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Wet Weather Impact on Trihalomethane Formation Potential in tributaries to Drinking Water Reservoirs

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Abstract During rain storm events, land surface runoff and resuspension of bottom sediments cause an increase in Trihalomethane (THM) precursors in rivers. These precursors, when chlorinated at water treatment facilities will lead to the formation of THMs and hence impact drinking water resources. In order to evaluate the wet weather impact on the potential formation of THMs, river samples were collected before, during and after three rain storms ranging from 15.2 to 24.9 mm precipitation. The samples were tested for THM formation potential and other indicators including UV254 absorbance, turbidity and volatile suspended solid (VSS). Average levels of THMs increased from 61 μg/l during dry weather to 131 μg/l during wet weather, and then went back to 81 μg/l after rain ended. Wet weather values of THM are well above the maximum contaminant level (MCL) 80 μg/l, set by EPA for drinking water. THM indicators also exhibited similar trends. Average levels increased from 0.6 to 1.8 abs; 2.6 to 6 ntu; and 7.5 to 15 mg/l respectively for UV254, turbidity and VSS. A positive correlation was observed between THM formation and THM indicators. The *t*-test of significance (*p*-value) was less than 0.05 for all indicators, and *R* values ranged from 0.85 to 0.92 between THMs and the indicators, and 0.72 to 0.9 among indicators themselves.

Keywords Trihalomethane · Wet weather · Sediment resuspension · THM precursors · Chlorination · Water treatment

Introduction

The most commonly used and economically feasible disinfection process in drinking water treatment is disinfection by chlorination. Such process is crucial to the safety of its consumption, yet with chlorination comes harmful organic by-products. These by-products are formed by the reaction of chlorine with naturally organic materials, mainly humic and fulvic acids (Rook 1976). The reaction mechanism of THMs formation can be explained in three steps: In the first step there is a nucleophilic attack of chloride ion at the major humic precursor to yield aromatic pentachloroketon intermediate. In the second step hydrolysis cleavages of the pentachloroketon occur to form halogenated carboxylic acid. In the third step there will be a series of electrophilic substitutions of chloride and subsequent hydrolysis reaction to form the major THM product chloroform (Hutton 1992). Trihalomethanes (THMs) as well as haloacetic acids are dominant by-products of chlorination. THMs encompass chloroform ($CHCl_3$),

bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). In prior studies, bromoform has been the dominant THM due to the amount of bromine present in the water (Golfinopoulos 1998). Formation of aldehydes and THMs were also monitored during intermediate ozonation of water pretreated with ozone and polyaluminium chloride. The study could not give an indication on how to split the required ozone dose between preozonation and intermediate ozonation, as the effect obtained regarding THMs formation potential was similar (Ivancev et al. 2004). Statistically, the THM content in drinking water was evaluated on the basis of common monitoring parameters. Levels of THMs in water seem to correlate directly with levels of combined residual chlorine and nitrate and inversely with the level of free residual chlorine (Espigares et al. 2003).

When present in large amounts in drinking water, THMs have proven to be carcinogenic (Morrow and Minear 1987). Due to the concern of the public, the Environmental Protection Agency (EPA) has set the maximum allowable level of trihalomethane in drinking water to 100 μg/l and then reduced it to 80 μg/l liter in 2005. In water distribution systems THMs can be fairly persistent. The half-life of THM ranges form 1 to 65 days with persistence of chloroform being highest and bromoform lowest (Pavelic et al. 2005). To ensure that proper legislation is applied, THMs research must be expanded and studied more closely. Although various institutions have already taken interest in THMs formation in drinking water, procedures for lowering THMs formation have not been fully understood. Various water quality and treatment characteristics were evaluated by many studies. Increasing pH from 6 to 8 was found to increase THMs formation but decreased trihaolacetic acid formation. In drinking water treatment coagulation generally removed more haloacetic acid precursor than trihalomethanes precursors (Liang and Singer 2003). Conventional alum treatment did not always reduce the THMs precursor levels formed in laboratory tests below 250 μg/l (Page et al. 2002). Prior studies have found that an increase in pH ultimately results in an increase in THMs formation (El-Dib and Ali 1995).

