SEASONAL CORRELATION BETWEEN WATER QUALITY PARAMETERS AND DISINFECTION BY-PRODUCTS IN SAKARYA RIVER

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ABSTRACT
This study focuses on investigating seasonal variations and relationships between water quality parameters and disinfection byproducts (DBPs) within the Sakarya River where is located in Turkey. This river water is rapidly endangered by urbanization, industrial and agricultural activities; so, research pollution of river samples have been taken from 5 different points along the river during one year. Within this scope, changes in the dissolved organic carbon (DOC), biological oxygen demand (BOD5), chemical oxygen demand (COD), ultraviolet absorbance at 254 nm (UV254), specific ultraviolet absorbance (SUVA254), trihalomethane formation potential (THMFP), and haloacetic acids formation potential (HAAFP) are measured. High coefficient of determination (R2) was 0.64 and 0.62 UV between THMFP and HAAFP respectively, also THMFP and HAAFP relationships between UV254 (R2) was found to be close to each other. COD, BOD and NBOM maximum coefficient of determination between DBPs was 0.62. High correlation coefficients (r) of 0.80 and 0.79 between SUVA254 and DBPs were obtained for THMFP and HAAFP respectively. The reactivity of the organic matter changed throughout the year; with the lowest reactivity for both THMFP and HAAFP in fall, increasing in spring and reaching a maximum in summer season. Understanding the seasonal changes and correlations between organic matter and their reactivity should lead to a better optimization of the treatment method and a more consistent water quality.

Keywords: THMFP, HAAFP, river water, seasonal correlation

1. INTRODUCTION

The water sources of drinking water generally contain natural organic matters (NOM) that contain heterogeneous mixture of organic compounds such as humic substances, polysaccharides, amino sugars, proteins, peptides, lipids, small hydrophilic acids, and others (Bhatnagar and Sillanpaa 2017). NOM cause both aesthetic concerns such as color, taste, odor and also produce undesirable disinfection by-products (DBPs) (Wei et al. 2008).

Therefore, understanding the properties of NOM has always been one of the most essential and vital topics for water quality control. Measuring NOM is difficult issue because no single parameter that include a complete characterization of NOM. For this reason collective parameters such as DOC, UV254, SUVA, COD, and BOD5 are commonly used (Hua et al. 2015).

Chlorination, is the most widely used strategy for drinking water disinfection, chlorine react with NOM and form harmful DBPs and these are vital concern for water sources, particularly surface waters are rich in NOMs. THMs and HAAs are the two DBPs which are found in the in chlorinated water all over the world (Khan et al. 2009, Zhang et al. 2011, Aydin et al. 2012). DBPs can potentially cause long-term adverse health effects and they are potentially carcinogenic to humans (Tubic et al. 2013, Reguero et al. 2013, Huang et al. 2015). Because of the potential health risks of DBPs, many countries like the UK, the USA, Turkey, Japan and some water agencies, i.e. USEPA (2013) and WHO (2011) have added these compounds in their drinking water quality standards (Zhang et al. 2011, Reguero et al. 2013, Kumari and Gupta 2015).

Seasonal changes will affect surface water quality, NOM characteristics, and molecular weight content and in consequence all this factors may challenge treatability. An understanding of the correlation of water quality parameters with NOMs can help to choose optimum treatment method for using the water source to drinking water. NOM could have negative effect to treatment, for example it can be increased of coagulant and disinfectant demand in drinking water treatment (Tubic et al. 2013). NOMs are critical to water quality parameters because, during drinking water treatment (e.g. chlorination and ozonation) components of the DOM react to form toxic halogenated compounds (Kraus et al. 2008). DOM includes; BOD5, COD or NBOPs, and TOC parameters.

Recent studies demonstrated complexity of NOMs makes difficult to develop universally applicable models with DBPs (Uyak et al. 2007). Ye et al 2009 studied chemical and physical parameters which possibly affect the DBPs formation and found that the correlations between THMFP with natural organic matter is higher than HAAFP (Ye et al. 2009).
Similarly, a study investigated THM and HAA formation relation with NOMs and reported that R² values could be >0.90 but it had high errors in their prediction accuracy because every water source has different NOM characterization and local data set is very important for exact prediction (Ged et al. 2015).

Therefore, this study investigated the relationships between BOD₅, COD or NBOPs, and TOC by evaluating the coefficient of determination (R²) and correlation coefficient (r) using the water quality data of Sakarya river for 1 year in Turkey. This study may provide valuable and unique relationships between representative water quality parameters because few studies have reported the relation between BOD₅, COD or NBOPs, and TOC for rivers. Notably, study will be focused on analyzing the impact that seasonal and spatial variations can be effected current and future regulations. Moreover, it helps choosing best available treatment method due to the temperature, NOM characterization, pH changes over the year, operational variations in water treatment plant importantly changes.

