial with the sample water, adding sufficient NaOCl solution to the remaining sample water to give the desired initial free-chlorine concentration, mixing, and immediately transferring the solution to the sample vials. All vials were filled completely so that no head space existed. The sample vials then were placed in the incubator at 25°C for 7.0 days. At the end of the 7.0-day period, 0.5 mL of a solution containing sufficient Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to quench the free chlorine was added to each vial to terminate the experiment. One extra vial was prepared with an initial free-chlorine concentration of 15 mg/L for determination of the residual free chlorine at the end of the 7.0-day period.

THM concentrations in the samples were determined using a solvent-extraction procedure (Federal Register, 1979b) with pentane as



Base from U.S. Geological Survey  
 Digital line graphs from 1:100,000 maps

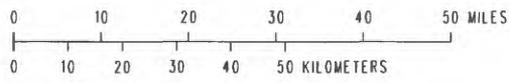


Figure 1.--Map of the Kentucky River basin.

the solvent. The procedure was modified slightly in that the extractions were done in the sample vials. The modified procedure consisted of removing and discarding 4.5 mL of the sample, adding 4.0 mL of pentane, and shaking vigorously for 1.5 minutes. The vials containing the water and pentane layers were stored upside down in a refrigerator at 4°C until analysis.

Because the volumes of the 40-mL vials were not always precisely 40.0 mL, the vials were weighed after each step of the procedure to determine the exact water/solvent volume ratio for each sample. Following analysis in a gas chromatograph with a capillary column and an electron capture detector, the observed peak areas for each sample were adjusted from the volume ratio of that sample to the average volume ratio for the standard samples for that particular run. This procedure resulted in all samples and standards being adjusted to one volume ratio.

Standard samples of known concentrations of the four THM's were prepared according to established procedures (Federal Register, 1979b). Briefly, a primary standard was prepared by adding each of the four THM compounds to methanol in a 10-mL volumetric flask. The exact amount of each compound added was determined by weighing on an analytical balance. Standards of the desired concentration were prepared by adding micro-liter-quantities of the primary standard to water in the 40-mL septum vials. To eliminate any matrix effects on the efficiency of the solvent extraction procedure, standards were prepared using the same river water as used for the THMFP experiments. Each standard was treated exactly as the samples except that the NaOCl was not added to the standards.

A relatively large number of standards was necessary for two reasons. First, the response of electron capture detectors is somewhat nonlinear. Second, the standards had to cover a wide range of concentrations for the four THM compounds. Generally, 12 to 14 stan-

dards were prepared for each run. These standards were analyzed twice each day, and sufficient standards were analyzed so as to bracket the peak areas of each of the four THM's in each of the samples. Usually, 25 to 30 percent of the samples analyzed each day were standards.

Final pH's of the samples were determined following completion of the gas chromatographic analysis. To do these measurements, the pentane was removed from the sample vials by evaporation.

DOC and bromide concentrations of each sample water were determined by the USGS National Water Quality Laboratory in Arvada, Colo. DOC was determined using a wet-oxidation method (Wershaw and others, 1983) and bromide was determined using segmented flow automated colorimetry (Fishman and Friedman, 1985). UV absorbances were determined at 254, 280, 330, and 400 nanometers (nm), and the specific conductance also was measured.

## RESULTS OF THE THMFP DETERMINATION

The THMFP was determined for 17 sample waters from the Kentucky River. The THMFP ranged from 59.7 to 731 and averaged 240 µg/L, compared with the EPA standard of 100 µg/L. The DOC ranged from 1.2 to 3.8 and averaged 2.1 mg/L. The bromide concentration ranged from 0.008 to 0.21 and averaged 0.053 mg/L. The bromide concentrations for the 1/90 and 2/90 waters were less than the limit of detection of 0.005 mg/L. Residual free chlorine concentrations were larger than 3.5 mg/L in all samples at the end of the 7.0-day period.

Duplicate determinations of the THMFP were done for all sample waters except 7/88. Coefficients of variations ranged from 0.01 to 11.0 and averaged 1.78 percent for the 144 pairs of measurements.

