# Impact of Biofilter Backwashing on the Biofiltration / Ultrafiltration Process

by

**Brad Wilson** 

A thesis

presented to the University of Waterloo
 in fulfillment of the
 thesis requirement for the degree of
 Master of Applied Science
 in
 Civil Engineering

Waterloo, Ontario, Canada, 2015

©Brad Wilson 2015

# **AUTHOR'S DECLARATION**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

#### **Abstract**

The use of ultrafiltration membrane technology for drinking water treatment has seen a marked increase in the past few decades, however, membrane fouling remains the top technological hurdle in the way of its widespread use. Multiple membrane pretreatment methods exist to alleviate this issue, however, they can be complicated and involve the addition of chemicals to the system. A novel method, known as biofiltration without pretreatment, is a green alternative to conventional membrane pretreatment, and has been shown effective at both the laboratory and bench scale in proof of concept studies.

It is unknown if the conventional biofiltration operational experience, applies to biofiltration without pretreatment especially as it relates to filter backwashing. To this end, the goal of this study was to investigate the performance of biofiltration without pretreatment as a membrane pretreatment under varying water quality conditions, as well as to test the effect of various backwashing parameter settings on the system performance.

To perform this study, a pilot plant was constructed at the Mannheim water treatment plant in Kitchener Ontario. This plant consisted of multiple identical biofilter columns running in parallel. For this study, dual identical biofilters run in parallel were used, with one being a control and run under constant backwashing conditions, while the other, an experimental filter, was run over a range of backwashing conditions according to a statistical experiment design. The dual media filters (anthracite over sand) used in this study were run with a 7 minute empty bed contact time.

This study was divided into two parts. In the first part, focus was placed on the performance of the biofilters and in the second part the combined process, that is the use of biofilters without pretreatment as a membrane fouling reduction pretreatment, was investigated. In both cases, the effect of changing inlet water quality parameters, as well as the effect of backwashing parameters (collapse pulsing time, wash time, wash expansion and membrane run delay) was investigated.

Performance of both sections of the plant was monitored through a combination of online and laboratory measured parameters. Biofilter turbidity, temperature, headloss, as well as membrane temperature and transmembrane pressure were monitored online. In the laboratory, liquid chromatography with organic carbon detection was used to measure the concentrations of various water constituents. Fluorescence emission and excitation matrices were also used for this purpose. In addition, dissolved organic carbon, and ultraviolet light absorption were also measured. The consumption of dissolved oxygen by biofilms attached to biofilter media was quantified as a means to determine biological activity within the biofilter.

In terms of biofilter performance, the backwashing factors studied were found to have no effect on the biological activity, either through the removal of nutrients, or by the amount of biomass on the biofilter media. However, these factors were found to influence turbidity removal and headloss accumulation by the biofilters as well as the removal of suspected membrane foulants, namely biopolymers and protein-like material

In terms of membrane performance, the irreversible fouling rate was found to be correlated to the amount of biopolymers applied to the membranes and reversible fouling was found to not be correlated to any of the parameters studied. The amount of turbidity applied to the membranes was shown to a play a complex, role in this fouling as well. Backwashing was also shown to have an effect on irreversible fouling, suggesting that the backwashing regime may be optimized for the reduction of irreversible fouling.

Although the backwashing procedure was found to have an effect on both the reduction of irreversible membrane fouling and the headloss buildup (hence biofilter run time), these two parameters were found to be affected in opposite, meaning that one may be optimized at the expense of the other. Therefore process optimization must be undertaken with specific goals in mind. It was found however, that the filter run time of the biofilters may be extended by optimizing the biofilter backwashing procedure.

The results of this study provide a frame work for which to further study the influence of backwashing on biofiltration without pretreatment used as a membrane pretreatment by pointing to the backwashing parameters which have the greatest effect on performance. Moreover, the results of this study may be used as a starting point for more in depth optimization exercises.

# **Acknowledgements**

Firstly, I would like to deeply thank my supervisors, Drs. Peter Huck and Sigrid Peldszus. Your continued support and expert guidance with this project from beginning to end was indispensable. This project, from the design and construction of the pilot plant to the data analysis and final thesis writing has been as difficult as it has been varied and without your support I would have been lost. I am extremely thankful to have a chance to work with you and to learn from you.

Secondly, I would like to thank my colleague Ahmed Elhadidy, with whom I've worked very closely with over the past three years in the design, construction and eventual operation of the pilot plant. Ahmed and I worked together to design and build the Mannheim pilot plant and I would like to formally acknowledge him in the sole design and manufacture of the roughing filter and the biofilters. It's been a pleasure working with him.

I would also like to thank the region of Waterloo staff at the Mannheim water treatment plant for without their generosity and support, this project would have never gotten off the ground. Specifically I would like to thank Tim Walton, Peter Clarke, Luis Figueiredo and Alex Lee for treating us like employees and allowing us full access to the plant at all hours. I would also like to thank them for being so generous in their time and being available for design meetings and to answer questions. I would also like to thank Ian Doyle of the region of Waterloo for all his help and guidance on the building of the pilot plant.

I would like to formally acknowledge and thank the following people for performing labwork that would go on to form parts of this thesis: Alex Chen for the FEEM analysis, Jangchuk Tashi for the DOC and UV measurements and Sylwia Kolaska for the DO measurements. I would also like to acknowledge and thank Dr. Monica Tudorancea for performing the LC-OCD analysis.

It's been a privilege and joy to study as part of the Natural Sciences and Engineering Research Council of Canada Chair in Water Treatment at the University of Waterloo. A big thank you to Dr. Michelle Van Dyke for help with interpreting the microbiology results of this study. Also thank you to Dr. Bill Anderson for lending his experience during the building of the pilot plant. A special thanks to Ms. Dana Herriman for all your support and assistance in this journey. I would like to extend a big thank you to all the students and personnel for the encouragement and support including Silvia Vlad who had the unfortunate luck of sharing an office with me and having to hear about the minutia of pump selection and piping design, but also for sharing in the joy that are many class projects.

Finally I would like to thank my family and friends and especially my partner Rachel for all your encouragement and support throughout this process. Without you I would not have made it.

Funding for this research is provided by the Ontario Research Fund and the Natural Sciences and Engineering Research Council of Canada (NSERC). In the form of an Industrial Research Chair in Water Treatment at the University of Waterloo. The current Chair partners include: Associated Engineering Group Ltd., the cities of Barrie, Brantford, Guelph, Hamilton and Ottawa, Conestoga-Rovers & Associates Limited, EPCOR Water Services, GE Water & Process Technologies Canada, Lake Huron and Elgin Area Water Supply Systems, the Ontario Clean Water Agency (OCWA), the Regions of Durham, Halton, Niagara and Waterloo, Toronto Water, RAL Engineering Ltd., and the Walkerton Clean Water Centre.

# **Table of Contents**

| AUTHOR'S DECLARATION                                 | ii   |
|--|------|
| Abstract   | iii  |
| Acknowledgements                                     | v    |
| Table of Contents                                    | vii  |
| List of Figures                                      | xi   |
| List of Tables                                       | xiii |
| List of Acronyms                                     | xiv  |
| Chapter 1 Introduction                               | 1    |
| 1.1 Problem Statement                                | 1    |
| 1.2 Objectives                                       | 4    |
| 1.3 Approach   | 4    |
| 1.4 Thesis Structure                                 | 5    |
| Chapter 2 Background                                 | 7    |
| 2.1 Biofiltration                                    | 7    |
| 2.1.1 Description                                    | 7    |
| 2.1.2 Establishing Biological Activity of Biofilters | 8    |
| 2.1.3 Design   | 9    |
| 2.1.4 Role of Ozonation                              | 10   |
| 2.1.5 Biofiltration Without Pretreatment             | 10   |
| 2.2 Filter Backwashing                               | 13   |
| 2.2.1 Backwashing Procedure                          | 14   |
| 2.2.2 Methods  | 14   |
| 2.3 Ultrafiltration Membranes                        | 18   |
| 2.3.1 Description                                    | 18   |
| 2.3.2 Membrane Fouling                               | 20   |
| 2.4 Biofiltration as a UF Membrane Pretreatment      | 23   |
| 2.4.1 Current Research                               | 24   |
| Chapter 3 Mannheim Pilot Plant Design                | 26   |
| 3.1 Overview   | 26   |
| 3.2 Introduction and Objectives                      | 27   |
| 3.2.1 Objectives                                     | 29   |

| 3.3 Design Scope Development   | 30 |
|--|----|
| 3.3.1 Detailed Design Requirements and Associated Features                         | 30 |
| 3.3.2 Design Constraints   | 35 |
| 3.3.3 Design Process   | 36 |
| 3.4 System Description   | 39 |
| 3.4.1 Location   | 39 |
| 3.4.2 Filtration Process Flow  | 40 |
| 3.4.3 Backwash Process Description   | 40 |
| 3.5 System Components  | 43 |
| 3.5.1 Piping Design  | 43 |
| 3.5.2 Filters  | 45 |
| 3.5.3 Pumps  | 49 |
| 3.5.4 System Control   | 50 |
| 3.5.5 Online Instrumentation   | 54 |
| 3.6 Conclusions  | 57 |
| Chapter 4 Influence of Backwashing on Biofiltration without Pretreatment Operation | 59 |
| 4.1 Overview   | 59 |
| 4.2 Introduction and Objectives  | 59 |
| 4.2.1 Objectives   | 61 |
| 4.3 Materials and Methods  | 62 |
| 4.3.1 Statistical Design.  | 62 |
| 4.3.2 Controlling for Systematic Errors  | 63 |
| 4.3.3 Experimental Setup Description   | 63 |
| 4.3.4 Biofilter Backwashing Procedure  | 66 |
| 4.3.5 Sampling Points and Method   | 67 |
| 4.3.6 Online data Collection   | 67 |
| 4.4 Results and Discussion   | 69 |
| 4.4.1 The Effect of Backwashing Parameters on Biofilter Metrics                    | 69 |
| 4.4.2 System Variability   | 76 |
| 4.5 Effect of Backwashing Parameters on Biofilter Performance                      | 79 |
| 4.5.1 Optimal parameter settings   | 87 |
| 4.6 Conclusions  | 89 |

| 4.7 Future Work   | 91  |
|---|-----|
| Chapter 5 Influence of Biofilter Backwashing on Ultrafiltration Membrane Fouling      | 92  |
| 5.1 Overview  | 92  |
| 5.2 Introduction and Objectives   | 92  |
| 5.2.1 Objectives:   | 93  |
| 5.3 Experimental Approach   | 93  |
| 5.3.1 Investigated Backwashing Parameters   | 93  |
| 5.3.2 Experimental Design   | 94  |
| 5.4 Materials and Methods   | 95  |
| 5.4.1 Biofilter Setup Description   | 95  |
| 5.4.2 Biofilter Backwashing Procedure   | 95  |
| 5.4.3 Membrane System Description   | 96  |
| 5.4.4 Membrane Operation  | 97  |
| 5.4.5 Sampling points and methods   | 100 |
| 5.4.6 Online Data Collection  | 100 |
| 5.4.7 Data Evaluation   | 101 |
| 5.4.8 Membrane Fouling  | 101 |
| 5.4.9 Statistical Calculations  | 103 |
| 5.5 Results and Discussion  | 104 |
| 5.5.1 Water Quality and Membrane Fouling over the Course of the Study                 | 104 |
| 5.5.2 Correlation of Control Train Parameters   | 110 |
| 5.5.3 System Variability between Control and Experiment Membranes                     | 114 |
| 5.5.4 Effect of Biofilter Backwashing on Reversible and Irreversible Membrane Fouling | 115 |
| 5.5.5 Conclusions   | 122 |
| 5.5.6 Future Work   | 123 |
| Chapter 6 Conclusions and Recommendations   | 124 |
| 6.1 Summary of Experiment   | 124 |
| 6.2 Experimental Conclusions  | 125 |
| 6.3 Toward Combined Process Optimization  | 127 |
| 6.4 Recommended Future Work   | 129 |
| References  | 131 |
| Appendix A Pilot Plant Piping Isometrics.   | 136 |

| Appendix B Chapter 4 Supplementary Graphics                               | 151 |
|---|-----|
| Appendix C Sample Calculation of Pressure Decay Velocity and Acceleration | 152 |

# **List of Figures**

| Figure 1-1 Relationship between the chemically assisted biofiltration process, the conventional    |    |
|--|----|
| membrane process and the novel $(BF_{wp}  /  UF)$ membrane process                                 | 3  |
| Figure 2-1 Transport efficiency under different mass transport mechanisms for hypothetical filter  |    |
| bed (Adapted from Crittenden et al., 2012)   | 12 |
| Figure 2-2 Membrane technology removal comparison (Crittenden et al. 2012)                         | 18 |
| Figure 2-3 Membrane flow regimes (Adapted from Crittenden et al., 2012)                            | 20 |
| Figure 2-4 Membrane fouling types  | 21 |
| Figure 2-5 Generalized schematic of the combined BF <sub>wp</sub> & UF membrane process            | 24 |
| Figure 3-1 Design Flowchart  | 30 |
| Figure 3-2 Mannheim pilot plant block flow diagram   | 38 |
| Figure 3-3 Mannheim pilot plant process & instrumentation diagram                                  | 42 |
| Figure 3-4 Biofilter piping (blue: effluent, grey: drain, orange: backwash)                        | 44 |
| Figure 3-5 Roughing filter   | 45 |
| Figure 3-6 CAD drawing of biofilter setup  | 46 |
| Figure 3-7 Reception trough.   | 47 |
| Figure 3-8 Acclimator diagram  | 48 |
| Figure 3-9 Backwash valve characteristics  | 51 |
| Figure 3-10 Biofilter effluent flow control loop   | 52 |
| Figure 4-1 Experimental setup including logical connections and sampling points                    | 65 |
| Figure 4-2 Biofilter organics removal and temperature  | 71 |
| Figure 4-3 Dissolved oxygen uptake of media samples (24h respiration period as per Urfer and       |    |
| Huck (2001))   | 72 |
| Figure 4-4 Absolute and log removal turbidity profiles for control and experiment filters          | 73 |
| Figure 4-5 Control biofilter backwash turbidity throughout study                                   | 74 |
| Figure 4-6 Control biofilter ripening peak statistics throughout study                             | 75 |
| Figure 4-7 Biofilter starting pressure and pressure loss profiles                                  | 76 |
| Figure 4-8 Centre point comparison of turbidity log removal for the control and experiment filters | 77 |
| Figure 4-9 Centre point comparison for column pressure for both control and experiment filters     | 79 |
| Figure 4-10 Biopolymer removal 2-factor interaction  | 83 |
| Figure 4-11 Significant 3-factor interactions.   | 87 |
| Figure 5-1 Zeeweed 1000 module (membrane fibers inside of housing)                                 | 96 |

| Figure 5-2 Simplified ultrafiltration pilot unit process diagram including temperature transmitter    |
|---|
| (TT), pressure transducer (PT) and flow transmitter (FT)  |
| Figure 5-3 Control TMP and temperature trends for November 3 to 7, 2014                               |
| Figure 5-4 One minute average start TMP values for November 3 to 7, 2014                              |
| Figure 5-5 UF membrane reversible and irreversible fouling as well as temperature over time 104       |
| Figure 5-6 Turbidity of control and experimental membrane influents (e.g. membrane feed) over         |
| time (4 hour moving average)  |
| Figure 5-7 Biofilter effluent DOC concentrations and UF membrane rejection                            |
| Figure 5-8 SUVA of biofilter effluent and UF membrane permeate  |
| Figure 5-9 Biopolymer concentration (Carbon (C) and nitrogen (N) detectors) in the control (Con)      |
| and experiment (Exp) membrane feeds (= membrane influents) and their removals through the             |
| membranes   |
| Figure 5-10 Carbon to nitrogen ratio of membrane influent biopolymers                                 |
| Figure 5-11 Humics rejection by UF membranes, and humics concentrations in the membrane feed          |
| and in the membrane permeates for both the control and experiment trains                              |
| Figure 5-12 Humic to biopolymer ratio in both the control and experiment membrane feeds and the       |
| corresponding permeates   |
| Figure 5-13 Relation of irreversible fouling rate to concentration of biopolymers applied to the      |
| membranes (membrane influent)   |
| Figure 5-14 (a-c) Irreversible fouling rate main effects for collapse pulsing time (a), wash time (b) |
| and membrane run delay (c)  |
| Figure 5-15 (a-c) Turbidity main effects for collapse pulsing time (a), wash time (b) and membrane    |
| run delay (c)   |
| Figure 5-16 (a-b) Biopolymer (measured as carbon) rejection main effects for collapse pulsing time    |
| (a), wash time (b)  |
| Figure 5-17 (a-b) Biopolymer (measured as nitrogen) rejection main effects for collapse pulsing       |
| time (a) and wash Time (b).   |

# **List of Tables**

| Table 1-1 Biofilter backwash parameters investigated and system performance response variables     | 5     |
|--|-------|
| Table 3-1 Design requirements and features   | 31    |
| Table 4-1 Factorial experiment design including setpoint values (non-random)                       | 63    |
| Table 4-2 Online data collection parameters  | 68    |
| Table 4-3 Source water quality   | 70    |
| Table 4-4 Collected ANOVA results for studied response variables                                   | 81    |
| Table 5-1 2 <sub>IV</sub> <sup>4-1</sup> Half fraction factorial design                            | 94    |
| Table 5-2 Membrane backpulse operation setpoints   | 99    |
| Table 5-3 Pearsons correlation coefficients for measured parameters (Green cells are statistically |       |
| significant at the a=0.05 level)   | . 113 |
| Table 5-4 Parameter variability between control and experimental train UF membranes                | . 115 |
| Table 5-5 Collected ANOVA results for factor effects on response variables                         | .116  |
| Table 6-1 Backwashing parameter settings for various process optimization objectives               | . 128 |

# **List of Acronyms**

| ANOVA  |   |
|--------|---|
| AOC:   | Assimilable organic carbon                          |
| BDOC:  | Biodegradable organic carbon                        |
| BF:    | Biofiltration                                       |
| BFD    | Block flow diagram                                  |
| BFM    | Biofilm monitor                                     |
| BFwp   | Biofiltration without pretreatment                  |
| BP     | Biopolymers   |
| CAD    |   |
| DBP    | Disinfection byproduct                              |
| DO     | Dissolved Oxygen                                    |
| DOC    | Dissolved organic Carbon                            |
| EBCT   | Empty bed contact time                              |
| FEEM   | Fluorescence emission excitation matrices           |
| FM     | Flowmeter   |
| FT     | Flow transmitter                                    |
| LC-OCD | Liquid chromatography with organic carbon detection |
| LMH    | Liter per square meter per hour                     |
| MF     | Microfiltration                                     |
| MFS    |   |
| NF     | Nanofiltration                                      |
| NOM    |   |
| NTU    |   |
| P      | Pump  |
| P&ID   | Piping & instrumentation diagram                    |
| PCA    | Principle component analysis                        |
| PFA    | Perfluoroalkoxy Alkane                              |
| PID    | Proportional integrative derivative                 |
| PT     | Pressure transmitter                                |
| PVC    |   |
| RF     | Roughing filter                                     |

| RO   | Reverse osmosis                 |
|------|---------------------------------|
| RTD  | Resistive temperature device    |
| SUVA | Specific ultraviolet absorbance |
| Tk   | Tank                            |
| TMP  | Transmembrane pressure          |
| TOC  | Total organic carbon            |
| TT   | Temperature transmitter         |
| Tu   | Turbidimeter                    |
| UF   | Ultrafiltration                 |
| V    | Valve                           |
| WTP  | Water treatment plant           |

# Chapter 1

## Introduction

#### 1.1 Problem Statement

Ultrafiltration (UF) membrane technology is rapidly becoming more prominent in the treatment of drinking water supplies in the face of more stringent regulations owing mainly to its inherent disinfection properties (due to the size exclusion of bacteria and viruses – depending on the type of membrane) and its small physical footprint as compared to conventional treatment options (AWWA 2005). However, major barriers still exist to its widespread use. Chiefly among these are costs stemming from the loss of productivity due to the accumulation of material on the membrane surface or within the membrane pores during operation – a phenomenon known as fouling (Escobar 2005). In practice at present, membrane fouling is commonly mitigated by the application of various pretreatment methods, including pH adjustment, peroxidation, screening and adsorption and coagulation (AWWA 2005). In industry, coagulation is the most common method of membrane pretreatment.

The causes of fouling are complex, but current research points to specific fractions of the natural organic matter (NOM) present in surface water sources as being primarily responsible (Lee et al. 2005). Of particular interest is the biopolymer fraction, which includes high molecular weight polysaccharides and protein-like material, as well as the interactions of the biopolymers with colloidal matter (Chen et al. 2014). Due to the biodegradability of the biopolymers, biologically active granular media filtration (biofiltration) is being investigated as a novel membrane pretreatment for fouling reduction in subsequent membrane filtration step.

Biofiltration is a well-developed treatment technology, which has been used at full scale since the 1970s. Specific applications of biofiltration have typically been ensuring microbiological stability in the treated water as well as the removal of specific chemical contaminants, such as disinfection by-product precursors and taste and odor compounds (Urfer et al. 1997). Biofiltration is typically applied after an ozone treatment step, as ozone has the effect of increasing the biodegradability of water constituents. Thus, when an ozone treatment step is added to an existing chemically-assisted filtration treatment train, which is done for a variety of treatment goals, filters are usually converted to biofilters by ensuring that the disinfection residual is removed from the filter backwash water. Hence, conventional biofilters are commonly preceded by coagulation, flocculation, sedimentation and ozonation (Figure 1-1). Thus, the treatment goals of conventional biofilters are twofold: the removal of turbidity (as with their conventional

counterparts) and the biodegradation of organic water constituents for ensuring the microbiological stability of biofilter effluent water (Crittenden et al. 2012).

However in the BF/UF process, the UF membrane acts as a barrier to turbidity, and the treatment goal for the biofilters becomes primarily the reduction of membrane foulants (Figure 1-1). Therefore coagulation, flocculation and sedimentation, which are a prerequisite to ensure high turbidity removals in conventional biofiltration, are not required for biofiltration as membrane pretreatment. Biofilters can therefore be operated without any prior coagulation and this process is termed biofiltration without pretreatment (BF $_{wp}$ ) (Huck et al. 2015). This process is advantageous over the conventional membrane pretreatment as it does not involve the application of chemicals, thus theoretically keeping operating costs low as well as being a so-called 'green' process. The relationship between the chemically-assisted biofiltration, conventional membrane, and BF $_{wp}$ /UF process is described in (Figure 1-1).

The combined  $BF_{wp}$  and UF membrane process has been investigated at both laboratory and pilot scale in proof-of-concept studies (Huck et al. 2011; Hallé et al. 2009; Peldszus et al. 2012). These have shown the effectiveness of the  $BF_{wp}$  process at reducing membrane fouling rates as compared to raw water alone. However a detailed operational study quantifying the impact of different biofilter backwashing regimes on biofilter and UF membrane performance, and providing guidance on optimizing biofilter backwashing strategies, has yet to be completed. The absence of influent coagulant dosing may have important effects on biofilter operation and backwashing regime employed. The nature of particles fed to the biofilters in the  $BF_{wp}$  process will be different in terms of size distribution and charge. Moreover, in the  $BF_{wp}$  process, the application of ozone is absent, and as such the natural organic matter character will be different between the two processes. Thus the biofilter influent water in the conventional process is much different than that of the  $BF_{wp}$  process in terms of both chemical and physical character. This is a condition which is not well studied in the scientific literature, which has traditionally focused on conventional biofiltration (with chemical pretreatment). As the  $BF_{wp}$  influent water character differs substantially from that used for conventional biofiltration, the applicability of operational knowledge from the current body of scientific literature to the novel  $BF_{wp}$ /UF process is unclear. This work aims to fill this knowledge gap.

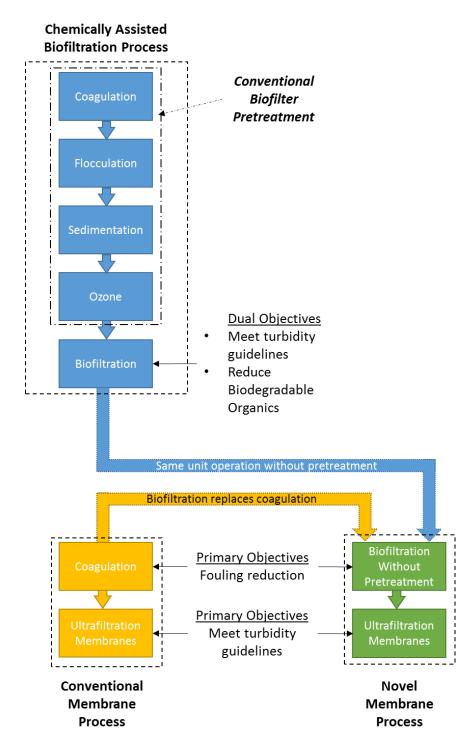


Figure 1-1 Relationship between the chemically assisted biofiltration process, the conventional membrane process and the novel  $(BF_{wp}\,/\,UF)$  membrane process

# 1.2 Objectives

The overarching objective of this study was to identify operational relevant parameters for the combined  $BF_{wp}$  / UF process with respect to the biofilter backwashing regime. To that end, the following goals were identified:

- Investigate the performance of BF<sub>wp</sub> in terms of conventional filter performance metrics and foulant removal over time.
- Investigate the performance of the combined BF<sub>wp</sub> and UF process over time.
- Determine the effect of biofilter backwashing parameters on the operation and performance of the biofilter.
- Determine the effect of backwashing parameters on the accumulation and rate of membrane fouling.

#### 1.3 Approach

A 10 week experimental statistically designed study to achieve the aforementioned goals was undertaken from September 22 to December 5 2015 using source water from the Mannheim Water Treatment Plant in Kitchener, Ontario. A number of backwashing parameters were investigated together with a number of performance metrics for the biofilter and membrane performance (shown in Table 1-1). For biofilter performance, the impact of the backwashing parameters collapse pulsing time, wash time and wash expansion were investigated. In terms of membrane fouling, a fourth biofilter backwashing factor, membrane run delay, was added. Water samples were taken weekly from the biofilter influent, effluent, and membrane permeate in addition to biofilter media samples. Water samples were analyzed in the laboratory for dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA), biopolymer concentration (using liquid chromatography and organic carbon detection or LC-OCD) (Huber et al. 2011), fluorescence excitation emission spectra (FEEM), and media dissolved oxygen (DO) respiration (Urfer & Huck 2001). The removals of the aforementioned parameters throughout the system was used to indicate performance and to determine the effect of backwashing regime. A  $2_{\rm HI}^3$  full and a  $2_{\rm IV}^{4-1}$  fractional factorial statistical experiment design were used for the investigation into the effect of backwashing on the performance of BF<sub>wp</sub> and of the combined process respectively. To accommodate the inherent variability in the source water quality, parallel control and experiment treatment trains were used. The operation of

the control train was kept consistent throughout the study, while the operational parameters of the experimental train were modified according to the experimental design. The response variables investigated were therefore the differences between the responses of each train.

Table 1-1 Biofilter backwash parameters investigated and system performance response variables

| Biofilter Performance (Full Factorial Design) |                       | Membrane Fouling (Fractional Factorial Design) |                              |
|---|-----------------------|--|------------------------------|
| Biofilter Backwash                            | Performance Response  | Biofilter Backwash                             | Performance Response         |
| Parameters                                    | Variables¹            | Parameters                                     | Variables <sup>2</sup>       |
| Collapse Pulsing Time                         | DOC Removal           | Collapse Pulsing Time                          | Biofilter Effluent Turbidity |
|   |                       |  |                              |
| Wash Time                                     | Biopolymer Removal    | Wash Time                                      | Reversible Fouling           |
| Wash Expansion                                | FEEM Protein Removal  | Wash Expansion                                 | Irreversible Fouling Rate    |
|   | Media DO Consumption  | Membrane Run Delay                             | DOC Removal                  |
|   | Log Turbidity Removal |  | SUVA Removal                 |
|   | Backwash Turbidity    |  | LC-OCD Biopolymer Removal    |
|   |                       |  | (Measured as Carbon)         |
|   | Ripening Peak         |  | LC-OCD Biopolymer Removal    |
|   |                       |  | (Measured as Nitrogen)       |
|   | Filter Headloss       |  | LC-OCD Humic Substances      |
|   |                       |  | Removal                      |
|   |                       |  | FEEM Humic Substances        |
|   |                       |  | Removal                      |
|   |                       |  | FEEM Protein Like Material   |
|   |                       |  | Removal                      |

<sup>1.</sup> Removal in this column refer to removal by the biofilter

A pilot plant was designed and built as part of this project to accommodate this study and others. This pilot plant included identical parallel treatment trains, a number of online sensors as well as constant effluent flow controls of the biofilters. Biofilter influent and effluent turbidity, biofilter headloss and influent temperature were measured online.

#### 1.4 Thesis Structure

Chapter 2 includes literature review and provides background into the information and concepts as they relate to the current study. Subsequent chapters are each written in the form of journal articles, which includes an introduction, detailed methods, results and conclusion sections. Chapter 3 discusses the design, procurement and construction of the pilot plant used for this work, placing an emphasis on the innovative features and design choices made. Chapter 4 describes a  $2_{\rm HI}$  full factorial design study used to determine the effect of backwashing parameters on the operation and performance of the BF<sub>wp</sub>. It also examines the operation of the control biofilter over time to gain an understanding of the BF<sub>wp</sub>

<sup>2.</sup> Removal in this column refer to removal by the membrane

performance at baseline operation conditions through changing water quality conditions. Chapter 5 describes a  $2_{\text{IV}}^{4\text{-}1}$  fractional factorial design study, which examined the effect of the backwashing parameters on the accumulation and rate of fouling on the UF membranes located downstream of the  $BF_{wp}$ . In addition, this chapter also examines the performance of the control UF membrane over time to understand the baseline performance of the  $BF_{wp}$ /UF process through changing water conditions. Chapter 6 presents overall conclusions and recommendations from the entire study.

## Chapter 2

# **Background**

#### 2.1 Biofiltration

#### 2.1.1 Description

The primary goal of modern drinking water treatment is to provide safe and aesthetically pleasing water to customers. Integral to achieving this goal is to reduce the number of particles, measured as turbidity, present in the finished water. A typical conventional water treatment train includes coagulation, flocculation, sedimentation, rapid media filtration and disinfection. Except for the latter, all processes focus mostly on the agglomeration, and removal of particles present in the water being treated.

In conventional rapid media filtration, raw water is chemically treated prior to being applied to the media filters. This chemical pretreatment encourages the aggregation of natural particles within the raw water, thus making them easier to be filtered. Biologically active granular media filtration, termed biofiltration, is a specific type of rapid deep bed filtration in which microorganisms, endemic to the applied source water, are allowed to proliferate on the filter media. This situation arises by ensuring that disinfectant is absent from both the influent stream, and from the backwash water. This latter condition precludes the backwashing of the filter with finished water which usually has a disinfection residual.

Encouraging the growth of microbial communities as a biofilm on the filter media is beneficial to meeting the treatment goal of providing biologically stable finished water as these microbial communities reduce easily biodegradable compounds by means of biodegradation. In this way, the bacterial regrowth within the water distribution system is minimized. Biodegradation of taste and odor causing compounds, disinfection byproduct (DBP) precursor reduction (Urfer et al. 1997). and as of late membrane foulants have also been areas of study for biofiltration (Hallé et al. 2009). In addition to degradation of organics, the biofilter is also often the final particle removal step in the treatment plant and if that is the case biofilter effluent has to meet stringent regulations. Biofiltration has seen widespread use in western European countries since the 1980s for ensuring biological stability of finished water, through the biodegradation of nutrients necessary for biological growth. It has also seen increasing use within North America in the past two decades. In both contexts, biofiltration is commonly preceded by ozonation due the ability of ozone to increase the biodegradability of the water being filtered.

#### 2.1.2 Establishing Biological Activity of Biofilters

Biofiltration commonly addresses dual treatment goals: organic removal (by biodegradation) and turbidity removal (as with conventional media filtration). As such, there are a number of additional criteria which are typically monitored, depending on treatment goals, as compared to conventional filtration.

As with conventional treatment, the measurement of turbidity is essential as the removal of particles by the filter (as measured by turbidity) is typically a regulated parameter. The measurement of filter headloss is an equally important performance parameter as this is directly related to filter run time – an important filter operational issue.

The treatment goals of biofilters include the biodegradation of certain contaminants, and as such, the biological activity of the biofilters is an important performance parameter. The biofilms that develop in biofilters are generally comprised of heterotrophic bacteria which degrade a portion of the dissolved organic carbon (DOC) present in the source water. Thus, the removal of this easily biodegradable portion of the DOC can be measured by biodegradable dissolved organic carbon (BDOC), as biofiltration performance indicator. Another type of measurement of the easily biodegradable DOC portion is known as assimilable organic carbon (AOC), which is defined as the portion of the DOC which may be turned into cell mass (Huck 1990). Determining the BDOC or AOC content of biofilter influent and effluent provides a sensitive measurement of the performance of biofiltration by measuring the amount of nutrients being degraded by the biomass on the filters, however they are cumbersome and lengthy incubation tests. DOC removal through the filters is easily performed either online or by grab sample, and is often used as a rough indication of biofilter performance. The typical DOC removals seen in biofilters is between 5 and 10 %.

The measurement of the amount and activity of the biofilm in biofilters is also commonly used to confirm the presence of biological activity in the biofilters. A number of methods are available for this cause. Adenosine Triphosphate (ATP) is a molecule present in all living systems as a so-called 'energy carrier'. Thus measurement of ATP is useful in determining the amount of active microorganisms present on filter media samples. The measurement of the amount of phospholipids in a sample is another useful method in confirming the presences of biological activity in biofilters, as phospholipids are integral in the makeup of every living cell (Findlay et al. 1989). Measuring the consumption of dissolved oxygen (DO) in biomass samples is another method of determining the activity of microorganisms present in the biofilter (Urfer & Huck 2001).

In addition the amount of biomass present on biofilter media has not been found to correlate to performance based on the removal of assimilable organic carbon (AOC) (Pharand et al. 2014). Although seemingly counter-intuitive, (Urfer et al. 1997) suggest that a threshold amount of biomass exists above which removals are independent of concentration.

#### 2.1.3 Design

Biofiltration is often used as a secondary process, by converting existing conventional filtration applications, after the installation of an ozonation facility. As such, the design of biofilters is quite often dictated by dual treatment goals: turbidity removal (as with conventional filtration) and the removal of specific chemical contaminants. However, a number of design considerations are important when filters are to be designed or converted to be operated as biologically active filters as discussed herein.

#### 2.1.3.1 Media

For conventional filtration applications, the selection of media type and depth is done with the goal of removing turbidity. Typical media types are sand, anthracite coal, Granular Activated Carbon (GAC), and any combination thereof. This selection depends mostly on the ratio of depth of the media to its effective size, termed the L/d ratio (Kawamura 1975). The L/d ratio is a convenient design parameter as it is easily relatable to relative amount of turbidity the filter may be expected to remove. Kawamura (1999) surveyed over 200 filter pilot plants in the United States and reported a number of minimum L/d values for different bed configurations and media effective sizes. For mono or dual media filter beds with effective sizes of the media up to 1.5mm; a L/d ratio greater than 1000 is found to be most efficient.

For biofilters, where the treatment goal is not only turbidity removal, but also the biodegradation of some chemical species, media selection criteria also includes the affinity for the proliferation of microbial biofilms. Urfer et al. (1997) conducted an extensive review of biofilter pilot studies. They have found that dual media beds of GAC over sand had the highest amount of attached specific viable biomass (nmol  $P/cm^3$  as measured by the phospholipid method).

#### 2.1.3.2 Loading Rate and Empty Bed Contact Time

The loading rate of filters is the flowrate of source water through the filter normalized to the bed area. This may be thought of as the velocity of water as it flows through the filter. From an operational perspective, this parameter should be maximized to maximize the throughput of the filter. However,

collection efficiency for turbidity generally relies on the velocity of particles through the filter bed, and as such loading rates need to be limited to ensure sufficient turbidity removal. In the United States, many state jurisdictions restrict the loading rate of mono media filters to 7.5 m/h and dual media filter beds to 10 m/h (Kawamura 1999).

The amount of time the water flowing through the filter is in contact with the active media is termed the Empty Bed Contact Time (EBCT). For biological filtration, where organics removal is one of the dual treatment objectives discussed previously, it has been shown that EBCT is positively correlated with organics removal efficiency, however with diminishing returns (Urfer et al. 1997). For example, the gain in efficiency from increasing EBCT decreases with the absolute EBCT. It's been shown that EBCT is more influential than loading rate in terms of degradation of biodegradable organic material (BOM) (Urfer & Huck 2001).

#### 2.1.4 Role of Ozonation

It's been shown that the oxidation of NOM by ozone in source water has the effect of breaking down large molecular weight molecules into smaller less complex ones, with increased hydroxyl, carbonyl and carboxyl groups (Urfer et al. 1997). These resultant molecules are easier to biodegrade, and as such the combined effect of pre-ozonation is an increase in BOM. This culminates in an increase in the risk of biological growth within the distribution system. The removal of this BOM to avoid this condition is a reason that biofiltration and ozonation are commonly coupled.

#### 2.1.5 Biofiltration Without Pretreatment

A variant on the biofiltration process, which has gained interest recently as a membrane pretreatment, is termed biofiltration without pretreatment ( $BF_{wp}$ ) as it has been shown to reduce membrane fouling (Huck et al. 2011; Gao et al. 2011; Halle et al. 2008; Peldszus et al. 2012). This process is used without chemical pretreatment and as such the process may be deemed 'green' as it does not use chemicals, however, this has implications with regards to operation. It should be noted that most of the available scientific literature on biofiltration is for biofiltration with chemical pretreatment i.e. coagulation/flocculation /sedimentation and usually ozonation. Hence, the operation of BFwp is largely untested.

Coagulation, flocculation and sedimentation and usually ozonation are the processes that typically precede a biofilter. Coagulation involves the addition of chemicals to the source water to destabilize suspended

particles by eliminating electrostatic repulsion between the suspended particles and encourage agglomeration. Flocculation refers to a gentle mixing of the source water to promote destabilized particle contact leading to aggregation and floc formation. Sedimentation is the process by which the particles are allowed to settle under the force of gravity and the resulting residual sludge is removed. After settling ozonation is commonly applied prior to the water being sent to the biofilters for final particle removal.

In the BF<sub>wp</sub> process, the aforementioned processes are absent and this affects the source water particles in two fundamental ways. Firstly, the particles in the biofilter influent, have not undergone changes in their surface charge and have not been agglomerated. They are likely much smaller which will impact the efficacy of adsorption onto the filter media grains. Three mechanisms govern the adsorption of particles by the filter media grains, diffusion, sedimentation and interception, and their efficacy depends on the properties of the particles, the media grains and the water being filtered. Of the highest importance is the size ratio between the particles and the collector grains (i.e. the filter media grains). Diffusion mechanisms dominate at low particle sizes, but the effect is inversely related to size. Sedimentation and interception mechanisms are positively related to particle size and dominate at higher particle sizes. Yao et al. (1971) modeled these phenomena and described a minimum in transport efficiency (and hence efficiency of particle adsorption/removal) at a particle size around 1 to 2 µm. For a hypothetical mono media filter bed with a collector diameter of 0.5 mm, a loading rate of 10 m/h, a temperature of 15°C and a media grain density of 1050 kg/m<sup>3</sup>. Liu (2005) has performed particle size analysis before and after coagulation on particles obtained in the source water of the Mannheim Water Treatment Plant in Kitchener, Ontario. He found that the mean particle diameter before coagulation was 6.3 um and 21.8 um after coagulation. These data points are shown respectively as red and orange points on Figure 2-1. This shows that the transport efficiency is much lower for the non- coagulated particles as compared to the coagulated ones, suggesting that filtration of raw source water in the BF<sub>wp</sub> process is much less efficient in terms of particle removal. Moreover, it can be seen that the dominating mass transport mechanism is different for each particle size, and that the non-coagulated particles exist in the minimum transport efficiency area of the graph.

Another consideration on the filtration of particles for the  $BF_{wp}$  process is that particles are unaltered when entering the  $BF_{wp}$  whereas in conventional biofiltration particles are destabilized by charge neutralization upon coagulation prior to entering the biofilter. Most colloids and particles in surface water sources are negatively charged, and the main purpose of the coagulation step is in reducing the particles double layer

repulsive force by raising of the particles zeta potential. When these altered particles come close enough in the subsequent flocculation step, the attractive but short ranging Van-der-Waals forces dominate and act to agglomerate particles.

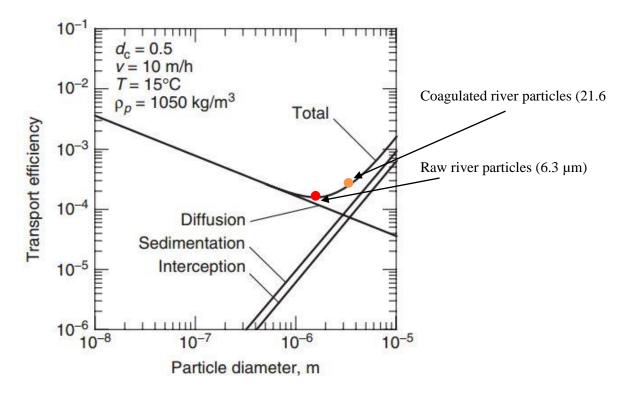


Figure 2-1 Transport efficiency under different mass transport mechanisms for hypothetical filter bed (Adapted from Crittenden et al., 2012)

When particle charge is neutralized in the conventional process, the zeta potential of the particles are brought close to zero. Although the zeta potential is not significant in the attachment of particles to collector grains during filtration, a change in particle zeta potential represents a change in the strength at which the particles are held. When investigating the fundamental forces that play a role in particle detachment during backwashing, Raveendran & Amirtharajah (1995), have shown that particles with low zeta potential (i.e. more negative) require less force to detach from media grains as compared to particles with higher zeta potentials. Thus, in the absence of a coagulation step, particles that become attached to the filter grains in the BF<sub>wp</sub> process, may be more easily removed during backwashing. Raveendran & Amirtharajah (1995) have also noted that the adhesive force varies proportionally with attached particle size. The combined effect of the lower zeta potential and smaller particle size in the BF<sub>wp</sub> process as

compared to the chemically assisted filtration process may be that particles are less tightly held to the collector grains and backwashing, with respect to turbidity removal, may require less effort.

## 2.2 Filter Backwashing

During filter operation, the routine accumulation of particles in the media leads to increased filter headloss, and (eventual) particle breakthrough, thus sustainable continued operation of the depth filter relies on the efficient periodic removal of these trapped particles through a process known as backwashing. This operation in its most general definition, involves any procedure which isolates the filter from operation, removes and disposes of attached particles so that filter operation may resume. This generally involves the use and / or combination of the following:

- Surface Wash in which the surface of the filter bed is cleaned by external jets of water
- Reverse Flow and Bed Expansion in which water flows up through the filter in reverse
  usually resulting in an expanded filter bed.
- Air Scour in which air is introduced to the filter from the bottom, usually coincident with reverse water flow
- Filter to Waste in which some of the filter effluent is sent to a waste immediately after the return of the filter to service.

With the exception of the filter-to-waste operation, the above methods induce particle detachment by creating shear stress in the media bed itself, and carry the dislodged particles through the overflow at the top of the filters to waste. With regards to biofiltration, the effect of backwashing on the organic removal capacity of biofilters as well as on the attached biomass has been investigated. It has been shown that the shear stress associated with backwashing is much less than the strength of the biomass to the media in full scale biofilters (Rittmann & McCarty 2001), and also that biological material is held to filter media more strongly than flocculated particles (Ahmad & Amirtharajah 1998). These investigations showed that backwashing optimized for particle removal should have little impact on biomass removal. Although some studies showed partial removal of biomass during backwashing (Liao et al. 2015; Hozalski & Bouwer 1998) these seemingly contradictory results have been explained by the quick regrowth of the microbial community following backwashing (Miltner et al. 1995). Others have studied the performance of biofilters in terms of BOM removal after backwashing under a number of different conditions and have

found it to be relatively unaffected (Miltner et al. 1995; Hozalski & Bouwer 1998; Niquette et al. 1998; Emelko et al. 2006).

#### 2.2.1 Backwashing Procedure

The goal of the filter backwashing operation of these down flow filters is to recondition the filter media by removing turbidity causing particles attached to the media collector grains from the previous filter run. This is accomplished by forcing the media grains to contact one another, causing abrasion and subsequent removal of particles attached to these grains, and by increasing the shear stress on the particles attached to the media grains relative to the liquid the grains are in. It has been shown that maximizing these parameters for a given filter media bed configuration leads to effective bed cleaning (Hewitt & Amirtharajah 1984).

A typical backwashing operation follows the following sequence:

- 1. Draining of the filter water to a level slightly above the media to avoid media loss in Steps 2 and 3.
- 2. Air Scour (i.e. introducing air from the bottom of the filter with or without concurrent water flow i.e. collapse pulsing).
- 3. Expanded bed wash by reversing the flow and applying high water flowrates from the bottom of the biofilter leading to media fluidization.
- 4. Slow reduction in water flow to allow the media to settle.
- 5. Filter-to-waste period immediately after putting the filter into service to avoid filter ripening peak.

The above steps are discussed in more detail in the following section.

#### 2.2.2 Methods

#### 2.2.2.1 Air Scour

Air scour refers to the bubbling of air from the bottom of the filter bed during a backwash operation. In practice this is sometimes done alone, but usually it is done in conjunction with a fluidized bed condition or simultaneously with a subfluidization velocity water flow (Cleasby & Arboleda 1977). Hewitt & Amirtharajah (1984) have found that for air scour alone, movement occurs only in the top part (6" in their study) of the filter bed. They concluded that this movement was due to the opening and closing of

channels within this part of the filter, and was not an effective method of filter cleaning, as compared to air scour with concurrent water flow. Hence, air scour alone is not recommended.

