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Biogenic Organic Carbon Compounds in Air and Rain

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A Master's Project Presented

by

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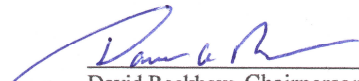

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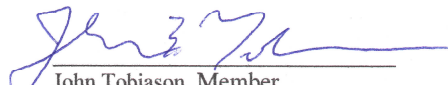
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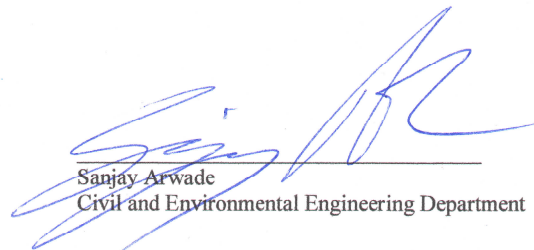
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Abstract

Rainwater quality has not been an issue of concern until recent decades of increasing urbanization and industrialization. Therefore, the role of biogenic contamination sources has been always underestimated as generally, anthropogenic contaminants are thought to be responsible for rainwater quality deterioration. This study aims to find the sources and reasons of biogenic VOC emission into the air and their changes in the air. Also, transfer of biogenic VOCs into the rainwater and their abundance have been investigated. The effects of these biogenic VOCs on rainwater quality have been studied by sampling of two rain events in the University of Massachusetts in Amherst. Key water quality parameters such as UV/VIS absorbance, DOC, SUVA, chlorine residual and DBPs formation potentials have been measured and analyzed. The results show a number of high concentrations of DOC and DBP formation potentials in rainwater samples suggesting that although rainwater is still the highest quality of drinking water, but it may have some quality issues especially in terms of DBPs formation potentials that can be caused mainly by the emission of biogenic VOCs.

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List of Abbreviations

1,1 DCP	1,1-Dichloropropanone
1,1,1 TCP	1,1,1-Trichloropropanone
BCAA	Bromochloroacetic Acid
BCAN	Bromochloroacetonitrile
BDCAA	Bromodichloroacetic Acid
CDBAA	Chlorodibromoacetic Acid
$CHBr_3$	Bromoform
$CHCl_2Br$	Bromodichloromethane
$CHCl_3$	Chloroform
$CHClBr_2$	Dibromochloromethane
CP	Chloropicrin
DBAA	Dibromoacetic Acid
DBAN	Dibromoacetonitrile
DBP	Disinfection By-Product
DCAA	Dichloroacetic Acid
DCAN	Dichloroacetonitrile
DiHAA	Dihaloacetic Acid
DOC	Dissolved Organic Carbon
FP	Formation Potential
HAA	Halacetic Acid
HAA_5	Summation of MCA, TCA, DCA, MBA and DBA
MBAA	Monobromoacetic Acid
MCAA	Monochloroacetic Acid
Sp. or Spec.	Specific
SUVA	Specific Ultraviolet Absorbance
TBAA	Tribromoacetic Acid
TCAA	Trichloroacetic Acid
TCAN	Trichloroacetonitrile
THM	Trihalomethane
TOC	Total Organic Carbon
TriHAA	Trihaloacetic Acid
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV/VIS	Ultraviolet Visible Spectrophotometry
VOC	Volatile Organic Compound

1 Introduction

1.1 Objectives

This study aims to explore the sources and identity of biogenic carbon compounds present in rainwater and assess their effect on rainwater quality, especially as it pertains to key drinking water parameters. The reasons for VOC release by plants as well as their chemical composition and abundance in the air is studied from the literature. Moreover, abundance of these carbon compounds and their transformations is discussed from source to final rainwater. Finally, time-variable rainwater quality is studied by collection of free falling rain and various points during a rain event, and the samples were subjected to measurement of key water quality parameters such as organic carbon content, chlorine demand, and DBP formation potential.

1.2 Background

1.2.1 Biogenic VOC Emission

Volatile organic compounds (VOCs) released by terrestrial plants account for over one third of the whole photosynthates. With this emission, the amount of available carbon to the plants is decreased significantly, thereby affecting the productivity and physiology of plants. Not surprisingly, plants are thought to expend valuable resources in producing and releasing VOCs for some very specific purposes that provide benefit to the plant community. As these compounds impact rainwater quality, its useful to understand the conditions under which biogenic VOCs (BVOCs) are released.

Many types of stress can induce the production of reactive oxygen species in the plants leading to a condition often referred to as "oxidative stress". Therefore, there is a

strong connection between the series of reactions to protect the plant from the source of stress and oxidative stress response. As VOC emissions change under stress conditions, it seems that VOC release is related to the biochemical response to stress in plants. Many abiotic stress conditions increase VOC emission. These can include leaf damage or water, heat or light stress. Ethylene and nitric oxide play the role of stress messengers to trigger defense mechanisms, but there are other VOCs such as isoprene and isoprenoids that have a direct role in protection against stresses. Generally, these VOCs are effective in protection against stress due to their antioxidant role [1]. In a recent study [2], emissions of seven VOCs were examined in drought stressed wheat seedlings. It was shown that three out seven VOCs can be used for the assessment of drought stress in crops. In another study on Truffles [3], fungal species that belong to the genus *Tuber,* VOCs rapidly and effectively caused leaf bleaching proving their phytotoxic role in stress conditions. Ethylene and salicylic acid are regarded as the main VOCs in plant signaling pathways and researchers have found that a number of VOCs cause induced systemic tolerance in reaction to abiotic stresses including drought and heavy metals [4]. While terrestrial plants and nearby soils harbor many of the same biogenic compounds, the amount and diversity of monoterpenes and VOCs are higher in plants compared to the soil. Soil VOC fluxes do not affect atmospheric chemistry very much [5]. Despite many recent studies, researchers still do not completely know how the emission rate and the severity of stresses are scaled to each other, but there is promising evidence indicating that the VOCs emission rate can be proportional to the severity of biotic and abiotic stress [6].

Biogenic VOCs may undergo chemical changes between release and reception by other plants or capture in rainwater. For example, ozone is reactive to many VOCs induced by

herbivory and is the main source of tropospheric air pollution in rural areas. These VOCs are degraded by ozone and therefore, the communication distances between the plants are shortened [7]. In a study on volatile communication between plants that affects herbivory [8], the authors indicate that those plants that have diverse taxonomic affinity and ecological condition show higher resistance to herbivory after receiving VOCs from their damaged neighbors. In another similar study on interplant volatile signaling [9], they "found evidence for the important role of interplant VOC signals in mediating interactions of herbivore and willows.

1.2.2   Controversial Role of Ethylene

Ethylene production in plant and its reactions and interactions with abscisic acid have been studied by many researchers. However, there is still no consensus on the role of ethylene in dealing with stresses. Different researchers have reported increase, decrease or no change in plant's ethylene production in stress conditions.

An increase of 6 to 12 fold in ethylene production has been measured in different growth periods of a species of heat susceptible wheat when faced with heat stress while no change has been observed in a heat tolerant species in the same condition [10]. Ethylene emission measurement in water stressed poplar leaves showed a primary increase proceeded by a decrease [11]. In water stressed paper birch plants, no significant increase has been detected in ethylene production prior to leaf abscission, suggesting a minor role of ethylene in the abscission process as a result of drought [12]. In Gerbera Jasemonii plants, production of ethylene has decreased under drought stress, returning to its normal level after rewatering [13]. Also in wheat, slight increase has been found in ethylene production under moderate or severe water stress [14]. Stress conditions have led to a decrease in ethylene production

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rate and a subsequent 2 to 5-fold increase upon rewatering in two wheat species [15]. Also, a study of three different plants under water deficit [16] showed no change in ethylene production in two and an increase in another plant. Similarly, a study of maize genotypes response to water deficit [17] showed no relation between water deficit and leaf ethylene production rate.

1.2.3 Terpenes Emission and Plant Stress

Terpenes $(C_5H_8)_n$ are major plant products that share a common isoprene biosynthetic origin. They are low molecular weight hydrocarbons and most are quite volatile. In a study on the effect of drought and herbivory stresses on terpenes [18], it was found that members of this group, such as (E) - β-ocimene and homoterpene DMNT (4,8-dimethyl-nona-1,3,7-triene) were emitted as a result of stress. In early stages of drought, plants released maximum VOC emissions. In another similar study, the proportion of a number of terpenes increased significantly in infested and water stressed plants [19]. In a study on the effects of water stress on the preference and performance of pine shoot beetles (Tomicus destruens) [20], it was observed that higher emission of β-pinene and lower emission of myrcene occurred in well-watered plants compared to the stressed ones. The results of a study on the effect of water stress and fungal inoculation on monoterpene emission from pine trees [21] suggest that monoterpenes play a role in pine-pest interactions and also water availability has an effect on their release.

1.2.4 VOCs in the Atmosphere

Not surprisingly, there are some strong similarities between the types of BVOCs noted from terrestrial plants and the VOCs measured in atmospheric samples not contaminated

by anthropogenic sources. Major groups of VOCs found in the atmosphere consist of acids, alcohols, aldehydes, hydrocarbons, ketones and terpenes. There are a number of other compounds mentioned in the literature such as esters or amino acids, but the absolute majority of VOCs in the atmosphere fall within the aforesaid groups. Table 1 contains the VOCs in the atmosphere:

Table 1- VOCs Found in Atmosphere

Acids			
1	Acetic acid [22] [23]	4	Formic acid [24] [23]
2	Acetoacetic acid [22]	5	Malic acid [22]
3	Butanedioic (succinic) acid [22]	6	Propanoic acid [22]
Alcohols			
1	1,8-cineol [25] [23]	14	5-Methyl-2-nitrophenol [26]
2	2,4-Dinitrophenol [26]	15	Dinoseb [26]
3	2,5-Dinitrophenol [26]	16	DNOC (Dinitro-ortho-cresol) [26]
4	2,6-Dinitro-p-cresol [26]	17	Eethanol [24]
5	2,6-Dinitrophenol [26]	18	Glycerol [22]
6	2-Methyl-3-nitrophenol [26]	19	Linalool [24] [25] [23]
7	3,4-Dinitrophenol [26]	20	m-Cresol [26]
8	3-Methyl-2-nitrophenol [26]	21	Myo-inisotol [22]
9	3-Methyl-4-nitrophenol [26]	22	Nerolidol [25]
10	3-Nitrophenol [26]	23	o-Cresol [26]
11	4-Methyl-2-nitrophenol [26]	24	p-Cresol [26]
12	4-Nitrophenol-2,3,5,6-d4 [26]	25	Phenol [26]
13	4-terpineol [23]	26	α+γ-terpineol [23]
		27	Methanol [24] [23]
Aldehydes			
1	Acetaldehyde [27] [24] [23]	4	Pinonaldehyde/Caronaldehyde [24]
2	Formaldehyde [27] [24]	5	Propionaldehyde [27]
3	Methacrolein [28]	6	Valeraldehyde [27]
Hydrocarbons			
1	Acyclic alkanes [29]	6	Glucose [22]
2	Arabinofuranose [22]	7	Glucose oxime [22]
3	Bicycloalkanes [29]	8	Tetralins [29]
4	Cycloalkanes [29]	9	Tricycloalkanes [29]
5	Galactopyranose [22]	10	β-D-galactofuranose [22]

Ketones			
1	Acetone [24] [23]	4	α-Thujone [25]
2	Methyl ethyl ketone [24]	5	β-Thujone [25]
3	Methylvinylketone [28]		
Terpenes			
1	(E)-β-Caryophyllene [25]	21	Pyrene [30]
2	(E)-β-Ocimene [25]	22	Sabinene [23]
3	(E,E)-α-Farnesene [25]	23	Steranes [29]
4	(Z)-β-Farnesene [25]	24	Terpinolene [23]
5	3-carene [23]	25	Trans-b-caryophyllene [23]
6	4,8-Dimethyl-1,3,7-nonatriene [25]	26	Trans-b-ocimene [23]
7	Benz(a)anthracene [30]	27	α-Cedrene [25]
8	Benz(e)pyrene [30]	28	α-Terpinene [28]
9	Benzene [29]	29	α-Humulene [25]
10	Benzo(a)pyrene [30]	30	α-Phellandrene [25]
11	Benzo(b)fluoranthene [30]	31	α-Pinene [28] [25] [23]
12	Benzo(ghi)pyrene [30]	32	α-Terpinene [25]
13	Benzo(k)fluoranthene [30]	33	α-Terpinolene [25]
14	Camphene [28] [23]	34	β-Phellandrene [25] [23]
15	Chrysene [30]	35	β-Pinene [28] [25] [23]
16	Cis-b-ocimene [23]	36	γ-Terpinene [28] [25]
17	Fluoranthene [30]	37	Isoprene [28] [24] [23]
18	Hopanes [29]	38	γ-terpinolene [23]
19	Limonene [28] [25] [23]	39	δ-Carene [25]
20	Myrcene [23]	40	Monoterpene, Sesquiterpene [24] [23]
Miscellaneous			
1	α-Glucopyranoside [22]	5	Cis-linalool oxide [23]
2	1,8-Cineole (Eucalyptol) [25]	6	Ioxynil [26]
3	Bornyl acetate [25]	7	L-threonine [22]
4	Bromoxynil [26]	8	Methyl salicylate [24] [25]

1.2.5   Abundant VOCs in Rainwater

Among the previously-mentioned VOCs that can be found in the atmosphere, some have

been measured in rainwater. Of these, simple aldehydes are most commonly reported (see

Table 2). Of course, the abundance of VOCs in rainwater can change based on the time

and location of measurement. Nevertheless, these data suggest that higher levels of

aldehydes can exist in fresh rainwater than one finds in nearly all treated drinking waters (i.e., including ozonated drinking waters).

