








Cite this: *Environ. Sci.: Water Res. Technol.*, 2018, **4**, 529

Partial renewal of granular activated carbon biofilters for improved drinking water treatment

Nashita Moona, ^{*a} Kathleen R. Murphy, ^a Mia Bondelind, ^a
Olof Bergstedt ^b and Thomas J. R. Pettersson ^a

There is a trend of increasing natural organic matter (NOM) in raw drinking waters of Nordic countries due to climate change. Seasonal deterioration in NOM quality imparts challenges for delivering a consistently high drinking water quality. In this study, a simple and cost effective operational strategy was investigated that improved short-term NOM removal in a full-scale treatment plant. Three granular activated carbon (GAC) media biofilters were modified by replacing a small fraction of saturated filter media with new media. Relative to replacing the entire biofilter media, this approach required lower capital cost and shorter down-time, and maintained conditions for biological filter functioning. NOM removal efficiencies were compared in modified *versus* unmodified (reference) filters using online UV absorbance, and offline fluorescence and dissolved organic carbon measurements. The modified biofilters showed improved organic matter removal lasting for at least four weeks. Partial replenishment of GAC in full-scale biofilters may be a useful and sustainable operational strategy for coping with temporarily high NOM loads in raw waters that might otherwise cause water quality problems.

Received 11th October 2017,
Accepted 6th February 2018

DOI: 10.1039/c7ew00413c

rsc.li/es-water

Water impact

Biologically activated carbon (BAC) filters are an integral part of many drinking water facilities that improve the stability of distributed water quality. This study investigates a promising, cost-effective strategy to improve short-term natural organic matter (NOM) removal by full-scale BAC filters.

1 Introduction

Drinking waters around the world are often produced from surface waters that contain natural organic matter (NOM) and pathogens. NOM impacts drinking water treatment causing problems with treatment process control and optimization, and increases coagulant requirements and disinfection dose.¹ NOM further affects drinking water quality by forming carcinogenic disinfection by-products (DBPs) in combination with chlorine, promoting bacterial regrowth within the distribution system, and causing undesirable colour, taste and odor.² Seasonal periods of elevated NOM and organic pollutant concentrations in raw water due to *e.g.* heavy rainfall, snow melt run-off, or lake turnover and algae bloom, lead to rapid changes in raw water quality,³ affecting treatment efficiency and making it difficult to meet water-quality standards year-round.^{4,5}

For economic and practical reasons, efforts to improve the removal of NOM in continuously-operating treatment plants are usually directed towards optimizing and improving existing treatment steps instead of implementing costly up-

grades.⁶ Granular activated carbon (GAC) filtration is a common component of drinking water treatment plants (DWTPs) that can effectively remove NOM from drinking water as well as trace organic contaminants, including pesticides, taste- and odor-causing compounds (in particular geosmin and 2-MIB), and reduce DBP precursors.^{7,8} Owing to their high adsorption capacity, GAC filters remove small- to intermediate-sized humic-like NOM fractions.^{9,10} However, the adsorption capacity of new GAC diminishes rapidly, and GAC filters convert naturally to biologically activated carbon (BAC) filters over time.¹¹ Due to the high specific surface area of GAC absorbers,¹² biofilms form that adsorb organic molecules and shelter microbes that additionally perform biological degradation. This biofilm effectively consumes biodegradable organic matter (BDOC) and removes certain organics more effectively than GAC, promoting a stable water quality in the drinking water distribution network.^{13–16}

One possible way to improve short-term NOM removal by BAC (or saturated GAC) filters is to replace a small fraction of the filter media with new media (new GAC). Furthermore, if effective, this may be an economical solution compared to replacing the entire filter media due to lower investment cost and a shorter interruption to normal operations. The retention of a large proportion of saturated filter media maintains

^a Department of Architecture and Civil Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. E-mail: nashita.moona@chalmers.se

^b City of Gothenburg, Box 123, SE-424 23 Angered, Sweden



biological filter functioning, while the new GAC improves the filter's adsorption capacity. Unlike powdered activated carbon, this technique produces minimal sludge and since the removed GAC can be regenerated, this is a more sustainable solution. Despite these possible advantages, the technique is not commonly used in DWTPs and to the best of our knowledge, has not been addressed by the scientific literature.

NOM removal by activated carbon filters is traditionally assessed by measuring specific absorbance (SUVA), colour, turbidity, total organic carbon (TOC) and/or dissolved organic carbon (DOC).^{9,17,18} UV_{254} is often used as a surrogate for TOC and is strongly correlated with regulated DBP formation potential (DBP-FP) in drinking waters and organic micro pollutant removal in wastewaters.^{19,20} However, DOC, UV_{254} and SUVA are bulk properties that do not distinguish between different NOM fractions, and do not track low-molecular-weight aliphatic compounds.²¹ Previous studies show that humic fractions of NOM are removed more effectively by adsorption,²² whereas protein-like fractions are removed more effectively by biodegradation.²³ These fractions can be distinguished sensitively using fluorescence spectroscopy.^{23–25}

In this study, a short-term strategy for enhancing NOM removal was investigated whereby a small fraction of saturated filter media was replaced with new GAC in a full-scale drinking water treatment plant. Using continuous UV_{254} monitoring we addressed the question: how does partial GAC replenishment influence NOM removal by saturated GAC filter media, and how long does this effect last? Using fluorescence spectroscopy, we further addressed the question: which NOM fractions are influenced the most by GAC replenishment and what are the possible mechanisms in play?