#### 2.2.2.2 Collapse Pulsing

Collapse pulsing refers to a backwashing condition by which air scour is used simultaneously with water flow at a subfluidization velocity. By analyzing the dynamics of air scouring of a filter media bed using soil mechanics principles, Amirtharajah (1984) theorized the existence of a particular set of air and water flowrates which would lead to the maximum amount of shear stress between grains. This condition, known as collapse pulsing, has been confirmed experimentally as indeed providing maximum agitation and shear stresses and producing the most efficient method of cleaning of filter beds (Amirtharajah 1993). During the collapse pulsing condition, air bubbles in the bed first coalesce into large air pockets, called 'lenses' deep in the filter bed. As this lens grows, a channel eventually forms in the top part of this pocket, which the air escapes through to form another pocket nearby, collapsing the first pocket and starting the process all over again. This occurs starting from deep in the bed and moving throughout to the top of the bed. The forming and then collapsing of these pockets is what causes the maximum shear stress between the grains, thereby removing the attached particles and making bed cleaning efficient (Hewitt & Amirtharajah 1984). The flowrates of both the air and water for this condition vary depending on the bed properties and are given as Equation 2-1.

Equation 2-1 
$$\left( \% \frac{V}{V_{mf}} \right) + aQ_a = b$$

Where:

 $\%V/V_{mf}$  = Water velocity as a percentage of minimum fluidization velocity

 $Q_a$  = Air flowrate

a, b = System constants

The system constants a and b in Equation 1, are functions of a number of system parameters including air pressure, surface tension, surface air cavity radii, media depth, amongst others. These vary from system to system, and set the units for the air flowrate. Details of this calculation are available in Amirtharajah (1993). Due to the complexity of the system constants a & b, in practice, the conditions for collapse pulsing are found by trial and error.

#### 2.2.2.3 Expanded Bed Wash

Expanded bed wash uses a high water flowrate to fluidize the filter bed and expand it by some fraction. It is inherently less efficient than air scour with concurrent water flow or collapse pulsing, due to the relatively low amount and veracity of grain to grain collisions (Amirtharajah 1993), and hence, expanded backwash is commonly used after an air scour operation at which point the primary function of the expanded bed wash is to discharge the detached particles through overflow at the top of the filter and to purge trapped air bubbles from the air scour within the bed (Kawamura 1999). Despite the advantages of this sequence there are instances of full scale filter plants using expanded bed wash as their primary backwashing method (Cleasby & Arboleda 1977), this may be in part due to the capital investments required to refurbish the filter underdrains to enable air scour.

Bed fluidization is defined by the point at which head loss across the bed is independent of upward water velocity. The velocity at which this occurs is known as the minimum fluidization velocity. At this point, the force of the water flowing upwardly through the bed equals the buyout weight of the media, and the media behaves like a fluid. This is a function of media and fluid properties. At flowrates higher than the minimum fluidization velocity, bed expansion varies linearly with velocity.

#### 2.2.2.4 Ripening Peak Mitigation

The ripening peak is a phenomenon seen in rapid media filters after the backwashing procedure when the filter is put back online. When going from the upflow mode during backwashing back to down flow mode when the filter is put back into service, filter effluent turbidity is seen to spike for a relatively short period before stabilizing out at normal levels. Mitigation of this peak by water utilities is important as it has been shown that increased cryptosporidium oocyst passage occurs during this ripening peak, For biofiltration though, it has been shown that cryptosporidium oocyst passage is only slightly higher in the ripening peak than during the remaining filtration run (Amburgey et al. 2004).

It has been shown that the magnitude and length of the ripening peak is a function of the particles that remain in the wash water above the media, of the remnant particles that remain in the filter bed and of the quality of the filter influent water. The theory put forth by Cranston & Amirtharajah (1987), is that particles which were not washed out of the filter by backwashing remain in the filter when it is put back in service. These particles, pass through the bed quickly (in a so called 'remnant phase') and manifest themselves as the first rise of the ripening peak. Moreover, once the filter bed is saturated with 'fresh'

influent water, the bed undergoes a so-called conditioning, in which the effluent turbidity decreases due to increasing capture efficiency of the bed during the latter part of the ripening peak. The underlying mechanisms for the ripening peak phenomenon relates to the different nature of the particles trapped in the filter compared to the ones in the influent of the filter. The flocs in the incoming water may be thought of as particle aggregates with a large size, and as such, a high propensity to be captured in the filter. After backwashing however, (Amburgey et al. 2004) showed that the particles involved in the ripening peak have a lower zeta potential than incoming particles, and thus have been restabilized by the backwash water. This suggests that the particles detached from the filter are much smaller than the aggregates they were part of in the filter influent water, and that, because they have been restabilized, are unlikely to form flocs again. A portion of these smaller particles do not get washed out during the backwashing and must be filtered again when the filter is put back in service. However, due to their small size, they are more likely to not be captured by the filter media, and thus get carried out through the filter effluent during the first part of the filter run. This is the proposed mechanism behind the ripening peak phenomenon.

Multiple strategies have been proposed for ripening peak mitigation including sending the effluent to waste during the ripening peak, which is commonly practiced and the addition of polymer or other chemicals to the backwash water (Cranston & Amirtharajah 1987) to aid in particle collection during the period when the filters are immediately put in service. More recently, extended terminal subfluidization wash (ETSW) (Amburgey 2005) has been found beneficial. This method involves the passage of subfluidization velocity water through the bed after the backwash in upflow mode in an effort to wash out the remnant particles from the bed. It could be shown that production loss in finished water is much less using ETSW compared to the filter to waste procedure as the filter to waste time is eliminated using ETSW.

#### 2.2.2.5 Conventional Filtration vs Biofiltration without Pretreatment

It should be noted that the backwashing procedures and results discussed thus far are valid for filtration or biofiltration with some type of chemical pretreatment in terms of coagulation, flocculation or sedimentation. Very little is known about the effect of backwashing on biofiltration without pretreatment – the subject of the current thesis. It is likely that in the absence of chemical pretreatment, some differences exist due to the difference in size and charge of particles being applied to the BF $_{\rm wp}$  as compared to the conventional BF process. As discussed in detail in Section 2.1.5, smaller particles

applied to the biofilter bed are more likely to not become attached due to the interplay of transport mechanisms being at a minimum around the size of natural particles. In addition, with the lower charge of natural particles, these are likely to be attached with less veracity than compared to chemically altered particles, suggesting particles may detach more readily from filter grains. Moreover, in terms of backwashing by expanded bed fluidization, many authors have recommended a 50% bed expansion level for sand only filters due to the maximum shear force between attached flocs and media grains being maximum at this level (for small grain filter beds) (Cleasby & Arboleda 1977). Although this value is smaller for modern filter beds, as noted by Kawamura (1999), the effect of fluidized bed expansion is likely to be different without pretreatment due to the nature of particle attachment in this case.

With regards to ripening peak, the prevailing theory on the phenomenon relies on the restabilization of flocs due to the influence of backwash water (Amburgey et al. 2004). Without pretreatment, the zeta potential of attached particles is likely to remain unchanged and as such, one may expect to see a smaller ripening peak with biofiltration without pretreatment.

#### 2.3 Ultrafiltration Membranes

#### 2.3.1 Description

Ultrafiltration (UF) is a type of pressure driven membrane filtration with pores sizes in the range of approximately 0.01 µm and 0.1 µm (AWWA, 2005) as shown in Figure 2-2.

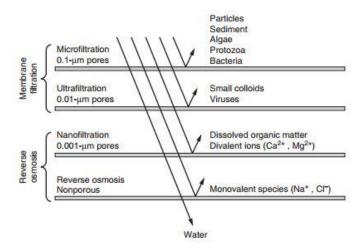


Figure 2-2 Membrane technology removal comparison (Crittenden et al. 2012)

UF membranes used in drinking water applications are typically made from polymeric materials in a number of geometric configurations. Micro- and ultrafiltration membranes also commonly referred to as low pressure membranes. Membranes with smaller pore sizes than UF i.e. Nanofiltration (NF) and Reverse Osmosis (RO) no longer operate by pressure driven transport of the water through the pores, but rather by diffusion of the water through the membrane material. NF and RO are also termed high pressure membranes.

UF membranes act as a physical barrier to contaminants smaller than the pore size i.e. removing contaminants predominantly through size exclusion. Due to their pore size UF membranes act as a barrier to protozoa, bacteria and most viruses, the removal of which is a major drinking water treatment objective. In the case of protozoa and bacteria, both of which are larger than the pores of UF membranes, log removals values as high as 7 and 8 respectively have been observed (Crittenden et al., 2012). In the case of viruses, which may be as small as 0.025 µm, removal may be accomplished with tighter UF membranes which have small enough pore sizes to retain the viruses, however, the exact mechanisms by which this occurs are rather complex and can go beyond simple size exclusion (Crittenden et al. 2012; ElHadidy et al. 2013). Typically, UF membranes in drinking water applications are configured as hollow fibers which are either arranged in a pressure vessel and pressure is employed to filter the water through the membrane or the hollow fibers are submerged as cassettes in an open tank and suction is applied to filter the water through the membrane. The flow regime in hollow fiber membranes can either be insideout where feedwater enters the lumen of the membrane fibers and the filtered water, i.e. the permeate, is collected on the outside of the membrane, or outside-in in which case the permeate is collected from the lumen of the membrane fibers. In addition MF and UF membrane filtrations are usually operated in deadend filtration mode, where influent water is fed to one side of the membrane and driven across via a pressure gradient and the motion of the water relative to membrane is perpendicular. Contaminants and particles accumulate on the feed side of the membrane and to remove these, the membrane vessel is periodically drained. This is typically accompanied by some type of hydraulic cleaning using air or reversed flows. In the case of cross-flow filtration, feed water flows in parallel to the membrane surface and water is driven across the membrane via a pressure gradient. Though only a portion of the feed flow water is filtered and the remaining feed flow water to together with the accumulated contaminants leaves the membrane unit as concentrate. Cross-flow is usually applied to high pressure membranes (NF and RO) which are configured as spiral wound membrane sheets. A comparison of both types of flow regimes is shown in Figure 2-3. The cross-flow is advantageous due to the scouring effect that the parallel feed

water flow has on fouling which accumulates on the membrane, but is typically more expensive to operate compared to the dead-end regime since the recovery, i.e. % of water produced relative to the feed water volume, is higher for the dead end operation.

#### 2.3.2 Membrane Fouling

The accumulation of material on the surface or within the pores of a membrane during filtration leading to flow resistance is a phenomenon known as fouling. This behavior occurs on all membrane types and has been identified as a major hurdle for the widespread adoption of membrane technology (Escobar 2005). A significant amount of research has gone into identifying the causes and the mitigation and reduction of membrane fouling.

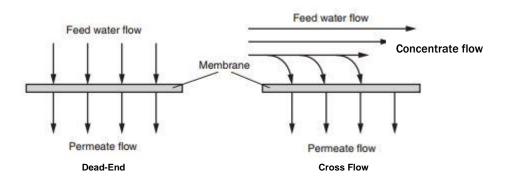


Figure 2-3 Membrane flow regimes (Adapted from Crittenden et al., 2012)

The flowrate through the membrane during operation is commonly expressed as flux, which is the flowrate normalized over the surface area of the membrane. As membranes are pressure driven processes, the differential pressure between the inlet and outlet sides of the membrane (i.e. the driving pressure) is an important performance parameter known as Transmembrane Pressure (TMP). UF membranes are usually operated at constant flux, where the pressure differential is increased to keep the membrane flux and hence, the output constant. Albeit less frequently employed, UF membranes can also be operated at constant TMP mode, in which the pressure gradient is kept constant and the membrane flux is allowed to decrease in response to the accumulation of fouling.

Fouling is typically identified as either reversible or irreversible, and by the method by which it may be reversed: hydraulic or chemical. The different types of fouling are illustrated in Figure 2-3. During a typical MF or UF membrane filtration cycle, periodic back pulsing is performed, analogous to granular media filtration, where flow is reversed through the membrane trapped material is removed. Air scour, or

other membrane agitation methods may or may not be used as well. This is followed by draining of the membrane tank to dispose of the removed material. The fouling that is removed during a backpulse operation is termed hydraulically reversible fouling (Figure 2-4). Not all of the flow resistance may be recovered by hydraulic means, and over time the fouling builds up to the point at which the membrane must be taken offline and cleaned by chemical means. The fouling removed during this process is termed chemically reversible fouling. This fouling is equivalent to hydraulically irreversible fouling since the hydraulic backpulse was not able to remove that fouling (Figure 2-4). Some amount of fouling is gained permanently and may be removed by more radical chemical cleaning or not at all. The latter is called irreversible fouling by many texts and is a function of both the membrane properties and the source water quality (Crittenden et al. 2012). However, for the purpose of many fouling studies, this is small compared with the timescale involved, and hydraulically reversible and hydraulically irreversible fouling types are referred to as simply reversible and irreversible fouling respectively. An explanation of the fouling types (for a constant flux system with fouling expressed as loss of TMP) is shown as Figure 2-4.

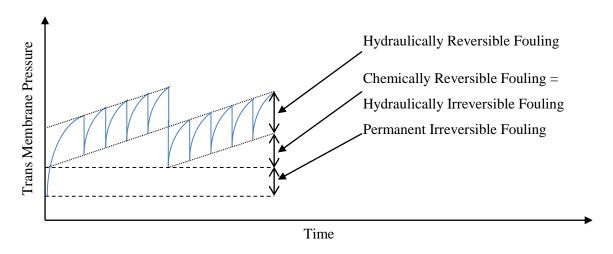


Figure 2-4 Membrane fouling types

Mechanistically, fouling is commonly broken down into three categories, pore blocking, pore constriction and cake formation. Pore blocking involves the complete blocking of a membrane pore by a particle. Pore constriction involves the deposition of material on the walls of the pore within the membrane itself. This mechanism works to decrease membrane permeability by effectively decreasing the diameter of pores. The quality of the source water as well as the surface properties of the membrane play a role in the

deposition of material within membrane pores. Cake formation involves the accumulation of material of larger diameter than the membrane pores and the creation of a cake layer along the surface of the membrane. This cake layer acts as a pseudo pre-filter, working to capture material which would have otherwise been free to deposit within the pores themselves. The description of these mechanisms hints at the complexity of the membrane fouling problem (Hermia 1985).

## 2.3.2.1 Role of Natural Organic Matter in Membrane Fouling.

It's been shown that natural organic matter (NOM) plays an important role in membrane fouling (Amy & Cho 1999; Kaiya et al. 1996), but the mechanisms are quite complex and not well understood (Amy 2008). NOM refers to the highly complex and varied organic molecules which are present from the decay of organic matter within natural water bodies (Crittenden et al. 2012). Numerous techniques exist for the determination of the composition of the NOM including liquid chromatography and organic carbon detection (LC-OCD) and flour essence emission and excitation matrices (FEEM). These are discussed in kind.

LC-OCD is a chromatography-based method which groups different NOM fractions present in natural water based on their size (Huber et al. 2011). Through the use of this method, it was found that the NOM content of the natural water was comprised mainly of humic substances, and also of large molecular weight molecules known as biopolymers. FEEM is a spectrometric method which measures the intensity of the emission spectra of water samples upon excitation over a range of light wavelengths. The output from this type of analysis is generally a 3D surface plot of intensities (with x and y coordinates corresponding to emission and excitation values). Each chemical species such as humic substances or amino acids which are present in protein like material emits a corresponding characteristic signal upon excitation at a particular wavelength and surface plots from these species are compared to the plots of a natural water sample. By using a number of data analysis techniques ranging from simple (peak picking) to complex (principle component analysis) it is possible to determine the relative amount of each species present.

No model has been successfully developed to describe the relationship between the adsorption of NOM and the decrease in membrane permeability (Crittenden et al. 2012), suggesting complex interactions between membrane surface chemistry and feed water quality. It has also been suggested that a small fraction of NOM plays a dominant role in the fouling of low-pressure membranes (Howe & Clark 2002),

namely high molecular weight macromolecules and colloids, mostly comprised of polysaccharides and protein like material (Amy 2008).

Recent studies using advanced analytical and statistical techniques (principle component analysis (PCA) of fluorescence emission and excitation matrices (FEEMs)) have shown a correlation of protein like material with irreversible fouling of UF membranes (Peldszus et al., 2011a, Chen et al., 2014). In addition, using the same techniques, (Peiris et al. 2010) were able to predict fouling events based on online analysis of the water quality of a particular source water. This suggests that the mitigation of a small fraction of the NOM material in the source water may help to reduce UF membrane fouling.

## 2.4 Biofiltration as a UF Membrane Pretreatment

Due to both the effectiveness of biofiltration in reducing NOM in source water and the large role NOM has been shown to play in membrane fouling, research has been undertaken into the use of biofiltration as an effective fouling reduction pretreatment to membrane technology. This new process has been shown to be effective by a number of authors specifically as it pertains to ultrafiltration membranes fouling (Huck et al. 2011; Gao et al. 2011; Halle et al. 2008; Peldszus et al. 2012). The new process is comprised of biofiltration without any chemical pretreatment followed by UF membranes. This means that source water is applied directly to biofilters without prior coagulation, flocculation or sedimentation steps before being fed to the UF membranes. Biofilters being operated in this manner have been termed biofiltration without pretreatment (BF<sub>wp</sub>) to distinguish them from biofilters with chemical pretreatment, and in many cases ozone (Figure 1-1) as UF membranes act as a final barrier to turbidity particles, bacteria and viruses. A generalized schematic of the combined BF<sub>wp</sub>/UF process is shown in Figure 2-5. Water is fed through a roughing filter, which is typically a media filter with a very coarse grain size with a low EBCT, and the roughing filter effluent serves as influent to the biofilter. After the biofilter, water is fed directly to the UF membrane (Figure 2-5). As the BF<sub>wp</sub> process is used without chemical pretreatment, there is very little buffer in the event of a large turbidity spike in the raw water. To allow for some buffering protection, a roughing filter is used and is intended to reduce the impact of large turbidity events and avoid excessive headloss within the biofilter.

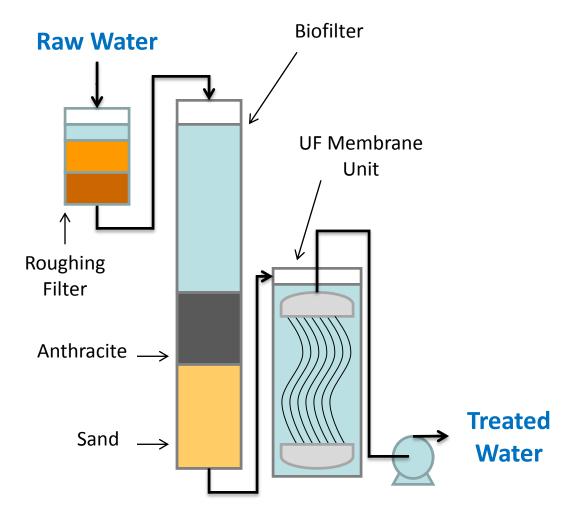


Figure 2-5 Generalized schematic of the combined  $BF_{wp}$  & UF membrane process

#### 2.4.1 Current Research

The use of BF<sub>wp</sub> as a pretreatment to UF membranes has been researched at both the bench scale (Hallé et al. 2009) and pilot scale (Huck et al. 2011; Peldszus et al. 2012). In these studies, the fouling rate of UF membranes was found to be greatly reduced by pretreatment as compared to no pretreatment. In addition, the authors in all cases found that this fouling reduction (for both reversible and irreversible fouling) increased with the EBCT of the biofilter being used as a pretreatment, however with diminishing rates of returns such that the reduction in fouling was greater for a move from 5 to 10 minutes EBCT than for the move from 10 to 15 minutes EBCT. These studies have focused on proof of concept and have not elucidated optimization strategies or the effect of biofilter backwashing on subsequent membrane fouling.

Advanced water analysis techniques to determine the character of the water being treated in an effort to elucidate the fractions of NOM causing membrane fouling have been used as well. This included techniques such as LC-OCD and FEEM.

Analysis of FEEM and LC-OCD results have been used by multiple authors in studying the fouling behavior of UF membranes (Peldszus et al. 2011a; Peiris et al. 2010; Chen et al. 2014; Hallé et al. 2009). These studies have underscored the influence of both protein like material (from FEEM analysis) and biopolymers (from LC-OCD analysis) as important membrane foulants. Chen et al. (2014) have performed extensive analysis regarding the nature of membrane foulants and have clustered the effects of protein like material and colloidal/particulate matter on fouling rates (both reversible and irreversible) depend on the relative rates present, suggesting complex behavior and interactions.

# **Chapter 3**

# Mannheim Pilot Plant Design

#### 3.1 Overview

Biologically active media filtration without pretreatment has shown promise at both the laboratory and pilot scales as being an effective pretreatment for a number of membrane technologies, however, to date detailed studies into the effect of differing operation regimes on process operation have yet to be completed. To address this research gap, an integrated and fully instrumented biofiltration/membrane research platform has been designed and constructed. This entailed extensive refurbishment and redesign of an existing pilot plant used by the NSERC Chair in Drinking Water Treatment at the University of Waterloo. The design incorporated a number of primary requirements for the planned studies including the ability to accommodate parallel studies, mirror full scale operation, account for factors outside of operator control and to minimize unintended microbial growth. In addition, a number of secondary requirements, relating to the ease of operation and maintainability, data availability and longevity concerns were also incorporated. A number of innovative design features have been developed to meet these primary and secondary design requirements.

Overall five biofilter columns were constructed allowing for multiple parallel studies to be conducted. These also included two sets of identical biofilters which can be run in a control / experiment configuration thereby accounting for factors outside the control of the operator and accommodating the use of statistically designed studies. Automatic biofilter effluent flow control was provided as well to mirror full-scale practice. Process piping was chosen so as to minimize biofilm growth within the piping. Opaque hard polyvinylchloride (PVC) piping material precluded the growth of photosynthetic organisms and moreover minimized the leaching of plasticizers, which can contribute to biofilm growth. By threading pipes adhesives did not have to be used during construction, the leaching of which may also contribute to biofilm growth. In addition, 'piping cleanliness monitors' were installed to assess potential biofilm growth occurring within the piping, and a number of tee sections were installed to allow for high velocity scouring of said piping. A newly designed, centralized roughing filter allowed for easy manual cleaning of said filter without interrupting pilot plant operation and provided a common influent water quality to all biofilters. Low shear influent pumps made of high end, inert materials were used to minimize pumping impacts on raw water characteristics.

A design/build structured methodology was followed. Detailed design drawings including block flow diagrams, process & instrumentation diagrams, and computer aided design models and piping isometrics were created as part of the design process. This chapter describes the entire design process, and includes descriptions of the operational flow of the pilot plant, the innovative features installed, as well as the equipment used and the reason for their selection, highlighting innovation.

# 3.2 Introduction and Objectives

Biological media filtration without pretreatment (BF<sub>wp</sub>) (coined by P. M. Huck et al., 2015) has been shown to be effective as a membrane pretreatment for fouling reduction, specifically in polymeric ultrafiltration membranes (Huck et al. 2011). Proof of concept studies have been conducted on both the laboratory (Hallé et al. 2009) and pilot scale (Peldszus et al. 2012). To date however, detailed investigations into the impact of backwashing procedures on the BF<sub>wp</sub> process and the coupled BF<sub>wp</sub> and UF process have not been undertaken. This is an important consideration as the BF<sub>wp</sub> process differs fundamentally from conventional biofiltration processes which are preceded by coagulation and in most cases also by ozonation. BF<sub>wp</sub>, however, treats raw water directly without any pretreatment other than roughing filtration. The bulk of the literature available on the operation of biologically active filtration considers the conventional process (i.e. chemically assisted filtration including ozonation) (Emelko et al. 2006; Urfer et al. 1997), and it is unknown whether findings in that literature also apply to BF<sub>wp</sub>. Moreover, detailed investigations into the applicability of the BF<sub>wp</sub> process as a pretreatment to other membrane technologies, specifically microfiltration (MF) and nanofiltration (NF), and other membrane materials (e.g. ceramic membranes) were lacking.

To elucidate answers to the research gaps identified, a number of experimental studies were scoped and planned by the NSERC Chair in Water Treatment in the Department of Civil and Environmental Engineering at the University of Waterloo in the fall of 2012. These studies were to use a pilot facility since pilot scale results would be more applicable to full scale operation than results obtained at bench-scale. The chair group operated an existing pilot plant facility at the Mannheim Water Treatment Plant in Kitchener, Ontario, which consisted of three biofilters operated at differing empty bed contact times (EBCTs) run in a declining rate flow mode. However, this facility was deemed inadequate for the studies planned and to that end, the author and a fellow graduate student, Ahmed El-Hadidy, undertook the task

of detailed design and construction of the refurbishment of this facility into a fully instrumented biofiltration research platform.

The redesigned biofilter pilot facility had to be able to accommodate a variety of studies including, optimizing biofilter operations for UF pretreatment, biofiltration pretreatment as a tool to prevent biofouling in nanofiltration membranes and proof of concept whether biofiltration pretreatment is beneficial for ceramic membrane filtration. The redesigned pilot plant needed to fulfill the specific experimental requirements of each of these studies, be able to accommodate some studies in parallel and provide a high degree of flexibility for future studies.

The original pilot plant with its three parallel biofilters each with a different EBCT did not have the necessary flows to accommodate the above mentioned parallel studies. To meet this requirement, the pilot plant biofilter columns needed to be replaced with larger diameter columns to accommodate the higher flow requirements. In addition, the studies being planned were focused on building a knowledge base of BF<sub>wp</sub> performance data which could be used to apply to full scale installations. To meet this requirement of more closely mirroring full scale operation, a number of changes to the original pilot plant would be necessary, such as changing from declining to constant rate filtration mode which required a complete overhaul and change of the biofilter effluent control system. It was also important to account for factors which were outside the control of the operator, such as changes in source water quality and temperature in order to conclusively interpret study results. The original pilot plant was equipped with single biofilters for each EBCT, but for the upcoming studies identical parallel biofilter trains for each EBCT were necessary. This would allow for a control train, which would be run with the same settings throughout the study period, to be operated in parallel to an experimental train where settings would be changed according to the study goals. Having parallel trains allowed for statistically designed experiments to be performed – a functionality lacking in the original pilot plant which due to cost reasons had only a single biofilter for each EBCT investigated. For the BF<sub>wp</sub> backwashing study further on-line sensors were required to be able to investigate parameters relating for example to filter headloss. The planned NF and RO studies, required the choices and use of materials to avoid organic leaching as these biofouling studies were expected to be very sensitive to organics contamination in the feed water. As such, piping and components in the original pilot plant were overhauled and changed from the original pilot plant to meet these requirements.

## 3.2.1 Objectives

To provide a pilot biofilter research platform with the capabilities required to meet the demands of the proposed study schedule, a complete refurbishment of the original pilot plant was undertaken. The goal of this refurbishment was to create an integrated pilot biofiltration plant, which would meet the following operational objectives:

- 1. Provide functionality for planned BF<sub>wp</sub>/UF process optimization tests
- 2. Provide functionality for planned BF<sub>wp</sub>/NF biofouling studies
- 3. Provide functionality for planned BF<sub>wp</sub>/ceramic MF proof of concept studies.

Each of these objectives required a unique set of features to be integrated into the pilot plant redesign. Moreover, as the planned experiments were using the entire spectrum of membrane filtration, and as it was expected that this pilot plant was to be used for less defined future studies, the new pilot plant was also redesigned with the following secondary objectives in mind:

- 1. Extend functionality wherever possible to allow for a variety of studies in the future
- 2. Incorporate lessons learned from previous pilot plant design iterations
- 3. Design for longevity and length of service.

# 3.3 Design Scope Development

Once the operational objectives for the pilot plant were defined, design requirements and features were developed. The design requirements were high level statements that were needed to meet the operational objectives. From this, a list of design features was developed, which would form the basis of the detailed design. These design features were also subject to design constraints, which were dictated by the location of the pilot plant. This is basic process is shown as Figure 3-1.

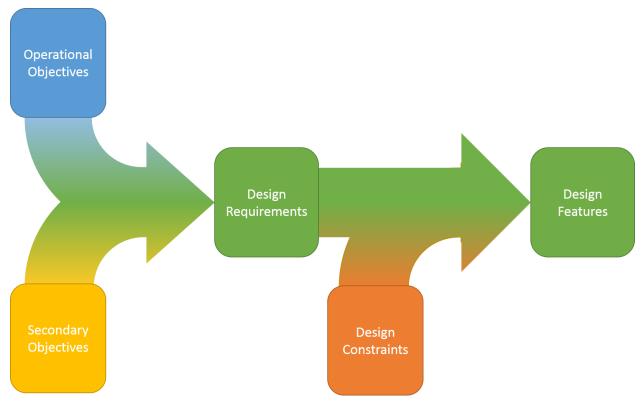


Figure 3-1 Design Flowchart

## 3.3.1 Detailed Design Requirements and Associated Features

From the primary objectives, the design requirements were defined. Design features that satisfied these requirements were also formulated. Both of these are shown in Table 3-1 and main points are discussed thereafter.

Table 3-1 Design requirements and features

| Design Requirement   | Design Feature  |
|--|---|
| Accommodate parallel research studies  | Centralized roughing filter facility with 4 independent filter sections providing a common  |
|  | influent water quality to all biofilters  |
|  | Two parallel biofilter trains for each EBCT   |
|  | One piece wise long EBCT filter   |
|  | Independent biofilter influent flow indication and control  |
|  | Online parameter measurement  |
|  | Large column diameters (8 inch)   |
| Closely mirror full scale operation  | Low shear force inlet pumps to reduce the shear on particulate matter in the raw water  |
|  | thereby preserving the original water characteristics   |
|  | Biofilter effluent flow control to ensure constant flow   |
|  | Online parameter measurement  |
| Account for factors<br>outside of operator<br>control                                | Two parallel biofilter trains for each EBCT investigated to provide a control and an  |
|  | experimental train  |
|  | Opaque schedule 80 PVC piping to minimize algae growth in pipes   |
|  | Periodically space unions on raw water line for manual disassembly and cleaning   |
|  | Low shear force inlet pumps to reduce the shear on particulate matter in the raw water  |
|  | thereby preserving the original water characteristics   |
|  | Biofilter effluent siphon protection to ensure that media stays wet during unplanned shut-  |
|  | downs   |
| Minimize unintended microbial growth  Increase the ease of operation and maintenance | Opaque Schedule 80 PVC piping to minimize algae growth in pipes   |
|  | Pipe Cleanliness monitors   |
|  | Tee' sections for high velocity water scour cleaning  |
|  | Periodically spaced unions on raw water line for manual disassembly and cleaning Threaded piping connections to avoid use of adhesives which could leach out organics |
|  | Centralized roughing filter facility with 4 independent filter sections providing a common  |
|  | influent water quality to all biofilters  |
|  | Close proximity of the raw water flow indication and control valve  |
|  | Pipe Cleanliness monitors   |
|  | Tee' sections for high velocity water scour cleaning  |
|  | Periodically spaced unions on raw water line for manual disassembly and cleaning  |
|  | Automatic pump protection   |
|  | Independent biofilter influent flow indication and control  |
|  | Periodically spaced unions on raw water line for manual disassembly and cleaning  |
|  | Backwashing flow indication and precise control   |
| Increase amount of data available  | Online parameter measurement  |
|  | Independent access to all filter effluent lines   |
|  | Biofilter media sampling ports space frequently along the depth of each biofilter   |
| Design for longevity   | Opaque Schedule 80 PVC piping to minimize algae growth in pipes   |
|  | Pipe Cleanliness monitors   |
|  | Tee' sections for high velocity water scour cleaning  |
|  | Periodically spaced unions on raw water line for manual disassembly and cleaning  |
|  | Automatic pump protection   |
|  | Biofilter effluent siphon protection to ensure that media stays wet during unplanned shut-  |
|  | downs   |

#### 1. Accommodate parallel studies

As stated, there were a number of studies planned that were required to be conducted in parallel with each other. This was one of the most important design requirements, as it involved the greatest amount of modification to the original pilot plant. The chief driving force behind this requirement was the amount of available biofilter effluent flowrate which must be large enough to accommodate all planned experiments. This was accomplished by increasing the diameter of the biofilters from 6 to 8 inches. The identical dual biofilter design also necessitated an increased plant flow. Moreover, the height of the biofilters was also increased, subject to space constraints (discussed in the next section). The increased height allowed a greater amount of driving force as compared to the previous pilot plant. In addition, a piece wise long EBCT filter column was also added, to accommodate the planned studies.

The biofilters used in the refurbished design were also equipped with independent influent flow control and indication to allow for independent operating conditions for parallel studies. In addition, a centralized roughing filter facility was added, with four independent filter sections. In this way, the roughing filter may be manually cleaned without impacting operation. The effluent from each of the four roughing filter sections were collected in a common tank from which all the bio filters were fed. In this way, the water quality applied to each of the membranes was the same.

#### 2. Closely mirror full scale plant operation

As many of the studies planned were focused on the creation of a BF<sub>wp</sub> performance data knowledge base to be applied eventually to full scale applications, it was imperative that the new pilot plant design mirror full scale operations as closely as possible. In the original pilot plant, biofilters were run at a constant head and hence, effluent flowrate declined as resistance within the filter bed accumulated. This resulted in changing EBCTs of the filter bed, and is not how filters in full scale are typically operated. In the refurbished plant design, biofilters can now be run at a constant flow and hence, the EBCT of each filter can be kept constant in between backwashing operations. To achieve this independent flow controllers were added to the biofilter effluent lines, which allowed for automatic set-point control. In addition, a number of online parameter measurements were planned for the refurbished design, which would closely mirror full scale operation.

#### 3. Account for factors outside of operator control

These factors were to be accommodated for and controlled in the design. The studies that were planned were performance tests and as such required a high level of precision. To this end, the refurbished pilot plant was envisioned with identical parallel biofilter trains, such that one could be run as a control while the other is run as an experiment, so as to control for variables fluctuating over time such as water temperature and quality. Moreover, it was important that the source water quality remain unaltered so as to minimize systematic error in the pilot plant studies. This was accomplished by utilizing a low shear force pump for the biofilter influent lines which minimized shear forces exerted on particles present in the water.

#### 4. Minimize unintended microbial growth

Specific to the NF/RO studies were requirements around organics contamination from the redesigned pilot plant. These experiments focused on biofouling of various membranes, which may be contaminated by organics leaching from system components, or from the growth of microorganisms within process piping. These were to be reduced to the greatest extent possible in the refurbished pilot plant design. This was accomplished by using opaque PVC piping, which would preclude photosynthetic organism growth within the pipe. The choice of PVC piping instead of flexible tubing was also a crucial design choice as this also precluded the leaching of plasticizer chemicals into the water stream, which may act as nutrients for the planned NF and RO experiments, contaminating results. In addition, organics leaching from PVC adhesives was of concern, and as such, its use was avoided. All piping connections within the system were to be threaded connections in pursuit of this aim.

In addition to these requirements catering to the specific requirements for the studies planned, the complete refurbishment of the pilot plant allowed a unique opportunity to improve upon day to day operations, and to design with longevity in mind. In addition, it was also an opportunity to increase the functionality of the pilot plant so as to allow for flexibility in future experiments. These principles were the thrust of the secondary objectives as shown in Section 3.2.1. The specific requirements stemming from these secondary objectives and their reasoning are:

## 1. Increase the ease of operation and maintenance

The increased complexity of the pilot plant refurbishment would require more frequent and complex operator interaction. As such, ease of operation was to be paramount. To this end, many design decisions, such as positioning of valves, number of process indications, etc. were done with operational ease in mind. The raw water inlet line control valve and local flow indicator were positioned very close to one another, for this reason. Moreover, all valves and indications throughout the system were placed in convenient locations. A greater number of flow indicators were placed in the system, as compared to the original pilot, to allow the operator a greater breadth of information when operating the plant.

As the system became more complex, it also required more complex maintenance procedures. This was at the forefront of the design, and system components designed and placed in such a way to ease maintainability.

The roughing filter on the refurbished design was made into a centralized easy to reach facility as compared to the previous design (which saw independent roughing filters atop each biofilter). In this way, it is easier for the operator to reach for manual cleaning purposes. In addition, the roughing filter consisted of four small filters running in parallel, such that each one could be manually cleaned independently of the others, so as to not interrupt system operation.

The raw water inlet line was also equipped with monitoring sections and so-called 'cleaning tees'. This allowed the monitoring of any biological growth within the system and allowed the system downstream of the tee to be isolated and a high velocity scour to clean the inlet lines. This section of piping was also equipped with easy disconnect unions for quick disconnect and manual cleaning.

A number of automatic control schemes were used on the system to minimize operator intervention. This was required as the operator was present at all times. The inlet pumps were to have automatic protection in case of loss of feed water flow.

#### 2. Increase amount of data available

The amount of information that could be gained from studies done with the original pilot plant was limited due to the relatively small amount of sampling points and online data. This was to be increased in the refurbished pilot plant, so that researchers would have access to a number of

online data streams as well as through an increase in the number of sample points available especially along the depth of each biofilter column.

Turbidity measurements of the inlet and outlet of each biofilter, system temperature and biofilter headloss measurements were available online. Independent access to all of the biofilter effluent flows as well as the system inlet was made available and easy to access. A number of sampling ports on the filter columns themselves was also to be included.

## 3. Design for longevity

Although the genesis of the pilot plant refurbishment was to accommodate for the three aforementioned studies, it was recognized that this pilot plant would be used in other future studies. To that end, pilot plant longevity was a requirement. Piping was made of hard PVC and anchored appropriately. Easy assessment of the cleanliness of the raw water piping, as well as a variety of cleaning methods was added to the system. In addition, the piping was to be constructed so that the biofilter media stay wet in the case of loss of inlet water. Components were to be chosen of sufficiently high quality and longevity to allow the system to operate for extended periods of time.

#### 3.3.2 Design Constraints

As the pilot plant to be refurbished was located on the lower level of the Mannheim Water Treatment (WTP) Plant, Kitchener, Ontario a number of design constraints were experienced by the location and put forth on by plant staff. These are listed and discussed as follows:

## 1. The pilot plant must meet all safety requirements

As the refurbished pilot plant was to include an increased number of larger filters, it was imperative to the Mannheim WTP management that this not violate safety standards, and the frame used to hold the filter columns was evaluated and redesigned by a professional engineer.

2. The operation of the pilot plant must not impact full-scale plant operations.

The Mannheim WTP management did not want the presence of the pilot plant, or any associated activities to disrupt the day to day operations of the full-scale plant. Moreover, as the refurbished pilot plant was to accommodate a flowrate much larger than the original one, it was imperative that the waste flow be diverted to an appropriate location. An automatic waste pump out system,

piped to the full scale flocculator tank drain line was to be designed. Moreover, this system was to have a high level of reliability to avoid flooding conditions in the plant.

3. The pilot plant must fit within the allotted space.

There was a finite area in which the pilot plant could operate. Moreover, there were full scale chlorine lines over top of the space, which were to be avoided. The biofilter columns were therefore to be designed in such a way to avoid contact with these lines. In addition, the system was to be designed to avoid routine operations close to these lines.

## 3.3.3 Design Process

The general design, procurement, construction and commissioning process that was followed for this project was broken into a number of steps. These steps were followed once the list of design features (Table 3-1) had been defined.

- 1. Create diagrams showing functional relationship between components needed to achieve design goals and features
  - a. Develop Block Flow Diagram (BFD)
  - b. Develop Piping & Instrumentation Diagram (P&ID)
- 2. Create mechanical design of custom components
  - a. Design biofilter columns
  - b. Design roughing filter
- 3. Conceptually place all equipment into location
  - a. Develop CAD drawings based on location constraints
  - b. Develop piping isometric drawings.
- 4. Create equipment list based on P&ID and CAD drawings
- 5. Procure materials identified in equipment list
- 6. Construct pilot plant
- 7. Commission pilot plant

The design steps shown above were treated fluidly. Design issues that arose during any part of the process were evaluated for their significance in the context of previous steps and documents developed were adjusted accordingly.

The design goals and features shown in Table 3-1 were developed through informal interviews with previous operators and in fulfillment of the operational design goals.

Once a general set of design features and constraints were agreed upon, a BFD was created (Figure 3-2). This document condensed the overall function of the pilot plant into various unit operations, and showed the functional relationships between each of them. Once this was done and agreed upon, a P&ID was synthesized (Figure 3-3). This schematic is a natural extension of the BFD which shows each of the pieces of equipment needed for the unit operations, their functional relationships, and valves. Also included on the P&ID were the various instrumentation and control functions. This document would form the blueprint for the rest of the design exercise.

Once the functional requirements and the relationships between conceptual equipment were established, the detailed mechanical design of the custom equipment was done. This included the biofilters, and the roughing filter. This activity was performed by a fellow graduate student, Ahmed ElHadidy, the details of which will be included in his forthcoming PhD thesis (ElHadidy 2016).

The design and construction of the pilot plant were restricted in terms of available floor space as well as the height available for equipment. Moreover, the main driving force for the water flow was gravity and as such required careful process piping placement. This issue was identified as being critical, and to allow for efficient design, a CAD model was created using Sketchup (Trimble Navigation Ltd.), using measurements taken from the pilot plant location. This enabled the quick and effective modeling of piping and equipment placement and to create piping isometric drawings which would be used in the construction phase. In addition, this also allowed a more accurate estimation of the amount of piping and related equipment (hangers etc.) required for the project thus keeping costs low. Multiple piping isometrics were done before settling on a final design (shown in Appendix A).

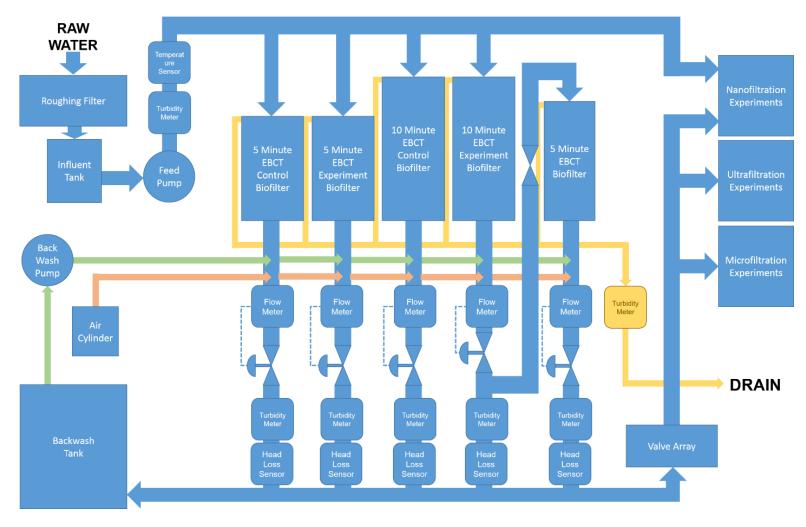


Figure 3-2 Mannheim pilot plant block flow diagram

Once the pilot plant design was conceptualized with the aforementioned documents, a detailed equipment list was generated. This formed the bulk of the procurement phase of the project. From the equipment list, quotes were requested from prospective suppliers, and cost estimates were generated. Equipment was ordered, and equipment which was first to arrive was installed first.

Parallel with the procurement phase, while equipment was still being ordered and received, the construction phase begun. This entailed the dismantling and disposal of parts of the original pilot plant infrastructure, and the installation of the new equipment. The biofilter columns of the new design were greater in number, larger and heavier than the original pilot columns. As such, upon suggestion of Mannheim plant staff, a structural engineering report was commissioned as to the integrity of the existing support structure with the new biofilter columns. From this, structural improvements were found to be necessary and carried out by a local welding shop. Once the new structure was in place and painted (to prevent rusting), the installation of the new equipment began. Installation of the equipment took approximately 6 months.

## 3.4 System Description

The P&ID for the pilot plant is shown as Figure 3-3. General descriptions of the pilot process flow is followed by in depth description of its components highlighting the novel and unique components for this pilot plant design. It should be noted that the flowrates indicated on this figure are for the original design, however due to a number of circumstances, they may or may not reflect the current field condition.

# 3.4.1 Location

The pilot plant is located at the Mannheim WTP in Kitchener, Ontario. The Mannheim WTP uses chemically assisted filtration and takes water from the Grand River located nearby. Water from the river is diverted and stored in a reservoir with a three day retention time prior to being pumped via high lift pumps to two holding tanks each with a 30 minute retention time and then fed by gravity into the treatment plant. It is then coagulated with acidified alum or poly aluminum chloride (depending on the season), flocculated and ozonated prior to being filtered by biologically active granular activated carbon. Following filtration, water is disinfected with ultraviolet light and chlorine gas prior to being pumped to the distribution system.

The Mannheim treatment plant is separated into two parallel treatment trains, called train 1 and train 2. Water for the pilot plant in this study takes water from train 2, directly behind the plant rapid mix unit.

#### 3.4.2 Filtration Process Flow

Raw water, taken directly from the influent to the Mannheim WTP, is filtered through each biofilter and either collected together in the biofilter effluent/backwash tank or used for experiments (Figure 3-2)

Raw water is ferried under line pressure through the raw water line (not detailed in Figure 3-3) and distributed equally to all four roughing filter portions shown in the top left hand corner of this figure. Water from these roughing filter sections is collected in a common reception tank (Tk1) and pumped via two low shear pumps in series (P1 & P2) into the top of each of the four main biofilters: 5 minute EBCT control biofilter (BF-5C), 5 minute EBCT experiment biofilter (BF-5E), 10 minute EBCT control biofilter (BF-10C) and 10 minute EBCT experiment biofilter (BF-10E). Water levels on top of the media in the biofilters is kept at a constant level via a drain installed at the top of each filter. Biofilter effluent flow is kept at a constant specified design flow by individual flow controllers specific to each filter (e.g. for BF-5E this is FT1 and V-31). Biofilter effluents are collected into their respective break tanks in the reception trough before flowing into the combined biofilter effluent/backwash tank. In addition, a portion of the effluent from BF-10C can be redirected from its specific break tank into the top of the 15 minute EBCT biofilter (termed BF-C for historical reasons) with the flowrate being monitored by FM 5 and controlled by the globe valve V-67. In this way, the effluent of BF-C has been subjected to the combined EBCT of both BF-10C and BF-C which at the design rate flow is 15 min.

## 3.4.3 Backwash Process Description

During the backwashing operation, collected biofilter effluent is pumped through the bottom of the biofilters, to dislodge and dispose of particles accumulated during the filtration cycle. Dirty water is discharged trough the overflow at the top of the column to the drain. The system is designed so that each filter may be backwashed separately thus not interfering with the operation of the other biofilters.

