A rapid technique to determine performance and efficiency of activated carbon water filters

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ABSTRACT

The performance of activated carbon water filters, with respect to the breakthrough of dissolved organic matter (DOM) and dangerous trihalomethanes (THMs) from supplied water, has been analysed by fluorescence spectroscopy. Fluorescence spectroscopy has been demonstrated as a viable technique to monitor carbon filter performance, using the fluorescently active DOM species as an indicator. Due to the relationship between DOM and THMs, where DOM is the precursor for THM formation during the chlorine treatment of water, fluorescence spectroscopy can be used to predict the breakthrough of both species from activated carbon filters. In order to establish a versatile measurement technique, the most appropriate fluorescence excitation and emission wavelengths for detecting the DOM in water were firstly determined. These fluorescence measurement parameters were then applied to effluent water samples from carbon filters, over a total filtrate volume of 4,200 L. The total THM concentration in filtered water samples was determined by headspace gas chromatography (HSGC), with the fluorescence and HSGC results showing a high degree of correlation for the amount of DOM and THM respectively. Importantly, this correlation is observed for both of the determined fluorescence measurement parameters, highlighting the validity and versatility of this technique.

Key words | activated carbon, dissolved organic matter, fluorescence, trihalomethanes, water filter

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INTRODUCTION

As the global demand for clean drinking water increases, there is a growing need to provide rapid and effective methods for analysing the quality of water purposed for human consumption. Currently, the common process of providing potable water involves multiple steps including flocculation, sedimentation and filtration of impurities, followed by disinfection to remove harmful pathogens (NHMRC 2011). The quality of treated water is routinely tested by techniques including measurement of pH, total organic carbon, conductivity, turbidity and assessment of sulfates, nitrates and chlorine (Briggs & Grattan 1990). While the treatment process can provide water that meets the minimum safe standard set by governing bodies, analysis confirms that trace amounts of harmful toxins and impurities remain at varying levels (Richardson 2003; Sadiq & Rodriguez 2004; Baghoth *et al.* 2011).

The major impurities in supplied water include dissolved organic matter (DOM) that is carried over from the source water and disinfection by-products (DBPs), which are formed during the chlorination treatment process (Stedmon *et al.* 2003; Sadiq & Rodriguez 2004; Ibrahim *et al.* 2016). DOM is a heterogeneous class of compounds, with the majority formed by the humification of organic matter (Ma *et al.* 2001; Rodríguez *et al.* 2014). This class of

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compounds are often catagorised as either protein like, humic like or fulvic like, based on the core structures of individual species (Her *et al.* 2003). The presence of DOM has been reported in naturally occurring bodies of water, including lakes, rivers and reservoirs, with the exact makeup of DOM governed by the local vegetation (Mostofa *et al.* 2013). DOM in water is significant as these species are the precursors to the formation of the above mentioned dangerous DBPs (Pifer & Fairey 2014). Chlorine, added to water to neutralise harmful pathogens can react with the DOM, specifically the humic and fulvic like species that contain a high degree of aromatic functionality, to form the harmful halogenated DBP species (Singer 1999). The formation rate of DBPs has been directly linked to the concentration of DOM, hence DOM levels are minimised prior to chlorine treatment flocculation, sedimentation and adsorption methods (Bougeard *et al.* 2010). Despite best efforts, enough DOM remains to cause DBP formation, which remains in the supplied water. Some of the most dangerous DBPs formed during this process are the trihalomethanes (THMs), which have been linked to adverse health effects in humans, including cancer (Wang *et al.* 2007).

Due to the presence of the residual contaminants in supplied water, there has been an increase in the use of end point water filter systems. Of the available systems, activated carbon filters are the most efficient and cost effective (Gupta & Saleh 2013). These filters remove harmful organic pollutants and toxic chemicals from water via adsorption processes, where these impurities are captured through non-covalent interactions (van der Waals, dipole-dipole, electrostatic etc.) within the porous matrix of the material (Moreno-Castilla 2004). Activated carbon can remove species ranging from agricultural and industrial pollutants to the naturally occurring DOM and toxic by-products present in supplied water (McKay *et al.* 1985; Sakoda *et al.* 1991; Dastgheib *et al.* 2004; Namasivayam *et al.* 2007; Rasheed *et al.* 2016). Domestic activated carbon filter systems are used to prevent exposure to the harmful contaminants in water and to improve its overall purity.

The working efficiency and lifetime of activated carbon water filters is of significant interest to people who have invested in these devices to deliver purified water. Generally, these parameters will be tested by manufacturers with a report of filter performance made available to consumers. Filter lifetime is commonly measured as a maximum volume of water that can pass through the filter before unacceptable breakthrough of certain compounds occurs. In reality however, the total volume that passes through a filter is likely unknown to the user(s) and therefore filter lifetime is commonly given as a time parameter (e.g. 12 months). However, the suggested filter lifetime is an estimated value, based on average use and influent water quality. The quality of the influent water will have the greatest effect on filter performance and lifetime and is generally the most variable parameter. Water is often supplied from a range of different sources including reservoirs, lakes and rivers and its quality (concentrations of dissolved contaminant species and sediments) can vary significantly from source to source as well as seasonally (Sharp *et al.* 2006; Hudson *et al.* 2007). Water quality (along with potential higher than recommended filtered volumes), will impact the duration over which the filter will perform adequately, with these two factors likely to lead to contaminant breakthrough in a shorter timeframe than the manufacturer's recommendation. The ability to rapidly monitor the performance of an activated carbon filter is therefore highly relevant for individuals who rely on these systems to deliver clean water.