### Final pH values

The final pH values of the various experiments are summarized in table 1. The maximum and minimum pH's and the coefficients of variation of the 17 values for each set of experiments are presented. The fact that the final pH's, particularly for the pH 6 and pH 8 experiments, are larger than the initial pH values indicates that the 2 percent by volume of buffer added to the water did not have sufficient buffering capacity to counteract the basicity of the NaOCl. Supplementary experiments indicated that the change in pH occurred immediately upon addition of the NaOCl, thus, the pH at which the THM reaction occurred was assumed to be that measured at the conclusion of the experiments.

squared improvement options all gave the same results for the experimental data.

The resultant equation was

$$\text{THMFP} = 0.714 \text{ DOC}^{1.19} \text{ PH}^{2.12} \text{ CL}^{0.0969} \quad (1)$$

where THMFP = trihalomethane formation potential, in micrograms per liter;

DOC = dissolved organic carbon concentration, in milligrams per liter;

PH = pH, in pH units; and

CL = initial free chlorine concentration, in milligrams per liter.

The bromide concentration was not a significant variable. The constant in equation

Table 1.--Maximum, minimum, and coefficients of variation of the final pH values

[mg/L = milligrams per liter; conc. = concentration]

Initial pH	Initial free-chlorine conc. (mg/L)	Maximum pH	Minimum pH	Coefficient of variation (percent)
6.00	15	6.93	6.60	1.14
6.00	30	7.37	6.89	1.76
6.00	50	7.97	7.28	3.01
8.00	15	8.69	7.83	2.79
8.00	30	9.30	8.10	3.78
8.00	50	9.67	8.51	3.89
10.00	15	10.04	9.44	1.64
10.00	30	10.11	9.40	1.94
10.00	50	10.18	9.47	1.97

### THMFP Prediction Equation

Multiple-linear regression analysis was used to develop an equation for predicting the THMFP as a function of the DOC, pH, initial free-chlorine concentration, and the bromide concentration. SAS Institute, Inc. programs (SAS, 1988) were used for these regression analyses. The forward selection, backward elimination, stepwise, and maximum R-

1 was adjusted from the regression-analysis value of 0.711 to 0.714 using the nonparametric correction of Duan (1983). This correction adjusts for the bias introduced when a log transformation of equation 1 is used to obtain a linear equation for the regression analysis.

The F value computed for each variable during the regression analysis is the ratio of the mean square error due to regression to the mean square error due to the residuals (Draper

and Smith, 1966). The larger the F value, the more significant the variable is, and the F values computed during the regression analysis indicated that the DOC and the pH were the most significant variables. The initial free-chlorine concentration had sufficient significance to be included in the equation, however, the correlation coefficient increased only from 0.976 to 0.981 when this variable was added. The standard error of estimate of equation 1 was 9.18 percent of the mean experimental THMFP value. Values of the THMFP predicted from equation 1 are plotted in figure 2 as a function of the experimental THMFP values.

One experiment was run to determine if the buffer added to the sample waters had any effect on the THMFP. This experiment was done with the 9/89 water and an initial free-chlorine concentration of 30 mg/L. The THMFP predicted from equation 1 and the experimental THMFP for this unbuffered experiment are presented in figure 3 together with the results for the nine buffered experiments. These results show that the unbuffered value is comparable to the buffered values, indicating that the buffer had no appreciable effect on the results, other than changing the initial pH of the water. This latter effect was incorporated into the results through the measurement of the final pH values.

### **Effect of the Bromide Concentration on the THMFP**

The percentages by weight of the total THM's that were brominated were determined by summing the concentrations of the brominated forms ( $\text{CHCl}_2\text{Br} + \text{CHClBr}_2 + \text{CHBr}_3$ ) and dividing by the total THMFP. Percentages ranged from 4.17 to 61.8 and averaged 20.6 percent. The two sample waters having bromide concentrations less than the limit of detection (1/90 and 2/90) both had measurable concentrations of the brominated THM's, with the percentages of the total ranging from 4.19 to 10.4 percent. This indicates that the

bromide concentrations for these two sample waters, although less than the limit of detection, were not zero.

The effect of the bromide concentration on the formation of the brominated THM's was determined using multiple-linear regression analysis. The forward selection, backward elimination, stepwise, and maximum R-square improvement options of the SAS regression program (SAS, 1988) all gave the same results for the experimental data. The data for the 1/90 and 2/90 waters were excluded from this analysis.

