

ASSESSMENT OF DISINFECTION BY-PRODUCT FORMATION
IN POLYMERIC PIPE DISTRIBUTION SYSTEMS

by

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Dedicated to my parents, the reason for my existence

ABSTRACT

In recent years, polymeric materials have become the dominant type of material used for drinking water pipe distribution systems. They have some advantages over other types of pipes such as cast iron, ductile iron, concrete, and copper. There are also concerns on the effect of polymeric pipes on water quality. The effect of polymeric pipes on desalinated water is an area that has not been significantly investigated in previous studies. The UAE is predominantly using a desalination plant in order to provide the water for the residents and industries. The purpose of this research was to investigate the effect of the combination of polymeric pipes and desalinated water on the formation of a disinfection byproduct. Three pipe loop systems were designed using polyvinyl chloride (PVC), polyethylene (PE), and polypropylene (PPR) materials to study the effect of polymeric pipes on trihalomethanes (THMs) formation. Natural organic matter (NOM) was used as a precursor for THMs. Experiments were conducted with different combinations of initial total organic carbon and initial calcium hypochlorite to study the effect of these operational parameters on the THM formation potential of the designed loop systems. The results of the experiments showed that PVC pipes have the most potential formation of THMs followed by PE and PPR pipes, respectively. High levels of bromide could shift the distribution of THMs by increasing the formation of brominated THMs. A statistical analysis of the obtained results showed that initial calcium hypochlorite has a significant effect on the formation of THMs. Initial total organic carbon (TOC) had the same effect; however, it did not have that strong correlation with THM formation like calcium hypochlorite.

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1 INTRODUCTION

1.1. Background Information

In recent years, polymeric pipes have replaced traditional pipe distribution systems such as copper, concrete, steel and iron pipes. Due to the high flexibility, ease of installment, high corrosion resistance, jointing properties, low weight, low cost, and durability, plastic pipes have become the dominant material for many different types of supply systems. They are used for different purposes like cold water, hot water, gas distribution, and drainage and sewerage systems. The most popular plastic pipes are PVC (polyvinyl chloride), polyethylene (PE), and polypropylene (PPR). These pipes have had a significant contribution in the construction of recent developments [1]. Recent statistics show that almost 69% of the pipes in drinking water distribution systems in United States are made of polymeric materials, mainly PVC [2]. Polymeric pipes have been shown to be better than other types of pipes in terms of forming fixed bacterial biomass on the surface of the pipes [3]. However, one study showed that the formation of microbial biofilm is slower in copper pipes than in plastic pipes [4].

After the treatment of water for domestic use, secondary disinfection of the water is carried out. This disinfection is done by chlorinating the water prior to entering the distribution system to deactivate the microbial growth in the pipes. Chlorine disinfection is the most popular method of disinfection due to the advantages it has over other disinfectants. The history of chlorine goes back to 1774 when it was prepared for the first time by Scheele. However, it was not known as a chemical until 1808 [5]. Chlorine was used as a water disinfectant in Chicago, USA in 1908 [6]. It took only a short period of time until chlorine became a well-known disinfectant to the world and was being used in small treatment plant. Chlorine disinfection is applied in different forms such as compressed gas and liquid. The liquid form is the solution that is prepared from calcium/sodium hypochlorite [6].

Chlorine is consumed in pipes through wall decay, or by reacting with the biofilm formed on the inner surface of the pipes by microbial growth. Chlorine decay should be monitored in distribution systems since it is considered to be a coupled phenomenon with DBP (disinfection byproduct) formation.

Disinfection byproducts are formed through a reaction between the chlorine and the natural organic matter present in the water. This problem mainly happens in treatment plants that use

surface water for their source of drinking water, since it has high concentration of organic matter. Leachate of volatile organic matter from the biofilm formed in the inner surface of polymeric pipes has been detected in the recent years [7]. The coatings and materials used to create polymeric pipes might leach chemicals that can be used as a source of nutrients for microorganisms to grow further and eventually increase the volatile organic carbon levels [8]. Another study showed leachate of organic compounds in PVC and PE pipes [9]. Although the organic content of desalinated water is negligible, leaching of organic compounds may cause the formation of a disinfection byproduct later when water is in the distribution system.

A high dosage of disinfection byproducts can have adverse effects on human health since they have been associated with cancer in some epidemiological studies [10]. Due to the threat of DBPs to human health, guidelines for levels of such contaminants have been regulated worldwide.

1.2. Problem Statement

Previous studies conducted on disinfection byproduct formation in distribution systems focused on conventional drinking water distribution systems or ground water as a source of drinking water. In the United Arab Emirates, the main supply of water is desalinated water. The effect of potential DBP formations and chlorine decay should be studied for desalinated water in polymeric pipe distribution systems. Therefore, this dissertation will be able to answer some of the questions regarding the effect of desalinated water and polymeric pipes on THM potential formation.

1.3. Objectives

The overall objective of this thesis is to assess the effect of polymeric materials on DBP formation potential in pipe distribution systems. The main objectives of this research are to determine:

- The effect of pipe material on trihalomethane formation
- The effect of initial total organic carbon on trihalomethane formation
- The effect of initial calcium hypochlorite concentration on trihalomethane formation

2 LITERATURE REVIEW

2.1. Disinfection

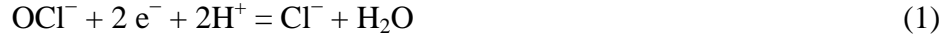
Disinfection of water is the most important part of the treatment before the water enters the distribution systems for maintaining the same quality when reaching the household plumbing units. The primary purpose of disinfection is to deactivate the microorganisms and bacteria that might contaminate the water during the time in which water travels through the distribution systems.

2.1.1. Free Available Chlorine

This term describes the summation of chlorine (Cl_2) molecular concentration, hypochlorous acid (HOCl), and hypochlorite ion (OCl^-) [6].

2.1.2. Source of Chlorine for Disinfection

Calcium hypochlorite is a solid/powdered material that is used as a source of chlorine for water disinfection. Since this bleaching powder contains hypochlorite ions, it will react with chloride as shown in Eq. 1 below.



As the equation shows, 1 mole of hypochlorite ions has a reaction with 2 electrons which results in forming available chlorine and water. Calcium hypochlorite ($\text{Ca}(\text{ClO})_2$) has two moles of hypochlorite ions. Around 99% of calcium hypochlorite is free available chlorine [6]. High available chlorine in calcium hypochlorite makes this chemical one of the most efficient materials in water disinfection.

2.1.3. Effects of Disinfectants on Water Quality

Table 2.1 shows the advantages and disadvantages of different disinfectants according to the American Chemistry Council [11]. Chlorine gas is considered as a disinfectant that is highly reliable and effective against pathogens. On the other hand, it has a low cost in comparison to other types of disinfectants. The formation of haloacetic acids (HAAs) and THMs is considered as the main disadvantage of chlorine gas. Another disinfectant that is used is chloramines. Chloramines do not have the same effect as chlorine gas in deactivation of microorganisms; however, they have less DBP potential formation [11]. The last one is chlorine dioxide which can give the water a better taste and odor, but has a high cost in comparison to other types.

Table 2.1: Advantages and Disadvantages of Different Disinfectants [11]

Disinfectants	Advantage	Disadvantage
Chlorine gas	<ul style="list-style-type: none">- The most reliable disinfectant- Highly effective against pathogens- Economic choice	<ul style="list-style-type: none">- DBP formation (HAAs, THMs)- Not effective against cryptosporidium
Chloramines	<ul style="list-style-type: none">- Reduced formation of HAAs and THMs- More stable residual	<ul style="list-style-type: none">- Weaker than chlorine- Toxic for kidney dialysis patients
Chlorine dioxide	<ul style="list-style-type: none">- Effective against cryptosporidium- Provides better taste and odor	<ul style="list-style-type: none">- DBP formation- High cost

2.2. Chlorine Decay

It has been a challenge for drinking water treatment plants to simultaneously minimize the risk of DBPs formation and provide sufficient chlorination to avoid further activities of microorganisms in distribution systems. This makes the study of chlorine decay in different pipe materials a major factor which has to be monitored in a distribution system. Polymeric pipes have shown lower reactivity with chlorine in comparison to other types of pipes. One of the important parameters that should be monitored in distribution systems is the aging of the pipes, as researchers studied the effect of aging on chlorine decay in different pipe materials and found that aging should not be ignored in some types of pipes such as cast iron, cement-lined ductile iron, cement-lined cast iron, steel, and ductile iron pipes [12]. Moreover, it was observed that according to the performance of polymeric pipes, aging was not a concern for chlorine decay and these types of pipes had less reactivity with chlorine [12].

PVC pipes have shown lower reactivity with chlorine than ductile iron or cast iron pipes [13]. One study on different types of pipe materials such as cast iron, spun iron, cement-lined ductile iron, PVC, and medium density polyethylene (MDPE) investigated the chlorine decay corresponding to the type of pipes used in the experiments [14]. The new polymeric pipes such as PVC and MDPE showed almost zero reactivity with the chlorine, resulting in no wall decay of chlorine. On the other hand, cast iron had the largest decay, followed by spun iron and cement-lined ductile iron [14].

Degradation of the polymeric pipes should be investigated since it has been noticed that chlorine dioxide can degrade the polymeric pipes leading to cracks on the surface of the pipes [15]. Many researchers only studied the wall decay of chlorine; however, degradation of the polymeric pipe should be considered as well, since oxidizers present in water can degrade the surface of the pipe resulting in cracks [16]. Polyethylene pipes are sensitive to chlorine dioxide. Results of one study which assessed the impact of different disinfectants like chlorine dioxide and sodium hypochlorite on the polyethylene pipes (PE) showed that after a few weeks of exposure, PE pipes showed significant antioxidant consumption using chlorine dioxide [16]. Chlorine dioxide had an adverse effect on the mechanical properties of polymeric pipes due to its high reactivity with the pipe material [16].

HDPE (high density polyethylene) pipes and chlorinated polyvinyl chloride pipes were studied regarding their chlorine residual. According to the results, the water that was exposed for 3-4 days to these types of pipes in stagnant conditions showed a decrease in disinfection residual which showed that chlorine had reacted with the pipe material [9]. Hydraulic modeling and wall decay of chlorine were studied using pipe column tests and also actual distribution systems. Results showed that the chlorine decay in cast iron pipes were more than PVC pipes. In general, the experiments showed that pipe material, diameter of the pipe, and the initial chlorine concentrations are the factors that affect the wall decay of the chlorine in distribution systems [17].

Most of the studies have focused on the comparative assessment between the polymeric pipes and conventional types of pipes used in drinking water distribution systems. With the emerging popularity of polymeric types of pipes and their short history, further investigation on comparative assessment between different types of polymeric pipes is an essential need. Table 2.2 shows previous studies on the chlorine decay of different types of pipes.

Table 2.2: Previous Studies on Chlorine Decay

Srl. No.	Pipe Material	Studied Variables	Samples	Experimental Conditions	Results	Reference
1	PVC, Cast Iron	Wall Decay of Chlorine	Conventional Treated Water	Pipe column tests and actual distribution systems	-Chlorine decay is more in CI pipes than in PVC pipes - Pipe diameter, pipe material, and initial chlorine are important factors in chlorine decay	[17]
2	PVC, Ductile Iron	Wall Decay of Chlorine, Bulk Consumption	Conventional Treated Water	Pipe loop systems with different flow rates in variable flow regions, initial chlorine concentration was studied as a variable	PVC pipes showed a lower chlorine decay rate than ductile iron	[13]
3	CI*, SI*, DICL*, PVC, MDPE	Chlorine Decay	Conventional Treated Water	In situ measurement of chlorine decay was done between two points	Chlorine reactivity showed the trend as below: CI>SI>DICL>PVC>MDPE	[14]
4	CI, DICL*, PVC, PE, DI	Chlorine Decay	Well Waters in Saudi Arabia	320 different pipes (used, new) were tested on their chlorine residual	-Cast iron showed the highest reactivity -Polymeric pipes showed less reactivity -Aging was an important issue in pipes having iron, but was less important in steel. It had almost no effect on polymeric pipes	[12]
5	Polyethylene	Oxidative Resistance and Mechanical Properties	Conventional Treated Water	A designed monitored test plant using PE pipes, using different disinfectants	PE pipes were studied on their performance while exposed to chlorine dioxide and sodium hypochlorite showing that mechanical properties of polyethylene changed by chlorine dioxide	[16]
6	HDPE, cPVC	Odor, Chlorine Residual	Conventional Treated Water	Utility quick test	Both pipes showed reduction in chlorine residual	[9]

*CI: Cast iron

*DICL: Cement-lined ductile iron

*SI: Spun iron

2.3. Disinfection Byproducts

Disinfection and disinfection byproduct formation are considered as a coupled phenomenon that can have adverse effects on the quality of the water in drinking water distribution systems. The reaction between the organic matter present in water and chlorine can form DBPs which are toxic and a serious threat to human health. Up to 700 different types of DBPs have been observed [18]. Among these, two types of DBPs are considered dominant in drinking water distribution systems: trihalomethanes (THMs) and haloacetic acids (HAAs). High concentrations of these two contaminants have been detected after disinfection in recent years [18]. Since these DBPs are potent carcinogens, many researchers have studied the effect of disinfection on the formation of byproducts. Table 2.3 shows different types of HAAs; however, only the first five acids are regulated [19]. The sum of the first five types should not exceed 60 micrograms per liter.

Table 2.3: Different Types of HAAs

NO	HAAs	Abbreviation
1	Monochloroacetic Acid	MCAA
2	Dichloroacetic Acid	DCAA
3	Trichloroacetic Acid	TCAA
4	Monobromoacetic Acid	MBAA
5	Dibromoacetic Acid	DBAA
6	Tribromoacetic Acid	TBAA
7	Bromochloroacetic Acid	BCAA
8	Bromodichloroacetic Acid	BDCAA
9	Dibromochloroacetic Acid	DBCAA

THMs consisting of different types are shown in Table 2.4:

Table 2.4: Different Types of THMs

NO	THMs	Abbreviation
1	Trifluoromethane	CHF_3
2	Chlorodifluoromethane	CHClF_2
3	Chloroform	CHCl_3
4	Bromodichloromethane	CHBrCl_2
5	Dibromochloromethane	CHBr_2Cl
6	Tribromomethane,	CHBr_3
7	Triodomethane	CHI_3

The EPA in the US regulated the maximum allowed concentration of TTHM (total trihalomethanes) as 80 ppm (parts per billion). TTHMs are considered as the sum of bromodichloromethane, dibromochloromethane, tribromomethane, and chloroform in treated water.

2.4. THM Precursors

Formation of THMs is mainly dependent on the characteristics of the source of water used prior to water treatment. The presence of natural organic matter (NOM) is the key factor for reactions forming disinfection byproducts. Hydrophilic acids, humic substances, and organic compounds are the primary precursors of THMs [20,21]. The presence of nitrite is considered as one of the precursors for THMs; however, other researchers proved that it did not have any significant effect on THM formation [22]. Since nitrite was not associated with THM formation in previous studies [22], it was not focused as a parameter in this dissertation. Besides the mentioned precursors, if bromide is present in the water, the available chlorine in the form of hypochlorous acid can react with bromide to form hypobromous acid. These reactions will

eventually result in the reaction of the precursors with the formed hypobromous acid causing the formation of chloro-bromo THMs [23].

Among the mentioned THMs, those which are associated with bromine are considered as brominated THMs, while those which do not have a bromide ion as a precursor are chlorinated types of THMs. Figure 2.1 shows the process of THM formation in the presence of NOM which was discussed earlier in this section.

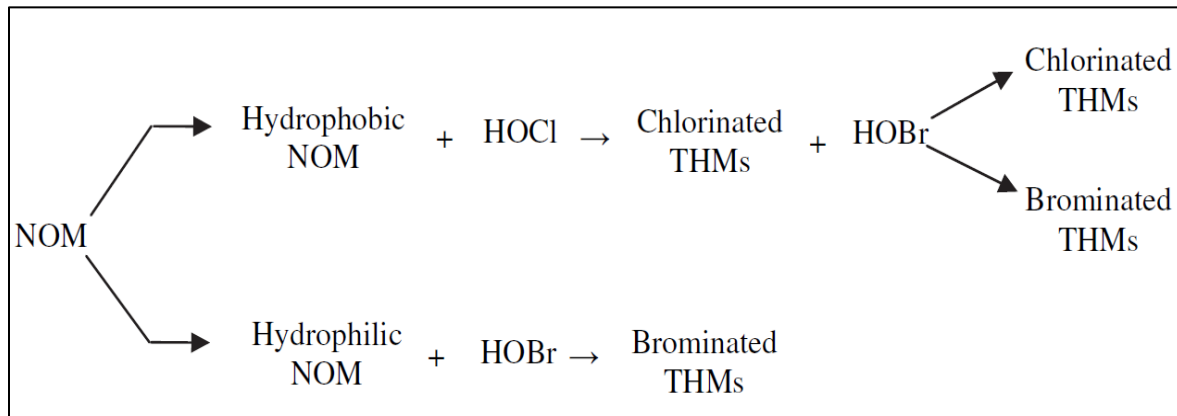


Figure 2.1: How NOM is Used to Form Chlorinated and Brominated THMs, Adapted from [24]

Total organic carbon can be a good measure of natural organic matter in water samples. Generally THMs showed higher potential formation with the increase in NOM and chlorine dose [25]. Also another study which was conducted on the effect of different parameters on THM formation showed a strong correlation ($r=0.90$) between TOC dose and THM formation [26].

One study found a strong correlation between dissolved organic carbon and total THM formation potential with $R^2=0.981$ [27] (Figure 2.2). However, increasing the organic content of water would not guarantee higher formation of THMs if residual chlorine is not sufficiently present in the system [26]. With the recent studies showing leachate or the occurrence of TOC in polymeric pipes [7,9], there is a need for studying the effect of initial TOC on THM formation potential in polymeric pipes.

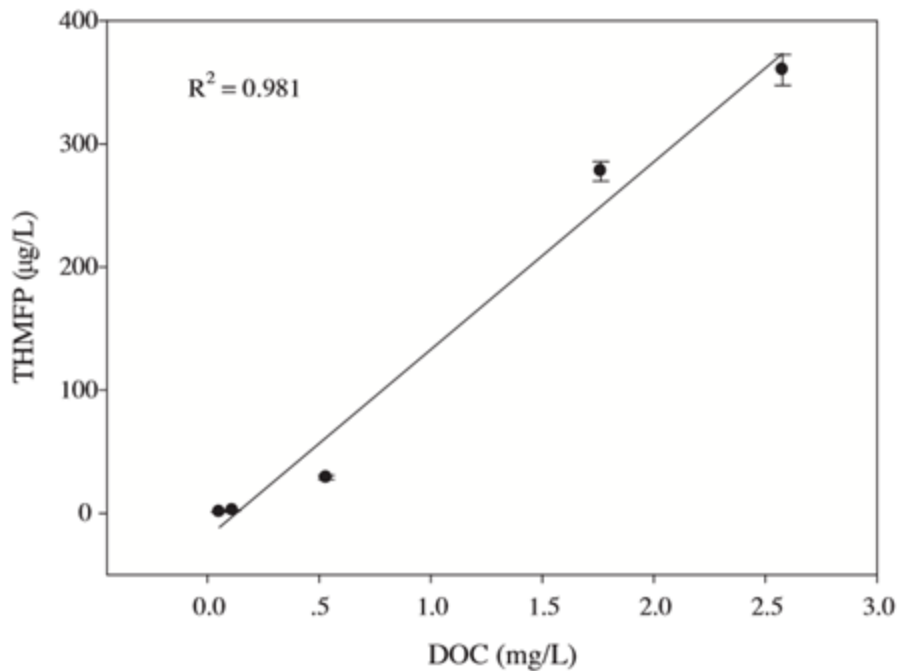


Figure 2.2: Strong Correlation of DOC and TTHM Formation Potential [27]

2.5. Vinyl Chloride Occurrence in Polymeric Pipes

One of the problems associated with PVC pipes is the leachate of vinyl chloride, a carcinogenic compound with health threats for human beings [28]. One case history in Doniphan County, Kansas showed that PVC pipes containing stagnant water for several days can leach vinyl chloride with a concentration of more than 2 ppb, with the potential to reach up to 14 ppb. The study showed that this leachate was more in dead-end zones of the distribution systems. Results of another study showed that vinyl chloride leached from PVC pipes, although it was less than the regulation which is 2 ppb [29]. Vinyl chloride leachate might have an effect on the formation of disinfection byproducts if it can release available chlorine inside the water in any forms discussed earlier in this report.

2.6. Effect of Pipe Material on DBP Formation

Due to the lower reactivity of polymeric pipes with disinfectants, lower potential formation of DBPs has been reported in the previous studies for polymeric pipes [13]. However, one study on different setups showed that THM formation was dependent on the pipe material in which the

same amount of biofilms were formed in the inner surface of all experimented pipes. The variations of THM formation were due to the pipe material as all other experimental conditions were controlled to be the same in different setups [30].

Experiments were conducted on copper and glass pipes and the results showed that there was no significant difference between the sum of HAAs and THMs in copper and glass pipes in the first 12 hours of chlorination [31]. However, the distribution of HAAs was different in each case. More MCAA, DCAA, DBAA, and THMs were formed in copper pipes. Pipe loop systems consisting of PVC and ductile iron pipes were studied in their DBP potential formation and PVC pipes showed lower potential formation of DBPs [13].

Experiments conducted on HDPE and PVC pipes showed that volatile organic components can leach from the polymeric pipes into the water [7]. Another problem associated with HDPE pipes was the odor, which was (TON=Threshold Odor Number >4). It was concluded that polymeric pipes can leach organics into the water inside the distribution system, potentially producing toxic byproducts [7]. Total organic carbon can leach from the polymeric pipes like polyethylene and chlorinated polyvinyl chloride pipes; however, it has been shown that DBP formation due to the organic materials leached into the water can be neglected [9].

One cannot say that the effect of chlorine decay by non-DBP reactions will lower the possibility of forming DBPs in a distribution system [32]; however, this should be investigated through an experimental procedure. The effect of pipe material should be assessed on potential DBP formation since the reactivity of pipe material with chlorine is different for each type of pipes.

2.7. Effect of pH and Temperature on DBP Formation

The effect of pH and temperature should be considered in DBP formations as well. Higher temperature can increase the byproduct formations [33]. High concentrations of HAAs and THMs can be formed rapidly if there is an increase in the temperature of the water [33].

A study showed that the concentration of DBPs is different in the flow of water in distribution systems than in the stagnant portion of the water which is in hot water tanks in housing plumbing systems [34]. Due to the high temperature of the hot water tanks, DBPs can generate quickly, creating high DBP concentration in water distribution systems [34]. DBP formations are also dependent on seasonal changes due to differences in temperatures, with

higher DBPs observed in summer than winter [35]. A report found that DBP formations are almost double in summer compared to winter [36].

