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Filtration efficiency following polymer addition

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Abstract

Natural organic matter has become an increasing concern in drinking water treatment, because of the potentially carcinogenic disinfection by–products that form when disinfectants react with the residual organic carbon not removed by the treatment process. Organic and inorganic matter at water treatment works (WTWs) is usually removed by aggregating the matter into large insoluble aggregates, known as *flocs*, and then separating the flocs from the water. Synthetic organic polymers are widely used to improve the characteristics of flocs. These polymeric additions enhance natural organic matter removal in the subsequent separation phase. The efficiency of the reaction between polymer and flocs is dependant on several factors such as the properties of the polymer and the particular site conditions. The choice of on–site polymer dosing is not simple because of the complex interactions between polymers and particulates, the influence of water quality and operating conditions. Polymer dosing in drinking water treatment does not follow a general rule and is usually based on trial and error or industrial experience.

This thesis details the work conducted to provide diagnostic support to existing on-site investigation on the optimum polymer dose and conditions required for the treatment of natural organic matter rich waters at Albert WTWs, Yorkshire, UK. Seasonal variations in water quality were investigated both at the laboratory scale and full-scale. The effect of polymer dosing on floc filterability was studied on water samples collected at Albert WTWs using a jar tester and two particle sizing instruments based on laser diffraction. Outlet turbidity and headloss were monitored during laboratory sand filtration experiments.

The results of the on–site data analysis showed great variability in the effect of site conditions on sand filtration performance. Polymer dosing as a filter aid improved particle removal by sand filtration during winter, that resulted in lower filtered turbidity and ultraviolet light at 254 nm wavelength. The results of laboratory experiments demonstrated that polymer dosing increased floc size and re-growth and

marginally improved floc strength, particularly for waters at low dissolved organic carbon content. Temperature had no significant impact on floc size or strength. The bench scale filter trials showed that there was an increase in the filter headloss with increasing polymer dose. Outlet turbidity was higher when no polymer was dosed and this was explained by performing particle count analysis on the inlet and the outlet of the bench sand filter. The results showed that when no polymer was dosed the filtrate contained a higher number of particles than when polymer was dosed. The number of particles in the inlet water decreased proportionally to the amount of polymer dosed, particularly after floc growth. Polymer dosing has the effect of mopping up small particles and so makes them easier to filter.

Polymer dosing engineers floc characteristics for improved filtration by reducing the concentration of particles onto the sand filters. The optimum dose of synthetic polyacrylamide on water after dissolved air flotation at Albert water treatment works is between 0.01 and 0.02 mg/L: such a dose ensures long filter runs and low outlet turbidity.

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Publications

- L. Fabrizi, P. Jarvis, A. Wetherill, "*Polymer dosing for filtration*", Poster for Yorkshire Water strategic partnership 2007 Annual Conference "*Disseminating and implementing results*", Leeds, May 2007.
- L. Fabrizi, P. Jarvis, B. Jefferson, S. Parsons, "*Polymer dosing for filtration: engineering results*", Water quality and technology conference, American Water Works Association, Charlotte, US, 7th November 2007

List of Contents

ABSTRACT ..... **II**

ACKNOWLEDGEMENTS ..... **IV**

PUBLICATIONS ..... **V**

LIST OF CONTENTS ..... **VI**

ABBREVIATIONS ..... **X**

LIST OF TABLES ..... **XI**

LIST OF FIGURES ..... **XII**

1. INTRODUCTION **1**

2. OBJECTIVES **4**

3. LITERATURE REVIEW **5**

3.1. Polymers 6

3.1.1. Definitions 6

3.1.2. Chemical description and structure 6

3.1.3. Synthesis 7

3.1.4. Synthetic organic polymers 7

3.2. Effect of polymer on flocs – Mechanism of action 9

3.2.1. Expansion of flexible polyelectrolytes in an aqueous solution 9

3.2.2. Polymer adsorption 10

3.2.3. Steric interaction 11

3.2.4. Bridging and flocculation 12

3.2.5. Charge neutralisation 13

3.2.6. Basic kinetic aspects 14
3.3. Coagulation and flocculation using polymers 16
3.3.1. Process fundamentals 16
3.3.2. Flocculation kinetics 17
3.3.3. Polymers as flocculation aids 20
3.3.3.1. Type of polymer 20
3.3.3.2. NOM and colour removal 26
3.3.3.3. Full scale studies 27
3.3.3.4. Parameters affecting polymer efficiency 29
3.3.3.4.1. Polyelectrolyte properties 29
3.3.3.4.2. Operating conditions 30
3.4. Polymer dosing in rapid sand filtration 32
3.4.1. Rapid sand filtration (RSF) 32
3.4.1.1. Process description 33
3.4.1.1.1. Headloss development in RSF 34
3.4.1.2. Particle removal mechanism 35
3.4.1.2.1. Transport mechanisms 37
3.4.1.2.2. Attachment mechanisms 41
3.4.2. Polymers dosing in direct filtration 42
3.4.2.1. Type of polymer 44
3.4.2.2. Effect on headloss development and turbidity removal 45
3.4.2.3. Zeta potential of filter grains 47
3.5. Summary of literature review 48

4. MATERIALS AND METHODS 50
4.1. On-site data analysis 50
4.2. Sampling 51
4.3. Characterisation of water samples 52
4.3.1. XAD resin fractionation 53
4.4. Measurement of floc properties 54
4.5. Data validation 57
4.6. Sand filtration 58

5. RESULTS 60
5.1. On-site data analysis 60
5.1.1. Introduction 60
5.1.2. Seasonal variations of WTWs parameters 61
5.1.2.1. Fixby WTW 61
5.1.2.2. Albert WTW 62
5.1.3. Seasonal RSF performance comparison 62
5.1.3.1. Fixby WTW 63
5.1.3.2. Albert WTWs 63
5.1.4. Polymer dosing effect on RSF performance 68
5.1.5. Summary of on-site data analysis 71
5.2. Water Characterisation 72
5.2.1. Introduction 72
5.2.2. Particle sizing 72
5.2.3. Water properties 75
5.2.3.1. NOM content 78
5.2.3.2. HPSEC results 79
5.3. Effect of polymer dosing on floc properties 80
5.3.1. Introduction 80
5.3.2. Water properties 81
5.3.3. Particle size measurements 82
5.3.3.1. Floc growth 82
5.3.3.2. Floc strength 85
5.3.3.3. Floc re-growth 89
5.3.4. Summary of effect of polymer dosing on floc properties 91
5.4. Effect of temperature on floc properties 92
5.4.1. Introduction 92
5.4.2. Water properties 92
5.4.3. Particle size measurements 93
5.4.3.1. Floc growth 93
5.4.3.2. Floc strength 95
5.4.3.3. Floc re-growth 95

5.4.4. Summary of effect of temperature on floc properties 97
5.5. Sand filtration experiments 97
5.5.1. Introduction 97
5.5.2. Results 97
5.6. Particle count analysis 100
5.6.1. Introduction 100
5.6.2. Particle count analysis on filtrate 100
5.6.3. Particle count analysis on clarified water 104
5.6.3.1. Comparison of volume and number distributions 106
5.6.4. Particle count analysis on September samples 108
5.6.5. Summary of particle count analysis 109

6. DISCUSSION 110
6.1. Effect of water quality on filterability 110
6.2. Effect of temperature on filterability 113
6.3. Effect of polyelectrolyte concentration on filterability 114
6.4. On-site implementation of research 118

7. CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK 120
7.1. Recommendations for future work 121

REFERENCES 122

APPENDIX A – ON-SITE DATA CHARTS 129

APPENDIX B – FLOC STRENGTH 156

Abbreviations

CD	:	Charge density
DAF	:	Dissolved air flotation
DOC	:	Dissolved organic carbon
DPB	:	Disinfection by products
FAF	:	Fulvic acid fraction
FTU	:	Formazin turbidity unit
HAF	:	Humic acid fraction
HPIAF	:	Hydrophylic acid fraction
HPINAF	:	Hydrophylic non acid fraction
HPSEC	:	High performance size exclusion chromatography
MLD	:	Mega litres per day
MW	:	Molecular weight
NTU	:	Nephelometric turbidity unit
RPM	:	Rotations per minute
RSF	:	Rapid sand filtration
THM	:	Trihalomethanes
TOC	:	Total organic carbon
UV_{254}	:	Specific ultraviolet light with 254 nm wavelength absorption
WTWs	:	Water treatment works

List of Tables

Table 3.1 : (adapted from Crittenden et al, 2005): Typical synthetic polymers used in water treatment

Table 3.2 : Research on polymer dosing as flocculation and filtration aid

Table 5.1 : On-site 2006 seasonal parameters for Fixby WTWs

Table 5.2 : On-site 2006 seasonal parameters for Albert WTWs

Table 5.3: Albert WTWs on-site data during polymer trials (summer 2006)

Table 5.4 : Water properties at different polymer dose

Table 5.5 : Floc growth rate and average standard deviation at different polymer doses for the September and the February samples

Table 5.6 : Breakage gradient for February and September sample at increasing polymer dose

Table 5.7 : Floc re-growth rate and average standard deviation at different polymer doses for the September and the February samples

Table 5.8: Water properties at different temperatures measured on the sample collected in April

Table 5.9 : D_{50} and standard deviation of the median particle diameter at different temperatures

Table 5.10 : Floc re-growth at different temperatures and at a constant polymer dose of 0.03 mg/L

Table 6.1 : Floc growth rate (D50/minute) at different polymer doses for February and September samples

List of Figures

Figure 1.1. Micrograph of a floc from Albert WTWs after DAF

Figure 1.2. Sand filter turbidity as a function of time (on-site data from Albert WTWs)

Figure 1.3. Schematic of the water treatment process used at Albert WTWs

Figure 3.1. Configuration of an adsorbed polymer chain (adapted from Gregory, 1996)

Figure 3.2. Processes involved in polymer adsorption and flocculation (adapted from *Gregory, 1996*)

Figure 3.3. Sand filter operation: turbidity Vs. time

Figure 3.4. Removal of particles as a function of their diameter according to *Rajagopalan and Tien* model *(1976)*

Figure 4.1. Sand filters operating at Albert WTWs

Figure 4.2. Schematic of the equipment for particle size measurement

Figure 4.3. Schematic of laboratory sand filter

Figure 5.1. Comparison of sand filter seasonal outlet turbidity (filter 2) at Fixby WTWs

Figure 5.2. Comparison of sand filter seasonal headloss growth (filter 2) at Fixby WTWs

Figure 5.3. Comparison of sand filter seasonal outlet turbidity (filter 3) at Albert WTWs

Figure 5.4. Comparison of sand filter seasonal headloss (filter 3) at Albert WTWs

Figure 5.5. Albert WTWs inlet flow and turbidity in February 2005, when no polymer was dosed, and February 2006, when polymer was dosed

Figure 5.6. RSF performance at Albert WTWs during summer polymer dosing trials

Figure 5.7. Effect of increasing raw water turbidity and works inlet flow on RSF performance

Figure 5.8. Initial particle size distribution before and after settling in water samples collected at Albert WTWs in different periods of 2007, measured with Mastersizer 2000

Figure 5.9. Particle growth with jar tester experiments in water samples collected at Albert WTWs in different periods of 2007

Figure 5.10. Physical and chemical properties of water samples collected at Albert WTWs in different periods of 2007

Figure 5.11. Organic fractions, isolated by ion exchange fractionation technique, making up NOM in the samples collected at Albert WTWs

Figure 5.12. Results of the HPSEC analysis performed on Albert samples

Figure 5.13. Effect of polymer dosing on zeta potential

Figure 5.14. Floc D_{50} and D_{10} growth in V% with increasing polymer dose (at 15 °C) with clarified water samples collected at Albert WTWs in February and September

Figure 5.15. Cumulative distribution in V% with increasing polymer dose (at 15 °C) for Albert February and September samples

Figure 5.16. Floc breakage for February and September clarified water temperature at increasing share dosing 0 and 0.03 mg/L of polymer

Figure 5.17. Typical floc growth graph (Jarvis, 2008)

Figure 5.18. D_{50} Vs share rate at increasing polymer dose and constant temperature (15 °C) in a log-log scale for Albert February and September samples

Figure 5.19. Floc re-growth with increasing polymer doses (at 15 °C) for February and September clarified water samples collected at Albert WTWs

Figure 5.20. Floc growth in V% at increasing temperature (0.03 mg/L polymer)

Figure 5.21. Cumulative distribution in V% at increasing temperature (0.03 mg/L polymer)

Figure 5.22. D50 Vs share rate at increasing temperature with a constant polymer dose (0.03 mg/L) in a log-log scale for Albert April sample

Figure 5.23. Floc re-growth at increasing temperature (0.03 mg/L of polymer) for Albert WTWs clarifies water sample collected in April 2006

Figure 5.24. Sand filtration experiments with the clarified water sample collected at Albert WTWs in July 2006

Figure 5.25. Sand filtration experiments with the clarified water sample collected at Albert WTWs in September 2006

Figure 5.26. Total particle count for filtrate at different polymer doses after increasing filtration intervals

Figure 5.27. Total particle count on the SF outlet at different polymer doses with the sample collected at Albert WTWs in September 2006

Figure 5.28. Filtrate particle size distribution after 15, 105 and 310 minutes on Albert WTWs sample collected in September 2006

Figure 5.29. Total count/ml for clarified water collected at Albert in September during floc growth at increasing polymer doses

Figure 5.30. Particle size distribution measured with Spectrex PC2200 during floc growth with Albert September clarified water sample

Figure 5.31. Comparison between measurement of particles with the Spectrex PC200 and with the Mastersizer 2000 for Albert September clarified water sample before and after floc growth at different polymer doses

Figure 5.32. Particle size distribution in number in September raw, clarified and filtered water: count /ml and percentage

Figure 6.1. On-site inlet turbidity to filters and combined outlet turbidity on 6 days intervals around the sampling dates

1. Introduction

Natural organic matter (NOM) is the main contaminant in water associated with moorland and mountain catchment areas (*Sharp et al., 2006*). Typically these waters are low in alkalinity and turbidity. NOM removal has become increasingly important in many drinking water treatment plants across the UK, in view of the potential carcinogenic disinfection-by-products (DBPs). DBPs are formed when a disinfectant, such as chlorine, reacts with any residual organic carbon present in the water. The most commonly studied DBPs formed in water by the reaction between chlorine and organic material are the trihalomethanes (THM). Recent legislation strictly controls DBPs in drinking water. Current legislation of the European Directive 98/83/EC and the US EPA enforce a limit value for the total concentration of THM of 100 µg/L and 80 µg/L respectively (*Gibbons and Laha, 1999*).

Coagulation and flocculation are the main processes used to limit the formation of DBPs in high NOM waters. Coagulation involves the addition of one or more chemical coagulants in order to modify the chemical properties of the particles in the water. The destabilisation of the particulate by neutralisation of the forces that keep them apart, enhances the subsequent flocculation phase. Flocculation involves the aggregation of destabilised particles into larger particles known as *flocs* (Figure 1.1), which can be removed by the subsequent separation procedures (*Crittenden et al., 2005*).

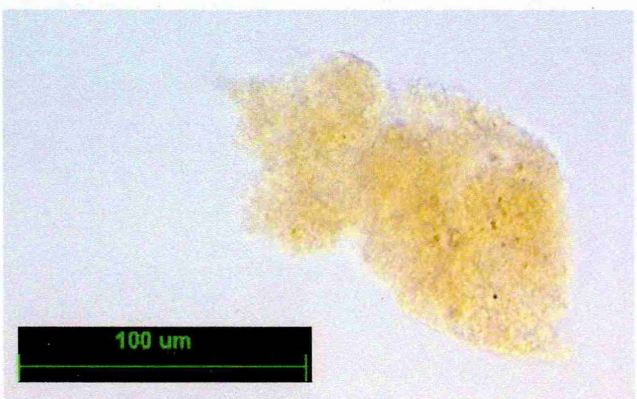


Figure 1.1 – Micrograph of a floc from Albert WTWs after DAF

Changes in raw water character often result in the formation of weaker and more unstable flocs. As a consequence there is more solid carryover onto the filters downstream of the flotation stage and causes early turbidity breakthrough at low headloss and reduces filter run times. This can have a detrimental impact on the final water quality and increase operational costs.

As an example, at Albert water treatment works (WTWs) in Yorkshire, an increase in solid carryover onto filters downstream of flotation has been observed, especially during winter. This results in early turbidity breakthrough at low headloss and reduces filter run times. As shown in Figure 1.2, turbidity breakthrough occurs in the filter operating under 'bad' conditions (December), and is avoided by reducing the filter run time from 24 to 12 hours. To overcome this problem Yorkshire Water has recently introduced dosing of synthetic polyacrylamide at their WTWs.

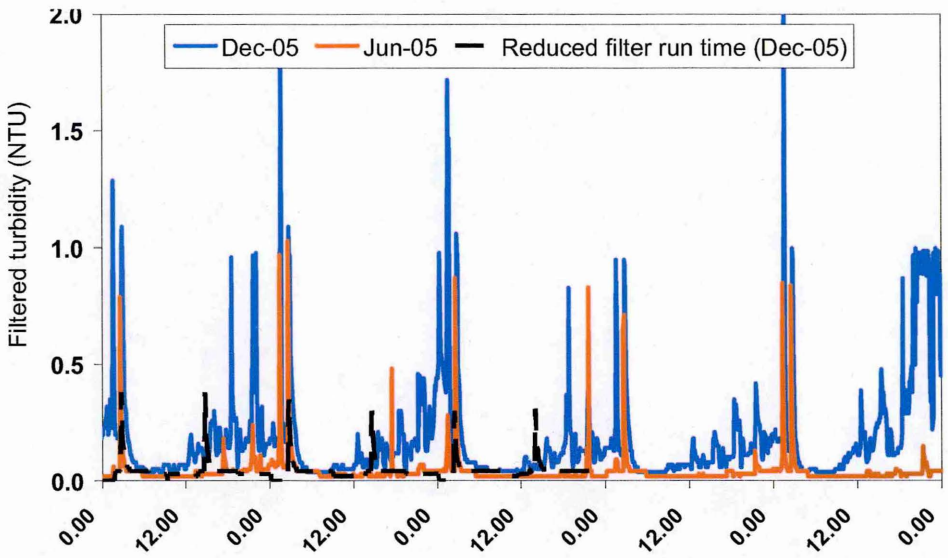


Figure 1.2 - Sand filter turbidity as a function of time (on-site data from Albert WTWs)

The polymer is dosed immediately after dissolved air flotation (DAF) (Figure 1.3) in order to improve the characteristics of the flocs that are not removed by flotation. The polymer assists in increasing floc size, density, compressibility and strength.

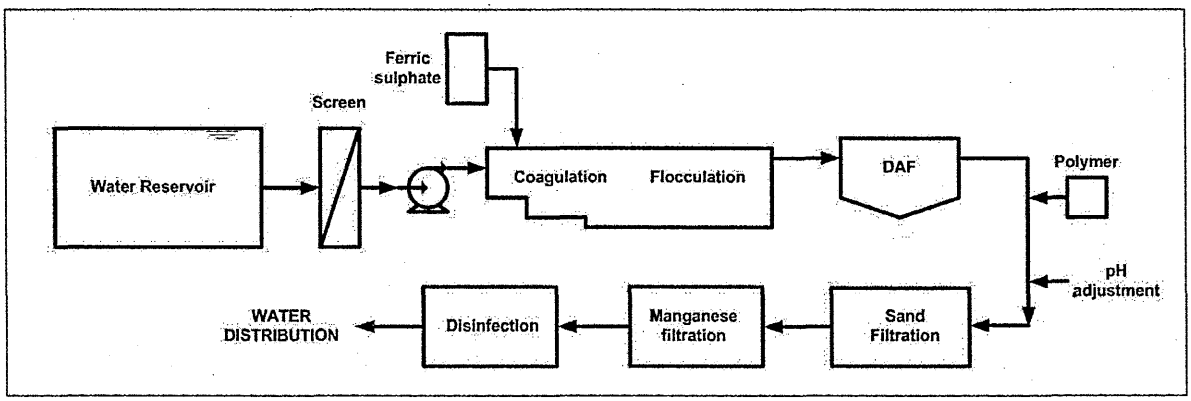


Figure 1.3 - Schematic of the water treatment process used at Albert WTWs

The aim of improving floc quality is to enhance the removal of small particles in the subsequent sand filtration step, particularly during long periods of deterioration in water quality. Polymer dosing delays turbidity breakthrough and enables the filters to operate at long run times. The main issue of on-site polymer dosing is to control and limit the rate of increase of headloss for sand filters. This is because polymer dosing before sand filtration clogs the filters more quickly and increases headloss build up. The filters then require more frequent filter backwash and so the operational costs are increased.

The work detailed in this thesis was part of a collaborative research project with Yorkshire Water. The overall research objective was to identify the optimum operational conditions for good sand filter performance at Albert WTWs. The work described in this thesis shows the effect of polymer dosing on the filterability of the particles entering the sand filtration stage. The effect of temperature and water quality on filterability with and without polymer dosing are investigated.

2. Objectives

The aim of this research is to provide diagnostic support to existing site investigations on the optimum polymer dose and conditions required for the treatment of NOM rich waters. The research is divided into three main parts: a literature review, on-site data analysis and laboratory experiments.

The literature review identifies and evaluates previous research on the effect of polymer dosing on floc properties and on synthetic polymer use in drinking water treatment, both as a flocculant and as a filtration aid.

The purpose of the analysis of on-site data was to identify the differences in on-site filterability. The effects of polymer dosing, seasonal variation in raw water quality, water temperature and inlet flow on sand filter performance were investigated in order to identify general trends and their effect of these variables on rapid sand filtration (RSF) performance.

The laboratory experiments consisted of characterisation of samples collected at Albert WTWs, measurement of floc properties, sand filtration experiments and particle count analysis. The overall objective was to explain how water quality and pre-filtered water particle size distribution and strength are related to floc filterability. The aim of the characterisation was to investigate the composition and properties of raw, clarified and filtered water, collected on-site at different periods of the year 2007. The characterisation results were related to the performance of the water treatment plant and to laboratory scale findings. Measurements of floc properties were conducted in order to investigate and understand the effect of polymer dosing and temperature on floc that remain in the water after DAF. The ultimate objective was to determine the optimum polymer dose and temperature required for efficient floc filterability. The aim of the sand filtration experiments was to investigate the polymer dosing effect on sand filter performance in terms of outlet turbidity and headloss. The particle count analysis was carried out to identify the effect of polymer dosing on particle filterability.

3. Literature review

Polymers are made up of large molecular chains consisting of a series of repeating chemical units. Their synthesis can be controlled to vary charge density (CD), molecular weight (MW), structure and size (*Bratby, 1980*). Synthetic polymers are used in drinking water production as coagulants either alone or in combination with metal salts.

Polymer dosing as a coagulant improves particle-particle interactions mainly through charge neutralisation and particle bridging. Polymer dosing enhances the growth of large flocs and leads to more efficient removal of fine particles through the subsequent solid-liquid separation phase. Flotation, sedimentation and filtration or combinations of the three are the most common particle separation processes in water treatment. Polymers are dosed in order to increase flotation and sedimentation rates, to produce larger and tougher flocs and to lower the required alum dosage (*Lee et al., 1998*). These features give significant cost savings by increasing the capacity of the treatment facility, delaying turbidity breakthrough during filtration and producing sludge with better dewatering properties (*Odegaard and Eikebrokk, 1985*).

Granular bed filtration in drinking water treatment reduces effluent turbidity by removal of colloidal and suspended material. The main processes involved in particle removal by filter grains are transport and attachment. The most important factor in achieving high attachment is destabilisation by coagulation (*Crittenden et al, 2005*). Polymeric coagulants are often dosed ahead of granular bed filtration in order to enhance turbidity removal.

The most relevant research on the use of polymer to control floc properties in drinking water treatment are reviewed in this chapter. Particular emphasis is given to polymer dosing in sand filtration.

3.1. Polymers

Polymeric macromolecules make up important natural materials such as silk, cellulose and proteins and synthetic products, such as plastics and synthetic rubbers. Polymers have many applications in industrial processes that include drinking water treatment. A brief description of polymer chemical properties, structure and their synthesis mechanism follows, which focuses on the polymers used in water treatment. However, polymer chemistry is rather complex and an exhaustive explanation is out of the scope of this review.

3.1.1. Definitions

A polymer is a natural or synthetic compound of high MW consisting of a structure of thousands of repeated linked units. This sequence is called the polymer's *primary structure*, while its localised shape is referred to as the *secondary structure*. Tertiary and quaternary structures are respectively the overall structure of the polymer and the arrangements in space of two or more polymer subunits (*McGraw-Hill, 2005*). A *polyelectrolyte* is a polymer whose repeating unit bears a functional group that may be ionisable. When this ionisable group dissociates, positively or negatively charged sites become available and the polymer molecule becomes charged. The polymer is then referred to as *cationic* or *anionic* respectively. Polymers without charge sites or with a low tendency to develop them are known as *non-ionic polymers*.

3.1.2. Chemical description and structure

Polymeric chemical structural units can have two or more bonding sites. Some examples of monomers are propylene (CH_2=$CHCH_3$), ethylene (CH_2=CH_2), vinyl chloride (CH_2=CHCl), styrene (CH_2=CHC_6H_5), acrytonitrile (CH_2=CHCN), tetrafluoroethylene (CF_2=CF_2) and isoprene (CH_2=CH-$C(CH_3)$=CH_2) (*Robert and Caserio, 1977*). In a linear polymer the structural units are connected in a chain arrangement, and have only two bonding sites. In a non linear molecule the structural units have three or more bonding sites. Polymers with two bonding sites are called *bifunctional*, polymers with more than two bonding sites are known as *polyfunctional.*

Polymers containing only a single type of structural unit are known as *homopolymers*, polymers containing more than one type are known as *copolymers* (*Robert and Caserio, 1977*). The total number of monomer units is referred to as *degree of polymerisation.*

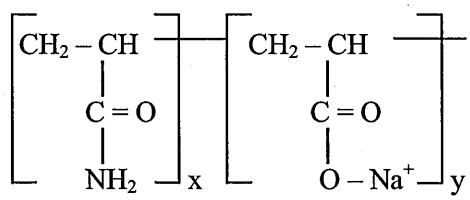
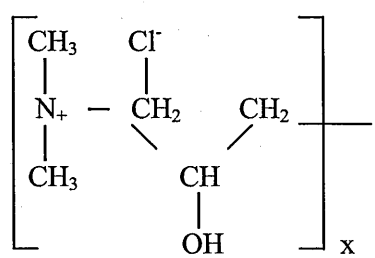
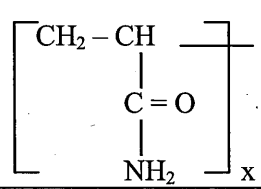
3.1.3. Synthesis

Polymers are formed by linking together of each monomer unit. Linear molecules assemble in chains through exothermic addition reactions. These chain-type reactions are initiated by a radical, an acid or a nucleophile and then proceed stepwise through reactive intermediate. The growth is mostly by carbon-carbon bond formation (*McGraw-Hill, 2005*). Polymers are also formed by a chemical reaction between polyfunctional monomer molecules. The growing chains can react with each other through the formation of carbon-heteroatom bonds. The reaction requires heat and may produce some molecular by-products. This kind of polymer synthesis is known as *condensation* and the polymers formed are known as *step-growth polymers.* Polymers formed by step-growth polymerisation have generally a lower MW than the polymers formed by chain-growth polymerisation and the terminal functional groups remain active (*McGraw-Hill, 2005*). Polymer synthesis can be manipulated to control the CD, structure and size of the final product.

3.1.4. Synthetic organic polymers

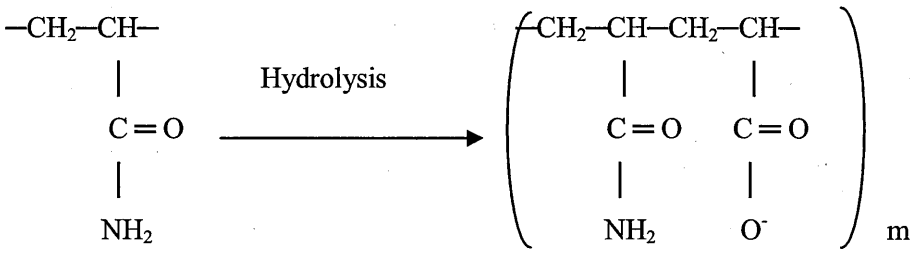
Synthetic polymers are normally used in water treatment, due to the possibility of controlling their properties (such as CD and MW). The principal synthetic organic polymers used in drinking water treatment are summarised in Table 3.1 (*Crittenden et al, 2005*).

Table 3.1 (adapted from *Crittenden et al, 2005*): – Typical synthetic polymers used in water treatment:

Type	Molecular weight [g/mol]	Example	Applications
Anionic	10^4 - 10^7	Hydrolysed polyacrylamides 	Coagulant aid, filter aid, flocculant aid, sludge conditioning
Cationic	10^4 - 10^6	Epichlorohydrin dimethylamine (epi-DMA) 	Primary coagulant, turbidity and colour removal
Nonionic	10^5 - 10^7	Polycarylamides 	Coagulant aid, filter aid, filter conditioning

x, y: number of monomer molecules in polymer

Most of the synthetic polyelectrolytes are based on polyacrylamide and its copolymers with polyacrylic acid. The structure of non-ionic polyacrylamide is shown below in the reaction describing its production. The monomer is acrylamide, this homopolymerises under appropriate conditions to form a non-ionic polymer. By subsequent hydrolysis under basic conditions polyacrylamide acquires carboxyl groups and assumes an anionic character (*Bratby, 1980*):



The structures of anionic polyacrylamide formed by hydrolysis and by copolymerisation with acrylate are identical. The higher the degree of hydrolysis, the higher the overall ionic charge. Cationic derivatives of polyacrylamide are also available. Many cationic polymers are based on polyethilenimine that usually has a MW lower then polyacrylamide. The reactions affecting the formation of the final polymeric structure are several and produce polyelectrolytes with different properties (MWs, CDs, charge distributions and sizes).

3.2. Effect of polymer on flocs – Mechanism of action

Synthetic polymers used in water treatment destabilise and aggregate particulate and natural organic matter (NOM) present in water. The main mechanisms involved in the process are polymer adsorption and particles bridging, which are described in this section.

3.2.1. Expansion of flexible polyelectrolytes in an aqueous solution

Synthetic polyelectrolytes used in water treatment possess either polar or ionisable groups that make them water soluble. Generally they also have hydrophobic groups and exhibit a tendency to associate in solution (*Budd, 1996*).

As repeatedly indicated by *Tanford* (*1961*) an uncharged flexible polymer molecule in a neutral water solution is expected to assume any configuration compatible with its bonds and in the course of time it is expected to take all these possible configurations. The average density of segments is roughly spherically symmetrical with respect to its centre of mass. This remains valid when the polymer is electrically charged, but the

free energy of the configuration is altered. Compact polyelectrolyte configurations will have higher free energy than an expanded one and will be less likely to form. Measurements on the intrinsic viscosity of polyelectrolytes in solution have shown that the degree of compaction increases with increasing ionic strength of the solution (*Fuoss, 1951*). This may be the reason for the lower degree of flocculation at high pH (or high ionic strength) than at a lower pH when polymer are used as coagulants in water treatment (*Yeho et al., 1991*).

3.2.2. Polymer adsorption

When a solid particle is immersed in a liquid it often combines with the molecules in the surrounding medium. The binding sites involved are on the surface of the particle but are often not easy to identify. This process is known as *adsorption* (*McGraw-Hill, 2005*). Polymers dissolved in an aqueous solution are adsorbed onto the particle surface. The adsorption causes a reduction in free energy. The adsorbed chain has restricted configuration if compared to the free chain. The reduction in free energy must be compensated by a favourable interaction between polymer segments and surface sites, which cause a favourable enthalpy change (*Gregory, 1996*). On the surface of the particle there are many attachment sites for the polymeric chain and the adsorption is often considered irreversible. *Gregory (1996)* and *Bolto and Gregory (2007)* described the main mechanisms of interaction that can cause adsorption of polymer on the surface of the particle as being either: hydrogen bonding, hydrophobic interaction, electrostatic interaction or ion binding. Hydrogen bonding is the result of the formation of H-bonds between the polymer chain and the particle surface; hydrophobic interaction generates from the adsorption of non-polar polymer segment on a hydrophobic surface; electrostatic interaction attracts oppositely charged ionic groups, as for instance cationic polyelectrolytes on the surface of negatively charged colloidal matter; ion binding results in the presence of some ions that make possible the adsorption of particles bearing a similar charge. The model of polymer adsorption that is now widely accepted is described by *Gregory (1996)* and is shown in Figure 3.1.

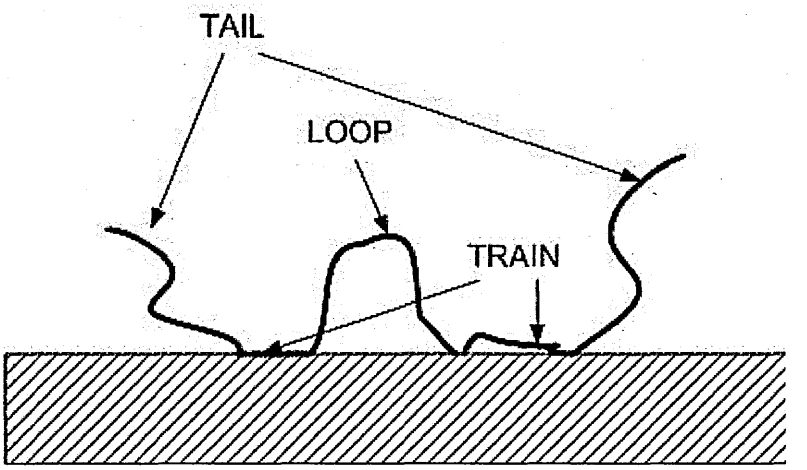


Figure 3.1 – Configuration of an adsorbed polymer chain (adapted from Gregory, 1996)

Polymer segments attach on the surface in trains and are extended in the solution in tails or loops. If the polymer is dissolved in a relatively poor solvent, usually the thickness of the adsorbed layer increases almost linearly with its MW. High MW polymers have longer chains to be absorbed by the solid particle. This dependence is weaker in good solvents such as water. However, the attachment rate is directly dependent on the concentration of polymer chains and mixing conditions (*Gosh et al., 1985*). In case of polyelectrolytes adsorbed on oppositely charged surfaces by electrostatic interaction, the chains assume a rather flat configuration, particularly if the solution has a low ionic strength. The electrostatic interaction is partially screened at high ionic strength and the polymer adopts a more coiled configuration. In the case of non-electrostatic interaction, as for instance in case of non-ionic polymers, tails are generally more extended in the solution and high ionic strength can lead to an increased amount of adsorption for higher MW (*Gregory, 1996*).

3.2.3. Steric interaction

Steric interaction occurs when two particles with a full layer of adsorbed polymer approach each other until the separation distance between the particles is lower than the sum of their thickness. The adsorbed layer partially overlap and polymer segments are mixed and interpenetrate. If the segments have a high affinity for the water the overlapping causes an increase in free energy, while if the segments are hydrophobic

the overlapping causes a decrease in free energy. In the first case there will be repulsion between the segments, while in the second case the segments will be attracted to each other. According to *Gregory (1996)* this kind of interaction is used for weak flocculation in water treatment. In case of hydrophilic polymer completely covering the particle surface, the adsorbed layer provides a barrier of moderate thickness, so that some kind of electrostatic attraction is sill active between the particles. The aggregates formed settle in a rather open structure easy to redisperse preventing the claying of the suspension. The polymer doses needed to provide steric interaction depend on polymer type and particle size.

3.2.4. Bridging and flocculation

Flocculation occurs when polymers are dosed in much lower concentrations than the amount required to give steric interaction. If long-chain polymers adsorbed on the surface of the particles have loops and tails that extend into the solution, these segments can attach on other particles linking them together. This phenomenon is known as *bridging* (*Bolto and Gregory, 2007).* The bridging mechanism suggests that since high MW polymers have a more extended molecular chain, the probability of particle-particle collision is greater and they should be more effective. *Caskey and Primus (1986)* found that the mean length of the adsorbed polymer molecules is a more important parameter than the amount adsorbed. When polymer is overdosed, it completely covers the surface of the particles not leaving any attachments site available for bridging. *Lee et al. (1998)* found that an excess of organic polymer can cause a secondary layer on the primary adsorption layer forming a surface that inhibits bridging and further adsorption. The optimum polymer dose for optimum flocculation is the amount that provides at the same time the most bridging links and bridging sites. An increase in the polymer dose above the optimum leads to a reduction in its performance (*Wilde and Dexter, 1972*). While determining the polymer dose that gave the highest settling rate for polymers with different MWs, *Wilde and Dexter (1972)* found that in all cases the settling rate decreased when exceeding the optimum dose. This was particularly evident for high MW polymers. Optimal doses varied between 2 mg/L for low MW polymer to 0.2 mg/L for high MW polymers. Bridging by polymer

can give stronger flocs than those formed in other ways (*Bolto and Gregory, 2007).* Nevertheless if flocs are subjected to a very high shear rate they can be irreversibly broken (*Muhle, 1993*). The CD of the polyelectrolyte plays an important role in the flocculation mechanism. High positive CD does not enhance bridging because positive polyelectrolyte is usually more strongly attached to negative particles and therefore assumes a flat configuration, preventing bridging bonds from forming. High negative CD causes repulsion of particles that usually bear a negative charge. Nevertheless the polyelectrolyte segments should be slightly charged in order to be able to assume a more extended configuration. Ionic strength effect is also important due to its influence on the polymer configuration.

3.2.5. Charge neutralisation

Cationic polyelectrolytes can enhance flocculation by neutralisation of the negative charge of particle dissolved in the water, in order to reduce inter-particle repulsion and promote aggregation. In this case bridging plays almost no role and the flocculation mechanism is the same as when adding metal salts. *Wilde and Dexter (1972)* found that the sign of the charge of the most effective flocculants is opposite to the charge of the particles to be flocculated. *Kam and Gregory (2001)* proved that optimum flocculation occurs at a polymer dose very close to that required for charge neutralisation. The authors did not find any direct effect of the polymer MW on the degree of removal, confirming that bridging did not play a major part in the process. When cationic high MW polymer are dosed both bridging and charge neutralisation are believed to contribute to particle flocculation. *Bolto and Gregory (2007)* described the case of a highly charged cationic polyelectrolyte adsorbed onto weakly charged negative surfaces. The distance between charged segments along the cationic polymer chain is lower than the distance between negatively charged sites. The total effect is a neutral particle with positive and negative areas that attract each other. This destabilisation effect can lead to attachment between particles and it is known as the *electrostatic patch effect.*

3.2.6. Basic kinetic aspects

The stages involved in flocculation following polymer dosing are mixing, adsorption, rearrangement and flocculation (*Gregory, 1996 and Bolto and Gregory, 2007*), as shown in Figure 3.2.

- Mixing: Mixing should take place immediately after dosing and it should ensure an even polymer distribution onto all of the particles throughout the suspension. *Leu and Gosh (1988)* found that vigorous mixing for a short period of time promoted floc formation. Vigorous mixing allows a better polymer distribution through the suspension, but at the same time can cause floc rupture. Short mixing periods reduce disaggregation of the flocs. Mixing promotes orthokinetic flocculation that is the dominant mechanism in polymer-aided flocculation (*Young et al., 2000*).
- Adsorption: After and during mixing polymer makes contact with particles and undergoes rearrangement until it reaches an equilibrium configuration with trains and loops as described in section 3.2.2. Adsorption can occur by diffusion or induced shear. Induced shear is obtained by physically stirring the solution and it is more important for high MW polymers, for which the rate of adsorption can depend on mixing conditions.
- Rearrangement: When polymer starts to be adsorbed onto the particle surface it first has just a few binding sites and afterwards it reaches an equilibrium configuration (Figure 3.2). The polymer is more likely to form bridging sites before this equilibrium is reached, because its chain is more extended into the solution and presents more loops and tails. *Pelssers et al. (1990)* developed a kinetic model in which they distinguished between active polymer molecules and inactive absorbed polymer chains. As the polymer configuration goes towards equilibrium, or *relaxation,* the number of active chains decreases. Relaxation rate depends on the nature of the polymer and on particle-particle interaction, but it should be independent on particle concentration (*Bolto and Gregory, 2007*).
- Flocculation: Flocculation occurs when particles are destabilised by polymer dosing, so that collisions result in attachment. *La Mer and Headley (1963)* proposed that flocculation rate depends on the square of particles concentration and always happens under some form of applied shear. The rate of floc formation is expressed by the equation:

$$-\frac{dn_0}{dt} = k \cdot n_0^2 \cdot \vartheta \cdot (1-\vartheta) \qquad \textbf{Eq. 3.1}$$

With n_0 : the number of primary particles,

k : flocculation rate constant

θ :fractionational surface coverage by polymer.

According to *La Mer and Headley* the optimum rate occurs when $\theta = 0.5$.

Flocculation by polymer bridging gives quite strong flocs, partly because polymer bridges between the particles are rather flexible allowing some molecules rearrangement under stress conditions.

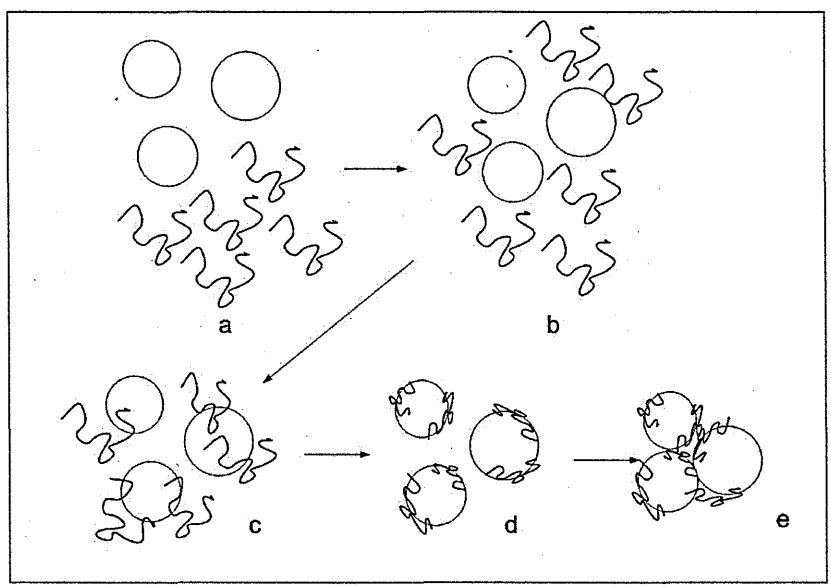


Figure 3.2– Processes involved in polymer adsorption and flocculation (adapted from *Gregory, 1996*)

3.3. Coagulation and flocculation using polymers

3.3.1. Process fundamentals

Natural surface waters contain matter both of organic and inorganic origin. Inorganic matter is mainly formed by products of natural erosion (clay, silt, minerals) (*Crittenden et al., 2005)*. Organic matter are often identified as NOM and may include colloidal material such humic and fulvic acids. Removal of NOM in drinking water treatment is important because many of its constituents are precursors to the formation of disinfection by-products and because NOM can impart colour to the water (*Crittenden et al., 2005*).

The most common method to remove organic and inorganic matter in WTWs is by aggregating it into large insoluble particles and separating them from the water by means of sedimentation, flotation or filtration. At WTWs flocculation usually takes place by gentle and continuous stirring in tanks or basins, known as *flocculators*.

Coagulants are typically metal salts such as iron and aluminium sulphates. Charge neutralisation is the main coagulation mechanism for removal of NOM (*Crittenden et al., 2005)*. When the coagulants are added to the water they hydrolyse following complex reactions. Hydrolysis products react with some molecules dissolved in the water forming both insoluble precipitates and soluble products that destabilise particles by reducing their repulsive forces (*Crittenden et al., 2005)*. Organic polyelectrolytes can be used for particle destabilisation. Their effect on particles is described in section 3.2. According to *Hawkes* (1970) one of the first applications of polymer in water treatment was in 1952, when a polyelectrolyte was used to increase floc dimensions. Since then, polymer dosing in water treatment has been investigated both on an industrial and on a scientific scale. Polymers as primary coagulants may not be as effective as metal salts to treat high turbidity waters, so they are rarely used alone but are generally coupled with ferric or aluminium sulphate (*Cleasby and Logsdon, 1999*). When the pre-treatment objective is to produce small, high density

aggregates for direct filtration, polymer coagulant used alone is often quite effective. The theory of particle removal by sand filtration is discussed in section 3.4.

3.3.2. Flocculation kinetics

After particle destabilisation is achieved by the use of chemical coagulants, particles are induced to approach together, make contact and progressively form large aggregates *(Bratby, 1980)*. This stage is called flocculation and consists in two discrete steps: transport and attachment. The transport step leads at the collision of two particles and is achieved by means of perikinetic flocculation, orthokinetic flocculation and differential sedimentation *(Thomas et al., 1998)*. Attachment occur after collision of destabilised particles. The forces that affect the particles attachment depend on their relative distance.

Perikinetic flocculation arises from thermal agitation (Brownian motion) and it is a random process that starts immediately after destabilisation. Perikinetic flocculation lasts only a few second as it is limited by floc size *(Bratby, 1980)*. The energy barrier existing between colloidal particles increases as the particles progressively coalesce, approximately proportionally to the area of the floc *(Bratby, 1980)*.

Orthokinetic flocculation derives from collisions due to imposed velocity gradients fluid/particles. Such velocity gradients may be induced by mechanical agitation, tortuous path through interstices of a granular filter bed or by sedimentation within a settling basin *(Bratby, 1980)*. Orthokinetic flocculation is governed by both the applied velocity gradients and time of flocculation: the greater the velocity gradients induced in the liquid the more particle contacts there will be within a given time. For a given velocity gradient there is a time beyond which flocs do not grow further. High velocity gradients cause the continuous breakdown of the larger flocs, leading to the formation of a smaller floc than at lower velocity gradients. The lower the velocity gradient the longer the time to reach the optimum floc size but the larger the final floc size *(Bratby, 1980)*. According to *Gregory (2003)*, the size of a floc for a given share rate indicates the strength of the floc. This definition of floc strength does not give an

indication of how floc will behave upon exposure of an increased share rate *(Jarvis et al., 2005)*. Floc strength is also defined by applying an increased share rate to the formed aggregates and measuring the maximum or average floc size remaining. The relationship between velocity gradient applied and the maximum or average size of the floc remaining gives an indication of floc strength *(Jarvis et al., 2005 c)*. This second approach is used in the experimental part of this work (section 4.4).

Collision between two particles can also be caused by their different settling speed. This flocculation mechanism is called differential *sedimentation*. When destabilized particles come in contact with each other attachment may occur depending upon a number of short range forces largely pertaining to the nature of the surfaces themselves *(Thomas et al., 1998)*.

Flocculation rate equations have been derived by assuming that in the aggregation process the rate of collisions between i and j- size particles is proportional to the product of their concentration (*Letterman et al, 1999)*. The general expression of the rate of successful collisions (N_{ij}) is:

$$N_{ij} = \alpha_{ij} \cdot \beta_{ij} \cdot n_i \cdot n_j$$

Where α_{ij} : collision efficiency

β_{ij} : collision frequency

n_i, n_j : particle concentrations

Thomas et al. (1998) compared the classical and modernised expressions for modelling the flocculation process. The first major attempt was made by *Smoluchowski (1917)* and his equations formed the chore of almost all the subsequent research into flocculation modelling. The basic equation given by *Smoluchowski* describes the rate of change in the number concentration of particles of size k as:

$$\frac{dn_k}{dt} = \frac{1}{2} \cdot \sum_{i+1=k} \beta(i,j) \cdot n_i \cdot n_j - \sum_{i=1}^{\infty} \beta(i,k) \cdot n_i \cdot n_k \qquad \textbf{Eq. 3. 2}$$

where subscripts i, j and k represent discrete particle sizes. In this expression the first term defines the increase in particles of size k due to flocculation and the second term describes the loss of particles of size k due to their aggregation with other particles.

The whole flocculation process was described by *Smoluchowski* by a series of non linear differential equations for each value of k. To simplify the model solution *Smoluchowski* made the assumption that $\alpha = 1$ for all collisions, that the fluid undergoes laminar shear, that the particles are monodispersed and sphericals, that the collisions involve only two particles that remain spherical and finally that no breakage of flocs occur (*Thomas et al., 1998).* Basing on these assumption *Smoluchowski* developed expressions for the collisions frequency both for perikinetic and ortokinetic flocculation:

$$\beta = \left(\frac{2 \cdot k \cdot T}{3 \cdot \mu}\right)\left(\frac{1}{d_i} + \frac{1}{d_j}\right)(d_i + d_j) \quad \text{for perikinetic flocculation} \quad \textbf{Eq. 3. 3}$$

$$\beta = \frac{1}{6} \cdot \left(\frac{du}{dy}\right)(d_i + d_j)^3 \quad \text{for orthokinetic flocculation} \quad \textbf{Eq. 3. 4}$$

where k : Boltzmann constant

T : absolute temperature of the fluid

μ : fluid viscosity

du/dy : velocity gradient of the fluid, later defined by *Camp and Stein (1943)* as the fluid root-mean-square velocity gradient G

Camp and Stein (1943) developed also the collision efficiency for differential sedimentation as:

$$\beta = \left(\frac{g \cdot \pi}{72 \cdot \mu}\right)(\rho_p - \rho_l)(d_i - d_j)^3 |d_i - d_j| \quad \textbf{Eq. 3. 5}$$

Where ρ_P and ρ_l : particle and fluid density.

The solution of the differential equation 3.2 gives the total particle count at time t based on the assumptions mentioned above. The validity of each assumption was considered in modern flocculation models. A detailed description of the flocculation models is considered out of the scope of this work and can be found in *Thomas et al., (1998).*

3.3.3. Polymers as flocculation aids

Polymers are widely used in drinking water treatment as coagulation and flocculation aids. Many benefits are derived from the use of organic polymers in water treatment as floc aids: because of their chemical properties they can improve floc characteristics, such as size, density, compressibility and strength, enhancing the flocculation process and leading to more efficient removal of fine particles (*Jun et al., 2001*). The increase in flocculation and sedimentation rates can allow smaller flocculation and sedimentation basins (*Odegaard and Eikebrokk, 1985*). Polymer dosing as a flocculation aid lowers the required coagulant dosage (*Lee at al, 1998*). This reduces residual coagulant concentrations and produces sludge with better dewatering properties and decrease sludge disposal costs.

The most common practice at WTWs is to add metal salts to the water to destabilise particles and subsequently dose polyelectrolytes to the solution. The required polymer dose and type varies depending on water characteristics and operating conditions. Typical dosages of cationic polydiallydimethyl ammonium chloride (poly-DADMAC) and epichlorohydrin dimethylamine (epi-DMA) before sedimentation are from 1 to 10 mg/L, while higher MW non-ionic polyacrylamides are added before granular bed filtration in lower concentrations, typically included in a range from 0.005 to 0.5 mg/L (*Crittenden et al., 2005*). Some scientific studies that have attempted to explain and describe the effect of polymers as flocculation aids during conventional coagulation-flocculation processes are reviewed below.

3.3.3.1. Type of polymer

Inorganic coagulants such as alum have been used as early as 1500 BC (*Parsons and Jefferson, 2006*). Today they are often coupled with synthetic polymers that minimise the consumption of primary coagulants. According to the survey carried out by the AWWA in 1989 on different plants in the United States, 47 out of 51 plants visited used a polymeric flocculant aid or filter aid (*Cleansby et al., 1989*). In this study polyelectrolytes were the most widely used flocculant aids, whilst alum was the most commonly used primary coagulant. However the choice between anionic, cationic and

non-ionic polymer flocculants does not follow a general rule and has for a long time been based on a trial and error basis (*Mishra, 1989*).

Laboratory studies developed in the last decades focused on the use of different types of polymers as coagulation and flocculation aids both together with aluminium or ferric sulphate and as a primary coagulant. According to *Choen et al. (1958), Black and Hannah (1961), Mueller et al. (1964), Lee et al. (1998), Jun et al. (2001) and Yukselen et al. (2006)* cationic polyelectrolyte gave the best performance in terms of turbidity and NOM removal. *Choen et al (1958)* dosed different types of polyelectrolytes both alone and in combination with metal coagulant. The authors found that while a cationic polyelectrolyte could be effectively used as a primary coagulant, an anionic polyelectrolyte needed aluminium sulphate addition to achieve significant turbidity removal. A non-ionic polyelectrolyte was found to be considerably less effective than both the anionic and the cationic form. These results were confirmed by *Black and Hannah (1961),* who investigated the effect of eight different flocculant aids on floc formation and turbidity removal with aluminium sulphate. In general the anionic aids worked best when particle charge had been reduced to near zero with aluminium sulphate. At low alum dosages the cationic aids were more efficient. *Mueller el al. (1964)* studied the effect of anionic, cationic and non-ionic polyelectrolytes in conjunction with ferric sulphate, pursuing a reduction in primary coagulant. The coagulants were dosed on water from the river Missouri and settling rate was measured. The cationic polyelectrolyte performed the best, producing a slight increase in settling rate as compared to ferric sulphate alone. With the non-ionic polyelectrolyte the settling rate of the Missouri river turbidity was greater than with ferric sulphate alone, while the anionic polyelectrolyte gave the worse result, with a high increase in turbidity and a decrease in settling rate. Further studies on the effect of different types of polymer as flocculation aids on water from WTWs were performed by *Jun et al. (2001)*. The authors used alum as the primary coagulant and 0.25 mg/L of cationic, non-ionic and anionic polymers on water samples taken from the intake of the ChongJu water treatment plant (central South Korea). The addition of cationic polymer improved removal of *Synedra* algae compared with alum alone, reaching 99% with 2.16 mg/L of alum. The addition of non-ionic and anionic

polymers did not improve *Synedra* removal. This suggested that at the pH used in the tests alum alone was not able to neutralise the surface charge of *Synedra* cells. As a consequence the repulsive electrostatic forces separated the particles at a distance larger than the bridging length of anionic and non-ionic polymers. Dosing cationic polymers the bridging action was accompanied by charge neutralisation that effectively reduced these electrostatic repulsive forces. Floc analysis by light microscopy showed that floc size, density and strength all increased as a result of the cationic polymer addition.

Lee et al. (1998) dosed cationic, anionic and non-ionic polymer coagulants in combination with polyaluminium chloride (PAC) on three different clay powders. The authors focused their research on the ability of synthetic organic polymers in removing non-ionic organic compounds (NOC) and on the formation of undesired toxic compounds following their reaction with chlorine. Results showed a residual turbidity of 20 NTU in all cases when PAC was used as the only coagulant. If polymer was added as a coagulation aid, the residual turbidity decreased to less than 10 NTU. According to previous work (*Mueller and Burbank, 1960, Black and Hannah, 1961)* the cationic polymer had the best efficiency, forming larger flocs than the other polymers. Optimum polymer doses were typically between 0.5 and 1.0 mg/L. Further experiments on NOC removal showed higher removal rates when polymer was used as coagulant aid than when it was used alone, reaching an optimum at 0.5 mg/L.

Yukselen et al. (2006) investigated the formation and properties of flocs formed from clay suspensions and polymer systems as coagulants. In their experiments the authors dosed a cationic low MW, an anionic high MW and a non-ionic polymer, determining the optimum amounts by a series of jar tests. Confirming the previous research, the cationic polymer gave lower breakage and recovery factor, and higher flocculation index when comparing the performance of single polymers (Table 3.2). Using dual systems the authors found that cationic-anionic polymers system gave the strongest flocs and the highest recovery after breakage (> 100%). Flocs formed using anionic and non-ionic polymers were larger than flocs formed using cationic and non-ionic or

anionic polymer, but were also the weakest. Floc breakage increasing the jar test speed from 50 to 400 RPM was monitored using a continuous optical flocculation monitor.

Yeoh et al. (1991) focused on the performance of four anionic polyelectrolytes as coagulant aids in combination with alum. In agreement with previous studies by *Choen et al (1958)* and *Black and Hannah (1961)* results confirmed the inefficiency of anionic polyelectrolytes alone and the best performance when used in conjunction with alum. Tests with polyelectrolyte alone showed an ineffective removal of colour and turbidity and a high residual total organic carbon (TOC) level. When 15 mg/L of alum were dosed in the samples before the polyelectrolytes the negatively charged colloidal particles were partially neutralised. This enabled bridging by anionic polyelectrolyte. Two polymers were more effective than the others and this was explained by the presence of additional bridging sites in their molecular structure. Optimum dosages were 0.5 and 1 mg/L depending on the polyelectrolyte type and the best performance was obtained at pH 6.6, giving turbidity lower than 1.0 NTU after settling, colour lower than 5 Hazen Units, conductivity of 63 and 62 μS/cm, TOC of 1.83 and 1.97 mg/L, fast settling rate and large flocs. The authors concluded that anionic polyelectrolytes as coagulation aids in conjunction with alum were very effective and able to produce high quality water.

