

1 Influence of granular activated carbon media properties on natural organic 2 matter and disinfection by-product precursor removal from drinking water

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7

8 **Abstract**

9 Operational and financial constraints challenge effective removal of natural organic matter
10 (NOM), and specifically disinfection by-product (DBP) precursors, at remote and/or small
11 sites. Granular activated carbon (GAC) is a widely used treatment option for such locations,
12 due to its relatively low maintenance and process operational simplicity. However, its
13 efficacy is highly dependent on the media capacity for the organic matter, which in turn
14 depends on the media characteristics.

15 The influence of GAC media properties on NOM/DBP precursor removal has been studied
16 using a range of established and emerging media using both batch adsorption tests and rapid
17 small-scale column tests. DBP formation propensity (DBPFP) was measured with reference
18 to trihalomethanes (THMs) and haloacetic acids (HAAs). All GAC media showed no
19 selectivity for specific removal of precursors of regulated DBPs; DBP formation was a
20 simple function of residual dissolved organic carbon (DOC) levels.

21 UV₂₅₄ was found to be a good surrogate measurement of DBPFP for an untreated water
22 source having a high DOC. Due to the much-reduced concentration of DBP precursors, the
23 correlation was significantly poorer for the coagulation/flocculation-pretreated water source.

24 Breakthrough curves generated from the microcolumn trials revealed DOC removal and
25 consequent DBP reduction to correlate reasonably well with the prevalence pores in the 5-10
26 nm range. A 3-6 fold increase in capacity was recorded for a 0.005 to 0.045 cm³/g change in
27 5-10 nm-sized pore volume density. No corresponding correlation was evident with other
28 media pore size ranges.

29 *Keywords: GAC, NOM, pore size, THM, HAA, formation propensity*

30 **1 Introduction**

31 Granular activated carbon (GAC) is used extensively in drinking water treatment in various
32 roles, including removal of pesticides, heavy metals and other micro pollutants, and more
33 recently in wastewater reuse (de Almeida Alves et al., 2019, Hoslett et al., 2018; Sun et al.,
34 2018). The process is also frequently applied downstream of conventional coagulation/
35 clarification for supplementary removal of natural organic matter (NOM) and to improve the
36 bio-stability of the water, through removal of assimilable dissolved organic carbon (DOC)
37 (Bhatnagar and Sillanpää, 2017; Graf et al., 2014; Velten et al., 2011, Liao et al., 2019). It
38 may also be employed at the beginning of the water treatment works (WTWs) as a
39 “roughing” filter to aid with NOM and pesticide removal (Ratnayaka et al., 2008; Reckhow
40 and Singer, 2010; Zeng et al., 2019).

41 One of the key drivers for NOM removal is the reduction of disinfection by-product (DBP)
42 forming compounds following chemical disinfection (Ndiweni et al., 2019), expressed as the
43 formation propensity (hence DBPFP). The trihalomethanes (THMs) and haloacetic acids
44 (HAAs) have been the most extensively studied DBPs since they are usually present at the
45 highest mass concentration (Gibert et al., 2013; Golea et al., 2017). In the EU, currently only
46 THMs are regulated, with the maximum permissible combined concentration being 100 µg/L.
47 Limits of 80 µg/L or 60 µg/L for 9 or 5 HAAs respectively are currently under consideration
48 in the EU, in alignment with US regulations (USEPA, 2010).

49 NOM is substantially removed by coagulation/clarification in large-scale potable WTWs,
50 provided rigorous monitoring and control is applied. However, this process is not always
51 appropriate at small scale in remotely located sites where low-maintenance processes are

52 preferred to reduce labour costs. These include membrane and adsorption technologies, with
53 GAC sometimes favoured on the basis of cost effectiveness and versatility (Bhatnagar and
54 Sillanpää, 2017; Iriarte-Velasco et al., 2008). It is known that the high molecular weight
55 (MW) hydrophobic (HPO) NOM fraction is readily removed by conventional coagulation,
56 such that the influent NOM to GAC processes in secondary potable treatment stages is
57 usually dominated by the low MW and relatively hydrophilic (HPI) fractions (Matilainen et
58 al., 2006). The HPO fraction is generally more reactive with chlorine, with thus a high
59 DBPFP (Golea et al., 2017). When GAC is used as a roughing filter, the main loading of
60 NOM is from HPO and high MW organic compounds. In this case, high MW NOM can
61 block the pores of the adsorbent, preventing other compounds from accessing the adsorbent.
62 The NOM characteristics and the corresponding required GAC media properties are thus
63 influenced by the position of the adsorption process in the treatment scheme (Valdivia-Garcia
64 et al., 2016).

65 One of the most significant GAC media properties is pore size (d_p) distribution; the useful
66 pore size range for NOM has been shown to be the secondary micropores (1-2 nm) and the
67 mesopores (2-50 nm), with pores smaller than 1 nm offering negligible adsorption (Dastgheib
68 et al., 2004; Velten et al., 2011). High MW (1-10 kDa) NOM such as humic substances with
69 molecular diameters above 2 nm are adsorbed largely within the mesopores. However,
70 adsorption is not solely governed by bulk physical properties, since physicochemical
71 properties – and specifically surface charge and hydrophobicity – also impact on adsorption;
72 HPO NOM is preferentially removed over hydrophilic material. It thus follows that the low
73 MW hydrophilic fraction, whilst less reactive with chlorine, poses the greatest challenge to

74 removal by GAC and may still have a sufficiently high DBPFP to be problematic (Golea et
75 al, 2017).

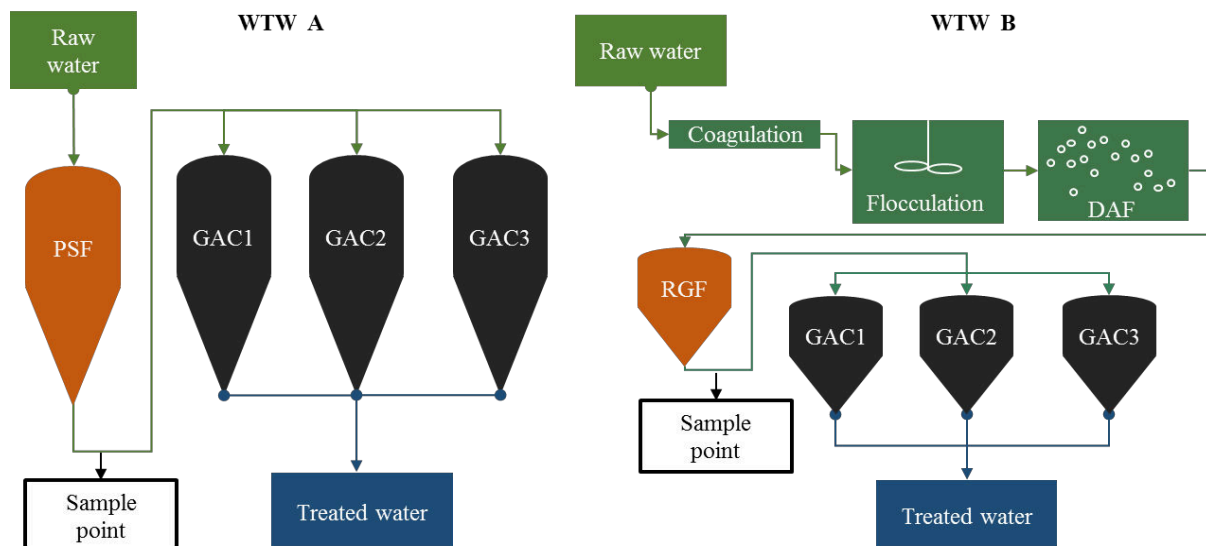
76 Given the above challenge presented by NOM removal by GAC it is of interest to determine
77 (a) the most effective GAC media for DBP precursor removal from different water sources
78 and (b) the most effective position of the GAC process in the treatment train. Previous studies
79 of GAC adsorption of NOM have tended to focus on physicochemical characteristics of the
80 NOM, rather than those of the GAC (Aschermann et al, 2018; Shimabuku et al, 2017; Velten
81 et al, 2011), with this work including the key area of competitive adsorption/desorption of
82 NOM and micropollutants (Aschermann et al, 2018; Piai et al, 2019). However, there have
83 thus far been few studies quantitatively correlating NOM or DBPFP adsorption with media
84 characteristics. Those studies that have encompassed GAC media with a range of pore sizes
85 (Gui et al, 2018) have not quantitatively correlated media capacity with pore-related
86 parameters.

87 The current study correlates GAC properties, specifically the media pore size distribution,
88 with NOM and DBPFP removal from two water sources having differing NOM chemistry
89 with reference to DBPFP. Tests encompassed both batch adsorption measurements and small-
90 scale media column tests for determining adsorption capacity, and DBPFP both as
91 trihalomethanes (THMFP) and haloacetic acids (HAAFP). Outcomes can then be expected to
92 (i) inform decisions regarding GAC media selection for NOM removal, and (ii) direct
93 developments on novel adsorptive media for maximum NOM capacity.

94 2 Methods and materials

95 2.1 Sampling

96 Source water was taken from two WTWs of differing process configuration (Fig. 1). WTW A
97 employs simple media filtration via a pressurised sand filter (PSF) followed by GAC
98 adsorption. WTW B uses clarification by conventional coagulation-flocculation followed by
99 dissolved air flotation (DAF), rapid gravity filtration (RGF) and GAC adsorption. The water
100 used in the current study was sampled from the filtrate, i.e. downstream of the PSF stage at
101 the WTW A site (*Water A*) and the RGFs at WTW B (*Water B*).



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103 Figure 1. Water treatment flow sheet at the 2 WTWs featuring rudimentary and advanced pretreatment
104 respectively. WTW A: Pressure sand filtration; WTW B: Coagulation/flocculation, dissolved air
105 flotation and rapid gravity filtration.

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107 2.2 GAC media

108 GAC media sourced from four different precursor materials were used, selected to encompass
109 a range of specific surface areas and d_p values, and comprised:

- 110 • Bituminous coal: *COL-L900* (Carbon-Activated LTD, Bristol, UK); *Filtrisorb F400*
111 (Chemviron, Tipton, UK).
- 112 • Coal: *208 EA* (Chemviron); *Hydraffin XC30* (Donau Carbon, Frankfurt, Germany).
- 113 • Coconut shell: *DEO, HT5* (Eurocarb, Bristol, UK); *FY5* (CPL Carbon Link, Wigan, UK))
- 114 • Bovine bones: *Brimac* (Inverclyde, UK).

115 **2.3 GAC preparation**

116 For the batch adsorption isotherm tests, the GAC media was crushed and fractionated by
117 sieving to generate a 38-90 μm size fraction. The media were then washed thoroughly in
118 ultrapure water, dried overnight at 105°C and kept in a desiccator until use for the adsorption
119 capacity batch tests. For the rapid small-scale column test (RSSCT), the GAC was crushed
120 using a hammer mill, and then sieved to between 212 and 300 μm , yielding a column
121 diameter:grain size ratio of >30:1 and so avoid channelling effects. The media were then then
122 rinsed and dried as with the isotherm tests (Philippe et al., 2010), then re-wetted prior to
123 testing by boiling in DI water for 10 minutes. Media preparation in this manner has been
124 shown to have no significant impact on the internal structural pore features (Ando et al.,
125 2010).

126 **2.4 GAC characterisation using N₂ pore size distribution**

127 The total pore volume V_{total} of the dried media was measured as the adsorbed volume of N₂
128 gas near the saturation volume ($P/P_0=0.98$) (Iriarte-Velasco et al., 2008), and the surface area
129 calculated from Brunauer–Emmett–Teller (BET) theory (Brunauer et al., 1938). The d_p
130 distribution was determined using density functional theory (DFT) for pores sizes quantified
131 between 0.7 and 36 nm (Velten et al., 2011). The DFT model was employed to provide a

132 more accurate interpretation of the isotherm data for non-homogenous liquids on
133 microporous materials (Lastoskie et al., 1993). Calculations assumed a graphite structure with
134 slit-like pore geometry (Iriarte-Velasco et al., 2008; Moore et al., 2001) using an *ASAP 2010*
135 (Micrometrics, St Andrews, UK) physisorption apparatus. GAC were primarily characterised
136 by the volume of the secondary micropores (1-2 nm) and mesopores (2-50 nm), since smaller
137 pores have been shown to exhibit negligible adsorption of NOM (Velten et al., 2011). Further
138 analysis of the d_p distribution was undertaken to correlate specific pore size ranges with
139 removal of NOM, with a maximum measured pore size of 30 nm.

140 **2.5 Adsorption capacity batch tests**

141 The prepared media were dosed at 0-0.1 g/L, with dose modulated based on the DOC of the
142 source water, and agitated continuously in an orbital shaker at 200 rpm for 24 hours at 20°C,
143 which preliminary trials established was a sufficient period for equilibration. The water
144 samples were then 0.45 µm-filtered prior to analysis. The equilibrium adsorption capacity
145 (q_e , mg DOC/g adsorbent) was calculated as the change in solution DOC concentration $C_i -$
146 C_e , C_i being the initial and C_e the equilibrium concentration, divided by the adsorbent
147 concentration D_o . Base D_o values of 150 and 50 mg/L for *Water A* and *B* respectively were
148 established as being appropriate for removing significant organic matter whilst still leaving a
149 sufficient (>1 mg/L) residual DOC concentration to permit subsequent THMFP and HAAFP
150 analysis. All tests were carried out in duplicate.

151 **2.6 Rapid small-scale column tests**

152 1000 L samples of water were taken from WTW A and B and were passed through media
153 beds of 15 mm diameter and 140 mm height for 14 days. The RSSCT columns were

154 undertaken according to the recommendations of [Crittenden et al. \(2012\)](#), following the
155 proportional intra-particle diffusivity (PD) model:

$$156 \quad \frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d_{G,SC}}{d_{G,LC}} = \frac{t_{SC}}{t_{LC}} \quad \text{Equation 1}$$

$$157 \quad M_{SC} = EBCT_{LC} \times \frac{d_{p,SC}}{d_{p,LC}} \times Q_{SC} \times \rho_{LC} \quad \text{Equation 2}$$

158 Where $EBCT_{LC}$ = empty bed contact time in full-scale adsorber; $EBCT_{SC}$ = empty bed
159 contact time for small experimental columns; $d_{G,SC}$ = diameter of GAC particles in small
160 column; $d_{G,LC}$ = diameter of GAC particles in full scale column; t_{SC}/t_{FS} = time required to
161 conduct a small-scale test (t_{SC}) relative to the time necessary to conduct a large-scale test
162 (t_{FS}); M_{SC} = the mass of media in the small column; Q_{SC} = the flow in the small column; ρ_{LC} =
163 density of the GAC media in the large column. Equation 2 was used to ensure that the
164 different GAC media densities were accounted for.

165 For NOM removal, the PD approach has proven to work well since the relatively high MW
166 organic matter diffuses significantly faster into the pores of the GAC when compared to
167 micropollutants ([Summers et al., 1995](#)). Scaled from an operational empty bed contact time
168 of 20 minutes for full scale adsorbers as typically used in Scottish Water ($EBCT_{LC}$), this
169 translated to an EBCT in the experimental columns ($EBCT_{SC}$) of 4.24 minutes for a 25 mL
170 bed volume.

171 **2.7 Sample chlorination and DBP formation potential determination**

172 250 mL water samples were diluted to a concentration of 1 mg C/L and buffered to pH 7 and
173 dosed with NaOCl at a Cl_2 :DOC weight ratio of 5:1. Samples were then sealed and stored in
174 the dark at a temperature of 25°C for seven days. The chlorine was then quenched with

175 excess sodium thiosulphate and the THM and HAA concentrations measured. The total THM
176 concentration (tTHM) was measured using gas chromatography spectrometry with headspace
177 injection using the standard USEPA 551 method (USEPA, 1998). The total concentration of
178 the five most predominant HAAs (tHAA₅) was measured using liquid-liquid separation and
179 analysis by gas chromatography with mass spectrometric detection following the USEPA
180 method 552.3 (APHA, 2012), with at least seven injections undertaken for each
181 measurement.

182 **3 Results and discussion**

183 **3.1 Source water characterisation**

184 Sample filtrate water quality varied significantly between the two sites (Table 1) due to the
185 differences in pre-treatment, *Water B* samples receiving full clarification whereas *Water A*
186 which was treated only by sand filtration (Fig. 1). Whilst the pH and conductivity values
187 were both lower for the *Water A* samples (6.8 and 166 $\mu\text{S}/\text{cm}$, cf. 8.1 and 569 $\mu\text{S}/\text{cm}$ for
188 *Water B*), reflecting the reduced chemical addition, the DOC of *Water A* was double that of
189 *Water B* and the UV₂₅₄ absorption 3.8 times higher. UV₂₅₄ absorption is recognised as
190 broadly reflecting the HPO content of the water (Bhatnagar and Sillanpää, 2017), which was
191 commensurately 3.4 times higher for *Water A*. Conversely, the HPI content was 2.8 times
192 lower. The elevated DOC and HPO concentrations of *Water A* were reflected in THMFP and
193 HAA₅FP values, respectively 1.25 and 4.2 times higher on average for *Water A* cf. *Water B*.
194 These factors increased to 2.4 and 8 respectively under worst-case conditions. No significant
195 change in the distribution of individual DBP species was observed between the two samples,
196 with trichloromethane being the predominant THM (85-90% by weight) and the

197 dichloroacetic and trichloroacetic acids making up 80-85% of the tHAA₅ concentration in
 198 both cases.

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207 **Table 1:** Physicochemical characteristics of the two different water sources.

<i>Parameter</i>	<i>Water A</i>	<i>Water B</i>
pH	6.8	8.1
DOC (mg/L)	5.98	3.12
UV ₂₅₄ (/cm)	0.254	0.068
SUVA (mg/L/m)	4.25	2.18
tTHM (µg/L)	676.3	282
THMFP (µg/L per mg DOC)	113.1	90.4
tHAA (µg /L)	1006.4	126
HAA ₅ FP (µg/L per mg DOC)	168.3	40.4
Colour (mg/L Pt/Co)	33	4.47
Turbidity (NTU)	0.37	0.1
Conductivity (µS/cm)	166	569
HPO (mg/L)	3.44	1
TPI (mg/L)	1.25	0.71
HPI (mg/L)	0.37	1.05

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209 **3.2 Physical media characteristics**

210 Total pore volumes ranged from 0.331 (*DEO*) up to 0.581 cm³/g (*HT5*) for the GAC media
 211 investigated. Mesopore volumes measured for the GAC media studied ranged from as low as
 212 0.004 cm³/g (*FY5*) up to 0.156 cm³/g (*XC30*). The secondary micropores were between 0.174
 213 cm³/g (*DEO*) and 0.401 cm³/g (*HT5*) (Table 2). None of the media had d_p values above 27.3

214 nm. The media with the highest total pore volume (*HT5*) had pores that were predominantly
215 in the 1-2 nm pore size range (0.401 cm³/g). The media with the most evenly distributed pore
216 sizes was the coal media *XC30* with 0.205 (57%) and 0.156 (43%) cm³/g distributed between
217 micro and mesopores respectively (Fig 2). *F400* had a 78:22 distribution of pore volume
218 between the micropore and mesopore size range. Further examination revealed pore size to be
219 predominantly below 5 nm, contributing 84.0-99.9% of the total pore volume (Fig 2). The
220 media with the highest proportion of small pores (<5) nm were the coconut shell media (*FY5*
221 and *DEO*) at 99.8 and 99.9%. Conversely, the GAC with the smallest proportion of small
222 pores were the coal-based *XC30* and the bone char media *Brimac*, at 83.9 and 85.7%
223 respectively.