Seasonal variations in THMs formation potential are associated with the variations in organic precursors and to change in temperature. The two parameters vary widely on a seasonal basis in surface waters, particularly in cold regions with the highest THMs formation potential in spring (Serodes et al. 2003). The increase in THMs due to the rise of temperature was indicated by past investigators as well (Urano and Takemasa 1986). Increases in THMs formation suggest that algal production, algal senescence and possibly photolysis increased THMs formation by as much as 50% (Jack et al. 2002).

During wet weather periods, rain increases the velocity of the river flow thus suspending solids that were previously settled on the river bottom. Also, surface runoff carries considerable amount of solids into the river. These solids consist of sand and silt as well as colloidal materials and humic acids, which react to form THMs when chlorinated at water treatment facilities. Thus, an increased river flow as well as surface runoff due to wet weather is expected to have a positive correlation with THMs formation and THMs indicators. Grain size distribution, porosity, and total organic contents of the sediment suggested that these parameters influence the redistribution of settleable solids in water column (Alkhatib and Castor 2000). One of the questions at hand is whether THMs formation potential and its indicators will remain elevated after the rainstorm has ceased. It is expected that THMs precursors should remain high due to colloidal molecules in the water column. It takes a longer time for colloidal molecules to settle on the riverbed due to their size. Other parameters such as turbidity and TSS should decrease at a faster rate after the rain ends because of the fast resettling of the non-colloidal particles on the riverbed.

For more effective treatment of drinking water, information concerning the formation potential of THMs is essential, particularly in tributaries to drinking water reservoirs, and the correlation of the formation potential of THMs with wet and dry weather is lacking. The study at hand also attempted to investigate a relation between THMs formation potential and THMs indicators and how rain storms influence these factors. Such relation can be valuable in helping water treatment authorities setting protocols to reduce THMs by-products.

Methods and materials

The study was conducted at the Mill River, a tributary to the Easton drinking water reservoir used by Aquarion Company in Bridgeport County, CT. The

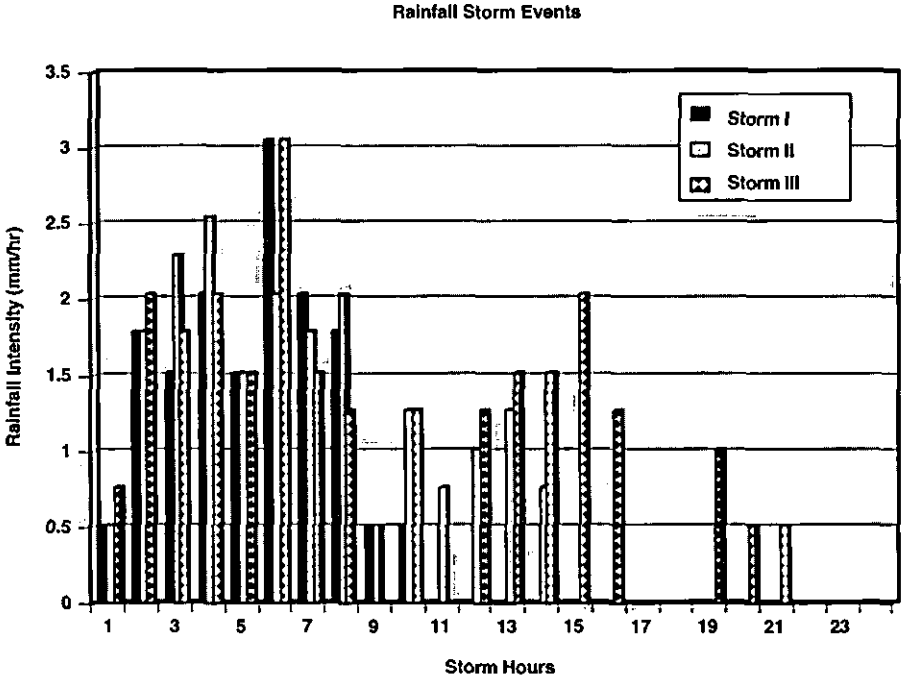
data included three rainstorm events. Storm I had a sampling period from November 9th through the 13th with a total precipitation of 15.2 mm over 11 h with average rainfall intensity 1.4 mm/h. Storm II had a sampling period from January 18th through January 27th with a total precipitation of 20.1 mm over 15 h and rainfall intensity of 1.33 mm/h. Storm III had a sampling period from March 5th through the 11th with a total precipitation of 24.9 mm over 21 h and average rainfall intensity of 1.18 mm/h. Figure 1 displays the rainfall distribution through the three storm events. For the three storms, the sampling periods began at the start of rain or only few hours earlier and always extended a few days after the rain stopped. In addition, a dry period of at least a week preceded each storm. This was essential in order to capture the wet weather impact on the resuspension of bottom sediment and to register the potential increase of THM precursors due to the storms. The samples were analyzed to determine THM formation potential and other THM formation indicator parameters. The THMs indicators analyzed include Turbidity, Volatile Suspended Solids (VSS), and UV254 absorbance analysis. Turbidity measures the amount of suspended and colloidal particles present in the water sample. UV254 absorbance determines the amount of water-soluble molecules present within the sample and is a useful surrogate measure of selected organic compounds in water (APHA–AWWA–WEF 1995).

