Spatial and Seasonal Variations of Disinfection Byproduct (DBP) Precursors in Relation with Total Organic Carbon (TOC)

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ABSTRACT

Disinfection is an essential process for both potable water and wastewater treatment plants. However, disinfection byproducts (DBPs) like trihalomethanes (THMs), haloacetonitriles (HANs), and nitrosamines (NOAs) are formed when organic matter precursors react with disinfectants such as chlorine, chloramine, and ozone. Formation of DBPs is strongly associated with the type of water source, type of disinfectant, and organic matter concentration, which can have seasonal variation. In this study, water samples were collected from 20 different intra-watershed locations, which included urban runoff (with and without the influence of unsheltered homeless populations), wastewater effluent discharges, and a large, terminal reservoir that serves as the local drinking water source. Samples were collected on dry and rainy days, which represent seasonal samples. DBP formation potential (FP) tests were conducted at consistent pH, contact time, and temperature. THMs, NOAs, and HANs were analyzed by gas chromatography-mass spectrometry (GC-MS). The FP tests performed on these water samples revealed that chlorine formed the highest THM concentrations, while THM concentrations were low for the ozone FP test as expected. Chloramine produced the greatest HAN concentrations, with dichloroacetonitrile representing the highest concentration. With respect to sample type, more DBPs were formed at the non-wastewater-impacted runoff sites as compared to the wastewater effluent discharge sites. With respect to TOC levels, rain event samples for all locations had higher TOC concentrations compared to dry sampling days. Similarly, rain event samples showed increased DBP formation; a significant amount of precursors for THMs was found in runoff waters that were influenced by wastewater effluent discharges and unsheltered homeless locations (concentration of total THMs for chlorine FP test was >200 μg/L). Therefore, urban runoff waters should be considered as potential sources of DBP precursors to drinking water source waters, and runoff water is prone to seasonal variation.

Keywords: Disinfection byproducts; DBPs; DBP precursors; wastewater; urban runoff; nitrosamines, trihalomethanes, haloacetonitriles

1 INTRODUCTION:

Global communities face water scarcity due to limited freshwater sources, increasing agriculture demand, climate change, and natural disasters (EPA, 2015). The sources of fresh water available on Earth are 2.5% of the global water supply (Perlman, 2013). Of this, only 1.2% of all freshwater is surface water, which serves most of our life's needs (Guamán & Yumisaca, 2015).

Most of the fresh water is used mostly for agricultural irrigation purposes (USDA, 2016). With such a limited supply of freshwater and greater agriculture demands to feed a growing population, the need for alternative water supplies for crop irrigation has increased rapidly.

Reclaimed wastewater and stormwater runoff can play a significant role in meeting water demands; however, the presence of contaminants like salts, pathogens, and organic matter influences the reusability of water from such sources. In addition, disinfection byproducts (DBPs) are formed when organic matter reacts with disinfectants. DBPs, due to their carcinogenic nature, are widely recognized to pose a risk to human health. The U.S. Environmental Protection Agency has set the regulation for trihalomethanes (THMs) with a maximum contaminant level (MCL) of 80 μg/L for the sum of four major THMs or total trihalomethanes (TTHM); similarly, five haloacetic acids (HAA5) are regulated with a MCL of 60 μg/L (Yang et al., 2018). More than 600 DBPs have been identified over the last thirty years (Richardson, 2011), and many are not regulated. Examples of unregulated DBPs are haloacetonitriles (HANs) and nitrosamines (NOAs).

The formation of DBPs depends on the type of water sources, type of disinfectant, and precursors. In general, most DBP precursors are organic materials and could be derived from terrestrial (i.e. natural organic matter), agriculture (e.g. fertilizer, pesticides), biological (e.g. algae, soluble microbial products) or anthropogenic sources (e.g., industrial chemicals, tire rubber, dyes). The availability of these organic materials in water systems will vary during dry and rainy (wet) seasons.