2 Materials and methods

2.1 Treatment plant description

This study was carried out during summer period (July–August, 2015) at Mariebergs DWTP in Uddevalla municipality,

Sweden. The DWTP has an average treatment capacity of 11 300 m³ per day. The DWTP receives surface water from Lake Köperödsjö, which receives its water from a small stream running through farmland. This treatment plant was selected since it experiences odor episodes during summer months and has detected geosmin and 2-methylisoborneol suggesting an algal source leading to seasonal issues with undesirable taste and odor in the finished drinking water. In the years before this study was initiated, the DWTP in response, had converted several rapid sand filters into BAC filters, which is a common odor-reduction strategy in Sweden.^{26,27}

Marieberg DWTP uses processes consisting of direct filtration by continuous-upflow rapid sand filters (DynaSand®) with polyaluminum chloride for coagulation. The Dynasand filters ($n = 46$), are located in two separate halls containing 24 filters (Hall A, Fig. 1) and 22 filters (Hall B, Fig. 1), respectively. The coagulation contact time differs between these two halls and results in a slightly better coagulation performance in Hall B, and a pH difference between Hall A and B (Table 1). Following direct filtration, water from both halls enter seven GAC filters (placed in parallel) in down-flow mode (Fig. 1). After GAC filtration, filtered water passes through two-step disinfection by UV irradiation and chlorine dioxide (the chlorine dioxide dose in finalized water, leaving the DWTP was 0.11 mg l⁻¹ as the water leaves the DWTP).

At the time of this study, the DWTP was operating without any significant variations in the operation of treatment processes, except for the modification of the three GAC filters. Incoming raw water parameters were stable during the experimental period with DOC in the range of 8.0–9.9 mg C L⁻¹ and UV_{254} in the range of 0.35–0.38 cm⁻¹. After Dynasand filtration, the DOC levels were reduced by 65 ± 4% and UV_{254} was decreased by 85 ± 4%.

2.2 GAC filters

Marieberg DWTP has seven BAC filters that receive the filtrate from the upstream Dynasand filters. Water from the

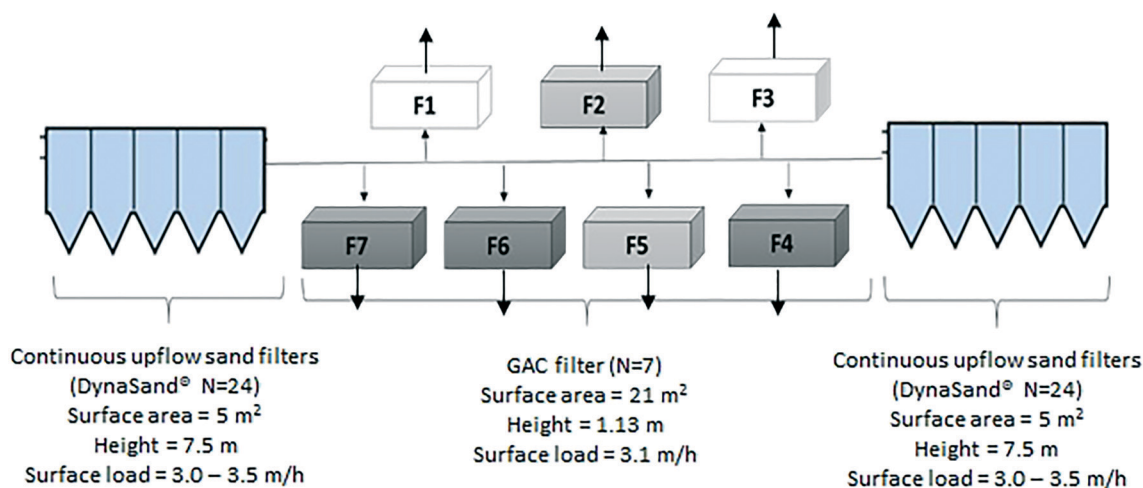


Fig. 1 Schematic of continuous-upflow sand filters and parallel downstream GAC filters in this study. Dark grey boxes (F4, F6, and F7) are modified GAC filters, light grey boxes (F1 and F3) are reference filters. Additional filters exist (F2 and F5), but were not studied in this experiment.



