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Investigating the Role of Chlorine Dosage and Pipe Material on Spatial and Temporal Variability of Trihalomethanes and Trihaloacetic acids Production in Water Networks

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The safety of drinking water is of paramount global concern, prompting an investigation into the prevalence of Trihalomethanes (THMs) and Trihalo acetic acids (THAAs), two major Chlorination Disinfectant Byproducts (DBPs) within High-Density Polyethylene (HDPE) water distribution networks. This study involved identifying and quantifying these DBPs, followed by evaluating two filtration setups, including Granular Activated Carbon (GAC) and Pack of Sand, filtration media. This research aimed to compare and assess these filtration techniques for DBP removal, accounting for production variations according to chlorine-controlled dosage and pipe material characteristics. Notably, gas chromatography-mass spectrometry (CG-MS(ECD)) was employed for DBP analysis, and laboratory-based distribution models were used. This study contributes valuable insights into the dynamics of THMs and THAAs in water distribution networks, offering guidance for mitigating these DBPs, thereby advancing the goal of providing safer drinking water in such distribution networks.

Keywords: Chlorination Disinfectant Products (DBPs), High-Density Polythene (HDPE), Chlorine Controlled Dosages, Abatement Techniques.

1. Introduction

Water is fundamental for sustaining life, and a sufficient, safe, and accessible supply must be made universally available. Enhancing access to clean drinking water can yield concrete health benefits [1]. Global freshwater distribution is uneven, affecting two billion people in water-stressed countries[2]. The World Health Organization (WHO) defines "safe drinking water" as water that poses no significant health risks throughout its consumption over a person's lifetime. According to the WHO's findings, in the developing world, 80% of all human diseases are attributed to biological or chemical contamination of water[3]. A staggering 2.3 billion people worldwide are exposed to the risk of waterborne illnesses due to the absence of safely managed drinking water services and inadequate sanitation systems[2]. The UNICEF Joint Monitoring Program (2000-2017) reveals limited global progress in water quality, with only a 10% rise in accessible safe drinking water and a 16% increase in managed sanitation services[4]. Urgent research is essential for a thorough understanding of exposure and health effects from contaminant mixtures in drinking water[5]. Global attention has been devoted to the importance of safe potable water, whereas DBP has gained attention worldwide as a serious issue.[6]. In Pakistan, around 30% of all infections and 40% of all deaths are attributed to the poor quality of water. Literature indicates that waterborne diseases account for approximately 0.6-1.44% of the country's Gross Domestic Product (GDP) loss according to[7]. Even though chlorination disinfectant is the most popular technique used to remove impurities in water it has some disadvantages i.e., long-term exposure causes cancer due to the production of DPBs and then this product has bad effects on kidney, liver, and other disabilities as well[8]. The primary causes of DBP development are anthropogenic pollutants, algal organic matter, and natural organic matter[9].

Chlorine and chloramine are widely used for drinking water disinfection due to their effectiveness against waterborne diseases. However, concerns arise from the formation of disinfection byproducts (DBPs), like (THMs) and (THAAs), identified as potential threats due to their teratogenic, carcinogenic, and mutagenic properties since their detection in 1974[10]. The formation of Chlorine DBP is mainly produced due to the presence of natural organic matter, algal organic matter, and anthropogenic contaminants[9]. For determination of chlorine residual which majorly contributes to the production of DBP. Trihalomethanes and halo acetic acids are the most important groups of CDBPs other are hala cetonitrites, haloketones, and chloropicrin. The drinking water distribution system commonly utilizes ductile iron (DI), polyethylene (PE), and stainless steel [11].Chlorine dioxide (ClO2) is gaining favor for its lower THMs and THAAs production, and recent studies show reduced developmental toxicity compared to chlorine, indicating its potential as an eco-friendly water treatment disinfectant[12]. Chlorine's widespread use as a disinfectant stems from its simplicity, cost-effectiveness, and residual disinfection potential, effectively controlling microbial regrowth throughout water distribution networks[13]. Mean concentrations of THM vary across different countries, ranging from zero to 1000mg/L. Due to potential health risks permissible limits have been established in several regions of the world. In Nigeria, the values in treated water samples have been observed to range from zero to 95 mg/L[14]. In the United States, it was shown that finished water included concentrations of up to 18 mg/L of DBPs, while distribution systems exhibited concentrations of up to 22 mg/L of DBPs in distribution networks have been studied[15]. According to[16] the average concentrations of THMs and THAAs in China for the entire treatment period were 19.9mg/L and 3.4mg/L, respectively. This suggests that the concentrations of THMs and THAAs in the water distribution system exhibit regional variability[17]. Chlorination is regulated by the U.S. EPA for disinfection byproducts (DBPs) like THMs and THAAs. A review of 500 major U.S. drinking water plants found mid-ppb levels of THMs and THAAs in chlorinated water[18]. Over the past four decades, additional organic and inorganic compounds, both halogenated and non-halogenated, have been identified as disinfection byproducts alongside THMs and THAAs. To address the health risks posed by (DBPs), countries have revised water quality standards. In the United