The system was designed so that individual filters could be isolated and drained (Figure 3-3). Isolation occurs by closing a shut off valve at the bottom of the biofilter (not shown) directly upstream of the effluent flow control valve for the biofilter in question. In the case of BF-5E, the valve to be closed would be V-20 located directly upstream of FT1, thereby isolating the flow control valve V-31. Following this, the water level in the biofilter is drained by the opening of the drain valve, which in the case of BF-5E is V-32. Once the water level in the biofilter has drained sufficiently, this valve is closed again, and another valve, the backwash valve can be opened. In the case of BF-5E this is V-41. At this

point, the backwash pump (P5) is energized, and biofilter effluent collected in Tk2 is pumped through the bottom of the biofilter being backwashed and out through the overflow near the top of the biofilter. Flow control of the backwash water is monitored by the variable area flowmeter, FM7, and controlled manually by the globe valve, V-65. The addition of air to the backwash water is also possible via an externally connected air cylinder. Dual isolation valves exist for each biofilter connection so as to minimize the risk of intrusion of water into these air lines. In the case of BF-5E, valves V-10 and V-17 would be opened to allow for air scour.

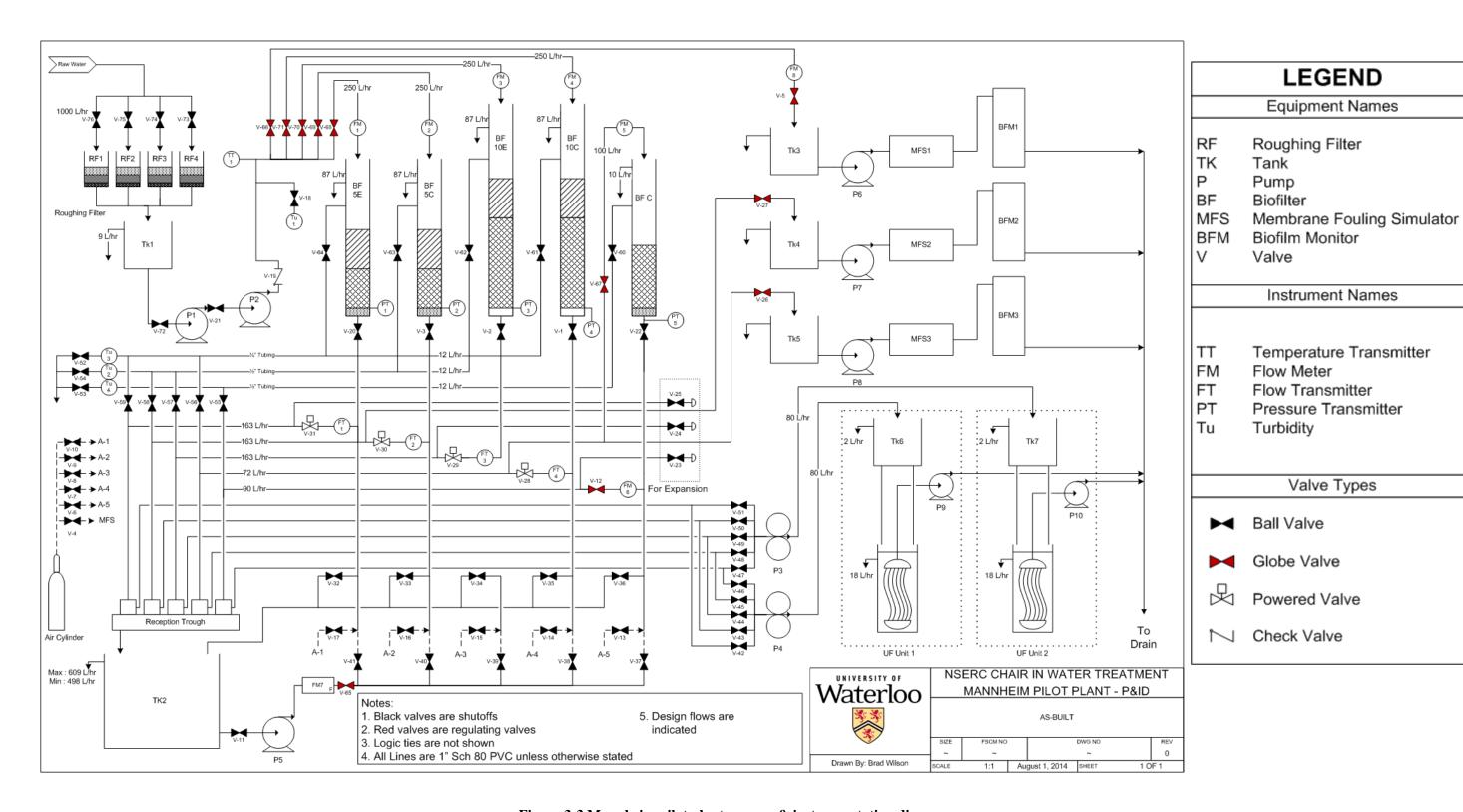


Figure 3-3 Mannheim pilot plant process & instrumentation diagram

# 3.5 System Components

The following section describes the technical details of the various components of the pilot plant, and places emphasis on the various innovative features of each.

## 3.5.1 Piping Design

In addition to being designed with the goal of connecting system components, process piping was designed with the following additional objectives: 1) minimization of the growth of microorganisms within the piping, 2) minimization of interferences laboratory testing of water quality parameters and 3) longevity. Moreover, the driving force for the flowrate for much of the system was gravity, and as such hydraulic conditions were carefully considered when choosing piping and equipment placing, as well as piping type and diameter.

All process piping was opaque 1" schedule 80 PVC with the exception of turbidimeter sampling lines, which were ½" Perfluoroalkoxy Alkane (PFA) tubing. Opaque PVC was chosen to minimize the growth of photosynthetic microorganisms within the piping. The growth of these organisms was undesirable for two reasons: Firstly, the accumulation of biomass within the piping has the effect of increasing pipe pressure loss, and could lead to a reduction of flowrate below design values. Secondly, these microorganisms may biodegrade dissolved organic carbon fractions within the water, effectively changing its character – a situation unacceptable for the planned NF and RO experiments. In addition, hard PVC piping was chosen to minimize the leaching of plasticizers, which enhance biofilm growth within the piping.

Longevity was another major process piping design goal, and to this end, piping was designed with split ring pipe hangers where appropriate. This ensured that piping would stay where they were designed to be, and the weight of the piping full of water would not cause undue stress of piping components, leading to failure over time.

Hydraulic considerations played a major role in piping design. As stated earlier, the driving force for all water flow after the biofilters, was gravity. To this end, all equipment to receive biofilter effluent water was placed below hydraulic grade to ensure adequate flow. In addition, as the amount of hydraulic head available was limited, the diameter of the piping had to be chosen carefully. If the piping diameter was chosen too small, undue pressure loss within the piping may have led to unacceptable low flowrates, given the length of piping after the biofilters. If the pipe diameter was too large, the weight of the piping as well as cost would have increased unduly. As a compromise 1" diameter PVC piping was chosen since it was large enough to minimize pressure loss, while keeping cost and weight at acceptable levels.

The filters used within the pilot plant were biologically active media filters, and as such they were submerged in water at all times to avoid loss of the microbial community within the media if they were to run dry. The pilot plant was designed to be semi-autonomous, with operator intervention required only multiple times a week to perform the backwashing operation. Hence, a loss of feed

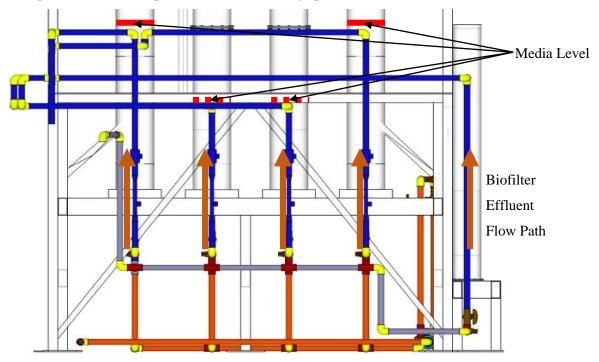


Figure 3-4 Biofilter piping (blue: effluent, grey: drain, orange: backwash)

water to the pilot plant (caused by equipment failure, or a Mannheim WTP shut down for example) would cause water to drain from the biofilters, potentially leading to significant loss of attached biomass on the media and compromising experiments. To avoid this event, and maintain water levels above the media at all times, the biofilter effluent pipes were designed and positioned to create an inverted siphon. The flow path of the biofilter effluent, with respect to earth, rises above the media height within the biofilter bed. Thus, if a loss of feed water event occurs, the media is assured to stay wet. This is shown in the CAD drawing in Figure 3-4.

## 3.5.1.1 Pipeline Cleanliness Monitors

To monitor the cleanliness of the raw water pipeline, so-called 'cleanliness monitors' were installed. These are 6" pieces of clear PVC pipe installed at the middle and at the end of the raw water line, wrapped in black foam during normal operation. This allows the operator to check the cleanliness of the raw water line to determine if cleaning is required. Directly downstream of the first monitor a tee section

of pipe was installed, which allows the operator to isolate the upstream portion of pipe and use high velocity water to scour built up material in the pipe.

#### 3.5.2 Filters

## 3.5.2.1 Roughing Filter (RF1 to RF4)

The roughing filter (Figure 3-5) located at the beginning of the process was installed to mitigate large turbidity spikes in the incoming raw water. It consisted of four independent rough gravel filters fed by a common influent and the effluents of the 4 individual roughing filters were collected in a common tank from where all biofilters were fed (not shown in Figure 3-5). This approach ensured a consistent influent water quality for all biofilters. In addition each independent roughing filter 'node' could be isolated and cleaned manually as part of the backwashing operation while keeping the roughing filter in operation.

The detailed design of the roughing filter was performed by Ahmed El-Hadidy and further information may be found in his forthcoming thesis (ElHadidy 2016).



Figure 3-5 Roughing filter

# 3.5.2.2 Biofilters (BF-5C, BF-5E, BF-10C, BF-10E & BF-C)

The biofilter section of the pilot plant was composed of five biologically active media filters columns all designed to be run at a loading rate of 5 m/h (Figure 3-6). As per the design requirements detailed in section 3.3.1, the biofilters were run in two parallel trains of identical filters, arranged in a control / experiment configuration to accommodate the UF optimization study. The EBCTs and loading rates were

chosen to correspond to the original pilot plant, for data consistency between studies conducted on the various iterations of the pilot plant. The height of each biofilter column was chosen to add clearance from the overhead chlorine gas lines (not pictured).

BF-5C and BF-5E are identically constructed 8 inch diameter dual media filters with an EBCT of 5 minutes and with 5 m/h loading this translates into a flowrate of 165 L/h. These filters feature 20 cm of anthracite on top of 20 cm of sand supported by a 15 cm layer of rough gravel. Due to flow sustainability limitations discovered during the commissioning phase of the project, the operating flowrate was reduced to 100 L/h, corresponding to a loading rate of 3.08 m/h and an EBCT of 7.79 minutes.

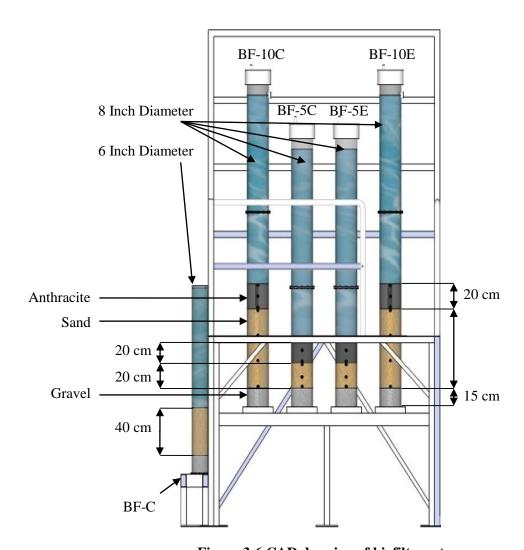


Figure 3-6 CAD drawing of biofilter setup

BF-10C and BF-10E, are also identically constructed 8 inch dual media filters designed to be run at a loading rate of 5 m/h, an EBCT of 10 minutes and a flowrate of 165 L/h. These feature 20 cm of anthracite on top of 63 cm of sand supported by a 15 cm layer of rough gravel. Like the previously described filters, flow limitations required the operating flowrate to be 100 L/h, corresponding to a loading rate of 3.08 m/h and an EBCT of 16.17 minutes.

BF-C is a 6" diameter vertically oriented mono-media filter with a 5 minute EBCT and is run as an extension to BF-10C. This filter features 40 cm of sand supported by 15 cm of rough gravel. BF-C was created as part of the original pilot plant to test the effect of a long EBCT on biofilter performance. However, due to space constraints, the building of a single filter capable of obtaining this high of a contact time was not feasible. Thus, BF-C was created as a piece wise filter. By using a portion of the BF-10C effluent as the influent to BF-C, the effluent of BF-C would be subjected to a total design EBCT of 15 minutes, in essence creating a large piece-wise filter. Due to flow limitations, the operating EBCT of BF-C is 21.17 minutes. The detailed design of the biofilters was performed by fellow graduate student Ahmed El-Hadidy, and more information can be found in his forthcoming PhD thesis (ElHadidy 2016).

## 3.5.2.3 Experimental Connections

The pilot plant was designed to allow for simultaneous access to the effluents of each biofilter as well as the pilot plant influent water, after the roughing filter. Two primary experiment setups are shown connected to the pilot plant in the right half of Figure 3-3 however the system was designed to offer the flexibility to attach any series of experimental setups.



Figure 3-7 Reception trough

The first set of water taps available for experimentation are shown by Valves V-23 to V-27, which take water directly downstream of the effluent flow control valves (Figure 3-3). The second set of water taps

for experimentation takes water directly from the reception trough shown in Figure 3-7, which allowed for simultaneous access to each of the biofilter effluent flows, with as short as possible break tank retention to minimize interferences. The reception trough is composed of five different small break tanks, corresponding to each filter, which sits across the top of the Tk2. The filter effluent of each filter flows via a pipe into the top of the respective break tank, fills the tank and overflows via a spout in the top and into Tk2 below. A port at the bottom of each break tank (not pictured) is connected via a PFA Swagelok tubing to the valve array consisting of V-42 to V-51. The output of each of these valves is connected to peristaltic pumps P3 and P4. The effluent from this location was not designed to go to biofouling experiments, and thus the leaching of plasticizers from the PFA is not a concern.

#### 3.5.2.4 Establishment of Biomass on the Media

During the startup of biofilters, microorganisms present in influent water are expected to become attached to the filter media and form biofilms in a processes known as colonization. Microbiological activity is typically higher in warmer temperatures, and as such, the growth of biofilms is typically faster during warmer weather. Due to this fact, the acclimation phase is commonly much faster in the warmer summer months as compared to the winter, especially given the Canadian climate. During the construction of the pilot plant, the commissioning was forecasted for the early months of 2014, and therefore the decision was made to acclimate the media concurrently during the construction phase of the pilot to take advantage of the summer temperatures.

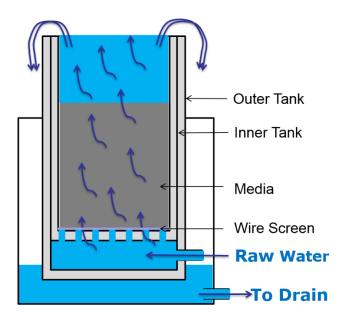


Figure 3-8 Acclimator diagram

Acclimation took place in custom built up flow filters, shown in Figure 3-8. Media was placed in the filters, and pilot plant inlet water was allowed to flow through from the bottom and overflow to drain. These acclimators were run for approximately 6 months prior to the media being transferred and installed in the newly constructed filters. During the operation of the acclimators, the accumulation of particles in the upflow filter bed created flow channels, and they were periodically cleaned, by increasing the flowrate and fluidizing the bed. The overall simple acclimator approach allowed for a much quicker start-up of these biofilters probably saving 3 month start up time, than if media acclimation had taken place in the newly constructed biofilters.

## **3.5.3 Pumps**

## 3.5.3.1 Main Feed Pumps (P1 & P2)

The main raw water feed pumps were seal-less, magnetically driven centrifugal pumps with high end, inert materials (i.e. PTFE and EPDM) for pump components in contact with the water. This design choice avoided leaching of any organics into the feed water from pump seals, leading to biofouling experiment contamination.

Although in this pilot plant, no coagulation pretreatment was used, the use of pumps was still of concern, as shear forces exerted during the pumping action may change the character of the particles in the water being pumped by destroying natural agglomerations of materials which occur in natural water (Buffle et al. 1998). The use of low shear pumps, such as positive displacement, piston or screw type pumps was highly desirable. However, they were excluded due to cost factors, the large minimum flow rate, as well the inherent pressure pulses present with these types of pumps. Albeit it is relatively rare to use centrifugal pumps for the main feed line for pilot plants, these were chosen here. To minimize the shear force placed on water being used with the centrifugal pumps chosen, a low RPM motor and coupling was used. Typically, centrifugal pumps used in similar applications, are coupled to a motor running at 3500 RPM. The motor used in this particular application was 1750 RPM, almost half of the typical running speed. This increased the cost of the pumps, but significantly reduced the velocity gradient (G value) of the pump impellers relative to the fluid, and hence the shear forces on the particles in the water.

The main feed pumps were two serially connected Promag M7 centrifugal pumps (Warrender, ltd.) each of which are magnetically coupled to a low RPM (1750) motor. These pumps were seal-less, and driven by magnetic coupling to the motor. The wetted materials within the pump itself were comprised of polypropylene with glass fiber, ceramics, PTFE and EPDM.

#### 3.5.3.2 Biofilter Effluent Transfer Pumps (P3 & P4)

The biofilter effluent transfer pumps were two peristaltic pumps chosen for this application due to a number of factors. Firstly, the relatively low biofilter effluent flowrate available for experimentation (<88 L/h), and the ability of the pumps to modify their speed and hence the flowrate made these especially suited to this application. Secondly, the low shear stress applied by these pumps ensured that the quality of the particles and dissolved components would not be impacted by the pumping action.

The pumps used were two parallel Masterflex peristaltic pump heads (ColeParmer LLC) attached to a 6 to 600 RPM variable frequency drives were used to transfer biofilter effluent from the reception trough to other experimental units for comparison. The pumps were connected to the valving array as shown in Figure 3-3 such that any biofilter effluent could be compared to any other biofilter effluent. ½" PFA tubing was used to connect the reception trough to the valving array and then again from the peristaltic pumps to the experimental units being used.

## 3.5.4 System Control

Although the pilot system was designed to be operated manually for many operations, the biofilter effluent flow, the main feed pump flows as well as the main drainage system were automated. These systems are typical of semi-automatic pilot plants, and not wholly innovative as such. The descriptions are included in this section for completeness.

#### 3.5.4.1 Backwashing System (P5)

A centrifugal pump, which was part of the original pilot plant, was used as a backwashing pump. This pump was wired to be run off of local electrical mains, and could be turned on and off by a local switch. Flow was monitored by a 3000 L/h maximum variable area flowmeter, and flow control was achieved manually by V-65, a high precision globe valve (Chemline ltd). This globe valve was chosen for flow control as it had a high turn to opening ratio and a relatively linear flow coefficient (Cv) to opening percentage in the flow range required for backwashing. In this way, operation of this valve would produce a linear flow response which could be precisely adjusted. It was estimated, based on previous knowledge of the pilot plant, that the flowrate required for the backwashing operation was between 100 to 2000 L/h, and that the backwash pump, unencumbered, could produce approximately 4000 L/h. Therefore, it was estimated that the opening of the globe valve to be installed should be below 50%, as the top range of the flowrate required for backwashing was half of the total flowrate capable by the backwashing pump. Figure 3-9 shows the globe valve characteristics, Cv through the valve as a function of opening fraction (percent open) of the valve. As can be seen, the relationship is approximately linear below 50%, and hence this valve was judged appropriate for this use.

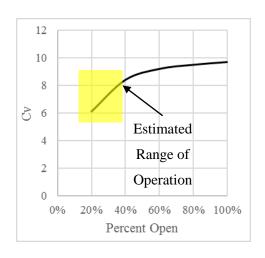


Figure 3-9 Backwash valve characteristics

#### 3.5.4.2 Biofilter Effluent Flow Control

Except for BF-C biofilter effluent flow control was achieved via a custom built feedback flow control loop. Only the effluent from BF-C featured a variable area flowmeter and manual flow control valve.

Each control loop featured an electromagnetic flow element (Siemens AG), called the 'primary', a remote flow transmitter (Siemens AG), called the 'secondary', a proportional integrative derivative (PID) controller (Omega Engineering) and an electromechanical valve positioner connected to a metering ball valve (Chemline Plastics Ltd.), connected as shown in Figure 3-10.

The electromagnetic flow element measures fluid flow through an application of Faradays Law. The flow element outputs a signal in a proprietary signal protocol to the flow transmitter, which converts this into engineering units for display, as well as outputs a 4-20 mA signal proportional to the flowrate (in the calibrated range) to the PID controller. In between the flow transmitter and PID controller, the signal is split for logging by the data logger as explained in Section 3.5.5.5.

The PID controller compares the signal received by the flow transmitter to the set-point entered by the user and follows the traditional PID control algorithm to minimize this error (OMEGA Engineering n.d.). It outputs a 4-20 mA signal which is sent to the flow control valve. The signal received by the flow control valve dictates the amount to open or close, adjusting the flow rate within the pipe. This in turn affects the flow measured by the flow element, and the cycle repeats until a steady state is achieved.

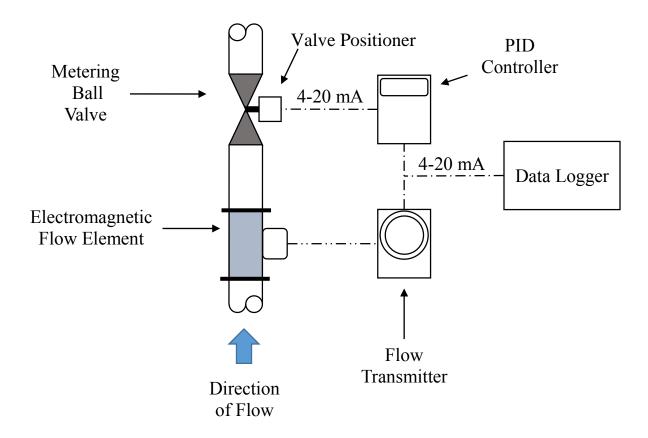


Figure 3-10 Biofilter effluent flow control loop

A major design issue encountered during the installation of the flow control loops was the relatively large pressure drop across the flow meters. The uncertainty in the flow measurement is proportional to the flow velocity through the meter, and as such, the flow area inside of the flowmeter is small (0.01") relative to the effluent pipe size (1"). To cope with the small internal diameter, a series of piping reductions were added to the pipe line to avoid a sudden large diameter reduction. Despite this effort, due to the small diameter of the flowmeter, the maximum sustainable flowrate for the filters was set at 100 L/h.

The flow control loops were tuned using the Zeigler-Nichols PID tuning method (Riggs & Karim 2006) as a starting basis and tweaked as necessary. In addition, due to large flow fluctuations within the pipeline, due to either external electrical noise, ungrounded flowmeters, or due to legitimate process fluctuations, high electrical dampening factors were used on both the transmitter and PID controller.

#### 3.5.4.3 Main Feed Pump Control

The feed water to the main feed pumps (P1 & P2) is fed from a small ~30 gallon tank (TK1 Figure 3-3) into which water from the roughing filter flows. The steady state level in this tank is a function of the flowrate in and out of the tank, and as these are set manually with relatively imprecise flowmeters, small errors between both flowrates may result in a gradual and virtually non-perceptive decline (or increase) in

water level in TK 1. A major concern if the water level declines too much is running dry of the pumps. To avoid this, float switches wired into the power mains for each of the feed pumps were placed into this tank. When the water level in the feed tank reaches a certain low level, the pumps automatically shut off until the water level in the tank recharges to a safe level. An unintended consequence of this type of pump protection is so-called feed cycling. This occurs when an imbalance between the influent and effluent flowrates to the main feed pumps, and power to them cycles on and off. This in turn causes the liquid level in the biofilters to drop and rise in response. This behavior was seen during commissioning oscillating behavior of the pressure transducer signals used to record the biofilter headloss. Later on during regular operation, the tolerances on the flowmeters are such that this behavior did not occur when the flowrates were set correctly. However, when the flow meters become dirty and are not cleaned in time, this behavior may be seen.

## 3.5.4.4 Drainage System

The total flowrate through the pilot system was designed to be between 600 and 800 L/h depending on the flowrate of the biofilters. As the pilot plant is a flow through system, this water, once treated and used for experimentation, is drained. Through discussions with Mannheim WTP plant staff, it was discovered that the flowrate through the pilot would quickly overwhelm the sump if the entire pilot plant effluent were to be discharged into the sump. Hence the bulk of the flow through pilot plant was to be discharged to another location. The decided upon location was the full-scale flocculation drain lines, which are connected to the full-scale residuals management plant on site.

In practice, the pilot effluent flow was split and drained in two locations, i.e. the sump and the flocculator waste line. Biofilter overflow, turbidity meter effluents, small tank overflows, biofilter backwash water and experiment water are drained to the local sump within the Mannheim WTP. These drain flows total approximately 200 to 400 L/h. The remaining flow up to 600 L/h, are the remaining biofilter effluents which are not used for experimentation and hence flow into the backwash tank. The overflow from this tank flows via a 4" diameter PVC pipe to another tank within a containment structure near the pilot plant. This second tank, called the 'waste tank' is connected to a centrifugal pump on a float switch. The waste tank is allowed to fill before the float switch activates the connected pump and drains the water into the flocculator waste line. This line drained by gravity to the sanitary sewer and the plant staff allowed the waste from the pilot plant to be discharged here. Normally empty, this pipeline is used to drain the flocculators when manual cleaning operations are scheduled (about once per year). When the draining operation commences, the pressure in this line is roughly 9 psi(g). To minimize the risk of backflow through the system connection, two check valves were placed on the drain line to ensure backflow prevention. Moreover, to minimize the risk of backflow in the event that the drain pump is running at the

same time as the flocculator drain operation is happening, the centrifugal pump used was oversized such that the discharge pressure would be able to overcome the increased pressure in this line.

#### 3.5.5 Online Instrumentation

The system was designed with a number of online measuring devices. These either provide local indication for manual readings with no data logging capability, such as variable area flowmeters, or they are instruments which provide a signal either for control purposes or as information which is logged by a nearby data logger, and stored on a local PC. The equipment described in this system control section is typical for pilot plants, and included here for completeness.

Biofilter effluent flowrate was measured by electromagnetic flowmeters used in the flow control loop for each biofilter. These are signified by 'FT' meaning 'Flow Transmitter' (Figure 3-3). The signal as logged by the data logger was tapped from the signal wire connecting the flow measuring device installed on the pipeline and the flow transmitter which was used by the flow controller to adjust flow (Figure 3-10). Temperature is measured by a resistive temperature device (RTD) installed at the biofilter influent stream. This instrument is signified by 'TT' signifying 'Temperature Transmitter'. Column headloss was measured by pressure transducers located at the bottom of each of the biofilters signified by 'PT' meaning 'Pressure Transducer'.

#### 3.5.5.1 Turbidimeters (Tu1, Tu2, Tu3, Tu4)

Turbidity monitoring of the effluent of all five biofilters, as well as the turbidity of all five biofilter backwash waters was required as part of the design. To avoid the use of 10 dedicated turbidimeters, which would elevate project cost, a unique valve arrangement was employed to use only 3 instruments for measuring these signals, as not all would be required to be measured at the same time. For example, the effluent turbidity and backwash turbidity of BF-5C would not need to be measured together and therefore could use the same turbidimeter.

Turbidimeters are signified by 'Tu' meaning 'Turbidity' (Figure 3-3). These measure turbidity after the roughing filter and prior to the biofilters (biofilter influent) as well as in the biofilter effluent and backwash water. Each turbidity meter has the ability to measure either a biofilter effluent or backwash water, as neither would be necessary at the same time. The effluent turbidity measurements can measure either the control filter of each train (BF 5C, 10C, C) or the control and experiment of a particular train (BF-5C and BF-5E for example). Tu1 was dedicated to the continuous monitoring of the influent turbidity.

Each turbidimeter was a HACH FilterTrack 1720E Low Range Turbidimeters with a published measurement range of 0.001 to 100 NTU, and an accuracy of +/-2% within the range of 0 to 40 NTU range and +/- 5% of the reading in the range of 40 to 100 NTU. A minimum flow to the turbidimeters of 12 L/h was required for adequate measurement. These turbidimeters were connected to the SC200 Universal Controller (HACH), which provided local indication as well as a facility to output the signal to the plant data logger. Calibration of these meters was performed at the commissioning of the pilot plant by the recommended 1-point calibration method using the HACH provided 20 NTU formazan standard and repeated as necessary.

The turbidimeters were connected to the pilot plant via ½" PFA tubing to the points shown in Figure 3-3. The waste from the turbidity meter was sent directly to the Mannheim WTP sump for wasting. The use of this water in a once over type arrangement allowed for the choice of a flexible tubing, which is prone to leaching of materials. It should be noted that the water being monitored for turbidity was not used in any laboratory analysis.

## 3.5.5.2 Flowmeters (FM1 to FM 8)

Local indication of flowrate was provided throughout. These were signified in Figure 3-3 as 'FM', meaning flow meter. These are inline variable area flowmeters (Chemline Plastics Ltd.), and provide indication of flow to the operator via a float in a tube.

All flow meters were placed in line in areas of the pilot plant where it was convenient for the operator to have local indication of flowrate for proper system operation, but were not critical values for projected experiments. Typically these were locations where the flow needed to be set manually, but was not expected to experience flow transients. Examples of locations include the inlet to each individual biofilter, the backwash piping and the raw water line.

A particular challenge with this type of flow meter is the accumulation of particles affecting the flow measurement. These type of flowmeters have a heavy float inside a cone shaped apparatus, and the float will rise in the meter proportionally to the flowrate, based on the area difference between the float and the outer wall. The accumulation of particles in these floats leads to this area difference being smaller than intended and the meter will indicate higher than actual flow readings. As such, it was important during the operation of this system to continuously monitor the accumulation of particles, and clean them when appropriate.

## 3.5.5.3 Resistance Temperature Detector (TT1)

Temperature of water flowing through the system was monitored by a Resistance Temperature Detector (RTD) (ColeParmer) placed at the common influent to all biofilters directly after the roughing filter. This type of temperature detector measures temperature by measuring the resistance in a coiled wire of a specific material within a sheath in the device which can be correlated to temperature. The range of this RTD was -40 to 70 degrees Celsius, and it produces a standard 4-20 mA signal in proportion to the temperature. The RTD comes calibrated from the manufacturer.

In this application, the RTD was a passive instrument, requiring an external voltage to be applied for measurement. This was provided by a power circuit, wired in parallel with the pressure transducers, and connected to the data logging modules.

## 3.5.5.4 Pressure Sensors (PT1 to PT5)

Headloss of each of the biofilters was measured by pressure transducers (ColeParmer) installed in the sampling ports in the gravel underdrain section in the biofilters. These transducers work by measuring the deflection of a flexible membrane exposed to the pressurized environment, and correlating this deflection with the perceived pressure. The range of these instruments was 0-5psi(g), and they output a 4-20mA signal in proportion to the pressure. These devices come calibrated from the manufacturer. Like the RTD, these devices required an applied external voltage to operate, and were connected in parallel with each other, along with the RTD, and wired into the data logging modules.

These devices were installed directly into the biofilters via the sampling port just above the underdrain gravel support layer. As such a fine mesh screen was included in the isolation valves directly in front of them to keep any media particles out and help protect the measuring membrane. The homogeneity of the media in the biofilters, as well as the pressure drop characteristics of the isolation valve and the mesh screen may contribute to the spread of pressure readings between all the filters. Although the absolute values of the driving pressure for each filter may differ slightly, the trends are comparable between all filters.

# 3.5.5.5 Data Logger

Data from all electronic online measurements were captured using two HOBO Energy Logger multichannel energy data logging systems (Onset Technologies ltd.). Each data logger was able to accept 3 active smart modules (capable of accepting two data signals), and six accessory ports, (capable of accepting a passive channel module which accepts only one data signal). These data loggers were connected to a nearby personal computer to store, convert and display the data. The data loggers work by collecting and storing the data locally in user defined intervals, and would be 'dumped' to the computer via user request. The units were powered by AC power adapters plugged into the wall nearby.

Signals which came from active sensors include turbidity and effluent flowrate, and were connected directly to one of the aforementioned modules via shielded twisted pair cables. The shield was connected to the ground of only the data logger, which was connected to the electrical ground of the AC power for the data logger units. As the flow control loops did not have a signal output facility, the signal was spliced from the signal wire between the pressure transmitter and the PID controller. Due to this fact, each flowrate signal was routed to a smart module due to the lower impedance across the positive and negative signal connections as compared to the other type of module.

Pressure and temperature signals were not active, and required a form of excitation energy. These signals were connected in a parallel circuit which included the modules they were connected to as well as an AC to DC power adapter. In this way, the data logger connection modules formed part of the monitoring circuit.

#### 3.6 Conclusions

A fully instrumented pilot plant using biofiltration without pretreatment capable of providing water to multiple membrane research studies has been designed and constructed at the Mannheim Water Treatment Plant in Kitchener, Ontario, using Grand River water as the influent. This pilot plant has been constructed to meet 4 primary design requirements: accommodate parallel studies, closely mirror full scale operation, account for factors outside the control of the operator and minimize microbial growth to allow for membrane biofouling studies. Large, parallel biofilters were constructed to accommodate parallel studies. Low shear pumps were included to closely mirror full scale operations. Opaque schedule 80 PVC piping as well as various pipe cleaning facilities were installed throughout to both account for factors outside of the operators control and to minimize unintended microbial growth.

In addition, a number of secondary design requirements have been addressed. These include: the ease of operation and maintenance, increasing the amount of data available and longevity. A centralized roughing filter, a large number of parameter measurements and automatic protection were some of the features applied in pursuit of this aim. Some features were chosen to address a number of design requirements.

A detailed P&ID was created for design and operation. A precise CAD model was created to virtually place equipment and to create piping isometrics. The CAD model and the P&ID facilitated the creation of a derailed equipment list and piping list. The pilot plant was constructed in a 6 month span. This pilot

plant was used for the studies described in Chapters 4 and 5, and is currently being used by other graduate students for a variety of studies.

# Chapter 4

# Influence of Backwashing on Biofiltration without Pretreatment Operation

#### 4.1 Overview

Direct Biofiltration without pretreatment ( $BF_{wp}$ ) (coined by (Huck et al. 2015) is a type of biologically active granular media filtration which differs from conventional chemically assisted media filtration in that it applies source water directly to the biofilter bed without prior treatment (i.e. coagulation or flocculation). Interest in this process is growing as a chemical free method of membrane fouling reduction. The current study examines the performance of the BF<sub>wp</sub> process under changing source water quality conditions as well under changing backwashing regimes using parallel identical biofilters configured in a control/experiment scheme. Three backwashing factors, collapse pulsing time, wash time and wash expansion, were studied using a full factorial statistical design. Collapse pulsing was found to have the largest effect, either as a main effect or in interaction with other factors, while wash expansion was found to have the least amount of influence. A number of three factor interactions were found to be significant, highlighting the complexity and interdependency of the factors studied. It was found that while backwashing was shown to not have an influence on DOC removal and biological activity of the biofilm on the media, it did have a profound effect on removal of turbidity and headloss reduction (and hence projected biofilter run time) during the subsequent biofilter run. Backwashing parameters were also shown to have a small influence on the removal of biopolymers which are known membrane foulants. Optimization of backwashing parameters was found to be goal dependent, and optimal settings for biopolymer removal did not coincide with those of turbidity and headloss reduction.

## 4.2 Introduction and Objectives

Rapid granular media filtration is a common unit operation employed by surface water treatment plants with the goal to reduce turbidity levels to well below regulated levels. Typically preceding rapid filters are chemical pretreatment and settling processes (coagulation, flocculation and sedimentation) which serve to chemically pretreat source water turbidity and encourage particle aggregation with the goal of enhancing gravity settling and biofilter grain attachment. Biofiltration (BF) is a specific type of rapid granular media filtration which encourages the proliferation of endemic microorganism communities to form a biofilm on the biofilter media with the goal of biodegrading organic compounds present in the source water. This is done by ensuring a disinfectant residual is absent from any water stream (influent or backwash) that is applied to the biofilter (Crittenden et al. 2012). Biofiltration as a unit operation has been

in use for a number of decades in western Europe, deployed with the goal of ensuring biological stability of the finished water (Urfer et al. 1997). Biological filtration without pretreatment ( $BF_{wp}$ ) is a specific application of biofiltration whereby the chemical pretreatment steps present in the conventional train are removed. This is a relatively new process that is currently being investigated as a pretreatment method for membrane filtration (Huck et al. 2011; Halle et al. 2008).  $BF_{wp}$  is an attractive membrane pretreatment method as it is chemical free, as compared to coagulation which is frequently employed in practice as membrane pretreatment for fouling reduction. When used in this way, the primary treatment goal for the  $BF_{wp}$  process is the removal of membrane foulants. Current research points to biopolymers as being one of the main components contributing to the fouling of UF membranes, and as such, the treatment goals of this process become the removal of these compounds. The removal of biopolymers by the conventional biofiltration process (i.e. including coagulation and ozone) has not been investigated. Detailed investigation of the effect of various operating parameters on biofiltration performance (excluding biopolymer removal) have been completed, however investigations to confirm that these findings apply also to the  $BF_{WP}$  process have not been performed as of yet.

Due to the accumulation of material in media filters, periodic backwashing operations, whereby flow is reversed through the biofilter and accumulated material is flushed out, are required to maintain performance. Multiple strategies are employed for backwashing, typically involving some combination of surface wash, air scour, and subfluidization flow and bed expansion. It has been found that in terms of turbidity removal from collector grains, a condition known as 'collapse pulsing' provides the greatest efficiency (Hewitt & Amirtharajah 1984). This is a condition by which air flow and sub fluidization water flow are applied to the bed concurrently and related by an empirical formula. The result is the growth and sudden collapse of large voids within the biofilter bed. It is the collapse at the end of this process which maximizes the shear force between the media grains during the backwash and causes the greatest amount of attached particles to dislodge from the media (Amirtharajah 1993). This process is typically done first in the backwashing operation as an efficient way to dislodge particles form the biofilter bed.

Biofilter bed expansion describes a condition in which fluid velocity above the fluidization velocity for a given biofilter bed is applied and the bed expands to a multiple of its resting volume. This is used in a typical backwashing operation after collapse pulsing as a secondary method to remove attached turbidity particles, but also to wash already detached particles out of the bed and into the drain. This process has also been shown to apply some amount of shear stress between the media grains, due to random collisions, however this shear force is less than that applied during the collapse pulsing condition

(Amirtharajah 1993). Others have found that very little additional turbidity removal from the bed is achieved above 50% bed expansion (Rasheed et al. 1998).

 $BF_{wp}$  is a relatively new and specialized process which differs significantly from conventional biofiltration due to the lack of chemical pretreatment preceding the biofilter. This affects the character of the turbidity applied to the biofilter in two fundamental ways. Firstly, without coagulation and flocculation, the size of the particles being attached to the biofilter is expected to be quite small in comparison to the conventional process. The efficiency of particle collection by the biofilter is a function of the size of the particles themselves, and this is expected to be much smaller in the  $BF_{wp}$  process as compared to conventional biofiltration. Secondly, without chemical pretreatment, the charge of the particles being applied is expected to be much lower than with chemical pretreatment as is done in conventional biofiltration. Coagulation serves to destabilize particles suspensions and encourage agglomeration by lowering the zeta potential of particles in source water. With this absent, the zeta potential of the particles applied to the biofilter is expected to be much more negative, which influences the strength of attachment to the biofilter media collector grains. Therefore, detachment of particles in the biofilter bed is expected to require less force for the  $BF_{wp}$  process compared to the conventional process.

For the above reasons, it is expected that particle removal by the  $BF_{wp}$  process will differ from the conventional biofiltration process, for which much of the scientific literature is written. Some investigations of the  $BF_{wp}$  process as it pertains to the reduction of UF membrane foulants have been undertaken (Huck et al. 2011; Peldszus et al. 2012; Hallé et al. 2009), however a detailed investigation on the effect of backwashing during of  $BF_{wp}$  which primarily seeks to reduce membrane foulants i.e. biopolymers, has not been undertaken to-date. This work aims to fill this knowledge gap by investigating the performance of the  $BF_{wp}$  process under seasonal variations as well as the effect of backwashing on  $BF_{wp}$  process performance.

#### 4.2.1 Objectives

The overarching objective of this work was to establish whether and to what extent the various backwashing parameters affect the performance of the  $BF_{wp}$  process in terms of removal of membrane foulants, turbidity reduction and biofilter run time thereby providing further information towards establishing this novel process in practice. As backwashing effects in  $BF_{wp}$  may differ substantially from conventional biofiltration, it is uncertain whether results published in literature on conventional biofiltration are applicable to  $BF_{wp}$ .

To this end, a comprehensive review of factors influencing the operation of biofilters was performed. These could be broadly categorized into either operational, design or backwash related. For the current study operational factors such as loading rate, and design factors such as particle size, were kept constant and close to the typical values of full scale water treatment plants to aid in scalability of this work.

Backwash factors were therefore chosen as the focus of this study. The chosen factors were: collapse-pulsing, wash time and wash expansion. These were selected on the basis of ease of manipulation and to resemble full scale practice.

In addition to the backwashing investigation, this study also examined the performance of  $BF_{wp}$  under changing water quality conditions. As this process differs from the conventional biofiltration process, it was important to establish further baseline performance data for  $BF_{wp}$ .

To this end, the following study objectives were defined:

- 1) Investigate the effect of varying water quality parameters on the performance of the  $BF_{wp}$  process.
- 2) Determine the influence of backwashing procedures on the performance of the BF<sub>wp</sub> process.

#### 4.3 Materials and Methods

### 4.3.1 Statistical Design

A full factorial experiment design was used in this study, augmented with two centre points as shown in **Table 4-1**. Experimental runs were performed on a weekly basis and lasted five days each. The use of this design allowed for the calculation of the main effects, as well as 2 and 3 factor interactions. For all response variables studied (Table 4-1) except for log turbidity removal and pressure related variables, the centre point runs were used to estimate the experimental error and to determine significance of factor effects in the subsequent ANOVA tables. The variance between the experimental and control responses was averaged between both center point weeks to obtain the pooled variance estimate for significance testing. Error estimates for turbidity and pressure related response variables were calculated from a pooled variance estimate of performance on the weekends between experimental runs. The variance of these variables were estimated for each weekend and an average of these was used as the error estimate for the subsequent ANOVA calculations. This was done because the weekends represented essentially replicates of the centre point runs as both control and experimental filters were backwashed in an identical fashion on Fridays. As there were 10 weekend replicates for the study, this had the effect of increasing the degrees of freedom for the ANOVA significance calculation and allowed for a high statistical power.

Table 4-1 Factorial experiment design including setpoint values (non-random)

|                 | Week       | _     | Pulsing<br>me | Wash  | Time   | Wash Ex | xpansion |  |
|-----------------|------------|-------|---------------|-------|--------|---------|----------|--|
| Run Number      | Starting   | Level | Value         | Level | Value  | Level   | Value    |  |
| 1               | 2014-09-22 | -     | 0 min         | -     | 5 min  | -       | 30%      |  |
| 2               | 2014-09-13 | +     | 6 min         | -     | 5 min  | -       | 30%      |  |
| 3               | 2014-10-06 | -     | 0 min         | +     | 15 min | -       | 30%      |  |
| 4               | 2014-10-20 | +     | 6 min         | +     | 15 min | -       | 30%      |  |
| 5 <sup>1</sup>  | 2014-10-27 | 0     | 3 min         | 0     | 10 min | 0       | 50%      |  |
| 6               | 2014-10-03 | -     | 0 min         | -     | 5 min  | +       | 70%      |  |
| 7               | 2014-11-10 | +     | 6 min         | -     | 5 min  | +       | 70%      |  |
| 8               | 2014-11-17 | -     | 0 min         | +     | 15 min | +       | 70%      |  |
| 9               | 2014-11-24 | +     | 6 min         | +     | 15 min | +       | 70%      |  |
| 10 <sup>1</sup> | 2014-12-01 | 0     | 3 min         | 0     | 10 min | 0       | 50%      |  |

<sup>&</sup>lt;sup>1</sup> Denotes Centre Point Runs

## 4.3.2 Controlling for Systematic Errors

To account for the variable nature of the source water being tested, this study used two parallel biofilters, with one acting as a control. The backwashing procedure of the control biofilter was kept constant with set-points at the centre point values while the experiment biofilter was varied according to the experimental design (Table 4-1). The response for each weekly run was then the difference between the response of the experiment biofilter and the control biofilter and was used in the subsequent ANOVA analysis.

### 4.3.3 Experimental Setup Description

This study was carried out using a portion of the pilot plant described in Chapter 3 which is shown as Figure 4-1. The pilot plant was located in the Mannheim Water Treatment Plant (WTP) in Kitchener, Ontario. The Mannheim WTP uses chemically assisted media filtration to treat water from the Grand River. Source water for this study was taken from the inlet to the Mannheim WTP, prior to the addition of treatment chemicals.

The setup consisted of two identical biofilter treatment trains which were run in parallel. For each treatment train, source water was fed to a common roughing biofilter and effluent was collected in a small volume tank (Tk1). From there, it was pumped by two low RPM pumps in series to the top of each separate biofilter (designated experiment and control). Water flowed through the biofilters by gravity, through an electromagnetic flow meter and control valve and into the backwashing tank (Tk2). Although the focus of this study was on these two biofilters, the entire pilot plant has a total of 5 biofilters running

in parallel which all fed into the same backwashing tank. Biofilter effluent from all filters, collected in the backwash tank was used to backwash the filters.

The roughing biofilter used in this study consisted of four sections, each containing two coarse gravel beds on top of one another. The four sections were run in parallel so that one section could be manually cleaned without impacting operation. The purpose of the roughing biofilter was to mitigate large turbidity spikes in the incoming water.

The two biofilters used in this study were identically constructed dual media filters consisting of 20 cm of anthracite over 20 cm of sand over a 15 cm coarse gravel underdrain. A 150 cm water depth was included on top of the media. The filters were constructed of two clear schedule 40 PVC column sections with an internal diameter of 8 inches (20.3 cm) connected in the middle with a slip flange. Sampling ports were located throughout the length of the biofilter bed to allow for media sampling. The filters were run in a constant rate mode with the effluent flow rate being controlled by a PID controller feedback loop. Flow rate was measured by an electromagnetic flowmeter and flow control was achieved through a coupled electromechanical positioner attached to a metering ball valve. Effluent flow rate was maintained at 100 L/h, corresponding to a loading rate of 3.08 m/h and an EBCT of 7.78 min in both biofilters.