2. MATERIALS AND METHODS

2.1 Taking the Samples from the River

Samples were taken from 5 different points along the Sakarya River in the context of the study. The first point is the Cifteler where the Sakarya River starts. The second and third points are Gokcekaya and Yenice Dams, respectively. As the fourth point, Geyve, which is a region where settlement and industry are intense, was chosen. The last sampling point is the Karasu area where the Sakarya Rivers runs to the Black Sea. Samples were taken from the river along 1 year during 4 seasons. In the sampling area, the highest temperatures are seen from summer and spring with a maximum temperature of 43.5 °C and an average temperature of 21 °C. Lowest temperatures (-14.5 °C) are observed in winter. He maximum rainfall can be seen in fall. Annual average temperature of 14.4 °C, measured at low temperature -14.5 °C, the highest temperature of 41.8 °C. Annual average moisture content of 73.9%, average annual rainfall of 1,016 mm and the seasonal distribution of rainfall; spring of 179.2 mm, 148.4 mm, summer, a fall 279.1 mm and 233.8 mm in winter months.

The sampling points are shown in Fig 1. The samples were taken from the water bodies after side branches of the river or after the discharges where there was full mixing of the water. For analyzing 3 samples were taken from each sampling point. The samples were kept at +4°C.

2.2 Analytical methods

2.2.1 Water quality analysis

DOC measurements were performed using a catalytic combustion based on DOC analyzer. DOC was measured by means of a DOC analyzer (Hach Lange, IL 550). The ultraviolet absorbance (UV₂₅₄) was determined using a UV-VIS scanning spectrophotometer (Genesys 10, Bonsay Technologies, Bhubaneswar, India) with 1-cm cells at 254 nm wavelength. Specific Ultraviolet Absorbance (SUVA) was calculated as the ratio of UV₂₅₄ to DOC. All the analyses were carried out following the Standard Methods for Water and Wastewater of American Public Health Association (APHA), American Water Work Association (AWWA) and Water Environment Federation (WEF).

THMFP and HAAFP analyses

All reagents and standards for THMs and HAAs were purchased from Supelco. THMFP, and HAAFP tests were analyzed according to the SM 5710B.

Sample was chlorinated and held for reaction for 7 days at 25°C in dark condition. After the reaction period the free chlorine residual was eliminated with a sodium sulfite solution. The chlorine residual concentrations were measured using the DPD ferrous titrimetric method (SM 4500 G) The residual chlorine concentration must be of 3-5 mg/L.
THMs including chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl), and bromoform (CHBr₃). They were extracted with methyl tert butyl ether (MTBE) according to the method of USEPA 551.1 and then analyzed by gas chromatography (Shimadzu, 2010) with a micro-electron capture detector. HAAs were measured using a liquid-liquid extraction gas chromatography (GC) according to EPA Method 552.3 (USEPA 552.3). A total of the nine HAA (monochloroacetic acid (MCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA) were extracted with MTBE.

3 RESULTS AND DISCUSSION

3.1 Characteristics of water

Table 1 summarizes the average, maximum and minimum measured raw water quality parameters in five sample points of Sakarya River. The average concentration of BOD₅, COD and DOC is 9 mg/L, 19 mg/L and 9 mg/L respectively during one year period, while the maximum concentration of BOD₅, COD, and DOC is 18 mg/L, 36 mg/L and 15 mg/L, the minimum concentration is 2 mg/L, 10 mg/L and 8 mg/L for 5 sample points in four seasons along the river. Especially Geyve showed the highest concentration, while Cifteler is lower. Moreover results showed that the highest UV₂₅⁴ absorbance was observed in Geyve (0.25 cm⁻¹) while Cifteler showed lowest value of UV₂₅⁴ absorbance (0.01 cm⁻¹). SUVA₂₅⁴ varies between 0.26 and 1.71 L/mg.m and this shows that the organic substances that form DOC generally have low-weight molecular (SUVA₂₅⁴<2) (Campagna et al., 2013). Similarly the highest THMFP and HAAFP concentration was measured in Geyve, due to the highest DOC and UV₂₅⁴ content of water. According to the studies UV₂₅⁴, DOC and SUVA₂₅⁴ have found to be good predictor of DBPs formation in water resources. (Hua et al. 2015)