States, stage II DBP regulations specify THMs and THAAs with maximum contamination levels (MCLs) below 80 and 60 µg/L, respectively. China's standards (GB5749-2006) also set varying MCLs for THMs and THAAs. The drinking water quality in the twin mega cities of Rawalpindi and Islamabad in Pakistan is found to be compromised for human consumption[19]. This study concluded that only 25% of the population has access to safe drinking water in the entire country. Most of the region is subjected to uncontrolled chlorination by non-technical workers, which may be caused by the excessive formation of THMs in the chlorinated drinking water. However, as stated by[20], there is currently no comprehensive literature review or study conducted to monitor the presence of THMs in the drinking water supplies of the twin cities of Rawalpindi and Islamabad. This lack of research could hinder the establishment of a solid foundation for future investigations. Another finding from the study conducted by[20] is that Islamabad has higher levels of total THMs compared to Rawalpindi. While vital for eradicating pathogens, chlorination leads to unintended DBPs, arising from chemical reactions with organic water compounds[21].In his study[22]observed that the decay parameters of chlorine walls in cement-lined cast iron pipes initially decrease and then increase over time. This suggests that iron corrosion increases with age, leading to higher consumption. However, the study did not include any experimental work or a valid model to support this conclusion. This notion contradicted the findings of the study conducted by[23] which determined that the walls of newly manufactured PVC pipes do not have a substantial impact on chlorine usage.Currently, plastic pipes have emerged as the prevailing material for a wide range of supply networks, mostly because of their exceptional flexibility, corrosion resistance, and jointing capabilities. However, it is important to note that these pipe materials have a significant impact on the manufacture of DBPs[24].Source water characteristics, influenced by geological conditions, watersheds, and bromide concentration, impact DBP formation. Different disinfectants contribute to distinct DBP types, with chlorine forming carbonaceous DBPs (C-DBPs) and chloramine generating nitrogenous DBPs (N-DBPs)[25].The studies conducted by[26] and[27] both observed a significant decline in the levels of free and total chlorine residual in water distribution systems as the duration of residence increased. In the study conducted by[22] a total of 350 pipe sections were examined for experimental work. These pipes were selected based on their age, ranging from fresh, recently installed pipes to older pipes of varying ages. The water source utilized in this study was derived from desalination plants. According to the findings of[22]the decay of chlorine at a pipe can be attributed to two factors: the transportation of masses from the bulk to the surface of the pipe wall, and the chemical reaction occurring with the pipe wall surface. In a study conducted by[28], it was observed that THMs were predominantly present in GI pipes. However, the creation of THAAs remained unaffected by the materials used in the pipes. It is worth noting that the investigation also identified the presence of undesired nitrogenous DBPs.One of the studies suggested that THAAs concentration in the four pipe loop systems was sequenced according following order: HDPE >PP > PVC >GS due to various factors involved[29].One of the other studies found by[30]states that DBPs increase with the increasing diameter of the pipe. Pipe materials play a crucial role in influencing the creation of (DBPs) and biofilms. The heterogeneous nature of biofilms leads to variations in their physical features, such as thickness, surface roughness, and porosity. These differences might have an impact on the transport and penetration of disinfectants[31].Various methods, including GC, LC, and ion exchange chromatography, are used to detect DBPs in water. GC, with detectors like ECD or MS, is suitable for known DBPs, while LC/MS methods are effective for polar and high-molecular-weight DBPs. Total organic halide (TOX) analysis quantifies both known and unknown DBPs[32].A separate investigation conducted by[33] revealed that the development of different DBPs is contingent upon a multitude of important circumstances. The dosage of 1. chlorine. 2. Temperature 3. pH 4. Duration of contact 5. Content of organic matter 6. Water constitution.

The identification of spatial and temporal variations in the production of THMs and THAAs under varying chlorine dosages is essential due to the potential impact on water quality[34].Different pipe materials can influence the formation of disinfection byproducts (DBPs) in drinking water distribution systems[35]. Pipe wall biofilms predominantly consist of microorganisms, corrosion byproducts, and inorganic deposits. Studies indicate that pipe wall biofilms, cultured in filtered water, exhibit a higher potential for THMs generation compared to filtered water alone after 48 hours of reaction at a chlorine concentration of 4 mg/L[35]. Biofilms on pipe walls impact disinfectant transport and reactions, influencing disinfection byproduct (DBP) formation. Studies suggest higher trihalomethanes (THMs) in simulated pipelines than in glass bottles, indicating THM precursor materials on pipe walls. Though initial findings showed no significant difference in haloacetic acids THAAs, subsequent research suggests potential HAA formation in tube wall biofilms. Biofilm-covered pipelines exhibit elevated chlorine consumption and THM production, emphasizing the need to address DBP risks from pipe wall biofilm[36] Understanding how THMs and THAAs vary spatially and temporally helps in optimizing chlorine dosages to mitigate DBP formation. By examining these variations, water treatment plants can tailor disinfection strategies to specific pipe characteristics, reducing the risk of elevated DBP levels[37]. This targeted approach contributes to ensuring compliance with water quality standards and minimizing potential health risks associated with DBPs in the water supply[38]. [13]study on ductile iron pipes revealed higher THMs and THAAs formation linked to DBP precursor matter on the pipe wall. According to[39], an investigation was conducted to examine the seasonal and regional fluctuations in the production of THM and THAAs across three distinct water distributions.