The resultant equation was

$$\text{TBR} = 18.1 \text{ DOC}^{0.319} \text{ PH}^{1.64} \text{ CL}^{-0.117} \text{ BR}^{0.784} \quad (2)$$

where TBR = the sum of the concentrations of the three brominated THM's, in micrograms per liter; and

BR = bromide concentration, in milligrams per liter.

The constant in equation 2 was adjusted from the regression-analysis value of 18.0 to 18.1 using the nonparametric correction of Duan (1983). The standard error of estimate of equation 2 was 12.5 percent of the mean experimental brominated THM value.

Although the bromide concentration was not a significant variable in equation 1 for the total THMFP, it was the most significant variable in equation 2 as indicated by the F values computed during the regression analysis. The pH was the next most significant, followed by the DOC. The initial free-chlorine concentration was sufficiently significant for inclusion in the equation, however, the correlation coefficient increased only from 0.980 to 0.983 when this variable was added. The sum of the concentrations of the brominated THM's predicted from equation 2 are plotted in figure 4 as a function of the sum of the experimental concentrations of the brominated THM's.

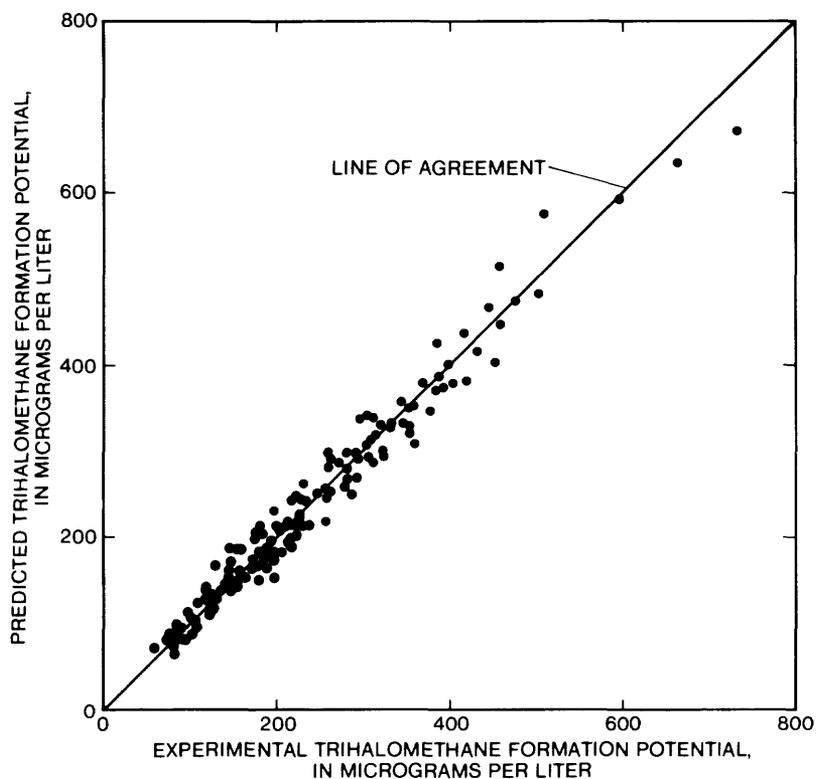


Figure 2.--Predicted trihalomethane formation potential as a function of the experimental trihalomethane formation potential.

