Comprehensive Analysis of Trihalomethanes (THMs) and Trihalo Acetic Acids (THAAs) in Drinking Water Supply: A Research Investigation

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Abstract: Water is the basic need of life. Chlorination is a well-known disinfection technique for potable water due to its cheap availability. Yet, some aspects are harmful to human health and found carcinogenic. An investigation has been made to quantify the occurrence of two prominent Chlorination Disinfectant byproducts (DBPs), i.e., Trihalomethanes (THMs) and Trihalo acetic acids (THAAs) in the water distribution network of galvanized iron Pipes Medium using GC-Mass Spectrometry equipped with Electron Capture Detector (ECD). Two filtration setups, i.e., Granular Activated Carbon (GAC) and a pack of sand, were evaluated as abatement techniques were introduced for removing these chlorination disinfectants by products according to the water source and pipe medium used. The chromatogram with mass spectrometry hints at the occurrence of these two DBPs and the filtration media's characterization and removal capacity. A combination of granulated activated carbon accompanied with sand media and based on gravel was found to be the more feasible and efficient setup to remove DBPs for the galvanized iron pipes distribution network medium.

Keywords: Chlorination Disinfectant by Products, Water Distribution Medium, GC-MS (ECD), Abatement Techniques.

1. Introduction

Clean drinking water is a fundamental human right to everyone on this planet. Population enhancement has dramatically impacted the demand for natural water resources. This increase in demand for potable water has involved us in different techniques to obtain cleaner water for drinking. Chlorination is one of the best yet least expensive methods to deactivate microorganisms and is a feasible agent for giving surety for procrastinating microorganisms' developmental activities in the supply network yet there are some harmful by-products formed when react with other precursors[1]. The formation of chlorine DBP is mainly produced due to natural organic matter, algal organic matter, and anthropogenic contaminants[2]. The findings by [3] found that the most prevalent group among DBPs is THMs and THAAs formed during the reaction of chloramine and chlorine with organic and inorganic species in drinking water. World Health Organization (WHO) statistics state that approximately 30% of humanity's diseases and 40% of morbidity across the globe are attributed to polluted water[4]. International Agency for Research on Cancer (IARC) and the U.S Environmental Protection Agency (EPA) include bromodichloromethane, bromate, bromoform, chloroform, and dichloroacetic acid as human carcinogenic[5].In contrast, investigators have investigated that brominated DBPs typically generate higher toxicity than corresponding chlorinated DBPs [6].[3] also reported that HAAs produced because of DBPs cause bladder cancer and other adverse reproductive anomalies. Another investigation done by [7] reported that THMs (750mg/L) are responsible for hepatotoxicity, hyperplasia in the urinary bladder, and metaplasia in the small intestine of male Wister rats at a dose of 16.17 mg in 1 month. Similarly,[8] concluded that THMs could that THMs could be responsible for almost 700 cancer cases in Canada, which endorses the harmful effect of DBPs on living bodies, and by [9] these produced halogens need to be minimized as much as possible.

Total chlorination for disinfection is divided into combined chlorine and free chlorine, so combined chlorine is a weak disinfectant inaccessible for disinfection. On the other hand, free chlorine is considered accessible for destroying pathogens. [1]. A free chlorine residual is maintained up to a maximum of 0.2 mg/L generally, which must be maintained in the distribution network because it reduces the likelihood of further contamination; however, chlorine concentration decreases with time due to dissolving behavior this finding by [10]is fully endorsed by the findings of [11]. The distribution system of drinking water plays a vital role in disinfectant by-products, and the possible growth of DBPs in distribution systems is felt impart by [12]to understand their concentration level at the system extremities.

Two important parameters, i.e., chlorine decay and transformation of DBPs under different chlorination conditions, were taken to investigate THMs and THAAs, respectively by [14] . For quantification of THMs and HAAs formation [14] conducted experiments for pipe setup [13]in which 56 days were selected to investigate the DBPs development of under-maintained booster chlorination dosages during the whole experiment. For this experimental setup [15] concluded that a chlorine decay experiment setup needs to be made, or a pilot scale study needs to be made by separate loops of ductile iron (DI) and stainless steel (SS).The diameter of each pipe was kept under 150 mm, and the length was approximately 80m.The velocity was kept at 0.2-0.8m/s. This pilot scale study was endorsed by quality parameters, i.e., turbidity, temperature, etc., and once checked weekly for quality assurance. The DBPs were measured for each sample by GC-MS equipped with an (ECD).In this, chlorine dosage concerns were separate, i.e., initial chlorination to booster chlorination dosages, i.e., 0.43mg/L to 1.03mg/L experimented for all chlorination results conducted by [16]. In another study, some elements like organic impurities, ammonia compounds, and unremoved metallic compounds such as ferrous ions and magnesia are prominent components that react with chlorine, and after the reaction, they disappear [10]. Both [17]and [18] found a rapid decrease in both free and total chlorine residuals in the water distribution system as residence time enhanced.[10]considered 350 pipe sections for the performance of experimental work, these pipes were either new, recently installed, or old pipes of different ages. This source of water was from desalination plants. This study studied eight pipe materials: cast iron, steel, asbestos cement, cement-lined cast iron, polyvinyl chloride (PVC), and UPVC. To avoid consistency between actual field conditions and lab conditions [10] different sizes of propellers to ensure almost complete mixing of the regime. Still, the sampling program stopped when chlorine concentration became low, about 10% of the initial concentration. So, the result concluded [10] that chlorine decay in the pipe is based on two aspects, i.e., the function of masses transport from bulk to the pipe wall surface and the second is the chemical reaction with the pipe wall surface. Mostly ductile iron (DI), polyethylene (PE), and stainless steel are widely used in the drinking water distribution system [19].Different countries have different mean concentrations of THM ranging from zero to 1000mg/L in Nigeria, and it has been found that between zero and 95mg/L in treated water samples [20]. Similarly, in the United States, up to 18mg/L of DBPs were detected in finished water and up to 22mg//L DBPs in distribution systems [21], while in China, the average concentrations of THMs, HAAs over the entire period of treatment were 19.9mg/L,3.4mg/L [22] therefore the concentrations of THMs and HAAs in the water distribution system are spatially variable.[23].In the [24] study THMs were prominently found in GI pipes, while HAAs formations were unaffected by pipe materials. Copper and iron are transition elements used widely in the distribution system of drinking water worldwide due to their killing effect on certain bacterial species.[25].For the investigation of HAAs and THMs [12] used a copper and glass pipes distribution network in which THMs quantification analysis was done by [26].[12]performed experiments regarding the monitoring of THMs and THAAs in pipe rigs. [12] also concluded the distribution of THMs and HAAs came into being in the first 12 h and more trihalomethanes and fewer halo acetic acids were formed in the copper and iron pipes than in the glass pipes. The percentage of THMs in the sum of HAAs and THMs at 12 h was 66.3% and 56.4% in copper and glass pipes, respectively. Hence, developed countries like the US EPA have set the maximum contamination level of HAAs at 60 µg/L. Another study by [27] shows that the formation of various DBPs depends on several influential factors: 1. chlorine dosage 2. Temperature 3. pH 4. Contact time 5. Organic matter content 6. Constitution of water 7. Type of pipe material. Plastic pipe has become the dominant material for various types of supply networks due to its high flexibility, corrosion resistance, and jointing properties. Still, these pipe materials greatly affect the production of DBPs [28].One of the studies suggested that HAA concentration in the four pipe loop systems was sequenced according to the 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 increasing diameter of the pipe. Some effective methods found by [31]for removing DBPs were adsorption, air stripping, and ozonation, followed by chlorination, enhanced coagulation, membrane technology, and advanced oxidation process. Importance should be given to pipe materials as they influence the factors of DBPs formation of Biofilms, and due to biofilms' heterogeneous character, their physical characteristics, e.g., thickness, surface roughness, and porosity, are different, henceforth affecting disinfectant transport and penetration[32]. Microbiological water quality in WDS was compromised for several reasons, including physiochemical water quality, pipe material, and water age. [29].[29] also studied the variation of HAAs in a laboratory-scale distribution system consisting of four sets of independent HDPE, PVC, PP, and Steel Galvanized pipe loops. The study [29] concluded that the development of HAA levels differed in the loop system for each pipe medium.