According to[39] an investigation was conducted to examine the seasonal and regional fluctuations in the production of THM and THAAs across three distinct water distributions. Five sampling locations were selected for the collection of samples. Two locations were chosen after filtration and chlorination, while three locations were chosen after the flow of distribution of lines. Gas chromatography equipped with an electron capture detector (GC-ECD) was employed to quantify THM, following the U.S Environmental Protection Agency Method 551.1 with several modifications[10]. The separation of trihalomethanes (THMs) was conducted using a capillary column named BPx50 and The generation of THMs was accomplished in triplicate. According to the findings of[34], it is crucial to take into account seasonal variation for both THM and THAAs when dealing with CDBPs. This consideration should not only be limited to broader seasonal variations but also extend to intra-seasonal variations in the near term. The study was done by[40] aimed to assess the effectiveness and practicality of using GAC adsorption to remove halogenate DBPs during chlorination. The purpose was to validate the novel method of GAC adsorption during chlorination for halogen DBPs removal, as opposed to GAC adsorption before chlorination for Natural Organic Matter (NOM) removal. In their study[40] employed the rapid small-scale column test (RSSCT) as a means to evaluate the effectiveness of a full-scale fixed-bed GAC filter in removing DBPs. The objective of the study conducted by[41] was to assess the effectiveness of pilot and full-scale treatment methods in reducing NOM and limiting the formation of DBPs. The initial choice for treatment involved the utilization of ultrafiltration, specifically employing a hybrid coagulation and submerged ultrafiltration membrane technique to study the removal of NOM.[41] discovered that GAC filtration was more effective than conventional treatment methods (coagulation, sand filtration) in removing NOM. The study compared two approaches and found that GAC filtering removed 23.4% of NOM. Experimental data employing transgenic bacteria, mammalian cell culture lines, and human cell culture lines has led to the suggestion of several biological processes that contribute to the detrimental effects of DBPs[42]. Epidemiological studies have utilized trihalomethanes as a measure of total DBP concentration, however, the connection between various DBPs may vary[42]. Epidemiological studies suggest a potential link between THM exposure and increased bladder cancer risk[43] According to[44]comprehensive case-control research undertaken in the United Kingdom revealed no substantiated indications of diminished semen quality in correlation with the presence of total trihalomethanes (THM), chloroform, or brominated THM in uncontaminated public drinking water.

Despite the generation of these prominent harmful chlorine DBPs in water supply according to the nature of the pipe is characterized and quantified yet there need for a cost-effective technique according to the nature of the pipe medium used. Some of the techniques discussed in[45]like adsorption, air stripping, and ozonation followed by enhanced coagulation then membrane technology are some of the well-known techniques through which it cannot be considered as cost-effective, and sustainable as compared to sand filtration media and GAC. Moreover, the introduction of sand filtration medium and GAC has been found by different studies that play an important role in removing Natural Organic Matter (NOM) which is considered a precursor of the DBPs.[46]. To our best knowledge, there has been no study reference investigating prominent DBPs for the cost-effective removal of HDPE nature water supply pipes in the water distribution network.

The study area, encompassing the region of Mardan, sets the stage for an in-depth investigation into the occurrence of (DBPs) in water distribution networks. The significance of this research lies in the potential health risks associated with DBPs, particularly their carcinogenic nature. Within this research framework, the three main domains are identification, quantification, and the formulation of remedial plans. The research was carried out in District Mardan, which is located within the geographical coordinates of 34°05 N-34°32 N and 71°48 E-72°25 E. District Mardan is recognized as one of the central districts in the Khyber Pakhtunkhwa province of Pakistan. The research area is partitioned into three distinct zones according to groundwater hydrology: the urbanized/industrial zone, encompassing Shergarh and Takhtbhai, and the non-industrial zone, referred to as the Surkhabi control region. The district is partitioned into three distinct zones, namely Zone 1, Zone 2, and Zone 3, as depicted in Figure 1. The industrial zones primarily consist of industrial activities such as car washing stations, commercial markets, and other commercial manufacturing processes. On the other hand, controlled or nonindustrial zones encompass anthropogenic activities that are not related to industrial or commercial processing.