The pH of water is considered as one of the factors that can affect DBP formation as well. The effect of pH is different based on the type of DBPs. Increasing the pH can increase the formation of THMs. On the other hand, decreasing pH value can increase the formation of HAAs [37]. Increasing the pH value from 6 to 9 can increase the formation of disinfection byproducts like THMs significantly [38]; however, this does not have the same effect on the HAA formation. pH values of less than 5.5 could have formed the same amount of HAAs and THMs; however, pH values of more than that could form more THMs only [39]. Increasing the pH level from 6-8.5 can increase the generation of THM, but it will decrease the HAA formation [40]. A summary of the results obtained from previous studies related to DBP formations is presented in Table 2.5.

Table 2.5: Previous Studies on DBP Formations

Srl. No.	Pipe Material	Test	Studied Variables	Experimental Conditions	Results	Reference
1	Copper, Glass	DBPs	THMs, HAAs	Pipe rigs were used, and Beijing tap water was used as samples of water	No significant difference between the sum of HAAs and THMs between copper and glass pipes.	[31]
2	PVC, Ductile Iron	DBPs	THMs	Pipe loop systems with different flow rates in variable flow regions, doses of chlorine were changed as variable	PVC pipes showed lower DBP potentials than ductile iron	[13]
3	HDPE, cPVC	THMs TOC	Conventional treated water	Utility quick test	TOC leached from both pipes into the water; however the formation of THM was not significant	[9]
4	N/A*	THMs HAAs	Treated water of a river	THM and HAAs were checked using variables such as pH, disinfectant concentration, etc.	The increase in pH had a great impact in formation of THMs; however, it did not have the same impact on HAA formation	[38]

5	N/A*	THMs HAAs	Raw water treated tater	THM and HAAs were checked for different variables like pH and temperature	Increasing pH from 6-8.5 showed a significant increase in THM formation and a decrease in HAA formation; higher temperature resulted in a higher formation of DBPS	[40]
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*N/A: Not Available

2.8. Desalination

Desalinated water is considered as the main source of water in some countries that do not have access to natural resources of water like surface or ground water. Almost 25% of the fresh water supply in Israel is desalinated water [41]. Desalinated water is the only source of drinking water in Gaza for more than 90% of the population of the Gaza Strip [42]. Many countries like Australia, China, Singapore, and the US are using desalination to supply water, but in recent years Middle Eastern countries around the Persian Gulf have become the hot spot for desalination plants [43]. The emerging use of desalinated water due to lack of access to natural drinking water has some environmental issues, such as air emissions and improper disposal to marine environments, which should be assessed. The United Arab Emirates produces 23% of the total world production of desalinated sea water. Figure 2.3 shows the desalinated water-producing countries worldwide [43]. Water scarcity is increasing at a rapid pace, and more countries are investigating the use of desalination plants for their drinking water supply. As shown in Figures 2.3 and 2.4, many countries are into producing drinking water using sea water desalination since they have access to sea water.

Polymeric pipes are gaining popularity worldwide as mentioned earlier for the purpose of drinking water distribution systems. Environmental impact assessments need to be done since these facilities are new to the environment and there are not significant histories or backgrounds for them. This shows that there is a need to investigate the effect of desalinated water combined with polymeric pipes since there are few studies done on this combination in drinking water distribution systems.

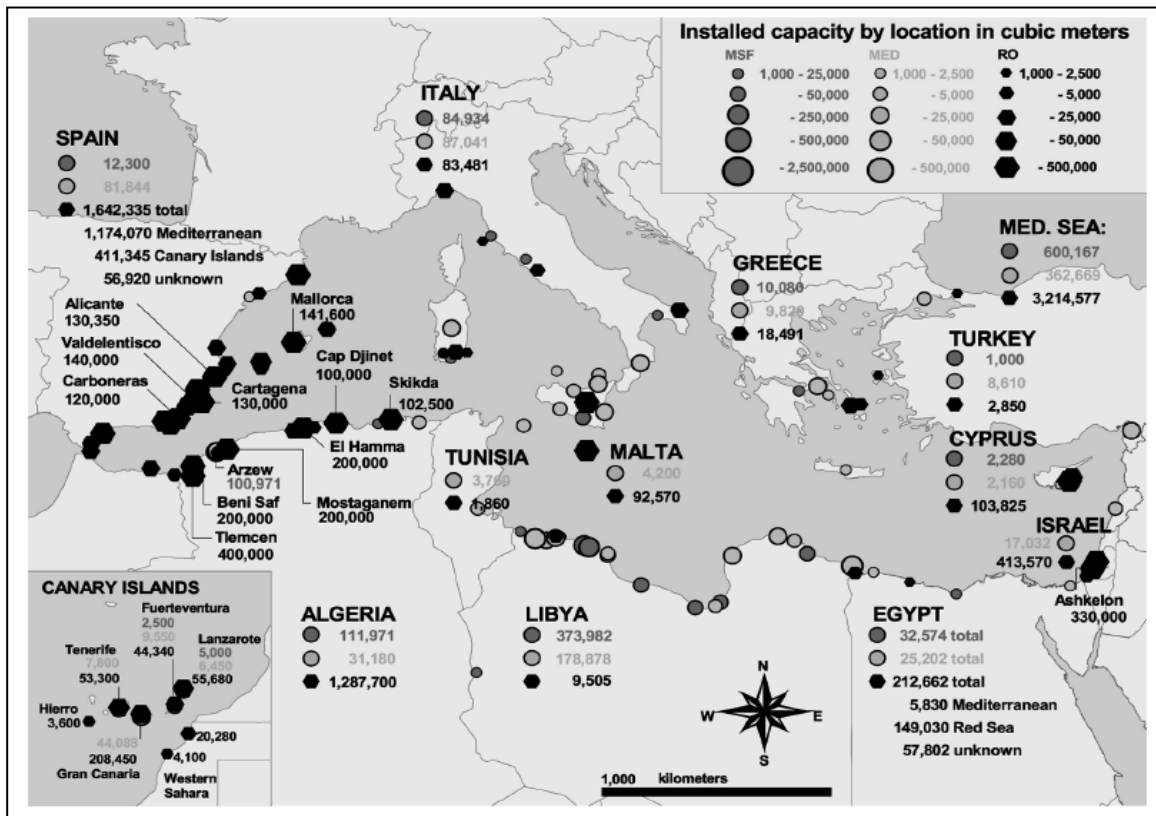


Figure 2.3: Sea Water Desalination Capacity in the World [43]

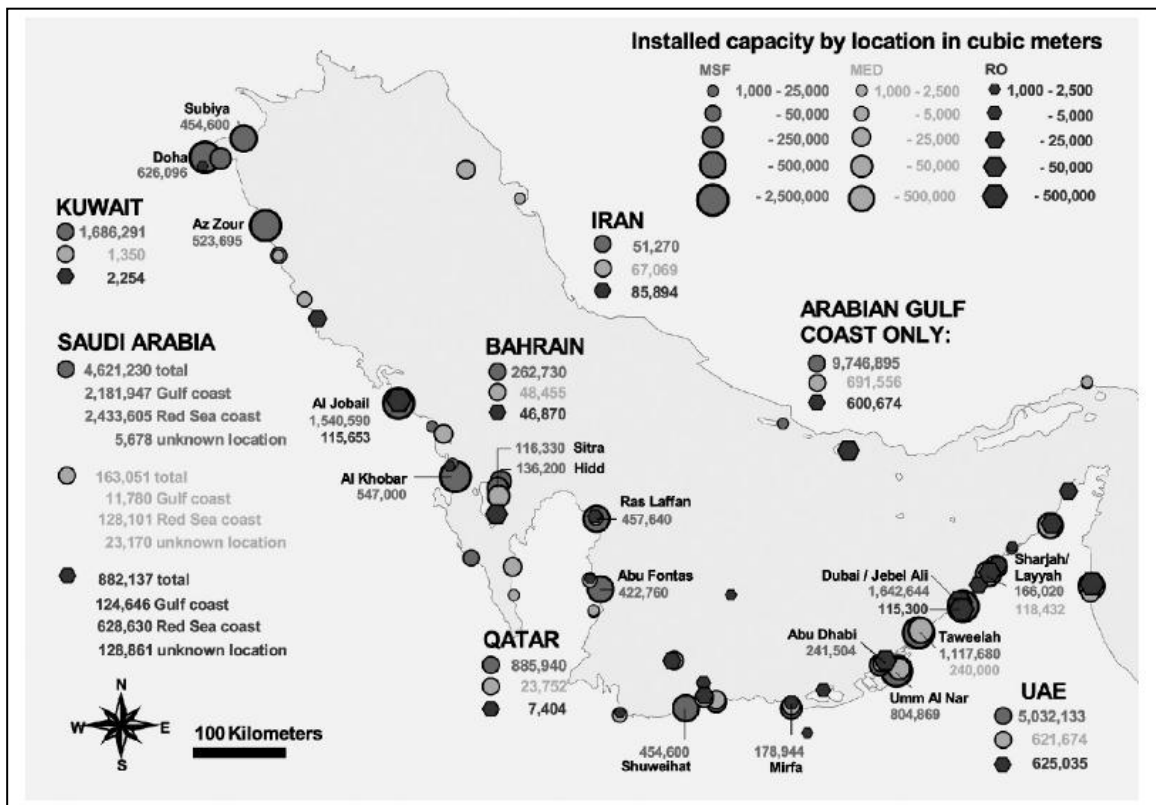


Figure 2.4: Sea Water Desalination Capacity in the Middle East [43]

3 MATERIALS AND METHODS

3.1. Materials

3.1.1. Water

Tap water from the geotechnical engineering lab of the American University of Sharjah was used for all the experiments conducted in this project. Desalinated water is the primary source of water used in Sharjah which is produced from processes such as reverse osmosis and distillation.

3.1.2. Disinfectant

Calcium hypochlorite, which is known as bleaching powder, was used in order to simulate the disinfection process of treatment plants prior to entering the distribution systems. Different reasons were behind the selection of calcium hypochlorite as a disinfectant in this project. Liquid and gas chlorine could not be used in the conducted experiments due to the properties of the designed setup such as the high temperature caused by the pumps and also the sampling point which was the cap of the tanks.

A major criterion which was the governing factor behind this selection was the long term availability of residual chlorine after using calcium hypochlorite as a disinfectant. Although using this disinfectant was the best option among other types available in the market, it had some issues such as causing an increase in the pH level, less solubility in water than other disinfectants, and high impurity which caused highly turbid water samples in the end of each experiment.

3.1.3. Precursor

Initially, decaying vegetation was used as the source of organic carbon in the experiment. However, preliminary results indicated that it is heterogeneous, difficult to control, and did not provide the required organic carbon to form necessary THMs. Having the preliminary results, coffee blend replaced decaying vegetation as a precursor due to lack of time (3 days for the duration of each cycle) and the lower ability of vegetation to reach the decay which was needed to produce the needed levels of TOC in the water samples within the time frame. Coffee was effective in forming THMs in the time span defined in this research.

3.2. Experimental Setup

3.2.1. Pipe Loop Systems

Pipe loop systems are widely used to simulate the movement of water in drinking water distribution systems and their storage in the laboratory conditions [13]. Three pipe loop systems were designed to simulate drinking water distribution systems made from different polymeric pipes (polyvinyl chloride, polypropylene, and poly ethylene) (Figure 3.1). All three setups were designed completely in the same style except the materials which were used for their pipes, elbows, and valves.



Figure 3.1: Setups Created with Different Polymeric Pipes

3.2.2. Circulation

In order to circulate the water, a 0.75 hp pump was used to move the water from a storage tank to the loop and back to the same tank after circulation. The volume of water used in all the conducted experiments was 20 L. The flow rate of the water was controlled as 0.56 L/s with a valve in all the experiments resulting in a velocity of 1.11 m/s which is a reasonable number for simulating the travel of water in a real distribution system. Water flowing in a loop is expected to reflect water flowing through a large section of pipes, thereby representing the actual distribution system. There was a check valve just before the pump that protected the pump from possible

damage due to the effect of water going back to the pump while it was not under use. Previous studies showed that the formation of THMs will reach an approximately steady state after 70 hours of residence time [44]. This is why the circulation duration was set as 3 days for all the conducted experiments to give enough residence time for the formation of trihalomethanes.

3.2.3. Pipe Network

The pipes used in the designed loop systems were made of polyvinyl chloride, polypropylene, and poly ethylene. The diameter of the pipes was selected as 1-inch for the entire loop systems as they were locally available with different materials used in this thesis and they were compatible with the capacity of the pumps used in this project. All the elbow connections used were made of the same material with 1-inch diameters. Like the previous parts of the loop systems, the valves (both check and normal) were used with same material to make the results of the experiments as reliable as possible.

3.2.4. Experimental Outline

The experimental plan was scheduled after the trial and error experiments were conducted. The main outcome of the preliminary results was the dose of calcium hypochlorite and organic added to each setup prior to water circulation. This is discussed in detail later in this dissertation. The effect of initial TOC and calcium hypochlorite dose were studied along with the main purpose of this project which was the effect of the pipe material.

In order to study the effect of TOC on THM formation, experiments were conducted with three different initial TOC values of 0.15, 0.69, and 0.75 mg/L which were due to the use of a coffee blend as natural organic matter in doses of 10, 15, and 20 mg/L. In all these experiments, the initial dose of calcium hypochlorite was constant combined with different initial doses of organic material. The same scenario was applied for different calcium hypochlorite doses with constant values of the organic dose. Table 3.1 shows the experimental plan that was used in this project.

Table 3.1: Experimental Plan

No	Calcium Hypochlorite (g/L)	Organics (mg/L)
1	0.50	10
2	0.50	15
3	0.50	20
4	0.75	10
5	0.75	15
6	0.75	20
7	1.00	10
8	1.00	15
9	1.00	20

3.3. Analytical Methods

Water samples were collected from the inlet of the storage tanks in 1 L dark amber bottles for THM measurements. They were kept under ice cubes to make sure the temperature did not have an effect on the measurements. All other parameters analyzed in this project were sampled from the same collection point and measured right after collection.

3.3.1. Trihalomethanes

The measurements of THMs were done in the GEOCHEM lab located in Techno Park, Jebel Ali. A purge and trap and gas chromatograph (GC) method was used for measurements (USEPA 524.2) [45]. The samples were collected in the tubes after being diluted 100 times so they could agree with the instrument limit (0-50 ppb) (Figure 3.2).

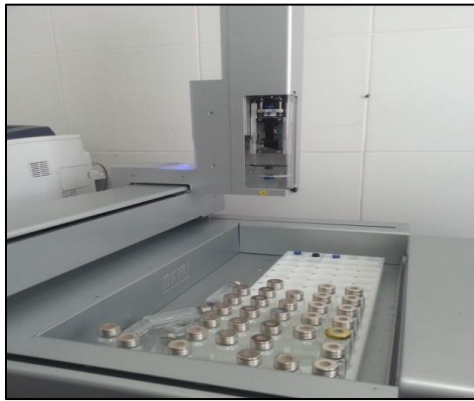


Figure 3.2: Dynamic Headspace for Purge and Trap

The incubation of the samples was processed at 70 °C for 10 minutes in the thermostatic oven. Moreover, stripping of the gases was for 5 minutes. The stripping process was followed by a drying state in which the water content was removed. During the injection process which was at 250 °C the trihalomethane gases were collected at the top of the container due to their lower density; in other words these inert gases of THMs were passed through the aqueous sample in order to get trapped by the sorbent material which in this case was tenaxgr (a polymeric material which is used to trap the THMs). Baking was the next process which was done to make sure that the trap was clean; this process was done at 280 °C (Figure 3.3).

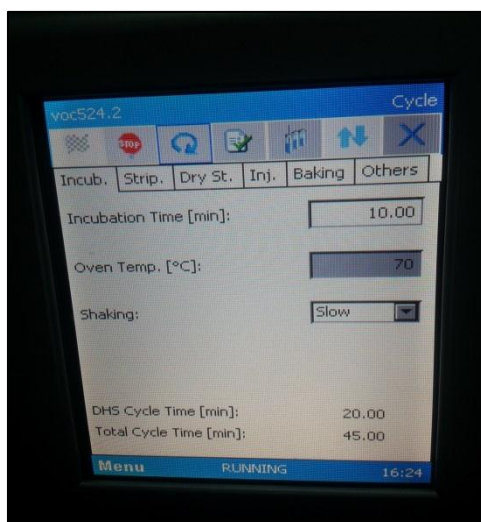


Figure 3.3: Processes During Purge and Trap

Helium gas was used as a carrier gas for GC which heated and desorbed the trapped sample components. The gas components were further carried to a mass spectrometer (Figure 3.4). In the column of the mass spectrometer (DB5) the separation of the THMs was done based on their masses. In this process the concentration of each THM was measured based on its MS response compared to a reference spectra of retention times. For the preservation of the samples the bottles were kept under ice cubes while taking them to the lab. The samples were kept at 4 °C and were taken for measurements no later than 1 week after collection of the samples. In order to avoid interference of chlorine, based on the chlorine residual of the samples sodium thiosulfate was added to the samples prior to preservation.



Figure 3.4: Mass Spectrometer

3.3.2. Total Dissolved Solids

The standard method (2540 solids) was used for TDS measurements [46]. 47 mm filters were used to pass through a certain known amount of water which was 20 ml in this project. The water which passed through the filter was kept in a container in the oven at 180 °C for 24 hours. The subtraction of the weight of containers before and after the tests represented the total dissolved solids in the water samples after each cycle of experiments.

3.3.3. pH and Temperature

A pH 100 probe manufactured by YSI Environmental was used for both temperature and pH measurements. The probe was calibrated prior to each measurement done after the run of each batch of experiments.

3.3.4. Chlorine

A HACH DR 5000 spectrophotometer was used to measure the chlorine after each run of the experiments. Method 8021 of HACH DR 5000, which has a range of 0-2 mg/L, was used. For this method DPD-free chlorine powder pillows were used as the required reagent. 1.0 N sulfuric acid was used to adjust the pH in the range of 6-7 before the measurements were carried out as required in the interference table.

3.3.5. Bromine

A HACH DR 5000 spectrophotometer was used to measure the bromine. Method 8016 of HACH DR 5000, which has a range of 0.05-4.50 mg/L, was used. For this method, DPD total chlorine powder pillows were used as the required reagent. 1.0 N sulfuric acid was used to adjust the pH in the range of 6-7 before the measurements were carried out as required in the interference table.

3.3.6. Other Parameters

An APHA 5310B high temperature combustion method was used for measurements of total organic carbon [46]. A HACH sensION5 Conductivity Meter was used for measurements of conductivity in milli Siemens (mS). HACH 2100P was used for measurements of turbidity in nephelometric turbidity units (NTU).

3.4. Statistical Analysis

Variance ANOVA (two-factor without replication) analysis was done using the results of each setup regardless of the effect of the pipe. The alpha value was set as 0.05 resulting in a 95 percent confidence interval. Calcium hypochlorite dose and initial TOC values were the two factors used as the studied variables in the analysis.

4 RESULTS AND DISCUSSION

4.1. Preliminary Results

Experiments were done in batches to identify the appropriate proportion of chlorine and precursor concentrations for trihalomethane formation. Using decaying vegetation (leaves of locally available trees and grass) as a precursor of trihalomethanes resulted in less than 10 ppb of TTHMs. The next phases of the preliminary experiments in the batches were done using coffee blend to simulate the dissolved organic matter present in the samples as a THM precursor. Results showed a reasonable formation of THMs (Table 4.1). Due to the significant effect of coffee, decaying vegetation was omitted in the main experimental approaches of this dissertation. The results of TOC did not represent the real TOC values of drinking water sources, which resulted in reducing the amount of coffee added in the combinations of main experiments. Calcium hypochlorite doses were also reduced significantly in order to simulate the real disinfection process in drinking water treatment plants.

Table 4.1: Preliminary Results of Batch Tests

Initial Conditions			
Volume of Water (L)	1	1	1
Organics (Leaves) (g/L)	0.4	0.2	0.5
Coffee (g/L)	0.1	0.05	0.5
Calcium hypochlorite (g)	5	5	8
Results			
Chloroform (ppm)	2.62	1.77	3.39
Bromodichloromethane (ppm)	0.06	0.3	NA*
Dibromochloromethane (ppm)	0.03	0.15	NA*
Tribromomethane (ppm)	0.009	0.07	NA*
Trihalomethanes (ppm)	2.719	2.29	3.39
TOC (ppm)	23.18	11.6	77.97

*N/A: Not Available

4.2. Effect of TOC on Trihalomethanes Formation

Results showed a logical pattern of increase in THM formation with increasing the dose of organic material. Figures 4.1-4.3 show the effect of organic dose on the formation of THMs with different initial doses of calcium hypochlorite as a disinfectant. The obtained results were consistent with the previous findings about the effect of TOC on THM formation. The general pattern shows that the initial organic dose is directly proportional to the formation of THMs. This agrees with the outcome of previous studies on the effect of dissolved organic matter on DBP formation potential [27,47]. A significant increase was observed in THM formation by using the first additional amount of organics, which showed that reactions were happening rapidly with the addition of the organics. Although the increasing pattern of THM formation due to higher dissolved organics has been observed in previous studies, the shape of the graphs was not consistent with the findings of the research [27]. Strong linear relationships were the outcome of previous research on the effect of TOC; however, Figures 4.1-4.3 do not represent a strong linear relationship. Although one can clearly observe an increase in THM formation in the last point of the graphs, the increase is not that significant in comparison with the second point of the graph which may be due to the fact that the reaction rate might have been reduced due to the addition of extra organic material, or the reaction rate might have been slow in the formation of THMs regardless of the initial organic dose.

Among the THM formation kinetic parameters, the rate of the reaction is one of the most important factors, since the nature of these reactions is heavily time dependent. Regardless of residence time, the initial TOC values were controlled which resulted in the higher potential formation of THMs with an increase in TOC.

Based on the results, the PVC setup showed more THM formation followed by the PE and PPR setups, respectively (Figures 4.1-4.3).