Table 2- Abundant VOCs in Rainwater

Compound	Mean Concentration	Measurement Time	Measurement Location	Ref.
Acetaldehyde	18 μg/l	Feb-Jun 2009	Singapore	[27]
	12 μg/l	Apr-Jun 91	Vosges Mountains, France	[30]
Formaldehyde	81 μg/l	Feb-Jun 2009	Singapore	[27]
	100 μg/l	Apr-Jun 91	Vosges Mountains, France	[30]
Propionaldehyde	31 μg/l	Feb-Jun 2009	Singapore	[27]
Valeraldehyde	12 μg/l	Feb-Jun 2009	Singapore	[27]

1.2.6 DOC in Rainwater

A study of 483 rainwater samples from 10 different sites in Northern China [31] showed a volume-weighted mean for rainwater dissolved organic carbon (DOC) in the range of 2.4 to 3.9 mg C/L leading to the annual wet deposition flux of 1.4 to 2.7 g C m^{-2} yr^{-1}, respectively. It was also observed that higher DOC concentrations occurred during winter and spring than summer and autumn mainly because of high domestic use of coal and less dilution of scavenged organic carbon. In this study, DOC to TOC ratios were 79% on average. They also found that the carbon wet deposition flux in Northern China in terrestrial ecosystems accounted for 8.6% of the carbon sink, and 22% of the anthropogenic carbon emissions proving that atmospheric wet deposition of total carbon plays a significant role in carbon flux, at least for sites that are prone to anthropogenic sources. Another group of researchers in China measured TOC and DOC to study the seasonality of carbon abundance and its contribution to acid rain [32]. The average concentrations of TOC and DOC in this study were 7.10 mg/L and 3.58 mg/L, respectively, confirming that a large amount of organic carbon loading can be attributed to rain. In a similar study in

Poland [33], DOC concentrations were measured at two sites to be 5.86 and 5.21 mg/L on average, and constituting 87% and 91% of TOC, respectively. They also found the same seasonal pattern in DOC fluctuations for similar reasons. By backward trajectory analysis they showed that air masses have been advected from polluted regions of Western Europe, and they affect the DOC in rainwater at both urban and non-urban sites. Carbon compounds are very important in wet deposition and atmospheric chemistry and reaction of substances in polluted environments. A study measured DOC and selected aldehydes in cloud and fog droplets [34] and they concluded that dissolved and insoluble aldehydes in the aqueous phase of clouds or fogs accounts for 2–~40% of TOC, respectively. Aged air masses showed higher values as organics are more oxidized and therefore more soluble in water. The DOC and aldehyde measurements revealed that clouds and fogs can be a good sink for atmospheric organics, esp. the aged air masses. Although only ~1% of DOC was comprised of aldehydes, especially formaldehyde, they may have remarkable impacts in the atmospheric oxidation capacity due to their scavenging and processing in the aqueous phase.

In a study in Puerto Rico [35], DOC and TOC values were measured in cloud and rainwater in a marine environment. In clouds, they found average DOC concentrations of 0.8 mg/L which was 80% of the TOC. A lower range of these concentrations (0.3 to 0.5 mg/l) was observed in rainwater. Concentration changes occurred due to the influence of anthropogenic sources, African dust, and air masses containing volcanic ashes. In these periods TOC and DOC concentrations increased 2 to 4 times higher than in the periods of trade winds. Their results show that 40‑80% of TOC in marine cloud and rainwater could have long-distance origins. A study in Texas was designed to investigate the quality of

rainwater harvested from roofs and found that after the first flush [36], the harvested rainwater contained a number of contaminants at levels above USEPA drinking water standards. Interestingly, green roofs were not the best option for rainwater harvesting if chlorination for disinfection of rainwater was used. Rainwater harvested from green roofs had the lowest levels of TSS, turbidity, nitrite, Al, Fe, Cu, and Cr. However, it contained the highest DOC concentrations, presumably due to leaching from plants and soils. Another review study on DOC in rainwater [37] concluded that in the existing models that are developed for global carbon cycling, the main focus is on inorganic forms of carbon and therefore, they are unable to include about 20% of the biogenic global carbon dioxide which is a great missing carbon sink.

Table 3 summarizes DOC measurements in rainwater:

Table 3- DOC Abundance in Rainwater

No.	Concentration or Range (mg/l)	Measurement Location	Ref.
1	N=11, Min=1.00, Max=9.12, Median=2.97	Guangzhou, China	[32]
2	1.44, 7.44, 21.60	Urban, Tokyo	[37]
3	1.32, 2.52	Rural, Sweden	[37]
4	1.09	Rural, Hubbard Brook NH	[37]
5	1.92	Rural, Ithaca NY	[37]
6	1.93	Rural, Dutch Delta, NL	[37]
7	0.82, 0.91, 1.91	Amazon, Amazonia	[37]
8	0.62	Coastal, Puerto Rico	[37]
9	0.70	Coastal, Costa Rica	[37]
10	1.37	Coastal, Wilmington NC	[37]
11	0.29	Marine, Del Mar CA	[37]

No.	Concentration or Range (mg/l)	Measurement Location	Ref.
12	0.67	Marine, N. of Samoa	[37]
13	0.26, 1.18	Marine, Enewetal Atoll	[37]
14	1.50	Marine, W. Pacific	[37]
15	0.29	Marine, S. New Zealand	[37]
16	N=9, Min=1.21, Max=9.55, Median=3.31	Ribeirao Preto, Brazil	[38]
17	N=7 Min=0.66, Max=2.34, Median=2.00	Araraquara, Brazil	[38]
18	N=5, Min=0.15, Max=0.80, Median=0.40	East Peak, Puerto Rico	[35]
19	15.00	Fresno, CA	[34]
20	18.50	Mount Tai, China	[34]
21	12.50	Davis, CA	[34]
22	10.40	Houston, TX	[34]
23	3.40	Whistler, Canada	[34]
24	6.90	Angiola, CA	[34]
25	5.30	Baton Rouge, LA	[34]
26	5.80	Schmucke, Germany	[34]
27	6.02	Mount Rax, Austria	[34]
28	7.60	Whiteface Mountain, NY	[34]
29	5.10	Poznań, Poland	[33]
30	4.72	Jeziory, Poland	[33]
31	0.18, 9.36	Seoul, Korea	[33]
32	0.70	Dunedin, New Zealand	[33]
33	2.90	Lower Wisconsin River Valley	[33]
34	4.70	Guandaushi, Taiwan	[33]
35	2.40, 3.90	Northern China	[31]

1.2.7 Aldehydes and Acids in Rainwater

Aldehyde concentrations as high as 0.6 mg/l have been reported in a 3-year study of Japanese rainwater. It is also observed that these concentrations are higher during rain events of lower total rainfall. The authors' interpretation is that the aldehydes are quickly washed out from the air due to their high solubility in rainwater [39]. A one-year study in Spain on the measurement of carboxylic acids and aldehydes in rain [40] showed that the most abundant acids and aldehydes are formic and acetic acids and formaldehyde and acrolein (7.0, 8.3, 0.42 and 1.25 μM, respectively). Also noted was a high degree of seasonality in these compounds which are mainly produced by biogenic sources [40]. Using FT-ICR/MS, it was possible to identify 522 unique organic compounds in New Jersey (USA) rainwater [41]. All contained the elements: CHO, CHOS, CHON or CHONS. Another team used fluorescence spectroscopy in a two-year study [42] in Birmingham, UK, to classify rainwater organic matter as humic-like, tyrosine-like and tryptophan-like substances, and they concluded the humic-like substances to have mostly anthropogenic sources. Total concentration of aldehydes in rainwater has been measured to be as much as 2000 μg/l, and most abundant in rains after a long period of dry weather. On average the aldehydes contributed about 3% of the TOC and in the extreme, as much as 14% [43]. In a thesis [44], higher concentrations of formaldehyde have been found in rains over the land which suggests the contribution of anthropogenic sources and also a significant biogenic source. Also, formaldehyde concentrations show an increase during spring, summer and growing seasons, reaffirming the importance of biogenic sources. In addition, aldehyde concentration increases during the period from 12 pm to 6 pm can be due to the increase in photochemical production and increased activity of plants, and also augmentation from

daytime anthropogenic sources. A study of rainwater in Los Angeles, USA [45] showed the concentrations of monocarboxylic acids, diacids and aldehydes to be 4.4%, 4.2% and 2.1% of the overall rainwater TOC, and the authors have suggested that most of the carboxylic acid content of rainwater had biogenic sources. In some early studies, formaldehyde was found to be the main aldehyde in rainwater samples [46]. Rainwater samples from two large urban regions taken along two highways had concentrations in the range of 0.05 to 10.7 mg/l confirming the importance of anthropogenic sources of formaldehyde from vehicular traffic in wet deposition [47]. Based on a study of carbonyl compounds in wet deposition [48], the deposition rates in most of the rainwater samples exceeded the production rates, indicating a substantial net flux of water soluble compounds from the atmosphere to the ground.

1.3   Summary

1.3.1   VOC Release from Plants to Air

As plants are exposed to different biotic and abiotic sources of stress such as drought or water stress, heat, cold, herbivory, etc., their main defense or signaling mechanism is the emission of VOCs. This is proceeded by considerable decrease of available carbon and therefore, plant's productivity reduction. Adjacent plants that can receive these signals also react to the stress in the same way even before coming into direct contact with the stress. This is an adaptive mechanism that plants have to undergo minimum loss and it has been shown that plants of the same species communicate more effectively with each other. Therefore, existence of a source of stress even over a limited area can result in a massive VOC release in plant communities.

Studies have shown that the major VOCs attributed to plant's stress are terpenes. Terpenes are categorized into different types according to the number of isoprene (C_5H_8) units they have. Different monoterpenes ($C_{10}H_{16}$ or $C_{15}H_{24}$) that have two or three isoprene molecules are directly related to the reaction of plants to stress. Limonene, camphene and pinene are examples of monoterpenes and normally can be recognized from their smell.

1.3.2   VOC Transfer from Air to Rain

There are six major groups of VOC measured in the air as acids, alcohols, aldehydes, hydrocarbons, ketones and terpenes. However, not all the VOCs found in the air are directly released from plants. In fact, oxidation plays an important role after the emission of VOCs. As for alcohols, depending on the type of alcohol, different compounds can be produced. Primary alcohols mainly become oxidized into aldehydes and after that and to a lesser extent, into acids, while secondary alcohols form ketones after oxidation. Tertiary alcohols do not get oxidized in the air. The final result of hydrocarbons oxidation is H_2O and CO_2. Terpenes also become oxidized very fast into aldehydes. Table 4 shows the lifetime of terpenes in reaction with oxidants which is only a matter of minutes or hours for the terpenes to become oxidized in air.

Therefore, it is normal that the most abundant compounds in rainwater are aldehydes and to a lesser extent, acids. Comparison of the volatility12

of terpenes and aldehydes is also helpful to verify this. Henry's law constants for terpenes are two to five orders of magnitude higher than those of aldehydes. This shows that terpenes tend to remain in the gas phase while aldehydes, by comparison, are much more soluble in water (Table 7).

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Table 4 – Terpenes Lifetimes in Reactions with Major Air Oxidants

Terpene Compound	Lifetimes for Reaction with Oxidants [49]		
	OH [a]	O$_3$ [b]	NO$_3$ [c]
Isoprene	1.4 h	1.3 d	1.6 h
3-Carene	1.6 h	11.0 h	7 min
Limonene	49 min	2.0 h	5 min
α-pinene	2.6 h	4.6 h	11 min
Myrcene	39 min	50 min	6 min
Longifolene	2.9 h	>33 d	1.6 h
Ocimene	33 min	44 min	3 min
β-Phellandrene	50 min	8.4 h	8 min
Linalool	55 min	55 min	6 min
β-Caryophyllene	42 min	2 min	3 min
β-Farnesene	52 min	26 min	-

[a] Assumed OH radical concentration: 2.0×10^6 molecule cm^{-3}, 12-h daytime average

[b] Assumed O$_3$ concentration: 7×10^{11} molecule cm^{-3}, 24-h average

[c] Assumed NO$_3$ radical concentration: 2.5×10^8 molecule cm^{-3}, 12-h nighttime average

1.4   Research Hypothesis

In studies of surface water quality and organic geochemistry, fresh rainwater is often considered of high purity and therefore its dissolved constituents are often ignored or presumed to be insignificant. Nevertheless, there is a growing body of literature that indicates the presence of organic compounds in rainwater that are similar in magnitude to many surface waters. This study aims to determine the total concentration of organic matter over the course of several rain events in a pristine location near the UMass Amherst, MA campus. Moreover, no published work has yet been done on the DBPs formation potentials even though high DOC concentrations have been reported in rainwater. This study also aims to investigate the rainwater quality in terms of DBP formation potentials. Finally, a comparison of rainwater and surface water quality will be made to see if fresh rainwater is really of substantially higher quality from the perspective of a potable water source, than typical surface waters.