It is of interest to detect THMs for the analysis of filter performance, as these are one of the significant classes of harmful species that the activated carbon filter should be removing. In practice however, the detection of THMs in water requires specialised analytical equipment and sample preparation and this species is not practical to target directly in order to determine filter performance (Kuivinen & Johnsson 1999; Cho *et al.* 2003). It is therefore necessary to identify another target compound that can be easily detected in water and can be used as an indicator for filter performance.

Importantly, there have been recent reports that show a linear correlation between the DOM concentration in water and the total THMs concentration (Yang *et al.* 2015; Li *et al.* 2016). This correlation however has only been reported in treated water and not for treated then end point filtered water. One study has investigated the relationship of DOM breakthrough from granular activated carbon water filters, to the breakthrough of trace organic impurities derived from pharmaceuticals contamination (Anumol *et al.* 2015).

This study showed a linear relationship between the measured DOM and specific trace organic impurities. As yet however, there has not been a direct investigation into the relationship of DOM and THMs concentration in activated carbon filtered water.

Significantly, the measurement of DOM in test water samples uses the relatively simple technique of fluorescence spectroscopy, with DOM being extensively analysed by this method (Hudson *et al.* 2007). The organic compounds that constitute the DOM (including protein like, humic like and fulvic like substances), contain a high amount of fluorescently active functional groups such as aromatic hydrocarbons (Her *et al.* 2003; Hudson *et al.* 2007). Therefore, even at low concentrations the presence of these species can be easily determined by fluorescence spectroscopy (Peiris *et al.* 2009). The detection of DOM in various water sources by fluorescence spectroscopy has been widely used for decades and is a well-established and understood phenomenon (Fellman *et al.* 2010). It should be noted however, that only a percentage of the DOM compounds give rise to the fluorescent signal; a parameter that will vary depending on the water source. Therefore, the exact concentration of DOM cannot be directly determined by fluorescence alone, however this measurement can be used as a comparison for other measurements made using water from the same source.

This investigation aimed to demonstrate the use of fluorescence spectroscopy as a viable and rapid technique to determine the running performance of activated carbon water filters. UV-Vis and fluorescence spectroscopy characterisation of tap water was used to identify the most appropriate excitation/emission wavelengths for fluorescence analysis of filtered water samples. Two specific ex./em. wavelength pairs were subsequently used to measure the fluorescence from activated carbon filtered water samples, at 150 L increments over a total filtrate volume of 4,200 L. The fluorescence intensity of each water sample over the filtered volume at each ex./em. pair was measured, along with the total concentration of THMs (as determined by headspace gas chromatography (HSGC)). This allowed the correlation of fluorescence intensity and THM concentration to be evaluated over the total filtered volume of water. Fluorescence spectroscopy and HSGC for THM concentration was also performed on tap water, at each filter sample increment. The compiled results for filtered and tap water samples allowed the percentage breakthrough of DOM and THMs to be determined and the relevant correlations to be explained. Principal component analysis (PCA) was also performed to demonstrate the clearly measurable differences in the obtained fluorescence spectra.

EXPERIMENTAL METHODS

Materials and equipment

Water filters were obtained from Puratap Pty. Ltd. (Stepney, South Australia) and consisted of an in-line sediment filter (cellulose mesh) and an activated carbon filter (coconut husk derived) in a single housed unit. For filtered water sample collection, a custom built filter rig was used (Figure S1), comprising housing and flow controllers for four filter units and a total volume meter. Humic acid mixture was purchased from Sigma Aldrich (Castle Hill, Australia). A stock humic acid solution was prepared by dissolving a pre-weighed amount of humic acid in 0.01 M NaOH and then adjusting the pH of solution to 7 by addition of $HCl_{(aq)}$. Standard solutions were made from dilutions of the stock in MilliQ water. THMs standard was purchased from Leco (Castle Hill, Australia) and consisted of the four major THM compounds, bromodichloromethane, bromoform, chloroform and dibromochloromethane at 2,000 μg/mL each in methanol. For preparation of gas chromatograph (GC) standards, MilliQ water (Millipore Academic A10, specific resistance 18.2 MΩ·cm) was heated at 100°C for 1 h under a nitrogen flow to remove any volatile organic compounds. The pretreated MilliQ water was used for preparing all GC blank solutions and standards. MilliQ water samples for fluorescence measurements were used untreated, directly from the Millipore filtration system.

Water filter operation and sample collection

Four filter units were placed into the custom built filter rig where tap water was passed through each, at a flow rate of 1.5 L/min. The pH of tap water was measured as 7.52. Two separate water samples were collected for each filter

at intervals of 150 L. The first was for fluorescence measurements and was collected in a screw cap vial. The second was for GC, where precisely 10 mL of sample water was collected and dispersed into a specific GC vial. The vial was then crimp sealed and placed at 4°C prior to analysis.

UV-Vis spectroscopy

UV-Vis spectroscopy was performed using a Varian Cary 50 Scan spectrometer. All samples were collected at 23°C, using a quartz cuvette with path length of 1 cm. Absorbance spectra were recorded over the wavelength range of 200–800 nm at a resolution of 80 nm/sec with MilliQ water used for baseline correction.