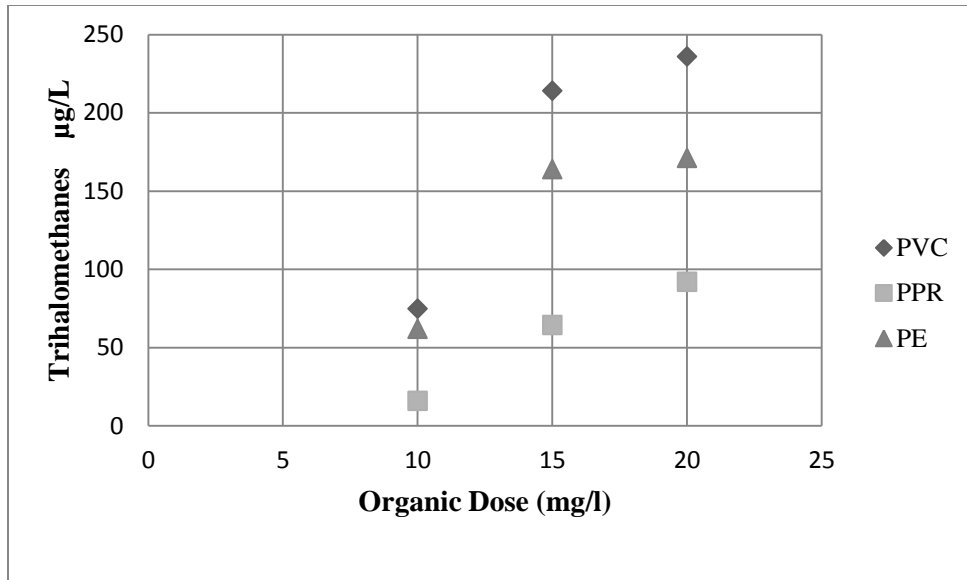


Figure 4.1: Effect of TOC on Trihalomethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

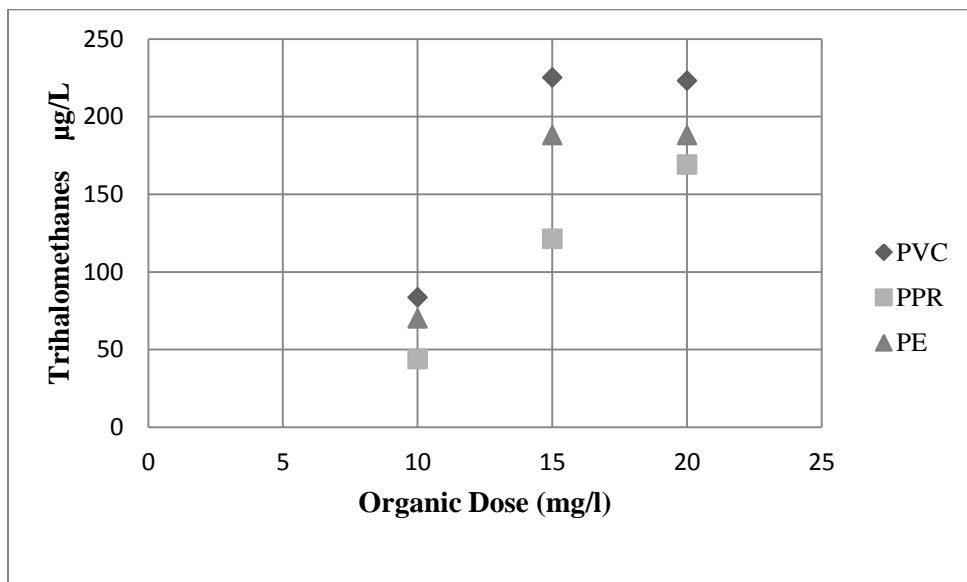


Figure 4.2: Effect of TOC on Trihalomethane Formation with an initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

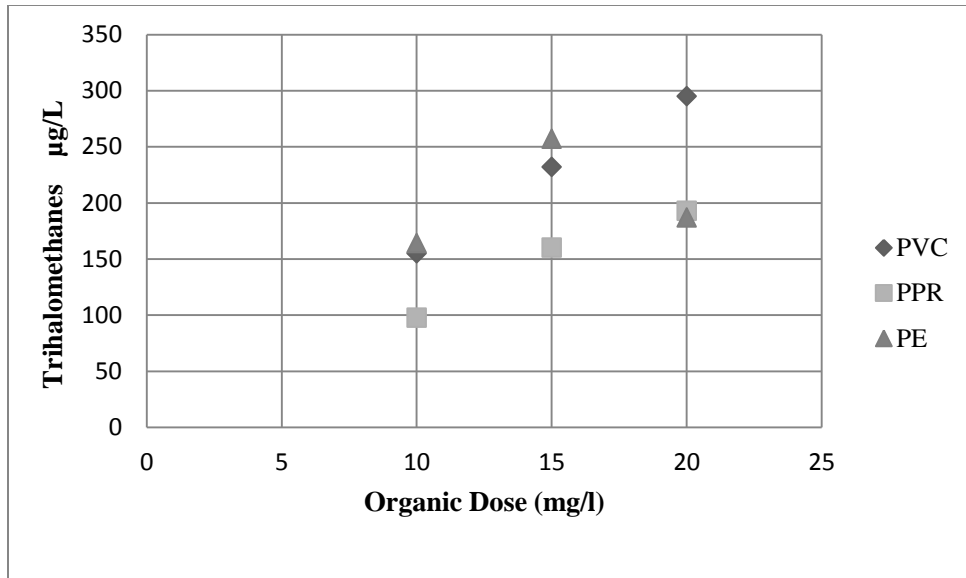


Figure 4.3: Effect of TOC on Trihalomethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

For the PVC pipe, the P-value from the ANOVA analysis was 0.060281, showing that the effect of TOC was significant in THM formation. Furthermore, the P-values for PE and PPR pipes were found to be 0.074238, and 0.020806 (Tables 4.2-4.4).

The obtained results from the ANOVA analysis showed evidence of correlation between TOC and values close to 0.05 for PVC and PE loop systems; however, they did not have same level of relevance as the PPR setup which had a value of 0.020806, which is close enough to 0.01 to be considered strongly related. It indicated that the effect of TOC was statistically significant in the formation of THMs.

Table 4.2: ANOVA Two Factor Without Replication for the PVC Pipe

<i>SUMMARY</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
TOC 0.15 (ppm)	3	313.4	104.4667	1933.703		
TOC 0.69(ppm)	3	671	223.6667	82.33333		
TOC 0.75 (ppm)	3	754	251.3333	1472.333		
Ca(ClO) ₂ of 0.5 g/L	3	524.9	174.9667	7631.003		
Ca(ClO) ₂ of 0.75 g/L	3	531.5	177.1667	6581.083		
Ca(ClO) ₂ of 1 g/L	3	682	227.3333	4916.333		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Rows	36543.9	2	18271.95	42.6681	0.002005	6.944272
Columns	5263.802	2	2631.901	6.145935	0.060281	6.944272
Error	1712.938	4	428.2344			
Total	43520.64	8				

Table 4.3: ANOVA Two Factor Without Replication for the PE Pipe

<i>SUMMARY</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
TOC 0.15 (ppm)	3	295.85	98.61667	3222.841		
TOC 0.69(ppm)	3	609	203	2331		
TOC 0.75 (ppm)	3	547	182.3333	96.33333		
Ca(ClO) ₂ of 0.5 g/L	3	396.85	132.2833	3732.891		
Ca(ClO) ₂ of 0.75 g/L	3	446	148.6667	4641.333		
Ca(ClO) ₂ of 1 g/L	3	609	203	2331		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Rows	18331.47	2	9165.736	11.90751	0.020681	6.944272
Columns	8221.372	2	4110.686	5.340327	0.074238	6.944272
Error	3078.977	4	769.7442			
Total	29631.82	8				

Table 4.4: ANOVA Two Factor Without Replication for the PPR Pipe

<i>SUMMARY</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>			
TOC 0.15 (ppm)	3	157.38	52.46	1721.425			
TOC 0.69(ppm)	3	345.6	115.2	2317.53			
TOC 0.75 (ppm)	3	454	151.3333	2784.333			
Ca(ClO) ₂ of 0.5 g/L	3	172.29	57.43	1479.778			
Ca(ClO) ₂ of 0.75 g/L	3	334.09	111.3633	3993.439			
Ca(ClO) ₂ of 1 g/L	3	450.6	150.2	2347.32			
ANOVA							
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>	
Rows	15017.86	2	7508.931	48.19503	0.001588	6.944272	
Columns	13023.36	2	6511.682	41.79433	0.002086	6.944272	
Error	623.212	4	155.803				
Total	28664.44	8					

4.2.1. Effect of TOC on Individual Trihalomethanes Formation

The effect of TOC on individual THMs showed a similar pattern as the effect of TOC on total THMs. However, as shown in the plotted figures, some values were erratic which makes it difficult to make conclusive comments on them individually. Chloroform is different from the other THMs in the sense that bromide is not considered one of its precursors. For chloroform the pattern was the same with the increase of organic dose, and data points were not far from each other in the first set of the experiment at 10 mg/l. As bromide has no relation with chloroform formation, one might clearly observe the effect of TOC in the second and third points of the graph at 15 and 20 mg/l of organic matter (Figure 4.4). The formation potential of other THMs such as bromodichloromethane, dibromochloromethane, and tribromomethane fell into a similar pattern like the total THMs. However, the difference between the values for PPR in comparison to the other two setups was significant. Looking into Figures 4.5-4.7, it is obvious that data points representing values for the PPR set up are at lower segments of the graph. This might be due to the fact that the bromide concentration in the PPR setup was almost close to 0 in all the

combinations tested in the experiments. The PVC setup showed higher potential formation of each one of the THMs followed by the PE setup.

Contrary to the outcomes of previous literature, chloroform was not the dominant THM in all the experiments; however, it was the highest value in the majority of the experiments. This might be due to the high concentrations of bromide present in the circulating water, as previous studies showed that the presence of bromide can have an effect on the distribution of THMs [48,49].

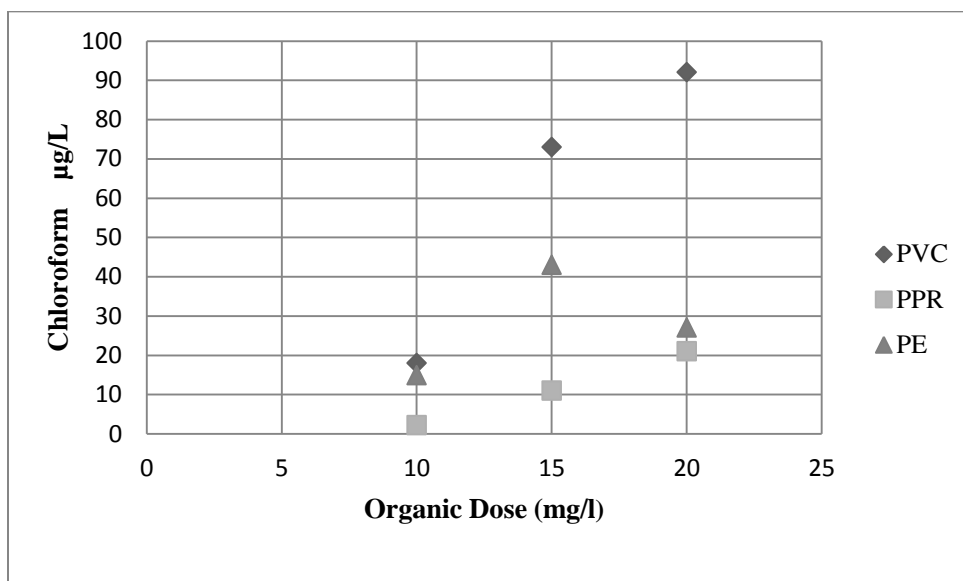


Figure 4.4: Effect of TOC on Chloroform Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

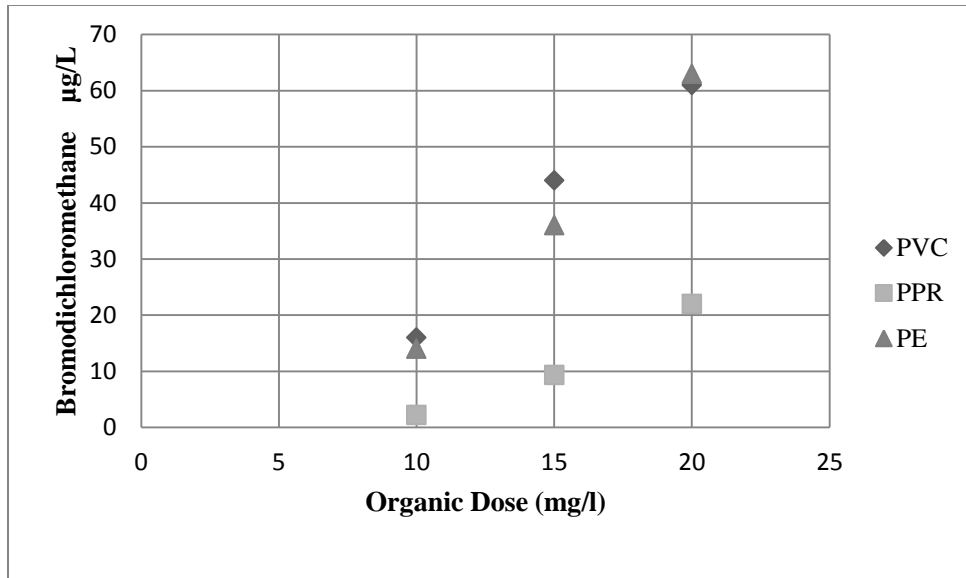


Figure 4.5: Effect of TOC on Bromodichloromethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

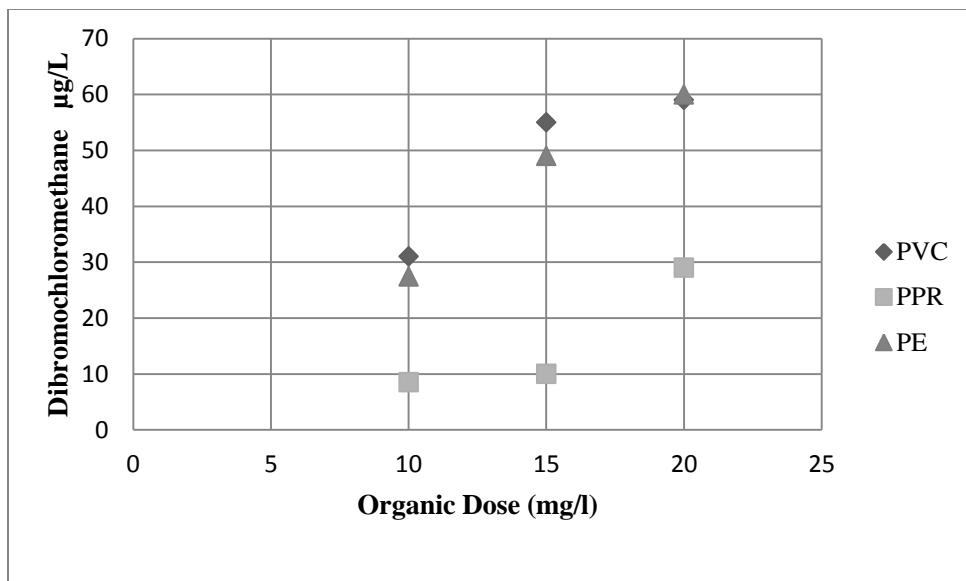


Figure 4.6: Effect of TOC on Dibromochloromethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

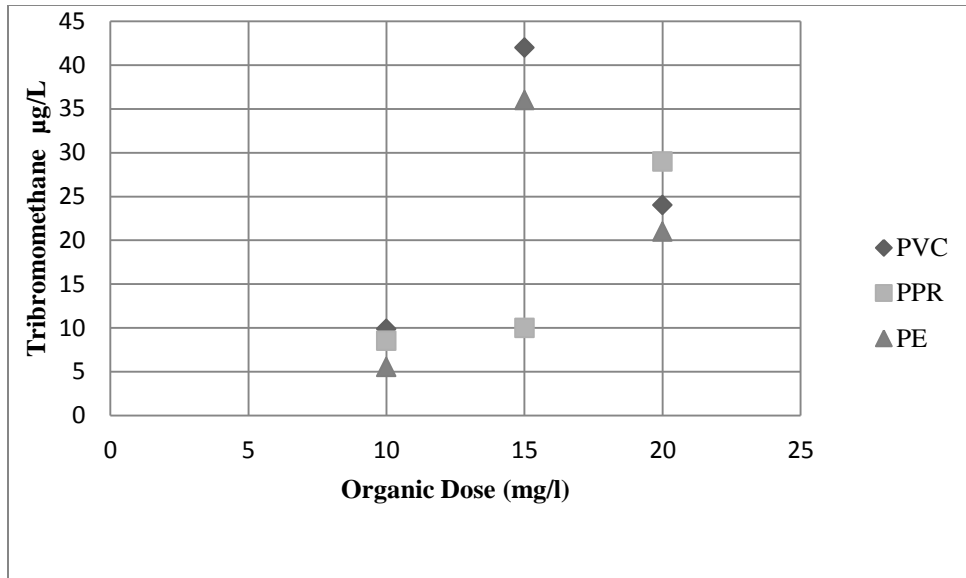


Figure 4.7: Effect of TOC on Tribromomethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

4.3. Effect of $\text{Ca}(\text{ClO})_2$ Dose on Trihalomethane Formation

Figures 4.8-4.10 showed an increase in THM formation with an increase in calcium hypochlorite dose. An additional dose of calcium hypochlorite would clearly increase the available chlorine in the water. There was a strong correlation between chlorine dose and disinfection byproduct formation. One previous study showed a strong correlation of chlorine and THM formation ($r=0.879$) [26]. Adding calcium hypochlorite or chlorine to water would eventually produce hypochlorous acid (HOCl) or hypochlorite ions (OCl^-), which are forms of available chlorine [50].

There was an increasing trend in all the graphs showing that results of these experiments were consistent with the previous researchers' works [26]. The rate of increase for THMs suddenly increased in the last data point which represents a TOC of 0.15 ppm as the initial condition (Figure 4.8); however, for other initial conditions of TOC as 0.69 ppm and 0.75 ppm, the rate of increase was somehow linear for all loop systems used in this project (Figures 4.9-4.10). This was due to the fact that having less organic matter in the water made the effect of the chlorine more significant in the first combination with a TOC of 0.15 ppm. Moreover, more organic matter present in the water made the trend closer to a linear relationship.

The comparative assessment of polymeric pipes in THM formation based on calcium hypochlorite dose showed the same pattern as the previous combinations with TOC as a variable of the study. PVC pipes showed more potential formation than PE and PPR loop systems in all the conducted experiments (Figures 4.8-4.10). Values of THMs for the PPR setup were the lowest values in comparison to the other two setups in the majority of the experiments.

For the PVC pipe, the P-value from the ANOVA analysis was 0.002005 showing that the effect of calcium hypochlorite dose was significant in THM formation. Furthermore, the P-value for PE and PPR pipes were found to be 0.020681 and 0.001588 (Tables 4.2-4.4). The results of the ANOVA analysis showed significance relevance in the PPR and PVC loop systems with P-values which were much less than 0.01. However, for PE loop systems, the 0.02 value shows a convincing and strong relevance which is considered less than the other two loop systems (Tables 4.2-4.4).

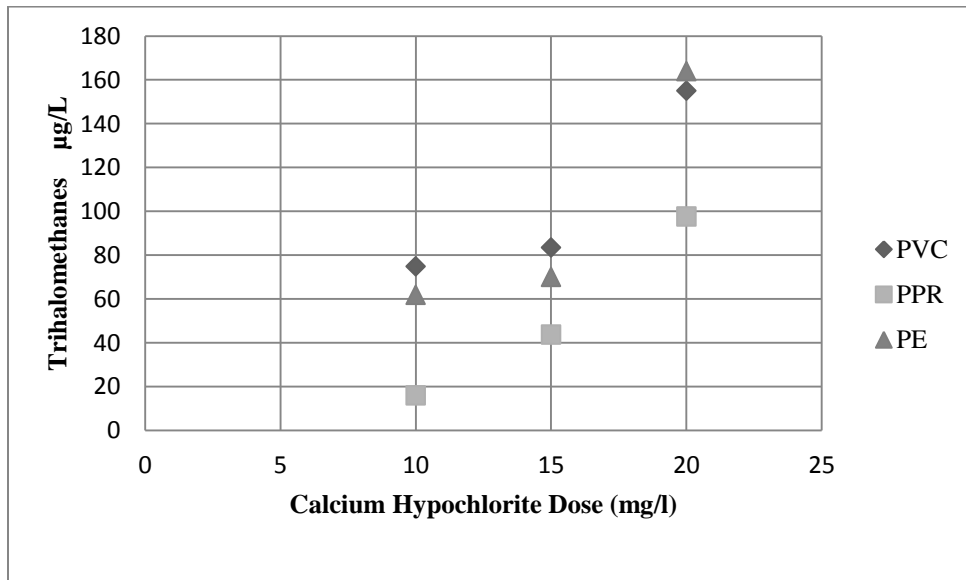


Figure 4.8: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Trihalomethane Formation with an Initial TOC of 0.15 ppm

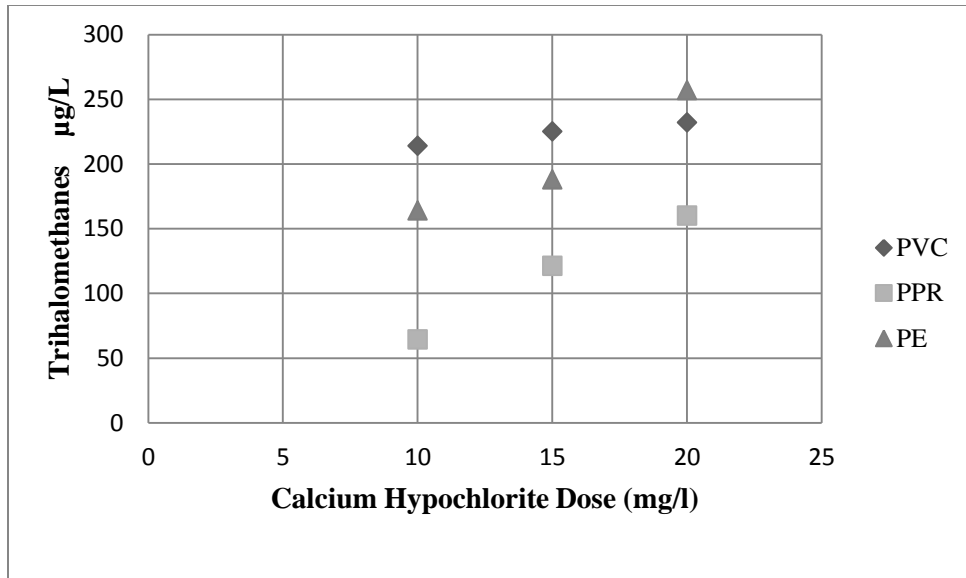


Figure 4.9: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Trihalomethane Formation with an Initial TOC of 0.69 ppm

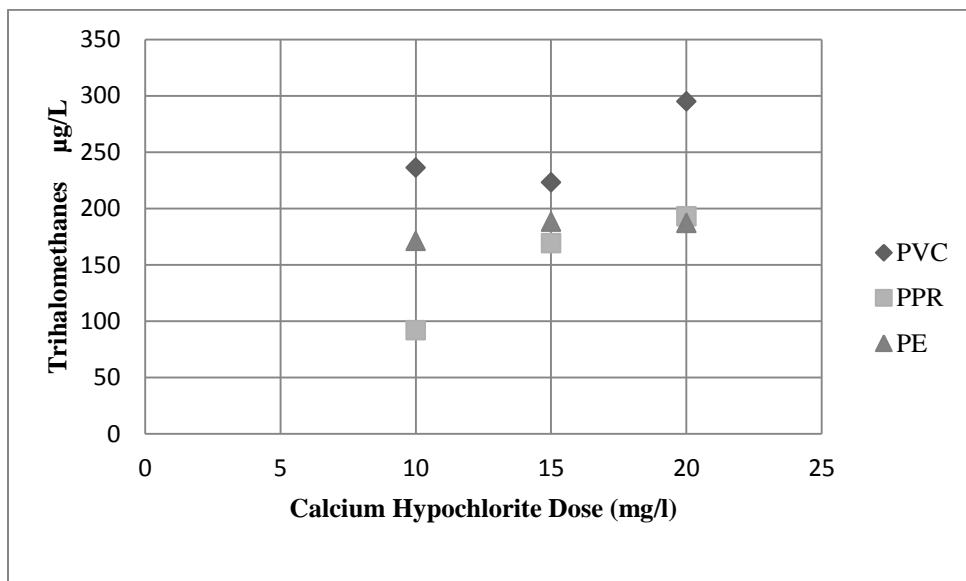


Figure 4.10: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Trihalomethane Formation with an initial TOC of 0.75 ppm

4.3.1. Effect of $\text{Ca}(\text{ClO})_2$ on Individual Trihalomethane Formation

Similar to the previous section, the results of the effect of a $\text{Ca}(\text{ClO})_2$ dose on chloroform, bromodichloromethane, dibromochloromethane, and tribromomethane formations did not show a trend, as clearly shown by the graphs (Figure 4.11-4.14). In general, an increase of calcium hypochlorite dose resulted in higher values for individual THMs, but in some cases one data point did not fall into the same behavior of the rest of the data points in the graph which might be due to the extremely sensitive type of analytical analysis needed to separate associated gases from THMs.