2   Materials & Methods

All the laboratorial experiments are conducted according to the standard methods practiced in the Civil and Environmental Engineering Department of the University of Massachusetts – Amherst. For more detailed information in this regard, please refer to http://cee.umass.edu/sops-and-methods.

2.1   Rainwater Sampling

Fresh rainwater was collected form a location on the UMass Amherst campus (N: $42^{\circ}24'$ 12.24" and W: $72^{\circ}32'$ 8.14") where there is at least a 50-foot clearance radius to make sure there was no canopy drip or direct contamination from terrestrial sources in the rainwater samples (Figure 1). As the region enjoys a prevailing western wind, the sampling site was located on the westernmost boundary of the university in order to have no trace of UMass produced air contamination in the samples.

Figure 1 – View of Sampling Site

In the first rainwater sampling, a 1.5-foot diameter funnel-like metal plate was used to catch rainwater (Figure 2) and no significant contamination was present in the samples as the DOC of the MilliQ water sprinkled over the funnel was measured to be 0.17 mg/l.

Figure 2 - Setting of First Sampling

Figure 3 - Setting of Second Sampling

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However, it took quite a long time to collect samples due to limited catchment area. To solve this issue, in the second rain event a pool's metal frame was used and covered with a PE film on top (Figure 3). The rain was conveyed then through a hole to the plate and from there to the bottle. This method resulted in good amounts of samples with no significant organic contamination as the DOC of the MilliQ water sprinkled over the funnel was measured to be 0.20 mg/l. All samples were filtered through GF/F filters using a suction pump and stored in RO (reverse osmosis) pre-rinsed bottles. Two samples were taken from the first rain event and nine from the second making together 11 samples for analysis.

2.2 UV/VIS Spectrophotometry

The UV/VIS spectrophotometry test employed in this study is in accordance with Standard Method 5910B, "Ultraviolet Absorbance Method". After passing the samples through 0.45 μm Teflon syringe filters, they were injected into a 1-cm wide cuvette and placed into the spectrophotometer (Agilent 8453 UV/VIS System). Samples absorbance was then measured and recorded at the conventional wavelength of 254 nm. For more detailed information in this regard, please refer to http://cee.umass.edu/sops-and-methods.

2.3 Dissolved Organic Carbon Measurement

DOC measurement was conducted in accordance with Standard Method 5310B, "Total Organic Carbon, High Combustion Method" as it contains both TOC and DOC measurement. Samples were filtered as mentioned in the UV/VIS section. Then, 80 μL of 6N-HCl acid was added to 30 ml samples to drop pH to 2. Samples were then placed on a tray of Shimadzu TOC-V$_{CPH}$ Analyzer for measurement. In case the DOC of samples were higher than the calibration range (1-10 mg/l), measurements were repeated with diluted

samples. For more detailed information in this regard, please refer to http://cee.umass.edu/sops-and-methods.

2.4   Chlorination and Chlorine Residual Measurement

As there is no generally accepted chlorination method in the lab, what has been exercised in the UMass Civil & Environmental Engineering Department labs is a combination of Standard Methods 2350 (Oxidant Demand) and 5710 (Formation of THMs and other DBPs). Samples were diluted with respect to their DOC concentrations. Dilution factor for the first rain samples was 10 and for the second rain samples was two. That is, from the 700 ml volume that was used in this test for each sample, 70 ml was rain water for the first rain samples and 350 ml for the second and the rest was MilliQ water. Seven ml of the phosphate buffer was added to each sample for pH control and samples' pH was recorded before and after buffer addition. The chlorine doses were determined based on target chlorine residual as 4 ± 1 mg Cl_2 /l after 7-day incubation at the temperature of 20 ºC. The samples were then fully mixed and poured into head space free capped bottles and covered with parafilm. All the samples were taken for incubation at 20 ºC in darkness for seven days before the chlorine residual test.

After the incubation period, the chlorine residual test was conducted by adding 5 ml of DPD (N,N-Diethyl-*p*-phenylene diamine) indicator and 5 ml of DPD buffer to 100 ml of each solution. The solution color was then turned into purple. It was then titrated rapidly with FAS (Ferrous Ammonium Sulfate) until the color was discharged. Volume of the added FAS was recorded. Chlorine demand was calculated by subtracting chlorine residual from the initial chlorine dose and was normalized by dividing by DOC. For more detailed information in this regard, please refer to http://cee.umass.edu/sops-and-methods.

2.5   Disinfection By-Products Precursors Measurement

DBP precursors measurements were done in two steps; measurement of trihalomethanes formation potential (THMs-FP) and haloacetic acids formation potential (HAAs-FP).

2.5.1   Measurement of Trihalomethanes Formation Potential

THM-FP measurement was conducted in accordance with the UMass Amherst protocol which is based on the USEPA Standard Method 551.1. An amount of 20 ml of each sample was placed into 40 ml amber vials. 40 mg of ammonium chloride (NH4Cl) and 1 gr of THM buffer salt were added to neutralize the effect of chlorine residual and control pH. The stock solution was also prepared based on the same standard containing chloroform ($CHCl_3$), bromoform ($CHBr_3$), chlorodibromomethane ($CHBr_2Cl$), and bromodichloromethane ($CHBrCl_2$). In the same manner and with 20 ml of MilliQ water, calibration standards were prepared within the range of 0-80 µg/l. Then, 4 ml of pentane (C_5H_{12}) and internal standard (1,2-dibromopropane) were added to the sample and finally, 15 gr of sodium sulphate (Na_2SO_4) were added to the vials. Vials were shaken for 15 min and the top organic layer of each vial was transferred to the autosampler vials. They were then put to freezer to remove water (if any) from the samples. The day after, samples were analyzed by an Agilent 6890 GC. THM-FP values were normalized by dividing by DOC. For more detailed information in this regard, please refer to http://cee.umass.edu/sops-and-methods.

2.5.2   Measurement of Haloacetic Acids Formation Potential

HAA-FP measurement was conducted in accordance with the UMass Amherst protocol which is based on the USEPA Standard Method 552.2. 30 ml of each sample was placed into 40 ml vials. The stock solution was also prepared based on the same standard

containing HAA stock (Supelco) and brominated stocks (Supelco). In the same manner and with 30 ml of MilliQ water, calibration standards were prepared within the range of 0-80 µg/l. 40 mg of sodium sulphate (Na_2SO4) and 5 µl of sodium azide solution (800 mg of sodium azide in 10 ml of MilliQ water) were added to the vials. Samples were acidified by 1.5 ml of concentrated sulfuric acid (H_2SO_4) and 3 ml of the pre-mixed MtBE+internal standard (Methyl-tert-butyl-ether and 1,2,3-trichloropropane) were added. Vials were shaken for 15 min and 2 ml of a solution of acidic methanol + 5% H_2SO_4 were placed into 20 ml vials. 1 ml of the first extract was also placed into 20 ml vials. The vials were then placed into a 50ºC water bath for 2 hours. Then, 5 ml of saturated $NaHCO_3$ and 1 ml of pure MtBE were added to each vial, they were shaken for 2 min and the top organic layer of each vial was transferred to the autosampler vials. They were then put to freezer to remove water (if any) from the samples. The day after, samples were analyzed by an Agilent 6890 GC. HAA-FP values were normalized by dividing by DOC. For more detailed information in this regard, please refer to http://cee.umass.edu/sops-and-methods.

2.6   Data Analysis

Precipitation data were obtained from a local rain gauge station at Cushman Village, North Amherst, MA (N: 42º24'30.38" and W: 72º30'17.25"). Although the station is located 2.6 km northeast of the sampling site (Figure 4), it represented the changes in rainfall intensity well. Measurement resolution in this station is five minutes and therefore, having the depth and duration of rainfall, intensities were calculated with the same resolution.
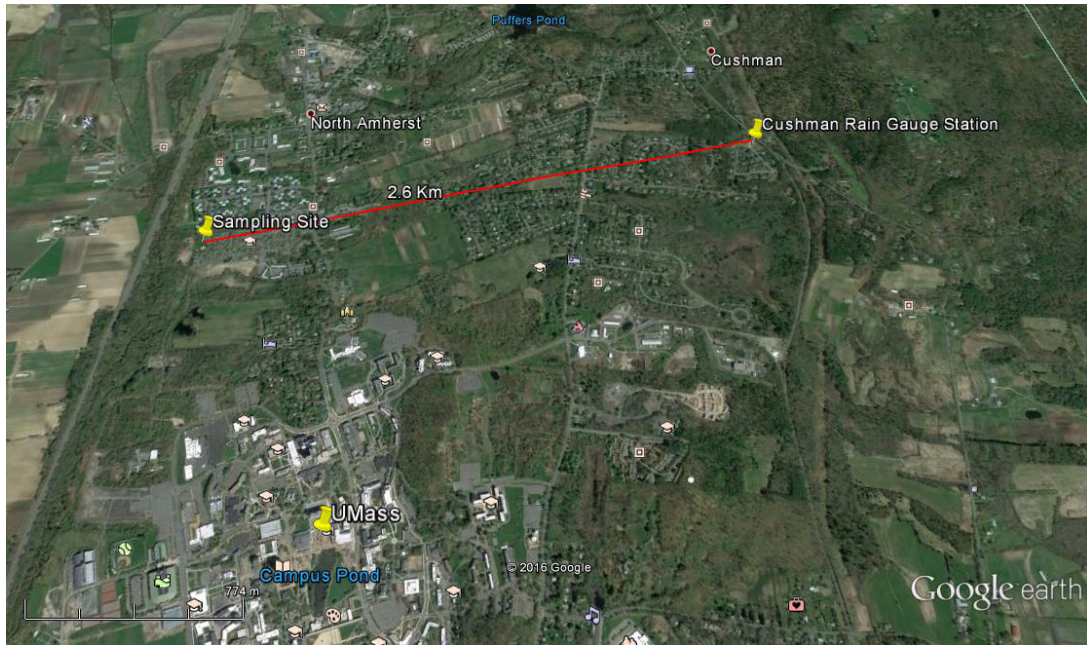
Figure 4 - Location of Sampling Site and Rain Gauge Station

Having UV/VIS absorbance and DOC, specific UV absorbance (SUVA) was calculated as:

$$\text{SUVA (l/mg.m)} = \frac{\text{UV/VIS Absorbance (/cm)} \times 100}{\text{DOC (mg/l)}} \qquad \text{(Eq. 1)}$$

Specific chlorine demand values were calculated by dividing chlorine demand by DOC as:

$$\text{Specific Cl Demand (μg/mg)} = \frac{\text{Cl Demand (μg/l)}}{\text{DOC (mg/l)}} \qquad \text{(Eq. 2)}$$

Likewise, specific values for DBP precursors were calculated as:

$$\text{Specific THM-FP (μg/mg)} = \frac{\text{THM-FP (μg/l)}}{\text{DOC (mg/l)}} \qquad \text{(Eq. 3)}$$

$$\text{Specific HAA-FP (μg/mg)} = \frac{\text{HAA-FP (μg/l)}}{\text{DOC (mg/l)}} \qquad \text{(Eq. 4)}$$

3 Results & Discussion

3.1 Rainwater Quality

As shown in Table 5, the duration of sampling in the first rain is much longer than the second and it is due to the sampling setting. In the second sampling, the area of rainwater catchment was increased by using a round PE film and that led to much lower sampling times (Figure 3). In addition, there is a difference in the time of day and duration of the two rain events. The first one happened in an afternoon (13:03 until 17:07) while the second one was at night and twilight (3:45 until 6:37). This has had its own effect on the results. As shown in Table 6, UV/VIS absorbance at 254 nm and DOC of the samples indicate a significant difference between the afternoon and night rains. While the minimum DOC in the afternoon rain is 10.95 mg/l, the maximum in the night rain is only 2.68 mg/l. This possibly shows the role of plants activity and their contribution to rainwater carbon compounds concentration as they increase their activity during the day as the temperature rises. However, in some regions this increase can be partly caused by anthropogenic sources such as car engines combustion exhaust. Although it is not the focus of this research, it should be noted that the sampling site (in the University of Massachusetts in Amherst) is located in a rural fabric where there is no significant urbanization or industrialization. Therefore, the remarkable changes in rainwater quality in this research can be attributed to the behavior of biogenic sources.