Table 1 Water characteristics

<table>
<thead>
<tr>
<th>Sample Point</th>
<th>Concentration</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>BOD₅ (mg/L)</th>
<th>COD (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UV₂₅⁴ (cm⁻¹)</th>
<th>SUVA₂₅⁴ (L/mg.m)</th>
<th>THMFP (µg/L)</th>
<th>HAAFP (µg/L)</th>
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<tr>
<td>Cifteler</td>
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<td>7.8</td>
<td>14.53</td>
<td>7.00</td>
<td>12.00</td>
<td>8.00</td>
<td>0.03</td>
<td>0.38</td>
<td>169.30</td>
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<tr>
<td></td>
<td>Maximum</td>
<td>7.93</td>
<td>20.87</td>
<td>12.00</td>
<td>14.00</td>
<td>9.72</td>
<td>0.04</td>
<td>0.42</td>
<td>209.60</td>
<td>220.00</td>
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<tr>
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<td>0.26</td>
<td>137.80</td>
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<td>Avarage</td>
<td>7.87</td>
<td>15.03</td>
<td>8.00</td>
<td>15.00</td>
<td>8.91</td>
<td>0.12</td>
<td>1.35</td>
<td>225.49</td>
<td>190.70</td>
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<tr>
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<td>Maximum</td>
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<td>21.1</td>
<td>12.00</td>
<td>18.00</td>
<td>10.68</td>
<td>0.19</td>
<td>1.80</td>
<td>294.03</td>
<td>250.83</td>
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<tr>
<td></td>
<td>Minimum</td>
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<td>8.22</td>
<td>4.00</td>
<td>12.00</td>
<td>6.38</td>
<td>0.06</td>
<td>0.97</td>
<td>142.67</td>
<td>132.62</td>
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<td>Yenice</td>
<td>Avarage</td>
<td>8.03</td>
<td>13.83</td>
<td>8.00</td>
<td>17.00</td>
<td>9.73</td>
<td>0.15</td>
<td>1.54</td>
<td>234.61</td>
<td>233.38</td>
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<tr>
<td></td>
<td>Maximum</td>
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<td>22.12</td>
<td>15.00</td>
<td>26.00</td>
<td>11.60</td>
<td>0.20</td>
<td>1.73</td>
<td>265.87</td>
<td>297.79</td>
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<td></td>
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<td>13.00</td>
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<td>0.08</td>
<td>1.21</td>
<td>187.96</td>
<td>166.97</td>
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<td>Geyve</td>
<td>Avarage</td>
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<td>15.09</td>
<td>8.00</td>
<td>30.00</td>
<td>11.64</td>
<td>0.19</td>
<td>1.63</td>
<td>327.73</td>
<td>367.90</td>
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<tr>
<td></td>
<td>Maximum</td>
<td>8.9</td>
<td>22.65</td>
<td>18.00</td>
<td>36.00</td>
<td>14.61</td>
<td>0.25</td>
<td>1.71</td>
<td>394.22</td>
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<td></td>
<td>Minimum</td>
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<td>0.18</td>
<td>2.53</td>
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<td>Karasu</td>
<td>Avarage</td>
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<td>10.00</td>
<td>21.00</td>
<td>10.92</td>
<td>0.15</td>
<td>1.37</td>
<td>243.76</td>
<td>238.26</td>
</tr>
</tbody>
</table>
3.2 The correlation and statistical analysis between water quality parameters

Many studies have indicated that a correlation may be established between DBPs and water quality parameters which representing organic matter measurement. In particular, parameters such as DOC, UV$_{254}$ absorbance and SUVA$_{254}$ were stated to be able to associate DBPs such as THM and HAA, and recently modeling studies were also made about this relationship. In this study, a correlation study was carried out for the parameters considered to represent DBPs and organic materials in Sakarya River. Fig. 2 shows the relationship between DOC, UV$_{254}$, SUVA$_{254}$ parameters and DBPs. The correlation coefficient ($R^2$) between THMFP and DOC is 0.528 while that value for HAAFP is very low (0.3922). It is stated that the structure of organic substances causing THM formation is different from the substances causing HAA formation (Ye et al. 2009, Guilherme and Rodriguez 2014). The correlation between THMFP, HAAFP and UV$_{254}$ was found to be higher than DOC (Fig 2). UV$_{254}$ represents humic substances, according to the results it can be seen that humic substances are the basic organic matter which causes DBPs.

The relationship between UV$_{254}$ and THMFP, HAAFP was found to be close to each other. According to this correlation it is understood that the UV$_{254}$ parameter can be used in DBPs estimation.

