

Sounding the Alarm on Water Quality: Predictive Modeling of Total Trihalomethanes Using Chlorine Residuals

Aditi V. Gopalakrishnan^{1,*} and Ragini Vittal²

¹Walton High School, Marietta, GA; ²Department of Medicine, Emory University, Atlanta, GA

Abstract — Flint water crisis in Michigan caused pathological fatalities traced to contamination of lead and Legionella bacteria in aging pipes. Elsewhere in Georgia, domestic Marietta waters registered abnormal carcinogen levels, including total trihalomethanes (TTHM, also detected in Flint crisis), due to chlorine disinfection which interacts with natural organic matter and forms TTHM. Further, industrial pollutants disrupt water chemistry by metal leaching and generating ammonia - making periodic testing an unmet public health responsibility. This study tests domestic Marietta waters for pH, lead, and chloride derivatives, hypothesizing that waters from metal versus polyvinyl chloride (PVC) plumbing will have high chloride derivatives and therefore, high levels of TTHM. Waters from homes aging 0-30 years or over 35 years, and mineral water controls were analyzed using TESPERT drinking water test kit. High-chlorine samples were tested for TTHM by gas chromatography/mass spectrometry (Paragon labs, Livonia, MI). Irrespective of year built, ~50% of homes had PVC/copper plumbing. Compared to PVC pipes, metal plumbing showed acidic waters (pH: 5-6.4) with higher levels of total and free chlorine (~1ppm) and demonstrating a trend that positively correlates with higher TTHM levels (10-30ppb) - predominantly chloroform and bromodichloromethane. Bromine was highest in waters from polybutylene (3ppm) and lead (1.5ppm) plumbing. Overall, these findings warrant free chlorine levels as an indicator of the presence of carcinogenic TTHM constituents and warrant preventive measures of boiling and stringent filtration, with periodic seasonal testing of chloride derivatives to monitor alteration patterns.

Introduction

Volatile halogen-based organic compounds are systematically detected in several samples of the drinking water aquifers in the United States[1], with concentrations exceeding health guidelines. Due to ubiquitous use of bleach as disinfectant and other halogen based compounds as pesticides, trichloromethanes were detected in upto 85% of drinking water samples[1]. The 2024 environmental protection agency (EPA) survey from thousands of water utilities and state officials indicates that ~9.2 million lead service lines are still in use. When lead pipes corrode, lead can contaminate water and increase acidity[2], thus triggering a vicious cycle. In 2015, the waters in Flint, Michigan, was contaminated with lead and Legionella bacteria leading to high incidences of Alzheimer's and Legionnaires' disease, respectively[3]. City officials reacted by adding more chlorine to disinfect the water which drove the TTHM levels high[4]. Water quality engineers blamed industrialization (mining sites, chemical dumps, power plants, farmyards, landfills), and use of detergents and disinfectants to acidity that can leach lead pipes, or alkalinity that can raise ammonia levels[5]. There also instances of occasional sewer overflow as reported in local Marietta

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^{*}Aditi V. Gopalakrishnan is a senior at Walton High School, Marietta, GA30062, USA (corresponding author: aditig2026@gmail.com).



waterways of Sewell Mill Creek[6], and the Chattahoochee River[7] in Marietta, a suburban city near Atlanta, Georgia.

In 2021, the US Environmental Protection Agency (EPA) working group reported that tap water in Marietta-Cobb County met Safe Drinking Water Act standards, but not health safety, due to lapses in updating legal limits[8]. Of the eight reported carcinogens over the health guidelines, one of them was TTHM at 259 times higher (total trihalomethanes – implicated in Flint crisis and generated when chlorine reacts with organic material), while nitrates/nitrites were 3.9 times higher[8]. The four TTHM analytes in this study are the most studied disinfection byproducts - chloroform, dibromochloromethane (DBCM), bromodichloromethane (BDCM), and bromoform whose maximum limits according to the World Health Organization is 300, 100, 60, and 100 μ g/L[9], which are significantly higher than the allowable maximum contaminant level set by the EPA at 80 μ g/L[8]. Both these guidelines are still significantly higher than the strict health guidelines set by the Environmental Working Group at 15 ppb to prevent chronic diseases including bladder and colorectal cancer[10,12]. Notably, ~308 Americans are consuming tap water with TTHM levels >15 ppb[10]. The need of the hour would be frequent monitoring of home waters for parameters that include turbidity, pH, and halogens, to alert local officials of abnormalities.