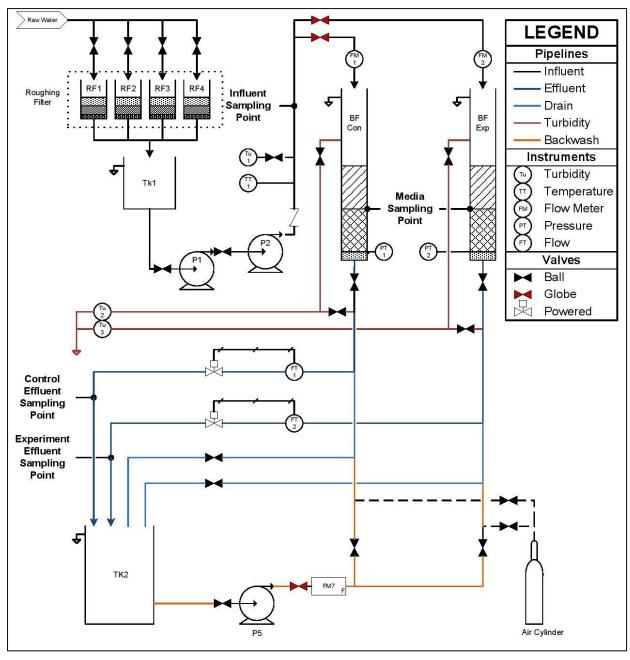


Figure 4-1 Experimental setup including logical connections and sampling points

## 4.3.4 Biofilter Backwashing Procedure

The biofilters were backwashed according to the following procedure.

- 1) Stop biofilter operation and isolate it from the system.
- 2) Open drain valve and drain the water level above the media to avoid biofilter media carry over during the biofilter backwash.
- 3) Initiate backwash according to the following steps (centre point conditions):
  - a. Air + water wash (collapse pulsing) 3 minutes
  - b. Water only wash -10 minutes at 50% bed expansion
  - c. Slowly lower flow to 0 L/h 1 minute
- 4) Open effluent valve and resume biofilter operation

The set points indicated as centre points in Table 4-1 were used for the control biofilter during the entire duration of the study and for the experiment biofilter during the centre point runs (Weeks 5 and 10). During the non-centre point runs, the experimental biofilter was backwashed according to the experimental design outlined in Table 4-1. In addition, the experiment biofilter was backwashed according to the control set-points on the Friday of every experimental run, effectively 'resetting' the biofilter performance over the weekend in preparation for the next experimental run in the following week. As the filters were run in parallel under identical conditions over the weekends, data from these weekends were used to estimate error in subsequent statistical calculations of log turbidity removal and all response variables relating to biofilter headloss.

During each weekly run, the biofilters were backwashed in the mornings on Monday, Wednesday and Friday, or when the headloss in one biofilter became such that a constant effluent flowrate could not be maintained, a condition termed 'critical headloss'. Through previous experience at the pilot plant from commissioning until the time that the current study began, it was found that the critical pressure as indicated by attached sensors at the bottom of the column was approximately 1.5 psi (g) (Figure B-1 in Appendix B)). It was also found that the biofilter pressure decay profile could be fit by a 2<sup>nd</sup> order polynomial function with roughly 4 hours of operation data and used to predict the time of critical pressure loss within a few hours (shown as Figure B-3 in Appendix B). This process was used to determine if premature backwashing was required. If backwashing was required for one biofilter, both filters were backwashed to ensure homogeneity between biofilter runs.

## 4.3.5 Sampling Points and Method

Weekly water and media samples were taken on Thursdays and analyzed in the laboratory for a number of parameters. This date and frequency was chosen as it was in the later part of the weekly run, and it was in between two backwashing operations. Water samples were taken prior to the draining of the biofilter to allow for the gathering of media for analysis. When the biofilters were refilled, if the headloss of either biofilter was at a point that could no longer support a design flowrate, both biofilters were backwashed. The sampling points for the biofilter influent, biofilter effluents and biofilter media are shown in Figure 4-1.

Water samples were analyzed for TOC, DOC, UV absorbance at 254 nm as well as by LC-OCD and FEEM. All samples for these parameters were filtered through an ultrapure water rinsed  $0.45\mu m$  PES filter prior to analysis and analyzed within 24 hours of collection. Between collection and analysis they were stored at  $4^{\circ}C$ .

TOC and DOC samples were analyzed by Jangchuk Tashi using the wet oxidation method (*Standard Methods for the Examination of Water and Wastewater*, method 5310D, 2012) using a OI Scientific model 1030 TOC analyzer. Biopolymer concentrations were determined by NOM fraction characterization using LC-OCD as described by Huber et al. (2011) with labwork done by Dr. Monica Tudorencia. UV absorbance at 254 nm was analyzed according to *Standard Methods for the Examination of Water and Wastewater* method 5910D (2012) with labwork being done by Jangchuk Tashi. A Cary Eclipse fluorescence spectrophotometer (Agilent Technologies) was used for the FEEM measurements with a 1 cm quartz cuvette. Excitation and emission wavelengths ranged from 250 to 380 nm and 300 to 600 nm respectively. The slit width used was 10 nm and the photomultiplier tube (PMT) voltage was 650 V. Emission/excitation coordinates for the protein-like substances was taken to be 330 nm by 280 nm and intensities at these coordinates were used for evaluation. Further details are provided in (Chen 2015).

Media samples were taken from each biofilter at the interface between the anthracite and sand. Media samples were taken on sampling days and analyzed for dissolved oxygen uptake as specified by Urfer and Huck (2001). Labwork for this parameter was done by Sylwia Kolaska. Media samples were gently washed using water obtained from the inlet to the biofilters to ensure only the attached biomass was contributed to the DO uptake reading.

## 4.3.6 Online data Collection

In addition to laboratory samples, a number of online measurements were made, as outlined in Table 4-2. Data from these instruments were collected using two HOBO Energy Loggers H22-001 made by Onset Technologies, which were periodically downloaded and saved to a nearby computer. Data collection

frequency for the backwashing turbidity measurements was set at 2 seconds, while all other parameters were collected once every 5 minutes. Data was downloaded to the computer at the end of every week.

**Table 4-2 Online data collection parameters** 

| Parameter   | Instrument                        | Location(s)   |  |  |  |  |  |
|-------------|-----------------------------------|---|--|--|--|--|--|
|             |                                   | Common influent   |  |  |  |  |  |
|             |                                   | Control biofilter effluent  |  |  |  |  |  |
| Turbidity   | HACH 1720E Low Range Turbidimeter | Experiment biofilter effluent Top of control biofilter (backwash) |  |  |  |  |  |
|             |                                   |   |  |  |  |  |  |
|             |                                   | Top of experiment biofilter (backwash)                            |  |  |  |  |  |
| Pressure    | Cole Parmer Pressure Transducer   | Control biofilter effluent  |  |  |  |  |  |
| Pressure    | Cole Farmer Fressure Transducer   | Experiment biofilter effluent                                     |  |  |  |  |  |
| Temperature | Cole Parmer Digi-Sense RTD Probe  | Common influent   |  |  |  |  |  |
| Flowrate    | ADD EED200 Mag Motor              | Control biofilter effluent  |  |  |  |  |  |
| riowrate    | ABB FEP300 Mag Meter              | Experiment biofilter effluent                                     |  |  |  |  |  |

#### 4.3.7 Data Evaluation

ANOVA methodology was employed for the calculation of the magnitude of effects (main and interaction) of the studied factors and their significance at the 5% level for the various response variables investigated. As a control biofilter was used for the study, the difference between the values of the experiment and control biofilter response at a specific weekly run (Table 4-1) was used as the response variable upon which statistical tests were conducted.

Error estimates for the ANOVA significance calculations were done using the pooled variance of the centre point weeks for all analyzed parameters except for turbidity removal and pressure loss. For these variables, error estimates were taken as pooled variances for the weekend data as outlined in 4.3.1.

Results from laboratory analysis of DOC percent removal, protein-like material percent removal, dissolved oxygen uptake, and biopolymer percent removal, were analyzed directly as one set of samples was taken on Thursdays per weekly run. On-line turbidity data was analyzed on a weekly basis per biofilter. For each data point, a log removal was calculated as the base 10 logarithm of the ratio of turbidity of biofilter effluent to the biofilter influent. These numbers were averaged over the entire experimental week for each biofilter.

Time series data of the turbidity in the backwash water was measured for each biofilter for each backwash. Data points above 100 NTU was not recorded as they exceeded the range of the turbidimeters. The time in seconds that the backwash turbidity spent above 5, 40 and 80 NTU was calculated and used to compare backwashing performance (shown as Figure B-2 in Appendix B). Moreover, the time difference between when the backwashing profile achieved a reading of 40 and of 80 NTU was used as an estimate of the slope of the backwashing turbidity profile.

A similar approach was used for analyzing the biofilter ripening peak turbidity i.e. the turbidity measured in the biofilter effluent immediately after putting it in service again after backwash. The time in seconds that the effluent turbidity spent above 2 NTU was used for this parameter. This limit was chosen due to turbidimeter scaling issues early in the study. The maximum turbidity of the ripening peak was also recorded and used as a response variable in the ANOVA calculations.

To analyze the headloss buildup for each biofilter, time series pressure data collected at the bottom of each biofilter was separated into the biofilter cycles performed in each experimental week. A quadratic function was fit to each pressure loss profile for each biofilter cycle (shown as Figure B-3 in Appendix B). The rate of pressure loss was then calculated as the derivative of this function averaged over the time of the backwashing cycle. The acceleration of the pressure loss rate was calculated as the second derivative of the fit quadratic function.

#### 4.4 Results and Discussion

## 4.4.1 The Effect of Backwashing Parameters on Biofilter Metrics

#### 4.4.1.1 Source Water Quality

Source water quality as measured prior to the roughing biofilter (except where noted) is shown in Table 4-3. This data was collected by the Mannheim WTP staff between October and December 2015. Water temperature fell consistently throughout the period. TOC and DOC concentrations steadily decreased from the beginning of the experiment until the middle of November, when they rose sharply again. Total Kjeldahl nitrogen and the nitrate concentration rose steadily throughout the measurement period. Measured Nitrite concentrations were below the detection limit throughout the measurement period. Like the nitrogen, phosphate concentrations, both total and ortho rose steadily throughout the experiment. These changing inlet water quality parameters point toward a change in water character and quality throughout the study. The decline and then rise of the TOC and DOC measurements was echoed in the results from the pilot plant and the decline was most likely due to cooler river temperatures, while the rise may be due to unseasonably warm and inclement weather near the end of November. The rise of key nutrients, namely nitrogen, nitrates and phosphates may signify a decrease of biological activity throughout the river system, and may be related to the falling temperature of the water.

Table 4-3 Source water quality

| Parameter                  | Range         | Units    | Number of Data Points |  |  |  |  |
|----------------------------|---------------|----------|-----------------------|--|--|--|--|
| Temperature                | 2.01 - 18.59  | Celsius  | 21916                 |  |  |  |  |
| pН                         | 7.52 - 7.93   | N/A      | 31                    |  |  |  |  |
| TOC                        | 6.05 - 7.01   | mg C/L   | 11                    |  |  |  |  |
| DOC                        | 5.95 - 6.98   | mg C/L   | 10                    |  |  |  |  |
| SUVA at 245nm <sup>1</sup> | 2.67 - 3.36   | L/mg C m | 11                    |  |  |  |  |
| Alkalinity                 | 270           | mg/L     | 1                     |  |  |  |  |
| Total Hardness             | 320           | mg/L     | 1                     |  |  |  |  |
| Total Kjeldahl Nitrogen    | 0.54 - 0.73   | mg N/L   | 6                     |  |  |  |  |
| Nitrate                    | 2.21 - 3.63   | mg/L     | 7                     |  |  |  |  |
| Nitrite                    | < 0.03        | mg/L     | 7                     |  |  |  |  |
| Total Phosphate            | 0.018 - 0.093 | mg P/L   | 4                     |  |  |  |  |
| Ortho-Phosphate            | 0.002-0.051   | mg/L     | 4                     |  |  |  |  |

<sup>&</sup>lt;sup>1</sup>SUVA measured after roughing biofilter

## 4.4.1.2 Organics and turbidity removal

The goal of the BF<sub>wp</sub> process is organics removal, specifically membrane foulant reduction. To that end, an important monitoring metric was the removal of DOC as this represented the entirety of the dissolved carbon in the source water, of which a portion is biodegradable by the biofilter microorganisms. Biopolymer removal by the biofilters was studied here as it is part of the biodegradable fraction of the DOC which is linked to membrane fouling. Figure 4-2 shows the DOC and biopolymer (BP) removal of both the experiment and control filters throughout the study as well as the system temperature. System temperature fell continuously throughout the duration of the study. For the control biofilter the removal of BPs (as measured by LC-OCD) fell from approximately 60% to 11%, while the removal of DOC fell from approximately 10% to 5% throughout the study. Over a similar temperature range, Pharand et al (2015) reported similar removals of BPs and DOC, from a full scale conventional biofiltration plant with pre-ozonation also located on the Grand River suggesting comparability between the two processes. In addition Figure 4-2 showed the removal of the aforementioned parameters by the experimental biofilter where backwashing conditions were varied from week to week. The trend for the DOC closely followed that of the control biofilter, suggesting that the backwashing procedure has little effect on the removal of the bulk of the biodegradable fraction of the DOC. For the BP differences were observed between the control and experimental biofilter indicating that backwashing may have some effect on BP removal.

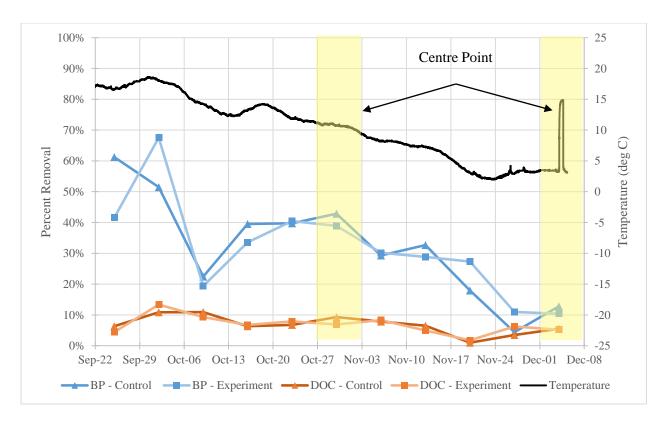


Figure 4-2 Biofilter organics removal and temperature

Figure 4-3 shows the dissolved oxygen uptake of the biologically active media samples taken from the interface between the sand and anthracite media of both control and experiment biofilters. This parameter was measured as an indicator of the degree of biological activity of the biofilters and is used to lend confidence that organics removal by the biofilter was due to biodegradation. Average values for the control and experiment filters were 1.83 and 1.99 mg DO /L cm³ respectively, which were higher than the values reported by Urfer and Huck (2001) (0.15 to 0.23 mg DO / L cm³), by which the method used was developed, suggesting that both biofilters used in this study were biologically active during the study period. As with the removals of the DOC, the DO consumption in both filters followed similar trends throughout the study, suggesting backwashing had little effect on DO consumption by the media and hence on biological activity.

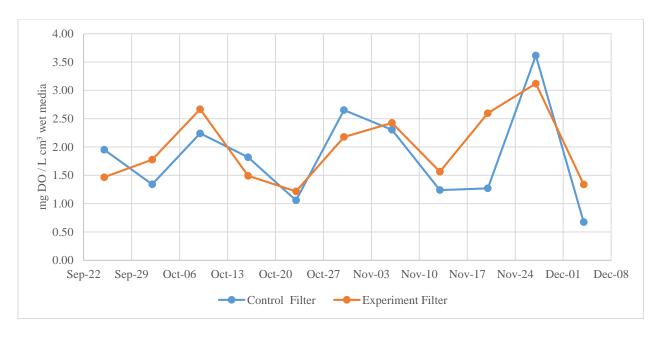


Figure 4-3 Dissolved oxygen uptake of media samples (24h respiration period as per Urfer and Huck (2001))

The turbidity profiles for both filters are shown in Figure 4-4. This was an important performance parameter because it is a main treatment goal in the conventional biofiltration context, and also because it relates to the filter run time. The inlet turbidity averaged about 3 NTU until the month of November when it rose sharply to 25 NTU for the remainder of the study. This may have been caused by premature snow melt and a high rainfall around this date. 10 cm of snow was reported to be on the ground on November 20th, but due to a large swing in temperatures in the following days (-4.6 °C to 8.3 °C) this snow melted shortly thereafter. Moreover, a 10 mm rainfall was experienced on November 23<sup>rd</sup>, which may have further contributed to high turbidity in the Grand River and into the setup. The system experienced three turbidity spike events, the first two being at the beginning of the study (September 22 to 25, and October 6 to 13 respectively) and the last and most severe, at the end of the study (November 26 to December 5). The consistency of the log removal of turbidity during these periods compared to other weeks suggests that the removal of turbidity by the biofilters was independent of raw water turbidity over the range studied. Also of note was the declining log removal performance of the control biofilter which fell steadily from 1 to 0.5 through the duration of the study despite the relative steady influent turbidity values (for the period between October 17 and November 17). This can be attributed to some external factors, such as the declining water temperature and/or potential differences in the size and shape of incoming particles, were influencing the performance of the biofilters. Thus it can be said that in terms of log removal of turbidity, the control biofilter performed best at the beginning of the study. Over the entire study, the experiment biofilter experienced discrete jumps in performance due to weekly changing

of backwashing conditions as per the experimental design, suggesting that the backwashing procedure likely has an effect on turbidity removals.

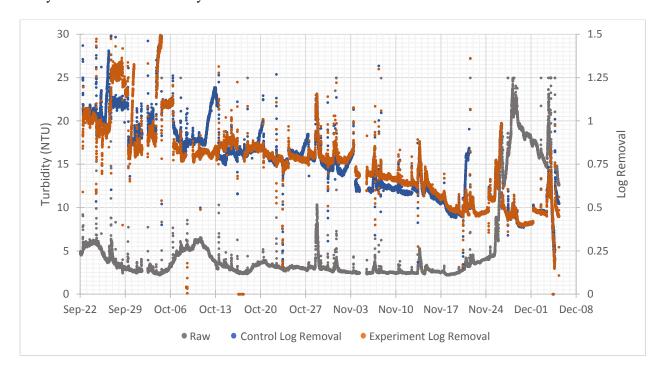


Figure 4-4 Absolute and log removal turbidity profiles for control and experiment filters

As the control biofilter backwashing procedure was not modified during the study, the performance of this filter is indicative of the effect of changing inlet water quality parameters (such as temperature) on general biofilter performance and thus the majority of the following discussion relates only to the performance of the control filter. The turbidity of the water above the control biofilter media bed during a backwash procedure, called here the backwash water turbidity, was tracked for each backwash event during the study. This parameter provides an estimation of the effectiveness of the backwashing procedure. To meaningfully compare backwashing turbidity curves between backwashing events, the time that the backwash water turbidity was above 5, 40 and 80 NTU was calculated and is shown in

Figure 4-5 for the length of the study. This figure shows a general increase in time spent at all three turbidity levels over time, but it is more pronounced for the 40 and 80 NTU levels.

The general increase in turbidity for all levels may reflect the changing quality of incoming particles for later experiment weeks and the marked increase in backwash turbidity for the 40 and 80 NTU levels at the end of the study (November 24<sup>h</sup> and onward) may reflect the increase biofilter influent turbidity as apparent from in Figure 4-4. It is interesting to note that the shape of the 40 and 80 NTU average lines follow the same trends, however the 5 NTU line does not. During the final two weeks (beginning on

November 24 and December 1), the backwash water turbidity did not fall below 5 NTU, and as such, the time indicated in

Figure **4-5** for these data points is the time between when the backwash water turbidity reached 5 NTU and the end of the backwash operation. It is probable that had the backwash continued, these points would be higher and follow the trend of the 40 and 80 NTU average lines. This corresponded with the weeks that the ripening peak turbidity did not fall below 2 NTU, as discussed later.

The biofilter ripening peak is a turbidity spike typically seen in the biofilter effluent after the biofilter is put back online following the backwashing operation. This parameter was measured as it is characteristic to media filters. Figure 4-6 shows the maximum turbidity of the ripening peak experienced by the control biofilter after the backwashing operation as well as the time the ripening peak was above 2 NTU. The maximum turbidity seen in the ripening peak increased over the length of the study, with the increase being most pronounced in the last two weeks (beginning on November 26 and December 1).

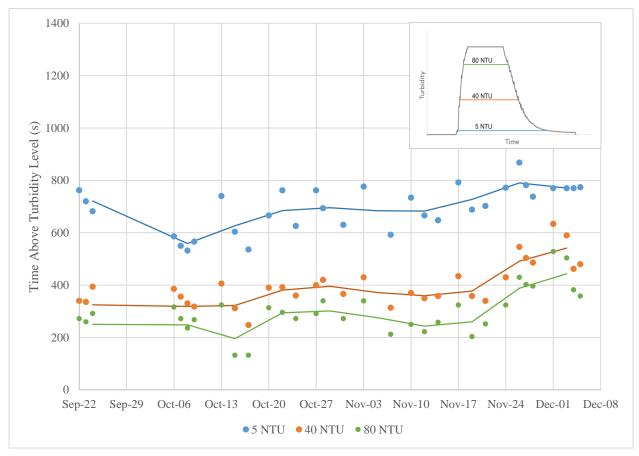


Figure 4-5 Control biofilter backwash turbidity throughout study. The data points represent the time the backwash water turbidity was above a specified turbidity level (as shown in insert), and the lines represent the weekly average.

The turbidity ripening peak is a function of the quality and quantity of particles that remain above the biofilter bed after the backwash procedure as well as of the collection efficiency of the biofilter (Amburgey 2005). As the study progressed, the collection efficiency of the control biofilter decreased, as can be seen by the decreasing turbidity log removal of the filters (Figure 4-4), which can be further explained by the increasing ripening peak turbidity. The time the ripening peak turbidity was above 2 NTU also increases over time and during the last two weeks (beginning on November 26 and December 1), the effluent turbidity did not drop below 2 NTU, and these points are therefore excluded from the figure. This corresponds to the large increase of turbidity seen at the end of the study as shown in Figure 4-4. This again suggests a progressive change in quality and quantity of particles in the biofilter influents throughout the study.

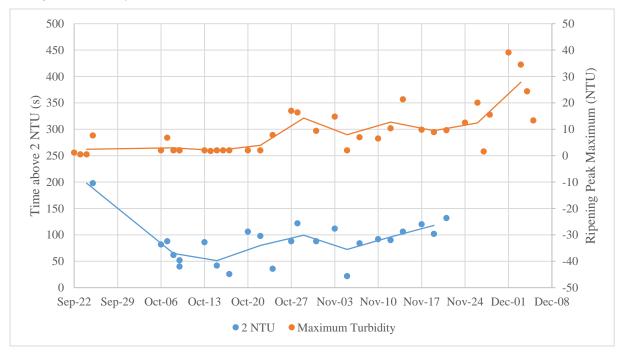


Figure 4-6 Control biofilter ripening peak statistics throughout study. The blue dots represent the time the effluent was above 2 NTU during the ripening peak following a particular backwash, while the orange dots represent the maximum turbidity during the ripening peak for a particular backwash. The lines represent the weekly averages of each data point.

The headloss (or pressure decay) character of the filters was measured as this is directly related to the accumulation of solids and the overall expected run time of the filter. The pressure at the bottom of each biofilter column at the beginning of each biofilter cycle steadily declined over the length of the study as shown in Figure 4-7 (with the hashed lines being read from the secondary ordinate axis). This behavior was expected since the temperature dropped over the same time frame (Figure 4-2) and water viscosity is inversely related temperature. However, the starting pressures for both the control and experiment filters

followed the same basic trend over the length of the study, lending confidence to the comparability of both. The average rate of change for the pressure decay for each biofilter during a filtration cycle is also shown in Figure 4-7. This is an expression of how quickly headloss builds up inside the biofilter, and how frequently the biofilters must be backwashed to maintain flow. The rates declined for both filters until approximately November 3<sup>rd</sup>, when they essentially became constant for the remainder of the study. This may be due to falling water viscosity throughout the study. As with the starting pressure for the columns, the rates for both filters followed the same basic trend. It should be noted that the rate of pressure decay following a media sampling event in which a backwash procedure was generally not undertaken is shown as a square in this figure.

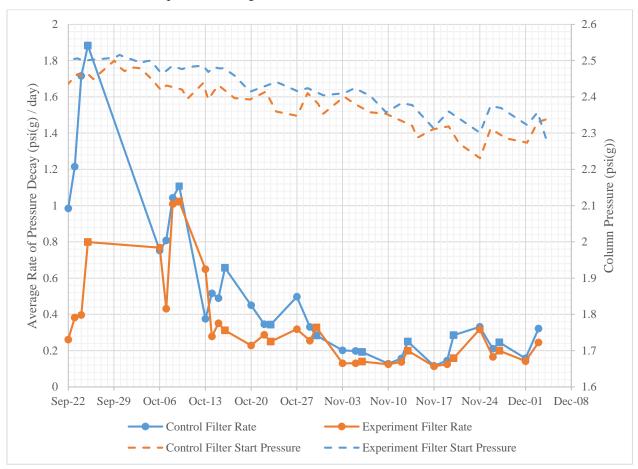


Figure 4-7 Biofilter starting pressure and pressure loss profiles. Pressure decay rates that occurred after a sampling event are shown as squares.

## 4.4.2 System Variability

The experiment and control biofilters were backwashed under identical conditions in study Week 5 and 10. This was done to ensure that the effects of the experimental treatments could be attributed to changes

in the backwashing parameters and not to performance differences between the trains and to calculate error estimates to be used in the ANOVA statistical methodology. As can be seen in Figure 4-2, the removal of DOC and biopolymers through both the control and experiment filters followed similar decreasing trends, and thus visually appear to be comparable. Trends for the DO uptake of the biofilm on the sampled media shown in Figure 4-3 also similarly decreased for both the control and experiment filters, but exhibited a large amount of week to week variation. The average of the DO uptake data also did not appear to change with time, suggesting that the microbial activity of the biofilm on the media samples (at the interface of the anthracite and sand media) was unchanged throughout the experiment.

**Figure 4-8** shows the turbidity log removal profiles for both the control and experiment filters during the centre point runs in Week 5 and 10 where both filters ran under identical operating conditions. In week 10, the source water was interrupted in the middle of the biofilter run due to the full scale plant being shut down for maintenance on December 3rd, thus data from this point on were excluded. As can be seen, the performance of both filters was quite similar for each week, with a maximum difference between the control and experiment biofilters of 0.07 and 0.09 log removals for Week 5 and 10 respectively. Thus, the declining log removal of the filters seen over the study period affected both filters to the same extent, and the difference between biofilter log removals stayed approximately the same for both centre point runs.

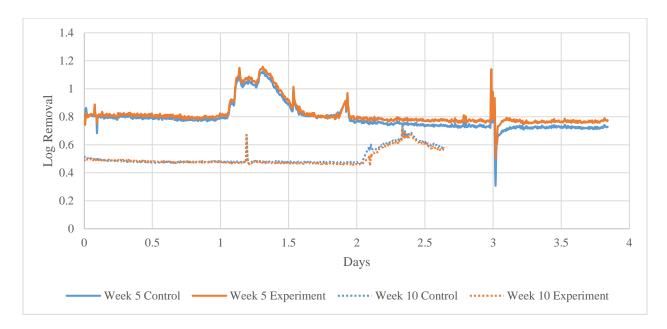


Figure 4-8 Centre point comparison of turbidity log removal for the control and experiment filters

During the end of the Week 5 center point run, however, the log removals were seen to diverge with the control filter removing less turbidity than the experiment filter. This may be due to the physical location of each filter in relation to the inlet water pipe coupled with the turbidity spike seen at the beginning of

the week. It is interesting to note that the experiment biofilter was slightly higher (that is had a higher log removal) in Week 5 than the control biofilter, while the opposite was true in Week 10.

Figure 4-9 shows the pressure decay profile for both the control and experiment filters during the centre point runs. In Week 10, the source water flow was interrupted for the later part of the run, and as such these data were excluded from 2.6 days onward (Figure 4-9). The maximum difference between the control and experiment filters was 0.39 and 0.13 psi(g) for Weeks 5 and 10 respectively. The larger difference between both biofilter pressures for Week 5 is due to the large loss of driving pressure due to an influx of turbidity seen on October 28th (Figure 4-4). In both centre point runs, the pressure at the bottom of the control biofilter was less than that of the experiment biofilter. This could be caused by the relative distance of each biofilter to the source pump, or by slight differences in biofilter bed depth. It is interesting to note that this difference was reversed after a sampling event (occurring on day 3 of the Week 5 run), suggesting that something shifted within the biofilter bed after sampling to allow for more flow through the biofilter, but both filters followed similar trends. The difference between the pressure loss profiles between Week 5 and 10 for the first biofilter cycle compared to the second cycle may be evidence of changing water quality parameters throughout the study. Also of note are the relative slopes between both weeks, and biofilter cycles. For the first biofilter cycle, the pre-turbidity spike slope of the Week 5 pressure loss was greater than that for Week 10. This is seemingly true for the second cycle as well, although not to as great of an extent. This may be due to the effect of the weekend as the weekend biofilter cycle was approximately 3 days, while during the experimental week a biofilter cycle was 2 days at most. During the weekend, the filters were not checked and if the flow control valve was not able to sustain flow, the biofilter flowrate would decrease. This may also explain the similarity of the pressure loss profile for the second biofilter cycle, as both filters were backwashed without experiencing a prior, possible decrease in flowrate.

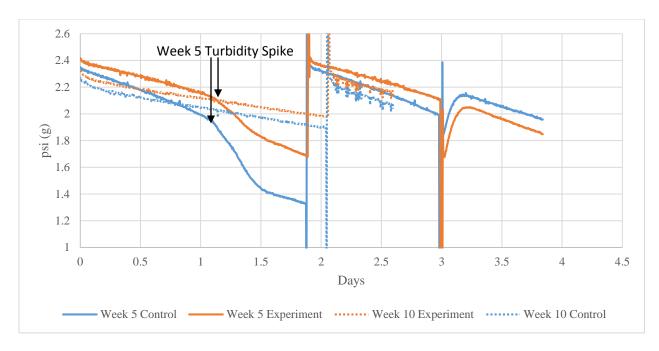


Figure 4-9 Centre point comparison for column pressure for both control and experiment filters

## 4.5 Effect of Backwashing Parameters on Biofilter Performance

The effect of backwashing operational parameters (collapse pulsing time, wash expansion and wash time) on biofilter performance metrics grouped by organics removal, turbidity removal, ripening peak character, backwash water turbidity and biofilter pressure loss is presented in this section. Table 4-4 shows the main and interaction effects of each studied factor on the aforementioned metrics. Factors were tested for significance at the  $\alpha=0.05$  level, and the factors affecting the response variable for which this criteria was met are highlighted in green. The largest absolute factor effect of those found to be significant are highlighted in red. Also indicated for each response variable is the estimated error, the critical F-value and the degrees of freedom used to calculate significance.

Table 4-4 shows that a number of response variables studied were also influenced by two and three factor interactions. When three factor interactions are present it may be thought of as a two factor interaction being moderated by a third factor. That is to say that a two factor interaction may not be present without the effect of a third factor, or the interaction effect is more pronounced by the presence of a third factor (Box 2005). Moreover, a number of cases exist in which main interaction effects were not significant, but their higher order interaction effects were. In these cases, this suggests that backwashing operation had an effect on the response variable in question, but its action was complex and required two or more factors working in concert. This is not surprising, as the backwashing operation involves sequential operations, and the effect of one factor may influence the effect of a subsequent action. In cases where higher interaction effects are present, analyzing main effects and/or lower interactions may not provide a

complete picture of the behavior present. To that end, a hierarchal approach was taken, and the significant effects with the largest number factor interaction for each response variable were examined closely. For example, one main, two of the two factor and the three factor interaction effects were shown to be significant for the log turbidity removal response variable in Table 4-4. In this case, the three factor interaction was examined the closest.

This section discusses the main effects, two factor interaction effects and three factor interaction effects as they pertain to the various groups of response variables studied, namely: organics removal and biological activity, turbidity removal and ripening peak character, backwash water turbidity and biofilter headloss profile.

Wash expansion, acting alone, had the least amount of influence on all the response variables studied, being shown to significantly impact only two responses. This suggests that, the low level bed expansion used in this study (30%) was sufficient for backwashing purposes. This has also been noted by others for conventional biofiltration (Rasheed et al. 1998). However, a number of interactions of the wash expansion factor were shown to be significant suggesting that this factors played a complex role in backwashing in concert with the other factors. In contrast, collapse pulsing time and wash time as main effects were both shown to be significant main effects for a number of response variables. However, these response variables were found also to have significant interaction effects, which are discussed later.

The removal of DOC was shown not to be influenced by main effects, or interaction effects, and the DO uptake was similarly unaffected. This suggests that the bacterial community in the biofilter remained largely active in spite of the action of backwashing. This finding echoes the finding seen by others for conventional biofiltration (Emelko et al. 2006; Urfer et al. 1997; Miltner et al. 1995). Main effects were also shown to not be significant in the removal of biopolymers or protein-like material, but some interaction effects were.

The parameters describing the ripening peak after a backwash cycle, (maximum turbidity achieved and the time the effluent turbidity is above 2 NTU), were not influenced by any of the factors studied. This suggests that the nature of the ripening peak was a function of water quality or biofilter design parameters, and not influenced by the backwash procedure, at least in so far as the parameter values studied here.

The turbidity of the backwash water was measured as a means of gauging biofilter cleaning efficiency.

The time above 40 NTU during backwashing was a measure of the middle of the turbidity curve, while 5 NTU was selected to provide a measure of the 'tail' of this curve (See insert in

Figure **4-5**).

**Table 4-4 Collected ANOVA results for studied response variables** 

|  |        | Collapse Pulsing |        | Wash Time |         | Wash<br>Expansion |         | Collapse Pulsing<br>Time x Wash<br>Time |         | Collapse Pulsing<br>Time x Wash<br>Expansion |        | Wash Time x<br>Wash Expansion |         | Three Factor<br>Interaction |          | Critical<br>f ratio | df1 | df2 |
|--|--------|------------------|--------|-----------|---------|-------------------|---------|---|---------|--|--------|-------------------------------|---------|-----------------------------|----------|---------------------|-----|-----|
| Response Variable                                      | Effect | f                | Effect | f         | Effect  | f                 | Effect  | f                                       | Effect  | f  | Effect | f                             | Effect  | f                           |          | a = 0.05            |     |     |
| DOC % Removal  | -0.72  | 2.84             | -0.06  | 0.02      | -0.12   | 0.07              | -0.10   | 0.05                                    | -2.40   | 31.10  | -1.09  | 6.37                          | 1.25    | 8.39                        | 1.48E-04 | 161.40              | 1   | 1   |
| Biopolymer % Removal                                   | 5.37   | 43.34            | 3.98   | 23.81     | 0.58    | 0.50              | -0.01   | 0.00                                    | -9.11   | 124.84                                       | -10.66 | 170.73                        | 5.90    | 52.42                       | 5.32E-04 | 161.40              | 1   | 1   |
| FEEM Protein % Removal                                 | -8.21  | 142.55           | -2.87  | 17.42     | 1.76    | 6.59              | 7.26    | 111.47                                  | -11.00  | 255.84                                       | -4.59  | 44.61                         | 10.57   | 236.29                      | 3.78E-04 | 161.40              | 1   | 1   |
| DO Update (mg/L/cm3)                                   | 0.86   | 49.73            | 0.46   | 14.39     | -0.30   | 6.03              | 0.07    | 0.36                                    | -0.07   | 0.32   | -0.43  | 12.38                         | -0.21   | 2.95                        | 1.18E-01 | 161.40              | 1   | 1   |
| Turbidity - Average Log Removal                        | 0.07   | 49.26            | -0.01  | 1.81      | -0.01   | 0.44              | -0.13   | 152.62                                  | -0.03   | 10.83  | 0.02   | 3.99                          | 0.04    | 13.04                       | 8.77E-04 | 4.38                | 1   | 19  |
| Backwashing Time Above 5 NTU (s)                       | 273.08 | 298.27           | 338.42 | 458.06    | 95.30   | 36.33             | -99.72  | 39.77                                   | -127.67 | 65.19  | -67.00 | 17.95                         | -140.97 | 79.48                       | 2.00E+03 | 161.40              | 1   | 1   |
| Backwashing Time Above 40 NTU (s)                      | 254.58 | 2724.79          | 120.18 | 607.20    | 21.04   | 18.61             | -51.21  | 110.25                                  | -12.34  | 6.40   | -68.74 | 198.67                        | 21.04   | 18.61                       | 1.90E+02 | 161.40              | 1   | 1   |
| Backwashing Time Above 80 NTU (s)                      | 241.03 | 15.31            | 168.48 | 7.48      | -27.39  | 0.20              | -109.78 | 3.18                                    | 62.36   | 1.02   | 19.81  | 0.10                          | -0.44   | 0.00                        | 3.04E+04 | 161.40              | 1   | 1   |
| Backwashing Slope (40 to 80 NTU) (NTU/s)               | -0.41  | 2.91             | -0.13  | 0.30      | 1.74    | 52.66             | 0.22    | 0.82                                    | 0.26    | 1.21   | -0.68  | 8.07                          | 0.13    | 0.29                        | 4.60E-01 | 161.40              | 1   | 1   |
| Ripening Peak Time Above 2 NTU (s)                     | 32.78  | 0.03             | 17.81  | 0.01      | -135.71 | 0.46              | 52.79   | 0.07                                    | 83.11   | 0.17   | 15.48  | 0.01                          | -71.54  | 0.13                        | 3.20E+05 | 161.40              | 1   | 1   |
| Maximum Ripening Peak Turbidity (NTU)                  | -6.89  | 37.59            | -5.16  | 21.05     | -4.49   | 15.92             | 1.87    | 2.77                                    | 0.40    | 0.13   | 2.53   | 5.06                          | -5.69   | 25.65                       | 1.01E+01 | 161.40              | 1   | 1   |
| Cycle 1 Rate Of Pressure Loss (psi(g)/day)             | 0.08   | 1.38             | 0.29   | 17.23     | 0.32    | 22.14             | -0.18   | 7.24                                    | -0.20   | 8.85   | -0.15  | 4.82                          | 0.03    | 0.21                        | 1.82E-08 | 4.45                | 1   | 17  |
| Cycle 2 Rate Of Pressure Loss (psi(g)/day)             | 0.18   | 6.65             | 0.24   | 12.42     | 0.07    | 1.19              | -0.04   | 0.41                                    | -0.23   | 11.60  | -0.16  | 5.39                          | 0.32    | 21.62                       | 1.82E-08 | 4.45                | 1   | 17  |
| Cycle 1 Acceleration of Pressure Loss (psi(g)/day/day) | 0.13   | 1.94             | 0.16   | 2.68      | 0.20    | 4.50              | -0.10   | 1.19                                    | -0.08   | 0.77   | -0.19  | 3.92                          | 0.07    | 0.60                        | 1.70E-14 | 4.45                | 1   | 17  |
| Cycle 2 Acceleration of Pressure Loss (psi(g)/day/day) | 0.22   | 5.32             | 0.40   | 17.54     | 0.07    | 0.58              | -0.04   | 0.15                                    | -0.46   | 22.71  | -0.25  | 6.68                          | 0.60    | 38.71                       | 1.70E-14 | 4.45                | 1   | 17  |

<sup>&</sup>lt;sup>1</sup> Green highlights indicate factor significance for a given response variable

<sup>&</sup>lt;sup>2</sup> Red highlights indicate the largest effect value for a given response variable

<sup>&</sup>lt;sup>3</sup> The responses shown in this table represent the difference between the response of the experiment filter and control filter

<sup>&</sup>lt;sup>4</sup> df = Degrees of Freedom

The large positive effect of both collapse pulsing time and wash time main factors on the backwash turbidity above 40 and 5 NTU (Table 4-4), indicate that the high setting of both of these factors independently released a large amount of particles from the biofilter bed during backwashing. The collapse pulsing factor was the factor which affected the 40 NTU backwashing variable to the greatest amount while the wash time affected the time above 5 NTU the greatest. Thus, both factors correlate with a large amount of particle removal during backwashing. Despite this, the turbidity after the backwashing operation during the ripening peak remained independent of backwashing regime as seen in Table 4-4. A large amount of particles being released by collapse pulsing, but staying atop the biofilter media bed with low wash time as compared to a high wash time, coupled with the independence of the ripening peak, suggests that a certain amount of particles reattached to the biofilter bed during the initial ripening peak. It is proposed that this initial particle loading contributes to the interaction of factors seen for turbidity removal in Figure 4-11b (discussed later).

The pressure loss profiles of the biofilter after the backwashing operation were shown to be significantly affected by all main factors: collapse pulsing time, wash time and wash expansion, showing that backwashing had a significant effect on the hydraulic operation of the biofilters. The pressure loss rate represents the average rate at which head loss in the filter bed accumulated. The pressure loss acceleration represented the rate at which the rate changed. A large pressure loss acceleration would indicate that the rate of headloss accumulation, which was found to be a function of time, was changing quickly over the filter cycle. A filter cycle is defined as the time in between successive backwashing operations. For backwashing Cycle 2, both the pressure loss rate and pressure loss acceleration were found to be significantly influenced by collapse pulsing, wash time, collapse pulsing / wash expansion interactions, wash time / wash expansion interaction and the three factor interaction. Pressure loss rate and pressure loss acceleration for Cycle 2 were also seen to be influenced by the same factors suggesting their interdependence. For backwashing Cycle 1 however, only wash expansion was found to be significant in both the pressure loss rate and acceleration. This suggests a fundamental difference between both cycles. This could be due to the fact that the first backwashing operation for a particular run occurred on a Monday preceded by a weekend of inactivity wherein the filters were allowed to reach a pressure loss beyond which the flow controllers could maintain flow. Thus the biofilter bed cleanliness during the first cycle may not have been the same as that for the second cycle, which may in part explain the difference in significant factors. Thus, as the second cycle was preceded by a back wash that was not preceded by the weekend biofilter run length, it may be more representative for backwashing conditions investigated as this more closely approximates 24/7 biofilter operation.

For the organic removals through the biofilter the biopolymer removal was influenced slightly by a 2 factor interaction, as signified by a f value just above the critical f ratio (p-value of 0.048), whereas the protein-like removal was influenced by 2 factor (p-value of 0.040) and 3 factor (p-value of 0.041) interactions both more pronounced (i.e. higher f values) than the 2 factor interaction observed for the biopolymers (Table 4-4). In the case of biopolymer removal, the effect of wash time was decreased when wash expansion was at a high level (as signified by its negative effect in Table 4-4). This can be also thought of as the slope of the line connecting the low level and high level wash time scenarios at high wash expansion (orange line in Figure 4-10) being 11 % removal / unit lower than the slope of the same line at low wash expansion (blue line in Figure 4-10). In this case, the cumulative effect was that, at a low level of wash expansion, the removal of biopolymers is proportional to wash time – the regression line had a positive slope (blue line in Figure 4-10). Whereas at high wash expansion, the removal of biopolymers was inversely proportional to the wash time; that is the slope of the regression line was negative (orange line in Figure 4-10). Therefore, maximum removal of biopolymers is achieved by a high level of wash time, but a low wash expansion. From Figure 4-10, the removal at this optimized condition was 5% higher in the experimental biofilter than in the control biofilter, which is a relatively small amount. Moreover, this data also indicates that collapse pulsing had no effect on the removal of biopolymers through the biofilter.

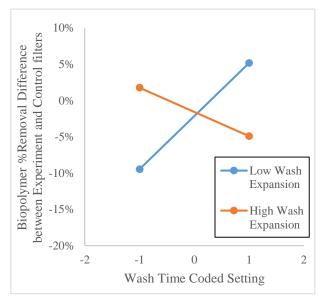


Figure 4-10 Biopolymer removal 2-factor interaction

In the case of the FEEM protein % removal, a three factor interaction existed, (Table 4-4) which may be thought of as an interaction effect between two factors moderated by a third factor (Figure 4-11a). This is a similar concept to the two factor interaction graph shown in Figure 4-10, but extended to the third dimension. In Figure 4-11 two way interactions are shown as surfaces with the corners representing the

setting of backwashing parameters (x and z coordinates) and the response (y coordinate). The two factor interaction graphs (the type shown in Figure 4-10) may be thought of as these surfaces viewed from one end. The different surfaces shown in Figure 4-11(a to d) represent the two way interactions at different settings of high (orange surface) and low (blue surface) of a third variable. A significant interaction between wash expansion and wash time factors existed, for the removal of protein like material as measured by FEEM and was moderated by the level of collapse pulsing. The high and low collapse pulsing surfaces converge at three corners - a low level of wash expansion and low level of wash time, and these also converge at a high level of wash expansion and high levels of wash time. There was a pronounced difference between the high and low collapse pulsing case at a low level of wash time but a high level of wash expansion. At this point, the effect of collapse pulsing was very pronounced and the largest amount of removal was seen with collapse pulsing set to the high level.

The trends followed by both the turbidity removal and the protein-like material removal were similar in that with a high collapse pulsing time setting, removal decreased with wash time, while at a low collapse pulsing time setting, the opposite was true. This suggests that the same underlying action was contributing to both phenomena, maybe some protein like material is being attached to the biofilter media and not biodegraded. This hypothesis is further supported by the fact that the removal of DOC through the filters as well as the overall microbial activity was unaffected by the backwashing effects studied. (Buffle et al. 1998) have shown that in natural water systems, proteins readily attach to natural colloids and may play a role in creating small natural aggregates. This may provide an explanation as to why the protein removal was similar to the turbidity removal.