The results for the study on the effect of initial calcium hypochlorite on individual THMs showed that it is not possible to bring conclusive comments into the discussion due to the erratic behavior of the data points in the graphs just like the previous discussion on the effect of initial TOC on individual THMs. Bromide's effect was clearly observed in the results as all the brominated THMs had a contribution just like chloroform. Other graphs representing an initial TOC of 0.69 and 0.75 ppm had the same erratic trends as mentioned earlier that were not able to prove some signs of consistency in the results (Figures A.9-16).

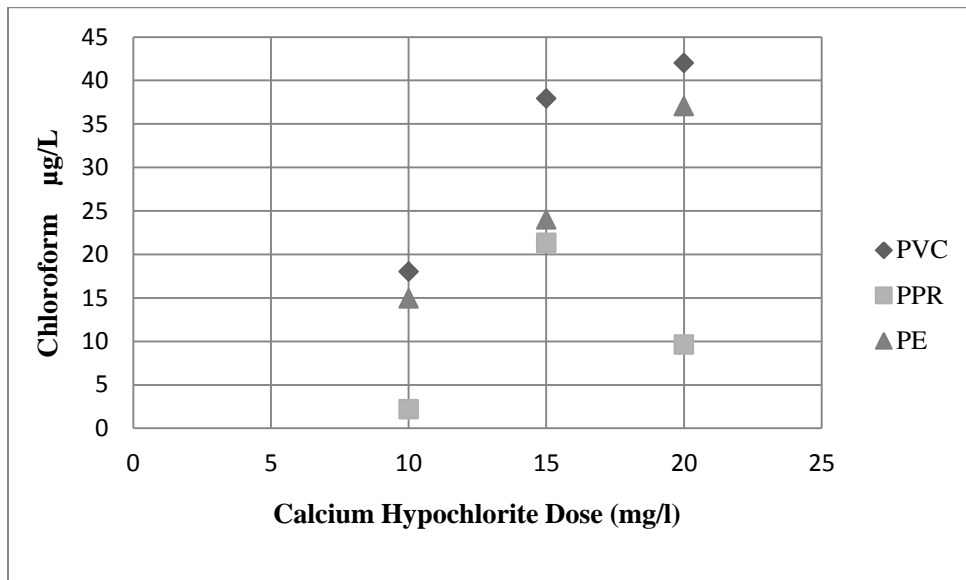


Figure 4.11: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Chloroform Formation with an Initial TOC of 0.15 ppm

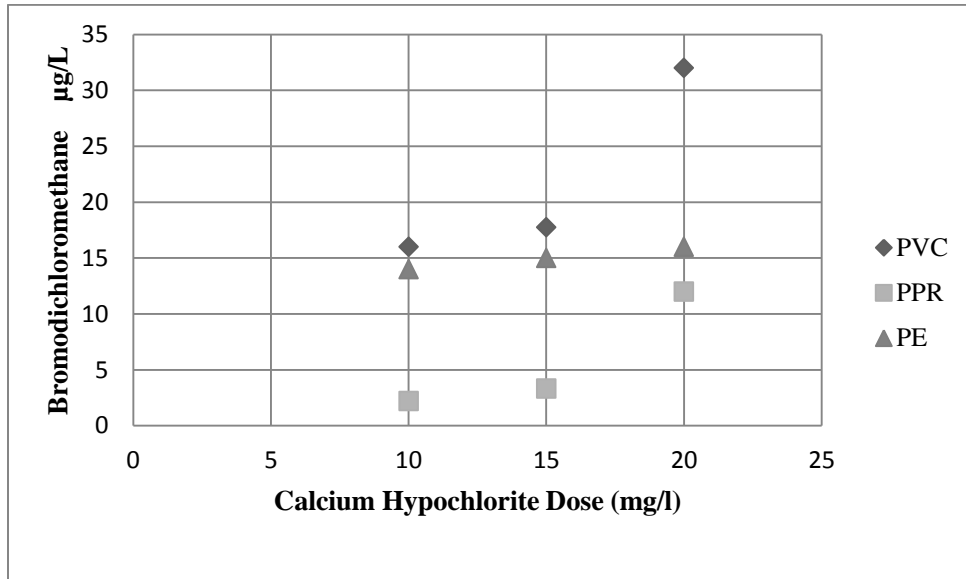


Figure 4.12: Effect of Ca(ClO)₂ Dose on Bromodichloromethane Formation with an Initial TOC of 0.15 ppm

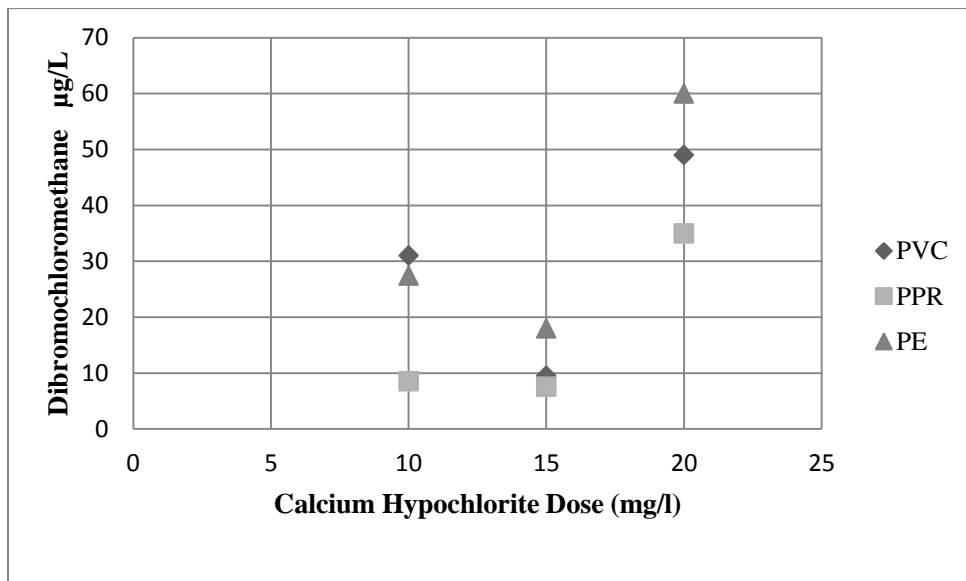


Figure 4.13: Effect of Ca(ClO)₂ Dose on Dibromochloromethane Formation with an Initial TOC of 0.15 ppm

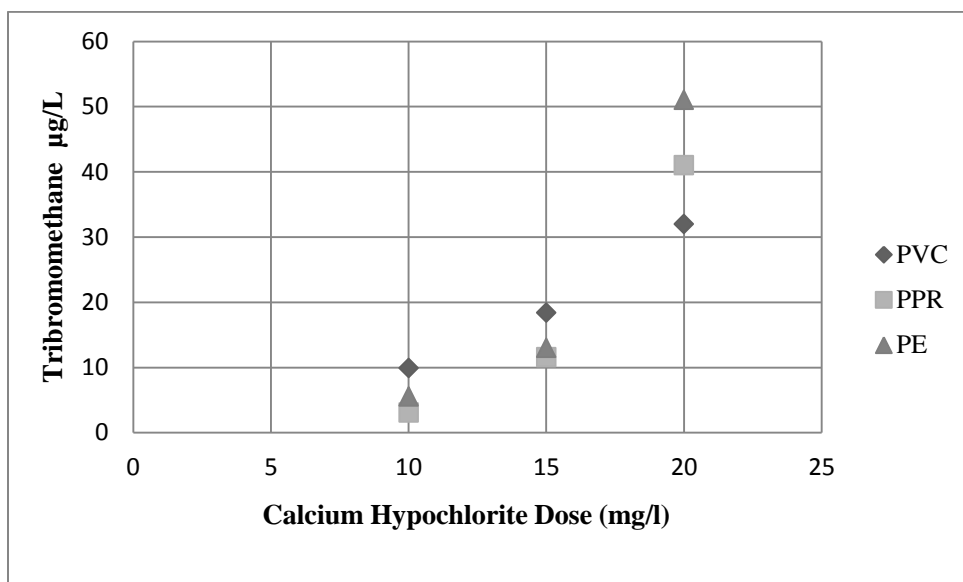


Figure 4.14: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Tribromomethane Formation with an Initial TOC of 0.15 ppm

4.4. Chlorine Residual

Chlorine loss was not that high in PVC pipes, as the values of chlorine residual in PVC pipes were higher than the other two pipes in all the combinations. The PE loop system was slightly less prone to chlorine loss compared to the PPR system; however values of chlorine were much less than chlorine residual in the PVC setup. PPR had the lowest amount of residual chlorine at the end of all the nine experiments, showing that chlorine decay was significant compared to other setups. The reason behind it might be the high temperature values, which were consistently recorded for the PPR setup as previous studies concluded that the chlorine decay rate can increase with higher temperature values [51]. Higher values of chlorine residual or less chlorine loss in PVC setups might be related to the previous works indicating leachate of vinyl chloride from PVC pipes [28,29]. The chlorine level would have been changed through leachate of vinyl chloride.

Figures 4.15-4.16 and A.17-A.20 clearly showed that adding a calcium hypochlorite dose would result in higher values of chlorine residual since more available chlorine in the form of hypochlorous acid and hypochlorite ion would be present in the pipe. On the other hand, more

organic matter can have an adverse effect on the chlorine residual since it will be using more of the available chlorine for the reactions to form THMs. A lower rate of decrease or increase in chlorine residual is observed after the second data point in the majority of the figures. This shows a lower effect of initial TOC than calcium hypochlorite dose, as discussed earlier.

In general, chlorine decay was observed using polymeric pipes in distribution systems which comes to agree with previous research done on chlorine decay [9]. The results of these experiments were not consistent with the findings of the previous studies that claimed that the reactivity of chlorine with polymeric pipes is negligible [12]. The trend of chlorine decay based on different pipe materials was not consistent with the finding of one previous experimental study on pipe effect on chlorine decay, where PVC showed less reactivity with chlorine than PE pipes. This was not the case reported in the previous research [14].

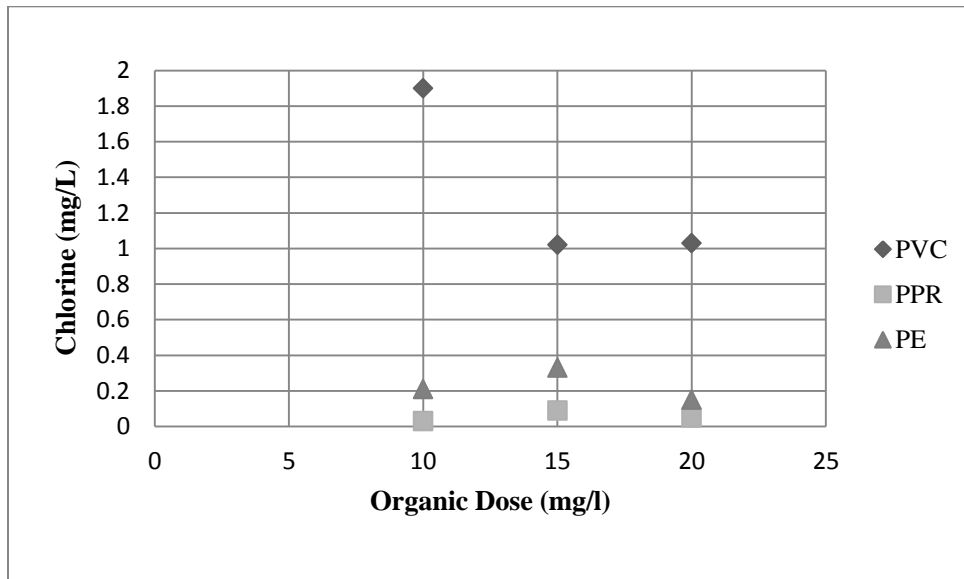


Figure 4.15: Effect of TOC on Chlorine Residual with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

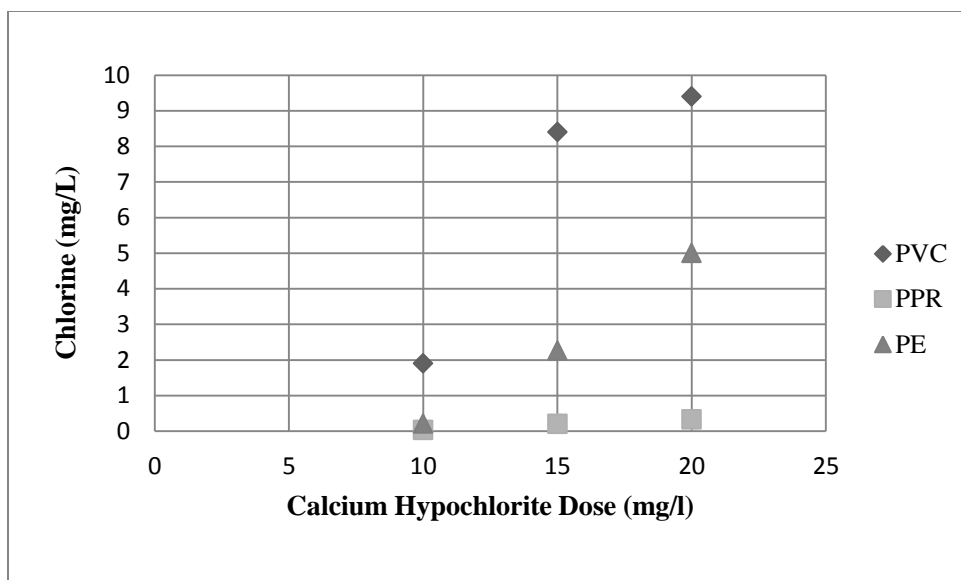


Figure 4.16: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Chlorine Residual with an Initial TOC of 0.15 ppm

4.5. Bromine Concentration

The results of the experiments showed that high doses of bromine were found in samples collected after each cycle in PVC and PE loop systems, although the initial tap water bromine dose was measured as 0.30 mg/L. As shown in Figures 4.17-18, PVC pipes had the most bromine concentration after each run in comparison to the other two pipe materials. PE pipes showed less bromine concentration, but PPR pipes showed almost no concentration of bromine. High doses of bromine in the PVC and PE setups might be due to the use of brominated flame retardants which are used for insulation of pipes to inhibit combustion [52], since thermal decomposition of polymeric materials which are flame retarded showed an occurrence of chlorinated and brominated products [53].

Previous studies on bromine indicated that calcium hypochlorite disinfectants showed formation of bromate in the water samples [54]. This might be another reason behind the high doses of bromine detected in the circulated water, as decomposition of ozone from bromate can result in the formation of bromide in water samples. The association of bromine in forming brominated trihalomethanes came to its maximum potential when it reached the maximum ratio of dissolved organic matter/available chlorine [55]. This means bromine was less utilized by the organic compounds if available chlorine was more. This argument explains the trend of increased

bromine which was observed in the figures showing effect of adding calcium hypochlorite on bromide concentration (Figure 4.18). The additional organic matter utilized the bromine available in the water resulting in the decreasing pattern which is shown in Figure 4.17.

Values of bromine were almost negligible in the PPR setup which comes to agree with the lowest concentration of THMs detected in the PPR setup compared to the other two setups as bromine is one of the major precursors of brominated THMs.

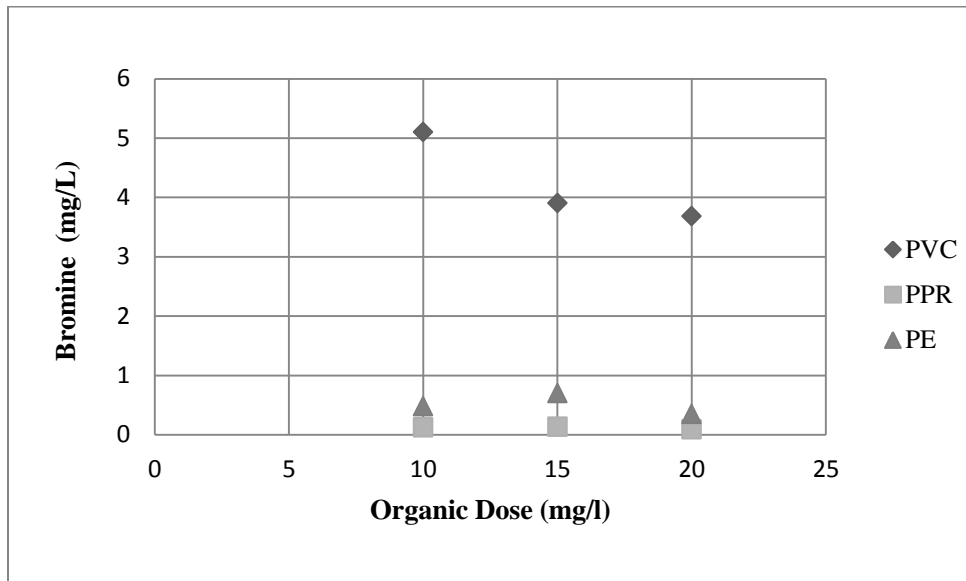


Figure 4.17: Effect of TOC on Bromine Concentration with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

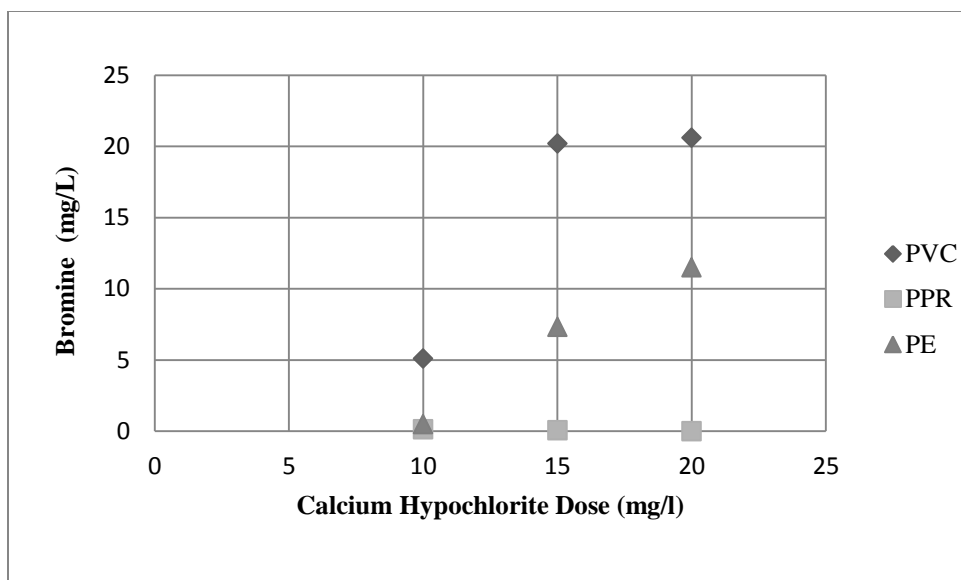


Figure 4.18: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Bromine Concentration with an Initial TOC of 0.15 ppm

4.6. pH Value

As shown in Figure 4.19, the pH of the samples showed an increasing trend with an increase in calcium hypochlorite dose. The addition of calcium hypochlorite increased the water pH since it was highly alkaline and caused a loss of the dissolved carbon dioxide to increase the pH value [56]. As mentioned in Section 4.4, additional organic matter reduced the chlorine residual, which means it was utilized for reactions of THMs; this argument is also supported by the decrease in pH values with an increase in organic matter dose (Figure 4.20). pH was not controlled as an initial condition in this research. The increase in pH values due to the nature of the disinfectant used resulted in pH values between 8 and 10 which could be a reason for the high values of THMs detected in all the experiments. High pH values could have a significant effect on the formation of THMs but as reported in the literature the effective range was mainly 6-8.5, which was not the range for most of the pH readings in this research [38,40].

Similar to other parameters discussed in this dissertation, pH as a measured component showed the same pattern regarding pipe material effect. PPR setups had the lowest pH values which might be due to the fact that they had the maximum chlorine loss among the other setups. PVC and PE loop systems had close pH values in all the measurements.

