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Use of Multiple Regression Analysis for Predicting Trihalomethane Formation in Water Supply

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Trihalomethanes represent between 5 and 20% of the total chlorinated products formed during the chlorination process in water treatment. Trihalomethanes are carcinogenic in nature and consequently their presence in drinking water has raised much concern both at national and international levels. The water quality data was collected for Mumbai water supply for the concentrations of individual species of trihalomethanes, chloroform, bromodichloromethane, dibromochloromethane and bromoform in finished water at the outlet of treatment process and master balancing reservoir. A multiple regression model for chloroform formation with respect to pH, turbidity and total organic carbon was generated for predicting trihalomethanes in the finished water at the outlet before leaving the treatment plant for the consumers, using the data of Panjrapur, Bhandup, Tulsi and Vehar treatment plants. In general this model was found to give acceptable fits. Overall 80% of the predicted values are within the 95% confidence interval.

Key Words: Regression, Analysis, Formation, Trihalomethane, Water.

INTRODUCTION

Chlorination is the most widely used technique for disinfection of drinking water. In 1974 Rook showed that trihalomethanes (THMs) are formed as a result of chlorination of natural water. The formation of THMs in drinking water results from the reaction of chlorine with naturally occurring organic materials, principally humic and fulvic acids[1]. The THMs formed are chloroform ($CHCl_3$), bromodichloromethane (BDCM) ($CHBrCl_2$), dibromochloromethane (DBCM) ($CHBr_2Cl$) and bromoform ($CHBr_3$).

THMs levels at low micrograms per litre concentrations have been reported in the nation's drinking water in India[2,3]. The presence of these compounds in water are linked with the occurrence of human cancer in many instances[4]. Jimenz *et al.*[5] have confirmed that between 5 and 20% of the total chlorinated products formed during chlorination are THMs. There is a national and international concern over the presence of these compounds in potable water[6] (Table-1). The concentrations of THMs, *e.g.*, chloroform, DBCM, BDCM and bromoform for Mumbai water supply were monitored[3] in September 1995 to August 1996. The data has been used to develop a multiple regression model for chloroform formation with respect to other dependent parameters for predicting the THMs in the finished water at the outlet of treatment plant.

TABLE-1
WHO GUIDELINE VALUES FOR TRIHALOMETHANES IN DRINKING WATER (1996)

Disinfectant byproducts	Guideline value ($\mu g\ L^{-1}$)	Remarks
Trihalomethanes	—	The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1
Bromoform	100	
Dibromochloromethane	100	
Bromodichloromethane	60[a]	For excess lifetime cancer risk of 10^{-5}
Chloroform	200[a]	For excess lifetime cancer risk of 10^{-5}

[a]For substances that are considered to be carcinogenic.

EXPERIMENTAL

Sample locations, collection and preservation

Water samples were collected from Bhandup, Panjrapur, Tulsi and Vehar treatment plants in Mumbai from their pre-identified locations and of six representative service reservoirs Bhandarwada, Borivali, Ghatkopar, Malabar, Trombay and Worli. All the treatment plants follow the conventional process and major features include prechlorination, coagulation, flocculation, sedimentation, gravity sand filtration and postchlorination. Two samples, one at the intake point after prechlorination, and the other at the final water discharge point after postchlorination were collected from each treatment plant for analysing THM formation potential (TFP). The reservoir samples were collected after chlorination at the outlets before supply to the consumers. Samples were collected during post-monsoon-I (1995), post-monsoon-II (1996), winter (1995) and summer (1996) seasons. The water samples were collected with minimum aeration and in especially available containers designed for volatile organics to minimize the loss of THMs during transit. Blanks and samples, collected at a given site (sample set) were stored together in a protected area known to be free from contamination. For each sampling site a duplicate set of samples were collected. Samples were analyzed within 14 days of collection.

Procedure

Liquid-liquid extraction method followed by qualitative and quantitative estimation by gas chromatograph (GC) equipped with Ni^{63} electron capture detector (ECD) has been used for the determination of THMs in aqueous samples. Vials of 24 mL capacity were used for the extraction of the THMs. Standards along with samples were placed in sample storage vials and identical procedures followed for preservation and transfer to the extraction vessel. The use of same lots of vessels for sample and standard extraction is mandatory. Carefully pour sample (10 mL) into sample vial, add 2 mL of *n*-hexane and seal with a TFE-faced septum, and shake vigorously for 1 min. Let stand until phases separate (60 s). Analyze sample by injecting 1 μL of the upper (organic) phase into GC-ECD. The minimum detection limit of the method for chloroform, BDCM, DBCM and bromoform and range of linearity are reported in the Table-2.

