Characterising natural organic matter flocs

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Abstract Using a dynamic optical technique and settling column apparatus, natural organic matter floc structural characteristics were monitored and evaluated over a one year period to monitor the seasonal variation in floc structure at optimum coagulation dose and pH. The results show that flocs changed seasonally with different growth rates, size, response to shear and settling rate. Autumn and summer flocs were shown to be larger and less resistant to floc breakage when compared to the other seasons, suggesting reduced floc strength. Floc strength was observed to increase with smaller median floc size. The results of the settling tests indicated that the autumnal flocs were of a more open structure which helped to explain why they settled faster. In summary, the autumnal flocs had significantly different floc characteristics although it was difficult to relate the floc structure with the incoming water characteristics.

Keywords Coagulation; floc strength; natural organic matter; removal; settling velocity

Introduction

The removal of natural organic matter (NOM) using coagulation, flocculation and solid–liquid separation techniques is now well established at water treatment works (WTW). The efficient removal of NOM is dependent upon a number of factors including pH, coagulant type and dose and the particular dosing strategy (Chow et al., 1999; Billica and Gertig, 2000; Fearing et al., 2004). In addition to this, floc structural quality plays a significant role in the removal process. There is a general conception that NOM flocs are weak and of low density when compared to turbidity flocs (Bache et al., 1999). Furthermore, the particular nature of the NOM and the coagulant being used can have a significant impact on floc structure (Collins et al., 1986). However, there is little evidence to clarify this as there has generally been no consideration and quantification given to the resulting floc physical properties. NOM is recognised as a complex mixture of organic compounds originating from one of the four main types of biopolymer; polysaccharides, peptidic material, N-acetylamine sugars and polyphenolic material (Christy and Egeberg, 2000; Nissinen et al., 2001). However, there is further evidence showing that there is considerable temporal variation in NOM (Wilkinson et al., 1997). An ongoing study by Goslan et al. (2002) has identified a change in the composition of NOM through fractionation studies. These were thought to be as a result of changes in climate, different seasonal land use and other unidentified reasons. During coagulation, NOM is removed through a combination of charge neutralisation, entrapment, adsorption and complexation with coagulant metal ions into insoluble particulate aggregates as shown in Figure 1 (Dempsey et al., 1984; Dennett et al., 1996; Vilge-Ritter et al., 1999). Further agglomeration of these micro-particles leads to the formation of flocs. The way in which these interactions occur and the efficient incorporation of these molecules into the floc aggregate is dependent upon the particular nature of the NOM components with regard to molecular size, functionality, charge and hydrophobicity. Because of the variable composition of NOM, the nature of removal will invariably be different for specific types of molecule within a NOM sample.

An accurate assessment of floc structure can be a crucial tool for predicting WTW performance under certain coagulation conditions and may be used in combination with removal data to find optimum coagulation pH and dose.
**Background and objectives**

Waterworks that are principally geared towards the treatment of water of a high organic content, low alkalinity and low turbidity are periodically faced with challenging conditions that occur as a result of either a seasonal increase in the organic concentration of the raw water or a seasonal change in the nature of the organic substances in the water. In the mountainous regions of America this coincides with the spring snow melt whilst in the uplands of Europe this usually corresponds to the first heavy rainfalls of autumn. A typical example of this occurs in Yorkshire, England. Figure 2 shows the seasonal change in coagulant demand at a WTW in Yorkshire over a two year period (Fearing et al., 2004). The coagulant dose remained around 12 mg L\(^{-1}\) as Fe during spring and summer months, whilst this was shown to increase to 17–20 mg L\(^{-1}\) Fe in some autumn and winter periods. The increase in coagulant demand between October and January coincides with water that is challenging to treat. Observed effects at the WTW include very short filter run times and early breakthrough. In addition, a decline in dissolved organic carbon (DOC), colour and trihalomethanes (THM) precursor removal is seen under normal operating conditions. A possible explanation for this being that this is as a result of deterioration in floc structural quality and reduced carbon removal efficiency during coagulation due to the changing NOM conditions. The objectives of this paper were to assess NOM floc structural quality in terms of floc size, settlement and strength for seasonal variation in water quality over a one year period.