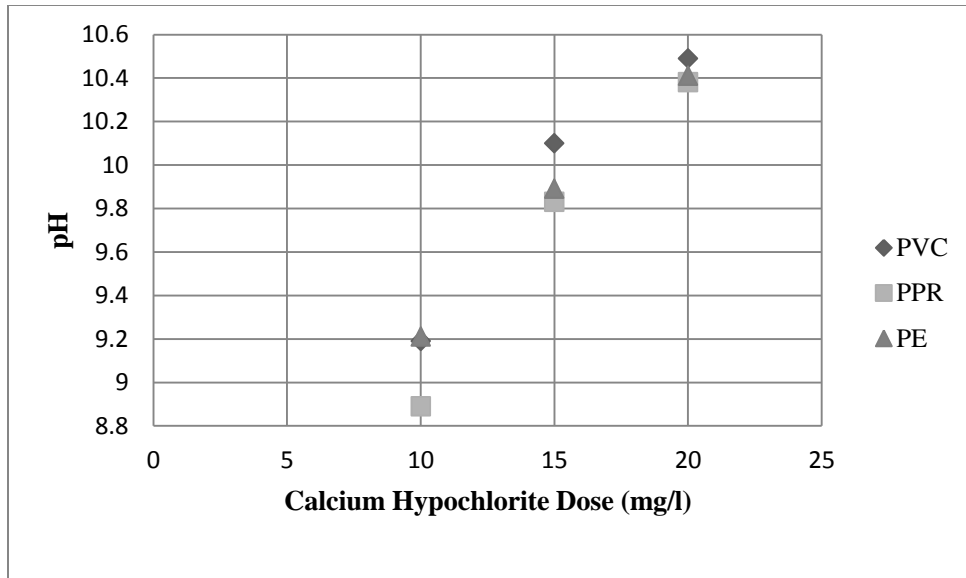


Figure 4.19: Effect of $\text{Ca}(\text{ClO})_2$ Dose on the pH of Water with an Initial TOC of 0.15 ppm

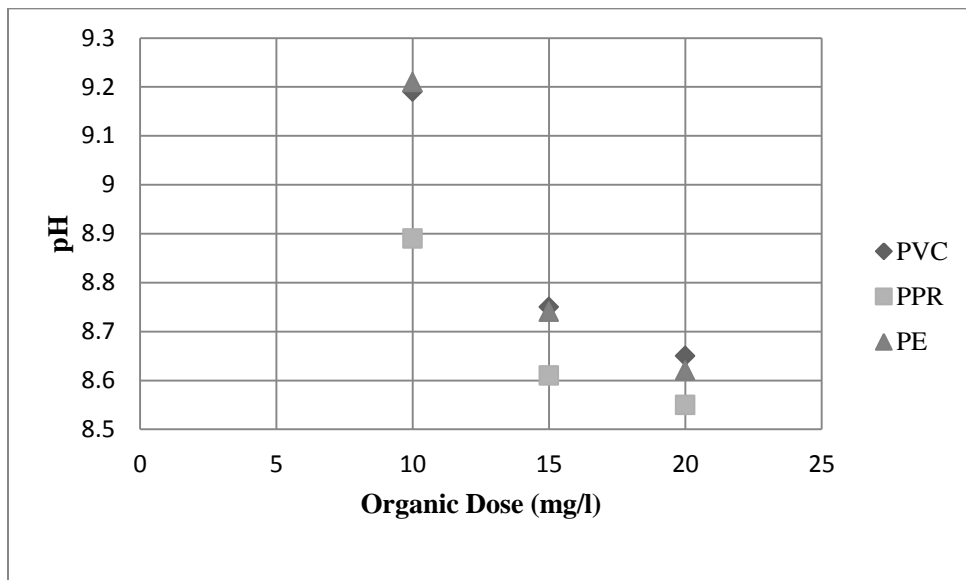


Figure 4.20: Effect of TOC on the pH of the Water with an Initial $\text{Ca}(\text{ClO})_2$ Dose of 0.5 g/L

4.7. Other Water Quality Parameters

As shown in the appendix, other water quality parameters which were checked in this project were turbidity and conductivity of water. In general, the results show that increasing the calcium hypochlorite dose increased the conductivity; however, increasing the organic dose did not show a considerable effect on the level of conductivity as the graph does not represent a constant increasing or decreasing pattern. Moreover, these graphs showed that data collected for conductivity were not dependent on the pipe material of the loop systems. In most of the combinations used in the experimental approach, conductivity values were close to each other regardless of the pipe material (Figures 4.21 and A.30-41).

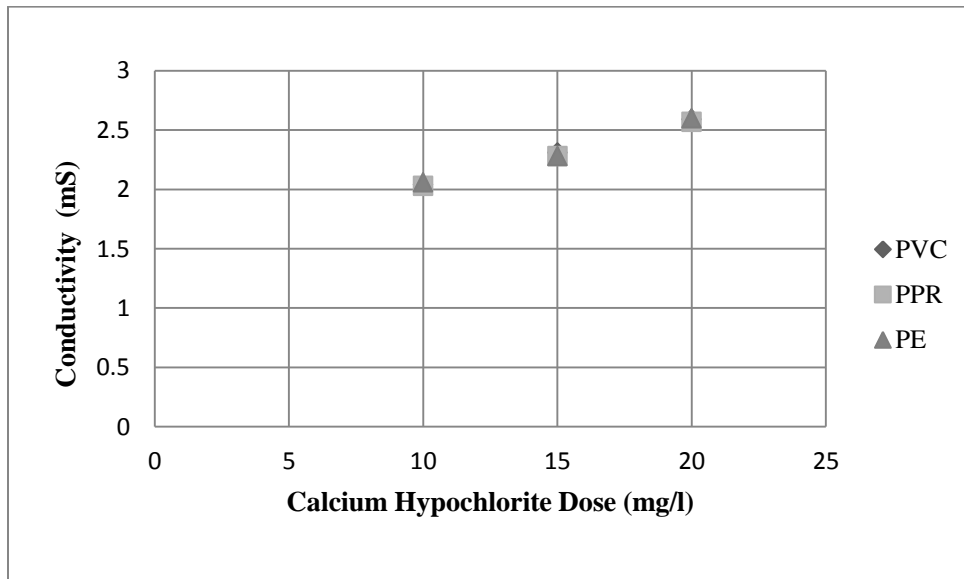


Figure 4.21: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Conductivity with an Initial TOC of 0.15 ppm

On the other hand, data collected for turbidity showed a pattern in all of the experiments. PPR pipes had the least amount of turbidity values in comparison to the other two setups, while PE loop system had the highest values of turbidity ranked first before the PVC loop system. Looking into the graphs, one can clearly observe that turbidity was increasing with the increase in calcium hypochlorite which was due to the highly impure bleaching powder used for disinfection. Increasing the organic dose mostly lowered the turbidity values in all the loop systems. The reason behind this may be the reaction between the additional doses of organic material with the calcium hypochlorite which was constant throughout these experiments. Such

reactions might have reduced the effect of calcium hypochlorite impurities in the tanks (Figures 4.22 and A.30-41).

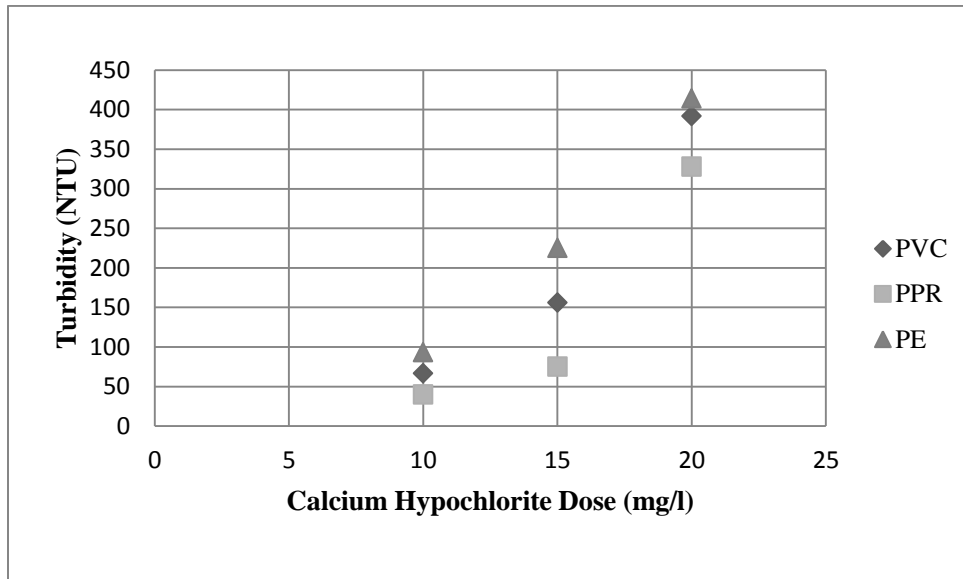


Figure 4.22: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Turbidity with an Initial TOC of 0.15 ppm

4.8. Effect of Pipe Material on Temperature

Figure 4.23 showed the effect of pipe material on the temperature of the water right after sample collections. Regardless of the initial conditions applied prior to running the experiments, PPR constantly had the highest values of temperature with an average of 45.05 °C. On the other hand, PVC and PE showed the same behavior on the temperature factor. One can observe the similar effect of these two pipes on temperature, as average temperature values are close to each other around 41 °C. Different properties of the pipe materials like rate of heat transfer and friction might be the reason behind the differences observed in the temperature values.

Unlike the previous studies, the formation of trihalomethanes was not affected significantly by the increase in temperature. The PPR setup had less formation potential of trihalomethanes in comparison to the other two setups, despite the fact that higher values of temperature were constantly observed in all the samples.

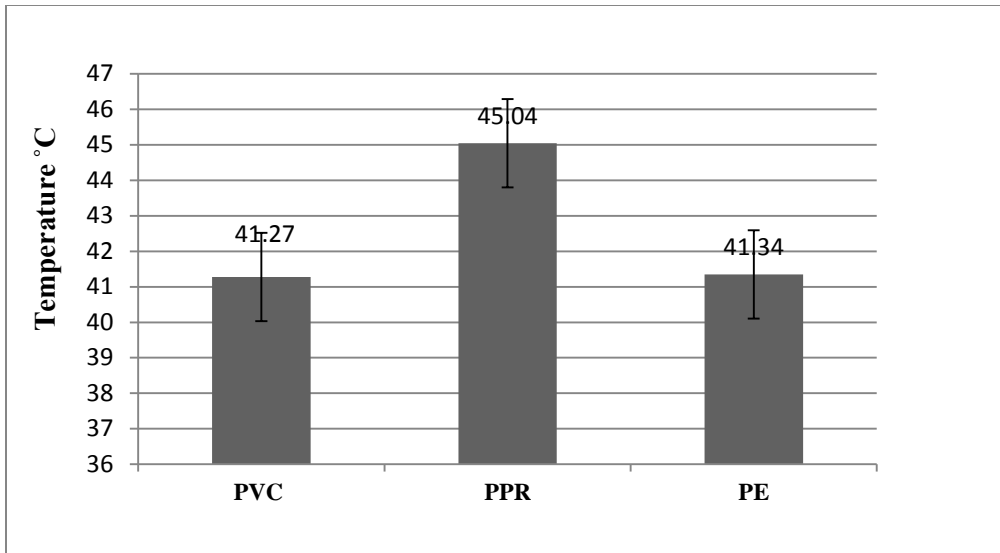


Figure 4.23: Effect of Pipe Material on Temperature

5 CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

The dominance of polymeric materials in pipe distribution systems and desalinated seawater as the primary source of water in local areas of the Gulf region created a need to investigate some concerns over contaminants such as disinfection byproducts in the combination of polymeric pipes and desalinated water.

In order to meet the objective of this dissertation, three pipe loop systems were designed with different polymeric pipe materials. All the operational components were controlled to avoid biased results. A total of nine experiments were conducted in a specific combination which was in two general styles:

1. Constant initial TOC with three different calcium hypochlorite doses
2. Constant initial calcium hypochlorite dose with three different initial TOCs

The outcome of the experiments was the assessment of the pipe effect on trihalomethane formation which showed that in general, polymeric pipes can have potential THM formation. PVC pipes are more prone to formation of trihalomethanes due to several factors like lower chlorine loss and higher occurrence of bromide. PE pipes are very similar to PVC pipes in terms of formation of THMs; however, lower amounts of THMs were formed in PE pipes than in PVC pipes in similar experimental conditions. The PPR pipe is far less prone to formation of THMs in comparison with the other two types of pipes. In general, it can be concluded that initial TOC and calcium hypochlorite dose were directly proportional to all the THMs like chloroform, dibromomethane, dibromochloromethane, and tribromomethane. However, the effect was not significantly observed through the visual representation of the data. On the other hand, the effect of pipe material was exactly the same for individual trihalomethanes and the total THMs. Having quite low concentrations of bromide in PPR loop systems showed bromide as a precursor of brominated trihalomethanes can have a significant effect on the total amount of trihalomethanes since PVC with the highest concentrations of bromide had highest the trihalomethane formation while PE and PPR had lower bromide concentrations resulting in less THM formation. The statistical analysis of the data showed that the effect of initial calcium hypochlorite dose was

more than initial TOC on THMs formation. In fact, calcium hypochlorite can be strongly correlated with THM formation with P-values close to 0.01 for all the pipes. However, the effect of TOC was not that significant as P-values were around 0.06 for PVC and PE setups in the ANOVA analysis done in this research. Other parameters like conductivity, turbidity, and TDS were also measured to provide more statistical data which might be used as evidence for future studies.

In conclusion, this research was able to contribute to the need for assessing polymeric materials in distribution systems through comparative assessment of three pipe materials used in the designed loop systems. THM formation was observed in all the loop systems in a consistent pattern which convincingly supported the validity of the early hypothesis of this research.

5.2. Recommendations

There are several directions for future research. The disinfectant used in this study was selected due to the limitations of the design used for the loop systems which means other types of disinfectants like chlorine dioxide, chlorine gas, chloramine, ozone, or UV radiation can be used to see their effect on THMs formation in polymeric pipes, especially as using calcium hypochlorite as a disinfectant in the conducted experiments made the pH values of water approximately within the range of 8-10 which is not the real case in distribution systems. Other disinfection byproducts like HAAs can be studied later with the same type of experimental plan. Different precursors can be used to check their effect on the potential formation of THMs. One of the main factors which can be studied is the effect of residence time. Time can be used as a variable using the same experimental design as more time will result in more possibility of reaction happening in the system resulting in better interpretation and judgment on the obtained data from the experiments. As previous studies showed, pH and temperature can have a significant effect on the formation of THMs [26]. These factors can also be used as variables to be studied in polymeric pipe distribution systems. Leachate of emerging contaminants like bisphenol-a can be studied to assess the effect of pipe materials. In the end, some factors like pipe diameter and flow rate of water can be used as variables using the same design as the experimental setups created in this project.

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APPENDIX

Table A.1: Results of First Experiment with an Initial $\text{Ca}(\text{ClO})_2$ of 1 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.69	0.69	0.69
Chloroform	$\mu\text{g/L}$	68	76	51
Bromodichloromethane	$\mu\text{g/L}$	54	62	40
Dibromochloromethane	$\mu\text{g/L}$	68	74	28
Tribromomethane	$\mu\text{g/L}$	42	45	41
Trihalomethanes	$\mu\text{g/L}$	232	257	160
Turbidity	NTU	224	314	213
Chlorine (final)	mg/L	8.7	3.6	1.6
Bromine	mg/L	21.3	9.4	0.5
pH	-	9.97	9.91	9.89
Temperature	$^{\circ}\text{C}$	41.2	40.9	46
TDS	mg/L	1269	1251	1261
Conductivity	mSi	2.54	2.5	2.52

Table A.2: Results of Second Experiment with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.69	0.69	0.69
Chloroform	$\mu\text{g/L}$	18	85	73
Bromodichloromethane	$\mu\text{g/L}$	94	37	6.3
Dibromochloromethane	$\mu\text{g/L}$	33	44	19
Tribromomethane	$\mu\text{g/L}$	80	22	23
Trihalomethanes	$\mu\text{g/L}$	225	188	121.3
Turbidity	NTU	137	182	65
Chlorine (final)	mg/L	4.2	0.66	0.31
Bromine	mg/L	7.6	1.39	1.32
pH	-	9.9	9.8	0.7
Temperature	$^{\circ}\text{C}$	41.8	41.2	44.8
TDS	mg/L	1318	1282	1272
Conductivity	mSi	2.35	2.34	2.31

Table A.3: Results of Third Experiment with an Initial Ca(ClO)₂ of 0.50 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.69	0.69	0.69
Chloroform	µg/L	73	43	11
Bromodichloromethane	µg/L	44	36	9.3
Dibromochloromethane	µg/L	55	49	10
Tribromomethane	µg/L	42	36	34
Trihalomethanes	µg/L	214	164	64.3
Turbidity	NTU	55.2	62	59.9
Chlorine (final)	mg/L	1.02	0.33	0.09
Bromine	mg/L	3.9	0.7	0.13
pH	-	8.75	8.74	8.61
Temperature	°C	41.1	41.3	45
TDS	mg/L	1022	1027	995
Conductivity	mSi	2.04	2.05	1.99

Table A.4: Results of Fourth Experiment with an Initial Ca(ClO)₂ of 0.75 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.15	0.15	0.15
Chloroform	µg/L	37.89	24	21.32
Bromodichloromethane	µg/L	17.73	15	3.32
Dibromochloromethane	µg/L	9.5	18	7.55
Tribromomethane	µg/L	18.38	13	11.6
Trihalomethanes	µg/L	83.5	70	43.79
Turbidity	NTU	156	225	75
Chlorine (final)	mg/L	8.4	2.26	0.2
Bromine	mg/L	20.2	7.32	0.05
pH	-	10.1	9.89	9.83
Temperature	°C	41.1	40.9	45.1
TDS	mg/L	1154	1139	1141
Conductivity	mSi	2.31	2.28	2.28

Table A.5: Results of Fifth Experiment with an Initial Ca(ClO)₂ of 1.0 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.15	0.15	0.15
Chloroform	µg/L	42	37	9.6
Bromodichloromethane	µg/L	32	16	12
Dibromochloromethane	µg/L	49	60	35
Tribromomethane	µg/L	32	51	41
Trihalomethanes	µg/L	155	164	97.6
Turbidity	NTU	392	414	328
Chlorine (final)	mg/L	9.4	5	0.33
Bromine	mg/L	20.6	11.5	0
pH	-	10.49	10.41	10.38
Temperature	°C	41.5	41.3	45.3
TDS	mg/L	1293	1299	1290
Conductivity	mSi	2.59	2.6	2.57

Table A.6: Results of Sixth Experiment with an Initial Ca(ClO)₂ of 0.5 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.15	0.15	0.15
Chloroform	µg/L	18	14.9	2.17
Bromodichloromethane	µg/L	16	14	2.19
Dibromochloromethane	µg/L	31	27.4	8.55
Tribromomethane	µg/L	9.9	5.55	3.08
Trihalomethanes	µg/L	74.9	61.85	15.99
Turbidity	NTU	66.4	93.4	39.9
Chlorine (final)	mg/L	1.9	0.21	0.03
Bromine	mg/L	5.1	0.48	0.12
pH	-	9.19	9.21	8.89
Temperature	°C	41.1	41.6	45.3
TDS	mg/L	1022	1030	1018
Conductivity	mSi	2.04	2.06	2.03

Table A.7: Results of Seventh Experiment with an Initial Ca(ClO)₂ of 1 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.75	0.75	0.75
Chloroform	µg/L	80	55	54
Bromodichloromethane	µg/L	65	42	36
Dibromochloromethane	µg/L	90	53	55
Tribromomethane	µg/L	60	37	48
Trihalomethanes	µg/L	295	187	193
Turbidity	NTU	198	286	126
Chlorine (final)	mg/L	7.2	2.85	0.25
Bromine	mg/L	19	8.15	0.35
pH	-	9.95	10.05	9.92
Temperature	°C	41.4	41.2	44.7
TDS	mg/L	1317	1300	1296
Conductivity	mSi	2.63	2.6	2.59

Table A.8: Results of Eighth Experiment with an Initial Ca(ClO)₂ of 0.75 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.75	0.75	0.75
Chloroform	µg/L	48	33	50
Bromodichloromethane	µg/L	53	35	51
Dibromochloromethane	µg/L	76	58	67
Tribromomethane	µg/L	46	43	20
Trihalomethanes	µg/L	223	169	188
Turbidity	NTU	124	61.3	137
Chlorine (final)	mg/L	2.34	0.16	0.37
Bromine	mg/L	6.32	0.19	1.34
pH	-	9.88	9.65	9.74
Temperature	°C	41.3	44.8	41.7
TDS	mg/L	1188	1188	1199
Conductivity	mSi	2.38	2.38	2.4

Table A.9: Results of Ninth Experiment with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

		PVC	PE	PPR
Initial TOC	mg/L	0.75	0.75	0.75
Chloroform	$\mu\text{g/L}$	92	27	21
Bromodichloromethane	$\mu\text{g/L}$	61	63	22
Dibromochloromethane	$\mu\text{g/L}$	59	60	29
Tribromomethane	$\mu\text{g/L}$	24	21	20
Trihalomethanes	$\mu\text{g/L}$	236	171	92
Turbidity	NTU	32.5	76	27.6
Chlorine (final)	mg/L	1.03	0.15	0.05
Bromine	mg/L	3.68	0.35	0.09
pH	-	8.65	8.62	8.55
Temperature	$^{\circ}\text{C}$	41	42	44.4
TDS	mg/L	1051	1041	1045
Conductivity	mSi	2.1	2.08	2.08

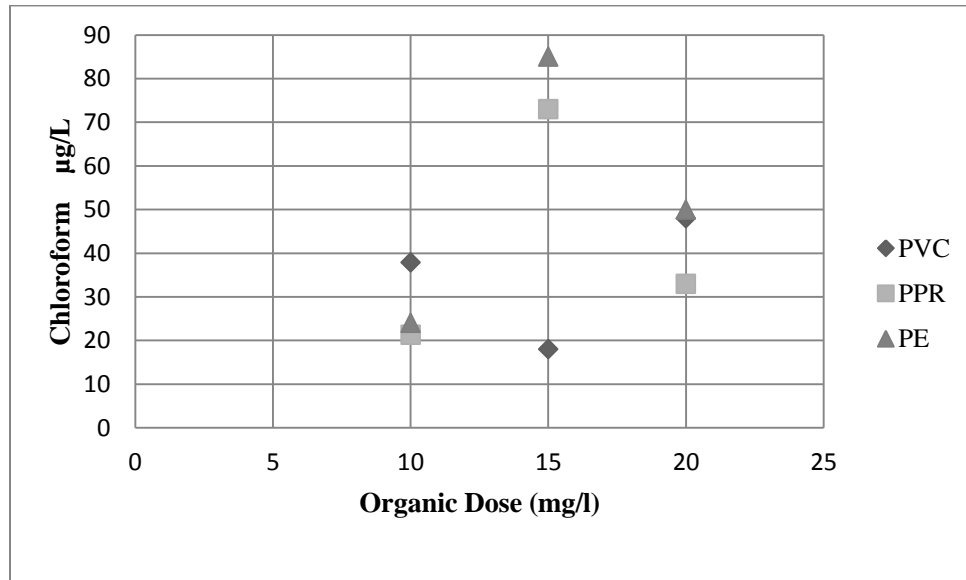


Figure A.1: Effect of TOC on Chloroform Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

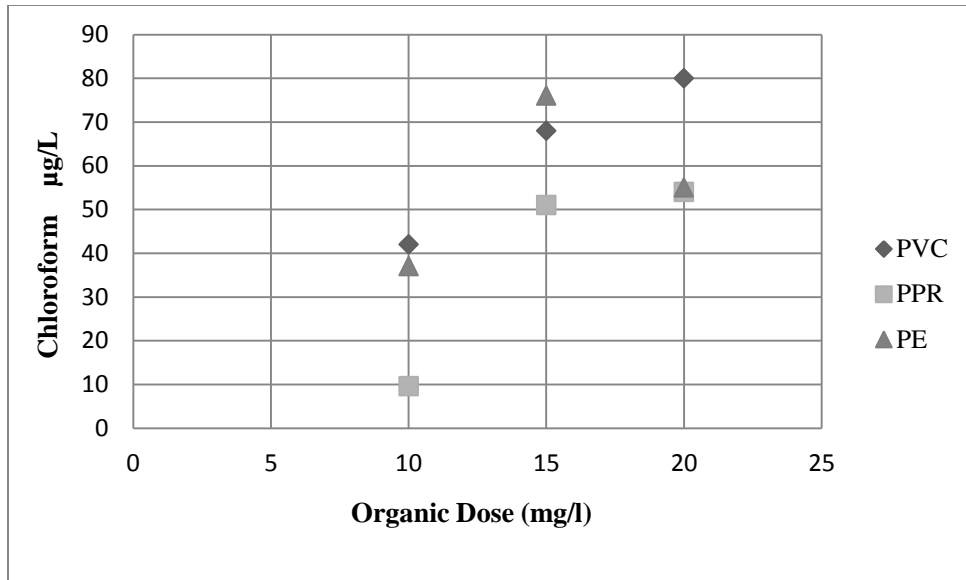


Figure A.2: Effect of TOC on Chloroform Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

