Role of Seasonal Algal growths on Disinfection by-products in Drinking Water of Greater Cairo

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ABSTRACT

According to the disinfection by-products (DBPs) measured in all the treatment plants and during the four seasons, it was found that there was seasonal variation in the DBPs especially CHCl3, CHCl2Br, DCAA and TCAA produced during the chlorination process associated with increasing the total algae count (TAC) and the chlorophyll "a" concentration (Method 10200 H Std Methods 2005). There was association between the increase in the TAC and DBPs in certain plants as N. helwan, Fustat, Ameria, Mostord, Shubra and El-Obour giving indication to the relation between these DBPs and the algal growth in these plants. During the fourth season, the TAC increased associated with these DBPs in all the plants. This was confirmed by the total organic carbon (TOC) values indicating the role of algae in elevation of these DBPs. The TOC did not represent the only factor affecting the total organic halogen (TOX) values. This indicated the presence of other factors which might involve in elevation of their values.

Keywords: Trihalomethanes, Total organic carbon, Total algae count, chlorophyll 'a', Disinfection By-products

INTRODUCTION

Disinfection for drinking water reduces the risk of pathogenic infection but may pose chemical threat to human health due to disinfection residues and their by-products (DBPs) when the organic and inorganic precursors are present in water [1]. The trihalomethanes (THMs) are disinfection by-products and suspected human carcinogens present in chlorinated drinking water [2,3]. Haloacetic acids (HAAs) and other DBPs have become a focus of attention in drinking water treatment.

The THMs and HAAs are the two most prevalent classes of DBPs, stringently regulated by the U.S. Environmental Protection Agency (USEPA) and the World Health Organization (WHO) due to their potential cancer risks [4,5]. It was found that there were seasonal variation and spatial fate of these DBPs in a drinking water distribution system located in a region where very significant seasonal variations in water temperature and surface water quality occur [6,7]. THMs have been used as surrogates for DBPs although the quantitative association between THMs and other DBPs is not well established [8]. More than 500 DBPs have been detected in drinking water [9]. THMs and HAAs are two primary species of DBPs that are found in water disinfected with chlorine. These DBPs are toxic, carcinogenic and mutagenic to humans, or induce reproductive and developmental problems [10,11]. Chloramine are used as secondary disinfectant in the water treatment systems because they are less reactive than free chlorine [5].

The increase in THMs was not directly proportional to the applied chlorine dose and increase in water temperature showed a rather limited effect compared to that reported by other investigators [12]. The previous studies suggested that there was relation between THMs, total organic carbon (TOC) and total...
organic halogen (TOX) [13]. The algae became equally potent as precursors as humic and fulvic acids in production of THMs [14]. It showed a linear relationship between chlorine consumption and the activated aromatic content of various humic and fulvic acids extracted from natural waters [15]. It was found that there were species of algae representing major taxonomic groups of phytoplankton, were utilized to investigate the potential of naturally occurring chlorophyll a of living algae to produce THMs during the chlorination process [16].

The biomolecules, including protein, carbohydrates and lipids in these algae species contributed in predicting DBPs formation especially THMs and HAAs upon chlorination of algal cells [17, 18]. This research focused on the evaluation of DBPs formation in all the treatment plants of the Cairo sector taking in the consideration role of algal extracellular products to enhance DBPs production.

The previous study showed that the predominant DBPs formed were CHCl₃, CHCl₂Br, CHClBr₂, DCAA, TCAA, BCAN, DCAN, TCAN, DBAN and TOX generated in all water treatment plants of greater cairo during 12 months. CHCl₃ was the major THMs followed by CHCl₂Br and CHClBr₂. The DCAA and TCAA yields indicated that the organic compounds possessing high DCAA formation potential than TCAA. Contribution of all haloacetonitriles to TOX is negligible compared to THMs compounds, DCAA and TCAA [19].

MATERIALS AND METHODS
The current experimental work has been carried out in the Fustat central water quality laboratory of Greater Cairo Water Company.

1. Samples
1. All the drinking water samples were collected from the treatment plants in the Cairo sector including Tebben, Kafr el elw, North helwan, Maadi, Fustat, Roda, Rodel farag, Ameria, Mostord, Shubra elkhheim and El-Obour during 12 months.
2. All the samples placed in brown bottles associated with dechlorinating agent represented by trace of sodium thiosulfate for THMs, TOX and EDBs analysis, 1 gm ammonium chloride for HAAs or without any dechlorinating agent for TOC analysis.
3. All the samples placed in plastic bottles associated with dechlorinating agent represented by trace of sodium thiosulfate for determining total algae count and the chlorophyll 'a' concentration.

