ORIGINAL ARTICLES

Characterization of Organic Matters (OM) in River Nile, Cairo, Egypt and their relation to the formation of disinfection by-products


ABSTRACT

This work investigated the characteristic of natural organic matters in the raw drinking water River Nile and their relation to the formation of Disinfection by-products (DBPs). Fractionation of dissolved organic carbon (DOC) content in river Nile to hydrophilic, transphilic and hydrophobic was carried out to assess the contribution of each fraction in forming THMs and HAAs. It was found that the DOC has high potentiality to form hazardous by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) during the chlorination process. The formation of these by-products is controlled mainly by operating factors like Cl₂ dosage, total organic carbon (TOC), pH, temperature of the water body and the contact time with Cl₂. So, the effect of all of these parameters were investigated in this study in addition to THMFP and HAAFP. The batch experiments showed that increasing Cl₂ dosage leading to increasing in the formation of THMs and HAAs. pH 7.5 was recognized as the optimum value for formation of THMs and HAAs. We found that from fractionation experiments that hydrophilic fraction is the major fraction in River Nile surface water and has the highest probability for the formation of THMs and HAAs.

Key words: THMs; HAAs; Fractionation; DOC; DBPs, Trihalomethane Formation Potential (THMFP), Haloaceticacid Formation Potential(HAAFP).

Introduction

During the last few decades, several authors reports confirmed that Natural Organic Matter (NOM) occurrence in water is a worldwide phenomenon (Eikebrokk et al., 2004) change in the climate (temperature, quality, and amount of precipitation) and the decline in acid deposition are reasonable explanations for the increasing in the NOM concentrations (Delpla et al., 2009).

NOM is a complex mixture of organic compounds present in all fresh water, particularly surface waters. The increased levels of NOM and changes in the quality of the matter present major challenges to the drinking water industry where it creates serious problems to drinking water quality and its treatment processes such as: (i) negative effect on water quality due to color, taste and odor, and this point was found in late 1980s, where an increase in color of NOM was first reported in Swedish surface waters (Forsberg et al., 1980).(ii) increasing the coagulant and disinfectant dose requirements, which in turn results in increased sludge and potential harmful disinfection byproduct (DBP) production, and (iii) promoting the biological growth in distribution system (Jacangelo et al., 1995). NOM consists of different compounds ranged from aliphatic to aromatics compounds. Some of these organic matter is negatively charged consisting of a wide variety of chemical compositions and molecular sizes (Thurman et al., 1985 and Sweitlik et al., 2004).

Reactions between natural organic matters (NOM) and chlorine form different types of disinfection byproducts (DBPs) in drinking water. Trihalomethanes were identified as the main DBPs as early as 1974. Later, other DBPs such as haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, haloaldehydes, chlorinatedphenols, chloropiricin, cyanogen halides and chloral hydrate (Rook et al., 1974, Alawi et al., 1994, Golfinopoulos et al., 2001, Nikolaou et al., 2001 and Christman et al., 1983).

Human exposure to DBPs can occur through ingestion of drinking water as well as inhalation and dermal contact during regular indoor activities (e.g., showering, bathing, swimming in chlorinated pools and cooking) (Mohamed A. EL-Dib et al., 1995). Some of these DBPs can be associated with human bladder cancer and other chronic and sub-chronic effects on human health (Anastasia D. Nikolaou et al., 2004). THMs were proven to have adverse effect on human beings. Specially, brominated species were suspected to be much stronger carcinogens and mutagens than their chloride containing analogues and these brominated compounds are formed...
due to the presence of bromide leads to the active halogen shifts from chlorine to bromine which means that the reactions incorporating bromine into natural organic matter are faster than those incorporating chlorine. Therefore, brominated THM species are considered as more toxic than non-brominated species (Uyak et al., 2007) so formation of brominated THMs during disinfection process is of great concern (Johnson et al., 1986 and Mok et al., 2005).