Table 5 – Rainwater Sampling General Info

Sampling Date	Sampling Time			Sample No.	Volume (L)	Rainfall (in)	Average Intensity (in/hr)
	Start	End	Duration (hr:min)				
10/9/2015	13:03	15:33	2:30	1	1.0	1.39	0.56
	15:33	17:07	1:34	2	1.0	0.83	0.53
10/25/2015	3:45	4:12	0:27	1	1.0	0.06	0.13
	4:12	4:20	0:08	2	1.0	0.03	0.23
	4:28	4:37	0:09	3	1.0	0.05	0.33
	4:37	4:42	0:05	4	0.5	0.04	0.48
	4:42	4:47	0:05	5	0.5	0.04	0.48
	5:15	5:20	0:05	6	0.5	0.05	0.60
	5:20	5:25	0:05	7	0.5	0.04	0.48
	6:22	6:30	0:08	8	0.5	0.07	0.53
	6:30	6:37	0:07	9	0.5	0.06	0.51

Table 6 - UV/VIS Absorbance and DOC Measurement Results

Sampling Date	Sample	UV/VIS at 254 nm (/cm)	DOC (mg/l)	SUVA ($l.mg^{-1}m^{-1}$)
10/9/2015	1	0.116	15.49	0.75
	2	0.108	10.95	0.99
10/25/2015	1	0.022	2.68	0.83
	2	0.013	1.96	0.69
	3	0.012	1.65	0.72
	4	0.009	1.37	0.65
	5	0.010	1.59	0.65
	6	0.011	2.02	0.55
	7	0.012	2.16	0.55
	8	0.014	2.16	0.64
	9	0.008	1.30	0.62

Rain intensity and UV/VIS absorbance vs. time are shown in Figure 5 and Figure 6 for rain events one and two, respectively. There is a small lag between the intensity recorded at the rain gauge station and the one at the sampling site due the 2.6 km distance between the two places. However, this is not disturbing the results as it is still obvious from these graphs that the absorbance values are inversely proportional to the rain intensity (see Figure 10). That is, the highest absorbance numbers are measured in the samples taken during the

lowest rain intensity and vice versa. This is also valid for the DOC levels shown in Figure 7 and Figure 8 that show rain intensity and DOC vs. time for rain one and two, respectively. This also can be verified for SUVA values in Figure 9 and Figure 10 that show rain intensity and SUVA vs. time for rain one and two, respectively. In addition, SUVA results suggest low weight molecular distribution of NOM in rainwater as they are all less than 1 ($l.mg^{-1}.m^{-1}$) while SUVA values in surface water are often much greater. Low SUVA value may also indicate low DBP formation potential.

DOC levels of the first rain event may seem very high with respect to the general understanding of rainwater quality. However, comparing DOC concentration of this study to other measurements reveals that these results are in a reasonable range. Figure 12 shows rainwater DOC measurements in different parts of the world. Although the average DOC of the first rain is among the high levels, but there are some even higher DOC concentrations recorded. The maximum belongs to Tokyo, Japan and it can be inferred that anthropogenic pollution sources may play a more important role in it.

Another point of concern is about the chemical composition of DOC. Although, with respect to the Henry's law constants, the DOC of rainwater can mainly be composed of aldehydes, but the measurements of these compounds in rain are around 100 µg/l maximum (Table 2), whereas the DOC levels are in the order of mg/l. It seems that there is a need to have the rainwater carbon compounds completely chemically characterized to see if there is a missing group of compounds in the rain or not.

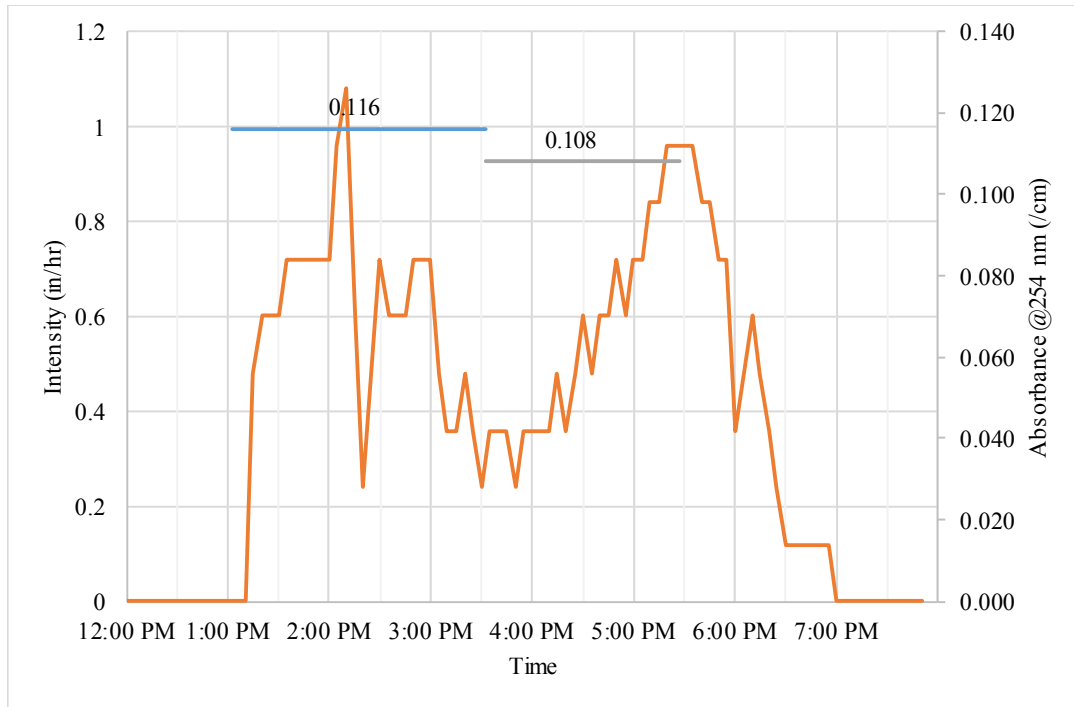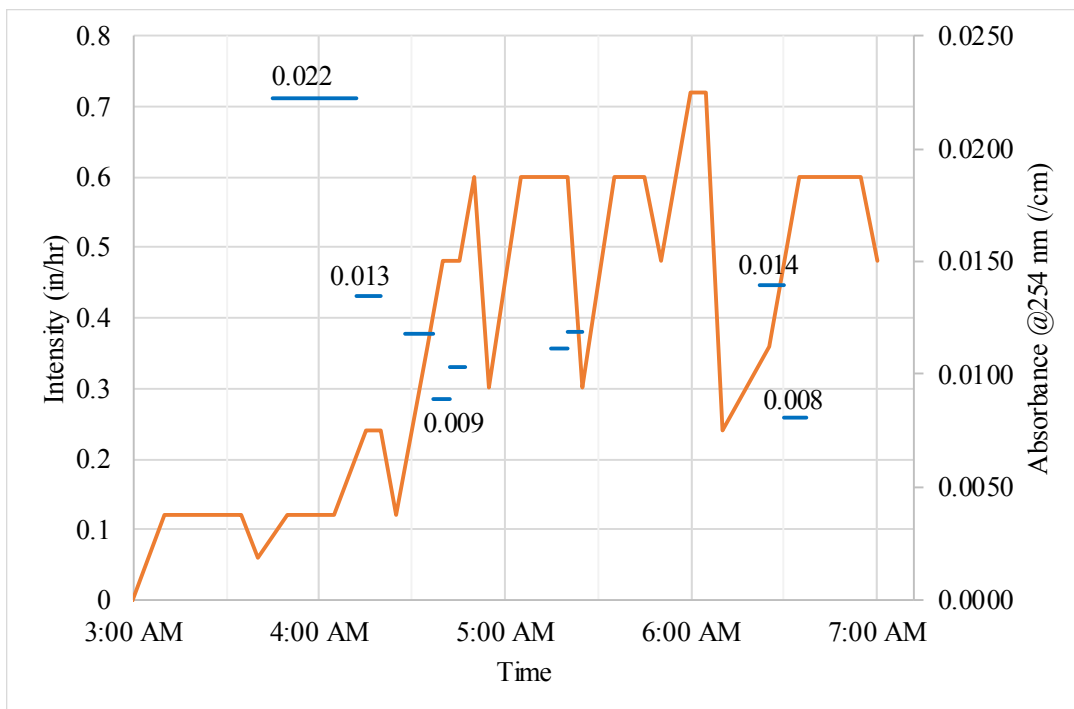Figure 5 - Rain 1 Intensity and UV/VIS Absorbance vs. Time

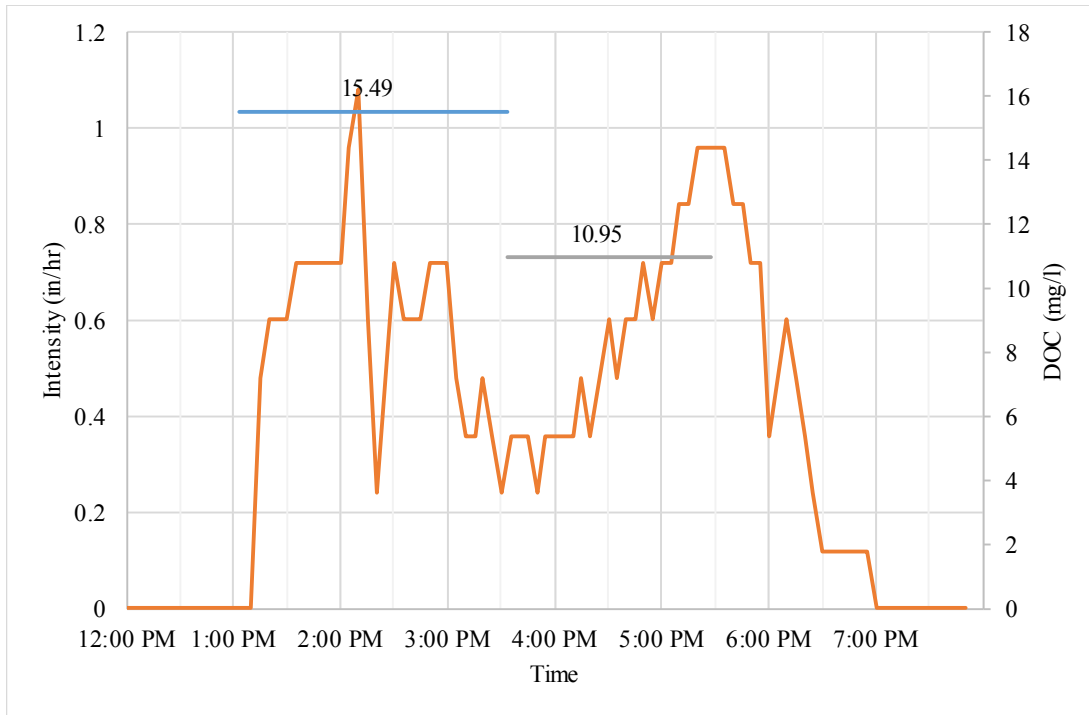Figure 6 - Rain 2 Intensity and UV/VIS Absorbance vs. Time

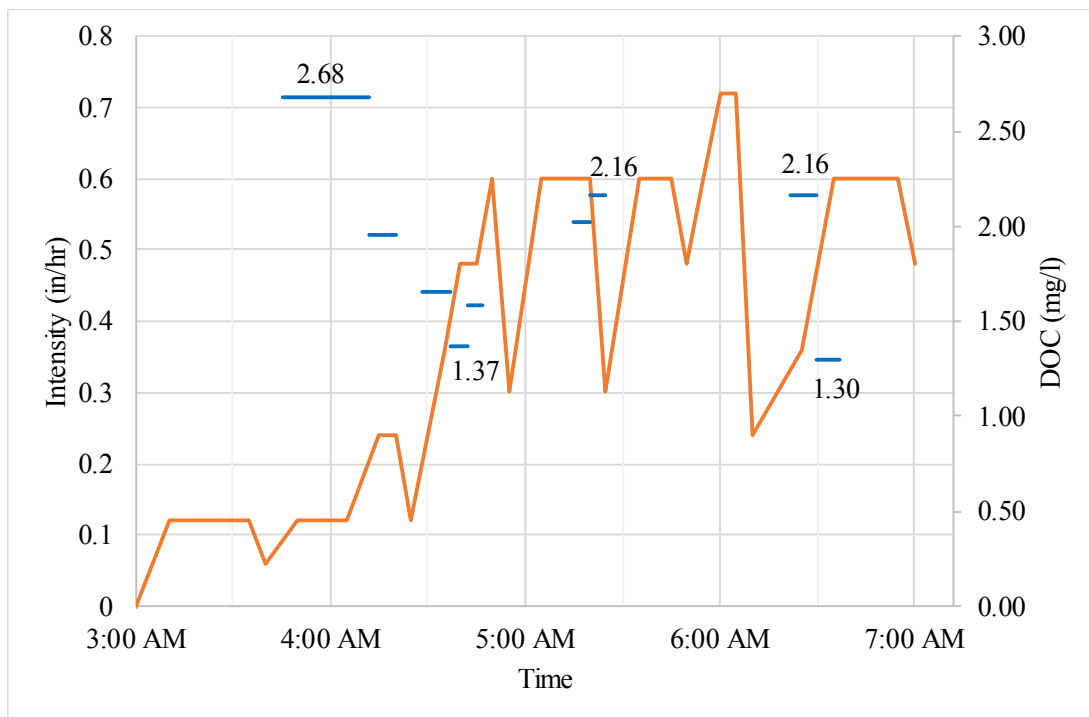Figure 7 - Rain 1 Intensity and DOC vs. Time
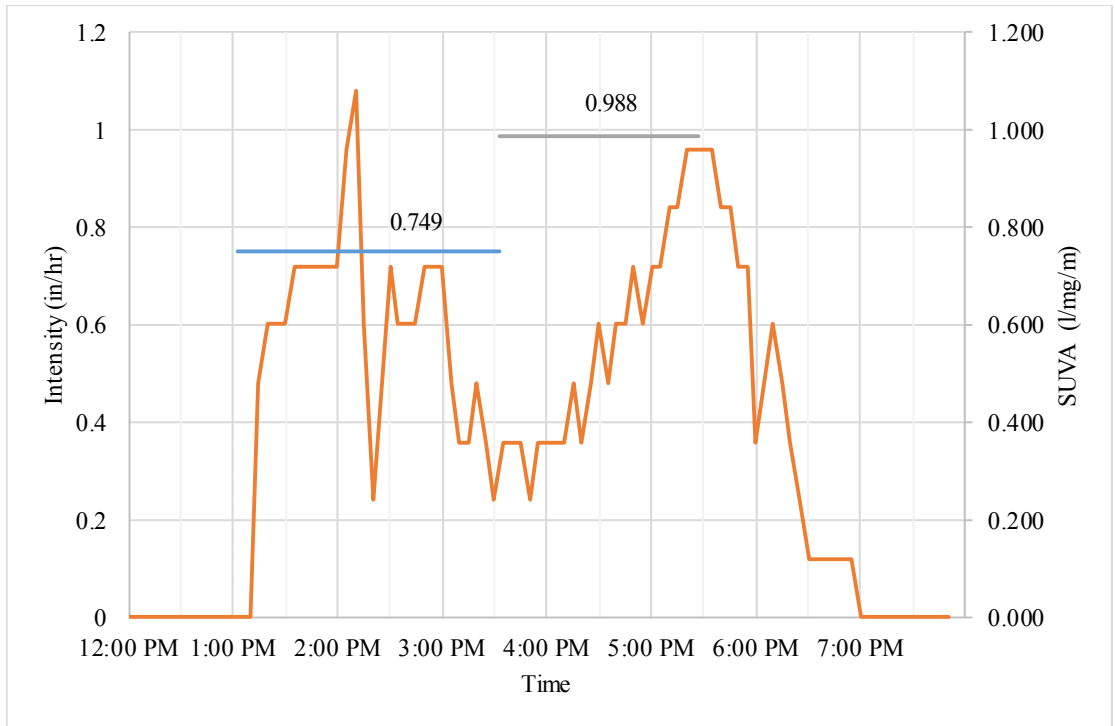