Environ. Sci.: Water Res. Technol., 2018, 4, 529–538 | 531



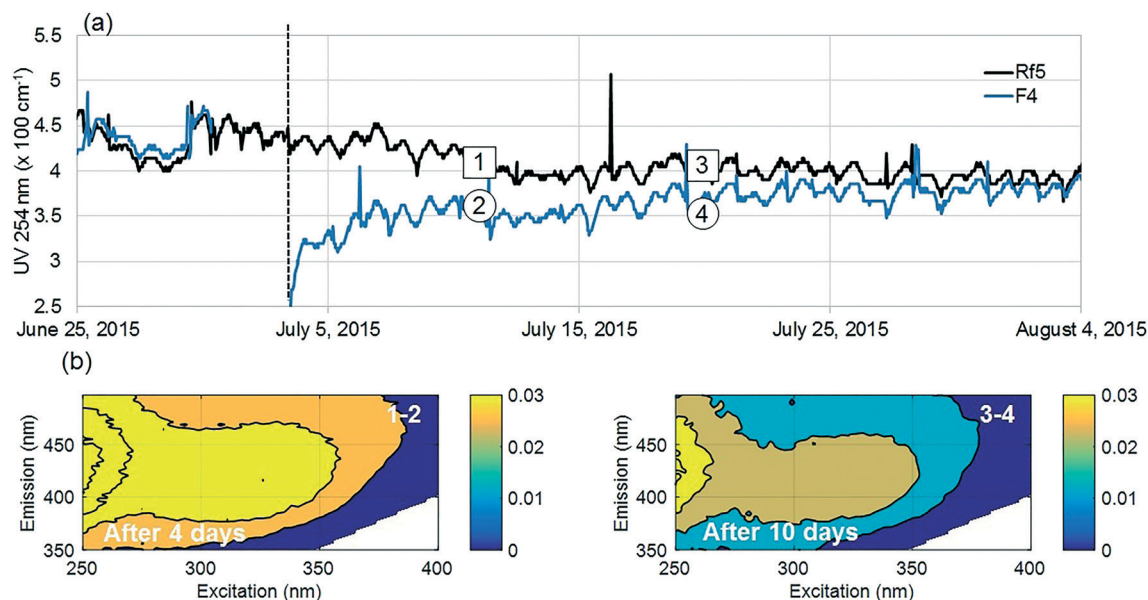


Fig. 2 Water quality in filtrates from modified (F4: blue line) and reference (Rf5: black line) filters. Vertical dotted lines denote filter start-up after GAC replenishment. Numbers denote grab sampling of Rf5 (squares) and F4 (circles). (a) UV₂₅₄ (m⁻¹) measured continuously; (b) fluorescence EEMs (in Raman unit) from filter F4 minus EEMs from filter Rf5. Data for 30 days are presented here.

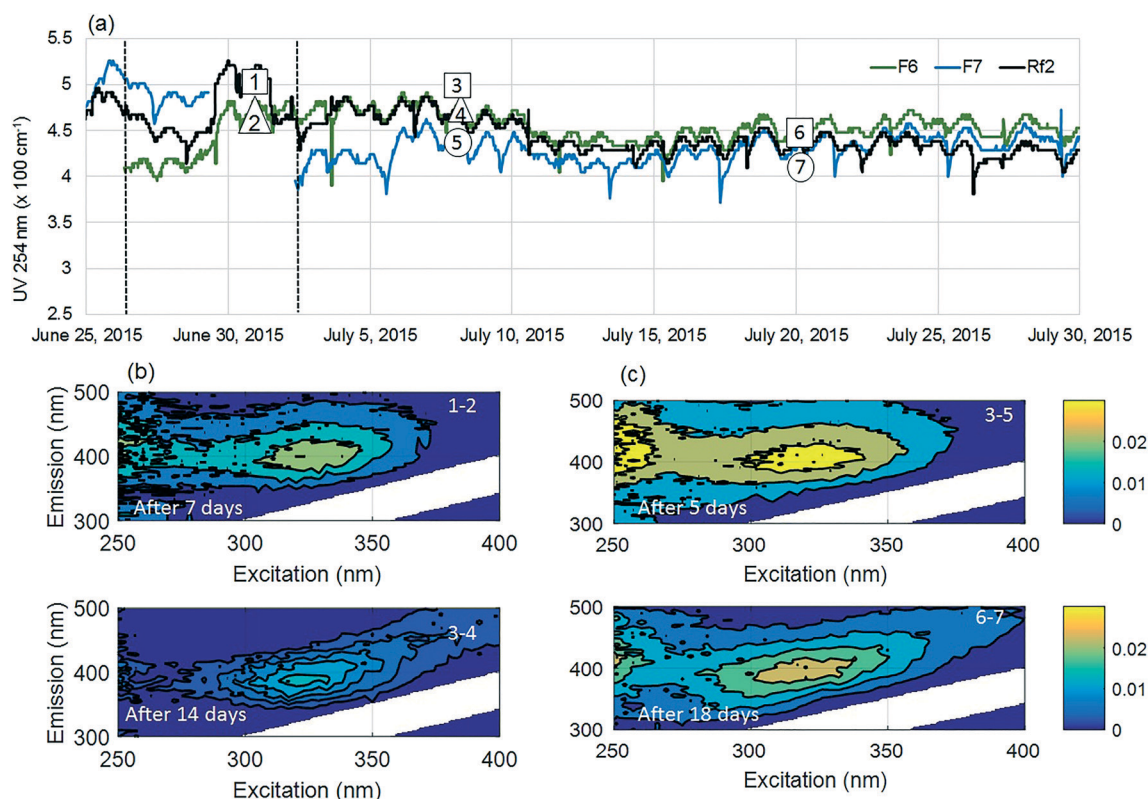


Fig. 3 Water quality in filtrates from modified (F6: green line, F7: blue line) and reference (Rf2: black line) filters. Vertical dotted lines denote filter start-up after GAC replenishment. Numbers denote grab sampling of Rf2 (squares), F6 (triangles) and F7 (circles). (a) UV₂₅₄ (m⁻¹) measured continuously; (b) fluorescence EEMs from filter F6 minus EEMs from filter Rf2, (c) fluorescence EEMs from filter F7 minus EEMs from filter Rf2. Data for 30 days are presented here.