The effect of collapse pulsing was prominent in the removal of turbidity from the filters, being significant as a main effect and in almost all significant interactions (Table 4-4) underscoring the importance of this operation in cleaning the biofilter. Indeed, it has been found that collapse pulsing is the most efficient way of cleaning granular media filters preceded by chemical pretreatment (Hewitt & Amirtharajah 1984), and the results of this study seem to indicate that this also applies to biofiltration without pretreatment. The effect value for the interaction of collapse pulsing time with wash time had the highest numerical value (Table 4-4) indicating this interaction as having the largest effect on turbidity removal. The sign on the effect is negative, suggesting that with collapse pulsing set to the high level, a high wash time has a negative effect on the average log removal recorded for that run. A three factor interaction is also present and illustrated in Figure 4-11b. From this figure it can be seen that at high collapse pulsing time settings, the turbidity log removal declines with increasing wash time, while at low collapse pulsing time settings, the log removal increases with increase wash time. A local maximum occurs with a high collapse pulsing level while all other factor levels are at their minimum, which is unsurprising as collapse pulsing has been

shown to be the most effective method at removing turbidity from the biofilter bed. However, the negative impact of wash time on turbidity removal with collapse pulsing at a high level suggests that the removal of too much turbidity from the bed, or removal of turbidity from the top of the bed that cannot be reattached to the media during the ripening peak causes a lower turbidity removal. As the opposite trend is seen for a low setting of collapse pulsing, it is suggested that low collapse pulsing conditions do not remove enough turbidity from the bed due to the inherent inefficiency of the bed expansion process (i.e. even at high bed expansion and high wash time) as compared to the collapse pulsing method. These finding suggests that there is an optimal particle loading on the biofilter bed meaning that a certain amount of particles needs to be deposited on the media grains to catch/attach further particles thereby removing turbidity (i.e. filter grain conditioning). This echoes the findings seen by Raveendran and Amirtharajah (1995) for filtration with chemical pretreatment. They have shown that the attractive force between particles and biofilter grains is higher for biofilter grains with a deposited layer, than without. Moreover, they have also shown that the required force to detach particles from the biofilter media is a function of zeta potential, with a lower detachment force required for particles with a lower zeta potential. As the charge of particles being filtered by the BF<sub>wp</sub> process have not been neutralized by coagulation and have therefore a low zeta potential, it is suggested that the backwashing force required for detaching particles from the media grain during backwashing in BF<sub>wp</sub> is less than that seen for conventional filtration. As such, the cleaning of the BF<sub>wp</sub> biofilter bed during backwashing may be more thorough than the conventional process, partly explaining the drastic effect that collapse pulsing time has on the turbidity removal of the biofilters.

The rate of pressure loss of the biofilter showed the highest amount of significant main and interaction effects (Table 4-4). Results are organized by average pressure decay rate and acceleration of that rate for the biofilter cycle immediately following a backwashing procedure. Thus, the average pressure loss rate and acceleration values for cycle 1 correspond to the biofilter performance for the time period after the first backwash (Mondays) up to the next backwash. The second cycle corresponds to the biofilter cycle after the second backwash. For experimental runs 4 through 10, only three backwashes were performed per week, as the pressure loss rate was less for these runs when compared to runs 1 through 3, which required more frequent backwashing. Sampling for water and media samples occurred on Thursdays between the second and third backwashing procedures and it was observed that media sampling of the filters disrupted their pressure loss profile. Thus for the runs 4 to 10 where this occurred in the filtration cycle following the second backwash, the data after the sampling procedure is excluded. The media sampling procedure effectively reduced the number of data points in the second biofilter cycle as compared to the first biofilter cycle. However, as a second order polynomial regression was used to

estimate the rate, this reduced number of data points was seen as adequate as the r<sup>2</sup> value of the fit for this cycle was always above 0.97.

The significant pressure loss rate and acceleration of pressure loss three factor interaction diagrams for cycle 2 are shown in Figure 4-11c-d. Cycle 2 was focused on as this cycle was the least likely to be influenced by the different weekend biofilter operation (as described in Section 4.4.2). As can be seen, both follow similar trends of a minimum occurring at the point of low wash expansion and low wash time but high collapse pulsing. The pressure loss rate and acceleration are essentially the same for all other combinations at the high collapse pulsing setting. At a low collapse pulsing setting, the values are also very similar. Rate of pressure loss and acceleration of pressure loss are also affected by a two factor interaction between wash time and wash expansion (Table 4-4), moderated heavily by collapse pulsing. The response variables in Figure 4-10c,d represent the difference between the performance of the experimental biofilter and the control biofilter. Thus, a negative value indicates that the pressure loss rate for the control biofilter was higher than the experimental biofilter and minimizing pressure loss optimizes/extends biofilter run time.

A clear minimum value of both pressure loss rate and acceleration can be seen at the point where collapse pulsing is at a high level, but wash time and wash expansion is at a low level. At this point, the difference in pressure loss rate between experimental and control filters is approximately 0.94 psi/day indicating that at these factor settings, the average pressure loss rate for the experimental biofilter was this value lower than for the control biofilter.

For this study, the starting pressure for experimental runs was in the range of 2.3 to 2.5 psi, while the critical pressure (the pressure at which point the flow controllers could no longer maintain the desired flow) was approximately 1.5 psi. Therefore, the difference noted here represents almost the entire available head, and optimizing the backwashing procedure for this parameter will likely lead to biofilter run times which are much longer than they are without optimization. It is interesting to note, that the parameter setting for which the pressure decay rate of the experiment biofilter is the lowest (Figure 4-11 b) occurs at the same parameter settings at which turbidity removal is at a maximum (Figure 4-11c) and as such, optimization of the backwashing procedure to maximize turbidity removal and biofilter run time is found at the same parameter setting.

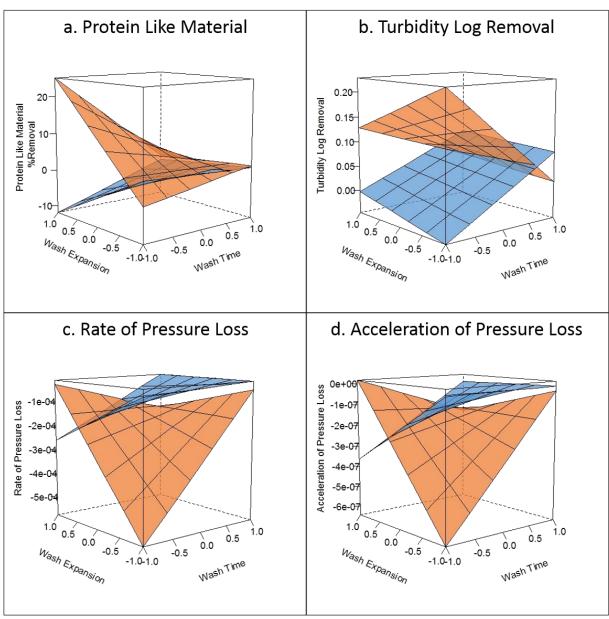


Figure 4-11 Significant 3-factor interactions. In each graph (a to d), the orange surface represents the collapse pulsing at a high level, while the blue surface represents the collapse pulsing at a low level. The responses here represent the difference in the response of the experiment filter and the control filter.

## 4.5.1 Optimal parameter settings

As can be seen from Table 4-4, Figure 4-10 and Figure 4-11, the response variables studied followed complex interactions, and as such, optimization of the biofilter backwashing depends on which factors are important to the end user as some tradeoffs are inevitable. From the perspective of maximizing turbidity

removal as well as minimizing the biofilter pressure decay rate thereby increasing biofilter run time, the optimal setting in experiment coded values (Table 4-1) are high collapse pulsing, low wash time and low wash expansion. In terms of absolute values, this corresponds to a total backwash time of 11 minutes, with a 6 minute collapse pulsing phase followed by a 5 minute fluidization cycle at 30% bed expansion (by volume). Compared to the biofilter backwash procedure currently employed by the control biofilter, this parameter setting results in a lower overall backwash time as well as a lower pump flow rate, thus lowering the overall water and energy consumption while increasing the removal of particles and lowering the pressure loss rate thereby extending biofilter run time. The drawbacks to this setting include somewhat lower biopolymer removal as well as protein like material removal being no better than the control case.

Optimization in terms of protein like material removal and biopolymer removal requires tradeoffs in turbidity removal and biofilter run time. As shown in Figure 4-11a, maximum protein like material removal occurs with high wash expansion, low wash time and high collapse pulsing, while the minimum occurs at the same point, but with low collapse pulsing. For all other corner points studied, the removal is shown to be no better than the control case. For biopolymer removal (Table 4-4, Figure 4-10), collapse pulsing has little effect, however the interaction of wash time and wash expansion are significant. Balancing the removal efficiency gains by adjusting parameters to maximize removals of protein like material and biopolymers, results in optimal backwash settings at high collapse pulsing and high wash expansion with low wash time. In this case, the maximum removal of protein like material is achieved, while biopolymer removal is slightly better than that of the control biofilter case. This combination of parameters results in non-optimal turbidity removal and pressure loss profiles (Figure 4-11 b and c), but performance at this setting is still better than that of the control biofilter. Moreover, in terms of energy and water use, this combination of settings may still be better than the control procedure. Although the wash expansion (and pump flow) is higher than for the control procedure, the time at that expansion is lower. A slightly higher biopolymer removal may be found under low wash expansion and high wash time conditions, however, all the other parameters discussed would be lower and energy use would be slightly higher.

As stated previously, optimizing the backwash procedure with the goal of biopolymer removal, is at odds with the goal of increased turbidity removal and biofilter run time. Therefore the optimization tradeoff is between a slight increase in biopolymer removal (~5%) and a significant turbidity removal increase (0.20 Log) and a substantial increase in biofilter run time. To fully elucidate this decision, the energy costs of each backwashing option must be evaluated, as compared to the benefits of each option. At first glance, it

is the author's opinion that the benefit of the decrease in biopolymers may not equal the gains made in turbidity removal and biofilter runtime.

It should be noted that the regression lines for the interaction and main effects for a number of studied response variables did not cross through the 'zero point' of the graphs. As the low and high factor levels were chosen symmetrically around the control backwashing regime (Table 4-1), the fact that these regression lines do not pass through the 0,0 coordinate suggest that the effect may not be linear between the levels chosen, and minima or maxima may occur in between these chosen levels. This behavior may be seen on Figure 4-10 and Figure 4-11. This suggests that some local maxima or minima exist for at least some of the factors studied. Thus, although this study has clearly established trends of response variables to factor effects, and points to the clearly significant effects, interpolating between these values should be done with caution. Further study using smaller ranges, or response surface methods, should be undertaken to truly appreciate the behavior of the system under all conditions.

#### 4.6 Conclusions

The work presented here studied the effect of seasonal water quality changes and backwashing factor effects on the performance of the  $BF_{wp}$  process. This process differs from the conventional biofiltration process, as it lacks chemical pretreatment, and as such operational wisdom for the conventional process, of which the majority of the scientific literature is comprised, does not necessarily apply. The aim of this work was to highlight the differences between the  $BF_{wp}$  process and the conventional process, as well as to begin to build a knowledgebase of performance data for optimization purposes. To that end, the goals of this study were to 1) study the effect of water quality changes on the  $BF_{wp}$  process and 2) to study the effect of the backwashing parameters: Collapse pulsing time, wash expansion and wash time on the performance of the  $BF_{wp}$  process. This was done by conducting experiments with identical biofilter trains run in parallel, with one running under constant backwashing conditions (control) while the other operated under varying backwashing conditions (experiment). It was shown that, when operated under the same conditions, these two trains had very similar performances.

The following conclusions were drawn about the effect of water quality changes on the  $BF_{wp}$  process performance:

Turbidity removal through the filters decreased over the duration of the study despite relatively
steady influent turbidity. This may be due to the increase in water viscosity due to lower water
temperatures throughout the study period. Turbidity removal was not majorly affected by large
increases in influent turbidity.

- The rate of pressure loss as well as the available pressure head for each biofilter decreased over the study period. This may have been caused by the quality of influent particles and the falling temperature seen throughout the study.
- Organics removal through each biofilter decreased coinciding with decreasing temperature, but biological activity as measured by DO uptake by media samples stayed constant throughout the study.

In addition, a full factorial statistically designed experiment was carried out to determine the effect of the length of collapse pulsing, wash expansion and wash time of the backwashing cycle on biofilter performance. With respect to this objective, the following conclusions were made:

- Optimal backwashing parameter settings in terms of subsequent biofilter turbidity removal coincide with the settings for the minimum biofilter pressure loss rate at 6 minutes of collapse pulsing followed by a 5 minute bed wash at 30% bed expansion. At this setting, the biofilter was shown to remove the maximum amount of turbidity with minimal headloss accumulation. This resulted in a significant biofilter run time gain (compared to the control biofilter) as well as an increase in log turbidity removal of 0.2 (compared to the control biofilter).
- The removal of biopolymers and protein like material by the filters after backwashing are shown to be marginally affected (<5% removal) by factor interactions. These are hypothesized to be interdependent on the removal of turbidity due to the similarity of the effect of backwashing on these response variables. This may be due to the interactions of biopolymers and protein like material and colloids as reported by Buffle et al. (1998)
- The removal of biopolymers by the biofilter after backwashing was found to be influenced only
  by the interaction of wash expansion and wash time. Optimal backwash parameter settings were
  found at 15 minute bed wash at 30% bed expansion. At this setting, removal of the biopolymers
  were expected to only be 5 percentage points higher than the control biofilter, which is a small
  increase.
- The optimal settings for the removal of biopolymers are at odds with the optimal settings for removal of turbidity and reduction of headloss, and optimization therefore requires a trade-off.
   The modest increase in biopolymer removal may result in shorter biofilter run times, which may prove to not be cost effective.
- The wash expansion factor had the least amount of influence on the response variables studied.

- Biological activity as measured by DOC removal and media DO uptake as is largely unaffected by the backwashing procedure.
- A number of three factor interactions exist for the response variables studied, suggesting the complexity of backwashing as a procedure.
- Collapse pulsing time has the largest effect on biofilter performance.
- The ripening peak seen by the filters studied are unaffected by the factors studied.
- An optimal particle loading condition appears to exist on the biofilter which leads to optimal turbidity removal following backwash.

#### 4.7 Future Work

To confirm and further the findings of this study, the author recommends research in the following directions:

- 1. Confirm the factor effects are present at warmer and more stable temperatures.
- 2. Perform further experiments using response surface methodologies within the regions bounded by the backwashing values studied herein. This will help to determine the linearity, or lack thereof of the response variables.

Once an optimal backwashing strategy has been elucidated, then it is suggested that the biological behavior of the filters be studied over a longer period of time than 1 week to confirm that the backwashing activities have little effect over the long term.

It is also recommended that the effects of alternative backwashing strategies not investigated in this work, such as the extended terminal subfluidization wash (ETSW) be investigated.

# Chapter 5

# Influence of Biofilter Backwashing on Ultrafiltration Membrane Fouling

#### 5.1 Overview

Biofiltration without pretreatment ( $BF_{wp}$ ) has been shown to be effective at reducing ultrafiltration polymeric membrane fouling on both the bench scale and the pilot scale, but to date, a detailed investigation into the effects of operational parameters on the system has not been undertaken. The current study aims to fill this gap by analyzing the effect of changing water quality parameters on the BF/UF system and to determine the significance of operator controllable biofilter backwashing parameters on membrane fouling behavior. The current study has shown that only the biopolymer fraction of the dissolved organic carbon measured correlated with irreversible membrane fouling, while reversible fouling was not found to have any correlation to any of the parameters investigated. The irreversible membrane fouling rate was also found to be influenced by the collapse pulsing time and the wash time of the preceding biofilter, and membrane run delay between putting the membrane back into service after biofilter backwashing.

## 5.2 Introduction and Objectives

The use of membrane filtration as a surface water treatment technology has grown significantly in the past two decades (Crittenden et al. 2012), however, the fouling of membranes remains a major operational barrier to greater acceptance and use (AWWA 1998; Escobar 2005). Membrane fouling refers to the accumulation of material on or within the membrane which restricts water flow effectively increasing the pressure drop across the membrane. The direct consequence of this depends on the method of operation of the membrane system. In constant flux systems, an increased pressure drop requires higher pressures to maintain flux, thus increasing electricity demand and operational costs. In systems where the pressure across the membrane is kept constant, fouling results in a decrease in membrane permeate (i.e. the filtered water coming out of the membrane) flux, resulting in a lower production rate. In both cases, fouling represents a major contributor to operational costs of the membrane system.

Typically, membrane fouling is characterized as reversible or irreversible in relation to the cleaning method used. Hydraulically reversible fouling refers to fouling which can be removed by hydraulic means – i.e. backpulse or backwash operation. Hydraulically irreversible fouling refers to fouling which cannot be removed hydraulically but its majority can typically be removed by chemical cleaning (Crittenden et al. 2012). This involves using chemicals, such as oxidizing agents and acids to dissolve the

attached foulants and requires the system to be offline. This chemical cleaning operation also results in an increase in system operating costs. In addition, the minimization of chemical cleaning operations is desirable as it has been shown that this operation can damage the membrane over time, thus shortening the lifespan of the membrane (Abdullah & Berube 2012).

The mechanism of fouling is complex and depends heavily on the influent source water quality, however, natural organic matter (NOM) and its fractions have been shown to play a critical role (Kennedy et al. 2005; Jermann et al. 2008; Peldszus et al. 2011b; Peiris et al. 2013). The biopolymer fraction of NOM, which consists of proteins, polysaccharides, amino sugars, and other dissolved chemical species (Huber et al. 2011), has been the particular focus of research, as it has been shown to not only contribute to membrane fouling, but also is biodegradable (Hallé et al. 2009). Therefore, the use of biologically active media filtration has been studied as a pretreatment technology for membrane fouling reduction (Persson et al. 2006; Hallé et al. 2009; Peldszus et al. 2012). Although the concept has been assessed, a detailed investigation into the effect of operational parameters on system operation has not been undertaken.

In the current study, the effect of changing water quality parameters on the operation of UF membranes within the BF/UF system, as well as the influence of biofilter backwashing operation on UF membrane fouling behavior was investigated in detail. This research was intended as a screening study to determine which biofilter operator controllable factors are significant in UF membrane fouling development, and to act as a guide for further, more detailed optimization studies.

## 5.2.1 Objectives:

The objectives for the current study were:

- 1) Investigate the effect of changing UF feed water quality parameters on the fouling of these membranes.
- 2) Determine the significant biofilter backwashing effects which influence fouling behavior and the rejection of water quality parameters by the UF membranes.

## 5.3 Experimental Approach

#### 5.3.1 Investigated Backwashing Parameters

All the backwashing parameters studied in Chapter 4 (collapse pulsing time, wash time, and wash expansion) and the rational used for their choice apply here as well. In addition, another parameter was added, which was termed "Membrane Run Delay". This refers to the amount of time between when the biofilter has been put back in service following a backwashing operation, and when the effluent from that

filter was fed to the membrane pilot unit. The inclusion of this parameter was intended to test for the effect of the filter ripening peak on the fouling behavior of the membranes.

## 5.3.2 Experimental Design

## 5.3.2.1 Controlling for systematic errors

To control for systematic errors, a two train approach was used. This approach was identical to that which was described in chapter 4. Two identical treatment trains running in parallel were used for this study, with one operating under constant operating conditions (termed 'control') and the other operating under varying conditions (termed 'experiment'). The setpoints used for the control filter were also used as the centre point conditions (Table 5-1), which were included to estimate system error for subsequent ANOVA calculations (described later). An analysis of the effects of backwashing parameters were on the difference in the response variables between both trains was conducted. In this way, systematic errors which may affect the fouling behavior of the membranes through time (such as temperature, varying water quality parameters etc.), could be accounted for.

#### 5.3.2.2 Statistical Design

The identical experimental design as was used in Chapter 4, was used here, but with the addition of the membrane run delay factor, thus making the design when applied to the membranes a half fractional factorial, as shown in Table 5-1. Thus one set of weekly experimental conditions, viewed from two parts of the system was used to conserve time. A half fraction design allowed for the determination of the significant main effects so as to provide input to future more in depth studies, thus the influence of higher factor interactions was not investigated. The centre point runs were performed in the middle and the end of the study to provide an estimate of error for the experimental analysis.

Table 5-1 2<sub>IV</sub><sup>4-1</sup> Half fraction factorial design

| Run    | Week       | Colla<br>Pulsing | -     | Wasl  | h Time |       | ash<br>nsion | Membrane Run<br>Delay |        |  |
|--------|------------|------------------|-------|-------|--------|-------|--------------|-----------------------|--------|--|
| Number | Starting   | Level            | Value | Level | Value  | Level | Value        | Level                 | Value  |  |
| 1      | 2014-09-22 | -                | 0 min | -     | 5 min  | -     | 30%          | -                     | 0 min  |  |
| 2      | 2014-10-13 | +                | 6 min | -     | 5 min  | -     | 30%          | -                     | 0 min  |  |
| 3      | 2014-10-06 | -                | 0 min | +     | 15 min | -     | 30%          | -                     | 0 min  |  |
| 4      | 2014-10-20 | +                | 6 min | +     | 15 min | -     | 30%          | +                     | 30 min |  |
| 5      | 2014-10-27 | 0                | 3 min | 0     | 10 min | 0     | 50%          | 0                     | 15 min |  |
| 6      | 2014-10-03 | -                | 0 min | -     | 5 min  | +     | 70%          | +                     | 30 min |  |
| 7      | 2014-11-10 | +                | 6 min | -     | 5 min  | +     | 70%          | +                     | 30 min |  |
| 8      | 2014-11-17 | -                | 0 min | +     | 15 min | +     | 70%          | -                     | 0 min  |  |
| 9      | 2014-11-24 | +                | 6 min | +     | 15 min | +     | 70%          | +                     | 30 min |  |
| 10     | 2014-12-01 | 0                | 3 min | 0     | 10 min | 0     | 50%          | 0                     | 15 min |  |

As the chosen design had an IV design resolution, two factor interaction effects were confounded with one another and main effects were confounded with three factor interactions. This was deemed an appropriate design as the objective of this portion of the study was to determine if a factor was statistically significant and warranted further study. It was hypothesized when designing this screening study that three factor interactions would not be significant and thus this design resolution would be appropriate to determine if factor effects were significant.

## **5.4 Materials and Methods**

## 5.4.1 Biofilter Setup Description

The experimental setup used in this study consisted of two identically constructed treatment trains running in parallel. Each train, with one being termed 'control' and the other 'experimental', consisted of a biologically active granular media filter followed by a custom built UF membrane pilot unit. The dual media biofilters (anthracite over sand) featured an 8 inch diameter and were operated under constant rate filtration mode. Effluent flowrate was kept constant at 100 L/h, corresponding to a loading rate of 3.08m/h and an EBCT of 7.78 minutes. Further details are discussed in Chapter 4.

# 5.4.2 Biofilter Backwashing Procedure

Biofilter backwashing was performed on Monday, Wednesday and Friday of each experimental week, or when the biofilter headloss built up to such a degree that a constant flowrate could not be maintained. Details of the backwashing procedure are provided in Chapter 4, but summarized here for clarity. The biofilters were backwashed as follows:

- 1) Stop filter operation and isolate filter from the system.
- 2) Open drain valve and drain the water level above the media to avoid filter media carry over (loss) during the filter backwash.
- 3) Initiate backwash according to the following steps:
  - a. Air + water wash (collapse pulsing) 3 minutes
  - b. Water only wash 10 minutes at 50% bed expansion
  - c. Slowly lower flow to 0 L/h 1 minute
- 4) Open effluent valve and resume filter operation

Setpoints and time for each step are shown in Table 5-1 for each train and experimental week. The control filter was backwashed at the setpoints indicated in the centre point weeks, while the rest of the table signifies the setpoints of for the experimental filter.

## 5.4.3 Membrane System Description

The focus of this part of the study was on the latter half of the treatment train, which was comprised of two identical custom built UF pilot test units shown in Figure 5-2. Each unit, termed 'control' and 'experiment', received effluent water from the corresponding biofilter, pumped via peristaltic pumps into the UF influent tanks. These tanks had an approximate available volume of 80 L. Levels in these tanks were maintained constant by an overflow i.e. constant head tanks.



Figure 5-1 Zeeweed 1000 module (membrane fibers inside of housing)

The membranes used for this study were hollow fiber Zeeweed 1000 (GE) arranged in membrane modules shown in Figure 5-1. These have an outside-in flow path (operated by applying a vacuum to the permeate side of the membrane) and had a nominal pore size of  $0.02~\mu m$ . The membranes modules were comprised of numerous fibers made from polyvinyldiene fluoride (PVDF) attached to headers at each end. These fibers had an inner diameter of 0.47~mm, an outer diameter of 0.95~mm and the permeation surface area of each module was  $1~m^2$  (GE Water 2013).

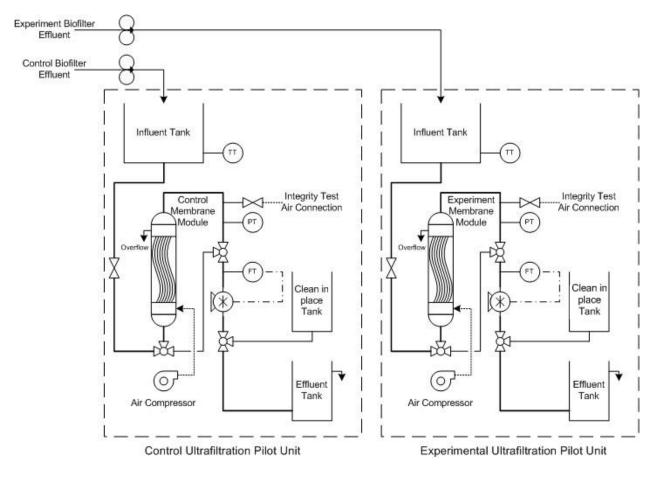


Figure 5-2 Simplified ultrafiltration pilot unit process diagram including temperature transmitter (TT), pressure transducer (PT) and flow transmitter (FT).

#### **5.4.4 Membrane Operation**

Operation of the UF pilot units was automatic and controlled by the on board programmable logic controller (PLC). Operator interface was provided via a touch screen computer. Operation was accomplished by an onboard sequencer which delineated each operation into a number of fundamental discrete steps, distinguished by a unique valve configuration, equipment state and setpoints. During the filtration cycle, water flowed from the inlet tank into the membrane tank housing the ZW-1000 module, which was kept at ambient pressure. The water level in the membrane tank was kept at a constant height by throttling the influent water flowrate such that a small amount of water was allowed to overflow. This throttling was set at the beginning of the experiments and not changed throughout. Water was then filtered through the membrane, the filtrate being termed 'permeate'. From the permeate connection in the module, water flowed through an electromagnetic flowmeter, through a reversible variable speed gear pump which provided suction to the membrane and into the effluent tank. A feedback loop between the

flowmeter and the pump, with the units PLC proportional-integral-derivative (PID) algorithm providing control function, allowed for flow control. An overflow was provided on the effluent tank.

Valving was provided on the units to allow for membrane permeate to be pumped from the effluent tank back through the membranes for a periodic backpulse cleaning operation (Table 5-2). An air compressor was connected to the membrane module to provide air scour during the back pulse. A tee connection was provided on the membrane effluent piping to allow for an air cylinder to be connected for membrane integrity testing. Temperature was measured by a thermocouple in the influent tank, and membrane effluent pressure was measured by a pressure transducer located slightly before the pump suction connection. The membranes were operated at a temperature corrected flux of 60 LMH at 20°C by Equation 5-1 (Crittenden et al. 2012).

Equation 5-1 
$$J_s = J_m (1.03)^{T_s - T_m}$$

Where:

 $J_s$  = Standard flux (60 LMH)

 $J_m$  = Measured flux

 $T_s$  = Standard temperature (20°C)

 $T_{\rm m}$  = Measured temperature

The membrane flux was corrected to account for temperature related viscosity changes of the water. Without correction, flow resistance due to the increase in water viscosity due to changing temperatures may be erroneously attributed to fouling, and membrane results occurring at different temperatures may not be comparable. At the beginning of each weekly run, an average temperature for that week was estimated and the temperature corrected operating flux corresponding to 60 LMH at 20°C was set for the remainder of the week. It was recognized that changing the flowrate through the membrane with a constant flowrate into the membrane tank effectively changed the flowrate through the drain and that this may affect the flowrate of solids flowing through the membrane module. It was assumed that this had no effect on the fouling behavior. Permeation occurred in 30 minute cycles followed by a back pulsing cycle. The back pulse cycle consisted of reversing the flow through the membranes with membrane tank aeration for 50 seconds, followed by an aeration-only step for 15 seconds. The membrane holding tank was then drained to waste, the membrane tank refilled with membrane influent water, and the next permeation cycle was started up again. Details of the back pulsing steps, including setpoints and times are shown in Table 5-2.

Table 5-2 Membrane backpulse operation setpoints

| Sequence<br>Step | Program<br>Step<br>Number | Description                 | Water Flowrate<br>(L/h) | Air<br>Flow | Time<br>(s) |
|------------------|---------------------------|-----------------------------|-------------------------|-------------|-------------|
| 1                | 30                        | Back Pulse Starting Step    | 0                       | Off         | 3           |
| 2                | 32                        | Backpulse ramp up           | 0-45 (Increasing)       | On          | 20          |
| 3                | 33                        | Back Pulse                  | 45                      | On          | 40          |
| 4                | 34                        | Back Pulse Pump Ramp Down   | 45-0 (Decreasing)       | On          | 3           |
| 5                | 35                        | Aeration                    | 0                       | On          | 15          |
| 6                | 36                        | Drain ZW Tank with aeration | 0                       | On          | 50          |
| 7                | 37                        | Drain no air                | 0                       | Off         | 20          |
| 8                | 38                        | Pause                       | 0                       | Off         | 5           |

Membrane recovery cleaning and integrity testing were performed at the end of each weekly run on Friday. Chemical cleaning consisted of a two-step chemical soak process. The first step consisted of soaking the membrane in a 500 mg/L solution of NaOCl for 6 hours. This was followed by a rinse step and then a 6 hour soak with a 5 g/L solution of citric acid.

Membrane integrity testing was performed after each chemical cleaning to establish that the membrane was clean and had not been damaged. During the integrity testing, the membrane permeate line was isolated and an external air cylinder was connected to the connection as shown in Figure 5-2. The membrane holding tank was filled with water and the air pressure within the fibers was brought to approximately 69 kPa(g) and held for 5 minutes to purge any water from the lumen of the membrane fibers. The air supply was then turned off, the isolation valve closed and the subsequent pressure decay within the membrane was monitored. Integrity was deemed intact if the pressure did not decay faster than 0.7 kPa in 2 minutes (Zeenon Environmetnal Inc. 2007).

Experiments/runs were performed on a weekly basis from Monday to Friday. On Friday, after the weekly run clean water permeability of the fouled membranes was determined, and a chemical cleaning followed by an integrity testing was performed. On the weekends, the membranes were put on hold by draining the influent membrane tanks and filling the system with membrane permeate. On Monday before starting an experimental run another clean water permeability test was performed on the clean membrane. During the clean water permeability test, membrane permeate water was recirculated through the membranes at 40, 50, 60 and 70 L/h. The test on the fouled membrane after a weekly run served as a measure of the irreversible fouling experienced over that week, whereas the clean water permeability test on the clean membrane was used to determine the efficacy of the membrane chemical cleaning.

Each time the biofilters were backwashed, the membrane pilot influent tank was drained and the system put on hold while the backwash operation was completed. Once membrane influent water was to be

applied to the membranes, the membrane influent tank was filled and the permeate in the system was drained. Permeation operation was resumed shortly thereafter (within three hours).

## 5.4.5 Sampling points and methods

Weekly water samples were taken on Thursdays and analyzed in the laboratory for a number of parameters. Samples were taken from the influent to the membrane pilot units (i.e. membrane influent) as well as from the permeate of each membrane unit. This provided a measure of the role of various water quality parameters on observed fouling behavior.

Samples were analyzed for TOC, DOC, and UV absorbance at 254 nm as well as NOM characterization as measured by LC-OCD and FEEM peak picking. All samples were analyzed within 24 hours of collection and were stored in a refrigerator at 4°C prior to analysis. TOC and DOC samples were analyzed by the wet oxidation method (Anon 2012) using a OI Scientific model 1030 TOC analyzer. Organic carbon and organic nitrogen biopolymers as well as humic acid concentration were determined by NOM fraction characterization using LC-OCD as described by Huber et al. 2011. UV absorbance at 254 nm was analyzed according to *Standard Methods for the Examination of Water and Wastewater* (2012). The details of the FEEM analysis as well as further details regarding the sampling and analysis of all parameters mentioned here can be found in Chapter 4.

#### 5.4.6 Online Data Collection

In addition to laboratory data analysis, a number of parameters were measured online. The turbidity of the membrane influents was measured by a HACH 1720E Low Range Turbidimeter connected to two HOBO Energy Loggers H22-001 (Onset Technologies), which logged measurements in 5 minute intervals.

A number of online measurements were included in the self-contained UF pilot units. The temperature of the influent was collected in the membrane influent water tank by a thermocouple. Pressure measurements for the calculation of transmembrane pressure (TMP) were taken at the effluent of the UF membrane module. TMP is defined as the pressure across the membrane wall. Flow measurement was also taken on the effluent line. These parameters were logged with a 2 second intervals by the on-board PLC system included in the UF pilot units.

#### 5.4.7 Data Evaluation

## 5.4.8 Membrane Fouling

Membrane fouling rates were calculated from the TMP data logged by the UF units. Prior to the calculation of fouling rates, the TMP data was adjusted based on the estimated average temperature selected for that week to account for temperature related water viscosity changes. This adjustment used Equation 5-2 and was done for each TMP point measured.

Equation 5-2 
$$TMP_C = TMP_m \times 1.025^{(T-T_{set})}$$

Where:

 $TMP_c$  = Corrected TMP (kPa)  $TMP_m$  = Measured TMP (kPa)

 $T_c$  = Corrected temperature (°C)

 $T_{set}$  = Set temperature (°C)

It was discovered in experimental week 8 that the temperature probe in each UF pilot unit was improperly calibrated, and that the indicated temperature was underestimating the actual temperature. This became apparent as the water temperature dropped, and the temperature probe began reading below zero degrees Celsius. A correction factor for each unit was established by comparing the thermocouple indicated temperature to that indicated on a laboratory thermometer for a range of temperatures from 2 to 30 °C. For the TMP correction calculation, the thermocouple indicated temperature was corrected using Equation 5-3 and then Equation 5-2.

Equation 5-3 
$$T_c = mT_m + b$$

Where:

m = Temperature correction slope (0.77 1/T)

 $T_m$  = Thermocouple measured temperature ( ${}^{\circ}$ C)

b = Temperature correction factor (6.56 for control and 6.78 for experiment trains)

An example of the temperature and TMP correction is shown in Figure 5-3, which shows the TMP and temperature trends for the control UF unit for the week of November 3 to 7 (experimental Week 6). On the Monday of that week it was estimated that the average actual water temperature for that week would be 12°C. Using Equation 5-1 the membrane flux corresponding to 60 LMH at 20°C was calculated to be 39 LMH and the experimental run for that week was performed at this flux. In the data analysis, the temperature probe indicated temperature (shown in grey in Figure 5-3) was corrected by Equation 5-3

(shown in orange). The measured TMP (shown in blue) was then corrected using this temperature in Equation 5-2 to the trend shown in yellow. This was done to account for the differences in temperature between the estimated 12°C for that week and the actual temperature which dropped down to 10°C.

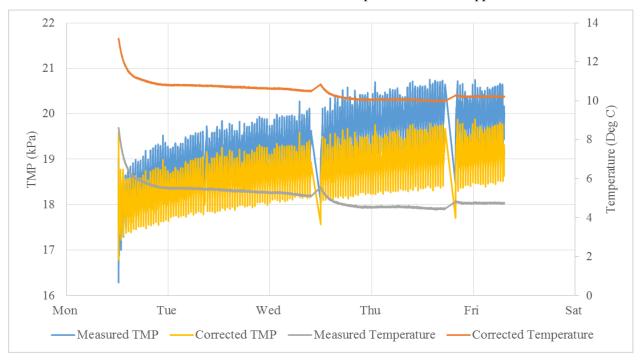


Figure 5-3 Control TMP and temperature trends for November 3 to 7, 2014

Hydraulically reversible fouling is defined as the fouling which can be removed by membrane back pulsing. This was calculated by subtracting the TMP reading from the end of one permeation cycle from the reading at the beginning of the next cycle. To obtain these readings for each cycle a 30 point (1 minute) average of the TMP readings at the end of one cycle and the beginning of next cycle were calculated to lessen the effect of noise present in these measurements. The reversible fouling reported for each run was the average of all cycles within that experimental run/week. Hydraulically irreversible fouling is defined as membrane fouling which cannot be removed by membrane back pulsing and accumulates over time. This can be determined as the difference between the starting TMP values of subsequent cycles. The rate of accumulation of hydraulically irreversible fouling, termed simply the irreversible fouling rate, was calculated by linear regression of these starting TMP values over an experimental run. As with the reversible fouling, a 30 point, or 1 minute average was used for each starting cycle TMP value to mitigate the effects of measurement noise. An example of this regression is shown in Figure 5-4 which shows the average control train TMP values for each cycle for the week of November 3 to 7 (experimental Week 6).

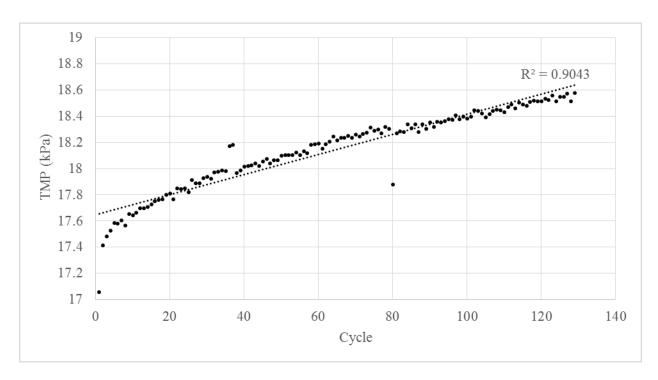


Figure 5-4 One minute average start TMP values for November 3 to 7, 2014

#### 5.4.9 Statistical Calculations

The statistical methodology followed for the half fraction factorial design analysis was the same as described in Chapter 4. Important points are highlighted here for completeness. ANOVA methodology was used in the analysis of the fractional factorial statistical experimental design used in this study. A significance level of 5% was used throughout. As a control / experiment configuration was used for the experimental setup, the difference between the values of the experiment and control train response for a specific week was used as the response variables upon which the statistical tests were conducted.

Error estimates were done using pooled variance of the centre point weeks except for the membrane influent turbidity parameter. For this response variable, error estimates were taken as pooled variances from the weekend data. This was the same procedure as described in chapter 4.

Pearson correlation coefficients (Devore 2004) were calculated to study the linear correlation between the responses variables investigated in this chapter. These were calculated by the analysis tool kit built into Microsoft Excel 2013. Significance of these coefficients was tested by a two-way t test at a significance level of 5%.

#### 5.5 Results and Discussion

# 5.5.1 Water Quality and Membrane Fouling over the Course of the Study

The weekly irreversible fouling rate and reversible fouling for the control and experiment UF membrane units are shown in Figure 5-5. Centre point weeks (Table 5-1) are highlighted in yellow, and temperature is also shown, on Figure 5-5. During the centre point weeks, the irreversible fouling behavior of the control and experiment membrane units were nearly identical, showing good comparability between both trains under consistent operating regimes. This low variability in the centre point weeks led to a low error estimate and a higher precision in estimating the significant factors from the ANOVA. For the reversible fouling behavior comparability between control and experiment trains was also quite good, but in the final centre point week reversible fouling between the trains deviated quite a bit more between the trains compared to the previous centre point. This resulted in higher error estimates for the reversible fouling rates and as such no factors were shown to be significant in the ANOVA tables. It was hypothesized that possible pinhole leaks in some of the valves and components of control UF unit may be responsible for this behavior, as it only affected this response variable.

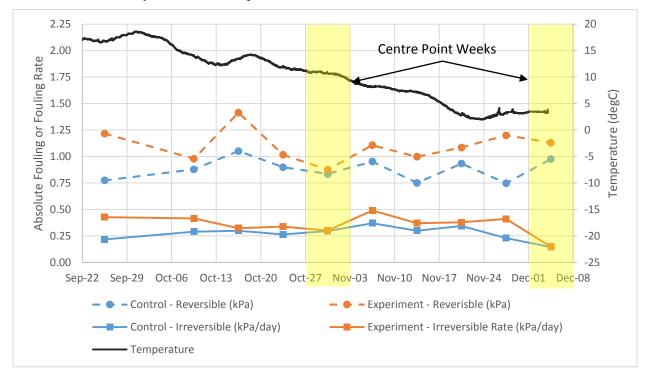


Figure 5-5 UF membrane reversible and irreversible fouling as well as temperature over time

The irreversible fouling rate for the control filter increased slightly over the length of the study, and dropped substantially in the final two weeks. This drop coincided with a large increase in turbidity

(Figure 5-6) as well as a elevated DOC (Figure 5-7) in the membrane influent. This suggests that a change in water quality may have played a role in the fouling behavior during these last two weeks.

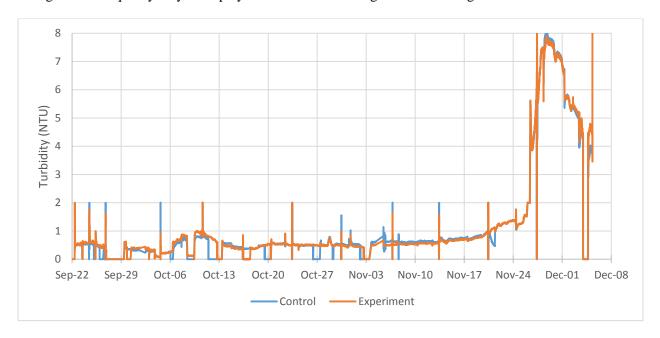


Figure 5-6 Turbidity of control and experimental membrane influents (e.g. membrane feed) over time (4 hour moving average)

The Membrane feed (membrane influent) DOC concentration as well as percent rejection by the control and experiment membranes are shown in Figure 5-7. Rejection of organics was analyzed as this provided a measure of what components would have been attached to the membrane and contribute to fouling. The dip in DOC rejection shown for October 16<sup>th</sup> was attributed to laboratory contamination as the measured DOC in the membrane permeate is higher than that of the membrane influent. This situation was also seen for the experimental train DOC rejections.

As shown on Figure 5-7, the membrane influent DOC for both the control and experimental filters ranged from approximately 5 to 7 mg C/L, while the last two experiment weeks (sampling dates on November 27<sup>th</sup> and December 4<sup>th</sup> respectively) were slightly higher than the rest of the study. This increase corresponded to the weeks in which the turbidity (Figure 5-6) was much higher than normal. Also of note was the similarity between the control and experimental membrane influents indicating that biofilter backwashing had little effect on the membrane influent DOC concentrations. This assertion is further supported by the ANOVA tables discussed in Section 5.5.4.

An overall slight upward trend can be seen in DOC rejections (dashed lines in Figure 5-7) by both the control and experimental UF membranes in the later part of the study, starting on the November 6<sup>th</sup> sample date. In this part of the study, the rejection of DOC by the membranes ranged from 7% to 9%,

while for the first half of the study, these rejections ranged from 1% to 6%. As during this time the DOC concentration in the water being filtered by the UF membranes (membrane influent) remained similar throughout the experiment, this increase in membrane DOC rejections may have been caused by a difference in the character of the DOC. The specific ultraviolet absorbance (SUVA) of the membrane influent as well as the membrane permeate for both the control and experimental trains are shown in Figure 5-8. This parameter is a measure of the aromaticity of the DOC. As can be seen in this figure, there was a distinct difference in the SUVA of the membrane influent and membrane permeate for the weeks starting on November 13<sup>th</sup> as compared to the rest of the study, with the later weeks being lower. This signifies a lower aromaticity of the membrane influent in these weeks, suggesting a shift in character of the DOC away from humic like aromatic compounds, which have been shown to easily pass through UF membranes. It is proposed that this was the reason for the shift in DOC rejections in the latter half of the study.

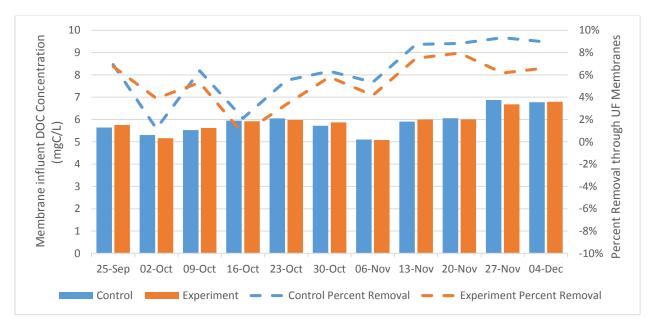


Figure 5-7 Biofilter effluent DOC concentrations and UF membrane rejection. The dates shown on the x-axis correspond to the sampling date, which occurred on Thursdays during each experimental week.

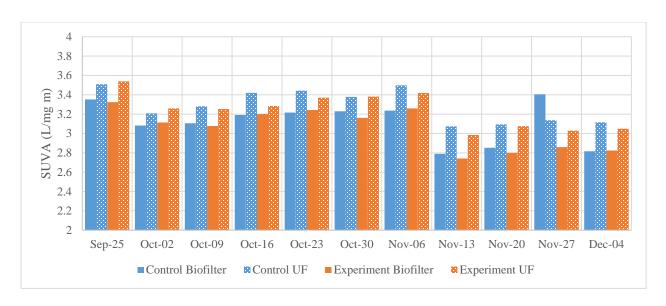


Figure 5-8 SUVA of biofilter effluent and UF membrane permeate. The dates shown on the x-axis correspond to the sampling date, which occurred on Thursdays during each experimental week.

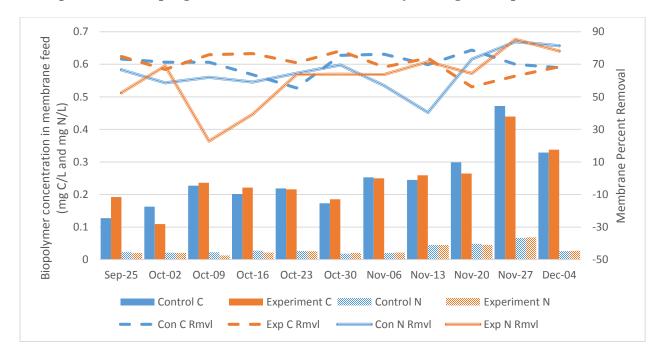


Figure 5-9 Biopolymer concentration (Carbon (C) and nitrogen (N) detectors) in the control (Con) and experiment (Exp) membrane feeds (= membrane influents) and their removals through the membranes. The dates shown on the x-axis correspond to the sampling date, which occurred on Thursdays during each experimental week.

