ABSTRACT
The objective of this pilot-study is to evaluate the Granular Activated Carbon (GAC) performance for the removal of specific disinfection by-products (DBPs), trihalomethanes (THMs) and haloacetic acids (HAAs), from Athens drinking water. For this purpose, a GAC pilot filter-adsorber was operated in Galatsi WTP, Athens, for 235 days, until the GAC removal efficiency for individual THMs, HAAs and DOC was almost eliminated (breakthrough). From the experimental results, GAC bed life, GAC loading, carbon usage rate, and operation time to breakthrough for most THMs and HAAs were calculated. The average influent concentrations of the more chlorinated THMs and HAAs were higher than those of less chlorinated and more brominated species and their mass adsorbed on the GAC column was also higher, as expected according to Freundlich isotherm. TCA, TCM and DCA had the highest influent concentrations and they seemed to be better adsorbed than the rest. TBM, TBA and DBCA were almost not detected in feed water. Comparison of the GAC loading at breakthrough for pairs of compounds with similar average influent concentration showed that TCA is better adsorbed than TCM and that BDCA is better adsorbed than MCA, BDCM and DBCM. Desorption phenomena of some THMs and HAAs, probably caused by a sudden drop in influent concentration, were also noticed. The above findings represent real operation conditions for Athens drinking water. Further research is recommended on methods to reduce desorption from carbon beds.

KEYWORDS: GAC, adsorption, DBPs, THMs, HAAs, DOC, TCM, BDCM, DBCM, DCA, TCA.

1. INTRODUCTION
Chlorination is the most common disinfection method of drinking water. Although it is important to the supply of safe drinking water, it also leads to the formation of undesirable organic-by-products (Disinfection-by-products, DBPs). The two main classes of these compounds are trihalomethanes (THMs)¹ and haloacetic acids (HAAs)² (Arora et al., 1997). They are formed when chlorine reacts with bromide (Br⁻) and natural organic matter (NOM) in source waters (Nikolaou et al., 2004; Chowdhury et al., 2008).

¹ THMs: chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM). The sum of THMs in this work: TTHMs.
² HAAs: monochloroacetic acid (MCA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), monobromoacetic acid (MBA), dibromoacetic acid (DBA), tribromoacetic acid (TBA), bromochloroacetic acid (BCA), bromodichloroacetic acid (BDC), dibromochloroacetic acid (DBCA). The sum of 9 HAAs in this work: THAAs (elsewhere: HAA9).
Toxicology studies have shown all THMs, HAAs (especially TCA and DCA) and other DBPs to be carcinogenic or to cause adverse reproductive or developmental effects in laboratory animals (AWWA, 1990; USEPA, 2001; WHO, 2004; Nieuwenhuijsen, 2005; Richardson, 2005). The above findings have demonstrated the importance of regulating DBPs in drinking water. The THMs and HAAs regulations are presented in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>TCM</th>
<th>BDCM</th>
<th>DBCM</th>
<th>TBM</th>
<th>TTHMs</th>
<th>MCA</th>
<th>DCA</th>
<th>TCA</th>
<th>MBA</th>
<th>DBA</th>
<th>HAA5</th>
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<tr>
<td>EC [1998]</td>
<td>100</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>USEPA [1998]</td>
<td>80</td>
<td>60</td>
<td></td>
<td>100</td>
<td>100</td>
<td>20</td>
<td>50</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
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<td>WHO [2004]</td>
<td>200</td>
<td>60</td>
<td>100</td>
<td>100</td>
<td>20</td>
<td>50</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Several treatment alternatives have been proposed for the control of halogenated DBPs in drinking water, such as the removal of precursor material before it interacts with chlorine (by enhanced coagulation, membrane filtration, GAC adsorption), the removal of DBPs after formation (by GAC adsorption, air stripping), moving the point-of-chlorination to the end of the treatment process, the use of alternative oxidants and disinfectants e.t.c. (Clark et al., 1991; 1994; 2001; Singer, 1994).