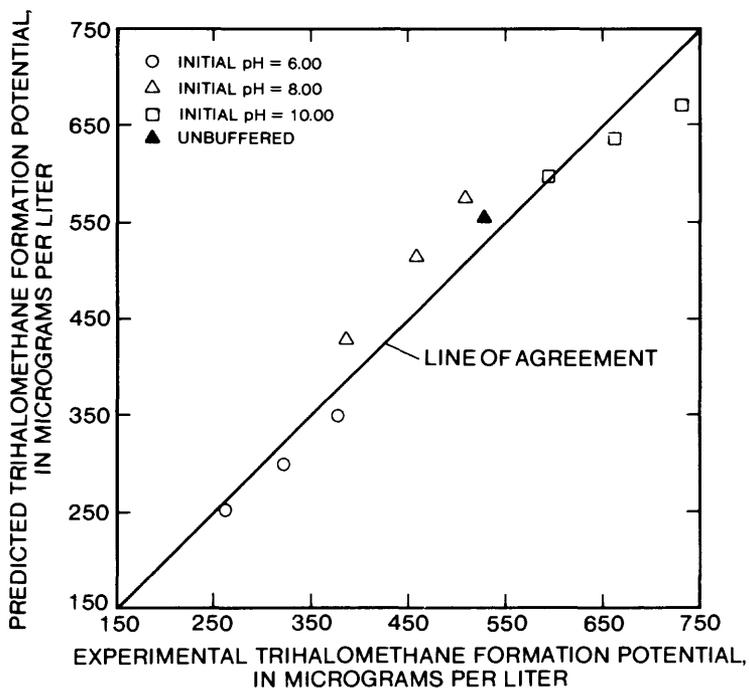


Figure 3.--Predicted trihalomethane formation potential as a function of the experimental trihalomethane formation potential for buffered and unbuffered experiments, September 1989 sample water.

### Estimation of the THMFP Using Predicted DOC Values

Estimation of the THMFP using equation 1 requires the pH, initial free-chlorine concentration, and the DOC concentration. The pH is determined by a combination of the natural pH of the source water and the particular process used for water treatment. The initial free-chlorine concentration also is determined by the water-treatment process. Determination of the DOC requires a relatively sophisticated laboratory analysis. To eliminate the necessity for a DOC determination, the ultraviolet (UV) absorbance has been used as a predictor of the DOC. Determination of the UV absorbance is simple and rapid, and absorbances at 254 nm (Edzwald and others, 1985; Ceraso, 1987; Chadick and Amy, 1987), 285 nm (Buffle and others, 1978), 330 nm (Moore, 1987), and 400 nm (Oliver and Thurman, 1981) have been used.

Linear regression of the logarithm of the DOC as a function of the logarithm of the UV absorbance resulted in standard errors of estimates of 8.84, 9.73, 14.6, and 19.6 percent for wavelengths of 254, 280, 330, and 400 nm, respectively. The equation for 254 nm is

$$\text{DOC} = 18.9 (\text{UV}_{254})^{0.767} \quad (3)$$

where  $\text{UV}_{254}$  = absorbance at 254 nm.

Equations for the other three wavelengths were similar, with the constant term increasing and the exponent decreasing as the wavelength increased. The constant in equation 3 was adjusted from the regression-analysis value of 18.8 to 18.9 using the nonparametric correction of Duan (1983). DOC values are plotted in figure 5 as a function of the UV absorbance at 254 nm. Equation 3 also is shown in figure 5.

Combining equation 3 with equation 1 permits prediction of the THMFP using only an easily-measured parameter and two parameters determined by the particular water-treat-

ment process being used. This combination of the two equations was tested by applying it to the experimental data. The standard error of estimate was 12.9 percent of the mean which compares favorably with the error of 9.18 percent for equation 1. This latter error is the minimum error by definition because the differences between the experimental and calculated values are minimized in a least-squares sense during the regression process. Thus, the error of 12.9 percent for the combination of equations 1 and 3 indicates that the UV absorbance at 254 nm is a good predictor for the DOC values of the sample waters of this study.

### Estimation of the Brominated THMFP

Estimation of the brominated THMFP using equation 2 requires the pH and concentrations of initial free-chlorine, DOC, and bromide. As indicated previously, the pH and initial free-chlorine concentration are controlled by the pH of the water source and the particular water-treatment procedure being used, and the DOC can be measured or predicted using the UV absorbance at 254 nm. The remaining parameter is the bromide concentration which requires a relatively sophisticated laboratory analysis for the low concentrations likely to exist in surface waters.

A review of the bromide and specific conductance data for the sample waters indicated an approximate relationship between these variables. Linear regression of the logarithm of the bromide concentration as a function of the logarithm of the specific conductance resulted in the equation

$$\text{BR} = 8.36 \times 10^{-7} (\text{SPCOND})^{1.94} \quad (4)$$

where  $\text{SPCOND}$  = specific conductance, in microsiemens per centimeter at 25°C.