Polymers adsorbed on particles can have tails extending in the solution that can attach to the polymer segments on other particles. Particles suspended in the water usually bear a negative charge. When cationic polymers are used this bridging action is accompanied by charge neutralisation that effectively reduced the electrostatic repulsive forces. On the other end, non-ionic or anionic polymers performed well when the surface charge on the particles was almost neutralised by metal coagulants. Further details on the mechanism of action of polymer dosing can be found in section 3.2. The polymer types and doses that give the best performances in most of the scientific studies considered in this review are summarized in Table 3.2.

Table 3.2 – Research on polymer dosing as flocculation and filtration aid.

Type of water	Optimum coagulant(s) type and dose	Effect *	Reference
Distilled water + 10 mg/L of synthetic fulvic acid + 200 mg/L of buffer $NaHCO_3$	Alum: 0.5 x 10^{-3} M, 0.188 x 10^{-3} M Non ionic polyacrylamide: (0.1 mg/L)	Settling: 50 % reduction of fulvic acids in solution after 20 min settling Filtration 45 µm: 94% of fulvic acids removal	Diamatopulos and Woods (1985)
Tap water + suspended bentonite clay and colloidal silica	Cationic polymer: Corcoat P600 (0.008 mg/L)	Flocculation: Particles remaining 24.6% Number-volume mean diameter: 2.49 µm	Gosh *et al.* (1985)
Raw water from Hasdeo River, Tunisia	Polymer not specified: (46 mg/L)	Turbidity: 30-50% reduction more than with conventional coagulant	Chourasia (1994)
Tap water + kaolin clay	Cationic high molecular weight copolymer of acrylamide and dimethylaminoethyl acrylate (10-1000 mg/L)	Settling rate: 0.2 mm/sec @ 10 mg/L 0.8 mm/sec @ 100 mg/L 3.6 mm/sec @ 1000 mg/L	Giubai and Gregory (1991)
Raw water from Yorkshire reservoir	Ferric sulphate (8 mg/L) AND Ferric sulphate (8 mg/L) + PolyDAMAC (1 mg/L)	Effect of poly addition: DOC removal: + 5% UV_{254} removal: -3% Settling velocity: -34 um/sec (500 µm floc), -134 um/sec (1000 um floc) D_{50} after 15 min breakage: -148 um	Jarvis *et al.* (2006)
Water from CheongJu WTWs (South Korea)	Alum (2.25 mg/L) Cationic polyelectrolyte C-599A (0.25 mg/L)	99% removal of Synedra algae	Jun *et al.* (2001)
Deionised water + reagents	Cationic polyelectrolyte L (MW 2 millons, CD 2.94 meq/g)	Flocculation index: increase from 0.3 @ 29.1 mg/L to 1.8 @ 47.6 mg/L after 15 minutes	Kam and Gregory (2001)
Tap water + anion exchange regenerant solution from WTWs	Poly-Epi-amine (MW 300000 g/mol, CD 7.0 meq/g)	Filtration @ 11 µm: 85 % removal	Kvinnesland and Odegaard (2004)
Boiled tap water + clay suspensions	Polyaluminium chloride (PAC 60 mg/L) + Cationic polymer (0.5 mg/L)	Non ionic organic compounds removal: between 15 and 75% depending on compound solubility Turbidity removal: 10 NTU more than with PAC	Lee *et al.* (1998)
Tap water + montmorillonite clay	Cationic polymer (Catfloc 21, 0.5 mg/L, MW 1.3 x 105, CD 1.05 coul/mg)	Number-volume particle diameter: 25 um after 15 min stirring @ 45 s^{-1}	Leu and Gosh (1988)

Type of water	Optimum coagulant(s) type and dose	Effect *	Reference
Surface water + bentinite clay	Polymeric coagulant (not specified, 1 mg/L)	Residual turbidity: from 80 to ca 5 NTU)	Orta de Velasquez *et al.* (1997)
Water with low organic content	Alum (not spec.) Polymer BTI A130 (0.3 mg/L)	Mean settling velocity: 0.09 mm/s	Packham (1972)
Raw water from Singapore reservoir	Alum (15 mg/L) Polymer: poly(Na 11AAuU) (0.5 mg/L)	Residual turbidity: 0.4 NTU Conductivity: 61 µS/cm TOC: 1.86 mg/L Floc size: 1.50 – 2.25 mm	Yeoh *et al.* (1990)
500 mL of DI water + 200 g of kaolin clay in tap water	PolyDAMAC (0.125 mg/L)	Flocculation index: 2.42 after 15 min growth 0.47 after breakage 2.20 after re-growth	Yukselen *et al.* (2006)
Kaolinite suspensions with 20 JTU turbidity	Cationic (Nalco 100 mg/L)	Absorption of polymer by sand: 3.8 – 4.2 mg/100 g sand	Loganathan and Maier (1975)
Raw water from water reservoir	Cationic polymer Catfloc T (0.75 mg/L)	Turbidity removal after sand filtration: 5 NTU Sand filter headloss: ca 200 cm	Cleasby *et al.* (1984)
Raw water from Grasse river (NY) and Glenmore reservoir (NY)	Cationic polyelectrolyte Magnifloc 573C (5, 2.5 mg/L)	Filtrate turbidity: < 0/2 NTU, UV removal: 58-51 %, TOC removal: 37-39%	Edzwald *et at.* (1987)
Tap water + 44 mg/L of bentonite clay and 22 mg/L of kaolin clay	Cationic polyelectrolyte CatFloc T (2 mg/L)	Filtrate turbidity: from 0.2 to less then 0.05 NTU	Letterman *et al.* (1979)
Tap water + 2 mg/L kaolinite clay and 4 ,g/L of bentonite clay	Alum (20 mg/L) Cationic polyelectrolyte CatFloc(1 mg/L)	Filtrate turbidity: <0.2 NTU in coarse media	Shea *et al.* (1971)
Distilled water + reagents (turbidity 80 FTU)	Cationic polymer (MW 10000 – 200000)	Volume of water filtered: 69 kL/m2, Filtrate turbidity: < 1.0 NTU	Stump and Novak (1979)
Raw water from E.L.Smith WTWs, Edmonton (Canada)	Alum Cationic low molecular weight diallyi dimethyl ammonium chloride (DDAC 0.01 mg/L)	Filtrate turbidity: 0.03 NTU with poly 0.06 NTU without poly Turbidity breakthrough: After 72 h with poly After 30-40 h without poly Filtration rate (declining mode): after 3 days operation 15 to 13 m/h no poly 15 to 10 m/h with poly	Zhu *et al.* (1995)

(*) as result of experimental procedures and operating conditions

3.3.3.2. NOM and colour removal

There is currently a paucity of information on the use of polymer as a coagulant for the treatment of NOM rich waters. Some researchers have investigated polymer dosing as primary coagulants and flocculation aids for the treatment of waters with a high content of NOM (humic and fulvic acids). Humic and fulvic acids are hydrophobic in nature and have a wide range of MWs. When coagulated, they generally form weak and low density flocs (*Bache et al., 1999*). Charge neutralisation is thought to be the most effective mechanism to coagulate humic and fulvic acids (*Kam and Gregory, 2001, and Kvinnesland and Odegaard, 2004). Kam and Gregory (2001)* investigated humic acid removal by a series of synthetic cationic polyelectrolytes, focusing on the role of charge effect. Humic acids and cationic polymers were flocculated by gentle stirring and absorbance of UV light at 300 nm was measured on the supernatant after centrifugation. The optimum removal of organic matter by coagulation and flocculation occurred together with charge neutralisation: the most highly charged polyelectrolyte gave up to 90% humic acid removal in a narrow range of dosages. As the CD decreased, the removal became worst (to about 75%) but the range of effective dosage became broader. Polymer MW did not affect the degree of removal. Similar research by *Kvinnesland and Odegaard (2004)* studied the effects of cationic polymer characteristics on the coagulation and flocculation of dissolved organic substance. Coagulation was measured as the extent of humic substances removal after filtration at 0.1 μm. In agreement with *Kam and Gregory (2001)* the authors found a relationship between the polyelectrolyte CD and the coagulation dose efficiency and a negligible effect of polymer MW on both coagulation and flocculation of humic substances. The optimum polymer dosages for flocculation deviated significantly from the dosage that gave optimum coagulation. Optimum humic acid removal occurred at different cationic charge dosages for different polyelectrolyes and therefore it was not explained by charge addition.

The settling rate of flocs formed from NOM rich waters was shown to increase following polymer addition. *Packham (1972)* tested seven commercial polyacrylamides as primary coagulants for the coagulation of water having a high NOM content. Although some polyelectrolytes gave good removal, in almost all cases

the flocs formed were very poor, settled slowly and gave rise to high final supernatant turbidity. In another series of tests the same polyelectrolytes coagulants were added to water of low organic content already coagulated with aluminium sulphate. The same dose of 0.3 mg/L of polyelectrolyte was used in all the tests. Results showed a significant variation in mean settling velocity depending on the polyacrylamide used, with values ranging from 0.09 mm/s to 0.02 mm/s. *Diamadopulos and Woods (1985)* varied pH, aluminium concentration and polymer dosage and noticed that the presence of polymer enhanced both flocs settleability and filtration. The most important variables affecting fulvic acid removal were pH and aluminium dose, with complete removal at $0.5x10^3$ mg/L of alum and pH 6. The authors found the best fulvic acid removal when adding 0.1 mg/L of non-ionic polymer at the optimum aluminium dose.

Jarvis et al. (2006) investigated the impact of polymer on floc structure, in combination with a ferric sulphate-based coagulant. The flocculant aid tested was a high MW cationic polymer and experiments were carried out on raw water from a reservoir source with high NOM content by performing a series of jar tests. A slight improvement in dissolved organic carbon removal was obtained at concentrations of 1 and 2 mg/L of polymer, but most of the polymer doses showed no improvement when compared with the coagulant alone. Maximum floc size was much reduced at polymer dose at and above 2 mg/L than at lower doses. A dose of 1 mg/L was chosen and comparative floc structural experiments were performed on three floc suspensions containing coagulant precipitate, NOM and optimum ferric sulphate dose, and NOM and optimum ratio ferric sulphate/polymer aid. In agreement with the previous study by *Packam (1972)* results showed that adding polymer to primary coagulant reduced floc size, settleability and compaction. The authors concluded that the high MW polymer chosen gave better floc properties when used as a primary coagulant rather than as a floc aid. However its poor NOM removal would preclude its operational use.

3.3.3.3. Full scale studies

Polymer dosing as a flocculation aid proved that in many cases it is successful on research conducted on full scale plants. A cationic polyelectrolyte was used for

several years to treat Kansas River water in order to remove organic matter (*Robinson, 1980*). Polymer dosing on raw water was followed by the traditional softening, alum coagulation and chlorine disinfection. Raw water pre-treatment using cationic polymer reduced organic matter with a consequent significant drop in chlorine requirements. *Bratby (1980)* mentioned the use of cationic polyelectrolytes in the state of New York to treat water from *Oswegatchie River*. A long chain anionic or non-ionic polyelectrolyte was added in a flocculation bay to the water after dosing of alum, activated silica and cationic polyelectrolyte. This resulted in the aggregation of flocs into large masses with higher settleability.

The effectiveness of the polymer is however very dependant on the conditions and the type of process considered. Environmental and operating conditions such as pH (*Odegaard and Eikebrokk, 1985*) and temperature (*Chourasia, 1994),* have a great effect on the final water quality. *Odegaard and Eikebrokk (1985)* investigated the optimisation of coagulation and flocculation in water treatment depending on the separation process used: sedimentation, flotation and filtration. The authors used data from different experiments on theoretically developed models, considering polymer dosing as a flocculation aid. According to their calculations, the use of polymer in combination with alum decreased the break-up coefficient of flocs, indicating that polymer treated flocs were stronger than flocs formed with no polymer. Studying the optimisation of flocculation followed by direct filtration the authors found that the absorbance capacity of flocs, defined as *storage capacity* was the key property. The addition of 0.1 mg/L of polymer increased both water production and filter run length at a given velocity. The pH value had a great impact on filtration performance: at pH 6 particle breakthrough occurred much earlier than at pH 4.7, when breakthrough did not occur even after 10 hours. Coagulation at low pH must however be carefully monitored because of the resulting high residual aluminium content. *Chourasia (1994)* studied the effect of polymer dosing in the clarification stage in a full-scale water treatment plant situated near Korba thermal power station, Tunisia. Monitoring the effluent before and after polymer dosing, the authors found turbidity values between 30 and 50% lower after polymer dosing than with alum alone. However a considerable increase in chloride content and a slight increase in water conductivity

made polymer dosing not a suitable option for the plant considered: the polymer was not stable at temperatures above 40°C, which were sometimes seen during summer. According to *Chourasia,* polymer could not be stored for long periods because their risk of deterioration. This is in contrast with the study by *Yeoh et al (1991)* who investigated the ageing effect on the performance of two anionic polymers and found that the quality of settled water treated using fresh polyelectrolyte solution was the same as the quality of settled water treated with the same polyelectrolyte solution after storing for up to 30 days at room temperature.

3.3.3.4. Parameters affecting polymer efficiency

The influence of operating conditions and polymer properties on coagulation efficiency using polymers have been researched at a laboratory scale, the most relevant research is reviewed in this section.

3.3.3.4.1. Polyelectrolyte properties

The influence of polyelectrolyte used in water clarification has been studied by *Wilde and Dexter, 1972.* The authors investigated the effect of polymer charge and MW, and the relationship between the polymer dose and the particle concentration in suspension. The authors noticed that the charge polarity of the most effective flocculants must be opposite to that of the particles being flocculated, even if some less effective flocculation occurred with polymers of similar charge. The type and optimum dose of polymer that provided the maximum supernatant clarity and the highest settling velocity appeared dependant on the type of metal coagulant used. The authors concluded that the best performance was associated with polymers having the lowest acceptable CD capable of yielding flocculation. In respect to polymer MW, increasing the MW improved the performance of non-ionic polymers. Nevertheless the authors noted that high MW polymers were effective when dosed in a very narrow range. *Leu and Ghosh (1988)* studied the inter-relationship between the chemical properties of several commercially available cationic polyelectrolytes and flocculated particle size distributions. The properties varied during the experiments were MW, CD, dosage and mixing intensity. Contrary to what was observed by *Wilde and Dexter*

with non-ionic polymers, the authors noticed that the optimum dosage of cationic polymers was independent from the MW of the polyelectrolyte and it was inversely related to its CD for a given colloid concentration. Optimum polyelectrolyte concentrations varied from 0.5 mg/L to 1.5 mg/L depending on the type. With respect to the floc size distribution the authors found that mixing conditions rather than the polyelectrolyte characteristics determined the shape of the particle size distribution curve. At low mixing intensities flocs were larger and distributed in a wider range that at high mixing intensities, reaching a maximum of about 20 μm. At constant mixing intensity and similar CD high MW polymers yielded larger and stronger flocs. At optimum polymer dose floc size and strength were directly related to the MW of the polymer, while CD played only a minor role. Re-growth tests showed that flocculation was a reversible process to a certain extent, even if re-aggregated flocs are always smaller than parents flocs.

3.3.3.4.2. Operating conditions

Operating conditions had a great influence on the polymer dosing effect. Polymer dose was shown to affect floc properties (size and strength) both for cationic, anionic and non-ionic polymer. The use of polymer dose higher than 1 mg/L made the floc less settleable (*Lee et al. 1998, Jarvis et al. 2006).* This may be due to the formation of a second polymer adsorption layer on the surface of metal precipitates, which inhibited the attachment of metal precipitates. *Yaremko et al. (1991)* used a kinetic model to study the effect of flocculant dose and method of introduction into a colloidal system. They found that differently charged high MW polymers showed a considerable similarity in pattern of stabilisation of colloid solutions. Increased polymer concentration was accompanied by a decrease in the stability of the suspension, followed by an improved stability and in some cases deterioration.

Flocculation time and mixing velocity were also found to be key variables in flocculation efficiency following polymer dosing. *Selvapathy and Reddy (1992)* found that cationic polyelectrolyte required increased flocculation period but decreased settling time when compared with alum. This might be due to the relatively large molecular size of the polyelectrolyte compared to the one with alum, and

consequently to a slower charge neutralisation and colloidal destabilisation. *Guibai and Gregory (1991)* found that flocculation of high turbidity waters was extremely dependent on the mixing process. Floc sizes reached a maximum by reducing the stirring rate shortly after polymer dosing and this plateau level could be held by maintaining this stirring rate, while rapid mixing caused floc breakage. The authors found also that flocculation of high-turbidity waters could be achieved by quite low dosages of polymer (from 0 to 0.02%) and an increase in polymer concentration caused an increase in the rate of flocculation and gave large floc sizes. *Young et al. (2000)* investigated the effect of mixing on flocculation kinetic parameters. Performing different model simulations, the authors found that alum flocculation with and without polymer dosing could be represented by the same type of kinetic model. The rate of floc growth was increased by increasing the mean velocity gradient of the slow mixing stage (G_f) up to 200 s^{-1}. Little improvement in performance occurred with values of G_f higher than 200 s^{-1}. The maximum mean floc diameter d_{max} reached its maximum with mixing intensities between 70 and 100 s^{-1}. With G_f values between 100 and 200 s^{-1} an increase in G_f is not followed by an increase in d_{max}, as previously found by *Guibai and Gregory (1991)* but by a decrease in flocculation time and an increase in flocculation rate. This confirms what found by *Selvapathy and Reddy (1991)*. According to the authors the improvements in kinetics did not justify the higher energy consumption required by higher mixing intensity. Finally the authors noticed that the use of polymers as coagulants aids strengthened the flocs, with significant break-up only at $G_f > 400$ s^{-1}.

Polymer used in drinking water treatment are dosed as primary coagulant or flocculation aids. Research showed that cationic polymer performs better than anionic and non-ionic polymer in terms of flocculation and settling. The better behaviour of cationic polymer is due to the combined effect of charge neutralisation and particle bridging. However, water characterised by high NOM content is more difficult to treat using polymers as primary coagulant as polymer dosing seems to reduce floc size, settleability and compaction. Aluminium and iron salts may be more effective for this type of water. Research showed that polymer efficiency both as primary coagulant and as flocculation aid is very sensitive to operating conditions, that is why the choice

of polymer type and dose on-site is often empirical. Research on full scale plants has proved that polymer dosing often improved effluent water quality.

3.4. Polymer dosing in rapid sand filtration

3.4.1. Rapid sand filtration (RSF)

Sand filtration is one of the oldest water treatment processes: the first reported application of sand and gravel as method for purifying water is described in Indian medical lore, dated probably around 2000 BC (*Crittenden et al., 2005)*. Early reported applications include the Romans in 150 AD, who took advantage of the natural filtration of water through soil when using lakes for water supply (*Crittenden et al., 2005*). The practice of filtering surface water on a municipal scale began in England and Scotland around 1800 and became more widespread as soon as people realised the possibility of controlling water born diseases (*Parsons and Jefferson, 2006*). The first regulation mandating filtration was adopted in 1852 in the Metropolitan District of London in order to control the increasing pollution in the river Thames (*Crittenden et al., 2005*). In the United States rapid filtration was first adopted in the 1880s and was made compulsory for surface water treatment plants in the latter part of the twentieth century with the *Surface Treatment Rule (U.S. EPA, 1989).* Granular media filters have been used for more than a century and today are still the most common type of filters used for removing particulate matter from the water. Sand filtration reduces the turbidity of the water by removal of colloidal and suspended materials (*Loganathan and Maier, 1973*).

The water passes through a submerged granular bed with a speed generally between 5 and 15 m/h (*Crittenden et al., 2005*). A typical sand filter consists of a rectangular or square concrete open-top tank containing the media that sits on top of an under-drain system that collects the filtered water and delivers the backwash flow (*Parsons and Jefferson, 2006*). The filter bed usually consists of a layer 0.6 m deep of coarse sand 0.5 – 1.0 mm in diameter and a layer of 12 – 25 mm gravel about 0.3 m deep, giving an overall depth of 0.9 – 1.2 m (*Gray, 2006*).

In WTWs, granular bed filtration can take place directly after the coagulation and flocculation stage (direct filtration) of after coagulation and flocculation and gravity separation.

3.4.1.1. Process description

The main stages involved in RSF are (Figure 3.3):

1. Ripening or *clean bed stage*
2. Effective filtration or *transient stage*
3. Breakthrough

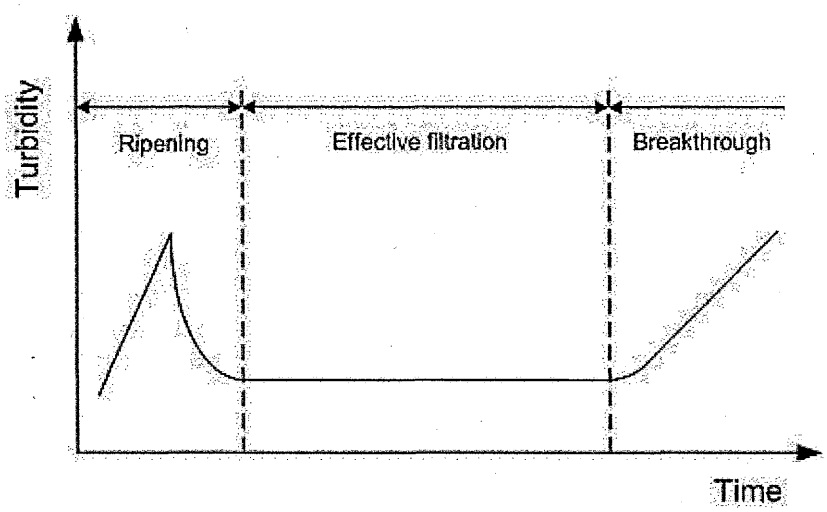


Figure 3.3. – Sand filter operation: turbidity Vs. time

To enhance particle removal by adhesion to filter grains, the particles must be previously destabilised by chemical dosing ahead of filters (coagulation). Polymeric coagulants are often used for this purpose. Ripening, filtration and breakthrough make up the so called *filter run* (figure 3.3). During the ripening stage, or *clean bed stage*, first turbidity increases to a peak because of the flushing of dirty backwash water remnants within the bed, then the water quality starts to improve because the filter media starts to capture particles and this provides a better collector surface, increasing filter efficiency (*Parsons and Jefferson, 2006*). At the end of the ripening the effluent turbidity reaches a minimum know as the *turbidity baseline* and can be maintained at

a steady-state below 1.0 NTU, and the effective filtration stage starts (*transient stage*). During the filtration stage the headloss constantly increases because the filter bed collects particles (*Crittenden et al., 2005*) (section 3.4.1.1.1.). The available head for rapid sand filters is generally within 1.8 to 3.0 m (*Crittenden et al., 2005*). If the headloss exceeds the designed headloss the filter must be backwashed. Backwash is carried out also when the filter experiences turbidity breakthrough. This happens when the filter bed contains so many particles that it can not longer filter them effectively. Particles pass through the filter bed and effluent turbidity increases. A filter is optimised when turbidity breakthrough and design headloss occur simultaneously. When either or the two or both occur together the filter is backwashed (*Gray, 2006*). In modern water treatment plants it is also very common to backwash filters at preset time intervals, usually between 20-60 hours, depending on loading and suspended solid concentration of the raw water (*Gray, 2006*). During the backwash stage the effluent is back pumped through the under drain system. Fluidisation goes on until turbidity value measured for the wash water is around 1.0 NTU (*Parsons and Jefferson, 2006*). The filter is then put back into operation.

3.4.1.1.1. Headloss development in RSF

Many studies have been developed in order to evaluate the pressure drop of fluid flowing through a granular sand filter bed. Kozeny (1927) was the first to establish the relationship between pressure loss, voidage and specific area and Carman (1937) extended his theory to cover transitional flows *(Sevenson, 1996)*. The Kozeny-Carman theory was based on the assumption that the relationship describing the fluid flow though a bed are similar to those which are valid for fluid flow though a model capillary *(Dolejs and Machac, 1994)*. The linear fluid velocity (u_e) of a Newtonian fluid in laminar flow though a capillary of arbitrary cross-section is (*Dolejs and Machac, 1994)*:

$$u_e = \frac{\Delta p \cdot r_h^{\,2}}{K_O \cdot \mu \cdot L_e} \qquad \textbf{Eq. 3. 6}$$

where Δp : pressure drop

μ : dynamic fluid viscosity

L_e : length of the capillary

K_o : coefficient depending on capillary shape (=2 for circular shape)

Kozeny and Carman modified the equation 3.6 for the creeping flow of a Newtonian fluid though a fix bed of particles. The Kozeny and Carman equation is (*Dolejs and Machac, 1994*):

$$\frac{\Delta p}{L} = 5 \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} \cdot \left(\frac{6}{D}\right)^2 \cdot u \cdot \mu \qquad \text{(in Pa)} \qquad \textbf{Eq. 3. 7}$$

By substituting in 3.6 the expressions:

$L_e = L \cdot q$

$u_e = \frac{u}{\varepsilon} \cdot q$

$r_h = \frac{\varepsilon \cdot D}{6 \cdot (1-\varepsilon)}$

$K_o \cdot q^2 = 5$: Kozeny coefficient

where L : Length of the bed [m]

q : tortuosity factor

u : superficial fluid velocity [m/s]

ε : bed porosity

D : particle diameter [m]

The Kozeny-Carman equation relates the pressure drop occurring in a sand filter to parameters characterising the bed structure. Increasing the diameter of the particles in the inlet and decreasing the velocity of the fluid contributes to a decrease in RSF headloss. A decrease in bed porosity contributes to an rapid increase in RSF headloss.

3.4.1.2. Particle removal mechanism

The mechanisms involved in particle removal by sand filtration are rather complex and depend on the physical and chemical characteristic of water, particles and filter medium. The main removal mechanism is transport attachment (*Loganathan and Majer, 1973*).

Iwasaki (1937) experimentally observed the removal within the filter depth to be directly dependent on the particle concentration, following a first order rate equation:

$$\frac{\partial C}{\partial z} = -\lambda C \qquad \textbf{Eq. 3.8}$$

Where C = mass or number concentration of particles [mg/L]

z = depth in filter [m]

λ = filtration coefficient [m^{-1}]

The main difficulty of this theory is the determination of the filtration coefficient, that can vary both in time and in depth and depends on the characteristics of both media and the influent suspension.

A macroscopic model to explain RSF behaviour examining the influence of actual transport and attachment mechanisms was presented by *Yao et al. (1971).* Yao defined the filtration coefficient λ as:

$$\lambda = \frac{-3(1-\varepsilon)\eta\alpha C}{2d_C} \qquad \textbf{Eq. 3. 9}$$

Where d_C = diameter of media grain [m]

ε = porosity

η = transport efficiency defined as the ratio between the particle contacting collector and the particle approaching collector

α = attachment efficiency defined as the ratio between particles adhering collector and particles contacting collector

Replacing λ in the equation 3.2 an expression of the variation in particle concentration as a function of depth (L) is obtained:

$$C = C_0 \exp\left[\frac{-3(1-\varepsilon)\eta\alpha L}{2d_C}\right] \qquad \textbf{Eq. 3.10}$$

The next step in the development of Yao's model was to evaluate on a microscopic scale the mechanism that influences particulate transport and attachment on filter grains. Yao's theory was later reviewed by *Jegatheesan and Vigneswaran (2005).* According to *Jegatheesan and Vigneswaran* the mechanisms that transport particle suspensions near filter grains are sedimentation, interception, diffusion, inertia and a hydrodynamic effect. Effective removal depends on the surface forces between

particles. *Jegatheesan and Vigneswaran* grouped these adhesive forces depending on the distances at which they are effective. Long terms forces are dominant for separation distances up to 100 nm (van der Waals and electric double layer), short terms forces are dominant for separation distances up to 5 nm (born and hydration force).

3.4.1.2.1. Transport mechanisms

In RSF processes the particles that are removed are usually between 0.1 – 50 μm (*Parsons and Jefferson, 2006*) and the sand used has a diameter between 0.5 and 1.2 mm (*Crittenden et al., 2005*).

The basic mechanisms for transporting particles onto media grain are described in this section.

- Straining

Straining is caused when particles larger than the void spaces in the filter arrive at the filtration surface and form a cake on top of the filter bed. The void volume in a RSF is usually 40-60% of the total bed volume. The cake can improve particle removal but can also rapidly increase the headloss to an unacceptable level. In addition, straining does not allow the filter to be used throughout all its depth. For these reasons straining should be avoided in RSF. Sand filters are designed to minimise straining and encourage filtration by transport and attachment. The vast majority of particles in the influent of RSF are smaller than about 30 – 80 μm (*Crittenden et al., 2005*). This is particularly evident when sedimentation is used ahead of filtration. *Barton (2004)* studied the effect of media grain shape on particle capture in granular filter bed. The author simulated contact removal for loosely packed limestone and densely packed limestone. The ratio of the grain diameter/particle diameter corresponding to 50% of the mass distribution that gave the best removal in case of almost monosized grain distribution was 9.2 for the loosely packed limestone and 14 for densely packed limestone. Therefore according to *Barton*'s study for a media having a mean grain

diameter of about 0.8 mm 50% of the best removed particles had a diameter of about 80 μm in a loosely packed filter bed and 50 μm in a densely packed bed.

- Diffusion

Particles less than 1 μm in diameter are affected by the thermal energy of the water that imparts a random movement to them. This random movement is known as *Brownian motion* and is the cause of particle diffusion in the filter bed. Diffusion can transport particles near filter grains causing collision and attachment.

- Interception

Interception occurs when particles are in a streamline that approach the grain surface to within a particle radius. As the fluid flows past the grain the particle will contact the grain. The interception efficiency (η_I) increases with the ratio particle size (d_P) to collector size (d_C), according to the following equation (*Yao et al., 1971)*:

$$\eta_I = \frac{3}{2} \cdot \left(\frac{d_P}{d_c} \right) \qquad \textbf{Eq. 3. 11}$$

- Inertia

Inertia occurs when particles maintain their trajectory while the streamline that approaches a filter grain diverges to pass around it. Inertia is difficult to calculate and its effect is insignificant in water filtration. For these reasons it has been generally ignored in water treatment models (*Crittenden et al., 2005*).

- Sedimentation

Sedimentation of particles onto filter grains is significant only for large particles having a density significantly higher than the density of the water. Such particles will move following a vector depending on the relative orientation of gravity velocity and velocity of the fluid streamline (*Jegatheesan and Vigneswaran, 2005*). According to *Yao et al (1971)* the collector efficiency due to gravity (η_G) is the ratio between the settling velocity and the filtration rate:

$$\eta_G = \frac{g(\rho_P - \rho_W) d_P^{\,2}}{10\mu \cdot v_F} \qquad \textbf{Eq. 3. 12}$$

Where ρ_P and ρ_W are the densities of the particles and the water, respectively, d_P is the particle diameter and μ is the hydrodynamic viscosity of the water.

- Hydrodynamic action

Hydrodynamic action imparts a random movement onto the particle, which may cause the particles to collide with filter grains. This action results from the variable shear field existing in the laminar water flow through the filter grains. This includes the unbalancing forces caused by particle shape and the irregularities due to the particle deformability. Hydrodynamic forces are very difficult to model in filtration beds, thus they have not been addressed on a fundamental basis (*Crittenden et al., 2005*).

The transport mechanisms do not act uniquely. Their relative importance depends on the characteristics of the fluid, the particles and the media (*Jegatheesan and Vigneswaran, 2005*). The Yao filtration model assumes that the transport mechanisms are additive (*Yao et al., 1971*), but when compared with experimental data it often under-predicts the number of collisions between particles and collectors. *Rajagopalan and Tien (1976)* refined the Yao model creating a semi empirical expression for the transport efficiency that correlated well with the results of numerical calculations. The *Rajagopalan and Tien* filtration model is currently considered the most accurate model because is correlates data better than the other filtration models (*Logan et al. 1995*). *Rajagopalan and Tien* developed the following semi empirical expression for the transport efficiency:

$$\eta = 4A_S^{1/3}Pe^{-2/3} + A_S N_{Lo}^{1/8} N_R^{15/8} + 3.38\times10^{-3} A_S N_G^{1.2} N_R^{-0.4} \qquad \textbf{Eq. 3. 13}$$

where $A_S = \dfrac{2(1-\gamma^5)}{2-3\gamma+3\gamma^5-2\gamma^6}$

$$N_{Lo} = \frac{4Ha}{9\pi\mu d_P^2 v_F}$$

$$N_R = \frac{d_P}{d_C}$$

$$N_G = \frac{v_S}{v_F} = \frac{g(\rho_P - \rho_W)d_P^2}{18\mu v_F}$$

$$Pe = \frac{3\pi\mu d_P d_C v_F}{k_B T}$$

with As = porosity function, dimensionless

N_{Lo} = London group, dimensionless

N_R = relative-size group, dimensionless

N_G = transport efficiency due to gravity, dimensionless

$\gamma = (1-\varepsilon)^{1/3}$ porosity function, dimensionless

Ha = Hamaker constant, $8*10^{-19}$ J

Pe = Peclet number, dimensionless

k_B = Boltzmann constant, 1.381 x 10^{-23} J/K

T = absolute temperature, K

ε = porosity, dimensionless

d_P = particle diameter, m

d_C = grain diameter, m

v_s = Stokes settling velocity, m/s

v_F = filtration rate, m/h

ρ_P = particle density, kg/m^3

ρ_W = water density, kg/m^3

μ = dynamic viscosity of fluid, kg/m*s

The *Rajagopalan and Tien* model *(1976)* can be used to examine the effect of important variables on filter performance. The removal efficiency as C/C_0 (equation 3.10) is a function of particle diameter. As an example, the following conditions: $\alpha = 0.7$, L = 1 m, $\varepsilon = 0.40$, d_C = 0.8 mm, v_F = 4 m/h, T = 15 °C, ρ_P = 1050 kg/m^3, ρ_W = 999 kg/m^3, $\mu = 1.14 \times 10^{-3}$ kg/m*s, have been put into the model and the ratio C/C_0 calculated as a function of the diameter of inlet particles (d_p). These calculations show how particle size influences removal of the particle in the filter (Figure 3.4). This shows that particles of 2 µm were the worst removed particles (C/C_0 = 0.531), and 0.1

and 8 μm particles were removed at a similar extent (C/C_0 = 0.064 and 0.065 respectively).

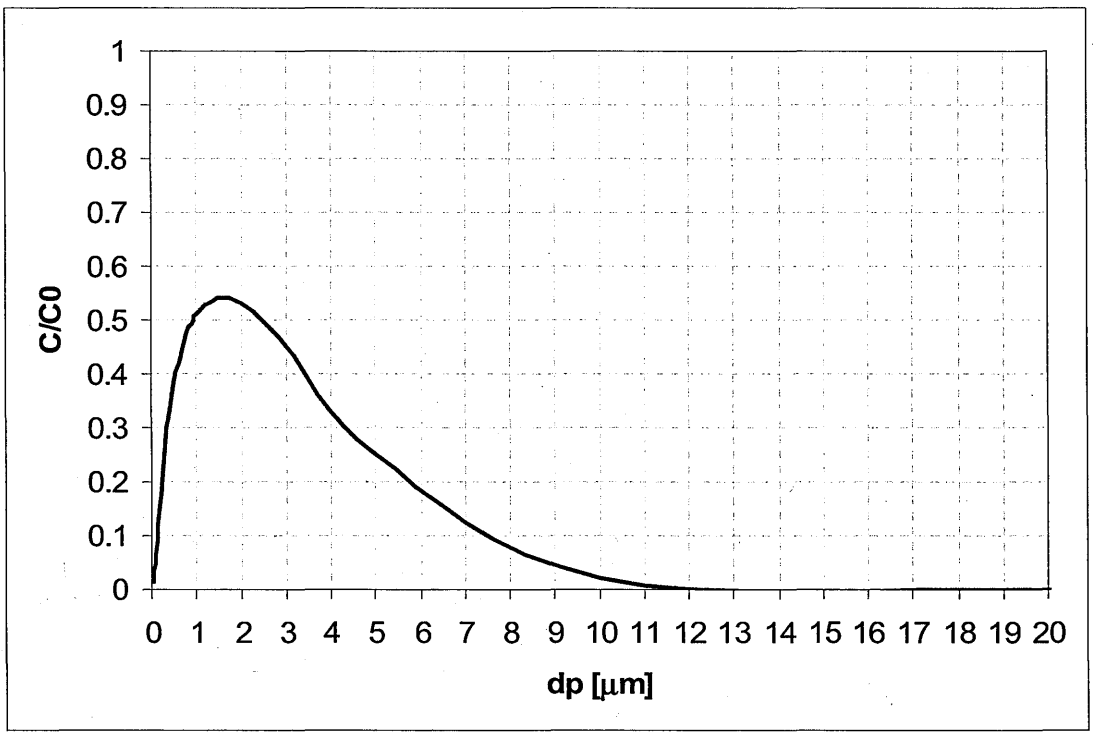


Figure 3.4 – Removal of particles as a function of their diameter according to *Rajagopalan and Tien* model *(1976)*

3.4.1.2.2. Attachment mechanisms

Particles that are transported onto the surface of filter grains must adhere to the collector in order to be removed. The forces that affect attachment of the particles onto the collector depend on the relative distance between particle and collector. The attachment efficiency can be controlled by the destabilisation of particles through coagulation (*Crittenden et al., 2005*).

Jegatheesan and *Vigneswaran (2000)* described the forces that arise between particles and filter grains. A temporary asymmetric distribution of electrons around the atomic nuclei produces the *London-van der Waals* forces. When solid particles are placed in a liquid they get a surface charge that is counterbalanced by the ions present in the solution. This interaction is known as the *electrical double layer.* The inner layer is composed of charged hydroxyl ions adsorbed onto the surface surrounded by an outer

layer of charged ions. The surface potential between these two layer is known as the *zeta potential.* The ionic strength of the solution directly influences the thickness of the double layer (*Stephan and Chase, 2001*). If two atoms get very close the electron clouds overlap and a strong repulsion force, known as a *born repulsive force* arises. *Hydration force* is generated by the incorporation of molecular water into a complex with the molecules or units of another species (*McGraw-Hill, 2003*). *Mutual adsorption* arises when coagulants adsorbed on the grain or particle surface interact forming link and bridges. Hydrophobic surfaces in an aqueous medium are attracted to each other. This phenomenon is known as the *hydrophobic effect.*

These forces form a resultant adhesive force depending on the distance between the particle and the surface of the filter grain. When the forces shearing the particles away from the media grain are greater than the adhesive force, detachment occurs (*Crittenden et al., 2005*).

3.4.2. Polymers dosing in direct filtration

The most important factor in achieving high attachment efficiency is proper destabilisation by coagulation (*Crittenden et al., 2005*). Polymer dosing before sand filtration further destabilises the particles in the water dosed to the filters. *Loganathan and Maier (1975)* studied how different types of polyelectrolyte affected the attachment mechanism. Cationic polymer dosing reversed the zeta potential of the sand from negative to positive, enhancing the attraction between filter grains and particles dissolved in the water by electrostatic interaction and van *der Waals forces.* This confirmed that found by *Graham (1988),* who developed a computer model to predict which filtration mechanisms are mostly affected by the addition of coagulant chemicals. The author found that the presence of cationic polymer on the surface of suspended particles or of filter grains enhanced attachment through *Van der Waals* forces assisted by polymer segment bridging. *Graham* also found that another mechanism enhancing particle attachment was a greater capture efficiency by deposited particles. In the study by *Loganathan and Maier (1975)* non-ionic polymer dosing did not affect the zeta potential of particle and filter grains. The main

mechanism of particles capture enhanced by non-ionic polymer dosing was *mutual absorption* by divalent cations. When anionic polymer was dosed negative zeta potential was decreased. Anionic polymers formed less attachments with filter grains than cationic and non ionic polymers, extending more into the free spaces between surfaces. Therefore particles were trapped by enmeshment.

The first authors mentioning polymer dosing before sand filters to control turbidity breakthrough were *Conley and Pitman (1960)*. In a filter evaluation program carried out at Hanford, Washington, from 1950 to 1955, the authors found that organic polymer caused a strong adhesion of flocs to filter grains. One of the first research to study polymer dosing as a filtration aid was performed by *Robeck et al. (1964)* in pilot plants treating water from Little Miami River. The treatment sequence involved coagulation using alum and activated silica, followed by flocculation, settling and filtration. Water samples were taken from the plant and dosed on bench-scale sand filters at three different points: after coagulation, after flocculation and after settling. A synthetic polyelectrolyte was used to strengthen floc entering the filters. Results showed that polymer dosing helped to decrease effluent turbidity extending filtration runs. Dosing synthetic polyelectrolyte as a filter aid at concentrations between 0.05 and 20 mg/L helped considerably to achieve the optimum floc strength, especially on settled water.

In direct filtration processes, the water is filtered directly after coagulation and flocculation. Sedimentation and flotation ahead of filtration are removed, reducing both capital and operating costs. Direct filtration is not able to rapidly respond to changes in raw water and the process is not suitable for waters high in either organics or turbidity (*Parsons and Jefferson, 2006*). Direct filtration is particularly promising in combination with polymer coagulation: polymer is dosed just ahead of filtration in small amounts, usually 1 mg/L or less and is superior to alum in both technical and economical aspects (*Shea et al., 1971*). In experiments carried out on four pilot filters containing different media *Shea et al.* found that adding 0.5 mg/L of cationic polyelectrolyte *Cat-Floc* to a single media sand filter produced floc of sufficient size and strength to be retained by the media. The headloss on the filter increased with

increasing polymer dose, and low polymer dose resulted in floc breakthrough. The optimum dose was reached when headloss and turbidity breakthrough occurred at almost the same time. The optimum polyelectrolyte dose appeared to be dependent on the type of filter media and in direct proportion to the concentration of suspended matter. This result was later confirmed by *Cikurel et al. (1999)*, who investigated the effect of coagulant addition on filtration efficiency. Dosing 0.5 mg/L of high MW cationic polymer as a primary coagulant was able to efficiently remove particulates larger than 10 μm, while dosing 3 mg/L of the same coagulant improved the removal of the whole range of particles. Headloss increased much faster adding 3 mg/L of polymer when compared to a dose of 0.5 mg/L of polymer. In order to find the best coagulation procedure that strengthened the floc and caused higher attachment to the media, *Cikurel et al. (1999)* carried out filtration experiments using alum as primary coagulant and polyelectrolyte as filtration aid. Dosing 7 mg/L of alum combined with very high MW cationic polyelectrolyte gave the largest and strongest flocs.

3.4.2.1. Type of polymer

Polymer that performed the best as a filtration aid appears to depend on several variables, including polymer properties, the properties of the water to be filtered and the operating conditions. The two main factors to consider when choosing a polymer as filtration aids are CD and MW. Cationic polymers were able to partially neutralize the negative charge of particles dissolved in the water or filter grains, reducing their repulsion and thus enhancing attachment by electrostatic forces *(Gosh et al., 1975)*. Non-ionic polymers enhanced removal through bridging between particles and filter grains. *Suthaker et al. (1995)* found that non-ionic polymer dosing did not significantly improved the filter performance at 12.5 m/h filtration rate, while the length of the filtration run and the water production capacity were reduced by polymer addition at 8 m/h filtration rate. Anionic polymers increased negative charges of media and dissolved colloids and therefore repulsion and did not seem effective as sand filtration aids *(Stump and Novak, 1979)*.

With respect to the MW of the polymer, high MW polymers were able to produce a clearer effluent, but at the same time caused a rapid increase in headloss (*Gosh et al., 1975, Stump and Novak, 1979).* The effects of five homologs of polyethilemine at different MW on particle removal from aqueous suspensions by sand filtration were studied by *Habibian and O'Melia (1975)* and the optimum polymer dose appeared to be independent from the MW of the polymer, contradicting the results of the study by *Gosh et al. (1975).* In the study by *Zhu et al. (1995)* the low or moderately low MW polymers performed the best in terms of turbidity removal and water production rate.

3.4.2.2. Effect on headloss development and turbidity removal

Laboratory research and industrial applications have proved the existence of a direct relationship between polymer dosing ahead of sand filters and headloss build-up in the filter bed. Polymer dosing prior to sand filtration increased the headloss growth rate (*Garnell, 1962).* This was more evident using high MW polymers. The rate of headloss development is higher when small particles are filtered, because they are retained in the filter pores (*Glaser and Edzwald, 1979).* Filtration is carried out in the bed by clearly defined working layers: in the layer above the working layer the sand is saturated, in the layer below the working layer the water is clean (*Adin and Rehbun, 1974 and Letterman et al. 1979).*

TOC removal was more effective using alum as a filtration aid rather than polymer (*Edzwald et al., 1987).* The optimum dose was mostly affected by the concentration of dissolved organic matter in raw water, rather by turbidity (*Edzwald et al., 1987).* *Saltnes et al. (2002)* compared turbidity and TOC removal in direct filtration testing a high MW, non-ionic, synthetic polymer as filter aid on a conventional filter and on a coarse filter. The conventional filter consisted in a 60 cm layer anthracite (0.8-1.6 mm) placed above a layer of sand (0.4-0.8 mm); the coarse filter consisted in a 48 mm of media FL NC (6-25 mm) placed above a layer of media (FL HC 0.6-1.6 mm). When 0.05 mg/L of polymer was dosed to the raw water in combination with aluminium sulphate, bigger flocs were clearly visible over the filter media. These flocs were much more filterable and the filter run-length was longer in the coarse

filter, while there was almost no reduction in effluent turbidity and surface deposition with exponential headloss development in the conventional filter. Improvement of direct filtration of humic acids on a coarse media combining alum and a high MW cationic polymer was previously demonstrated by *Adin and Rebhun (1971)* and *Rebhun et al. (1983)*, who suggested that deep bed filtration proceeds in working layers. *Cleasby et al. (1984)* compared the performance of rapid in-line filters using cationic polymer coagulant and alum. The cationic polymer produced longer filter cycles but a slightly inferior filtrate than alum. Alum proved to be less sensitive to changes in raw water quality, therefore the optimum dose selection was easier than with cationic polymer. When low MW polymer are dosed in high turbidity water the filtration run is often terminated because of turbidity breakthrough. *Logsdon et al. (1993)* investigated the feasibility of direct filtration during periods of high raw water turbidity following heavy rainfalls. A key factor influencing the filtration performance was the selection of the appropriate filter aid dosage. Non-ionic polymer was used as filter aid and productivity was best dosing 0.01 mg/L. Lower doses gave early turbidity breakthrough, while higher doses resulted in filter runs with satisfactory filtered-water turbidity, but excessive headloss growth rates. In Brasilia, Brazil and Amman, Jordan, the water reservoirs became turbid for short periods during the raining season, with turbidity values for raw water in excess of 40 NTU (*Wagner and Hudston, 1982)*. Bench scale studies on this water gave a satisfactory direct filtration performance with alum coagulation and 0.5 mg/L of the polymer *CatFloc* as filtration aid.

Yao et al. (1971), Habibian and O'Melia (1975), and *Glaser and Edzwald (1979)* found some similarities in the results of coagulation and filtration experiments. These similarities can be explained by the fact that both processes to be effective require a transport and an attachment stage. In both processes the particles to be removed must be destabilised and suspended particles must be transported so that contact may be achieved.

3.4.2.3. Zeta potential of filter grains

Most particles in the water as well as the filter grains bear a negative charge which produces a repulsion force that can be measured by zeta potential. The mutual repulsion created by typical colloidal zeta potential of -15 mV to -30 mV is sufficient to maintain particles discreteness (*Riddick 1966).* The zeta potential is dependant on the ionic strength of the solution. *Chang and Vigneswaran (1990)* found that by increasing the ionic strength of the solution the zeta potential can be increased creating a lower energy barrier and thus enhancing particles attachment on filter grain and consequently filter efficiency. In a later study *Jagatheesan and Vigneswaran (1999)* found also that charge accumulation on filter grains due to particles deposition caused a significant deterioration in the filtration removal efficiency at all ionic strengths.

Polymer dosing on sand filters can increase the negative zeta potential on filter grains, neutralising the barrier between particles and grains/collectors and enhancing particle/grain attachment. *Riddick (1966)* mentioned the use of a cationic polyelectrolyte for zeta potential control in the Governeur water utility, New York. First alum was dosed to increase the zeta potential from about -20 mV to a range between -6 and -3 mV, and than 0.3 mg/L of cationic polyelectrolyte was added to further rise the zeta potential to 0 – 3 mV, maximising colour removal. *Jackson (1980)* studied the filtration efficiency of cationic polymers of varying charge densities as filtration aid. The author found that filtration efficiency appeared to decrease with decreasing CD of the polymer and a minimum CD (between 25 and 30%) was required on the polymer to be effective as filtration aid. This was confirmed two years later by *Terashima and Ozaki (1982),* who evaluated the dependence of filter removal efficiency on the zeta potential of filter grains. The authors found that cationic polymer pre-treatment reversed the zeta potential of the sand from negative to positive, favouring the attachment between the negatively charged particles and the filter grains. Particles with a zeta potential of 1.0 mV can be obtained dosing 0.01 mg/L of polymer *(Kim et al., 2006).* Such particles were detached only at certain filter depth and are easily re-attached at subsequent filter depth *(Kim et al., 2006)*

Table 3.2 (section 3.3.2.1) summarizes the main research on the effect of polymer dosing both as flocculation and as a filtration aid. Best performances in terms of settling velocity, NOM removal and filtrate turbidity were generally obtained by dosing a primary metal coagulant together with a cationic polyelectrolyte. The effects of polymer properties as MW and CD are not yet completely understood and more research is required in this direction.

3.5. Summary of literature review

- A generally held conception in water treatment is that the addition of polymer improves floc characteristics enhancing particles removal in the following separation phase. This statement appears to be partially true but the efficiency of the reaction between polymer and flocs depends on many factors such as polymer properties (polymer type, CD and MW) and site conditions (temperature, mixing intensity, NOM content and turbidity).
- Polyelectrolytes used in drinking water treatment are dosed as a primary coagulant or a flocculation aid. Primary polymeric coagulants are generally cationic and have a relatively low MW while polymeric flocculation aids are generally anionic or non ionic and have a relatively high MW (*AWWA, 1999*).
- The main mechanisms involved in polymer-floc interaction are polymer adsorption on particle surface and bridging of particles within the polymeric coagulant. Laboratory research has proved that cationic polymers give the best performance because of the combination of bridging action and charge neutralisation, which reduces electrostatic repulsive forces.
- Water characterised by high NOM content is more difficult to treat using polymers as a primary coagulant as polymer dosing seems to reduce floc size, settleability and compaction. Aluminium and iron salts may be more effective for this application in this type of water.
- A primary polymeric coagulant is effective when the pretreatment objective is to produce small high-density aggregates for direct filtration. Non ionic or anionic high MW polymers are often added after the flocculation process in order to increase size and strength of particle aggregates by particle *bridging*. General effects found

after polymer dosing are lower residual turbidity in filtered water and higher rate of headloss growth.

- The effect of polymer dosing on floc properties and the interaction between flocs and filter bed grains was difficult to measure accurately due to the inherent fragility and complexity of floc structures. There has not been a great deal of work carried out in this field over the past two decades and previous research is sometimes contradictory. Further work is required in order to adequately quantify the effects of polymeric coagulants.
- Because of the complex interactions between polymers and particulates and the influence of water quality and operating conditions on these interactions, polymer selection on-site is often empirical.

4. Materials and methods

4.1. On-site data analysis

Data stored within the central database of Yorkshire Water were collected for both Fixby and Albert WTWs. Albert WTWs treats water from a moorland catchment area which has drained down though a peat system before reaching the reservoir. The water enters the treatment works through a screen to prevent large material from entering the plant. The water is then coagulated with ferric sulphate, flocculated and floated with a DAF system (Figure 1.3). After pH adjustment the effluent is fed to six deep sand filters operating in parallel (Figure 4.1) and finally chlorinated. Fixby WTWs is very similar to Albert, the main difference is that sedimentation tanks are used for particulate removal after coagulation and flocculation, in place of DAF.

Figure 4.1 – Sand filters operating at Albert WTWs

The time period covered for the data analysis was from 1st January to 31st December 2006. This period was considered sufficient to highlight seasonal variations in water quality and includes intervals when polymer was dosed. Polymer was dosed on-site during winter, generally from January to the end of March or the beginning of April. However exact dates and polymer concentrations were not available from the database.

The analysis focused on understanding the impact of on-site conditions on RSF performance. The variables considered relevant for this analysis were: inlet turbidity, inlet flow to the WTWs, raw water temperature, raw water specific UV_{254} absorbance (UV_{254}), coagulant (ferric sulphate) dose. The effect of these explanatory variables on RSF performances in terms of outlet turbidity and headloss (dependent variables) was studied.

On-line measurements were taken every 10 minutes for Fixby and every 5 minutes for Albert for the total duration of the period investigated and grouped according to season. Winter was defined as from January to March, spring from April to June, summer from July to September and autumn from October to December. Graphs summarising on-site data are shown in Appendix A. The performance of only one out of the six operative sand filters is shown at a time, in order to make the charts clearer. However in the data analysis at least two of the six operating filters were considered, in order to make the analysis more reliable.

4.2. Sampling

Water samples were collected from Albert WTWs (schematic in Figure 1.3), Halifax, UK, at three different sampling points: after screening (raw water), after coagulation with ferric sulphate and DAF (clarified water), and after rapid sand filtration (filtered water). The sampling took place on the 21st February, 17th April, 10th July and 6th September 2007. The samples were transported to Cranfield University and stored in a cold room at approx 5 °C for no longer than 2 months. Each sample was characterised investigating the chemical properties and the size distribution of the particles dispersed in the water samples (section 4.3). In order to investigate the ageing effect on the sample properties, characterisation was repeated after 40 days on the water samples that were collected in April 2007. The clarified water sample collected in February 2007 was used to investigate the effect of dosing different synthetic polyelectrolyte concentrations (0, 0.01, 0.02 and 0.03 mg/L) on floc properties at a constant temperature of 15°C (section 4.4). The clarified water sample collected in April 2007 was used to investigate the properties of the floc at different temperatures (5°C, 10°C, 20°C and 30°C) using a constant polymer dose of 0.03 mg/L (section

4.4). The clarified water collected in July 2007 was used to study the impact of polymer dosing on sand filter performance using a bench scale filter (section 4.5). The water that was collected in September was used to perform the analysis of the impact polymer dosing on floc properties and clarified water filterability and to study the particle size distribution in clarified and filtered water in number (section 4.4).

4.3. Characterisation of water samples

The parameters measured were UV_{254}, TOC, turbidity, zeta potential, pH and particle size distribution. A brief explanation of these parameters follows:

UV_{254}: The sample is filtered through filter paper *Munktell*, Falum, Sweden, with pore size of 1.2 μm in order to remove the interference of particles larger than 1-2 μm. Specific molecular structures (*chromopores*) within NOM absorb UV light having a wavelength of 254 nm, so UV_{254} is an indicator of chromoporous NOM content (*Crittenden et al, 2005, p.86*). UV_{254} was measured using a *Jenway 6505 UV Vis* spectrometer, Felsted, Dunmow, UK.

TOC: determination of the organic carbon content of a sample. TOC was measured using a *Shimadzu TOC-500A* analyzer, Milton Keynes, UK. In order to determine the TOC the analyser measured total carbon and inorganic carbon. The difference between the two was the TOC. As samples were filtered through *Munktell* filter paper with pore size of 1.2 μm before being analysed, the TOC value measured was referred as the dissolved organic carbon (DOC).

Turbidity: measurement of the interference of the passage of light through the water by suspended matter. Turbidity can be caused by a variety of suspended materials, ranging from colloidal to coarse dispersions (*Sawyer at al., 1994*). Turbidity was measured using a *Hach 2100N* turbidimeter, Loveland, Colorado, US.

Zeta potential: Zeta potential is the electrostatic potential between the surface of a particle and the bulk solution generated by the accumulation of ions at the surface of the particle. The stability of hydrophilic compounds depends upon their electrical charge. When two particles bearing a similar charge approach each other the similar charge results in repulsive forces. Zeta Potential was measured using a *Zetasizer 2000 HAS*, Malvern, UK.

pH: pH is the measurement of the acidity or alkalinity of a solution. The pH of the water is a highly important characteristic as it affects equilibria between many chemical species (*Sawyer et al, 1994*). pH was measured using the pH/temperature meter *Jenway 3150,* Felsted, Dunmow, UK.