modified filters were highest (15–80%) for the first 10 days compared to reference filters (Fig. 2a and 3a). Filter F4 was modified last and showed improvements for longer than

the other filters, possibly since it did not receive an increased surface load while other filters were out of operation.



3.2 Comparison of DOC measurements of modified and reference biofilter samples

DOC removal by the reference filters in this study was moderate initially (12–14%) and improved only marginally after GAC replenishment (18–23%). Previous work shows that new GAC filters typically remove around 40–90% of DOC through adsorption, depending on incoming water quality.^{38–41} After formation of biofilm, DOC removal by adsorption decreases gradually and both adsorption onto biofilm and biological degradation process contribute to DOC reduction at a lower removal efficiency (15–45%).^{23,42–44} In our study, the low DOC removal can be explained by the fact that the GAC in the filters was over three years old, although the relatively high DOC loading (Table 2) would have caused saturation within few months of regeneration.²¹

At the end of experiments, the relative DOC removal continued to be 15–45% higher by modified filters than the reference filters. Since biodegradation is the main removal mechanism within the reference filters, this additional removal by the modified filter is probably due to combination of biological degradation and adsorption.

3.3 Comparison of FEEM measurements of modified and reference biofilter filtrate samples

Fluorescence monitoring extended the results from UV₂₅₄ and DOC monitoring by revealing changes in NOM composition. Differential EEM ($EEM_{\text{Referencefilter}} - EEM_{\text{Modifiedfilters}}$) represents the portion of fluorescence removed after GAC replenishment by the modified filter. Differential EEM showed that during the first few weeks following GAC replenishment, modified filters were more efficient in removing all types of fluorescent organic matter (*i.e.* the complete range of excitation and emission wavelengths) compared to reference filter (Fig. 2b and 3b and c). With filter running time, as the active sites of new GAC became exhausted, the modified filters gradually returned to their original performance which is visible from the changes in intensity of the differential EEMs (Fig. 2b and 3b and c). The differential EEM results shows that modified filters were most efficient at removing FDOM with excitation/emission wavelengths Ex/Em of <250, 340/410–450 nm and <250, 290/340–380 nm region. These fluorescence peaks with emission <380 nm are generally attrib-

uted to protein-like fluorescence while peaks with emission >380 nm are attributed to humic-like FDOM.^{45–48}

PARAFAC analysis revealed three independently-varying fluorescent components were present in the samples (Fig. 4). Cross-referencing the components C1–C3 with the OpenFluor database³⁶ identified statistically similar signals in other studies. The first identified component, C1, with Ex/Em of <250, 330 nm/480 nm appears in many studies where it is believed to originate from terrestrial humic material.^{46,49,50} The emission at longer wavelengths suggests that C1 comprises of conjugated, aromatic, larger molecules with several functional groups.^{51,52} The second identified component, C2, with Ex/Em of <250, 330 nm/410 nm has fluorescence characteristic of productive freshwaters impacted by agriculture and of terrestrial humic-like NOM modified by microbial reprocessing.^{36,53} The third identified component, C3, with Ex/Em of <250, 290 nm/360 nm has a tryptophan protein-like character and may be associated with algal or microbial-derived organic matter and anthropogenic inputs.^{36,54,55}

Previously all of these identified PARAFAC components have been found to correlate with regulated and unregulated DBPs precursors.^{56–59} Thus their presence could indicate a risk for producing DBPs in chlorinated finished water.

3.4 Removal efficiency of NOM components in modified filters

Overall removal efficiencies of all optically-active (absorbing/fluorescing) NOM and DOC by the GAC filters are illustrated in Fig. 5. Error bars on this figure represent standard error calculated by the error propagation method⁶⁰ and are smallest for fluorescence measurements. Fig. 5 shows that the biofilters in this study preferentially removed FDOM fractions compared to both the wider DOM pool represented by DOC, and the UV-absorbing fractions that did not fluoresce. The relatively low removal of DOC indicates that a large fraction of the DOM pool consists of non-fluorescent fractions with relatively poor removal. However, removal of all three fractions including DOC improved following GAC replenishment, indicating a positive overall effect on NOM removal. Since there would be no biological removal associated with the new GAC, the increased removal is most-likely attributable to adsorption onto the new GAC filter material.