The constant in equation 4 was adjusted from the regression-analysis value of  $7.69 \times 10^{-7}$  to  $8.36 \times 10^{-7}$  using the nonparametric correction

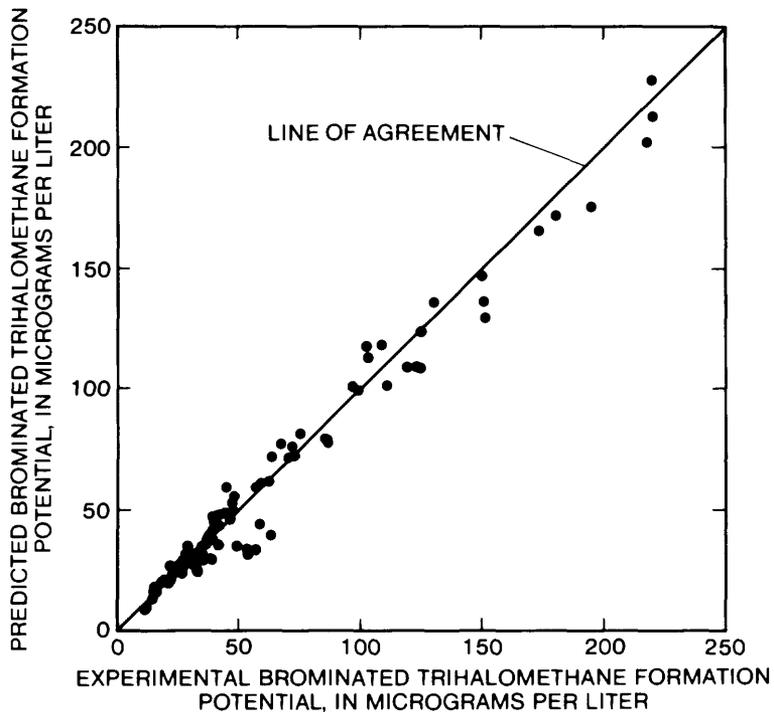


Figure 4.--Predicted brominated trihalomethane formation potential as a function of the experimental brominated trihalomethane formation potential.

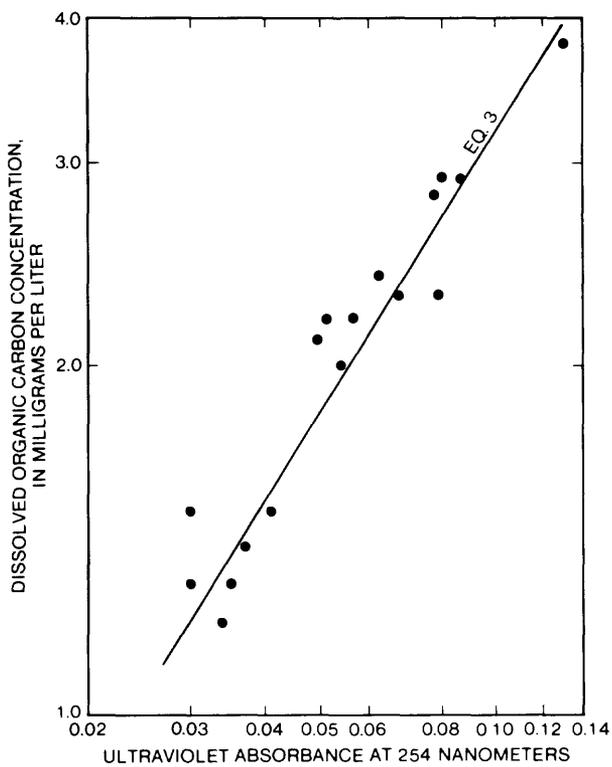


Figure 5.--Dissolved organic carbon concentration as a function of the ultraviolet absorbance at 254 nanometers.

of Duan (1983). The standard error of estimate for equation 4 was 33.7 percent of the mean. Equation 4 is specific for the Kentucky River and most likely will not be applicable to other surface waters. Also, it is for the time period of this study and may not be applicable to other time periods on the Kentucky River because of the variable way in which bromide is transported in this river system (Evaldi and Kipp, 1990).