In this study, water samples were collected from a wide range of sources including intra-watershed locations, urban runoff (with and without the influence of unsheltered homeless populations), wastewater effluent discharges, and a large, terminal reservoir that serves as the local drinking water source. All sampling locations either serve as tributaries to the Las Vegas Wash or are impacted by the Las Vegas Wash, including the principal drinking water source for Southern Nevada—Lake Mead. Some of the sample locations were selected to capture areas within the urban flood control network with high density homeless encampments. As there are no sanitary facilities for unsheltered homeless populations, the waste generated from these locations enters the wash network through stormwater runoff. Other sample locations included areas heavily influenced by treated wastewater effluent and areas that lacked contributions from wastewater effluent or unsheltered homeless populations.

The objective of this study is to determine DBP precursor loads for the local urban watershed at various locations and under different seasonal conditions. Therefore, DBPs, their precursors and total organic carbon (TOC) were measured under dry (sampling at 20 locations) and wet (sampling at 2 locations; 4 different time intervals) conditions. This paper presents initial findings for an ongoing study with a goal of better understanding the DBP precursor loadings from flood control and wastewater infrastructure on the existing drinking water infrastructure.

2 MATERIALS AND METHODS:

2.1 Sampling locations and FP tests

Dry event samples were collected from 20 different locations (A to T) along the Las Vegas Wash, reaching Lake Mead, as shown in Figure 1. The wet (rain) event samples were collected from two locations (A and K), each at four different time intervals. Sites A, B, and C were in close proximity to unsheltered homeless populations. Locations D, E, G, H, M, I, Q, L, and K were collected along the Las Vegas Wash. Sampling locations T, O, N, and J were collected from the Las Vegas Wash just after the discharge from wastewater treatment plant effluents, and locations R and S were collected from nearby drinking water source intakes.

The DBP (THMs, NOAs, and HANs) precursors were assessed through formation potential tests with different disinfectants: chlorine, chloramine, and ozone. The DBP formation potential (FP) tests were conducted at consistent pH 7–7.5, reaction time (24 h for ozonation, seven days for chlorination, and ten days for chloramination), and room temperature (Chen & Westerhoff, 2010; Kanan & Karanfil, 2020). During the ozonation FP test, ozone was added to achieve a ratio of 0.8 mg O_3/mg TOC following an established procedure (Zeng et al., 2016). In contrast, the chlorine dose for chlorination FP was estimated based on the excitation-emission matrix (EEMs) of the respective samples and dosed at multiple concentrations to achieve a residual of 3–5 mg/L as Cl_2 after seven days following Standard Method 5710 (Federation, 1999). For the chloramination FP test, a monochloramine solution was prepared and samples were initially spiked at 140 mg/L following an established procedure (Mitch & Sedlak, 2004). Chlorine and chloramine residuals were quenched using sodium thiosulfate.