Fluorescence spectroscopy

Fluorescence spectroscopy was performed on a Varian Cary Eclipse spectrometer. A fluorescence excitation scan was performed over the wavelength range of 200–400 nm, while monitoring the fluorescence intensity at 430 nm. Emission spectra were recorded using an excitation wavelength of 250 or 365 nm with emission measured over the range of 300–700 nm or 395–600 nm respectively. Maximum fluorescence intensity was measured as the emission intensity at 425 nm or 446 nm for 250 or 365 nm excitation respectively. Fluorescence intensities for filtered water samples are reported as the average of four measurements from four individual filter units.

Headspace gas chromatography

Samples were analysed using an Agilent 7890A GC-μECD GC with headspace sampler (HP 7694). The headspace gas was generated by heating samples in the sampler oven for 10 min at 100°C and then injected into the capillary column (DB624, J & W scientific 122-1334) of 30 m length, 0.25 mm internal diameter and 1.40 μm film thickness. The initial and final temperatures of the column were 35 and 230°C, with a temperature increment rate of 12°C/min to 105°C, then held for 5 min, and then 50°C/min to 230°C, then held for 2 min. The retention times for chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochlormethane ($CHClBr_2$) and bromoform ($CHBr_3$) were 6.35, 8.46, 10.75 and 14.05 min, respectively (see Figure S2). Detector signals were analysed through Agilent's ChemStation software package. Sample concentrations were compared with standard calibration curves. Mixed standard solutions (200, 20 and 2 μg/mL) were prepared in 2 mL amber glass vials by diluting the stock solution using methanol. Working standard solutions were prepared daily in 10.0 mL volumes using the pretreated MilliQ water, in 20 mL headspace vials and crimp sealed. Each stock solution and the corresponding dilutions were stored in a refrigerator below 4°C before analysis. The method was sensitive and accurate by headspace GC with a detection limit of 0.1 μg/L and calibration range of 0.1–250 μl/L ($R^2 = 0.9995$).

RESULTS AND DISCUSSION

Determination of appropriate excitation/emission wavelengths for characterising filter performance

In order to demonstrate a versatile fluorescence technique for monitoring the performance of activated carbon water filters, appropriate excitation and emission wavelengths for analysis must be determined. To identify ex./em. wavelengths, UV-Vis spectroscopy of tap water was performed, with the spectrum displayed in Figure 1(a). In parallel to UV-Vis spectroscopy, a fluorescence excitation scan was also performed, while monitoring the intensity at 430 nm (Figure 1(b)). The emission wavelength of 430 nm was selected as an indicative wavelength, based on the previously reported emission properties for DOM in water (Birdwell & Engel 2010). It is observed in the UV-Vis spectrum (Figure 1(a)) that tap water absorbs strongly in the wavelength range <370 nm, with significant absorbance at shorter wavelengths. When analysing the fluorescence excitation scan, a significant peak is observed at 250 nm, with smaller peaks at 290 nm and 365 nm. These peaks correlate with the wavelengths of higher absorbance observed in the UV-Vis spectrum. One other feature to note in the fluorescence excitation spectrum of MilliQ is the peak at 370 nm that corresponds to the Raman emission band of water (Parker 1959). While this feature partially overlays with

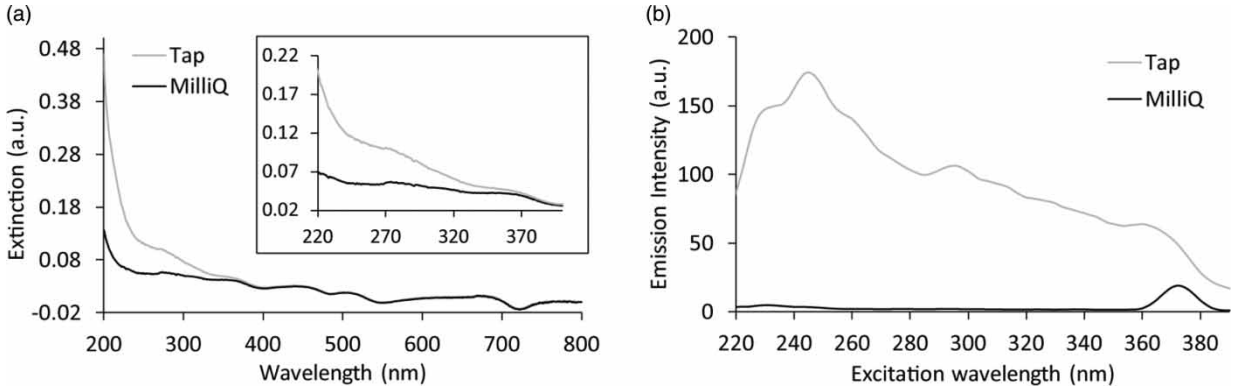

Figure 1 | (a) UV-Vis spectra of tap and MilliQ water samples, inset displaying the UV-Vis absorbance over the range of 220–400 nm. (b) Fluorescence excitation scan for tap and MilliQ water, monitoring the fluorescence intensity at 430 nm.

(and contributes to) the excitation peak at 365 nm, it can be corrected for by baselining the water samples to MilliQ.