224 There was good agreement between the specific surface area values measured in the current
225 study (S_{BET}) and those reported by the supplier ($S_{BET,s}$) and other researchers (Table 2). The
226 exception was the S_{BET} for *Brimac* (bone char). For *Brimac*, S_{BET} has been previously reported
227 as being 130-283 m²/g, with a V_{total} of 0.287 cm³/g (Moreno et al., 2010; Nili-Ahmadabadi,
228 2011), compared to the much higher values of 841 m²/g and 0.430cm³/g respectively
229 recorded in the current study. For *F400*, there was a small difference in the $V_{micropores}$
230 measured in the current study (0.271 cm³/g), a value which was 20-33% lower than the 0.30-
231 0.41 cm³/g range previously reported (Summers et al., 2010, Dastgheib et al., 2004, and
232 Gibert et al., 2013, Table 2). Differences are likely to reflect the media sample heterogeneity,
233 a point noted by other researchers (Ando et al., 2010) and differences in the range of pore
234 sizes quantified during the analysis. The surface area of the *Brimac* media was nonetheless
235 the lowest measured of all those investigated.

236 **Table 2:** The physicochemical properties of the media used for removal of NOM from two different water sources.

<i>GAC media</i>	V_{total}^1 cm ³ /g	d_p nm	$V_{micropores}^2$ cm ³ /g	$V_{meso-pores}^3$ cm ³ /g	$DFT\ area\ (m^2/g)^4$			<i>Granulation</i> ⁵ mm	$S_{BET,s}^5$ m ² /g	S_{BET} m ² /g	$IN^{5,6}$ mg/g	<i>Precursor</i> ⁵
					0.7-1.7	1-2	>2					
<i>COL-L900</i>	0.460	≤26.1	0.347	0.112	444	506	72	0.425-1.70	900-1000	977±5	900	Bituminous coal
<i>F400</i>	0.442	≤26.1	0.271	0.073	431	416	49	0.425-1.70	1050	1032±5	1050	Bituminous coal
<i>208EA</i>	0.517	≤16.1	0.301	0.120	424	465	67	0.6-1.7	1000	1078±6	1000	Coal
<i>XC30</i>	0.511	≤26.1	0.205	0.156	325	340	66	0.6-2.36	1000	986±6	950	Coal
<i>DEO</i>	0.331	≤27.3	0.174	0.013	274	285	8	0.6-1.70	800	809±11	825	Coconut shell
<i>HT5</i>	0.581	≤27.3	0.401	0.029	621	652	14	0.42-1.70	1400	1419±12	1300	Coconut shell
<i>FY5</i>	0.400	≤16.1	0.288	0.004	452	471	3	1.40-3.35	1150	1043±11	1100	Coconut shell
<i>Brimac</i>	0.430	≤25	0.246	0.131	334	373	62	0.7-2.38	200	841±3	700	Bovine bones

237 ¹According to DFT (density functional theory), determined to <30nm; ²1-2 nm pore size range; ³>2 nm pore size; ⁴with reference to pore size range indicated; ⁵Data
 238 sourced from supplier technical sheets; ⁶Iodine number.

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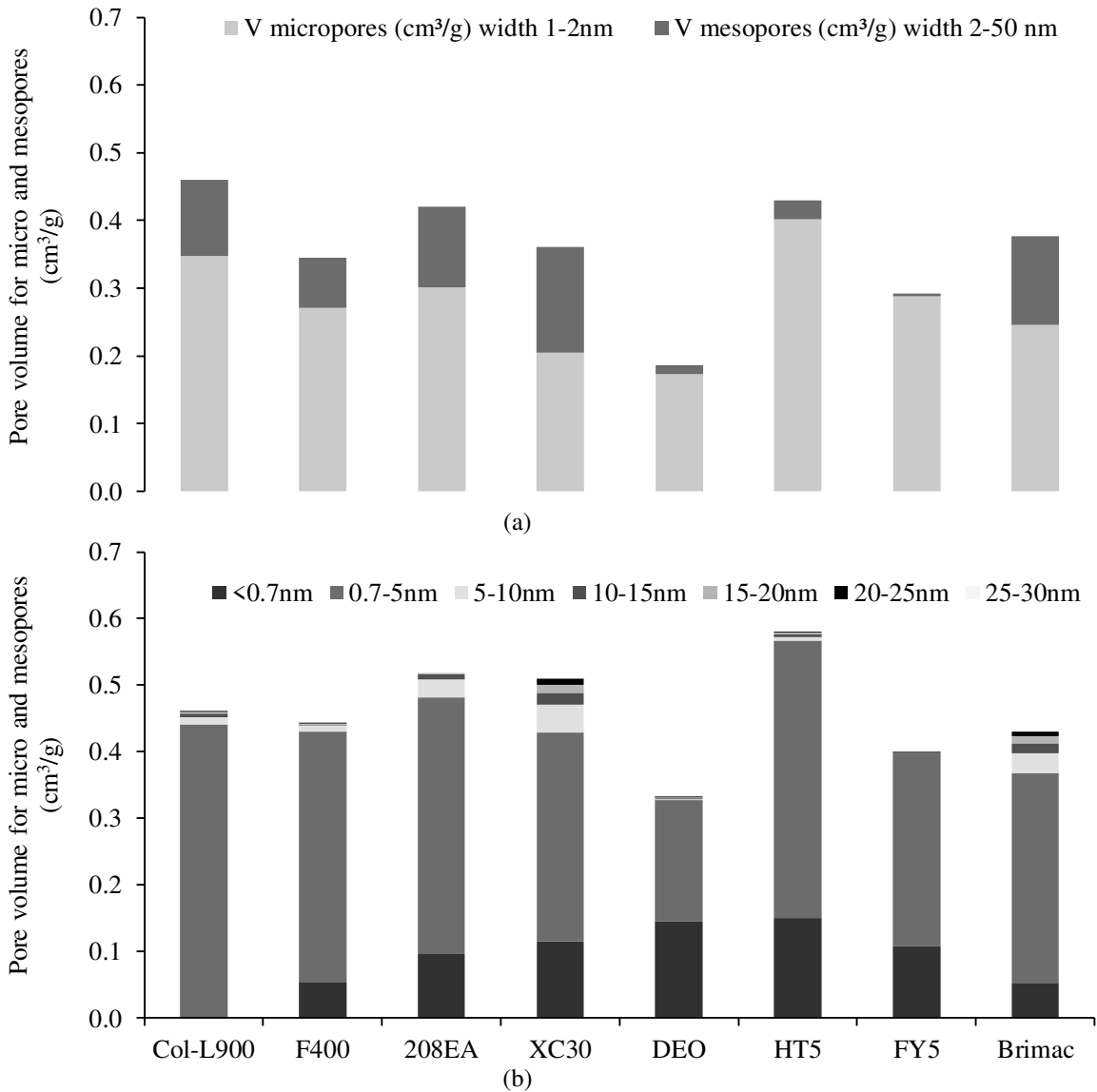
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Table 3: Volumetric pore size distribution, determined from DFT for pores sizes <30 nm.

<i>Media/pore size:</i>	<0.7nm	0.7-5nm	5-10nm	10-15nm	15-20nm	20-25nm	25-30nm	Total
<i>Col-L900</i>	0.001	0.440	0.011	0.006	0.002	0.001	0	0.460
<i>F400</i>	0.055	0.375	0.010	0.002	0	0	0	0.442
<i>208EA</i>	0.096	0.386	0.027	0.008	0.001	0	0	0.517
<i>XC30</i>	0.115	0.314	0.042	0.018	0.012	0.009	0.001	0.511
<i>DEO</i>	0.144	0.183	0.001	0.002	0.000	0	0	0.331
<i>HT5</i>	0.151	0.417	0.005	0.004	0.003	0.002	0	0.581
<i>FY5</i>	0.108	0.291	0	0.001	0	0	0	0.400
<i>Brimac</i>	0.053	0.316	0.029	0.016	0.010	0.007	0	0.430

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Figure 2. GAC pore volumes for (a) the micro (1-2 nm) and mesopores (2-50 nm) pore size, and (b) the full distribution of pore sizes.

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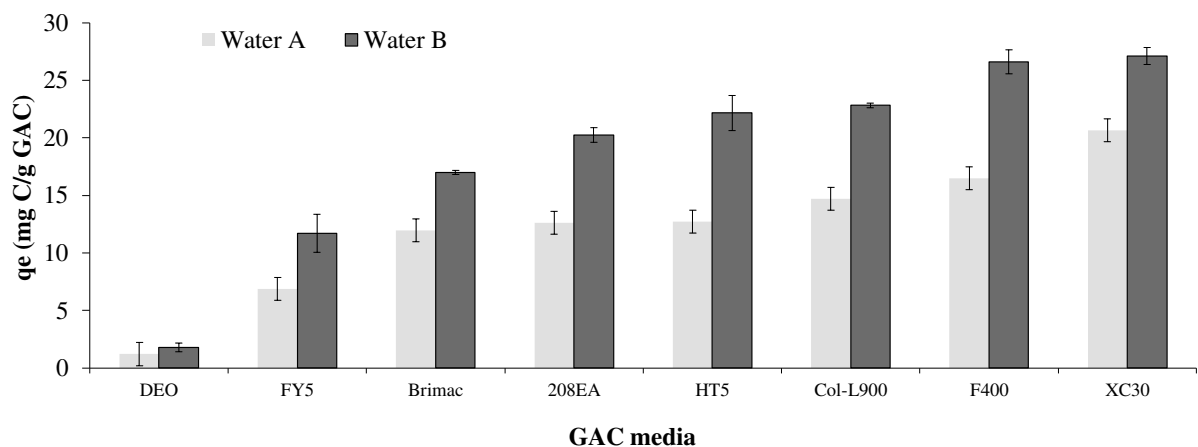
250 3.3 Batch adsorption isotherms

251 Batch adsorption isotherms revealed significant differences in DOC capacity across the
252 different media (Fig. 3), with *DEO* having the lowest capacity (1.19 and 1.76 mg/g for
253 *Waters A* and *B* respectively) and *XC30* the largest (20.7 and 27.1 mg/g respectively).

254 The higher capacity for the *Water B* organic matter reflects the impact of the
 255 coagulation pre-treatment on the DOC characteristics, which similarly accounts for the
 256 difference in THMFP. Increased GAC capacity following coagulation has been noted
 257 by [Karanfil et al. \(1999\)](#), and was attributed to the removal of high MW HPO NOM
 258 which otherwise cause pore blockage and so reduce media capacity. Two-fold changes
 259 in THMFP between raw and treated waters have been previously reported for
 260 predominantly upland water samples ([Golea et al, 2017](#)).

261 No selective removal of THM precursors was observed for any of the media, the
 262 THMFP values all lying between 100 and 113 $\mu\text{g THM} / \text{mg DOC}$ for *Water A* and 75-
 263 83 for *Water B* (Fig. 4a), despite a >10 times change in capacity. THMFP tended to
 264 decrease with increasing media capacity regardless of the media characteristics, a trend
 265 more readily recognisable from the non-normalised THM concentration data (Fig. 4b).
 266 However, no other trend in THM concentration vs bulk media characteristics,
 267 specifically IN and S_{BET} , was evident.

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Figure 3. Organic carbon capacity (q_e) of the 8 media.

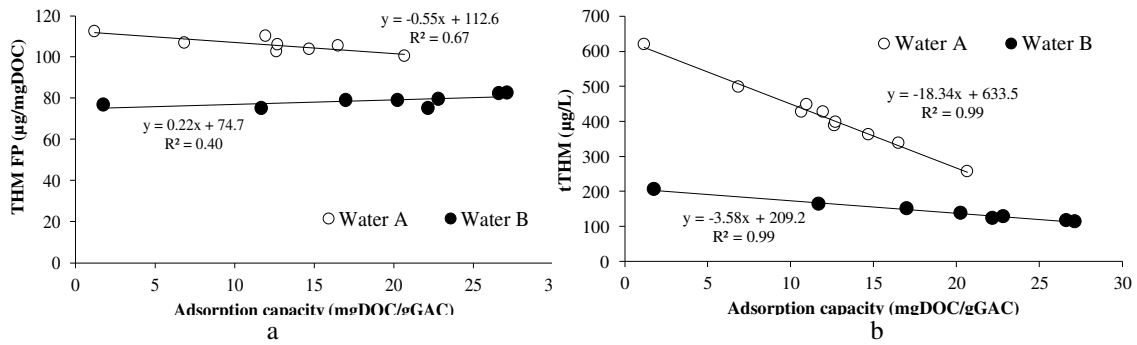


Figure 4. (a) Normalised THMFP and (b) tTHMs for Waters A and B. Each datum corresponds to a single GAC media.

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276 3.4 Rapid small-scale column tests

277 The breakthrough curves for the individual media inferred relative capacities which
 278 generally followed the trends recorded for the batch tests (Fig. 5). Breakthrough curves
 279 were steeper for Water A due to the higher organic loading for this source water and the
 280 impact of the larger and HPO organic carbon fraction exhausting the GAC surface area.

281 Overall, the two coal-based media (208EA and XC30) offered the highest capacities,
 282 reflected in shallower breakthrough curves. For Water A, the DOC removal efficiency
 283 for these media progressively decreased from 92-94% to 25-27% after 22,000 BVs (Fig.
 284 5a), the maximum volume reached for this campaign. For Water B, XC30 provided the
 285 shallowest curve, from 92% DOC removal initially to an end value of 50%, with two
 286 other coal-based media (F400 and 208EA) removing 90-91% DOC initially and
 287 progressively declining to 36-38%.

288 Differences in performance between Waters A and B again reflect the impact of
 289 clarification pre-treatment, which both decreases the DOC concentration and the
 290 proportion of the high MW organic compounds which otherwise block the media pores.

291 The lower MW NOM fraction, reported to be in the 0.5-5 nm size range (Dastgheib et
292 al., 2004; Karanfil et al., 1999; Moore et al., 2001; Velten et al., 2011) can then access
293 the media pores (Graf et al., 2014; Iriarte-Velasco et al., 2008) with the 2-50 nm
294 mesopores expected to provide the most accessible adsorption sites for such NOM
295 macromolecules. This was consistent with the two media having the lowest mesopore
296 volumes (*FY5* and *DEO*, derived from coconut shell, with mesopore volumes of 0.004-
297 0.013 cm³/g) offering the lowest DOC removal (Fig. 5b) despite their relatively high
298 surface area (S_{BET} values). Conversely, the mesopore volume of the *208EA* and *XC30*
299 media were amongst the highest of those tested. The *Brimac* media performed
300 comparatively well for both water sources despite its low S_{BET} value due to its high
301 mesopore volume.

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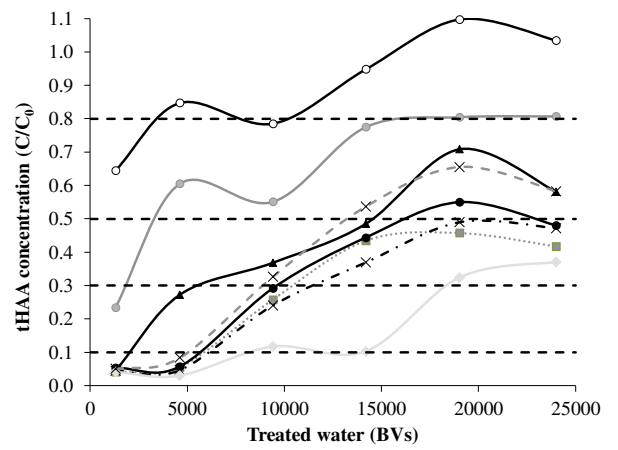
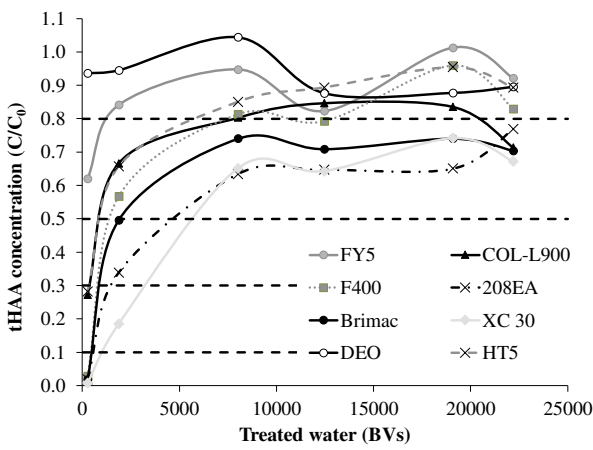
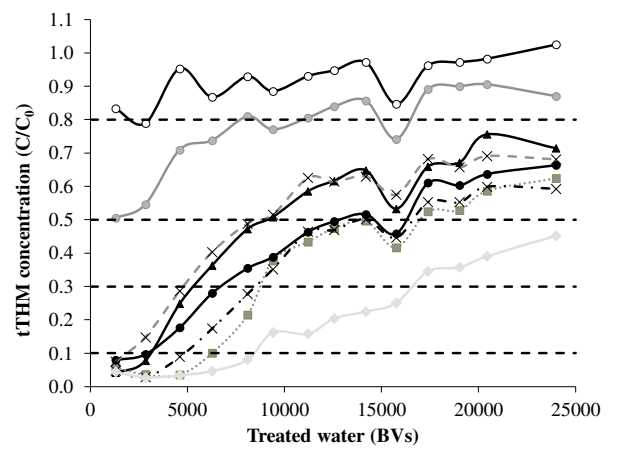
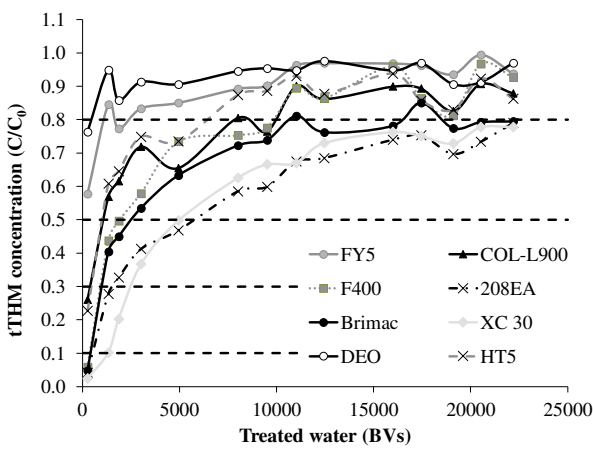
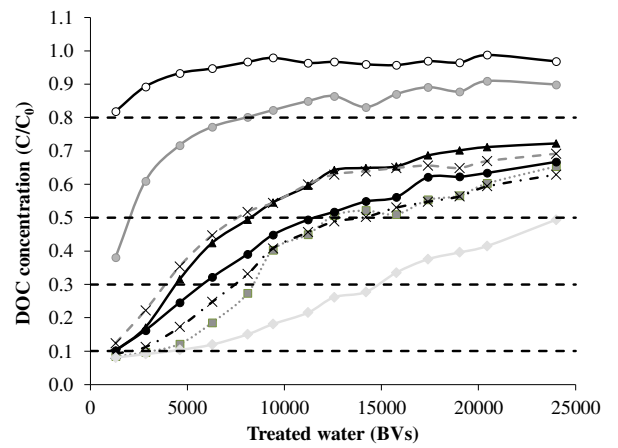
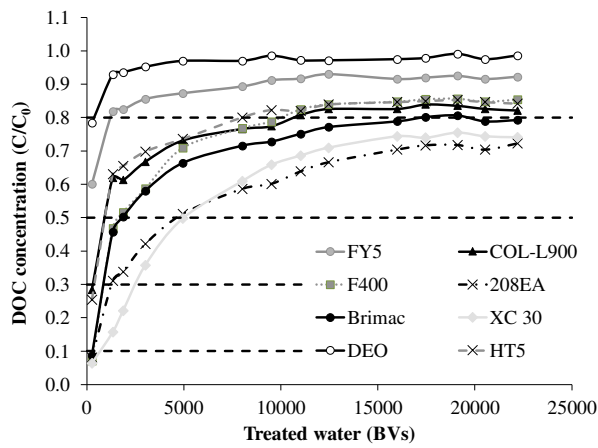


Figure 5. Removal of (a-b) DOC and precursors of (c-d) tTHM and (e-f) tHAA for waters A (a, c, e) and B (b, d, f), for up to 24,000 bed volumes (BV) of treated water.