For fluorescent NOM, removal efficiencies in all modified and reference filters followed the trend $C2 > C3 > C1$, *i.e.* were highest for the microbial or processed humic-like component C2, lowest for the “terrestrial” humic-like component C1, and intermediate for the protein-like fraction (Fig. 5). This trend has previously been observed in BAC filter studies^{53,57,61} where it was concluded that C3 and C2 were more bioavailable and hence better removed by biodegradation than terrestrial humic-like component (C1). At the same time, other trends have been observed, for example, Peleato *et al.* observed highest removal of C3, while Fu *et al.* observed lowest removal of C3.^{18,62} These differences may be a function of different types of GAC supporting different biological communities, or may reflect differences in NOM composition in

Table 2 DOC concentration in incoming water and filtrates from GAC filters

Sample location	DOC ^a (mg C L ⁻¹)	Removal efficiency (%)
Filtrate from Hall A	3.5 ± 0.2	—
Reference GAC (Rf2)	3.0 ± 0.2	14
Modified GAC (F6)	2.8 ± 0.1	20
Modified GAC (F7)	2.7 ± 0.2	23
Filtrate from Hall B	3.3 ± 0.2	—
Reference GAC (Rf5)	2.9 ± 0.4	12
Modified GAC (F4)	2.7 ± 0.1	18

^a DOC removal measured from weekly sampling data averaged over one month after GAC replenishment.



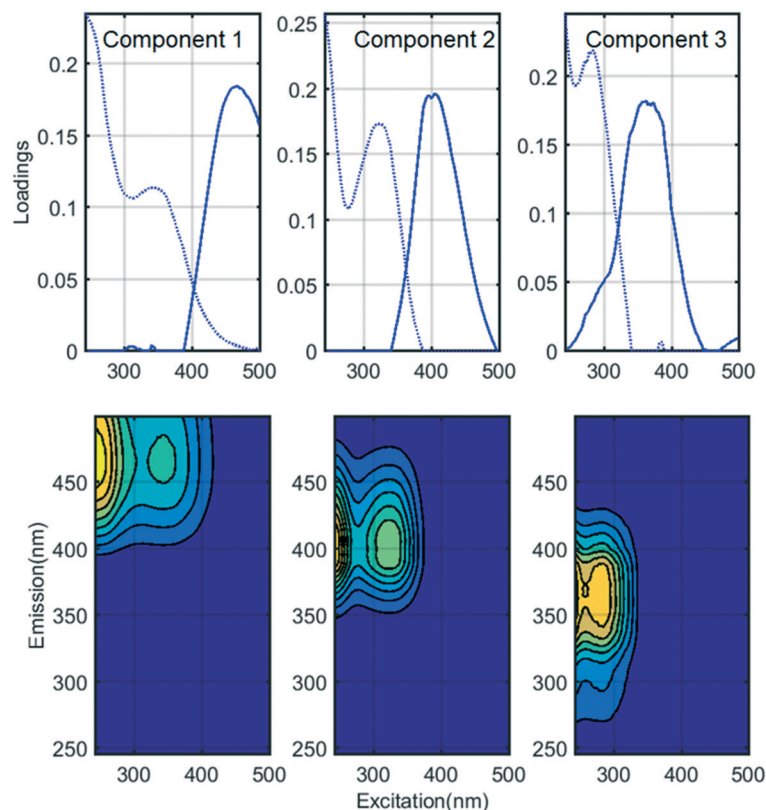


Fig. 4 Spectral properties of the three independent fluorescence components identified by PARAFAC in the DWTP dataset. Top: Excitation (dotted line) and emission (solid line) spectra for each component. Bottom: Fluorescence fingerprints; colors denote relative intensity.

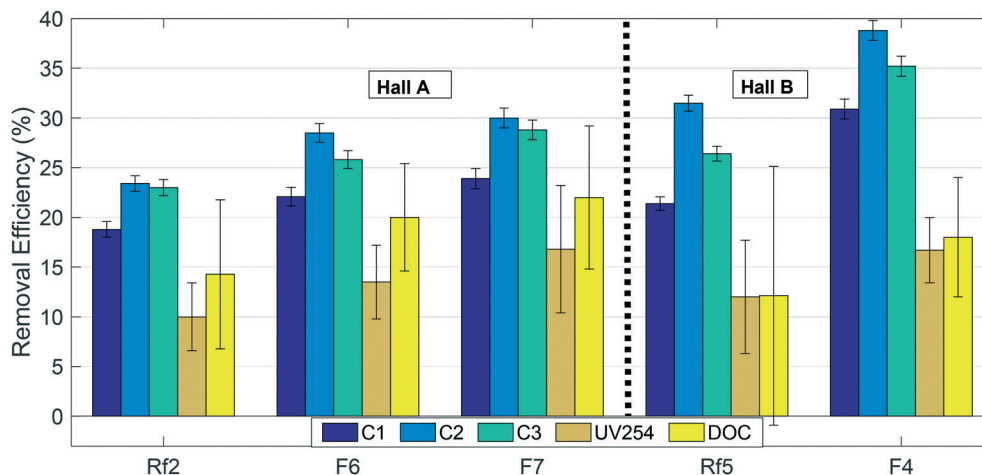


Fig. 5 Removal efficiencies of NOM fractions in modified (F6, F7 and F4) and reference (Rf2 and Rf5) filters. Error bars indicate standard errors calculated by error propagation ($N = 4$).

the incoming water. In this study, all the filters receiving water from Hall B showed better removal of fluorescent fractions and poorer removal of non-fluorescent fractions than all the filters receiving water from Hall A.