High performance size exclusion chromatography (HPSEC): Size Exclusion Chromatography (SEC) is a technique used for the separation of complex mixtures based on molecular hydrodynamic volume. The underlying principle of SEC is that molecules of different sizes will elute (filter) through a stationary phase at different rates. This results in the separation of a solution of molecules based on size. Provided that all the molecules are loaded simultaneously or near simultaneously, molecules of the same size should elute together. HPSEC analysis was carried out on samples filtered at 1.2 µm with *Munktell* filter paper. The instrument used was a Shimadzu VP series, Milton Keynes, UK, high performance liquid chromatogram using UV_{254} detection.

4.3.1. XAD resin fractionation

The organic matter contained in the collected samples was fractionated by XAD resin (*Amberlite*, France) adsorption technique into hydrophobic (HPOAF) and hydrophilic (HPIAF) acids using a method adopted by *Malcom and MacCharthy (1992).* The DOC of each fraction was then measured using the TOC analyzer and recalculated to the initial volume.

Two 2.5 cm diameter chromatography columns *Econo-columns* by *Bio-Rad,* Hemel Hempstead, UK, were filled with about 60 g of clean resins Amberlite XAD 4 and XAD 8. Sample preparation consisted of filtering 2 L of raw water, 10 L of clarified water and 16 L of filtered water with *Munktell*, Falum, Sweden, filter paper with pore size of 1.2 µm and to regulate the pH of the sample at 2. At this pH the HPOAF of the NOM dissolved in the water can be absorbed by the resin Amberlite XAD 8. The whole sample volume was slowly fed to the first column, containing the resin XAD 8, using a peristaltic pump. The outlet was fed to the second column containing the resin XAD 4. The resin XAD 8 absorbed the HPOAF and the resin XAD 4 absorbed the

HPIAF. The non-absorbed fraction was categorised as hydrophilic non acid fraction (HPINAF). To remove the NOM absorbed on the resin 300 ml of 0.1 M NaOH where passed through both of the columns and stored. Afterwards the resins were regenerated by filtering 300 ml of a HCl 0.1 M and 300 ml of ultrapure water. The pH of HPOF, extracted from the first column, was then reduced to 1, because at such extreme pH HAF precipitate and FAF remains in solution. The HAF was left settle overnight and subsequently separated from the FAF by centrifugation. The DOC of each fraction (HAF, FAF, HPIAF and HPINAF) was then measured using the TOC analyzer and recalculated to the initial volume. The portion of each fraction was calculated out of the total (fractionation) for the raw, clarified and filtered water samples collected at Albert WTWs. Further details on the methods can be found in *Goslan et al. (2002).*

4.4. Measurement of floc properties

Floc growth was measured in the water samples after DAF (clarified water) by performing a series of jar test, following the same method and arrangement successfully applied by *Jarvis et al. (2005 a).*. A *PB-900* variable speed jar tester, *Phipps and Bird,* Virginia, USA, was used with 76x25 mm flat paddle impellers with cylindrical jars containing 1 L samples. To measure the effect of polymer dosing on floc formation in clarified water, synthetic polyacrylamide was dosed to the samples in concentrations increasing from 0.00 to 0.03 mg/L and at a constant temperature of 15°C. The polymer used was *FLOPAM™ AH 912 SEP*, produced by *SNF Ltd,* slightly anionic, bearing a charge of 0.6 meq/g. The jar tester sequence was repeated three times for every polymer dose and consisted of 90 seconds rapid mixing followed by a slow stir phase of 15 minutes. After the slow stir phase the effect of increased shear rate was investigated by increasing the RPM on the jar tester for a further 15 minutes. Floc breakage was performed with jar tester stirrer speeds of 40, 50, 70, 100, 150 and 200 RPM. Floc re-growth was measured by returning the stirrer speed to 30 RPM for 20 minutes, after breakage at 200 RPM. The effect of the temperature on floc properties was investigated performing the same experiments at 5, 10, 20 and 30 °C with a constant polymer dose of 0.03 mg/L. The sample temperature was kept constant by placing the jar was into a 50x28x18 cm water bath with an immersion

thermostat *GD100, Grant*, Shepreth, UK. Cold water temperatures were achieved by adding ice to the water bath.

A laser diffraction instrument (*Malvern Mastersizer 2000,* Malvern, UK) was used to measure the dynamic floc size during floc growth, breakage and re-growth. The instrument allowed continuous measurement of the distribution of particles within the sample by drawing water through the optical unit of the Mastersizer and back into the jar with a peristaltic pump (Figure 4.2). The inflow and the outflow tubes were positioned in the jar opposite to one another at a depth just above the paddle. Size measurements were taken every minute for the duration of the jar test and logged onto a PC. The range of size measured was between 20 nm and 2 mm. The size distribution was expressed in term of volume percent (V%). For example if the result indicated that 15% of the distribution was within a defined size range, it meant that the total volume of all particles in that size range represents 15% of the total volume of all particles in the distribution. Using the *Mastersizer* instrument, the volume of very small particles may not be relevant as it may make up only a small percentage of the total volume, but very small particles size range can contain a very high number particles, representing a high percentage of the total number of particles in the distribution.

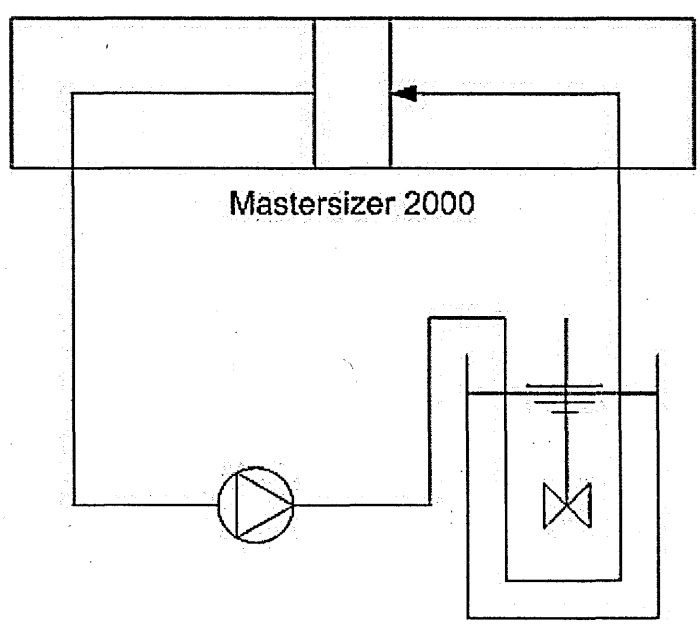


Figure 4.2 – Schematic of the equipment for particle size measurement

Characterisation of particle concentration in the water at different polymer doses was considered fundamental for understanding sand filtration performance and polymer dosing effect. The laser particle counter *PC2200, Spectrex,* Redwood city, California, USA was used. The instrument is able to count and size individual particles from 500 nm to 100 μm; it takes a measurement every 15 seconds, giving the average at the output. One minute measurement duration was set in order to obtain the average of four measurements. As the Spectrex instrument was not able to perform continuous measurement, every 5 minutes during floc growth 3 ml of clarified water were taken from the jar in the jar tester using a plastic pipette with an inlet-outlet diameter of 6 mm. The sampling point chosen was in the middle of the jar, at the lowest extremity of the jar tester mixing pad. In order to obtain consistent measurement the same sampling procedure was repeated five times for every polymer dose at each time interval and measured with the instrument. As the measurement count had to be kept below 1000 count/mL in order to avoid coincident counts, the 3 mL sample was diluted in 100 mL of ultrapure water by injecting the pipette content in a 20 cm bottle containing 97 mL of ultrapure water. The bottle was placed in the instrument and the particles number distribution was measured. This procedure was repeated five times at polymer dosing of 0, 0.01, 0.02 and 0.03 mg/L using the September sample. It was not possible to use the *Spectrex PC 2200* with the samples collected in February, April and July as the instrument was only available for use in September. However, particle count analysis was performed on the outlet of RSF experiments carried out with the September sample. As a lower count was expected for the filtrate, the dilution ratio adopted was 15:100.

The main difference between the two laser diffraction instruments used in this work (*Mastersizer 2000 and Spectrex PC 2200*) is summarised below:

- The Mastersizer 2000 is able to detect particles from 2 nm to 2000 μm, the Spectrex PC 2200 sizes and counts particles between 0.5 μm and 100 μm
- When measuring an heterogeneous mix of particles the Mastersizer 2000 is dominated by large particles, while the Spectrex PC2200 is able to count and size individual particles

- The Mastersizer 2000 operates by a continuous flow through cell, the Spectrex PC 2200 is not able to operate continuously
- With the Mastersizer 2000 a high particle concentration in the sample is required for having a sufficient cell obscuration that allows a reliable measurement. With the Spectrex PC 2200 samples need to be diluted in order to avoid coincident counts.

4.5. Data validation

The calibration of the laboratory instruments was checked before starting every measurement session following the procedure described in the laboratory manuals. The calibration of the pH meter *Jenway 3150* was checked using standard solutions at pH 4 and 7. The calibration of the turbidity meter *Hach 2100N* was checked using six turbidity standards that ranged from 0.02 to 1.6 NTU. The spectrometer *Jenway 6505 UV* was calibrated with DI water before starting the measurements. The calibration of the TOC instrument was checked with DI water and standards at 5 mg/L and 10 mg/L DOC before measuring the samples. The calibration of the *Zetasizer* was checked weekly using standard samples. The calibration of the *Mastersizer 2000* and the HPSEC instrument *Shimadzu VP series* were periodically checked by the laboratory technicians. Before and after every measurement the *Mastersizer 2000* was flushed with de-ionised (DI) water. Subsequently the response of the detectors and the obscuration levels were checked on the screen when running DI water, in order to verify that the cell was clean and no bubbles were present.

The calibration of the *Spectrex PC 2200* was checked daily using three calibration standards containing polystyrene spheres in an alcohol-Freon mix. This special diluents is able to create very stable suspensions with slow settling characteristics. The three bottles used contained 930 count/mL, 550 count/mL and less than 20 counts/mL. If the average of ten counts was between ± 15% of these numbers the instrument was calibrated correctly and working properly.

All the water collected at Albert WTWs was used within a maximum period of two months. In order to determine if there was any deterioration in water properties, water properties were checked in a time period of 40 days. Validation was carried out on the sample collected in April. Particle size distribution, pH, zeta potential, turbidity and UV_{254} measured after 40 days were very similar to the values measured after 5 days. The variations for the clarified sample were -15% for pH, -4% for turbidity and -10% for zeta potential. Therefore from the results of these experiment it was concluded that the data obtained from fresh and aged samples were comparable.

4.6. Sand filtration

Sand filtration experiments were performed on the July and September samples using a laboratory sand filter (Figure 4.3), consisting in a glass graduated column with a diameter of 5 cm and a length of 60 cm, filled with gravel and 16-30 sand. On the bottom of the column 2 cm of gravel were placed in order to avoid clogging of the outlet. A layer of sand of about 7 cm was then laid on the gravel. Clarified water was poured into a 1 L jar and 0, 0.01, 0.02 and 0.03 mg/L of polymer were dosed for each run. The jar was placed on a jar tester and the solution mixed at 200 RPM for 90 sec and subsequently at 30 RPM for 15 minutes. This mixing sequence enabled polymer dispersion followed by floc growth. The solution was then fed to the sand filter using a peristaltic pump at a constant filtration rate of 3.5 m/h. Filtration was carried out for 3.5 hours and filtrate turbidity and headloss were measured every 15 minutes. Turbidity was measured using a *Hach 2100N* Loveland, Colorado, US, turbimeter. Headloss was calculated as the difference between the water level in the column (H) and the pressure (p) measured at the outlet using an *Ashcroft*, Stratford, Connecticut, US, low pressure gauge. The size distribution and number of particles in the filtered water were measured using the *Spectrex* instrument. At the end of each run the sand was removed by the column and washed for 10 minutes using running tap water. Filter runs were repeated twice for each polymer dose with the September sample.

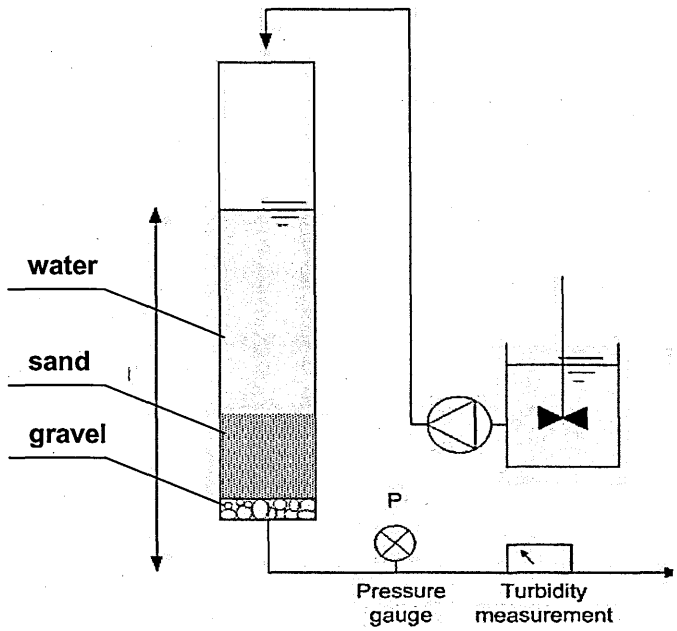


Figure 4.3 – Schematic of laboratory sand filter

5. Results

Chapter 5 describes the results of on-site data analysis and laboratory experiments. On-site data from Albert WTWs covering the year 2006 were analysed in order to identify the effect of seasonal variation of inlet water parameters and of polymer dosing on RSF performance. Laboratory experiments consisted of the characterisation of Albert WTWs samples, jar tests and RSF experiments dosing 0, 0.01, 0.02, 0.03 mg/L of the synthetic polyelectrolyte *FLOPAM™ AH 912 SE* as a filter aid. The overall objective was to explain to what extent water quality influences floc filterability, and to investigate the effect of polymer dosing on pre-filtered water particle size distribution and strength.

5.1. On-site data analysis

5.1.1. Introduction

On-site data from Albert and Fixby WTWs, Yorkshire, UK, covering the year 2006 were collected and analysed. The variations of inlet flow, coagulant dose, raw water temperature, turbidity and UV_{254} throughout the year were considered and their effect on RSF performance was investigated. A chart showing on-site parameters (raw water turbidity, UV_{254}, flow, coagulant dose, temperature, filtered water turbidity, sand filter headloss, outlet flow to sand filters) Vs. time was drawn for every month of the year for Albert WTWs and every season for Fixby WTWs (Appendix A). Polymer aid was dosed as a filtration aid both at Albert and Fixby during winter and some summer dosing trials were also carried out at Albert WTWs. The polymer dosing effect on filtered water quality and RSF performance was analysed.

5.1.2. Seasonal variations of WTWs parameters

5.1.2.1. Fixby WTW

The average coagulant dose was around 8.7 mg/L Fe in spring and 9.0 mg/L Fe in summer. The ferric sulphate dose was kept almost constant during spring and summer: the standard deviation was 0.7 mg/L Fe in spring and 1.8 mg/L Fe in summer (Table 5.1.). In autumn the coagulant dose was a little more variable: 9.2 ± 2.4 mg/L Fe. However the main variability occurred in winter, when a standard deviation of ± 6.5 mg/L Fe was calculated. Raw water UV_{254} was higher and more variable in winter and autumn than in spring and summer: 41.46 ± 5.85 and 40.78 ± 7.59 m^{-1} in winter and autumn respectively against 32.57 ± 2.22 and 32.03 ± 4.01 m^{-1} in spring and summer. Higher and more variable coagulant dose in winter and autumn mirrored higher and more variable raw water UV_{254}: higher UV_{254} indicated higher NOM in the raw water. When this occurred the operators on-site responded by dosing more coagulant in order to improve NOM removal by coagulation.

Inlet turbidity onto filters was the highest in winter, when its average exceeded 4.5 FTU and the lowest in spring (3.4 FTU). In summer and autumn inlet turbidity was around 4.0 FTU. Inlet turbidity variability was also slightly higher in winter: ± 1.2 FTU compared to less than ± 1 FTU during the other seasons. Raw water temperature was the highest in summer (15.0 ± 0.7 °C average) and the lowest in winter (3.3 ± 0.9 °C average). During spring and autumn raw water temperature was more variable: 10. 3 ± 2.5 °C in spring and 8.4 ± 2.9 °C in autumn. Inlet flow to the WTWs was almost constant through the year, with an average around 24.5 ± 2.0 MLD during all the seasons.

Table 5.1: On-site 2006 seasonal parameters for Fixby WTWs

	AVERAGE			
	WINTER 06	**SPRING 06**	**SUMMER 06**	**AUTUMN 06**
Coagulant dose [mg/L Fe]	9.9 ± 6.5	8.7 ± 0.7	9.0 ± 1.8	9.2 ± 2.4
Raw water UV_{254} [m-1]	41.4 ± 5.8	32.5 ± 2.2	32.0 ± 4.0	40.8 ± 7.6
Inlet turbidity to filters [FTU]	4.5 ± 1.2	3.3 ± 0.8	4.0 ± 0.7	3.9 ± 0.9
Raw water temperature [°C]	3.3 ± 0.9	10.2 ± 2.5	15.0 ± 0.7	8.4 ± 2.9
Inlet flow [MLD]	24.4 ± 2.5	24.7 ± 2.1	24.6 ± 2.6	24.1 ± 2.4

5.1.2.2. Albert WTW

Looking at the averages and standard deviations for the on-site parameters shown in Table 5.2, the average coagulant dose was higher in summer: 10.0 ± 2.5 mg/L Fe compared to 8.8 ± 0.6, 8.4 ± 1.8, and 8.9 ± 0.8 mg/L Fe in winter, spring and autumn respectively. The average raw water UV_{254} values measured were between 50 and 55 m^{-1} in all the seasons with a standard deviation between 3.7 and 5.1 m^{-1}. The inlet turbidity was very variable in winter (3.7 ± 5.5 FTU), while it fluctuated around 3.7 ± 0.7 FTU and 2.0 ± 0.7 FTU in summer and autumn respectively. Between winter and spring the average raw water temperature value rose by almost 10 °C (from 3.8 ± 0.8 °C to 12.0 ± 3.5 °C). Summer average raw water temperature was 4.3 °C higher than the spring average and its value decreased by more than 8 °C between summer and autumn. Inlet flow to the WTWs was kept high and fairly constant in winter: the average measured was 52.8 ± 2.6 MLD. During spring and summer inlet flow was more variable (49.0 ± 5.9 MLD in spring and 44.1 ± 8.0 MLD in summer). In autumn is it was again less variable and higher (51.9 ± 4.1 MLD).

Table 5.2: On-site 2006 seasonal parameters for Albert WTWs

	AVERAGE			
	WINTER 06	**SPRING 06**	**SUMMER 06**	**AUTUMN 06**
Coagulant dose [mg/L Fe]	8.8 ± 0.6	8.4 ± 1.8	10.0 ± 1.8	8.9 ± 0.8
Raw water UV_{254} [m-1]	NA	53.1 ± 5.1	50.0 ± 3.7	55.0 ± 4.9
Inlet turbidity to filters [FTU]	3.7 ± 5.5	NA	3.6 ± 0.7	2.0 ± 0.7
Raw water temperature [°C]	3.8 ± 0.8	12.0 ± 3.5	16.3 ± 1.1	8.1 ± 2.9
Inlet flow [MLD]	52.8 ± 2.6	49.0 ± 5.9	44.1 ± 8.0	51.9 ± 4.1

5.1.3. Seasonal RSF performance comparison

Three sets of RSF outlet turbidity and headloss data covering a period of five days were compared during winter, spring, summer and autumn for two of the six operating filters at Fixby and Albert WTWs. Polymer as a filtration aid was dosed during winter. This comparison was performed in order to highlight seasonal differences. 5 days snapshots were investigated. These covered the following days:

- 1^{st}-5^{th} February (winter), 1^{st}-5^{th} May (spring), 1^{st}-5^{th} August (summer), 1^{st}-5^{th} November (autumn);

- 10th-15th February (winter), 10th-15th May (spring), 10th-15th August (summer), 10th-15th November (autumn) ;
- 25th-30th February (winter), 25th-30h May (spring), 25th-30th August (summer), 25th-30th November (autumn).

5.1.3.1. Fixby WTW

Seasonal sand filter performance was compared for two of the six filters (filter 4 and filter 2) operating at Fixby WTWs. Outlet turbidity for filter 2 (Figure 5.1) was almost always below 0.3 FTU during summer, in autumn and winter it exceeded 0.4 FTU one hour after backwash with turbidity breakthrough occurring before backwash. During May (spring) outlet turbidity was lower between the 1st and the 5th, remaining below 0.4 FTU, than between the 10th and the 15th and between the 25th and the 30th, when breakthrough occurred. The headloss in filter 2 followed a similar growth trend in each season (Figure 5.2), rising from 0 m up to between 1.2 and 1.6 m in 24 h before backwash. Headloss growth was slower in early November and late August, when it stayed below 1.2 m. Sand filter performance of filter 4 was rather similar to the performance of filter 2, the only relevant difference is a higher headloss between the 10th and the 15th May, when reached 2 m, and lower outlet turbidity between the 1st and the 5th of November, when no breakthrough occurred.

5.1.3.2. Albert WTWs

Seasonal sand filter performance was compared for two of the six filters (filter 3 and filter 5) operating at Albert WTWs. Performances of filter 3 and filter 5 were similar. RSF were backwashed every 24 hours during winter, summer and autumn and every 32 hours during spring, in order to keep the outlet turbidity below 0.2 FTU. Polymer was dosed as a filtration aid in February. In May and August both filter 3 and filter 5 performed well, maintaining outlet turbidity below 0.1 FTU, while in February and November outlet turbidity exceeded 0.2 FTU a few hours before backwash (Figure 5.3). Headloss growth was lower during summer when it stayed below 1.0 m (Figure 5.4). In spring, autumn and winter it reached 1.6 m before backwash. Headloss build-up was particularly high at the end of May, when it reached 1.9 m. Headloss data for the 30th of May are missing. This could be due to malfunctioning of the pressure meter or because the filter operation was temporally modified. It was not possible to retrieve the cause of these data anomalies.

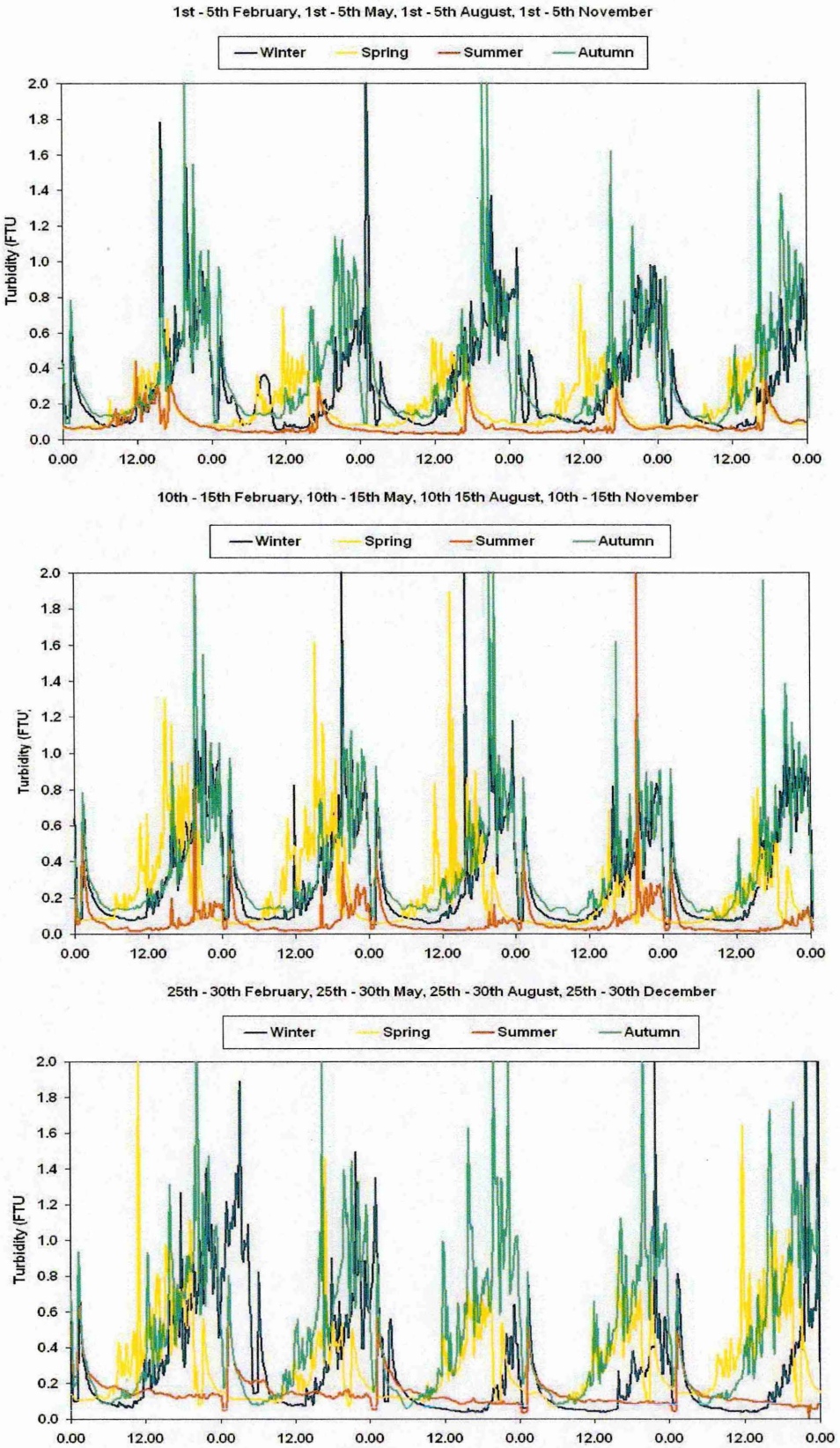


Figure 5.1– Comparison of sand filter seasonal outlet turbidity (filter 2) at Fixby WTWs

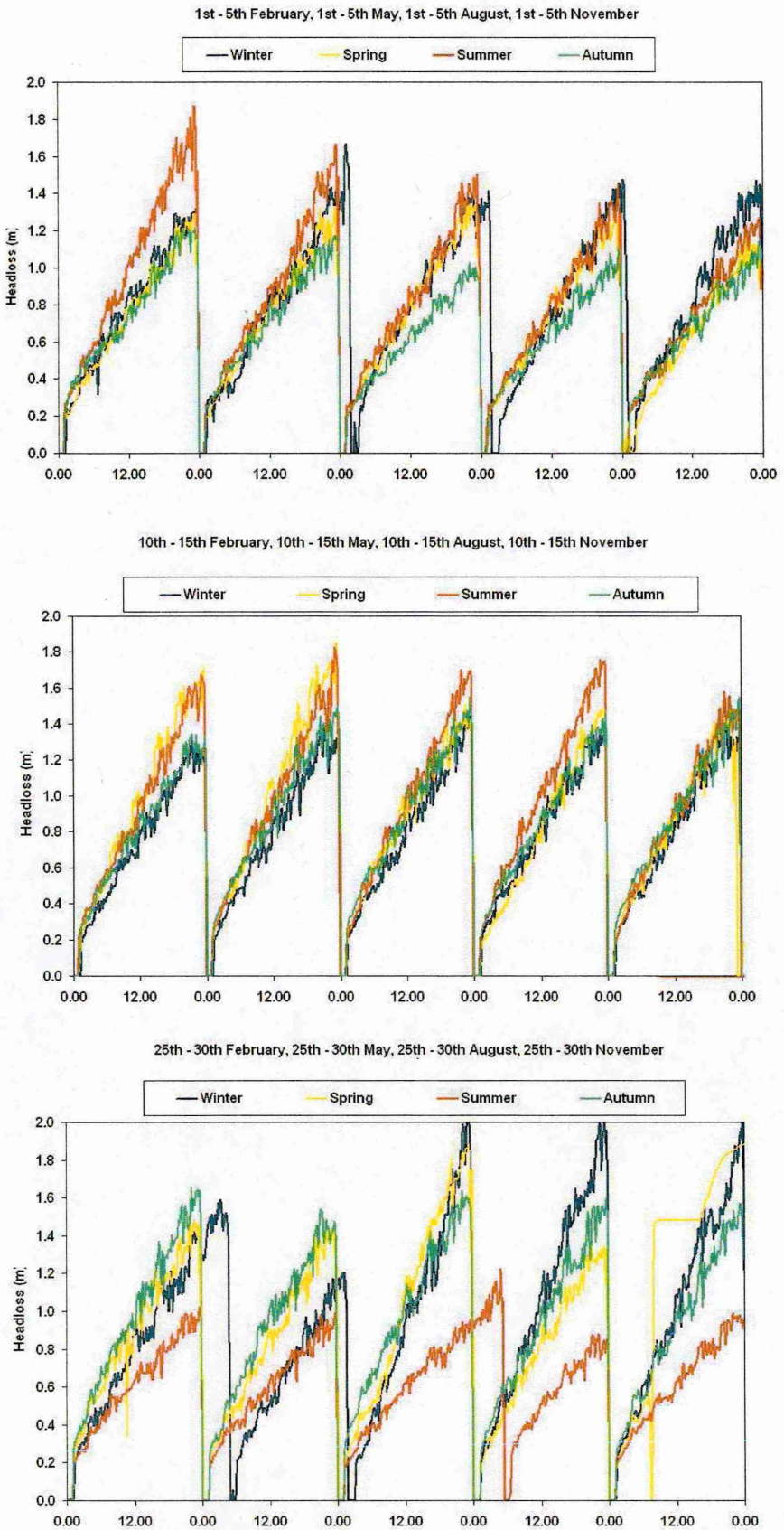


Figure 5. 2 – Comparison of sand filter seasonal headloss (filter 2) at Fixby WTWs

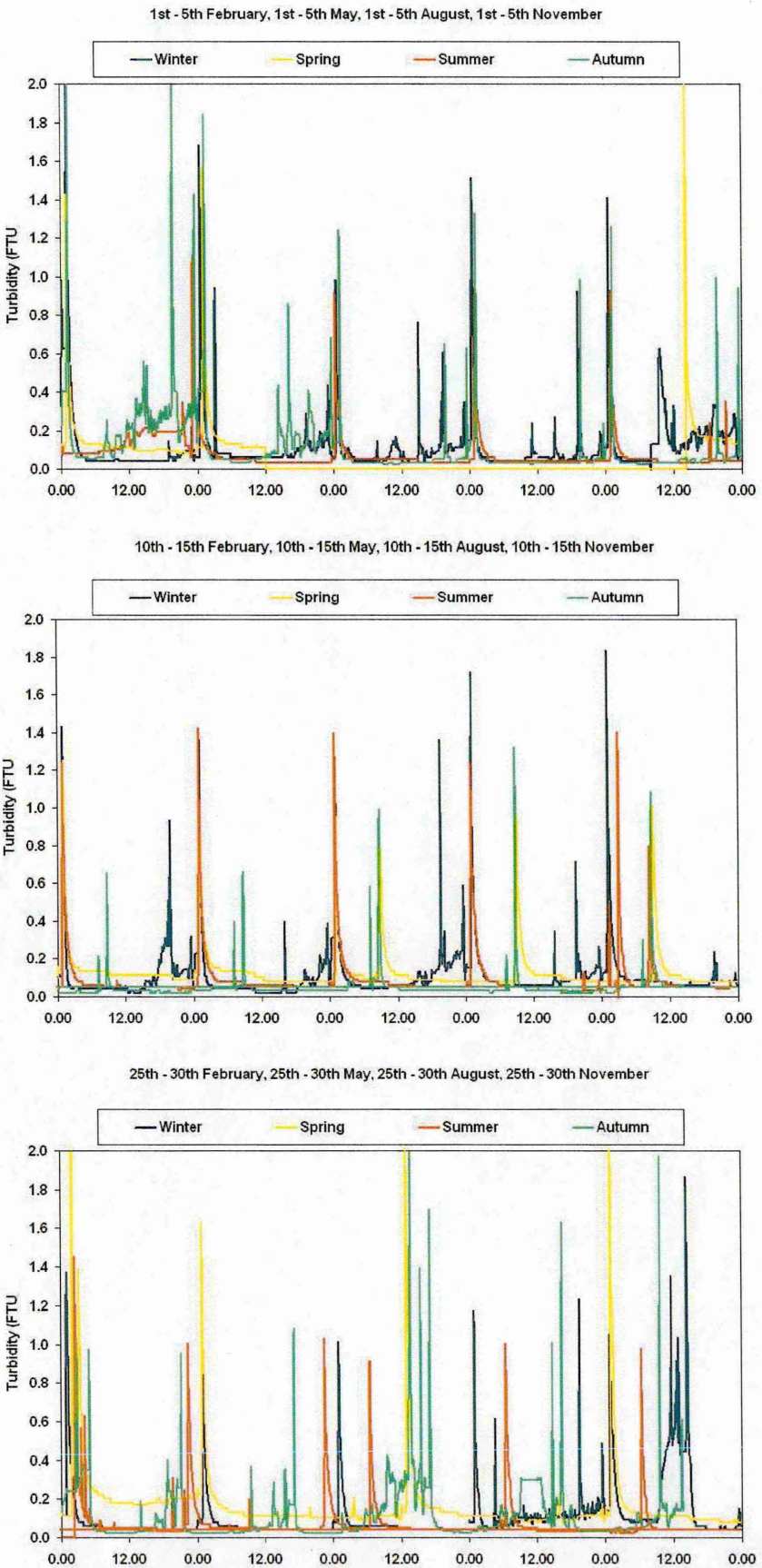


Figure 5.3–Comparison of sand filter seasonal outlet turbidity (filter 3) at Albert WTWs

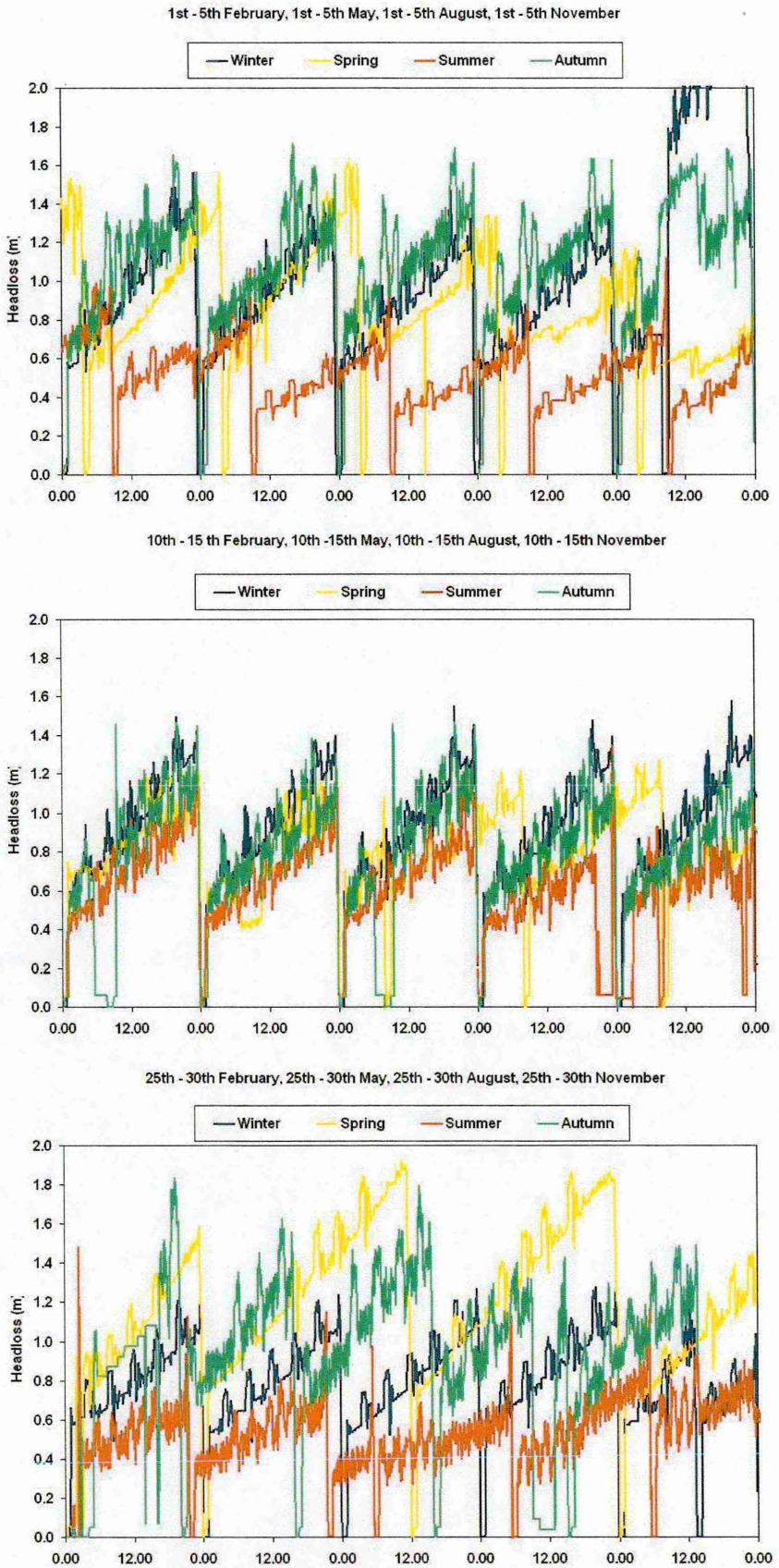


Figure 5.4 – Comparison of sand filter seasonal headloss (filter 3) at Albert WTWs

5.1.4. Polymer dosing effect on RSF performance

A comparison of the outlet turbidity and works inflow data of February 2005, when no polymer was dosed, and 2006, when polymer was dosed, suggests that polymer dosing at Albert WTWs had a beneficial effect on the performance of RSF (Figure 5.5). In 2005 turbidity breakthrough occurred after 10-11 h operation, with turbidity peaks reaching 1.0 FTU with a works inlet flow between 47 and 50 MLD. The RSF backwash had therefore to be performed every 12 h rather then every 24 h, in order to clean the filters. Throughout February and March 2006, when polymer was dosed, the works inflow reached up to 55 MLD with 24 hour filter runs whilst maintaining filtered water turbidity below 0.1 FTU. An extra 7000 m^3 of treated water flow per day was gained that is 5000 m^3 per day in extra inflow and 2000 m^3 per day by washing at 24 hour intervals compared to 12 hour intervals.

Polyelectrolyte dosing started at Albert WTW on 20th July 2006. The dosed concentration was 0.02 mg/L. Following the commencement of dosing the filtered water turbidity lowered slightly and the gradient of the headloss trends increased (Figure 5.6), causing higher than previous values at the end of the filter runs. There was also a slight reduction in the filtered water UV_{254}.

Looking at a selection of daily mean data values before and after polymer dosing (Table 5.3), prior to polymer dosing (12th July) filtered water UV_{254} of 4.8 m^{-1} was obtained with a coagulant dose to raw UV_{254} ratio of 0.2 mg /L of ferric sulphate per raw UV_{254} (absorbance/m) and works inflow of 50 MLD. The flow increase on 18th July resulted in a significant increase in filtered water UV_{254} from 4.8 to 6.1 m^{-1}. Polyelectrolyte dosing started on 20th July and resulted in a reduction of filtered water UV_{254} to 5.5 m^{-1}, still significantly higher than the 4.8 m^{-1} that was achieved at the lower flow of 50 MLD. Filtered water UV_{254} returned to 4.8 m^{-1} when the inlet flow was reduced to 38 MLD on 3rd August with polymer dosing. Filtered water UV_{254} was expected to be lower at flow of 38 MLD with polymer dosing (3rd August) than at 50 MLD without polymer dosing (12th July). Since this did not happen, polymer did not have a significant effect on the filtered water UV_{254} during July 2006 at plant flow of less than 50 MLD and at the ambient raw water quality, with a coagulant dose to

raw UV_{254} ratio of 0.21 mg/L of ferric sulphate per raw UV_{254} (absorbance/m). The combined filtered water turbidity trend followed a similar pattern.

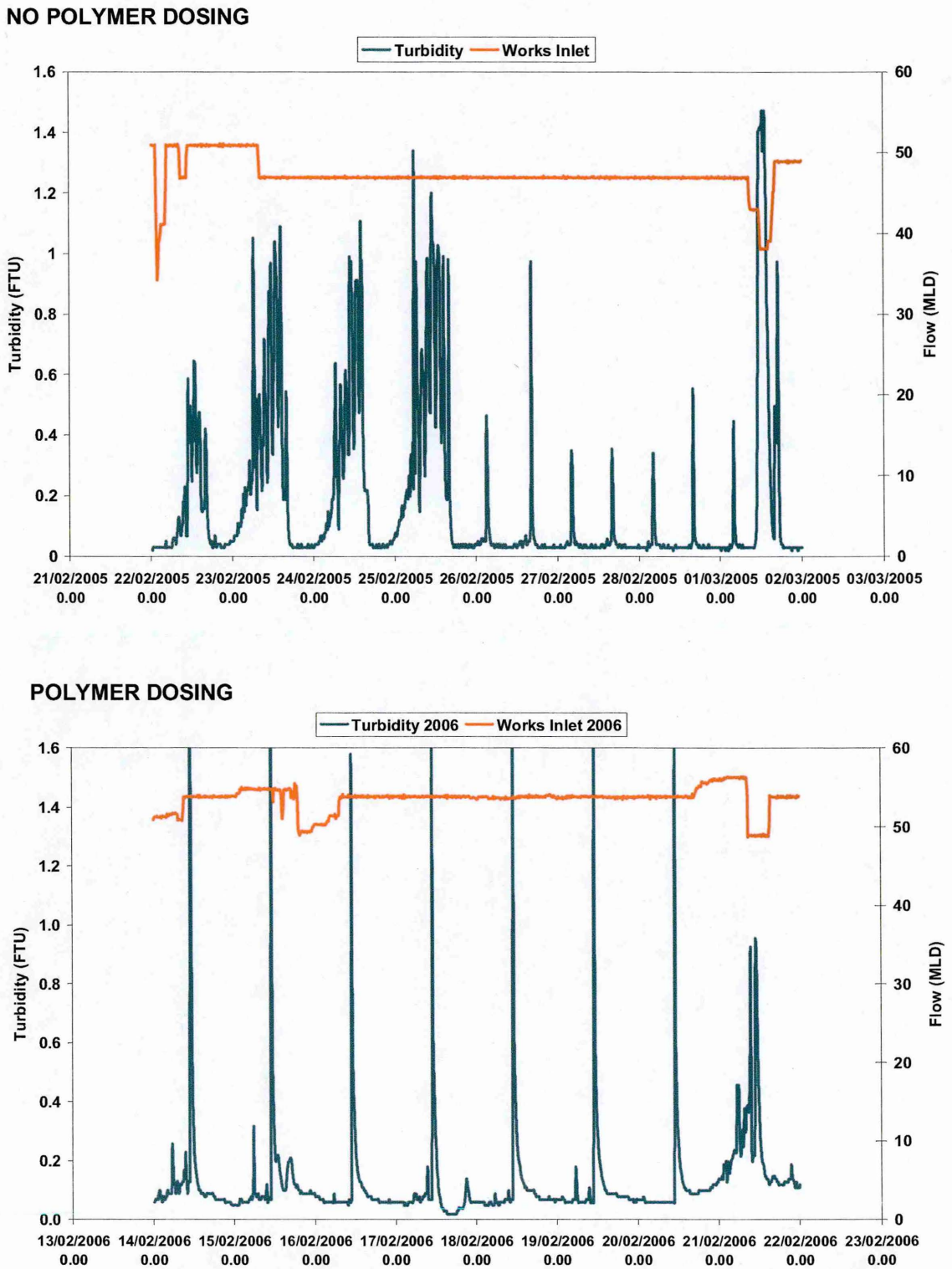


Figure 5.5 – Albert WTWs inlet flow and turbidity in February 2005, when no polymer was dosed, and February 2006, when polymer was dosed

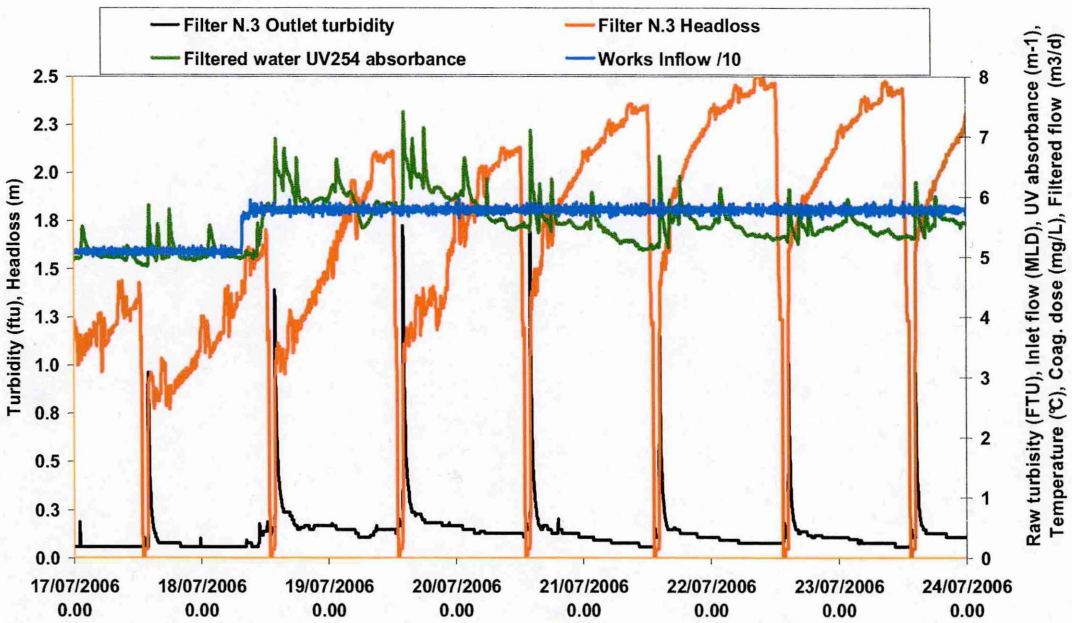


Figure 5.6 – RSF performance at Albert WTWs during summer polymer dosing trials

Table 5.3: Albert WTWs on-site data during polymer trials (summer 2006)

Date (2006)	Works Inflow (MLD)	Combined filtered UV absorbance (m^{-1})	Combined Filtered Turbidity (FTU)	Coagulant Dose (mg/L Fe) to Raw UV (abs/m) Ratio	Polymer Y/N
12th July	49.9	4.8	0.07	0.21	N
19th July	56.8	6.1	0.18	0.21	N
22nd July	56.8	5.5	0.12	0.21	Y
3rd August	34.5	4.8	0.05	0.22	Y
18th August	38.0	5.9	0.08	0.19	Y

5.1.5. Summary of on-site data analysis

Data from two WTWs in Yorkshire, UK, shown in the data chart in Appendix A, were analysed in order to highlight the effect of seasonal variations and site conditions on sand filter performance. The combined effect of the on-site variables were considered, as it was not possible to isolate the effect of individual variables on RSF performance. Polymer as filter aid was dosed mainly during winter and its effect on RSF performance was also analysed.

- Analysis of seasonal variation of on-site data at Fixby WTWs (section 5.1.2.1) showed direct dependence between UV_{254} and coagulant dose and higher and more variable inlet turbidity in winter. Both at Albert and at Fixby WTWs the raw water temperature was the highest in summer and more variable in spring and autumn than in winter and summer. Inlet flow to the WTWs was lower and more constant at Fixby WTWs, where about 24 MLD of raw water entered the works and higher and more variable at Albert WTWs, with about between 45 and 55 MLD treated.
- A comparison of RSF performance for Albert and Fixby WTWs showed lower outlet turbidity in spring and summer than in winter and autumn, when turbidity breakthrough occurred sometimes (section 5.1.3). RSF headloss followed a similar growing trend in each season at Fixby WTWs, while headloss was lower during summer than during winter, spring and autumn at Albert WTWs.
- Polymer dosing as filter aid improved particles removal by sand filtration during winter, resulting in lower filtered turbidity and UV_{254}. Summer trials showed that polymer dosing did not have a significant effect on the filtered water UV_{254} at plant flow of less than 50 MLD at ambient raw water quality (section 5.1.4).
- Increase inlet turbidity and inlet flow contributed to increasing headloss and increasing outlet turbidity in all of the season. This was evident also looking at some intervals in data charts in Appendix A, that show RSF performance and on-site data parameters during 2006 (Figure 5.7). On-site data registered in 2006 at Fixby and Albert WTWs showed higher RSF outlet turbidity values on average in winter than in summer

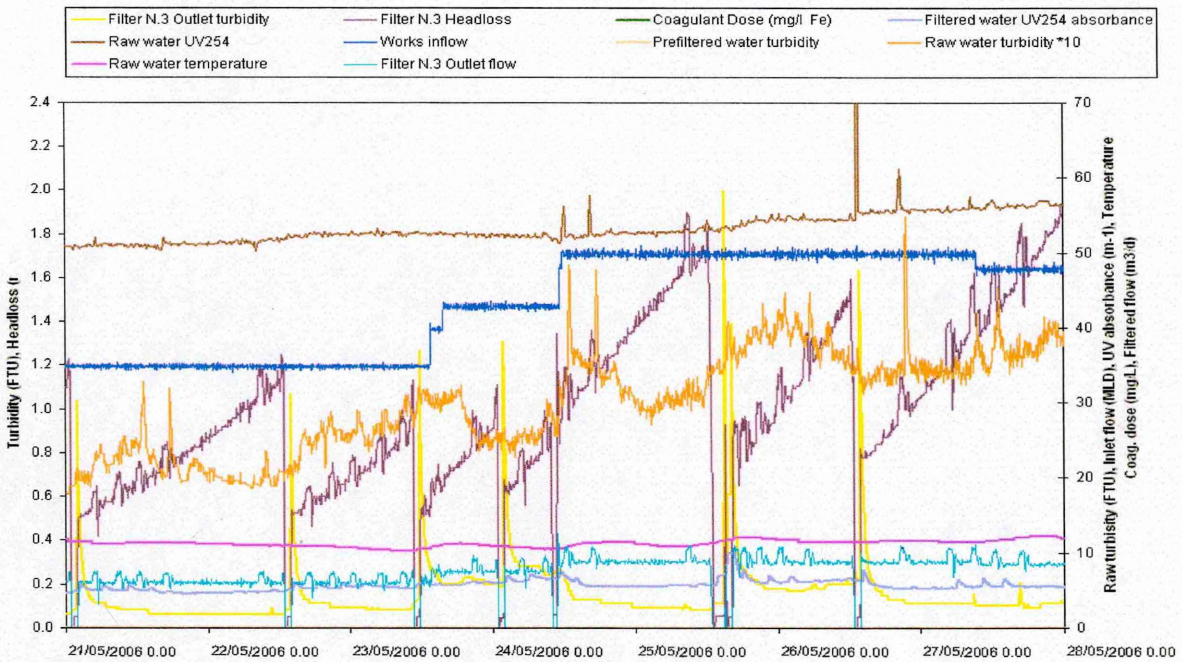


Figure 5.7 – Effect of increasing raw water turbidity and inlet flow on RSF performance at Fixby WTWs

5.2. Water Characterisation

5.2.1. Introduction

The aim of the characterisation stage was to investigate the composition and properties of raw, clarified and filtered water from Albert WTWs from different periods of the year and relate the outputs to the performance of the water treatment plant and to laboratory scale findings. The results of particle sizing measurements for the samples collected at Albert WTWs in February, April, July and September have been described first, followed by the measurement of pH, turbidity, UV_{254} and zeta potential. Results of the DOC measurements for the fractions, obtained through the ion exchange procedure described in section 4.1.2, and of the HPSEC measurements are finally shown and discussed.

5.2.2. Particle sizing

Particles dispersed in raw water were included in a range between 0.1 and 1000 µm in the February sample, 2 and 1000 µm in the April sample, 0.1 and 800 µm in the July sample and 1 and 100 µm in the September sample (Figure 5.8). The distribution was

narrower in the September raw water. The median size (D_{50}) before floc growth on the jar tester was higher in the February and April than in the July and September raw water: D_{50} without settling was 42.3 µm in April, 29.2 µm in February and only 15.2 and 16.9 µm in July and September respectively. Settling did not significantly affect particle size, as D_{50} before and after settling are very similar in raw and clarified water in all the samples. Samples after settling were indicated as *residual* (Figure 5.8).

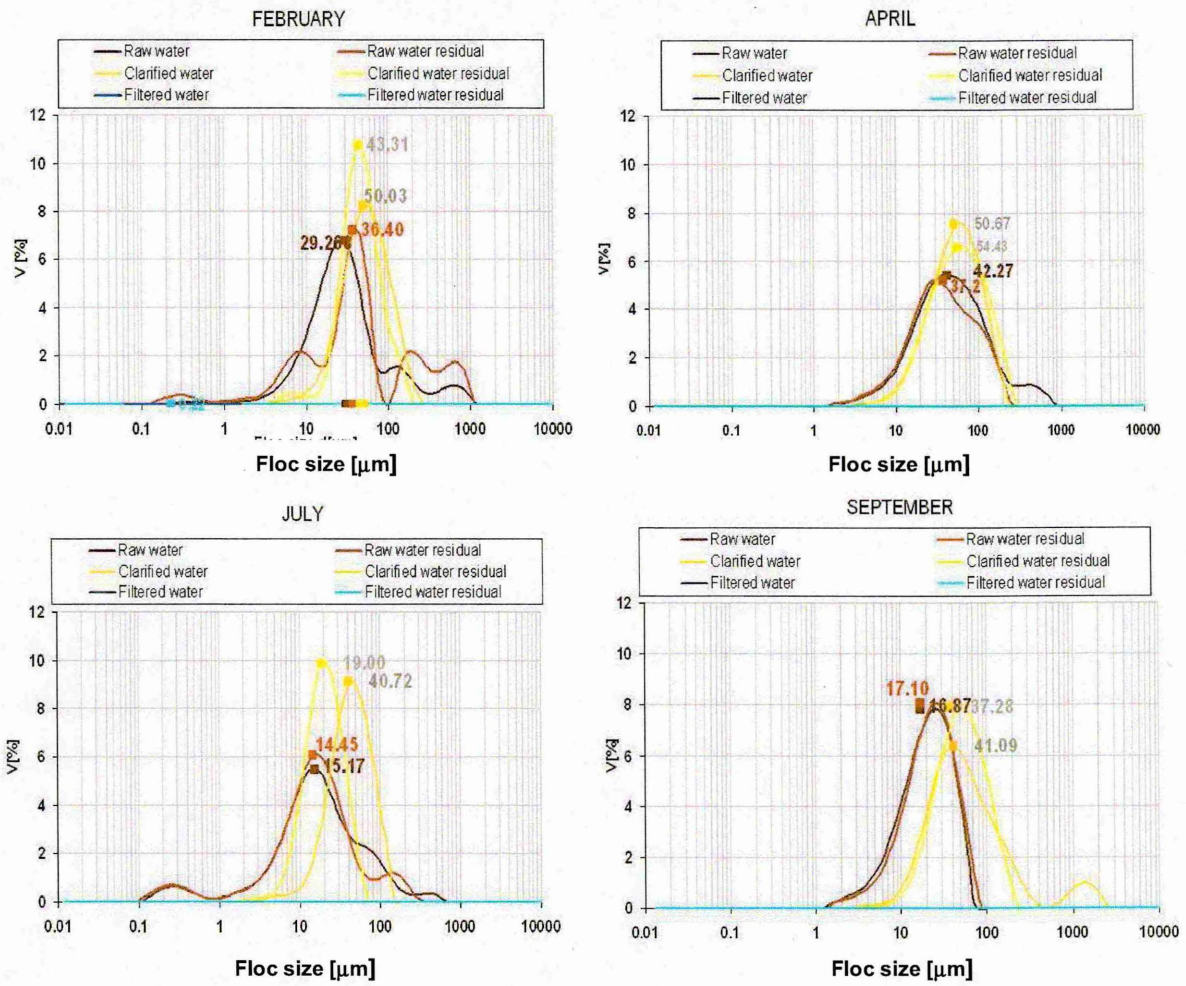


Figure 5.8 – Initial particle size distribution before and after settling in water samples collected at Albert WTWs in different periods of 2007, measured with Mastersizer 2000

Looking at the size distribution there was no significant difference in the initial distribution before and after settling for Albert raw water in all the samples studied. Clarified water particle had a narrower particle distribution than raw water particles, being approximately between 5 and 200 µm in all the clarified water samples. The median size before growth was slightly higher in the February and April samples

(50.0 and 50.7 µm) than in the July and Sept. samples (41.7 and 41.1 µm). Particle concentration in filtered water was very low and did not give a sufficient obscuration of the instrument cell to obtain a reliable measurement.

