Study of Presence of Trihalomethanes in Chlorinated Drinking Water of Bhopal City

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ABSTRACT
Trihalomethanes have many adverse health effects. Chlorinated drinking water is the largest source of trihalomethanes (THMs) for human exposure. The experiment was conducted to study the presence of THMs in Chlorinated drinking water of WTPs (water treatment plants) of Bhopal city. For this experiment Perkin Elmer clarus 500 gas chromatography – Mass Spectroscopy instrument was used. The key findings emerge that the concentration of THMs was significantly lower than the set acceptable limits of BIS:10500 (2012) and WHO Standard.

Keywords: Water treatment plant, Chloroform, Dichlorobromomethane, Dibromochloromethane, Bromoform, Natural organic matter

INTRODUCTION
Water disinfection by the action of oxidation with chlorine known as chlorination is a global practice for reducing health hazards caused by pathogenic growth in drinking water. In chlorination of water along with its beneficial disinfection property, various classes of harmful by-products such as trihalomethanes are also produced. These substances carry mutagenic and cancerogenic effects (Rook, 1974). The mainly important structural development factors for THMs are the rate of formation increase as a function of the concentration of chlorine and pH, humic acid, temperature and the bromide ion. In nature contains humus organic compounds. Natural organic matters (NOMs) in surface waters, including humus and fulvic acids, mostly result from decomposition of substances secreted from algae and other aquatic organisms as well as human activities (industrial, city sewage, agricultural waste waters, and trash disposal secretions (Alicia, C., 2000 & Bodzek, M. 2002).
Trihalomethanes development in drinking water depends on operational procedures implemented in water treatment plants (WTP), such as chlorine quantity, contact time between chlorine and pH, temperature, organic matter, and others (Navalon et al., 2008 & Sadiq et al., 2004). THMs are produced when free available chlorine reacts with natural organic matter in raw water when the water is being treated with disinfection (Rook, 1974 & Bellar et al., 1974).

More than 780 types of disinfection by-products (DBPs) are generate as a product of reaction of additive disinfectants including chloric compounds in water distillation systems (Atarchi et al., 1999). Dissolved Organic Matter (DOM) and Natural Organic Matter (NOM) present in water sources are the primary precursor for the formation of harmful by products in drinking water (Fathiyah et al., 2016) conventional treatment systems reduce THM precursor concentrations in water before disinfection using flocculation, activated carbon, coagulation and membrane filtration processes, in the absence of such pretreatment processes greater THM formation is observed (Reckhow & Singer, 1984). These water treatment processes can only remove 30% of the precursors of THMs (Ramanvandi et al., 2015). Increased contact with chlorine and high concentrations of chlorine, natural occurrence and source of bromide in surface water and natural organic matter in water are the prominent factors leading to the formation of these compounds. Rise in temperature increases reaction rate which leads to increase in production of THMs. Chemicals excessively used by treatment plants during rainy season such as chlorine, Poly Aluminium chloride (AlCl₃), Maxfloc T etc to reduce the turbidity of raw water, generate residual chlorine which reacts with natural organic matter as well as other chemicals leading to the formations of THMs. If residual chlorine present, the concentrations of THMs depended on the contact time between organics and residual chlorine. The removal of natural organic matter in water decreases the concentration of THMs, as natural organic matter act as precursor for the THMs formation More than simply drinking THMs containing water ,Skin contact with THMs by the means of Dermal absorption and inhalation can cause higher blood THM concentration [EHP 113:863–870]. Formation of THMs in conventional water treatment systems has been studied extensively to help suppliers comply with national drinking water standards (Serodes et al., 2003).

Madhya Pradesh Pollution Control Board has performed a study during the year 2017-18 to assess whether the THMs (Chloroform, Dichlorobromomethane (DCBM), Dibromochloromethane (DBCM) and bromoform) in chlorinated drinking water being supplied to the localities of Bhopal city from different filtration plants are within the BIS 10500: 2012 norms as depicted in 1.1. For this study samples were collected from different parts of the Municipal Corporation representing main distribution network of water supply of Bhopal city.