To determine the appropriate excitation wavelengths for DOM analysis in water, the nature of the adsorbing species is investigated. The excitation peak at 250 nm corresponds to π-π* excitation in the aromatic functional groups present in the DOM (Sutton & Sposito 2005) and is the dominant excitation event. The 290 nm excitation peak corresponds to fluorescently active amino acids tryptophan, tyrosine and phenylalanine (Stedmon & Markager 2005). The 365 nm peak corresponds to the n-π* excitation event, which is again present in the DOM species and relevant for characterising filter performance (Rodríguez *et al.* 2014). From the UV-Vis and fluorescence excitation analysis of tap water, it can be determined that two appropriate excitation wavelengths for monitoring activated carbon filter performance are 250 nm and 365 nm.

With appropriate excitation wavelengths selected, the resulting fluorescence emission at these wavelengths is characterised. Figure 2 displays the raw and baseline corrected fluorescence spectra for tap and MilliQ (raw only) water samples using 250 nm and 365 nm excitation wavelengths. Figure 2(a) and 2(b) display the raw and baseline corrected spectra using 250 nm excitation, where a prominent fluorescence band is observed. The position of the peak maximum for the emission band is centred at 425 nm, in both the raw and corrected spectra respectively. Figure 2(c) and 2(d) displays the raw and corrected spectra for tap water using the excitation wavelength of 365 nm. In Figure 2(c) the previously mentioned Raman emission band associated with water is clearly present at 416 nm (Parker 1959). When the fluorescence spectrum of the sample is baseline corrected using the MilliQ spectrum, a conventional fluorescence band is resolved. In this case the position of the peak maximum is at 446 nm, a red shift of 21 nm compared to that for 250 nm, due to the lower energy wavelength of excitation. This analysis shows the ex./em. pairs of 250/425 nm and 365/446 nm are appropriate measurement parameters for the fluorescence analysis of DOM in tap and filtered water. As the observed fluorescence intensity correlates to DOM concentration, breakthrough of these species from the activated carbon filter should result in higher fluorescence intensity.

Analysis of filtered water samples

Activated carbon water filter performance was assessed based on the fluorescence intensity (i.e. indicative concentration of DOM) and the total concentration of THMs, at 150 L intervals over the total test volume. Figure 3(a) and 3(b) display the results of these measurements, with Figure 3(a) showing the peak fluorescence intensity (average from the four filter units tested) for each water sample collected. In this figure, data using the ex./em. pair of 250/425 nm is presented, with data for the 365/446 nm pair presented in the supporting information, Figure S3. Figure 3(a) also displays the average peak fluorescence intensities of both MilliQ water and tap water as two references for ultrapure and influent water respectively. It can be immediately observed that the initial filter performance (low volumes)

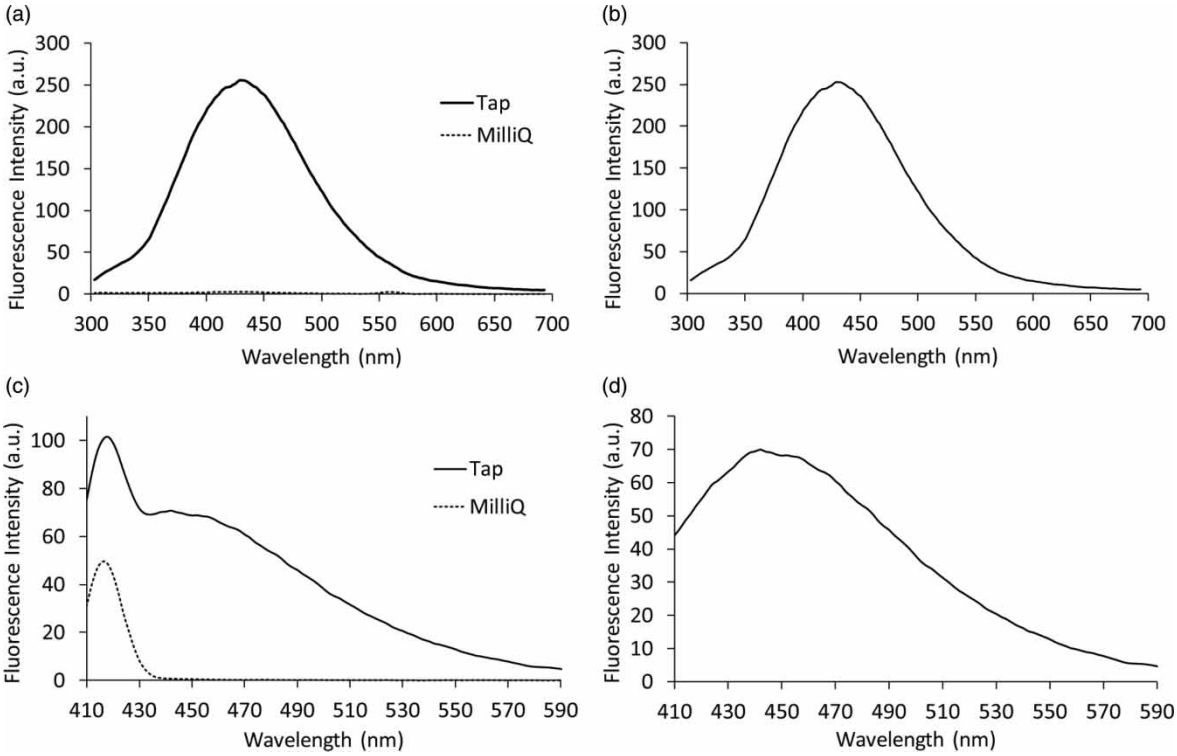

Figure 2 | (a) Raw fluorescence spectra for tap and MilliQ water samples and (b) background corrected fluorescence spectra for tap water, using 250 nm excitation. (c) Raw fluorescence spectra for tap and MilliQ water samples and (d) background corrected fluorescence spectra for tap water, using 365 nm excitation.