TABLE-2
MINIMUM DETECTION LIMITS AND RANGE OF LINEARITY OF TRIHALOMETHANES

Compounds	Minimum detection limits ($ng\ L^{-1}$)	Range of linearity
Chloroform	45	45 ngL^{-1} to 880 μgL^{-1}
Bromodichloromethane	20	20 ngL^{-1} to 900 μgL^{-1}
Dibromochloromethane	65	65 ngL^{-1} to 900 μgL^{-1}
Bromoform	100	100 ngL^{-1} to 1000 μgL^{-1}

The percentage recovery of the extraction and analysis procedure was established by analyzing replicate samples of known THMs concentration under identical conditions. The quality assurance/quality control (QA/QC) in the form of percentage recovery, standard deviation and relative standard deviation of the extraction process were established for all the four THMs at the concentration of 200 μL^{-1} and are reported in Table-3.

TABLE-3
QUALITY ASSURANCE AND QUALITY CONTROL DATA FOR TRIHALOMETHANES ESTIMATIONS

Parameter	Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform
RSD	2.93	0.23	0.15	1.11
SD	0.90	0.05	0.05	0.33
Recovery (%)	98.00	84.00	96.00	97.00

Total organic carbon (TOC) concentrations in the samples were determined using a TOC analyser of Ionics 1555B. Typical data including water temperature, pH, turbidity, chlorine dose and free residual chlorine were collected for all the finished water samples.

Data Set

The variables examined in the present work were pH, turbidity and TOC. TOC was included in the model for limited sites only, since the results in other cases were not reliable. The concentrations of total THMs (TTHMs) are expressed in μgL^{-1}. The individual species of THMs concentrations, chloroform, DBCM, BDCM, pH, turbidity and TOC values used were of the final water samples of Bhandup, Panjrapur, Tulsi and Vehar treatment plants of three different seasons, *i.e.*, post-monsoon, winter and summer collected during 1995–96. Bromoform was not included in the data due its concentration below not detectable level (NDL).

Data Analysis

The variables were tested for normality and data transformations, and applied to approximate a normal distribution[7]. The inter relationships between the chemical variables were examined by calculating the Pearson's correlation coefficient. The multiple regression analysis was applied using statistical software SPSS version 6.0. The level of significance for conclusion of a variable was 0.05.

The *F*-criterion based on the sum of squares due to regression (SSREG) over the sum of squares for error divided by the respective degrees of freedom (S_e^2) was used to eliminate statistically insignificant variable[7].

RESULTS AND DISCUSSION

Correlation between THMs and pH: The correlation between the pH and formation levels of chloroform, DBCM and BDCM were studied. After removal of suspected outliers it was found that the treated water pH had a positive correlation