Statistical analysis was applied in order to find a possible correlation between THM formation potential and the indicator parameter. EPA quality assurance/quality control protocol was followed in all sampling and analysis methods. Preparation and analysis of THM formation potential was in accordance with the Standard Operation Procedure (SOP) set by Aquarion Hydraulic 2005, Bridgeport, CT. The river depth at the sampling location ranged between 4 to 6 feet. Samples were collected in air tight amber 250 ml glass bottles with TFE-lined screw caps (for THM analysis) and Nalgene 1,000 and 250 ml bottles (for THM indicators analysis).

THMs analysis

Stock chlorine dosing solution of 5000 mg Cl_2/l was prepared from a solution of 5% sodium hypochlorite. A phosphate buffer was also prepared. Both solutions were refrigerated, air sealed, and used up to one week after preparation. Three samples were gathered for each sampling period, one as a control and two for duplicate chlorination. All were spiked by 5 ml of phosphate buffer to maintain the pH at 7.2 and two received 1 ml of stock chlorine dosing solution.

Fig. 1 Rainfall storm events



Immediately after, samples were sealed with TFE-lined screw caps and incubated for 7 days at 25°C. At the end of the seven-day reaction period, samples were analyzed for total THMs by a purge and trap/capillary gas chromatography (HP 6890 Series GC System) equipped with a HP 5973 mass selective detector. The instrument was calibrated by preparing four standard stock solutions, each containing a different concentration of total THMs. Batches were made at 50, 100, 200, and 400 μg/l.

THMs indicator analysis

Turbidity and pH were measured immediately after the samples were transported back to the laboratory. For the three storms, tested pH measurement ranged from 7.1 to 7.25 and thus was considered constant for the purpose of this study. A Cole Parmer turbidimeter was calibrated with two solutions, one at 0.5 ntu and the other at 10 ntu. VSS analysis was performed within 48 hours after collection. UV254 absorbance analysis samples were vacuum filtrated using Wattman filter papers with 0.7 μm pore size and brought to room temperature before analysis. A Perkin Elmer UV/VIS Lambda 20 Spectrometer was used to determine the UV absorbance. UV analysis was conducted in accordance with the standard method for examination of water and wastewater (APHA–AWWA–WEF 1995).

Results and discussion

The averages of rainfall intensity of the three storms were fairly comparable. Thus, the duration of the storms and total precipitation were the major factors influencing THM precursors over the sampling period. Longer storm periods have led to higher THM precursors due to sustained increase of river velocity as well as surface runoff over time.

In the three storm events, THM formation potential was substantially lower during the dry weather periods before the rain started. As shown in Fig. 2, the THM formation potential during the dry weather periods preceding the three storms and during the base-flow of the stream ranges from 20 to 50 μg/l. However, during the periods of wet weather, THM formation potential began to rise steadily. The peak of THM concentration was essentially reached after the rainstorm had subsided for 12 to 36 h. THM concentrations reached a peak of 228 μg/l in storm III. In storm