Figure 8 - Rain 2 Intensity and DOC vs. Time

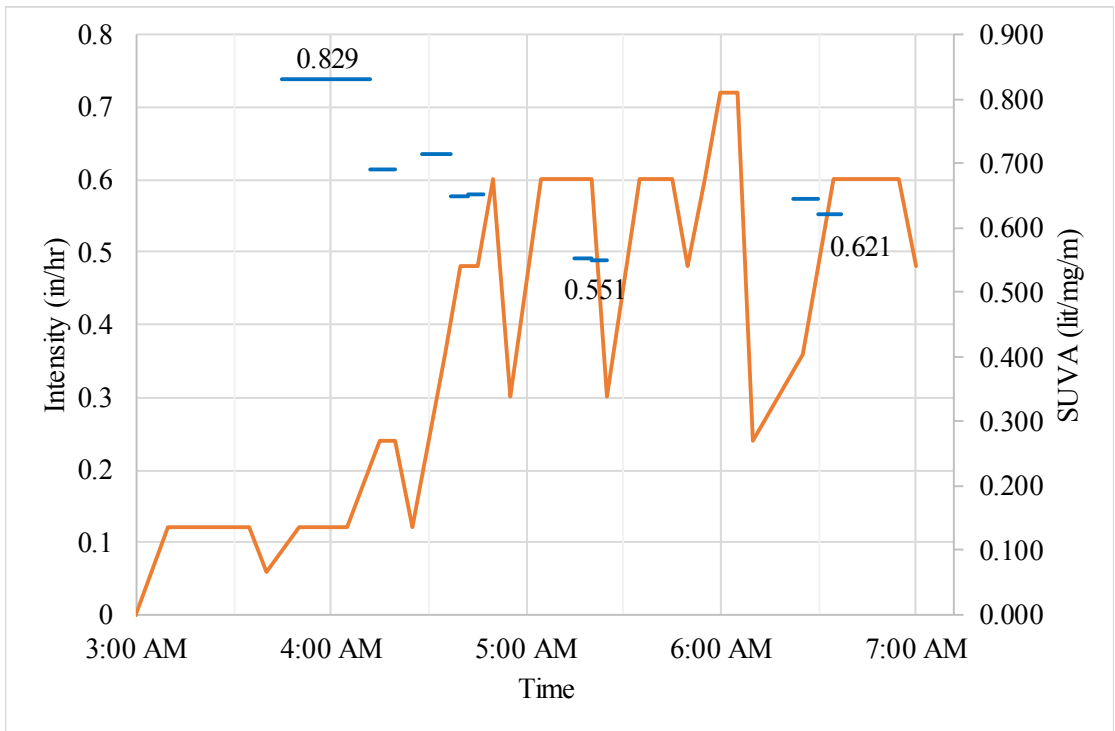Figure 9 - Rain 1 Intensity and SUVA vs. Time

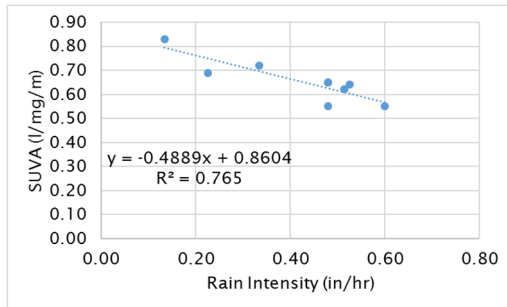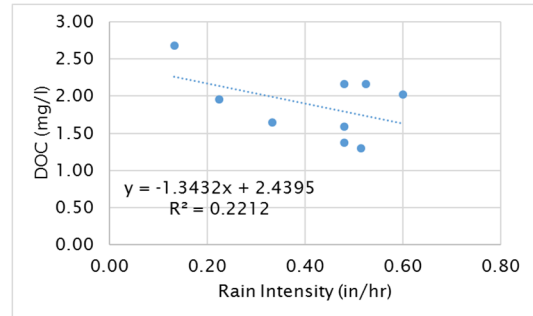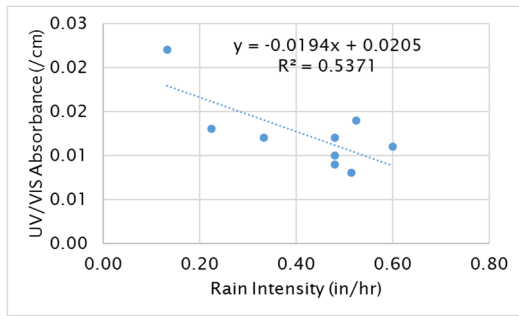Figure 10 - Rain 2 Intensity and SUVA vs. Time

Figure 11 – Inverse Proportionality of UV/VIS Absorbance, DOC & SUVA with Second Rain Intensity

Table 7 - Mean Concentrations of Aldehydes and Terpenes in Air and Rain

(Underlined numbers are measured)

Compound		Henry's Law Constant (Pa m³ mol⁻¹) [50]	Molar Mass (g/mol)	Mean Concentration in Atmosphere (ppt)	Partial Pressure (Pa)	Mean Concentration in Rain (ppt)	Measurement Time	Measurement Location	Ref No
Aldehydes	Acetaldehyde	7.00	44.05	58	2.94E-03	1.85E+04	Feb-Jun 2009	Singapore	[27]
		7.00	44.05	37	1.91E-03	1.20E+04	Apr-Jun 91	Vosges Mountains, France	[30]
	Formaldehyde	0.0305	30.03	1	8.25E-05	8.12E+04	Feb-Jun 2009	Singapore	[27]
		0.0305	30.03	1	1.02E-04	1.00E+05	Apr-Jun 91	Vosges Mountains, France	[30]
Terpenes	α-Pinene	13600	136.24	186	3.06E-03	31	Summer 2009	Remote site, South-west of France	[28]
		13600	136.24	106	1.73E-03	17	2001	Elevated plateau, South California	[28]
		13600	136.24	250	4.11E-03	41	2000	Tropical forest, Amazonia	[28]
		13600	136.24	320	5.26E-03	53	2003	Cultivated plain, central Portugal	[28]
		13600	136.24	395	6.49E-03	65	2003	Eucalyptus forest, central Portugal	[28]
	β-Pinene	6830	136.24	41	6.74E-04	13	Summer 2009	Remote site, South-west of France	[28]
		6830	136.24	125	2.06E-03	41	2000	Tropical forest, Amazonia	[28]
		6830	136.24	290	4.77E-03	95	2003	Cultivated plain, central Portugal	[28]
		6830	136.24	370	6.08E-03	121	2003	Eucalyptus forest, central Portugal	[28]
	α-Terpinene	1960	136.24	115	1.88E-03	131	Summer 2009	Remote site, South-west of France	[28]
		1960	136.24	69	1.13E-03	79	2003	Cultivated plain, central Portugal	[28]
		1960	136.24	48	7.89E-04	55	2003	Eucalyptus forest, central Portugal	[28]
	γ-Terpinene	3590	136.24	8	1.32E-04	5	Summer 2009	Remote site, South-west of France	[28]
	Limonene	2850	136.24	33	5.43E-04	26	Summer 2009	Remote site, South-west of France	[28]
		2850	136.24	31	5.10E-04	24	2001	Elevated plateau, South California	[28]
		2850	136.24	50	8.22E-04	39	2000	Tropical forest, Amazonia	[28]
		2850	136.24	57	9.29E-04	44	2003	Cultivated plain, central Portugal	[28]
		2850	136.24	39	6.33E-04	30	2003	Eucalyptus forest, central Portugal	[28]
	Camphene	1600	136.24	50	8.14E-04	69	Summer 2009	Remote site, South-west of France	[28]
		1600	136.24	31	5.10E-04	43	2001	Elevated plateau, South California	[28]
		1600	136.24	33	5.34E-04	45	2003	Cultivated plain, central Portugal	[28]
		1600	136.24	35	5.75E-04	49	2003	Eucalyptus forest, central Portugal	[28]
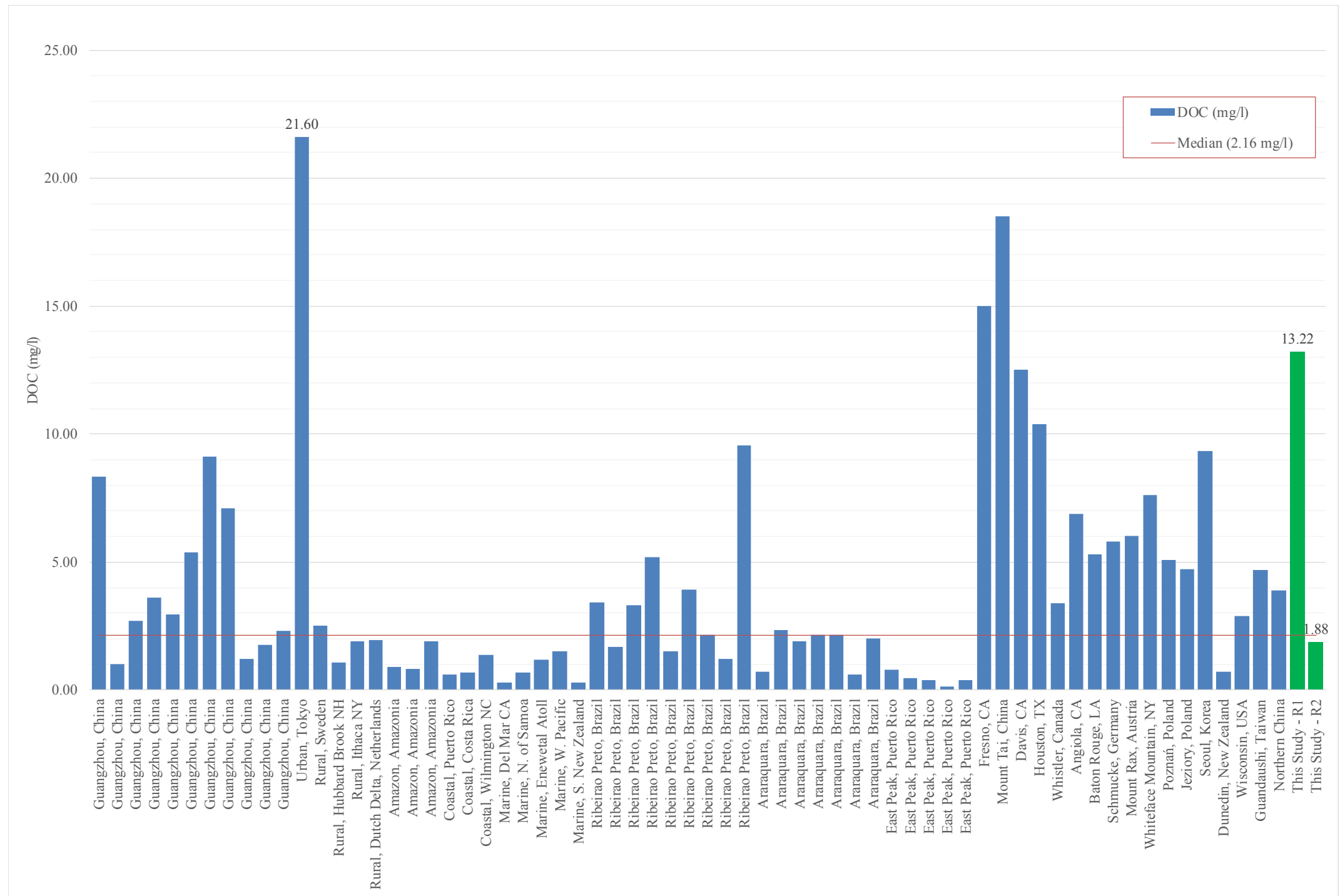
Figure 12 - Rainwater DOC Content in Different Locations Including This Study