The objective of the present study is to test domestic water quality for pH, lead, and chloride derivatives; and to compare samples from polyvinyl chloride(PVC) versus metal plumbing. Therefore, the questions posed were: (i) acidic or alkaline pH leach heavy metals from older lead or metal pipes versus newer PVC pipes; how will this impact drinking water levels of pH, lead, chlorides and nitrates? (ii) since chlorinated water may contain higher levels of the carcinogen, TTHM, than health guidelines in Flint-Michigan and Marietta-Georgia, what is the current TTHM levels in our drinking water? We hypothesized that older lead or metal plumbing will have imbalanced pH, higher levels of lead, chloride and nitrate derivatives, including TTHM, compared to newer homes with PVC plumbing.

Methods

Methodology. Of the randomly chosen total sampling of 21 homes, as shown in Table 1, 11 newer homes were aged 0-30 years (blue), 10 older homes were aged over 35 years (red). The type of plumbing used was recorded. Tap water was allowed to flow for 30 seconds prior to collection in sterile containers at the same time of the day and stored at 4°C, until analyses as per protocol in the TESPERT drinking water test kit (Catalog #788081195647). 16 parameters were recorded as

TABLE 1. Details of water sample sources

IADLE	i. Details	o oi wai	er Sample	Sources
Sample No.	Sample ID	Year Built	Plumbing	Age (years)
1	AL	1980	PVC	44
2	VT	1999	PVC	25
3	TB	1980	Polybutylene	44
4	WHS	2017	PVC	7
5	AM	1997	Copper	27
6	HG	1978	Lead	46
7	RV	1997	Copper	27
8	AC	2005	PVC	19
9	SM	2007	Copper	17
10	YJ	1980	PVC	44
11	MA	1986	Copper	38
12	HC	1987	Copper	37
13	CD	1987	Copper	37
14	SVG	1988	Copper	36
15	AbG	2002	Lead	22
16	TgR	2008	Copper	16
17	PE	2006	Lead	18
18	JW	2017	Copper	7
19	MK	2012	PVC	12
20	IW	1965	Iron	59
21	SI	1960	Iron	64

TABLE 2. Safe limits of TESPERT kit parameters

	Parameters	Safe limits
Nitrogen derivatives	Nitrates	<10ppm (mg/L)
	Nitrites	<1ppm (mg/L)
Halogens	TOTAL Cl ₂	<4ppm
	FREE Cl ₂	pure water:0.2-1ppm; <4ppm
	Br	minimal or none
Disinfectants	MPS	Potassium bisulfate
	Cyanuric acid	minimal or none
Metal ions	Cu	1.3ppm
	Fe	0.3ppm
	Pb	<15ppb
	Ni	minimal or none
Acid ions	SO3	minimal or none
	CO3	minimal or none
Acidity and	TOT ALK	minimal or none
dissolved substances	pН	6.4-8.2
(Ca and Mg)	HARDNESS	0-60ppm (mg/L)

listed in Table 2. High chlorine samples were collected carefully as per guidelines from Paragon lab and sent for TTHM analyses by GC/MS (gas chromatography and spectrometry; mass Paragon labs, Livonia, MI). Controls used were Smart Water®, Just Water® and Pure Life® as mineral water control samples against the 16-



parameter TESPERT kit and TTHM analyses.

Data and Statistical analyses. MS Excel was used to tabulate data. GraphPad Prism (ver. 10.0.1) was used to generate graphs and analyze statistical differences by comparing two means (unpaired Student's 2-tailed t test) or three means (one-way ANOVA, *post hoc* comparison test by Bonferroni) for the analytes in water from lead or metal vs. PVC pipes. Pearson's and Spearman's correlation analyses was performed between analytes. Values were expressed as Means ± SEM. Significance was set at 0.05: *p<0.05, **p<0.01, ***p<0.001.

Results

Prevalent plumbing in new and old Marietta homes. Figure 1 illustrates the plumbing types in the randomly selected homes. The distribution for each plumbing type is expressed as fraction of the total: the 11 newer homes had 4/6 PVC pipes, 5/9 copper pipes and 2/3 lead pipes; while the 10 older homes had only 2/6 PVC, but 4/9 copper, 1/3 lead, and 1/1 polybutylene.