Granular activated carbon (GAC) has been of a special interest due to its ability to remove a wide range of compounds such as odor and color causing compounds, NOM, THMs, HAAs and other toxic compounds (Speth and Miltner, 1990; 1998; Clark et al., 1991; Xie et al., 2002; Zhou et al., 2002; Babi et al., 2003; 2007; Kannan and Murugavel, 2008). GAC has already been used as the medium in a filter-adsorber or a postfilter-adsorber in many water treatment plants in Europe and in the U.S.A. (Graese et al., 1987; AWWA, 1990; Clark et al., 1991; Black et al., 1996).

2. BACKGROUND

The adsorption capacity of GAC varies widely, depending on the quality of the source water and the pretreatment given to it. In carbon adsorption columns treating natural water, many factors can reduce a carbon’s adsorption capacity such as: competition for adsorption sites by natural organic matter or other compounds, preloading of organics onto the carbon, development of biofilms, temperature, pH, variable influent concentrations and adsorption kinetics. On-site pilot studies can give a good approximation of full-scale performance of GAC for the removal of NOM and organic DBPs (AWWA, 1990; Black et al., 1996; Graese et al., 1987; Speth and Miltner, 1998).

Isotherm results for THMs in distilled-deionized water and activated carbon (Speth and Miltner, 1990) have shown that the higher the number of bromine atoms THMs molecules contain, the better they are adsorbed on carbon. This has been confirmed by pilot-plant and full-scale plant studies (Clark et al., 1991; AWWA, 1990). Also, it has been shown that activated carbon’s isotherm capacity for TCA in organic-free water is higher than for DCA, both being much higher than the capacity for each of THMs (Speth and Miltner, 1990; 1998). More recent research by others (batch experiments with synthetic finished water) showed that the more halogen atoms a HAA contains, the higher GAC adsorption capacity for it, but the lower its biodegradation rate. Also, for two HAAs with the same number of halogen atoms, the HAA with more bromine atoms is more readily adsorbed to GAC (Zhou et al., 2002).

Previous research on the drinking water of Athens, Greece, has showed the occurrence of THMs, HAAs and natural organic matter in the chlorinated finished drinking water (Golfinopoulos et al., 2003; Nikolaou et al., 2004). The removal of total THMs, total HAAs and dissolved organic matter from the drinking water of Athens by GAC treatment has been studied on a pilot-scale (Babi et al., 2003; 2007).

The objective of this pilot study is to evaluate the performance of a GAC filter-adsorber for the removal of the individual members of THMs and HAAs from water intended for human consumption in Athens.
3. MATERIALS AND METHODS

3.1 Pilot-plant operation.
The pilot-plant experiments were conducted in the Water Treatment Plant of Galatsi, Athens (GTP), which is of conventional design. Water treatment applied in the Plant includes prechlorination, coagulation, flocculation, sedimentation, rapid gravity sand filtration and postchlorination.
The pilot-plant consists of a rapid gravity GAC filter. The GAC filter column is constructed of plexiglass and stainless steel to avoid problems of possible contamination or adsorption of organics from the treated water (APHA, 1992; Babi et al., 2003; 2007). In this study the adsorption efficiency of a GAC (10x20 U.S.mesh) filter-adsorber (Loading rate: 7.2 m h\(^{-1}\), Empty Bed Contact Time (EBCT): 9.5 min, bed depth:1.14 m, 1 Bed Volume: 32.29 L, Mean duration of filter run: 29.2 h) receiving prechlorinated water from the overflow of the sedimentation tanks, was evaluated.
The operation of the GAC filter was interrupted by regular backwashing with chlorinated sand-filtered water, when the pressure drop through the filter reached a maximum desirable level. The operation of the GAC filter-adsorber continued, until the GAC removal efficiency for individual THMs, HAAs and DOC was almost eliminated (235 days). The amount of GAC used was 13.89 kg. The whole experimental cycle was defined as adsorption cycle for the purpose of this research.

3.2 Sampling and analytical procedure.
Ten sampling events were performed regularly during the operation period of the GAC filter-adsorber. A little after the start of a filter run, water samples were taken with a peristaltic pump through silicon tubing from the inlet, outlet and different depths in the GAC column. Sample preparation and preservation were performed according to Standard Methods (APHA, 1992).

