

Assessment of Low pH Coagulation Performance Using Fluorescence Spectroscopy

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Abstract: Optimization of organic matter (OM) removal is of key importance for effective water treatment, as its presence affects treatment processes. In particular, OM increases the operational cost of treatment caused by increased coagulant and disinfectant demands. In the work reported here, fluorescence spectroscopy is used to assess the effect of changing coagulation pH on OM removal, character, and composition. The results of a 3-month trial of low pH coagulation operation at a major surface water treatment works in the Midlands region of the UK are discussed, together with the effect upon total organic carbon (TOC) removal. OM removal was assessed on the basis of both measured removal and fluorescence-inferred removal (through intensity-reduction measurements). Fluorescence spectroscopy demonstrated that optimized coagulation affects the quantitative and qualitative OM properties. Fluorescence analyses were shown to complement other OM measurements, with reductions of peak intensities correlating well with removal of TOC in a range of different treatment conditions. DOI: 10.1061/(ASCE)EE.1943-7870.0000371. © 2011 American Society of Civil Engineers.

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Introduction

Water-treatment works optimization involves changes to the treatment processes and treatment infrastructure to increase the water-treatment effectiveness, secure supplies of potable water, reduce the production of undesirable treatment by-products [e.g., sludge, disinfection by-products (DBPs)], prolong the life of treatment infrastructure, and lower operational costs. Optimization of organic matter (OM) removal is of key importance to effective water treatment, as its presence affects treatment processes and treated water quality. Poor removal of OM can result in the formation of potentially carcinogenic DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs) formed when residual natural organic matter (NOM) reacts with disinfectants such as chlorine. In England and Wales, drinking-water regulations stipulate an absolute maximum contaminant level value of 100 $\mu\text{g}/\text{L}$ for four combined THMs (chloroform, dichlorobromomethane, dibromochloromethane, bromoform) measured at the customers' taps. HAAs are currently unregulated. In the United States, the U.S. Environmental Protection Agency's (U.S. EPA) Disinfectants and DBPs Rule regulates the same four THMs and five HAAs (monochloro-ClAA, monobromo-BrAA, dichloro-Cl₂AA, dibromo-Br₂AA, and trichloroacetic acid Cl₃AA). The U.S. EPA limit on selected HAAs is 60 $\mu\text{g}/\text{L}$ (U.S. Environmental Protection Agency 1999).

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The extent of OM removal by coagulation, flocculation, and clarification is dependent on raw-water OM properties and the treatment conditions (Randtke 1988; Kim and Yu 2005; van Leeuwen et al. 2005; Fabris et al. 2008). The hydrophobic, high-molecular-weight fraction is known to be preferentially removed, whereas the low-molecular-weight hydrophilic OM is more recalcitrant to removal. The relative contribution of the more recalcitrant OM fraction to the total OM is specific to the particular raw water and exhibits seasonal changes induced by natural and anthropogenic effects. Consequently, coagulation optimization can be achieved by appropriate adjustment of the coagulant type, dosage, pH, and pretreatment processes (e.g., ozonation). However, although OM character and coagulant type and dose are critical, for a given raw water and coagulant, the coagulation pH has been found to be the most significant treatment parameter affecting the extent of OM removal by coagulation (Edzwald and Tobiason 1999; O'Melia et al. 1999; Yu et al. 2007).

Fluorescence Spectroscopy

River, waste, and potable-quality waters all have distinctive spectrophotometric properties in both absorption of light and fluorescence. As well as strong absorption in the ultraviolet (UV) region, much dissolved organic matter (DOM) is present in water fluoresces. Recent studies have demonstrated that fluorescence spectroscopy is a useful tool for determining qualitative aspects of OM character and functional properties, such as alumina adsorption, hydrophilicity, and buffering capacity (Baker et al. 2008); and technological advances now allow rapid acquisition (< 1 min) of three-dimensional excitation-emission matrices (EEMs) from just a few milliliters of sample volume.