Although the generation of these prominent harmful chlorine DBPs in water supply according to the nature of the pipe is characterized and quantified, there is a need for a cost-effective technique according to the nature of the pipe medium used. Some of the methods discussed in[31]like adsorption, air stripping, and ozonation followed by enhanced coagulation and 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.[33]. To the best of our knowledge, no study has analytically investigated prominent DBPs for the environment-friendly, cost-effective removal of G.I. nature water supply pipes in the water distribution network.

Our study was conducted in District Mardan (geographic coordinates between 34°05`N-34°32`N and 71°48`E-72°25`E), one of the central districts of Khyber Pakhtunkhwa province of Pakistan. The study area can be divided into three zones based on groundwater hydrology: the urbanized/ industrial zone (shergarh and Takhtbhai) and the non-industrial zone (control area called Surkhabi). These divisions divide the whole district into 3 zones known as Zone 1, zone 2, and Zone 3, respectively, as shown in (Figure S1). The industrial zones mainly comprise industrial activities, car washes, markets, and other commercial manufacturing processes, while controlled or nonindustrial zones comprise anthropogenic activities other than industrial or manufacturing processes.

A total of 5 samples were selected based on specified samples for identification and quantification in every 3 zones of district jurisdiction, and 2 separate samples were chosen for each filtration medium. Each sample was investigated under controlled chlorine dosages. A prototype experimental lab setup was built to replicate a vast water supply network flow in G.I. nature pipes for the uninterrupted water flow in distribution pipes under controlled conditions. Under the continuous flow without filtration and by introducing abatement techniques like sand filtration media, sand cum (GAC) filter media in a form rapid small-scale column test. The two main chlorination disinfectant by-products specifically Trihalomethanes and Trihalo acetic acids were investigated for quantification under GC-MS equipped with (ECD) with and without filtration media.

2. Materials and Method

2.1. Chemicals and Reagents

Chlorine granular powder i.e. Calcium Hypochlorite was obtained from the Water Quality Labs Public Health Engineering Department KP, Pakistan. Two DBP standardization chemicals, i.e., Chloroform and Trihalo acetic acids, were purchased from standard sales in Pakistan. Separating chemicals for separation of solute and solvent Ethyl acetate(separator) as a liquid-liquid separation was obtained from the Public Health Engineering Department KP. Distilled water was obtained from the Public Health Engineering Department KP, Pakistan Water Quality Labs.

2.2. Sampling Site

For coherent sampling, we use a multi-staged random sampling for all three zones of the district Mardan region, Pakistan's second-largest district in KP province. The primary sampling units (PSU) were selected for each of the three areas, i.e., two from industrial and one from controlled zones, to identify and quantify the production of Chlorination DBPs. In contrast, for secondary sampling units (SSU), two samples were collected, one from the industrial zone and one from the controlled/nonindustrial zones for DBPs abatement techniques quantification and qualification. In these three district zones, water from the ground source was selected, and the pumping water system elevated head tank or overhead reservoirs were utilized to give head elevation and distribute to the consumers. Groundwater, or tubewell, was the intake source for all inputs. The groundwater potential of almost every groundwater source was below 90-120m, while the static water level was about 18-30m. The average yield of tubewell was 6-8m, and the average discharge of each groundwater source was about 0.00315 m^3/s to 0.00526 m^3/s. For consideration of the sample analysis, at least 10-year-old tubewell water with at least a 5km distribution network was taken, and all water samples were collected at terminal /end-user points. Before the sampling analysis in GC-MS (ECD) water important parameters that influence DBPs production were analyzed and quantified including pH with a pH meter, Dissolved Oxygen with a DO meter, turbidity with a nephelometer, taste with human sense, Total Organic Matter (TOM) with fluorescence spectrometry, temperature with thermometer and water sample hardness with test kits(Calorimeter).

2.3. Setup

For all sampling, considerable glassware was used during the whole analysis. Unique sampling medium washing was washed with detergents, rinsed with tap and ultrapure water, and then placed in an oven at 150ºC for 1-2 Hours. Samples were collected in 100ml amber glass bottles with polypropylene screw caps and TFE-faced septa. Further, for more investigation, vials were carefully filled so that trapping of air bubbles inside was not allowed.