Bromide concentrations are plotted in figure 6 as a function of the specific conductance. Equation 4 also is shown in figure 6. Largest deviations from equation 4 are at the lower end of the concentration range which is near the limit of detection (0.005 mg/L) of the analytical procedure used for bromide.

Equations 4 and 3 were combined with equation 2 to predict the brominated THMFP for the experimental data. The standard error of estimate was 33.8 percent of the mean.

Figure 6 indicates that there are three points which deviate considerably more from equation 4 than the other points. Residuals for these points were two to three times larger than the largest residual for the other points. Analysis of the data indicated no basis for rejecting these three points, other than that the concentrations were near the lower limit of the concentration range and therefore, just above the limit of detection for the analytical procedure. If these three points are neglected, the standard error of estimate for the bromide-specific conductance relationship decreases from 33.7 to 16.7 percent, and the resultant equation is

$$BR = 3.24 \times 10^{-8}(\text{SPCOND})^{2.50}. \quad (5)$$

The constant in equation 5 was adjusted from the regression-analysis value of  $3.20 \times 10^{-8}$  to  $3.24 \times 10^{-8}$  using the nonparametric correction of Duan (1983). If equation 5 is used with equations 2 and 3 to predict the brominated THMFP, then the standard error estimate is 24.6 percent of the mean.

The standard errors of estimate for predicting the brominated THM'S using estimated values of the bromide concentration are two to three times larger than the standard errors for predicting the total THM formation potential. These larger errors result from the large errors in the bromide-specific conductance relationship (equations 4 and 5). Intuitively, we might expect some relationship between the bromide concentration and the specific conductance, but a direct relationship may not be justified for all flow conditions. Also, the fact that many of the bromide concentrations are near the limit of detection of the analytical procedure probably contributes to the large errors in equations 4 and 5. Therefore, results from these equations should be used only as qualitative indicators of the brominated THM's that will be formed when Kentucky River water is chlorinated.

#### Flow Conditions in the Kentucky River for the Study Period

There are 14 locks and dams on the Kentucky River (White and others, 1987). These locks and dams maintain a minimum water depth of 1.8 m from a point just downstream of the confluence of the North, Middle, and South Forks of the Kentucky River to the mouth at Carrollton (fig. 1). This system is operated seasonally for commercial and recreational traffic (White and others, 1987).

Water discharges at Lock 10 for the time period of the THM study ranged from 5.41 m<sup>3</sup>/s for the 10/88 sample time to 1,450 m<sup>3</sup>/s for the 2/89 sample time. Water discharges for each of the sample times are presented in table 2. Also presented in table 2 are the percentages of the historical flows at Lock 10 that were greater than or equal to the observed flows for each month. These percentages were determined from monthly flow duration data (Quinones and others, 1980). The flow of 1,030 m<sup>3</sup>/s in 6/89 has been equaled or exceeded only 0.23 percent of the time. Conversely, the minimum flow in 10/88 during the Midwestern drought has been equaled or