When put on the jar tester and slowly stirred for 15 minutes, the clarified water samples showed considerable particle growth even when no polymer was dosed, with the D_{50} reaching 240 µm in both the February and April samples (Figure 5.9)..

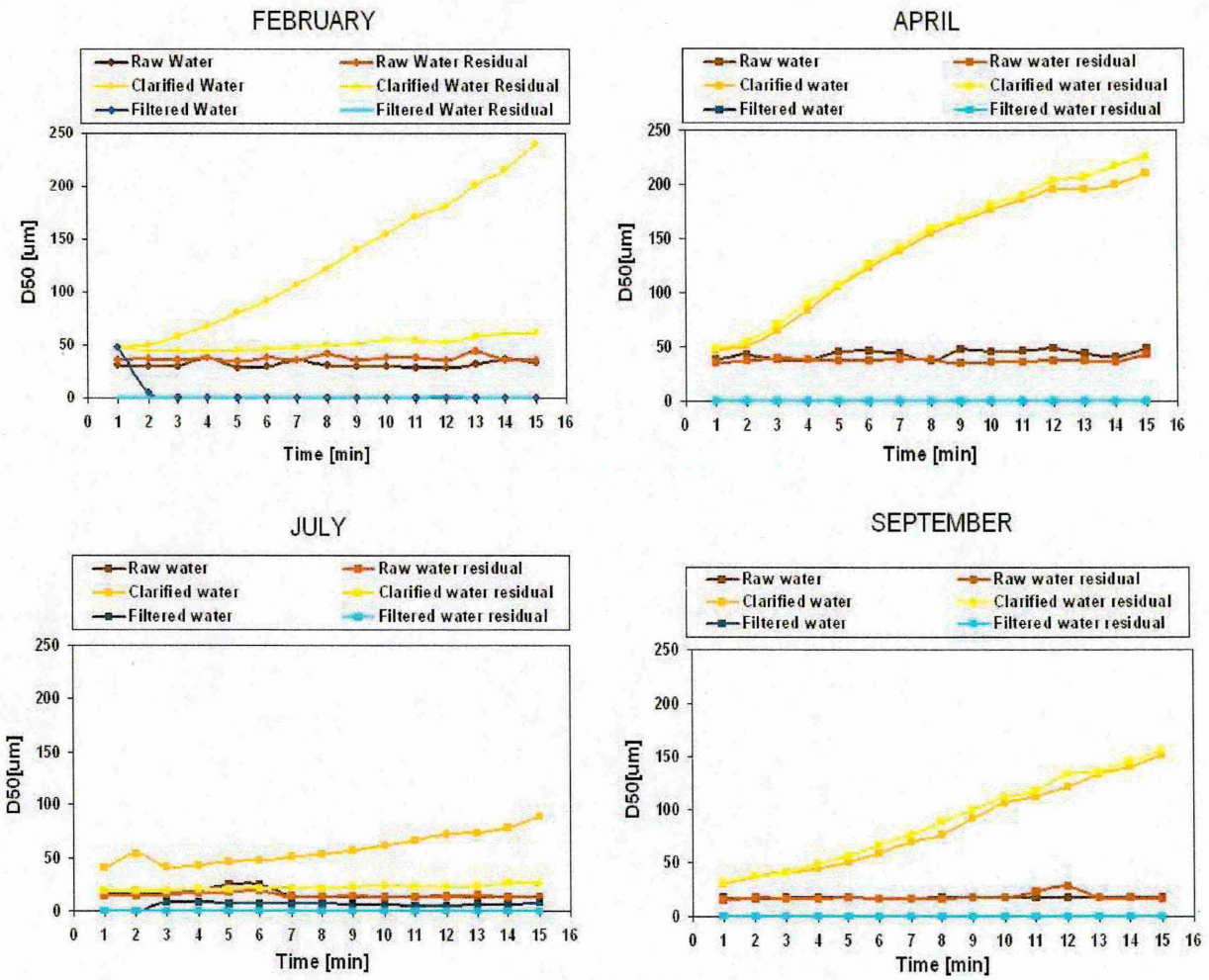


Figure 5.9 – Particle growth with jar tester experiments in water samples collected at Albert WTWs in different periods of 2007

Clarified water was collected on-site after coagulation, flocculation and DAF (section 4.2). The growing capacity of the particles in the clarified water was due to the residual ferric sulphate dosed during the coagulation phase and left in the water after DAF. Clarified water particle growth was the lowest for the September and July

samples, when particles reached less than 100 and 160 μm respectively. Particles remaining in the water after settling (*residual*) did not grow during the slow stir phase for the February and July clarified water samples, while they had the same growing trend as seen before settling for the April and September samples. The diameter of the particles in the raw water samples stayed constant during the slow stir phase. Laser diffraction measured almost no particles in the filtered water samples, because they were either too small or too few in concentration

5.2.3. Water properties

pH, turbidity, zeta potential and UV_{254} were measured on the four samples collected during the different seasons. The aim was to identify properties of Albert WTWs raw, clarified and filtered water, and to relate the outputs to laboratory scale findings and on-site data. Properties of the four samples were compared (Figure 5.10).

The **pH** value measured for the raw water varied from 5.0 in April to 6.6 in September. Clarified water collected after DAF had a lower pH, with values between 4.5 and 5.0. This was due to the acidification of the water by the addition of ferric sulphate, dosed before the DAF to an optimum pH for floc growth and removal of NOM. At Albert WTWs the pH was increased before sand filtration in order to enhance particle attachment to filter grains and to encourage precipitation of metals. This explains why the filtrate had a pH of between 6.0 and 6.5.

In the February sample **turbidity** decreased from 3.7 NTU in the raw water to 2.4 NTU in clarified water and 0.3 NTU in filtered water. In the April sample turbidity was 2.4 NTU higher in the clarified water than in the raw water, reaching 5.0 NTU. The raw water turbidity was 1.2 NTU lower than in the February sample. The turbidity in the July sample decreased from 3.7 NTU in the raw water to 1.0 NTU and 0.2 NTU in the clarified and filtered water respectively. Raw water turbidity was the same in the July and in the February samples and it was the highest in the September sample (4.5 NTU). The turbidity of clarified water varied the most during 2007. The April raw water turbidity was the lowest indicating good water quality. On-site data indicated also low raw water turbidity and UV_{254} absorption on the 17th of April 2007

(Appendix A): raw water UV_{254} was between 40 and 38 m^{-1}, and raw water turbidity was between 2.3 and 3.0 FTU. This was probably due to the dry weather water at Albert during April: the UK Met Office reports for East and North East of England a mean temperature of 10.5 °C in April 2007, over 5 °C higher than the average 1971-2000, 211.3 hours of sunshine and 10 mm of rain. The average data for the same month registered between 1971 and 2000 are 133.1 hours of sunshine and 51.0 mm of rain (*Met Office* web site). The turbidity of the filtered water samples collected in April at Albert WTWs was also the lowest.

Raw water had negative **zeta potential** values, and the values were very similar in the four samples: -15.8 mV in the February, -15.7 mV in the April; -16.20 mV in the July and -18.10 mV in the September sample. Negative zeta potential values were due to the presence in raw water of naturally oxidised organic structures (i.e. humic acids). The values measured for clarified water were less negative (-2.8, -8.3, -7.4, -7.1 mV in February, April, July and September respectively) because of ferric sulphate dosing. The metal has a positive charge that partially neutralizes the negative charge of the dissolved matter, reducing their repulsion and helping them to aggregate. Zeta potential for clarified water was the highest in the February sample, about 5 mV higher than in the samples collected in April, July and September. Zeta potential in the filtered water was more negative than in the clarified water, with values between -8.0 and -13.7 mV. This is due to the regulation of pH from about 4.5 to 6.5 carried out on-site before RSF: if alkali are added to the water suspension than the particles tend to acquire a more negative charge.

UV_{254} was measured for raw and filtered water: UV_{254} was reduced by coagulation from 44.6 to 3.3 m^{-1} in February, from 20.4 to 3.4 m^{-1} in April, from 49.0 to 13.0 m^{-1} in July and from 67.0 to 4.0 m^{-1} in September.

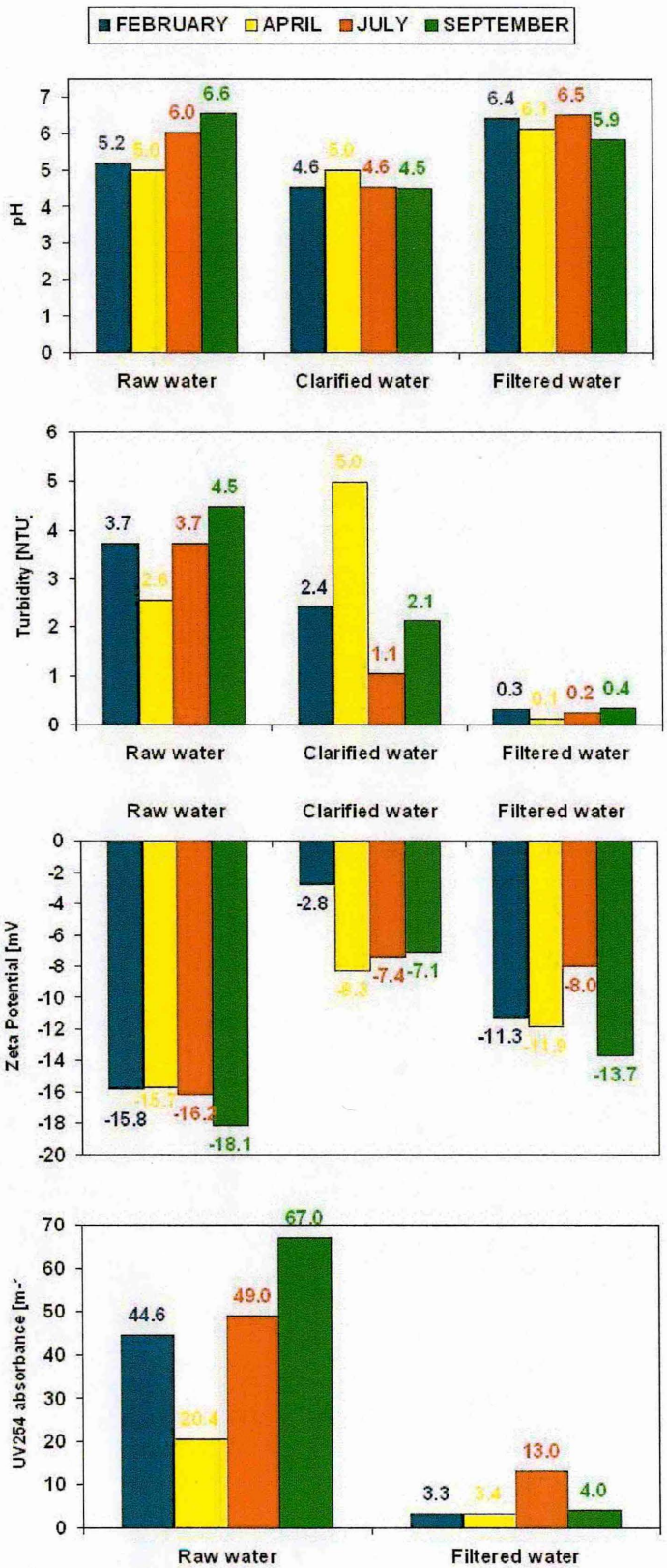


Figure 5.10 – Physical and chemical properties of water samples collected at Albert WTWs in different periods of 2007

5.2.3.1. NOM content

The DOC of the raw water was the highest in the sample collected in September, which reached 12.9 mg/L and the lowest in April (6.2 mg/L), as shown in Figure 5.11. The DOC measured in the raw water samples collected in February and July was 7.9 and 8.8 mg/L respectively. DOC decreased considerably in the clarified water and in the filtered water to between 2.7 and 1.6 mg/L.

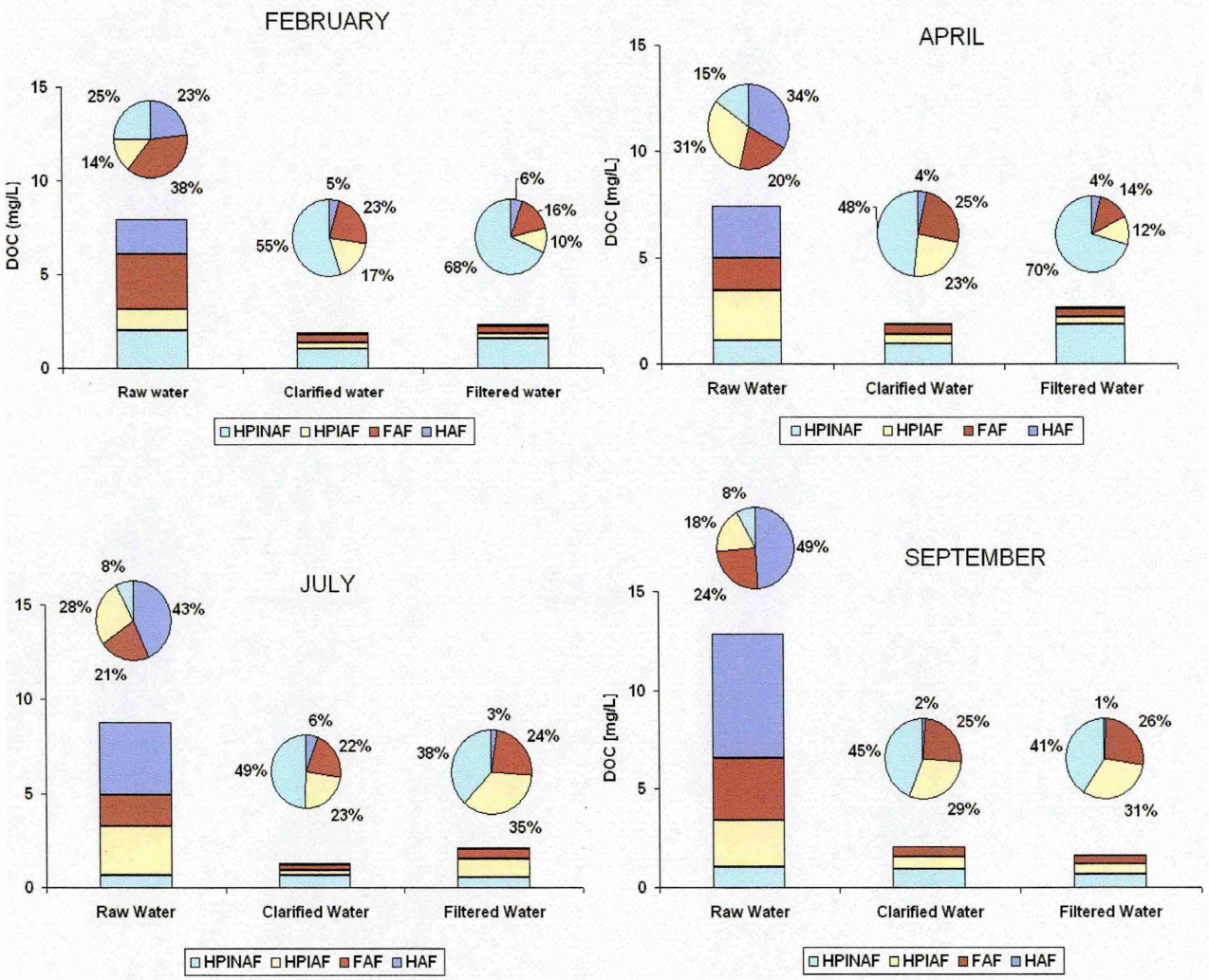


Figure 5.11 – Organic fractions, isolated by ion exchange fractionation technique, making up NOM in the samples collected at Albert WTWs

Looking at the composition of the samples in terms of their hydrophobicity, HAF and FAF made up more than the half of the whole NOM present in the raw water in all of

the samples (61% in February, 54% in April, 64% in July and 73% in September). In clarified water HIPOF percentage decreased to 27% in February, 29% in April, 28% in July and 27% in September. The main fraction in filtered water was HPINA, which was particularly high in April (1.7 mg/L): HPINA made up 68% of the filtered water NOM in February, 70% in April, 38% in July and 41% in September. The fractions best removed by the treatment in all the samples were HAF and FAF, with over 90% removal: total humic and fulvic acid content was below 0.6 mg/L in clarified and filtered water in all the samples. HPIA were also reduced by 50-60 %, while no significant variation occurred for the HPINA.

5.2.3.2. HPSEC results

HPSEC can provide information on molecular size distribution of the samples. Molecules of different sizes will elute (filter) through a stationary phase at different rates. The elution time (x axis) in HPSEC charts refers to molecules having different MW. Each peak represents a specific chemical compound or a mixture of compounds with the same rate of movement. The peak height is proportional to the material content. Similar experiments conducted on NOM revealed that peaks at 6.4 – 6.7 minutes, 7.6 – 7.8 minutes and 9.7 – 9.9 minutes refer to molecular weight bands of approximately > 5 kDA, 3-4 kDa and 0.5-1 KDa respectively (*Jefferson et al.,* 2004). Comparison of the HPSEC graphs for the four samples collected at Albert WTWs (Figure 5.12) indicated that raw water contained a much greater proportion of high MW molecules. Peaks at 6 minutes and between 8 and 9 minutes for the February, July and September raw water samples revealed that most of the molecules in the samples were heavier than 5 kDa and between 3 and 4 kDa. The highest peaks were measured for the September sample, indicating a higher concentration of molecules than in the other samples. April raw water HPSEC analysis showed only one peak at 9 minutes elution time, indicating a MW of about 1 kDa for most of the molecules in this sample. Clarified water in the April sample contained molecules of the same size of raw water, even if in much lower proportion. Clarified water collected in February, July and September and filtered water eluted at between 8 and 11 minutes, indicating the presence of molecules between 3 and 0.5 kDa. Comparing the raw water and the clarified and filtered water chromatograms, a higher absorbance occurred for raw

water, indicating that raw water contained a larger quantity of molecules than clarified and filtered water. Higher quantity of organic molecules in raw water than in clarified and filtered water was also shown by the higher DOC value measured (section 5.2.3.1).

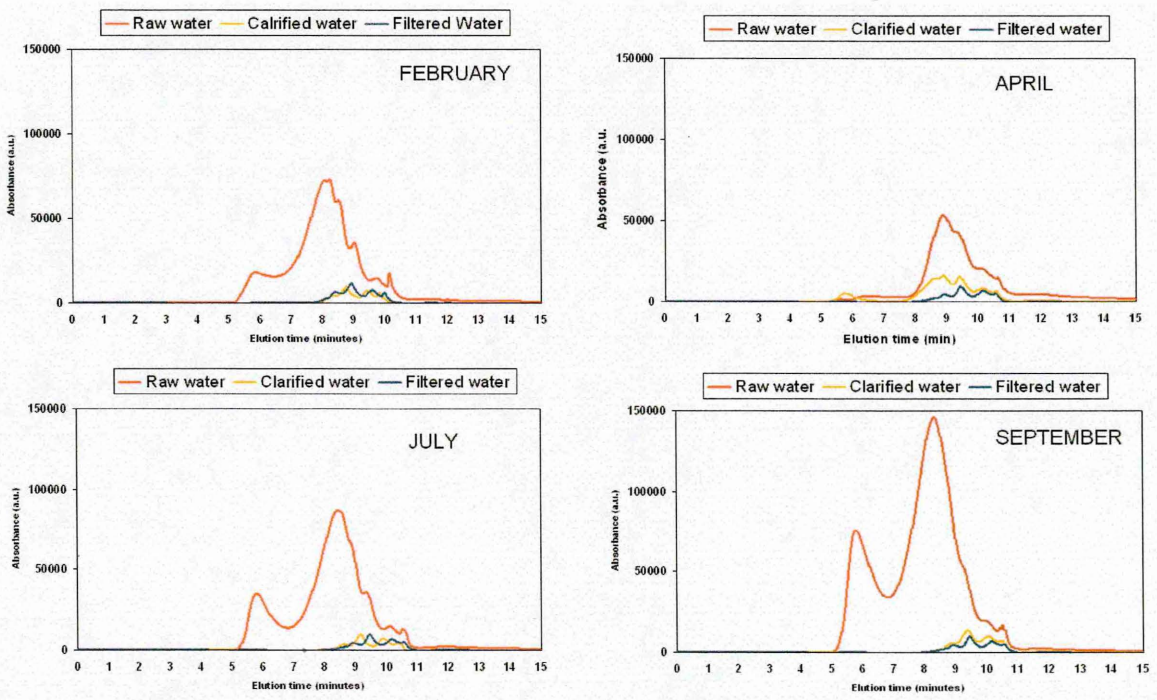


Figure 5.12 – Results of the HPSEC analysis performed on Albert samples

5.3. Effect of polymer dosing on floc properties

5.3.1. Introduction

Measurements of floc properties and chemical-physical characteristics were carried out on clarified water samples collected in February and September at polymer dose concentrations increasing from 0 to 0.03 mg/L, following the experimental procedures described in section 4.4. The same measurements were performed on the sample collected in April in order to investigate effect of temperatures from 5 to 30 °C. The purpose was to investigate to what extent polymer dosing and water temperature affected floc filterability.

5.3.2. Water properties

The physical and chemical properties of the February and September clarified water samples were measured after floc growth at different polymer doses (Table 5.4). The pH and zeta potential were not significantly affected by polymer dosing. Polymer dosing reduced turbidity in the February clarified water sample: turbidity decreased from 4.5 to 2.5 NTU when polymer was dosed from 0 to 0.03 mg/L. Turbidity was lower in September than in the February sample and was not significantly affected by polymer dosing.

Table 5.4 : Water properties at different polymer dose

Polymer dose [mg/L]		0	0.01	0.02	0.03
pH	FEB	4.3	4.5	4.9	4.4
	SEPT	4.4	4.8	4.5	4.6
Z potential [mV]	FEB	-6.0	-4.9	-5.2	-4.5
	SEPT	-7.1	-5.9	-6.1	-5.9
Turbidity [NTU]	FEB	4.5	3.2	2.5	2.5
	SEPT	2.1	1.8	2.4	1.8

To investigate the effect of polymer dosing on zeta potential, further measurements using the *Zetasizer 2000* were performed on the April clarified water with an increasing polymer concentration from 0.01 to 0.1 mg/L. The polyelectrolyte dosed was only slightly anionic with a charge density of 0.6 meq/g of DOC, therefore it did not alter significantly the floc surface charge as zeta potential stayed around -4.7 ± 1.8 mV (Figure 5.13).

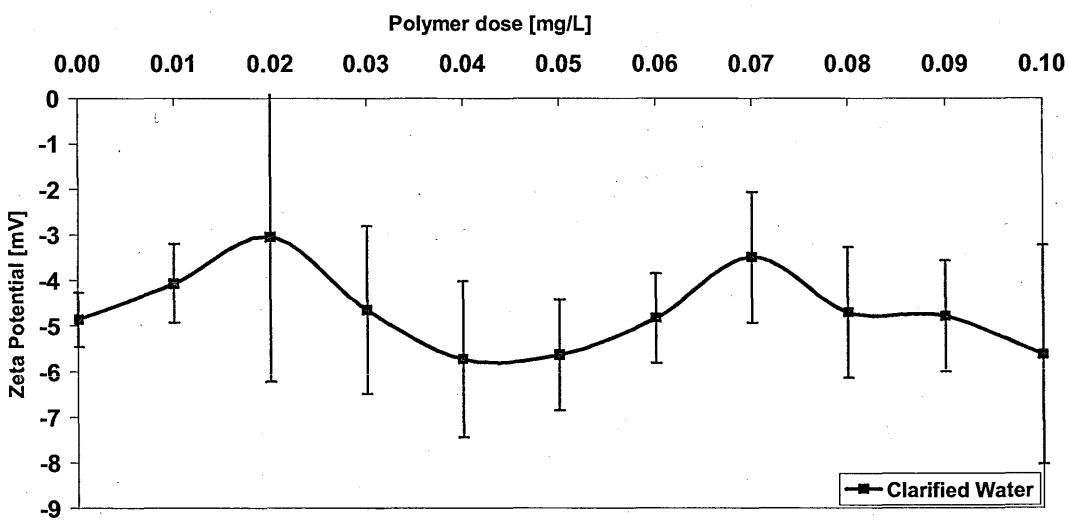


Figure 5.13 – Effect of polymer dosing on zeta potential

5.3.3. Particle size measurements

5.3.3.1. Floc growth

The flocs in the samples grew proportionally to the polymer concentration dosed, as shown by the slope of the curves in Figure 5.14. Floc growth rate over 15 minutes for the February sample at different polymer doses was (Table 5.5): 10.6 µm/min with no polymer, 12.8 µm/min with 0.01 mg/L of polymer, 14.5 µm/min with 0.02 mg/L and 16.2 µm/min with 0.03 mg/L. These data show that the growth gradient for the February sample increased by approximately 2 µm/min by adding 1 µg/L of polymer. The floc in the September sample had a lower growth rate, particularly when no polymer was dosed. The floc growth rate at different polymer doses with the September water was 7.6 µm/min with no polymer, 10.7 µm/min with 0.01 mg/L of polymer, 10.8 µm/min with 0.02 mg/L, 13.7 µm/min with 0.03 mg/L. D_{50} with no polymer dosing reached 226.7 ± 9.2 µm in the February clarified water and 171.0 ± 17.0 µm in the September clarified water. The standard deviation of the D_{50} for the 21 measurement carried out at each polymer dose was higher at higher polymer dose: the average standard deviation values measured at 0, 0.01, 0.02, 0.03 mg/L of polymer dose were 9.2, 12.3, 21.5, 34.3 µm respectively for the February sample and 13.4, 26.2, 21.2, 37.6 µm respectively for the September sample. Increasing standard deviation with increasing polymer dose indicated the random nature of polymer bridging between flocs.

The polymer dose effect was less important during the first 5 minutes compared to the last 5 minutes of floc growth. The floc grow rate during the first 5 minutes was: 13.2, 14.6, 16.7 and 17.0 µm/min at 0, 0.01, 0.02, 0.03 mg/L for the February sample and 7.1, 9.6, 9.6, 11.4 µm/min at 0, 0.01, 0.02, 0.03 mg/L for September sample. During the last 5 minutes the floc growth rate was very dependant on polymer dose: 6.9, 9.1, 10.1, 13.1 µm/min at 0, 0.01, 0.02, 0.03 mg/L for the February sample and 7.4, 11.2, 12.6, 15.1 µm/min at 0, 0.01, 0.02, 0.03 mg/L for the September sample. These data indicated that when no polymer was dosed flocs growth was much reduced at the end of the growth phase. When polymer was dosed flocs went on growing until the end of the growth phase, as a consequence of polymer bridging between flocs.

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Table 5.5 : Floc growth rate and average standard deviation at different polymer doses for the September and the February samples

		NO polymer	0.01 mg/L polymer	0.02 mg/L polymer	0.03 mg/L polymer
Total floc growth rate [µm/min]	February	10.6	12.8	14.5	16.2
	September	7.6	10.7	10.8	13.7
Floc growth rate min. 3-7 [µm/min]	February	13.2	14.6	16.7	17.0
	September	7.1	9.6	9.6q	11.4
Floc growth rate min. 12-17 [µm/min]	February	6.9	9.1	10.1	13.1
	September	7.4	11.2	12.6	15.1
Average standard deviation (± µm)	February	9.2	12.3	21.5	34.3
	September	13.4	26.2	21.2	37.6

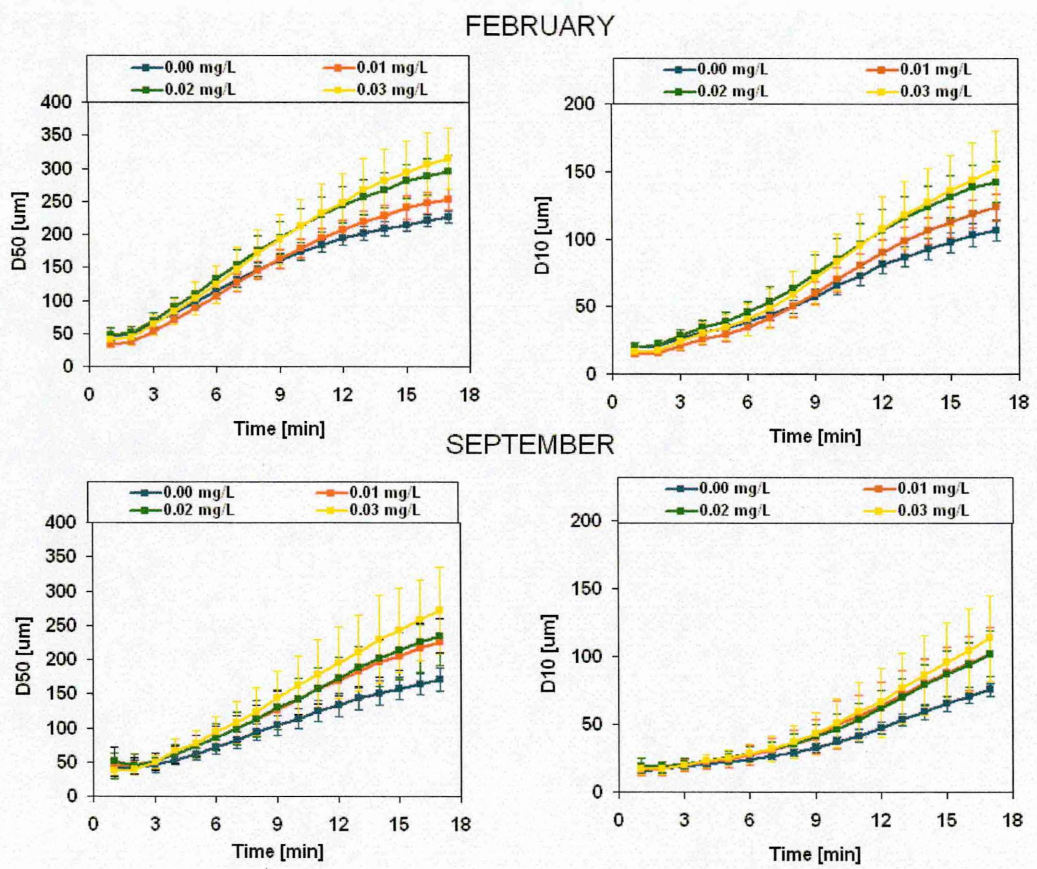


Figure 5.14 – Floc D_{50} and D_{10} growth in V% with increasing polymer dose (at 15 °C) with clarified water samples collected at Albert WTWs in February and September

Floc growth in terms of the D_{10}, which represents the value of the particle size distribution such that 10% of the total volume of particles has an equal or smaller diameter, gave us a better understanding of the smaller flocs in the system. As seen

for the D_{50}, floc growth was proportional to polymer dose and was higher in the February than in the September sample. This reflected the results of the particle size measurements on the February and the September sample, which also showed larger particles in the February sample. The D_{50} measured was 29.3 µm in the raw water and 50.0 µm in the clarified water in February sample, 16.9 µm in the raw water and 41.9 µm in the clarified water in September sample (section 5.2.2).

The particle size distribution measured with the *Mastersizer 2000* after 2 and 17 minutes during floc growth on the jar tester at different polymer doses were compared (Figure 5.15). This comparison showed how polymer dosing influenced particle size distribution after floc growth.

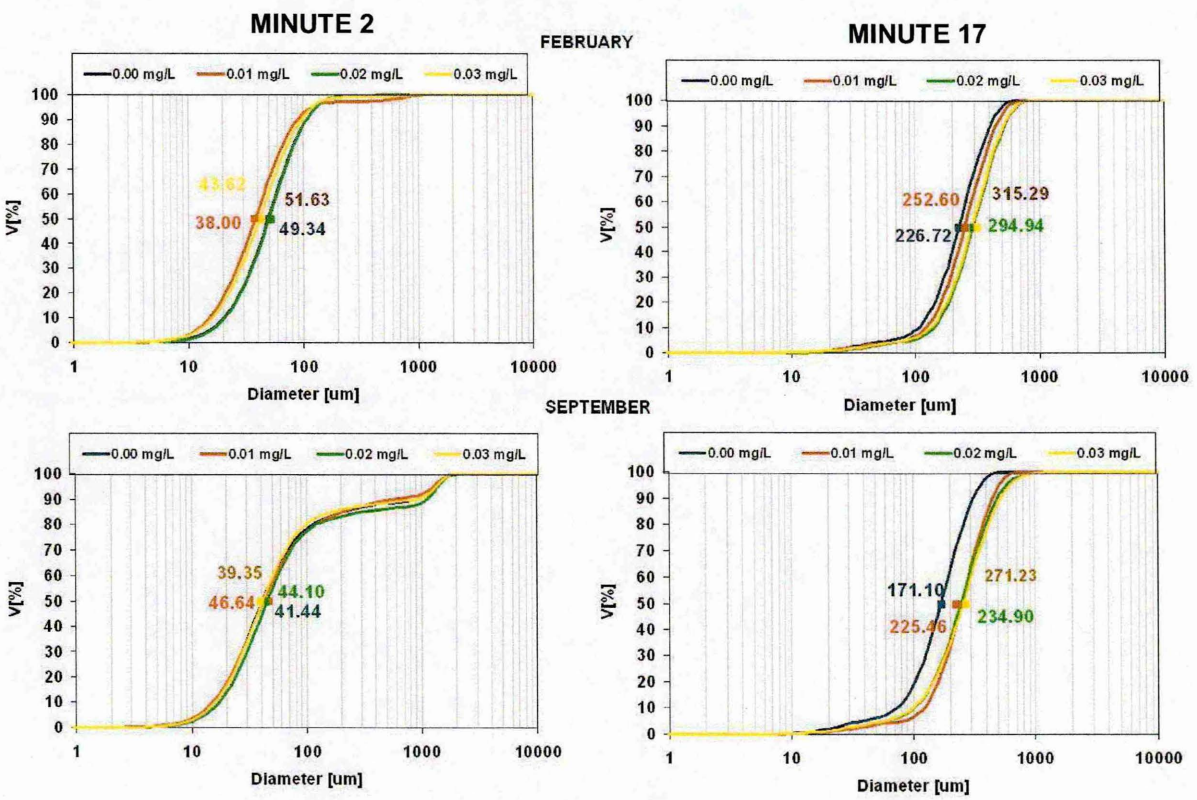


Figure 5. 15 – Cumulative distribution in V% with increasing polymer dose (at 15 °C) for Albert February and September samples

In both the February and September sample flocs were distributed within a narrower range after growth (minute 17) than at the beginning of the measurements (minute 2). The median floc sizes (D_{50}) shown in Figure 5.15 at minute 2 and minute 17 revealed

that 50% of flocs in the sample dosed with 0.03 mg/L of polymer were 60-70 μm higher than 50% of the floc in the sample containing no polymer. During floc growth in February sample D_{50} increased from 45.9 ± 3.9 μm to 226.7 ± 9.2 μm μm with no polymer dosing and from 43.2 ± 11.1 μm to 315.3 ± 46.5 μm with 0.03 mg/L of polymer; in the September sample floc grew from 41.2 ± 9.9 μm to 171.0 ± 17.0 μm with no polymer and from 39.4 ± 8.2 μm to 271.2 ± 63.0 μm dosing 0.03 mg/L of polymer.

After floc growth 80% of the particles were smaller than 360 μm and 257 μm for the lowest polymer dose, and smaller than 480 μm and 416 μm for the highest polymer dose in the February and September sample respectively.

5.3.3.2. Floc strength

Floc growth and breakage tests were plotted in terms of D_{50} and D_{10} (Figure 5.16 and Appendix B). Results showed a dual-stage response of floc to increased levels of shear rate. For high RPM a large decrease in floc size occurred during the first 2 minutes after exposure to higher RPM and during the remaining 13 minutes floc size was steady or slightly increasing. For low RPM (40 and 50) there was no characteristic jump in floc size, just a gradual decline. At 30 RPM the flocs continued to grow and the D_{50} reached 260.6 ± 9.3 μm, 301.9 ± 26.2 μm, 361.9 ± 34.5 μm, and 404.2 ± 22.2 μm with 0, 0.01, 0.02, 0.03 mg/L of polymer respectively with the February sample and 232.0 ± 23.5 μm, 325.5 ± 30.6 μm , 357.7 ± 12.3 μm, 410.8 ± 22.5 μm with the September sample. Flocs were larger after breakage at high shear rate (200 RPM) when dosing polymer: comparing lowest and the highest polymer dose used at the end of the breakage phase the D_{50} was 83.5 ± 16.8 μm and 136.6 ± 12.5 μm respectively with the February sample and 78.3 ± 5.1 μm and 139.4 ± 51.1 μm with the September sample, as shown in Figure 5.16. For mixing speeds up to 100 RPM the D_{50} rose on average 30-40 μm every μg/L of polymer used.

The standard deviation tended to increase together with polymer dose: for the February sample at the lowest polymer dose the standard deviation reached 9.9 μm during breakage at 30 RPM and 18.0 μm during breakage at 200 RPM, while at the highest polymer dose standard deviation reached 23.5 μm during breakage at 30 RPM

and 27.4 µm during breakage at 200 RPM. The same trend was seen with September sample with a highest standard deviation of 24.2 and 14.7 µm during breakage at 30 and 200 RPM respectively with no polymer dosing at and of 40.0 and 51.0 µm during breakage at 30 and 200 RPM respectively with 0.03 mg/L of polymer. Increasing standard deviation with increasing polymer dose was already seen during the floc growth measurement and indicated the random nature of polymer bridging between flocs.

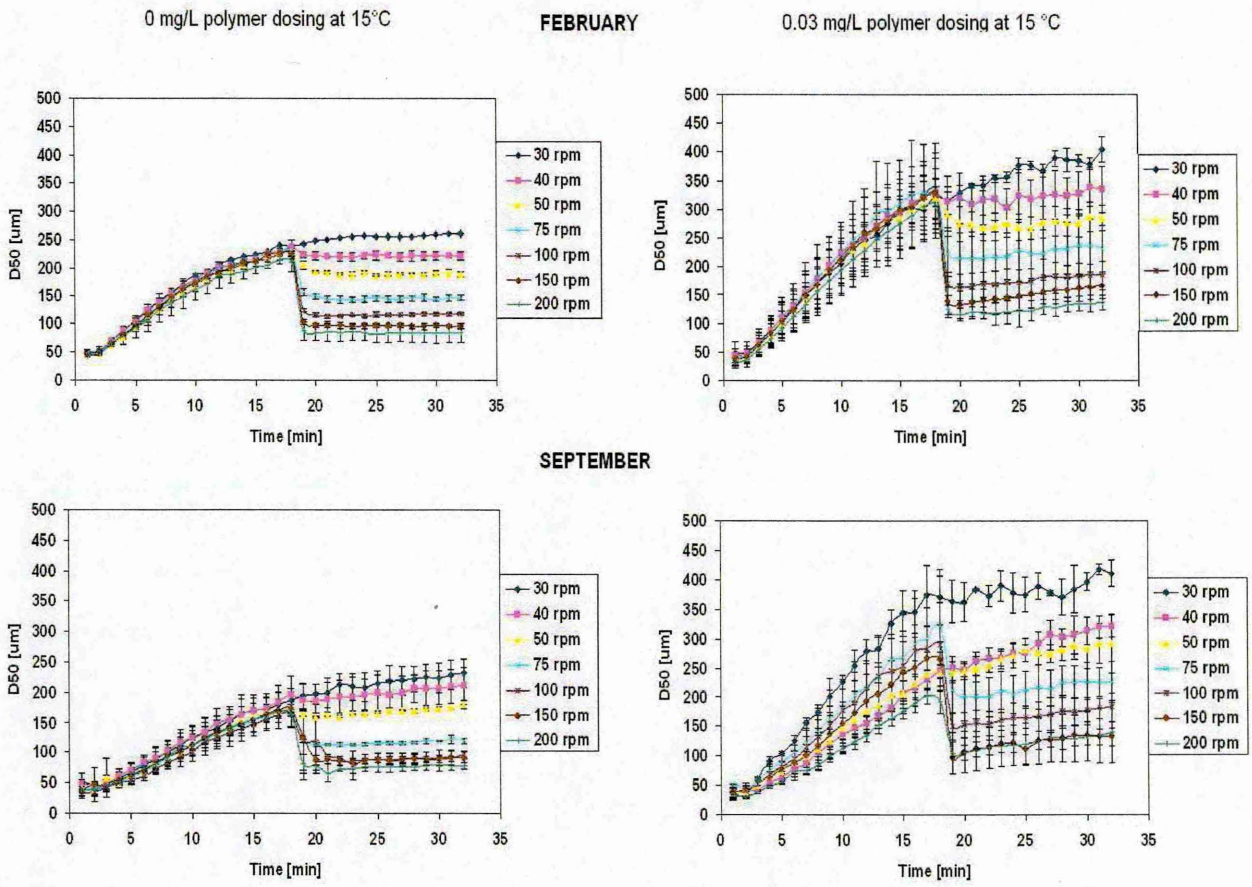


Figure 5.16 – Floc breakage for February and September clarified water temperature at increasing share dosing 0 and 0.03 mg/L of polymer

The floc breakage graphs for Albert clarified water (Figure 5.16) were compared with the breakage graph for raw water of the same reservoir coagulated using a dose of 8 mg/L of ferric sulphate ($Fe_2(SO_4)_3$) (Figure 5.17). Breakage was performed on the jar tester using the same procedure. In February and September clarified water flocs continued growing during the all 15 minutes slow stir, reaching a median value

between 150 and 250 µm when no polymer was dosed. In the coagulated raw water flocs grew during the first 5 minutes, reaching a D_{50} of about 700 µm, and stayed constant around this value for the following 15 minutes. When the breakage phase started, flocs formed in clarified water first brake down to less than 100 µm, but then started growing, even if very slowly, particularly when polymer was dosed (Figure 5.16). Flocs in the raw water decreased in size as a consequence of increasing shear rate. The decline was very pronounced during the first 2 minutes and was then more gradual.

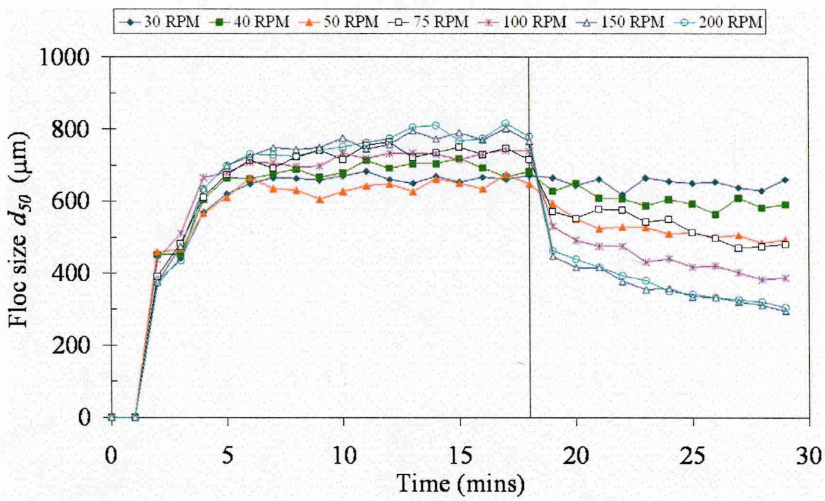


Figure 5.17 – Typical floc growth graph for NOM flocs formed using 8 mg/L as Fe coagulant (*Jarvis et al., 2008*)

After 10 minutes exposure to the shear the floc size was steady and reduced proportionally to the mixing speed used (Figure 5.17). The rate at which a floc suspension decays on exposure to shear is indicative of the strength of the flocs (*Jarvis et al., 2006)*. The size of the steady-state floc is governed by the prevailing shear condition within the containing vessel. A characteristic strength-size relationship was seen when plotting the gradients of the lines interpolating the D_{50} and the D_{10} at the end of breakage phase as a function of the mixing speed on a log-log scale (Figure 5.18 and Table 5.6). Dosing 0.01 mg/L caused a slightly lower breakage gradient with the February sample (-0.48 µm/RPM) than with the September sample (-0.67 µm/RPM), indicating slightly stronger floc at 0.01 mg/L of polymer in February than in September.

The breakage gradient measured for both the February and the September sample was -0.62 µm/RPM, floc had the same breakage behaviour with no polymer dosing in the February and in the September clarified water (Table 5.6). The breakage gradient, dosing 0.03 mg/L of polymer, was -0.62 µm/RPM in the September, and -0.56 µm/RPM in the February sample, therefore flocs broke more easily in the September than in the February sample when dosing high polymer concentrations. This was due to the higher NOM content in the September sample (section 5.2.3.1.): the higher concentration of organic molecules in the floc might have weakened the polymeric bridges (section 3.2.4.). Polymer dosing slightly increased the strength of the median size floc in the February sample by reducing the breakage gradient for the D_{50}. The same was not evident for smaller floc, as the breakage gradient of the D_{10} was the same for the February sample at the highest and the lowest polymer dose and only slightly lower for the September sample.

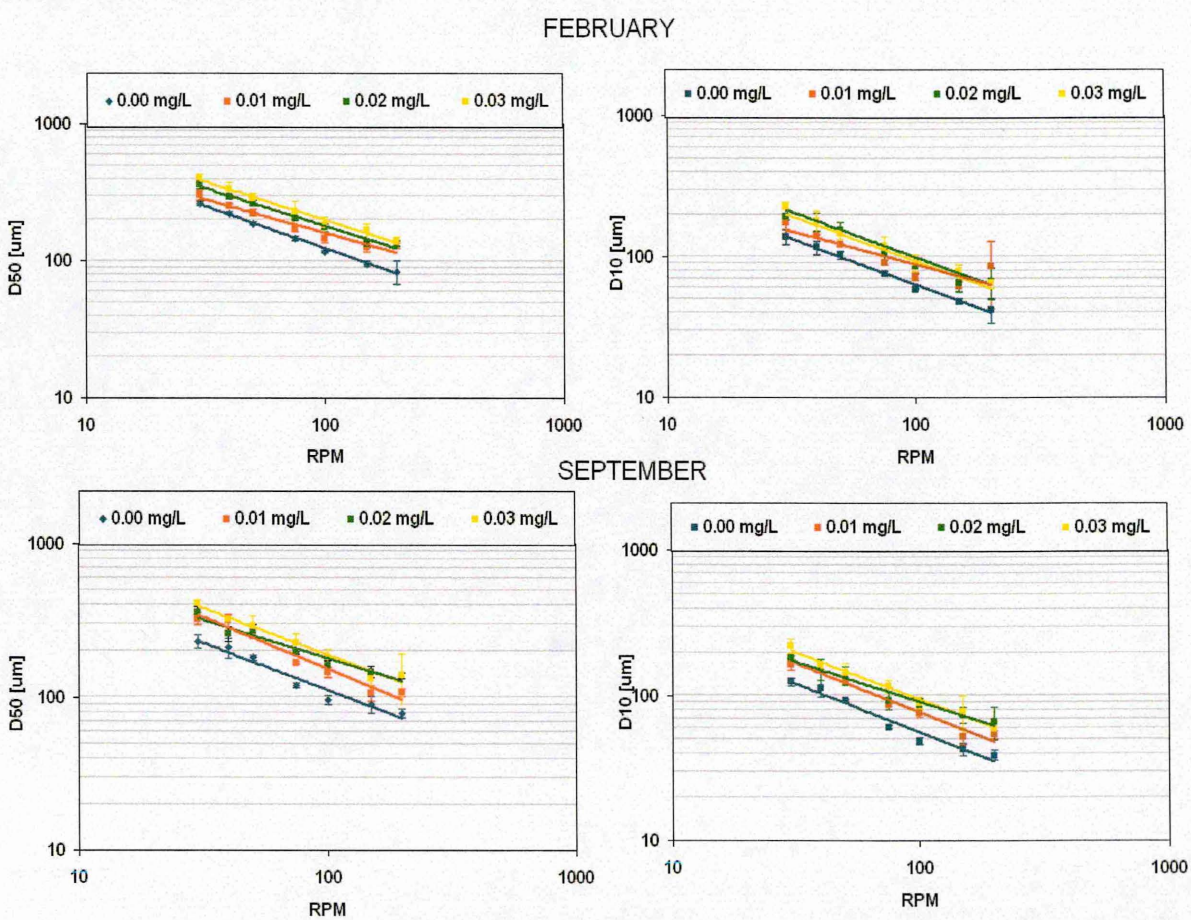


Figure 5.18 – D_{50} Vs share rate at increasing polymer dose and constant temperature (15 °C) in a log-log scale for Albert February and September samples

Table 5.6 : Breakage gradient for February and September sample at increasing polymer dose

		NO polymer	0.01 mg/L polymer	0.02 mg/L polymer	0.03 mg/L polymer 30 °C
D50 Breakage Gradient [µm/RPM]	February	- 0.62	- 0.48	- 0.55	- 0.56
	September	- 0.62	- 0.67	- 0.50	- 0.61
D10 Breakage Gradient [µm/RPM]	February	- 0.65	- 0.48	- 0.64	- 0.65
	September	- 0.69	- 0.68	- 0.55	- 0.65

5.3.3.3. Floc re-growth

The polymer concentration of 0.03 mg/L gave the best re-growth of the floc after breakage on the jar tester at 200 RPM. The worst re-growth occurred when no polymer was dosed (Figure 5.19). The re-growth rate was 6.8 and 5.2 µm/min with no polymer for the February and September samples respectively. The D_{50} before and after re-growth dosing no polymer was 85.1 ± 15.9 and 221.5 ± 16.6 µm for the February sample, and 81.1 ± 8.1 and 184.9 ± 7.3 µm for the September sample. The re-growth rate dosing 0.03 mg/L of polymer was: 13.6 µm/min for the February sample, with the floc D_{50} growing from 135.6 ± 10.9 to 408.5 ± 71.6 µm, and 14.5 µm/min for the September sample, with the flocs D_{50} growing from 133.3 ± 31.5 to 422.6 ± 45.1 µm (Table 5.7). Re-growth rates were similar at 0.01 and 0.02 mg/L of polymer dosing: 9.6 and 11.2 µm/min with 0.01 mg/L of polymer, 8.7 and 10.4 µm/min with 0.02 mg/L of polymer for the February and the September sample respectively. The re-growth rate for the September sample was up to 1.7 µm/min higher than for the February sample after polymer dosing but 1.6 µm/min lower with no polymer dosing.

The standard deviation during re-growth was higher for the measurement carried out when dosing 0.03 mg/L of polymer then when dosing less polymer concentrations. The highest standard deviation of the D_{50} was 45.1 µm for the September sample and 71.5 µm for the February sample and it was measured on the 20th minute of re-growth dosing 0.03 mg/L of polymer. The higher standard deviation at higher polymer doses

confirms the random nature of polymer bridging between flocs. already seen during floc growth and strength measurements.

Floc re-grew almost three times faster during the first 5 minutes: at 0, 0.01, 0.02 and 0.03 mg/L of polymer dosing floc re-growth rates for the February sample were 11.5, 17.0, 14.8 and 23.0 μm/min during the first 5 minutes and 4.7, 6.3, 5.5 and 8.2 μm/min during the remaining 15 minutes; for the September sample growth rates were 9.1, 18.2, 17.3 and 24.3 μm/min during the first 5 minutes and 3.3, 7.7, 6.6 and 9.9 μm/min during the remaining 15 minutes.

Table 5.7 : Floc re-growth rate and average standard deviation at different polymer doses for the September and the February samples

		NO polymer	**0.01 mg/L polymer**	**0.02 mg/L polymer**	**0.03 mg/L polymer**
Total floc re-growth rate [μm/min]	February	6.8	9.6	8.7	13.6
	September	5.2	11.2	10.4	14.5
Floc re-growth rate min. 3-7 [μm/min]	February	11.5	17.0	14.8	23.0
	September	9.1	18.2	17.3	24.3
Floc re-growth rate min. 17-22 [μm/min]	February	4.7	6.3	5.5	8.2
	September	3.3	7.7	6.6	9.9
Average standard deviation (± μm)	February	15.5	12.3	72.1	38.9
	September	5.2	31.0	33.2	62.1

Looking at floc re-growth in term of the D_{10}, the February and September samples had the same behaviour: the re-growth rate increased from 2.7 to 6.7 μm/min at 0.00 and 0.03 mg/L of polymer respectively. The standard deviation of the D_{10} re-growth measurement is again higher when dosing polymer

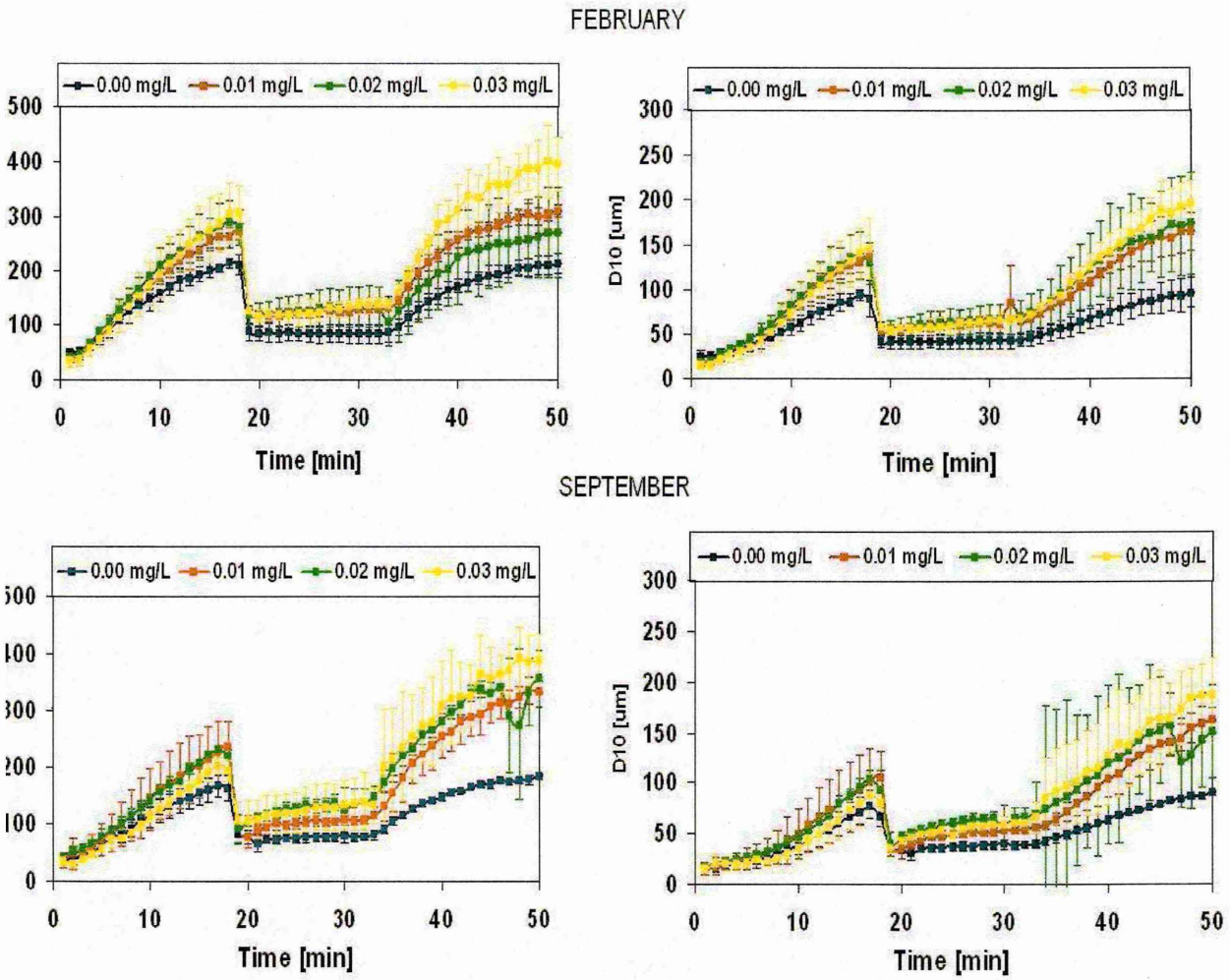


Figure 5.19 – Floc re-growth with increasing polymer doses (at 15 °C) for February and September clarified water samples collected at Albert WTWs

5.3.4. Summary of effect of polymer dosing on floc properties

Floc properties were measured on the water samples collected at Albert WTWs after DAF (clarified water) by performing a series of jar test dosing 0, 0.01, 0.02 and 0.03 of synthetic polyelectrolyte. The aim of the experiments was to identify the optimum polymer dose required for the formation of large and strong floc and to investigate the effect of polymer dosing on floc properties. The optimum dose was found to be 0.03 mg/L: dosing such polymer concentration, D_{50} after growth was 60-70 µm higher than when dosing no polymer in both the samples analysed. Sand filtration outlet turbidity will reduce when filtering larger and strong floc aggregates, more easily trapped by filter grains than small particles or aggregates that tend to break giving rise to

turbidity breakthrough (section 3.4.1.3). The results of floc growth, strength and re-growth measurements showed that polymer dosing enhanced floc growth and the formation of floc aggregates that were easily reformed after breakage. Polymer dosing produced slightly stronger flocs when treating water characterised by 7.9 mg/L DOC.