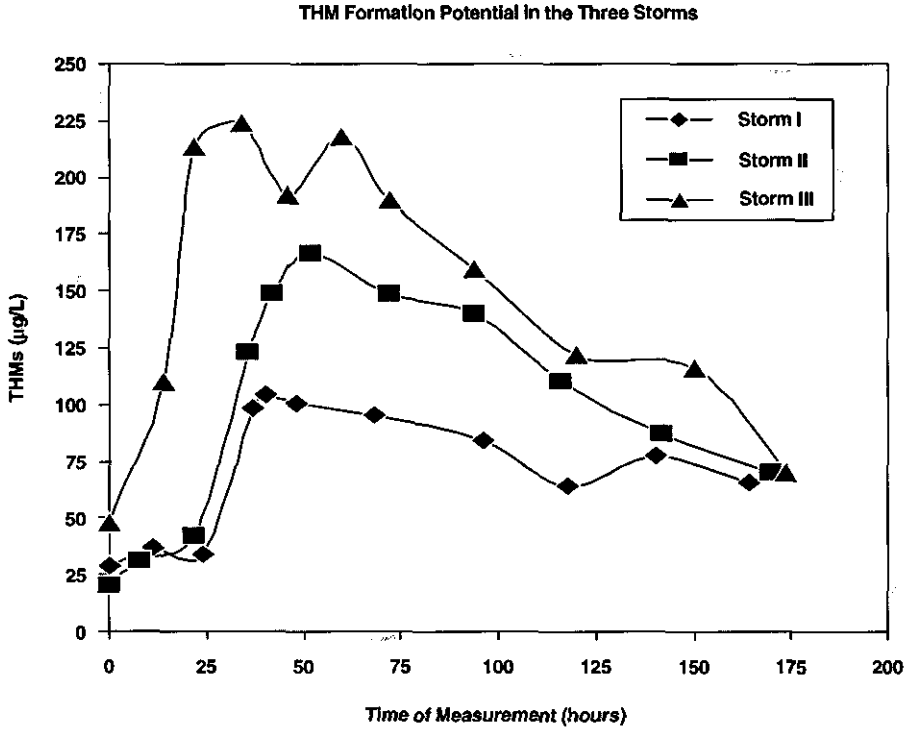
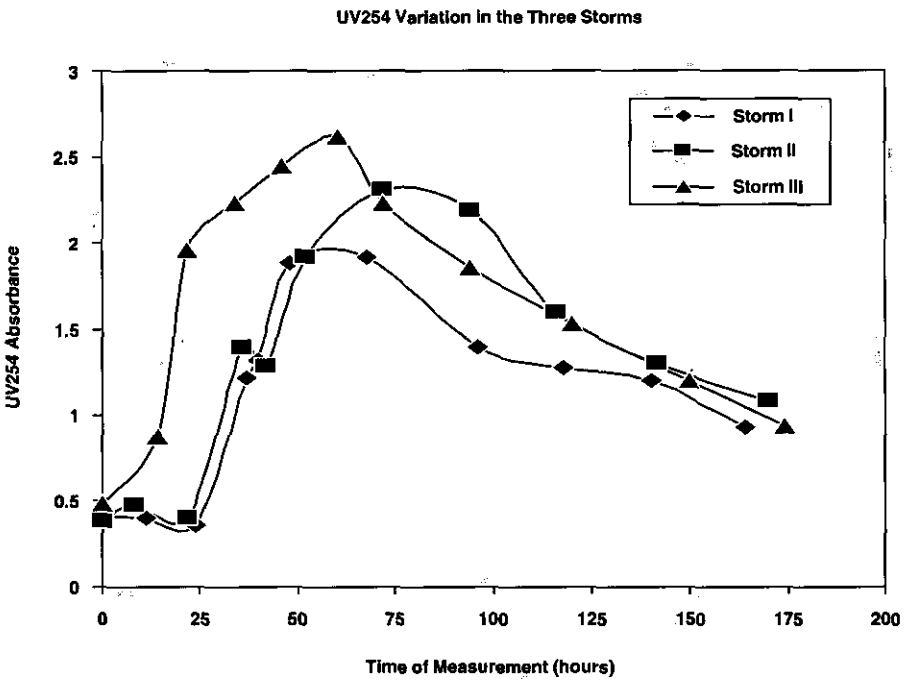


Fig. 2 THM formation potential in the three storms

Fig. 3 UV254 variation in the three storms



I and II THM concentrations reached highs of 105 and 166 μg/l respectively. Theses periods correspond with the rising limb and the falling limb of the hydrograph of the river when overland flow, interflow, and direct precipitation are the major contributors to the flow in the stream. Such values substantially exceeded the EPA set level of 80 μg/L and more than doubled in storm III. The averages of THM concentrations in the three storms were 72, 98, and 151 μg/l for storm I, II, and III respectively. Also, as shown in Fig. 2, THM concentrations did not begin to significantly decrease until approximately 3 days after the wet weather periods had ceased. This illustrates that the material responsible for the formation of THMs stayed in the water column for