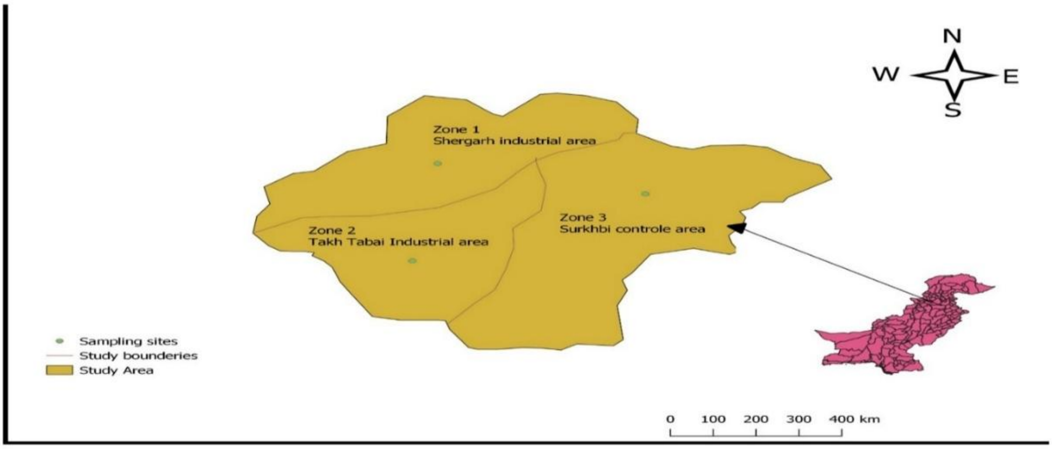

Figure 1 Study Area Division

For identification and quantification, a total of five samples were chosen from each of the three zones under the district jurisdiction. Additionally, two distinct samples were picked for each filtration medium, namely sand filter media and (GAC). The investigation of each sample was conducted using controlled amounts of chlorine. To simulate the continuous flow of water in distribution pipes under regulated conditions, a laboratory-based model was constructed to duplicate the flow of a large water supply network in HDPE-type pipes. By implementing filtration techniques such as sand filtration media and sand cum (GAC) filter media, a small-scale filtration setup can be established under continuous flow conditions without filtration. The measurement of trihalomethanes and trihaloacetic acids was conducted under headspace conditions. The experimental setup involved the utilization of (GC-ECD), both with and without filtration media, while maintaining regulated settings.

2. Methodology

2.1 Chemical and Reagents

Chlorine granular powder i.e.calcium hypochlorite was acquired from the water quality labs of the Public Health Engineering Department in Khyber Pakhtunkhwa, Pakistan. THMs and THAAs which are two DBP standardization chemicals, were acquired from Standard Sales in Pakistan. Ethyl acetate, a liquid-liquid separator, was acquired from the Public Health Engineering Department KP to separate solute and solvent. The distilled water was acquired from the water quality laboratories of the Public Health Engineering Department in KP, Pakistan for washing pipe networks.

2.2 Sampling Site

A multi-staged random sampling technique is employed to provide coherent sampling over all three zones of District Mardan Region, which is the second-largest district in Pakistan's KP Province. To detect and quantify the production of Chlorination DBPs, primary sampling units (PSU) were chosen for each of the three regions, specifically two from industrial areas and one from regulated zones. On the other hand, in the case of secondary sampling units (SSU), two samples were obtained, with one sample collected from the industrial zone and one sample collected from the controlled/nonindustrial zones, to quantify and qualify DBPs abatement procedures. Water from the ground source was chosen for distribution in these three district zones, with which elevated head tanks or overhead reservoirs were employed to provide head elevation and deliver it to the consumers. The intake source for all inputs was groundwater, sometimes known as tubewell. Nearly all groundwater sources exhibited a groundwater potential below 300-400ft, with a static water level ranging from 60-100ft. The mean yield of the tubewell ranged from 20 to 25 feet, whereas the mean flow rate of each groundwater source was around 0.00315 m^3/s to 0.00526 m^3/s. To conduct the sample analysis, it was necessary to have tubewell water that was at least 10 years old and had a distribution network spanning at least 5 kilometers. Additionally, all water samples were obtained at terminal or end-user points.

2.3 Setup

A significant amount of glassware was utilized during the entirety of the analysis for all sampling purposes. The distinctive sampling medium was cleansed using detergents, rinsed with tap and ultrapure water, and after that subjected to an oven at a temperature of 150°C for 1-2 hours. The sampling procedure involved the collection of samples in 100ml amber glass vials equipped with polypropylene screw tops and TFE-faced septa. Additionally, to conduct a more thorough investigation, the vials were meticulously filled to prevent the entrapment of air bubbles within.

To achieve the objective of the research, a laboratory model pilot-scale water distribution system was constructed to accommodate varying chlorine dosages as shown in Figure 2. This system incorporates loops composed of HDPE nature. The length of each loop approximately ranged from 5 to 10 feet, while maintaining a pipe diameter of 1 inch. To examine the characteristics of water and regulate water pressure and velocity, the loops were equipped with ball valves, elbows, unions, and sockets. Additionally, they have been employed to redirect the flow of water in the desired direction. The water's velocity was regulated within the range of 0.2m/s to 1.8m/s. Additionally, a centrifugal pumping machine with a power output of 0.3 HP was implemented to ensure a continuous flow of water. Within the distribution network, a reservoir containing 50 gallons of water is immediately supplied with samples from the location. The Public Health Engineering Department KP mobile water quality testing laboratory was utilized to collect water samples from several zones to monitor temperature and sunlight exposure. Before introducing the water sample into the pilot scale laboratory distribution system, a thorough cleansing of the system was conducted using ultrapure water for 30 minutes to eliminate any residual contaminants. The distribution network methodology consists of four components: flushing, parameter adjustment, chlorination dosing, and sampling. Following the cleansing process with uncontaminated water, the samples were introduced into a 50-gallon reservoir and subjected to suction using pumping pumps. The water flow from each loop exhibited uniformity and uninterrupted velocity, hence ensuring equal opportunities for particle mixing with the addition of chlorine dosages. Following the establishment of a consistent flow, chlorine dosages were introduced in proportions of 0.2 mg/L, 1.8 mg/L, and 2.4 mg/L, respectively, for each attempt. For zone 1, the concentrations were 0.2 mg/L, zone 2 had 1.8 mg/L, and zone 3 had 2.4 mg/L. THMs and THAAs were successfully identified and quantified at various chlorine doses.