Previous work indicates that new GAC is most efficient at removing small to intermediate sized NOM fractions, because the GAC surface does not admit large-sized and condensed DOM.^{63–66} Longer-wavelength emitting components like C1 are generally believed to reflect a larger size fraction than

shorter-wavelength emitting components like C2,⁶⁷ which is consistent with the lower removal efficiency of C1 compared to C2. On the other hand, this does not explain the relatively poor removal of DOC, much of which consists of substances with lower molecular weights than humic acids.⁶⁸ If biological processing on the GAC filters converts fluorescent organic matter to non-fluorescent (and UV absorbing) soluble microbial products, this could account for the relatively high removal of FDOM despite low removal of DOC.



GAC replenishment caused a short-term improvement in the filters' capacity to remove NOM. Our results indicate differences in the treatment efficacy of various NOM fractions and differences in their removal mechanisms. Because only part of the GAC was replaced, the biological activity of the majority of the BAC was retained. Whether the modifications affected the biological activity of the remaining BAC in any way cannot be reliably determined from this study; in future, it would be worthwhile to study the effect of replacing different amounts of GAC to determine how much GAC can be replaced before the biodegradation function is unduly hampered.

3.5 Economic aspects of GAC replenishment

From economic perspective, adding a layer of GAC is much more economical than regenerating or replacing a complete GAC filter. While there are some fixed costs associated with modifying a GAC filter (e.g. administration and set-up time, acquisition and installation of pumps, biological tests), the majority of costs are proportional to the amount of GAC that will be replaced (e.g. new GAC purchase, extraction and distribution pump time, backwashing time, transportation and disposal costs). The operation cost for BAC systems is far less than for GAC systems with estimated savings around 2–3 fold including a 4–5 fold extension of service life.⁶⁹ Since the strategy maintained 90% of the filter media within the existing BAC filters, biodegradation continued to contribute to NOM removal at the same time that adsorption was boosted by new GAC. For many DWTPs, this simple strategy may be preferable to alternative options that would deliver similar improvements due to its relatively low cost and ease of implementation. Data obtained from Marieberg DWTP as well as a second DWTP in Sweden that recently implemented a similar strategy estimated costs in the range of 1750–2300 USD per m³ of GAC. Costs for DWTPs in other locations would be expected to vary depending on the total amount of GAC to be replaced and local labour, transport and waste management costs.

4 Conclusion

- Experiments performed on GAC filters at full-scale DWTPs indicated that replenishing a small fraction (10% bed height) of saturated filter media with new filter media temporarily improved the removal of various organic matter fractions. Some variations in performance could be attributed to variations in incoming water quality and flow rates.

- Online monitoring of UV₂₅₄ absorbance for four weeks following GAC replenishment indicated enhanced removal of the UV-absorbing NOM fraction lasting at least four weeks. The UV-absorbing fraction is known to include precursors of regulated DBPs.

- In all filters, removal efficiencies for fluorescent organic matter fractions followed the trend C2 > C3 > C1, i.e. highest for the microbial or processed humic-like component C2, lowest for the terrestrial humic-like component C1, and intermediate for the protein-like fraction.

- In all filters, DOC was removed much less efficiently than fluorescent fractions suggesting that some fluorescent organic matter was converted to non-fluorescent organic matter in the filter media.

- Partial GAC replacement is a relatively simple and cost-efficient strategy that could deliver short-term improvements in NOM removal to cope with temporarily strained operating conditions.

Abbreviations

BDOC	Biodegradable organic matter
BAC	Biological activated carbon
DBP	Disinfection-by-product
DBP-FP	DBP formation potential
DOC	Dissolved organic carbon
DWTPs	Drinking water treatment plants
EEMs	Fluorescence excitation-emission matrixes
FDOM	Fluorescent dissolved organic matter
GAC	Granular activated carbon
NOM	Natural organic matter
PARAFAC	Parallel factor analysis
R.U.	Raman units
SUVA	Specific absorbance
TOC	Total organic carbon
UV ₂₅₄	UV absorption at 254 nm

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This research was funded by the National drinking water research center DRICKS at Chalmers University of Technology, Göteborg Stad (Kretslopp och Vatten), Swedish Water and Wastewater Association (SVU), Västvatten AB, VIVAB, Trollhättan Energi, Sydsvatten and Norrvatten. The authors would like to thank the Marieberg DWTP (Västvatten AB) staff for their valuable and fruitful collaboration and especially Elisabet Edlund (water plant operator during the experimental period) for her cooperation in the collection of the water samples.

References

- A. Matilainen, E. T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar and M. Sillanpää, *Chemosphere*, 2011, **83**, 1431–1442.
- P. C. Singer, *Water Sci. Technol.*, 1999, **40**, 25–30.
- E. Hood, D. M. McKnight and M. W. Williams, *Water Resour. Res.*, 2003, **39**, 1188.
- S. A. Parsons, B. Jefferson, E. H. Goslan, P. R. Jarvis and D. A. Fearing, *Water Sci. Technol.: Water Supply*, 2005, **4**, 43–48.
- R. Vogt, *Increase in colour and amount of organic matter in surface waters*, In NORDTEST Position paper, 2003.
- M. R. Collins, G. L. Amy and P. H. King, *J. Environ. Eng.*, 1985, **111**, 850–864.