Fig. 4 VSS variation in the three storms events

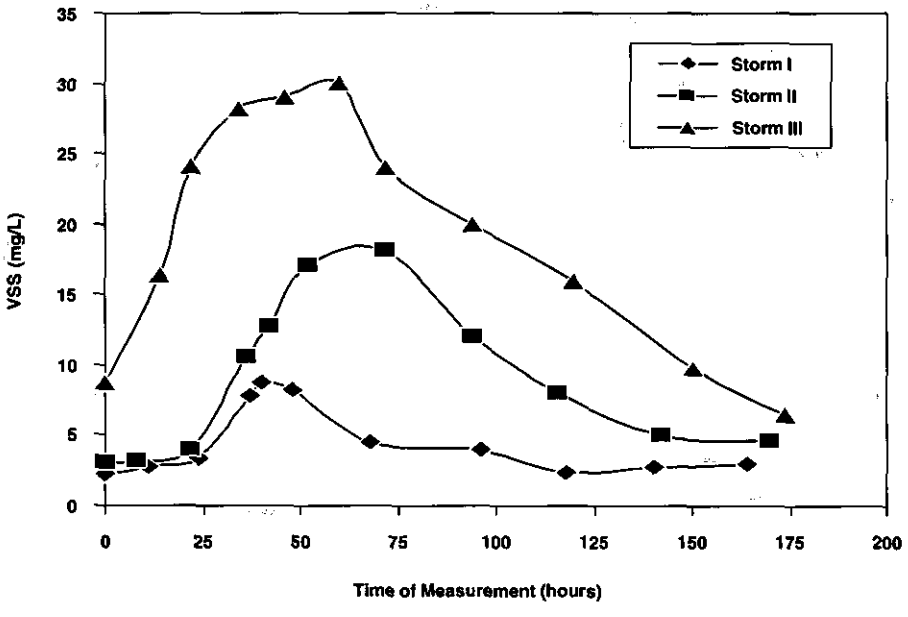
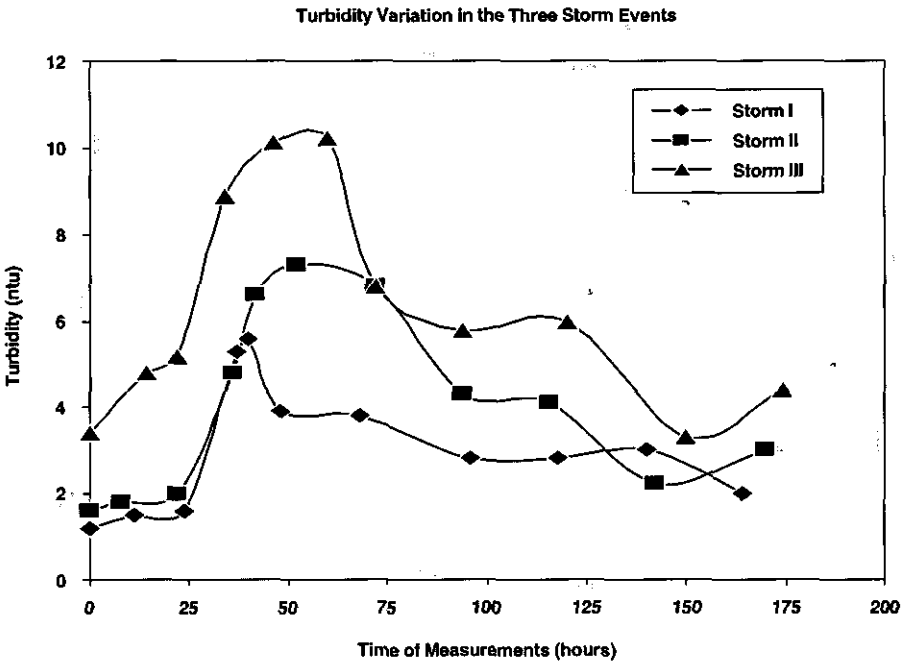