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309

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311 The reduction in THMFP (Figure 5c-d) and HAAs (Figure 4e-f) generally followed the
312 removal profile of the DOC. There was no indication of selective removal of DBP
313 precursors from either water by any of the GAC media, a result consistent with that
314 observed from the batch experiments.

315 The throughput to 30, 50 and 80% breakthrough (BV_{30} , BV_{50} and BV_{80}) of DOC (Table
316 4) confirm *XC30* as achieving the highest BV_{30} for both water sources. For *Water A*,
317 *XC30* treated almost double the amount of water (2514 BVs) than the next best GAC
318 (*208EA*), and respectively three and seven times more water than *Brimac* and the best
319 coconut shell-based media *HT5*. The *Brimac* GAC performed at a similar level to the
320 *F400* media. Both *FY5* and *DEO* failed to achieve a quantifiable BV_{30} due to rapid
321 exhaustion at <267 BVs, the point when the first sample was taken. The same order of
322 removal was seen when the BV_{50} was considered, although the differences were less
323 pronounced, with the best performing media being *XC30* with a BV_{50} of 5059 compared
324 with only 946 BVs for *HT5*. The BV_{80} indicated more significant differences between
325 the media, with no BV_{80} value obtained after 23,980 BVs for two of the media (*XC30*
326 and *208EA*) for *Water A* indicating removal was always >20%. This compares with a
327 BV_{80} of only 503 for *DEO*. For the other GAC, *Brimac* treated 40% more water than
328 *F400*, while *COL-L900* treated the same number of BVs as *HT5* (946).

329

330 **Table 4:** Throughput to a filtrate DOC of 30%, 50% and 80% of the feed concentration (BV₃₀, BV₅₀
 331 and BV₈₀ respectively) for the GAC media studied by RSSCT, waters A and B, EBCT_{LC} = 20
 332 minutes.

GAC media	WTW A			WTW B		
	BV ₃₀	BV ₅₀	BV ₈₀	BV ₃₀	BV ₅₀	BV ₈₀
<i>COL-L900</i>	355	946	10,710	4,467	8,284	>>23,980
<i>F400</i>	858	1,775	10,030	8,402	12,308	>>23,980
<i>208EA</i>	1,301	4,704	>>22,194	7,455	13,728	>>23,980
<i>XC30</i>	2,514	5,059	>>22,194	14,911	23,964	>>23,980
<i>DEO</i>	<<267	<<267	503	<<1,302	<<1,302	1,302
<i>HT5</i>	355	946	8,047	3,875	7,633	>>23,980
<i>FY5</i>	<<267	<<267	1,242	<<1,302	2,041	8,284
<i>Brimac</i>	858	1,775	17,101	5,798	11,657	>>23,980

333
 334 For *Water B*, *XC30* was again the best performing media with a BV₃₀ of 14,911, a value
 335 substantially higher than the next best GAC *F400*, having a BV₃₀ of 8,402. No BV₃₀
 336 value was recorded for *DEO* and *FY5* since the 30% target was exceeded before the first
 337 sample taken at 1,302 BVs. This was also the case for the BV₅₀ value for *DEO*, whereas
 338 the corresponding value for *FY5* was 2,041. This value was less than 10% of the BV₅₀
 339 values recorded for *XC30*. All media other than *FY5* and *DEO* removal achieved
 340 removal exceeding 20% throughout the run, thus providing no measurable BV₈₀, with
 341 *XC30* maintaining $\geq 50\%$ removal.

342 **3.5 UV₂₅₄ for monitoring of DBP formation propensity breakthrough**

343 It is of practical significance to correlate DBP breakthrough with a more readily
 344 monitored water quality determinant, such as UV₂₅₄ absorbance. UV₂₅₄ is widely
 345 acknowledged as being a reasonable analogue measurement for DBPFP due to its
 346 association with the more labile HPO organic content of the NOM (Bougeard et al.,
 347 2010; Karapinar et al., 2014). Breakthrough data based on number of BVs passed

348 recorded for 10, 30 and 50% breakthrough (BV_{10} , BV_{30} , and BV_{50} respectively) for
349 *Waters A* and *B* (Fig. 6) indicate a consistently better correlation for the former. R^2
350 values range from 0.98 to 1.00 for *Water A* data, compared with 0.75-0.99 for *Water B*.
351 This is a consequence of the increased HPO content of the DOC in *Water A* compared
352 with *Water B*, which was subject to pre-clarification. Similar increases in DBPFP data
353 scatter for residual DOC following clarification have been reported by [Golea et al](#)
354 [\(2017\)](#).

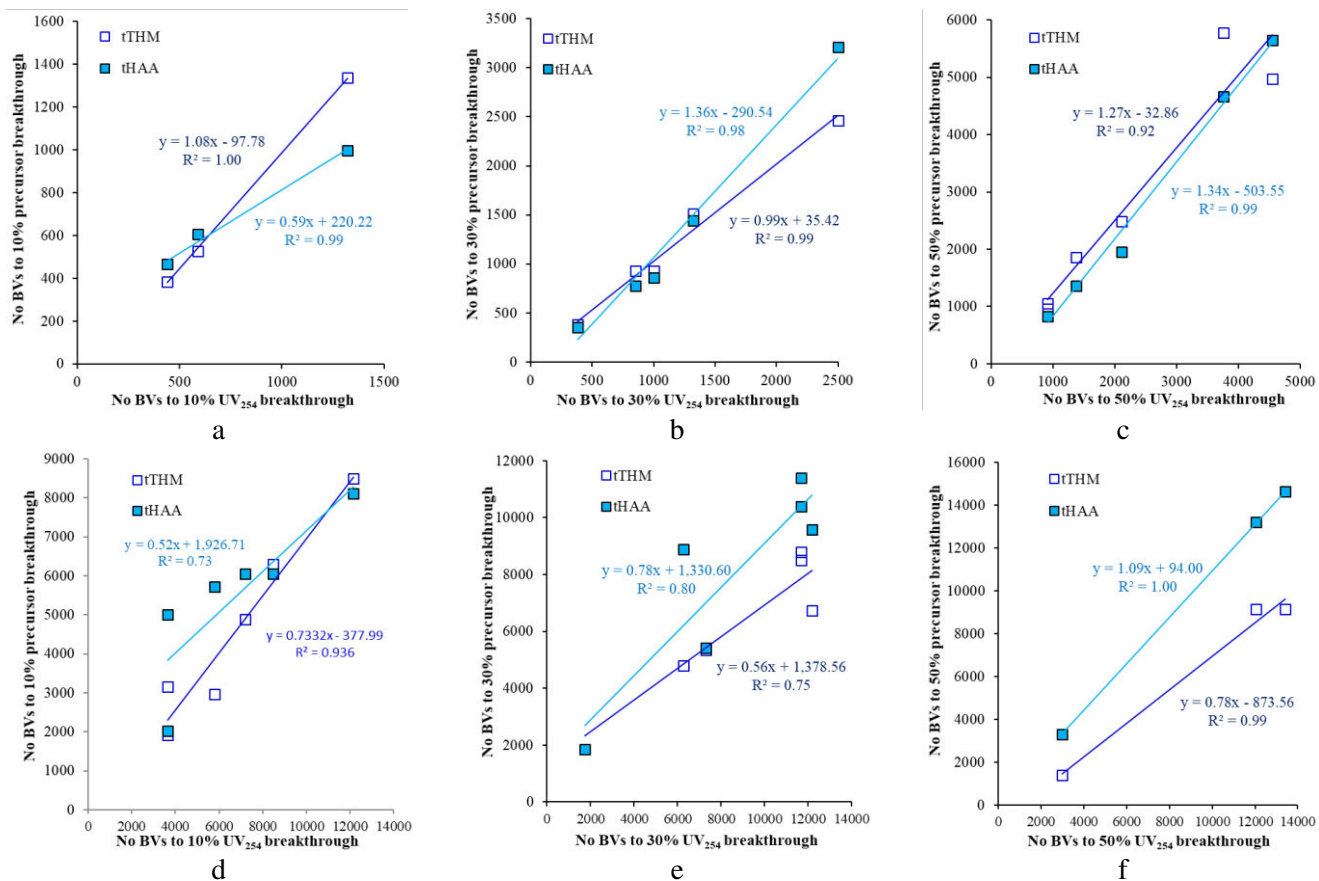
355 However, the slope for these correlations varies significantly across the different data
356 sets, from 0.99 to 1.36 for *Water A* and 0.52-1.09 for *Water B* with no pattern evident.
357 This may reflect the vagarious nature of the reactivity of the organic carbon, as noted by
358 previous authors ([de la Rubia et al, 2008](#); [Golea et al, 2017](#)). Thus, whilst UV_{254}
359 provides a reasonable representation of DBPFP for both raw and treated waters, and is
360 apparently unaffected by the GAC media characteristics, the coefficient is dependent on
361 the DOC characteristics.

362

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366
 367 Figure 6. Correlation of bed volumes passed until target percentage breakthrough is reached, DBP
 368 precursor concentration vs. UV₂₅₄ for waters A (a-c) and B (d-f) at 10% (a, d), 30% (b, e) and
 369 50% (c, f) breakthrough. For a single correlation each individual datum relates to a single
 370 GAC media.

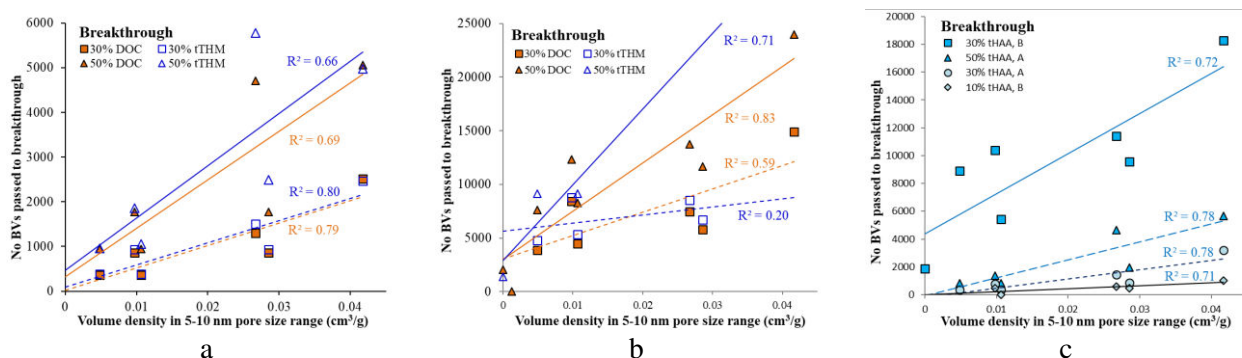
371

372 3.6 Correlation of DOC removal with GAC characteristics

373 A consideration of the impact of media characteristics on the removal of DOC and
 374 THMFP from the RSSCTs (Fig. 7) indicates a reasonable correlation of the BV₃₀ and
 375 BV₅₀ data for both DOC and tTHM concentration with the absolute pore volume density
 376 for the 5-10 nm pore size range $V_{p,5-10}$ (Fig. 7a-b). The tHAA breakthrough data also
 377 correlated reasonably with this pore size range (Fig. 7c). Across these 12 data sets R²
 378 values ranged from 0.59 to 0.83 for all but the BV₃₀ data set for tTHM breakthrough, for

379 which there was no evident correlation ($R^2 = 0.20$). Against this, all correlations
 380 between the breakthrough BV and pore volume density produced for the other pore size
 381 ranges generated R^2 values below 0.27 (Supplementary Information, Table S1).
 382 Evidence therefore suggests that removal of NOM-derived DOC, and subsequently the
 383 THM and HAA byproducts generated from the residual DOC in the treated water, is
 384 primarily a function of the density of 5-10 nm-sized pores in the GAC media. This is a
 385 result consistent with that of Velten et al (2011), who advocated selection of 1-50 nm
 386 pore-sized GAC media for NOM removal. The present research suggests that the key
 387 pore size range to be 5-10 nm.

388



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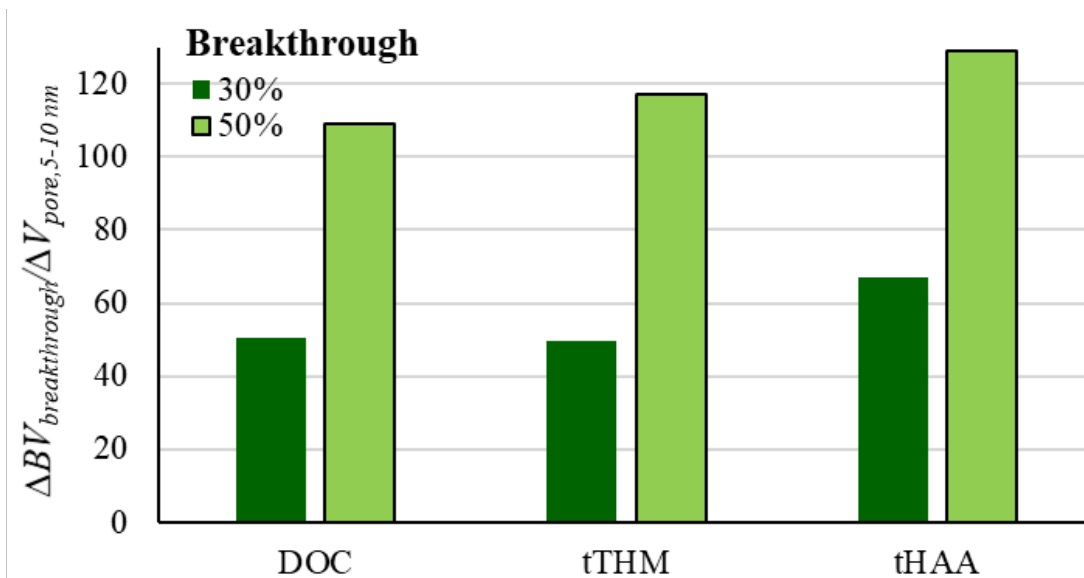
390 Figure 7. No. BVs passed to 30% and 50% breakthrough of DOC and tTHMs vs. total volume of pores
 391 within 5-10 nm size range for waters (a) A, and (b) B, and for (c) 10-50% breakthrough of
 392 tHAAs.

393

394 The values of the slopes depicted in Figure 7, i.e. $\Delta BV_{\text{breakthrough}}/\Delta V_{p,5-10}$, provide an
 395 indication of the extent to which the practical adsorption capacity of the media is
 396 influenced by the 5-10 nm pore volume. Accordingly, in the case of *Water A* (Fig. 8),
 397 the volume treated to 50% breakthrough increases by 105-125 BVs per cm³/kg 5-10nm

398 pore volume density based on either DOC or DBPFP concentration. The corresponding
 399 range for *Water B*, for an organic carbon concentration around half that of *Water A*, is
 400 500-670 BVs per cm³/kg – the difference being attributable to the pore-blocking effect
 401 of the HPO in *Water A*. In both cases, the tHAA data forms the top of the range.

402 There is evidently a significant influence of the total 5-10 nm pore volume per kg
 403 material on the media capacity; 3-6 fold capacity changes arise, the precise value
 404 depending on the % breakthrough value, as $V_{p,5-10}$ changes from 0.005 to 0.042 cm³/g.
 405 Whilst previous authors have qualitatively identified the importance of pores above 3
 406 nm in size, specifically for removing humic and fulvic acid-like substances (Gui et al,
 407 2018), the quantification of practical capacity in terms of breakthrough volume against
 408 the total volume provided by pores within a specific size range has not previously been
 409 reported.



410
 411 Figure 8. Values of slopes in Fig. 7a and c, i.e. the change in treated volume to breakthrough as a
 412 function of the volume of pores in the 5-10 μm size range ($\Delta BV_{\text{breakthrough}}/\Delta V_{p,5-10}$) in units of
 413 BV per cm³/kg, for *Water A*.