For better understanding of DBPs formation, it is worth to study the factors affecting the formation in chlorinated water. Such understanding will help in the design of a mathematical model for the prediction of DBPs formation. The major categories of chlorination by-products (CBPs) are trihalomethanes (THMs) and haloacetic acids (HAAs) according to our previous results and other studies (Johnson et al., 1986, Mok et al., 2005, Singer et al., 2002, USEPA 2003, Richardson et al., 2007, Health Canada Guidelines for Canadian Drinking Water Quality 2008 and Hrudey et al., 2009) Therefore, it was decided to use them as a model for the other DBPs. So the main objective from this work is to assess information about the parameters that have an influence on formation of THMs and HAAs in the distribution system such as contact time, chlorine dose, NOM concentration, pH and temperature.in addition to the reactivity of the DOC fractions that forming THMs and HAAs was determined by fractionation experiments and measuring their THMFP and HAAFP.

Methods and Materials

Water Samples were collected in transparent amber glass bottles and from two Drinking Water Treatment Plants (DWTP) located in Greater Cairo Governorate including Giza and Cairo cities during 2012. Embaba DWTP was selected in Giza Governorate, and Fostat DWTPs in Cairo Governorate were selected. Water sampling program was planned in advance. Several samples were collected at each treatment step namely inlet, after clarifier, after filtration and the plant outlet.

Chemicals:

All chemical solutions were prepared from reagent grade chemicals or stock solutions. Dilution to target aqueous concentrations was accomplished with double distilled water. Solutions were stored at 4°C and brought to room temperature before use. A free chlorine (HOCl) stock solution (2500 mg/L) was prepared from 5% sodium hypochlorite (NaOCl) (from sigma aldrich) and it was periodically standardized using DPD/FAS titration (Standard Methods, 1998). Standards of THMs and HAAs in addition to XAD resins were brought gently from Sigma Aldrich. Humic acid (from Sigma Aldrich) stock solution is prepared by dissolving 2 g in 1 L of distilled water and using NaOH to dissolve it due to it precipitate at low pH.

DOC fractionation:

NOM fractionation was carried out through the simplified NOM fractionation scheme, using small (~8 mL) resin volumes packed into a 30 cm (24 mL) glass column. XAD-8 and XAD-4 resins were used for all fractionation procedures, in order to separate NOM into hydrophobic (HPO), transphilic (THP) and hydrophilic (HPI) fractions, following the procedure developed by Croue and co-workers (1999). Waters used in these experiments were first filtered through a 0.45 μm nylon membrane filter to remove particulate matter and acidified to pH 2.0 with perchloric acid (HClO4). The acidified sample was passed through a small XAD-8 column at a flow rate of approximately 5 mL/min, resulting in removal of the hydrophobic fraction. The effluent was then passed through a small XAD-4 column, removing transphilic material and leaving only hydrophilic matter in the final effluent. After each use, columns were rinsed with a total of 100 mL 0.1 N NaOH and 100 mL 0.1 N HCl, alternating between acid and base, followed by 200 mL Milli-Q water (flow rate was 20 mL/min). Fractionation was repeated 4 times for every sampling round. Fractionated effluent samples from XAD-8 and XAD-4 columns were adjusted at pH 7.0 with 0.1 N sodium hydroxide and buffered with 0.03 mol/L of phosphate buffer prior to be analyzed or used for chlorination experiments.

Analytical measurements:

The measured parameters were total organic carbon and dissolved organic carbon (TOC & DOC) which gives an indication on the natural organic matter (NOM), Ultraviolet absorption at 254 nm (UV254) was used for the determination of aromatic organic compounds, Specific Ultraviolet Absorption at 254 nm (SUV254) was calculated which is obtained by dividing a sample's ultraviolet absorption at a wavelength of 254 nm (UV 254) (path width = 1 m) by its concentration of dissolved organic carbon (DOC) (mg/L).