To accomplish the aim of the study, the lab model pilot-scale water distribution system was prepared for different chlorine dosages, which contain loops made of G.I nature as shown in Figure 1. Each loop's length was approximately 1.5-3m, and the diameter of the pipe was kept at 25mm . The loops were provided with ball valves, elbows, unions, and sockets to investigate water behavior and control water pressure and velocity. They have also been used to divert water flow in the required direction. The velocity flow of the water was controlled between

0.2m/s to 1.8m/s. A 0.3 HP centrifugal pumping machine was also installed for the continuous water flow. In the distribution network, 50 Gallons of water reservoir receives samples directly from the site. Special attention was paid to grab samples of water from different zones to monitor temperature and exposure to sunlight by using the Public Health Engineering Department KP Mobile Water quality testing laboratory. Before running the water sample in the pilot scale Laboratory distribution system, the system was washed with ultrapure water for 30 minutes to clean any leftover residue. The methodology of the distribution network comprises four components, i.e., flushing, adjusting parameters, chlorination dosages, and sampling. After washing with clean water, samples were added to a reservoir of 0.189m3(50 Gallons) and given a suction by pumping matching. The water flow from each loop, flow, and velocity were uniform and uninterrupted, so mixing particles may have equal opportunities when chlorine dosages are added. After ensuring the flow was uniform, chlorine dosages were added in weightage of 0.2 mg/L, 1.8 mg/L, and 2.4 mg/L, respectively, for each turn. i.e. 0.2 mg/L for zone1,1.8mg/L for zone 2 and 2.4mg/L for zone 3. Identification and quantification of THMs and THAAs were achieved for different dosages of chlorine added.

For the abatement technique, two filtration mediums, i.e., Granular Activated Carbon (GAC) and a Pack of Sand, were introduced as rapid small-scale column tests followed by a ball valve between the distribution networks for the fixed chlorine control dosage of 2.4mg/L. This ball valve diverted the flow towards filtration mediums while shutting the other valve towards the reservoir. This rapid small-scale filter represents the pilot or full-scale fixed bed GAC and sand filter. The quick small-scale column test (RSSCT) was conducted to assess the performance of GAC and sand adsorption. The carbon fraction with a particle size of 170-230 mesh (with a mean particle diameter of 76 microns) was selected, washed with ultrapure water, and dried overnight. This dried carbon has been stored in a desiccator. The GAC column was filled with prepared GAC particles. The minimum velocity is already defined using the Reynolds number (Remin), and according to the U.S EPA /CR manual, the Re min is recommended up to the range of 0.5 -1.0 [34]. The physical properties of GAC were characterized by the American Society for Testing and Materials (ASTM) standard test methods. This includes moisture (ASTM D2867), ash contact (ASTM D2866), iodine number (ASTM D4607), bulk density (ASTM D2854), hardness number (ASTM D3802), and uniformity coefficient (ASTM D2862) of the activated carbon. For sand filtration media, a column shape setup was used to observe SF media, comprised of a 1000mm quartz sand layer, and the column was operated in downflow media with a specified filtration rate. The bed depth on the sand filtration column was 700mm, containing silica with an adequate size of 0.7mm and a uniformity coefficient of 1.4. The granular filtration column has been operated at a 4.6m/h filtration rate with a rising head.

Before determining the produced DBPs, a slight modification was done in EPA method 551.1[35], which includes liquid-liquid extraction (LLE) with Ethyl Acetate instead of MTBE due to environmental concerns as mentioned in [35]. The consequences of MTBE prevail in the environment and specifically in drinking water.[36]. This separation was performed once the sample finished the distribution/rotation in the laboratory-prepared water distribution model pipes. For liquid-liquid extraction (LLE), a separation funnel was used as the procedural requirements in a 1:2 ratio of solute and solvents were considered. Here, in this case, the solutes were THMs and THAAs. The solvent was ethyl acetate separation initiated with placement of solute and solvent partially along with mixing/shaking for 5 mins and then again adding solvent (separator) in 10 ml, which was further accompanied by constant shaking for 5mins and further so on overall for 5 times hence making 100ml sample separation by adding 50 ml solvent (separator) with 5mins shaking intervals. After obtaining two different layers separating the funnel by the LLE technique, water was removed from the solute using a funnel dropper, and the remaining residual was solute.

To determine THMs and THAAs already recommended by EPA 551.1[35](Environmental Protection Agency, n.d.-b),Gas Chromatography-Mass Spectrometry equipped with an electron capture detector (GCMS-5977B AGILENT TECHNOLOGIES USA)was used. The column was fused silica capillary DB-1,30m × 0.32 mm i.d. × 0.25μm film thickness. The Gas used was helium (99.99% pure) as a carrier and nitrogen(99.99%) as makeup gas. The analytical conditions are presented in Table 1

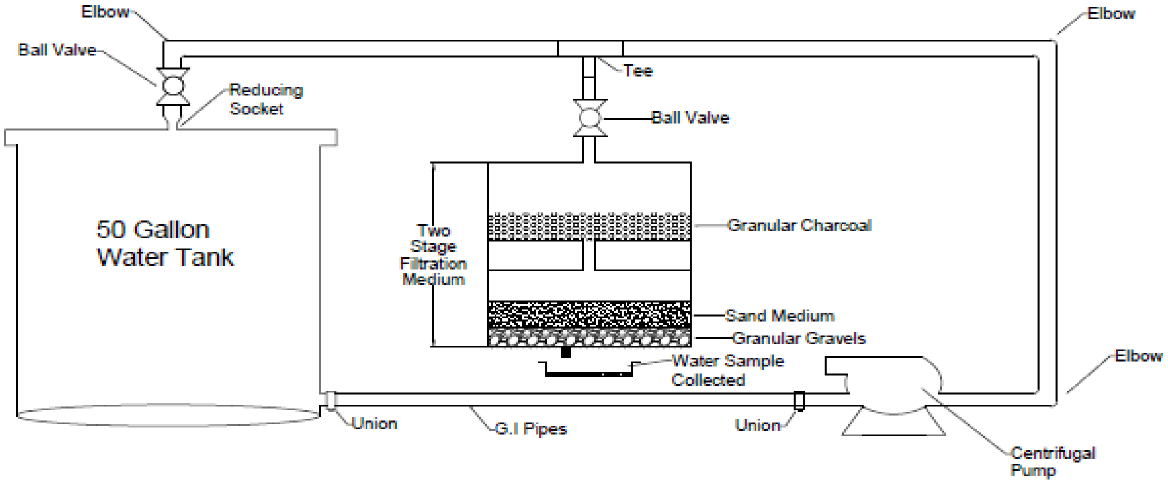


FIGURE 1| Schematic of Experimental Setup

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°C	18	Gas Saver	Off
4	Hold Time	3 mins	19	Split Ratio	20:1
5	Post Run	50°C	20	Split Flow	20mL/min
6	Temperature Rate	10°C/min	21	Thermal annex(initial)	280°C
7	Equilibrium Time	2 mins	22	Post Run	0°C
8	Max Temp	300°C	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°C	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 and discussion

3.1. Fraction of DBPs in selected zones

To obtain occurrence results of Chlorine DBPs [15]I made a sequence-wise batch supply of chlorine dosage for the water distribution network model and observed the production weightage/variations accordingly against the chlorine-controlled dosages supplied. Here for the sample of water of zone 1, zone 2, and zone 3, the fraction of discovered DBPs was different. Essential characteristics to produce DBPs were sorted out for each water sample, as shown in Table 2. The analysis was conducted in a stepwise phase, i.e., initially for 0.2mg/L, then 1.8mg/L, and then 2.4mg/L, respectively. For the initial control dosage of 0.2 mg/L with parameters as shown in Figure 2, the production of DBPs, specifically THMs and THAAs, was not seen in the obtained chromatogram. Other than halogens compounds with retention time have been shown in (Table S1). The reason for non-identified THMs and THAAs was the meager presence of chlorine residual and negligible chlorine rate.