is close to that of the MilliQ filtration system, for removal of DOM. As higher volumes of water are passed through the filter the performance gradually decreases, up to the point where the filtration ability is nearly lost and the fluorescence intensity is reaching that of tap water. This indicates that by this volume the concentration of DOM in the filtered water and tap water is similar.

A fluorescence calibration curve using a commercial humic acid mixture was made and used to estimate the concentration, in mg/L, of the DOM in the collected water samples. Figure S4(a) displays the calibration and (b) determine DOM concentration for each water sample (calculated using the average fluorescence intensity of each). The concentration of DOM in the effluent water samples is initially around 0.17 mg/L and rises to over 1.6 mg/L after 4,200 L filtrate volume. At 2,000 L filtrate volume (the manufacturers recommended filter lifetime), the concentration of DOM is approximately 1 mg/L, which corresponds to a breakthrough of 72%. This data serves as an estimate of the DOM concentration in the water samples, as the fluorescence properties and proportions of fluorescent and non-fluorescent organic compounds are different between the humic acid mixture and constituents of local DOM. For a more accurate representation of the real samples, the fluorescent intensities of the water samples and not the calculated DOM concentrations have been used, when making comparisons to other measurements.

One feature to note in the average filter fluorescence intensity trace (Figure 3(a)) is the appearance of steps at regular sample intervals. These steps, appearing as slight decreases in the observed fluorescence intensity, correspond to the first water sample collected following an overnight halt in water flow through the filter. This phenomenon is observed for each overnight stop of water flow and is most pronounced for the sample collected at ~2,400 L, corresponding to the beginning of the additional 1,800 L volume and after the filter had no flow for 10 days. The overnight and 10 day stops were included in order to observe the effect of a rest period on the immediate and continuing performance of the filters. The observed decreases in the measured intensity is attributed to the increased adsorption of organic species from the void water, which was static in

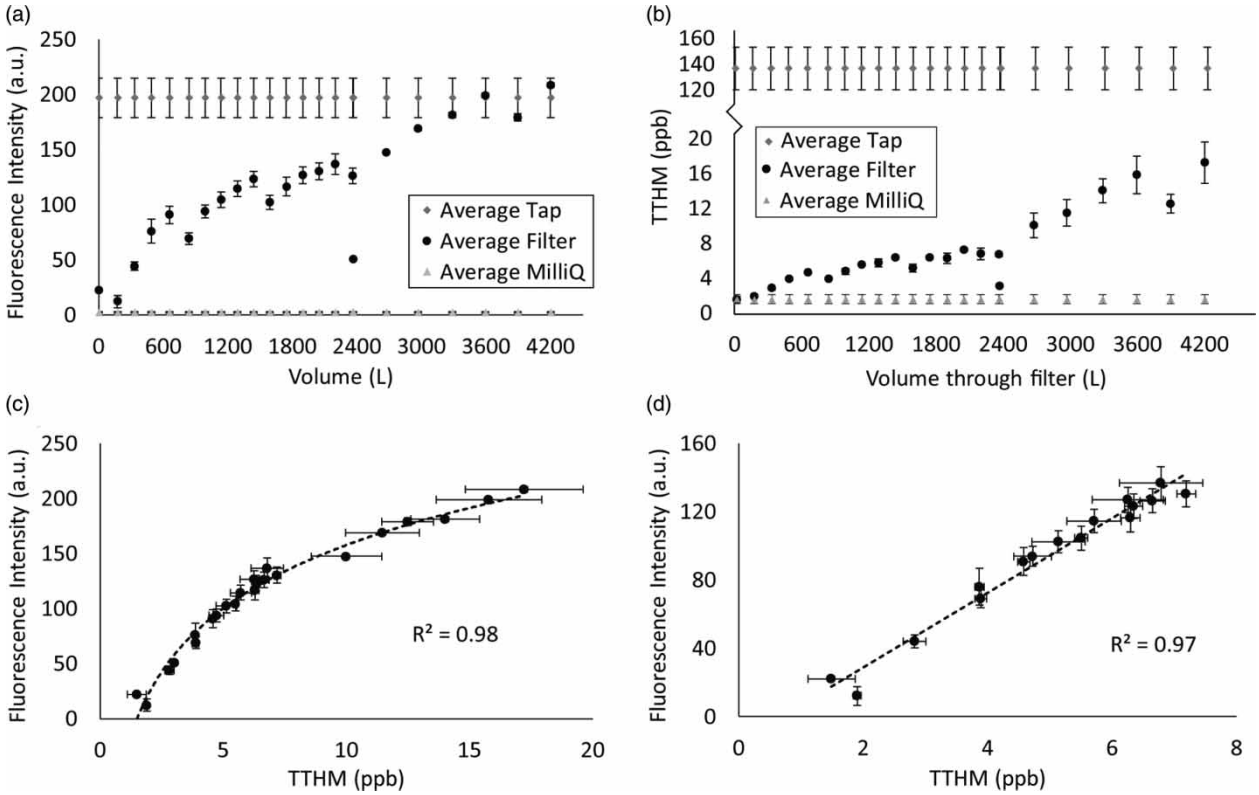

Figure 3 | (a) Average fluorescence intensity measured using the 250/425 nm ex./em. pair for MilliQ, all filter samples and tap water. (b) Average THM concentration for MilliQ, all filter samples and tap water. (c) Correlation of fluorescence intensity and THM concentration for all filter water samples. (d) Correlation of fluorescence intensity and THM concentration for filter water samples up to 2,000 L filtrate volume.