MATERIALS AND METHODS

Study Area:
Bhopal is the capital of Madhya Pradesh also known as the City of Lakes for its natural & artificial lakes. Bhopal is situated in the central part of India between 23.25° N, 77.41° E, and is in just north of the Vindhya mountain ranges. The city is surrounded by Idgah hills, Shyamala hills in the northern region and Katara hills in southern region. City's geography has two lakes, namely.There are two raw water water sources to provide drinking water to entire Bhopal city that is Upper Lake and kolar dam.

The Upper Lake is raw water source for 8 water treatment plants of different capacities. The lake is spread over 6.25 sq.km area. Discharge of wastewater into the lake and direct inflow of surface runoff are prevented to protect the water quality of the lake. Uptake of water from the lake is about 146 MLD for these 8 treatment plants located at different places in the city.
Raw water supply from Kolar dam to Kolar WTP is 162 MLD. The dam on Kolar River was constructed near Birpur village, which is about 32 km from Bhopal city. The capacity of the dam is 265 MCM and present water supply to city from this treatment plant is 153 MLD.

Total 11 sampling locations were selected for the study. Measurement of free residual chlorine was carried out at field and analysis of THMs (CHCl₃, CHCl₂Br, CHClBr₂ and CHBr₃) was carried out by using Standard Methods for the Examination of Water and Waste Water 23rd Edition (2017), American Public Health Association (APHA).

**Sample Handling:**
Sample collection and storage was performed using standard procedure (APHA (2017). Samples collected as:
1) Raw water
2) Treated water
3) Finish water (user end)
125 ml sample have been collected in Amber glass bottles along with glass stoppers to avoid direct contact with sunlight. Samples were collected with minimum turbulence and filled completely to avoid loss of THMs already present.
Collected samples were transported to the laboratory in ice box (Temp. ≤ 6°C), extracted and analysed. Analysis was done as soon as possible because significant degradation can occur in unpreserved samples within 24 hrs.
Liquid-Liquid extraction technique using separatory funnel was performed for sample preparation. 40 ml sample vigorously shaken with 5ml n-hexane in separatory funnel. Two different layers of solvent and sample were formed and 2 ml of solvent layer was separated in a pre-cleaned vial ensuring zero moisture content.

**Analysis:**

THMs analysis method has been developed and standardized at Centre Laboratory, MPPCB. Analysis was performed as per the Standard Method (APHA 2017) using Perkin Elmer Clarus 500 Gas Chromatography instrument.

Gas Chromatography Instrument’s operating condition during analysis is detailed below:

- Column- Elit-608,
- 30m x 0.32 mm x 0.5 μm (film thickness),
- Detector- Electron Capture,
- Carrier Gas- Nitrogen,
- Flow rate- 1 ml/min,
- Makeup flow for detector- Nitrogen 30 ml/min,
- Injector Temperature- 200°C,
- Detector Temperature-290°C,
- Oven Temperature-35-180°C.

**Standard**

As per the guidelines of **BIS:10500 (2012)** the maximum acceptable limits for trihalomethanes in portable water are,

| Trihalomethanes                  | Acceptable limit |
|----------------------------------|------------------|
| Bromoform , µg/l , max           | 100              |
| Tribromochloromethane µg/l , max | 100              |
| Trichlorobromomethane , µg/l,max | 60               |
| Chloroform , µg/l, max           | 200              |

**OBSERVATION I.**

**Concentration of Chloroform, µg/l**

| Location                              | Sample Type | Raw | Treated | Reservoir | User End | RO Water |
|---------------------------------------|-------------|-----|---------|-----------|----------|----------|
| WTP Idghal Hills Bhopal (3 MGD)       | Raw         | 0   | 21.89   | 18.16     | 6.01     | 0        |
| WTP Idghal Hills Bhopal (2 MGD)       | Treated     | 0   | 24.04   | 13.90     | 12.05    | 0        |
| WTP Shyamla Hills Bhopal (4.5 MGD)    | Reservoir   | 0   | 3.23    | 20.61     | 3.43     | 0        |
| WTP Shyamla Hills Bhopal (2 MGD)      | User End    | 0   | 9.57    | 23.03     | 28.6     | 0        |
| WTP NewVidhanSabha Bhopal(5MGD)       | RO Water    | 0   | 7.45    | 22.01     | 10.67    | 0        |
| WTP Bairagarh Bhopal (2 MGD)          | Raw         | 0   | 4.61    | 13.92     | 48.74    | 0        |
| WTP Bairagarh Bhopal (1 MGD)          | Treated     | 0   | 10.84   | 25.61     | 11.76    | 0        |
| WTP Kolar Bhopal (34 MGD)             | Reservoir   | 0   | 3.84    | 10.7      | 11.76    | 0        |
| WTP Badal Mahal Bhopal (1 MGD)        | User End    | 0   | 1.83    | 23.43     | 30.11    | 0        |
| WTP AKVN Mandideep (3 MGD)            | RO Water    | 0   | 12.31   | 16.23     | 20.62    | 0        |
| WTP Narmada,Shahaganj (184 MLD)       | Raw         | 0   | 15.33   | 14.01     | 35.53    | 0        |