TABLE 2 Water Sample Characteristics Ranges

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			

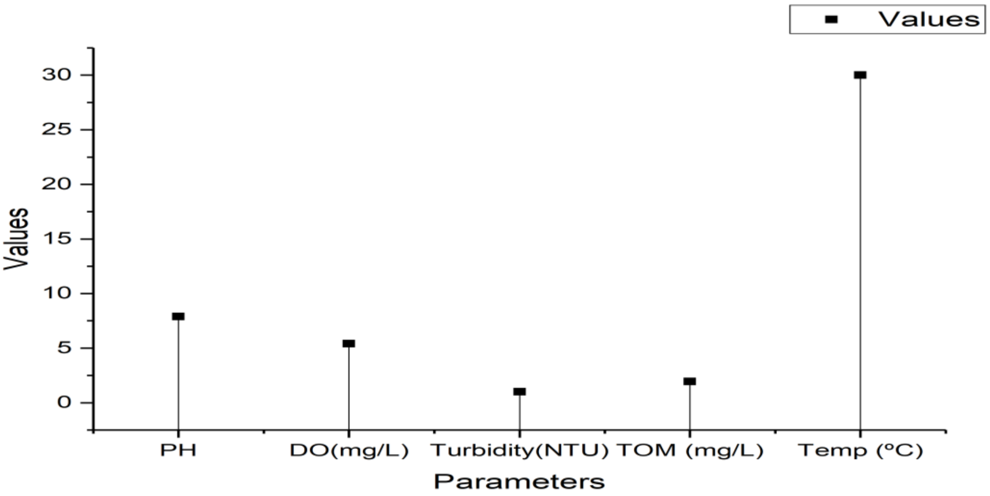


FIGURE 2 Water Sample Parameters Specifically for Zone 1.

Then for 1.8mg/L chlorine dosage rate sample from zone 2 was taken to investigate the availability of two chlorine DBPs, i.e., THMs and THAAs. Important water sample parameters were noted before further investigations in G-C Mass Spectrometry, i.e., PH, DO, Turbidity, Taste, Temperature, etc., as shown in Figure 3. For GC-MS sample analysis, 11 elements were traced out in a chromatogram as shown in (Table S2). In contrast, subject DBPs one element Trichloromethane was recognized at 1.532 mins with Peak Number 4 with a molecular weight of 119 g/mol and having mass spectrometry area of 3029057 as shown in Figures 4&5.So here we observe that earlier at 1.552 mins trichloromethane was detected due to being more volatile than other obtained hexadenoic acids and oleic acids which are considered fatty acids.

This hints at the initial occurrence of one of the focused Chlorine DBPs, Trihalomethane, while increasing the chlorine dosage quantity from 0.2mg/L to 1.8mg/L, respectively.

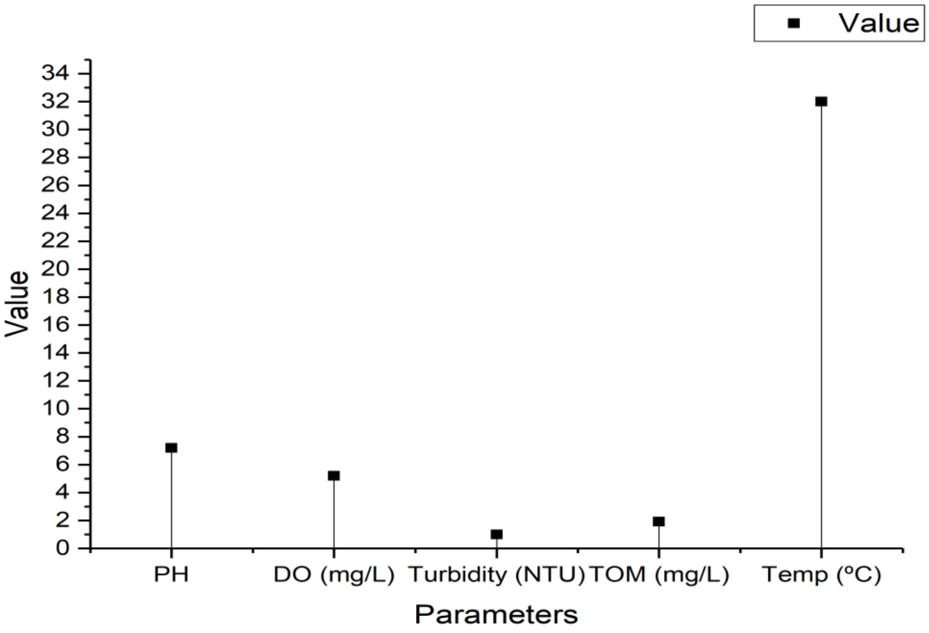


FIGURE 3 Water Parameters for 1.8mg/L Chlorine for Zone 2 sample.