**Methods**

Floc structural characteristics were measured from the same upland reservoir water source during four separate time periods: spring, summer, autumn and winter. Seasonal raw water was characterised by fractionation of organic material into hydrophilic and hydrophobic components using XAD4 and XAD8 resins following the method of Goslan et al. (2002).
Flocs were formed by performing a series of jar tests. A PB-900 variable speed jar tester (Phipps and Bird, Virginia USA) was used with 76 × 25 mm flat paddle impellers with 1 L cylindrical jars containing 1 L samples of water. Two speeds were used with a rapid mix at 200 rpm for 1.5 minutes followed by a slow stir phase at 30 rpm for 15 minutes followed by a 10 minute settling time. The coagulant was a pre-polymerised ferric sulphate based coagulant as used by the WTW (Ferripol XL, Huntsman Tioxide Europe Ltd). The coagulant was added at optimised doses based upon maximum achievable NOM removal, similar to those as used by the WTW at the time of abstraction. Adjustment of pH was achieved using 1 mol L⁻¹ NaOH (Fisher Scientific UK, Loughborough). In all cases the coagulation pH was around 4.5 as this corresponds to the pH as used by WTW for optimum NOM removal using this iron based coagulant.

**Floc size and strength**

A laser diffraction instrument (Malvern Mastersizer 2000, Malvern UK) was coupled with the jar tester to measure dynamic floc size as the coagulation and flocculation process proceeded. A 1 litre cylindrical jar was used with holding ports for the inflow/outflow tubing secured onto the sides of the jar. This type of arrangement has previously been successfully applied in the analysis of other floc systems (Spicer et al., 1998; Biggs and Lant, 2000). However, due to the delicate nature of the organic flocs in these experiments it was necessary to have a comparatively reduced flow rate through the tubing to prevent floc breakage. The suspension was monitored by drawing water through the optical unit of the Mastersizer and back into the jar by a peristaltic pump on the return tube using 5 mm internal diameter peristaltic pump tubing at a flow rate of 1.5 L/hr. The inflow and outflow tubes were positioned opposite to one another at a depth just above the paddle in the holding ports. Coagulant and pH adjustment chemicals were added at the start of the rapid mix. Size measurements were taken every minute for the duration of the jar test and logged onto a PC. Each size experiment was repeated three times for each set of conditions. For the determination of floc response to shear, the jar tester was programmed as before; however, after the slow stir phase the suspension was exposed to increased shear for a further 15 minutes. Separate experiments were carried out and replicated three times at increased shears of 30, 40, 50, 75, 100, 150 and 200 rpm. Particle size was monitored before and after exposure to each level of shear.

**Floc settling velocity**

The measurement of floc settling velocity followed a similar protocol to numerous studies that have used photography and image analysis to observe falling flocs (Johnson et al.,

![Figure 2](https://iwaponline.com/ws/article-pdf/4/4/79/417479/79.pdf)
Briefly, the system involved floc aggregates falling into a central settling column that was enclosed by a water bath. The water bath was connected to a ThermoHaake K10 heat-refrigerated circulator (Hakke, Germany) to ensure a constant temperature was maintained in the column at 21.5–22.0°C and a period of 2 hours was left for quiescent conditions to be reached. The settling column was filled with de-ionised water and left to reach the required temperature. Flocs were introduced into the settling column after flocculation on a jar tester jar using a wide mouthed pipette. Visual observation showed that little change in floc macrostructure occurred using the pipettes; however, if flocs were observed to break during the transfer procedure then they were discarded. Falling floc images were captured using a CV M90 colour close-coupled device (CCD) camera (JAI UK Ltd, England). As a focused floc passed in front of the camera, the image grabber was manually triggered to take a series of 10 images with a gap of 1 second between each frame. Image analysis software (Image Pro Plus from Media Cybernetics, Maryland USA) was used to determine floc size and distance travelled. The projected area of the floc presented in front of the camera was determined using the image analysis software and converted to an equivalent diameter. This standardised diameter was recorded along with its settling velocity for 100 aggregates for each set of coagulation conditions.