For the analyses of the samples the following methods were used: THMs: LLE (with MTBE)-GC-ECD: USEPA method 551.1 (USEPA, 1998a; Nikolaou et al., 2002a); HAAs: LLE (acidic methanol esterification) - GC-ECD: a modification of USEPA method 552.2 (USEPA, 1998b; Nikolaou et al., 2002b); DOC: Persulfate-Ultraviolet oxidation for most of the sampling events after sample filtration through 0.45 µm syringe filter (APHA, 1992); Free chlorine: DPD colorimetric method; Bromide: Ion Chromatography; Temperature, pH: Standard Methods (APHA, 1992).
The analyses for THMs and HAAs were performed in the Water and Air Quality Laboratory of the Department of Environmental Studies of the University of the Aegean. The analysis for DOC was performed in Kιourka Laboratory of EYDAP, while the rest of the analyses and measurements were carried out in Galatsi Laboratory of EYDAP.

4. RESULTS AND DISCUSSION

4.1 Experimental results and calculations.
From the measurements and analyses performed, the following results came out:
The influent values for some parameters, like temperature, pH and bromide concentration, did not change significantly through the GAC bed. Free residual chlorine in the feed water was about 0.6 mg l\(^{-1}\), while it became zero after the first 20 cm depth of the GAC bed as expected due to the catalytic action of the activated carbon (AWWA, 1990). The temperature of the influent water varied seasonally, with an average value of 13 °C. The mean pH of water was 7.5 and the mean bromide concentration was 23.4 µg l\(^{-1}\).

4.2 Removal profiles.
The breakthrough point for individual THMs and HAAs was defined as the point of 0 % removal, which was not significantly and continuously exceeded during the further operation of the GAC adsorber. The measured influent and effluent concentrations of the individual THMs and HAAs have been plotted versus the volume of treated water (removal profiles: Figures 1-6). The analytical error in the detection of concentrations of THMs and HAAs (Nikolaou et al., 2002a; 2002b) was taken into account in the assessment of the results.
The cumulative influent and effluent mass of the specific compounds at each sampling point was also calculated from the area between the respective curves and the axis of water
volume in Figures 1-6. This was based on the assumption that between two successive sampling events the influent and effluent concentrations were constant and equal to the arithmetic mean of the respective values of the two sampling events. The cumulative mass removal of the compounds by GAC was calculated by subtracting the cumulative influent and effluent mass during the filter-adsorber operation. It was plotted versus time of operation for some species (GAC loading profiles: Figures 7, 8).

The final results at breakthrough, including GAC bed life (Bed Volumes of water), GAC loading (total adsorbed mass of a specific compound per unit mass of carbon), carbon usage rate (g of GAC per m$^3$ of treated water, CUR) and time of operation were calculated by linear interpolation. All the above results are presented in Table 2.

The interpretation of the results was made under the hypothesis that at breakthrough, as it was defined, equilibrium had been established between the concentration of the adsorbed compounds on the whole GAC bed and their average concentration in the influent water - and not complete saturation of GAC. The equilibrium is described by the Freundlich isotherm (Treybal, 1980).

The average influent concentration of each compound of interest until breakthrough (Table 2) was calculated by dividing the cumulative influent mass of the compound until breakthrough by the total volume of treated water, which we considered to represent the real mean concentration in contact with the GAC better than does the simple average of the measured influent concentrations.