The abatement strategy involved the introduction of two filtration media, namely (GAC) and a Pack of Sand, as rapid small-scale column experiments. These tests were subsequently followed by the implementation of a ball valve between the distribution networks. The ball valve was utilized to redirect the flow into the filter mediums, while simultaneously closing the valve aimed at the reservoir. This compact filter is a prototype of the pilot or full-scale fixed bed GAC and sand filter. The performance of GAC and sand adsorption was evaluated through the implementation of the rapid small-scale column test (RSSCT). The carbon fraction exhibiting a particle size ranging from 170 to 230 mesh, with an average particle diameter of 76 microns, was chosen for further purification. Subsequently, it was rinsed with ultrapure water and subjected to overnight drying. The desiccator has been used to store this desiccated carbon. The GAC column was filled with GAC particles that had been manufactured in advance. The determination of the minimum velocity is established by the Reynolds number (Remin), and as stated in the U.S. EPA/CR guidance, the suggested range for Re min is between 0.5 and 1.0 [41]. The physical characteristics of GAC were assessed using the standard test techniques established by the American Society for Testing and Materials (ASTM). The parameters evaluated for the activated carbon are moisture content (ASTM D2867), ash contact (ASTM D2866), iodine number (ASTM D4607), bulk density (ASTM D2854), hardness number (ASTM D3802), and uniformity coefficient (ASTM D2862). A column-shaped arrangement was employed to monitor sand filtration media, consisting of a 1000mm layer of quartz sand. The column was operated in a downflow medium with a predetermined filtration rate. The sand filtration column had a bed depth of 700mm, which consisted of silica particles with a size of 0.7mm and a homogeneity coefficient of 1.4. The filtration rate of the granular filtration column was set at 4.6m/h, while the rising head was maintained.

Before determining the produced DBPs, a slight modification was done in EPA method 551.1[47], which includes liquid-liquid extraction (LLE) with Ethyl Acetate instead of MTBE due to environmental concerns as mentioned in [47]. The consequences of MTBE prevail in the environment and specifically in drinking water.[48]. The separation occurred after the sample completed the distribution/rotation in the prepared water distribution model pipes in the laboratory. To do (LLE), a separating funnel was employed, adhering to the procedural specifications of a 1:2 ratio between the solute and solvents. In this instance, the solutes consisted of THMs and THAAs. The ethyl acetate solvent was used to separate the solute and solvent. The separation process began by placing the solute and solvent partially and mixing/shaking for 5 minutes. Then, 10 ml of solvent (separator) was added, followed by constant shaking for 5 minutes. This process was repeated 5 times, resulting in a 100 ml sample separation. 50 ml of solvent (separator) was added with 5-minute shaking intervals. The LLE technique was employed to separate the funnel into two distinct layers. Subsequently, water was extracted from the solute using a funnel dropper, leaving behind the solute as the residual.

Gas Chromatography-Mass Spectrometry (GCMS-5977B AGILENT TECHNOLOGIES USA) Analytical conditions as shown in Table 1, were employed to identify THMs and THAAs, as per the guidelines set forth by the Environmental Protection Agency (EPA) in 55.1. The column consisted of fused silica capillary DB-1 with dimensions of 30m ± 0.32 mm i.d. and a film thickness of 0.25µm. Helium (99.99% pure) was employed as the carrier gas, while nitrogen (99.99%) served as the makeup gas.

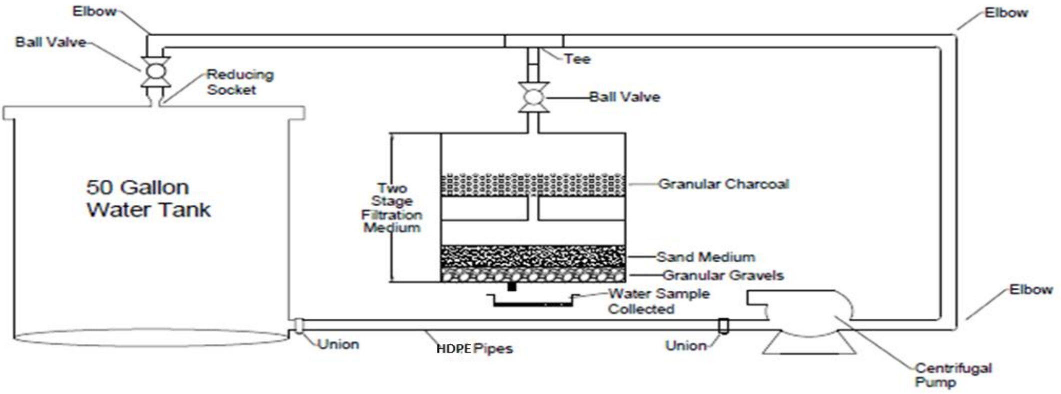

Figure 2 Prototype Model Setup

Table 1 Analytical Conditions of Gas chromatographic-mass Spectrometric Determination of DBPs