Chlorine residuals were analyzed at the time of sampling. THMs and HAAs measurements were conducted using EPA 551.1 method and EPA 552.3 respectively (27-28) (All the samples were refrigerated at 4°C and analyzed within 2 weeks.) THMs were quantified by liquid/liquid extraction with pentane followed by gas
chromatography and electron capture detection (GC/ECD) according to Standard Method (APHA, 1995). Methyl-tertbutyl-ether extraction of the HAAs samples was done immediately in accordance with the EPA method (2003).

The quality control program was applied including the following:
1-Laboratory reagent blank (LRB) was run with each set of analysis.
2-Quantification of DBPs was carried out using external standards with coefficient for calibration curves higher than 0.995.
3-The Calibration program was verified on each working day by the measurement of one or more standards.
4- A random sample was run in triplicate. Laboratory control sample was analyzed with each series of samples (10 samples). Q-chart was used and two values of ±2 slandered deviations are the lower and upper limits. For THM species, analytical procedures ensured detection limits of 0.5 \( \mu \text{g/L} \) for chloroform (CF) and 0.3 \( \mu \text{g/L} \) for bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. The efficiency of the extraction of HAAs was determined by addition of known concentration of 2-bromobutanoic acid as surrogate standard. Recovery for water samples ranged from 83 to 103\% (C). The Egyptian Ministry of Health 2007) and United States (USEPA 2003) drinking water quality standards were used as a basis for assessing the water quality data obtained in the study.

Results and Discussion

DOE fractions and their contribution in DBPs formation:

The major source of DBPs is NOM present in raw and the treated water represented by DOC. Dissolved organic carbon can be classified according to their hydorphilicity to hydrophilic (HPL), hydrophobic (HPO), and transphilic (TPL) fractions. It is significance to identify which fraction is responsible for the formation of DBPs. To assess the DOC and fractionated dissolved organic matter at DWTPs, samples were collected from the treatment stages. The collected data from each treatment step in DWTPs under study are presented in Table 1.

Table 1: DOC content and different fractions through DWTP stages

<table>
<thead>
<tr>
<th>DWTP</th>
<th>Treatment Stage</th>
<th>DOC (mg/l)</th>
<th>Hydrophilic (HPL)</th>
<th>Hydrophobic (HPO)</th>
<th>Transphilic (TPL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Embaba</td>
<td>Inlet</td>
<td>4.36 - 6.78</td>
<td>5.57</td>
<td>3.38 - 2.17</td>
<td>2.77</td>
</tr>
<tr>
<td></td>
<td>clarifier outlet</td>
<td>3.81 - 5.7</td>
<td>4.83</td>
<td>2.84 - 1.90</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>Filter outlet</td>
<td>3.46 - 5.39</td>
<td>4.56</td>
<td>2.69 - 1.72</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>Outlet</td>
<td>3.44 - 5.04</td>
<td>4.37</td>
<td>2.51 - 1.71</td>
<td>2.18</td>
</tr>
<tr>
<td>Fostat</td>
<td>Inlet</td>
<td>4.32 - 5.93</td>
<td>4.98</td>
<td>2.95 - 2.15</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>clarifier outlet</td>
<td>3.87 - 5.38</td>
<td>4.36</td>
<td>2.68 - 1.93</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>Filter outlet</td>
<td>3.54 - 4.81</td>
<td>4.05</td>
<td>2.40 - 1.76</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>Outlet</td>
<td>3.32 - 4.69</td>
<td>3.87</td>
<td>2.34 - 1.65</td>
<td>1.93</td>
</tr>
</tbody>
</table>

The values in the table is given by mg/l.

DOC content in raw water was ranged 4.36 - 6.78 mg/L with mean value of 5.57 mg/L, while hydrophilic fraction ranged from 3.38 - 2.17 mg/L with mean 2.77 mg/L, while hydrophobic fraction ranged from 1.17 - 1.82 with mean 1.49 mg/L and the transphilic fraction is ranged from 0.77 to 1.58 mg/L. Figure 1 showed the speciation of DOC fractions in Embaba and Fostat DWTPs, and illustrated that the hydrophilic fractions were always the dominant species leading to the preliminary conclusion, that removal of hydrophilic fraction was not efficient at the different treatment stages which is in consistent with (Eikebrokk et al., 2004). About 13\% of the DOC was removed in the coagulation unit, and a much less decrease was obtained in the following treatment processes.