the filter during the period of no flow. This water was in contact with the carbon filter for approximately 16 h between day to day sample measurements (or 10 days in the extreme case), in which time a significant amount of the organic species could have been adsorbed from the water. The improved capture of DOM from the following 150 L filter volume, may also be attributed to the ingress of the organic species into the pores of the activated carbon during the static period. This would free up a portion of peripheral binding sites in the porous matrix that would initially capture the DOM efficiently once the water flow was recommenced. It should be noted that the improved adsorption following the stop in flow is short lived, with the effect only lasting for 150–200 L once flow has been restored. After this volume the level of DOM returns to that of the previous sample and for subsequent samples a continuing increase in DOM level is then observed.

The step phenomenon is associated with the kinetics of adsorption by the carbon filter, which depends upon parameters such as flow rate, pressure and the type of activated carbon. It is likely that the extent to which this effect is observed may vary for different types of activated carbon filters (Abouleish & Wells 2015). This phenomenon is potentially significant, as an intermittent flow would be normal for individuals using activated carbon water filter systems. This observation suggests that filter performance will be determined by individual use and confirms the need for real time monitoring of filter systems.

The concentration of THMs was also measured for each water sample collected, by using HSGC. The THM concentration results are presented in Figure 3(b) in a similar layout as for the fluorescence measurements. The graph displays average THM concentrations for MilliQ and tap water as a reference of ultrapure and unfiltered samples respectively. In correlation to the fluorescence measurements, the filter performance for removal of THMs is close to that of MilliQ water for low filter volumes. A gradual increase in the THM concentration is observed as the total filtered

volume increases, however the THM concentration in the filtered water samples do not reach the same level as in tap water. This indicates a sustained performance for removal of THMs by the activated carbon filter, even over the 4,200 L filtrate volume. The observation of superior filtration of the THMs over the larger DOM species is expected, as the smaller species will be able to achieve a higher adsorption density on the carbon surface as well as access to a greater fraction of the material's microporous structure. The effect of molecular size on adsorption capacity to activated carbon filters has been previously investigated and characterised (Schreiber *et al.* 2005). Again, the extent to which this effect is observed will depend on the type of activated carbon filter in use. Another observation of importance from Figure 3(b) is the presence of the same step features in the average filter THM concentration graph. It appears that stopping the flow through the filter has the same effect on adsorption of THMs as for the DOM and is again attributed to the prolonged adsorption time for the void water in the filter.

When the measured fluorescence intensity and THM concentration is compared for each sample, a high degree of correlation is observed. This correlation is presented in Figure 3(c) and 3(d). Figure 3(c) shows the correlation between fluorescence intensity and THM concentration across the entire 4,200 L filtered volume. In this case a logarithmic function has been fit to the data, resulting in a regression coefficient of 0.98. There is a non-linear trend for this correlation because for higher filtration volumes the fluorescence intensity begins to plateau as it approaches that of tap water. The highest fluorescence intensity that can be observed in the filtered water will be that of the influent tap water. Therefore, once the filter completely loses its ability to remove DOM, the measured fluorescence intensity will remain constant (i.e. that of tap water). In contrast, over the measured sample volume the THM concentration gradually increases at a constant rate, and remains far lower than that of the influent tap water. When the correlation is limited to the data collected over the reported filter lifetime (2,000 L, as given by the manufacturer), the observed trend is linear with a regression coefficient of 0.97 (Figure 3(d)). It should be noted that extrapolation of this graph will not pass through the origin. This is due to the fact that a percentage of the DOM is non-fluorescent, but can give rise to THMs. Therefore, at zero observed fluorescence, there will still be THMs present that may pass through the filter. These results indicate that over the manufacturer's reported filter lifetime, the measured fluorescence intensity of filtered water can be used as an indicator for both DOM amount (with respect to influent water) and THM concentration. Significantly, the data indicates that the rate of DOM breakthrough is proportional to the rate of THM breakthrough. This makes DOM (measured by fluorescence spectroscopy) an ideal target for determining activated carbon water filter performance.