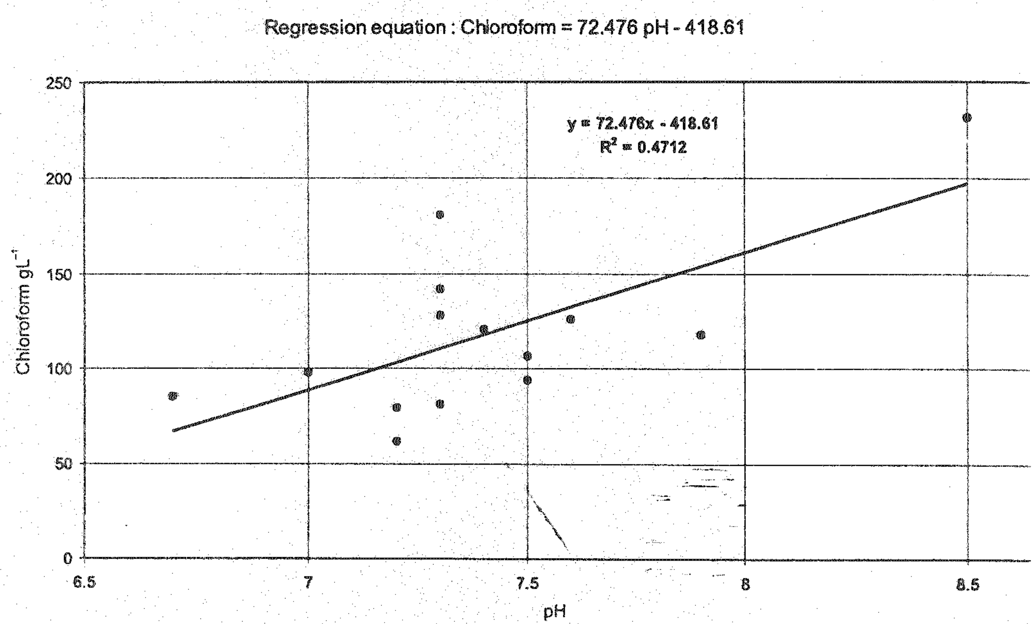

Fig. 1. Relationship between chloroform and pH

with chloroform (Pearson's correlation coefficient $r = 0.6865, p = 0.007$) (Fig. 1). A similar positive correlation was observed between pH and BDCM (Fig. 2) ($r = 0.6365$; $p = 0.035$), and pH and DBCM (Fig. 3) ($r = 0.7428$, $p = 0.004$). The positive values of correlation coefficients obtained indicate that pH has a positive linear relationship with chloroform, BDCM and DBCM. In all the cases a high value of pH was accompanied with a high value of the three main constituents of THMs. The inter relationship between pH and TFP was also studied (Fig. 4). After removal of outliers the correlation between pH and TFP was found to be $r = 0.599$; $p = 0.003$. The value indicates that a positive linear relationship exists between pH and TFP.

Regression Analysis: On the basis of the observed results the following linear regression equations were established:

(i) Chloroform = 72.476 pH – 418.61
(ii) BDCM = 4.357 pH – 27.067
(iii) DBCM = 13.240 pH – 88.816
(iv) TFP potential = 72.503 pH – 402.33