EEMs display the intensity of fluorescence within the sample against the excitation wavelengths and the wavelength at which excited fluorophores emit light. Fluorescence regions can be attributed to both natural fluorescence (humic- and fulviclike, defined as Peaks A and C), and microbial-derived organic matter (tryptophan- and tyrosine-like fluorescence, defined as Peaks T and B) at shorter

emission wavelengths (Coble 1996). Chlorophyll fluorescence is found at longer wavelengths and is indicative of algal activity. In standard fluorescence EEM data analysis, the maximum fluorescence intensity for each peak is recorded along with its spectral location (excitation and emission wavelengths).

To date, fluorescence has been used for monitoring river water quality, specific pollutants in industrial wastewater, oil in water, and failures in recycled water treatment and distribution systems (e.g., Hudson et al. 2007; Kuzniz et al. 2007; Lambert 2003; Henderson et al. 2008). However, few studies have investigated the use of fluorescence in drinking-water treatment works (WTWs). Bieroza et al. (2009) investigated OM removal across the coagulation, flocculation, and clarification processes at 16 WTWs in the UK and found that Peak C characterized the OM and that Peak T characterized microbial activity. The authors also demonstrated that OM fluorescence properties could be used to determine temporal variations of OM at specific sites and spatial variations of OM between different sites.

Investigation of the link between fluorescence and DBP formation has received some attention in recent years; and results from two studies that indicate a correlation between fluorescence intensity, chlorine demand, and DBP formation have now been published (Roccaro et al. 2009; Beggs et al. 2009). The research undertaken at drinking-water plants thus far demonstrates that fluorescence is a promising tool for characterizing OM; however, the number of studies undertaken remains limited. Further research is required to determine, inter alia, the effect of specific processes on fluorescent OM. The work reported here goes into addressing this limitation in the available literature. Specifically, an investigation was undertaken to assess improvements in TOC removal efficiency by coagulation pH reduction. The work reported in this paper discusses a 3-month trial of low pH coagulation operation at a major surface water treatment works in the Midlands region of the UK and the effect on TOC removal. OM removal was assessed on the basis of both measured removal and fluorescence-inferred removal (through intensity-reduction measurements). The results were combined with a larger data set from 15 other WTWs to assess the capability of fluorescence measurements to describe TOC removal.

Materials and Methods

Site Description

WTW A abstracts raw water from the river Leam in the Midlands region of the UK. This lowland source is stored in an impounding reservoir with a theoretical retention time of 2 days. The catchment area is 372.9 km² and comprises 65% nonirrigated arable land and 25% pasture (European Environmental Agency 2007). The process flow sheet at the works incorporates screening, preozonation, coagulation, flocculation, intermediate ozonation, clarification, filtration, granulated activated carbon (GAC), and disinfection. Maximum and minimum flows to the works are 45 and 10 ML/day, respectively. Water leaving the WTW is held in a final water storage reservoir (nominal retention time is approximately 20–22 h under normal operating circumstances) before entering the distribution system.

Fluorescence spectroscopy analysis was carried out on samples of raw and clarified water from WTW A and 15 other surface WTWs in the Midlands region of the UK, collected monthly between August 2006 and February 2008 (Bieroza et al. 2009). All WTWs sampled are owned and operated by Severn Trent Water Ltd. Fluorescence properties for WTW A are presented and

Table 1. Raw and Clarified Water Properties for WTW A and All 16 Water Treatment Sites (August 2006–February 2008)

Parameter	WTW A		All sites	
	Mean	SD	Mean	SD
Tryptophan-like intensity RAW (au)	42.2	6.8	34.9	15.8
Tryptophan-like intensity CLA (au)	36.1	5.7	27.8	15.8
Peak C emission wavelength RAW (nm)	423	5	428	11
Peak C emission wavelength CLA (nm)	418	8	422	10
Peak C intensity RAW (au)	162.9	46.9	141.1	48.0
Peak C intensity CLA (au)	127.8	25.9	86.2	40.4
TOC RAW (mg/L)	6.1	1.3	6.4	16.6
TOC CLA (mg/L)	5.1	1.0	4.1	9.1
OM removal fluorescence Peak C (%)	21.5	9.7	37.8	20.2
OM removal TOC (%)	20.0	11.8	40.6	21.7
Coagulation dose (mg/L Fe)	6.8	1.5	7.6	3.6
Coagulation pH	7.4	0.1	6.6	1.1

Note: RAW: raw water; CLA: clarified water; SD: standard deviation.

compared to the average values for all 16 surface water treatment sites in Table 1. The high and seasonally variable Peak C intensity and TOC values indicate the presence of substantial amounts of organic matter in WTW A raw water. The average raw-water Peak C emission wavelength for WTW A is slightly lower than the average for all sites and indicates the predominance of the hydrophilic fraction of organic matter (Baker et al. 2008). High tryptophan-like fluorescence intensity suggests the presence of a microbial organic matter fraction including algae-derived material.