The organic substances being composed of less hydrophobic substances with a lower molecular weight so as a result of this SUVA$_{254}$ and DBPs relationships was rather weak. Similar results are obtained by Ates et al (Ates et al. 2009).
Fig. 2 Relationships between DBPs and DOC, UV254, SUVA254

The correlation coefficients (r) between water quality parameters and THMFP and HAAFP in Sakarya River are shown in Table 2. The correlation coefficient (r) revealed a strong linear relationship between UV 254, THMFP and HAAFP 0.80 and 0.79 respectively In addition SUVA 254 correlation with THMFP and HAAFP was weak and found 0.57 and 0.51 respectively. This poor correlations between SUVA and THM and HAA concentrations means the presence of NOM with low molecular weight, less hydrophobicity and aromaticity in Sakarya River. Ates et al.,(2007) found similiar results in surface waters from different regions of Turkey.(Ates et al. 2007)

COD and BOD5 correlation between DBPs is similiar to each other. These results revealed that the structure and composition organic matter play vital role formation of THMFP and HAAFP. However, The NBOM correlation was also found rather high (0.69,0.51), this indicates that non biodegradable organic matters also affect the formation of DBPs.

Table 2 The correlation coefficient (r) between water quality parameters and DBPs in Sakarya River

<table>
<thead>
<tr>
<th>Classification</th>
<th>Correlation coefficient, r</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC/THMFP</td>
<td>0.73</td>
</tr>
<tr>
<td>DOC/HAAFP</td>
<td>0.63</td>
</tr>
<tr>
<td>UV254/THMFP</td>
<td>0.80</td>
</tr>
<tr>
<td>UV254/HAAFP</td>
<td>0.79</td>
</tr>
<tr>
<td>SUVA254/THMFP</td>
<td>0.57</td>
</tr>
<tr>
<td>SUVA254/HAAFP</td>
<td>0.51</td>
</tr>
<tr>
<td>BOD5/THMFP</td>
<td>0.76</td>
</tr>
<tr>
<td>BOD5/HAAFP</td>
<td>0.77</td>
</tr>
<tr>
<td>COD/THMFP</td>
<td>0.78</td>
</tr>
<tr>
<td>COD/HAAFP</td>
<td>0.67</td>
</tr>
<tr>
<td>NBOM/THMFP</td>
<td>0.69</td>
</tr>
<tr>
<td>NBOM/HAAFP</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Fig 3 shows the relationship between temperature and pH. Accordingly, in general, both THMFP and HAAFP increased with increasing temperature. The highest temperature was 22.65 °C in the summer and measured 394.22 μg/L and 633.90 μg/L in the highest THMFP and HAAFP, respectively. Many researchers showed that THMs and HAAs level were higher in summer, the main reasons could be explained by water temperature, chlorine residue and on the water source. (Aschermann et al. 2016, Azzouz and Ballesteros 2013, Guo et al. 2016). The lowest DBPs levels found during winter may be attributed to slower rate of reaction which might have contributed to lower formation.

pH is significant parameter which affected the rate and speciation of DBPF. Most researchers revealed that pH has positive correlation with THM (Kumari and Gupta 2015). According to Fig 3 with increasing pH at some points THMFP
and HAAFP were increased and some points were reversed. Studies have indicated that THMFP is generally increased with increasing pH, while the effect of pH for HAAFP is less and generally decreasing with increasing pH. Guilherme et al. (Guilherme and Rodriguez 2014) observed that the two main HAAs were DCAA and TCAA, and pointed pH is effected two DBPs differently. For example, the effect of pH on DCAA was found to be negligible, while the concentration of TCAA decreased with increasing pH. There could be different possible explanations; DCAA and TCAA have different precursors (Guilherme and Rodriguez 2014, Charisiadis et al. 2015).

The relationship DBPs between BOD5 and COD has also been examined. While BOD5 is used as an indicator of organic pollutants, COD and DOC not only contain biodegradable organics but also non-biodegradable organic substances. The NBOPs are calculated from the differences between COD and BOD5. There was a higher correlation between DBPs and COD and BOD5 correlations than TOC (Fig 4.).

When the relationship between THM and HAA is examined, it is seen that R2 between THM and NBOM is rather high (0.4765) According to this results understood that biodegradable organic material contributes to DBPFP. It was observed that anthropogenic pollution was present in the Sakarya River. The relationships between BOD5, COD, TOC and NBOM is given Fig 5.

Lee et al. (Lee et al. 2016) pointed out that NBOM is the determinant of human-induced pollutants in rivers and analytical methods should be developed to measure this compounds. Because of NBOM concentration it is obvious that Sakarya River is polluted by human induced pollutants.