Table 8 - Chlorine Demand Calculations

Sampling Date	Sample No.	Dilution Factor	Chlorine Dose (mg/l)	Chlorine Addition (µL)	pH before Adding Buffer	pH after Adding Buffer	Chlorine Residual (mg/l)	Chlorine Demand (mg/l)	chlorine residual (mg/l) before Dilution	Chlorine Demand (mg/l) before Dilution	Normalized Chlorine Residual (mg/mg DOC)	Normalized Chlorine Demand (mg/mg DOC)
10/9/2015	1	10	7.30	88.3	6.73	7.13	2.13	5.17	21.30	51.74	1.38	3.34
	2	10	7.29	88.1	6.18	7.15	2.30	4.99	23.00	49.87	2.10	4.56
10/25/2015	1	2	7.29	88.2	7.30	7.01	2.35	4.94	4.70	9.89	1.75	3.69
	2	2	7.20	87.0	8.03	7.16	4.95	2.25	9.90	4.50	5.06	2.30
	3	2	7.18	86.8	7.90	7.11	2.90	4.28	5.80	8.56	3.51	5.18
	4	2	7.15	86.4	7.79	7.18	3.65	3.50	7.30	7.00	5.32	5.10
	5	2	7.16	86.6	7.69	7.20	3.50	3.66	7.00	7.33	4.40	4.61
	6	2	7.17	86.7	7.84	7.20	3.80	3.37	7.60	6.74	3.76	3.33
	7	2	7.18	86.8	8.15	7.20	4.52	2.66	9.04	5.32	4.18	2.46
	8	2	7.20	87.1	8.00	7.17	2.75	4.45	5.50	8.91	2.54	4.12
	9	2	7.14	86.3	6.58	7.21	4.79	2.35	9.58	4.70	7.37	3.61

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As shown in Table 8, chlorination of rainwater samples has resulted in relatively high chlorine residuals which can eventually lead to high DBP formation potentials. With respect to some high DOC levels and chlorine residuals, high concentrations of TTHM-FP for the first rain samples cannot be surprising. Based on the data in Table 9, both samples have elevated TTHM-FP levels which can be due to the abundance of humic-like substances and direct chlorination of this water would result in concentrations well beyond the USEPA limit (80 µg/l). However, the second rain samples had much lower DBP-FPs. As for the HAA_5-FP, all the samples are below the USEPA limit (60 µg/l).

Table 9 – Disinfection By-Products Formation Potential Values

Sampling Date	Sample	DOC (mg/l)	TTHM-FP (µg/l)	HAA_5-FP (µg/l)	Spec. TTHM-FP (µg/mg)	Spec. HAA_5-FP (µg/mg)
10/9/2015	1	15.49	217	42	14.0	2.7
	2	10.95	204	6	18.6	0.6
10/25/2015	1	2.68	39	10	14.5	3.6
	2	1.96	50	5	25.6	2.4
	3	1.65	26	9	15.8	5.3
	4	1.37	26	13	19.2	9.1
	5	1.59	31	10	19.7	6.2
	6	2.02	27	4	13.3	2.2
	7	2.16	31	10	14.5	4.6
	8	2.16	28	9	12.7	4.2
	9	1.30	21	4	15.9	3.4

Chemical composition of TTHM-FP (Table 10) shows that it is mainly attributed to chloroform ($CHCl_3$) and other compounds were formed in very marginal amounts. Very little amounts of dichlorobromomethane ($CHCl_2Br$) are also observed. This is presumably a reflection of the low bromide content of the fresh rainwater. As Table 11 shows, chemical composition of HAA_5-FP is dominated by dichloroacetic acid (DCAA) and to a lesser

extent by trichloroacetic acid (TCAA) chlorodibromoacetic acid (CDBAA). Figure 13 also shows that chloroform is the dominant TTHM-FP compound and as expected from DOC levels, its concentration is much higher in the first rain event. Generally, HAA5-FP is mainly composed of dihaloacetic acids (Table 11) and DCAA forms the majority of dihaloactic acids concentration (Figure 14), whereas trihaloacetic acids are mostly attributed to TCAA and CDBAA (Figure 15).
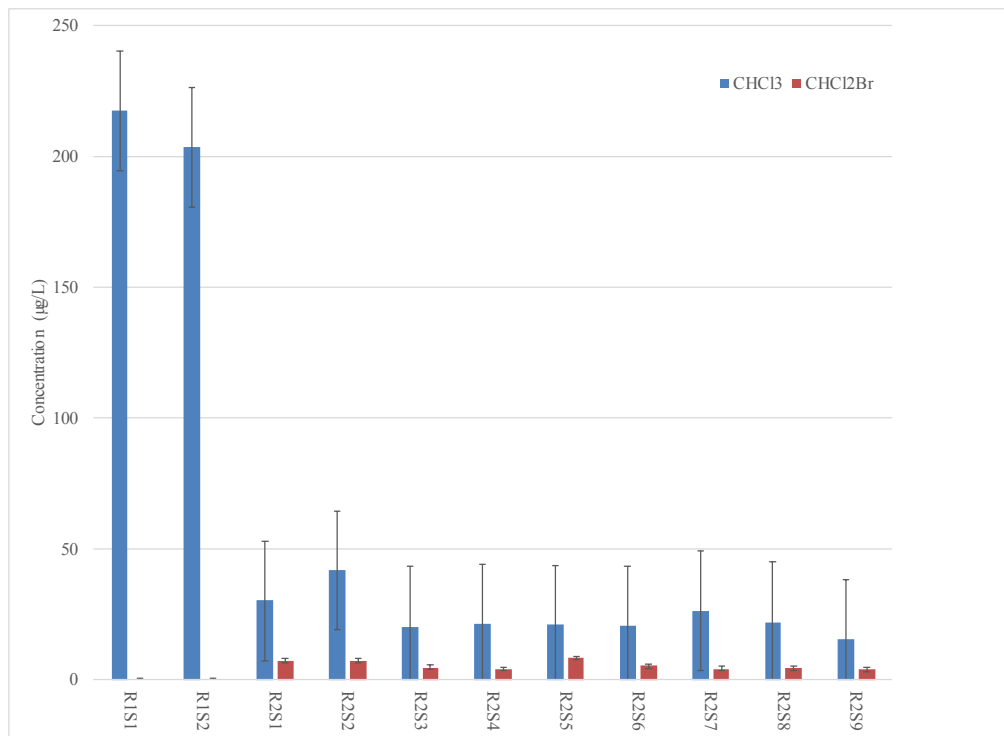
Figure 13 - TTHM Formation Potentials Concentrations

Table 10 – Neutral Extractable DBPs in Rainwater Samples

Rain Sample No.	Concentration (μg/l)											
	TTHM-FP	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TCAN	DCAN	BCAN	DBAN	1,1 DCP	CP	1,1,1 TCP
R1S1	217	217	0	0	0	0	1	0	0	0	1	0
R1S2	204	204	0	0	0	0	2	0	0	2	1	0
R2S1	39	30	7	1	0	0	1	0	0	1	1	5
R2S2	50	42	7	1	0	0	1	0	0	2	2	5
R2S3	26	20	5	1	0	0	1	0	0	2	1	3
R2S4	26	22	4	1	0	0	1	0	0	2	1	3
R2S5	31	21	8	2	0	0	1	0	0	2	1	4
R2S6	27	21	5	1	0	0	1	0	0	2	1	2
R2S7	31	26	4	1	0	0	1	0	0	2	1	3
R2S8	28	22	5	1	0	0	1	0	0	2	1	2
R2S9	21	16	4	1	0	0	0	0	0	2	1	2

Table 11 – Haloacetic Acids in Rainwater Samples

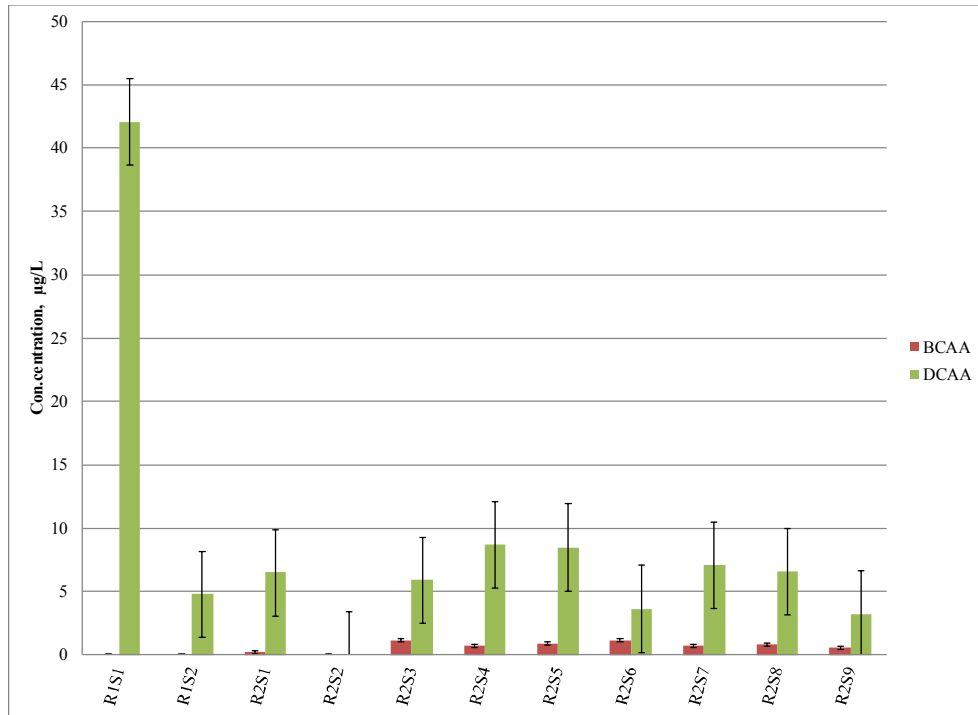| Rain Sample No.	Concentration, µg/L											
	HAA$_5$ -FP	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	CDBAA	TBAA	DiHAA -FP	TriHAA -FP
R1S1	42	0	0	42	0	0	0	0	0	0	42	0
R1S2	6	0	0	5	0	1	0	0	1	0	5	2
R2S1	10	0	0	7	0	3	0	0	0	0	7	3
R2S2	5	0	0	0	0	5	0	0	0	3	0	7
R2S3	9	0	0	6	1	2	0	0	1	0	7	4
R2S4	13	0	3	9	1	1	0	0	3	0	10	4
R2S5	10	0	0	8	1	1	0	0	2	0	9	4
R2S6	4	0	0	4	1	1	0	0	8	0	5	8
R2S7	10	0	0	7	1	3	0	0	2	0	8	5
R2S8	9	0	0	7	1	2	0	0	1	0	7	3
R2S9	4	0	0	3	1	1	0	0	1	0	4	2

Figure 14 - Dihaloacetic Acids Formation Potentials Concentrations
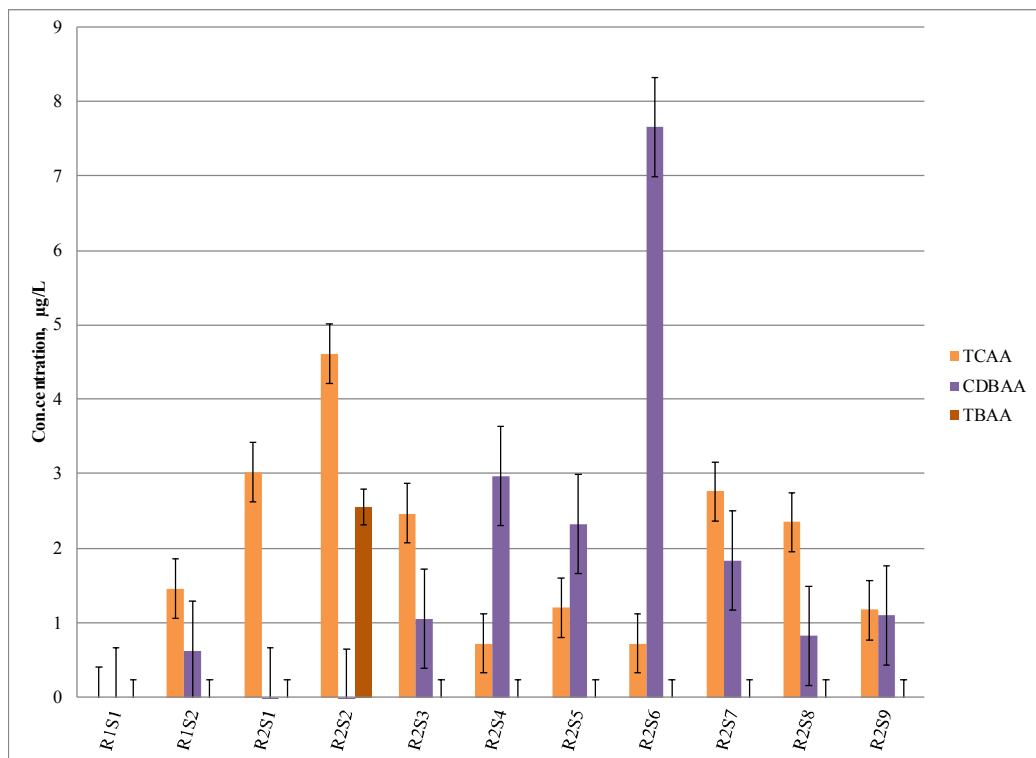