414 Results are comparable with previous work on NOM removal by GAC, with relatively
415 low water volumes treated prior to significant breakthrough (e.g. 50% DOC
416 breakthrough at 5-10,000 BVs for the treatment of water containing ~1 mg/L of DOC
417 (Li et al., 2007; Velten et al., 2011). In comparison, removal of micropollutants
418 normally provides higher removal levels for more sustained periods (e.g. 80% removal
419 of the antibiotic sulfamethoxazole after ~68,000 BVs, Greiner et al., 2018). In the
420 current study most of the media removed 20-30% DOC after extended run times for
421 both water sources, with the most effective media removing >50% DOC after >20,000
422 BVs for water pre-treated by coagulation. This shows potential for continuous precursor
423 removal, particularly for the two coal-based media and the bone char GAC, provided
424 20-30% removal is acceptable. However, the relatively fast breakthrough to 50% DOC
425 and tTHM/tHAA for the higher-DOC, substantially untreated water source (*Water A*)
426 indicated limited capacity for long-term bulk removal of NOM for source waters having
427 a high DBP-FP. Against this, GAC was found to be an effective polishing process for
428 pre-clarified water (*Water B*), where longer term reduction in DOC and DBP precursors
429 was recorded.

430 **4 Conclusions**

431 Granular activated carbon (GAC) media of various origins (coal, coconut shell and
432 bovine bone), and providing a range of physical characteristics with reference to pore
433 size, have been appraised with reference to their capacity for natural organic matter
434 (NOM). Experiments comprised (a) batch adsorption experiments for determination of
435 equilibrium capacity, and (b) tests on micro-columns to represent capacity under normal

436 operating conditions. Two different water sources were tested, a raw water with
437 rudimentary pretreatment (pressure sand filtration) and one pre-treated by full
438 clarification. The media capacity both for organic carbon and for chlorinated
439 disinfection byproduct formation propensity (DBPFP), with reference to both
440 trihalomethane (THM) and haloacetic acid (HAA) formation, was determined. The
441 applicability of UV_{254} absorption as a surrogate for was also assessed.

442 Results revealed:

- 443 a. The 8 media tested were found to have a wide range of pore size distributions and
444 pore volume densities (V_p in cm^3/g), specifically within the key range of 5-10 nm
445 ($V_{p,5-10}$).
- 446 b. There was no evidence of any selectivity for DBPFP removal by any of the media
447 tested: the ratio of THM and HAA concentrations generated from DOC in treated
448 waters did not change significantly between the different media.
- 449 c. In view of (b) above, UV_{254} provided a reasonable surrogate measurement of both
450 DOC and DBPFP.
- 451 d. Batch adsorption tests provided a good indicator of media performance in terms of
452 NOM removal: ranking of media capacities from batch testing generated the same
453 sequence as that from microcolumn testing.
- 454 e. The media capacity, quantified in terms of bed volumes treated to breakthrough, was
455 found to correlate with the pore volume density of the 5-10 nm pores ($V_{p,5-10}$), in
456 terms of pore volume provided per unit mass of media. A 3-6 fold increase in
457 capacity was recorded for a change in $V_{p,5-10}$ from 0.005 to 0.042 cm^3/g .

458 f. Correlations were stronger for the water with rudimentary treatment than for the
459 preclarified water due to both its increased organic carbon concentration and the
460 hydrophobic content, the latter having a higher reactivity.

461 **Acknowledgments**

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593

Figure 1

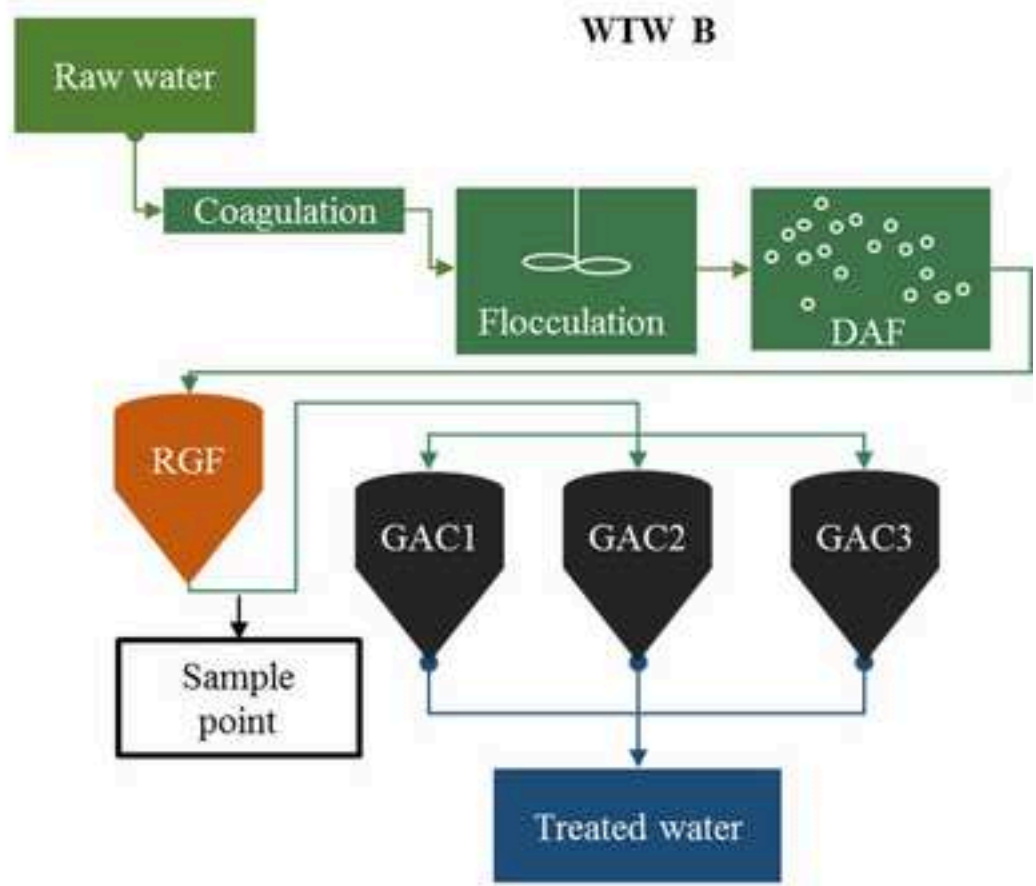
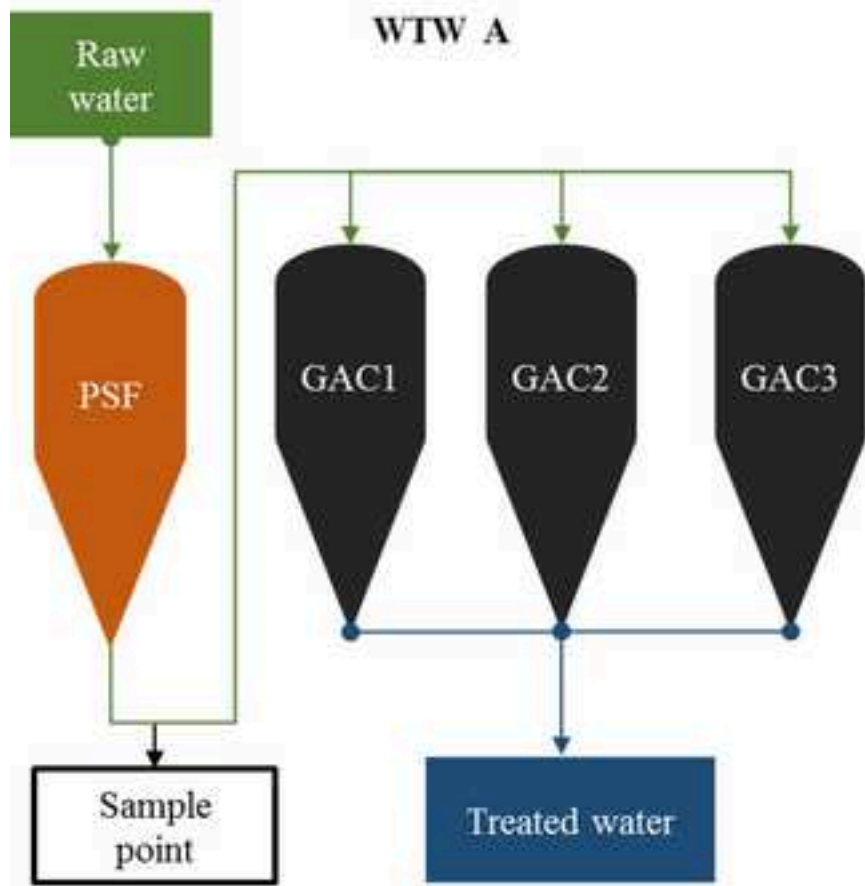