Calculated breakthrough of DOM and THMs

The percentage breakthrough of the organic species (DOM and THMs) was determined with respect to the amounts of each species in tap water, as this will be the highest concentration possible in the effluent water. The percentage breakthrough of DOM was calculated based on the fluorescence intensity of each filter water sample, in relation to the fluorescence intensity of the tap water collected at the same time as the filtered sample. The results for DOM breakthrough are displayed in Figure 4(a) and display a similar trend to the absolute fluorescence intensity for each sample. Again, the data that is presented has been acquired using the 250/425 nm ex./em. pair. The percentage breakthrough calculated using the 365/446 nm ex./em. pair is presented in the supporting information (Figure S5). It is observed that for the reported filter lifetime (2,000 L) the breakthrough of DOM reaches 72%, indicating that the filter is operating at less than 30% efficiency by this stage. The breakthrough increases to 82% after 4,200 L, which further highlights the filter's loss of efficiency for removal of DOM. This loss of efficiency is expected, as the DOM will only adsorb into the mesopores of the activated carbon and not into the micropores (Lee *et al.* 1981; Pelekani & Snoeyink 1999; Quinlivan *et al.* 2005). As the mesopores become saturated with the large DOM species the filter can no longer facilitate the adsorption of further compounds (Pelekani & Snoeyink 1999).

In contrast to the DOM, the percentage breakthrough of the THMs remains relatively low over the total filtered volume of water (Figure 4(b)). In this case the percentage breakthrough is calculated based on the total concentration

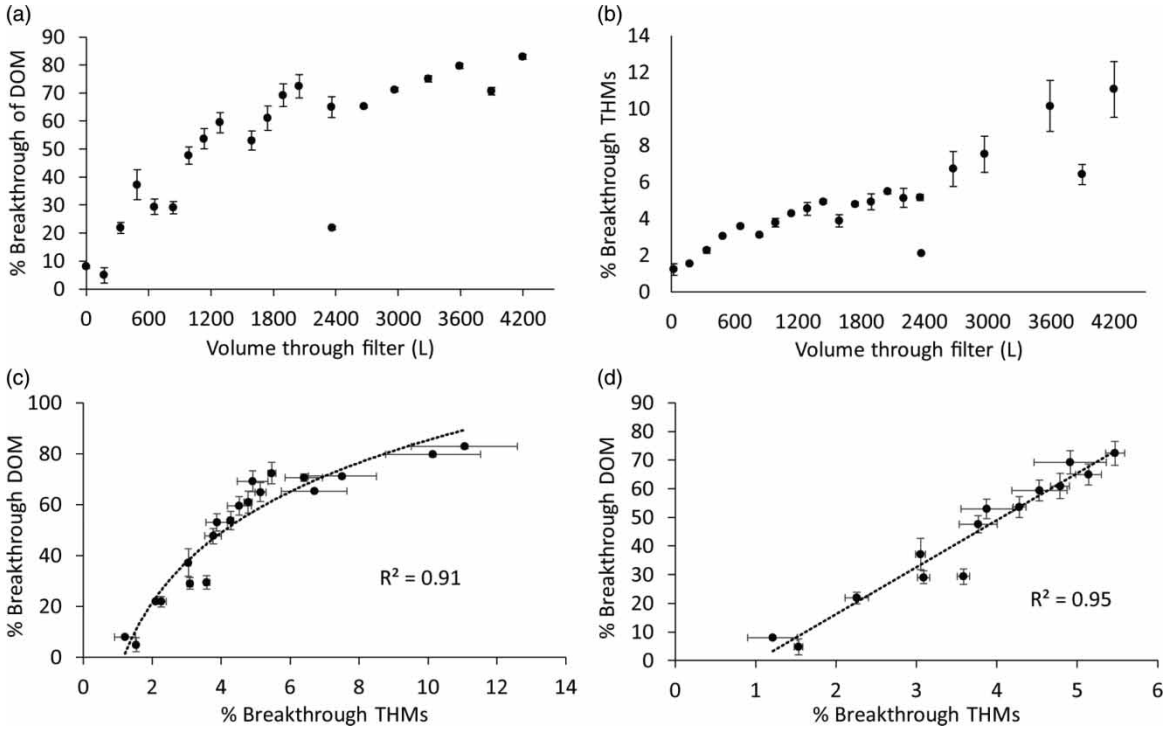

Figure 4 | Percentage breakthrough of (a) DOM and (b) THMs over the total volume of filtered water (4,200 L). Correlation of DOM and THM % breakthrough over (c) the entire filtered volume and (d) over 2,000 L filtered volume.

of THM in the filtered water sample, relative to the total THM concentration in the corresponding tap water sample (as determined by HSGC). It can be observed that the breakthrough of THMs is substantially lower across all filter volumes, with a maximum breakthrough of 11% after 4,200 L. This improved capture can be attributed to the small size of these species and the high affinity and access to micropores on the activated carbon surface (Sakoda *et al.* 1991). The size of these compounds allow them to penetrate the micropores of the activated carbon and access binding sites unavailable to the larger DOM compounds. The enhanced removal of the THMs is important, as these compounds are considered carcinogenic to humans (Wang *et al.* 2007). Importantly, over the reported filter lifetime (2,000 L) the breakthrough of these species is less than 6%, corresponding to a concentration of approximately 7 ppb. The reported safe level of THMs concentration in water for human consumption ranges from 80–250 ppb, according to various guidelines from the World Health Organisation, USA, UK, Australia and Canada (Sadiq & Rodriguez 2004). The presented result for THM breakthrough highlights the effectiveness of end point activated carbon filters to remove harmful species from supplied water.