Analytical Methods

Fluorescence

Organic matter fluorescence was measured using a Cary Eclipse fluorescence spectrophotometer (Varian, Surrey, UK), by scanning excitation wavelengths from 200 to 400 nm in 5-nm steps, and detecting the emitted fluorescence in 2-nm steps between 280 and 500 nm. Excitation and emission slit widths were set to 5 nm and the photomultiplier tube voltage to 725 V. To maintain the consistency of measurement conditions, blank scans with a sealed cell containing deionized (DI) water were run systematically following the procedure described by Baker (2001), and the intensity of the Raman line of water at 348 nm excitation wavelength was recorded. To enable comparison between samples, all the fluorescence intensities were corrected and calibrated to a Raman peak intensity of 20 units at 396 (392–400) nm emission wavelength. OM fluorescence was measured on unfiltered samples in 4-ml cuvettes. TOC values observed in the water samples obtained were well below 25 mg/L; and therefore, any inner-filter effect was negligible, thereby negating the need for dilution (Hudson et al. 2007). Fluorescence intensities were measured in the following spectral areas:

Peak A : λ_{em} (400:450), λ_{ex} (225:260)

Peak C : λ_{em} (400:450), λ_{ex} (300:355)

Peak T₁ : λ_{em} (330:370), λ_{ex} (225:235)

Peak T₂ : λ_{em} (330:370), λ_{ex} (270:280)

A Java script was written to facilitate basic fluorescence data processing and automated extraction of the fluorescence peak data.

TOC was measured using a Shimadzu TOC-V-CSH analyzer with autosampler TOC-ASI-V. HCl was added to the samples, which were then sparged with CO₂-free air to strip inorganic

carbon before catalytically aided platinum 680°C combustion. The nonpurgable organic carbon (NPOC) determination method was employed and the resulting NPOC was calculated as a mean of three valid measurements. The typical error of the duplicated analyses was less than 10%.

UV absorbance was measured in duplicate with the Biochrom Libra S12 spectrophotometer between 200 and 800 nm, with DI water as the blank. Samples were filtered through a 0.45- μ m membrane. A quartz cuvette with 1.0-cm path length, rinsed with DI before each analysis, was used.

Results

Organic matter removal at WTW A is limited, as calculated both on the basis of fluorescence analysis (reduction in Peak C intensity between raw and clarified water, 21.5%) and from the reduction in measured TOC concentrations (20.0%). The OM removal at WTW A is significantly lower than the average value for all 16 WTWs, and the WTW A coagulation pH is higher compared to all sites, as a result of the initial high raw-water pH (raw-water average for the work reported here was pH 8.1).

Edzwald and Tobiason (1999) considered the extent to which OM would be removed by different coagulants for different values of specific UV absorbance (SUVA) at 254 nm. The authors predicted more than 50% removal for SUVA values in excess of 4, less than 25% removal for SUVA values below 2, and between 25 and 50% removal for SUVA values between 2 and 4. The high raw-water SUVA (in a range of 2.9 to 5.6 mg/L-m, average value of 3.8 mg/L-m, Table 2) observed at WTW A indicates the presence of a relatively hydrophobic OM fraction that could therefore be favorably removed by coagulation. It was considered that the efficiency of the coagulation process could potentially be improved by manipulation of the coagulation pH. Thus, to investigate the potential improvements in TOC removal efficiency by coagulation pH reduction, the removal of OM on the basis of both TOC removal and fluorescence intensity reduction measurements was evaluated.