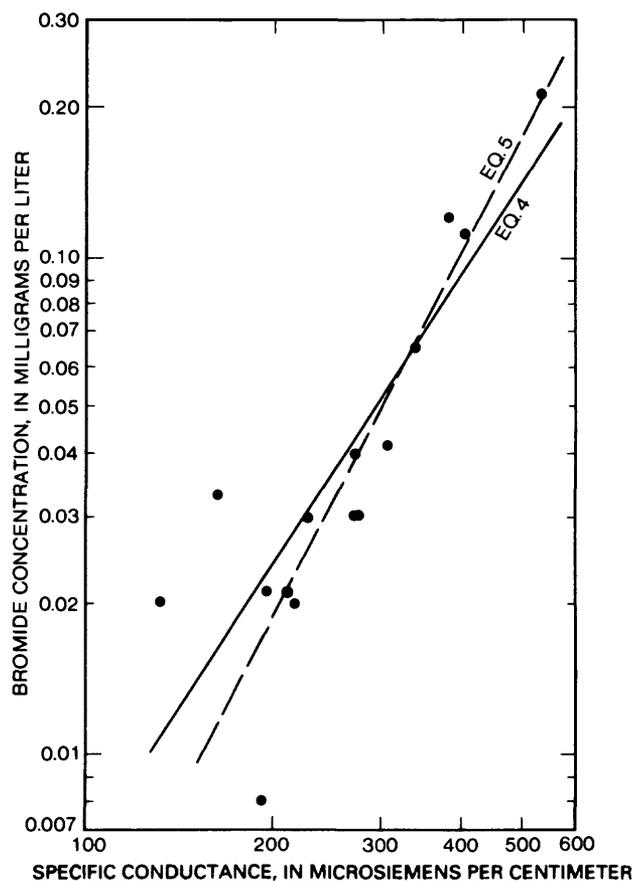


Figure 6.--Bromide concentration as a function of the specific conductance.

exceeded 95.8 percent of the time. The maximum flow during the floods of 2/89 has been equaled or exceeded only 0.83 percent of the time. The water discharges in table 2 reflect the dry conditions of the summer and fall of 1988 and the wetter-than-normal conditions in 1989.

The specific conductance of a river usually decreases as the water discharge increases. Because an approximate relationship between the bromide concentration and the specific conductance was determined for the Kentucky River at Lock 10, some dependence of the

formation of the brominated THM's on discharge was expected.

The maximum concentration of the brominated THM's was obtained for the 10/88 sample water which had the largest bromide concentration (0.21 mg/L) of all the waters. The water discharge for this sample time was the minimum observed during the study (table 2). Conversely, the minimum concentration of the brominated THM's was obtained for the 6/89 water which had the smallest measurable bromide concentration (0.008 mg/L) of all the sample waters. Two other waters (1/90 and 2/90) had bromide concentrations less than the

Table 2.--Water discharges and flow duration percentages for the study period

[m<sup>3</sup>/s = cubic meters per second]

Date (Month/year)	Water discharge (m <sup>3</sup> /s)	Percentage of flows greater than or equal to (percent)
7/88	9.88	90.0
10/88	5.41	95.8
1/89	617	9.2
2/89	1,450	0.83
3/89	148	72.0
4/89	149	54.5
5/89	183	30.0
6/89	1,030	0.23
7/89	182	2.3
8/89	73.1	15.5
9/89	396	1.3
10/89	351	1.3
11/89	138	21.0
12/89	52.1	68.5
1/90	283	30.0
2/90	1,180	2.1
3/90	170	66.0

detection limit of 0.005 mg/L, and the concentrations of brominated THM's formed for these waters were similar to those for the 6/89 water. The water discharge for 6/89 was large, but it was not the largest observed (table 2). It did, however, follow a period of sustained relatively high discharges. Discharges for 1/90 and 2/90 also were relatively high. These observations indicate that the formation of the brominated THM's is likely to be inversely dependent on the water discharge, with the antecedent flow conditions also having some influence.

A qualitative relationship also was observed between the THMFP and the water discharge. This relation results from the effect of discharge on the DOC in the river, which is the precursor for the THM formation, and the flushing effect (Thurman, 1985). As the discharge increases, the DOC also increases, even though lower DOC concentrations might

be expected because of dilution by the increased flow. The exact source of this DOC is unknown, but possible sources are runoff into the river from the surrounding land surfaces and the bottom sediment interstitial waters which have larger DOC concentrations than the overlying river water (Thurman, 1985).

Water discharges for the study period and the minimum and maximum THMFP values for each sample water are presented in table 3. Little can be inferred from the 7/88 and 10/88 data because of the three-month interval between the samples. The other data, however, generally indicate that when the discharge increases, the THMFP also increases. There are some exceptions. Between 7/89 and 8/89, the water discharge decreased but the THMFP increased. This increase in the THMFP may have occurred because the vegetation was actively growing at this time, and vegetation is a source of DOC. Between 1/90

Table 3.--Water discharges and minimum and maximum trihalomethane formation potentials for the study period

[m<sup>3</sup>/s = cubic meters per second; µg/L = micrograms per liter]

Date (Month/year)	Water discharge (m <sup>3</sup> /s)	Trihalomethane formation potential	
		Minimum (µg/L)	Maximum (µg/L)
7/88	9.88	127	322
10/88	5.41	203	447
1/89	617	81.2	228
2/89	1,450	152	393
3/89	148	80.6	214
4/89	149	80.4	195
5/89	183	91.6	225
6/89	1,030	144	369
7/89	182	118	353
8/89	73.1	217	478
9/89	396.	264	731
10/89	351	142	385
11/89	138	124	360
12/89	52.1	59.7	160
1/90	283	180	501
2/90	1,180	117	319
3/90	170	74.6	181

and 2/90, the discharge increased more than four fold; however, the THMFP decreased. This was during the winter when the production of DOC is minimum, and thus, the supply may have been limited.