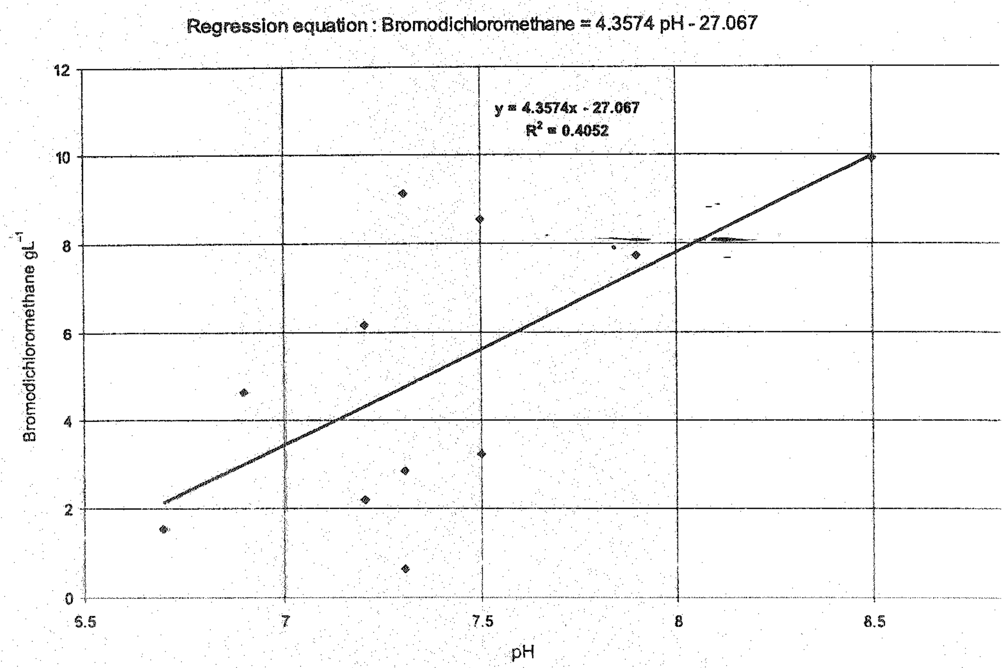

Fig. 2. Relationshp between bromodichloromethane and pH

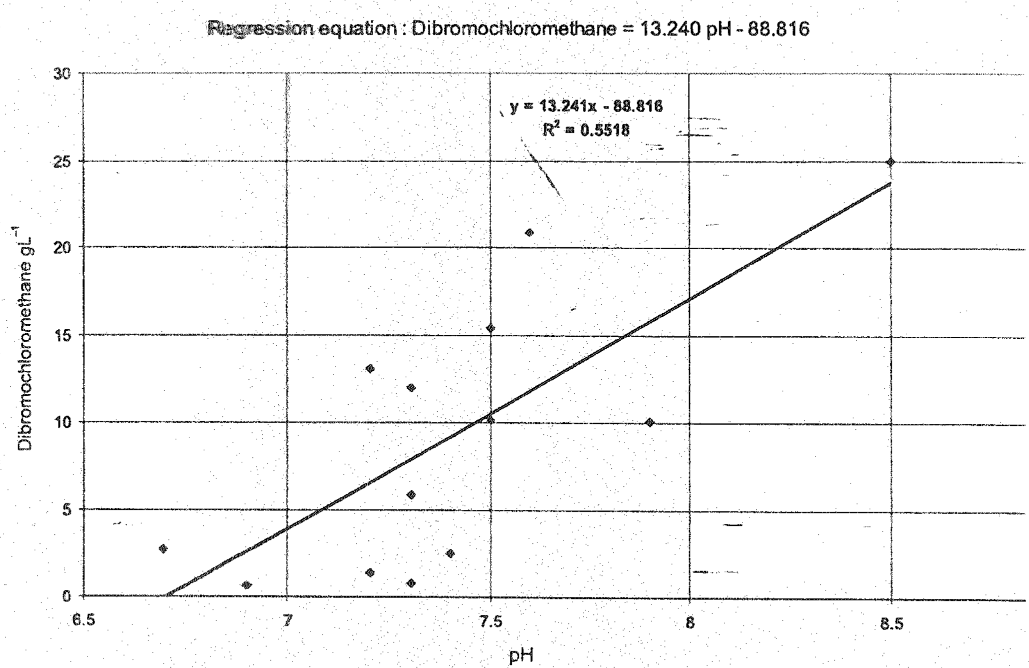

Fig. 3. Relationship between dibromochloromethane and pH

These equations derived from the available water quality data suggest that the formation of THMs is more in alkaline pH (7.0).

Correlation between chloroform, TOC and turbidity

The corelation between TOC, chloroform and turbidity for ~~postmonsoon~~ and winter 95 data was studied for the limited set of values to establish the regression equation. This set of values suggests a positive linear relationship between chloro-