S.no	Nomenclature	Details	S.no	Nomenclature	Details
1	Run Time	36 mins	16	Total Flow	On 24mL/min
2	Post Run Time	0 mins	17	Septum Purge	On 3mL/min
3	Oven Temperature	70℃	18	Gas Saver	Off
4	Hold Time	3 mins	19	Split Ratio	20:1
5	Post Run	50℃	20	Split Flow	20mL/min
6	Temperature Rate	10℃/min	21	Thermal annex(initial)	280℃
7	Equilibrium Time	2 mins	22	Post Run	0℃
8	Max Temp	300℃	23	Column 1 Flow	On
9	Slow Fan	Disabled	24	Initial (Post Run)	1mL/min
10	Mode	Split	25	Column	DB-1
11	Heater	On 250℃	26	Length	25mX0.250mmx0.25um
12	Pressure	On 8.805 psi	27	Gas Used	Helium
13	Jet Cleaning	No Clean	28	Scan Low Mass	30
14	Solvent Delay	2 mins	29	Scan High Mass	650
15	Scanning	Norma	30	Threshold	150

3. Results

To obtain occurrence results of Chlorine DBPs [13]made a sequence-wise batch supply of chlorine dosage for the water distribution network model and observed the production weightage/variations accordingly against chlorine-controlled dosages supplied. The proportion of detected DBPs varied among the water samples from zone 1, zone 2, and zone

3. The identification of essential parameters for the production of DBPs was conducted for each water sample, average range of parameters as presented in Table 2. The study was performed sequentially, starting with a concentration of 0.2mg/L, followed by 1.8mg/L, and finally 2.4mg/L. Initially, for chlorine dosage of 0.2 mg/L, no focused elements DBPs i.e. Trihalo acetic acids and Trihalomethanes were traced rather than any other of their family derivates. Water Sample Parameters for Zone 1 including pH, DO, Turbidity, TOM, and Temperature were traced out separately as shown in Figure.3

S. No	Parameters	Range	S. No	Parameters	Range
1	pH	7.2-7.8	5	Temperature	30-38 ºC
2	DO	5-5.7 mg/L	6	Hardness	Soft water
3	Turbidity	1-3 NTU	7	Total Organic Matter	1.8-2.2mg/L
4	Taste	Fair			

Table 2 Water Parameter Range for All Samples Taken

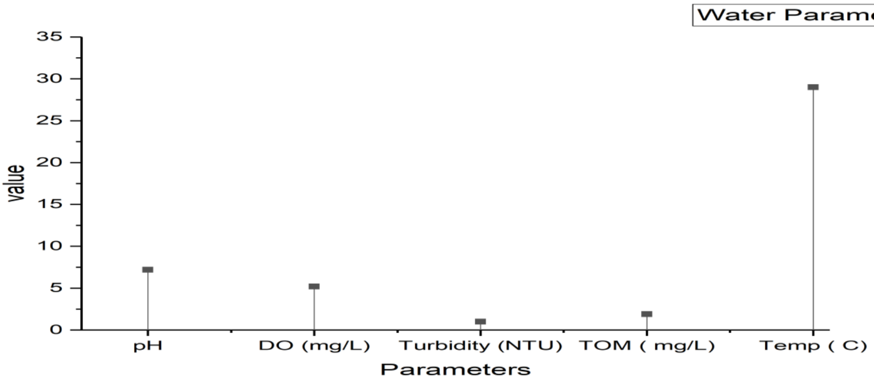

Figure 3 Water Sample Characteristic for Zone 1 with 0.2mg/L Chlorine Dosage

For zone 2 with enhancement in chlorine dosage to 1.8mg/L sample parameters attached in Figure 4, for searching of chlorine DBPs the sample was investigated under GC.MS (ECD) for about 5-6 hours and it couldn’t be discovering any halogenated Chlorine DBPs but rather any of their family members. This non-tracing of none of any members of THMs or THAAs in even the second sample from zone 2 diverts our results towards the lesser amount of Chlorine DBPs production in the HDPE nature of pipe medium due to a lesser amount of reaction between pipe material and water sample in presence of organic matter this no identification of DBPs family elements also diverts our attention towards the issue of lesser contact time of pipe nature reaction with chlorine and precursors due to HDPE smooth surface this make the sense of lower production.

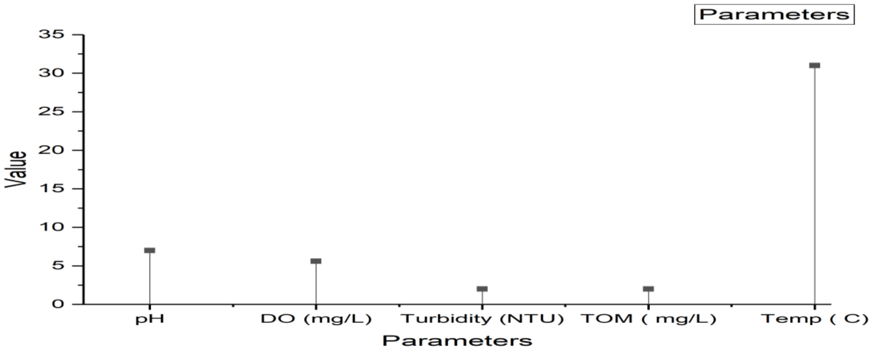

Figure 4 Water Sample Parameters for Zone 2 with 1.8mg/L chlorine Dosage.