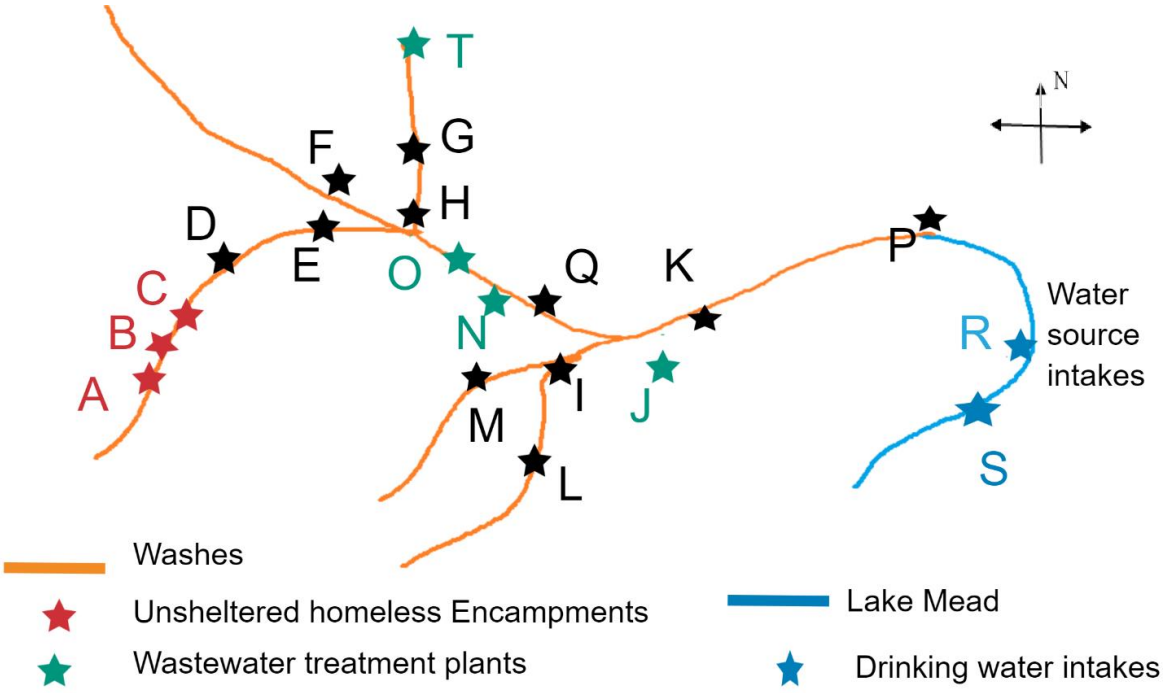


Figure 1: Location of sampling points along the urban channels to Lake Mead. Locations are color-coded to show influence of unsheltered homeless populations and treated wastewater effluent.

DBPs were analyzed directly in all samples as well. These values indicate the presence of the DBPs in the water as opposed to the presence of DBP precursors. These values are denoted as ambient concentrations.

2.2 Analytical methods

The 18 selected DBPs for this study include 4 THMs, 8 NOAs, and 6 HANs as summarized in Table 1. All DBPs were analyzed by gas chromatography mass spectrometry (GC-MS) using USEPA or modified USEPA methods. Only the target DBPs above the minimum reporting limit (MRL) are reported in the study. For NOAs, only NDMA was measured above the MRL; all other NOAs are below the MRL and, therefore, not mentioned in the study. All chemicals and solvents

were purchased from commercial suppliers at 95% purity or higher, and all solvents were of HPLC grade. TOC samples were collected in 40 mL vials, acidified, and analyzed for non-purgeable organic carbon using Standard Method 5310A (Federation, 1999).

Table 1: Target disinfection byproducts for trihalomethanes (THMs), nitrosamines (NOAs) and haloacetonitriles (HANs) with the analytical methods and references

DBPs Group	Target DBPs	Analytical method	References
THMs	trichloromethane (TCM), dibromochloromethane (DBCM), bromodichloromethane (BDCM), tribromomethane (TBM)	USEPA 524.3 method	(Munch, 1995)
NOAs	*N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosomorpholine (NMOR), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosopiperidine (NPIP), *N*-nitrosodi-*n*-butylamine (NDBA)	Modified USEPA 521 method	(Holady et al., 2012)
HANs	monochloroacetonitrile (MCAN), dichloroacetonitrile (DCAN), monobromoacetonitrile (MBAN), bromochloroacetonitrile (BCAN), monoiodoacetonitrile (MIAN), dibromoacetonitrile (DBAN)	Modified USEPA 551.1	(Chuang & Mitch, 2017)

3 RESULTS & DISCUSSION

3.1 Total organic carbon

The TOC values during dry event samples were in the range of 0.91 – 8.21 mg/L (Figure 2) depending on the influence of wastewater effluents, storm runoff, etc., Locations where treated wastewater effluent was discharged (J, N, O, T) or shortly downstream (G, K, P, Q) showed the highest TOC values. Urban runoff water in the channels at locations A-I, L and M was mainly due to excess water from irrigation of lawns or parks.

For the wet sampling event, two locations were selected in the study. One location (A) had the influence of the unsheltered homeless population, and the second location (K) was influenced by wastewater effluent. The locations were selected to study the impact of the unsheltered homeless population and wastewater effluents on DBPs FPs in relation to TOC. Figure 3 shows the TOC values of locations A and K measured at four different time intervals (7 AM, 8 AM, 9 AM, & 10 AM). It can be observed that the TOC values of both locations are higher than those measured during the dry sampling event. The average value for location A, influenced by unsheltered homeless population, increased by 12-fold, whereas location K—influenced by wastewater effluents—increased by two-fold or less. Compared to the non-rain sampling event, there is significantly higher TOC in the urban runoff at location A. With the onset of rain, the TOC values

increased rapidly within 2 h of the rain. This may be attributed to the unsheltered homeless population and materials that build up on streets during the dry season, which must be further investigated. Higher TOC means a greater chance of DBP precursors, which has the potential to result in higher DBP formation as this runoff water joins the drinking water source at the terminus of the Las Vegas Wash.