The correlation of DOM and THM breakthrough is also reported, with Figure 4(c) and 4(d) displaying the correlation for 4,200 L volume and 2,000 L filtrate volume respectively. In agreement with the previous results, the correlation over 4,200 L is non-linear (a logarithmic function has been applied to the data), as the breakthrough of DOM approaches 100% (i.e. the same as tap water) and plateaus, while the breakthrough of THMs remains gradual and constant. Over the 2,000 L filter lifetime, the correlation is linear, supporting the fluorescence measurement technique as a reliable method to report filter performance and efficiency, within the manufacturers reported filter lifetime.

Validation of measurement parameters for fluorescence spectroscopy analysis of filter performance

In order to validate the selected measurement parameters a correlation of fluorescence intensity for each ex./em. wavelength pair as well as PCA of the individual spectra has

been performed. Figure 5(a) displays the correlation of fluorescence intensity at 425 nm and 446 nm (using excitation wavelengths of 250 nm and 365 nm respectively), for all of the filtered water samples. The correlation is linear with a regression coefficient of 0.98, indicating that the same trend is observed using both measurement parameters (i.e. increasing fluorescence intensity for prolonged filter use). This finding is important as it shows that measuring the fluorescence from the π-π* excitation or the n-π* excitation within the DOM gives the same result. This has implications for example where the exact constituency of the DOM or the pH of water samples may vary, with the two measurement parameters able to be used interchangeably. This result is also important in that it shows that the Raman band associated with water has no significant effect on the fluorescence measurement process.

Figure 5(b) and 5(c) show PCA graphs for the fluorescence spectra of water samples collected using 250/425 nm and 365/446 nm ex./em. respectively. Selected background corrected spectra from each measurement parameter (250/425 nm and 365/446 nm ex./em.), have been grouped based on their filtered volume and have been subject to PCA. The first principal component can describe 96.4% and 99.7% of the difference between the measured spectra for 250/425 nm and 365/446 nm ex./em. respectively. The plots of PC 1 vs PC 1 for the spectra of each measurement parameter show a clear discrimination between the sample groups (filter volume) and a clustering of individual data points from each group. Tap water has been included as a reference and a clear trend can be observed where data points for higher filtrate volumes approach that of tap water. The PCA data clearly indicates there are specific, measurable differences in the fluorescence spectra over the lifetime of the filters. This validates the fluorescence technique, whereby either parameter (250/425 nm or 365/446 nm ex./em.) can be used as a reliable method to determine the performance of activated carbon water filters.

CONCLUSION

Fluorescence spectroscopy has been demonstrated and validated as a rapid and accurate technique to determine the real time performance and of activated carbon water filters. The detection of DOM in filtered water and the strong correlation of fluorescence intensity to the total THM concentration has been successfully characterised. Fluorescence characterisation of DOM was performed at two ex./em. wavelength pairs, corresponding to the π-π* and n-π* excitation transitions. The resulting fluorescence intensities for both ex./em. parameters were shown to correlate very strongly with the total THM concentration in water samples. Filter performance has been evaluated through to

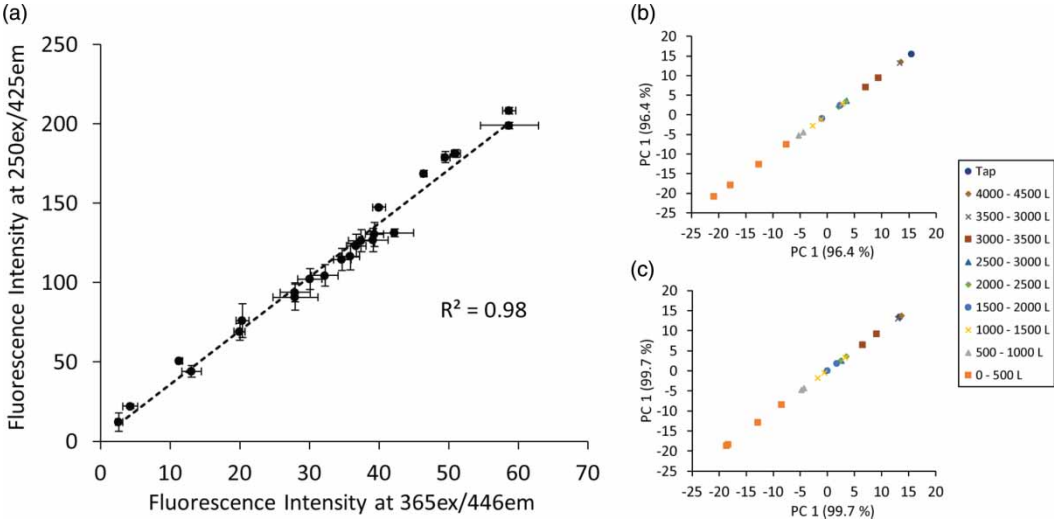

Figure 5 | (a) Correlation of fluorescence intensity at 425 nm and 446 nm for 250 and 365 nm excitation wavelengths respectively, for all filtered water samples. Principal component analysis of selected background corrected fluorescence spectra for (b) 250/425 nm ex./em. and (c) 365/446 nm ex./em.

a volume of more than twice that of the manufacturers reported filter lifetime, with the breakthrough of DOM at over 80% by the end volume. Interestingly, the breakthrough of THMs was relatively low at just 11% by the end volume, confirming the applicability and high capture capacity of activated carbon water filters for removal of these harmful compounds. An important observation to note is the increased absorbance of organic species during periods of no water flow through the filter. This highlights the necessity for real time monitoring of filter performance, as individual use (flow, water quality) will vary significantly.

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