- 7 G. Newcombe, J. Morrison and C. Hepplewhite, *Carbon*, 2002, **40**, 2135–2146.
- 8 C. Kim, S. I. Lee, S. Hwang, M. Cho, H.-S. Kim and S. H. Noh, *Journal of Water Process Engineering*, 2014, **4**, 91–98.
- 9 J. L. Weishaar, G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii and K. Mopper, *Environ. Sci. Technol.*, 2003, **37**, 4702–4708.
- 10 T. Karanfil and J. E. Kilduff, *Environ. Sci. Technol.*, 1999, **33**, 3217–3224.
- 11 P. Servais, G. Billen and P. Bouillot, *J. Environ. Eng.*, 1994, **120**, 888–899.
- 12 R. M. Hozalski, S. Goel and E. J. Bouwer, *J. - Am. Water Works Assoc.*, 1995, **87**, 40–54.
- 13 W. H. Joe, I. C. Choi, Y. A. Baek, Y. J. Choi, G. S. Park and M. J. Yu, *Water Sci. Technol.*, 2007, **55**, 111–116.
- 14 S. Velten, M. Boller, O. Köster, J. Helbing, H.-U. Weilenmann and F. Hammes, *Water Res.*, 2011, **45**, 6347–6354.
- 15 S. Velten, *Adsorption capacity and biological activity of biological activated carbon filters in drinking water treatment*, ETH, 2008.
- 16 P. M. Huck, *Optimizing filtration in biological filters*, American Water Works Association, 2000.
- 17 AWWA, *Operational Control of Coagulation and Filtration Processes*, American Water Works Association, 3rd edn (M37), 2011.
- 18 J. Fu, W.-N. Lee, C. Coleman, M. Meyer, J. Carter, K. Nowack and C.-H. Huang, *Chemosphere*, 2017, **166**, 311–322.
- 19 P. C. Singer and S. D. Chang, *J. - Am. Water Works Assoc.*, 1989, **81**, 61–65.
- 20 J. Altmann, A. S. Ruhl, F. Zietzschmann and M. Jekel, *Water Res.*, 2014, **55**, 185–193.
- 21 A. Matilainen, N. Vieno and T. Tuhkanen, *Environ. Int.*, 2006, **32**, 324–331.
- 22 S. Ciputra, A. Antony, R. Phillips, D. Richardson and G. Leslie, *Chemosphere*, 2010, **81**, 86–91.
- 23 N. M. Peleato, M. McKie, L. Taylor-Edmonds, S. A. Andrews, R. L. Legge and R. C. Andrews, *Chemosphere*, 2016, **153**, 155–161.
- 24 K. R. Murphy, A. Hambly, S. Singh, R. K. Henderson, A. Baker, R. Stuetz and S. J. Khan, *Environ. Sci. Technol.*, 2011, **45**, 2909–2916.
- 25 R. K. Henderson, A. Baker, K. R. Murphy, A. Hambly, R. M. Stuetz and S. J. Khan, *Water Res.*, 2009, **43**, 863–881.
- 26 B. Johansson, *Dricksvattenteknik 3 (Publikation U8) Ytvatten*, Svenskt Vatten, 2011.
- 27 F. Persson, G. Heinicke, T. Hedberg, O. Bergstedt, C. Wångsell, H. Rydberg, I. Kjellberg and S.-E. Kristenson, *Mikrobiologiska barriärer i vattenrening*, Stockholm, 2005.
- 28 J. Kim and B. Kang, *Water Res.*, 2008, **42**, 145–152.
- 29 L. A. Rossman, *EPANET: Model for Water Distribution Piping Systems*, US Environmental Protection Agency, 2008.
- 30 Z. K. Chowdhury, R. S. Summers, G. P. Westerhoff, B. J. Leto, K. Nowack and C. J. Corwin, *Activated carbon: solutions for improving water quality*, American Water Works Association, 2013.
- 31 A. F. Hess, M. J. Chipps and A. J. Rachwal, *Filter maintenance and operations guidance manual*, American Water Works Association, 2002.
- 32 K. R. Murphy, K. D. Butler, R. G. M. Spencer, C. A. Stedmon, J. R. Boehme and G. R. Aiken, *Environ. Sci. Technol.*, 2010, **44**, 9405–9412.
- 33 E. E. Lavonen, M. Gonsior, L. J. Tranvik, P. Schmitt-Kopplin and S. J. Köhler, *Environ. Sci. Technol.*, 2013, **47**, 2264–2271.
- 34 R. Bro, *Chemom. Intell. Lab. Syst.*, 1997, **38**, 149–171.
- 35 K. R. Murphy, C. A. Stedmon, D. Graeber and R. Bro, *Anal. Methods*, 2013, **5**, 6557–6566.
- 36 K. R. Murphy, C. A. Stedmon, P. Wenig and R. Bro, *Anal. Methods*, 2014, **6**, 658–661.
- 37 Y. Tan, T. Lin, F. Jiang, J. Dong, W. Chen and D. Zhou, *Chemosphere*, 2017, **181**, 569–578.
- 38 D. S. Chaudhary, S. Vigneswaran, H.-H. Ngo, W. G. Shim and H. Moon, *Korean J. Chem. Eng.*, 2003, **20**, 1054–1065.
- 39 B. W. Dussert and G. R. Van Stone, *Water Eng. Manage.*, 1994, **141**, 22–24.
- 40 J. Lohwacharin, Y. Yang, N. Watanabe, A. Phetrak, H. Sakai, M. Murakami, K. Oguma and S. Takizawa, *presented in part at the WA Specialty Conference on Natural Organic Matter*, Costa Mesa, CA, USA, 2011.
- 41 E. E. Lavonen, D. N. Kothawala, L. J. Tranvik, M. Gonsior, P. Schmitt-Kopplin and S. J. Köhler, *Water Res.*, 2015, **85**, 286.
- 42 B. W. Dussert and G. R. Van Stone, *Water Eng. Manage.*, 1994, **141**, 22–24.
- 43 W. H. Kim, W. Nishijima, E. Shoto and M. Okada, *Water Sci. Technol.*, 1997, **35**, 147–153.
- 44 M. B. Emelko, P. M. Huck, B. M. Coffey and E. F. Smith, *J. - Am. Water Works Assoc.*, 2006, **98**, 61–73.
- 45 P. G. Coble, C. E. Del Castillo and B. Avril, *Deep Sea Res., Part II*, 1998, **45**, 2195–2223.
- 46 P. G. Coble, C. E. Del Castillo and B. Avril, *Deep Sea Res., Part II*, 1998, **45**, 2195–2223.
- 47 M. Li, X. Sun, F. Qian, H. Xu and Y. Liu, *Asian J. Chem.*, 2013, **25**, 10095–10101.
- 48 A. Li, X. Zhao, R. Mao, H. Liu and J. Qu, *J. Hazard. Mater.*, 2014, **271**, 228.
- 49 P. G. Coble, *Mar. Chem.*, 1996, **51**, 325–346.
- 50 Y. Yamashita and R. Jaffé, *Environ. Sci. Technol.*, 2008, **42**, 7374–7379.
- 51 J. Hur and G. Kim, *Chemosphere*, 2009, **75**, 483–490.
- 52 B. M. Lee, Y. S. Seo and J. Hur, *Water Res.*, 2015, **73**, 242–251.
- 53 S. A. Baghoth, S. K. Sharma and G. L. Amy, *Water Res.*, 2011, **45**, 797–809.
- 54 D. M. Reynolds and S. R. Ahmad, *Water Res.*, 1997, **31**, 2012–2018.
- 55 N. Hudson, A. Baker and D. Reynolds, *River Res. Appl.*, 2007, **23**, 631–649.
- 56 K. M. H. Beggs, R. S. Summers and D. M. McKnight, *J. Geophys. Res.: Biogeosci.*, 2009, **114**, 10.
- 57 N. M. Peleato and R. C. Andrews, *Water Sci. Technol.: Water Supply*, 2015, **15**, 589–598.
- 58 D. W. Johnstone, N. P. Sanchez and C. M. Miller, *Environ. Eng. Sci.*, 2009, **26**, 1551–1559.