WTP : water treatment plant
II. Concentration of Dichlorobromomethane, µg/l

| Location                          | Sample Type | Raw | Treated | Reservoir | User End | RO Water |
|----------------------------------|-------------|-----|---------|-----------|----------|----------|
| WTP Igdah Hills Bhopal (3 MGD)   |             | 0   | 0.67    | 2.99      | 1.56     | 0        |
| WTP Igdah Hills Bhopal (2 MGD)   |             | 0   | 0.59    | 7.64      | 2.94     | 0        |
| WTP Shyamla Hills Bhopal (4.5 MGD) |            | 0   | 0       | 2.52      | 1.93     | 0        |
| WTP Shyamla Hills Bhopal (2 MGD) |             | 0   | 0.18    | 4.07      | 4.77     | 0        |
| WTP NewVidhanSabha Bhopal (5MGD) |             | 0   | 3.92    | 15.57     | 1.25     | 0        |
| WTP Bairagarh Bhopal (2 MGD)     |             | 0   | 0.13    | 0         | 6.19     | 0        |
| WTP Bairagarh Bhopal (1 MGD)     |             | 0   | 3.25    | 1.88      | 7.18     | 0        |
| WTP Kolar Bhopal (34 MGD)        |             | 0   | 1.49    | 2.80      | 1.91     | 0        |
| WTP Badal Mahal Bhopal (1 MGD)   |             | 0   | 3.86    | 1.93      | 2.79     | 0        |
| WTP AKVN Mandideep (3 MGD)       |             | 0   | 8.83    | 3.44      | 0.51     | 0        |
| WTP Narmada, Shahaganj (184 MLD) |             | 0   | 4.27    | 4.30      | 5.13     | 0        |
III. Concentration of Dibromochloromethane, µg/l

| Location                                      | Sample Type | Raw | Treated | Reservoir | User End | RO Water |
|------------------------------------------------|-------------|-----|---------|-----------|----------|----------|
| WTP Idgah Hills Bhopal (3 MGD)                |             | 0   | 0.68    | 4.75      | 0.33     | 0        |
| WTP Idgah Hills Bhopal (2 MGD)                |             | 0   | 23.91   | 19.14     | 0.43     | 0        |
| WTP Shyamla Hills Bhopal (4.5 MGD)            |             | 0   | 1.55    | 0.19      | 1.98     | 0        |
| WTP Shyamla Hills Bhopal (2 MGD)              |             | 0   | 4.28    | 13.61     | 4.32     | 0        |
| WTP New Vidhan Sabha Bhopal (5 MGD)           |             | 0   | 2.05    | 0.05      | 0.48     | 0        |
| WTP Bairagarh Bhopal (2 MGD)                  |             | 0   | 0       | 0         | 25.34    | 0        |
| WTP Bairagarh Bhopal (1 MGD)                  |             | 0   | 23.26   | 1.15      | 0.31     | 0        |
| WTP Kolar Bhopal (34 MGD)                     |             | 0   | 0.06    | 1.81      | 26.82    | 0        |
| WTP Badal Mahal Bhopal (1 MGD)                |             | 0   | 20.34   | 26.01     | 1.21     | 0        |
| WTP AKVN Mandideep (3 MGD)                    |             | 0   | 15.48   | 0.36      | 0.31     | 0        |
| WTP Narmada Shahaganj (184 MLD)               |             | 0   | 1.61    | 5.53      | 6.18     | 0        |