The main results of the laboratory experiments are:

- The pH and zeta potential were not significantly affected by polymer dosing.
- The flocs grew proportionally to the polymer concentration dosed.
- Polymer dosing slightly increased the strength of the median size floc in floc formed in during the treatment of low NOM raw water (February sample).
- The polymer concentration of 0.03 mg/L gave the best re-growth, while the worst re-growth occurred when no polymer was dosed.

5.4. Effect of temperature on floc properties

5.4.1. Introduction

Measurements of floc properties and chemical-physical characteristics were performed on the sample collected in April in order to investigate effect of temperatures from 5 to 30 °C. The purpose was to find out to what extent water temperature affected floc growth, strength and re-growth.

5.4.2. Water properties

Water properties were measured on the April clarified water sample after stirring the samples at 30 RPM for 15 minutes at constant temperatures of 5, 10, 20 and 30 °C, with and without polymer dosing (Table 5.8). The polymer dose used was 0.03 mg/L. Slow stirring at different temperatures did not have any clear effect on the properties of the samples. Polymer dosing did not significantly affect pH and zeta potential. Turbidity was lower when measured on the samples containing polymer. This can be explained by the ability of polymer to increase NOM removal. Turbidity was affected

by the temperature used during the slow stirring phase: lower turbidity values were measured at higher temperatures (Table 5.8).

Table 5.8: Water properties at different temperatures measured on the sample collected in April

Temperature		5 °C	10 °C	20 °C	30 °C
Polymer dose: 0.03 mg/L	pH	4.7	4.6	3.7	3.3
	Z potential [mV]	-7.7	-6.7	-4.3	-5.6
	Turbidity [NTU]	2.0	2.1	2.1	1.4
No polymer	pH	5.1	4.5	4.0	4.3
	Z potential [mV]	-9.0	-7.6	-7.1	-7.8
	Turbidity [NTU]	3.4	3.8	2.5	2.4

5.4.3. Particle size measurements

5.4.3.1. Floc growth

Measurements were performed at constant temperatures of 5, 10, 20 and 30 °C with the clarified water sample collected in April adding a constant polymer dose of 0.03 mg/L. Some obscuration problems on the measurement cell of the instrument arose during the tests at 5 °C due to condensation. This was solved by lowering the room temperature and stopping the measurement when condensation occurred. The standard deviation of the D_{50} measured was high indicating high variability of the median diameter of the flocs at the same temperature, reaching 60 µm at the end of floc growth. The error bars for the series in Figure 5.20 overlap each other and therefore there was no significant difference between floc sizes at different temperatures and a polymer dose of 0.03 mg/L. The results of floc growth measurements in term of D_{10} are not shown because of the high standard deviation.

Table 5.9 : D_{50} and standard deviation of the median particle diameter at different temperatures

		5 °C	10 °C	20 °C	30 °C
Minute 2	D_{50} [µm]	29.97 ± 6.09	25.35 ± 2.91	26.18 ± 6.73	31.24 ± 15.66
Minute 17	D_{50} [µm]	278.17 ± 61.59	302.94 ± 52.85	321.02 ± 52.84	288.61 ± 29.99

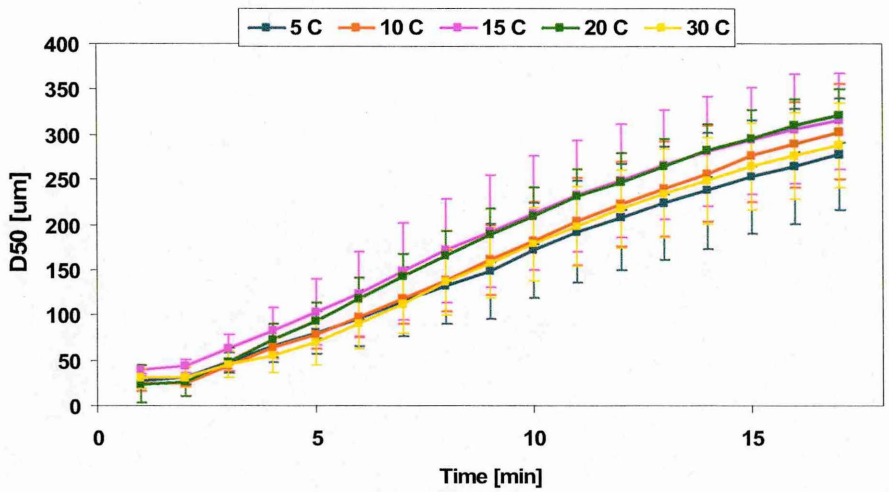


Figure 5. 20 – Floc growth in V% at increasing temperature (0.03 mg/L polymer)

The standard deviations of the median diameter for the cumulative distributions in V% at different temperature before and after floc growth (Figure 5.21) were almost a quarter of the total value (Table 5.9). Floc growth rate at different temperature was very similar: 14.7 µm/min at 5 °C, 16.3 µm/min at 10 °C, 16.2 µm/min at 15 °C, 17.5 µm/min at 20 °C and 15.0 µm/min at 30 °C.

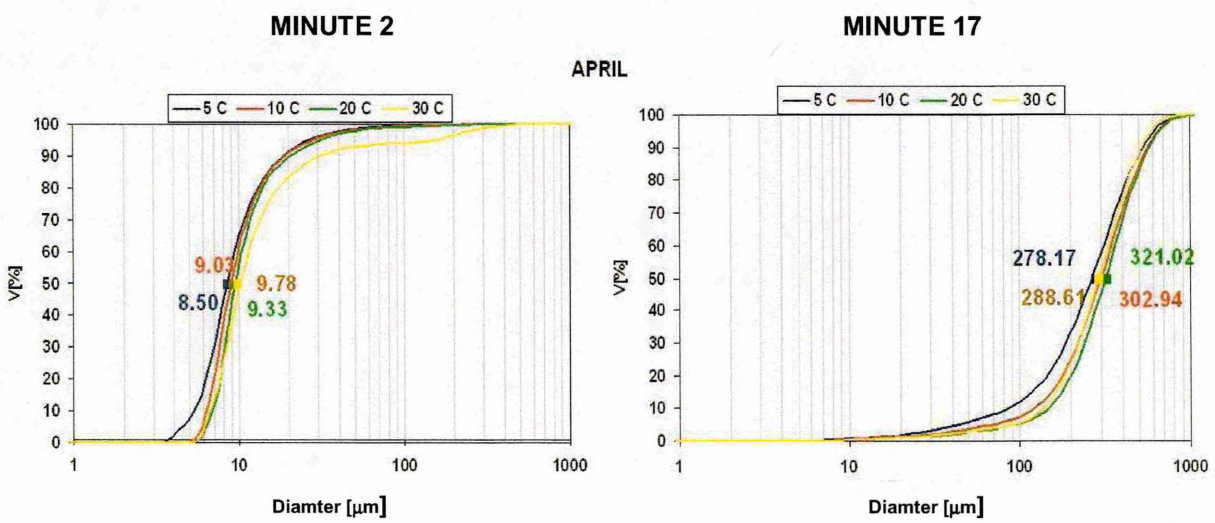


Figure 5.21 – Cumulative distribution in V% at increasing temperature (0.03 mg/L poly)

5.4.3.2. Floc strength

The breakage of the flocs under increasing shear rate at different temperatures is shown in Appendix B. Standard deviation values were high (± 60 µm) particularly during the breakage phase. This was due to some difficulties in carrying out long measurements at low and high temperatures, because of condensation and bubble formation on the measurement cell. At high temperatures, dissolved gases tended to form and bubbles escaped from the solution. The high variability in the results indicated that breakage at the same temperature was not repeatable and that temperature had no relevant effect on floc strength (Figure 5.22).

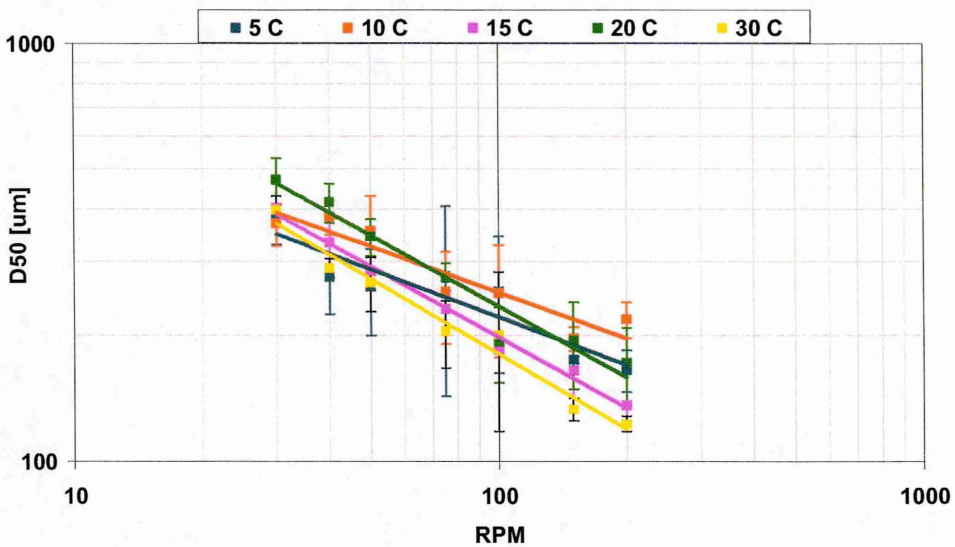


Figure 5.22 – D_{50} Vs. shear rate at increasing temperature with a constant polymer dose (0.03 mg/L) in a log-log scale for Albert April sample

5.4.3.3. Floc re-growth

The re-growth rates at different temperatures were quite similar (Figure 5.23). The values measured were 16.0 µm/min at 5 °C and 19.0 µm/min at 10 °C: flocs re-grew from a D_{50} of 150.2 ± 27.3 µm to 470.9 ± 56.0 µm at 5 °C, and from 240.8 ± 22.8 µm to 615.4 ± 67.5 µm at 10 °C. The re-growth rated measured at 20 °C and 30 °C were 14.5 µm/min and 12.0 µm/min respectively, with flocs re-growing from 185.5 ± 51.6 µm to 431.5 ± 47.5 µm at 20 °C and from 122.3 ± 8.3 µm to 366.5 ± 14.5 µm at 30 °C

(Table 5.10). Standard deviation values were quite high showing that the temperature had no effect on floc re-growth, as already seen on floc growth and strength.

Floc re-growth was faster during the first 5 minutes, particularly at low temperatures. The re-growth rate was 24.6, 41.3, 23.0, 29.9 and 26.7 µm/min during fist 5 minutes at 5, 10, 15, 20 and 30 °C respectively and 14.9, 10.8, 8.2, 4.8 and 5.8 µm/min during the remaining 15 minutes at 5, 10, 15, 20 and 30 °C.

5.10 : Floc re-growth at different temperatures and at a constant polymer dose of 0.03 mg/L

Temperature	5 °C	10 °C	15°C	20 °C	30 °C
Total floc re-growth rate [µm/min]	16.0	19.0	13.6	14.5	12.0
Floc re-growth rate min. 3-7 [µm/min]	24.6	41.3	23.0	29.9	26.7
Floc re-growth rate min. 17-22 [µm/min]	14.9	10.8	8.2	4.8	5.2
Floc size before regrowth [µm]	150.2 ± 27.3	240.8 ± 22.8	135.6 ± 10.9	185.5 ± 51.6	122.3 ± 8.3
Floc size after regrowth [µm]	470.9 ± 56.0	615.4 ± 67.5	408.5 ± 71.4	431.5 ± 47.5	366.5 ± 14.5

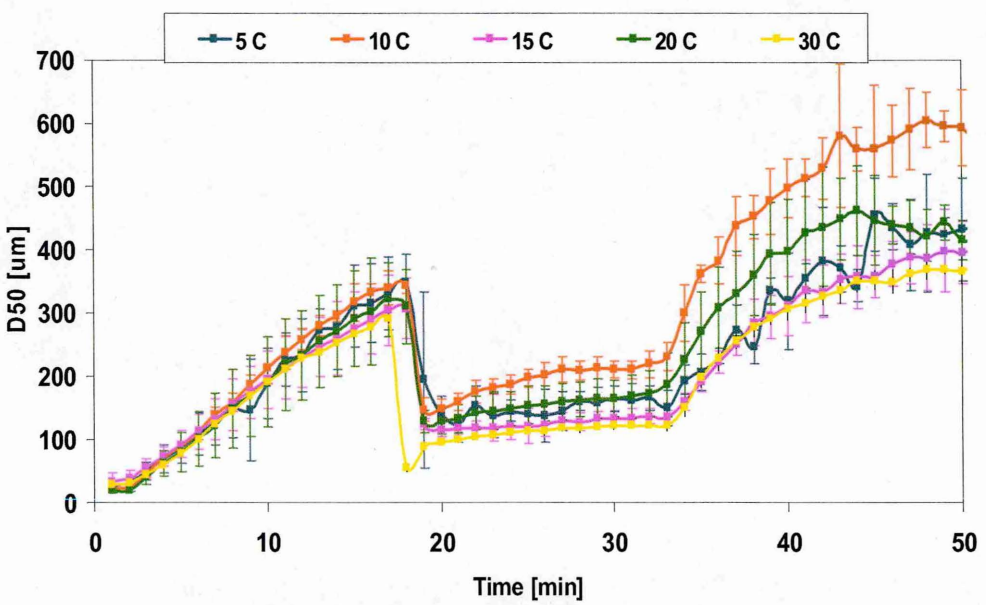


Figure 5.23 – Floc re-growth at increasing temperature (0.03 mg/L of polymer) for Albert WTWs clarified water sample collected in April 2006

5.4.4. Summary of effect of temperature on floc properties

Floc properties were measured at different temperatures on the sample collected in April, dosing 0.03 mg/L of polymer. Results were compared with floc properties measured on the sample collected in February at 15 °C and dosing the same polymer concentration. During floc growth, breakage and re-growth there was no significant difference between floc sizes at different temperatures.

5.5. Sand filtration experiments

5.5.1. Introduction

Sand filtration experiments were performed on the July and the September sample with the laboratory sand filter described in section 4.6, in order to evaluate the effect of polymer dosing on sand filtration performance. The same sand and filtration rate used at Albert WTWs were used during the tests, as the research study aimed to investigate the polymer dosing effect on floc filterability at Albert WTWs.

5.5.2. Results

Results showed that headloss build-up rate was proportional to polymer dose: headloss stayed constant when no polymer was dosed both in July for 3 h run and in September for two 3.5 h runs (Figure 5.24 and 5.25). When polymer was dosed headloss after one hour started to differentiate depending on polymer concentration. At the end of the run total headloss for the July sample reached almost 28.3 cm with 0.03 mg/L of polymer, 17.1 cm with 0.02 mg/L, 13.5 cm with 0.01 mg/L and stayed constant at about 8-9 cm when no polymer was dosed. The September sample had a similar behaviour: headloss increased from 20 cm to 59, 43 and 27 cm at 0.03, 0.02 and 0.01 mg/L of polymer respectively and stayed constant around 20 cm when no polymer was dosed. The headloss built up more quickly when polymer was dosed because the total load to the filters was higher and floc tended to clog the filter pores. Particularly, when 0.03 mg/L of polymer were dosed straining tended to occur (section 3.4.1.2.1).

Results in terms of outlet turbidity (Figure 5.24 and 5.25) were different for the July and the September samples.

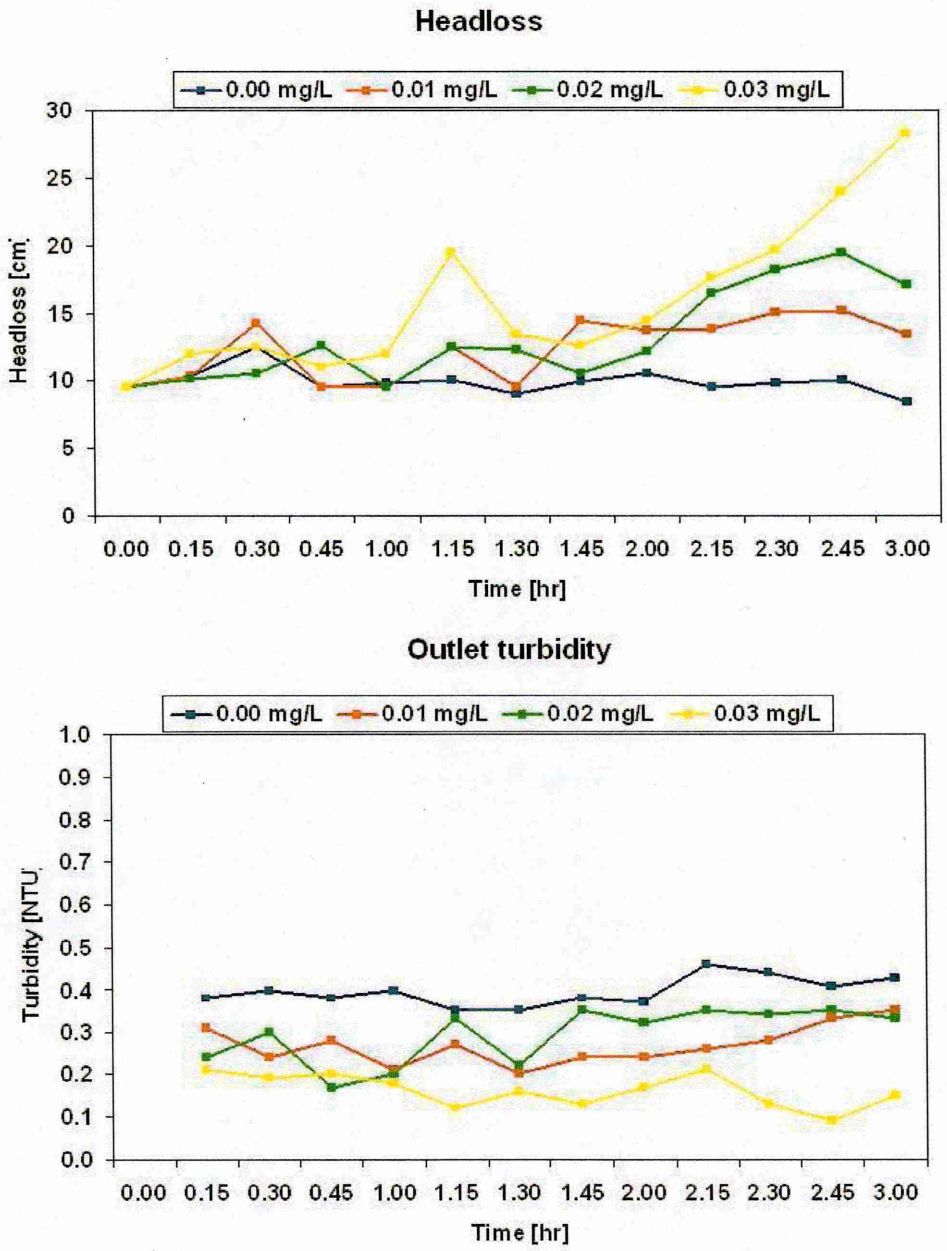


Figure 5.24 – Sand filtration experiments with the clarified water sample collected at Albert WTWs in July 2006

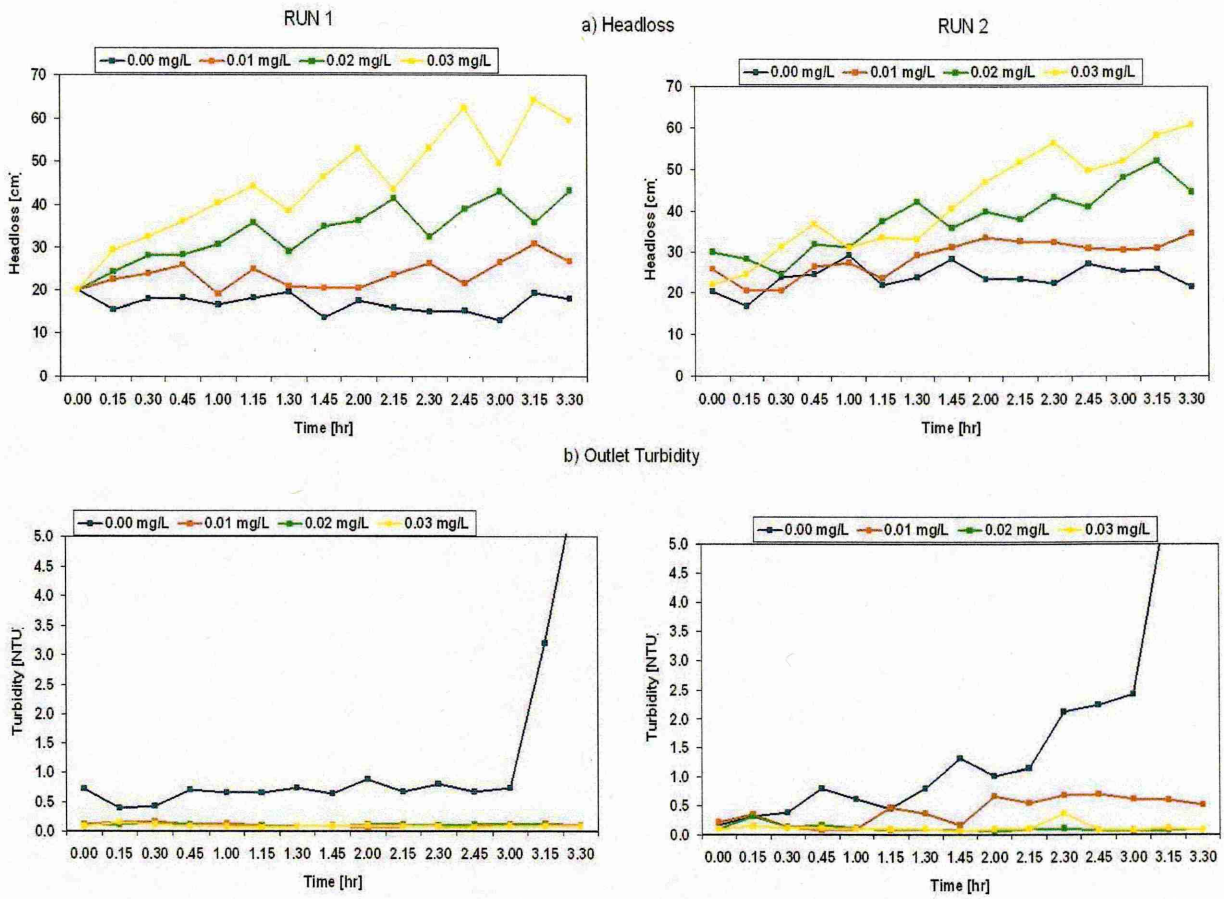


Figure 5.25 – Sand filtration experiments with the clarified water sample collected at Albert WTWs in September 2006

Outlet turbidity was higher for the September sample with breakthrough occurring after 3 h and 1.5 h with no polymer dosing during the first and second run respectively. In all the samples and runs outlet turbidity was the lowest with the highest polymer dose: with the July sample outlet turbidity was about 0.4 NTU with no polymer dosing, around 0.3 NTU with 0.01 and 0.02 mg/L of polymer and between 0.2 and 0.1 NTU with 0.03 mg/L of polymer. With the September sample outlet turbidity stayed generally around 0.1 NTU dosing 0.01, 0.02 and 0.03 mg/L of polymer during the first run. No breakthrough occurred when dosing 0.01 mg/L of polymer even after 8 hours run of filter. When no polymer was dosed outlet turbidity was about 0.6 NTU higher and breakthrough occurred after 3 hours, with outlet turbidity reaching 6.2 NTU. The second run gave higher outlet turbidity than the first run dosing 0.01 mg/L and no polymer: outlet turbidity reached 0.5 NTU after 1 hour.

While at 0.01 mg/L of polymer outlet turbidity stayed constant around this value for the two following hours, with no polymer dosing it rose up to 8.9 NTU after 3:30 hours. Outlet turbidity at 0.02 and 0.03 mg/L of polymer was around 0.1 NTU.

5.6. Particle count analysis

5.6.1. Introduction

For understanding sand filtration performance and polymer dosing effect it was important to determine the number of particles in the filtrate at different polymer concentrations and to evaluate the effect of polymer dosing on the total number of particle dispersed in the clarified water sample. The laser diffraction instrument *Mastersizer 2000* calculates the volume moment mean (or *De Broukere mean diameter*), expressed as:

$$D[4,3] = \frac{\sum d^4}{\sum d^3} \qquad \textbf{Eq. 5.1}$$

This formula indicates around which central point of the frequency the volume distribution would rotate (*Rawle, 2007*). The distribution in V% is based around this value. This method of calculation of the mean and distribution does not require knowledge of the particle count involved. Therefore the particle counter *Spectrex PC 2200* was used on the filtrate of sand filtration tests and on clarified water after floc growth in the jar tester at different polymer doses, as described in sections 4.4 and 4.3. Particle count was also carried out on the raw, clarified and filtered water samples collected at Albert WTWs in September.

5.6.2. Particle count analysis on filtrate

By solving the *Rajagopalan and Tien* model *(1976)* with inlet particle size diameters from 0.1 to 100 μm at the same operating conditions as the ones existing at Albert WTWs, it was found that particles that are more likely to pass trough the sand pores of the filters have a diameter between 0.1 and 10 μm (Figure 3.4). The model simulated what would happen in an ideal system characterised by filter grains all of

the same size (d_C = 0.8 mm) and constant porosity (ε = 0.40), temperature (T = 15 °C), filtration rate (v_F = 4 m/s), particles density (ρ_P = 1050 kg/m^3) and water density (ρ_W = 999 kg/m^3). In order to find if the size of the particles not retained by RSF was the same as predicted by *Rajagopalan and Tien* model *(1976)*, particle count analysis on the RSF outlet with September water was performed.. Comparing the total count per ml of sample after 15, 105, and 310 minutes during the first of the two runs (Figure 5.26), it was evident that after 15 minutes, filtrate with no polymer dosing had a total of 8000 particles more than filtrate with polymer dosing. The total count was almost 10000 particles/mL with no polymer dosing and less than 2000 particles/mL when dosing polymer, irrespective of the amount dosed. The number of particles in the filtrate after filtration for 105 and 310 minutes was compared: the total count/mL increased from 13200 to 92100 when filtering with no polymer dosing, decreased slightly from 2920 to 2230 when dosing 0.01 mg/L, from 990 to 970 when dosing 0.02 mg/L and from 1440 to 970 when dosing 0.03 mg/L. Results of the particle count analysis on RSF outlet correlated well with the outlet turbidity measurement (Figure 5.27). The size distribution analysis of the filtrate showed that most of these particles were smaller than 10 µm (Figure 5.28). After 3 hours turbidity breakthrough occurred with no polymer dosing and most of the particles that passed through the RSF after 310 min creating breakthrough were smaller than 5 µm.

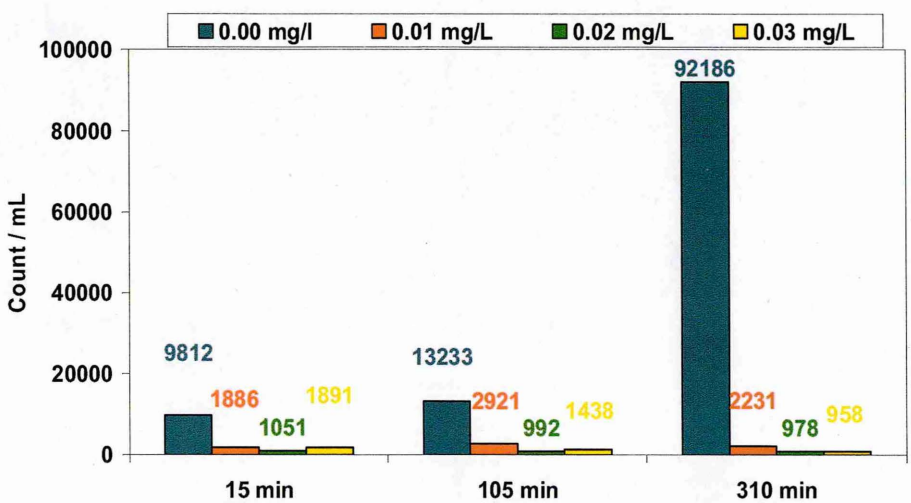


Figure 5. 26 - Total particle count for filtrate at different polymer doses after increasing filtration intervals

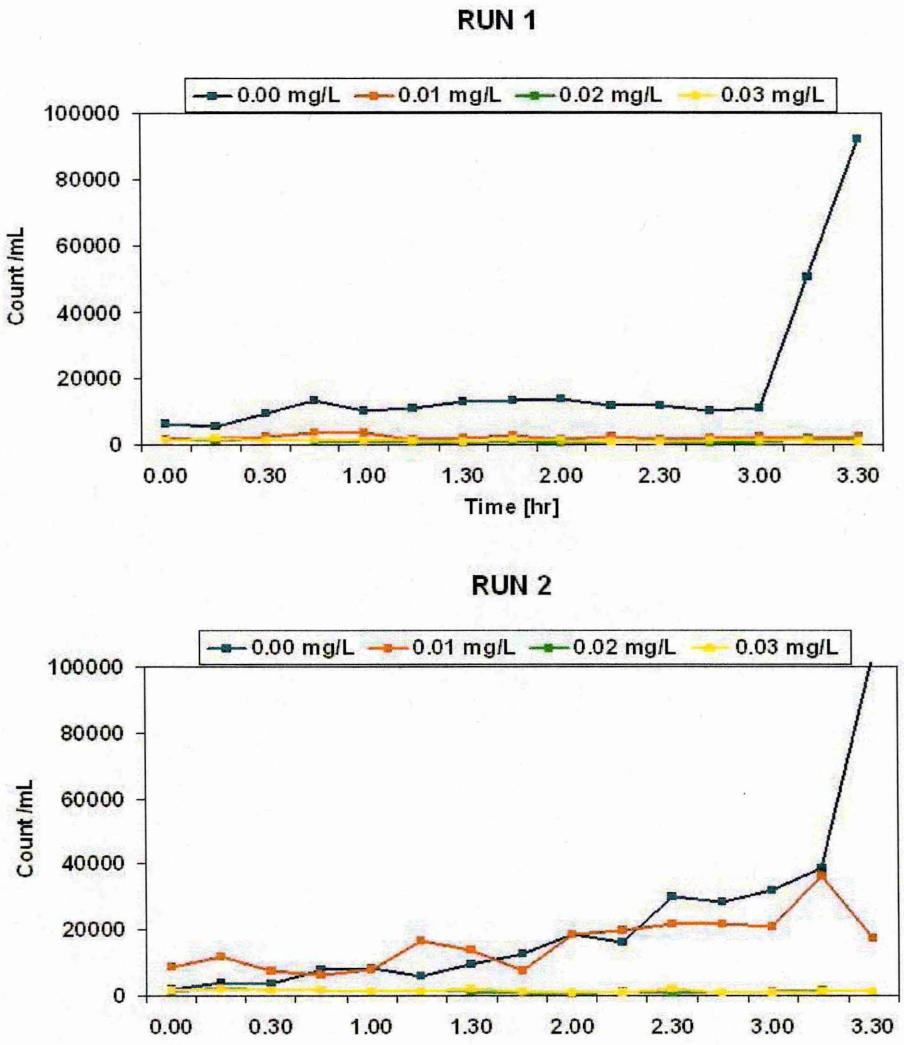


Figure 5.27 – Total particle count on the RSF outlet at different polymer doses with the sample collected at Albert WTWs in September 2006

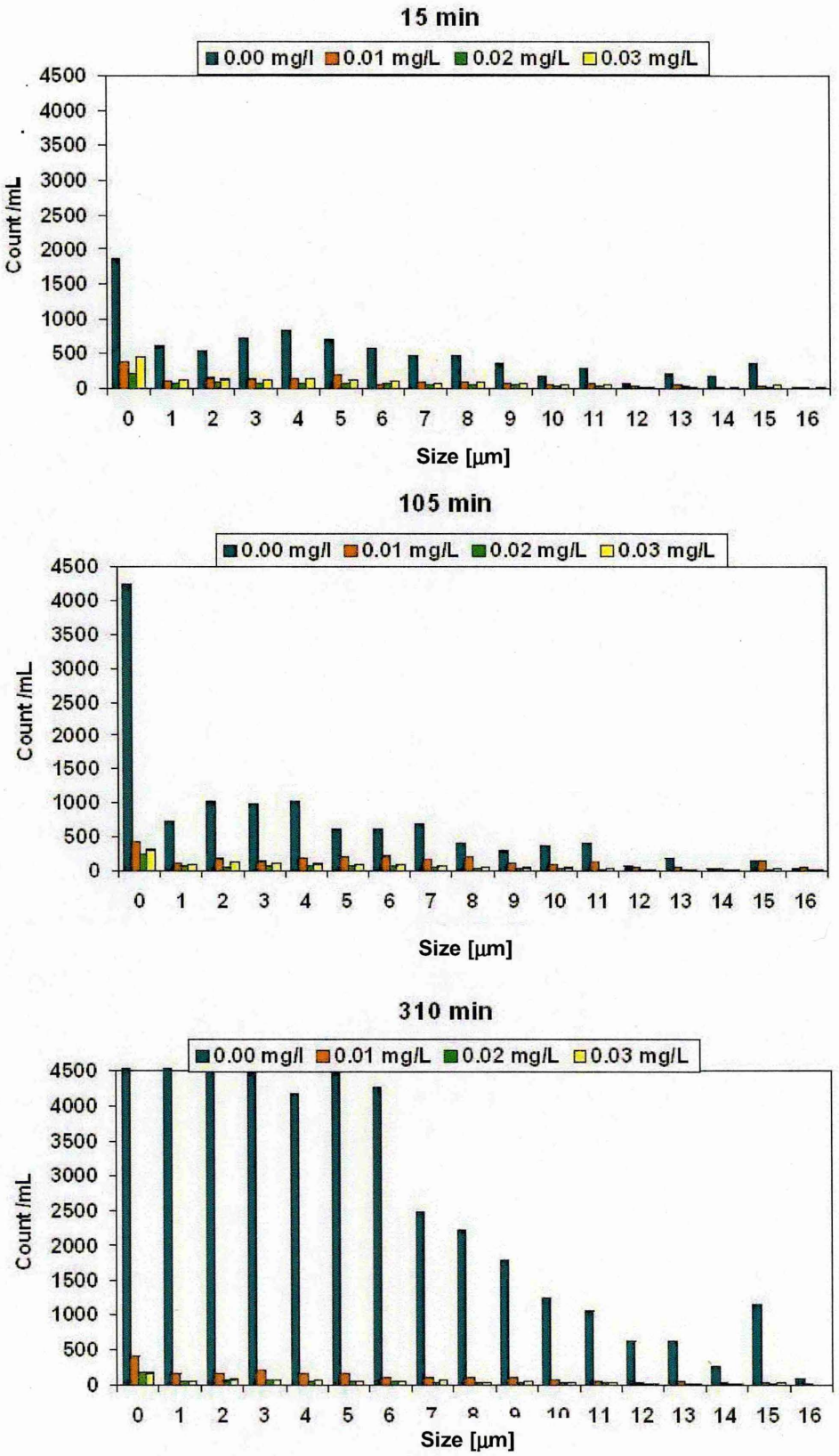


Figure 5. 28 – Filtrate particle size distribution after 15, 105 and 310 minutes on Albert WTWs sample collected in September (run 1)

5.6.3. Particle count analysis on clarified water

Particle count analysis was performed on clarified water in order to investigate how polymer dosing and floc growth affected the number and the size of the particles subsequently fed onto the sand filters. As the particle counter was not able to operate in a continuous mode, a sample was collected every 5 minutes during floc growth at 0, 0.01, 0.02 and 0.03 mg/L of polymer as described in section 4.4. Particles decreased proportionally to the amount of polymer dosed, particularly at the end of the growth phase. The total count fluctuated around 20000 and 25000 particles/mL when no polymer was dosed, it decreased from about 23000 to 17000 particles/mL when 0.01 mg/L was dosed, from 25500 to 15500 particles/mL with 0.02 mg/L of polymer and from 24000 to about 14000 particles/mL with 0.03 mg/L (Figure 5.29).

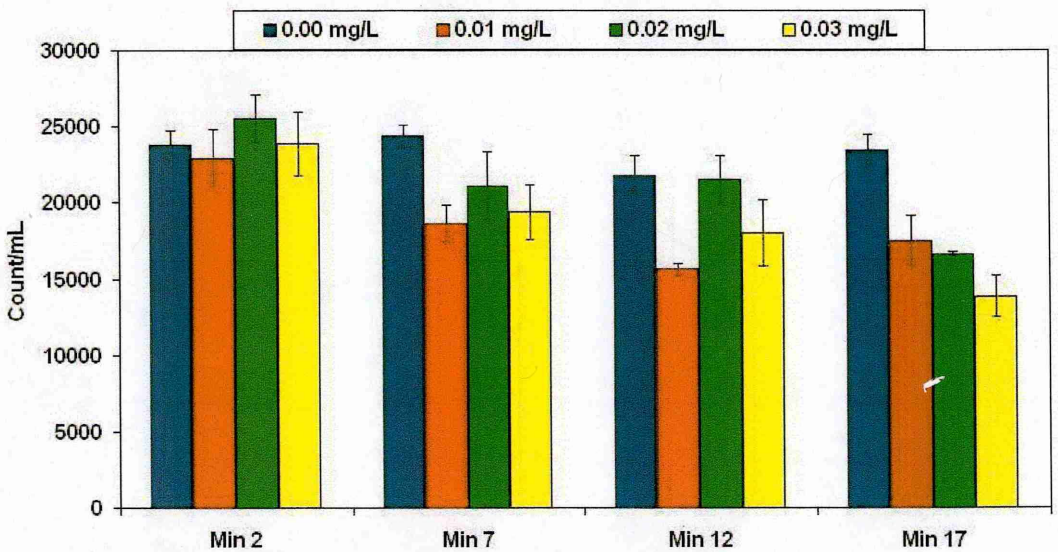


Figure 5.29 – Total count/mL for clarified water collected at Albert in September during floc growth at increasing polymer doses

The number of particles smaller than 4 µm was reduced by the greatest extent following polymer dosing and floc growth (Figure 5.30): when no polymer was dosed the number of particles between 2 and 4 µm contained in 1 mL of clarified water remained constant after 2 min (5814 ± 725) and 17 min (5733 ± 415). When polymer was dosed the number of particles/mL decreased from 5493 ± 542 count/mL after 2 min to 3911 ± 449 count/mL after 17 min with 0.01 mg/L of polymer dosing, from 6135 ± 707 count/mL to 3743 ± 262 count/mL with 0.02 mg/L of polymer dosing and

from 5768 ± 136 to 2794 ± 215 count/mL with 0.03 mg/L of polymer dosing. The same occurred to the particles smaller than 2 µm: they decreased from between 11000 and 15000 count/mL to less than 6000 count/mL after floc growth when dosing polymer, while particle numbers remained 10480 count/mL when no polymer was dosed. The count of particles between 4 and 8 µm contained in 1 mL of clarified water varied from 5455 ± 92 with 0.01 mg/L, 4823 ± 347 with 0.02 mg/L and 5089 ± 629 with 0.03 mg/L of polymer to 5602 ± 449, 5710 ± 532 and 4395 ± 527 respectively.

Results showed that polymer dosing was able to link small particles together in larger and fewer structures. The main mechanism responsible of this effect was particle bridging: polymers chains adsorbed on the surface of the particles and extending into the solution attached to each other linking them together (section 3.2.4).

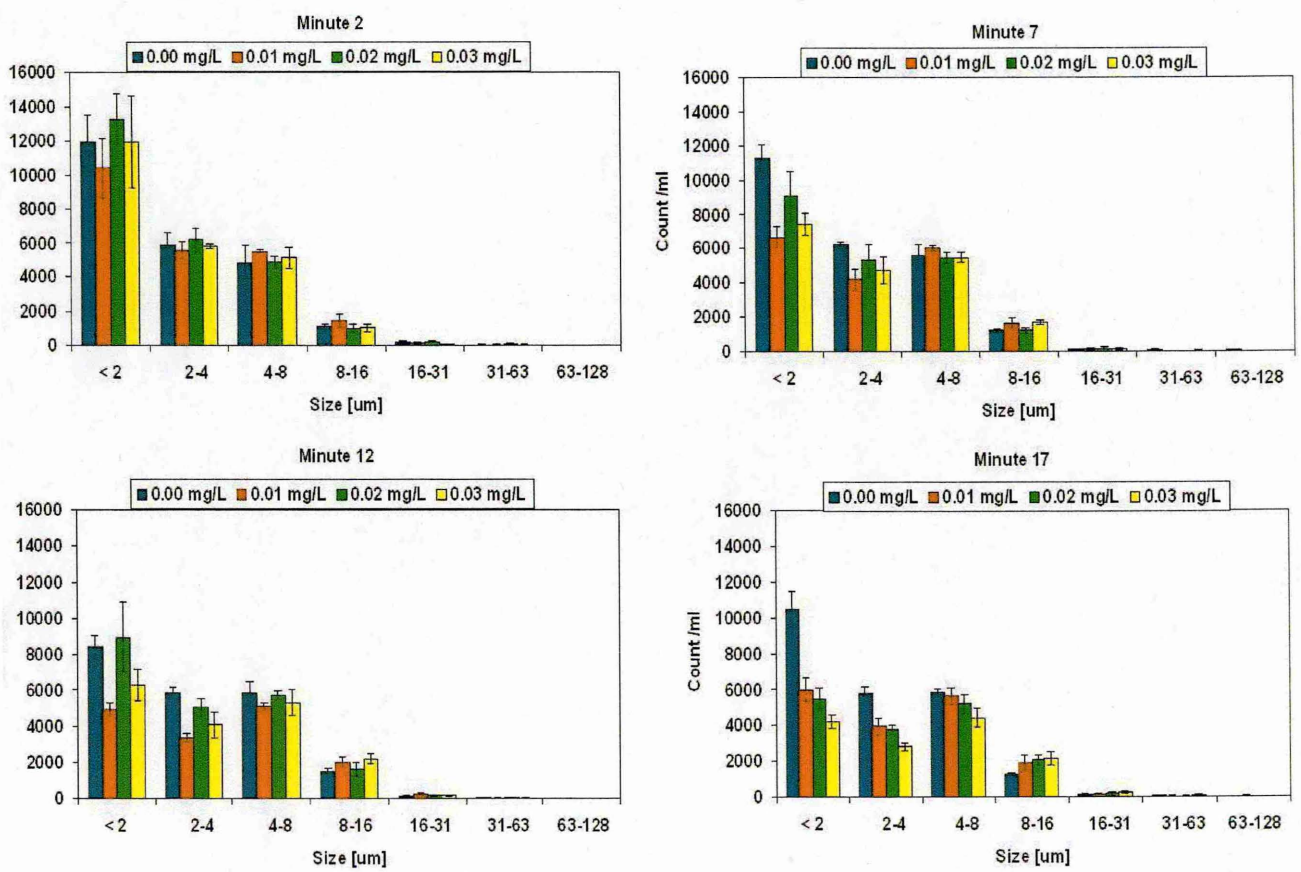
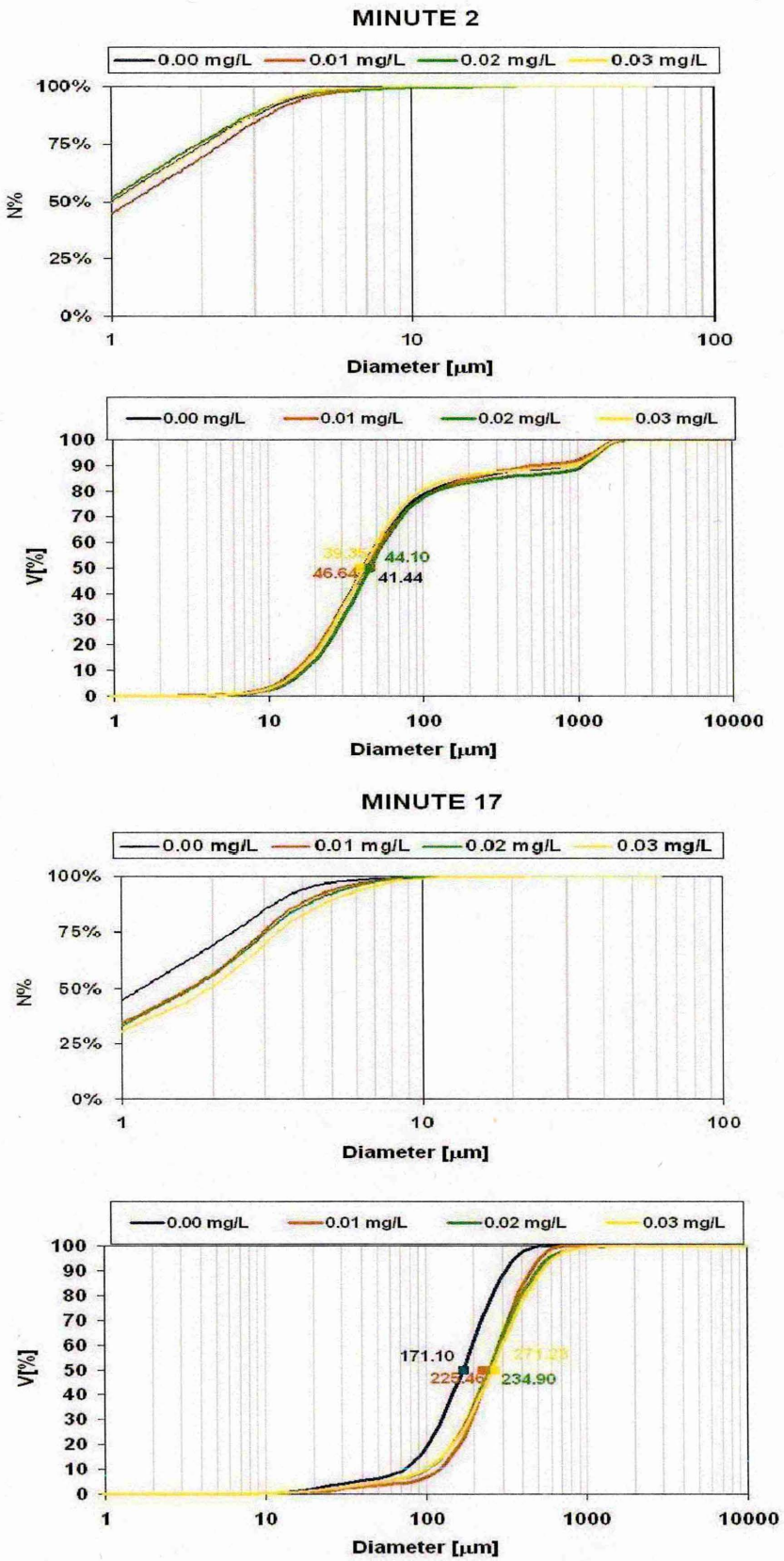


Figure 5. 30 – Particle size distribution measured with Spectrex PC2200 during floc growth with Albert September clarified water sample

5.6.3.1. Comparison of volume and number distributions

When comparing the floc size distributions before and after floc growth at different polymer doses (Figure 5.31) with the September sample, the sizes of the flocs appeared very different. For example, 50% of the total number of particles counted with the *Spectrex PC 2200* were smaller than 2 μm before growth, and between 2 and 4 μm after growth, while the *Mastersizer 2000* indicated that particles smaller than 40 μm before growth and smaller than 170-270 μm after growth represented 50% of the total volume, depending on the polymer concentration dosed (section 5.3.3.). This difference may be due to the following:

- Volume and number distributions are very different, even when they refer to the same system: it can happen that 99.9 % of the particles in a system are very small, but if we sum their volume they make up only a very small fraction of the total volume. A few big particles, that in frequency are less than 0.5% of the total, could however make up the largest percentage of the total volume.
- The measurement range of the *Spectrex PC 2200* was between 0.5 and 100 μm, while the measurement range of the *Mastersizer 2000* was between 0.2 and 2000 μm. The measurement of particles larger than 100 μm with the *Spectrex PC2200* was not reliable as it was outside the measurement interval.
- The *Mastersizer 2000* allows continuous measurement of the particle distribution and the solution containing the dispersed particle was re-circulated to the jar by means of a peristaltic pump. The *Spectrex PC2200* was only able to carry out discrete particle distribution measurements. The solution containing the flocs was taken from the jar by means of a plastic pipette (section 4.4). The sampling procedure could have altered the real sample distribution. However, in order to obtain consistent data the same procedure was repeated five times.



- **Figure 5. 31 – Comparison between measurement of particles with the Spectrex PC200 and with the Mastersizer 2000 for Albert September clarified water sample before and after floc growth at different polymer doses**

5.6.4. Particle count analysis on September samples

Particles in each size class were counted using the *Spectrex* instrument for raw, clarified and filtered water samples collected from Albert WTWs in September. The percentage of particles belonging to each size class was calculated. Results in Figure 5.32 show that clarified water contained approximately half the number of particles in raw water: the total average count for three samples was 45060 particles/mL in raw water, 23830 particles /ml in clarified water and only 993 particles /mL in filtered water. Particle count measurement performed on tap water gave an average value of 850 count/mL. The count for filtered water was therefore close to the count for tap water. In all of the three samples more than 55% of the particles were smaller than 2 µm and about 35% had a diameter beween 2 and 8 µm. Particles between 8 and 31 µm were 6 % of the total in raw water, 8 % in clarified water and 3 % in filtered water. Less than 1% of the total number of particles were bigger than 31 µm in all of the samples.

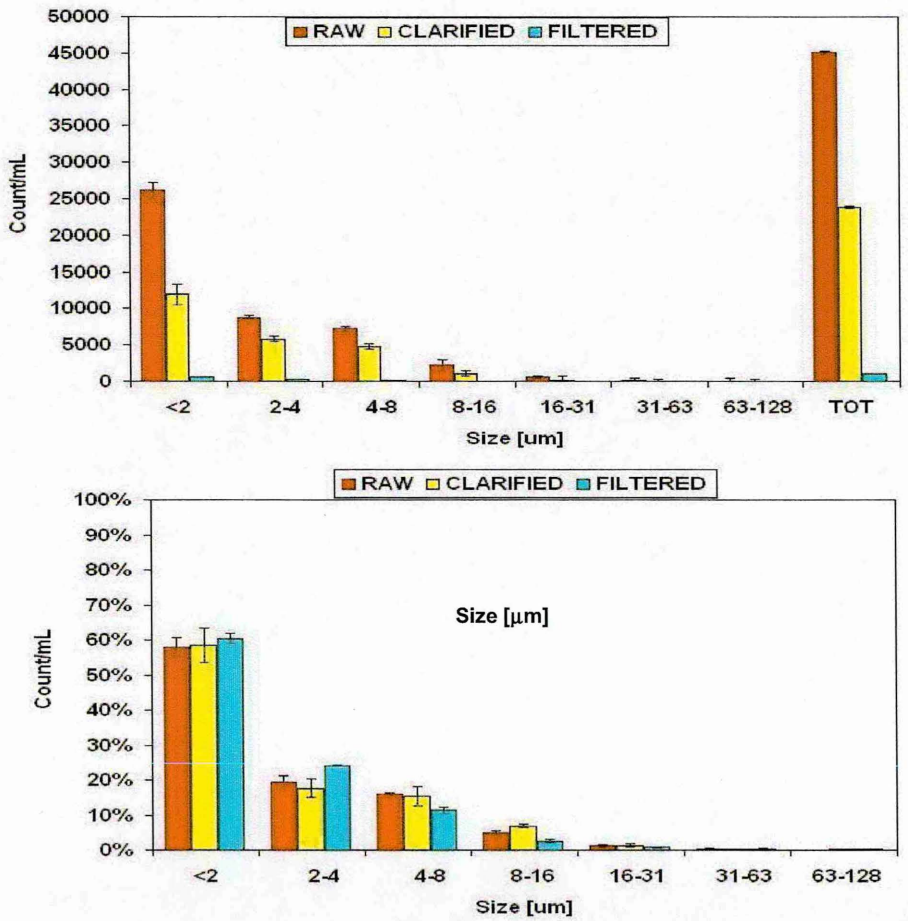


Figure 5.32 – Particle size distribution in number in September raw, clarified and filtered water: count /ml and percentage

5.6.5. Summary of particle count analysis

Particle count analysis was conducted using the instrument *Spectrex PC 2200* on the filtrate during RSF laboratory experiments, on clarified water during floc growth with different polymer doses and on raw, clarified and filtered water samples collected from Albert WTWs. All the measurements were carried out using the sample collected in September. The particle count analysis showed that:

- Filtrate of RSF runs conducted using clarified water with no polymer had a total of 8000 particles/mL more than filtrate with polymer dosing. The number of particles in the filtrate increased as the filtration run progressed with no polymer dosing (+3500 count/mL), while decreased slightly (from -100 to -800 count/mL) as the filtration run progressed with polymer dosing. Most of the particles in the filtrate were smaller than 10 μm.
- The number of particles in the clarified water decreased proportionally to the amount of polymer dosed, particularly at the end of the growth phase. The number of particles smaller than 4 μm was reduced the most.
- Clarified water contained approximately half the number of particles in raw water and filtered water contained a number of particle similar to the number of particles measured by the *Spectrex* for tap water (< 1000 count/mL).

6. Discussion

This chapter discusses the results described in the previous chapter. The operating variables that influence sand filtration performance have been studied for Albert WTWs, Yorkshire, UK, as described in section 5.1. Also, the effects of polymer dosing and particle size distribution on floc properties and RSF performance have been investigated.

Experiments were performed on water having different properties, and the effect of water quality on floc filterability was studied. The particle sizing tool *Mastersizer 2000* gave a good indication of floc properties and the *Spectrex PC2200* instrument was able to more accurately identify which particles are at risk of passing through the RSF.

This chapter contains the discussion and analysis of results presented in chapter 5. The aim of this chapter is to provide a meaningful comparative study on the effects of raw water quality, operating temperature, polyelectrolyte concentration and filter inlet particle concentration on floc filterability and discuss possible on-site implementation of the research.

6.1. Effect of water quality on filterability

NOM in drinking water is a highly heterogeneous mixture of organic compounds that vary spatially and temporally (*Sharp et al.,* 2006). Many studies have been carried out on identifying organics in raw water and their effect on water quality. Some of these studies involved resin fractionation, which allows the determination of the hydrophobocity of NOM in the water (*Volk et al., 2002).*

The DOC of the raw water samples varied across the period of investigation from a low of 6.2 mg/L in April 2007 to a high of 12.9 mg/L in September 2007. The DOC values were similar to the values measured by *Jefferson et al. (2004)*, in a study

carried out on raw water from the same reservoir. Raw water UV_{254} also reflected the change in organic concentration, varying from a minimum of 45.0 m^{-1} in April to a maximum of 67.0 m^{-1} in September. The high UV_{254} values measured suggested that the raw water was predominantly hydrophobic in character. This was confirmed by water fractionation, with between 60 and 73% of NOM associated with the hydrophobic FAF and HAF, and was in agreement with that found by *Jefferson et al. (2004)* and *Sharp et al. (2006)* studying the character of the water from the same reservoir. The HPIAF had a smaller variability throughout the sampling period: 3.1 ± 0.2 mg/L DOC compared to 5.8 ± 2.8 mg/L DOC for the HPOAF. The contribution of the HAF was the highest for the September raw water sample (73%), which was also very highly coloured. The concentration of the HPIAF was approximately the same in all of the raw water samples (ca 3 mg/L).