The concentration of biopolymers (measured using carbon and nitrogen detectors) in the membrane influents as well as their percent rejection for both control and experimental membranes are shown in Figure 5-9. The concentration of carbon based biopolymers was much higher than the concentration of biopolymers (measured as nitrogen) in the samples and increased toward the later part of the study. There was also a marked increase in the nitrogen component occurring between the November 13<sup>th</sup> and November 27<sup>th</sup> sample dates, returning to baseline levels in the final experimental week. This is seen more clearly in Figure 5-10 which shows the ratio of carbon to nitrogen content in the biopolymers measured, and indicates that the character of the membrane influent water was different for these three weeks as compared to the rest of the study, with a higher nitrogen component. These changes corresponded to the slightly higher membrane influent DOC concentrations as well as the increase in DOC membrane rejection in the later portion of the study (Figure 5-9) and may indicate that the composition of water near the end of the study was different than at the beginning of the study. This was further evidenced by the increased biopolymer concentration as measured by the nitrogen detector rejection in the last two weeks of the study.

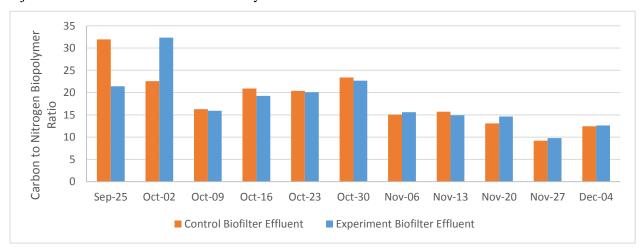


Figure 5-10 Carbon to nitrogen ratio of membrane influent biopolymers. The dates shown on the x-axis correspond to the sampling date, which occurred on Thursdays during each experimental week.

The humic acid concentrations in the membrane influent and in membrane permeate are shown in Figure 5-11. A marked increase was observed on the sampling dates between October 16 to 30, as well as during the last two weeks of the study (November 27 to December 4). Despite this, the rejection by the membranes remained consistent and low (0% to 5%) throughout the study, indicating that humic substances were likely not contributing to membrane fouling as they pass through the UF membranes.

The ratio of humic substances to biopolymers in the membrane influent is shown in Figure 5-12. The overall decreasing trend in the humics to biopolymer ratio in the membrane influent indicates that the DOC composition changed and that the biopolymer fraction within the DOC increased over the length of the study. In addition, this declining behavior is also seen in the membrane permeate, indicating that the fraction of biopolymers in the permeate increases for this half of the study. This was expected as the membrane rejection was also high in this portion of the study. Both of these trends further the claim of changing water quality throughout the study.

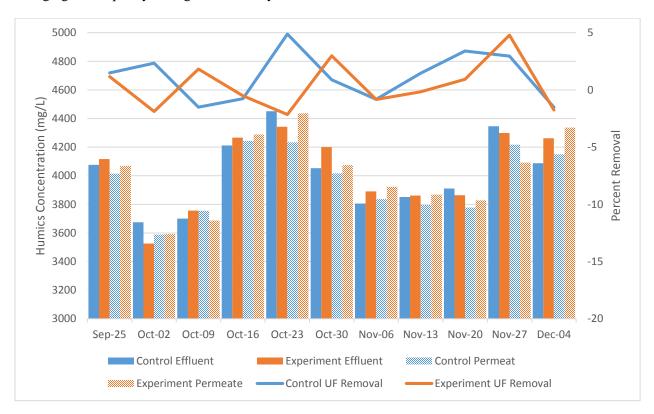


Figure 5-11 Humics rejection by UF membranes, and humics concentrations in the membrane feed and in the membrane permeates for both the control and experiment trains. The dates indicated on the x-axis correspond to the sampling date, which occurred on Thursday during each experimental week.

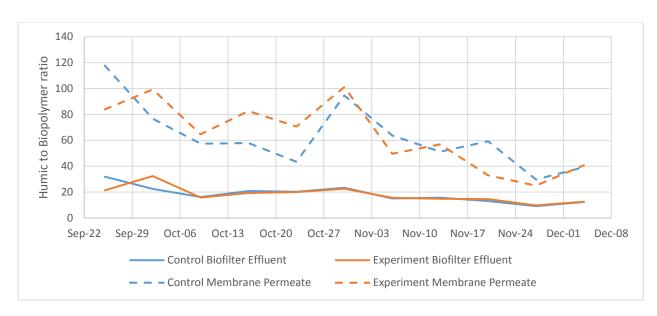


Figure 5-12 Humic to biopolymer ratio in both the control and experiment membrane feeds and the corresponding permeates. The dates indicated on the x-axis correspond to the sampling date, which occurred on Thursday during each experimental week.

#### **5.5.2 Correlation of Control Train Parameters**

The control train was operated under consistent conditions for the length of this study, and therefore allowed for the investigation of the effect the presence of different water quality parameters in the membrane feed have on membrane fouling. To that end, Pearson correlation coefficients between all the measured values obtained from the control membrane for this study, including reversible fouling and irreversible fouling rate were calculated and are shown in Table 5-3. This analysis was done to gain a better understanding of how membrane fouling was correlated with the concentrations of water quality parameters applied to the membrane (i.e. in the membrane influent) under constant conditions. That is to say, the variation in water quality parameters originated from the changing raw water conditions. The correlation analysis was done to identify water quality parameters as potential foulants in the conditions present during this study.

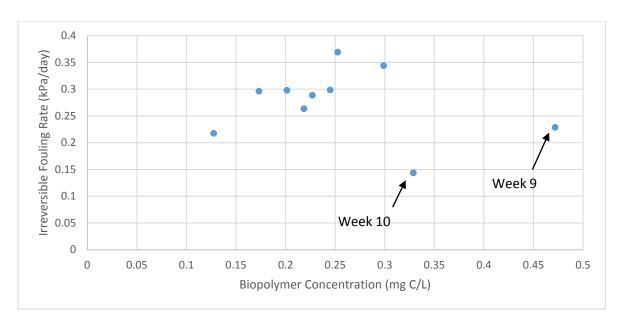


Figure 5-13 Relation of irreversible fouling rate to concentration of biopolymers applied to the membranes (membrane influent). Week 9 and 10 as marked here had significantly higher turbidity then the rest of the dataset.

The significance of each calculated coefficient was tested using a two-tailed t-test. Values for which the null hypothesis (coefficient equal to zero) could be rejected at the  $\alpha$ =0.05 level, indicating a statistically significant correlation, are highlighted in green. This table analyzes only values for Weeks 1 to 8 (Sept 22 to Nov 21) with a membrane influent turbidity range of 0.46 to 0.80 NTU. Weeks 9 and 10 showed significantly higher turbidities (3.5 to 4.8 NTU average range), and were significant outliers in the resulting scatter plots of significantly influencing correlation (Figure 5-13). Turbidity has been shown to play a complex role in fouling, and authors who have previously investigated membrane fouling have found it useful to group fouling in terms of turbidity (Peldszus et al. 2011b; Chen et al. 2014). It was determined that correlations should be done on the basis of turbidity groups, and values for Weeks 9 and 10 were therefore excluded from Table 5-3.

In the turbidity range studied, the rate of irreversible fouling was found to be statistically significant and positively correlated to the concentration of biopolymers (measured in mg C/L) in the membrane feed (Table 5-3). This confirmed the behavior seen by others (Chen et al. 2014; Halle et al. 2008). Irreversible fouling was also positively correlated to week number (i.e. fouling was found to increase through time) and negatively correlated with temperature. The correlation of irreversible fouling rate to temperature was unexpected, especially since the membranes were operated at a temperature corrected flux to take changes in viscosity with changing water temperatures into account. However, in this data set temperature and week number were highly correlated ( $\rho = -0.9686$ ), as is also apparent in Figure 5-5

where the temperature decreased throughout the study period. Moreover, the concentration of biopolymers in the membrane feed was strongly correlated to the week number, and temperature (Table 5-3 and Figure 5-5), and as Figure 5-9 shows the biopolymer concentration in the membrane influent stream increased throughout the study. Due to these two facts, it is speculated that the correlation of the week number to the irreversible fouling rate was indicative of changing water quality which has been documented and discussed in the previous section.

Biopolymer concentration (as mg C/L) applied to the membranes was found to be positively correlated to the protein like material (as measured by FEEM) applied to the membranes (Table 5-3). This may be due to the fact that proteins may be thought of as long chain polypeptides, and polypeptides are a component of biopolymers. Thus the FEEM instrument measures a subset of the biopolymer concentration, which is measured by the LC-OCD instrument. Moreover, the irreversible fouling rate was found to be correlated with incoming biopolymer concentration, but not to protein like material as measured by FEEM. This suggested that only a subset of the biopolymers that does not include the material measured by FEEM, is contributing to irreversible fouling seen in this study. This is a surprising result as previous authors have found protein like material to play a large role in irreversible fouling rates (Chen et al. 2014; Peldszus et al. 2011b). These different findings may also be explained by the method in which protein like material was measured and enumerated in those studies compared to this one. Principle component analysis (PCA) of the entire FEEM data was used in the aforementioned studies, which is a statistical method that takes into account all data points in the FEEM of each sample, while here, peak picking was used. In the case of peak picking, a single value at a particular set of excitation emission coordinates known to be related to the presence of proteins was used to determine the relative amount of proteins present in each sample. It may be that the presence of other NOM fractions, such as humic acids which comprises the bulk of the measurement, may have been influencing the results. Moreover, the p-value of the correlation coefficient between protein like material and irreversible fouling was p = 0.0610, which is very close to the critical value chosen (p = 0.0500). Thus it is likely that the protein like material may be playing a role in irreversible fouling here, but is not detected due to either the small sample size (n = 8) or due to the method by which it was determined.

The concentration of biopolymers in the membrane feeds was also positively correlated with turbidity in the same feeds. This is likely due to the fact that biopolymers interact with colloid material to form aggregates (Buffle et al. 1998), which may be detected as turbidity. In chapter 4 it was shown that the removal of biopolymers through the biofilters was influenced only by the interaction of wash time and wash expansion factors.

Table 5-3 Pearsons correlation coefficients for measured parameters (Green cells are statistically significant at the a=0.05 level)

|        |  |                                |  |                           |                           |                          | LC/OCD                   |                              | FEEN                                     | 1                         |                  |                        |                    |
|--------|--|--------------------------------|--|---------------------------|---------------------------|--------------------------|--------------------------|------------------------------|--|---------------------------|------------------|------------------------|--------------------|
|        |  | Reversible<br>Fouling<br>(kPa) | Irreversible<br>Fouling<br>Rate<br>(kPa/day) | DOC<br>Applied<br>(mgC/L) | TOC<br>Applied<br>(mgC/L) | BP<br>Applied<br>(mgC/L) | BP<br>Applied<br>(mgN/L) | Humics<br>Applied<br>(mgC/L) | Applied<br>Protein Like<br>Material (Au) | Humics<br>Applied<br>(Au) | SUVA<br>(L/mg m) | Temperature<br>(Deg C) | Turbidity<br>(NTU) |
|        | Irreversible Fouling Rate<br>(kPa/day) | 0.44                           |  |                           |                           |                          |                          |                              |  |                           |                  |                        |                    |
|        | DOC Applied (mgC/L)                    | -0.32                          | -0.30  |                           |                           |                          |                          |                              |  |                           |                  |                        |                    |
|        | TOC Applied (mgC/L)                    | -0.37                          | -0.42  | 0.98                      |                           |                          |                          |                              |  |                           |                  |                        |                    |
|        | BP Applied (mgC/L)                     | 0.46                           | 0.80   | 0.11                      | 0.00                      |                          |                          |                              |  |                           |                  |                        |                    |
| CC/OCD | BP Applied (mgN/L)                     | -0.43                          | 0.14   | 0.35                      | 0.29                      | 0.43                     |                          |                              |  |                           |                  |                        |                    |
| 3      | Humics Applied (mgC/L)                 | -0.32                          | -0.47  | 0.57                      | 0.65                      | -0.37                    | -0.23                    |                              |  |                           |                  |                        |                    |
| FEEM   | Applied Protein Like Material<br>(Au)  | 0.52                           | 0.63   | -0.12                     | -0.13                     | 0.83                     | 0.14                     | -0.21                        |  |                           |                  |                        |                    |
| E      | Humics Applied (Au)                    | -0.28                          | -0.51  | 0.47                      | 0.58                      | -0.48                    | -0.43                    | 0.95                         | -0.26                                    |                           |                  |                        |                    |
|        | SUVA (L/mg m)                          | 0.05                           | -0.22  | -0.54                     | -0.37                     | -0.34                    | -0.50                    | 0.01                         | 0.16                                     | 0.23                      |                  |                        |                    |
|        | Temperature (Deg C)                    | -0.04                          | -0.78  | -0.19                     | -0.10                     | -0.85                    | -0.48                    | 0.30                         | -0.62                                    | 0.34                      | 0.29             |                        |                    |
|        | Turbidity (NTU)                        | 0.34                           | 0.42   | 0.18                      | 0.11                      | 0.74                     | 0.35                     | -0.58                        | 0.55                                     | -0.54                     | -0.17            | -0.68                  |                    |
|        | Week                                   | 0.03                           | 0.73   | 0.10                      | 0.04                      | 0.81                     | 0.49                     | -0.37                        | 0.63                                     | -0.36                     | -0.12            | -0.97                  | 0.69               |

The removal of turbidity through the filters was not influenced by this interaction but was influenced by the three factor interaction (which included wash time, wash expansion and collapse pulsing time factors). Thus although the concentration of biopolymers and turbidity in the membrane influent appear strongly correlated, optimizing the biofilter backwashing operation for the removal of turbidity may, counter intuitively, not result in a lower membrane influent concentration. The reversible fouling of the membranes was found to not correlate to any of the parameters studied. This could be due in part to the large variability seen in the reversible fouling measurements as indicated in the next section.

## 5.5.3 System Variability between Control and Experiment Membranes

The differences between measured parameter values for both control and experiment trains during the centre point weeks (i.e. the weeks in which both trains operated under identical conditions since the backwash protocol for both biofilters was the same) are shown in Table 5-4. Differences were measures as the experiment value minus the control value. Also shown in this table is the difference as a percentage of the control train measurement. In cases where the difference was larger than the control measurement, this is shown as a percentage of the experiment measurement and marked with a 1. The difference between both trains in each week was small when compared to the control measurement, with the majority of all values being below 10% with the exception of the biopolymer concentration (mg N/L), protein like material and the reversible fouling rate. This indicates that for almost all parameters this small variability provides a high degree of confidence in the results of the statistical tests discussed in section 5.5.4 to determine the significance of the main effects studied.

The high variability in the reversible fouling measurement in Week 10 as compared to Week 5 has been hypothesized earlier as a result of UF pilot plant components degradation. The high variability seen in the biopolymer concentration (measured as nitrogen) in the membrane permeate may be due to the fact that the concentrations were very close to the method detection limit. Similar reasoning holds true for the protein like material as measured by FEEM.

Table 5-4 also shows that in general the influent and effluent concentration of many of the parameters increased in Week 10 as compared to Week 5. This again adds evidence to the difference in water quality as the study progressed. Although the concentration of these parameters increased in Week 10, the difference between both trains decreased, indicating very good comparability between the trains.

Table 5-4 Parameter variability between control and experimental train UF membranes

|            |   |           |            | Wee        | ek 5                  |         | Week 10    |            |                       |         |  |  |
|------------|---|-----------|------------|------------|-----------------------|---------|------------|------------|-----------------------|---------|--|--|
|            | Parameter   | Control   | Experiment | Difference | Percent of<br>Control | Control | Experiment | Difference | Percent of<br>Control |         |  |  |
|            | Reversible Fouling (kPa)  |           | 0.8357     | 0.8743     | 0.0386                | 4.61%   | 0.9755     | 1.1301     | 0.1547                | 15.86%  |  |  |
|            | Irreversible Fouling Rate (kPa/day) Membrane influent Turbidity (NTU) |           | 0.2962     | 0.3006     | 0.0045                | 1.51%   | 0.1438     | 0.1467     | 0.0029                | 2.05%   |  |  |
|            |   |           | 0.5454     | 0.5074     | 0.0380                | 6.97%   | 4.9157     | 5.1340     | 0.2184                | 4.44%   |  |  |
|            | DOC   | Influent  | 5.71       | 5.87       | 0.15                  | 2.66%   | 6.7693     | 6.79       | 0.02                  | 0.34%   |  |  |
|            | DOC<br>(mgC/L)  | Effluent  | 5.50       | 5.53       | 0.03                  | 0.55%   | 6.18       | 6.34       | 0.16                  | 2.55%   |  |  |
|            | (mgC/L)   | Rejection | 3.83%      | 5.81%      | 1.98%                 | 51.67%  | 8.64%      | 6.62%      | -2.02%                | 23.35%  |  |  |
|            |   | Influent  | 3.23       | 3.16       | -0.07                 | 2.12%   | 2.80       | 2.80       | 0.00                  | 0.29%   |  |  |
|            | SUVA  | Effluent  | 3.38       | 3.38       | 0.0034                | 0.10%   | 3.12       | 3.05       | -0.07                 | 2.14%   |  |  |
|            |   | Rejection | -4.60%     | -6.97%     | 2.37%                 | 51.42%  | -10.66%    | -7.98%     | 2.68%                 | 25.11%  |  |  |
|            | Biopolymer<br>(mgC/L)   | Influent  | 0.1732     | 0.1852     | 0.0120                | 6.95%   | 0.3290     | 0.3379     | 0.0089                | 2.69%   |  |  |
|            |   | Effluent  | 0.0424     | 0.0403     | 0.0022                | 5.13%   | 0.1058     | 0.1064     | 0.0006                | 0.59%   |  |  |
|            |   | Rejection | 75.49%     | 78.26%     | 2.77%                 | 3.67%   | 67.85%     | 68.51%     | 0.66%                 | 0.97%   |  |  |
| $\alpha$   | Biopolymers<br>(mgN/L)  | Influent  | 0.0184     | 0.0205     | 0.0021                | 11.41%  | 0.0263     | 0.0270     | 0.0007                | 2.66%   |  |  |
| C/OCD      |   | Effluent  | 0.0056     | 0.0074     | 0.0018                | 32.14%  | 0.0049     | 0.0059     | 0.0010                | 20.41%  |  |  |
| $\Gamma C$ |   | Rejection | 69.57%     | 63.90%     | 5.66%                 | 8.14%   | 81.37%     | 78.15%     | 3.22%                 | 3.96%   |  |  |
|            |   | Influent  | 4.0525     | 4.2000     | 0.1475                | 3.64%   | 4.0873     | 4.2621     | 0.1748                | 4.28%   |  |  |
|            | Humic   | Effluent  | 4.0166     | 4.0745     | 0.0579                | 1.44%   | 4.1496     | 4.3367     | 0.1871                | 4.51%   |  |  |
|            | (mgC/L)   | Rejection | 0.89%      | 2.99%      | 2.10%                 | 237.34% | -1.52%     | -1.75%     | 0.23%                 | 14.87%  |  |  |
|            |   | Influent  | 39         | 41         | 1                     | 4.58%   | 36         | 37         | 0                     | 0.63%   |  |  |
|            | Protein Like Material   | Effluent  | 46         | 39         | -7                    | 15.06%  | 36         | 35         | -1                    | 2.92%   |  |  |
| FEEM       | (au)  | Rejection | -17.71%    | 4.39%      | 22.10%                | 124.78% | 0.21%      | 3.73%      | 3.52%                 | 94.37%1 |  |  |
| FE         |   | Influent  | 390        | 390        | -1                    | 0.25%   | 410        | 405        | -6                    | 1.34%   |  |  |
| _          | Humic Substances  | Effluent  | 391        | 392        | 1                     | 0.34%   | 405        | 407        | 3                     | 0.81%   |  |  |
|            | (au)  | Rejection | -0.08%     | -0.67%     | -0.59%                | 88.06%1 | 1.20%      | -0.95%     | -2.16%                | 179.19% |  |  |

<sup>&</sup>lt;sup>1</sup> Denotes percentage calculated from the experimental train results

## 5.5.4 Effect of Biofilter Backwashing on Reversible and Irreversible Membrane Fouling

The effect of collapse pulsing, wash time and wash expansion of the pretreatment biofilter and of membrane run delay on a number of response variables was studied using ANOVA, and the results are compiled in Table 5-5. Response variables included membrane influent turbidity, reversible and irreversible membrane fouling rate, and also rejection of a range of water quality parameters through the UF membranes. As a control / experiment treatment train configuration was used in this study, entries in Table 5-5 are the difference between the response of the experimental and control train. In this way the influence of changing inlet water conditions could be accounted for. Factors which were found to have a statistically significant effect ( $\alpha = 0.05$ ) on the responses are highlighted in green. For each response that has more than one significant effect, the maximum absolute value is highlighted in red.

The results shown in Table 5-5 represent the difference in response between the experiment train and the control train, and therefore the value of the effect represents the slope of the line for the effect normalized to the control train. The responses shown in Table 5-5 can be thought of as the slope of a line drawn between the average response at the high and low factor levels (Table 5-1). A negative effect therefore indicates a negative slope between the responses at a high and low level. Under this condition, at a high

parameter value, the difference between the response of the experimental and control trains is lower than at a low parameter setting (see for example plots in Figure 5-15). This would indicate that for a particular response variable, at a high factor setting, the experimental train would have a lower average response than the control train.

UF membrane rejections of a range of water constituents were predominantly chosen as response variables as they represent the accumulation of material on the membrane, and may be linked to fouling. Thus if a particular factor affected both the fouling and the rejection of a particular water constituent that was applied to the membrane, it may be evidence that this constituent may be influencing the fouling behavior. In addition, the membrane run delay factor was included in this study as a way to investigate the effect that ripening peak had on the UF membrane performance. The membrane influent turbidity was included in this analysis as it has been seen previously that turbidity plays a role in UF membrane fouling (Hallé et al. 2009; Peldszus et al. 2012).

Table 5-5 Collected ANOVA results for factor effects on response variables

|                   |  |        | se Pulsing<br>ime | Was    | h Time  |        | ash<br>nsion |        | ane Run<br>lay |          | Critical f value |      |      |
|-------------------|--|--------|-------------------|--------|---------|--------|--------------|--------|----------------|----------|------------------|------|------|
| Response Variable |  | Effect | f value           | Effect | f value | Effect | f value      | Effect | f value        | Error    | α=0.05           | df 1 | df 2 |
| Tuı               | bidity (NTU)                           | 0.06   | 18.43             | -0.10  | 47.14   | 0.01   | 0.55         | -0.07  | 24.85          | 1.65E-03 | 4.38             | 1    | 19   |
| Rev               | versible fouling (kPa)                 | -0.07  | 5.73              | -0.18  | 40.60   | 0.07   | 6.95         | -0.02  | 0.62           | 6.35E-03 | 161.45           | 1    | 1    |
|                   | eversible fouling rate<br>Pa / day)    | -0.06  | 3684.98           | -0.08  | 7920.12 | -0.01  | 92.43        | 0.01   | 199.08         | 7.19E-06 | 161.45           | 1    | 1    |
| DC                | C Rejection (%)                        | 0.14   | 0.11              | 0.47   | 1.26    | -0.62  | 2.18         | -1.07  | 6.43           | 1.42E-04 | 161.45           | 1    | 1    |
| SU                | VA Rejection (%)                       | 2.70   | 18.22             | 5.06   | 64.27   | -2.79  | 19.57        | -1.88  | 8.84           | 3.19E-04 | 161.45           | 1    | 1    |
| D                 | Carbon Biopolymer<br>Rejection (%)     | 0.54   | 1.17              | -6.99  | 193.09  | 6.94   | 190.62       | 1.93   | 14.80          | 2.02E-04 | 161.45           | 1    | 1    |
| COCI              | Nitrogen Biopolymer<br>Rejection (%)   | 2.03   | 3.10              | 15.52  | 181.73  | -2.36  | 4.21         | 30.17  | 686.54         | 1.06E-03 | 161.45           | 1    | 1    |
| 1                 | Humic Substances<br>Rejection (%)      | -2.38  | 40.59             | -0.42  | 1.24    | 3.41   | 83.43        | -1.90  | 25.87          | 1.12E-04 | 161.45           | 1    | 1    |
| FEEM              | Protein Like Material<br>Rejection (%) | -9.62  | 5.91              | 21.74  | 30.19   | 6.22   | 2.47         | -23.60 | 35.60          | 1.25E-02 | 161.45           | 1    | 1    |
| FEI               | Humic Substances<br>Rejection (%)      | -0.33  | 0.70              | -0.92  | 5.41    | -0.20  | 0.26         | 0.69   | 3.02           | 1.25E-04 | 161.45           | 1    | 1    |

<sup>&</sup>lt;sup>1</sup> Significant factors for a specific response variable are highlighted in green

The rate of irreversible fouling of the membranes was found to be the most influenced by biofilter backwashing, with the greatest effect being from backwashing wash time factor (Table 5-5). This is shown graphically in the main effect plots in Figure 5-14 (a-c). Values of the response, while a particular factor was at a low level, are shown in blue while the values at the high level are shown in orange. The grey dots represent the average response at each factor level and included is a line drawn from the average at each level indicating the general trend of the response over the effect levels. The effect values from Table 5-5 are the slopes of these lines. Also included on each plot are the values of the response at the

<sup>&</sup>lt;sup>2</sup>. The largest magnitude factor effects of the ones found to be significant are highlighted in red for the specific response variables

<sup>3.</sup> df signifies degrees of freedom

centre point runs, shown as yellow dots. It can be visually confirmed from these plots that wash time showed the largest influence, and hence the largest absolute slope.

Irreversible fouling was found to be inversely related to both collapse pulsing and wash time, indicating that at the high levels of these factors, 6 and 15 minutes respectively, the difference between the experiment and control irreversible fouling rates were at a low. The opposite is true with membrane run delay, with a slight positive relation to irreversible fouling. This indicates that at the low level of membrane run delay (no delay), a low level of irreversible fouling was observed. Although the membrane run delay was found to be significant (Table 5-5), largely due to the low variability seen of the centre point runs, the scatter in the response differences as indicated by the spread on Figure 5-14c for both levels is high. This may suggest that the effect is very slight, if present at all.

The irreversible fouling observed during the two centre point runs is shown as yellow dots in Figure 5-14 (a-c). These values are relatively close to one another, and very close to zero effect, indicating that the difference between the experiment and control trains were essentially nonexistent when both trains were run under identical conditions. This was to be expected and confirms that both trains were operating very similarly and that no systematic error or bias was present. In contrast, the difference between the experiment and control trains was positive at both the low level and high level, indicating that, as compared to the control train, the experiment train exhibited higher fouling in both cases. This suggests that the behavior between the factor levels chosen was not linear and a maximum or minimum may occur between the factor levels chosen. Moreover, this also suggests that the centre point backwashing strategy was better at reducing irreversible fouling rates than the factors at the levels studied. That is to say, the irreversible fouling rate of the experimental train was found to be higher (i.e. worse) than of the control filter at both high and low factor level conditions. Despite this fact, it is still clear that the backwashing effects studied still have an appreciable effect on irreversible membrane fouling.

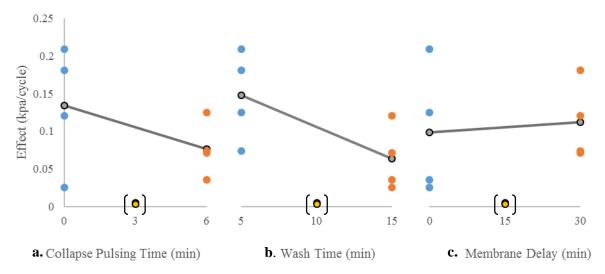


Figure 5-14 (a-c) Irreversible fouling rate main effects for collapse pulsing time (a), wash time (b) and membrane run delay (c). The orange and blue dots represent the high and low coded experimental response differences (between the experimental and control train), while the grey dots represent the average response at each level. The yellow dots represent the response at the centre point (i.e. when the backwashing parameters were identical).

The amount of reversible fouling accumulated on the membranes was found to not be influenced by the biofilter backwashing procedure (Table 5-5). This was a somewhat surprising result, as previous studies have found that biopolymers contribute to reversible fouling. However, in those studies the fouling rates were higher than those seen here and they did not measure the difference in treatment trains as was done here. The lack of influence may have been a result of the high measurement variability in the centre point weeks for the reversible fouling response variable. The total error used in assessing significance was three orders of magnitude higher than that for the irreversible fouling (Table 5-5). In addition, the variability between control and experiment trains was much higher for the centre point weeks as compared to the irreversible fouling measure (Table 5-4). The reason for this high variability has been hypothesized in section 5.5.1 as being due to the possible UF membrane component degradation that may have happened during the study period. This manifested as a large increase in the TMP reading of the control UF unit approximately 3 to 5 minutes before the end of some permeation cycle. This behavior was seemingly random with respect to permeation cycles and was not seen in the experimental membrane. As the reversible fouling rate was calculated as the difference between the TMP averaged over one minute of the end of one cycle and the beginning of the next, the large increase in the ending TMP caused a large variability. As this large variability existed in the reversible fouling data, it may have been expected that no effect could be seen. In addition, it should be noted that if an effect of biofilter

backwashing does exist, but cannot be detected due to the variability in the data, this effect can be said to be small, and for practical purposed be neglected.

The difference in average membrane influent turbidity was found to be significantly influenced by the collapse pulsing, wash time and membrane run delay factors (Table 5-5). This is shown graphically in Figure 5-15. The difference in average turbidity on the centre point weeks were found to be different, and are shown as yellow dots on these graphs. This was because of the turbidity increase seen in Week 10 as compared to Week 5. As was explained earlier, the centre point weeks were not used to calculate error of this response parameter.

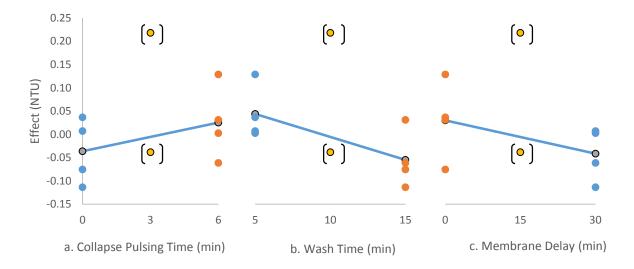


Figure 5-15 (a-c) Turbidity main effects for collapse pulsing time (a), wash time (b) and membrane run delay (c). The orange and blue dots represent the high and low coded experimental response differences (between the experimental and control train), while the grey dots represent the average response at each level. The yellow dots represent the response at the centre point.

Wash time and membrane run delay were both inversely related to their factor level settings indicating that a high setting, the average turbidity in the membrane influent was seen to be low. In addition, at the high setting of both the wash time and membrane run delay, the differences between the experimental and control responses were negative, indicating that the experimental train saw a lower turbidity as compared to the control train. Interestingly, the opposite was found for the collapse pulsing factor, as the difference in responses was found to be positively related to factor level setting. As such, it could be expected that a high collapse pulsing, the membrane influent turbidity was higher in the experimental train than in the control train. Moreover, it is surprising to see membrane run delay as having an significant impact, as this should have no effect on biofilter effluent turbidity (as this parameter was measured continuously regardless of the membrane run delay).

The removal of humic substances by the membranes was not found to be influenced by the factors studied. This was unsurprising as it has been established by others that humic substances are not retained by UF membranes to any appreciable amount. As they do not accumulate on the membrane, they have also not been indicated as contributing in an appreciable way to fouling of this UF membrane (Chen et al. 2014).

The rejection of biopolymers (measured as carbon) by the membranes was found to be affected by backwashing time and backwash expansion to a similar but opposite amount. This is shown graphically as Figure 5-16 (a-b). In both cases, the response line passes very close to the responses of the centre point runs suggesting the effect was linear between the factor levels chosen. A large amount of scatter exists in the observed responses at the high level of wash time and the low level of wash expansion, suggesting that other non-studied or controlled factors play a role in the rejection of biopolymers (measured as carbon) by the membranes.

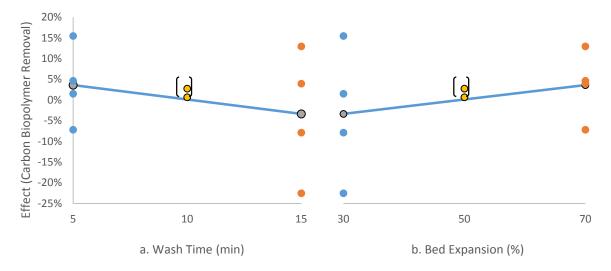


Figure 5-16 (a-b) Biopolymer (measured as carbon) rejection main effects for collapse pulsing time (a), wash time (b). The orange and blue dots represent the high and low coded experimental response differences (between the experimental and control train), while the grey dots represent the average response at each level. The yellow dots represent the response at the centre point.

As was shown in Chapter 4, the removal of the biopolymers through the biofilters, and hence the concentration applied to the membranes was influenced by backwashing procedure. However, as shown in Figure 5-9 the rejection of biopolymers by the membranes was relatively consistent despite varying influent concentration. In addition, the concentration of applied biopolymers to the membranes was found to correlate with irreversible fouling rate whereas wash expansion was not. However, wash expansion was shown to influence the rejection (and hence accumulation) of biopolymers by the

membranes (Table 5-5) which adds further evidence to support the notion that biofilter backwash affects the type of biopolymers in the membrane influent.

The rejection of biopolymers (measured as organic nitrogen) by the membranes was shown to be influenced by the biofilter wash time as well as the membrane run delay. This is shown graphically as Figure 5-17. For both factors studied, the response line intersected the response at the centre points, suggesting that, much like the biopolymer (measured as carbon) rejection, the effect is linear over the range of the factor setpoints chosen. Both factor effects are seen to have positive slopes, suggesting biopolymer (measured as organic nitrogen) rejection (and hence accumulation on the membranes) was greatest at high factor levels. In terms of the wash time factor, this is the opposite behavior that was seen with the biopolymer (measured as carbon) rejections, suggesting that the biofilter backwashing protocol may affect the character of the water being filtered. However, the irreversible fouling rate is seen to be lower at high wash time (Figure 5-14a), despite the increased accumulation of biopolymers (measured as organic nitrogen) on the membrane. This finding suggests that biopolymers, measured as organic nitrogen, do not contribute to irreversible fouling.

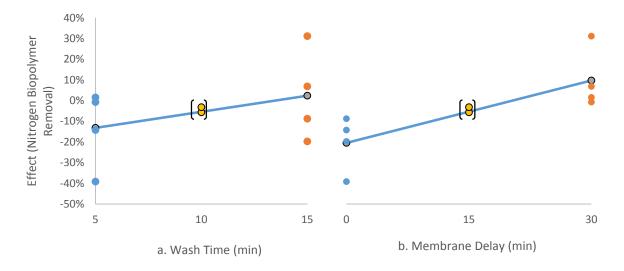


Figure 5-17 (a-b) Biopolymer (measured as nitrogen) rejection main effects for collapse pulsing time (a) and wash Time (b). The orange and blue dots represent the high and low coded experimental response differences (between the experimental and control train), while the grey dots represent the average response at each level. The yellow dots represent the response at the centre point.

This echoes what also seen in Table 5-3as biopolymers (measured as organic nitrogen) were not seen to be correlated with fouling. This seems counter intuitive as one might expect the accumulation of material on the membrane to have some contribution to fouling. A possible reasoning for this result is that the

nitrogen containing biopolymers become loosely attached to the fouling layer formed on the membrane, and are easily removed by membrane back pulsing.

Taken together, the results shown in Table 5-5 show a clear pattern indicating the wash time parameter as the most important biofilter backwashing parameter relating to irreversible fouling. Wash time is the significant factor with the largest effect on irreversible fouling, turbidity and biopolymer (measured as carbon) rejection, as well as being significant (but not the largest effect) in nitrogen biopolymer rejection. Moreover, these response variables, with the exception of nitrogen biopolymers, were seen to have a negative effect of wash time, indicating that at high parameter settings of wash time, all these parameters may be expected to be low. Thus the rejection of biopolymers by the membrane and membrane influent turbidity are very likely contributing factors in irreversible fouling. This suggests that some material which is rejected by the membrane, may become attached and contribute to flow resistance through the membrane.

In addition, DOC rejection and SUVA rejection was not found to be influenced by any of the backwashing factors studied, thus the accumulation of these parameters on the membranes was unaffected by the backwashing regime. This is similar to the results discussed in Chapter 4, which found that DOC removal by the biofilters was unaffected by backwashing regime. Although rejection of fractions of the DOC by the membranes, namely biopolymers, were found to be influence by the factors studied, the rejection of humic substances were not. This may be the reason for the lack of influence of the studied factors of the rejection of the DOC, as humic substances form the largest fraction of the DOC.

#### 5.5.5 Conclusions

A study has been conducted which investigated the effects of changing water quality parameters and the effects of varying biofilter backwashing regimes on the operation of the biofiltration/ultrafiltration process. Reversible and irreversible fouling rates of the ultrafiltration membranes have been correlated with membrane feed water quality parameters to elucidate which parameters influence fouling behavior. ANOVA methodology was employed to determine which biofilter backwashing parameters may have an effect on membrane fouling behavior as well as chemical species rejection by the membrane. The following conclusions could be drawn:

- The amount of reversible fouling remained largely unchanged throughout the study.
- The rate of irreversible fouling increased slightly over the length of the study, with the exception of the last two study weeks, which showed a marked decline. This decline corresponded with a change in membrane influent water quality in terms of turbidity and concentration of biopolymers (measured as carbon and as nitrogen).

- The rate of irreversible fouling of the membrane was found to be significantly influenced by biofilter collapse pulsing time and wash time factors as well as the membrane run delay.
- The biofilter wash time factor was found to be the most significant of the 4 factors investigated in terms of membrane fouling development.
- Irreversible fouling rate showed no correlation with protein like material applied to the membranes. This is contradictory to what was seen by others, and this discrepancy may be a result of the type of FEEM analysis used in this study and the small sample size (n = 8).
- It is suggested that turbidity plays a significant and complex role in fouling development
- It is suggested that the factors which were found to significantly influence the irreversible fouling rate do not vary linearly over the range of factor levels studied.
- Due to the incongruence of significant factors influencing the rejection of protein like material as measured by FEEM and the rejection of biopolymers (as mgC/L) by the membranes, it is suggested that biofilter backwashing parameters affect the nature of the biopolymer DOC fraction in membrane influent. As the term biopolymers as used within this study refers to a large number of organic molecules having similar size, it is possible that some of these molecules exhibit a stronger affinity for natural colloids than others, as biopolymers have been shown to form weak aggregates with organic colloids (Buffle et al. 1998). It is suggest that these biopolymers are more readily affected by the backwashing operation, hence shifting the molecule population of the biopolymers as measured within this study.

#### 5.5.6 Future Work

To confirm and further the findings of this study, the author recommends research in the following directions:

- 1. Confirm the behavior of the effects present using water from a different season with more stable temperature.
- 2. Investigate the connection between membrane fouling, biopolymer concentration and turbidity.
- Perform more in depth experiments using response surface methodology for the significant
  effects seen here to determine the optimal backwash settings for the process, as well as determine
  if interaction effects exist.

# Chapter 6

# **Conclusions and Recommendations**

The study presented in this thesis was performed to assess the effect of backwashing on the operation of the combined biofiltration without pretreatment ( $BF_{wp}$ ) and UF membrane process, and to determine the effects that changing water quality parameters have on the performance of this process. To that end the following goals were addressed:

- Investigate the performance of the BF<sub>wp</sub> process under changing water quality conditions.
- Investigate the accumulation and rate of fouling of UF membranes being pretreated with BF<sub>wp</sub>.
- Determine the effect of backwashing on the performance of the BF<sub>wp</sub> process.
- Determine the effect of backwashing on the performance of the combined BF<sub>wp</sub> and UF membrane process specifically as it pertains to the accumulation and rate of fouling.

These goals were achieved through the use of a custom built pilot plant using source water from the Mannheim Water Treatment Plant in Kitchener, Ontario. The pilot plant was composed of two identical parallel train biofilter columns of 7.78 minute EBCT, which were run in a control / experiment configuration, whereby one train was operated in the same way throughout the experiment, while the other was modified according to the experimental design. A full and a fractional factorial statistical design were used to determine the effect of backwashing on the operation of the system. Four backwashing operational parameters were chosen for study and these were: 1) collapse pulsing time 2) wash expansion percentage 3) wash time and 4) membrane run delay. When studying the effect of backwashing on the BF $_{\rm wp}$  process, only factors 1 to 3 were considered. When studying the effect on the combined process all 4 factors were considered.

## 6.1 Summary of Experiment

The experimental work presented in this thesis took place over a 10 week period from September to December 2014. Each study week of 5 days formed an experimental run, in which the backwashing regime of the experimental filter train was modified according to the experimental design. Throughout the experiment, the backwashing regime of the control filter remained constant, and the various responses measured were taken as the difference between each train. The experimental filter backwashing was set to the conditions as the control filter over the weekends. Moreover, the centre point weeks (5 and 10) saw the experimental filter operating in the same fashion as the control filter and these weeks served to produce an estimate of error in the subsequent statistical calculations. The performance of the control

train, which did not change throughout the study, was monitored to determine the performance of the process under varying water quality conditions.

# **6.2 Experimental Conclusions**

The following conclusions below summarize the performance of the control  $BF_{wp}$  and  $BF_{wp}/UF$  combined process through changing water quality conditions:

- The removal of turbidity by the biofilters generally decreased from week to week despite
  relatively steady influent turbidity. This reflects a change in water temperature over the length of
  the study. Moreover, the removal of turbidity was not substantially affected by large influent
  turbidity spikes.
- The rate of pressure loss decreased for the first half of the study and then remained essentially
  constant until the end. The available pressure head for each biofilter steadily declined as the
  study progressed. It is suggested that this is due to the steady temperature decline seen
  throughout the length of the study.
- Removal of organics through each biofilter decreased in concert with temperature. However, biological activity as measured by DO uptake by the filter media remained essentially constant throughout the experiment.
- The rate of hydraulically irreversible membrane fouling increased over the length of the study, possibly relating to an increase in biopolymer concentration (as mg C/L) in the membrane feed water over time.
- The removal of DOC through the UF membranes increased throughout the experiment despite relatively constant DOC concentrations being applied to the membranes. This finding suggests a possible change in the nature of the DOC.
- The removal of biopolymers through the UF membranes remained constant over time, despite the
  applied biopolymer concentration (both as mgC/L and mgN/L) to the membranes increasing over
  the same time period. This suggests a change in the nature of the biopolymers throughout the
  study.
- Hydraulically reversible fouling of the membrane was not found to significantly correlate to any of the parameters measured ( $\alpha = 0.05$ ). This may be due to the relatively small filter run times (4 days). This may also be due to the increase in variability seen by the control UF unit possibly relating to some component degradation occurring near the end of the study. In the case of the

- latter, any effect that biofilter backwashing may have had on the accumulation of reversible fouling would be smaller than the error estimate for this parameter, which was small.
- Irreversible membrane fouling was found to significantly and positively correlate to the amount of biopolymers rejected by the membranes (as measured by LC-OCD in mg C/L and  $\alpha = 0.05$ ).
- Irreversible membrane fouling was found to be significantly negatively correlated to temperature, which declined throughout the study ( $\alpha = 0.05$ ), despite the membrane flux being temperature corrected. This suggests a change in water quality throughout the study.
- The amount of protein-like material as measured by FEEM was found to positively correlate to the amount of biopolymers (mg C/L) applied to the membranes, however, protein-like material was not found to correlate to the irreversible fouling rate, unlike the concentration of applied biopolymers. This suggests that a fraction of the biopolymers that is not protein-like material is contributing to the increase in irreversible fouling rate experienced by the UF membranes during this study. It is hypothesized that this is due to the interactions of a small fraction of biopolymers with natural colloids, which was seen to be affected by the backwashing procedure (as measured by turbidity).
- Turbidity applied to the membranes was seen to play a complex role in membrane fouling.

The effect of biofilter backwashing on  $BF_{wp}$  performance and the accumulation and rate of membrane fouling was also studied using ANOVA methodology for the same study. The conclusions for this work are as follows:

- Biological activity and removal of some biodegradable organic fractions were largely unaffected by the backwash procedure.
- A number of significant three factor interactions were found, pointing to the complexity of the backwashing procedure as it pertains to biofilter performance.
- Collapse pulsing time was the factor that was found to have the largest effect on biofilter performance.
- The ripening peak seen by the filters studied was found to be unaffected by the backwashing regime.
- An optimal particle loading condition appears to exist for the filter in terms of particle removal.
- In terms of BF<sub>wp</sub> performance, the setting of the wash expansion factor had the least effect.

- Response variable minimum and maximum values may exist within the factor values studied suggesting non-linear responses for these variables in this region.
- Optimal backwashing in terms of turbidity and pressure loss occurs at a different condition setting
  than optimal for biopolymer removal. This suggests that an overall optimization scheme should
  be goal-specific and trade-offs are necessary.
- Reversible fouling of the UF membranes was found to be not impacted by the biofilter backwashing regime.
- The rate of irreversible fouling was found to be significantly influenced by collapse pulse time, wash time and membrane run delay (the amount of time between the end of the biofilter backwash procedure and the starting of the membrane units) factors.
- It is suggested that the factors that were found to significantly influence the irreversible fouling rate do not vary linearly over the range of the factor levels studied.
- Due to the difference in significant factors influencing the removal of protein-like material as
  measured by FEEM and the removal of biopolymers (as mgC/L) by the membranes, it is
  suggested that biofilter backwashing parameters affect the nature of the biopolymer DOC fraction
  in biofilter effluent.

# **6.3 Toward Combined Process Optimization**

The results of this work show that the operation of the  $BF_{wp}$  as a pretreatment to reduce membrane fouling has a measureable effect on the rate of irreversible fouling of the downstream UF membranes. However this effect is less than the backwashing regime has on the operation of the  $BF_{wp}$  process in terms of turbidity removal and filter headloss. This is not surprising as the results show that the DOC removal by the filters, as well as biological activity on the media as measured by DO uptake, remains unaffected by the backwashing regime, and the prevailing theory is that biodegradation of membrane foulants is the primary pretreatment method. Therefore, it is hypothesized that the effect that backwashing has on membrane fouling has to do with the removal of colloidal and macro molecule biopolymers that have not been biodegraded.