**Table 2. Final results for THMs and HAAs at breakthrough**

<table>
<thead>
<tr>
<th>Average infl. conc</th>
<th>units</th>
<th>TCM</th>
<th>BDCM</th>
<th>DBCM*</th>
<th>MCA*</th>
<th>MBA*</th>
<th>DCA*</th>
<th>BCA*</th>
<th>TCA</th>
<th>DBA*</th>
<th>BDCA*</th>
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<tbody>
<tr>
<td>µg l$^{-1}$</td>
<td></td>
<td>13.25</td>
<td>3.61</td>
<td>3.14</td>
<td>3.36</td>
<td>0.64</td>
<td>7.10</td>
<td>0.90</td>
<td>13.34</td>
<td>0.50</td>
<td>2.93</td>
</tr>
<tr>
<td>GAC capacity</td>
<td>mg kg$^{-1}$ GAC</td>
<td>458.0</td>
<td>149.4</td>
<td>130.4</td>
<td>174.6</td>
<td>42.7</td>
<td>516.0</td>
<td>35.0</td>
<td>585.7</td>
<td>28.5</td>
<td>242.6</td>
</tr>
<tr>
<td>Time to BT</td>
<td>days</td>
<td>210.5</td>
<td>215.2</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>223.6</td>
<td>235</td>
<td>235</td>
</tr>
<tr>
<td>GAC bed life</td>
<td>bed volumes</td>
<td>31917</td>
<td>32626</td>
<td>35632</td>
<td>35632</td>
<td>35632</td>
<td>35632</td>
<td>35632</td>
<td>33899</td>
<td>35632</td>
<td>35632</td>
</tr>
<tr>
<td>CUR</td>
<td>g GAC m$^{-3}$ water</td>
<td>13.47</td>
<td>13.18</td>
<td>12.07</td>
<td>12.07</td>
<td>12.07</td>
<td>12.07</td>
<td>12.07</td>
<td>12.07</td>
<td>12.07</td>
<td>12.07</td>
</tr>
</tbody>
</table>

(*) For DBCM, MCA, MBA, DCA, BCA, DBA, BDCA at the end of experimental cycle, that is before breakthrough.

**4.2.1 THMs**

THMs are small volatile molecules, which are hydrophobic and non biodegradable. They are adsorbed on GAC to some extent (AWWA, 1990; Arora et al., 1997). The average influent concentration of each of THMs was different (Table 2). TBM was detected in influent water only 3 times (mean con. 0.22 µg l$^{-1}$).

THMs removal profiles are presented in Figures 1,2. The available experimental data for TBM were not enough for a proper removal profile.

The above removal profiles indicate that breakthrough for TCM and BDCM occurred between the 8th and 9th sampling event, while for DBCM it occurred between the 9th and 10th sampling event. The time of operation to breakthrough was 210.5, 215.2 and more than 235 days respectively.

The experimental results indicate that the GAC loading for THMs with higher number of chlorine atoms was higher (highest for TCM). These results seem to be opposing those by other researchers, according to which the higher the number of bromine atoms THMs molecules contain, the better they are adsorbed on carbon (Speth and Miltner 1990; AWWA, 1990; Clark et al., 1991).

However, they can be justified if we consider the fact that the average influent concentration of THMs species of higher number of chlorine atoms was higher (Table 2) and resulted in higher adsorbed mass by the activated carbon, according to the Freundlich isotherm (Treybal, 1980), in which the constants 1/n are supposed to be almost equal for all THMs, as have been referred in the relevant literature (Speth and Miltner, 1990).
Some desorption incidents of TCM and BDCM were also noticed, when a sudden drop in influent concentration occurred or near the breakthrough point (Figure 1). These incidents are expected for weakly adsorbing compounds and are usually caused by either sudden decreases in influent concentration or the presence of stronger adsorbing compounds (Thacker et al., 1983; Voudrias et al., 1986; AWWA, 1990).

4.2.2 HAAs
HAAs are soluble in water and biodegradable. They are ionized under the pH conditions of the drinking water and they are reported to be removed by GAC adsorption and biodegradation (Arora et al., 1997; Speth and Mittner, 1998; Xie and Zhou, 2002).

The average influent concentration was different for each of HAAs (Table 2). DBCA was detected in influent water only once (mean con. 0.04 µg l⁻¹) and TBA was not detected at all. MBA was detected few times in influent water.

HAAs removal profiles for the 7 HAAs are presented in Figures 3-6.

The above removal profiles show that breakthrough occurred only for TCA (between the 8th and 9th sampling event), while for the rest HAAs it had not occurred yet (BT time more than 235 days). The total removed mass of the above HAAs (TCA at breakthrough and the rest HAAs at the end of the experimental cycle) is also presented in Table 2.