The DOC content of clarified water was approximately the same for the sample collected in September and the sample collected in February (Figure 5.11). In September a higher concentration of ferric sulphate was dosed on-site than in February: on-line data gave an actual coagulant dose of 10.9 mg/L in September and 7.6 mg/L in February. This correlates with the higher HPOF in September (9.5 mg/L) than in February (4.8 mg/L) water in addition to a higher overall NOM content: a higher coagulant dose was used on-site in September to treat water characterised by high MW NOM. Higher NOM and consequent higher coagulant dose caused higher load to DAF, which resulted in worse floc removal. As a consequence more particles ended up in the inlet to RSF in September than in February: inlet turbidity to filters reached 3.7 NTU on the 7th September 2007, while its value stayed constant around 2.0-2.3 NTU during the first week of February 2007 (Figure 6.1). Higher inlet turbidity contributed to high outlet turbidity: the RSF outlet turbidity combined for the 6 filters measured on-site reached 0.3 FTU on the 6th September, whereas it reached a maximum value of only 0.03 FTU on 21st February. Increased concentrations of NOM and the consequential inlet turbidity to filters caused higher deterioration in floc properties in the September sample than in the February sample. This deterioration was observed in laboratory experiments that showed that flocs were weaker in September than in February when dosing polymer (Table 5.6). Furthermore, that flocs

growth and re-growth rates were higher in the February sample than for the September sample (Table 5.5 and Table 5.9).

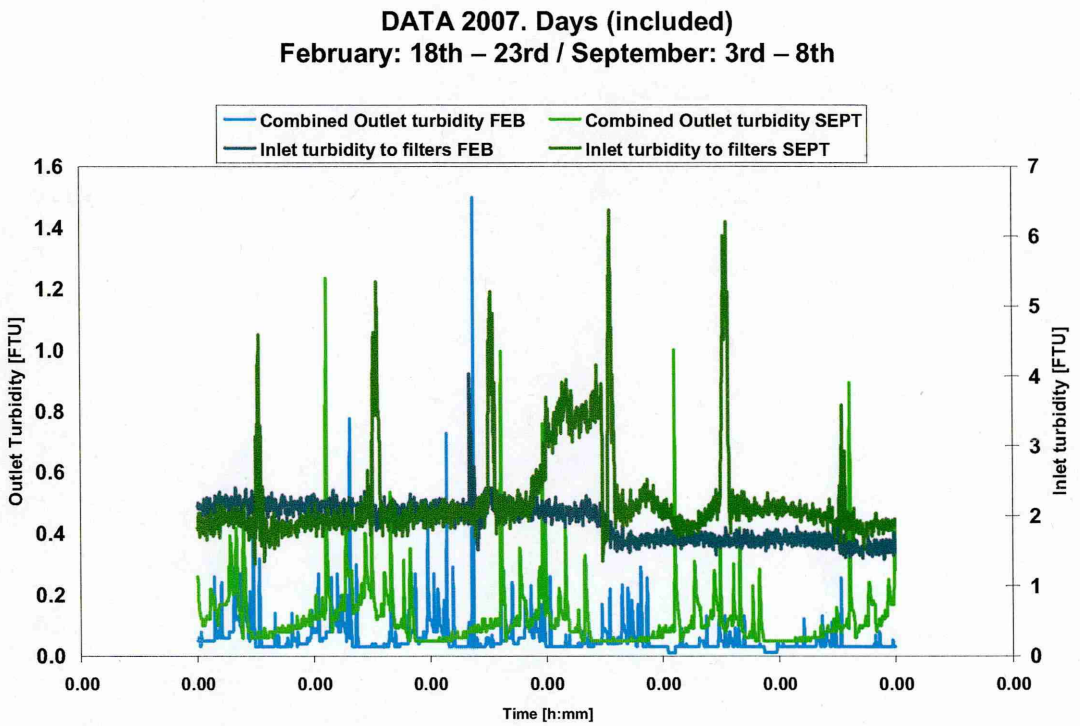


Figure 6. 1 – On-site inlet turbidity to filters and combined outlet turbidity on 6 days intervals around the sampling dates

Flocs containing a high concentration of NOM have been shown to result in smaller and weaker aggregates (*Dulin and Knocke, 1989, Jarvis et al., 2005 b*). This can be attributed to the fact that in water characterised by low NOM-coagulant ratio adsorption the organic molecules only partially cover the primary particles of the floc. This allows the molecules to come into close contact and form stronger bonds. Increasing NOM concentrations causes an increase in the separation distance between primary particles and the formation of weaker bonds. The results of this work support this hypothesis. The high DOC September water resulted in smaller weaker flocs compared to the February water.

The results of turbidity measurements on clarified water after floc growth at different temperatures showed lower turbidity after growth at 20 and 30 °C than at 5 and 10 °C, both with and without polymer dosing (Table 5.8). This can be explained by the fact

that at low temperature chemical-physical reactions between NOM and flocs are slower than at higher temperature. According to *Le Chatelier's* principle if a chemical system at equilibrium experiences an external interaction that disturbs its equilibrium the system will tend to reduce the effect of this interaction *(Sawyer at al, 1994)*. Particle aggregation in floc is a destabilisation process that increases the entropy of the system. When particles aggregate, heat is released, this process was more favourable at high rather than at low temperature. This explains why turbidity of clarified water was higher on flocs formed at low temperature. Further discussion on the effect of temperature on floc properties is in section 6.2

The impact of raw water quality on sand filtration performance was studied also by analysing on-site data registered at Albert and Fixby WTWs over the year 2007 (Appendix A). At Fixby WTWs high inlet turbidity resulted in higher RSF outlet turbidity and headloss growth. This occurred because RSF were not always able to remove the high particle content at the inlet, therefore inlet turbidity above 6 FTU often resulted in outlet turbidity higher than 0.1 FTU. At Albert outlet turbidity increased following an increase in inlet turbidity and of coagulant dose. The coagulant dose is normally increased when treating raw water characterised by high NOM content. High NOM concentration contributed to cause high outlet turbidity and occasional breakthrough.

6.2. Effect of temperature on filterability

The results of laboratory experiments showed that clarified water turbidity was higher at lower temperatures. During floc growth, breakage and re-growth there was no significant difference between floc sizes at different temperatures: polymer dosing enhanced floc growth independently of the operating temperature. *Fitzpatrick et al. (2004)* investigated the effect of temperature on flocs using a kaolin clay suspensions in tap water and alum, ferric sulphate and three polyaluminium chloride coagulants. The authors measured floc formation, breakage and recovery at temperatures ranging from 6 °C to 29 °C and found that at lower temperatures flocs are smaller and flocculation slower than at higher temperatures. Aluminium based coagulants

produced flocs that vary more with temperature than ferric sulphate flocs. The low variation of floc size with temperature when dosing ferric sulphate is confirmed by the results on the laboratory experiments carried out in this work, as the raw water at Albert WTWs is coagulated with ferric sulphate. This work also shown that temperature has no effect on flocs properties when dosing synthetic polyacrylamide as filtration aid.

6.3. Effect of polyelectrolyte concentration on filterability

Previous research on polymer dosing in drinking water treatment showed that cationic polyelectrolyte dosed in combination with a metal coagulant gives the best performance in terms of floc settling rate, NOM removal and residual turbidity, as discussed in chapter 3 and summarised in Table 3.2 (*Choen et al., 1958, Black and Hannah, 1961, Mueller et al., 1964, Lee et al., 1998, Jun et al., 2001 Jarvis et al., 2006 and Yukselen et al., 2006).* Anionic and non-ionic polymers are mainly used in conjunction with direct filtration, as they enhance floc size and strength through particle bridging (section 3.2.4.). The effect of polyelectrolyte dosing on floc filterability is discussed in this section. Floc filterability is a function of floc size distribution and strength and is influenced by on-site conditions and water quality (*Loganathan and Majer, 1973*).

Floc growth experiments simulated the industrial process at Albert WTWs: water after DAF is fed into six sand filters operating in parallel and polyelectrolyte coagulant is dosed at the entrance of an open channel that connects DAF basins to sand filters. Flocs grow while the water flows in this channel. Floc growth experiments with Albert clarified water showed that floc growth rate increased significantly with increasing polyelectrolyte concentration, as described in section 5.3.2.1. and summarised in Table 6.1. Floc growth rate was between 2 and 4 μm/min slower in the September than in the February sample, because of the higher NOM concentration in September than in February sample, as discussed in section 6.1.

Table 6.1 : Floc growth rate (D_{50}/minute) at different polymer doses for February and September samples

Polymer dose	Growth rate [µm/min]	
	February	September
0.00 mg/L	10.63 ± 0.31	7.64 ± 0.42
0.01 mg/L	12.85 ± 0.72	10.69 ± 0.90
0.02 mg/L	14.51 ± 0.99	10.85 ± 0.23
0.03 mg/L	16.20 ± 2.08	13.70 ± 3.23

This result agrees with the findings of *Rawlings et al. (2006).* The authors measured the flocculation index during floc growth and re-growth dosing between 0 and 0.01 mg/L of anionic and non-ionic polycarilamyde and found larger flocs formed at higher polyelectrolyte doses.

In section 5.3.3. the addition of polymer after coagulation and DAF was shown to give rise to improved floc structure by engineering a larger and more resistant floc aggregate, particularly when treating low DOC content raw waters. The production of a more robust floc following polymer dosing enables better filtration of this residual particulate material. Importantly, flocs that were formed with polymer were able to re-grow to their previous size, as described in section 5.3.2.3. and shown in Figure 5.19. During filtration, particles that are captured on filter sand grains must resist shear forces to remain fixed on to the sand (*Kim and Tobiason, 2004).* Additionally, the retained particles may be used to capture more particles if an attractive force still exists between the two (*Parsons and Jefferson, 2006*). Broken flocs can re-grow for systems with and without polymer dosing which enables the particle capture mechanism outlined above to take place. However, when polymer dosing was employed the flocs showed slight increased resistance to shear which would explain why polymer dosing should be used to improve filter performance. Flocs should be considered stronger in this way because flocs captured on sand will be less likely to break from the sand surface and release other components of the floc that may eventually be released from the filter and give rise to turbidity.

In drinking water treatment, granular media filters are used to capture particles primarily as a result of attachment, detachment and reattachment of detached particles in deeper layers of the filters (*Kim and Tobiason, 2004).* In sand filtration experiments the improved capture of particles resulted in the increased RSF headloss seen with increasing polymer dose: increased polymer dose contributes to a faster depletion of the voids in the sand filter bed. Therefore polymer dosing causes a reduction in the bed porosity and a consequent rapid increase in headloss, in accordance with the Kozeny-Carman equation (section 3.4.1.1.1.). *Boller and Kavanaugh (1995)* developed a predictive model of headloss increase based on particulate characteristics and using data from several filtration studies found that the increase in hydraulic gradient in a RSF layer was due to a more rapid depletion of the available pore space for particle collection. For this reason according to *Boller and Kavanaugh (1995)* the aim of RSF pre-treatment should be to produce small and dense flocs which are destabilised and react easily with filter grains without causing excessive headloss development. Small and dense flocs also detach less easily from sand filters, as shown by *Kim and Tobiason (2004).* The authors found that the degree of detachment was higher for particles between 6 and 12 μm, followed by particles between 3 and 5 μm and between 1 and 2 μm. This occurred because of the greater effect of hydraulic shear as particle size increases (*Kim and Tobiason, 2004).* Results of particle count analysis of filtrate carried out in this work (section 5.6.2.) confirmed that the particle passing through the sand filter after 15 minutes were between 0.5 and 12 μm. As the filtration run progressed the number of particles smaller than 1 μm passing through increased significantly (Figure 5.28). The headloss build-up is an operational issue at Albert WTWs: the concentration of polymer dosed on inlet water to RSF should not be too high in order to avoid high rate of increase in headloss and filter clogging.

To be able to identify an improvement in filtration performance it is important to understand the behaviour of particles smaller than 10 μm: it is the capture and release of small floc that is responsible for the turbidity in the filtered water (*Boller and Kavanaugh, 1995*). Improved removal of this range of turbidity causing particles is therefore of great importance during filtration. Particle counts on clarified water was performed in order to understand the effect of polymer dosing on particles with a

median diameter between 0.5 and 100 μm. Experimental results (section 5.5) showed that increasing polyelectrolyte concentration caused a decrease in the total particle count after floc growth. During floc growth particles interact with each other and aggregate into flocs. The presence of polyelectrolyte destabilised and linked together the particles, entrapping them with its polymer loops and tails (*Gregory, 1996)*. The more polyelectrolyte was dosed the more this interaction became stronger and the lower was the particle count on clarified water at the end of the floc growth. The mechanism of reaction between polymer and particles could be investigated by analysis of microscopic images of flocs with and without polymer dosing. This was not possible due to the limited timeframe of the project but is included in the recommendations for future work (section 7.1).

The particle count analysis showed that during floc growth the percentage of particles in clarified water smaller than 10 μm stayed constant around 98 % with no polymer dosing, while it decreased from 98.5 ± 0.5 % to 93.7 ± 1.2 % dosing 0.03 mg/L of polymer.

According to the model of *Rajagopalan and Tien (1976)*, particles that were more difficult to retain during sand filtration have a median diameter between 0.1 μm and 10 μm (section 3.4.1.4.). Particle count was therefore expected to be higher and turbidity breakthrough more likely to happen with no polymer dosing. This was proved by RSF experiments: the total particle count on filtered water, shown in Figure 5.26, was about 8000 particles/mL higher when no polymer was dosed than when polymer was dosed. Particles causing breakthrough had a median diameter between 0.5 and 15 μm, as discussed in section 5.5.1. and shown by the filtrate particle size distribution at different RSF stages (Figure 5.28). Experiments conducted by many researchers (*Yao et al, 1971, Habibian et al., 1975, Ghosh et al., 1975*), showed that RSF efficiency of sub-micron particles is minimum at 1 μm and increases with increased particle size above the micron size. Particle size distribution of the filtrate confirms that the most abundant particles both in filtrate and clarified water are in the sub-micron particle range (Figure 5.28).

In this study removal of submicron particles by RSF was similar after filtering for 15 minutes (clean bed stage, as described in section 3.4.1.) and after filtering for 1 h and 45 minutes (transient stage). Filter effluent contains both the influent particles that are not removed by RSF and particles detached after being part of the deposited material in the filter pores (*Kim et Tobiason, 2004*). *Aim et al. (1997)* studied the variation of filter performance under varying particle and filter grain sizes. Focusing on sub-micron particles the authors found a minimum filtration efficiency filtering 0.825 μm rather than 0.460 and 2.967 μm particles in a clean bed, while during the transient stage the efficiency improved with an increase in particle size also when filtering sub micron particles.

Due to polyelectrolyte-particles interactions (*Gregory, 1996*), polyacrylamide dosing on coagulated and floated water resulted in larger flocs that were able to maintain a larger size after exposure to increased shear rates compared to flocs formed with no polymer dosing. Floc re-growth potential was also higher when dosing polymer. The bench scale RSF trials showed that there was an increase in the filter headloss with increasing polymer dose, due to the increasing floc size and the consequent rapid depletion of the pore spaces of RSF top layer. Outlet turbidity was higher when no polymer was dosed, and this was demonstrated performing a particle count analysis on the inlet and outlet water to filters. Results showed that the total particle count after floc growth was lower when polymer was dosed, as described in section 5.5.2. This resulted in a lower particle load to the bench filter and in a consequent lower outlet turbidity (section 5.4).

6.4. On-site implementation of research

Granular media filters are capable of efficiently and economically removing a wide range of particle types from the water and are the most common type of filters used for particulate removal in WTWs. RSF is a rather simple process from an engineering point of view, but the chemical and physical reactions and mechanisms behind particle transport and attachment are scientifically very complex. The effectiveness of RSF depends on several variables, parameters and conditions and, although granular

media filtration has been the subject of much research and many previous studies, there are still no accepted analytical models that combine all these parameters into a non-empirical model to predict efficiency. Granular media filters are mostly designed on extrapolation of previous experience or from the result of pilot scale studies. However a non-empirical model would allow process optimisation, that is minimisation of operational costs. In theoretical terms, the operating costs are at a minimum when limiting headloss and deterioration in filtered water quality below the preset minimum standard occur at the same time (*Boller and Kavaugh, 1995*).

The Yorkshire Water research and development team is currently involved in the extrapolation of an empirical model, applicable to Albert WTWs, that outputs the rate of increase in headloss and the timing of the onset particle breakthrough for given filtration rate, filtration media, and floc filterability. Floc filterability derives from particle size distribution and concentration, and floc resistance to shear. Floc filterability is significantly affected by polyacrylamide dosing as filtration aid, and knowing the effect of polymer dosing on floc filterability is necessary for the development of the empirical model.

In this work floc properties at different polymer doses were performed with two samples containing different NOM content (section 5.2.3.). The results showed that floc formed in the high NOM water sample were smaller and weaker than floc formed in the low NOM water sample. Polymer dosing increased floc growth and re-growth in both samples and marginally improved floc strength in the low NOM sample. This research found that it is recommended to start polymer dosing on-site when treating water at high NOM content (i.e. DOC > 8 mg/L) and when inlet turbidity to filters is high, particularly in autumn and winter. The suggested polymer dose was between 0.01 and 0.02 mg/L, as this dose ensures low headloss build-up rate and low outlet turbidity. Before being fed to RSF the water should be slowly mixed for at least 15 minutes, in order to allow enough time to for floc growth and particle-polymer interaction.

7. Conclusions & Recommendations for future work

This thesis has presented an in depth study on:

- The effect of water quality and synthetic polyacrylamide dosing on floc filterability;
- The effect of variation of on-site variables on filtration efficiency.

The main conclusions arising from this work are:

1. Polymer dosing engineers flocs for improved filtration by reducing the concentration of small particles (0-10 μm) onto RSF.
2. The optimum dose of synthetic polyacrylamyde on water after DAF at Albert WTWs was between 0.01 and 0.02 mg/L. Such doses ensure long filter runs: low outlet turbidity and low headloss build-up rate.
3. The *Mastersizer 2000* particle sizing tool gives a good indication of floc growth, strength and re-growth, while the *Spectrex PC 2200* is able to better identify which particles are at risk of passing through the RSF.
4. When no polymer was dosed before RSF a higher load of particles between 0.1 and 16 μm was fed to the filters than when polymer was dosed and the concentration of particles in the filtrate was also higher, resulting in higher RSF turbidity.
5. Headloss development on RSF increased with increasing polymer dose.
6. Polymer dosing increased floc size for all the classes and improved floc reformation after breakage. Polymer dosing slightly increased floc strength in the samples characterised by lower DOC in the raw water.
7. Raw water at high NOM content was characterised by reduced clarified water floc growth when no polymer was dosed. Polymer dosing solved this problem.
8. Water temperature did not have a significant effect on floc properties.
9. RSF headloss tended to increase with increasing inlet flow, in accordance with the Kozeny-Carman equation. Outlet RSF turbidity increases at increasing raw

water turbidity and coagulant dose, particularly in winter and autumn. Coagulant dose is controlled by UV_{254}, which mirrors the NOM concentration is the water. Therefore during winter and autumn RSF turbidity increases following increasing NOM concentration in the raw water.

7.1. Recommendations for future work

Research to extend from this work should concentrate on:

1. Particle count analysis should be performed for different types of clarified water to identify the seasonal variation in the number of particles going onto the filter.
2. The relationship between RSF inlet and outlet particle concentration should be investigated in order to highlight the role of non-attachment and detachment of turbidity breakthrough.
3. Albert WTWs typically experienced problems with filter breakthrough occurring at low headloss during winter. Some further measurements on the temperature effect on floc filterability should be carried out by performing bench-scale RSF experiments at different temperatures with and without polymer dose.
4. It would be interesting to study the influence of coagulant dose and coagulation pH on floc filterability and particle distribution, as coagulant dose and coagulation pH are two variables to take into account in the empirical filtration model (section 6.4). This analysis should be repeated with and without polymer dosing.
5. Microscopic image analysis of polymer-floc reaction should be performed in order to have a better understanding of the mechanisms involved.

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Appendix A – On-site data charts

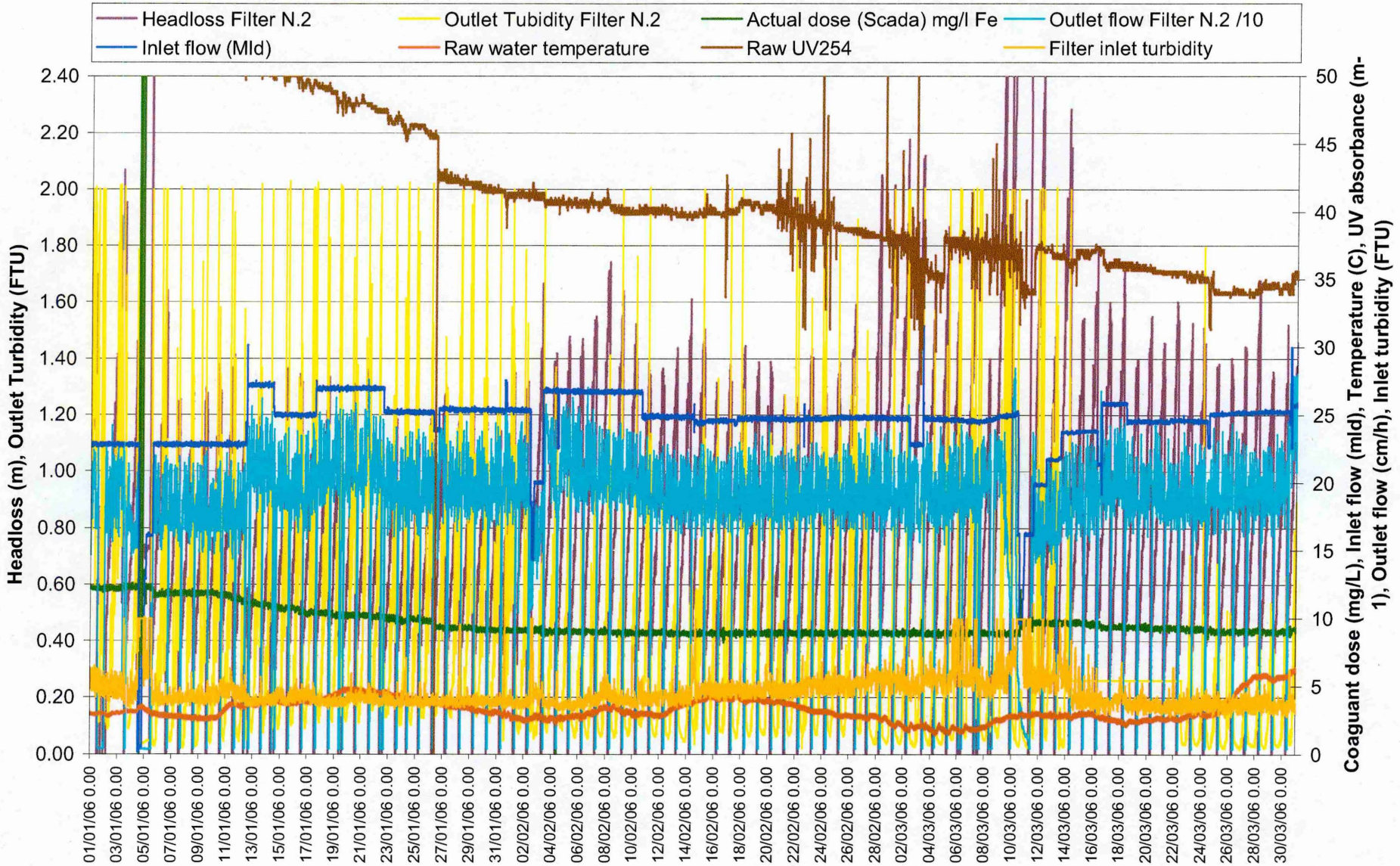
Fixby WTWs

- Winter 2006
- Spring 2006
- Summer 2006
- Autumn 2006
- Winter 2007
- Spring 2007

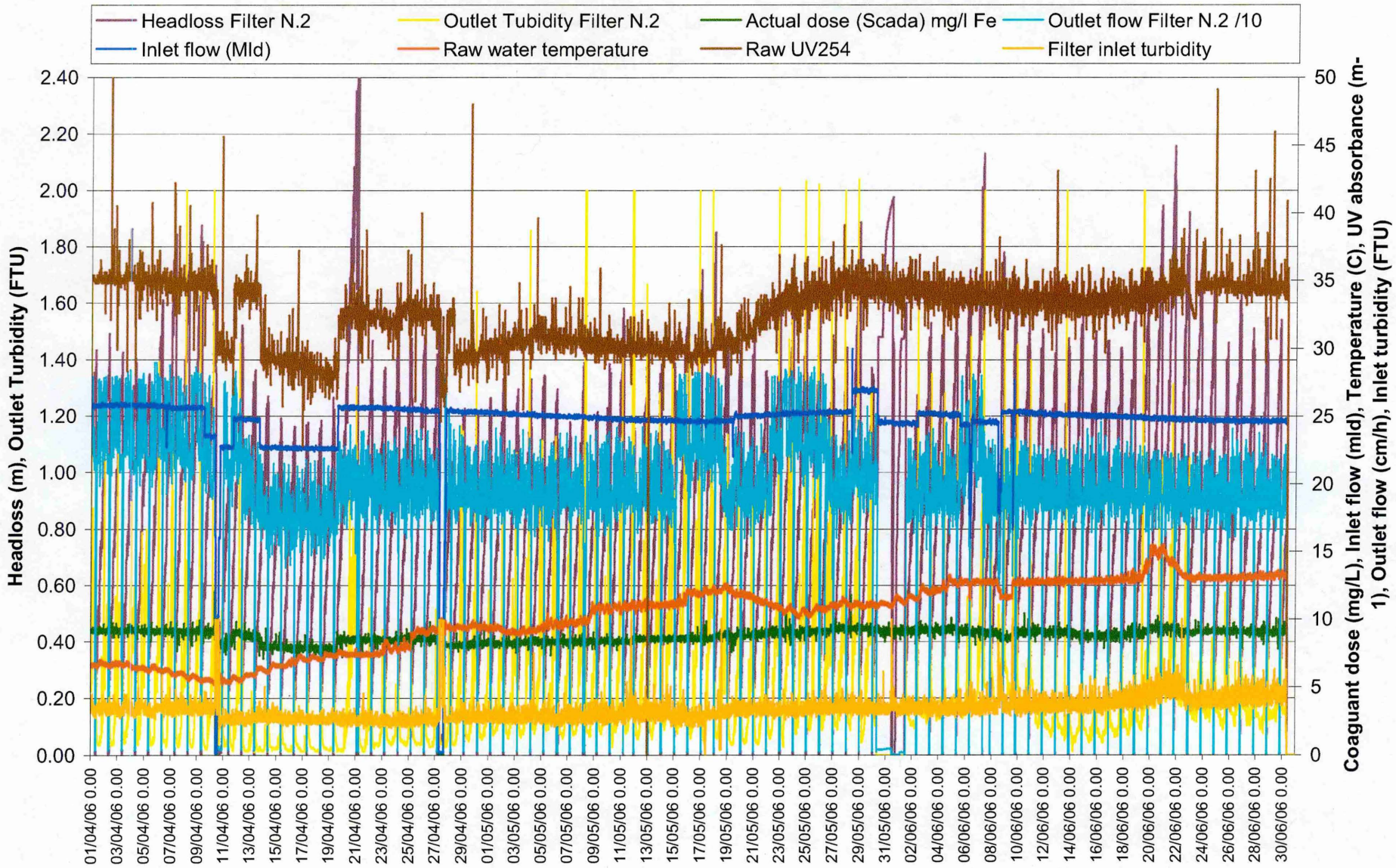
Albert WTWs

- December 2005
- January 2006
- February 2006
- March 2006
- April 2006
- May 2006
- June 2006
- July 2006
- August 2006
- September 2006
- October 2006
- November 2006
- December 2006
- January 2007
- February 2007
- March 2007
- April 2007
- May 2007
- June 2007
- July 2007