Figure 2a

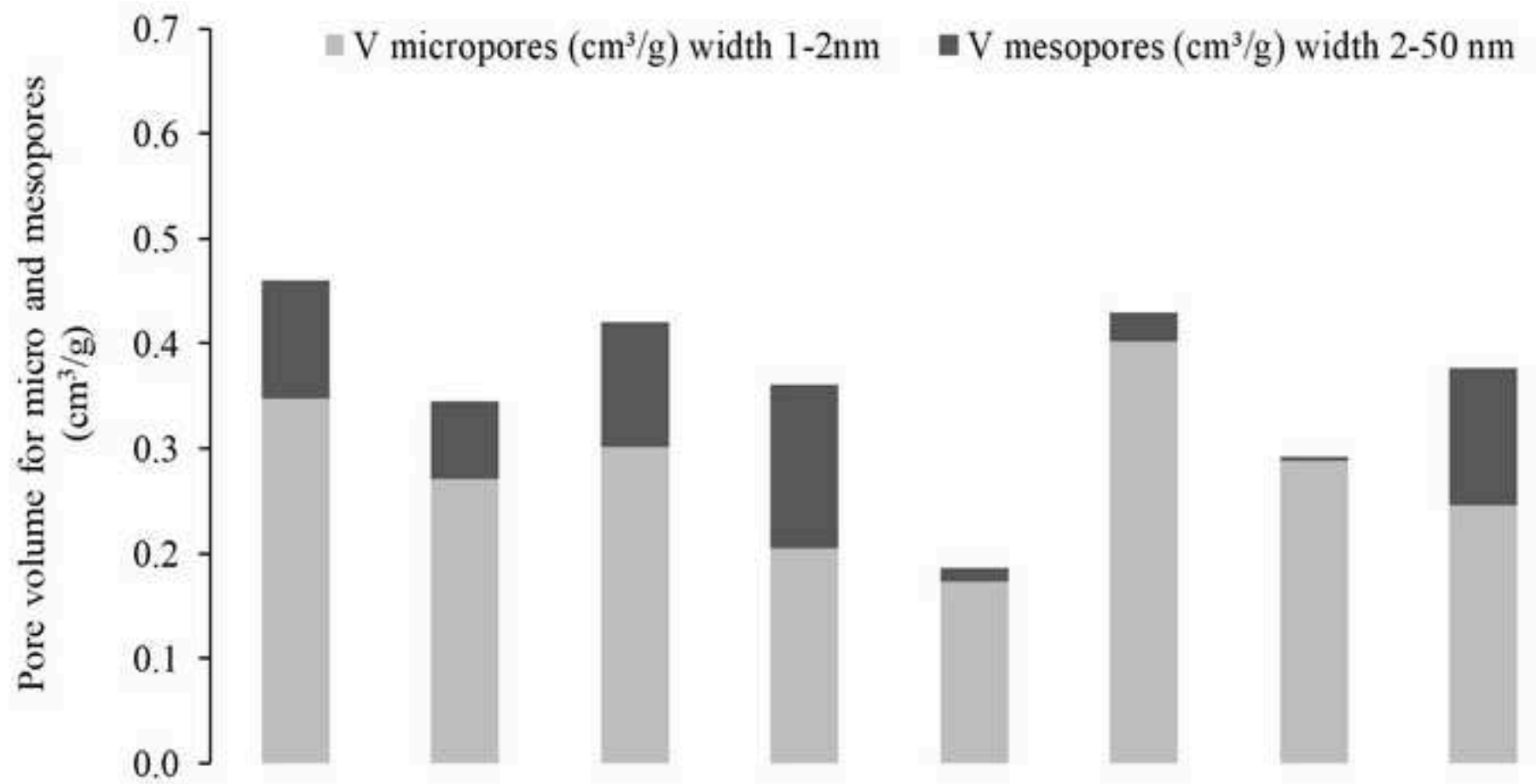


Figure 2b

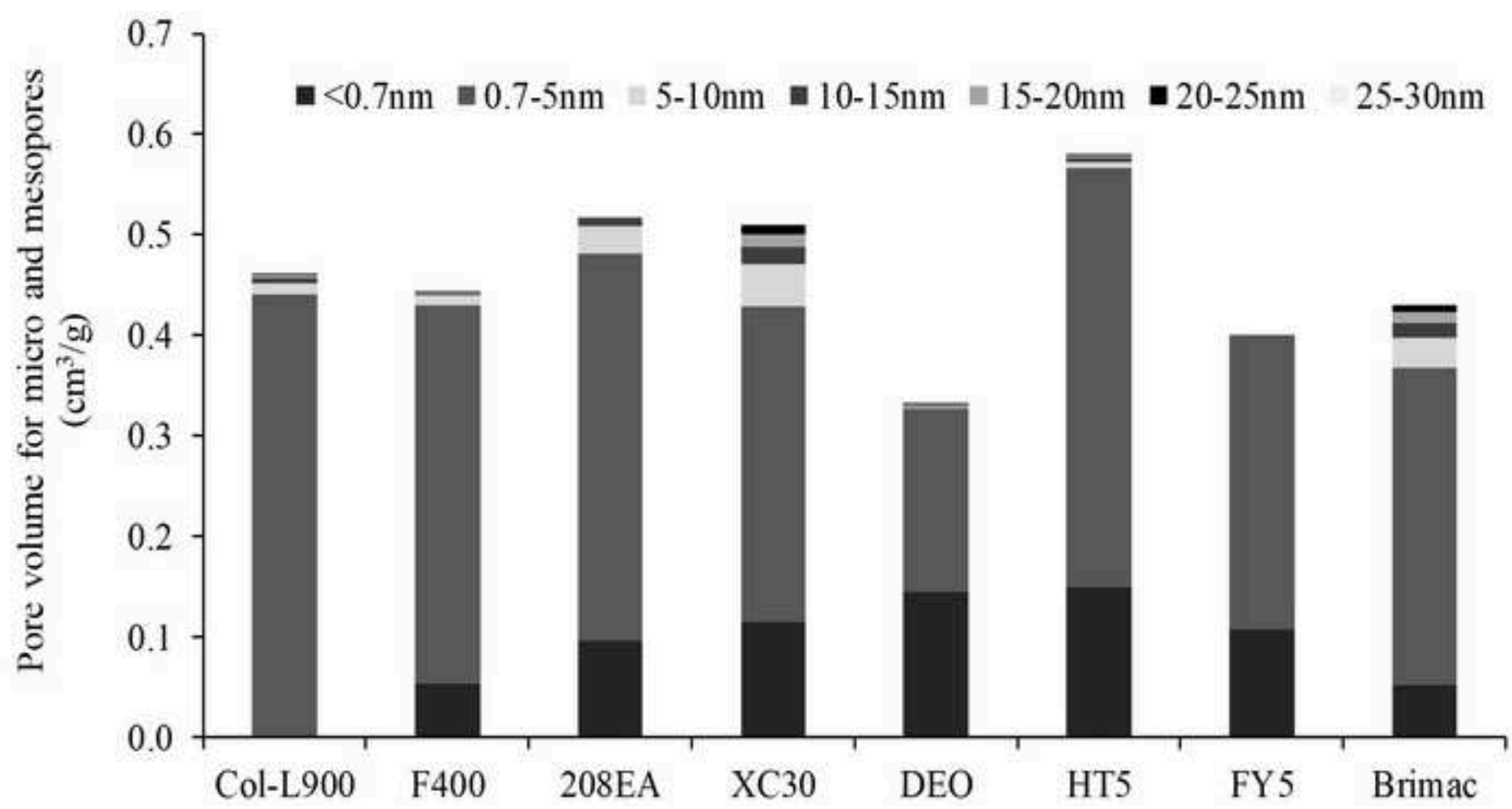


Figure 3

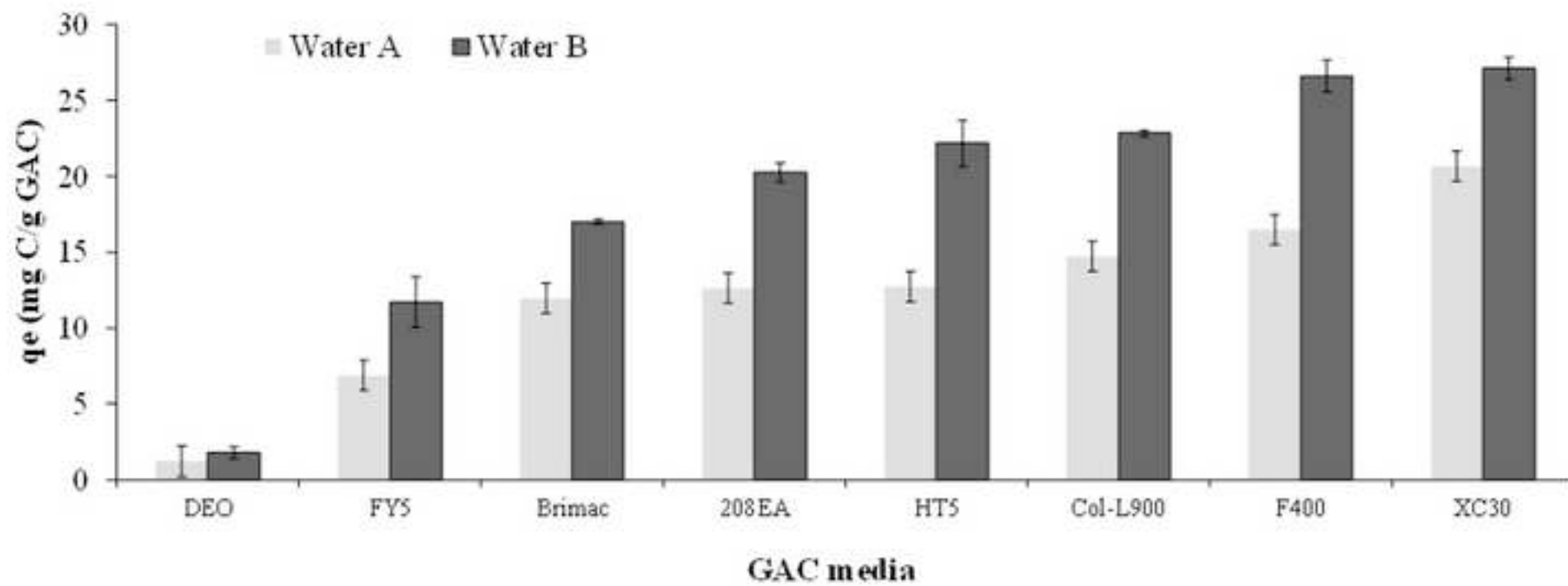


Figure 4a

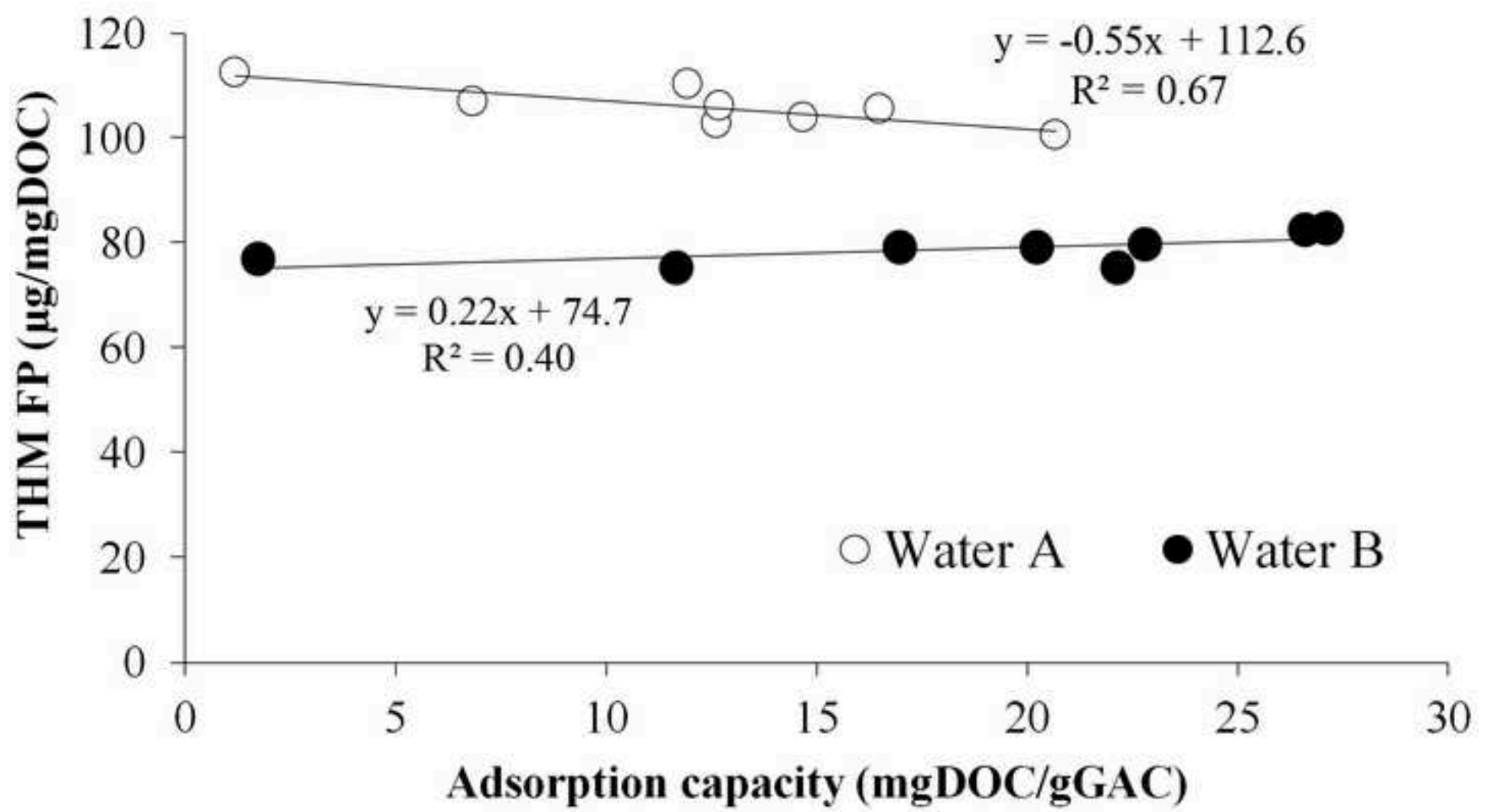


Figure 4b

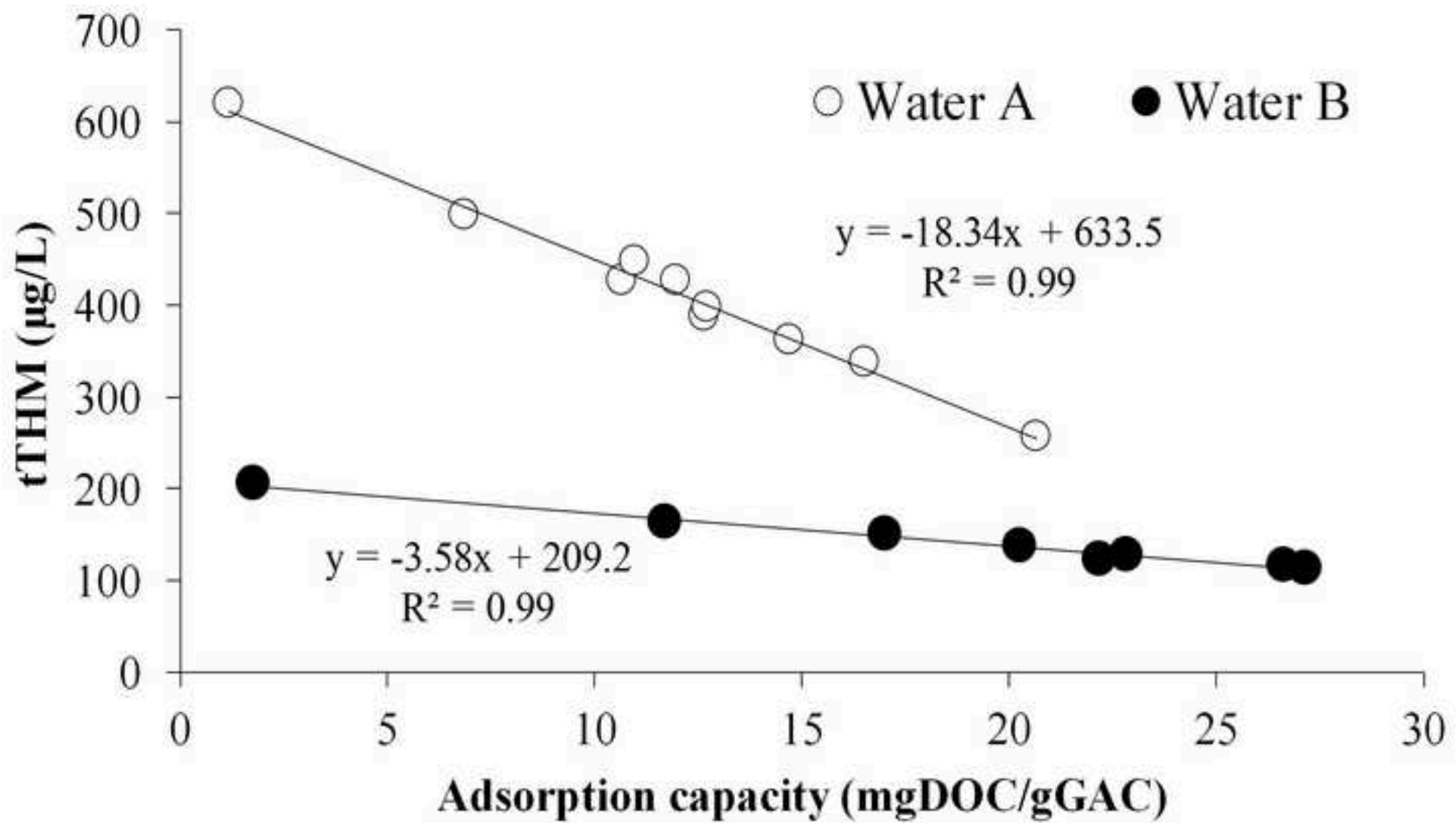


Figure 5a

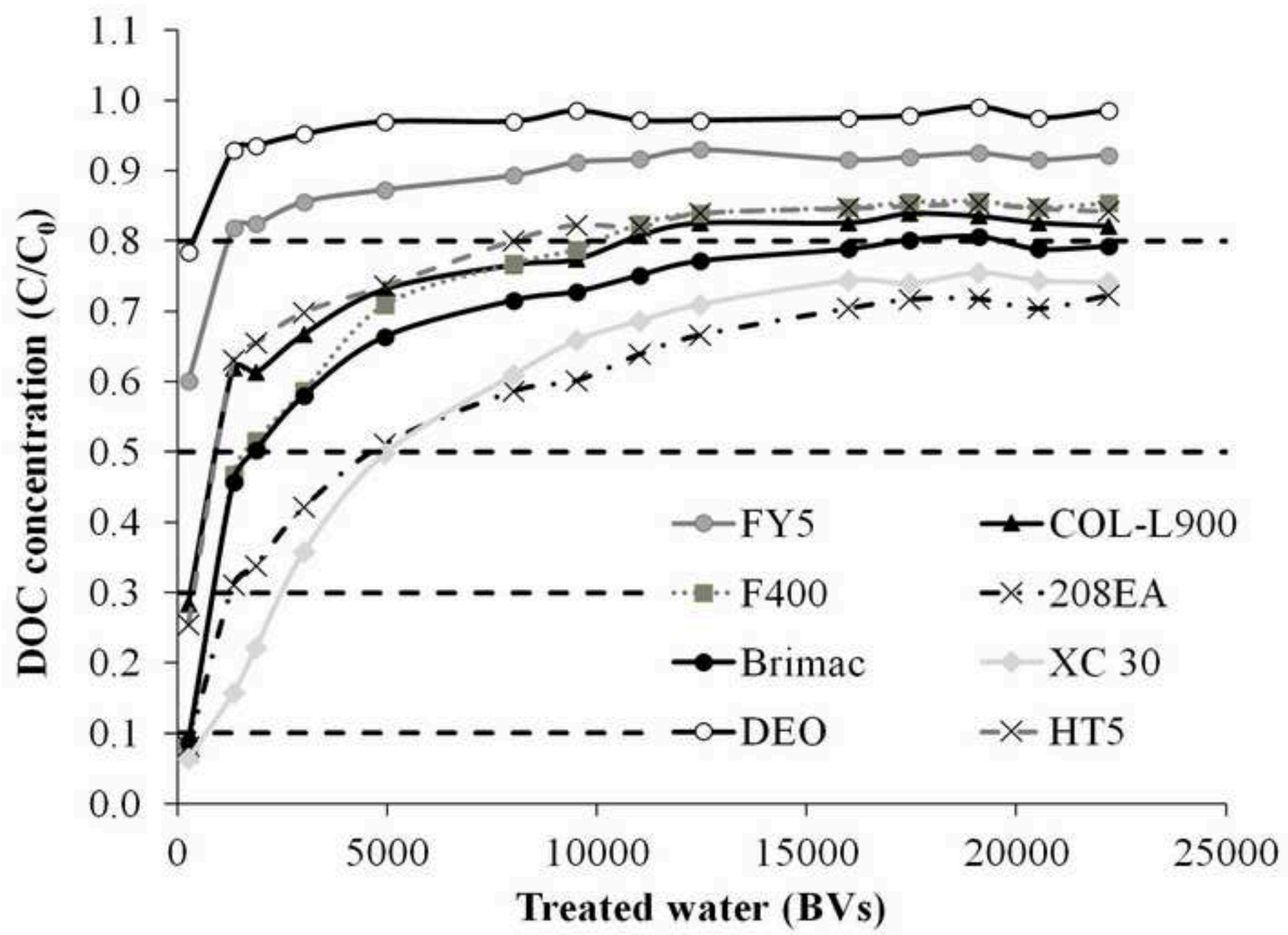


Figure 5b

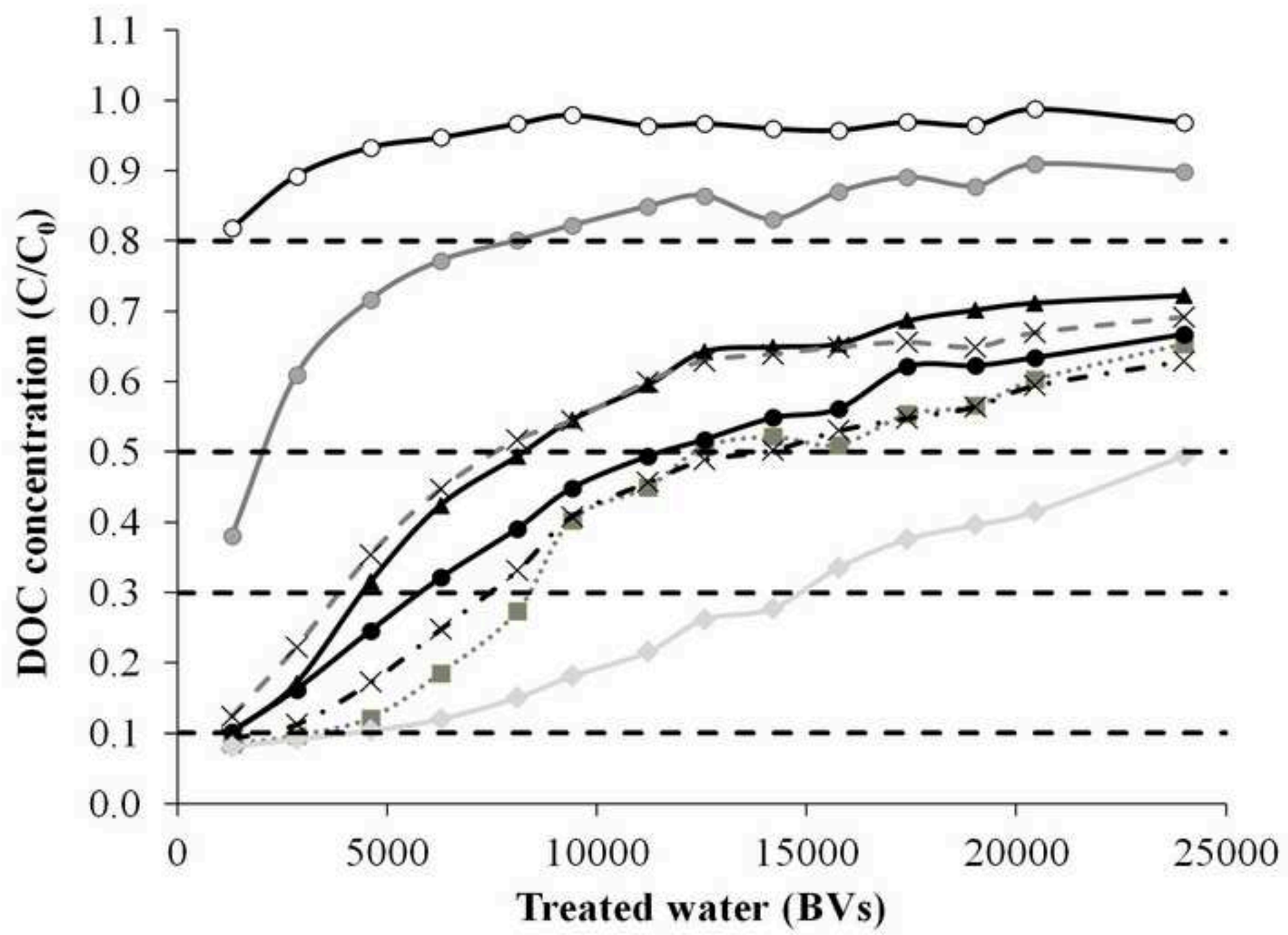


Figure 5c

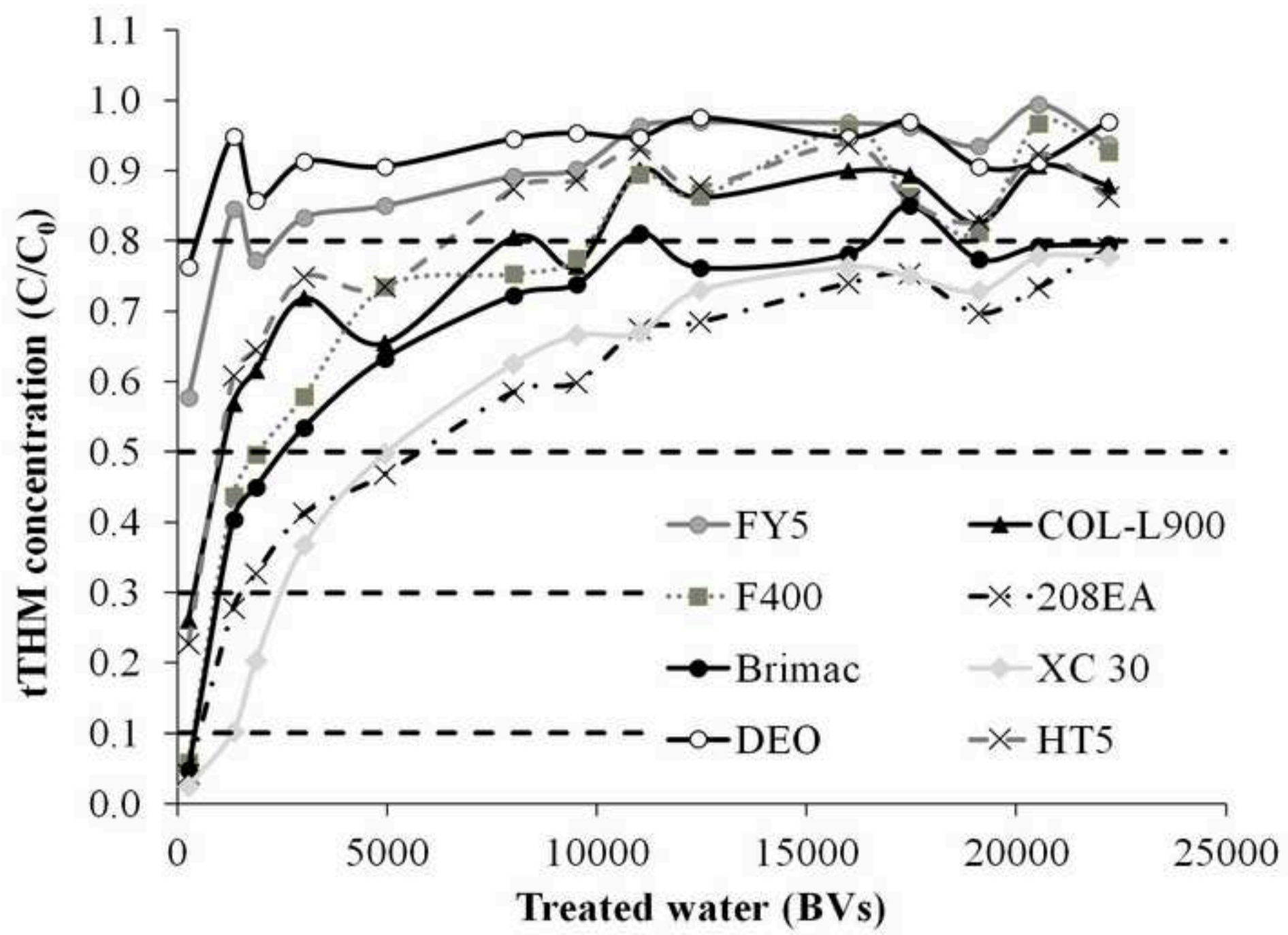


Figure 5d

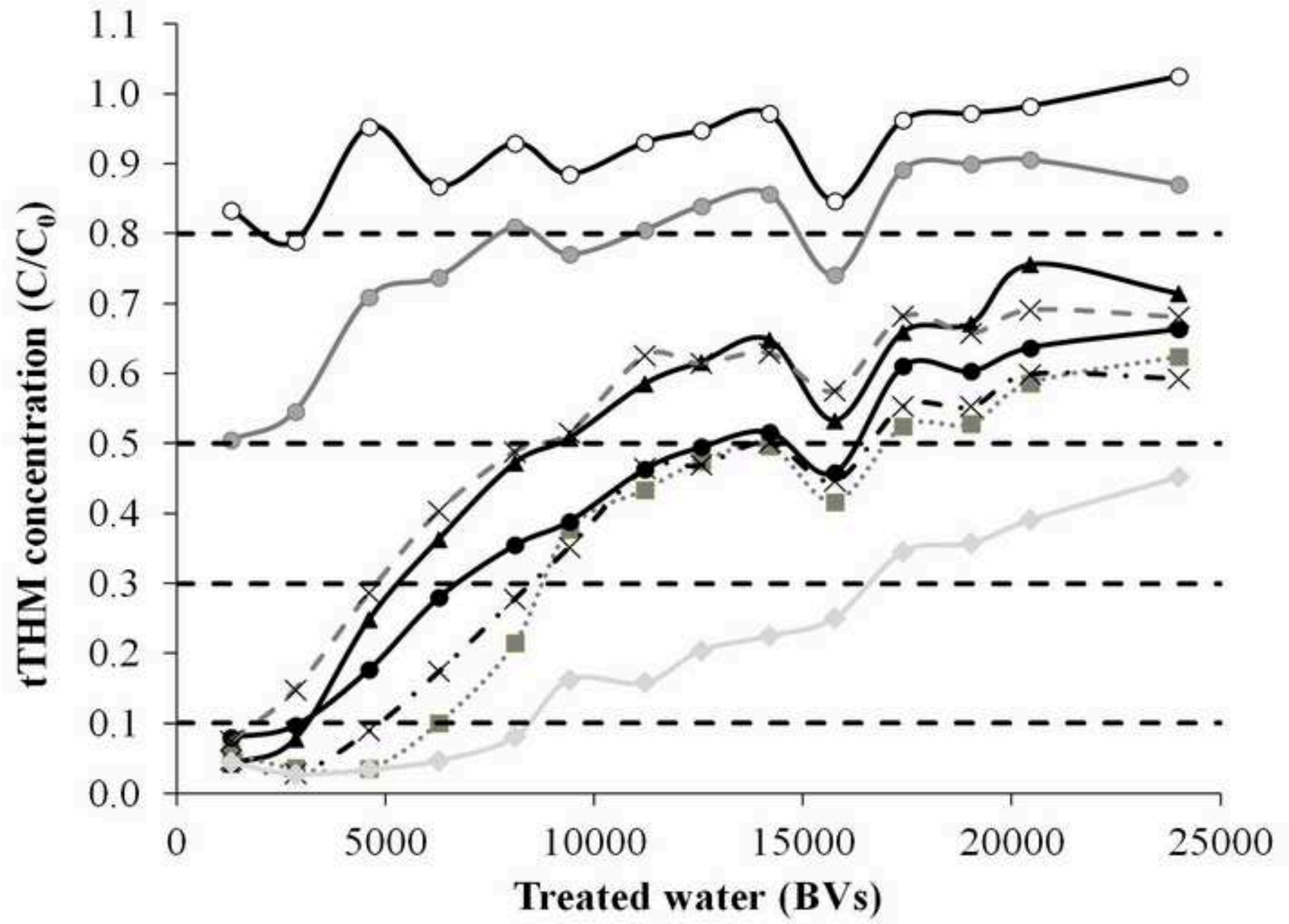


Figure 5e

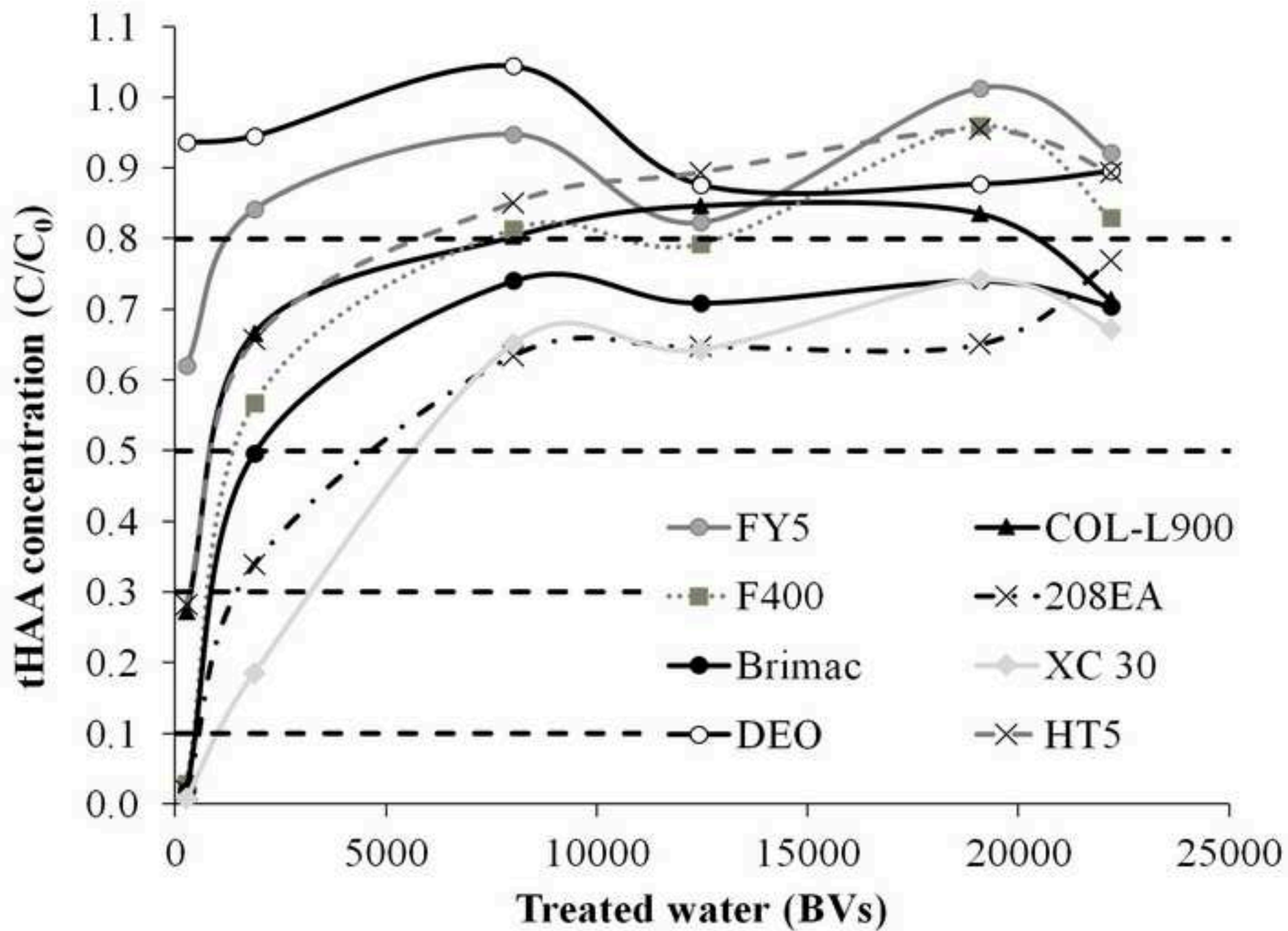


Figure 5f

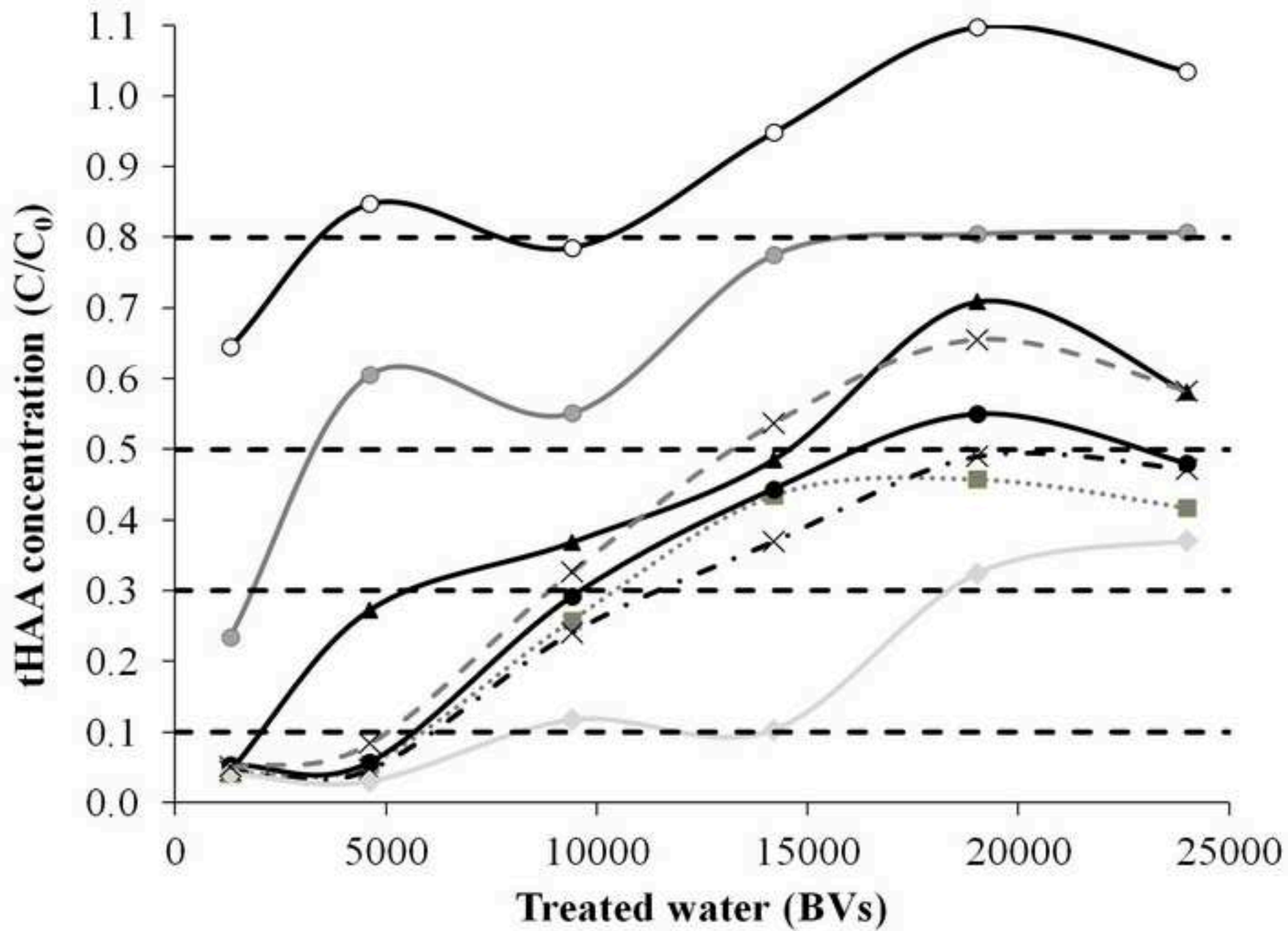


Figure 6a

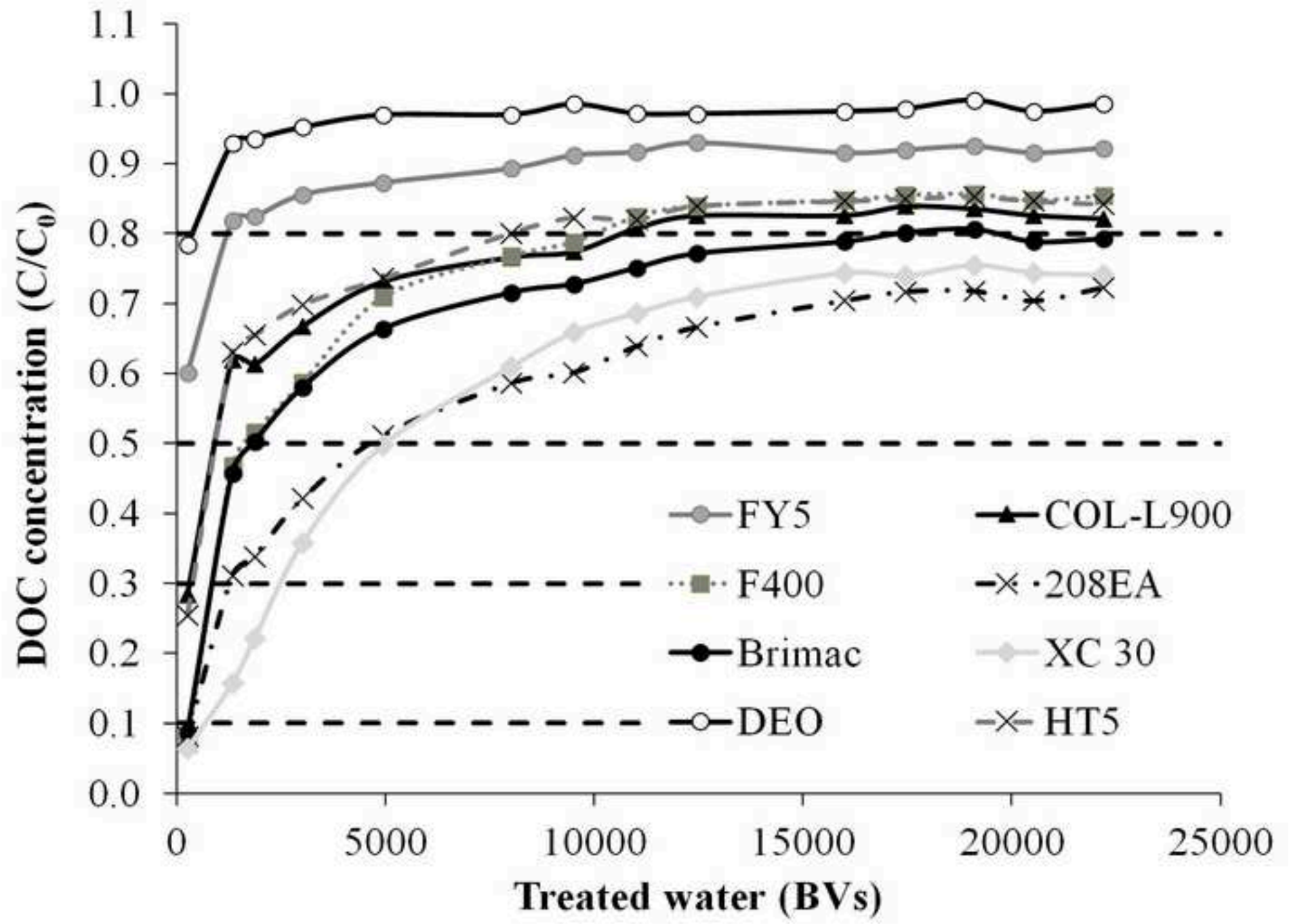


Figure 6b

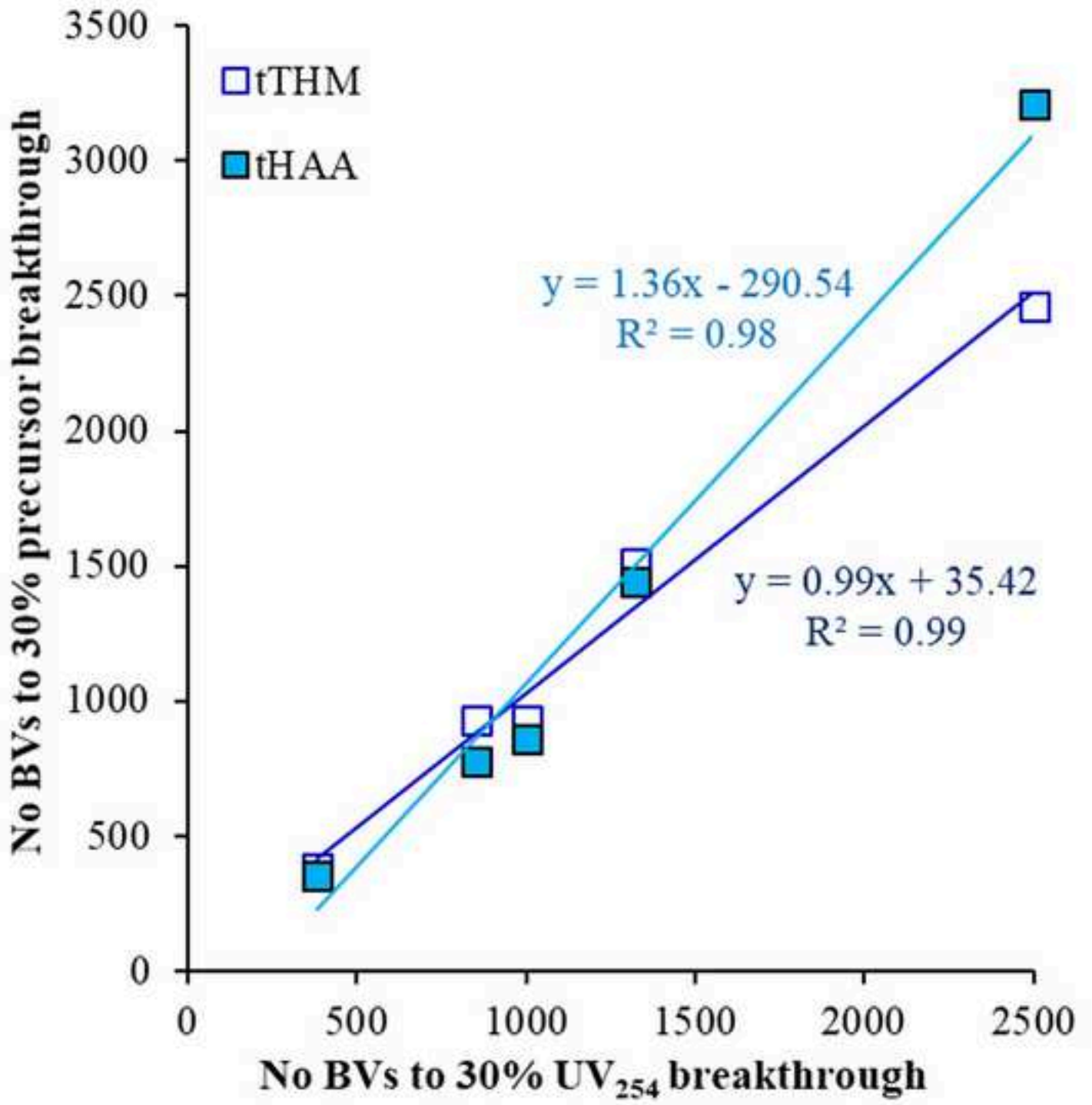


Figure 6c

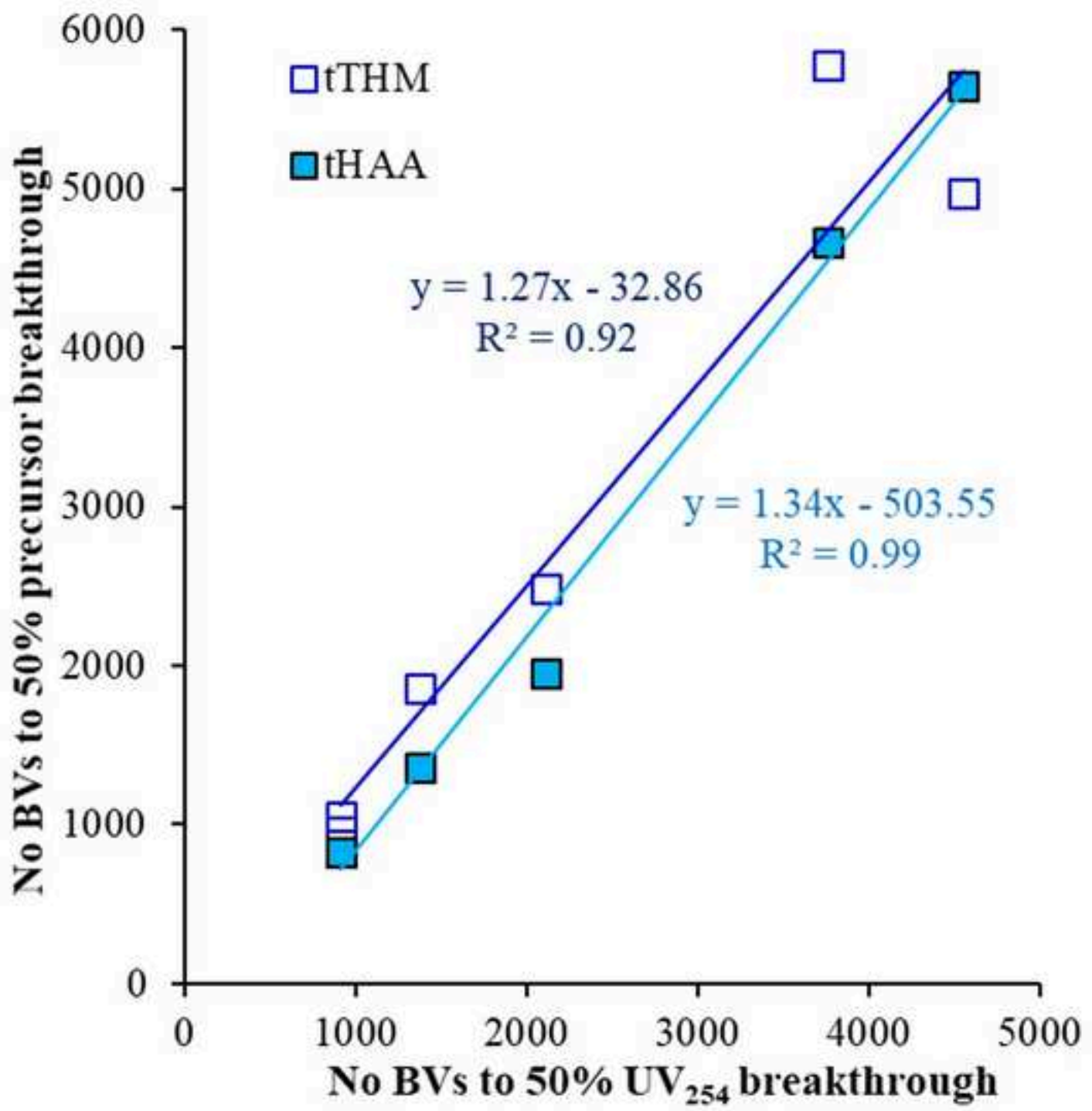


Figure 6d

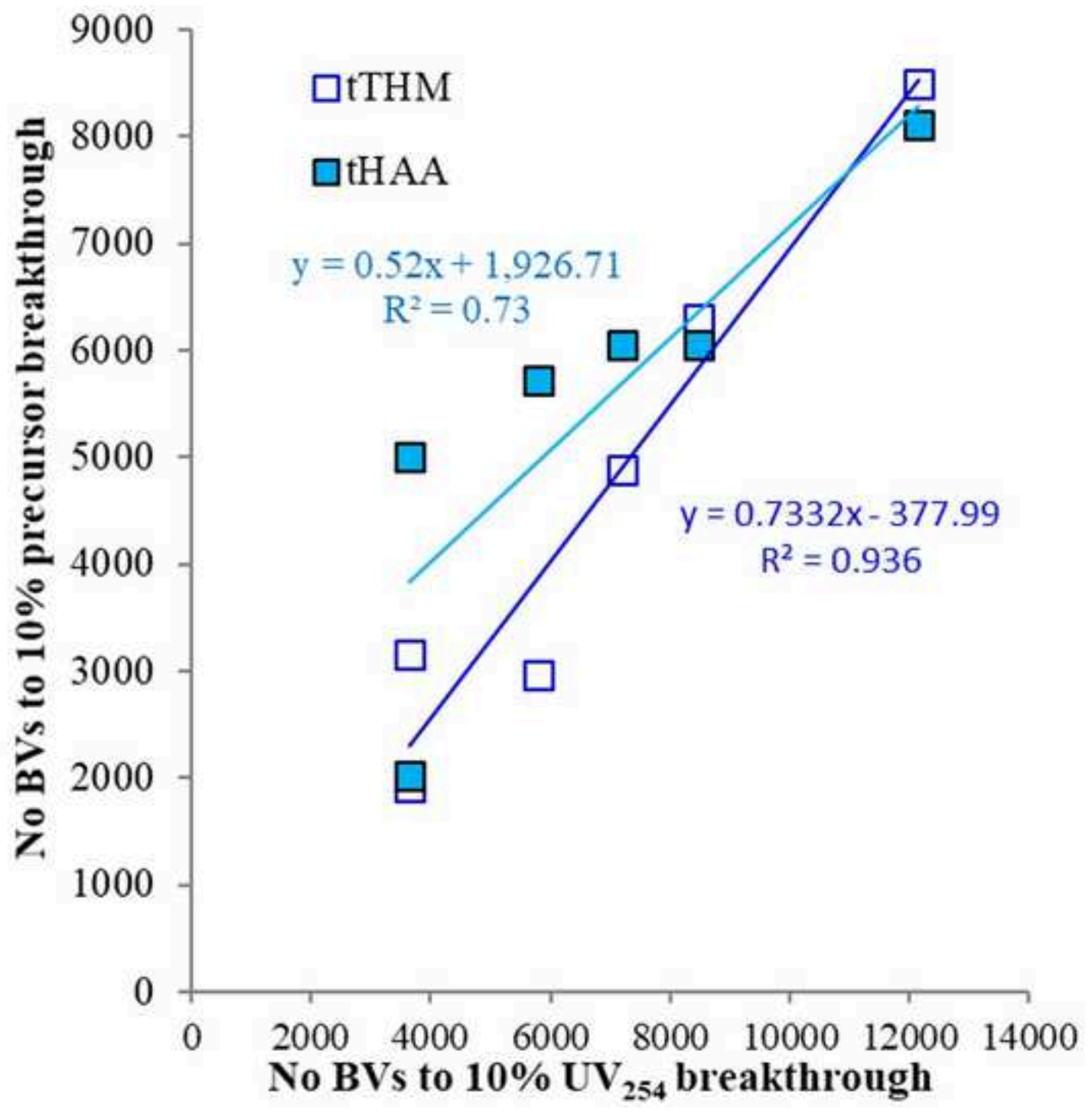


Figure 6e

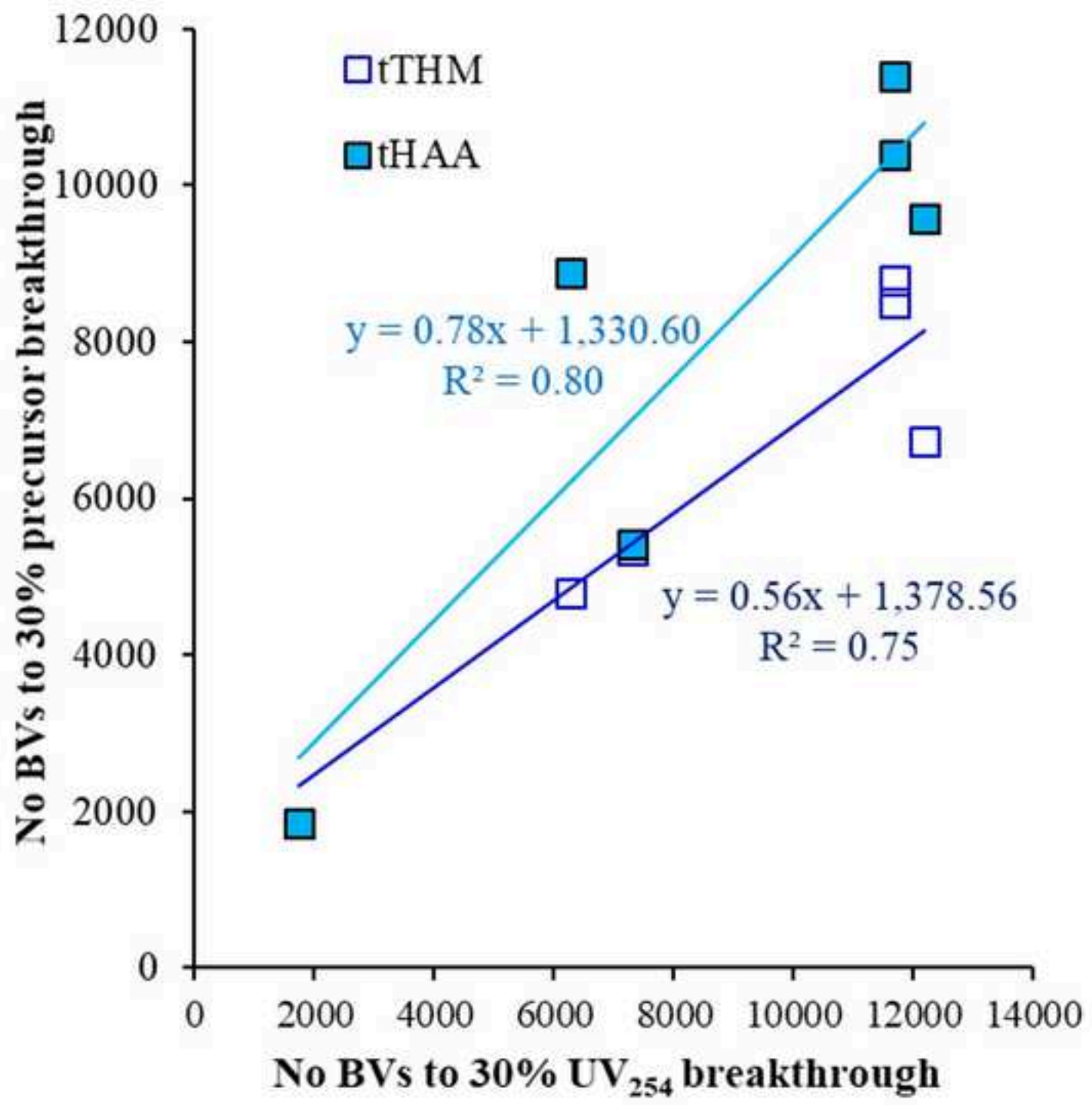


Figure 6f

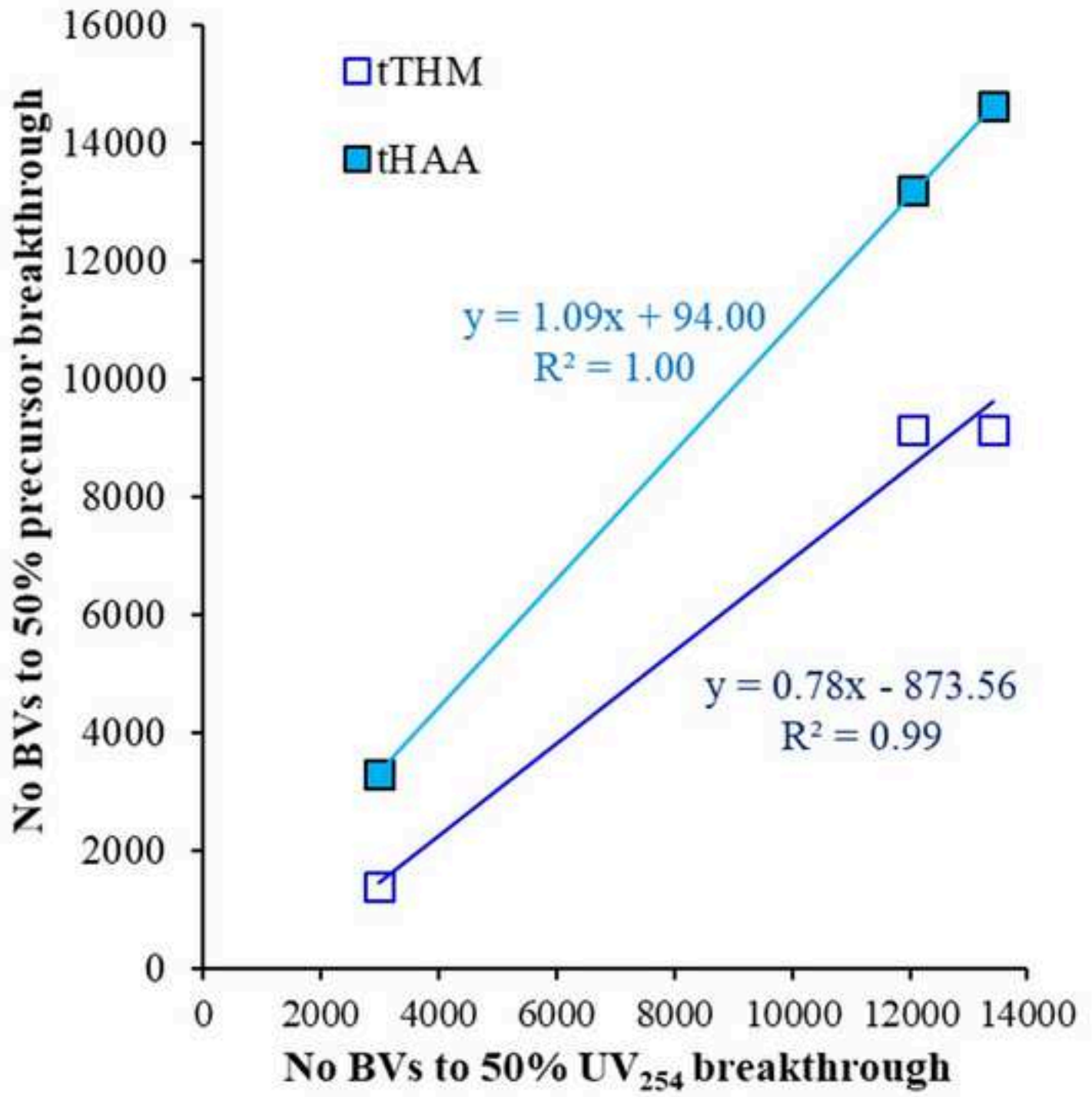


Figure 7a

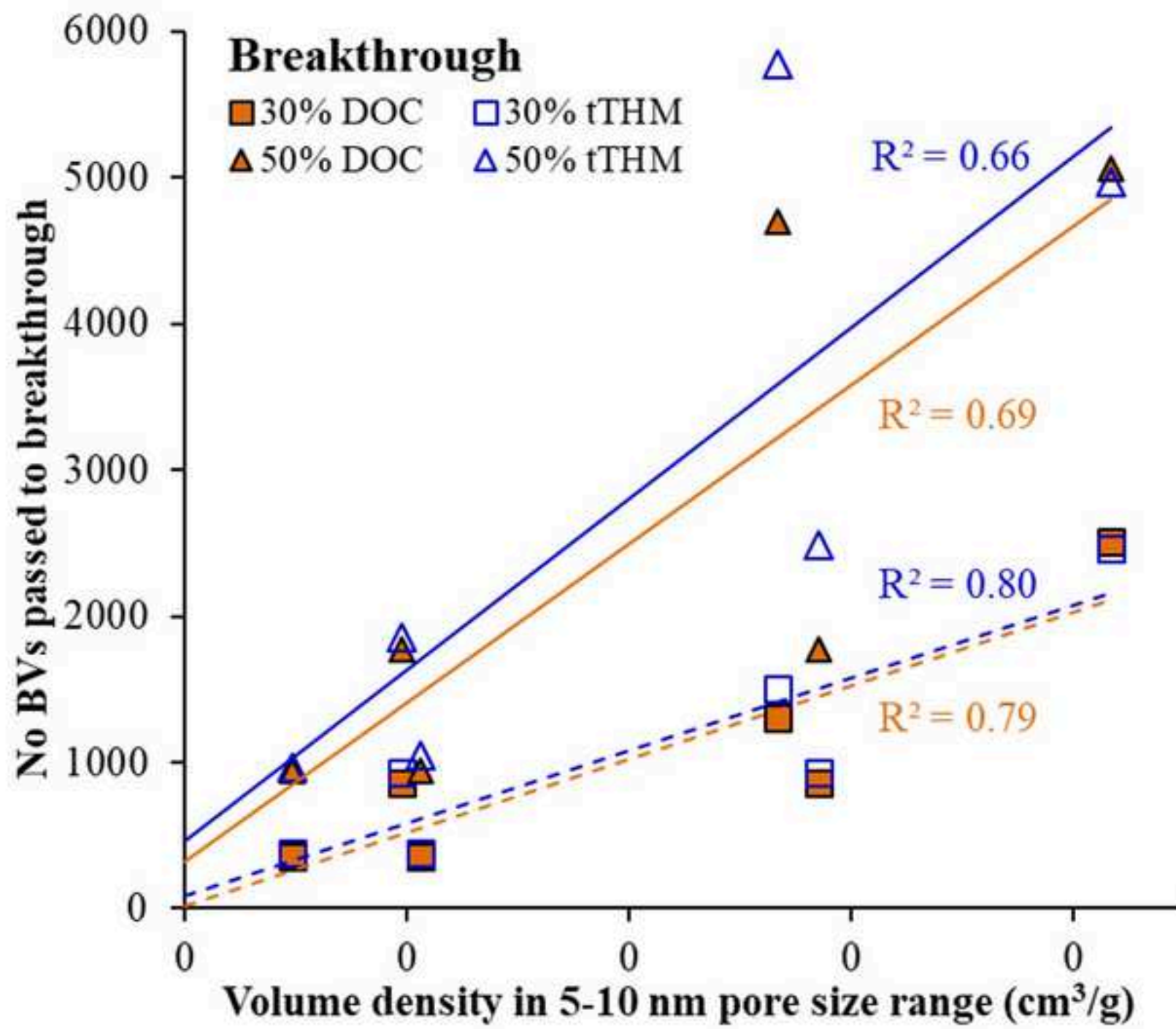


Figure 7b

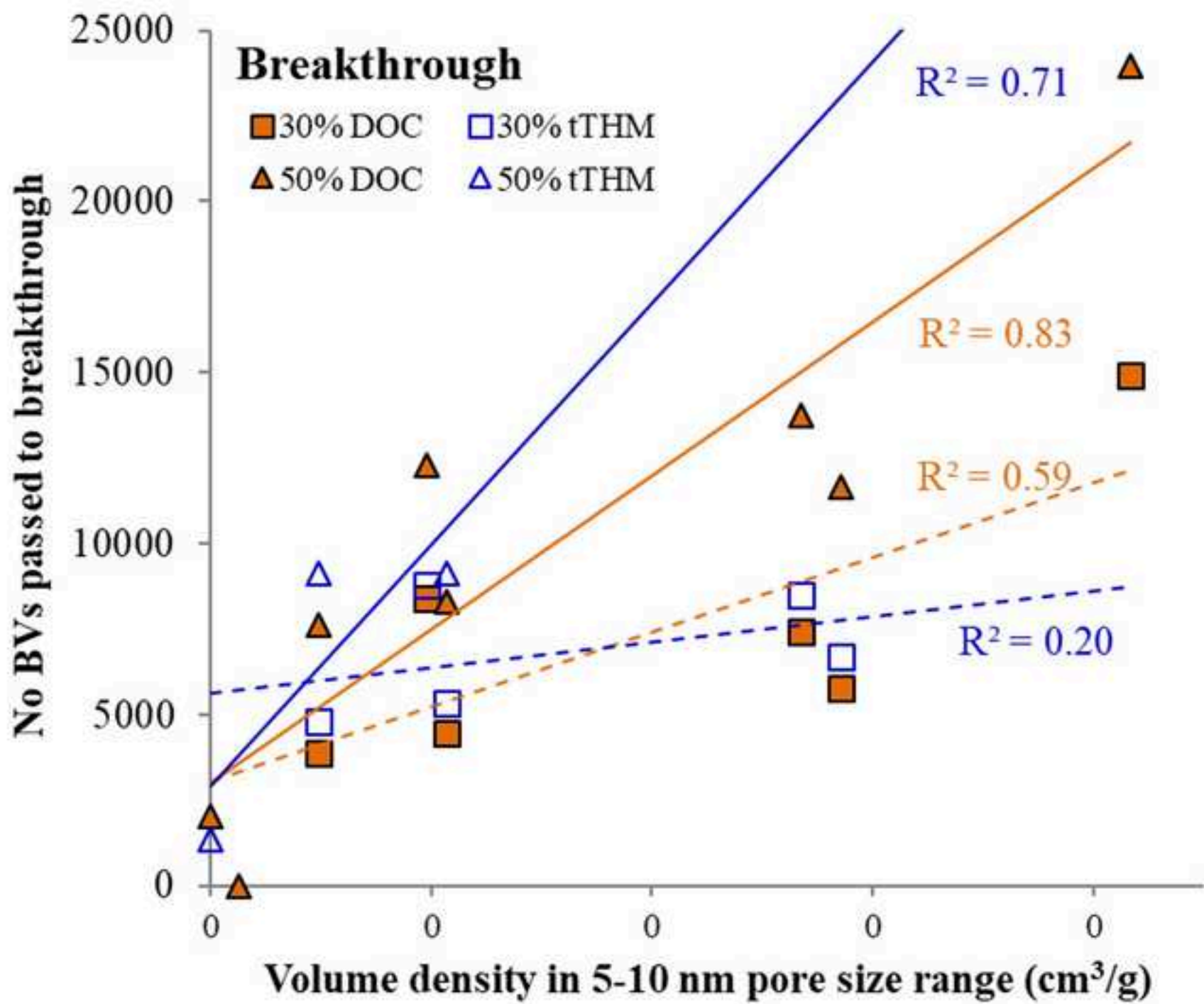


Figure 8

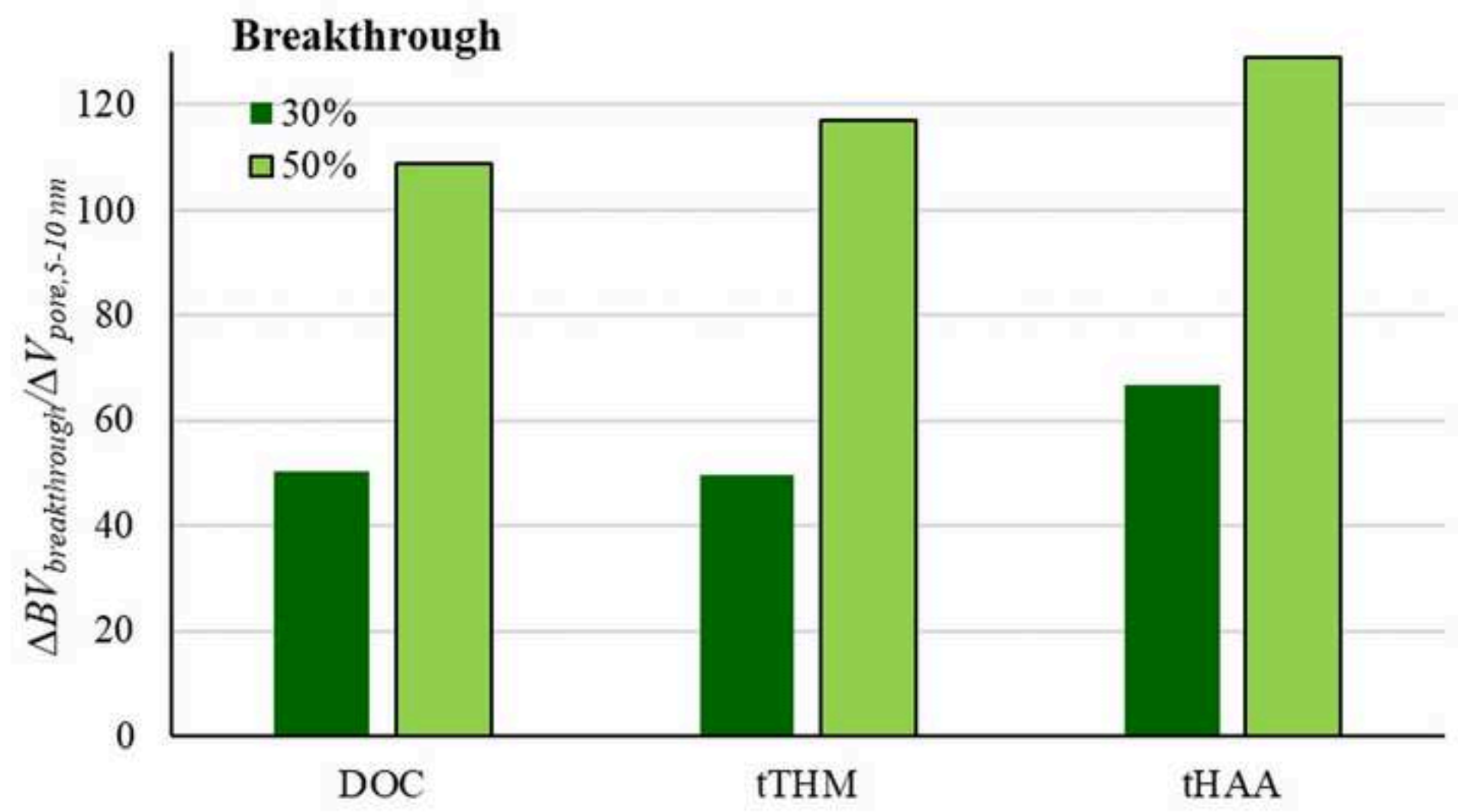


Table 1: Physicochemical characteristics of the two different water sources.

<i>Parameter</i>	<i>Water A</i>	<i>Water B</i>
pH	6.8	8.1