To determine the impact of pH adjustment on organic matter removal efficiency at WTW A, a full-scale coagulation enhancement experiment was carried out over the period November 2008 to February 2009. For four successive weeks, the coagulation pH was decreased from the current operational level of 7.5 to 5.5; and in February, the coagulation conditions were initially evaluated at a coagulation pH of 6.5, followed by a period at pH 5.0 (Table 2). For each week of pH change, samples of raw, clarified, and final water were collected on three separate days. For all samples, fluorescence and absorbance measurements were performed along with determination of TOC. The data were then used to assess the impact of pH lowering on organic matter removal effectiveness.

Fig. 1 shows the raw-water fluorescence properties (Peak C and Peak T) annotated with TOC removal for two sets of data from WTW A. The data have been derived from a historic fluorescence data set (August 2006–February 2008) and from the low pH coagulation investigation (November 2008–February 2009). Raw-water hydrophobicity (Peak C emission wavelength) and microbial fraction content (tryptophan-like intensity) of the low pH coagulation samples are similar to the historic OM properties. However, the TOC removal of the low pH samples is significantly higher than TOC removal obtained historically. Thus, by lowering the coagulation pH, TOC removal was improved with no change in raw-water OM character.

For each coagulation pH, an average TOC removal was calculated and compared to the historic removal at pH 7.0 (34.0%) (Table 2). A decrease in coagulation pH enabled more effective TOC removal; removal increased from 34.0% at pH 7.0 to 39.7% at pH 6.5, 50.9% at pH 6.0, 66.2% at pH 5.5, and 54.7% at pH 5.0. The greatest TOC removal was observed for pH 5.5, and not for the lowest pH 5.0. As the coagulation pH investigation was carried out over several weeks, the raw-water OM concentrations varied over the study period (from 6.2 mg/L on February 8, 2009, to 10.8 mg/L on December 10, 2008). The higher raw-water TOC concentrations would require higher coagulant doses for effective removal of DBP precursors. Thus,

Table 2. Coagulation Enhancement Measurements at WTW A from November 2008 to February 2009

Date	Coag dose mg/L Fe	Coag dose/ TOC R	Coag pH	TOC			SUVA			OM removal (%)		
				R	C	F	R	C	F	TOC	FLU	UV ₂₅₄
11.18.08	7.5	1.1	7.0	7.0	4.8	3.3	4.4	3.4	1.7	32.0	37.4	47.8
11.19.08	6.4	0.9	7.0	6.9	4.7	3.3	3.9	3.1	1.9	32.0	33.1	46.3
11.20.08	5.4	0.8	7.0	6.8	4.7	3.3	4.1	3.4	1.9	29.9	31.6	41.5
11.25.08	6.1	0.8	6.5	7.4	4.5	3.2	3.5	2.2	2.6	39.9	30.8	62.7
11.26.08	6.6	1.0	6.5	6.6	3.7	2.7	4.0	2.6	0.7	43.0	42.4	62.6
11.27.08	7.2	1.0	6.5	7.2	3.7	2.6	3.7	2.5	0.3	49.0	46.1	65.2
12.02.08	8.3	1.3	6.0	6.3	3.8	2.4	3.5	2.3	1.2	39.7	48.3	61.0
12.03.08	7.5	1.2	6.0	6.3	3.3	2.4	3.8	2.7	0.9	47.6	52.3	63.0
12.04.08	7.4	1.2	6.0	6.3	3.3	2.5	3.7	2.1	0.7	47.6	52.1	71.0
12.09.08	12.8	1.3	5.5	10.1	3.7	2.0	5.4	2.4	1.6	63.4	67.0	83.9
12.10.08	14.1	1.3	5.5	10.8	3.3	1.7	5.6	3.7	1.8	69.4	70.0	79.8
12.11.08	14.1	1.4	5.5	9.9	3.9	1.6	4.1	2.3	1.8	60.6	61.7	78.1
02.06.09	9.2	1.6	6.5	5.8	3.3	2.7	3.3	2.2	1.3	43.0	40.3	61.7
02.07.09	7.6	1.3	6.5	6.0	2.9	1.9	3.2	2.7	1.2	50.8	49.6	58.9
02.08.09	6.4	1.0	6.5	6.2	2.9	1.9	2.9	2.8	1.0	53.5	47.8	55.9
02.10.09	5.4	0.8	5.0	6.5	3.7	2.2	3.1	2.3	0.9	42.9	44.1	58.1
02.11.09	6.6	1.0	5.0	6.6	3.1	2.0	3.1	2.6	0.7	53.1	52.0	60.3
02.12.09	9.9	1.4	5.0	7.2	2.4	1.8	3.3	2.1	0.6	66.6	67.9	78.5

Note: TOC (mg/L) and SUVA (mg/L-m) of raw (R), clarified (C), and final water (F). Organic matter removal (%) measured as a reduction in TOC, fluorescence intensity of Peak C (FLU), and UV₂₅₄ absorbance.