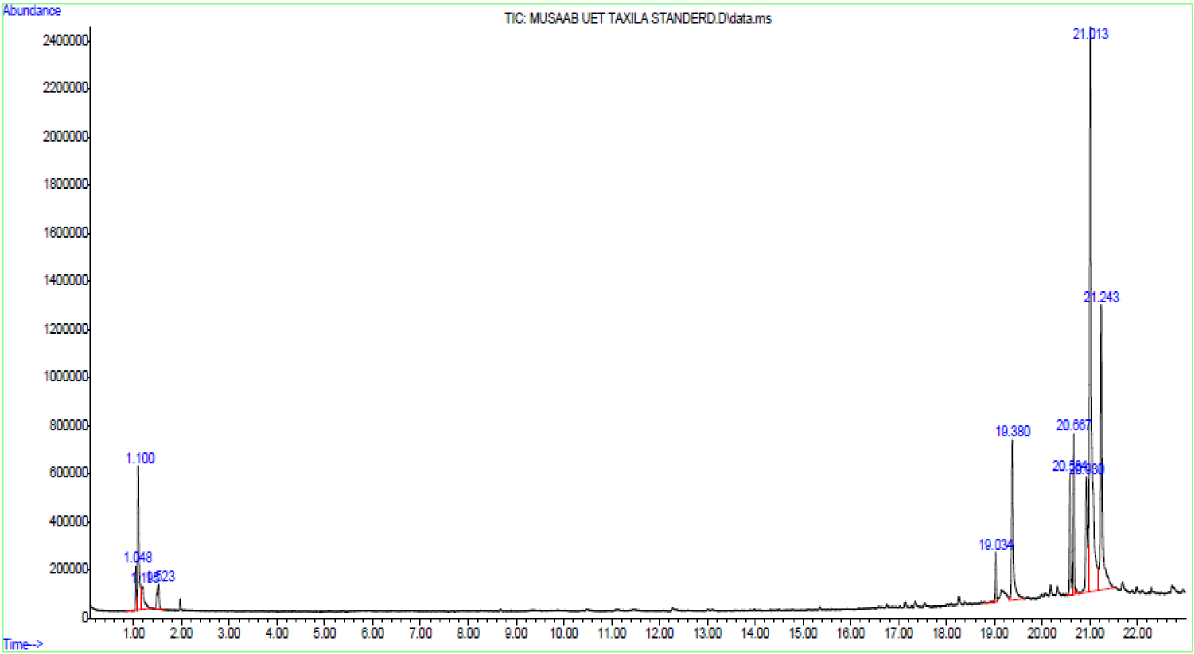
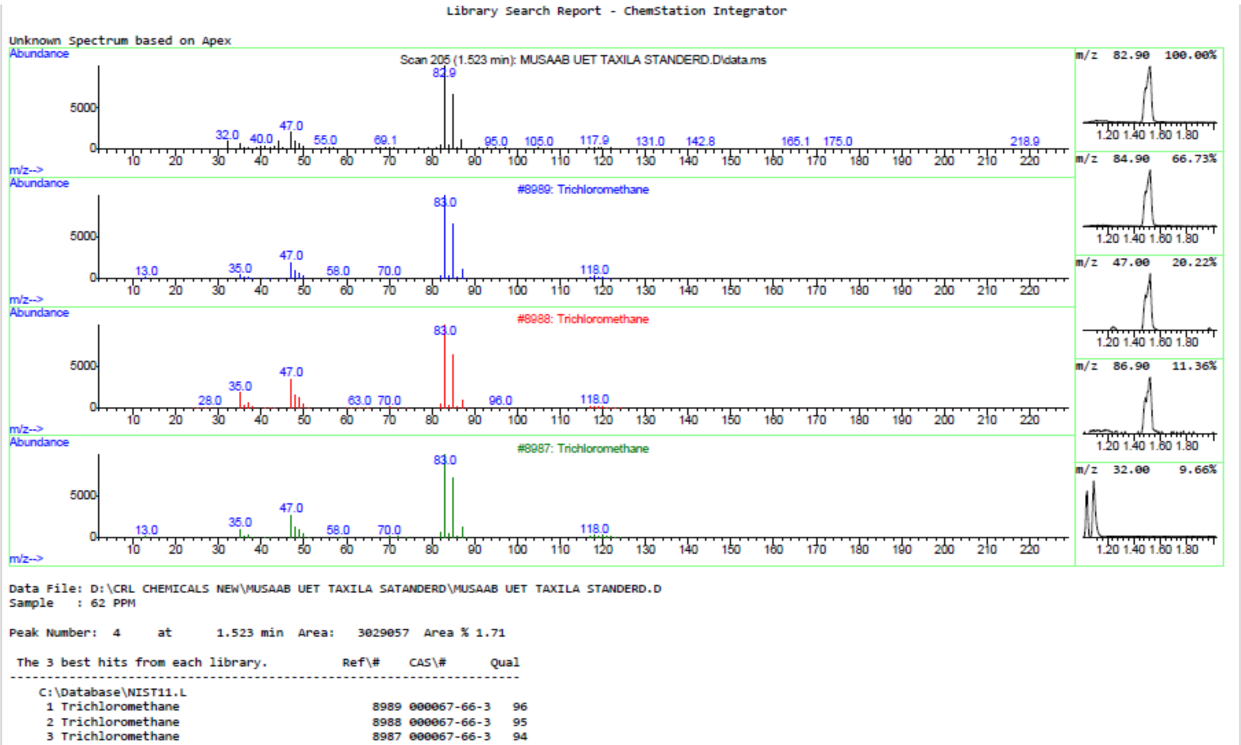


FIGURE 4 Chromatograph of 1.8mg/L Chlorine Dosage



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Library Search Report - ChemStation Integrator

Unknown Spectrum based on Apex
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Sample   : 62 PPM

Peak Number:  4     at      1.523 min  Area:   3029057  Area % 1.71

 The 3 best hits from each library.          Ref\#    CAS\#      Qual
---------------------------------------------------------------------
    C:\Database\NIST11.L
     1 Trichloromethane                         8989 000067-66-3   96
     2 Trichloromethane                         8988 000067-66-3   95
     3 Trichloromethane                         8987 000067-66-3   94
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FIGURE 5 Trichloromethane Mass Spectrometry for Chlorine Dosage of 1.8mg/L.

For chlorine dosage of 2.4mg/L parameters as shown in Figure 6, the focused Chlorine DBPs presence peaks were detected starting at 3.329 mins and then at 4.452 mins. Specifically, at 3.329 mins, only trichloroacetic acid with a molecular mass of 149 g/mol and a mass spectrum area of 6061939 with other elements with retention time is shown in (Table S3). Further, considering the obtained chromatogram in Figure 7, at 4.452mins trichloroacetic acid with 164g/mol molecular mass, trichloronitromethane with 128 g/mol molecular mass was seen in spectrum Figure 8. The Spectrum area of these traced elements was 57186815. Thus, this shows the formation of chlorine DBPs when the dosage of residual chlorine content in water is increased and endorses the idea of [2] which concluded in variations of DBPs production with controlled chlorine dosages with known water parameters.[37]found by increasing residual chlorine dosage from 1.0mg/L to 3.0 mg/L during pre-chlorination the concentration of THMs and THAAs enhanced even in filter media.