DOC (mg/L)	5.98	3.12
UV ₂₅₄ (/cm)	0.254	0.068
SUVA (mg/L/m)	4.25	2.18
tTHM (µg/L)	676.3	282
THMFP (µg/L per mg DOC)	113.1	90.4
tHAA (µg /L)	1006.4	126
HAA ₅ FP (µg/L per mg DOC)	168.3	40.4
Colour (mg/L Pt/Co)	33	4.47
Turbidity (NTU)	0.37	0.1
Conductivity (µS/cm)	166	569
HPO (mg/L)	3.44	1
TPI (mg/L)	1.25	0.71
HPI (mg/L)	0.37	1.05

Table 2[Click here to download Table: Table 2.docx](#)**Table 2:** The physicochemical properties of the media used for removal of NOM from two different water sources.

<i>GAC media</i>	V_{total} ¹ cm ³ /g	d_p nm	$V_{micropores}$ ² cm ³ /g	$V_{meso-pores}$ ³ cm ³ /g	$DFT\ area\ (m^2/g)^4$			<i>Granulation</i> ⁵ mm	$S_{BET,s}$ ⁵ m ² /g	S_{BET} m ² /g	IN ^{5,6} mg/g	<i>Precursor</i> ⁵
					0.7-1.7	1-2	>2					
<i>COL-L900</i>	0.460	≤26.1	0.347	0.112	444	506	72	0.425-1.70	900-1000	977±5	900	Bituminous coal
<i>F400</i>	0.442	≤26.1	0.271	0.073	431	416	49	0.425-1.70	1050	1032±5	1050	Bituminous coal
<i>208EA</i>	0.517	≤16.1	0.301	0.120	424	465	67	0.6-1.7	1000	1078±6	1000	Coal
<i>XC30</i>	0.511	≤26.1	0.205	0.156	325	340	66	0.6-2.36	1000	986±6	950	Coal
<i>DEO</i>	0.331	≤27.3	0.174	0.013	274	285	8	0.6-1.70	800	809±11	825	Coconut shell