2. DBPs Quantification
2.1. Methods
The samples were analyzed after the chlorination process to determine levels of THMs, EDB, HAAs and TOX. THMs and EDB concentrations were detected by using simple liquid-liquid extraction gas chromatographic method (GC/ECD, EPA method 501.2), HAAs concentrations were detected by using liquid-liquid extraction gas chromatographic method (GC/ECD, EPA method 552.3), TOX concentration was detected by shaking method (ISO method 9562) using TOX analyzer, TOC concentration was determined by UV-persulfate TOC analyzer (EPA method 415.1) and the chlorine residues were measured by the DPD colorimetric method according to APHA 1998 [20].

2.2. Equipments
HP gas chromatograph equipped with auto-injector and 30 meter DB-1701 fused silica capillary column and an electron capture detector (ECD) was used for analysis of THMs, EDB and HAAs. Data acquisition and processing were controlled by chemstation. High purity (99.99 %) grade gases were used. Helium was used as a carrier gas, nitrogen was used as make-up gas. Oxygen gas was used for furnace heating. All sample extracts including standards and blanks were injected in splitless mode.

2.3. Standards
Concentrations of THMs, EDB and HAAs were calculated by using external standard calibration method. A certified mixture standards of THMs including (chloroform, bromodichloromethane, dibromochloromethane and bromoform), HAAs including (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and Dibromoacetic acid (DBAA)) and EDB including (ethylene dibromide (EDB) and dibromochloropropane (DBCP)) obtained from Suppelco Inc. were used.

2.4. The operating conditions of the gas chromatograph
For THMs and EDB
- Injector temperature was 220°C in splitless mode.
- ECD temperature was 320°C.
- Carrier gas flow was 1 ml/minute and make-up gas flow was 60 ml/minute.
- Capillary column temperature program was: start with 40°C, ramp 10°C/minute to 100°C and holding for 5 min.

For HAAs
- Injector temperature was 210°C in splitless mode.
- ECD temperature was 290°C.
- Carrier gas flow was 1 ml/minute and make-up gas flow was 60 ml/minute.
- Capillary column temperature program was: start with 40°C, ramp 2.5°C/minute to 65°C, ramp 10°C/minute to 85°C, ramp 20°C/minute to 205°C.

2.5. Quality Control and Data Analysis
A procedural blank and the certified standards were analyzed routinely with each batch of samples. The detection limits of the methods were verified and carefully noticed. The linearity response of ECD for THMs, EDB and HAAs compounds, in area count, was observed. It was showed that the ECD was responding
linearly for all compounds during the current experiment. Mean concentrations of individual compounds in addition to sum of compounds were calculated.

3. The microbiological parameters
The total algae count (TAC) measured in all the treatment plants and during the four seasons using counting cell to enumerate plankton to limit the volume and area for ready calculation of population densities [21]. The low magnification method is the most suitable method for the plankton counting. It is easily manipulated providing with reasonably reproducible data.

The chlorophyll "a" concentration measured in all the treatment plants and during the fourth season only using the spectrophotometric technique [22] filtered after acidification. The chlorophyll "a" extraction was carried out in subdued light to avoid degradation by centrifuging large volume of water and the chlorophyll "a" concentrated in the extract with aqueous acetone followed by determining the optical density (absorbance).

RESULTS AND DISCUSSION
The results showed that the predominant DBPs formed were CHCl₃, CHCl₂Br, DCAA and TCAA generated during this experiment. CHCl₃ was the major THMs species followed by CHCl₂Br and TCAA followed by DCAA. The yields of CHCl₃, CHCl₂Br, DCAA and TCAA upon the chlorination process are presented in Tables 1 and 2.

Table 1. Concentration of Chloroform, Dichlorobromo methane and Residual chlorine in all the treatment plants in Cairo sector.