Results and discussion

Raw water characterisation

The water under investigation was characteristic of a moorland catchment being of high colour and NOM concentration, low turbidity (<3 NTU) and low alkalinity (<10 mg L⁻¹ as CaCO₃). Some of the raw water characteristics are shown in Table 1. It can be seen that the general water characteristics do not significantly change across the periods of measurement. The specific UV₂₅₄ absorbance (SUVA) was seen to increase by 24–30% in the summer and autumn months. DOC removal was seen to increase with increasing coagulant dose other than in summer when high removal was seen for a low dose. There was a drop in organic removal rates in autumn and winter at optimum doses suggesting these waters were more recalcitrant to treatment. As can be seen in Figure 3, fractionation of these waters shows there to be only small changes in the character of the water throughout most of the year. The hydrophobic fractions (the humic and fulvic acids) were the dominating components throughout the year, accounting for between 60–70% of the total DOC. The largest change in the fractional composition was seen in winter when the fulvic acid fraction (FAF) was seen to increase by 20% when compared to the other seasons. This was commensurate with a similar decrease in the humic acid fraction.

Floc size and breakage

The size profiles of flocs upon exposure to increasing levels of shear on a jar tester are shown in Figure 4 for the seasonal waters. The data shows the 50 percentile floc size expressed as an equivalent volumetric diameter (d₅₀). The d₅₀ was chosen as the representa-

<table>
<thead>
<tr>
<th>Seasonality</th>
<th>DOC (mg/L as C)</th>
<th>UV Absorbance at 254 nm (1/m)</th>
<th>SUVA, (L/mg/m)</th>
<th>Coagulant dose applied (mg/L Fe)</th>
<th>% DOC removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>11.4</td>
<td>52.6</td>
<td>4.6</td>
<td>14.4</td>
<td>81</td>
</tr>
<tr>
<td>Summer</td>
<td>8.9</td>
<td>50.8</td>
<td>5.7</td>
<td>8.0</td>
<td>88</td>
</tr>
<tr>
<td>Autumn</td>
<td>10.2</td>
<td>60.2</td>
<td>5.9</td>
<td>12.2</td>
<td>75</td>
</tr>
<tr>
<td>Winter</td>
<td>9.2</td>
<td>40.1</td>
<td>4.4</td>
<td>10.0</td>
<td>63</td>
</tr>
</tbody>
</table>
The floc size after 15 minutes of slow stir was of the following general trend: autumn (median floc size 764 µm ± 34) > summer (724 µm ± 65) > spring (649 µm ± 38) > winter (594 µm ± 45). However, the overlap of adjacent error bands suggest this size order was indicative only. The rate of floc formation was quicker for the spring, autumn and winter waters than for the summer water which had the lowest coagulant dose, suggesting low dose significantly slows the rate of floc formation. In comparison to other studies using similar floc sizing techniques, these flocs were 6–7 times larger than activated sludge flocs (Biggs and Lant, 2000) and 5–6 times larger than kaolin coagulated with polyaluminium chloride (Lin et al., 2002). There has been no previous work using a similar laser based differentiation technique to observe the size of Fe-NOM flocs; however, the range of floc sizes found were of a similar size to metal-NOM flocs observed using CCTV with image analysis (Bache and Rasool, 2001).

Figure 3  A demonstration of the change in composition of NOM with season for the Albert Reservoir, Yorkshire

![Figure 3](image_url)

Figure 4  The growth and breakage behaviour of flocs with increasing shear from three seasonal periods in 2003

![Figure 4](image_url)
With increasing rpm on a jar tester the steady-state floc size was shown to decrease. At high rpm there was an initial large-scale decrease in floc size followed by a more gradual decline. At low rpm there was a more gradual decline in floc size until a steady state size was approached after 15 minutes exposure to shear. The sizes after 15 minutes at increased RPM are shown in Figure 5. The rate at which a floc suspension degrades with increasing RPM gives an indication of floc strength. A steeper slope suggests a floc suspension will undergo a larger proportional reduction in floc size when compared to a degradation curve with a shallower slope. The summer and autumn floc suspensions had similar degradation slopes (0.47 and 0.49 respectively) whilst the initially smaller spring and winter flocs degraded at a significantly lower slope (0.34 and 0.31 respectively). However, it should be noted that the autumn flocs remained larger than the other seasons until very high shears (>100 rpm) when flocs converged on a similar microfloc size.