<i>HT5</i>	0.581	≤27.3	0.401	0.029	621	652	14	0.42-1.70	1400	1419±12	1300	Coconut shell
<i>FY5</i>	0.400	≤16.1	0.288	0.004	452	471	3	1.40-3.35	1150	1043±11	1100	Coconut shell
<i>Brimac</i>	0.430	≤25	0.246	0.131	334	373	62	0.7-2.38	200	841±3	700	Bovine bones

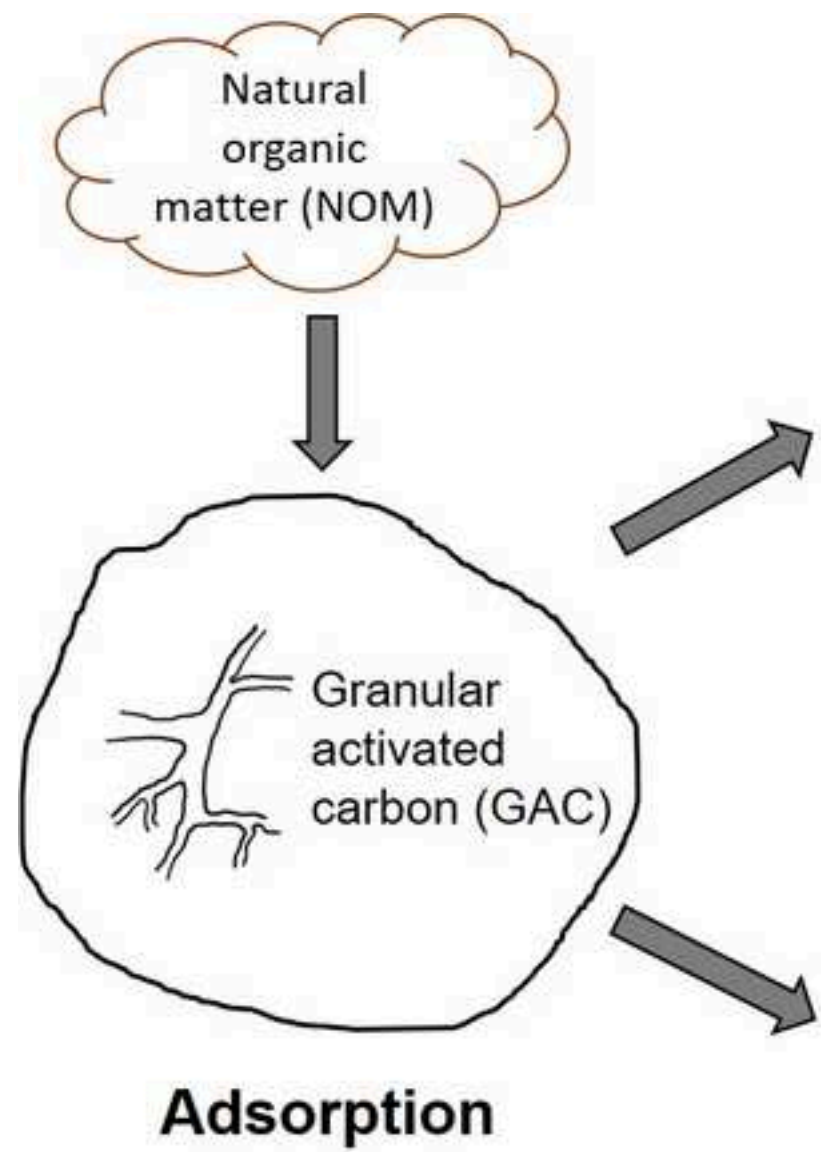
¹According to DFT (density functional theory), determined to <30nm; ²1-2 nm pore size range; ³>2 nm pore size; ⁴with reference to pore size range indicated; ⁵Data sourced from supplier technical sheets; ⁶Iodine number.

Table 3[Click here to download Table: Table 3.docx](#)**Table 3:** Volumetric pore size distribution, determined from DFT for pores sizes <30 nm.

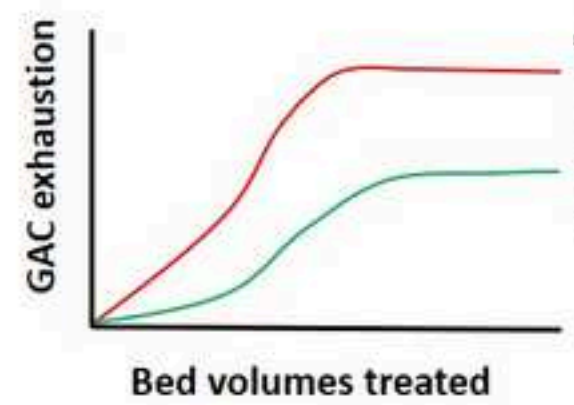
<i>Media/pore size:</i>	<i><0.7nm</i>	<i>0.7-5nm</i>	<i>5-10nm</i>	<i>10-15nm</i>	<i>15-20nm</i>	<i>20-25nm</i>	<i>25-30nm</i>	<i>Total</i>
<i>Col-L900</i>	0.001	0.440	0.011	0.006	0.002	0.001	0	0.460
<i>F400</i>	0.055	0.375	0.010	0.002	0	0	0	0.442
<i>208EA</i>	0.096	0.386	0.027	0.008	0.001	0	0	0.517
<i>XC30</i>	0.115	0.314	0.042	0.018	0.012	0.009	0.001	0.511
<i>DEO</i>	0.144	0.183	0.001	0.002	0.000	0	0	0.331
<i>HT5</i>	0.151	0.417	0.005	0.004	0.003	0.002	0	0.581
<i>FY5</i>	0.108	0.291	0	0.001	0	0	0	0.400
<i>Brimac</i>	0.053	0.316	0.029	0.016	0.010	0.007	0	0.430