Fig. 5 Turbidity variation in the three storm events

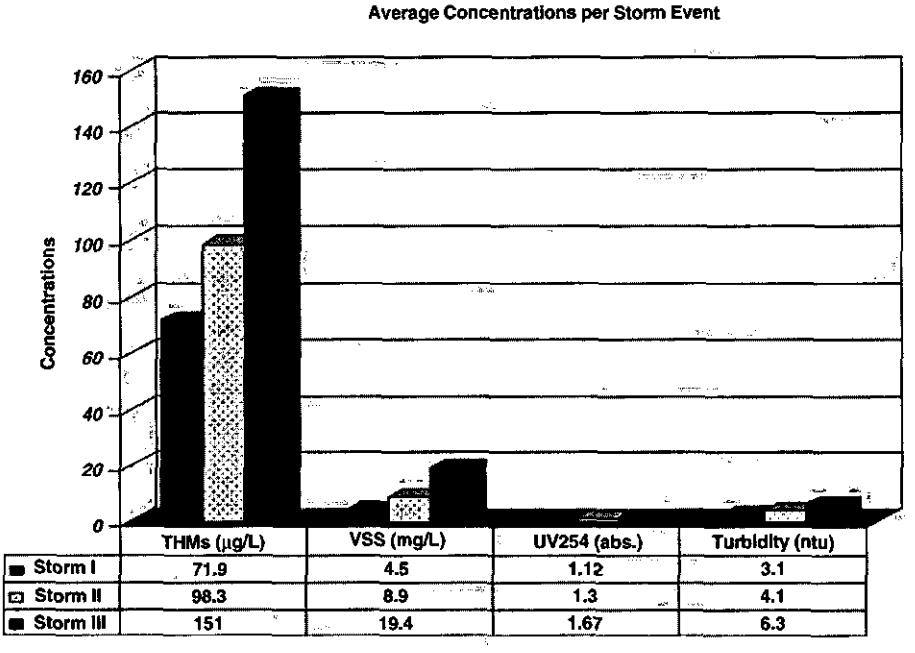


a longer period of time, which is attributed to their colloidal nature and slow settling rates compared with larger size particles in the water column. The dominant species of the THMs formed was chloroform making up approximately 60 to 90% of the THMs. This was probably due to a lack of bromine present in the river water.

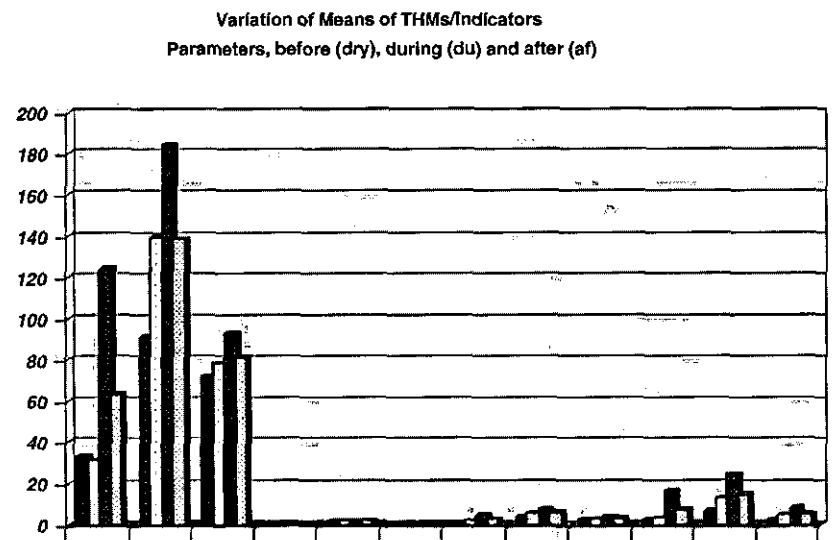
THM formation indicators

In the three storms a positive trend can be observed between THMs and the indicator parameters UV254, turbidity, and VSS. With the increase of the indicator value, there is associated an increase of THM formation. The three storms tested generated THM

Fig. 6 Average concentrations per storm event



	THMs (µg/L)	VSS (mg/L)	UV254 (abs.)	Turbidity (ntu)
Storm I	71.9	4.5	1.12	3.1
Storm II	98.3	8.9	1.3	4.1
Storm III	151	19.4	1.67	6.3



	dry	du	af	dry	du	af	dry	du	af	dry	du	af
	THMs µg/L			UV254 abs.			Turbidity ntu			VSS mg/L		
Storm I	33.4	91.2	71.8	0.39	1.5	1.07	1.4	4.3	2.6	2.8	6.7	2.7
Storm II	31.1	139.3	78.7	0.42	1.79	1.2	1.8	5.7	2.6	3.4	13.1	4.8
Storm III	124	184	93	1.11	2.15	1.07	4.5	8	3.9	16.4	24.6	8.2
Average	62.8	138.2	81.2	0.64	1.81	1.1	2.6	6	3	7.5	14.8	5.2