The zone 3 water sample with 2.8 mg/L chlorine dosage with water parameters is attached in Figure 5. Focused halogens family members including trichloroacetic acid and trichloronitromethane were traced with peak number 2 at 4.340 mins. The other elements traced at peak number 3 were carbon tetra chloride, at peak number 4 phthalic anhydride, at peak number 5 hexadecanoic acid, at peak number 6 hexadecanoic acid, at peak number 7 octadecanoic acid, at peak number 8 methyl stearate, at peak number 9 Bis phthalate were identified. The identification of both chlorine DBPs trichloroacetic acid and trihalomethanes or their family members for zone 3 under GC.MS (ECD) were traced for zone 3 majority due to increased dosage of chlorine content under known water parameters as shown in Figure 6. However, it has been found that for chlorine dosage of 2.8mg/L about 0.2mg/L THAAs were quantified as a result and about 0.167 mg/L THMs were found after running under a controlled environment and HDPE pipe medium as shown in Figure 7.

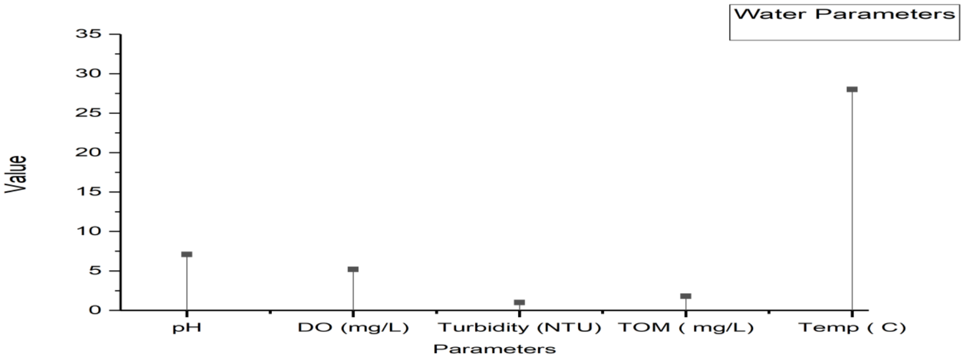

Figure 5 Water Samples Parameters for Zone 3 with 2.8mg/L Chlorine Dosage

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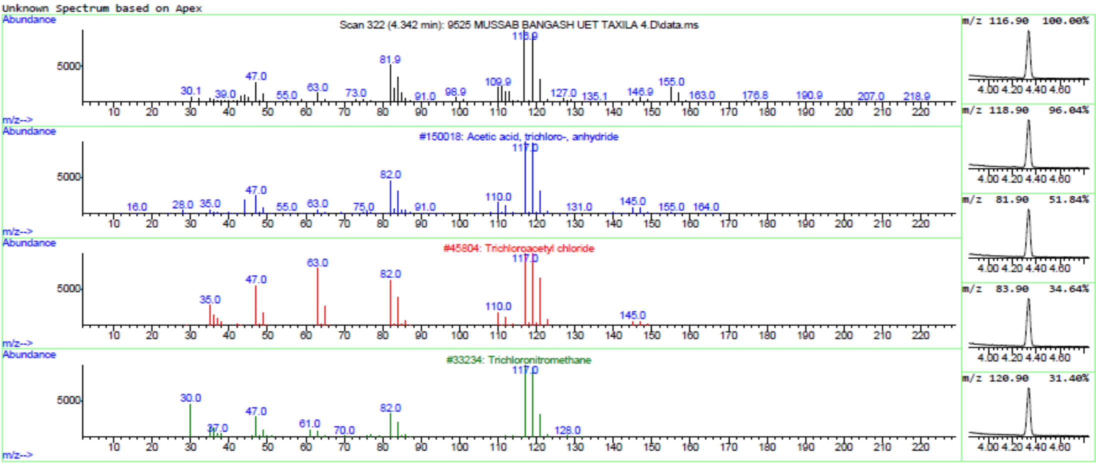

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Sample   : 4

Peak Number:  2     at      4.340 min  Area:  13920662  Area % 0.40

 The 3 best hits from each library.          Ref\#    CAS\#      Qual
----------------------------------------------------------------------
    C:\Database\NIST11.L
     1 Acetic acid, trichloro-, anhydride      150018 004124-31-6   83
     2 Trichloroacetyl chloride                 45804 000076-02-8   72
     3 Trichloronitromethane                    33234 000076-06-2   64

                                                              Library Search Report

  Data Path : D:\GCMS RESULTS DATA\
  Data File : 9525 MUSSAB BANGASH UET TAXILA 4.D
  Acq On    : 21 Mar 2024  18:43
  Operator  : CRL
  Sample    : 4
  Misc      :
  ALS Vial  : 4   Sample Multiplier: 1