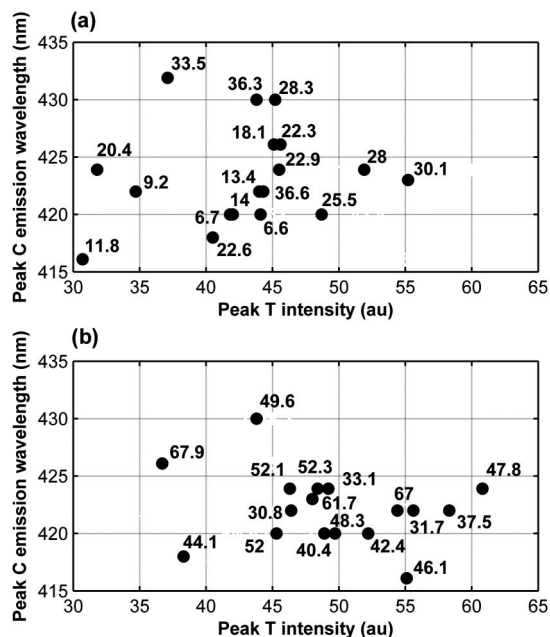


Fig. 1. WTW A raw-water spectral properties; Peak C emission wavelength versus Peak T intensity with % TOC removal shown for all data August 2006–February 2008 [baseline conditions, (a)] and coagulation experiment data [optimized coagulation conditions, (b)]

the difference in TOC removal efficiency between the two lowest coagulation pH values may result from higher TOC concentrations of raw water and higher coagulant doses applied (pH 5.5, average TOC = 10.3 mg/L; pH 5.0, average TOC = 6.8 mg/L, Table 2). To address the change in TOC and its effect on OM removal, a ratio of coagulant dose to raw-water TOC was calculated (Table 2). It can be seen that for pH 5.5, a higher coagulant dose to raw-water TOC ratio (average 1.3) was observed compared to conditions at pH 5.0 (average 0.9, excluding February 12, 2009). However, at a given coagulant dose to TOC ratio, the degree of OM removal depends on coagulant pH, TOC, and SUVA. For example, on both December 11, 2008, and February 12, 2009, the coagulant dose to TOC ratio was 1.4, while pH was 5.5 and 5.0, respectively. A higher TOC removal was observed for the lower coagulation pH and lower SUVA (3.3 mg/L-m and 4.1 mg/L-m for December 11, 2008, and February 12, 2009, respectively). On December 9, 2008, and December 10, 2008, the coagulant dose to TOC ratio was 1.3, coagulation pH was 5.5, and SUVA values were 5.4 and 5.6 mg/L-m, respectively. Here TOC removal was 63.4% and 69.4%, respectively.

The impact of low pH coagulation on OM removal is shown in Fig. 2 and Table 2. OM removal was calculated from the reduction in TOC concentration, UV_{254} , and fluorescence intensity of Peak C between raw and clarified water. Fig. 2 shows that the fluorescence-derived OM removal (calculated as Peak C intensity reduction) correlates strongly with TOC removal ($R^2 = 0.91$). The decrease in absorbance in percentage plotted against the TOC removal yielded a poorer correlation (coefficient value of $R^2 = 0.69$). The percentage removal of UV-absorbing material, however, is higher than TOC removal (average 15%), indicating that coagulation preferentially removes the aromatic organic matter fraction (Chow et al. 1999; Volk et al. 2000).