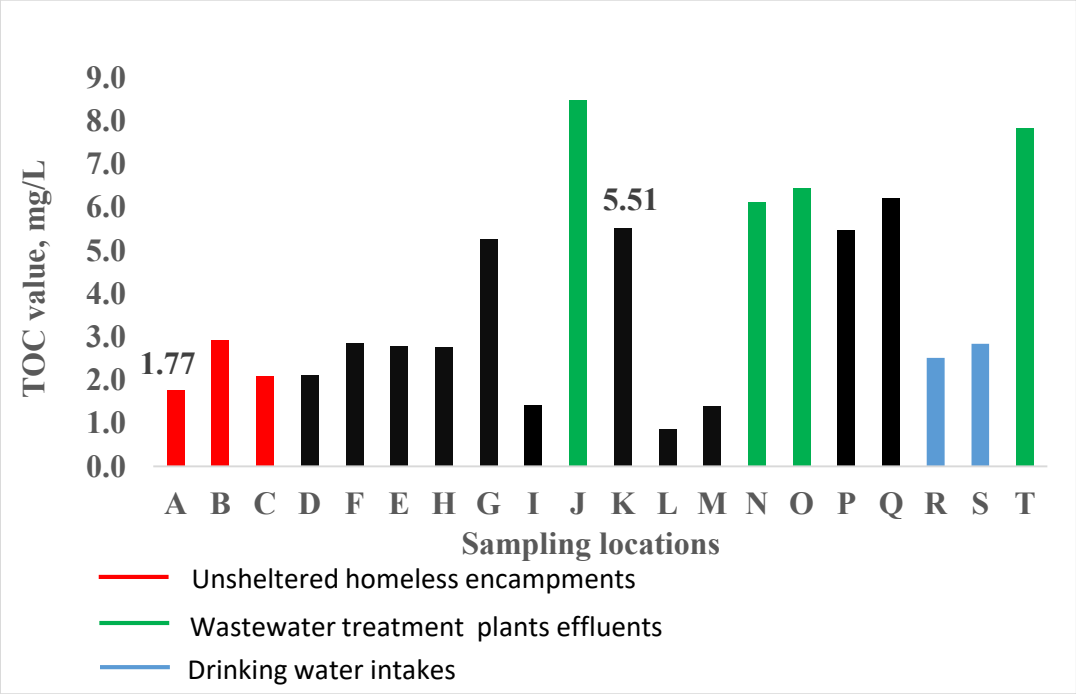


Figure 2: Total organic carbon (TOC) values for 20 different locations collected during dry (non-rain) sampling events

3.2 Disinfection byproduct formation potential during a rain event

Table 2 shows the DBP FP values at location A and K at different time intervals after raining. Among all the three disinfectants used, only the disinfectants which formed the highest DBP FPs are mentioned in Table 2. The ambient samples (not subjected to FP testing) for all HANs, NDMA, and BDCM are below the MRL for both the locations A and K. However, for location A, TCM, DBCM, and TBM are 5.7, 0.9, and 0.11 µg/L respectively; whereas, for location K, the average TCM, DBCM, and TBM are 5.2, 0.57, and 0.11 µg/L respectively. These could be due to the irrigation runoffs from previously chlorinated tap waters. It can be observed that the THM FP and HAN FP increased by 40% and 140%, respectively, just after 2 h of rain at location A. At location K, just downstream from a wastewater effluent discharge point, THM FPs increased by 47%, while HANs amplified by 30% within 2 h. This clearly shows that stormwater runoff TOC contains significant precursors for THMs and HANs. This might be attributed to lack of proper disposal of excrement containing low molecular dissolved organic matter that are THM and HAN precursors (Huang et al., 2016). While natural organic matter and amino acids have been known for a number of years to be precursors for THMs and HANs (Bond et al., 2012; Hong et al., 2009; Huang et al., 2016; W. Lee et al., 2007; Tak & Vellanki, 2018; Trussell, 1978), more work remains to identify

specific precursors in urban watersheds. The chloramine formation potential of NDMA was observed in the second hour of rain; it was below the method reporting limit at other times.