Settling behaviour
An example of settling behaviour of Fe-NOM flocs is shown in Figure 6 for flocs formed from the summer and autumn water. Due to the relative scatter and crossover of the data, it was not possible to present all of the data for all of the seasonal waters on the same graph. For this reason, a review of the settling data for organic flocs is summarised in Table 2 as typical settling velocities obtained from the regression line through the data points. The floc settling data showed that the autumnal water flocs had generally faster settling rates.

Floc structure and NOM composition
These experiments have established a seasonal change in floc characteristics with the autumnal flocs showing the most marked difference in structure. Explaining the reasons for

![Figure 5](https://iwaponline.com/ws/article-pdf/4/4/79/417479/79.pdf)

**Figure 5** The rate of degradation of NOM flocs with increasing shear for the seasonal waters

<table>
<thead>
<tr>
<th>Type of floc</th>
<th>Settling velocity range (µm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Small floc (400 µm diameter)</td>
</tr>
<tr>
<td>Spring</td>
<td>290</td>
</tr>
<tr>
<td>Summer</td>
<td>267</td>
</tr>
<tr>
<td>Autumn</td>
<td>423</td>
</tr>
<tr>
<td>Winter</td>
<td>315</td>
</tr>
</tbody>
</table>

*Table 2* The settling velocity and fractal dimension of different types of flocs
the resulting floc structure was made difficult due to the different initial NOM concentrations and coagulant doses for each of the seasonal waters. The different DOC removals achieved with optimum coagulant doses based on NOM removal and as used at the WTW reflect a seasonal change in NOM. During winter and autumn the organics became more recalcitrant to removal as reflected by lower percentage DOC removals. However, there was no obvious correlation between the floc growth, size and breakage and the coagulant dose or the initial DOCs of the water. It was therefore likely that the seasonal NOM composition had a considerable impact on the floc structure. The increase in the FAF seen during winter may be a factor that influenced the reduced floc size seen during this season when smaller flocs formed. However, significant changes in floc structure were seen during the other seasons which could not be explained by the small scale changes in NOM fractions observed during these times. It was therefore difficult to interpret how the specific fractions impacted on floc structure.

While the specific reactions of NOM fractions with coagulant chemicals has not been fully understood, a possible explanation for the observed floc characteristics was SUVA. The autumn and summer waters had the highest SUVA and this was concurrent with flocs that were initially large whilst the low SUVA, high FAF winter water gave rise to small weak flocs. Large flocs are indicative of strong flocs (Bache and Papavasilopoulos, 2003; Yukselen and Gregory, 2004). This is because in order to maintain a large floc size for a given shear these flocs must have higher resistance to breakage and should therefore be considered stronger. Higher SUVA values are indicative of an increase in hydrophobic, highly charged and high molecular weight NOM molecules (Edzwald and Tobiason, 1999). It is likely that an increase in these charged components will react better with coagulants and become better incorporated in the floc when compared to lower charged molecules. This may help to explain why waters give periodic operational problems at WTW. However, given the previously mentioned differences in initial DOC and coagulant dose this impact needs further investigation.

An understanding of the impact of NOM on floc structure provides important information at WTW with regard to the likely removal efficiency of NOM flocs during solid–liquid separation processes. In addition, being able to quantify floc structure will allow the development of improved dosing strategies in terms of combining improved floc quality with optimum NOM removal. However, more work is required to understand further the

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**Figure 6** An example of the settling behaviour of NOM flocs in relation to their size

![Diagram showing floc settling velocity vs. floc equivalent diameter size for Summer and Autumn](image-url)
specific impact of NOM components and concentration and coagulant dose on floc structure. Furthermore an investigation of a wider range of NOM rich waters is required in order to assess the wider ranging impacts of NOM on floc structure.

Conclusions

• A seasonal change in floc structure was observed as a result of the combined effects of variation in NOM composition, NOM concentration and coagulant dose, although the specific effects of each of these factors could not be quantified.
• The most marked difference in structure was observed for autumnal water flocs. These flocs were larger and settled faster.
• Smaller floc structures showed reduced proportional breakage with increased shear.

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