Figure 15 - Trihaloacetic Acids Formation Potentials Concentrations

Commenting on this study's rainwater quality in terms of its DBP-FP is not possible as there has been no published work in this issue yet. As it is the first time that DBP-FP is being measured in rainwater, these data have been compared to the surface water quality of the neighboring Wachusett Reservoir watershed and its tributaries. For this, some data including DOC, SUVA and specific DBP formation potentials have been compared. Wachusett Reservoir surface water data has been taken from the master's project done by Cynthia M. Castellon in UMass Amherst in 2008 (Table 12). [51]

Table 12 – Surface Water Quality Data in Wachusett Reservoir Watershed

| Sampling Site	DOC (mg/l)	SUVA (l.mg^{-1}.m^{-1})	THM-FP (µg/l)	TriHAA-FP (µg/l)	DiHAA-FP (µg/l)	SpTHM-FP (µg/mg)	Sp-TriHAA-FP (µg/mg)	SpDiHAA-FP (µg/mg)
Quinapoxet	3.9	4.5	298	598	158	78	152	42
At MPR	3.5	4.4	202	363	122	59	104	37
At Crowley	3.7	4.3	255	380	129	69	104	37
At Rt 62	3.4	4.3	224	353	138	65	104	41
At SRR	3.6	6.2	237	391	145	66	106	41
Wachusett	3	4.1	156	306	117	53	99	39
Wauschacum	4.4	3.3	253	548	130	55	124	30
Justice	4.1	5.2	235	453	161	58	112	40
Keyes	4.5	3.9	272	320	160	61	71	36
Gates	2.7	4.9	182	214	88	70	84	33
French	5.3	4	309	591	156	62	120	31
Rocky	2.5	4.8	154	332	117	61	132	46
Malden	2.2	3.9	146	4.3	71	66	81	39
Scalon	3.4	5	222	387	131	66	116	40
Houghton	3.6	4.2	197	284	122	59	83	35
Malagasco	5.4	6.8	538	1090	326	97	191	62
Ball	3.1	4.6	177	465	141	57	148	48
Muddy	2.6	2.9	148	350	83	56	126	32
Bailey	2.4	5.2	147	224	94	64	95	41
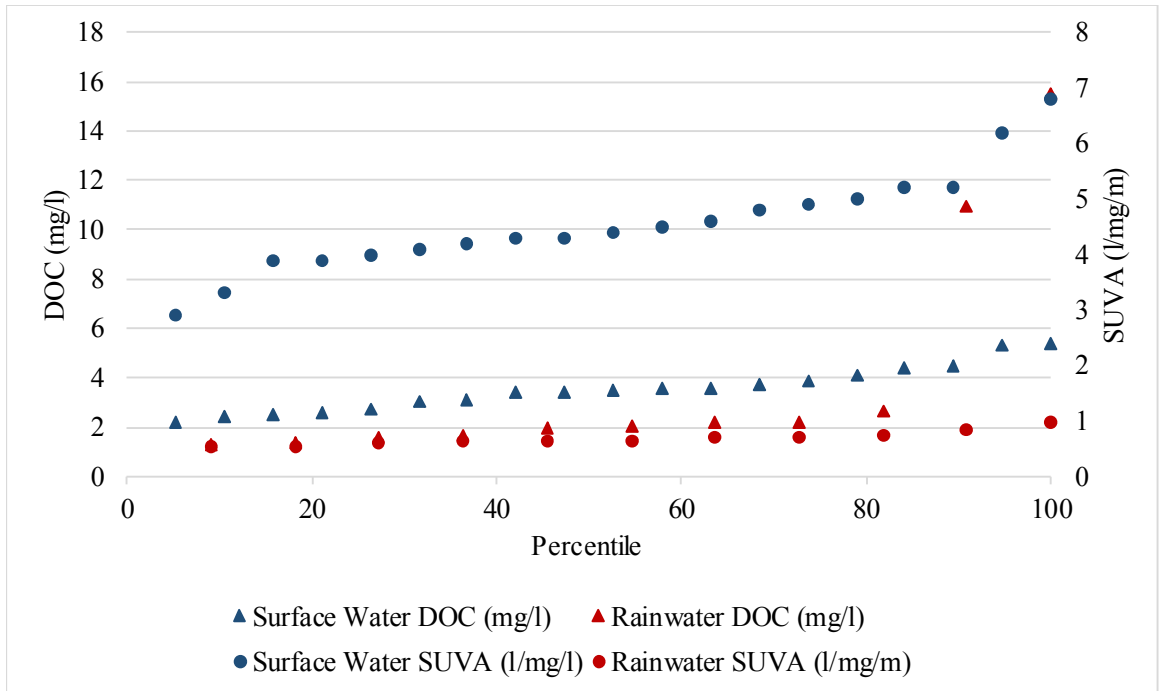
Figure 16 – Comparison of DOC and SUVA in Rain and Surface Water
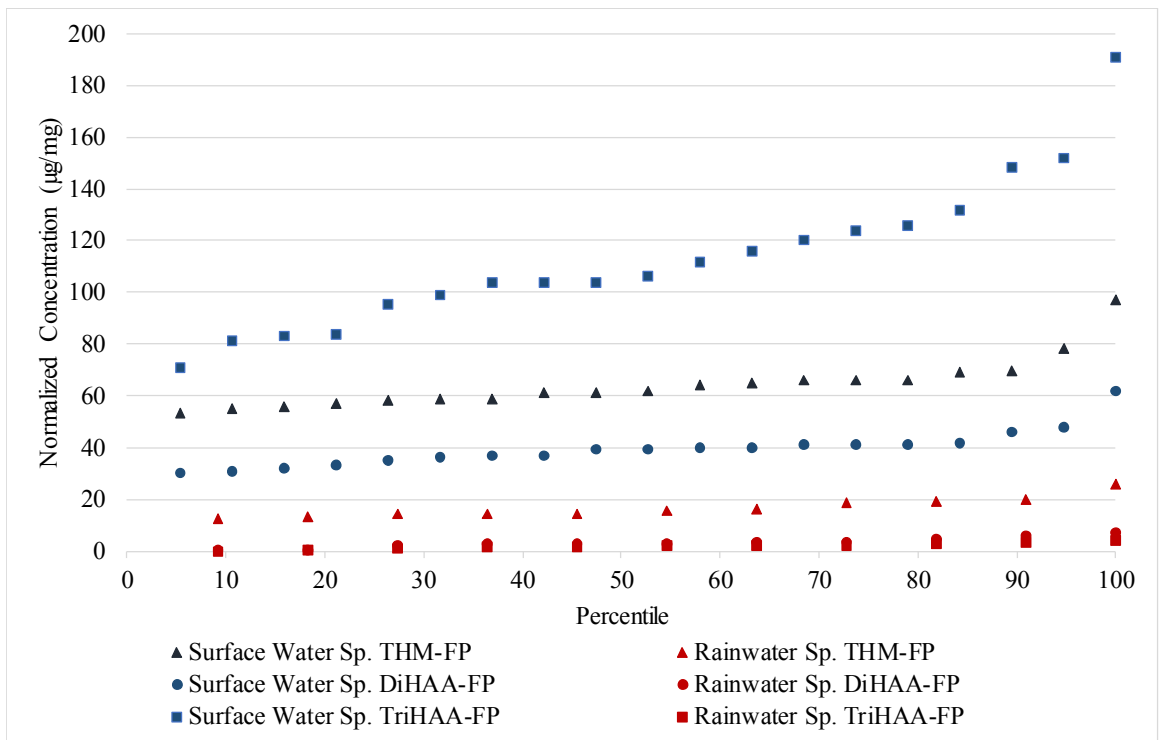

Figure 17 – Comparison of Specific DBP-FP in Rain and Surface Water

The selected rain and surface water DBP-FP data from Wachusett Reservoir and its tributaries have been sorted in an ascending order for comparison purposes in Figure 16 and Figure 17. Comparison of DOC and SUVA in rain and surface water (Figure 16) shows that unlike what is generally assumed, rainwater DOC is not significantly lower than the surface water DOC. In fact, in some cases, it can very well surpass it. However, SUVA numbers are much lower in the rain. Comparison of specific DBP-FPs in Figure 17 reveals that although rainwater DOC can be high as compared to surface water, but it is not leading to very high DBP-FPs. Comparing specific THM-FPs shows much lower levels in the rain. It is also the same for specific dihaloacetic acids. More interestingly, it seems that specific trihaloacetic acids are a water quality issue in the mentioned watershed while these numbers are insignificant in the rain.

3.2   Conclusions

3.2.1   Conclusions from Literature

Different biotic and abiotic sources of stress such as drought or water stress, heat, cold, herbivory, etc., cause plants to release VOCs as their main defense mechanism. Adjacent plants that can receive these signals also react to the stress in the same way. Therefore, existence of a source of stress even at a limited area can result in a massive VOC release in plant communities. Major VOCs attributed to plant's stress are terpenes.

In general, six major groups of VOCs are measured in the air; acids, alcohols, aldehydes, hydrocarbons, ketones and terpenes. However, oxidation eventually transforms VOCs into the aldehydes, acids and ketones. Due to their abundance in air and solubility, aldehydes and, to a lesser extent, acids are the most abundant biogenic organic carbon compounds in rainwater.

3.2.2 Conclusions from This Research

Rainwater sample measurements indicate a significant difference between the afternoon and night rains mainly due to plants activities. It can also be inferred that the carbon content of the rainwater is inversely proportional to the rain intensity. Low SUVA values suggest low weight molecular distribution of NOM in rainwater and low DBP formation potential.

Although the DOC of rainwater may be mainly composed of aldehydes, the measurements of these compounds in rain does not prove that. It seems that there is a need to have the rainwater carbon compounds more completely characterized to really understand the chemical composition of pristine rain.

Some samples have shown TTHM-FP levels that would be considered quite high based on the USEPA limit, probably as a result of the abundance of humic-like substances whereas the HAA_5-FP concentrations are relatively low. Chloroform is the main component of TTHM-FP probably due to very low amounts of bromine. In addition, DCAA which is a dihaloacetic acid is the main component of the HAA_5-FP.

Comparison of DOC and SUVA in rain and surface water shows that rainwater DOC is not significantly lower than the surface water DOC. However, SUVA numbers are much lower in the rain. Also, comparison of DBP-FP shows much lower numbers in the rain especially in case of trihaloacetic acids.

Although by most parameters, rainwater is of a higher quality than surface water, there are some elements of water quality that are not substantially different (e.g., DOC, and THM precursors). Therefore, the general understanding of rainwater quality and its impacts on surface water needs to be revised. The most likely adverse effect of rainwater on surface

water quality is by high DOC concentration leading to high values of some DBPs following chlorination.

4 References

[1]   Francesco Spinelli, Antonio Cellini, Livia Marchetti, Karthik Mudigere Nagesh and Chiara Piovene, "Emission and Function of Volatile Organic Compounds in Response to Abiotic Stress,," in *Abiotic Stress in Plants - Mechanisms and Adaptations*, Rijeka, Croatia, InTech, 2011, pp. 365-394.

[2]   Timmusk S, Abd El-Daim IA, Copolovici L, Tanilas T, Kannaste A, et al., "Drought-Tolerance of Wheat Improved by Rhizosphere Bacteria from Harsh Environments: Enhanced Biomass Production and Reduced Emissions of Stress Volatiles," *PLoS ONE 9(5): e96086,* pp. 1-13, 2014.

[3]   Mika T. Tarkka and Birgit Piechulla, "Aromatic weapons: truffles attack plants by the production of volatiles," *New Phytologist,* pp. 381-383, 2007.

[4]   Mohamed A. Farag, Huiming Zhang & Choong-Min Ryu, "Dynamic Chemical Communication between Plants and Bacteria through Airborne Signals: Induced Resistance by Bacterial Volatiles," *Chemical Ecology,* pp. 1007-1018, 2013.