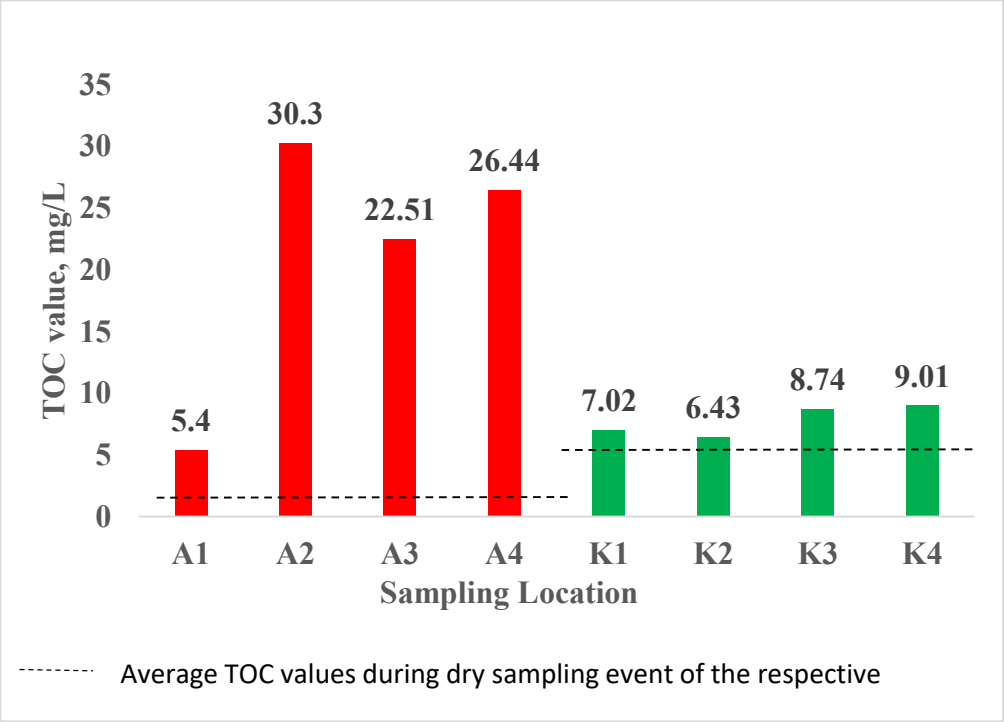


Figure 3: Total organic carbon (TOC) values of wet sampling locations (A & K) taken at four different time intervals (7, 8, 9, & 10 AM) after the first rain of the season.

Table 2: The formation potentials (FPs) of trihalomethanes (THMs), *N*-nitrosodimethylamine (NDMA), and haloacetonitriles (HANs) during a wet sampling event at locations A and K

Location		Time (h) β	THM FP[a] (µg/L)	NDMA FP[b] (µg/L)	HAN FP[c] (µg/L)
A (nearby homeless community)	A1	1	233.16	< MRL	0.22
	A2	2	249.40	1.32	0.53
	A3	3	1229.90	< MRL	0.48
	A4	4	1230.2	< MRL	0.43
K (nearby wastewater effluent discharge)	K1	1	293.1	< MRL	0.79
	K2	2	399.8	< MRL	1.03
	K3	3	337.8	< MRL	1.32
	K4	4	271.4	< MRL	1.14

β Hours after raining; [a] formed using chlorine as disinfectant; [b] formed using chloramination; [c] formed using chloramine as disinfectant; MRL – minimum reporting level; MRL for NDMA is 0.46 µg/L

From the THM FPs, chloroform formed the highest concentration; whereas, tribromomethane was the lowest out of all. At both the locations, the THMs FP are in the trend TCM > BDCM > DBCM > TBM as shown in the Figures 4a & 4b. Chlorinated THMs had the highest formation potential compared to brominated THMs.