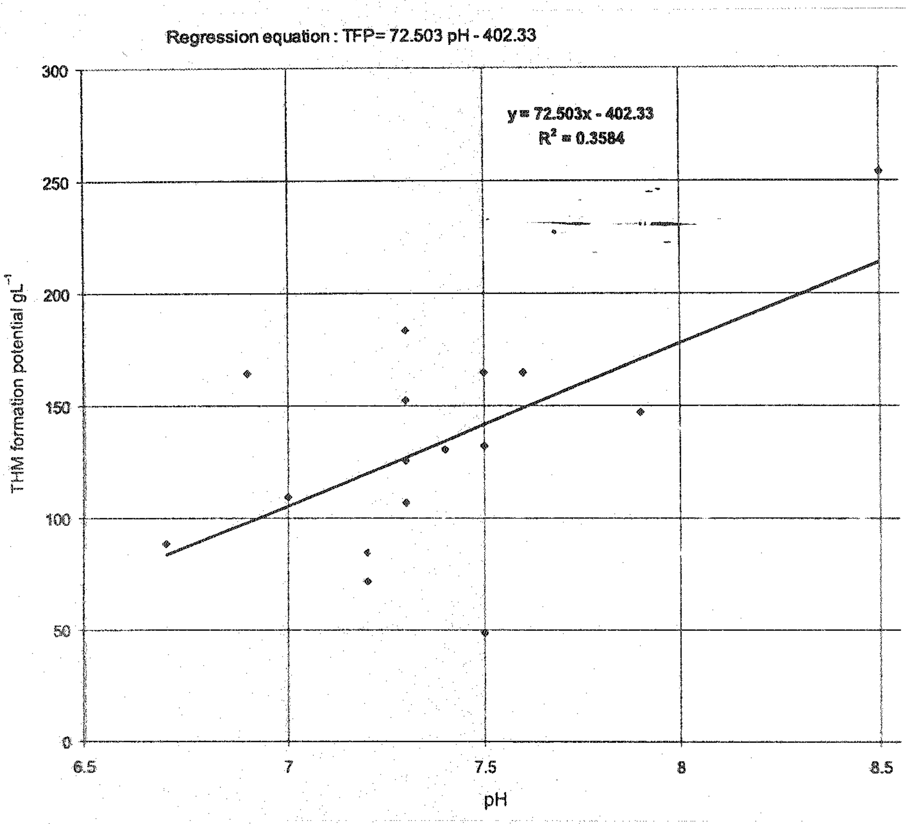

Fig. 4. Relationship between THM formation potential and pH

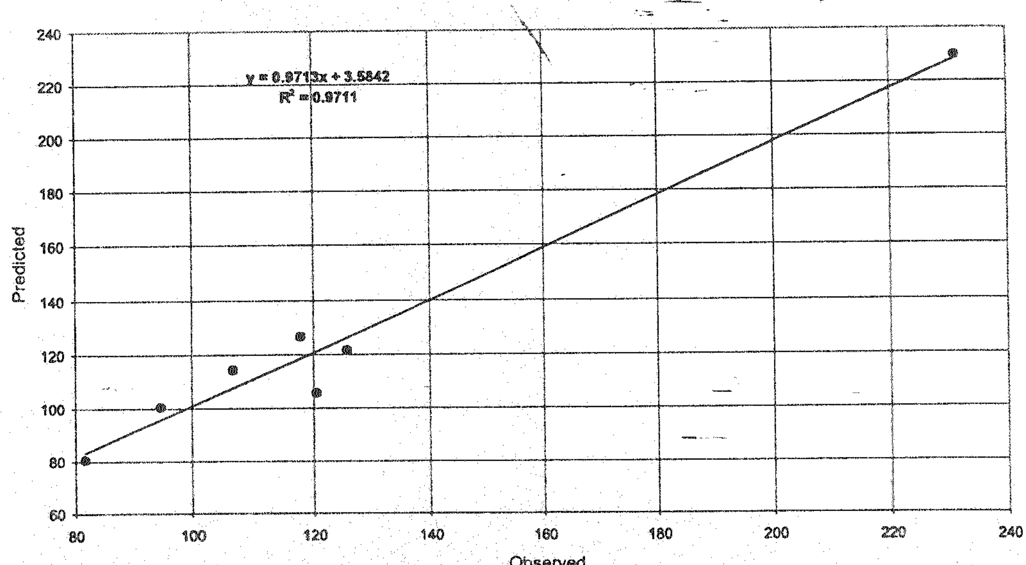

Fig. 5. Observed and predicted chloroform levels (μgL^{-1})

form, TOC and turbidity. The relationship between observed and predicted chloroform levels is shown in Fig. 5. The following regression equation has been derived.

$$\text{Chloroform} = 24.185\ \text{TOC}^* + 76.366\ \text{turbidity}^* - 8.254$$

The developed equation may be applicable to identical set of conditions for a water supply.

Conclusion

Water quality data collected for the finished water supplied by Bhandup, Panjrapur, Tulsi and Vehar treatment plants for the levels of chloroform, BDCM, DBCM and bromoform and other dependable variables, *viz.*, pH and TOC, were used to generate a multiple regression model in predicting the THMs concentrations in the final water before leaving the plant. The model has been found satisfactory with 80% of the predicted values within the 95% confidence interval. The complexity of the trihalomethanes formation reaction makes it difficult to develop it as a universally applicable model. The model can be applicable to other field data only if the values of dependent variables fall within the minimum and the maximum levels of values used in the model developed. It recommends further studies involving large water quality data for dependent variables to develop a widely acceptable model in predicting trihalomethanes formation on chlorination.

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*Turbidity and TOC values were taken from the treated water samples.