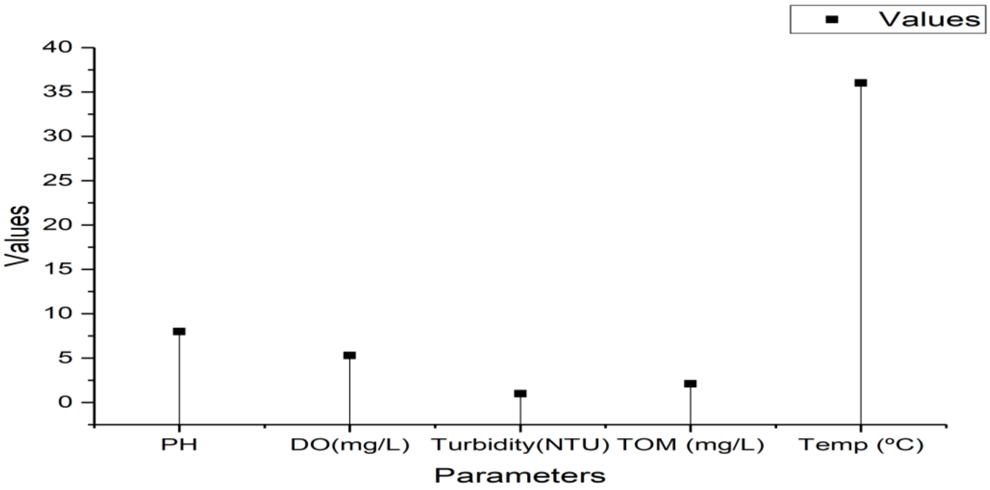


FIGURE 6 Parameters of 2.4mg/L of water sample of zone 3

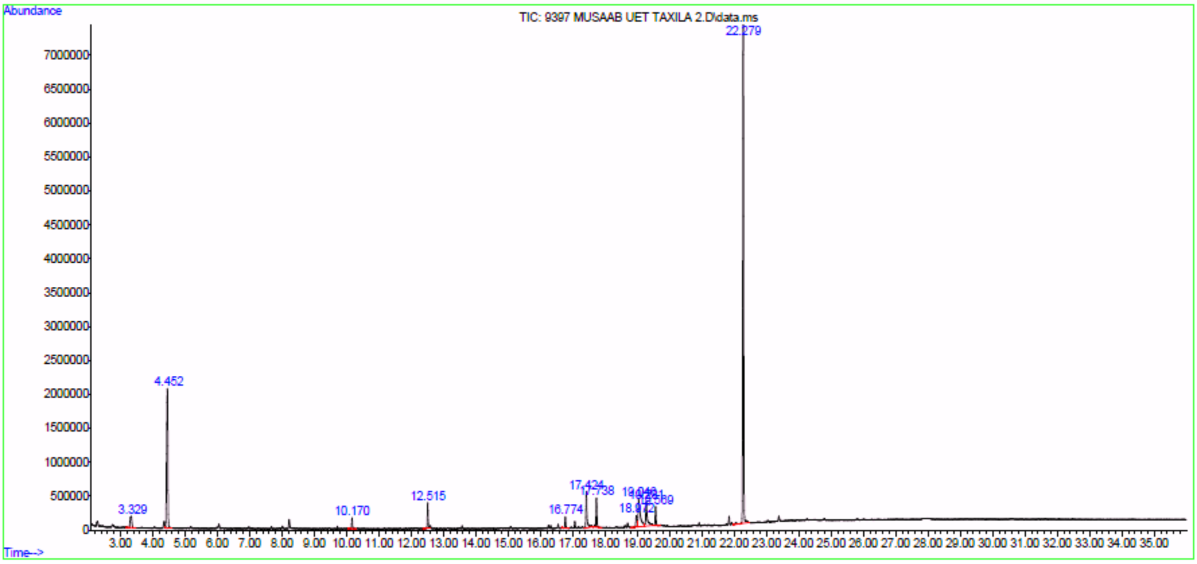
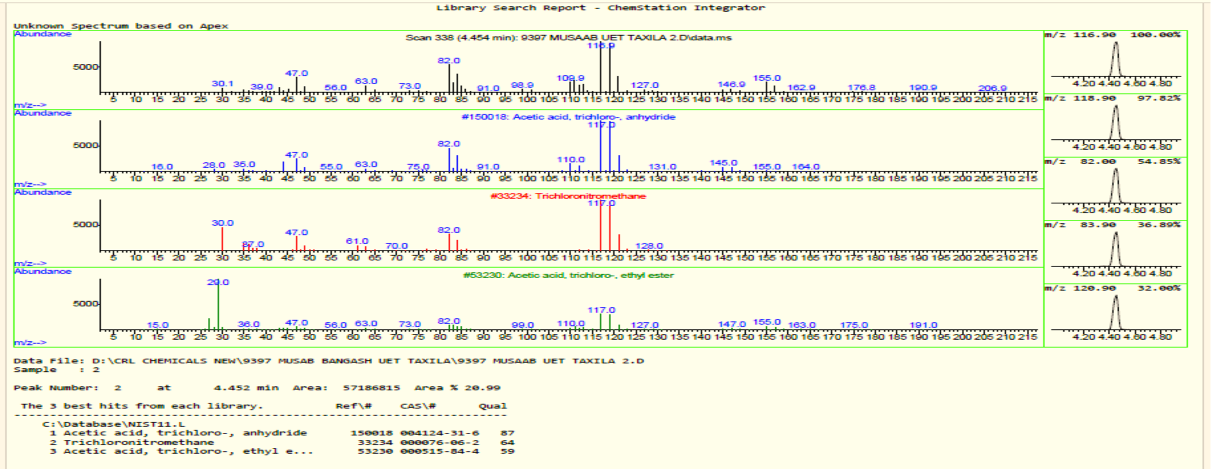


FIGURE 7| Obtained Chromatogram of 2.4mg/L of Chlorine dosage



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Library Search Report - ChemStation Integrator

Unknown Spectrum based on Apex
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Sample    : 2

Peak Number:  2      at       4.452 min  Area:  57186815  Area % 20.99

 The 3 best hits from each library.          Ref\#    CAS\#       Qual
--------------------------------------------------------------------------
    C:\Database\NIST11.L
     1 Acetic acid, trichloro-, anhydride       150018 004124-31-6   87
     2 Trichloronitromethane                     33234 000076-06-2   64
     3 Acetic acid, trichloro-, ethyl e...       53230 000515-84-4   59
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FIGURE 8| Mass Spectrometry obtained for a chlorine dosage of 2.4mg/L