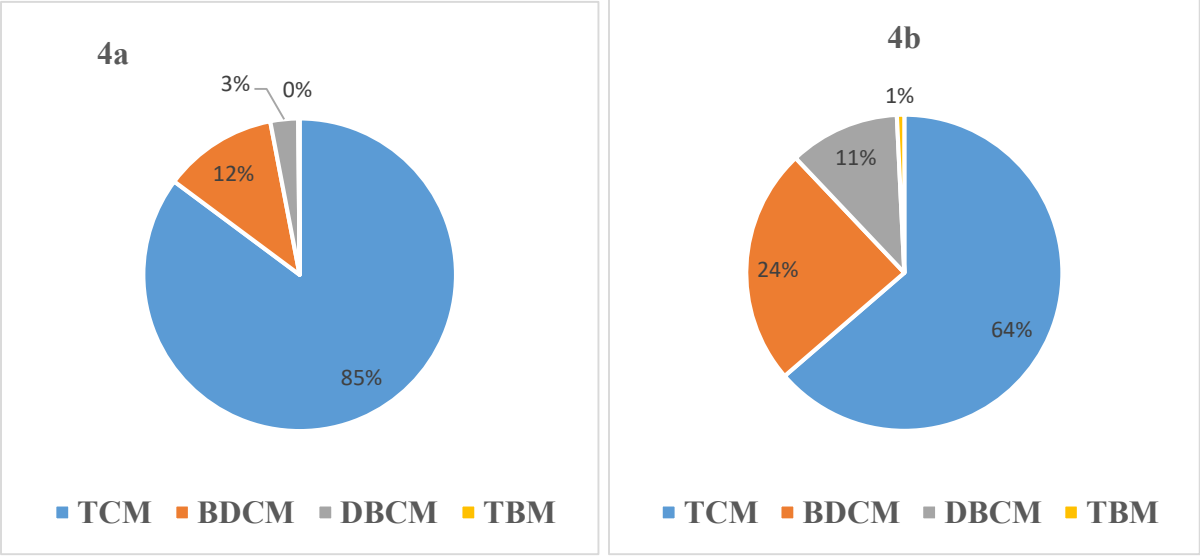


Figure 4a & 4b: The average trihalomethane formation potential (THM FP) composition formed using chlorine as the disinfectant at locations A (4a) and K (4b)

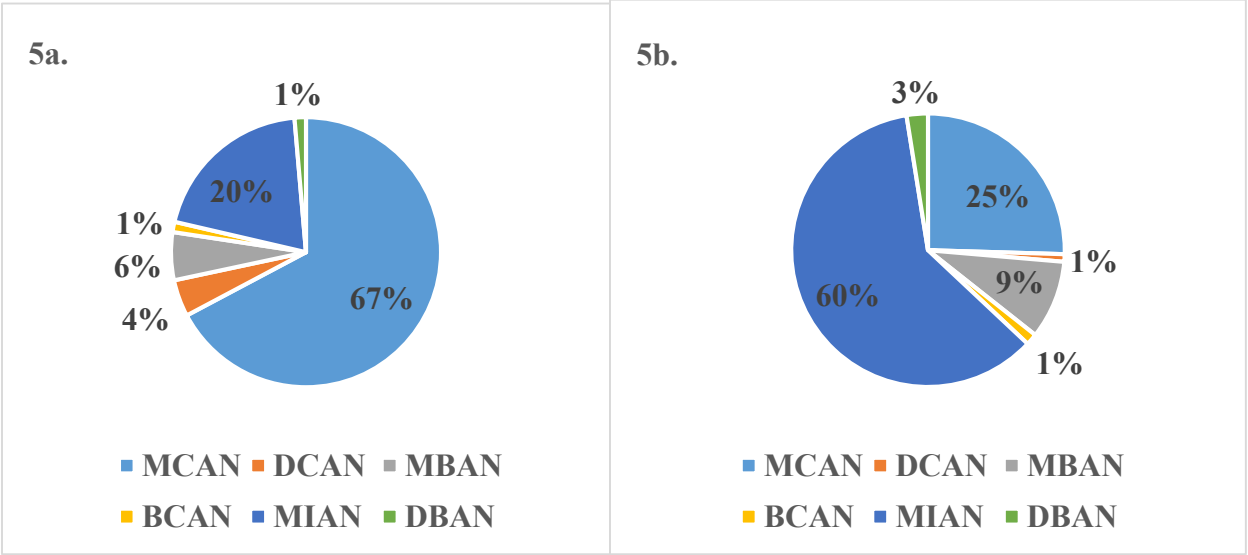


Figure 5a & 5b: The average haloacetonitrile formation potential (HAN FP) composition formed using chloramine as the disinfectant at locations A (5a) and K (5b).