According to recent research (batch experiments with synthetic finished water), the more halogen or bromine atoms a HAA contains, the higher GAC adsorption capacity for it (Zhou et al., 2002).
Also, activated carbon’s isotherm capacity for TCA is higher than for DCA, both being much higher than the capacity for each of THMs (Speth and Mittner, 1990; 1998). The above have been proved in case of equal influent concentrations of the compounds of interest. In our case, this does not happen for all HAAs. The average influent concentrations of more chlorinated HAAs were much higher compared to those of less chlorinated or more brominated ones and so was the GAC loading for them (MCA loading higher than MBA, DCA higher than DBA, TCA higher than DCA), as should be expected according to the Freundlich isotherm. GAC loading at breakthrough was highest for TCA and seemed to be lower for DCA and much lower for the rest species. From the above results general conclusions cannot be drawn, since the average influent concentrations of the HAAs species differed from one another and breakthrough had not occurred for all HAAs until the end of the experimental cycle.

However, we could compare some pairs of HAAs as to their adsorbability on GAC during the experimental cycle. The more halogen atoms containing BDCA was better adsorbed than MCA, although its average influent concentration was probably lower. This result is indicative of the fact that the more halogen atoms in a HAA, the better it is adsorbed on the GAC column.

In addition, although MBA seems to be better adsorbed than DBA and with a higher average influent concentration (Table 2), no conclusion can be drawn because of the high analytical error of the low concentrations of MBA (Nikolaou et al., 2002b). We can also compare some pairs of HAAs - THMs of similar average influent concentration. Between TCA and TCM which were almost at the same level in feed water, TCA was much better adsorbed until breakthrough (Table 2, Figure 7). BDCA, with an influent concentration almost at the same level as those of BDCM and DBCM, was much better adsorbed than both
of them (Table 2, Figure 8). These results indicate that probably HAAs are better adsorbed than THMs with the same number and/or kind of halogen atoms. All the above findings represent real operation conditions for Athens drinking water. The possible contribution of biodegradation to individual HAAs removal has not been studied. Desorption phenomena of MBA, DCA and TCA, probably caused by a sudden drop in influent concentration were observed towards the end of the adsorption cycle (Figures 3, 4).

4.2.3 DOC
DOC parameter includes humic substances which are hydrophobic and adsorbable on GAC and non-humic substances which are hydrophilic, non adsorbable and more easily removed by biodegradation (AWWA, 1990). The average influent concentration of DOC was 1.8 mg L⁻¹. DOC breakthrough – that is 0% removal – was not observed until the end of the experimental period. At that time, the DOC loading of GAC was 55.83 g DOC kg⁻¹GAC and the carbon usage rate (CUR) was 11.96 g m⁻³. The contribution of biodegradation to DOC removal was not studied.

5. CONCLUSIONS
This work has evaluated the performance of a GAC filter-adsorber for the removal of the individual THMs and HAAs from drinking water of Athens. From the experimental data, the GAC bed life, GAC loading, carbon usage rate and time of operation to breakthrough for most THMs and HAAs were calculated.

The average influent concentrations of more chlorinated THMs and HAAs were higher than those of less chlorinated and more brominated species and therefore the GAC loading for them was also higher, as expected according to Freundlich isotherm. TCA, TCM and DCA had the highest concentrations and seemed to be better adsorbed than the rest. TBM, TBA and DBCA were almost not detected in feed water. Comparison of GAC adsorption efficiency for pairs of compounds with similar average influent concentration showed that TCA is better adsorbed than TCM and that BDCA is better adsorbed than MCA, BDCM and DBCM.

The above results probably support the conclusion by other researchers that the more halogen atoms in a HAA, the better it is adsorbed on GAC. They also indicate that probably HAAs are better adsorbed than THMs with the same number and/or kind of halogen atoms. The above findings represent real operation conditions for Athens drinking water. Desorption phenomena of THMs and HAAs, probably caused by a sudden drop of influent concentration, were also noticed. Further research is recommended on methods to reduce desorption from carbon beds.

ACKNOWLEDGEMENTS
The authors gratefully acknowledge the Athens Water Supply and Sewerage Company (EYDAP), for supporting this work.

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