In the range of the factor levels studied, some combinations of backwashing settings have been shown to impact irreversible fouling rate, as well as a number of  $BF_{wp}$  performance parameters. It has been shown here that the biopolymer concentration applied to the UF membranes correlates with irreversible fouling rates in low turbidity conditions. Thus, from the perspective of the reduction of membrane fouling, the backwashing regime should be optimized to maximize the amount of biopolymer removal by the

biofilters. At the location investigated and for the levels of the factors studied, this condition is present with a 15 minute wash time at a 30% bed expansion. From the results in Chapter 4, this corresponds with an increase in biopolymer removal of 5 percentage points for the experimental biofilter compared to the control biofilter. This result is independent of the collapse pulsing setting.

However, in terms of biofilter headloss, which is affected by a three factor interaction, the optimal setting (for the second filtration cycle) is found at a collapse pulsing time, wash time and wash expansion of 6 minutes, 5 minutes and 30% respectively. The minimization of the rate of biofilter headloss is an attractive optimization goal, as this has a direct impact on the length of time a biofilter can be operated in between backwashing operations. Maximizing the filter run time (i.e. the time in between filter backwash operations) is worthwhile as this represents an increase in biofilter productivity as well as a conservation of resources (water and electricity) used during a backwashing operation. Moreover, it's been shown that in the system studied, the log removal of turbidity by the biofilter is maximized under the same set of conditions that filter headloss is minimized.

The goal of maximizing filter run time is in conflict with the goal of minimizing membrane irreversible fouling rate as shown in Table 6-1. The transition between both objectives is controlled by the setting of the wash time factor, as the other backwashing parameters are identical for each goal.

Table 6-1 Backwashing parameter settings for various process optimization objectives

|                          |  | Optimizat                                       | ion Goal                       |
|--------------------------|--|---|--------------------------------|
|                          | Parameter  | Minimize<br>Irreversible<br>Membrane<br>Fouling | Maximize<br>Filter Run<br>Time |
| Diefilter                | Collapse Pulsing Time (min)                      | 6   | 6                              |
| Biofilter<br>Backwashing | Wash Time (min)                                  | 15  | 5                              |
| Parameters               | Wash Expansion (%)                               | 30  | 30                             |
| Parameters               | Membrane Run Delay (min)                         | 0   | 0                              |
| Performance              | Irreversible Fouling Rate (kpa/day)              | +0.1  | +0.15                          |
| Change                   | Biofilter Biopolymer Removal (measured as C) (%) | +5  | -10                            |
| Compared to              | Biofilter Turbidity Log Removal                  | +0.12   | +0.22                          |
| Control                  | Average Rate of Headloss (psi(g) / day)          | -0.13   | -0.86                          |
| Biofilter                | Total Backwash time (min)                        | 21  | 11                             |

When maximizing filter run time, the irreversible fouling rate of the experimental membrane was found to be 0.15 kPa/day higher than that of the control membrane. This is 0.05 kpa/day higher than under the conditions found to minimize the irreversible fouling rate. This is a relatively small amount, as the

membranes used in this study have an ultimate limit of 90 kPa (GE Water 2013). Assuming a constant daily irreversible fouling increase of 0.3 kPa, which was seen by the control membrane in the week from November 10 to 14, 2014, the membrane could be expected to operate for 225 days under the minimal irreversible fouling rate scenario and 200 days under the maximum filter run time scenario.

The rate of headloss was seen to be 0.86 psi(g)/day lower than the control filter under the maximize filter run time scenario and 0.13 psi(g)/day lower under the minimize irreversible fouling scenario. On the week of November 10 to 14, the control filter saw a starting biofilter pressure of 2.35 psi(g), and required backwashing at 1.5 psi(g). Under these conditions, the maximum filter run time scenario could be expected to see a filter run time of 1.16 days longer than the minimal irreversible fouling rate case. Assuming a maximum control biofilter backwashing frequency of 3 days, as seen by the control filter on the week of November 10 to 14, 2014, this extra day of filter run time would represent a savings of 50 backwashing operations over the 200 days of membrane operation expected for this condition. Moreover, the total backwash time for the maximum filter run time scenario is less than that of the minimal irreversible fouling rate scenario.

In summary, the optimization conditions for the combined  $BF_{wp}$  / UF membrane process are optimization goal specific, and the aforementioned tradeoffs must be considered. Under the conditions analyzed, optimizing the backwashing rate to for the reduction of irreversible fouling results in 25 extra days of membrane operation, with a 21 minute backwashing cycle. However, optimizing the backwashing process for maximum filter runtime results in a savings of 50 backwashing cycles over 200 days of membrane operation with a lower backwashing cycle time. A full cost analysis is required to determine the most appropriate method of backwashing.

### **6.4 Recommended Future Work**

Based on the results of this study, the following is recommended as future work:

- The current study investigated the operation of the BF<sub>wp</sub> and combined BF<sub>wp</sub> / UF membrane process through a time of the year with a large amount of variability in terms of source water quality and temperature. It is recommended that baseline studies be repeated at a time of the year where water quality and temperature are expected to be more stable to confirm these results and further quantify the effect of the seasons as well.
- Despite the fact that a control / experiment parallel train methodology was used in the present study, some evidence seems to point toward temperature and water quality having a moderating influence on the factors studied. It is recommended that the experimental studies be repeated under more constant water quality conditions to confirm these results.

- The difference between factor levels was chosen to be wide by design for this study to attempt to quantify the outer reaches of the design envelope for this process. However, as can be seen by the center points for a number of the main effect graphs not coinciding with assumed linearity, there may be local maxima and minima present in some of the responses. It is therefore recommended that studies be done using more precise methodology such as Response Surface Methods (RSM), which may help to more precisely define the extent and shape of operational subspaces. It is expected that this would lead to much better understanding of the role the factors play in the operation of this process as well as a more accurate optimization strategies.
- The choice of a resolution IV experimental design for the combined process investigation was a relatively inexpensive screening experiment design at the expense of higher level interaction quantification. Now that this work has been done and determined the significance of each factor studied, it is recommended that a high resolution design be employed in future experimental design studies with the significant factors only to elucidate higher level interaction effects.

#### References

- Abdullah, S.Z. & Berube, P.R., 2012. Effects of Chemical Cleaning on Membrane Operating Lifetime. In *American Water Works Association Membrane Technology Conference Proceedings*. pp. 1–9.
- Ahmad, R. & Amirtharajah, A., 1998. Detachment of particles during biofilter backwashing. *Journal of the American Water Works* ..., 90(12), pp.74–85.
- Amburgey, J.E., 2005. Optimization of the extended terminal subfluidization wash (ETSW) filter backwashing procedure. *Water research*, 39(2-3), pp.314–30.
- Amburgey, J.E., Amirtharajah, A., Brouckaert, B.M. & Spivey, N.C., 2004. Effect of washwater chemistry and delayed start on filter ripening. ... American Water Works ..., (January), pp.97–110.
- American Water Works Association, 2005. *Microfiltration and Ultrafiltration Membranes for Drinking Water*,
- Amirtharajah, A., 1984. Fundamentals and Theory of Air Scour. *Journal of Environmental Engineering*, 110(3), pp.573–590.
- Amirtharajah, A., 1993. Optimum backwashing of filters with air scour: a review. *Water Science & Technology*, 27(10), pp.195–211.
- Amy, G., 2008. Fundamental understanding of organic matter fouling of membranes. *Desalination*, 231, pp.44–51.
- Amy, G. & Cho, J., 1999. Interactions between natural organic matter (NOM) and membranes: rejection and fouling. *Water science and technology*.
- Anon, 2012. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation.
- AWWA, 1998. Committee Report--Membrane Processes (PDF). ... American Water Works ..., (June), pp.91–105.
- AWWA, 2005. Microfiltration and Ultrafiltration Membranes for Drinking Water Manual of Water Supply Practices, M53 (1st Edition), American Water Works Association (AWWA).
- Box, G.E.P., 2005. *Statistics for experimenters : design, innovation, and discovery* 2nd ed. CN. J. S. Hunter 1923- & W. G. Hunter 1937-, eds., Hoboken, N.J.: Wiley-Interscience.
- Buffle, J., Wilkinson, K. & Stoll, S., 1998. A generalized description of aquatic colloidal interactions: the three-colloidal component approach. ... *Science & Technology*, 32(19), pp.2887–2899.
- Chen, F., 2015. Development of an improved approach to monitor and optimize the performance of biofiltration as a pre-treatment prior to ultrafiltration using LC-OCD and fluorescence-based techniques.

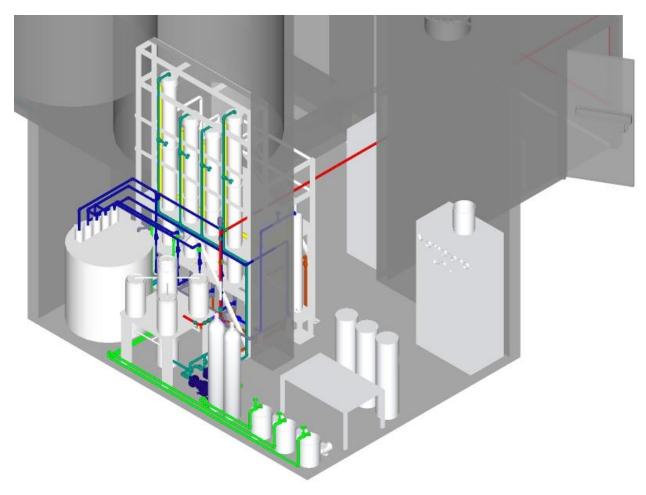
- Chen, F., Peldszus, S., Peiris, R.H., Ruhl, A.S., Mehrez, R., Jekel, M., Legge, R.L. & Huck, P.M., 2014. Pilot-scale investigation of drinking water ultrafiltration membrane fouling rates using advanced data analysis techniques. *Water research*, 48, pp.508–18.
- Cleasby, J. & Arboleda, J., 1977. Backwashing of granular filters. *Journal (American Water ...*, (February).
- Cranston, K. & Amirtharajah, A., 1987. Improving the Initial Effluent Quality of a Dual-Media Filter by Coagulants in Backwash., (C).
- Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J. & Tchobanoglous, G., 2012. MWH's Water Treatment: Principles and Design, Third Edition thrid., John Wiley & Sons.
- Devore, J.L., 2004. *Probability and Statistics for Engineering and the Sciences* Sixth. C. Crockett, ed., Toronto: Nelson.
- ElHadidy, A., 2016. Evaluating Direct Biofiltration as a Pre-treatment for Membrane Biofouling Control.
- ElHadidy, A.M., Peldszus, S. & Van Dyke, M.I., 2013. An evaluation of virus removal mechanisms by ultrafiltration membranes using MS2 and φX174 bacteriophage. *Separation and Purification Technology*, 120, pp.215–223.
- Emelko, M., Huck, P., Coffey, B. & Smith, E., 2006. Effects of media, backwash, and temperature on full-scale biological filtration. *Journal (American Water ...*, 98(12).
- Escobar, I., 2005. Committee report: recent advances and research needs in membrane fouling. *Journal* ..., (August), pp.79–89.
- Findlay, R.H., King, G.M. & Watling, L., 1989. Efficacy of Phospholipid Analysis in Determining Microbial Biomass in Sediments. , 55(11), pp.2888–2893.
- Gao, W., Liang, H., Ma, J., Han, M., Chen, Z., Han, Z. & Li, G., 2011. Membrane fouling control in ultrafiltration technology for drinking water production: A review. *Desalination*, 272(1-3), pp.1–8.
- GE Water, 2013. ZeeWeed 1000 Modules Fact Sheet., p.2.
- Halle, C., Huck, P., Peldszus, S., Haberkamp, J. & Jekel, M., 2008. Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water Supplementary Information. *Journal (American Water Works Association)*.
- Hallé, C., Huck, P.M., Peldszus, S., Haberkamp, J. & Jekel, M., 2009. Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water. *Environmental science & technology*, 43(10), pp.3878–84.
- Hermia, J., 1985. Blocking Filtration. Application to Non-Newtonian Fluids. In A. Rushton, ed. *Mathematical Models and Design Methods in Solid-Liquid Separation*. Springer Netherlands, pp. 83–89.

- Hewitt, S.R. & Amirtharajah, A., 1984. Air Dynamics Through Filter Media During Air Scour. *Journal of Environmental Engineering*, 110(3), pp.591–606.
- Howe, K. & Clark, M., 2002. Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environmental science & technology*, 36(16), pp.3571–3576.
- Hozalski, R. & Bouwer, E., 1998. Deposition and retention of bacteria in backwashed filters. *Journal-American Water Works Association*, (January), pp.71–85.
- Huber, S. a, Balz, A., Abert, M. & Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography--organic carbon detection--organic nitrogen detection (LC-OCD-OND). *Water research*, 45(2), pp.879–85.
- Huck, P., 1990. Measurement of biodegradable organic matter and bacterial growth potential in drinking water. *Journal (American Water Works Association)*, (C).
- Huck, P., Peldszus, S., Halle, C. & Ruiz, H., 2011. Pilot scale evaluation of biofiltration as an innovative pre-treatment for ultrafiltration membranes for drinking water treatment. *Water science & Technology; Water Supply*, (2007), pp.23–29.
- Huck, P.M., Peldszus, S., Anderson, W.B., Chen, F., ElHadidy, A.M., Legge, R.L., Siembida-Lösch, B., Van Dyke, M.I., Wilson, B. & Walton, T., 2015. Biofiltration With and Without Pre-treatment Are There Differences? In *IWA Specialized Conference of Biofilms in Drinking Water Systems*.
- Jermann, D., Pronk, W. & Boller, M., 2008. Mutual Influences between Natural Organic Matter and Inorganic Particles and Their Combined Effect on Ultrafiltration Membrane Fouling., pp.9129–9136.
- Kaiya, Y., Itoh, Y., Fujita, K. & Takizawa, S., 1996. Study on fouling materials in the membrane treatment process for potable water. *Desalination*, 6(96).
- Kawamura, S., 1999. Design and operation of high-rate filters. *Journal-American Water Works Association*, (DECEMBER), pp.77–90.
- Kawamura, S., 1975. Design and operation of high-rate filters-part 1. *Journal (American Water Works Association)*, pp.535–544.
- Kennedy, M.D., Chun, H.K., Quintanilla Yangali, V. a., Heijman, B.G.J. & Schippers, J.C., 2005. Natural organic matter (NOM) fouling of ultrafiltration membranes: fractionation of NOM in surface water and characterisation by LC-OCD. *Desalination*, 178(1-3), pp.73–83.
- Lee, N., Amy, G. & Lozier, J., 2005. Understanding natural organic matter fouling in low-pressure membrane filtration. *Desalination*, 178(1-3), pp.85–93.
- Liao, X., Chen, C., Zhang, J., Dai, Y., Zhang, X. & Xie, S., 2015. Operational performance, biomass and microbial community structure: impacts of backwashing on drinking water biofilter. *Environmental science and pollution research international*, 22(1), pp.546–54.

- Liu, G., 2005. An investigation of UV disinfection performance under the influence of turbidity & particulates for drinking water applications.
- Miltner, R., Summers, R. & Wang, J., 1995. Biofiltration performance: part 2, effect of backwashing. *Journal of the American Water* ..., 87(12), pp.64–70.
- Niquette, P., Prevost, M. & Maclean, R., 1998. Backwashing first-stage sand-BAC filters. ... American Water Works ..., 90(1), pp.86–97.
- OMEGA Engineering, CN 142 Controller User's Guide.
- Peiris, R.H., Hallé, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P.M. & Legge, R.L., 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices. *Water research*, 44, pp.185–94.
- Peiris, R.H., Jaklewicz, M., Budman, H., Legge, R.L. & Moresoli, C., 2013. Assessing the Role of Feed Water Constituents in Irreversible Membrane Fouling of Pilot-scale Ultrafiltration Drinking Water Treatment Systems. *Water Research*, pp.1–11.
- Peldszus, S., Benecke, J., Jekel, M. & Huck, P.M., 2012. Direct biofiltration pretreatment for fouling control of ultrafiltration membranes. *Journal American Water Works Association*, 104, pp.E430–E445.
- Peldszus, S., Hallé, C., Peiris, R.H., Hamouda, M., Jin, X., Legge, R.L., Budman, H., Moresoli, C. & Huck, P.M., 2011a. Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment. *Water research*, 45(16), pp.5161–70.
- Peldszus, S., Hallé, C., Peiris, R.H., Hamouda, M., Jin, X., Legge, R.L., Budman, H., Moresoli, C. & Huck, P.M., 2011b. Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment. *Water research*, 45(16), pp.5161–70.
- Persson, F., Heinicke, G., Uhl, W., Hedberg, T. & Hermansson, M., 2006. Performance of direct biofiltration of surface water for reduction of biodegradable organic matter and biofilm formation potential. *Environmental technology*, 27(9), pp.1037–45.
- Pharand, L., Dyke, M. Van, Anderson, W. & Huck, P., 2014. Assessment of biomass in drinking water biofilters by adenosine triphosphate. *JOURNAL AWWA*, (October), pp.433–444.
- Pharand, L., Van Dyke, M.I., Anderson, W.B., Yohannes, Y. & Huck, P.M., 2015. Full-scale Ozone-Biofiltration: Seasonally-related effects on NOM Removal (In Press)(PDF). ... American Water Works ..., pp.1–32.
- Rasheed, A., Amirtharajah, A., Al-Shawwa, A. & Peter, M., 1998. Effects of backwashing on biological filters. *Journal American Water Works Association*, 90(12), pp.62–73.
- Raveendran, P. & Amirtharajah, A., 1995. Role of short-range forces in particle detachment during filter backwashing. *Journal of environmental* ..., pp.860–868.

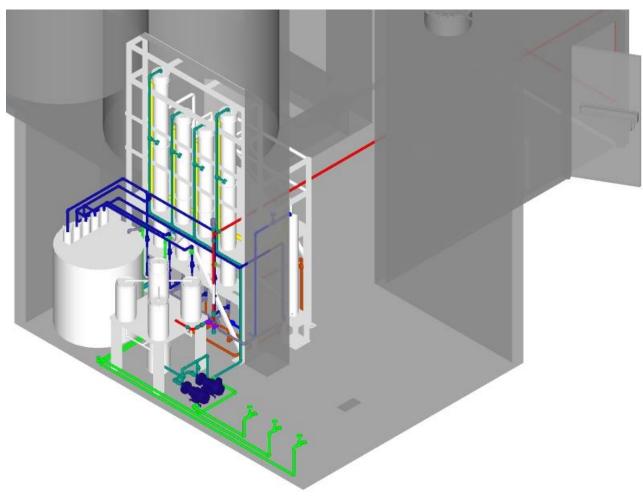
- Riggs, J.B. & Karim, M.N., 2006. *Chemical and Bio-Process Control* thrid., Lubbock, Texas: Ferret Publishing.
- Rittmann, B.E. & McCarty, P.L., 2001. *Environmental Biotechnology: Principles and Applications*, Boston: McGraw-Hill.
- Urfer, D. & Huck, P., 2001. Measurement of biomass activity in drinking water biofilters using a respirometric method. *Water research*, 35(6), pp.1469–1477.
- Urfer, D., Huck, P., Booth, S. & Coffey, B., 1997. Biological Filtration for BOM and Particle Removal: A Critical Review (PDF). *Journal-American Water* ..., (December), pp.83–98.
- Yao, K., Habibian, M. & O'Melia, C., 1971. Water and waste water filtration. Concepts and applications. *Environmental Science* & ..., 5(11), pp.1105–1112.
- Zeenon Environmetnal Inc., 2007. Installation & Operating Manual for ZeeWeed 1000 Jr., (December 2007), p.30.

Appendix A
Pilot Plant Piping Isometrics



| Color             | System                             |
|-------------------|------------------------------------|
| Red               | Raw Water Line                     |
| Green             | High Pressure Membrane Experiments |
| Teal              | Influent Piping                    |
| Dark Blue         | Effluent piping                    |
| Yellow            | Drain                              |
| Orange (not seen) | Backwashing                        |
| Bright Blue       | Biofilter B to C Piping            |

Figure A - 1 Full Mannheim Pilot Plant Piping Isometric



| Color             | System                             |
|-------------------|------------------------------------|
| Red               | Raw Water Line                     |
| Green             | High Pressure Membrane Experiments |
| Teal              | Influent Piping                    |
| Dark Blue         | Effluent piping                    |
| Yellow            | Drain                              |
| Orange (not seen) | Backwashing                        |
| Bright Blue       | Biofilter B to C Piping            |

Figure A - 2 Piping Isometric without NF/RO experiments

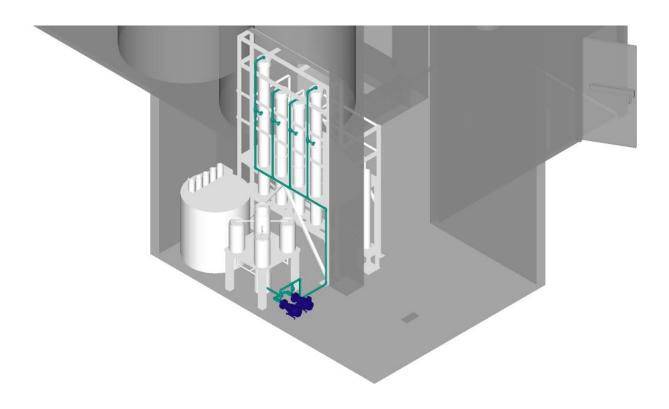
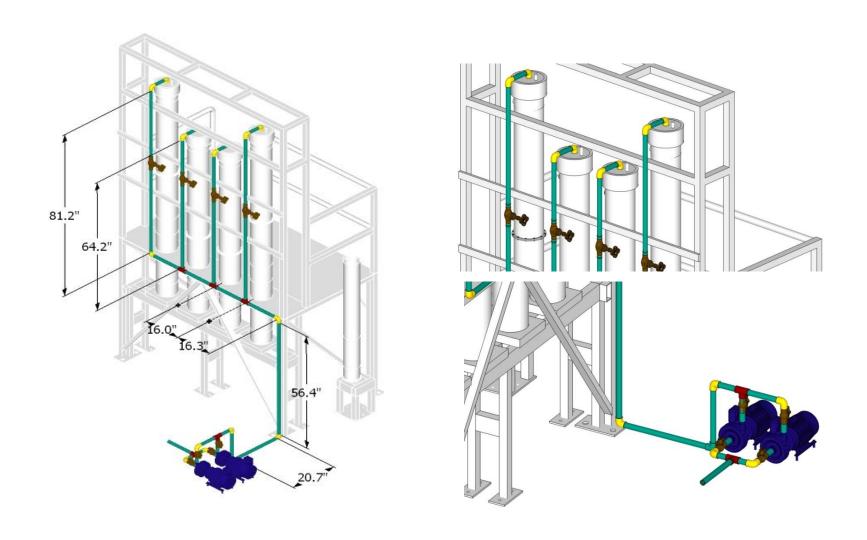


Figure A - 3 Piping Isometric showing only influent piping



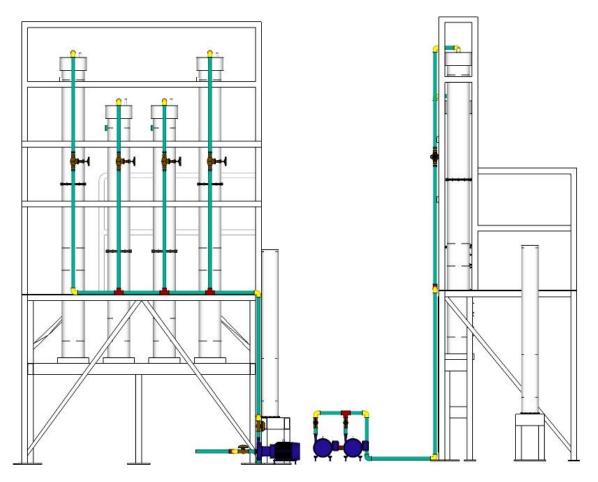


Figure A - 5 Projection view of piping run from inlet pump to top of biofilters  $\,$ 

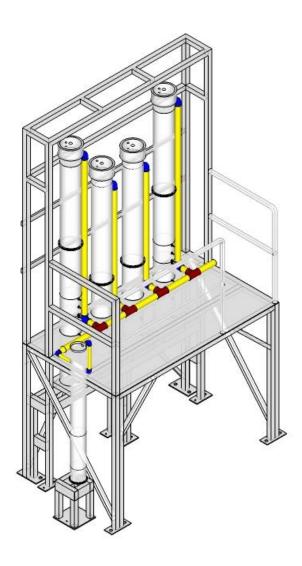
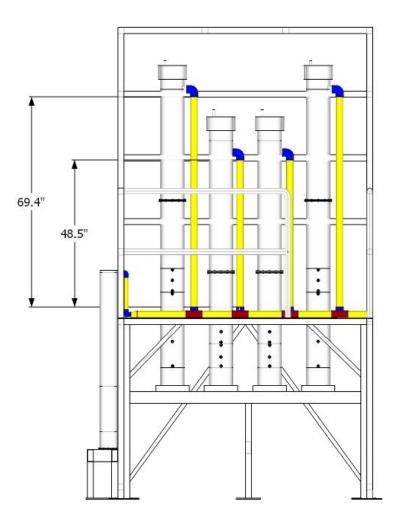


Figure A - 6 Biofilter drain piping isometrics



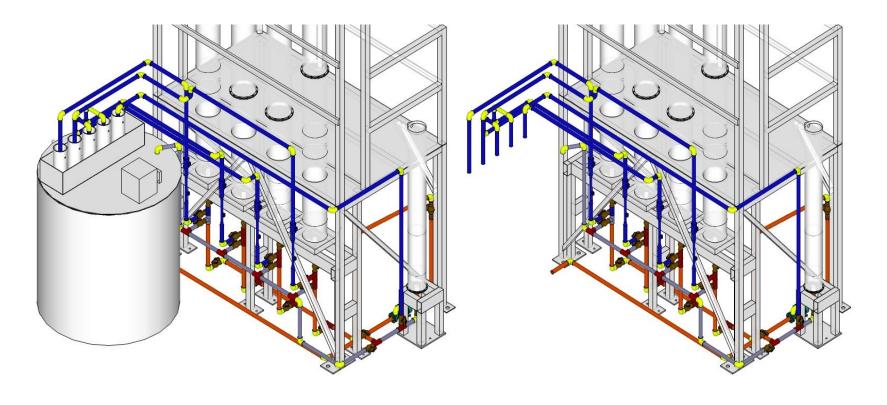


Figure A - 7 Biofilter effluent and drain piping isometrics

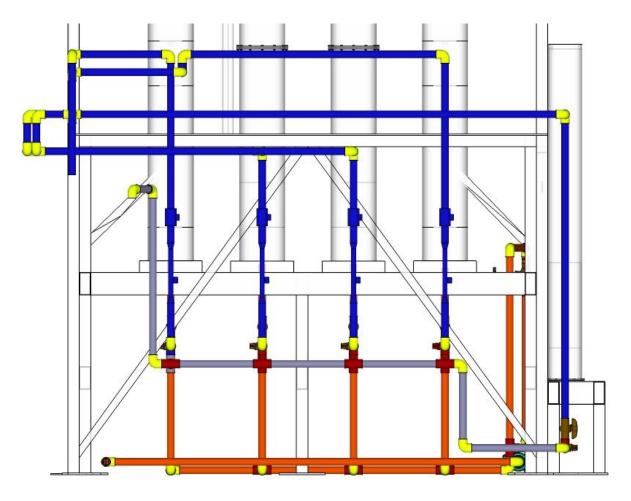


Figure A - 8 Detail of biofilter drain and effluent piping  $\,$ 

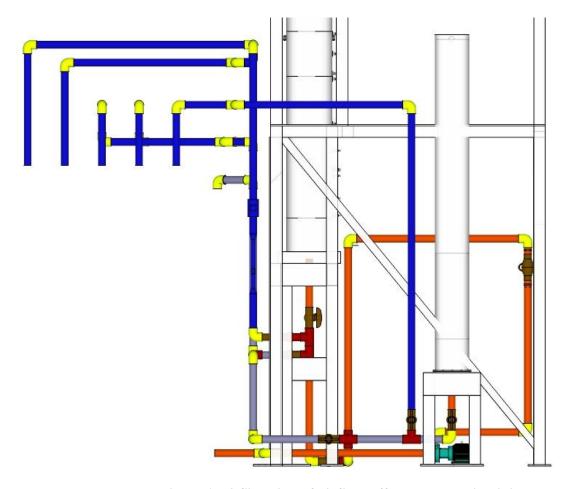


Figure A - 9 Side view of biofilter effluent and drain piping

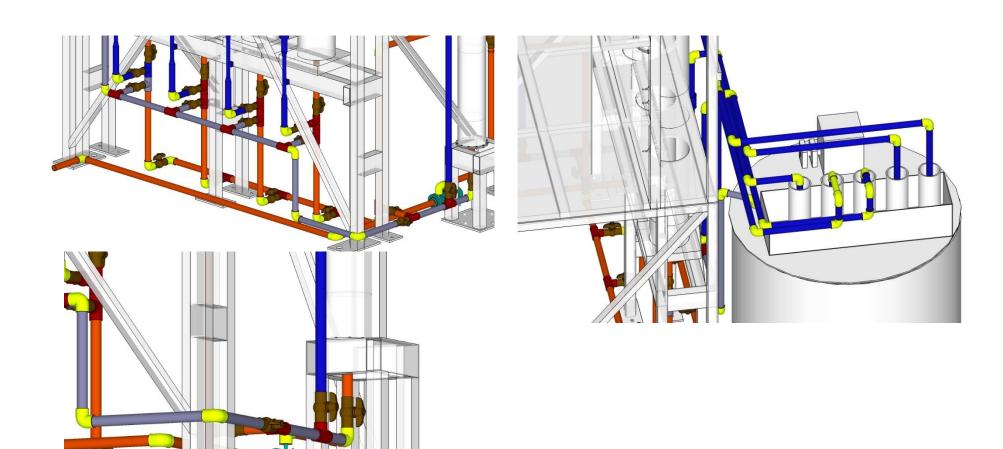


Figure A - 10 Details of piping isometrics

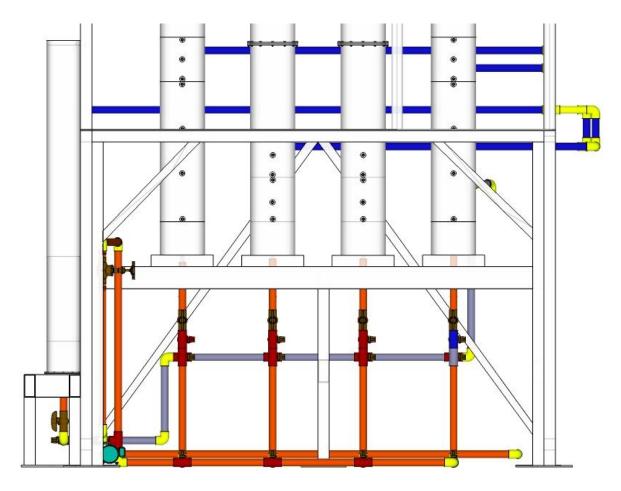


Figure A - 11 Detail of biofilter drain piping (front view)

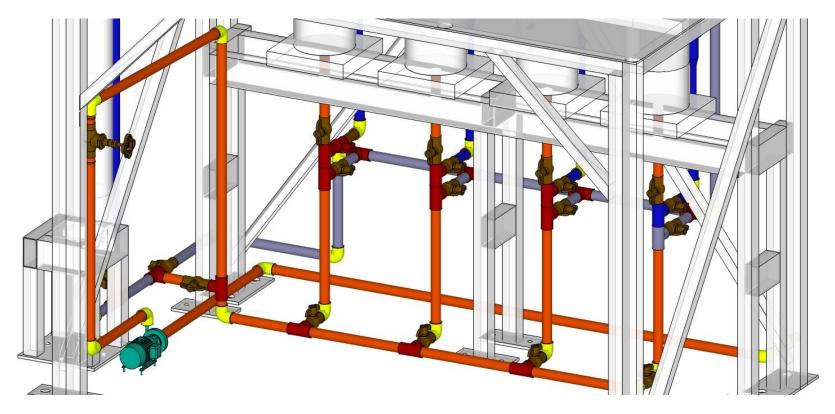


Figure A - 12 Isometric view of biofilter drain piping

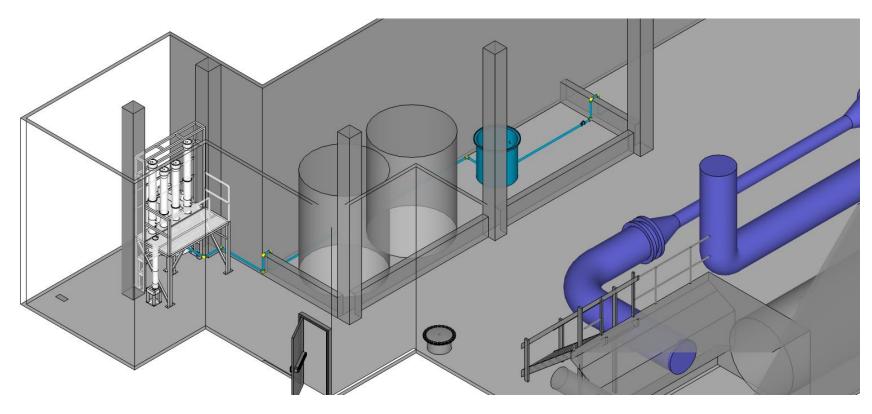


Figure A - 13 Mannheim pilot plant position in full scale plant

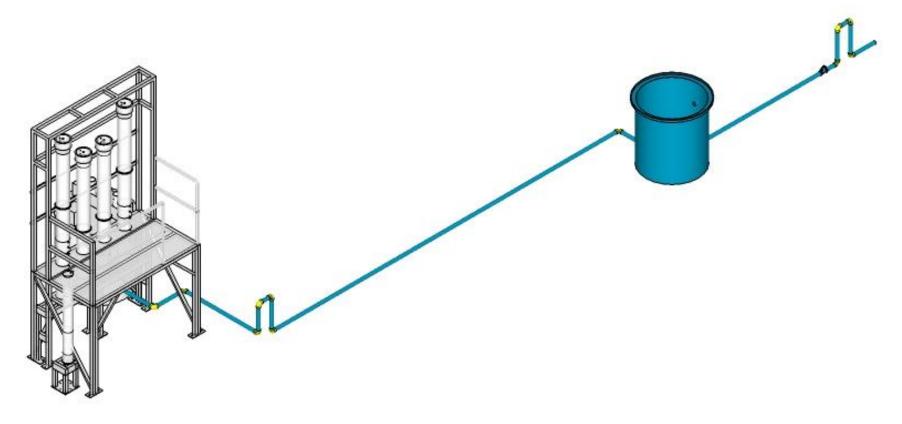


Figure A - 14 Drain piping isometric

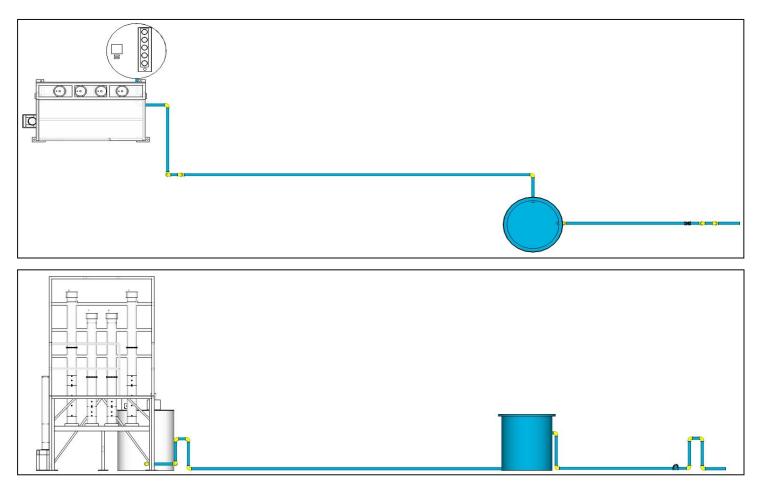


Figure A - 15 Drain piping overhead view

# Appendix B Chapter 4 Supplementary Graphics

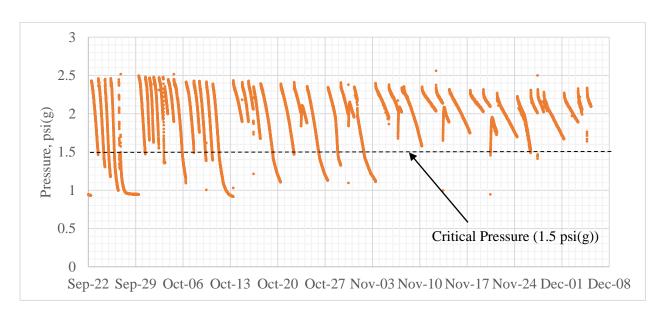


Figure B - 1 Control biofilter pressure decay throughout entire study

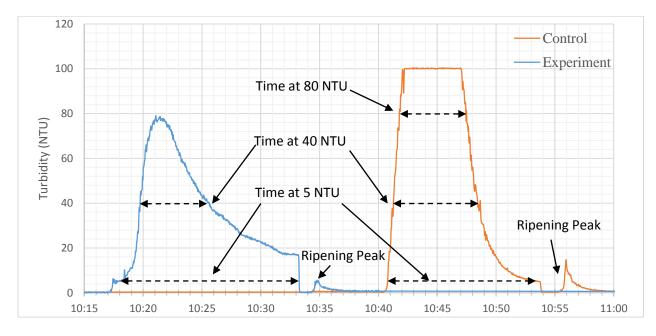


Figure B - 2 Backwash water turbidity example - Week 6 (November 3 to 7, 2014)

## **Appendix C**

## Sample Calculation of Pressure Decay Velocity and Acceleration

The water pressure at the bottom of both the experimental and control filter columns was recorded at 5 minute intervals. An example of this is shown for experimental week 4, October 20 to 24 2014, in Figure C - 3. Analysis of this was carried out separately for filter cycle, which was defined as the filter run time in between backwashing operations. To compare the filter pressure loss profiles, an average rate of change was calculated for each filter cycle. First, a second-order polynomial equation was fit to the filter pressure measurements for a given filter cycle using the built-in trend line function in Microsoft Excel 2013. This equation was of the form shown below

$$P=at^2+bt+c$$

Where:

P = Pressure (psi(g))

t = Time (minutes)

a,b,c = Fit constants

For the fit of the first cycle for the control filter as shown in Figure C-1 a, b and c were equal to  $-4.68 \times 10^{-8} \, \mathrm{psi}(\mathrm{g})/\mathrm{min}^2$ ,  $-1.84 \times 10^{-4} \, \mathrm{psi}(\mathrm{g})/\mathrm{min}$  and  $2.36 \, \mathrm{psi}(\mathrm{g})$  respectively. The  $r^2$  value for this fit was found to be equal to 1.00.

The rate of change of Equation C-1 may be calculated as this equations first derivative and is shown in Equation C-2:

**Equation C - 2** 
$$\frac{dP}{dt} = 2at + b$$

Thus the rate of change of the pressure profile for each cycle was found to be a function of time. To calculate a single value for which statistical analysis could be employed, an average was taken over the entire length of the cycle. This was accomplished by calculating the rate of change for each measured data point and dividing by the number of total measurements in a cycle. For the first filter cycle for the control filter this was found to be  $-3.13 \times 10^{-4} \, \text{psi}(g)/\text{min}$ .

As the rate of change of the pressure at the bottom of the column changed with time, a pressure loss acceleration was also calculated to provide information to the magnitude of this change over time. This was calculated as the second derivative of Equation C-1, shown as Equation C-3:

Equation C - 3  $\frac{d^2P}{dt^2} = 2a$ 

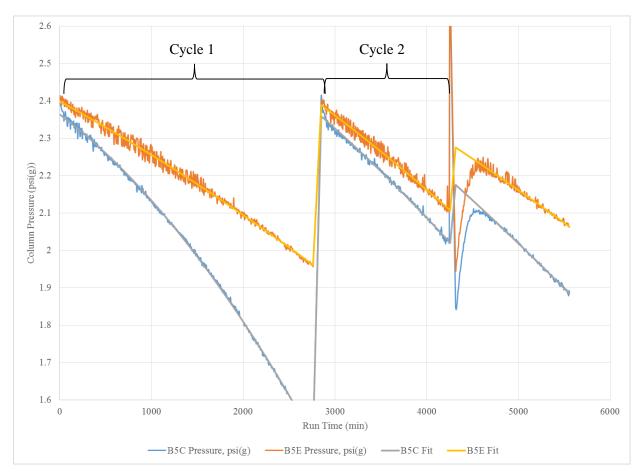


Figure C - 3 Column pressure decay profile example including quadratic fit - Week 4 (October 10 to 15,2014)

This procedure was carried out for both the control and experimental filters for each filter cycle. Results and raw data are shown as tables C-1, C-2 and C-3.