In order to correlate the formed DBPs with the detected in DOC fractions, the fate of DBPs through the assessment treatment stages. The averages of obtained data from each treatment step in DWTPs under study are presented in Tables (1-3). The concentration of all DBPs increased through the treatment stages due to long contact time with chlorine applied in pre-chlorination step. The results in (Table 1 and Tables 2&3) revealed that DBPs concentration increases with the increase in hydrophilic fraction indicating that hydrophilic fraction responsible for the formation of DBPs.
Table 2: Fate of DBPs through Embaba drinking water treatment plant stages

<table>
<thead>
<tr>
<th>DBP(µg/L)</th>
<th>Coagulation-Floculation</th>
<th>Sand Filtration basin outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Range</td>
<td>Mean Range</td>
</tr>
<tr>
<td>CHCl_3</td>
<td>9.70 - 12.21</td>
<td>16.73 - 29.01</td>
</tr>
<tr>
<td>CHCl_2Br</td>
<td>1.14 - 2.44</td>
<td>4.78 - 13.47</td>
</tr>
<tr>
<td>CHClBr_2</td>
<td>1.36 - 1.94</td>
<td>2.77 - 4.37</td>
</tr>
<tr>
<td>CHBr_3</td>
<td>0.28 - 0.87</td>
<td>1.52 - 2.88</td>
</tr>
<tr>
<td>MCAA</td>
<td>33.57 - 48.61</td>
<td>28.33 - 35.57</td>
</tr>
<tr>
<td>DCIA</td>
<td>19.72 - 27.13</td>
<td>17.61 - 25.05</td>
</tr>
<tr>
<td>TCIA</td>
<td>29.74 - 37.41</td>
<td>22.74 - 32.05</td>
</tr>
<tr>
<td>MBAA</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BCAA</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>DBAA</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table 3: Fate of DBPs through Fostat drinking water treatment plant stages

<table>
<thead>
<tr>
<th>DBP</th>
<th>Coagulation-Floculation</th>
<th>Sand Filtration basin</th>
<th>Chlorination tank</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Range</td>
<td>Mean Range</td>
<td>Mean Range</td>
</tr>
<tr>
<td>CHCl_2Br</td>
<td>2.02 - 2.53</td>
<td>2.38</td>
<td>4.89</td>
</tr>
<tr>
<td>CHClBr_2</td>
<td>0.89 - 1.11</td>
<td>1.08</td>
<td>6.97 - 8.73</td>
</tr>
<tr>
<td>CHBr_3</td>
<td>0.66 - 0.82</td>
<td>0.79</td>
<td>0.27 - 0.34</td>
</tr>
<tr>
<td>MCAA</td>
<td>31.10 - 41.09</td>
<td>36.29</td>
<td>24.15 - 31.91</td>
</tr>
<tr>
<td>DCIA</td>
<td>17.22 - 19.54</td>
<td>18.36</td>
<td>16.41 - 19.93</td>
</tr>
<tr>
<td>MBAA</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BCAA</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>DBAA</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND: Not Detected.

**MCAA: monochloroacetic acid, DCAA: dichloroacetic acid, TCAA: trichloroacetic acid, MBAA: monobromoacetic acid, BCAA: bromochloroacetic acid, and DBAA: dibromoacetic acid.**

Fig. 1: Distribution Percentages of DOC fractions in (a) Embaba and (b) Fostat DWTP

Fig. 2: Contribution of DOC fractions in DBPs formations, (a) THMs and (b) HAAs
For better understanding of the correlation between DOC fractions and DBPs formation, a series of bench scale experiments were conducted. Raw water sample was collected from Nile River and then fractionated. Finally, each fraction was chlorinated with 5 mg/L Cl₂ for one hour. Figure 2 shows the DBPs formation for the hydrophilic species was usually higher than that of hydrophobic species. This indicated that the hydrophilic fraction was a more reactive precursor for THMs than the hydrophobic fraction.