<table>
<thead>
<tr>
<th>PLANT</th>
<th>CHCl₃ (ppb)</th>
<th>CHCl₂Br (ppb)</th>
<th>R. Chlorine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEBBIN</td>
<td>33.24</td>
<td>10.12</td>
<td>1.95</td>
</tr>
<tr>
<td>KAFR EL-ELV</td>
<td>44.04</td>
<td>9.87</td>
<td>1.59</td>
</tr>
<tr>
<td>NORTH HELW</td>
<td>44.03</td>
<td>22.34</td>
<td>0.74</td>
</tr>
<tr>
<td>MAADI</td>
<td>40.20</td>
<td>9.22</td>
<td>0.67</td>
</tr>
<tr>
<td>FUSTAT</td>
<td>40.20</td>
<td>9.22</td>
<td>0.67</td>
</tr>
<tr>
<td>ROJA</td>
<td>39.35</td>
<td>9.78</td>
<td>0.69</td>
</tr>
<tr>
<td>ROO AL-FARAG</td>
<td>38.99</td>
<td>7.24</td>
<td>0.69</td>
</tr>
<tr>
<td>AMERIA</td>
<td>44.03</td>
<td>21.64</td>
<td>0.74</td>
</tr>
<tr>
<td>MOSTOROD</td>
<td>50.45</td>
<td>20.21</td>
<td>1.84</td>
</tr>
<tr>
<td>SHUBRA AL-KHENA</td>
<td>50.45</td>
<td>15.15</td>
<td>1.75</td>
</tr>
<tr>
<td>AL-OBOUR</td>
<td>52.25</td>
<td>24.62</td>
<td>1.89</td>
</tr>
</tbody>
</table>

As evident in Fig. (1, 2 and 3), the highest yields of CHCl₃, CHCl₂Br, DCAA, TCAA and TOX observed in N. helwan, Fustat, Ameria, Mostord, Shubra and El-Obour treatment plants. This was in agreement with the TOC values indicating to the correlation between all these parameters in these treatment plants. It was observed according to the data collected annually through the four seasons from all these plants that most of these parameters (CHCl₃, CHCl₂Br, DCAA and TCAA) increased during the last four months of the year (Sept., Oct., Nov. and Dec.). This was in agreement with many previous studies [23].

The total organic carbon (TOC) level used as indicator of the presence of organic matter in drinking water. The fulvic and humic acid components of the TOC are important precursors for THMs [26]. It was found that the higher the TOC value, the higher the levels of THMs formation. Increasing the TOC levels resulted in substationally increased total THMs production [27].
The microbiological data collected annually showed that the TAC increased obviously during the last season associated with increasing the chlorophyll "a" concentration (Table 3). The chlorophyll "a" concentration culpedied the "Eutrophic zone" during this season. It was found that the highest yields of TAC found in N. helwan, Fustat, Ameria, Mostord, Shubra and El-Obour plant. This was completely related to the DBPs produced after the chlorination process.

Table 3. Concentration of Chlorophyll "a" and Algae count in all treatment plants of Cairo sector.

<table>
<thead>
<tr>
<th>PLANT</th>
<th>Chlorophyll &quot;a&quot;</th>
<th>Algae count (Unit/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEBBIN</td>
<td>31.052</td>
<td>6.937</td>
</tr>
<tr>
<td>KAFF EL-ELW</td>
<td>28.866</td>
<td>6.909</td>
</tr>
<tr>
<td>NORTH HELWAN</td>
<td>24.866</td>
<td>7.350</td>
</tr>
<tr>
<td>MAADI</td>
<td>24.223</td>
<td>6.872</td>
</tr>
<tr>
<td>FUSTAT</td>
<td>31.739</td>
<td>7.913</td>
</tr>
<tr>
<td>RODA</td>
<td>26.740</td>
<td>6.830</td>
</tr>
<tr>
<td>ROD AL- FARA</td>
<td>32.336</td>
<td>6.602</td>
</tr>
<tr>
<td>AMERIA</td>
<td>32.018</td>
<td>8.086</td>
</tr>
<tr>
<td>MOSTOROD</td>
<td>15.716</td>
<td>7.960</td>
</tr>
<tr>
<td>SHOUBRA AL-KHEMA</td>
<td>26.870</td>
<td>7.367</td>
</tr>
<tr>
<td>AL-OBOUR</td>
<td>20.704</td>
<td>7.532</td>
</tr>
</tbody>
</table>

During this season, there was obvious increase in the TAC (Fig. 4) and this was indirect agreement between the TOC and TOX values (Table 4) or the other DBPs. The TOC represent one of the factors affecting the DBPs especially the THMs produced during the chlorination process. As evident in Fig. 5, there was association between the TAC and TOC in all the plants.