Graph – III

IV. Concentration of Bromoform, µg/l

| Location                                      | Sample Type | Raw | Treated | Reservoir | User End | RO Water |
|------------------------------------------------|-------------|-----|---------|-----------|----------|----------|
| WTP Idgah Hills Bhopal (3 MGD)                |             | 0   | 1.04    | 0.09      | 0        | 0        |
| WTP Idgah Hills Bhopal (2 MGD)                |             | 0   | 0.06    | 0.28      | 0.34     | 0        |
| WTP Shyamla Hills Bhopal (4.5 MGD)            |             | 0   | 0.11    | 0         | 0        | 0        |
| WTP Shyamla Hills Bhopal (2 MGD)              |             | 0   | 0.17    | 1.01      | 0.15     | 0        |
| WTP New Vidhan Sabha Bhopal (5 MGD)           |             | 0   | 0       | 0.05      | 0.19     | 0        |
| WTP Bairagarh Bhopal (2 MGD)                  |             | 0   | 0       | 0.05      | 0.19     | 0        |
| WTP Bairagarh Bhopal (1 MGD)                  |             | 0   | 0.15    | 0         | 0        | 0        |
| WTP Kolar Bhopal (34 MGD)                     |             | 0   | 0       | 0.89      | 0.34     | 0        |
| WTP Badal Mahal Bhopal (1 MGD)                |             | 0   | 0.23    | 0.15      | 0.35     | 0        |
| WTP AKVN Mandideep (3 MGD)                    |             | 0   | 0.38    | 0.25      | 1.10     | 0        |
| WTP Narmada Shahaganj (184 MLD)               |             | 0   | 0.28    | 0.71      | 0.22     | 0        |
V. Concentration of Residual Chlorine, µg/l

| Location                        | Raw | Treated | Reservoir | User End | RO Water |
|---------------------------------|-----|---------|-----------|----------|----------|
| WTP Idgah Hills Bhopal (3 MGD)  | 0   | 1.77    | 1.37      | 0.82     | 0        |
| WTP Idgah Hills Bhopal (2 MGD)  | 0   | 1.77    | 1.25      | 0.55     | 0        |
| WTP Shyamla Hills Bhopal (4.5 MGD) | 0 | 1.87   | 1.4       | 1        | 0        |
| WTP Shyamla Hills Bhopal (2 MGD) | 0 | 1.82   | 1.32      | 0.9      | 0        |
| WTP New VidhanSabha Bhopal (5MGD) | 0 | 1.62   | 1.2       | 0.75     | 0        |
| WTP Bairagarh Bhopal (2 MGD)    | 0   | 1.45    | 1         | 0.55     | 0        |
| WTP Bairagarh Bhopal (1 MGD)    | 0   | 0.92    | 0.52      | 0.3      | 0        |
| WTP Kolar Bhopal (34 MGD)       | 0   | 1.95    | 1.32      | 0.95     | 0        |
| WTP Badal Mahal Bhopal (1 MGD)  | 0   | 1.52    | 1.2       | 0.8      | 0        |
| WTP AKVN Mandideep (3 MGD)      | 0   | 1.62    | 1.32      | 1        | 0        |
| WTP Narmada,Shahaganj (184 MLD) | 0   | 1.7     | 1.32      | 0.95     | 0        |
The occurrence pattern of THMs compounds in Potable water samples of Bhopal city during 2017-18 is as follow;

**RESULT AND DISCUSSION**

In the present study it was observed that the no concentration of THMs present in raw water of upper lake and kolar dam which indicate that no chlorine is present in water reservoirs which generally depends on the geographical condition as predicted by table I and Fig. I. samples drawn from household RO purification system had zero chloroform concentration, see Table I graph I. Among all the WTPs , Bairagarh Bhopal 2 MGD had highest Concentration of chloroform which was found as 48.74 µg/l. Average Values of chloroform concentration found to be 10.44 µg/l ,18.32 µg/l ,19.93 µg/l in treated, reservoir and user end water samples respectively .

As per the guidelines of BIS: 10500 (2012) the maximum acceptable limit of chloroform in portable water is 200 µg/l.In chlorination technique, oxidation of bromide ions also takes place generating traces of bromine which cause analogous health effects (Rook, 1977). In the present study among all the sampling points highest concentration of bromoform was found to be 1.10 µg/l in Idgah Hills Bhopal (3 MGD) water treatment plant. This treatment plant also had highest concentration of residual chlorine which is 1.95µg/l (see table VI graph VI and table V graph V respectively).