This analysis of the effect of discharge on the THMFP through its effect on the DOC should be considered qualitative for two reasons. First, the analysis is based on monthly samples, and variations in both the discharge and the DOC likely occurred between the monthly sample times. Second, the analysis assumes that the characteristics of the DOC and its THMFP were constant during the period of the study. This assumption may not be completely valid because the DOC, as it is produced, is subject to bacterial degradation. The most-easily degraded compounds are likely to be degraded first, and because the degradation and the production processes are temperature dependent, both the quantity and

the character of the DOC will vary seasonally. It was established previously (equation 1) that the THMFP depended on the DOC concentration, and while not considered in the present study, it seems likely that the THMFP would also depend on the characteristics of the DOC.

## SUMMARY AND CONCLUSIONS

Trihalomethane compounds are chlorinated and brominated derivatives of methane that are formed when a natural water is disinfected with free chlorine to produce drinking water. These compounds result when the free chlorine used for disinfection reacts with the dissolved organic carbon of the water. Control of the formation of these compounds is necessary because of possible health effects from their ingestion.

The trihalomethane formation potential of water from the Kentucky River was determined for the period from July of 1988 through March of 1990. Multiple-linear regression analysis of the experimental data indicated that the trihalomethane formation potential was strongly dependent on the pH and dissolved organic carbon concentration and was only slightly dependent on the initial free-chlorine concentration. The equation resulting from the regression analysis predicted the experimental trihalomethane formation potential with a standard error of estimate of 9.18 percent of the mean.

The percentages by weight of the total trihalomethane compounds that were brominated ranged from 4.17 to 61.8 and averaged 20.6 percent. Multiple-linear regression analysis of the experimental data indicated that the brominated trihalomethane formation potential was strongly dependent on the bromide concentration, was also dependent on the pH and the dissolved organic carbon concentration, but was only slightly dependent on the initial free-chlorine concentration. The equation resulting from the regression analysis predicted the experimental brominated trihalomethane formation potential with a standard error of estimate of 12.5 percent of the mean.

The dissolved organic carbon concentration of the sample waters could be predicted from the ultraviolet absorbance at 254 nanometers with a standard error of estimate of 8.84 percent of the mean. Such a relationship permits replacing the relatively sophisticated laboratory analysis for dissolved organic carbon with the simple measurement of the ultraviolet absorbance. Using values of the dissolved organic carbon concentration calculated from this relationship, the multiple-linear regression analysis equation predicted the experimental trihalomethane formation potential with a standard error of estimate of 12.9 percent of the mean.

An approximate relationship between bromide concentration and specific conductance was determined for the sample waters of

the Kentucky River. This relationship had a standard error of estimate of 33.7 percent of the mean, and permitted replacing the relatively sophisticated laboratory analysis for bromide with the simple measurement of the specific conductance. Using values of the bromide concentration calculated from this relationship, the multiple-linear regression analysis equation predicted the experimental brominated trihalomethane formation potential with a standard error of estimate of 33.8 percent of the mean. Thus, errors in the bromide-specific conductance relationship limit this procedure to qualitative estimates of the brominated trihalomethane formation potential. Some of this error is because several of the bromide concentrations were near the limit of detection of the analytical procedure. This bromide-specific conductance relationship is specific for the Kentucky River for the time period of this study.

The experimental results indicated qualitatively that the formation of the brominated compounds was inversely dependent on the water discharge and that previous flow conditions also had some influence. Conversely, the results indicated that the total trihalomethane formation potential increased as the discharge increased, presumably because of the flushing of dissolved organic carbon into the system. Both of these observations were inferred from monthly data, therefore, they should be considered as qualitative only.

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