To compare the effect of enhanced coagulation on OM character, fluorescence data corresponding to baseline operational (November 18, 2008, coagulation pH 7.0) and optimized

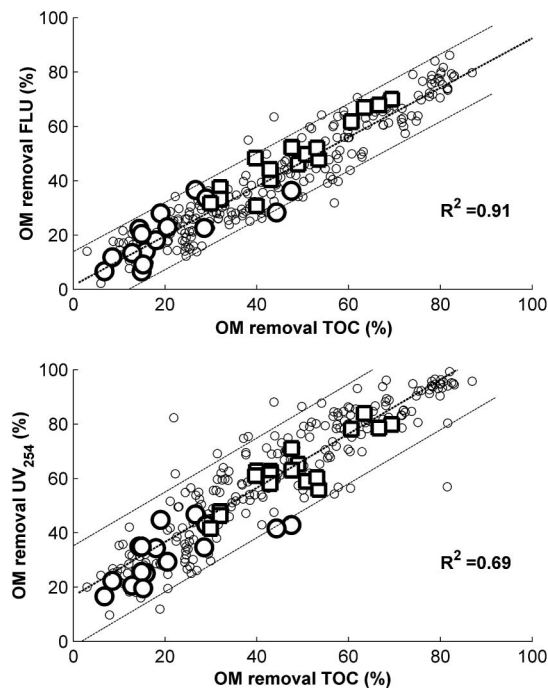


Fig. 2. OM removal calculated as a change in Peak C intensity (OM removal FLU) and as a change in UV₂₅₄ (OM removal UV₂₅₄) between raw and clarified water versus TOC removal (OM removal TOC); correlation coefficients obtained for all historic data (circles); results obtained for WTW A for baseline conditions (large circles) and optimized coagulation conditions (large squares); dotted lines represent trend line and 95% confidence intervals

conditions (February 12, 2009, coagulation pH 5.0) were evaluated (Table 3). The raw-water properties (pH and TOC concentrations) were similar for both sets of samples: pH 8.0 and TOC 7.0 mg/L for baseline, and pH 8.2 and TOC 7.2 mg/L for optimized conditions, respectively. This suggests that raw-water properties were relatively similar before coagulation. There was, however, a difference in SUVA for both sampling events, with a lower value of 4.4 mg/L-m observed for the baseline conditions compared to 5.4 mg/L-m for optimized conditions. Raw water EEMs for the baseline and optimized coagulation regimes are shown at Figs. 3(a) and 3(c). Visual inspection of these raw-water EEMs indicates very similar OM composition for the two samples, with higher fluorescence intensities in the Peak A region for the baseline raw-water EEM. Figs. 3(b) and 3(d) show differences in fluorescence properties of clarified waters obtained for baseline and optimized coagulation conditions. The results for clarified water indicate a greater reduction in all fluorescence peak intensities for the optimized conditions compared with the baseline conditions (increased reduction: Peak A: 74 units, Peak C: 30 units, Peak T2: 27 units) (Table 3). Furthermore, the difference in emission wavelengths between raw and clarified water was also found to be greater for the optimized samples (Peak A: 20 nm, Peak C: 6 nm), indicating that the residual OM is more hydrophilic. Final water-fluorescence intensities for the baseline case are consistently higher than the corresponding low pH coagulation values (Table 3), indicating that there was more NOM removal at the lower pH. Thus, the reduced residual OM content arising from low pH coagulation can reduce costs of OM removal postcoagulation and reduce problems arising from the presence of OM in downstream treatment processes.