In the case of location, A influenced by homeless communities, the trend for HANs FP is in the order MCAN > MIAN > MBAN > DCAN > DBAN > BCAN as shown in Figure 5a. Whereas, the location K influenced by wastewater effluent, the HANs FP are in the trend MIAN > MCAN > MBAN > DBAN > BCAN > DCAN as shown in Figure 5b. The FP for NDMA formed at

location A after 2 hours of rain was measured as 1.32 µg/L. The precursors of NDMA are known to be small organic amine and nitrite compounds (C. Lee & Yoon, 2007; Sgroi et al., 2018). Small amines and nitrous salts are highly soluble in water (Davison et al., 1960). Thus, when it rains, they easily dissolve into water. This might explain why their formation potential increased within the first 2 h and thereafter decreased as the sources of amine and nitrite were no longer available. DBP FPs were relatively steady over time at location K. This is likely caused by the continuous discharge of wastewater effluent, providing a consistent precursor load.

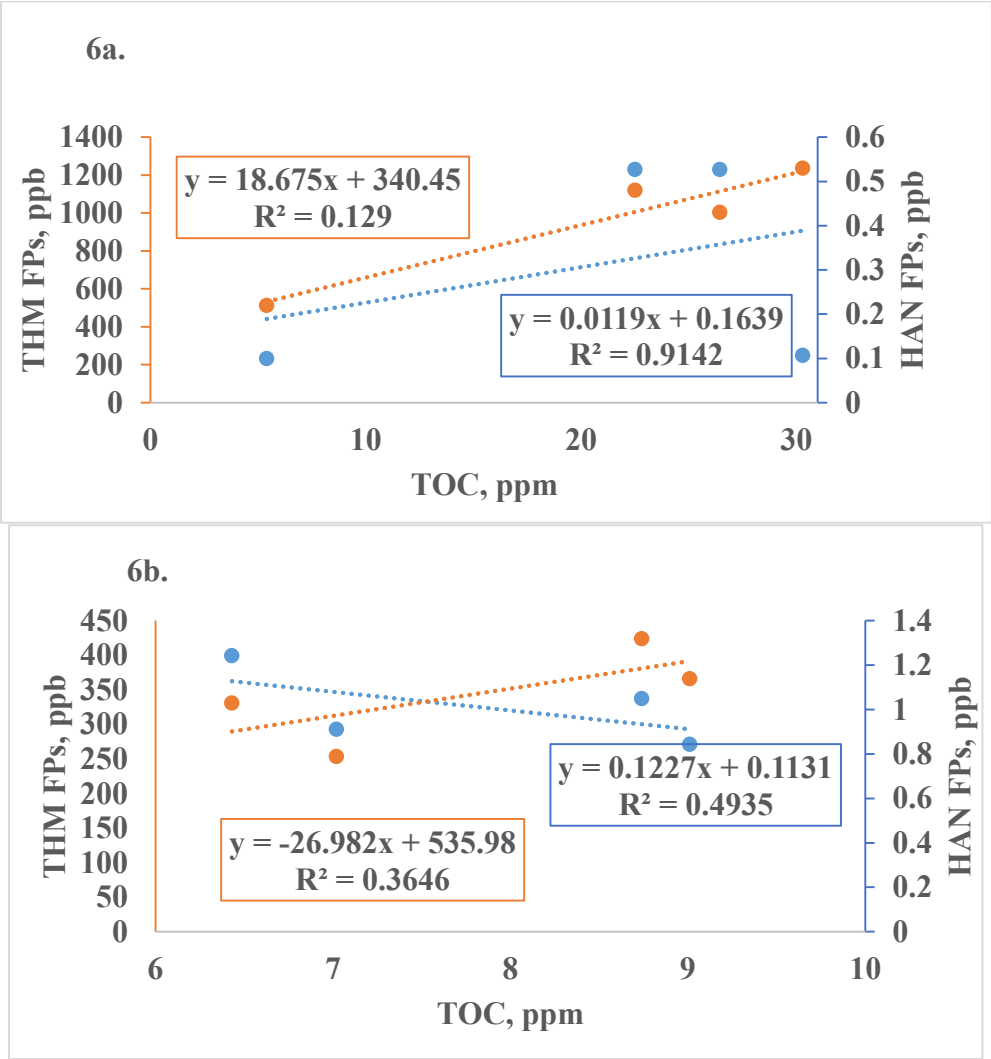


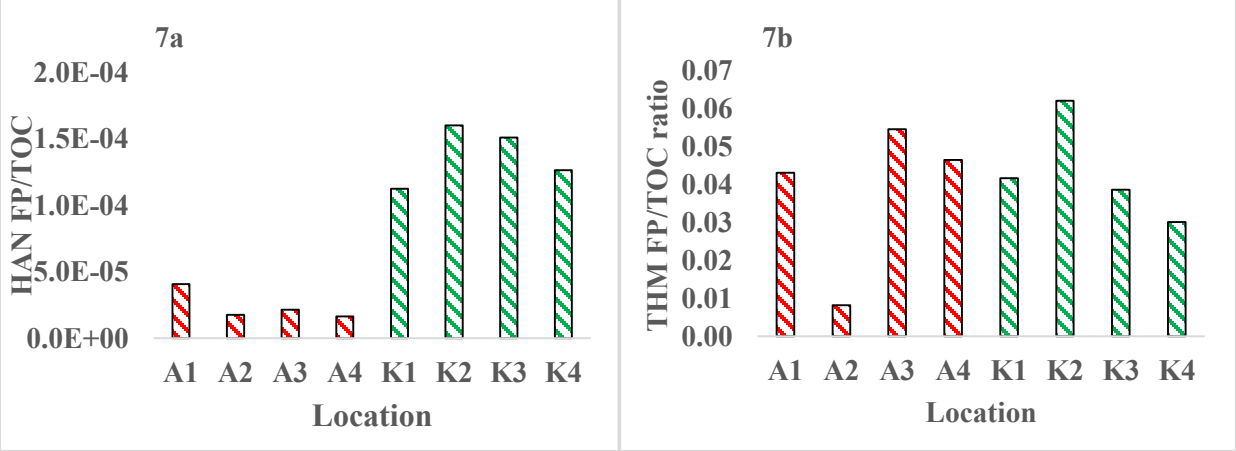
Figure 6a & 6b: Trihalomethane (THM) and haloacetonitrile (HAN) formation potential (FP) with respect to total organic carbon (TOC) for location A (6a) and K (6b). THM FP appears in orange and HAN FP appears in blue.

3.1 Correlation between disinfection byproduct formation potential and total organic carbon

Figures 6a & 6b show the relationship between DBP (THM and HAN) FP and TOC. At location A, the correlation between HAN FP and TOC was more significant ($R^2 = 0.91$), and the relationship between THM FP and TOC was not strong ($R^2 = 0.129$; low). Similarly, the