The highest R2 between THM, HAA and UV254 absorbance, was found to be 0.642 and 0.6187 respectively. After the UV254 absorbance value, COD and BOD5 could also be identifier parameters for the determination of DBPs.
Fig. 4 Relationship between DBPs and COD, BOD5

THMFP

HAAFP

THMFP $\gamma = 7,0804x + 106,72$

$R^2 = 0,6234$

HAAFP $\gamma = 10,087x + 34,418$

$R^2 = 0,4501$

THMFP $\gamma = 17,05x + 132,77$

$R^2 = 0,5734$

HAAFP $\gamma = 29,205x + 40,565$

$R^2 = 0,5985$

THMFP $\gamma = 8,7573x + 130,28$

$R^2 = 0,4765$

HAAFP $\gamma = 10,916x + 87,565$

$R^2 = 0,2634$
3.3 Spesifik THM ve HAA

The specific DBPs parameter is expressed in the literature as the water reactivity (Uyak et al. 2008). Specific THM and HAA values were seasonally monitored throughout the year.

The seasonal organic reactivity of the Sakarya River is given in Fig 6 Reactivity changed throughout the year and for both THM and HAA the highest value was found in the summer at the Geyve point. The lowest reactivity of the organic matter value for THM and HAA was found as 14.18 and 12.16 μg/mg TOC in Çifteler at spring, respectively. The specific THM HAA values were highest at the season and the point at which the DYÜOP and TOC concentrations were highest.

In general, it has been found that specific THM is higher than specific HAA, and it is believed that the main reason is that THM-forming organic compounds are composed of high molecular weight hydrophobic substances whereas HAA-forming organic materials are composed of hydrophilic low molecular weight substances (Tian et al. 2008). Similar results were found in the study carried out in Uyak et al. (Uyak and Toroz 2007). The water reactivity is directly proportional to the amount of organic matter removed from the water, and the amount of organic matter removed from the water reactant is also increased.

The highest reactivity during the year was observed in Geyve and when the removal efficiencies of the treatments were examined it was found that Geyve had both the highest THM removal and specific THM.

It is understood that the as the water reactivity increases; it means hydrophobicity increase, as a result; the removal efficiency of the organic matter increases. Many studies in the literature have indicated that organic materials with high hydrophobicity, i.e., reactivity, can be treated efficiently, especially by the coagulation process (Ates et al. 2009, Tian et al. 2008, Sadırnourmohamadi and Gorczyca 2015).
4. Conclusions

This study has provided the relationships between DBPs and water quality parameters and evaluated the effect of seasons and the possible relationships between organic matters during one year from five important point along the river. The concentration of THMFP and HAAFP ranged between 138 - 350 µg THMFP/L and 118 - 634 µg HAAFP/L, respectively. The samples collected from the river had a considerable differences depending on the sampling point and time. These differences are presumably because of anthropogenic pollution sources like domestic or industrial wastewater and agricultural runoff. Moreover, a high correlation of NBOM with DBPFP is evidence of this uncontrolled runoff.

The highest correlation coefficient (r) value was observed 0.80 and 0.79 between TMHFP and HAAFP, respectively for UV_254 while the lowest r value was 0.57 and 0.51 between SUVA_{254}&THMFP and SUVA_{254}&HAAFP, respectively. Because of the presence of NOM with low molecular weight, less hydrophobicity and aromaticity were caused poor correlations with SUVA_{254}. Due to the low SUVA_{254} correlation this type water difficult to treat such with traditional drinking water treatment methods such as; coagulation flocculation, so it is more appropriate to select advanced treatment methods like membrane and ozone.

In addition, the maximum coefficient of determination (R^2) was in UV_{254} 0.64 and 0.61 between THMFP and HAAFP, respectively.

Increased pH results in high THM formation, there was a linear relationship between pH and THM formation. This parameter seems to be very important in controlling THM formation. DBPs during summer and winter along the Sakarya River is higher in summer than in winter, due to a higher water temperature and chlorine demand. It is seen that anthropogenic pollution in the river more affected than the effect of organic pollution.

Throughout the year the lowest reactivity (THMFP and HAAFP) of the organic matter has shown in winter, increasing in spring and reaching a maximum in summer season. Similarly this results lowest and maximum DOC concentration seen in winter and summer respectively. These observations indicate that water can be treated more effectively and easier summer than winter due to the content of the NOM.

To sum up, it is understood that; not only one parameter effect THM and HAA formation organic precursor such as DOC, UV_254, SUVA, BOD_5, COD and external factors like pH, temperature and NBOMs are also very important and significantly influences of formation DBPs.
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