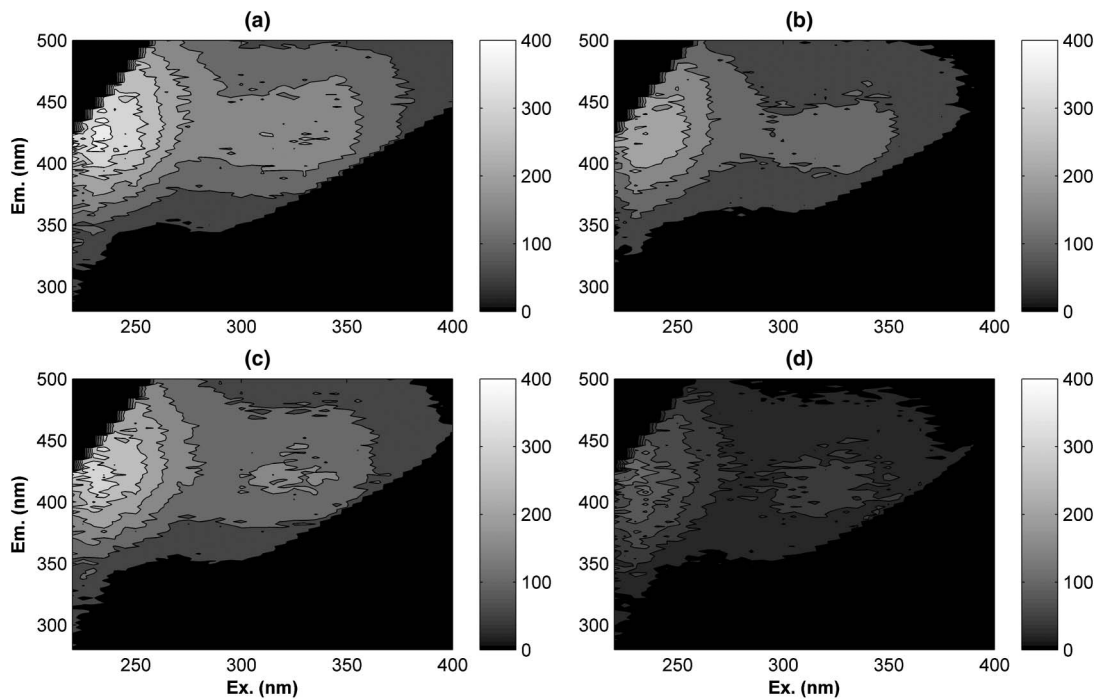


Fig. 3. Raw and clarified water EEMs for baseline and optimized coagulation conditions: (a) November 18, 2008, represents raw-water characteristics for baseline conditions; (b) November 18, 2008, represents clarified water characteristics for baseline conditions; (c) February 12, 2009, represents raw-water characteristics for optimized coagulation conditions; (d) represents clarified water characteristics for optimized coagulation conditions

Table 3. Fluorescence Peak Intensities for the Optimized Conditions Compared with Baseline Conditions

Conditions	Water	Peak A			Peak C			Peak T2		
		Em	Ex	Int	Em	Ex	Int	Em	Ex	Int
Base	RAW	420	235	401.8	420	330	214.6	258	275	70.1
	CLA	416	230	255.6	410	330	127.6	366	270	60.1
	FIN	412	230	99.0	412	320	46.7	344	275	11.6
Opt	RAW	432	230	352.4	426	325	172.4	360	280	64.0
	CLA	408	235	132.4	410	315	55.3	362	275	27.4
	FIN	420	235	64.2	400	330	26.4	350	280	9.2

Note: Fluorescence peak emission (nm), excitation wavelength (nm), and intensity (au) for raw, clarified, and final water for baseline (November 18, 2008) and optimized (February 12, 2009) coagulation conditions (RAW: raw water, CLA: clarified water, FIN: final water).

Conclusions

The ability of fluorescence spectroscopy to characterize OM properties and removal effectiveness under a range of different coagulation scenarios was studied on the basis of an optimization investigation carried out at a full-scale WTW. The results show that fluorescence spectroscopy was able to provide an insight into the effect of coagulation on changes in NOM character and concentration across treatment processes. A greater reduction in fluorescence intensity (and hence, TOC removal) between raw and clarified water was observed for optimized coagulation conditions. An analysis of fluorescence EEMs demonstrated that lowering the coagulation pH from a baseline pH of 7.5 to pH 5.5 yields significant improvements in OM removal (from 30% for baseline to 60% for optimized conditions). The fluorescence response is consistent with changes in TOC and UV because of coagulation and implies a change in character that is in agreement with the accepted observation that residual OM exhibits an increased degree of hydrophilicity. Furthermore, TOC removal was found to correlate well with percentage reduction of Peak C fluorescence intensity.

Fluorescence-derived OM removal (calculated as Peak C intensity reduction) correlated strongly with TOC removal ($R^2 = 0.91$), whereas the correlation between UV absorbance removal and TOC removal was less robust ($R^2 = 0.69$). Thus, fluorescence spectroscopy was shown to be an effective OM characterization technique in a range of different treatment conditions.

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