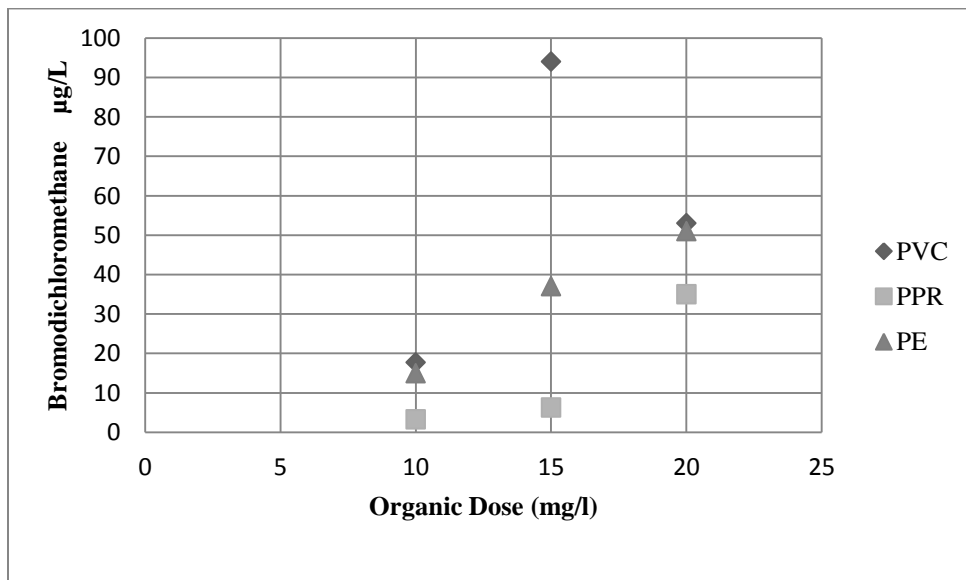


Figure A.3: Effect of TOC on Bromodichloromethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

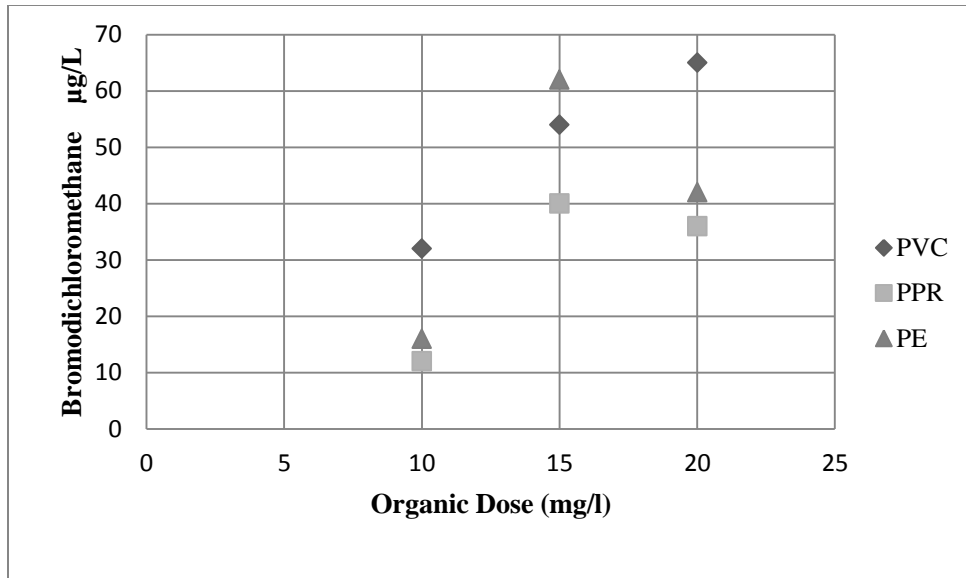


Figure A.4: Effect of TOC on Bromodichloromethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

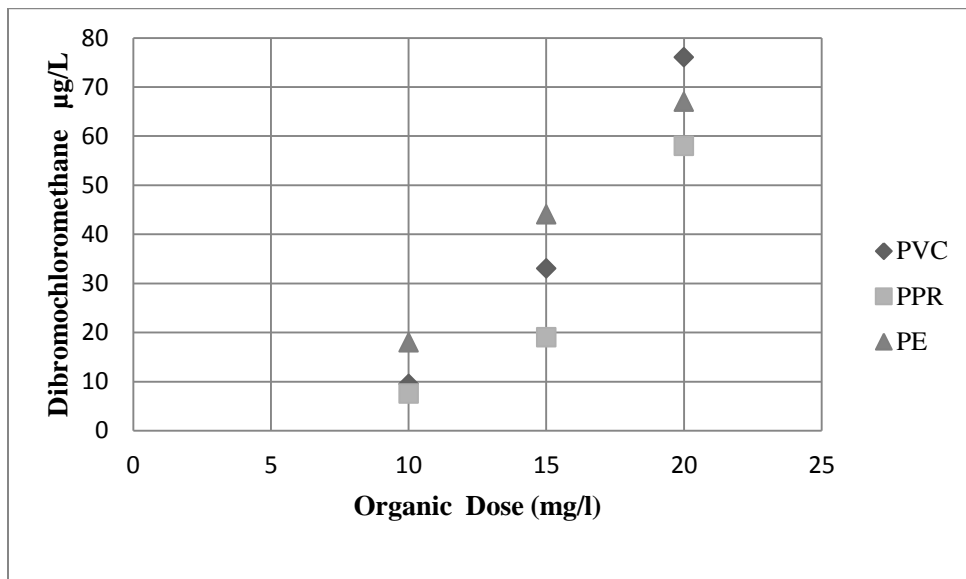


Figure A.5: Effect of TOC on Dibromochloromethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

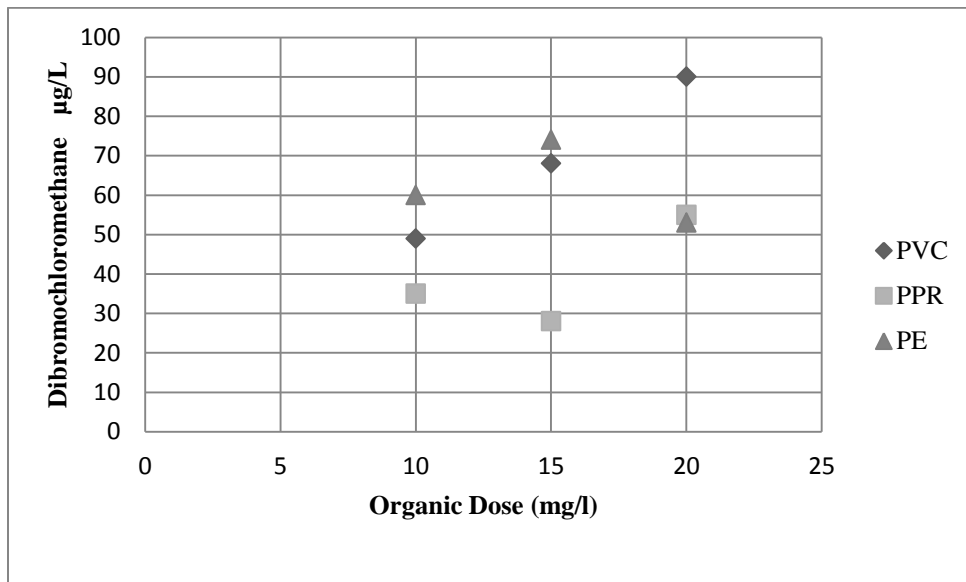


Figure A.6: Effect of TOC on Dibromochloromethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

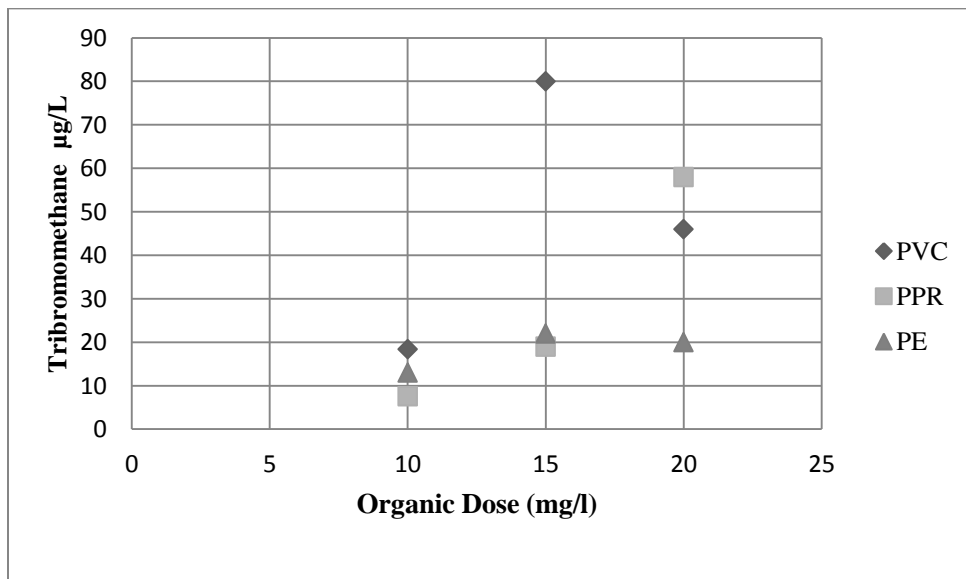


Figure A.7: Effect of TOC on Tribromomethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

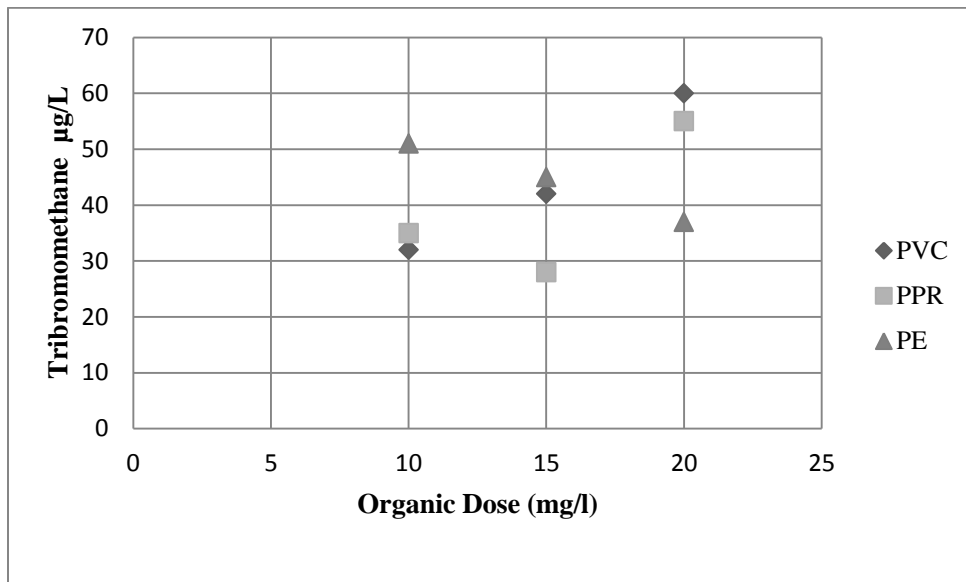


Figure A.8: Effect of TOC on Tribromomethane Formation with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

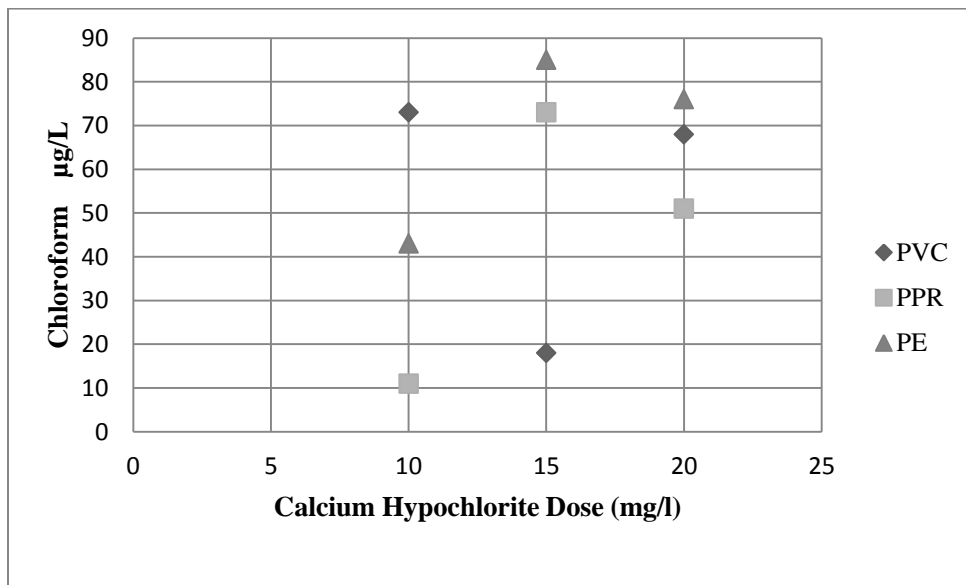


Figure A.9: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Chloroform Formation with an Initial TOC of 0.69 ppm

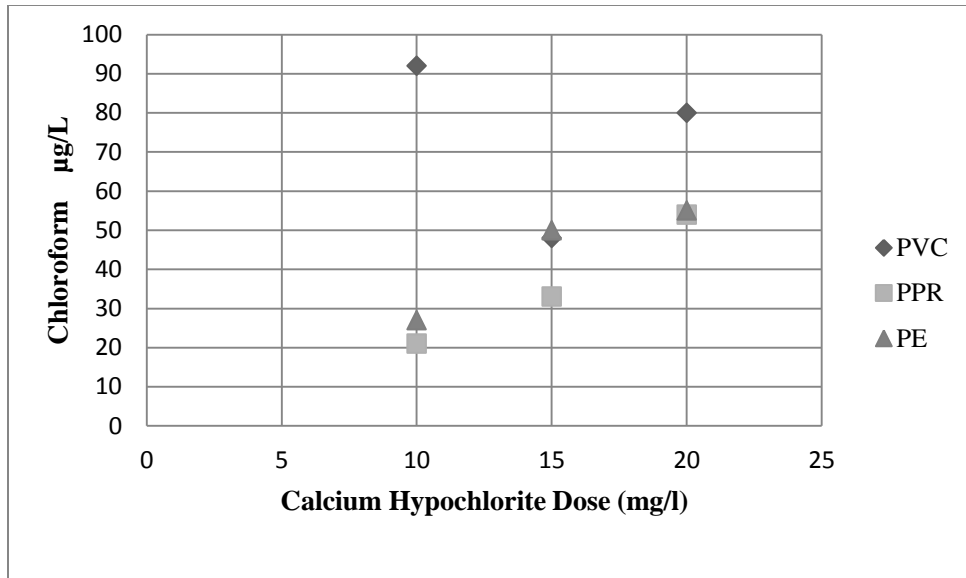


Figure A.10: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Chloroform Formation with an Initial TOC of 0.75 ppm

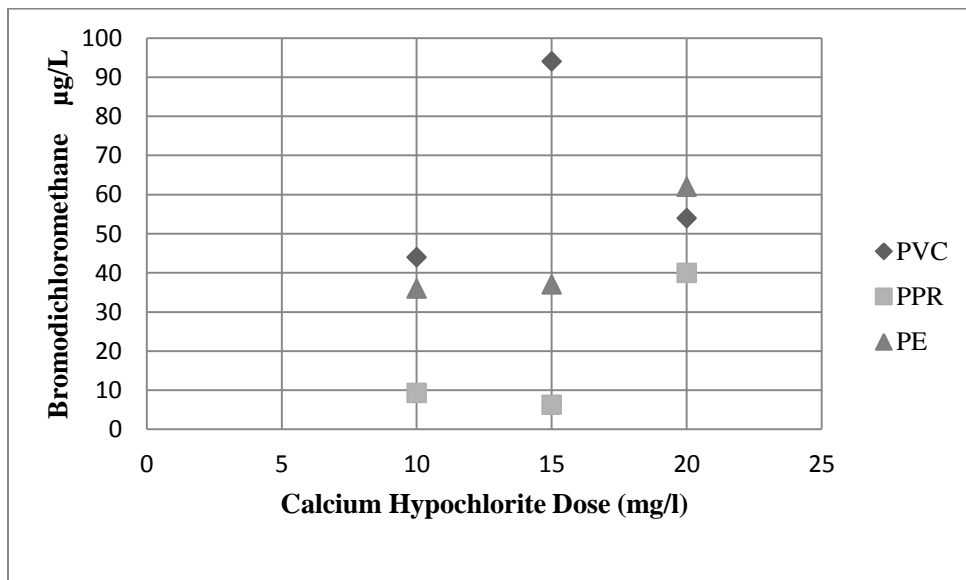


Figure A.11: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Bromodichloromethane Formation with an Initial TOC of 0.69 ppm

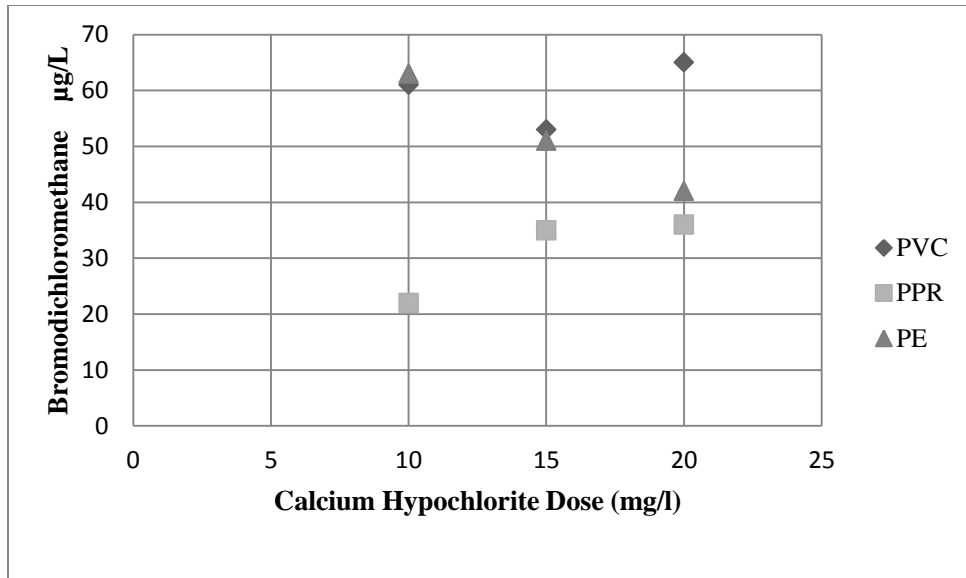


Figure A.12: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Bromodichloromethane Formation with an Initial TOC of 0.75 ppm

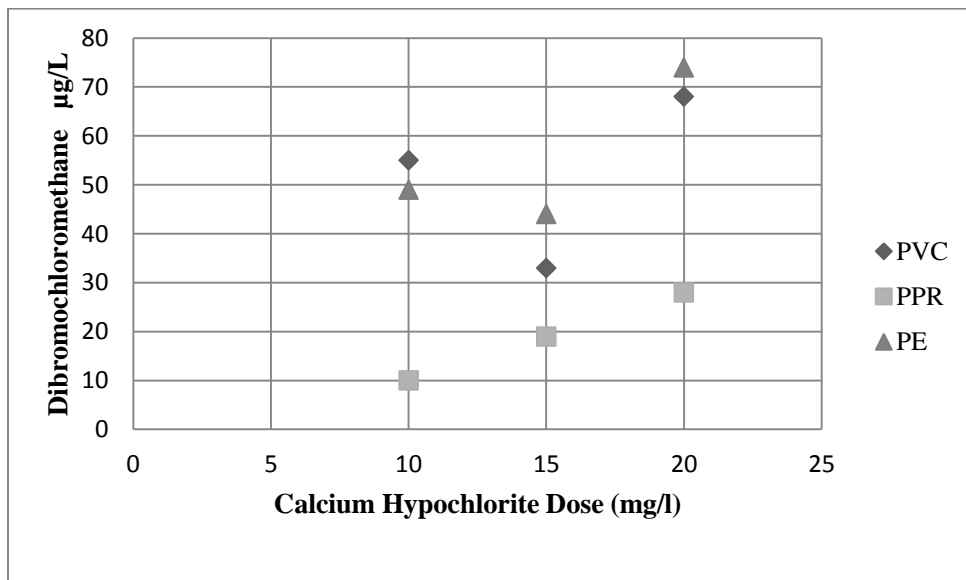


Figure A.13: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Dibromochloromethane Formation with an Initial TOC of 0.69 ppm

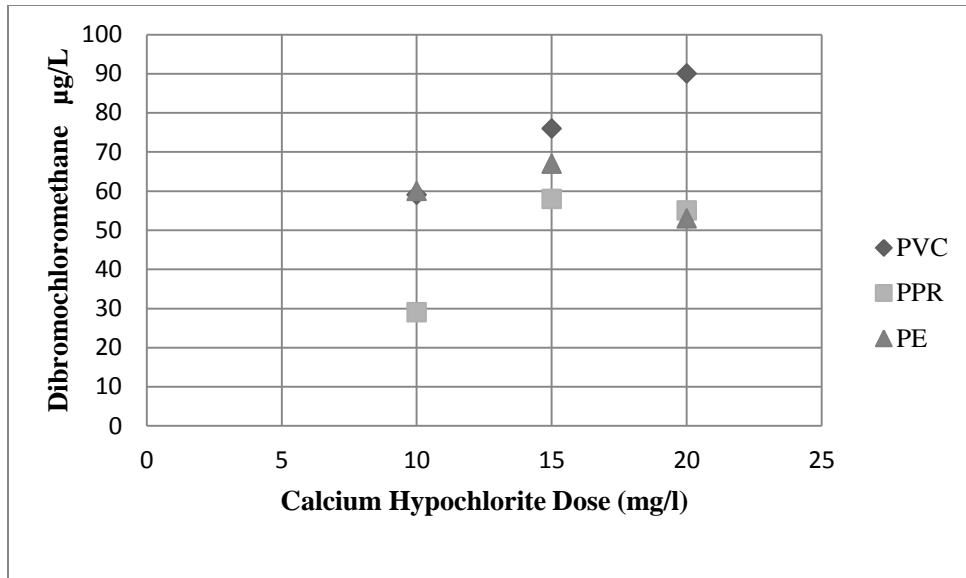


Figure A.14: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Dibromochloromethane Formation with an Initial TOC of 0.75 ppm