[5]   Dolores Asensio, Josep Penuelas, Roma Ogaya, Joan Llusia, "Seasonal soil VOC exchange rates in a Mediterranean holm oak forest and their responses to drought conditions," *Atmospheric Environment 41,* p. 2456–2466, 2007.

[6]   Kaia Kask, Astrid Kännaste, Ülo Niinemets, "Emission of volatile organic compounds as a signal of plant stress," *Scientific Bulletin of ESCORENA vol. 8,* pp. 1-15, 2013.

[7]   James D. Blande, Jarmo K. Holopainen and Tao Li, "Air pollution impedes plant-to-plant communication by volatiles," *Ecology Letters 13,* p. 1172–1181, 2010.

[8]   Richard Karban, Louie H. Yang and Kyle F. Edwards, "Volatile communication between plants that affects herbivory: a meta-analysis," *Ecology Letters,* vol. 17, pp. 44-52, 2014.

[9]   Ian S. Pearse, Kathy Hughes, Kaori Shiojiri, Satomi Ishizaki and Richard Karban, "Interplant volatile signaling in willows: revisiting the original talking trees," *Oecologia,* vol. 172, p. 869–875, 2013.

[10] Dirk B. Hays, Jung Hwa Do, Richard E. Mason, Gaylon Morgan, Scott A. Finlayson, "Heat stress induced ethylene production in developing wheat grains induces kernel abortion and increased maturation in a susceptible cultivar," *Plant Science,* no. 172, pp. 1113-1123, 2007.

[11]   D. Acosta-Avalos, J.J. Alvarado-Gil and H. Vargas, "Monitoring ethylene and oxygen emission during water stress of Populus alba leaves," *Jornal of Physiology,* no. 125, pp. 817-819, 2015.

[12]   Mengmeng Gu, James A. Robbins, Curt R. Rom, "The Role of Ethylene in Water-deficit Stress Responses in Betula papyrifera Marsh," *HortScience,* vol. 42, no. 6, pp. 1392-1395, 2007.

[13]   C. Olivella, M. Vendrell, R. Save, "Abscisic acid and ethylene content in Gerbera Jamesonii plants submitted to drought and rewatering," *Biologia Pantarum,* vol. 41, no. 4, pp. 613-616, 1998.

[14]   Jose Beltrano, Edgardo Montaldi, Carlos Bartoli and Alejandra Carbone, "Emission of water stress ethylene in wheat (Triticum aestivum L.) ears: effects of rewatering," *Plant Growth Regulation,* vol. 21, pp. 121-126, 1997.

[15]   Maria Balota, Simona Cristescu, W. A. Payne, S. te Lintel Hekkert, L. J. J. Laarhoven, and F. J. M. Harren, "Ethylene Production of Two Wheat Cultivars Exposed to Desiccation, Heat, and Paraquat-Induced Oxidation," *Crop Science,* vol. 44, pp. 812-818, 2004.

[16]   Page W. Morgan, Chuan-Jin He, Jan A. De Greef, and Maurice P. De Proft, "Does Water Deficit Stress Promote Ethylene Synthesis by Intact Plants?," *Plant Physiology,* vol. 94, pp. 1616-1624, 1990.

[17]   Anne-Sophie Voisin, Beat Reidy, Boris Parent, Gaelle Rolland, Elise Redondo, Denise Gerentes, Francois Tardieu & Bertrand Muller, "Are ABA, ethylene or their interaction involved in the response of leaf growth to soil water deficit? An analysis using naturally occurring variation or genetic transformation of ABA production in maize," *Plant, Cell and Environment,* vol. 29, pp. 1829-1840, 2006.

[18]   Lucian Copolovici, Astrid Kännaste, Triinu Remmel and Ülo Niinemets, "Volatile organic compound emissions from Alnus glutinosa under interacting drought and herbivory stresses," *Environmental and Experimental Botany,* vol. 100, pp. 55-63, 2014.

[19]   Dieu-Hien Truong, Pierre Delaplace, Yves Brostaux, Stéphanie Heuskin, Frédéric Francis, Georges Lognay, "Myzus persicae Feeding on Water Stressed-Arabidopsis Affects the Emission Profile of Plant Volatile Organic Compounds," *Journal of Environment and Ecology,* pp. 276-291, 2014.

[20]   Manuela Branco, Joao Santos Pereira, Eduardo Mateus, Catarina Tavares, Maria Rosa Paiva, "Water stress affects Tomicus destruens host pine preference and performance during the shoot feeding phase," *Annals of Forest Science,* pp. 608p1-608p7, 2010.

[21]   Inka Lusebrink, Maya L. Evenden, F. Guillaume Blanchet, Janice E. K. Cooke and Nadir Erbilgin, "Effect of Water Stress and Fungal Inoculation on Monoterpene

Emission from an Historical and a New Pine Host of the Mountain Pine Beetle," *Journal of Chemical Ecology,* pp. 1013-1026, 2011.

[22]   Barbara A. Cottrell et al., "A regional study of the seasonal variation in the molecular composition of rainwater," *Atmospheric Environment,* pp. 588-597, 2013.

[23]   Silvano Fares, Ralf Schnitzhofer, Xiaoyan Jiang, Alex Guenther, Armin Hansel and Francesco Loreto, "Observations of Diurnal to Weekly Variations of Monoterpene-Dominated Fluxes of Volatile Organic Compounds from Mediterranean Forests: Implications for Regional Modeling," *Environmental Science & Technology,* p. 11073−11082, 2013.

[24]   Efstratios Bourtsoukidis, Boris Bonn and Steffen M. Noe, "On-line field measurements of BVOC emissions from Norway spruce (Picea abies) at the hemiboreal SMEAR-Estonia site under autumn conditions," *Boreal environment research,* pp. 153-167, 2014.

[25]   Lucian Copolovici, Astrid Kännaste and Ülo Niinemets, "Gas Chromatography - Mass Spectrometry Method for Determination of Monoterpene and Sesquiterpene Emissions from Stressed Plants," *STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA,* pp. 329-339, 2009.

[26]   Claude Schummer, Christine Groff, Jamal Al Chami, Farouk Jaber and Maurice Millet, "Analysis of phenols and nitrophenols in rainwater collected simultaneously on an urban and rural site in east of France," *Science of the Total Environment,* p. 5637–5643, 2009.

[27]   Chanbasha Basheer, Shruti Pavagadhi, Huixin Yu, Rajasekhar Balasubramanian and Hian Kee Lee, "Determination of aldehydes in rainwater using micro-solid-phase extraction and high-performance liquid chromatography," *Journal of Chromatography A,* p. 6366–6372, 2010.

[28]   A. Detournay, S. Sauvage, V. Riffault, A. Wroblewski and N. Locoge, "Source and behavior of isoprenoid compounds at a southern France remote site," *Atmospheric Environment,* pp. 272-282, 2013.

[29]   Chan, A. W. H., et al., "Detailed chemical characterization of unresolved complex mixtures in atmospheric organics: Insights into emission sources, atmospheric processing, and secondary organic aerosol formation," *J. Geophys. Res. Atmos.,* vol. 118, p. 6783–6796, 2013.

[30]   K. Levsen, S. Behnert, P. Muβmann, M. Raabe and B. Prieβ, "Organic Compounds in Cloud and Rainwater," *Intern. J. Environ. Anal.Chem.,* pp. 87-97, 1993.

[31] Yuepeng Pan, Yuesi Wang, Jinyuan Xin, Guiqian Tang, Tao Song, Yinghong Wang, Xingru Li, Fangkun Wu, "Study on Dissolved Organic Carbon in Precipitation in Northern China," *Atmospheric Environment,* pp. 2350-2357, 2010.

[32] XU Tao, SONG Zhi-guang, LIU Jun-feng, WANG Cui-ping, "Seasonality and Contribution to Acid Rain of the Carbon Abundance in Rainwater," *Environmental Science,* pp. 322-326, 2008.

[33] Patrycja Siudek, Marcin Frankowski, Jerzy Siepak, "Seasonal variations of dissolved organic carbon in precipitation over urban and forest sites in central Poland," *Environmental Science and Pollution Research,* pp. 11087-11096, 2015.

[34] B. Ervens, Y. Wang, J. Eagar, W. R. Leaitch, A. M. Macdonald, K. T. Valsaraj, and P. Herckes, "Dissolved organic carbon (DOC) and select aldehydes in cloud and fog water: the role of the aqueous phase in impacting trace gas budgets," *Atmospheric Chemistry and Physics,* pp. 5117-5135, 2013.

[35] Adriana Gioda, Olga L. Mayol-Bracero, Gabriel J. Reyes-Rodriguez, Gilmarie Santos-Figueroa, Jeffrey L. Collett Jr., "Water-soluble organic and nitrogen levels in cloud and rainwater in a background marine environment under influence of different air masses," *Atmospheric Chemistry,* pp. 85-99, 2008.

[36] Carolina B. Mendez, Brigit R. Afshar, Kerry Kinney, Michael E. Barrett, Mary Jo Kirisits, "Effect of Roof Material on Water Quality for Rainwater Harvesting Systems," Texas Water Development Board, Texas, 2010.

[37] Joan D. Willey, Robert J. Kieber, Mary S. Eyman, and G. Brooks Avery Jr., "Rainwater dissolved organic carbon: Concentrations and global flux," *Global Biochemical Cycles,* pp. 139-148, 2000.

[38] M.L.A.M. Campos, R.F.P. Nogueira, P.R. Dametto, J.G. Francisco, C.H. Coelho, "Dissolved organic carbon in rainwater: Glassware decontamination and sample preservation and volatile organic carbon," *Atmospheric Environment,* p. doi:10.1016, 2007.

[39] Shigeru Taguchi, Keita Murai, Mizuho Takamatsu, Yukari Hayakawa, Shinya Tamizu, Makoto Kuwata, Yuuki Katayama, Hideki Kuramitz, Noriko Hata, "Interpretation of the concentrations of aldehydes in rainwater over a wide area and local areas of Japan by some dominant factors," *Atmospheric Environment,* vol. 61, pp. 588-596, 2012.

[40] Rosa M. Pena, Sagrario Garcia, Carlos Herrero, Marta Losada, Ana Vazquez, Tomas Lucas, "Organic acids and aldehydes in rainwater in a northwest region ofSpain," *Atmospheric Environment,* vol. 36, pp. 5277-5288, 2002.

[41] K. E. Altieri, B. J. Turpin, and S. P. Seitzinger, "Oligomers, organosulfates, and nitrooxy organosulfates in rainwater identified by ultra-high resolution electrospray

ionization FT-ICR mass spectrometry," *Atmospheric Chemistry and Physics,* vol. 9, pp. 2533-2542, 2009.

[42]   Catherine L. Muller, Andy Baker, Robert Hutchinson, Ian J. Fairchild, Chris Kidd, "Analysis of rainwater dissolved organic carbon compounds using fluorescence spectrophotometry," *Atmospheric Environment,* vol. 42, pp. 8036-8045, 2008.

[43]   D. A., "Aliphatic Aldehydes as Undesirable Contaminants in Precipitation," in *International Conference on Environmental Science and Technology*, Rhodes, Greece, 2015.

[44]   J. D. Felix, "Methanol, Formaldehyde, and Acetaldehyde in Rain," Masters Thesis, University of North Carolina Wilmington, 2008.

[45]   Kimitaka Kawamura, Spencer Steinberg, Lai Ng, Isaac R. Kaplan, "Wet deposition of low molecular weight mono- and di-carboxylic acids, aldehydes and inorganic species in Los Angeles," *Atmospheric Environment,* vol. 35, pp. 3917-3926, 2001.

[46]   Kiyoshi Matsumoto,Shunji Kawai,Manabu Igawa, "Dominant factors controlling concentrations of aldehydes in rain, fog, dew water, and in the gas phase," *Atmospheric Environment,* vol. 39, pp. 7321-7329, 2005.

[47]   Zaneta Polkowska, Kamila Skarzinska, Tadeusz Gorecki, and Jacek Namiesnik, "Formaldehyde in Various Forms of Atmospheric Precipitation and Deposition from Highly Urbanized Regions," *Atmospheric Chemistry,* vol. 53, pp. 211-236, 2006.

[48]   Sou N. Matsunaga, Alex B. Guenther, Yusuke Izawa, Christine Wiedinmyer, Jim P. Greenberg, Kimitaka Kawamura, "Importance of wet precipitation as a removal and transport process for atmospheric water soluble carbonyls," *Atmospheric Environment,* vol. 41, pp. 790-796, 2007.

[49]   Jarmo K. Holopainen, Anne-Marja Nerg, and James D. Blande, "Multitrophic Signalling in Polluted Atmospheres," in *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*, 2013, pp. 285-314.

[50]   P. C. Harley, "The Roles of Stomatal Conductance and Compound Volatility in Controlling the Emission of Volatile Organic Compounds from Leaves," in *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*, 2013, pp. 181-208.

[51]   C. M. Castellon, *DBP Precursors in a Central MA Watershed and DBP Occurence in MA Water Supplies,* 2008.

[52]   A. Wenda-Piesik, "Volatile Organic Compound Emissions by Winter Wheat Plans (Triticum aestivum L.) under Fusarium spp. Infestation and Various Abiotic Conditions," *Polish Journal of Environmental Studies,* pp. 1335-1342, 2011.