3.2. Abatement Technique

In the study by [2] where these prominent DBPs were partially removed by introducing cost-effective environment-friendly sand filtration media and GAC filter. A consolidated filtration media comprising a sand pack layer, below that GAC filter media which is considered most versatile for removing water impurities by [38] , and then again, a thin layer of sand was developed. The small size of gravel ranges between (2-4mm) for assessment of water quality passing through it. The size of the sand column was kept at 1000mm, and the charcoal column was observed at 600mm. For assessment of filtration media for removing chlorine DBPs, two significant aspects of filtration setup, i.e., sand media, which is marked as 1st filtration setup, and then activated granular charcoal media, which is marked as 2nd filtration media setup, were investigated separately. As per previous studies, sand filtration media is usually helpful for removing turbidity as suspended particles in water samples if passed accordingly. So here, in the case of sand filtration after running the sample of chlorine dosage of 2.4mg/L in GC-MS, the obtained chromatogram shows that a notable improvement in the removal of trihalomethane was achieved. Still, trichloroacetic acid was traced at time intervals with peak no 1 at 3.196 mins with an area of 1115036 along with in mass spectrum traced molecular mass of 165g/mol as shown in Figure 9 along with three best hits mass spectrometry in Figure 10. This nonexistence of trihalomethane and detection of trihalo acetic acid shows the capability of the sand filtration media setup for partial removal of chlorine DBPs up to some extent. This also shows the understanding of the removal of trihalomethane by controlling the source of DBP generation, specifically the controlling of suspended dissolved particles and mainly holding of organic matter in water, which is considered the catalyst of these chlorine DBPs but on the other side of the tracing of trichloroacetic acid with mass spectra challenges the capability of 1st filtration media setup. On the other side, 2nd the filtration media setup, water samples were analyzed using GC-MS (ECD), under controlled conditions. According to the nature of the pipe under controlled chlorine dosage, the capacity and feasibility were analyzed through chromatograms and mass spectrometers. The obtained chromatograms for 2nd filtration media didn’t recognize the presence of specific DBPs, i.e., THMs or THAAs, rather than any of their family compounds. The removal of both these DBPs through a second filtration media setup shows the capability of removal.

The nonidentification of these two DBPs shows the capacity of the 2nd filtration media to control the precursors of these produced chlorine DBPs, with the phenomenon of having granular charcoal media beside the sand layer followed by gravel pack hints initially the removal of suspended particles mainly organic matter then penetrating in fine activated carbon medium the adsorption takes place through which after passing by these generated DBPs get removed followed by gravels which furtherly filter the water neutralize physical properties thus qualified for the removal of traced TCMs and TCAAs under controlled conditions.

The quantification of prominent DBPs and filter media removal capacity was assessed and compared using Equation 1. For concentration in the extract, we used Equation 2, while for concentration of DBPs in water was sorted by using Equation 3 as detailed in (Supplementary Material (S1)).On the reliance on analysis as shown in Figure 12 (a,b) for chlorine dosage of 2.4mg/L THAAs were traced in the range of a maximum of 0.212mg and a maximum range of 0.199mg THMs were traced while for the chlorine dosage of 1.8mg/L maximum THMs were traced with a maximum range of 0.193mg. After this, the abatement techniques removing capacity were analyzed for a fixed chlorine dosage of 2.4mg/L for which only 0.134mg THAAs were detected under passing by sand filtration media rest of THMs in GAC and sand filtration media were not detected either any of THAAs were detected after passing by GAC filter media.

$$\mathrm{TTHMs + THAAs = promient\ chlorine\ DBPs} \qquad \text{Equation 1}$$

$$\mathrm{Concentration\ in\ Extract} = \frac{\mathrm{Measured\ Peak\ area}}{\mathrm{Peak\ area\ of\ Internal\ Standard}}\ \mathrm{X}\ (\mathrm{m} + \mathrm{b}) \qquad \text{Equation 1}$$

$$\mathrm{Cw} = \frac{\mathrm{Ce\ X\ Ve}}{\mathrm{Vw}} \qquad \text{Equation 2}$$

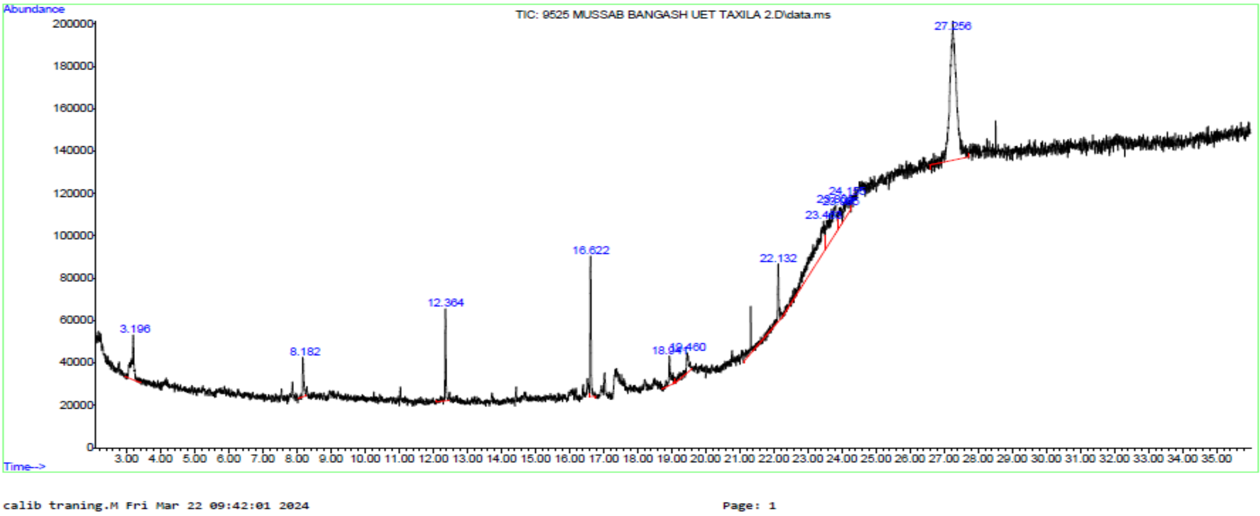
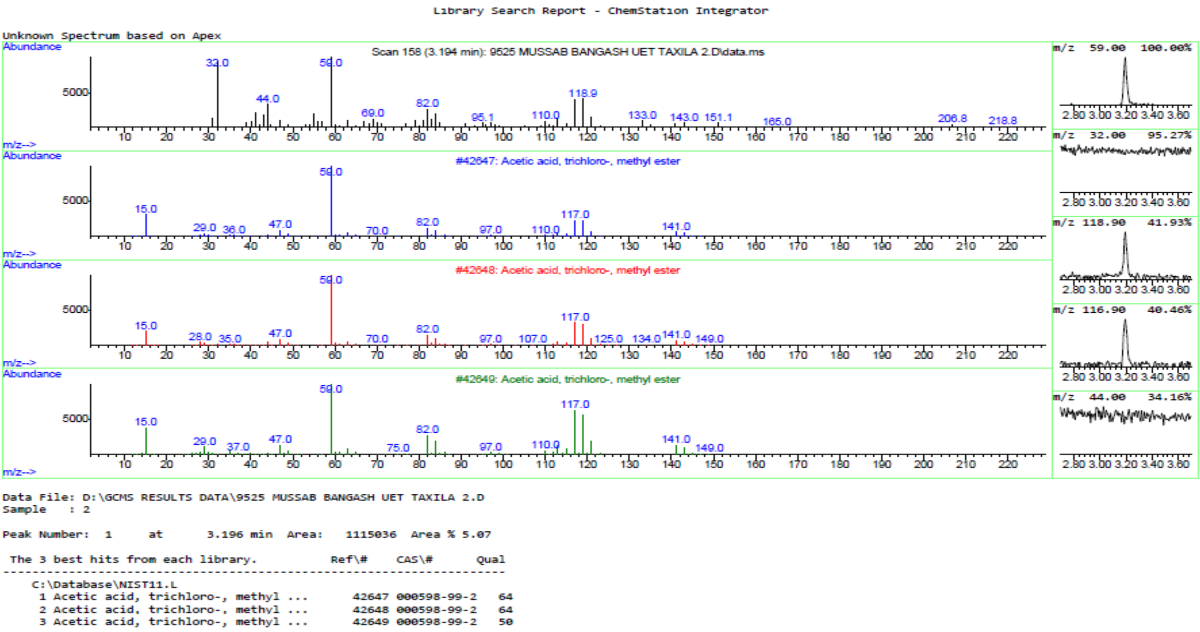