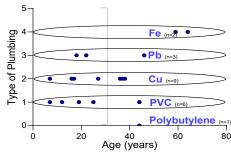


Figure 1. Plumbing distribution in Marietta

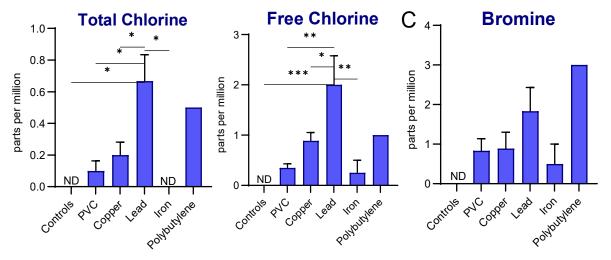


Figure 2. Chlorine and bromine levels in domestic waters.

Free chlorine levels were highest in lead plumbing. Among the 16 parameters, chlorine and bromine levels are shown in Figure 2. Water samples from lead plumbing demonstrated higher levels of total and free chlorine compared to other plumbing types (Figure 2A, 2B).

Free chlorine from all types of metal pipes were higher than waters from PVC pipes (Figure 3A, 3B). Lead, polybutylene and copper plumbing demonstrated higher total/free chlorine (~1 ppm) levels. Bromine was highest in polybutylene (3 ppm) and lead (1.5 ppm) but bromine levels in metal plumbing were not significantly different from that in the PVC plumbing (Figure 3C).

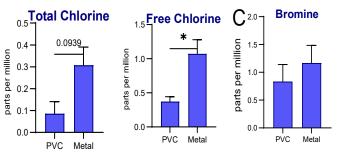


Figure 3. Chlorine and bromine levels in PVC vs metal pipes.



High TTHM levels in metal plumbing. TTHM levels were measured by gas chromatography and mass spectrometry, (GC/MS; Figure 4, Table 3). The spectrometry results in Figure 4 shows

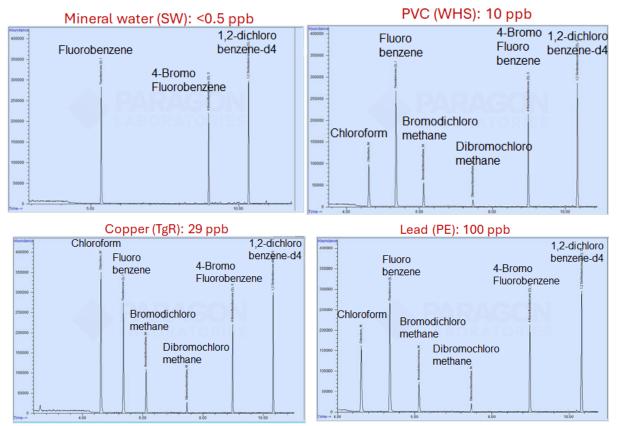


Figure 4. TTHM analytes by GC/MS spectrometry. Representative readouts are shown.

representative samples with each peak indicating a specific organic compound as shown in the graphs. The area under the curve in each peak indicates the analyte concentration (ppb). Mineral water indicated presence of three non-carcinogenic organic analytes, which are also seen in domestic water samples collected from the various plumbing.

Table 3 shows each of the four individual analytes that are classified as human carcinogens by U.S. Department of Health and Human Services and the International Agency for Research on

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ppb/µg per L	Bromodichloromethane	Bromoform	Chloroform	Dibromochloromethane	TTHM	X higher	plumbing
SW	>0.5	>0.5	>0.5	>0.5	>0.5	unknown	mineral water control
WHS	3.4	<0.5	6	0.91	10	67	PVC
TgR	6.2	>0.5	21	1.6	29	193	Copper
HC	1.2	>0.5	3.7	>0.5	5	33	Copper
SVG	4.2	<0.5	7.5	1.2	13	87	Copper
AbG	2.9	0.88	3.6	2.3	9.6	64	Lead
PE	4.3	<0.5	9.9	1.1	15	100	Lead
EWG health	0.06	0.1	0.4	0.1	0.15		
	0.06	0.1	0.4	0.1	0.13		
Legal limit	none	none	none	none	80		



Cancer – bromodichloromethane, bromoform, chloroform, and dibromochloromethane, indicate TTHM levels[10-12]. Each of these analytes were higher in water samples collected from metal plumbing compared to PVC plumbing and were multiple fold significantly higher than the EWG health safety guidelines. Chloroform was the most dominant analyte, followed by bromo dichloromethane, dibromo chloromethane and bromoform, and this finding is consistent with other reported findings[11,12]. Overall, TTHM levels were higher in metal plumbing (range: 5-29 ppb) versus PVC plumbing (10 ppb), but undetectable in mineral water (<0.5 ppb).