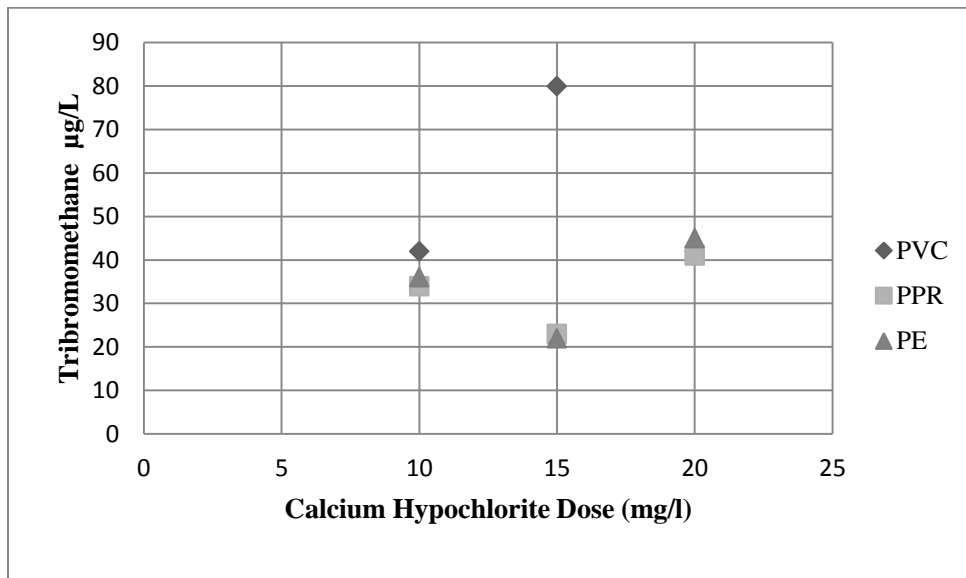


Figure A.15: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Tribromomethane Formation with an Initial TOC of 0.69 ppm

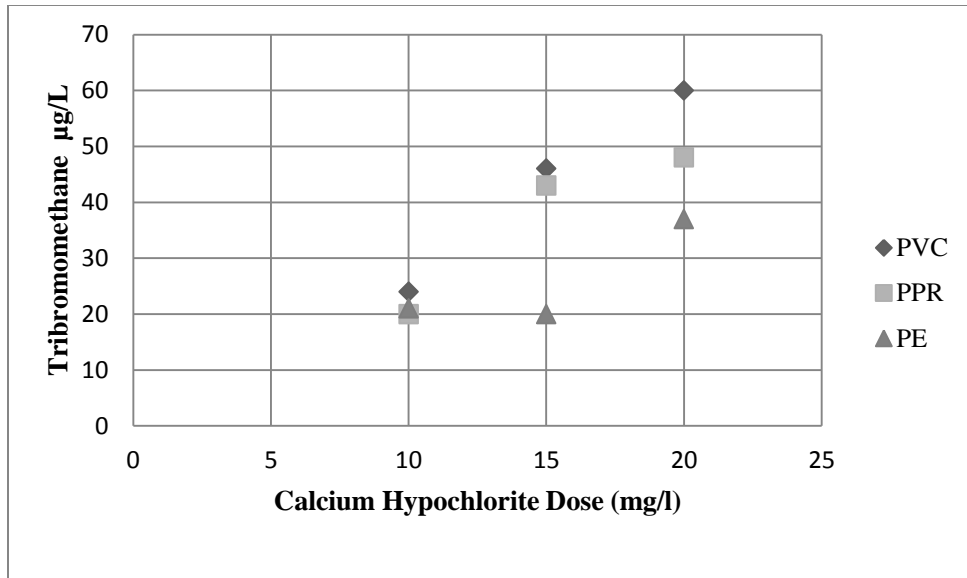


Figure A.16: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Tribromomethane Formation with an Initial TOC of 0.75 ppm

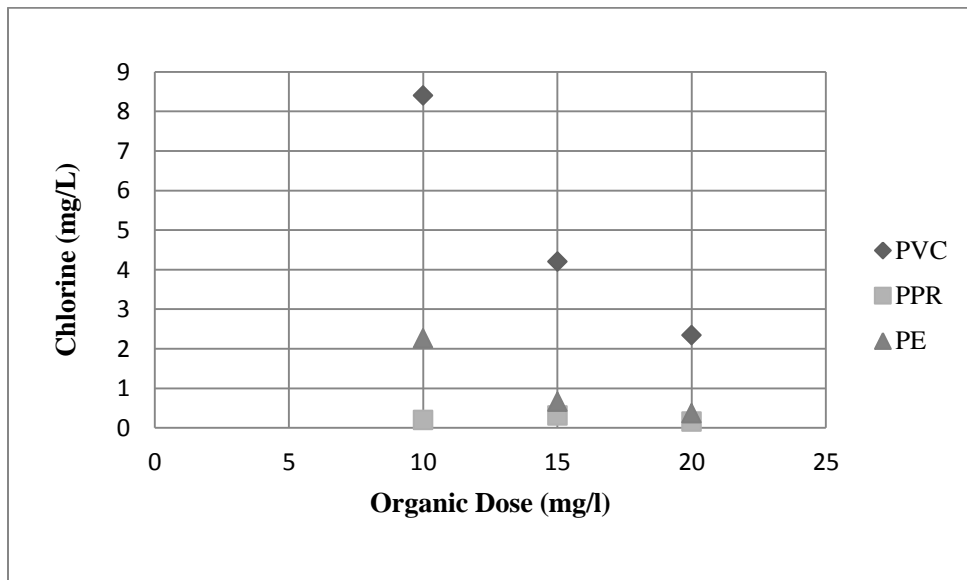


Figure A.17: Effect of TOC on Chlorine Residual with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

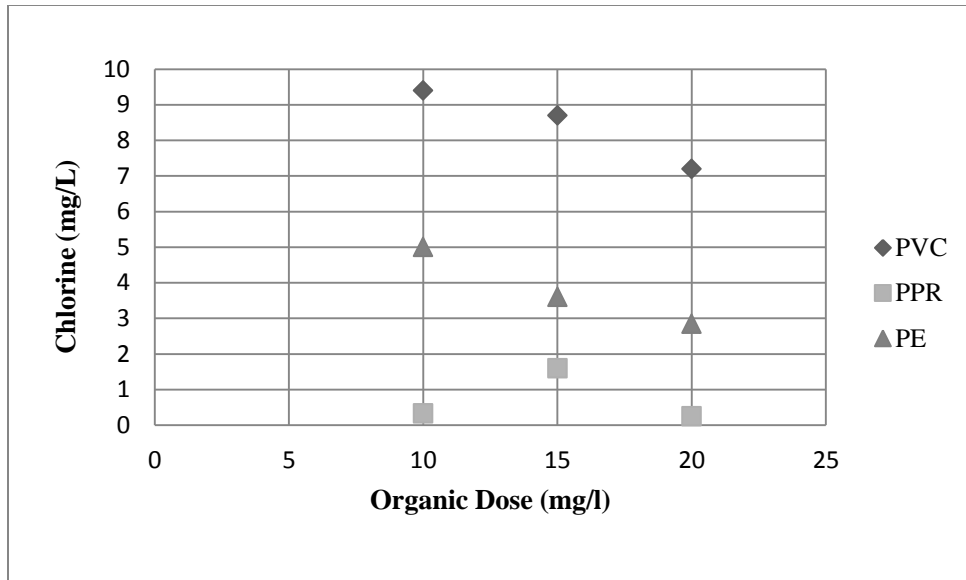


Figure A.18: Effect of TOC on Chlorine Residual with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

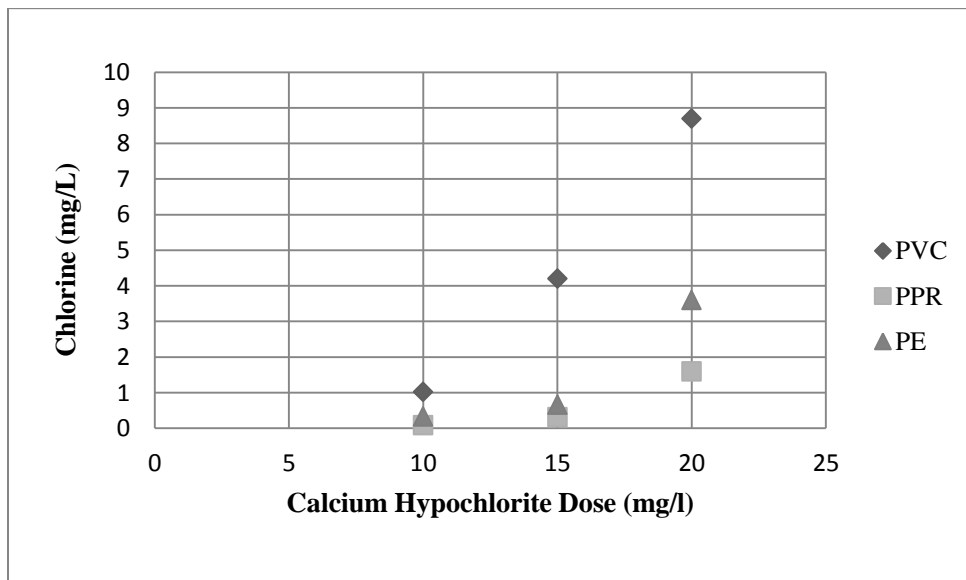


Figure A.19: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Chlorine Residual with an Initial TOC of 0.69 ppm

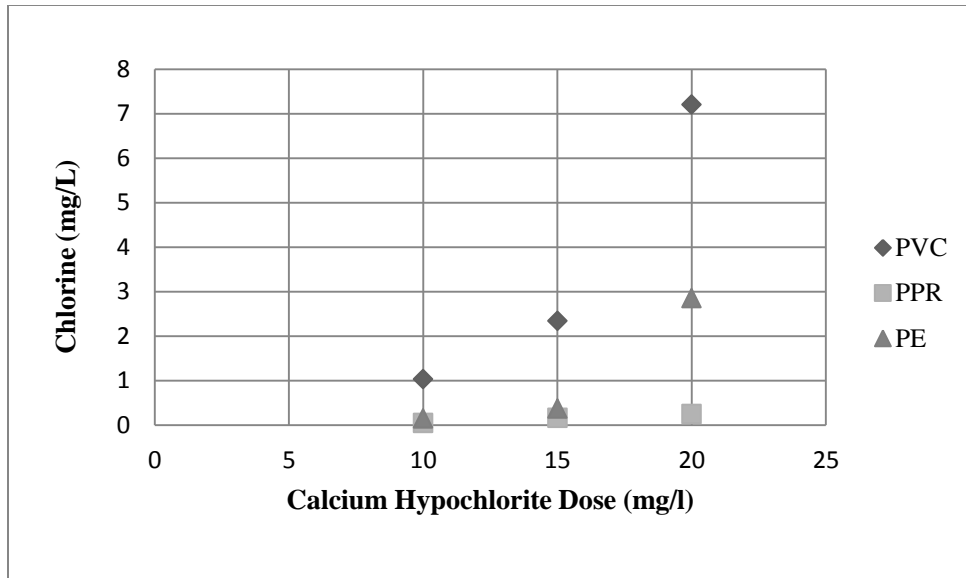


Figure A.20: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Chlorine Residual with an Initial TOC of 0.75 ppm

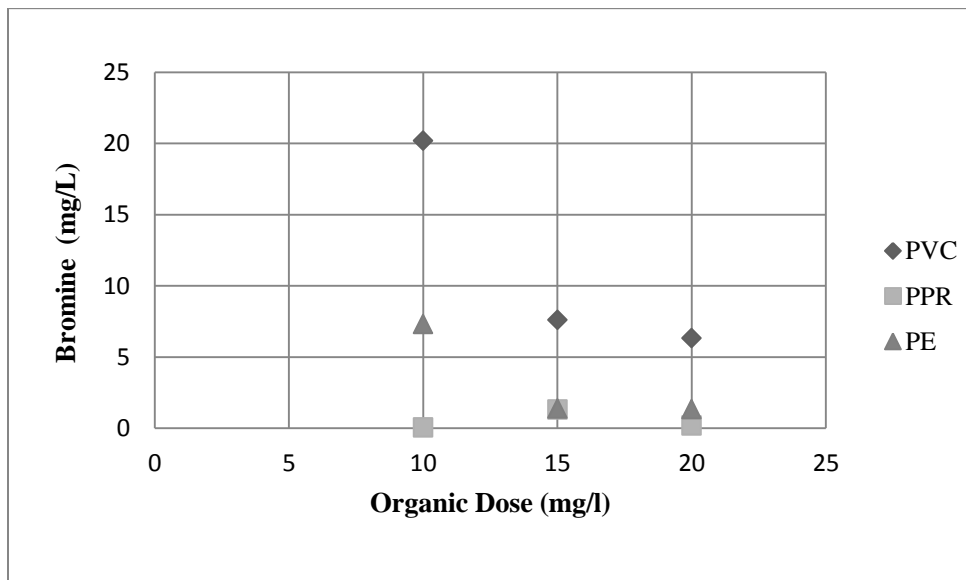


Figure A.21: Effect of TOC on Bromine Concentration with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

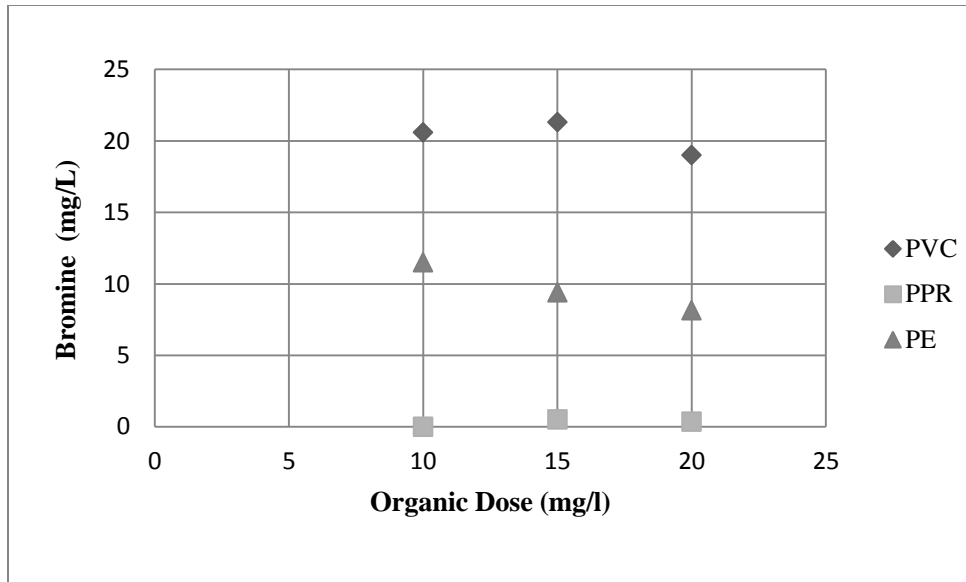


Figure A.22: Effect of TOC on Bromine Concentration with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

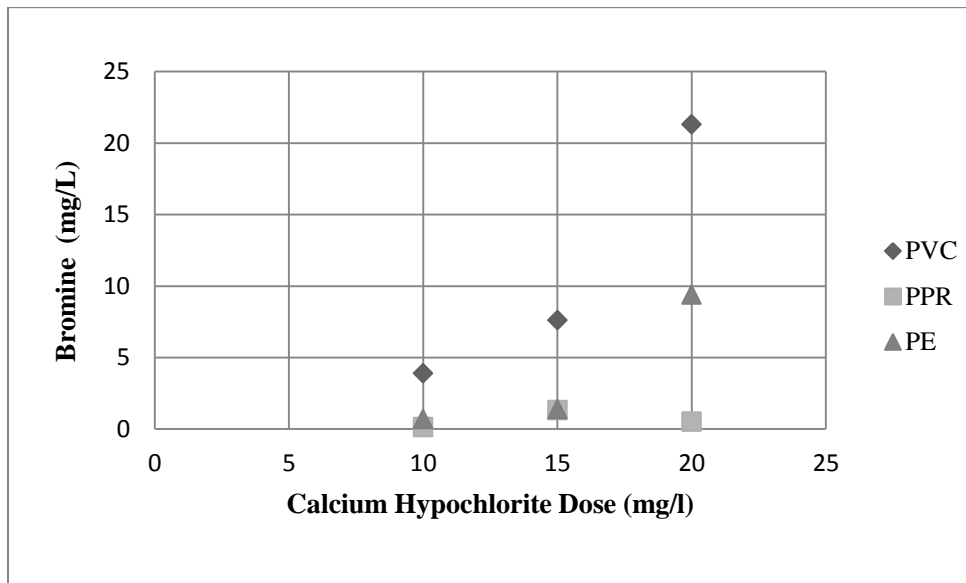


Figure A.23: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Bromine Concentration with an Initial TOC of 0.69 ppm

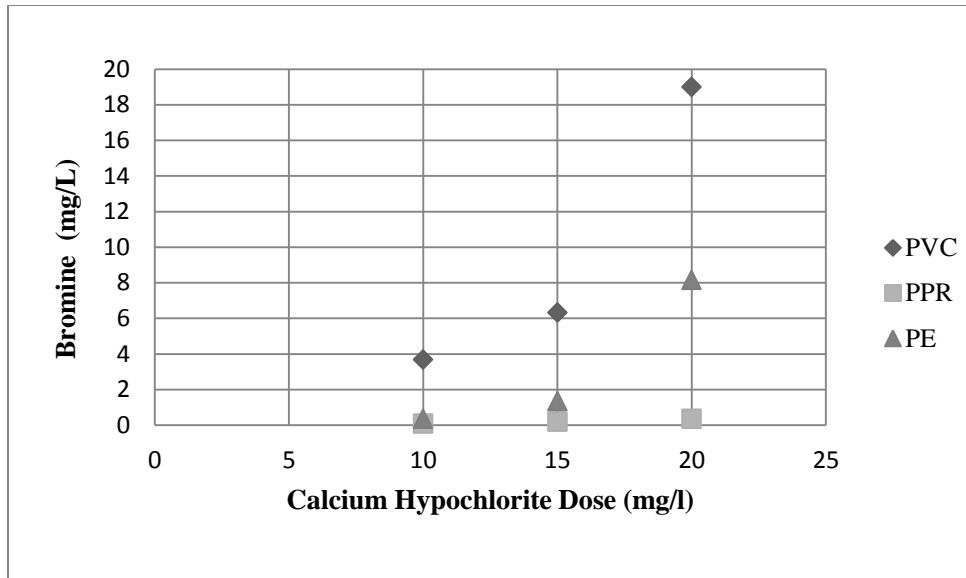


Figure A.24: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Bromine Concentration with an Initial TOC of 0.75 ppm

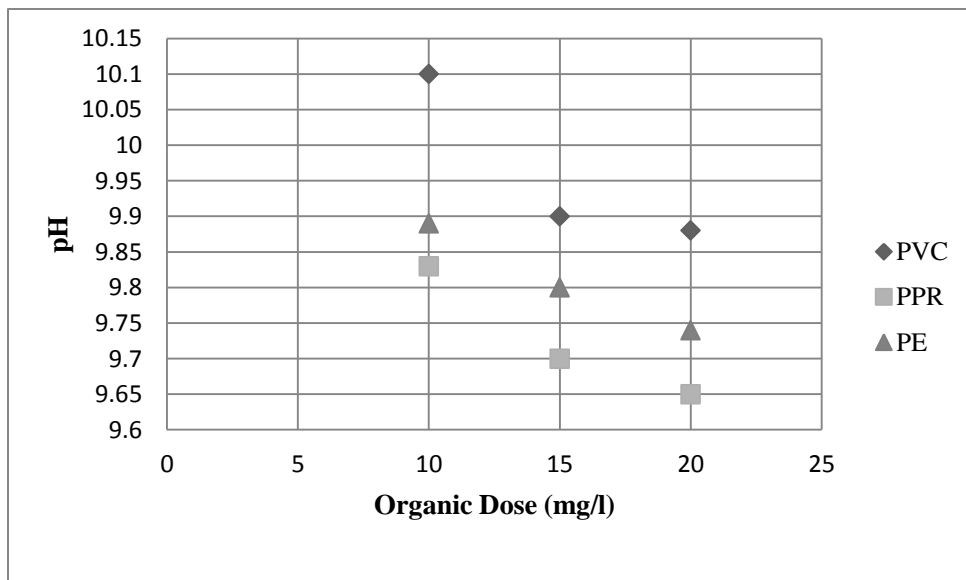


Figure A.25: Effect of TOC on pH of Water with an Initial $\text{Ca}(\text{ClO})_2$ Dose of 0.75 g/L

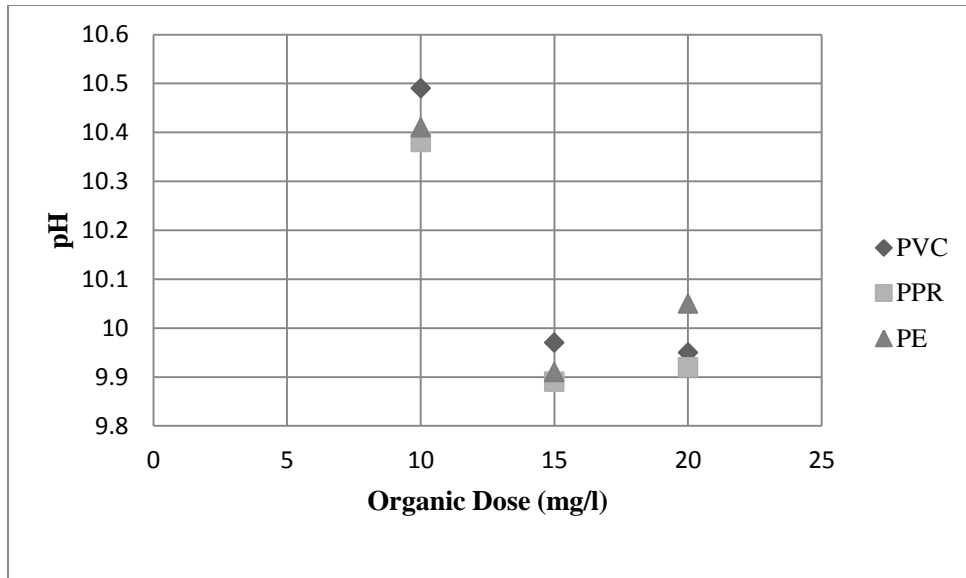


Figure A.26: Effect of TOC on pH of Water with an Initial $\text{Ca}(\text{ClO})_2$ Dose of 1.0 g/L