FIGURE 9| Obtained Chromatograph Passing by First Filter Media



```
Data File: D:\GCMS RESULTS DATA\9525 MUSSAB BANGASH UET TAXILA 2.D
Sample   : 2

Peak Number:  1     at      3.196 min  Area:   1115036  Area % 5.07

 The 3 best hits from each library.          Ref\#    CAS\#      Qual
------------------------------------------------------------------------
    C:\Database\NIST11.L
     1 Acetic acid, trichloro-, methyl ...      42647 000598-99-2   64
     2 Acetic acid, trichloro-, methyl ...      42648 000598-99-2   64
     3 Acetic acid, trichloro-, methyl ...      42649 000598-99-2   50
```

FIGURE 10| Obtained Mass Spectrometry Result for 1st Filtration Media

3.3. Comparison

Comparing the capacity of the two-filter media 1st, filter media is purely based on silica medium, which is known for the removal of dissolved and suspended particles yet found in result for the removal of chlorine DBPs precursor particles through sand filter media which is found to be known for removing trichloromethane up to some extent, yet cannot be able to remove TCAAs which were also traced as DBPs in water samples while analyzed in GC-Mass. Although TCAAs found in the water samples after 1st filtration media were low compared to those without filtration media, which also endorses the 1st filtration media capabilities for removing these chlorine DBPs as shown in Figure 11. For the comparison point of view, through 2nd filtration media focus chlorine DBPs, i.e., THMs and THAAs, were not traced when the sample passed by the 2nd filtration media, which shows the capability of the 2nd filtration media. In this setup, the initial sand layer resists the suspended particles besides the GAC column, retaining the precursor elements of chlorine DBPs as an adsorption phenomenon. Under controlled dosage, this non-tracing of DBPs shows the way out as a cost-effective abatement technique for removing halogens in G.I pipe nature media.

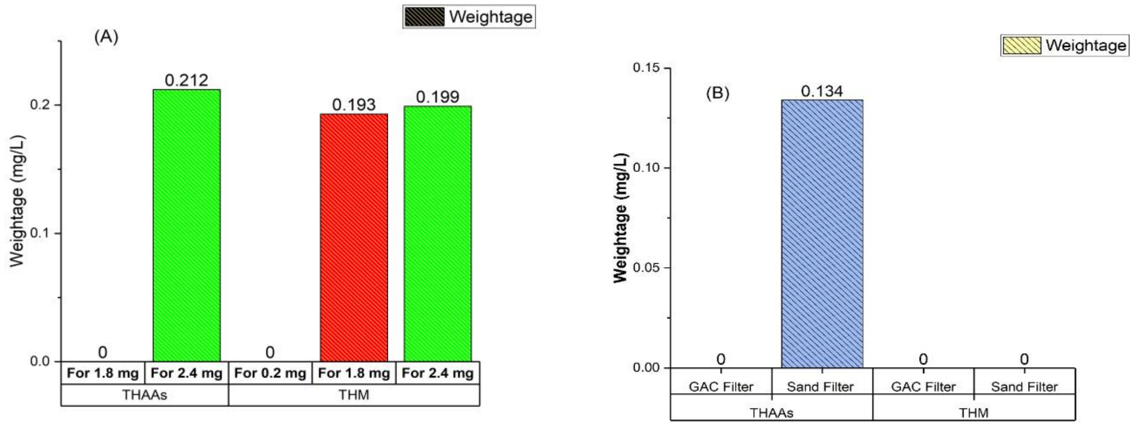


FIGURE 11| a. Chlorine DBPs generated By Products obtained weightage without filtration media b. Chlorine DBPs generated By Products obtained weightage with filtration media.

4. Conclusions

In consideration of the above discussion and results, the chlorine DBPs generation, the tracing of Trichloromethane, Trichloronitromethane, and Trichloroacetic acid, which are classified members of THMs and THAAs under controlled dosage and controlled environment endorses the idea of production of chlorine DBPs as halogens after reaction with precursors in a water sample. The result also supports the production of these DBP halogens by varying the water's physical-chemical parameters and the pipe nature. Secondly, it has also been found that the adsorption phenomenon, including sand filter media and granular activated carbon (GAC), is one of the prominent abatement techniques to remove these halogenated by-products under controlled conditions up to a great extent for G.I pipe nature medium. This analytical analysis of DBPs including identification, monitoring, and reduction can play a significant role in green chemistry and environment preservation.

Author Contributions

Musaab Habib Bangash Conceptualization, methodology, original writeup, Naeem Ejaz Leading supervision, Sadia Nasreen Leading supervision.

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Conflict of Interest

The author declares no conflict of interest.

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Data Availability Statement

The data supporting the study's findings are available from the corresponding author upon request.

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