In addition to being higher than health guidelines issued by Environmental Working Group from the EPA[10], in certain cases, the analyte levels exceeded the legal limits. The chlorine levels in the samples showed a strong trend towards positive correlation TTHM against the levels albeit significant (Figure 5). Thus, free chlorine levels can potentially serve as predictors of elevated levels of carcinogenic chloride derivatives since these derivatives are generated when chlorine disinfectants react with natural organic matter in the waters.

Nitrates and other parameters. While elevated levels of nitrates were detected in metal plumbing, no significant differences were noted among the parameters (Figure 6). pH/alkalinity, carbonates and water hardness were variable among the different type of plumbing; however, it should be noted that these are essential analytes to consider in terms of leaching of the plumbing.

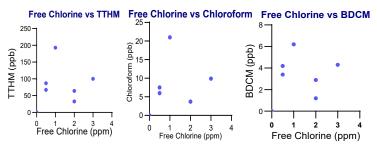
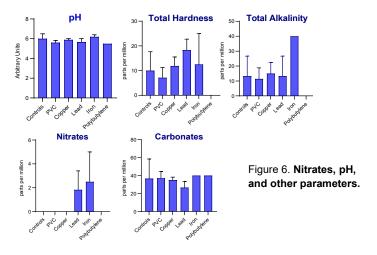


Figure 5. Correlation of free chlorine levels to predict TTHM presence



Health implications. TTHM are proxy measures of disinfection by-products analyzed via the four carcinogenic organic constituents chloroform (group 2B), bromoform _ bromodichloromethane (group 2B), and dibromochloromethane (group 3), according to the International Agency for Research on Cancer and World Health Organization[12]. Recent studies as shown in Table 4 has implicated prolonged exposure of TTHM with detectable levels in the blood and increased risk and prevalence of several chronic diseases that include cancer, cardiovascular, respiratory, renal, and thyroid-dysfunction-related diseases. It should also be noted that chloroform was the predominant analyte detected in our study, and Table 4 shows that serum chloroform was observed to be linked to non-cancer/non-heart disease mortality. The reported PUBMED findings in Table 4 are prevalent in both adolescent and aged adults as investigated via the NHANES (National Health and Nutrition Examination Study) and the California Teachers



Study, thus widely encompassing the length and breadth of the United States.

TABLE 4. Recent PUBMED reports on role of TTHM in chronic human diseases.

Year/PMID	Publication	Subjects	Health Implication
2023/ 38091484	Exposure to Trihalomethanes and Bone Mineral Density in US Adolescents: A Cross-Sectional Study (NHANES)	NHANES adolescents	adversely affects bone mineral density
2023/ 36764558	Blood trihalomethane concentrations and allergic sensitization: A nationwide cross-sectional study	NHANES adolescents	adverse risk to multiple allergies
2021/ 34617747	Relationship between Blood Trihalomethane Concentrations and Serum Thyroid Function Measures in U.S. Adults	NHANES adults	altered serum thyroid hormone levels but not thyroid autoimmunity
2023/ 37852642	Blood Trihalomethane Concentrations and Osteoarthritis among U.S. Population Aged over 50 Years	NHANES adults>50 years	elevated serum gamma-glutamyltransferase with high risk of osteoarthritis
2021/ 34152769	Association of Blood Trihalomethane Concentrations with Risk of All-Cause and Cause- Specific Mortality in U.S. Adults: A Prospective Cohort Study	NHANES adults>40 years	serum Br-THMs linked to high cancer mortality risk, and serum chloroform linked to high noncancer/nonheart disease mortality.
2023/ 37657551	Association of blood trihalomethane concentrations with hypertension in US adults: A nationwide cross-sectional study	NHANES adults	blood Br-THMs positively correlated with hypertension and high BMI
2025/ 40601319	Community Water Trihalomethanes and Chronic Kidney Disease	California Teachers Study	exposure to THM<80 μg/L (US current standard) increased CKD risk, particularly Br-THM
2022/ 34625481	Association of blood trihalomethane concentrations with asthma in US adolescents: nationally representative cross-sectional study	NHANES adolescents	exposure to THM linked to higher risk of asthma, particularly if exposed to tobacco smoke