Table 4[Click here to download Table: Table 4.docx](#)**Table 4:** Throughput to a filtrate DOC of 30%, 50% and 80% of the feed concentration (BV₃₀, BV₅₀ and BV₈₀ respectively) for the GAC media studied by RSSCT, waters A and B, EBCT_{LC} = 20 minutes.

GAC media	WTW A			WTW B		
	BV₃₀	BV₅₀	BV₈₀	BV₃₀	BV₅₀	BV₈₀
<i>COL-L900</i>	355	946	10,710	4,467	8,284	>>23,980
<i>F400</i>	858	1,775	10,030	8,402	12,308	>>23,980
<i>208EA</i>	1,301	4,704	>>22,194	7,455	13,728	>>23,980
<i>XC30</i>	2,514	5,059	>>22,194	14,911	23,964	>>23,980
<i>DEO</i>	<<267	<<267	503	<<1,302	<<1,302	1,302
<i>HT5</i>	355	946	8,047	3,875	7,633	>>23,980
<i>FY5</i>	<<267	<<267	1,242	<<1,302	2,041	8,284
<i>Brimac</i>	858	1,775	17,101	5,798	11,657	>>23,980

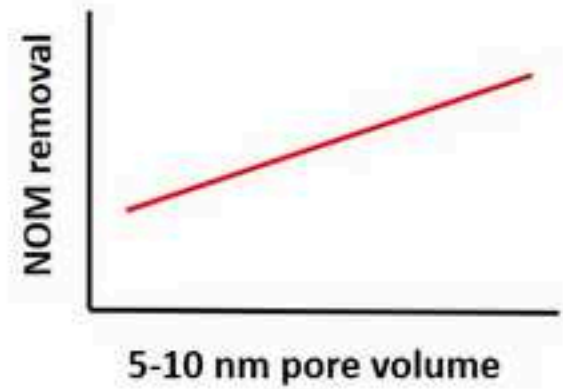


NOM character



High molecular weight, pore blocking organic matter decreases capacity

GAC pore structure



5-10 nm pore size range most important in determining capacity

2020-02-15

Influence of granular activated carbon media properties on natural organic matter and disinfection by-product precursor removal from drinking water

Golea, D. M.

Elsevier / IWA

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