**Effect of contact time on THMs and HAAs formation:**

![Fig. 3: Formation of (a) THMs and (b) HAAs as a function in time; pH = 7.5, Temperature = 25°C, TOC = 10 mg C/L and Cl₂ = 5 mg/L.](image)

Figure 3 represents the concentration levels of THMs and HAAs formed on chlorination of authentic water samples at various contact times. It is clear that Cl₂ reacts very fast to produce reasonable amounts of THMs and HAAs within short time (30 min); the subsequent increase is slightly slow. The increase in THMs and HAAs concentration with time is due to more contact between Cl₂ and NOM present in water. It is interesting to note that the extent of formation varies from one compound to another. For example chloroform concentration increased from 1050 to 1391 µg/L, i.e., 27%, within 100 min while only 14% and 20% increase in dibromochloromethane and tribromomethane was obtained in the same time interval. Bromodichloromethane was the most affected by the reaction time; 55% increase in 100 min. on the other hand, monochloroacetic acid (MCAA) increased from 794.64 µg/L to 988.87 i.e. 16.5 % within 90 min, while dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were increased by 26, and 25 %, respectively in the same time intervals. Brominated acetic acid compounds were not detected due to absence of bromide ion (Amy et al., 1995)

**Effect of pH on THMs and HAAs formation:**

![Fig. 4: Effect of pH on the formation of (a) THMs and (b) HAAs; contact time = 120 min, Temperature = 25°C, TOC = 10 mgC/L and Cl₂ = 5 mg/L.](image)

Another important factor that affects the formation of THMs and HAAs is pH value of water containing NOM. Figure 4 shows the concentrations of THMs and HAAs after dosing with chlorine at 5 mg/L in NOM
solution (10 mgC/L) at different pH values. The pH of treated water exhibited a profound influence on the THMs and HAAs yield as the formation of THMs varied significantly with pH from 5 to 9 and the maximum yields of THMs occurred at pH 7. However, the maximum yield of HAAs was taken place at pH 8. The formation of THM detected at near neutral condition was two times more than that of pH value at 5. At high pH values, hydrolysis of many halogenated DBPs occurs (Singer et al., 2002). As a result, total organic halide (TOX) concentration is lower at pH>8. Maximum concentration was obtained under neutral conditions.

Effect of initial TOC concentration on THMs and HAAs formation:

![Fig. 5](image)

**Fig. 5:** Effect of initial TOC concentration on (a) THMs and (b) HAAs formation

THMs and HAAs are produced from the reaction between NOM and Cl₂ used for disinfection. Figure 3 represents the variation of THMs and HAAs concentration with the initial TOC concentration. Chloroform is the most affected compound by the change in TOC concentration; 1490 µg/L CHCl₃ was formed when TOC value was 15 mg C/L. Other compounds were slightly affected by TOC value. Also, MCAA concentration was increased by 20% as TOC concentration increased from 10 mg/L to 15 mg/L. While DCAA, and TCAA concentration were increased by 49 and 40%, respectively (Cowman et al., 1994)

Effect of Temperature on THMs and HAAs formation:

![Fig. 6](image)

**Fig. 6:** Effect of temperature on (a) THMs and (b) HAAs formation

Increase in THMs and HAAs yield by rise of temperature was indicated (Figure 6). The most dominant DBPs species were chloroform and MCAA at any temperature of reaction. Doubling of the rate constant for every 10°C increase in temperature, between 0 and 30°C was shown by EL-Dib and Ali (1995). However in this study, the yields of THAA in chlorination of sample increased slightly with increasing reaction temperature from 18 to 30°C. It was found that, the formation of THAA in chlorination of water sample less sensitive to temperature change. The rather limited effect of temperature on TTHMs yield attained by this work is most probably due to the variation in the nature of organic precursors found in raw river water (Owen et al., 1993).
Effect of initial Cl₂ dose on THMs and HAAs formation:

The chlorine demand and THMFP of synthetic samples with different contents of dissolved organic carbon were analyzed. Figs. 5 shows that the chlorine demand as function of dissolved organic carbon. As expected, an increase in the humic content in the samples (measured as TOC) produces an increase in the chlorine demand (CD) (Figure 5) and in the quantity of THMs and HAAs generated after chlorination (Figure 6).

Chlorine Demand has linear dependence as function of the dissolved organic indicates that the concentration present in the samples (Figs. 5). Furthermore, the results show a production of THMs and HAAs in concentrations higher than those determined by other authors (Panyapinyopol et al., 2005) due to the fact that synthetic samples prepared by dilution of a humic solution (THM precursor) were used in this study instead of real samples. The dissolved organic concentration in real surface waters is a contribution of different organic compounds and some substances are not THM precursors. As chlorine dose is increased, THMs and HAAs yield attains higher values (Figure 8). However, THMs formation was not directly proportional to the applied chlorine dose. Results given in Table 3 indicate that THMs formation proceeds as a pseudo first order reaction with respect to THMs. According to EL-Dib and Ali (1995) the reaction of THMs tends to be first order with respect to chlorine and third order with regard to precursors. Variation in the reaction kinetics may be attributed to the fact that not all organics act as THMs precursors and/or that chlorination yields several halogenated organics other than THMs (Nikolaou, A.D., et al., 2004). At low chlorine dose, substituted chloro products dominated whereas at higher doses oxidation and cleavage products, including THMs, become more important (Sorlini et al., 2005).

CHCl₃, CHCl₂Br, CHClBr₂ and CHBr₃ were observed in the experimental scope and raised gradually with increasing available chlorine concentration (as shown in Figure 6 (a). Among the three, CHCl₃ was the dominant species and occupied over 69% of the total THMs concentration (TTHM), represented by the total height of the stacked bars, in the chlorination of both water samples.
Trihalomethane and Haloacetic acid formation potential (THMFP and HAAFP):

Fig. 1: Formation potential of (a) THMs and (b) HAAs.

THM formation potential (THMFP) is often the term employed to indicate the amount of THMs that could be produced during the chlorination process. The tests for THMFP can be quite tedious and time-consuming. Water Sources from different DWTPs inlets were analyzed for their THM content and it was found that THMs could not be detected in these samples, i.e., THM0 < detection limit. An addition of chlorine to the samples and 7 days incubation resulted in the formation of THMs (THM7) in the range from 2134 to 2881.54 μg/L (Summers et al., 1996). The difference between THM7, HAA7 and THM0, HAA0, respectively, in a sample is considered as its THMs and HAAs formation potential or (THMFP and HAAFP) (Figure a). This range of THMFP was considered a very high figure as the maximum contaminant level (MCL) for THMs in drinking water was set at as low as 80 μg/L. Also, chloroform was increased by 43 % after 7 days. Chloroform formation potential represents 69 % of THMFP. While HAA7 concentration changed from 1951 to 2619 μg/L as shown in Figure b.

Conclusion:

This study showed that:-
1. The levels of THMs and HAAs released from the Fosat and Embaba DWTPs below the MCL regulations established by the USEPA and Ministry of Health in Egypt 2007.
2. The hydrophilic fraction represents the higher part of DOC fractions.
3. The hydrophilic fraction has the largest probability in the contribution of THMs and HAAs formation.
4. Increasing the chlorine dose, temperature and the contact time enhancing the formation of THMs and HAAs while the optimum pH is around 8.

References


EPA, 552.3 2003. Determination of HAAs and dalapon in drinking water by liquid-liquid extraction, derivatization and GC/ECD detection.