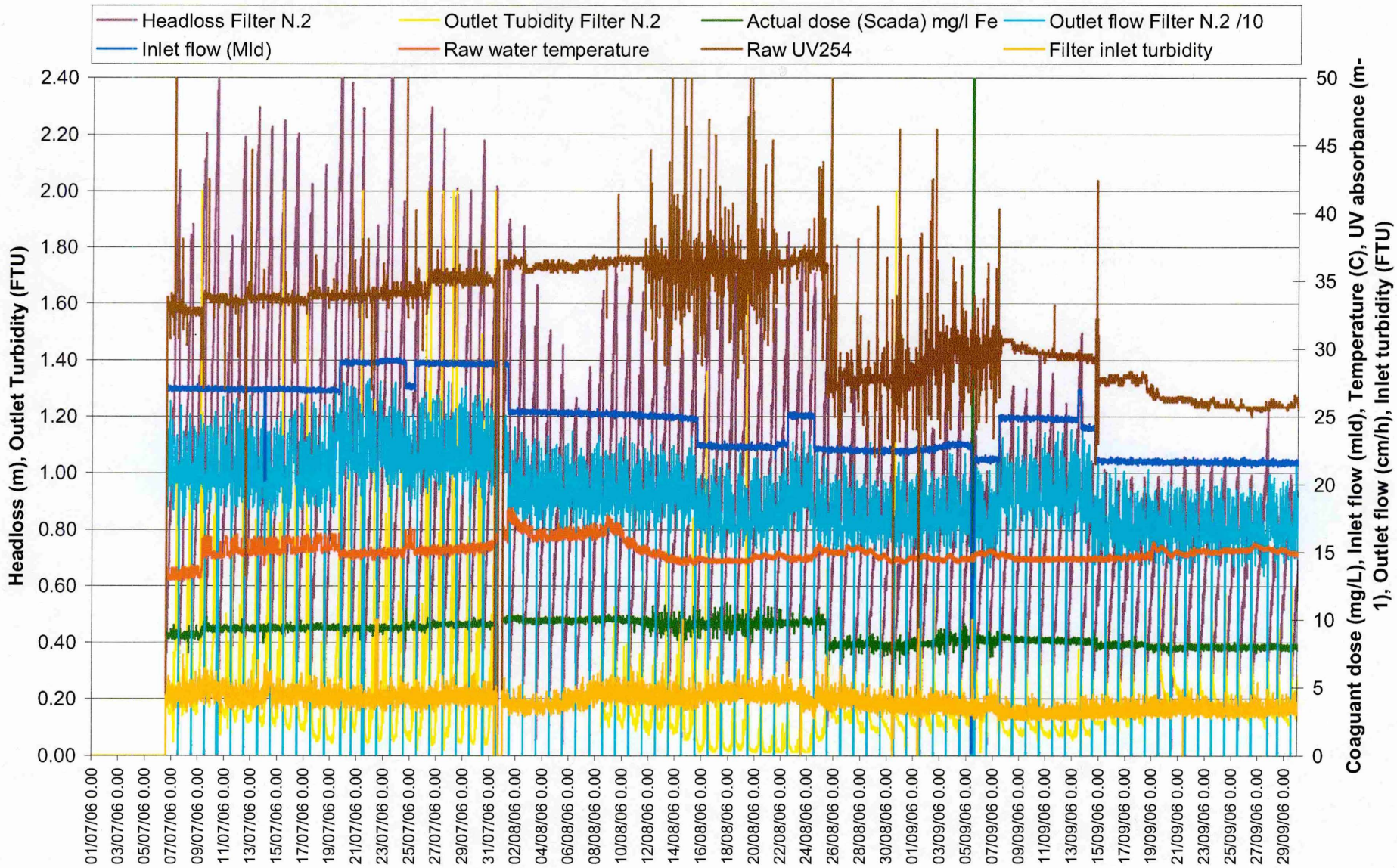
FIXBY – WINTER 2006



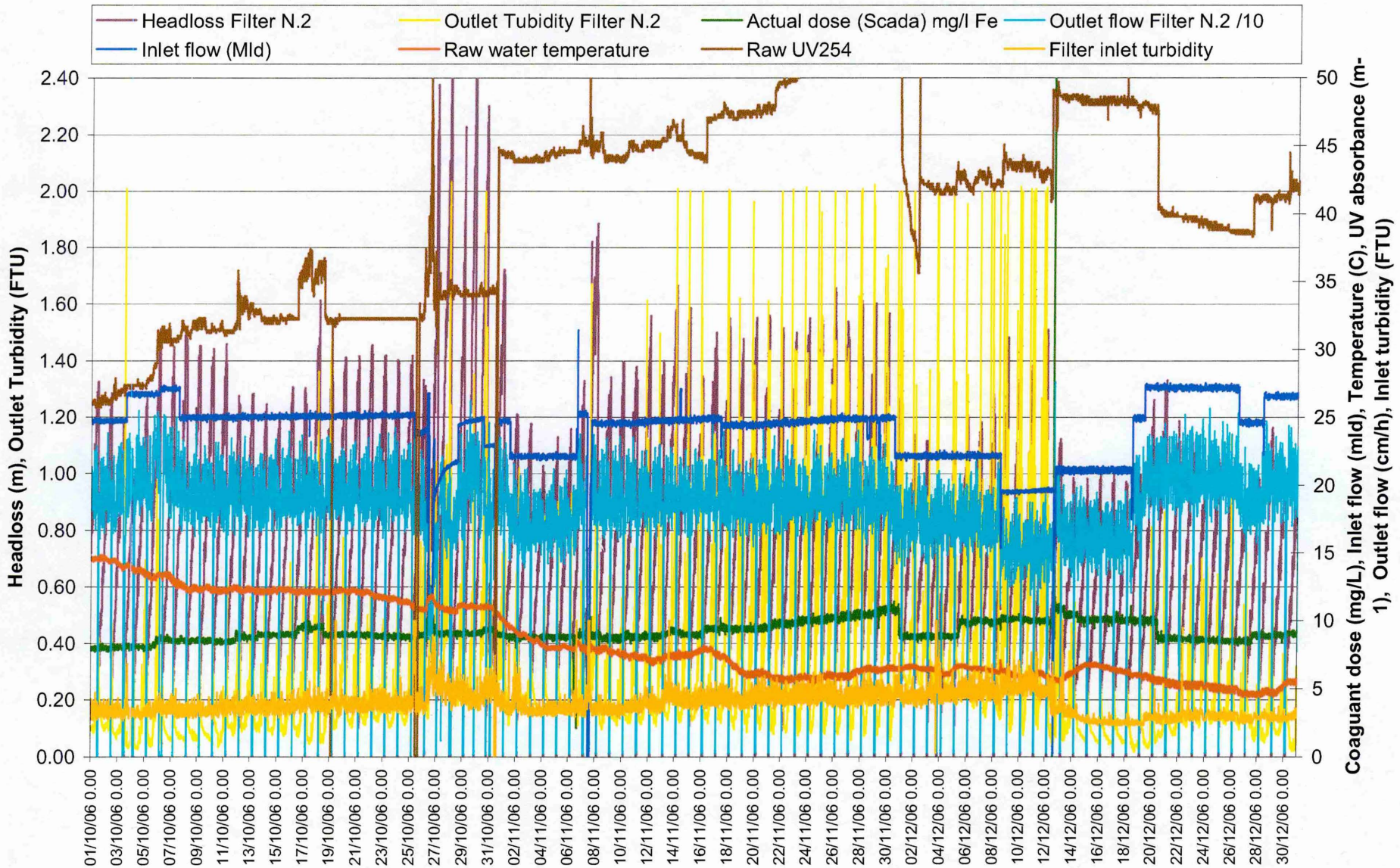
FIXBY – SPRING 2006



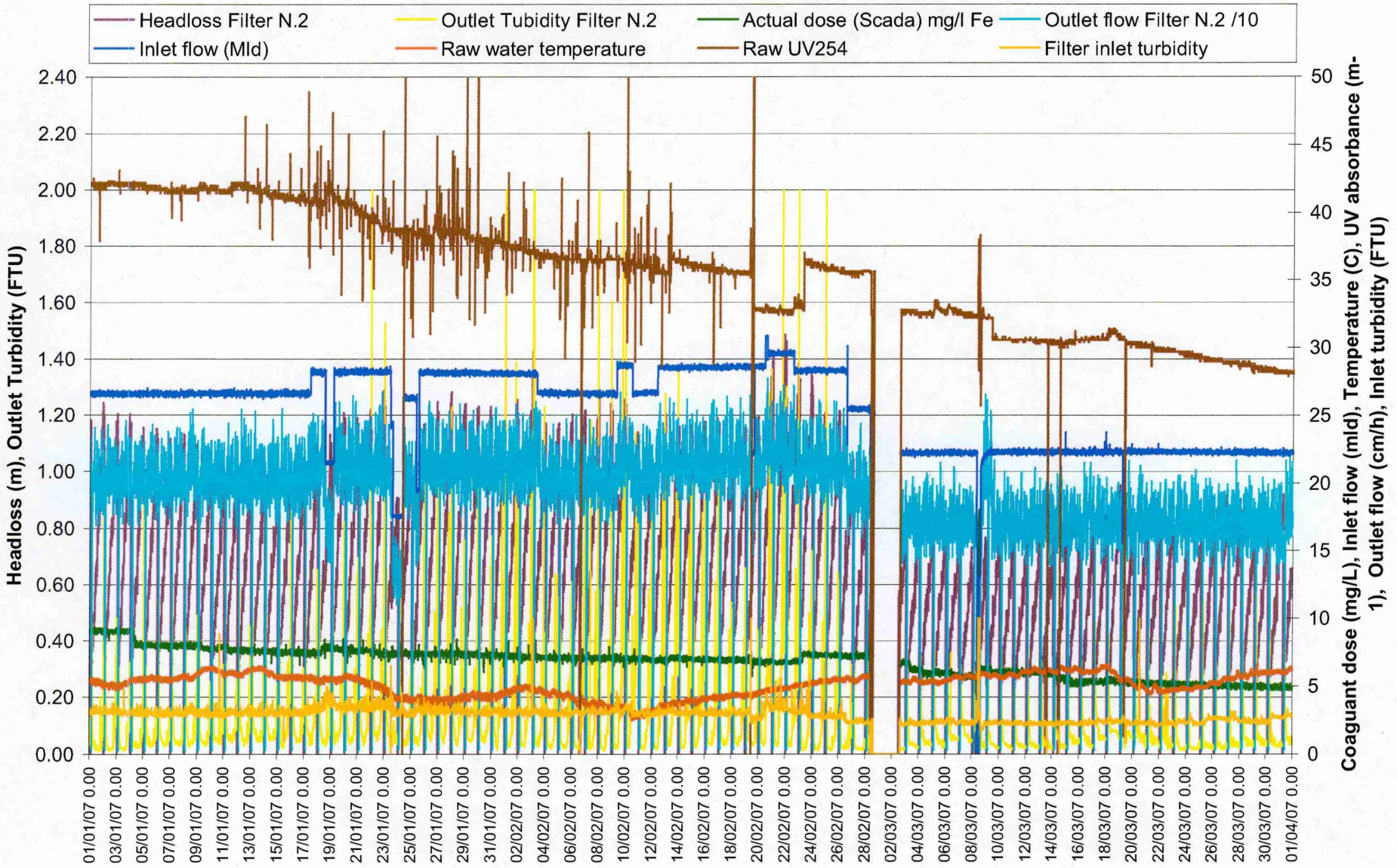
FIXBY – SUMMER 2006



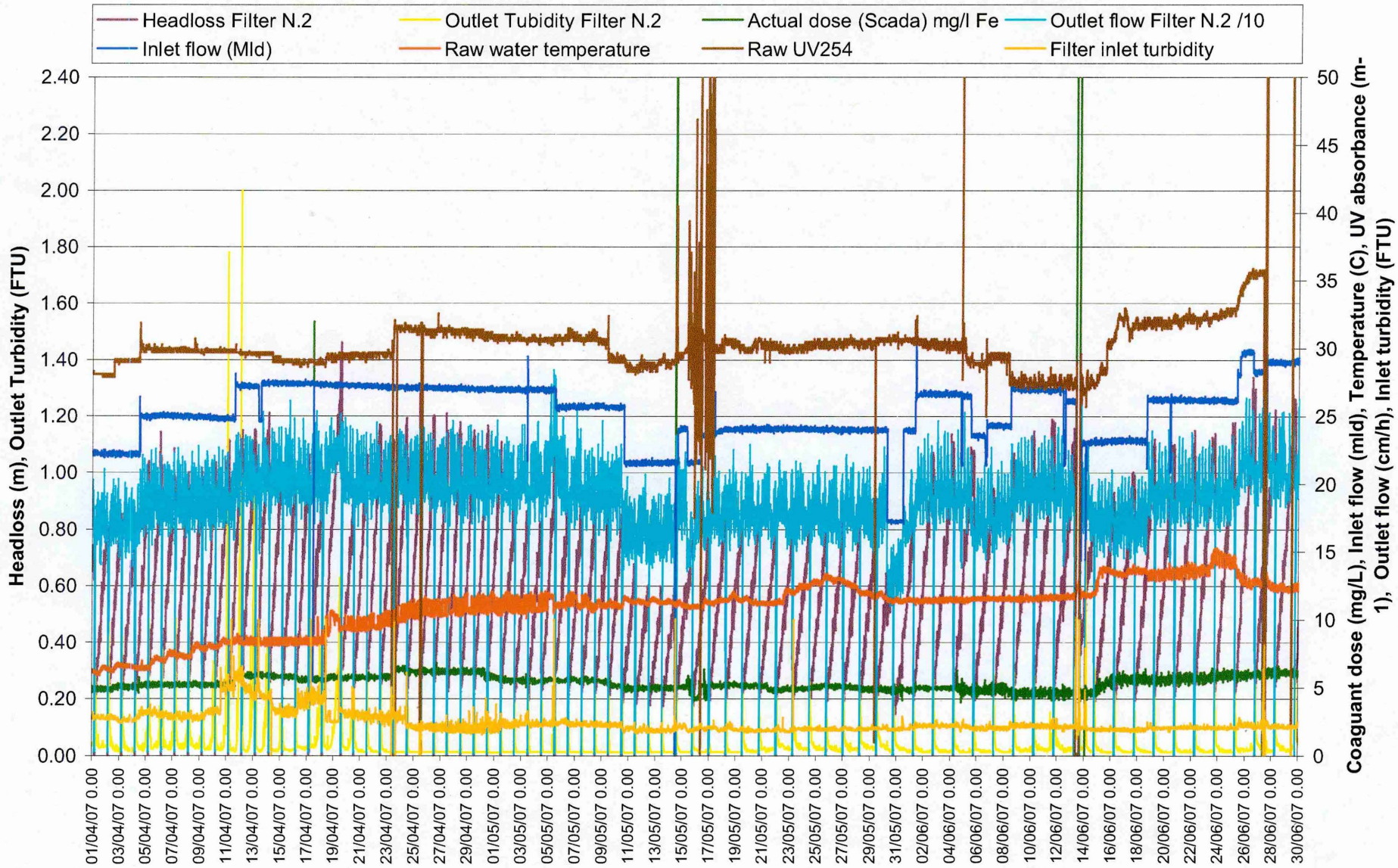
FIXBY – AUTUMN 2006



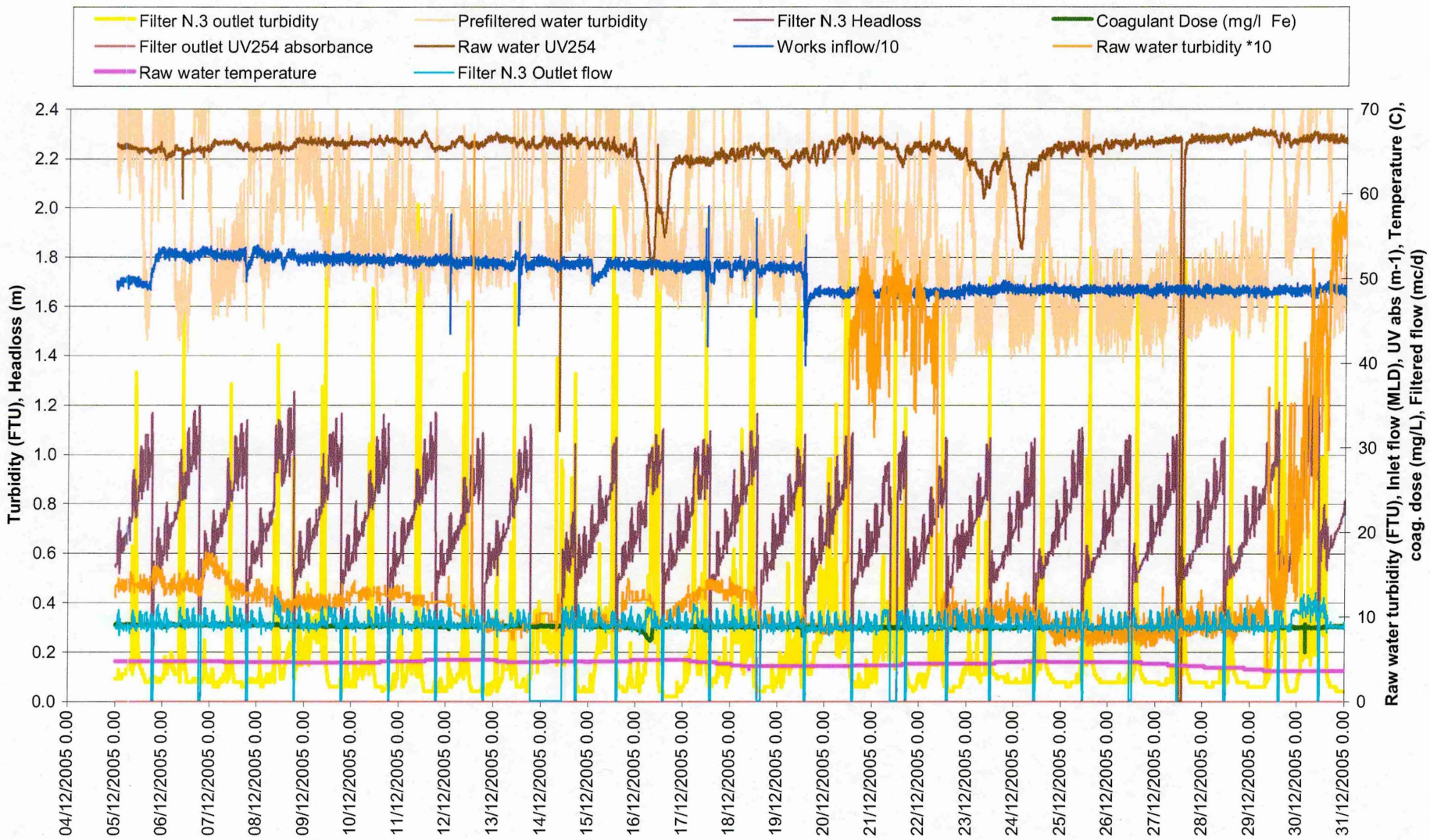
FIXBY – WINTER 2007



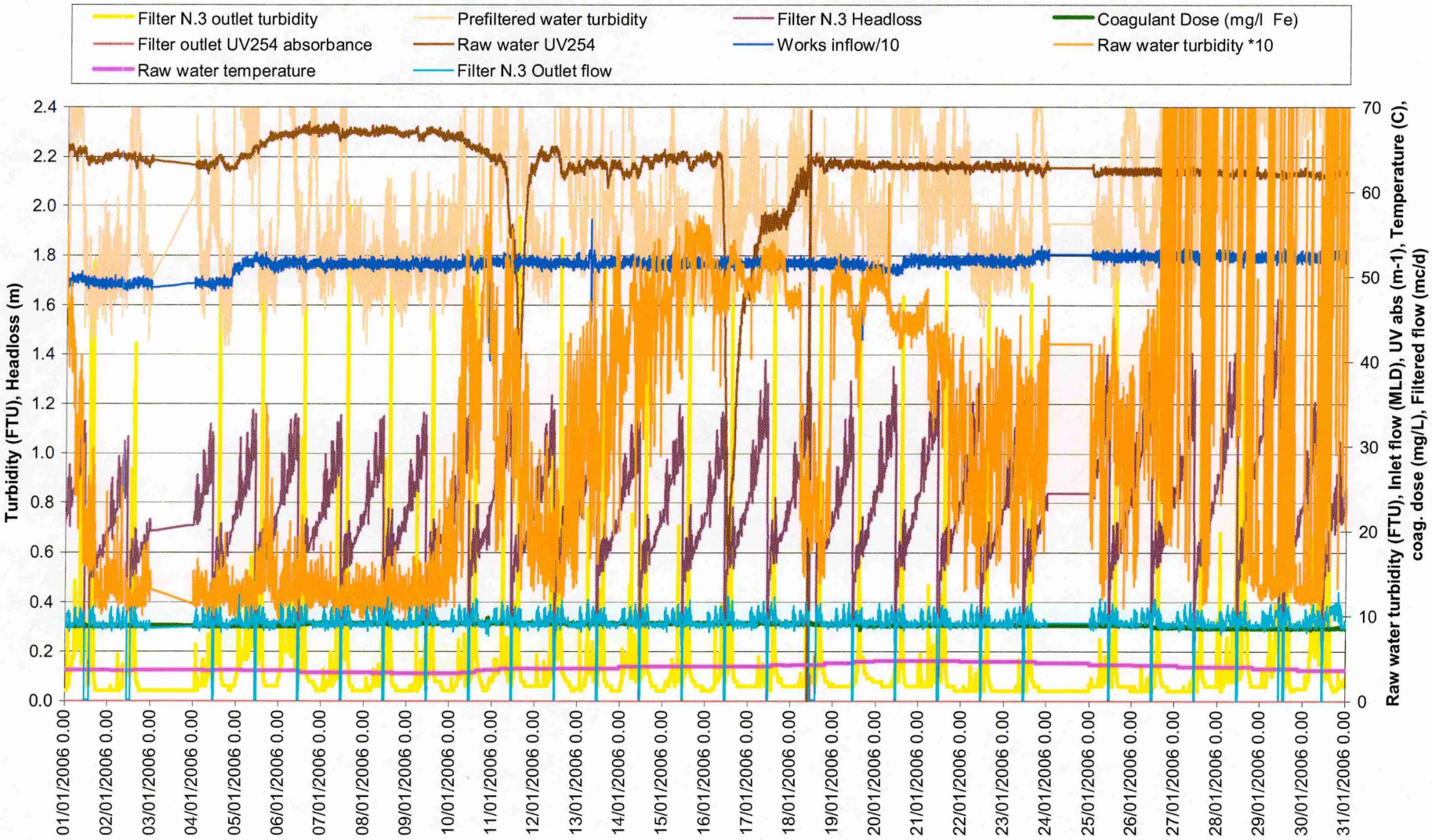
FIXBY – SPRING 2007



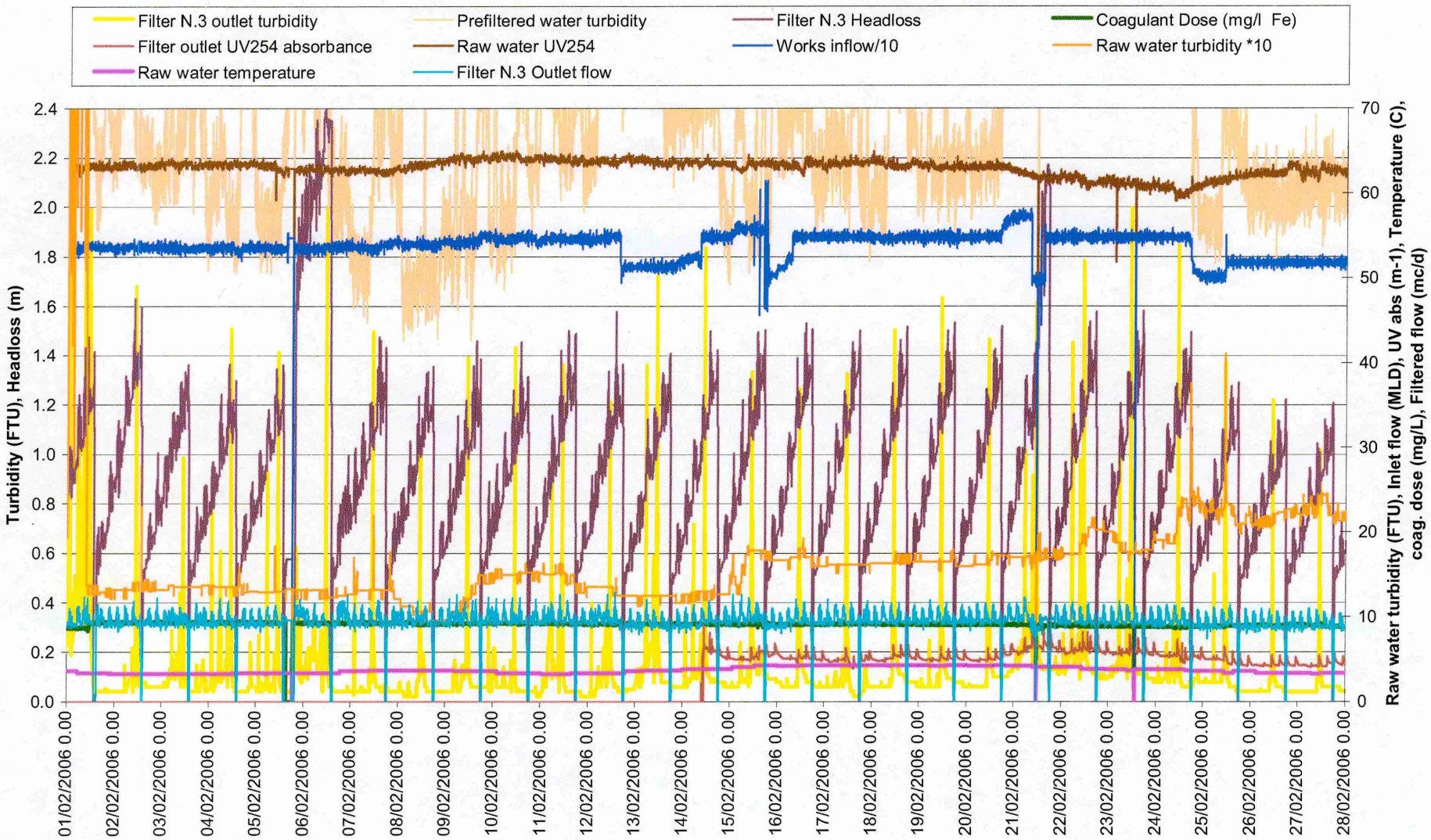
ALBERT – DECEMBER 2005



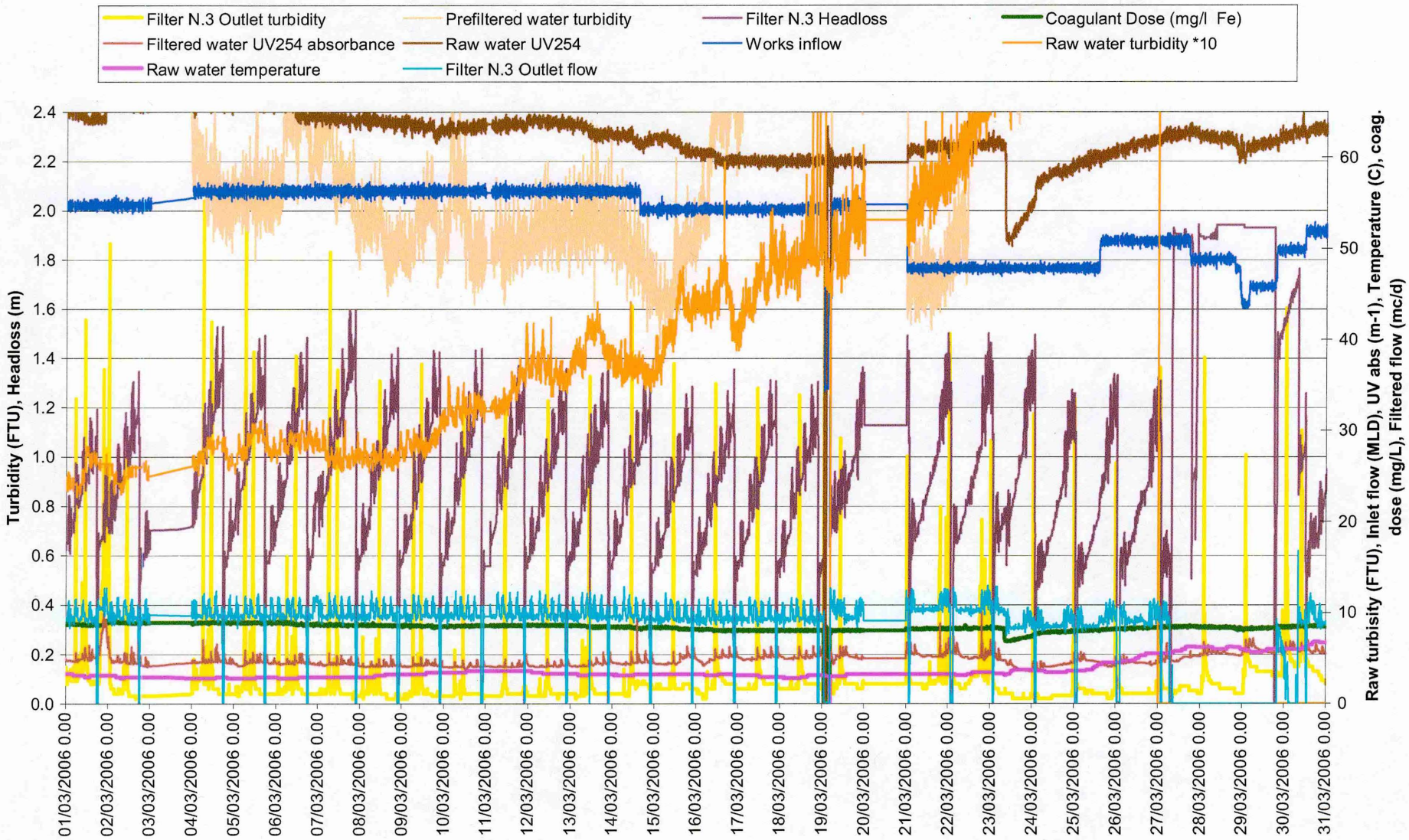
ALBERT – JANUARY 2006



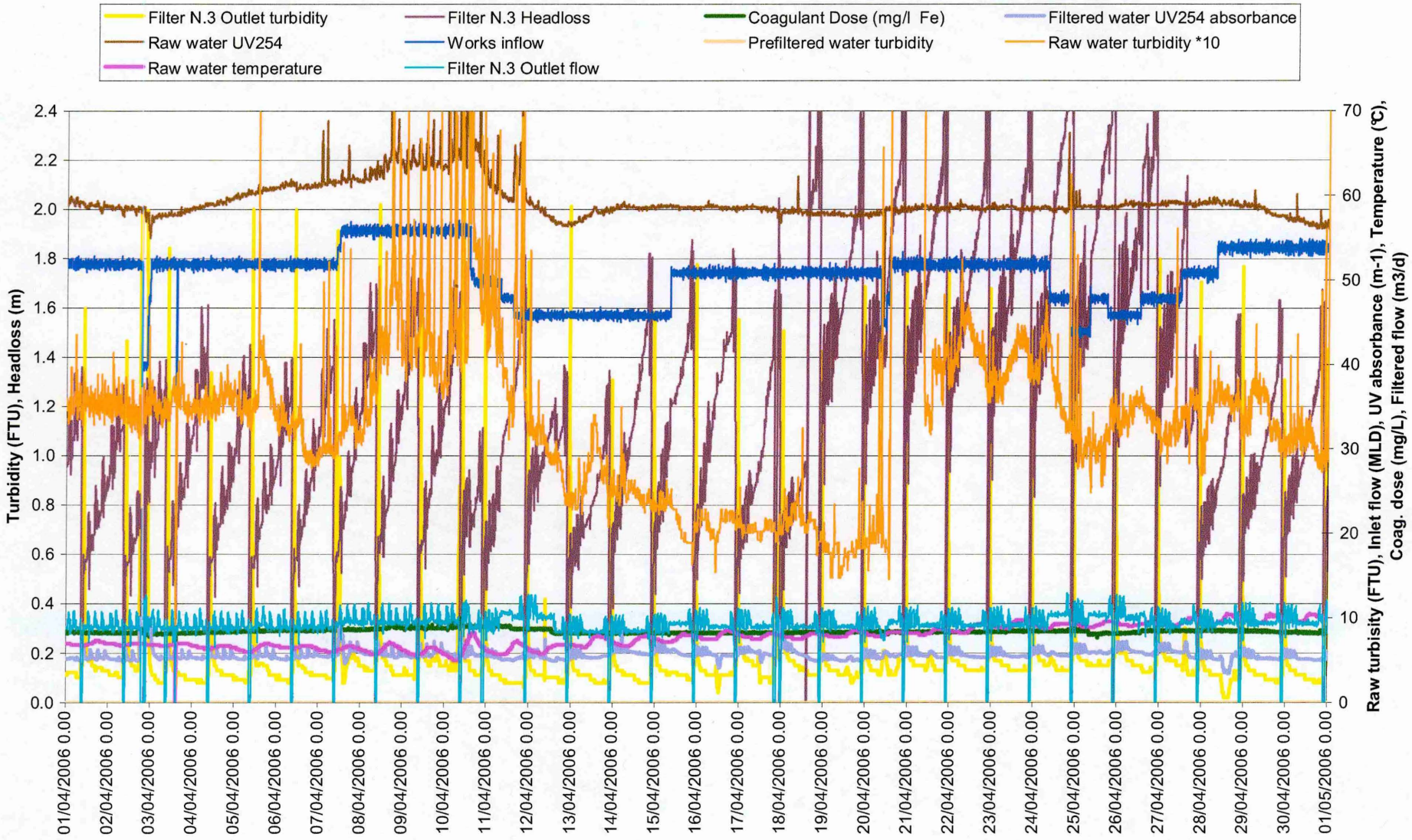
ALBERT – FEBRUARY 2006



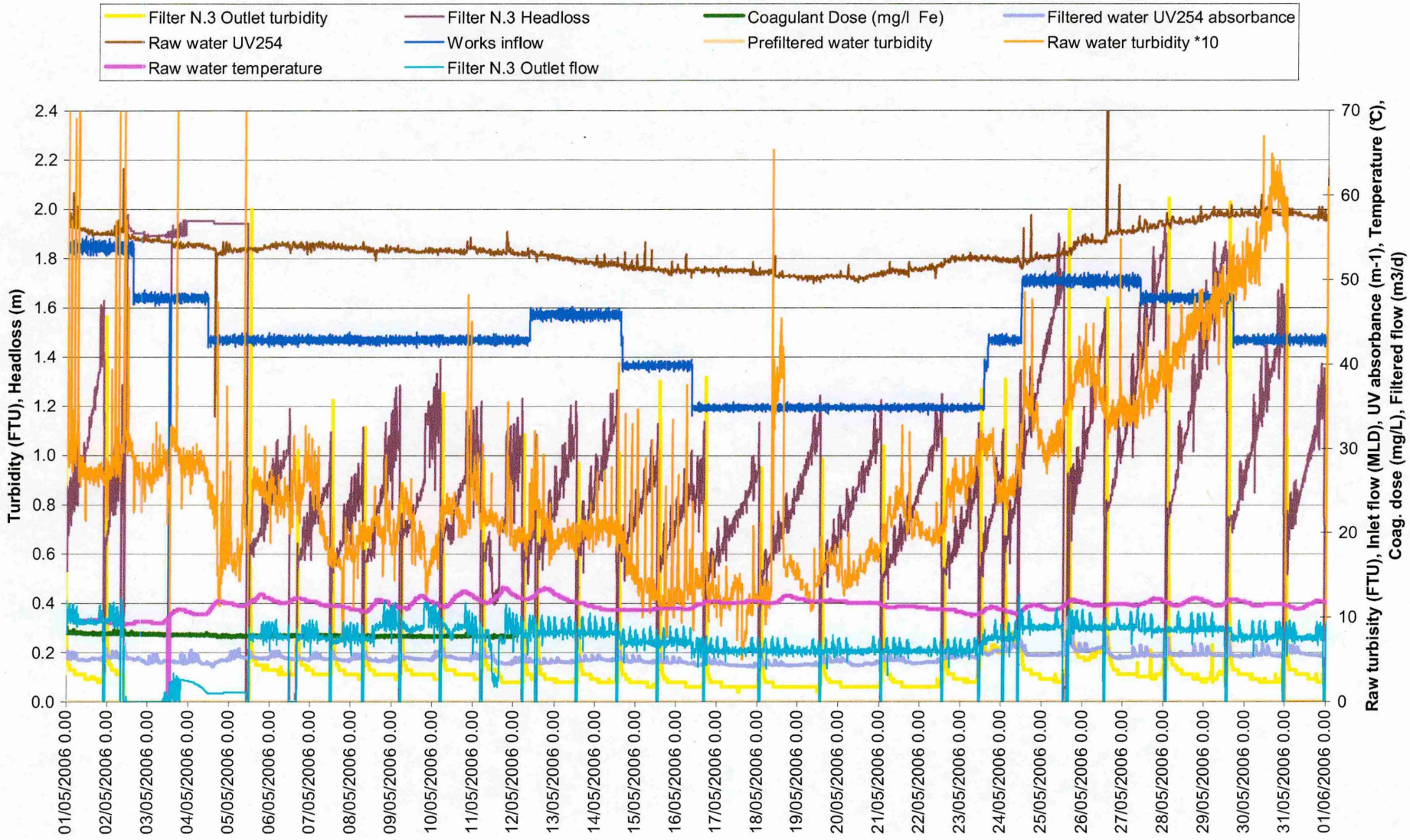
ALBERT – MARCH 2006



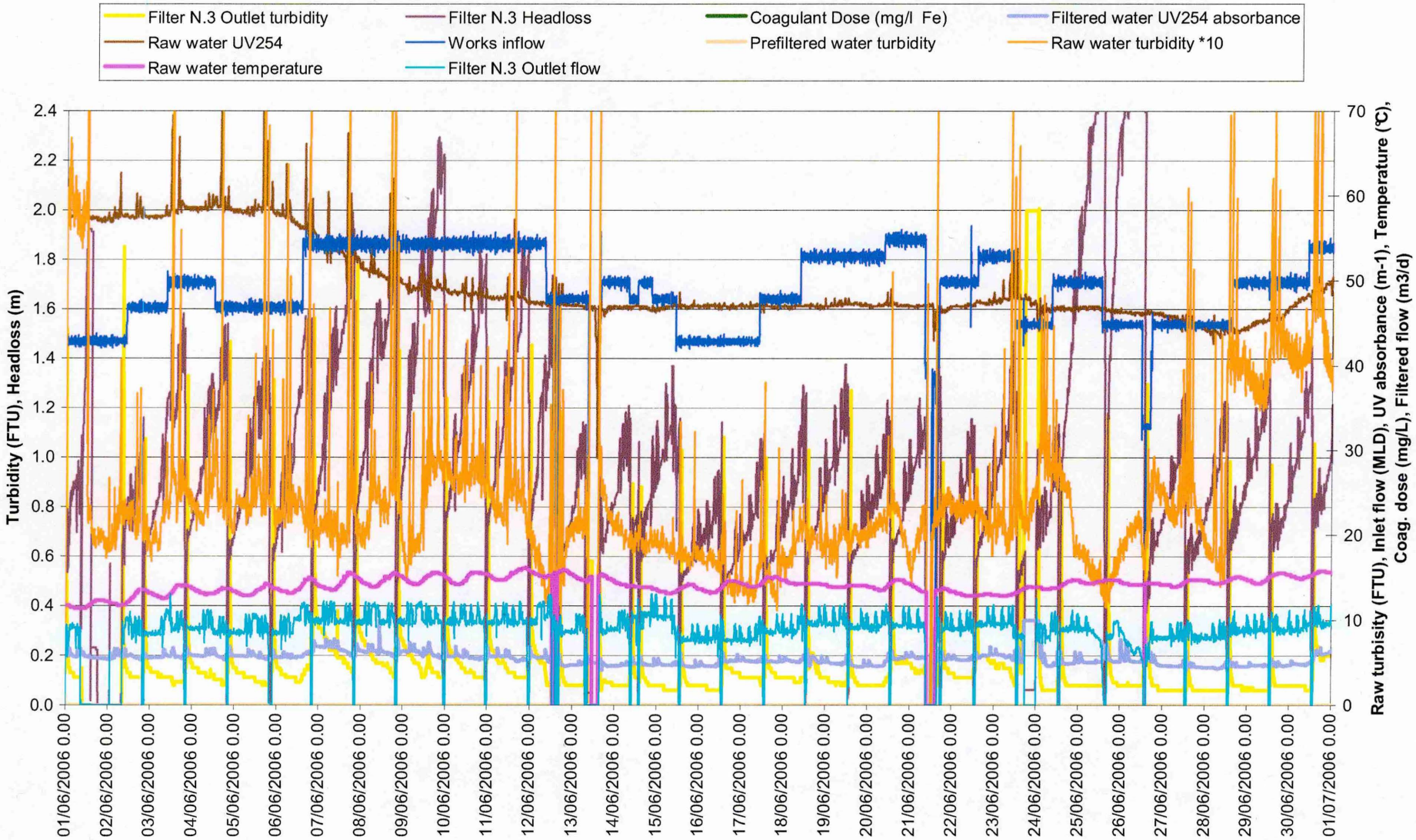
ALBERT – APRIL 2006



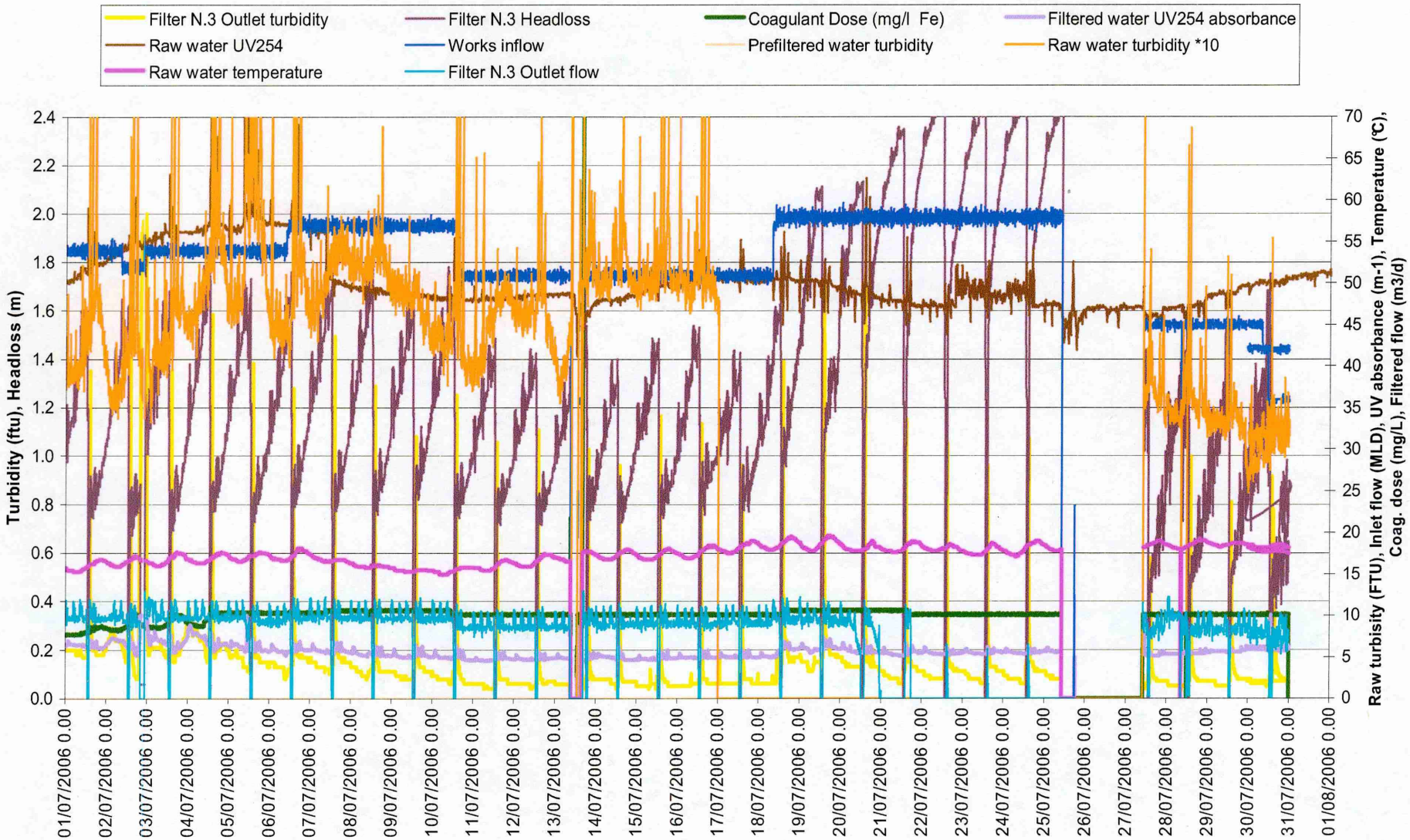
ALBERT – MAY 2006



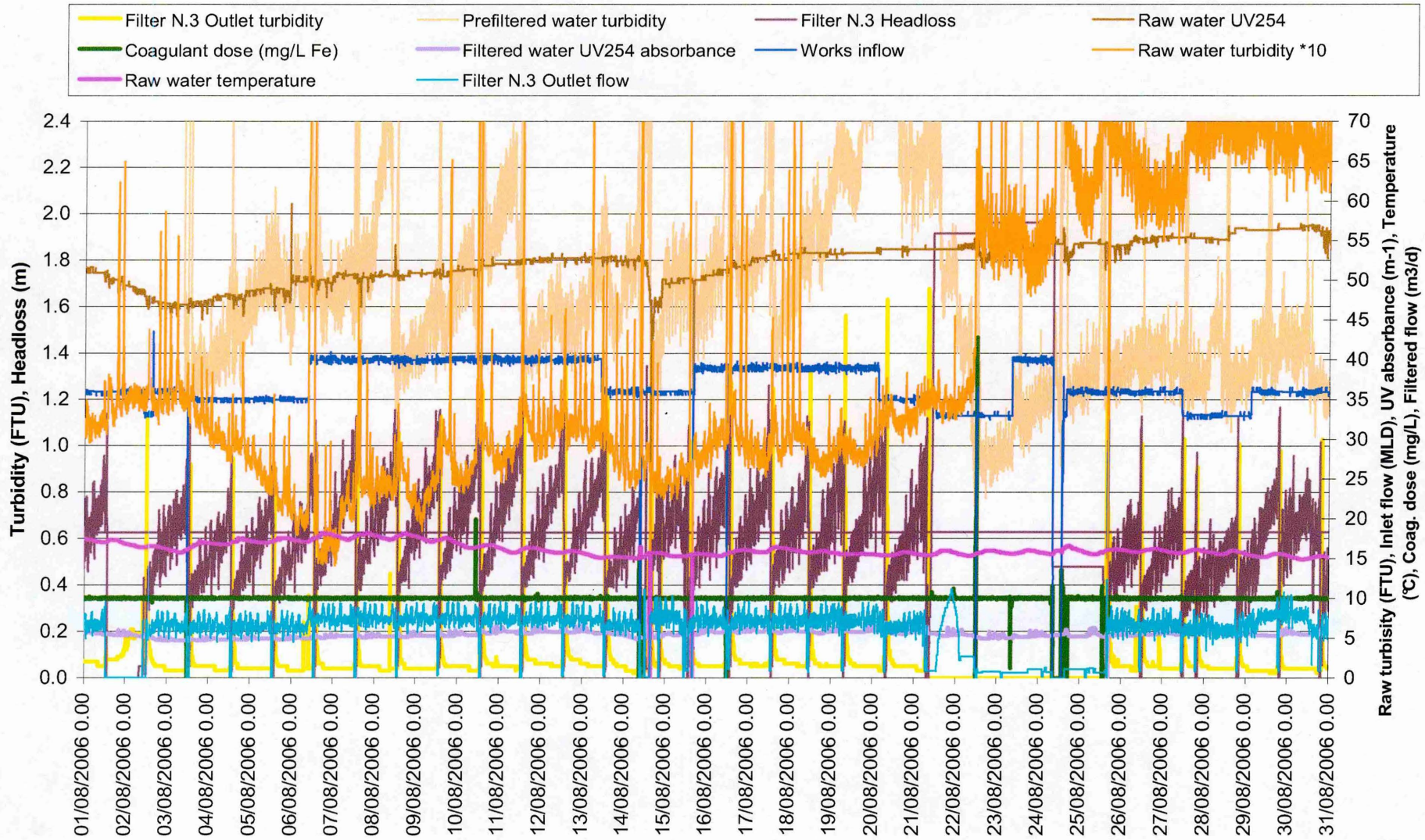
ALBERT – JUNE 2006



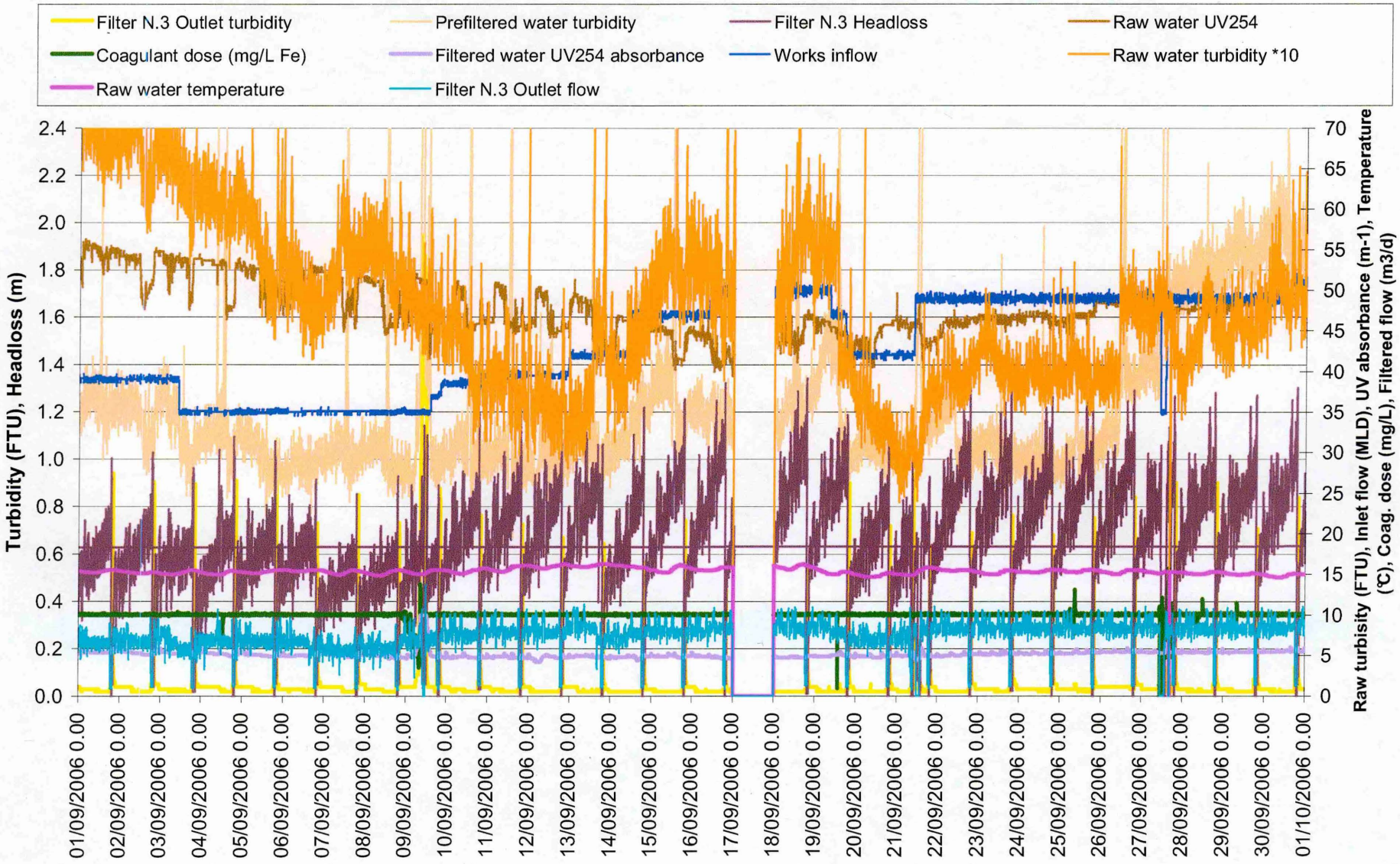
ALBERT – JULY 2006



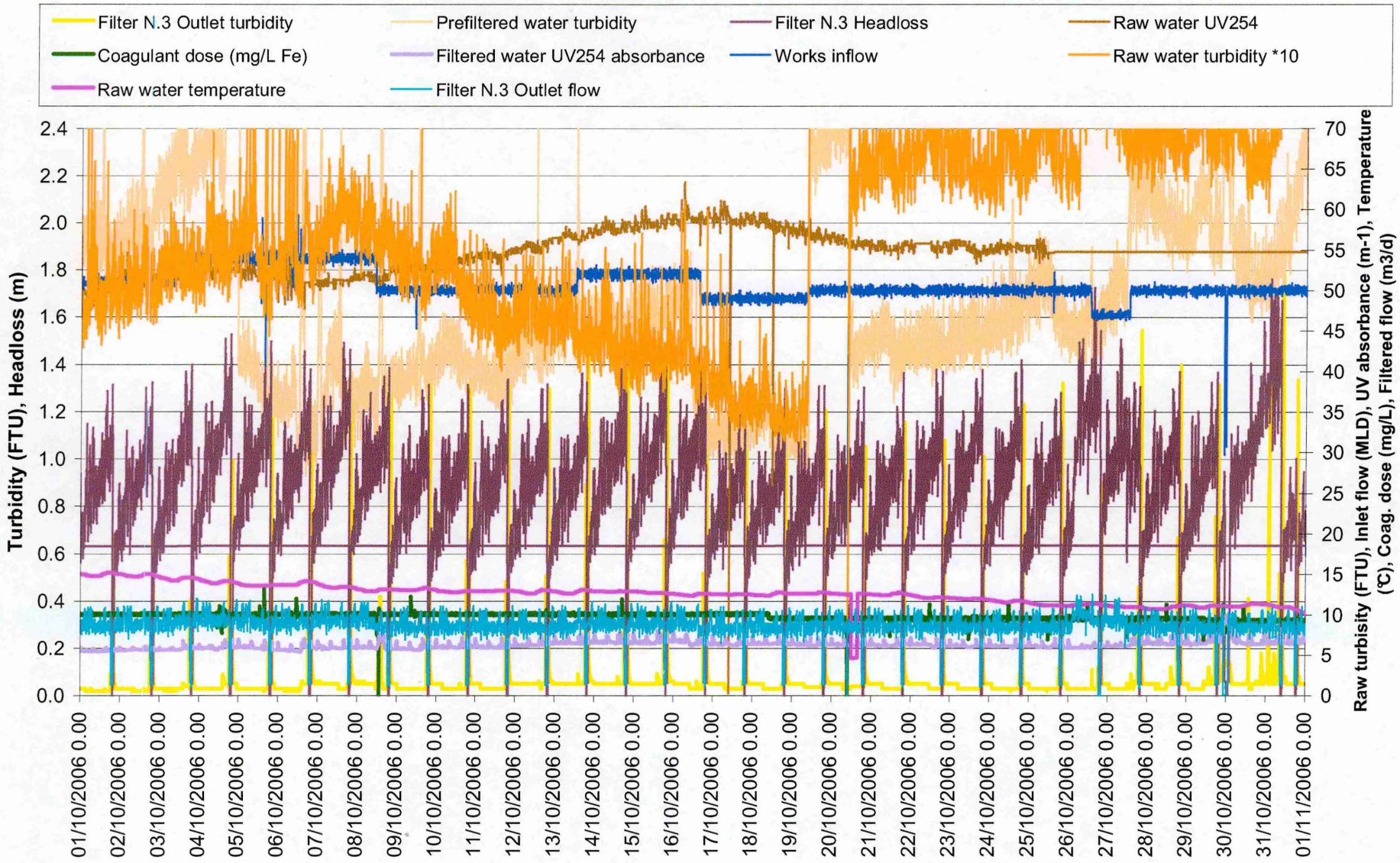
ALBERT – AUGUST 2006



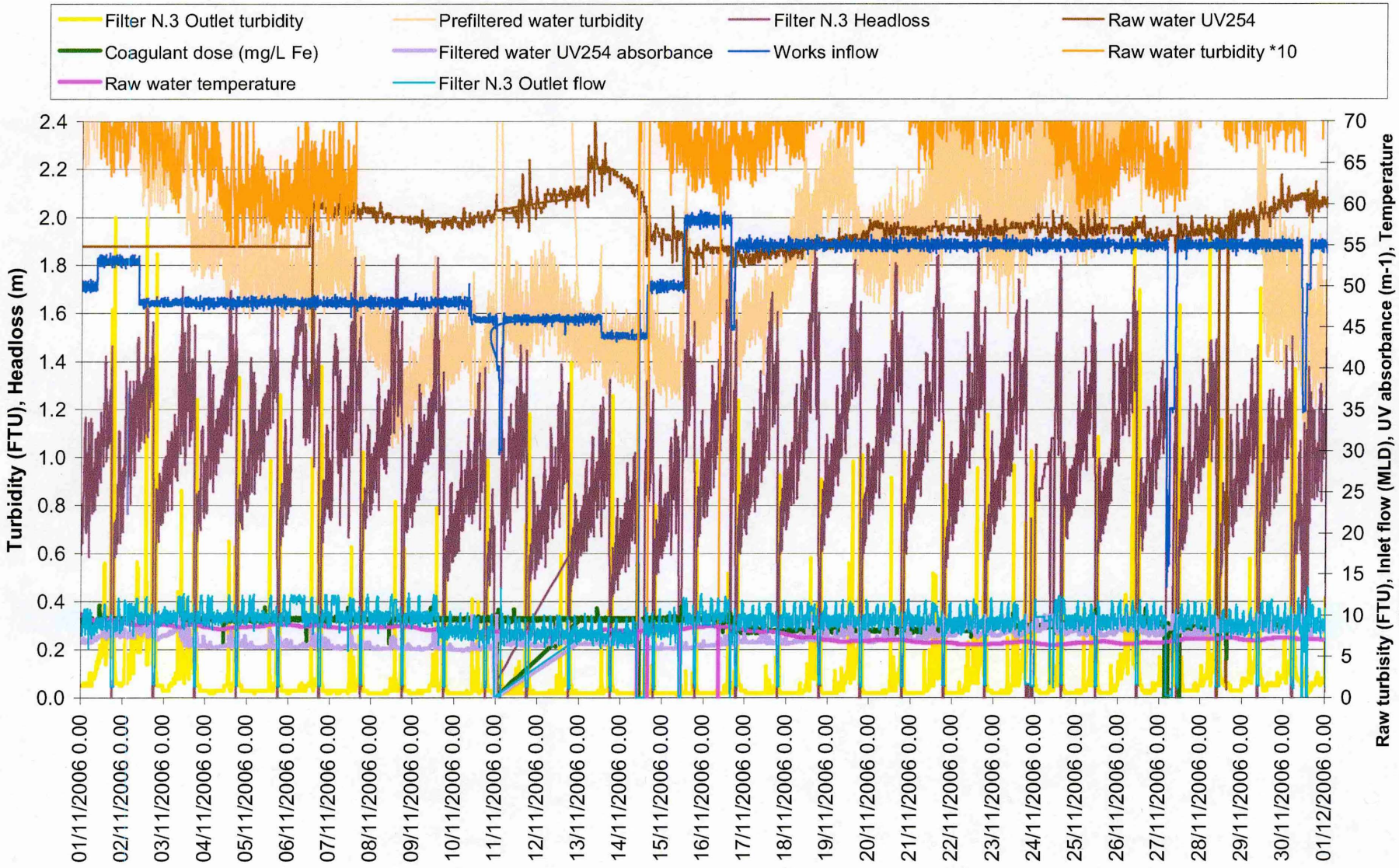
ALBERT – SEPTEMBER 2006

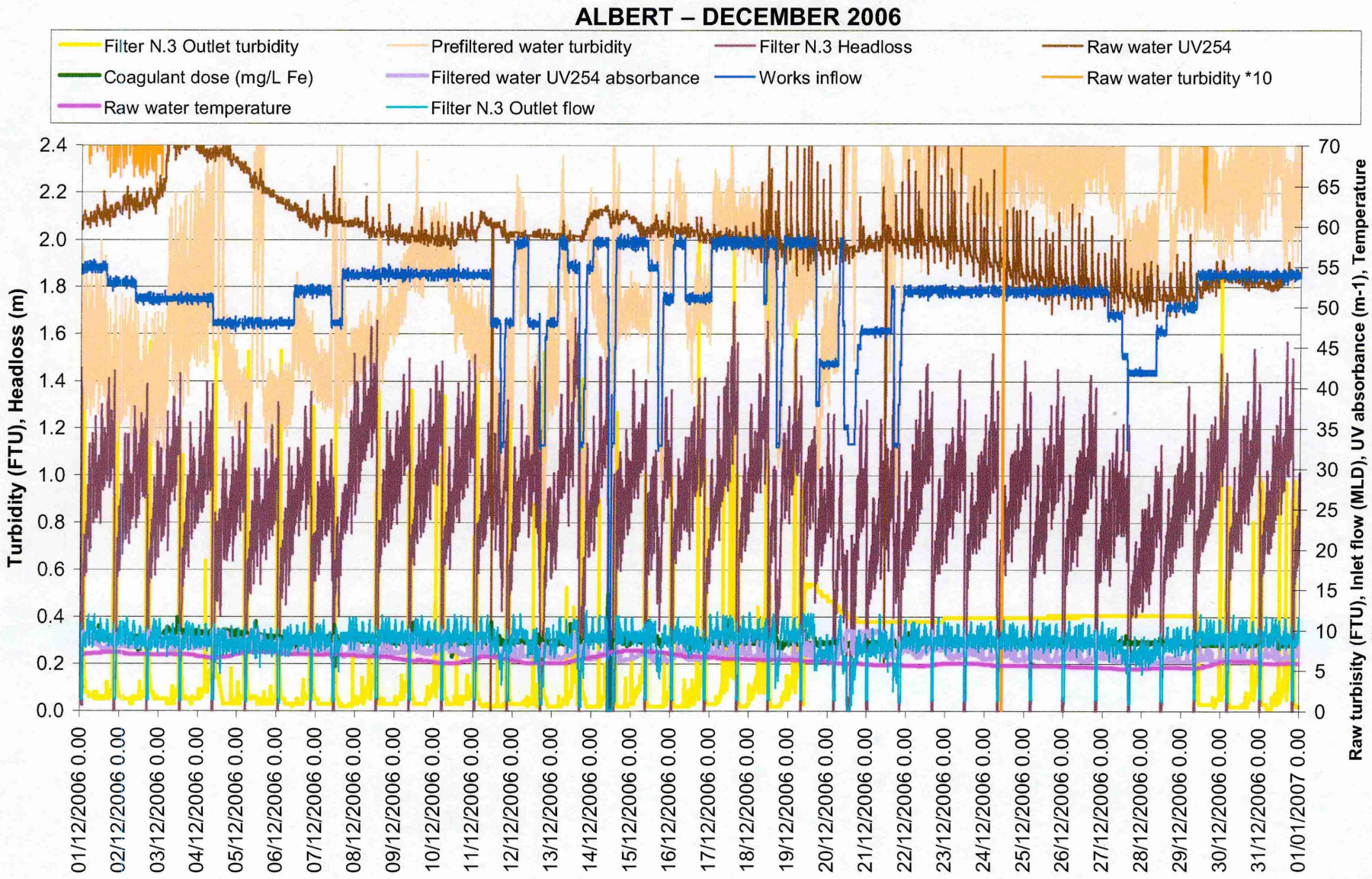


ALBERT – OCTOBER 2006

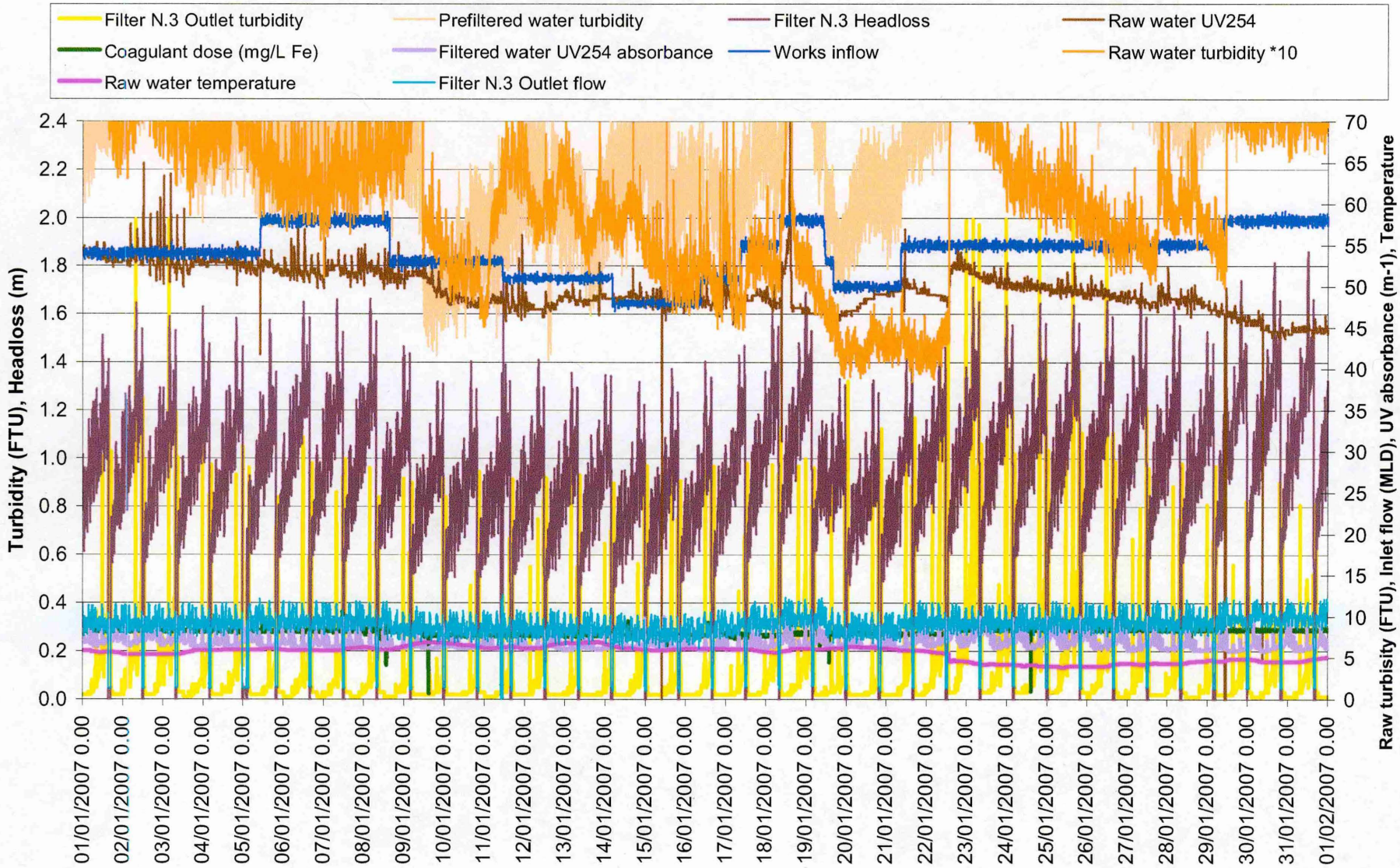


ALBERT – NOVEMBERT 2006

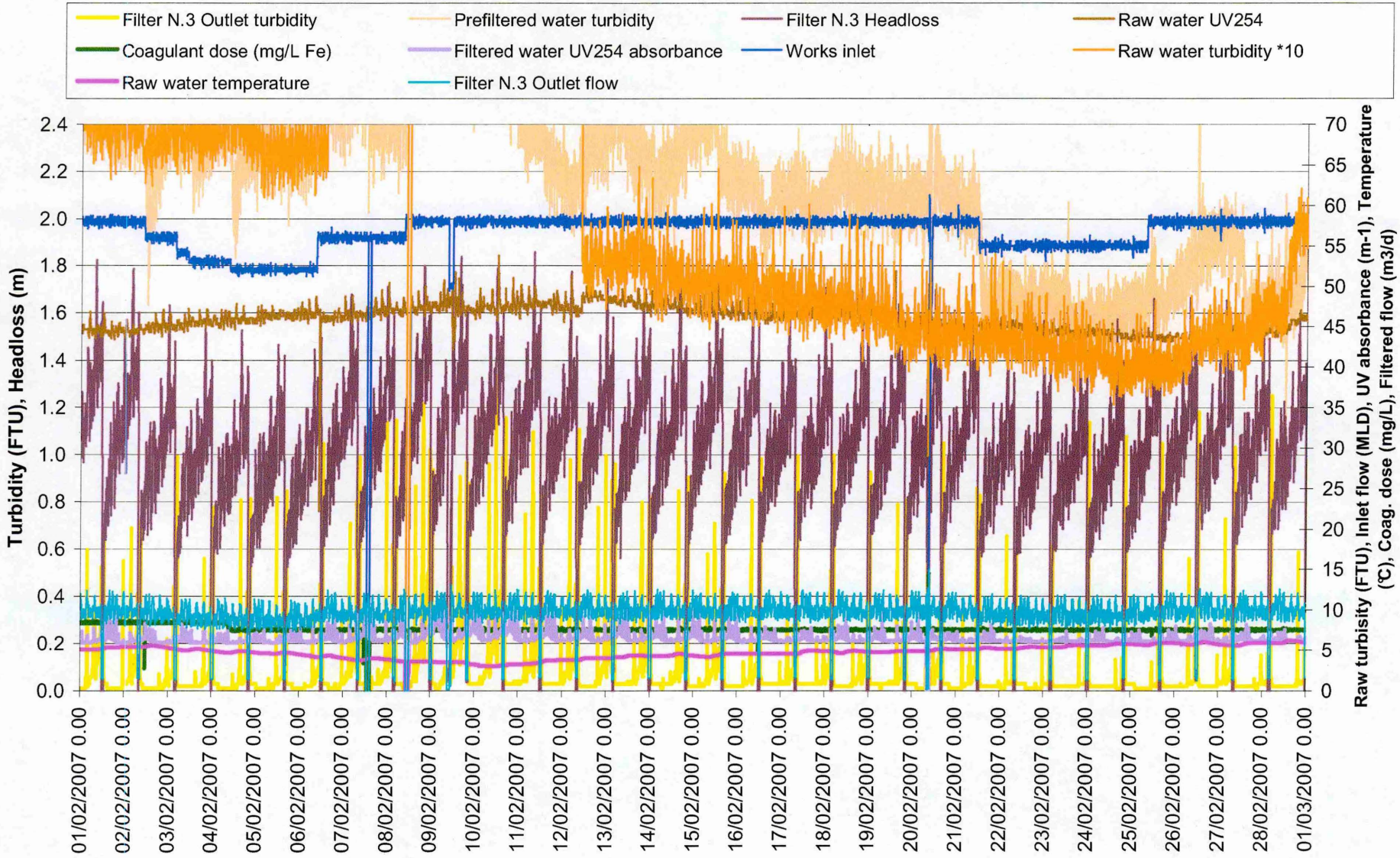



ALBERT – DECEMBER 2006
Filter N.3 Outlet turbidity
Prefiltered water turbidity
Filter N.3 Headloss
Raw water UV254
Coagulant dose (mg/L Fe)
Filtered water UV254 absorbance
Works inflow
Raw water turbidity *10
Raw water temperature
Filter N.3 Outlet flow
Turbidity (FTU), Headloss (m)
Raw turbisity (FTU), Inlet flow (MLD), UV absorbance (m-1), Temperature (°C), Coag. dose (mg/L), Filtered flow (m3/d)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
01/12/2006 0.00
02/12/2006 0.00
03/12/2006 0.00
04/12/2006 0.00
05/12/2006 0.00
06/12/2006 0.00
07/12/2006 0.00
08/12/2006 0.00
09/12/2006 0.00
10/12/2006 0.00
11/12/2006 0.00
12/12/2006 0.00
13/12/2006 0.00
14/12/2006 0.00
15/12/2006 0.00
16/12/2006 0.00
17/12/2006 0.00
18/12/2006 0.00
19/12/2006 0.00
20/12/2006 0.00
21/12/2006 0.00
22/12/2006 0.00
23/12/2006 0.00
24/12/2006 0.00
25/12/2006 0.00
26/12/2006 0.00
27/12/2006 0.00
28/12/2006 0.00
29/12/2006 0.00
30/12/2006 0.00
31/12/2006 0.00
01/01/2007 0.00