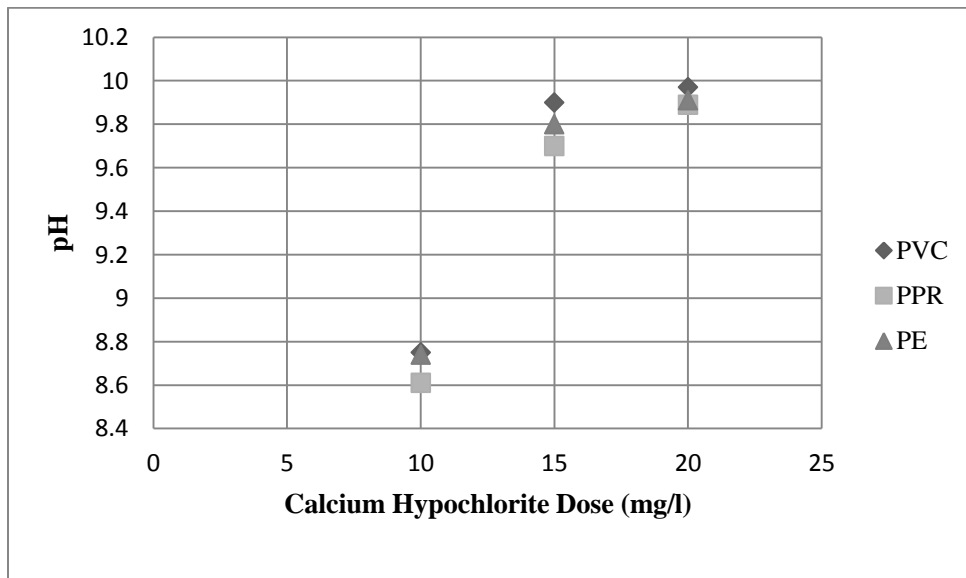


Figure A.27: Effect of $\text{Ca}(\text{ClO})_2$ Dose on pH of Water with an Initial TOC of 0.69 ppm

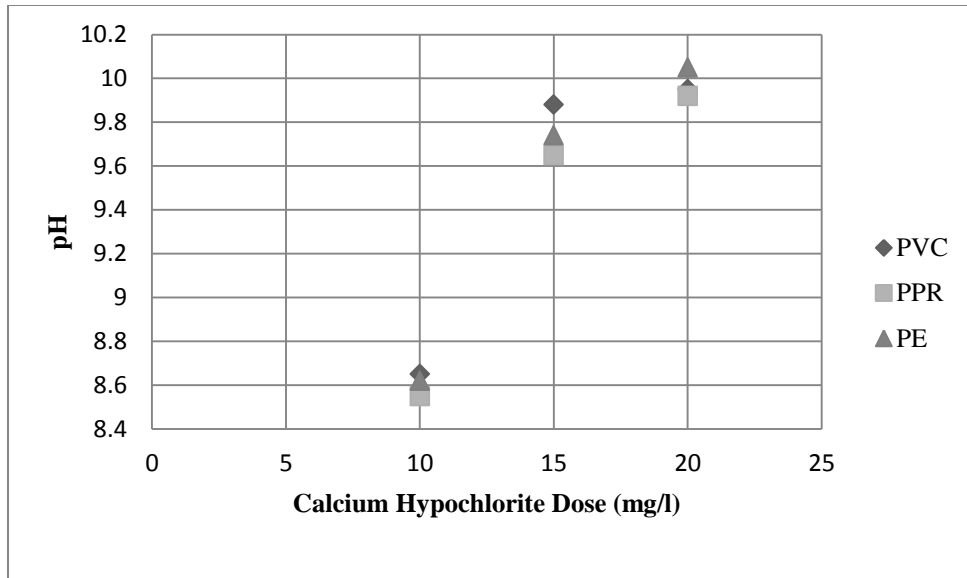


Figure A.28: Effect of $\text{Ca}(\text{ClO})_2$ Dose on pH of Water with an Initial TOC of 0.75 ppm

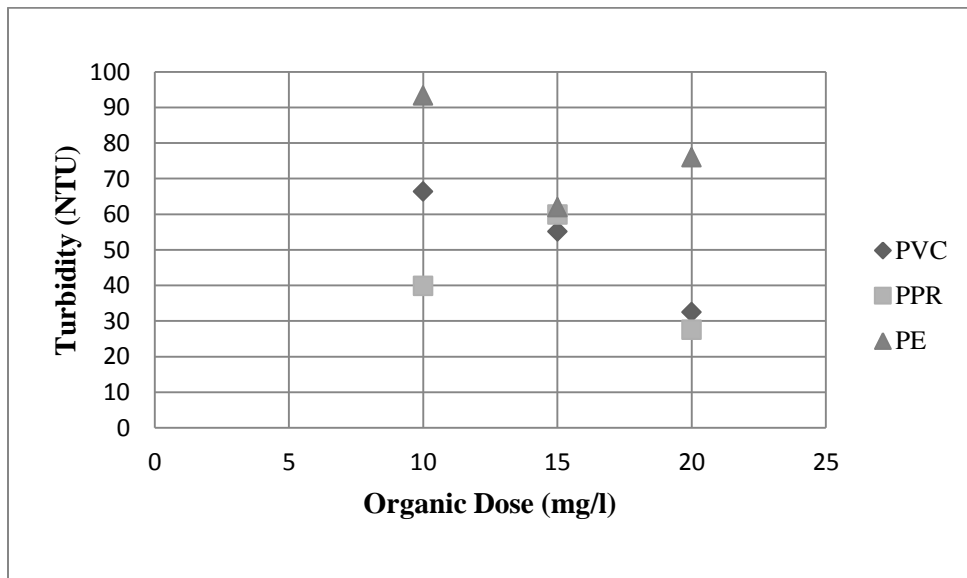


Figure A.29: Effect of TOC on Turbidity with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

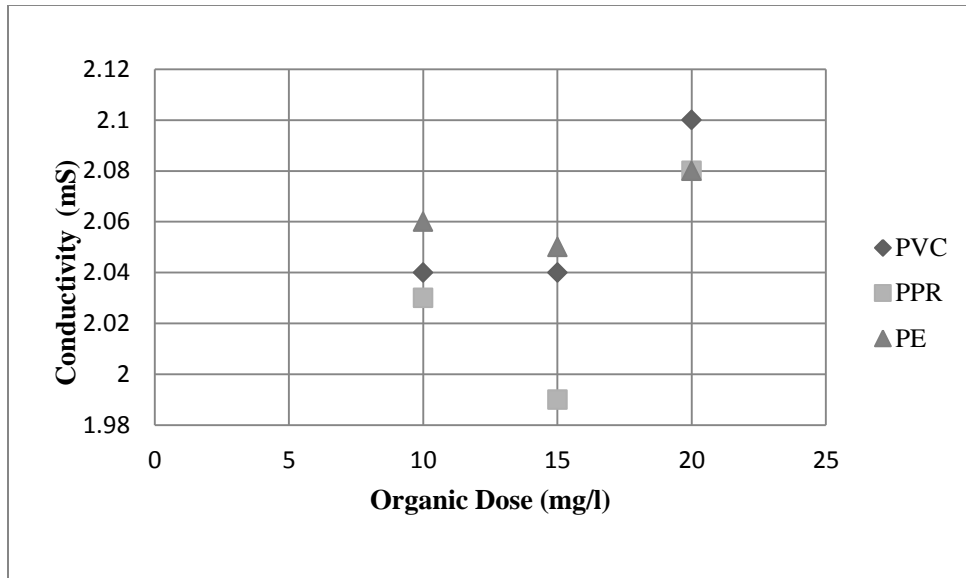


Figure A.30: Effect of TOC on Conductivity with an Initial $\text{Ca}(\text{ClO})_2$ of 0.5 g/L

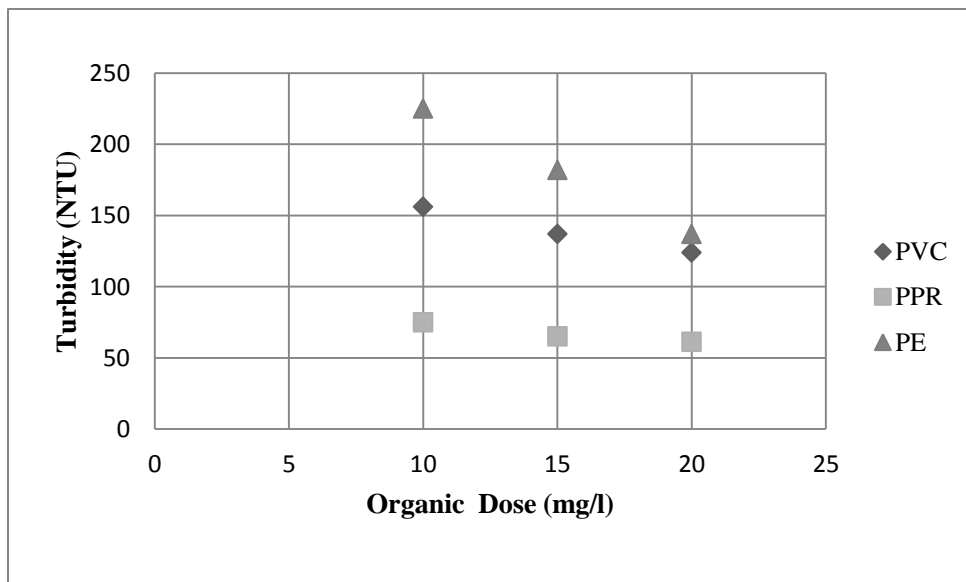


Figure A.31: Effect of TOC on Turbidity with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

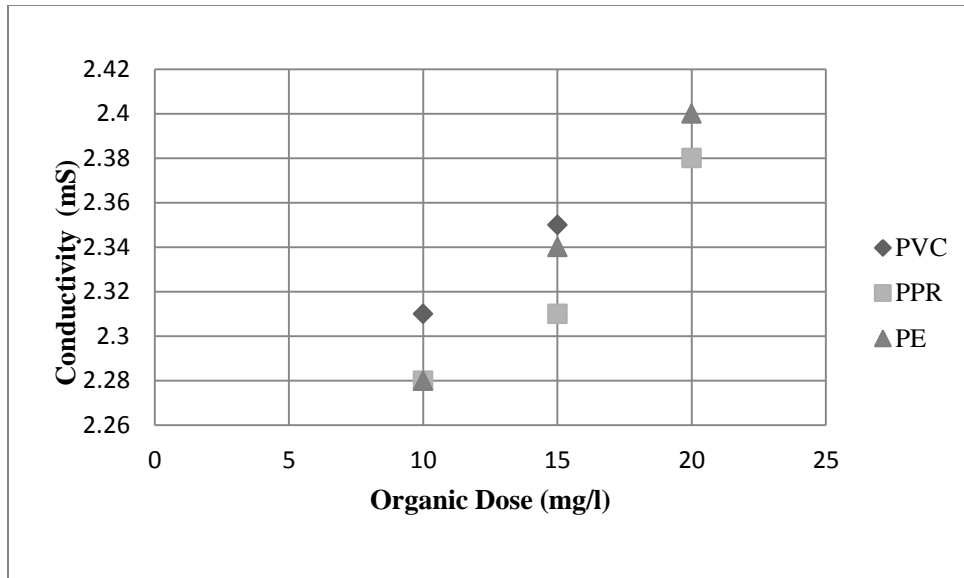


Figure A.32: Effect of TOC on Conductivity with an Initial $\text{Ca}(\text{ClO})_2$ of 0.75 g/L

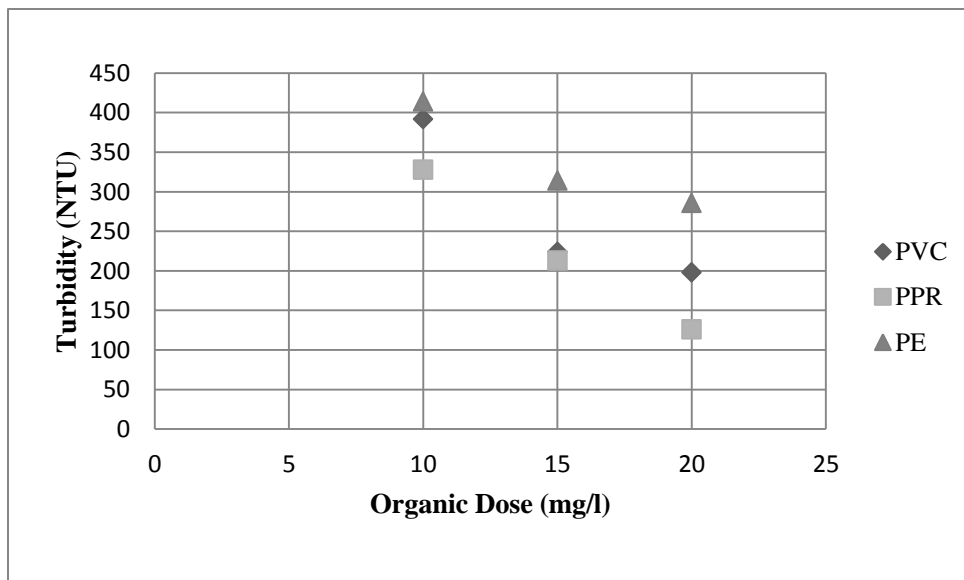


Figure A.33: Effect of TOC on Turbidity with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

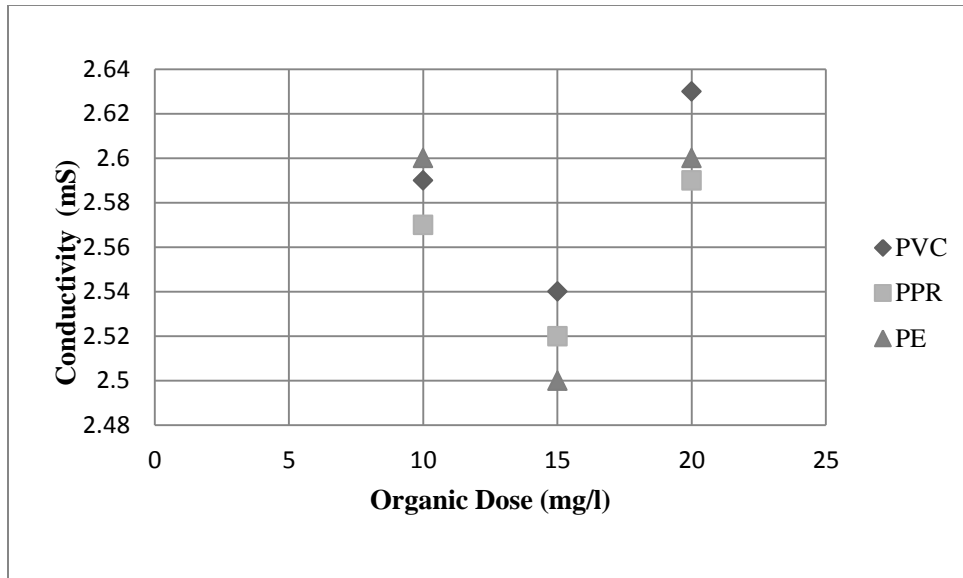


Figure A.34: Effect of TOC on Conductivity with an Initial $\text{Ca}(\text{ClO})_2$ of 1.0 g/L

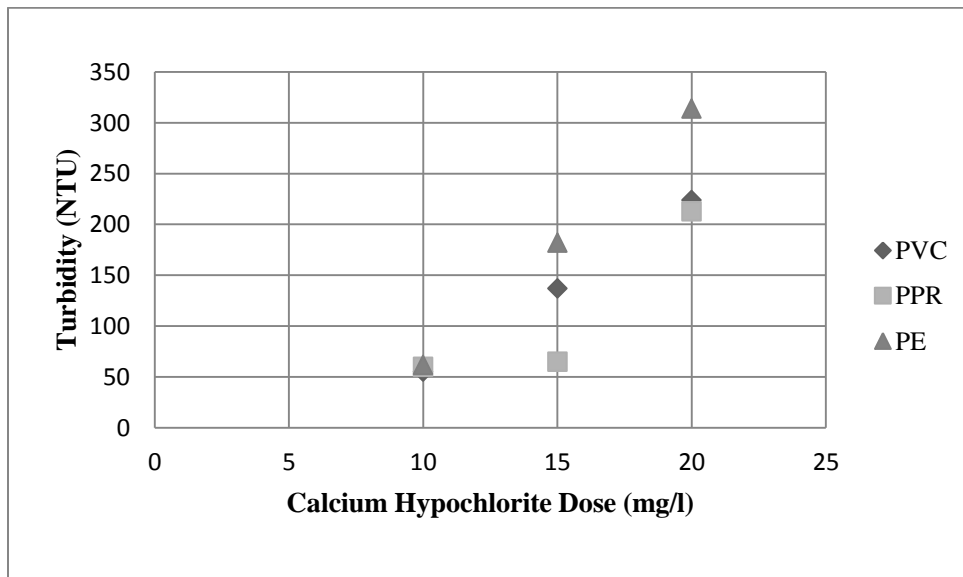


Figure A.35: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Turbidity with an Initial TOC of 0.69 ppm

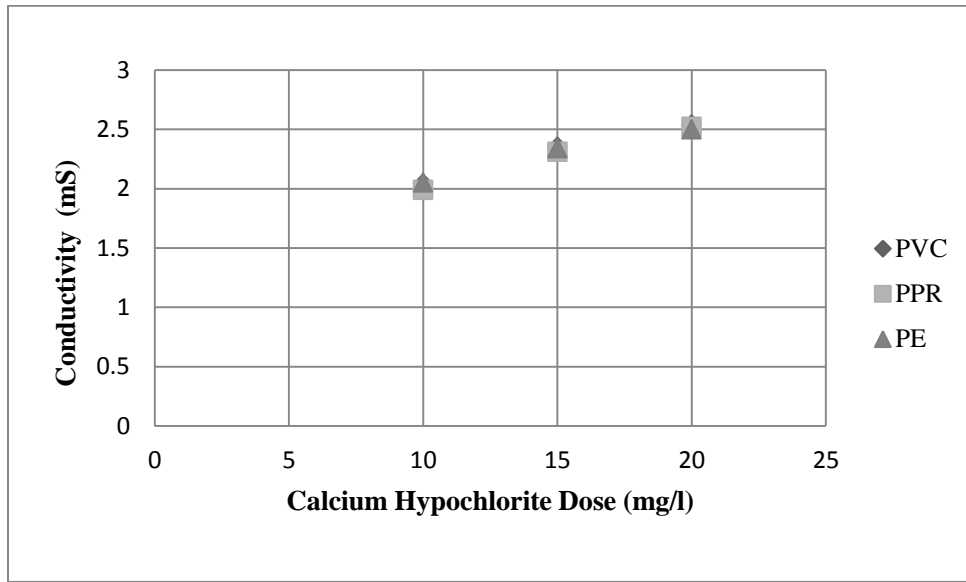


Figure A.36: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Conductivity with an Initial TOC of 0.69 ppm

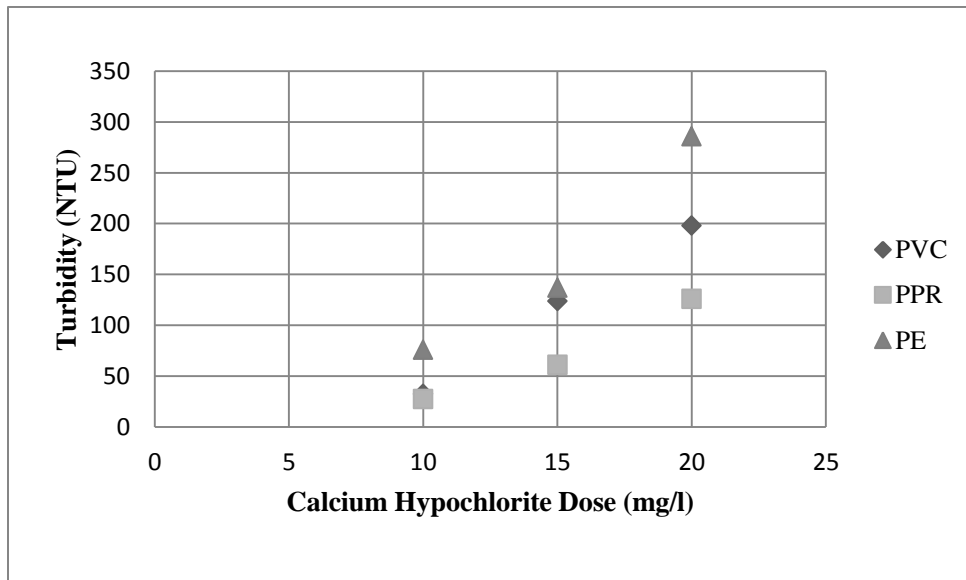


Figure A.37: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Turbidity with an Initial TOC of 0.75 ppm

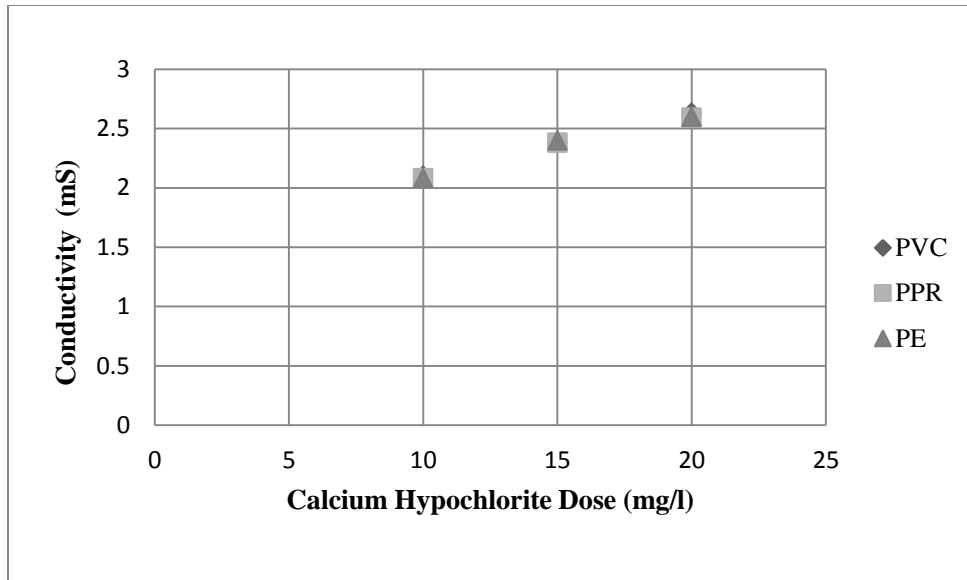


Figure A.38: Effect of $\text{Ca}(\text{ClO})_2$ Dose on Conductivity with an Initial TOC of 0.75 ppm

Vita

Sina Shabani was born on April 14, 1988, in Norrköping, Sweden. He migrated to his home country Iran at the age of 6 and started his education at Amir Kabir Primary School. He graduated from Amir Kabir High School in 2005.

He moved to the United Arab Emirates in 2006 and finished preuniversity at Towhid Iranian School of Dubai. He continued his education at the American University of Sharjah and graduated in January, 2011 with a B.S. degree in Civil Engineering. In 2011, he started his graduate studies at the American University of Sharjah in the Master's program in Civil Engineering Science. During his studies he worked as a research and teaching assistant. He was in charge of several courses and mainly had lab duties in the environmental engineering laboratory. He is expected to receive the M.S. degree in Civil Engineering in June 2013.