Discussion

Irrespective of the year built, the plumbing systems varied as homeowners replaced them or had a combination of pipes. Copper and lead pipes registered higher degree of water hardness, and acidic pH. As hypothesized, lead pipes had elevated levels of chlorine, bromine, and nitrogen derivatives, as well as disinfectants. Some of the concerning findings were marginally higher levels of iron (house #11), lead (houses #10, #15) and nickel (house #16), independent of the type of plumbing.

The most concerning finding was the elevated levels of trihalomethanes, both brominated and chlorinated forms, as measured by GC/MS in the high-chlorine samples. Large cohort studies demonstrate trihalomethanes-associated mortality, with brominated compounds linked to cancer, while chlorinated compounds were linked to nonheart/noncancer disease mortality[13,14]. With widespread use of chlorine as a disinfectant, it forms hypochlorous acid which interacts with natural organic matter to form disinfection byproducts, including TTHMs. Furthermore, acidic water with a pH of less than 6.5 as in this case is more likely to be contaminated, making water unsafe to drink and corroding metal pipes. It should be noted that although peak TTHM formation



typically occurs at ~pH 7–8, detectable amounts are still produced at pH 5–6.5, with ideal levels of dissolved organic carbon, chlorine, long contact time and warm temperatures.

Practical preventive measures such as reverse osmosis[15] and presence of corrosion inhibitors[16] may help reduce the production of harmful chemicals. Another practical preventive measure would be boiling water for one minute followed by use of activated carbon filters[17], or reverse osmosis or ion exchange filters, each of which could potentially reduce the presence of the chloride derivatives and therefore the halogen-based carcinogens.

There are multiple ways to expand this study. More homes need to be analyzed over a longer period, both winter and summer, to monitor changes in water quality and the effects of using disinfectants and detergents. Monitoring of samples after using the suggested preventive measures might shed light on the most effective outcome with better cost to benefit ratio. The sensitivity of the testing kit is critical and it may not have yielded detectable signals for the nitrates and nitrites. So other mode of nitrate/nitrite analyses are warranted. Testing of carcinogens such as total trihalomethanes are cost- prohibitive, so possibly greater samples might fetch a better cost of analyses, as the findings outweigh the cost. Further, comparative evaluation of water samples filtered utilizing multiple devices for the presence of TTHM analytes will provide better understanding of water treatment in areas of prolonged exposure. Small-scale sample collection has generated enthusiasm which could drive greater curiosity and awareness to evaluate water quality. Next steps would be to explore IO-driven water sensors to evaluate waters from various areas of Marietta for carcinogens and nitrate derivatives and ensure safety of water quality.

In conclusion, our study reports elevated levels of total and free chlorine levels, which are critical for the generation of the carcinogens, TTHM. Specifically, chlorine levels were found to be higher in metal plumbing as compared to PVC pipes, and hence chloroform was the predominant analyte detected. This study is critical from an overall perspective of quality of life since prolonged exposure to TTHM causes a plethora of chronic diseases in addition to cancer, while on the other hand, use of plumbing made of heavy metals such as lead, copper, and iron, could accumulate systemically at toxic levels, especially in the vulnerable population subsets of younger children and the aged[18]. The toxic accumulation of these metals in the body could affect neuromuscular coordination[19], hematopoiesis[20], and eventually manifests in the form of chronic ailments, including Alzheimer's disease[21].

Considering the growing presence of harmful contaminants such as lead, and disinfection byproducts like TTHMs in domestic water supplies, proactive measures are critically essential. Prioritizing routine water quality assessments, fostering public awareness, and ensuring access to affordable filtration solutions must become standard practice. Only through collective vigilance and strengthened regulatory oversight can we protect our communities, especially the most vulnerable among us such as the elderly and immunocompromised population.



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