Fig. 7 Variation of means of THMs/Indicators parameter, before (*dry*), during (*du*), and after (*af*)

precursors as well as indicator parameter concentrations proportional to the amount of rain precipitation as well as the duration of the rain period. Most of the THM indicators exhibited the same pattern as THM until the rain ended i.e. exhibited an increase during wet weather periods as well. However, while THM concentrations and UV254 remained elevated during the days after the storm (Figs. 2 and 3), VSS levels and, to a lesser extent, Turbidity began to drop considerably (Figs. 4 and 5). The THM indicators are dependent on the river flow and the precursor content in water. During wet weather conditions the velocity of the river increases resulting in bottom sediment resuspension in the water column. Also, surface runoff input into the river increases, resulting in higher loads of precursors in water. When the velocity of the river decreased, the THM indicators also decreased. The samples scanned by the UV/VIS for UV254 were vacuum filtrated and brought to room temperature before measurement. The positive correlation between UV254 and THM formation suggests that a high percentage of the THM precursors are colloidal and soluble in nature (i.e. less than 0.7 µm the pore size of the filter paper used in the study). The storm averages of THM concentrations as well as the THM formation indicators were plotted for the three storm events in Fig. 6. Notable in the figure is the increase in THMs and indicators proportional to the amount of precipitation as well as the rainfall duration. In order to isolate the signal from rain impact on THM formation and indicator parameters, the averages were calculated before, during and after rain fall stops for each of the three storm events. Results are presented in Fig. 7, and labeled as "dry," "during," and "after". The "dry" period represents the period before rain as well as the period of the baseflow at the start of the rising limb of the hydrograph. The "during" period represents the period of the rising limb and half way during the falling limb which

Table 1 Correlations matrix of THM formation with UV254, VSS, and turbidity

	THMs	UV254	VSS	Turbidity
THMs	–	0.85 (<0.05) [33]	0.92 (<0.05) [33]	0.90 (<0.05) [33]
UV254	–	–	0.72 (<0.05) [33]	0.76 (<0.05) [33]
VSS	–	–	–	0.90 (<0.05) [33]

Key: Correlation *R* (*P*-value) [no. of samples]

included the period of rain. The "after" period represents the period following rain fall until all sampling ended. For THMs the average "dry," "during," and after were 63, 138 and 81 mg/l, i.e. more than doubled due to rain fall. The other indicators showed a similar trend, as presented in Fig. 7.

Correlation analysis

Correlation analysis was generated to determine whether THM formation potential is significantly dependent on the selected indicators UV254, Turbidity, and VSS. The results of correlation in terms of Pearson's correlation (R) and t-test are presented in Table 1. The total number of samples tested was 33. Pearson's coefficient assumes that both populations are well approximated by normal distribution and their joint distribution is bivariate normal, the closer the number to "one" the better the correlation is. The t-test of significance of rho (the population correlation coefficient) reports a p-value. A low p-value (<0.05) is usually taken to indicate that the correlation is significant. In the correlation matrix Table 1, THMs indicate good correlation with all indicators tested with R values between 0.85 and 0.92, with VSS and turbidity being best. The p-values were all less than 0.05 indicating significant correlation. Among the indicator parameters, the correlation was also fairly well with R-values ranging from 0.7 to 0.9 with turbidity/VSS being the highest. p-Values were also less than 0.05.

Conclusion

1. Wet weather conditions impact THM formation potential in tributaries of drinking water reservoirs. Average THM concentration values more than doubled during wet weather, violating EPA set standards of 80 μg/l in drinking water.
2. The impact of wet weather on THM formation potential extends beyond the wet period for many days after the rain stops. Such an effect is attributed to the colloidal nature of THM precursors and slow settling rates compared with the larger size particles in the water column.
3. The dominant THM present in the water samples was chloroform. This could be due to a lack of bromine present in Mills River.
4. In order to reduce the potential of THM formation in drinking water, special attention should be given by water treatment facilities, particularly during wet weather conditions.
5. THM indicators effectively increased during the wet weather period, illustrating a positive correlation between wet weather and THM indicators. This has been statistically verified by correlation coefficient R close to one and the by the t-test p value <0.05.

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