The CHCl₃, CHCl₂Br, DCAA and TCAA increased in N. helwan, Fustat, Ameria, Mostord, Shubra and El-Obour plant. This may be due to variation in the water quality (pH and temperature), treatment conditions (disinfectant dose and contact time) or increase in the organic pollutants (26). This increase may be due to the increase in the algal growth. All the algae species are rich in chlorophyll contents especially chlorophyll "a". This represented potent as precursors as humic and fulvic acids in production of these DBPs. This increasing yield could be due to the release of breakdown products of cell constituents [17].

Table 4. Concentration of Total organic carbon and Total organic halogen in all treatment plants of Cairo sector.

<table>
<thead>
<tr>
<th>PLANT</th>
<th>TOC (ppm)</th>
<th>TOX (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEBBIN</td>
<td>3.48</td>
<td>0.16</td>
</tr>
<tr>
<td>KAFF EL-ELW</td>
<td>3.53</td>
<td>0.14</td>
</tr>
<tr>
<td>NORTH HELWAN</td>
<td>3.63</td>
<td>0.19</td>
</tr>
<tr>
<td>MAADI</td>
<td>3.48</td>
<td>0.17</td>
</tr>
<tr>
<td>FUSTAT</td>
<td>3.74</td>
<td>0.18</td>
</tr>
<tr>
<td>RODA</td>
<td>3.54</td>
<td>0.17</td>
</tr>
<tr>
<td>ROD AL- FARA</td>
<td>3.53</td>
<td>0.13</td>
</tr>
<tr>
<td>AMERIA</td>
<td>3.60</td>
<td>0.16</td>
</tr>
<tr>
<td>MOSTOROD</td>
<td>3.46</td>
<td>0.20</td>
</tr>
<tr>
<td>SHOUBRA AL-KHEMA</td>
<td>3.75</td>
<td>0.18</td>
</tr>
<tr>
<td>AL-OBOUR</td>
<td>3.68</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The DBPs especially CHCl₃ could be dependent on the variation of the cellular biochemical composition (protein, lipids and carbohydrate) of the algae. The relative percentage of the cellular biochemical composition in the different algae may have a major influence as DBPs precursors [27, 28]. The bacterial contamination may be cause of the increase in some of DBPs [29]. The bacteria may be associated with algae in elevation of the DBPs but their contribution to the overall DBPs formation was likely to be minor relative to that from algae [14].

It has been observed that concentrations of the CHCl₃ were increased as the reaction time extended, but 60% of the CHCl₃ was formed during the first 5 minutes of the reaction. The CHCl₃, CHCl₂Br, DCAA and TCAA did not represent the only by-products which cause elevation of the TOX and also the increase in TOC may not be associated with increase in the TOX. This suggested that there were other factors added to the TOC to enhance the TOX values. It was found that the EDB and DBCP can not be produced during the chlorination steps in any treatment plant. It was showed that the organic impurities or the algae present naturally in the Nile water cannot involve in production of EDB and DBCP.

http://ijps.aizeonpublishers.net/content/2013/3/ijps211-215.pdf
The DCAA and TCAA yields indicated that the organic compounds possessing high DCAA formation potential than TCAA. These results were in agreement with the previous experimental studies [30]. It was proved that DCAA is a more potent carcinogen than CHCl₃ and TCAA [26, 31]. These results were not expected since the aquatic humic substances contain more aromatic carbon than algae’s organic matter, in the same time these results can indicate that algae may be a significant contributor to DBPs precursor, especially the most dangerous DCAA.

CONCLUSION
The DBPs varied seasonally after chlorination of the Nile water. The yields of CHCl₃, CHClBr, DCAA, TCAA and TOX increased in N. helwan, Fustat, Ameria, Mostord, Shubra and El-Obour water treatment plants associated with increasing the TAC during the four seasons. The TAC and DBPs as CHCl₃, CHClBr, DCAA and TCAA increased in all the Cairo treatment plants during the last season only. There was obvious relation between all these DBPs and the algal growth associated with the chlorophyll content. There was indirect relation between the TOC and TOX. The TOX values in all the treatment plants and during the four seasons did not depend only on the TOC or these DBPs. There were other factors in addition to the TOC involved in elevation of the TOX values. Finally the DBPs affected by many factors related to the treatment conditions and/or seasonal factors.

REFERENCES

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