- 59 B. Hua, K. Veum, J. Yang, J. Jones and B. Deng, *Environ. Monit. Assess.*, 2010, **161**, 71–81.
- 60 J. C. Pezzullo, Propagation and Compounding of Errors, <http://statpages.info/erpropgt.html>, (accessed January 18, 2018).
- 61 S. Peldszus, C. Hallé, R. H. Peiris, M. Hamouda, X. Jin, R. L. Legge, H. Budman, C. Moresoli and P. M. Huck, *Water Res.*, 2011, **45**, 5161–5170.
- 62 N. M. Peleato, B. S. Sidhu, R. L. Legge and R. C. Andrews, *Chemosphere*, 2017, **172**, 225–233.
- 63 E. Vuorio, R. Vahala, J. Rintala and R. Laukkanen, *Environ. Int.*, 1998, **24**, 617–623.
- 64 A. Matilainen, N. Vieno and T. Tuhkanen, *Environ. Int.*, 2006, **32**, 324–331.
- 65 C. J. Corwin and R. S. Summers, *Environ. Sci. Technol.*, 2010, **44**, 5403–5408.
- 66 J. E. Kilduff, T. Karanfil, Y.-P. Chin and W. J. Weber, *Environ. Sci. Technol.*, 1996, **30**, 1336–1343.
- 67 S. K. L. Ishii and T. H. Boyer, *Environ. Sci. Technol.*, 2012, **46**, 2006–2017.
- 68 F. Zietzschmann, C. Stützer and M. Jekel, *Water Res.*, 2016, **92**, 180–187.
- 69 C.-K. Lin, T.-Y. Tsai, J.-C. Liu and M.-C. Chen, *Water Res.*, 2001, **35**, 699–704.