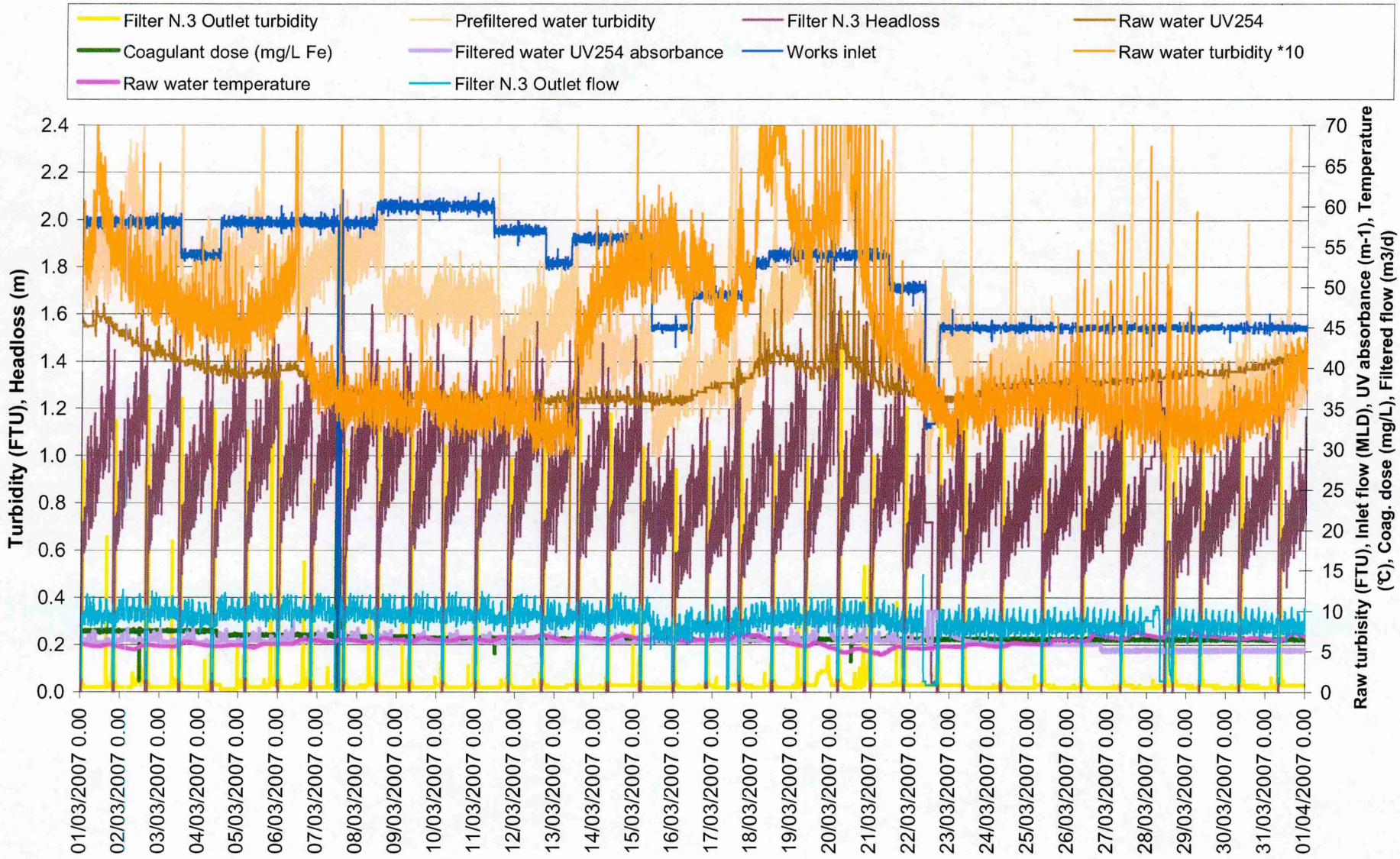
ALBERT – JANUARY 2007



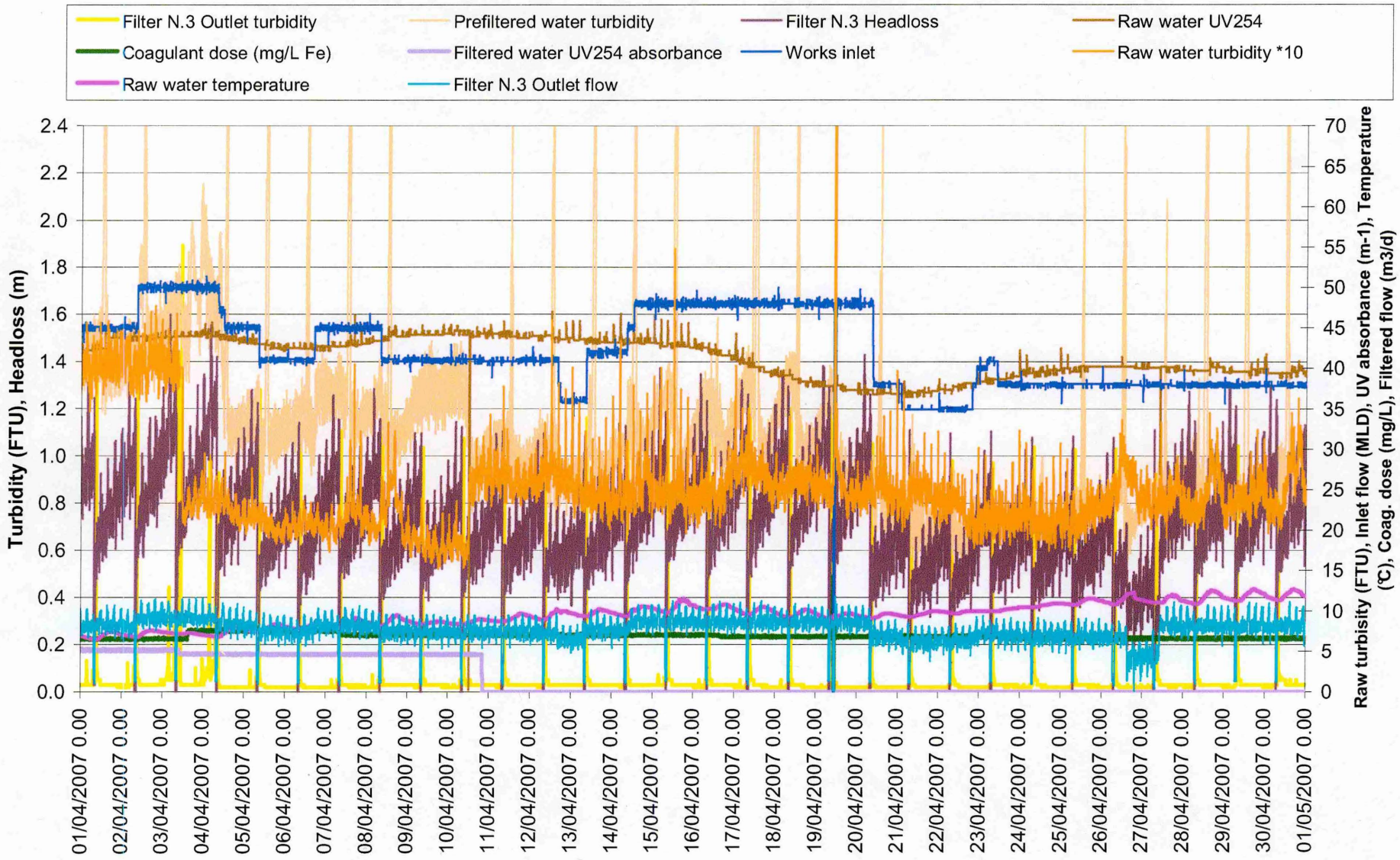
ALBERT – FEBRUARY 2007



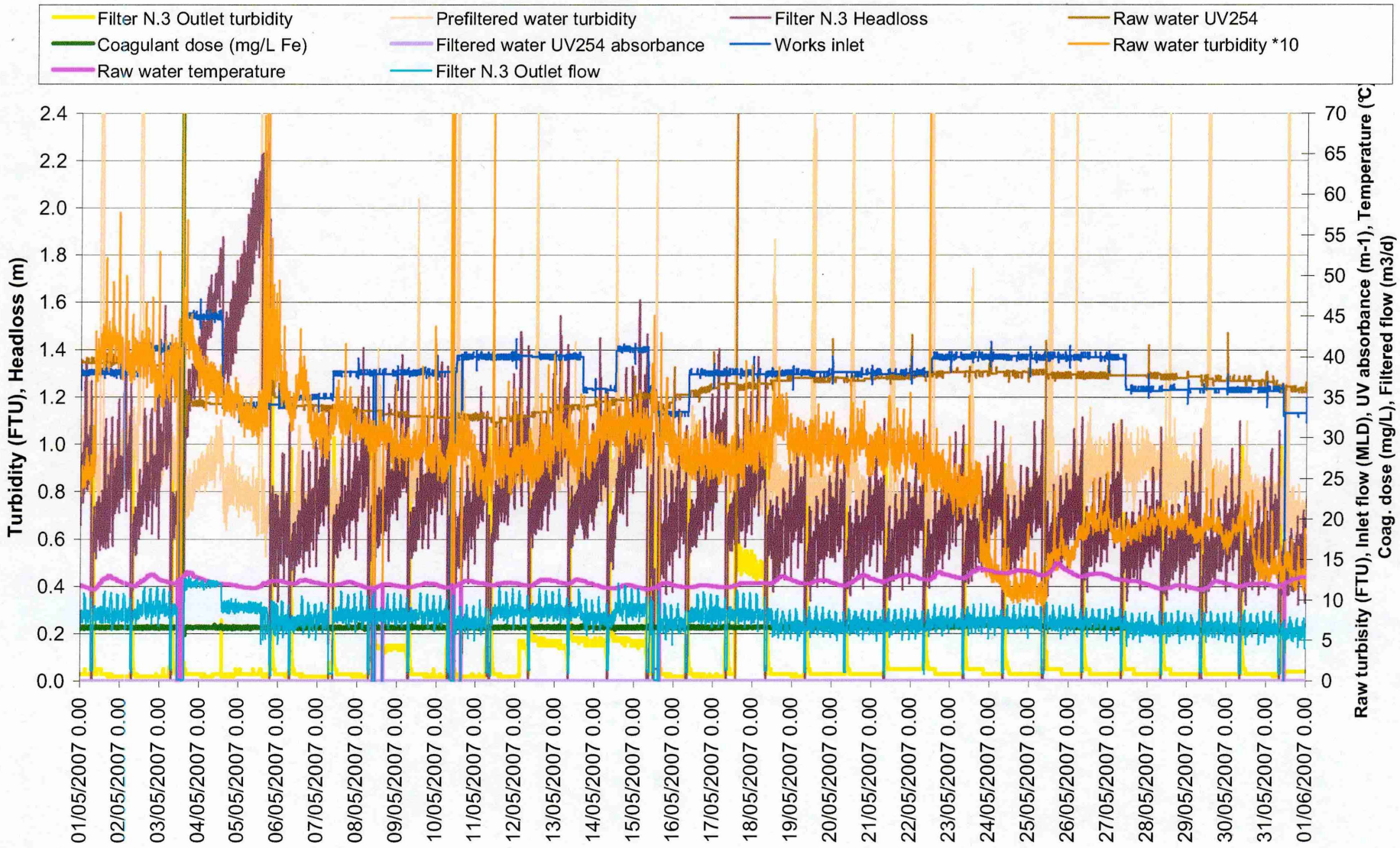
ALBERT – MARCH 2007



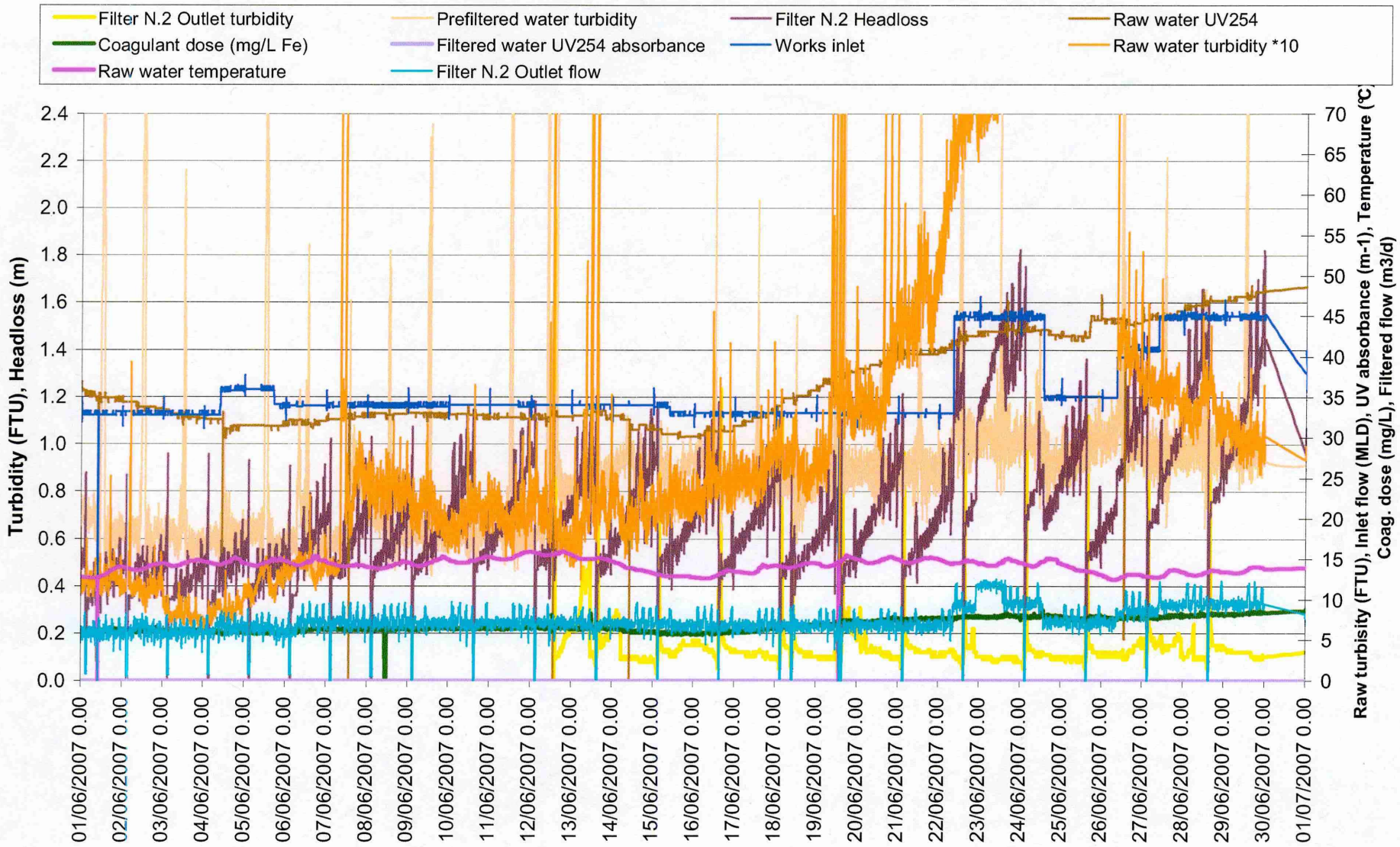
ALBERT – APRIL 2007



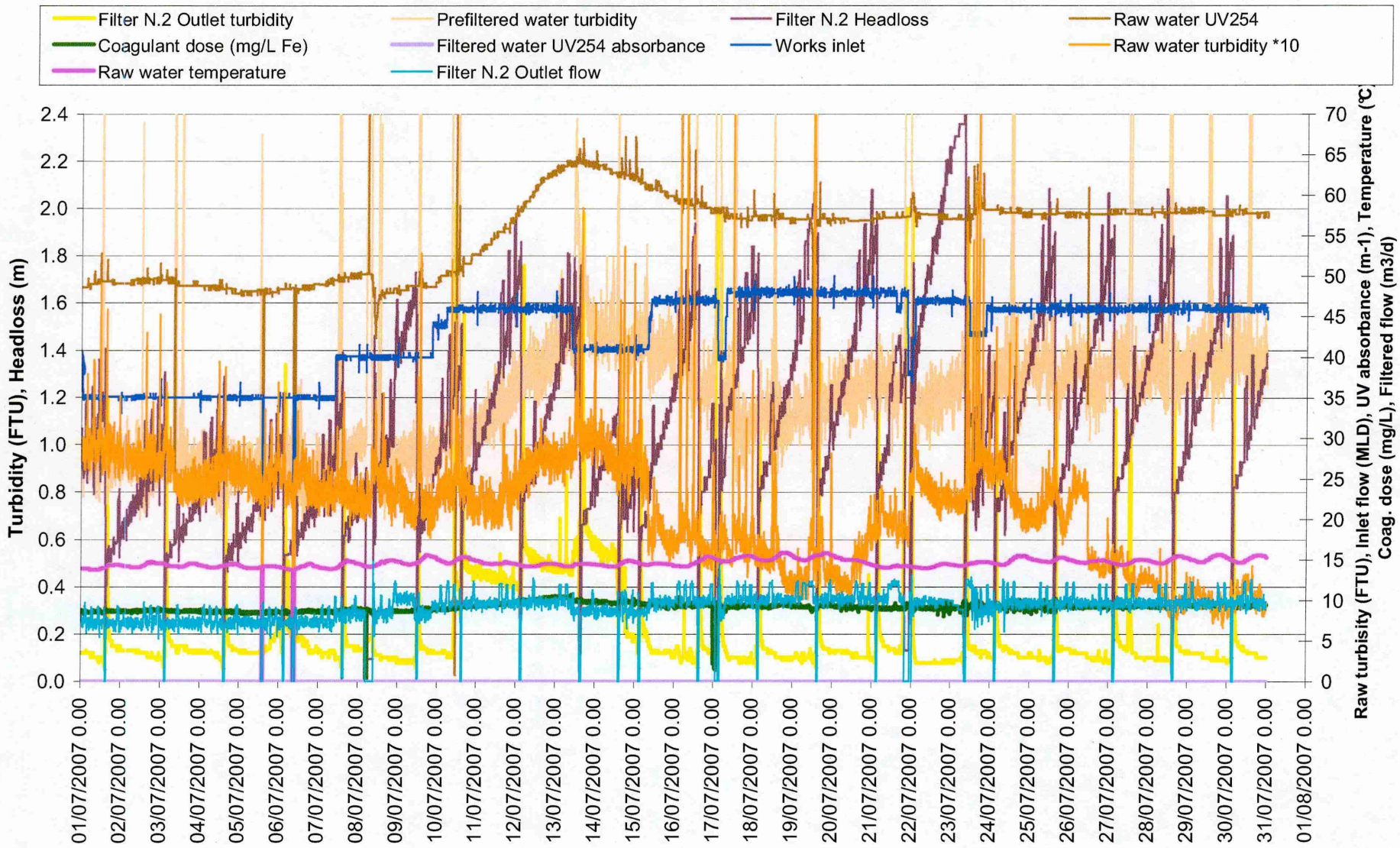
ALBERT – MAY 2007



ALBERT – JUNE 2007



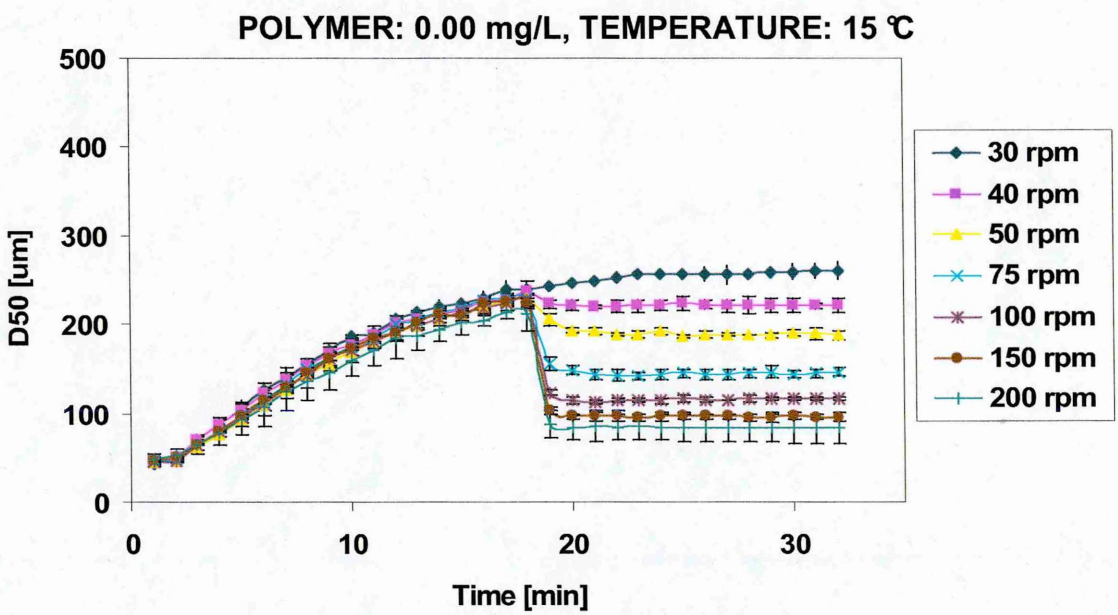
ALBERT – JULY 2007

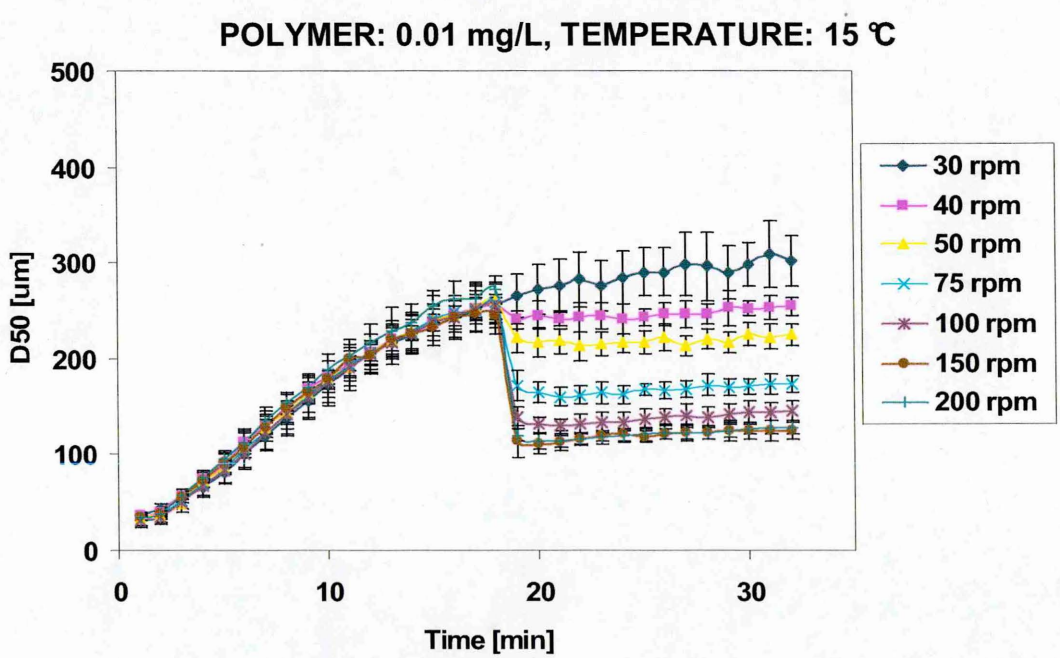


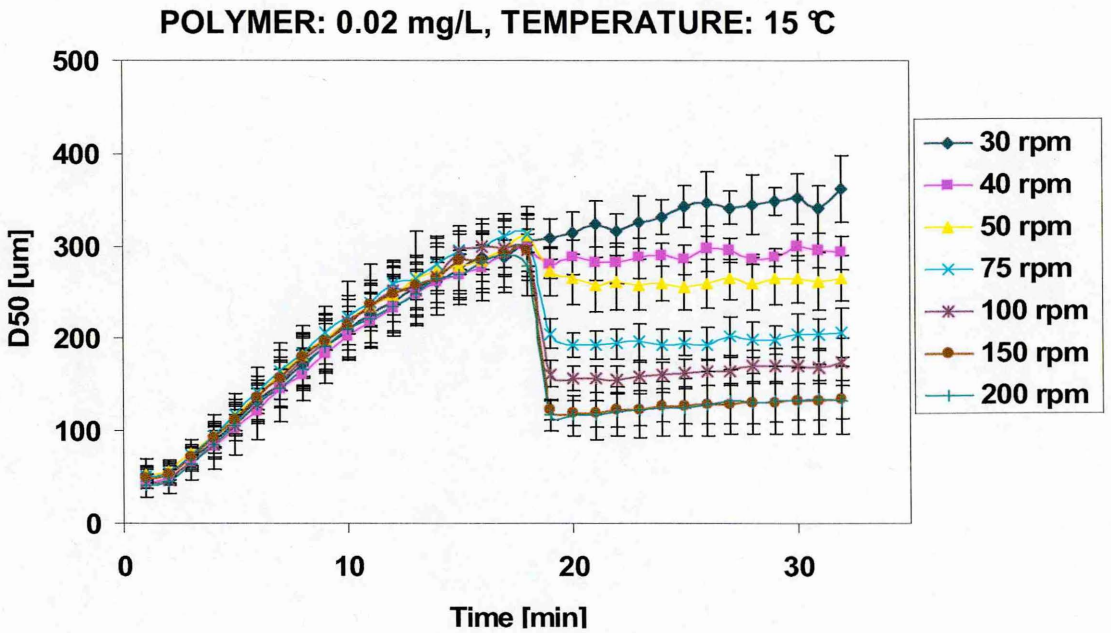
Appendix B – Floc strength

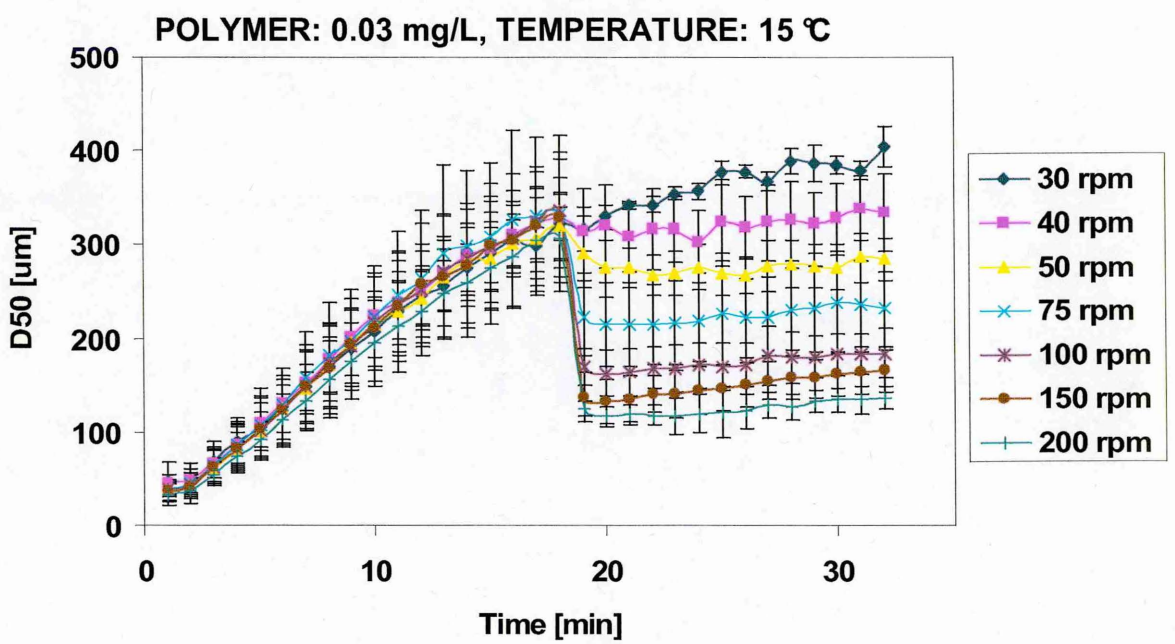
Charts showing floc breakage at different polymer dose and temperature are shown in this Appendix. Both D_{50} and D_{10} are shown in order to highlight the behaviour of small particles. Floc strength measurement were repeated with the samples collected in February and September.

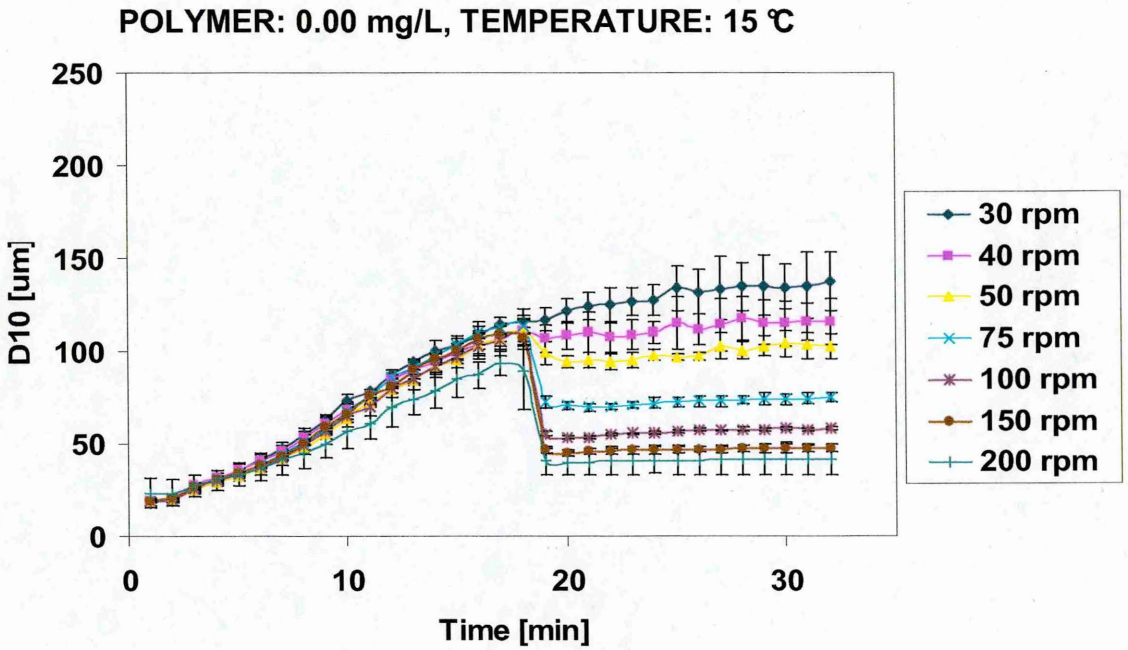
- Floc strength for February sample

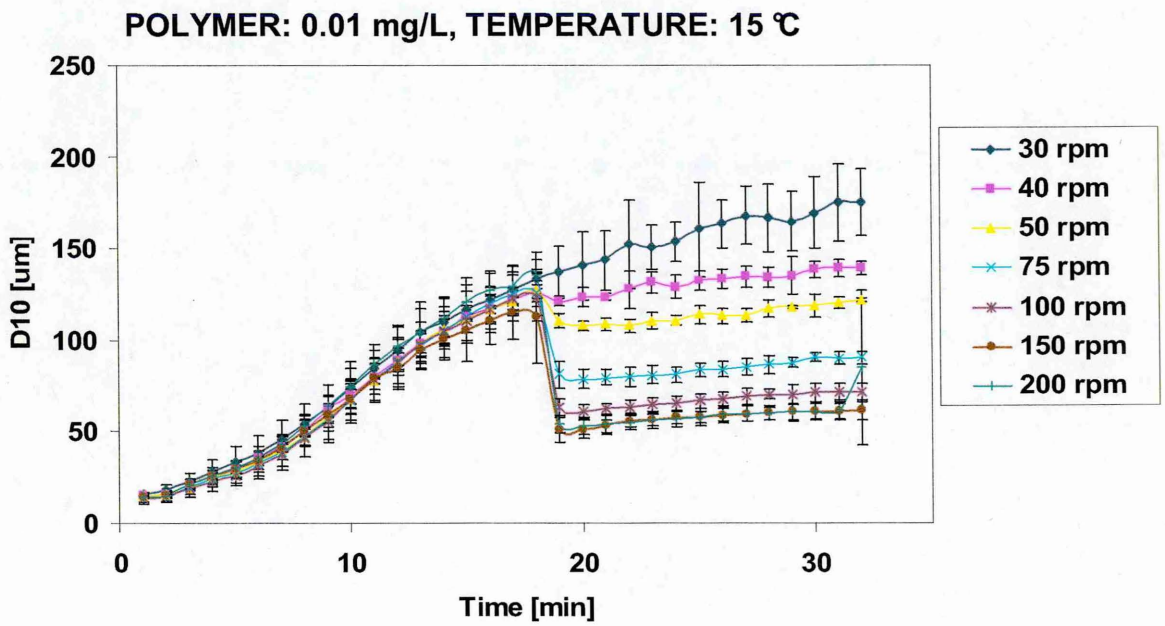


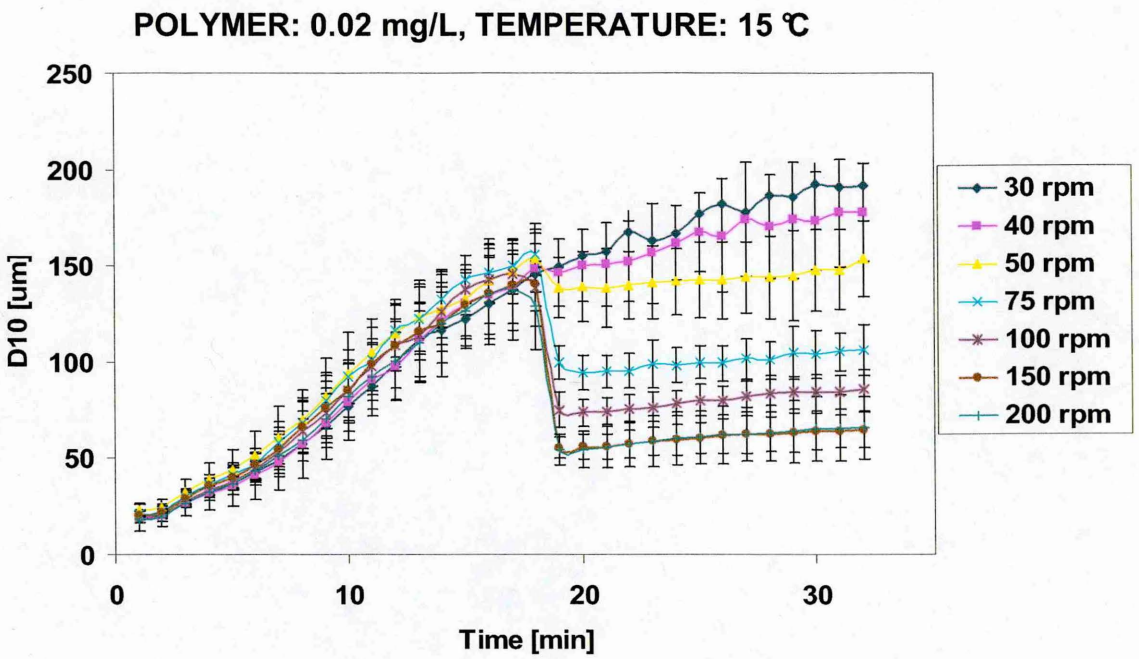


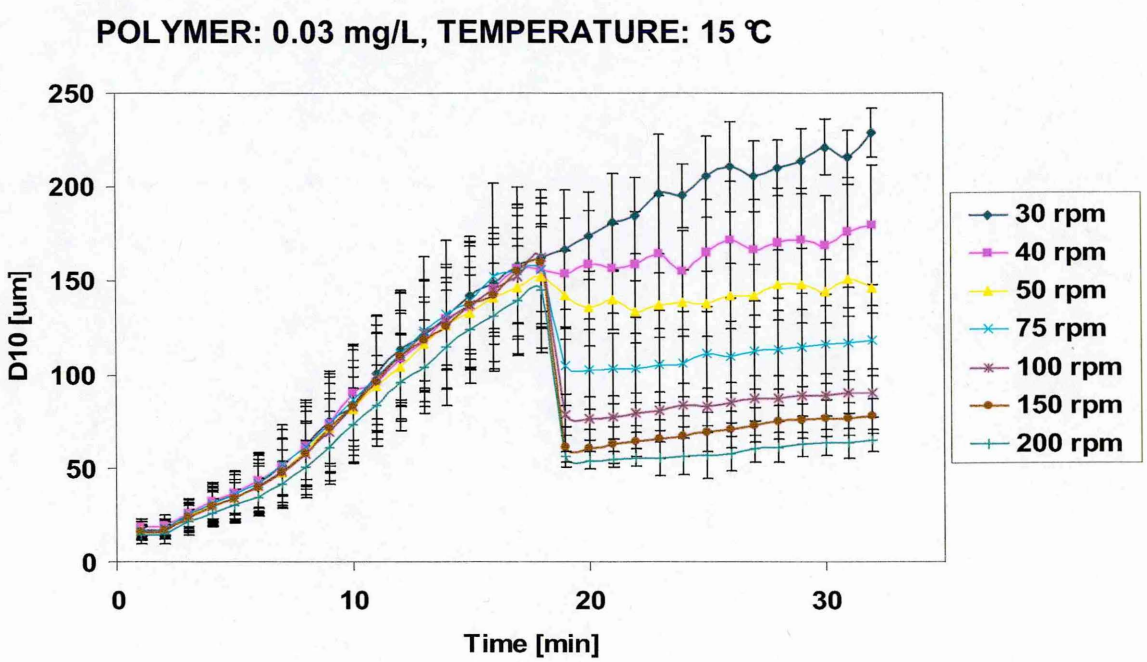

POLYMER: 0.02 mg/L, TEMPERATURE: 15 ℃
D50 [um]
500
400
300
200
100
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm


POLYMER: 0.03 mg/L, TEMPERATURE: 15 ℃
D50 [um]
500
400
300
200
100
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

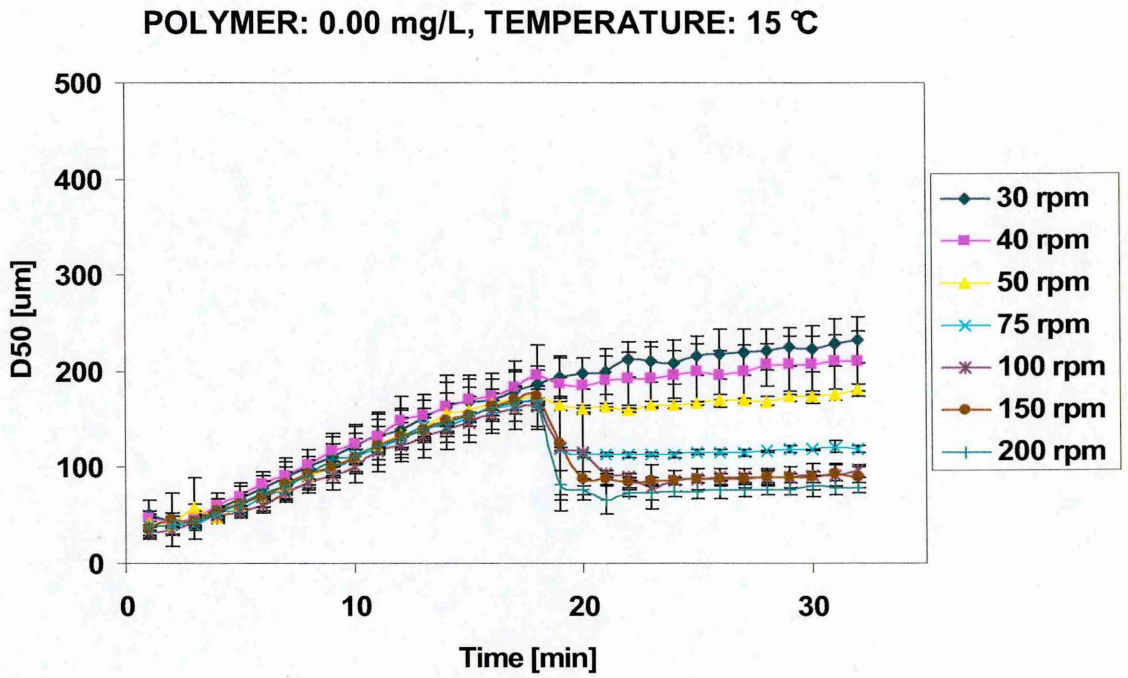

POLYMER: 0.00 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

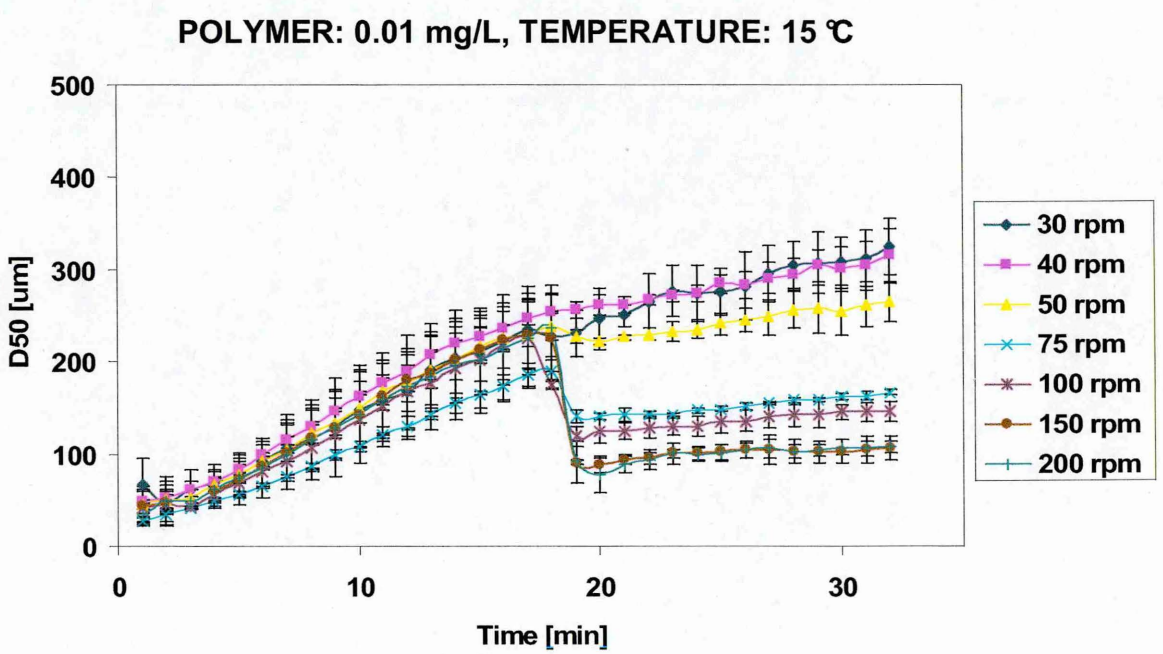

POLYMER: 0.01 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

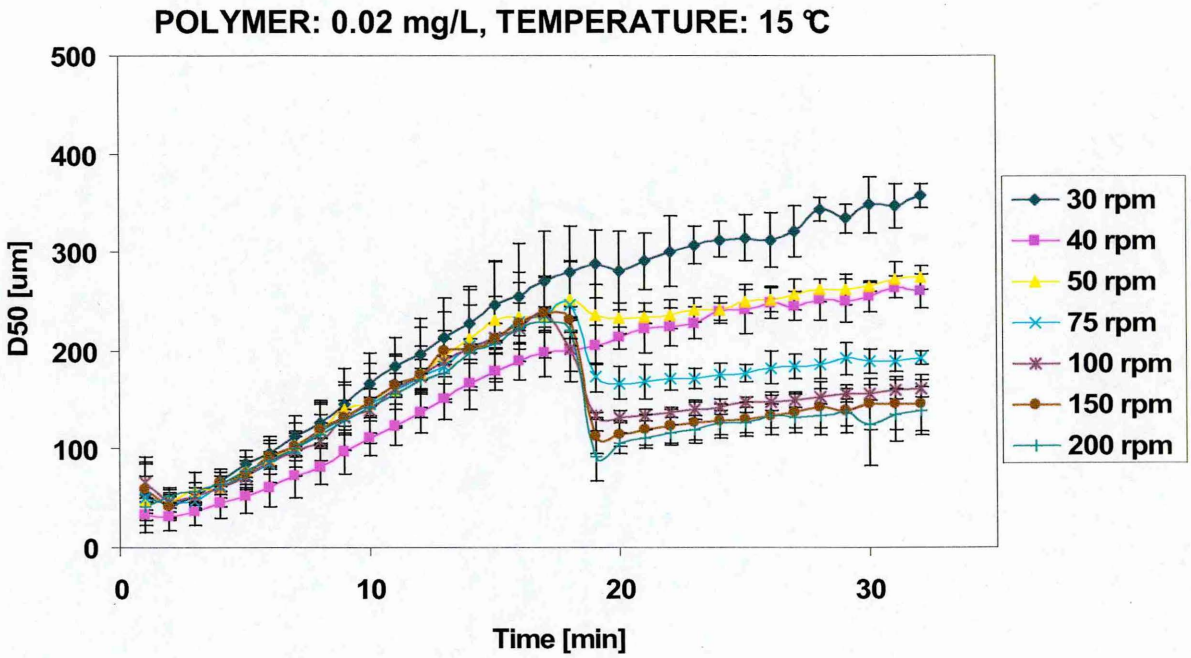

POLYMER: 0.02 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

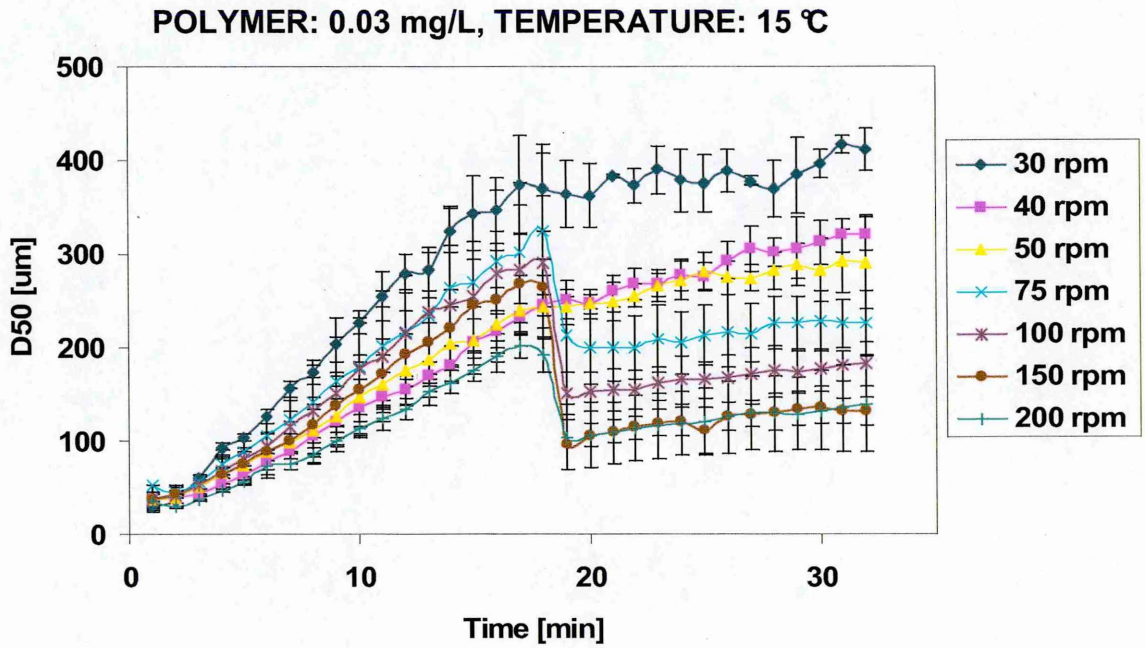

POLYMER: 0.03 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

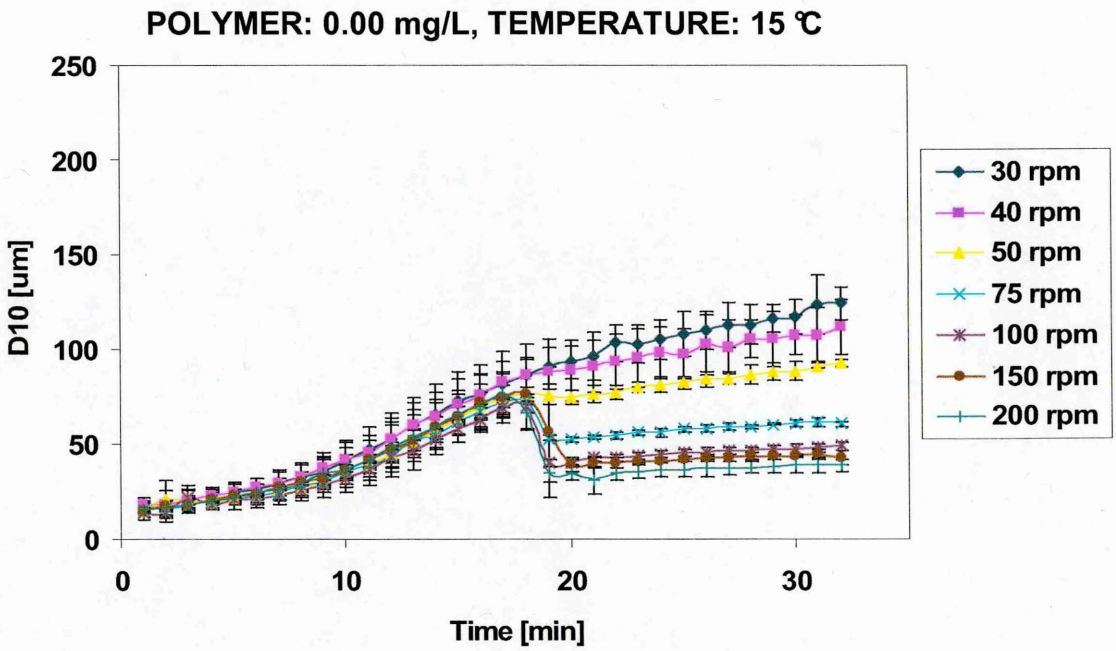
- Floc strength for September sample

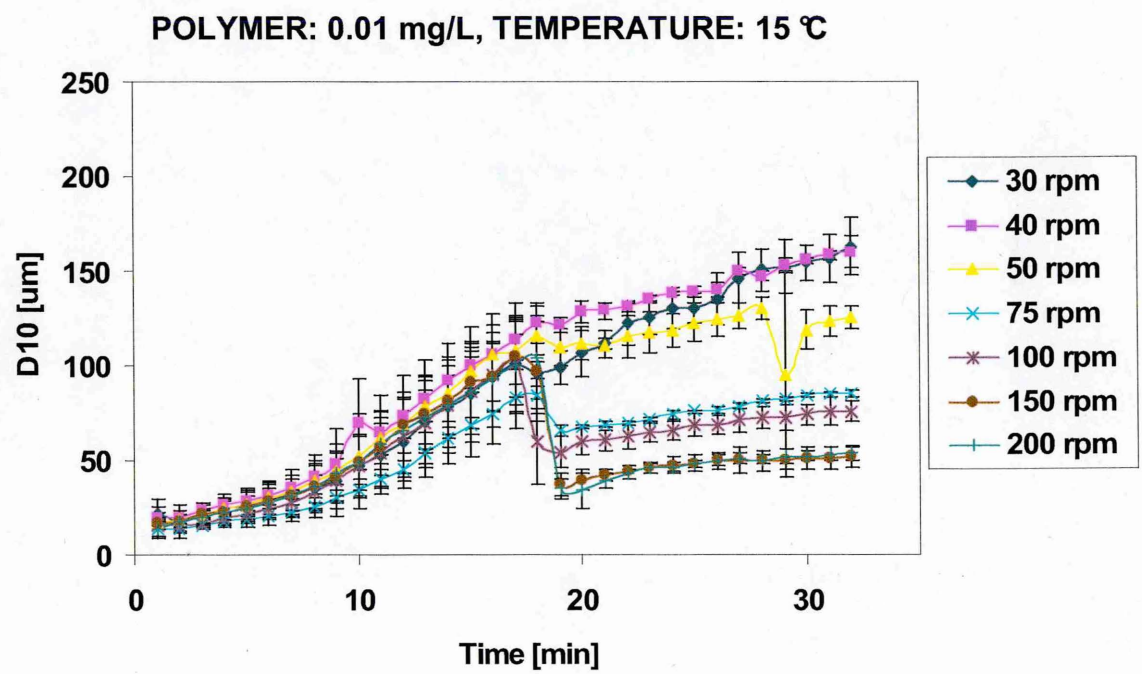


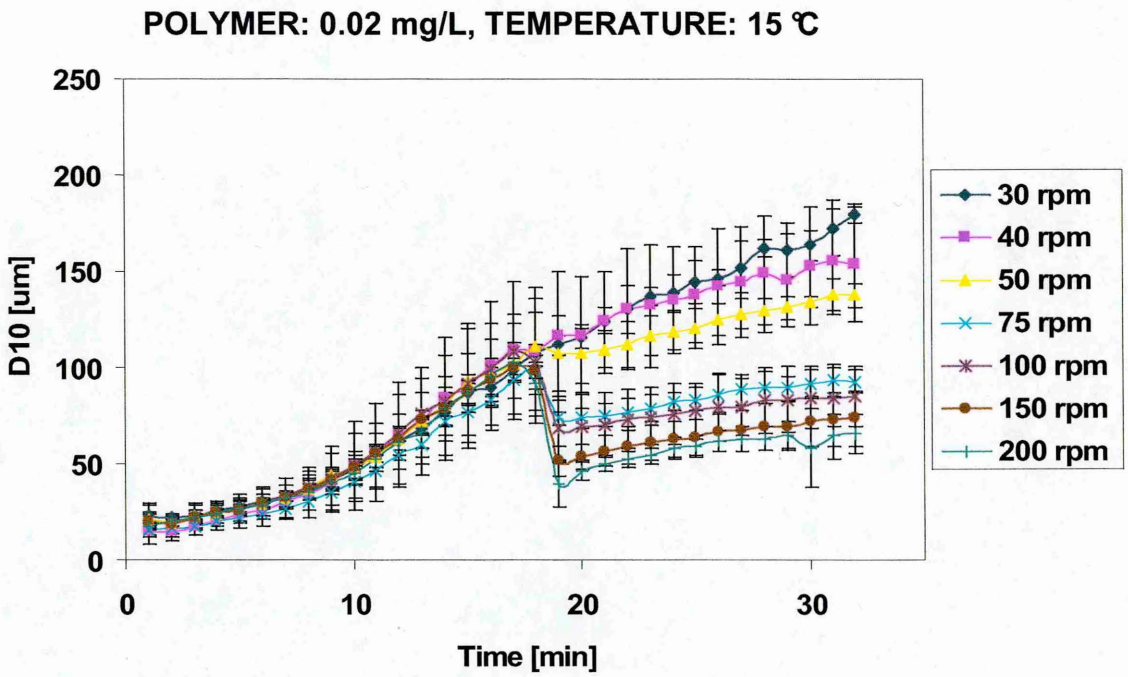


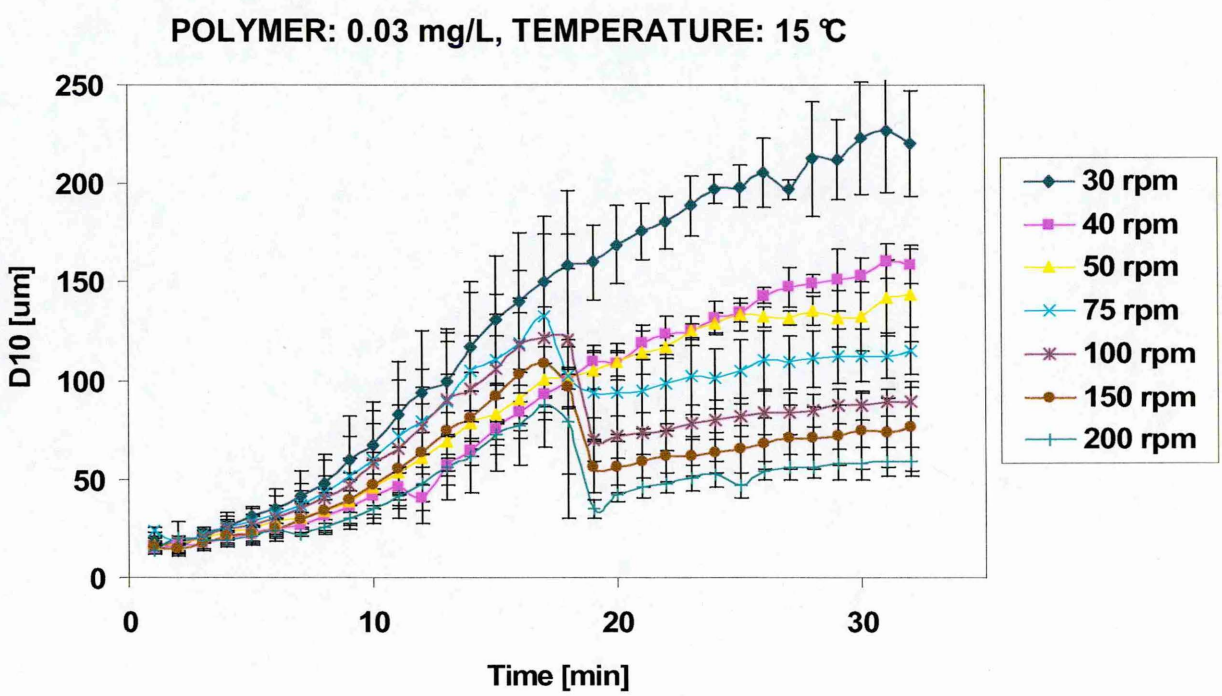

POLYMER: 0.02 mg/L, TEMPERATURE: 15 ℃
D50 [um]
500
400
300
200
100
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm


POLYMER: 0.03 mg/L, TEMPERATURE: 15 ℃
D50 [um]
500
400
300
200
100
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

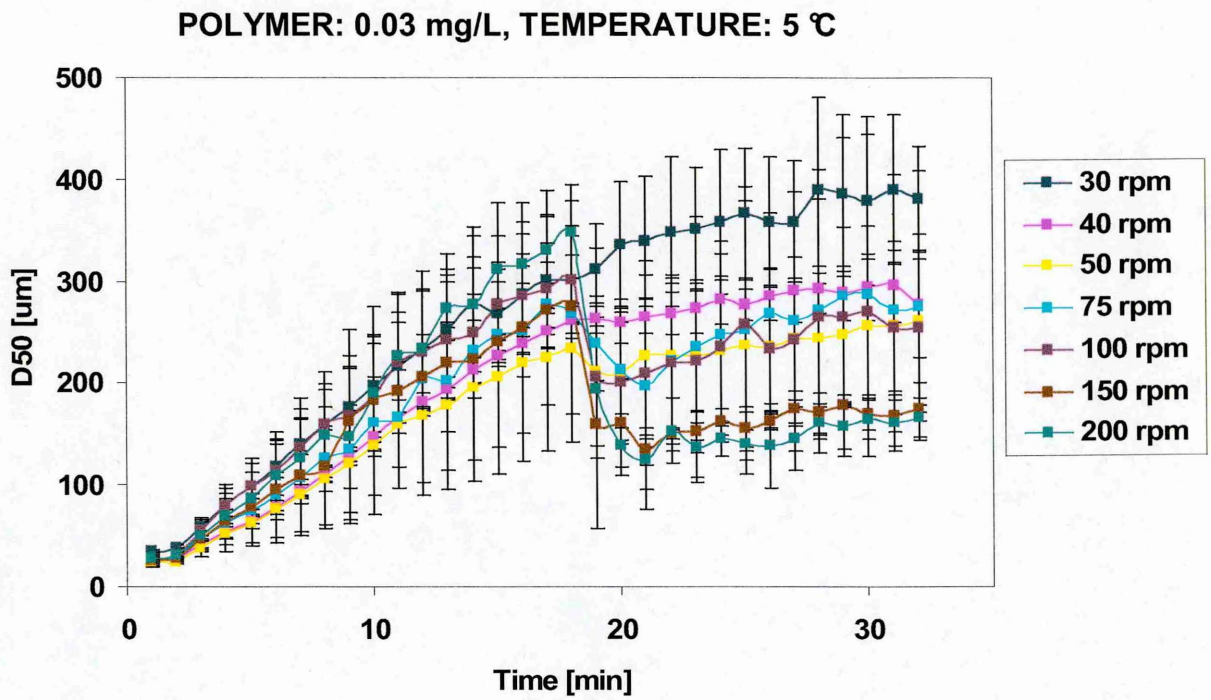

POLYMER: 0.00 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

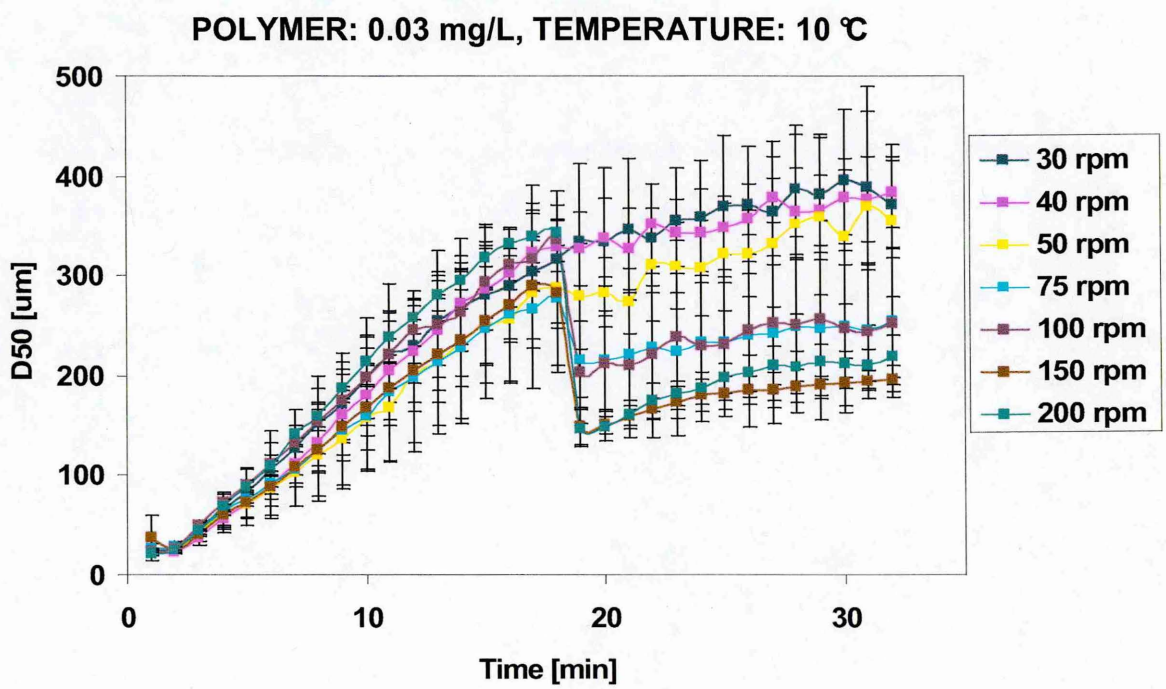

POLYMER: 0.01 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

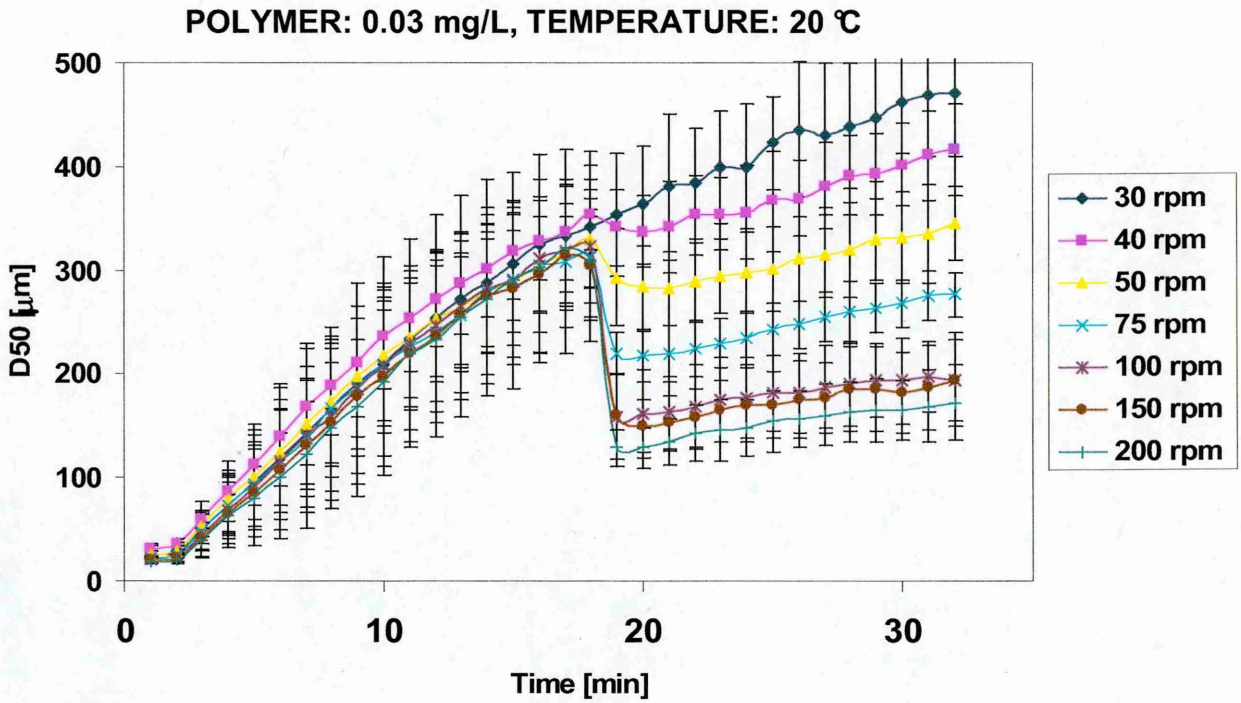

POLYMER: 0.02 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

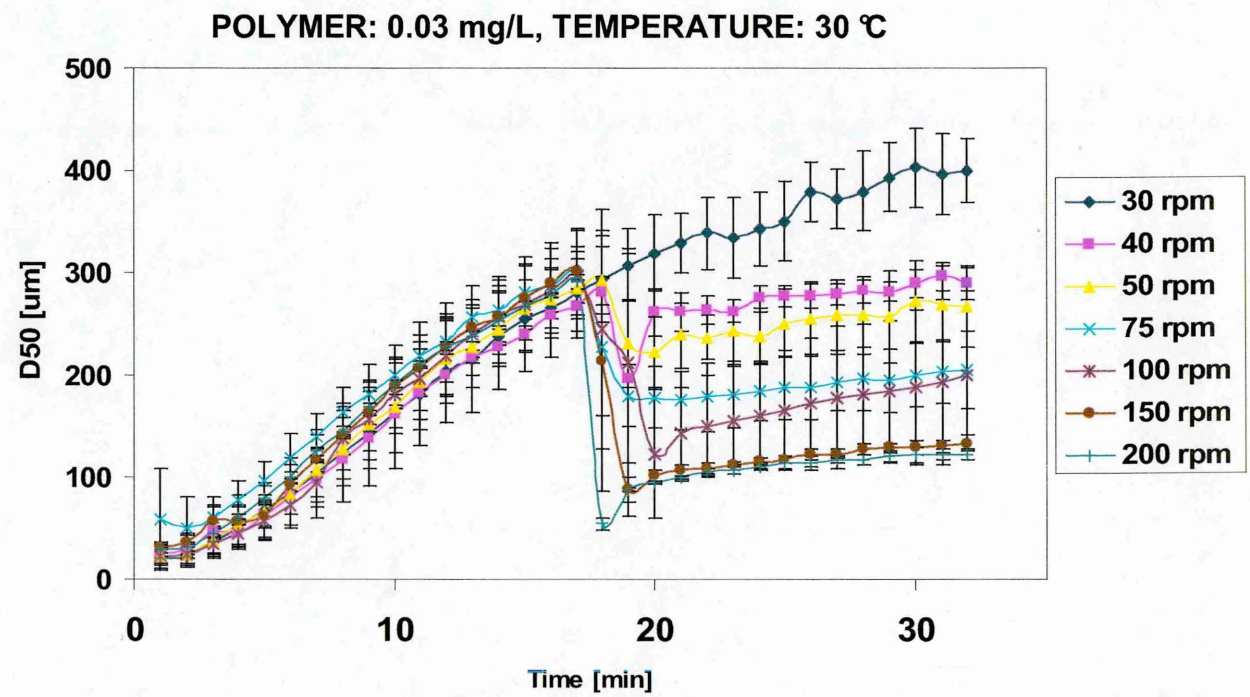

POLYMER: 0.03 mg/L, TEMPERATURE: 15 ℃
D10 [um]
250
200
150
100
50
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm

- Floc strength for April sample






POLYMER: 0.03 mg/L, TEMPERATURE: 20 ℃
D50 [µm]
500
400
300
200
100
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm


POLYMER: 0.03 mg/L, TEMPERATURE: 30 ℃
D50 [um]
500
400
300
200
100
0
0
10
20
30
Time [min]
30 rpm
40 rpm
50 rpm
75 rpm
100 rpm
150 rpm
200 rpm