correlation at location K between HAN FP and TOC was moderate ($R^2 \sim 0.5$) and the correlation between THM FP and TOC was low ($R^2 = 0.36$).

Results (Figures 7a & 7b) show that location K has higher HAN FP/TOC than location A at all given times of sampling. HAN FP/TOC ratio was consistent across the time intervals at location A while the THM FP/TOC ratio fluctuated. The data suggest that HAN precursors were evenly distributed, while THM precursors lagged. Insufficient information is available to know the cause, but possible reasons are that fewer THM precursors—relative to TOC—end up in the 'first flush' after the rain or the THM precursors are located further away from sampling location A and did not arrive at the same time as the initial increase in TOC.



Figures 7a & 7b: Haloacetonitrile (HAN) formation potential (FP) and trihalomethane (THM) FP normalized to total organic carbon (TOC) at locations A (7a) and K (7b) over time

4 CONCLUSIONS

In respect to TOC levels, wet event samples for all locations had higher TOC concentrations compared to dry sampling days. Similarly, wet event samples showed a significant quantity of THM precursors were found in wastewater effluent discharges and urban runoff. With respect to sample type, more HAN FP precursors were formed at the non-wastewater-impacted runoff sites as compared to the wastewater effluent discharge sites, though the TOC values where lower. Therefore, urban runoff waters, such as those impacted by unsheltered homeless populations, should be considered as potential sources of DBP precursors to drinking water source waters, and runoff water is prone to seasonal variation.

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