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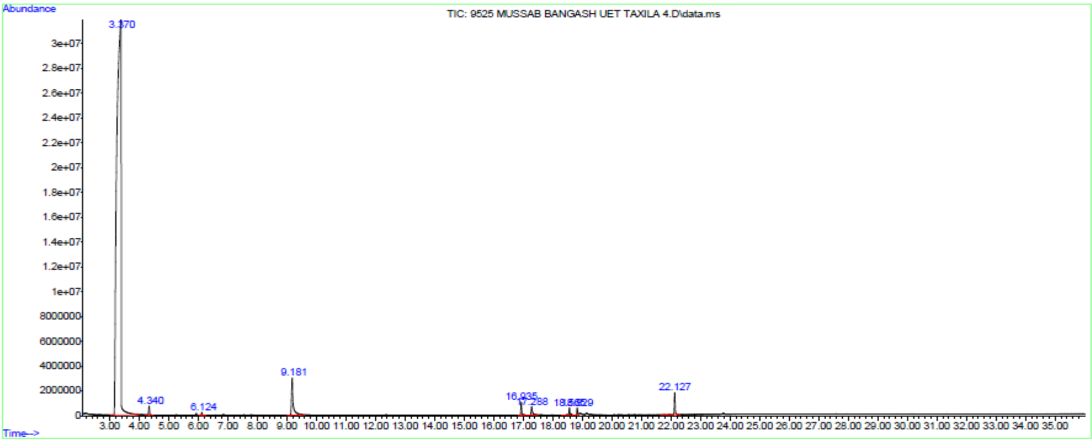

Figure 6 (a). Obtained Chromatogram for Zone 3 Water Sample (b) Obtained Mass Spectrometry for traced DBPs for Zone 3 Water Sample.

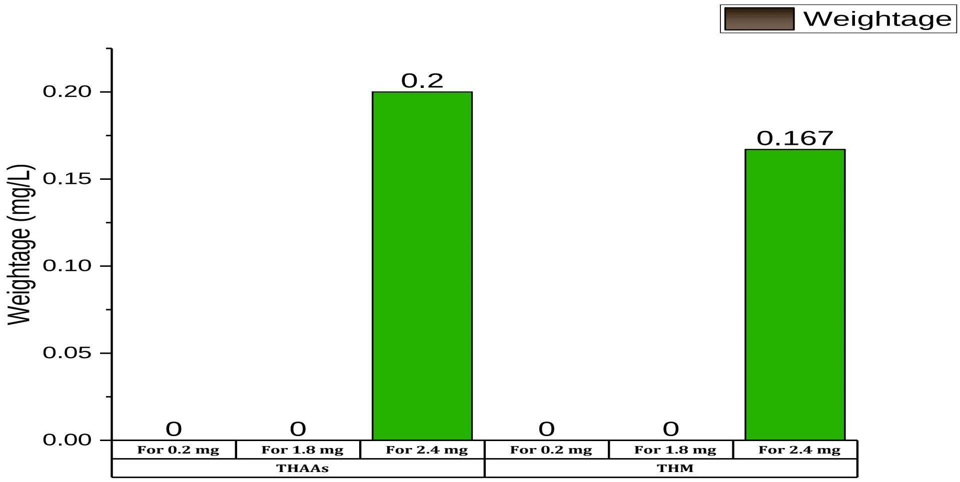

Figure 7 Founded THAAs and THMs for Different Chlorine Dosages

The quantification of prominent DBPs and filter media removal capacity was assessed and compared using eq.1.The traced element eq.3 was used based on eq.2 as provided in Text S1.

$$\text{TTHMs} + \text{THAAs} = \text{promient chlorine DBPs} \qquad (1)$$

$$\text{Chromatogram Peak Height}\ \alpha\ \text{Chromatogram Peak Area} \qquad (2)$$

$$\text{TE Peak Height (TE mg/l)} = \text{SR Element Area} \times \text{TE Peak Height} \big/ \text{SR Element Peak Height} \qquad (3)$$

In the study by[9] where these prominent DBPs were partially removed by introducing cost-effective sand filtration media and GAC filter.According to previous studies done by the introduction of filtration setup which may control these halogens up to some extent. So here we introduce consolidated filtration media which comprises of majority two filtration setups, one comprises the sand filter medium which was considered as 1st filtration media and the second one majorly comprises (GAC) filter media and has been considered as 2nd filtration media. To evaluate the water quality that passes through it, gravel's tiny size ranges from 2-4 mm. The charcoal column was measured at 600 mm, and the sand column's size was maintained at 1000 mm. Here in the water samples for Zone 2, and Zone 3, the samples were studied by passing both the filter setup i.e. 1st filtration setup, and the 2nd filtration setup as well. After obtaining a chromatogram no prominent chlorine DBPs were traced out nor any Prominent DBPs family members were discovered. This no existence /non-tracing of THMs and THAAs after passing by filtration media shows the capacity of the medium to reduce precursors including dissolved and suspended particles and also endorses the adsorption technique as a cost-efficient abatement technique.

4. Conclusion

Considering different controlled chlorine dosages with the trend in increasing the chlorine quantity familiar with the more prominent tracing of chlorine DBPs and with the proportionality of enhancement in quantification as well likely here happened for 0.2 mg/L,1.8mg/L,2.8mg/L chlorine dosage. This behavior of identification and non-identification were observed and variated according to the nature of the pipe medium used and other important water quality parameters including pH, Hardness, DO, turbidity with discharge, and flow duration time frame. It has also been concluded that introducing abatement techniques specifically adsorption and absorption plays a vital role in reducing or removing chlorine DBPs up to a great extent under a controlled environment hence showing the spatial and temporal variations behavior in HDPE pipe nature.

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