Average concentration of DBCM was found maximum 4.28 µg/l in reservoir, 3.28 µg/l in user end and 2.47µg/l in treated water samples of all the WTP’s of Bhopal city. The average DBCM concentration was found highest 8.47µg/l in Treated water sample and the least 6.15 µg/l in user end water sample. THMs were not present in Raw water samples of Upper Lakes and Kolar Dam. From the obtained data it was also observed that the concentrations of THMs were found maximum during rainy season. Due to the rainfall, enrichment of natural organic matter in the aquatic resources occurs, which may enhance the formation of THMs. The largest source of human exposure to THMs is in from the consumption of chlorinated drinking water.

**CONCLUSION**

From this study, key findings emerge that the concentrations of THMs were significantly lower than the set limits of these compounds in drinking water by guideline value set by BIS, WHO and various environmental organizations. Concentration of chloroform among all the sampling points of water treatment plants is maximum however it is within the limit of BIS:10500 (2012). Observed concentration of DCBM and DBCM in all WTP’s were in traces.

These basic THMs compounds found maximum during the month of June to August as during these months there was active rainfall all around the city, surface water dissolves much more solids and natural organic matter. For removing organic matter Alum coagulation is an effective way . In a
moderately coloured water 50–90 percent of all by product precursors tested are removed by Alum coagulation. The study shows that reverse osmosis method is effective in removal of chlorine since chlorine concentration has not been found in RO water samples. However, significant concentration of Trihalomethanes was found in the treated water sample, water stored in sumps or reservoir and in User End samples indicating the formation of THMS. The concentration of organic chlorine in a public water supply can be minimized by avoiding prechlorination, avoiding higher concentrations of chlorine than are necessary for good disinfection, using combined chlorine rather than free chlorine, maintaining a high pH, and withdrawing from a source with a low concentration of precursor material and a cool temperature.

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REFERENCES
Atarchi, M. F., Chaleshkesh, M. (1999). Risk Evaluation related to Chlorination Method Disinfection for Drinking Water. Annual Journal of Chemical Engineer Department of Esfahan Technical University: 227.
Alicia, C. (2000). DBP formation during the chlorination. JAWWA; 92(6), 76-90.
APHA (2017). Standard Methods for the Examination of Water and Waste Water. 24th Ed. American Public Health Association.
Bellar, T. A, Lichtenberg, J.J., & Kroner, R.C. (1974). The occurrence of organohalides in chlorinated drinking waters. J Am Water Works Assoc. 66(12), 703–6
Bodzek, M. (2002). Pressure driven membranes techniques in the treatment of Water containing THMs. Desalination; 147, 101-7.
Fathiyyah, M.Z., Hassimi, A.H and Siti Rozaimah S.A., (2016). Characterization of Trihalomethanes (THMs) Levels in Surface Water, Domestic and Industrial Wastewater. Journal of Environmental Science and Technology, 9, 268-276.
Navalon,S., Alvaro,M. & Garcia, H. (2008).Carbohydrates as trihalomethanes precursors. Influence of pH and the presence of Cl(-) and Br(-) on trihalomethane formation potential Water Res., 42, pp. 3990-4000
Ramavandi, B., Farjadfard, S., Ardjmand, M. & Dobaradaran, S. (2015). Effect of water quality and operational parameters on trihalomethanes formation potential in Dez River water, Iran. Water Resources and Industry 11, 1–12
Rook, J.J. (1974). Formation of Haloforms During Chlorination of Natural Waters. Water Tymt. Exam., 23, 234.
Rook, J.J. (1977). Chlorination Reactions of Fulvic Acids in Natural Waters. Enuivy. Sci. & Technol., 11(5), 478.
Reckhow, D.A., & Singer, P.C. (1984). The Removal of Organic Halide Precursors by Preozonation and Alum Coagulation. Jour. A WWA, 76(4), 151.
Sadiq, R., & Rodriguez, M.J. (2004). Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review Sci. Total Environ., 321, 21-46
Sérodes, J.B, Rodriguez, M.J., Li, H., & Bouchard, C. (2003). Occurrence of and HAAs in experimental chlorinated waters of the Quebec City area (Canada). Chemosphere 51, 253–263.