Table C - 1 Results of Week 4 Pressure Loss Analysis

| Cycle                            |           | 1                  | 2         |            |  |
|----------------------------------|-----------|--------------------|-----------|------------|--|
| Filter                           | Control   | Control Experiment |           | Experiment |  |
| a                                | -4.68E-08 | -8.48E-09          | -1.92E-08 | -1.31E-08  |  |
| b                                | -1.84E-04 | -1.35E-04          | -1.04E-04 | -1.07E-04  |  |
| С                                | 2.36      | 2.40               | 2.81      | 2.80       |  |
| r2                               | 1.00      | 0.99               | 0.99      | 0.97       |  |
| Average Rate of Change (psi/min) | -3.13E-04 | -1.59E-04          | -2.40E-04 | -2.00E-04  |  |
| Acceleration (psi/min/min)       | -9.36E-08 | -1.70E-08          | -3.85E-08 | -2.62E-08  |  |

Table C - 2 Week 4 Control and Experiment Raw and Calculated Data

| Timestamp        | Normalized | Control  | Control   | Experiment | Experiment |       |
|------------------|------------|----------|-----------|------------|------------|-------|
|                  | Time       | Pressure | Pressure  | Pressure,  | Pressure   |       |
|                  | (Minutes)  | (psi(g)) | Rate      | (psi(g))   | Rate       |       |
|                  |            |          | (psi/min) |            | (psi/min)  | Cycle |
| 2014-10-20 10:41 | 0          | 2.39     | -1.84E-04 | 2.41       | -1.35E-04  | 1     |
| 2014-10-20 10:46 | 5          | 2.39     | -1.84E-04 | 2.40       | -1.35E-04  | 1     |
| 2014-10-20 10:51 | 10         | 2.39     | -1.85E-04 | 2.40       | -1.35E-04  | 1     |
| 2014-10-20 10:56 | 15         | 2.38     | -1.85E-04 | 2.41       | -1.35E-04  | 1     |
| 2014-10-20 11:01 | 20         | 2.38     | -1.85E-04 | 2.39       | -1.35E-04  | 1     |
| 2014-10-20 11:06 | 25         | 2.37     | -1.86E-04 | 2.41       | -1.36E-04  | 1     |
| 2014-10-20 11:11 | 30         | 2.37     | -1.86E-04 | 2.41       | -1.36E-04  | 1     |
| 2014-10-20 11:16 | 35         | 2.37     | -1.87E-04 | 2.40       | -1.36E-04  | 1     |
| 2014-10-20 11:21 | 40         | 2.37     | -1.87E-04 | 2.41       | -1.36E-04  | 1     |
| 2014-10-20 11:26 | 45         | 2.35     | -1.88E-04 | 2.40       | -1.36E-04  | 1     |
| 2014-10-20 11:31 | 50         | 2.36     | -1.88E-04 | 2.38       | -1.36E-04  | 1     |
| 2014-10-20 11:36 | 55         | 2.36     | -1.89E-04 | 2.40       | -1.36E-04  | 1     |
| 2014-10-20 11:41 | 60         | 2.37     | -1.89E-04 | 2.39       | -1.36E-04  | 1     |
| 2014-10-20 11:46 | 65         | 2.36     | -1.90E-04 | 2.40       | -1.36E-04  | 1     |
| 2014-10-20 11:51 | 70         | 2.36     | -1.90E-04 | 2.38       | -1.36E-04  | 1     |
| 2014-10-20 11:56 | 75         | 2.35     | -1.91E-04 | 2.39       | -1.36E-04  | 1     |
| 2014-10-20 12:01 | 80         | 2.33     | -1.91E-04 | 2.40       | -1.36E-04  | 1     |

| 2014-10-20 12:06 | 85  | 2.33 | -1.92E-04 | 2.39 | -1.37E-04 |   |
|------------------|-----|------|-----------|------|-----------|---|
|                  |     | 1    | 11,722 0. |      | 1.57E 01  | 1 |
| 2014-10-20 12:11 | 90  | 2.36 | -1.92E-04 | 2.38 | -1.37E-04 | 1 |
| 2014-10-20 12:16 | 95  | 2.34 | -1.93E-04 | 2.38 | -1.37E-04 | 1 |
| 2014-10-20 12:21 | 100 | 2.35 | -1.93E-04 | 2.39 | -1.37E-04 | 1 |
| 2014-10-20 12:26 | 105 | 2.35 | -1.93E-04 | 2.38 | -1.37E-04 | 1 |
| 2014-10-20 12:31 | 110 | 2.35 | -1.94E-04 | 2.39 | -1.37E-04 | 1 |
| 2014-10-20 12:36 | 115 | 2.32 | -1.94E-04 | 2.38 | -1.37E-04 | 1 |
| 2014-10-20 12:41 | 120 | 2.35 | -1.95E-04 | 2.40 | -1.37E-04 | 1 |
| 2014-10-20 12:46 | 125 | 2.34 | -1.95E-04 | 2.37 | -1.37E-04 | 1 |
| 2014-10-20 12:51 | 130 | 2.34 | -1.96E-04 | 2.37 | -1.37E-04 | 1 |
| 2014-10-20 12:56 | 135 | 2.34 | -1.96E-04 | 2.38 | -1.37E-04 | 1 |
| 2014-10-20 13:01 | 140 | 2.34 | -1.97E-04 | 2.39 | -1.38E-04 | 1 |
| 2014-10-20 13:06 | 145 | 2.34 | -1.97E-04 | 2.38 | -1.38E-04 | 1 |
| 2014-10-20 13:11 | 150 | 2.35 | -1.98E-04 | 2.37 | -1.38E-04 | 1 |
| 2014-10-20 13:16 | 155 | 2.33 | -1.98E-04 | 2.36 | -1.38E-04 | 1 |
| 2014-10-20 13:21 | 160 | 2.33 | -1.99E-04 | 2.38 | -1.38E-04 | 1 |
| 2014-10-20 13:26 | 165 | 2.34 | -1.99E-04 | 2.37 | -1.38E-04 | 1 |
| 2014-10-20 13:31 | 170 | 2.31 | -2.00E-04 | 2.36 | -1.38E-04 | 1 |
| 2014-10-20 13:36 | 175 | 2.34 | -2.00E-04 | 2.37 | -1.38E-04 | 1 |
| 2014-10-20 13:41 | 180 | 2.33 | -2.00E-04 | 2.37 | -1.38E-04 | 1 |
| 2014-10-20 13:46 | 185 | 2.33 | -2.01E-04 | 2.38 | -1.38E-04 | 1 |
| 2014-10-20 13:51 | 190 | 2.34 | -2.01E-04 | 2.37 | -1.38E-04 | 1 |
| 2014-10-20 13:56 | 195 | 2.30 | -2.02E-04 | 2.36 | -1.38E-04 | 1 |
| 2014-10-20 14:01 | 200 | 2.33 | -2.02E-04 | 2.36 | -1.39E-04 | 1 |
| 2014-10-20 14:06 | 205 | 2.32 | -2.03E-04 | 2.37 | -1.39E-04 | 1 |
| 2014-10-20 14:11 | 210 | 2.34 | -2.03E-04 | 2.38 | -1.39E-04 | 1 |
| 2014-10-20 14:16 | 215 | 2.32 | -2.04E-04 | 2.37 | -1.39E-04 | 1 |
| 2014-10-20 14:21 | 220 | 2.30 | -2.04E-04 | 2.36 | -1.39E-04 | 1 |
| 2014-10-20 14:26 | 225 | 2.31 | -2.05E-04 | 2.37 | -1.39E-04 | 1 |
| 2014-10-20 14:31 | 230 | 2.33 | -2.05E-04 | 2.38 | -1.39E-04 | 1 |
| 2014-10-20 14:36 | 235 | 2.31 | -2.06E-04 | 2.37 | -1.39E-04 | 1 |
| 2014-10-20 14:41 | 240 | 2.33 | -2.06E-04 | 2.38 | -1.39E-04 | 1 |
| 2014-10-20 14:46 | 245 | 2.30 | -2.07E-04 | 2.37 | -1.39E-04 | 1 |
| 2014-10-20 14:51 | 250 | 2.32 | -2.07E-04 | 2.36 | -1.39E-04 | 1 |
| 2014-10-20 14:56 | 255 | 2.31 | -2.07E-04 | 2.35 | -1.39E-04 | 1 |

| 2014-10-20 15:01 | 260 | 2.31 | -2.08E-04 | 2.37 | -1.40E-04 | 1 |
|------------------|-----|------|-----------|------|-----------|---|
| 2014-10-20 15:06 | 265 | 2.31 | -2.08E-04 | 2.37 | -1.40E-04 | 1 |
| 2014-10-20 15:11 | 270 | 2.31 | -2.09E-04 | 2.37 | -1.40E-04 | 1 |
| 2014-10-20 15:16 | 275 | 2.31 | -2.09E-04 | 2.36 | -1.40E-04 | 1 |
| 2014-10-20 15:21 | 280 | 2.31 | -2.10E-04 | 2.34 | -1.40E-04 | 1 |
| 2014-10-20 15:26 | 285 | 2.29 | -2.10E-04 | 2.37 | -1.40E-04 | 1 |
| 2014-10-20 15:31 | 290 | 2.30 | -2.11E-04 | 2.37 | -1.40E-04 | 1 |
| 2014-10-20 15:36 | 295 | 2.31 | -2.11E-04 | 2.36 | -1.40E-04 | 1 |
| 2014-10-20 15:41 | 300 | 2.29 | -2.12E-04 | 2.38 | -1.40E-04 | 1 |
| 2014-10-20 15:46 | 305 | 2.30 | -2.12E-04 | 2.34 | -1.40E-04 | 1 |
| 2014-10-20 15:51 | 310 | 2.30 | -2.13E-04 | 2.37 | -1.40E-04 | 1 |
| 2014-10-20 15:56 | 315 | 2.30 | -2.13E-04 | 2.34 | -1.40E-04 | 1 |
| 2014-10-20 16:01 | 320 | 2.31 | -2.14E-04 | 2.37 | -1.41E-04 | 1 |
| 2014-10-20 16:06 | 325 | 2.30 | -2.14E-04 | 2.36 | -1.41E-04 | 1 |
| 2014-10-20 16:11 | 330 | 2.30 | -2.15E-04 | 2.35 | -1.41E-04 | 1 |
| 2014-10-20 16:16 | 335 | 2.31 | -2.15E-04 | 2.35 | -1.41E-04 | 1 |
| 2014-10-20 16:21 | 340 | 2.30 | -2.15E-04 | 2.37 | -1.41E-04 | 1 |
| 2014-10-20 16:26 | 345 | 2.30 | -2.16E-04 | 2.33 | -1.41E-04 | 1 |
| 2014-10-20 16:31 | 350 | 2.30 | -2.16E-04 | 2.34 | -1.41E-04 | 1 |
| 2014-10-20 16:36 | 355 | 2.29 | -2.17E-04 | 2.36 | -1.41E-04 | 1 |
| 2014-10-20 16:41 | 360 | 2.28 | -2.17E-04 | 2.33 | -1.41E-04 | 1 |
| 2014-10-20 16:46 | 365 | 2.27 | -2.18E-04 | 2.36 | -1.41E-04 | 1 |
| 2014-10-20 16:51 | 370 | 2.29 | -2.18E-04 | 2.35 | -1.41E-04 | 1 |
| 2014-10-20 16:56 | 375 | 2.30 | -2.19E-04 | 2.35 | -1.42E-04 | 1 |
| 2014-10-20 17:01 | 380 | 2.29 | -2.19E-04 | 2.35 | -1.42E-04 | 1 |
| 2014-10-20 17:06 | 385 | 2.28 | -2.20E-04 | 2.36 | -1.42E-04 | 1 |
| 2014-10-20 17:11 | 390 | 2.28 | -2.20E-04 | 2.36 | -1.42E-04 | 1 |
| 2014-10-20 17:16 | 395 | 2.29 | -2.21E-04 | 2.36 | -1.42E-04 | 1 |
| 2014-10-20 17:21 | 400 | 2.28 | -2.21E-04 | 2.35 | -1.42E-04 | 1 |
| 2014-10-20 17:26 | 405 | 2.28 | -2.22E-04 | 2.36 | -1.42E-04 | 1 |
| 2014-10-20 17:31 | 410 | 2.29 | -2.22E-04 | 2.36 | -1.42E-04 | 1 |
| 2014-10-20 17:36 | 415 | 2.28 | -2.22E-04 | 2.35 | -1.42E-04 | 1 |
| 2014-10-20 17:41 | 420 | 2.28 | -2.23E-04 | 2.35 | -1.42E-04 | 1 |
| 2014-10-20 17:46 | 425 | 2.27 | -2.23E-04 | 2.35 | -1.42E-04 | 1 |
| 2014-10-20 17:51 | 430 | 2.28 | -2.24E-04 | 2.33 | -1.42E-04 | 1 |
|                  |     |      |           |      |           |   |

| 2014-10-20 17:56 | 435 | 2.27 | -2.24E-04 | 2.33 | -1.43E-04 | 1 |
|------------------|-----|------|-----------|------|-----------|---|
| 2014-10-20 18:01 | 440 | 2.28 | -2.25E-04 | 2.33 | -1.43E-04 | 1 |
| 2014-10-20 18:06 | 445 | 2.27 | -2.25E-04 | 2.33 | -1.43E-04 | 1 |
| 2014-10-20 18:11 | 450 | 2.27 | -2.26E-04 | 2.31 | -1.43E-04 | 1 |
| 2014-10-20 18:16 | 455 | 2.28 | -2.26E-04 | 2.34 | -1.43E-04 | 1 |
| 2014-10-20 18:21 | 460 | 2.27 | -2.27E-04 | 2.34 | -1.43E-04 | 1 |
| 2014-10-20 18:26 | 465 | 2.27 | -2.27E-04 | 2.35 | -1.43E-04 | 1 |
| 2014-10-20 18:31 | 470 | 2.26 | -2.28E-04 | 2.33 | -1.43E-04 | 1 |
| 2014-10-20 18:36 | 475 | 2.26 | -2.28E-04 | 2.32 | -1.43E-04 | 1 |
| 2014-10-20 18:41 | 480 | 2.26 | -2.29E-04 | 2.33 | -1.43E-04 | 1 |
| 2014-10-20 18:46 | 485 | 2.25 | -2.29E-04 | 2.32 | -1.43E-04 | 1 |
| 2014-10-20 18:51 | 490 | 2.26 | -2.29E-04 | 2.31 | -1.43E-04 | 1 |
| 2014-10-20 18:56 | 495 | 2.26 | -2.30E-04 | 2.31 | -1.44E-04 | 1 |
| 2014-10-20 19:01 | 500 | 2.26 | -2.30E-04 | 2.33 | -1.44E-04 | 1 |
| 2014-10-20 19:06 | 505 | 2.26 | -2.31E-04 | 2.34 | -1.44E-04 | 1 |
| 2014-10-20 19:11 | 510 | 2.25 | -2.31E-04 | 2.34 | -1.44E-04 | 1 |
| 2014-10-20 19:16 | 515 | 2.25 | -2.32E-04 | 2.33 | -1.44E-04 | 1 |
| 2014-10-20 19:21 | 520 | 2.25 | -2.32E-04 | 2.31 | -1.44E-04 | 1 |
| 2014-10-20 19:26 | 525 | 2.24 | -2.33E-04 | 2.34 | -1.44E-04 | 1 |
| 2014-10-20 19:31 | 530 | 2.24 | -2.33E-04 | 2.30 | -1.44E-04 | 1 |
| 2014-10-20 19:36 | 535 | 2.25 | -2.34E-04 | 2.33 | -1.44E-04 | 1 |
| 2014-10-20 19:41 | 540 | 2.25 | -2.34E-04 | 2.30 | -1.44E-04 | 1 |
| 2014-10-20 19:46 | 545 | 2.24 | -2.35E-04 | 2.34 | -1.44E-04 | 1 |
| 2014-10-20 19:51 | 550 | 2.24 | -2.35E-04 | 2.34 | -1.44E-04 | 1 |
| 2014-10-20 19:56 | 555 | 2.24 | -2.36E-04 | 2.34 | -1.45E-04 | 1 |
| 2014-10-20 20:01 | 560 | 2.24 | -2.36E-04 | 2.32 | -1.45E-04 | 1 |
| 2014-10-20 20:06 | 565 | 2.25 | -2.37E-04 | 2.31 | -1.45E-04 | 1 |
| 2014-10-20 20:11 | 570 | 2.24 | -2.37E-04 | 2.33 | -1.45E-04 | 1 |
| 2014-10-20 20:16 | 575 | 2.24 | -2.37E-04 | 2.32 | -1.45E-04 | 1 |
| 2014-10-20 20:21 | 580 | 2.23 | -2.38E-04 | 2.31 | -1.45E-04 | 1 |
| 2014-10-20 20:26 | 585 | 2.24 | -2.38E-04 | 2.33 | -1.45E-04 | 1 |
| 2014-10-20 20:31 | 590 | 2.23 | -2.39E-04 | 2.28 | -1.45E-04 | 1 |
| 2014-10-20 20:36 | 595 | 2.23 | -2.39E-04 | 2.31 | -1.45E-04 | 1 |
| 2014-10-20 20:41 | 600 | 2.23 | -2.40E-04 | 2.30 | -1.45E-04 | 1 |
| 2014-10-20 20:46 | 605 | 2.24 | -2.40E-04 | 2.31 | -1.45E-04 | 1 |
|                  |     |      |           |      |           |   |

| 2014-10-20 20:51 | 610 | 2.23 | -2.41E-04 | 2.31 | -1.45E-04 | 1 |
|------------------|-----|------|-----------|------|-----------|---|
| 2014-10-20 20:56 | 615 | 2.23 | -2.41E-04 | 2.29 | -1.46E-04 | 1 |
| 2014-10-20 21:01 | 620 | 2.23 | -2.42E-04 | 2.29 | -1.46E-04 | 1 |
| 2014-10-20 21:06 | 625 | 2.23 | -2.42E-04 | 2.32 | -1.46E-04 | 1 |
| 2014-10-20 21:11 | 630 | 2.23 | -2.43E-04 | 2.29 | -1.46E-04 | 1 |
| 2014-10-20 21:16 | 635 | 2.22 | -2.43E-04 | 2.29 | -1.46E-04 | 1 |
| 2014-10-20 21:21 | 640 | 2.22 | -2.44E-04 | 2.33 | -1.46E-04 | 1 |
| 2014-10-20 21:26 | 645 | 2.22 | -2.44E-04 | 2.32 | -1.46E-04 | 1 |
| 2014-10-20 21:31 | 650 | 2.22 | -2.44E-04 | 2.31 | -1.46E-04 | 1 |
| 2014-10-20 21:36 | 655 | 2.23 | -2.45E-04 | 2.32 | -1.46E-04 | 1 |
| 2014-10-20 21:41 | 660 | 2.22 | -2.45E-04 | 2.31 | -1.46E-04 | 1 |
| 2014-10-20 21:46 | 665 | 2.22 | -2.46E-04 | 2.32 | -1.46E-04 | 1 |
| 2014-10-20 21:51 | 670 | 2.21 | -2.46E-04 | 2.30 | -1.47E-04 | 1 |
| 2014-10-20 21:56 | 675 | 2.21 | -2.47E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:01 | 680 | 2.21 | -2.47E-04 | 2.29 | -1.47E-04 | 1 |
| 2014-10-20 22:06 | 685 | 2.21 | -2.48E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:11 | 690 | 2.21 | -2.48E-04 | 2.31 | -1.47E-04 | 1 |
| 2014-10-20 22:16 | 695 | 2.21 | -2.49E-04 | 2.30 | -1.47E-04 | 1 |
| 2014-10-20 22:21 | 700 | 2.20 | -2.49E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:26 | 705 | 2.21 | -2.50E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:31 | 710 | 2.21 | -2.50E-04 | 2.31 | -1.47E-04 | 1 |
| 2014-10-20 22:36 | 715 | 2.21 | -2.51E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:41 | 720 | 2.20 | -2.51E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:46 | 725 | 2.20 | -2.51E-04 | 2.28 | -1.47E-04 | 1 |
| 2014-10-20 22:51 | 730 | 2.20 | -2.52E-04 | 2.30 | -1.48E-04 | 1 |
| 2014-10-20 22:56 | 735 | 2.20 | -2.52E-04 | 2.27 | -1.48E-04 | 1 |
| 2014-10-20 23:01 | 740 | 2.20 | -2.53E-04 | 2.30 | -1.48E-04 | 1 |
| 2014-10-20 23:06 | 745 | 2.19 | -2.53E-04 | 2.31 | -1.48E-04 | 1 |
| 2014-10-20 23:11 | 750 | 2.20 | -2.54E-04 | 2.27 | -1.48E-04 | 1 |
| 2014-10-20 23:16 | 755 | 2.19 | -2.54E-04 | 2.28 | -1.48E-04 | 1 |
| 2014-10-20 23:21 | 760 | 2.19 | -2.55E-04 | 2.27 | -1.48E-04 | 1 |
| 2014-10-20 23:26 | 765 | 2.19 | -2.55E-04 | 2.28 | -1.48E-04 | 1 |
| 2014-10-20 23:31 | 770 | 2.19 | -2.56E-04 | 2.28 | -1.48E-04 | 1 |
| 2014-10-20 23:36 | 775 | 2.19 | -2.56E-04 | 2.31 | -1.48E-04 | 1 |
| 2014-10-20 23:41 | 780 | 2.19 | -2.57E-04 | 2.30 | -1.48E-04 | 1 |
|                  |     |      |           |      |           |   |

| 2014-10-20 23:46 | 785 | 2.19 | -2.57E-04 | 2.30 | -1.48E-04 | 1 |
|------------------|-----|------|-----------|------|-----------|---|
| 2014-10-20 23:51 | 790 | 2.19 | -2.58E-04 | 2.30 | -1.49E-04 | 1 |
| 2014-10-20 23:56 | 795 | 2.18 | -2.58E-04 | 2.31 | -1.49E-04 | 1 |
| 2014-10-21 0:01  | 800 | 2.18 | -2.59E-04 | 2.30 | -1.49E-04 | 1 |
| 2014-10-21 0:06  | 805 | 2.18 | -2.59E-04 | 2.28 | -1.49E-04 | 1 |
| 2014-10-21 0:11  | 810 | 2.18 | -2.59E-04 | 2.27 | -1.49E-04 | 1 |
| 2014-10-21 0:16  | 815 | 2.18 | -2.60E-04 | 2.30 | -1.49E-04 | 1 |
| 2014-10-21 0:21  | 820 | 2.18 | -2.60E-04 | 2.26 | -1.49E-04 | 1 |
| 2014-10-21 0:26  | 825 | 2.18 | -2.61E-04 | 2.26 | -1.49E-04 | 1 |
| 2014-10-21 0:31  | 830 | 2.18 | -2.61E-04 | 2.29 | -1.49E-04 | 1 |
| 2014-10-21 0:36  | 835 | 2.17 | -2.62E-04 | 2.30 | -1.49E-04 | 1 |
| 2014-10-21 0:41  | 840 | 2.16 | -2.62E-04 | 2.30 | -1.49E-04 | 1 |
| 2014-10-21 0:46  | 845 | 2.17 | -2.63E-04 | 2.30 | -1.49E-04 | 1 |
| 2014-10-21 0:51  | 850 | 2.17 | -2.63E-04 | 2.30 | -1.50E-04 | 1 |
| 2014-10-21 0:56  | 855 | 2.17 | -2.64E-04 | 2.28 | -1.50E-04 | 1 |
| 2014-10-21 1:01  | 860 | 2.17 | -2.64E-04 | 2.25 | -1.50E-04 | 1 |
| 2014-10-21 1:06  | 865 | 2.16 | -2.65E-04 | 2.26 | -1.50E-04 | 1 |
| 2014-10-21 1:11  | 870 | 2.17 | -2.65E-04 | 2.26 | -1.50E-04 | 1 |
| 2014-10-21 1:16  | 875 | 2.16 | -2.66E-04 | 2.30 | -1.50E-04 | 1 |
| 2014-10-21 1:21  | 880 | 2.16 | -2.66E-04 | 2.29 | -1.50E-04 | 1 |
| 2014-10-21 1:26  | 885 | 2.16 | -2.66E-04 | 2.30 | -1.50E-04 | 1 |
| 2014-10-21 1:31  | 890 | 2.15 | -2.67E-04 | 2.26 | -1.50E-04 | 1 |
| 2014-10-21 1:36  | 895 | 2.17 | -2.67E-04 | 2.28 | -1.50E-04 | 1 |
| 2014-10-21 1:41  | 900 | 2.16 | -2.68E-04 | 2.24 | -1.50E-04 | 1 |
| 2014-10-21 1:46  | 905 | 2.17 | -2.68E-04 | 2.26 | -1.50E-04 | 1 |
| 2014-10-21 1:51  | 910 | 2.16 | -2.69E-04 | 2.29 | -1.51E-04 | 1 |
| 2014-10-21 1:56  | 915 | 2.15 | -2.69E-04 | 2.28 | -1.51E-04 | 1 |
| 2014-10-21 2:01  | 920 | 2.15 | -2.70E-04 | 2.25 | -1.51E-04 | 1 |
| 2014-10-21 2:06  | 925 | 2.15 | -2.70E-04 | 2.25 | -1.51E-04 | 1 |
| 2014-10-21 2:11  | 930 | 2.15 | -2.71E-04 | 2.24 | -1.51E-04 | 1 |
| 2014-10-21 2:16  | 935 | 2.16 | -2.71E-04 | 2.28 | -1.51E-04 | 1 |
| 2014-10-21 2:21  | 940 | 2.15 | -2.72E-04 | 2.28 | -1.51E-04 | 1 |
| 2014-10-21 2:26  | 945 | 2.14 | -2.72E-04 | 2.25 | -1.51E-04 | 1 |
| 2014-10-21 2:31  | 950 | 2.14 | -2.73E-04 | 2.28 | -1.51E-04 | 1 |
| 2014-10-21 2:36  | 955 | 2.14 | -2.73E-04 | 2.24 | -1.51E-04 | 1 |
|                  |     |      |           |      |           |   |

| 2014-10-21 2:41 | 960  | 2.14 | -2.73E-04 | 2.24 | -1.51E-04 | 1 |
|-----------------|------|------|-----------|------|-----------|---|
| 2014-10-21 2:46 | 965  | 2.14 | -2.74E-04 | 2.24 | -1.52E-04 | 1 |
| 2014-10-21 2:51 | 970  | 2.14 | -2.74E-04 | 2.27 | -1.52E-04 | 1 |
| 2014-10-21 2:56 | 975  | 2.13 | -2.75E-04 | 2.23 | -1.52E-04 | 1 |
| 2014-10-21 3:01 | 980  | 2.13 | -2.75E-04 | 2.25 | -1.52E-04 | 1 |
| 2014-10-21 3:06 | 985  | 2.13 | -2.76E-04 | 2.28 | -1.52E-04 | 1 |
| 2014-10-21 3:11 | 990  | 2.13 | -2.76E-04 | 2.28 | -1.52E-04 | 1 |
| 2014-10-21 3:16 | 995  | 2.13 | -2.77E-04 | 2.28 | -1.52E-04 | 1 |
| 2014-10-21 3:21 | 1000 | 2.13 | -2.77E-04 | 2.26 | -1.52E-04 | 1 |
| 2014-10-21 3:26 | 1005 | 2.13 | -2.78E-04 | 2.28 | -1.52E-04 | 1 |
| 2014-10-21 3:31 | 1010 | 2.13 | -2.78E-04 | 2.26 | -1.52E-04 | 1 |
| 2014-10-21 3:36 | 1015 | 2.13 | -2.79E-04 | 2.23 | -1.52E-04 | 1 |
| 2014-10-21 3:41 | 1020 | 2.12 | -2.79E-04 | 2.26 | -1.52E-04 | 1 |
| 2014-10-21 3:46 | 1025 | 2.12 | -2.80E-04 | 2.26 | -1.53E-04 | 1 |
| 2014-10-21 3:51 | 1030 | 2.12 | -2.80E-04 | 2.23 | -1.53E-04 | 1 |
| 2014-10-21 3:56 | 1035 | 2.12 | -2.81E-04 | 2.26 | -1.53E-04 | 1 |
| 2014-10-21 4:01 | 1040 | 2.11 | -2.81E-04 | 2.22 | -1.53E-04 | 1 |
| 2014-10-21 4:06 | 1045 | 2.12 | -2.81E-04 | 2.23 | -1.53E-04 | 1 |
| 2014-10-21 4:11 | 1050 | 2.12 | -2.82E-04 | 2.23 | -1.53E-04 | 1 |
| 2014-10-21 4:16 | 1055 | 2.12 | -2.82E-04 | 2.26 | -1.53E-04 | 1 |
| 2014-10-21 4:21 | 1060 | 2.11 | -2.83E-04 | 2.25 | -1.53E-04 | 1 |
| 2014-10-21 4:26 | 1065 | 2.11 | -2.83E-04 | 2.25 | -1.53E-04 | 1 |
| 2014-10-21 4:31 | 1070 | 2.12 | -2.84E-04 | 2.25 | -1.53E-04 | 1 |
| 2014-10-21 4:36 | 1075 | 2.11 | -2.84E-04 | 2.25 | -1.53E-04 | 1 |
| 2014-10-21 4:41 | 1080 | 2.11 | -2.85E-04 | 2.22 | -1.53E-04 | 1 |
| 2014-10-21 4:46 | 1085 | 2.10 | -2.85E-04 | 2.25 | -1.54E-04 | 1 |
| 2014-10-21 4:51 | 1090 | 2.11 | -2.86E-04 | 2.23 | -1.54E-04 | 1 |
| 2014-10-21 4:56 | 1095 | 2.10 | -2.86E-04 | 2.22 | -1.54E-04 | 1 |
| 2014-10-21 5:01 | 1100 | 2.10 | -2.87E-04 | 2.26 | -1.54E-04 | 1 |
| 2014-10-21 5:06 | 1105 | 2.11 | -2.87E-04 | 2.25 | -1.54E-04 | 1 |
| 2014-10-21 5:11 | 1110 | 2.10 | -2.88E-04 | 2.25 | -1.54E-04 | 1 |
| 2014-10-21 5:16 | 1115 | 2.10 | -2.88E-04 | 2.22 | -1.54E-04 | 1 |
| 2014-10-21 5:21 | 1120 | 2.10 | -2.88E-04 | 2.25 | -1.54E-04 | 1 |
| 2014-10-21 5:26 | 1125 | 2.10 | -2.89E-04 | 2.21 | -1.54E-04 | 1 |
| 2014-10-21 5:31 | 1130 | 2.10 | -2.89E-04 | 2.23 | -1.54E-04 | 1 |
|                 |      |      |           |      |           |   |

| 2014-10-21 5:36  |                 |      |      |           |      |           |   |
|--|-----------------|------|------|-----------|------|-----------|---|
| 2014-10-21 5:46  | 2014-10-21 5:36 | 1135 | 2.10 | -2.90E-04 | 2.24 | -1.54E-04 | 1 |
| 2014-10-21 5:51   1150   2.09   -2.91E-04   2.22   -1.55E-04   1   | 2014-10-21 5:41 | 1140 | 2.10 | -2.90E-04 | 2.24 | -1.54E-04 | 1 |
| 2014-10-21 5:56   1155   2.09   -2.92E-04   2.23   -1.55E-04   1   | 2014-10-21 5:46 | 1145 | 2.09 | -2.91E-04 | 2.22 | -1.55E-04 | 1 |
| 2014-10-21 6:01  | 2014-10-21 5:51 | 1150 | 2.09 | -2.91E-04 | 2.22 | -1.55E-04 | 1 |
| 2014-10-21 6:06  | 2014-10-21 5:56 | 1155 | 2.09 | -2.92E-04 | 2.23 | -1.55E-04 | 1 |
| 2014-10-21 6:11  | 2014-10-21 6:01 | 1160 | 2.09 | -2.92E-04 | 2.21 | -1.55E-04 | 1 |
| 2014-10-21 6:16  | 2014-10-21 6:06 | 1165 | 2.09 | -2.93E-04 | 2.21 | -1.55E-04 | 1 |
| 2014-10-21 6:21  | 2014-10-21 6:11 | 1170 | 2.08 | -2.93E-04 | 2.21 | -1.55E-04 | 1 |
| 2014-10-21 6:26  | 2014-10-21 6:16 | 1175 | 2.08 | -2.94E-04 | 2.24 | -1.55E-04 | 1 |
| 2014-10-21 6:31   1190   2.08   -2.95E-04   2.21   -1.55E-04   1   2014-10-21 6:36   1195   2.08   -2.95E-04   2.21   -1.55E-04   1   2014-10-21 6:41   1200   2.07   -2.96E-04   2.23   -1.55E-04   1   2014-10-21 6:46   1205   2.07   -2.96E-04   2.23   -1.56E-04   1   2014-10-21 6:51   1210   2.07   -2.97E-04   2.24   -1.56E-04   1   2014-10-21 6:56   1215   2.07   -2.97E-04   2.22   -1.56E-04   1   2014-10-21 7:01   1220   2.07   -2.98E-04   2.22   -1.56E-04   1   2014-10-21 7:06   1225   2.07   -2.98E-04   2.21   -1.56E-04   1   2014-10-21 7:11   1230   2.06   -2.99E-04   2.21   -1.56E-04   1   2014-10-21 7:16   1235   2.07   -2.98E-04   2.21   -1.56E-04   1   2014-10-21 7:26   1245   2.06   -3.00E-04   2.20   -1.56E-04   1   2014-10-21 7:31   1250   2.06   -3.00E-04   2.21   -1.56E-04   1   2014-10-21 7:36   1255   2.06   -3.01E-04   2.22   -1.56E-04   1   2014-10-21 7:36   1255   2.06   -3.01E-04   2.22   -1.56E-04   1   2014-10-21 7:36   1255   2.06   -3.01E-04   2.22   -1.56E-04   1   2014-10-21 7:46   1265   2.06   -3.02E-04   2.21   -1.57E-04   1   2014-10-21 7:56   1275   2.06   -3.03E-04   2.22   -1.57E-04   1   2014-10-21 7:56   1275   2.05   -3.03E-04   2.22   -1.57E-04   1   2014-10-21 8:01   1280   2.05   -3.03E-04   2.20   -1.57E-04   1   2014-10-21 8:01   1280   2.05   -3.03E-04   2.20   -1.57E-04   1   2014-10-21 8:06   1285   2.05   -3.05E-04   2.20   -1.57E-04   1   2014-10-21 8:06   1285   2.05   -3.05E-04   2.20   -1.57E-04   1   2014-10-21 8:01   1290   2.05   -3 | 2014-10-21 6:21 | 1180 | 2.08 | -2.94E-04 | 2.21 | -1.55E-04 | 1 |
| 2014-10-21 6:36         1195         2.08         -2.95E-04         2.21         -1.55E-04         1           2014-10-21 6:41         1200         2.07         -2.96E-04         2.23         -1.55E-04         1           2014-10-21 6:46         1205         2.07         -2.96E-04         2.23         -1.56E-04         1           2014-10-21 6:51         1210         2.07         -2.97E-04         2.24         -1.56E-04         1           2014-10-21 6:56         1215         2.07         -2.97E-04         2.22         -1.56E-04         1           2014-10-21 7:01         1220         2.07         -2.98E-04         2.22         -1.56E-04         1           2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -3.00E-04         2.20   | 2014-10-21 6:26 | 1185 | 2.07 | -2.95E-04 | 2.23 | -1.55E-04 | 1 |
| 2014-10-21 6:41         1200         2.07         -2.96E-04         2.23         -1.55E-04         1           2014-10-21 6:46         1205         2.07         -2.96E-04         2.23         -1.56E-04         1           2014-10-21 6:51         1210         2.07         -2.97E-04         2.24         -1.56E-04         1           2014-10-21 6:56         1215         2.07         -2.97E-04         2.22         -1.56E-04         1           2014-10-21 7:01         1220         2.07         -2.98E-04         2.22         -1.56E-04         1           2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.22   | 2014-10-21 6:31 | 1190 | 2.08 | -2.95E-04 | 2.21 | -1.55E-04 | 1 |
| 2014-10-21 6:46         1205         2.07         -2.96E-04         2.23         -1.56E-04         1           2014-10-21 6:51         1210         2.07         -2.97E-04         2.24         -1.56E-04         1           2014-10-21 6:56         1215         2.07         -2.97E-04         2.22         -1.56E-04         1           2014-10-21 7:01         1220         2.07         -2.98E-04         2.22         -1.56E-04         1           2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22   | 2014-10-21 6:36 | 1195 | 2.08 | -2.95E-04 | 2.21 | -1.55E-04 | 1 |
| 2014-10-21 6:51         1210         2.07         -2.97E-04         2.24         -1.56E-04         1           2014-10-21 6:56         1215         2.07         -2.97E-04         2.22         -1.56E-04         1           2014-10-21 7:01         1220         2.07         -2.98E-04         2.22         -1.56E-04         1           2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.01E-04         2.21         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.01E-04         2.22   | 2014-10-21 6:41 | 1200 | 2.07 | -2.96E-04 | 2.23 | -1.55E-04 | 1 |
| 2014-10-21 6:56         1215         2.07         -2.97E-04         2.22         -1.56E-04         1           2014-10-21 7:01         1220         2.07         -2.98E-04         2.22         -1.56E-04         1           2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:56         1255         2.06         -3.03E-04         2.22   | 2014-10-21 6:46 | 1205 | 2.07 | -2.96E-04 | 2.23 | -1.56E-04 | 1 |
| 2014-10-21 7:01         1220         2.07         -2.98E-04         2.22         -1.56E-04         1           2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22   | 2014-10-21 6:51 | 1210 | 2.07 | -2.97E-04 | 2.24 | -1.56E-04 | 1 |
| 2014-10-21 7:06         1225         2.07         -2.98E-04         2.21         -1.56E-04         1           2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20   | 2014-10-21 6:56 | 1215 | 2.07 | -2.97E-04 | 2.22 | -1.56E-04 | 1 |
| 2014-10-21 7:11         1230         2.06         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20   | 2014-10-21 7:01 | 1220 | 2.07 | -2.98E-04 | 2.22 | -1.56E-04 | 1 |
| 2014-10-21 7:16         1235         2.07         -2.99E-04         2.21         -1.56E-04         1           2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.04E-04         2.20   | 2014-10-21 7:06 | 1225 | 2.07 | -2.98E-04 | 2.21 | -1.56E-04 | 1 |
| 2014-10-21 7:21         1240         2.06         -3.00E-04         2.20         -1.56E-04         1           2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:11         1290         2.05         -3.05E-04         2.19   | 2014-10-21 7:11 | 1230 | 2.06 | -2.99E-04 | 2.21 | -1.56E-04 | 1 |
| 2014-10-21 7:26         1245         2.06         -3.00E-04         2.21         -1.56E-04         1           2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:11         1290         2.05         -3.05E-04         2.20         -1.57E-04         1           2014-10-21 8:16         1295         2.05         -3.05E-04         2.19   | 2014-10-21 7:16 | 1235 | 2.07 | -2.99E-04 | 2.21 | -1.56E-04 | 1 |
| 2014-10-21 7:31         1250         2.06         -3.01E-04         2.23         -1.56E-04         1           2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:11         1290         2.05         -3.05E-04         2.19         -1.57E-04         1           2014-10-21 8:16         1295         2.05         -3.05E-04         2.20         -1.57E-04         1           2014-10-21 8:21         1300         2.05         -3.05E-04         2.20   | 2014-10-21 7:21 | 1240 | 2.06 | -3.00E-04 | 2.20 | -1.56E-04 | 1 |
| 2014-10-21 7:36         1255         2.06         -3.01E-04         2.22         -1.56E-04         1           2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:11         1290         2.05         -3.05E-04         2.20         -1.57E-04         1           2014-10-21 8:16         1295         2.05         -3.05E-04         2.19         -1.57E-04         1           2014-10-21 8:21         1300         2.05         -3.05E-04         2.20         -1.57E-04         1  | 2014-10-21 7:26 | 1245 | 2.06 | -3.00E-04 | 2.21 | -1.56E-04 | 1 |
| 2014-10-21 7:41         1260         2.06         -3.02E-04         2.19         -1.57E-04         1           2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:11         1290         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:16         1295         2.05         -3.05E-04         2.19         -1.57E-04         1           2014-10-21 8:21         1300         2.05         -3.05E-04         2.20         -1.57E-04         1   | 2014-10-21 7:31 | 1250 | 2.06 | -3.01E-04 | 2.23 | -1.56E-04 | 1 |
| 2014-10-21 7:46         1265         2.06         -3.02E-04         2.21         -1.57E-04         1           2014-10-21 7:51         1270         2.06         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 7:56         1275         2.05         -3.03E-04         2.22         -1.57E-04         1           2014-10-21 8:01         1280         2.05         -3.03E-04         2.20         -1.57E-04         1           2014-10-21 8:06         1285         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:11         1290         2.05         -3.04E-04         2.20         -1.57E-04         1           2014-10-21 8:16         1295         2.05         -3.05E-04         2.19         -1.57E-04         1           2014-10-21 8:21         1300         2.05         -3.05E-04         2.20         -1.57E-04         1  | 2014-10-21 7:36 | 1255 | 2.06 | -3.01E-04 | 2.22 | -1.56E-04 | 1 |
| 2014-10-21 7:51     1270     2.06     -3.03E-04     2.22     -1.57E-04     1       2014-10-21 7:56     1275     2.05     -3.03E-04     2.22     -1.57E-04     1       2014-10-21 8:01     1280     2.05     -3.03E-04     2.20     -1.57E-04     1       2014-10-21 8:06     1285     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:11     1290     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:16     1295     2.05     -3.05E-04     2.19     -1.57E-04     1       2014-10-21 8:21     1300     2.05     -3.05E-04     2.20     -1.57E-04     1   | 2014-10-21 7:41 | 1260 | 2.06 | -3.02E-04 | 2.19 | -1.57E-04 | 1 |
| 2014-10-21 7:56     1275     2.05     -3.03E-04     2.22     -1.57E-04     1       2014-10-21 8:01     1280     2.05     -3.03E-04     2.20     -1.57E-04     1       2014-10-21 8:06     1285     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:11     1290     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:16     1295     2.05     -3.05E-04     2.19     -1.57E-04     1       2014-10-21 8:21     1300     2.05     -3.05E-04     2.20     -1.57E-04     1  | 2014-10-21 7:46 | 1265 | 2.06 | -3.02E-04 | 2.21 | -1.57E-04 | 1 |
| 2014-10-21 8:01     1280     2.05     -3.03E-04     2.20     -1.57E-04     1       2014-10-21 8:06     1285     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:11     1290     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:16     1295     2.05     -3.05E-04     2.19     -1.57E-04     1       2014-10-21 8:21     1300     2.05     -3.05E-04     2.20     -1.57E-04     1   | 2014-10-21 7:51 | 1270 | 2.06 | -3.03E-04 | 2.22 | -1.57E-04 | 1 |
| 2014-10-21 8:06     1285     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:11     1290     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:16     1295     2.05     -3.05E-04     2.19     -1.57E-04     1       2014-10-21 8:21     1300     2.05     -3.05E-04     2.20     -1.57E-04     1  | 2014-10-21 7:56 | 1275 | 2.05 | -3.03E-04 | 2.22 | -1.57E-04 | 1 |
| 2014-10-21 8:11     1290     2.05     -3.04E-04     2.20     -1.57E-04     1       2014-10-21 8:16     1295     2.05     -3.05E-04     2.19     -1.57E-04     1       2014-10-21 8:21     1300     2.05     -3.05E-04     2.20     -1.57E-04     1   | 2014-10-21 8:01 | 1280 | 2.05 | -3.03E-04 | 2.20 | -1.57E-04 | 1 |
| 2014-10-21 8:16 1295 2.05 -3.05E-04 2.19 -1.57E-04 1<br>2014-10-21 8:21 1300 2.05 -3.05E-04 2.20 -1.57E-04 1   | 2014-10-21 8:06 | 1285 | 2.05 | -3.04E-04 | 2.20 | -1.57E-04 | 1 |
| 2014-10-21 8:21 1300 2.05 -3.05E-04 2.20 -1.57E-04 1   | 2014-10-21 8:11 | 1290 | 2.05 | -3.04E-04 | 2.20 | -1.57E-04 | 1 |
|  | 2014-10-21 8:16 | 1295 | 2.05 | -3.05E-04 | 2.19 | -1.57E-04 | 1 |
| 2014-10-21 8:26   1305   2.05   -3.06E-04   2.20   -1.57E-04   1   | 2014-10-21 8:21 | 1300 | 2.05 | -3.05E-04 | 2.20 | -1.57E-04 | 1 |
|  | 2014-10-21 8:26 | 1305 | 2.05 | -3.06E-04 | 2.20 | -1.57E-04 | 1 |

| 2014-10-21 8:31  | 1310 | 2.05 | -3.06E-04 | 2.22 | -1.57E-04 | 1 |
|------------------|------|------|-----------|------|-----------|---|
| 2014-10-21 8:36  | 1315 | 2.04 | -3.07E-04 | 2.20 | -1.57E-04 | 1 |
| 2014-10-21 8:41  | 1320 | 2.04 | -3.07E-04 | 2.19 | -1.58E-04 | 1 |
| 2014-10-21 8:46  | 1325 | 2.04 | -3.08E-04 | 2.22 | -1.58E-04 | 1 |
| 2014-10-21 8:51  | 1330 | 2.04 | -3.08E-04 | 2.19 | -1.58E-04 | 1 |
| 2014-10-21 8:56  | 1335 | 2.04 | -3.09E-04 | 2.22 | -1.58E-04 | 1 |
| 2014-10-21 9:01  | 1340 | 2.04 | -3.09E-04 | 2.21 | -1.58E-04 | 1 |
| 2014-10-21 9:06  | 1345 | 2.04 | -3.10E-04 | 2.19 | -1.58E-04 | 1 |
| 2014-10-21 9:11  | 1350 | 2.03 | -3.10E-04 | 2.19 | -1.58E-04 | 1 |
| 2014-10-21 9:16  | 1355 | 2.04 | -3.10E-04 | 2.18 | -1.58E-04 | 1 |
| 2014-10-21 9:21  | 1360 | 2.03 | -3.11E-04 | 2.20 | -1.58E-04 | 1 |
| 2014-10-21 9:26  | 1365 | 2.03 | -3.11E-04 | 2.19 | -1.58E-04 | 1 |
| 2014-10-21 9:31  | 1370 | 2.03 | -3.12E-04 | 2.18 | -1.58E-04 | 1 |
| 2014-10-21 9:36  | 1375 | 2.03 | -3.12E-04 | 2.21 | -1.58E-04 | 1 |
| 2014-10-21 9:41  | 1380 | 2.02 | -3.13E-04 | 2.21 | -1.59E-04 | 1 |
| 2014-10-21 9:46  | 1385 | 2.03 | -3.13E-04 | 2.21 | -1.59E-04 | 1 |
| 2014-10-21 9:51  | 1390 | 2.02 | -3.14E-04 | 2.21 | -1.59E-04 | 1 |
| 2014-10-21 9:56  | 1395 | 2.02 | -3.14E-04 | 2.19 | -1.59E-04 | 1 |
| 2014-10-21 10:01 | 1400 | 2.02 | -3.15E-04 | 2.18 | -1.59E-04 | 1 |
| 2014-10-21 10:06 | 1405 | 2.02 | -3.15E-04 | 2.18 | -1.59E-04 | 1 |
| 2014-10-21 10:11 | 1410 | 2.01 | -3.16E-04 | 2.18 | -1.59E-04 | 1 |
| 2014-10-21 10:16 | 1415 | 2.02 | -3.16E-04 | 2.20 | -1.59E-04 | 1 |
| 2014-10-21 10:21 | 1420 | 2.02 | -3.17E-04 | 2.18 | -1.59E-04 | 1 |
| 2014-10-21 10:26 | 1425 | 2.01 | -3.17E-04 | 2.20 | -1.59E-04 | 1 |
| 2014-10-21 10:31 | 1430 | 2.01 | -3.17E-04 | 2.21 | -1.59E-04 | 1 |
| 2014-10-21 10:36 | 1435 | 2.01 | -3.18E-04 | 2.19 | -1.59E-04 | 1 |
| 2014-10-21 10:41 | 1440 | 2.00 | -3.18E-04 | 2.17 | -1.60E-04 | 1 |
| 2014-10-21 10:46 | 1445 | 2.00 | -3.19E-04 | 2.20 | -1.60E-04 | 1 |
| 2014-10-21 10:51 | 1450 | 2.00 | -3.19E-04 | 2.18 | -1.60E-04 | 1 |
| 2014-10-21 10:56 | 1455 | 2.00 | -3.20E-04 | 2.21 | -1.60E-04 | 1 |
| 2014-10-21 11:01 | 1460 | 1.99 | -3.20E-04 | 2.17 | -1.60E-04 | 1 |
| 2014-10-21 11:06 | 1465 | 2.00 | -3.21E-04 | 2.19 | -1.60E-04 | 1 |
| 2014-10-21 11:11 | 1470 | 2.00 | -3.21E-04 | 2.20 | -1.60E-04 | 1 |
| 2014-10-21 11:16 | 1475 | 2.00 | -3.22E-04 | 2.17 | -1.60E-04 | 1 |
| 2014-10-21 11:21 | 1480 | 1.99 | -3.22E-04 | 2.20 | -1.60E-04 | 1 |
|                  |      |      |           |      |           |   |

| 2014-10-21 11:26 | 1485 | 1.99 | -3.23E-04 | 2.17 | -1.60E-04 | 1 |
|------------------|------|------|-----------|------|-----------|---|
| 2014-10-21 11:31 | 1490 | 1.99 | -3.23E-04 | 2.20 | -1.60E-04 | 1 |
| 2014-10-21 11:36 | 1495 | 1.99 | -3.24E-04 | 2.17 | -1.61E-04 | 1 |
| 2014-10-21 11:41 | 1500 | 1.99 | -3.24E-04 | 2.20 | -1.61E-04 | 1 |
| 2014-10-21 11:46 | 1505 | 1.98 | -3.25E-04 | 2.19 | -1.61E-04 | 1 |
| 2014-10-21 11:51 | 1510 | 1.98 | -3.25E-04 | 2.19 | -1.61E-04 | 1 |
| 2014-10-21 11:56 | 1515 | 1.97 | -3.25E-04 | 2.17 | -1.61E-04 | 1 |
| 2014-10-21 12:01 | 1520 | 1.98 | -3.26E-04 | 2.18 | -1.61E-04 | 1 |
| 2014-10-21 12:06 | 1525 | 1.98 | -3.26E-04 | 2.16 | -1.61E-04 | 1 |
| 2014-10-21 12:11 | 1530 | 1.98 | -3.27E-04 | 2.17 | -1.61E-04 | 1 |
| 2014-10-21 12:16 | 1535 | 1.98 | -3.27E-04 | 2.19 | -1.61E-04 | 1 |
| 2014-10-21 12:21 | 1540 | 1.97 | -3.28E-04 | 2.20 | -1.61E-04 | 1 |
| 2014-10-21 12:26 | 1545 | 1.97 | -3.28E-04 | 2.18 | -1.61E-04 | 1 |
| 2014-10-21 12:31 | 1550 | 1.96 | -3.29E-04 | 2.16 | -1.61E-04 | 1 |
| 2014-10-21 12:36 | 1555 | 1.97 | -3.29E-04 | 2.17 | -1.62E-04 | 1 |
| 2014-10-21 12:41 | 1560 | 1.97 | -3.30E-04 | 2.15 | -1.62E-04 | 1 |
| 2014-10-21 12:46 | 1565 | 1.97 | -3.30E-04 | 2.19 | -1.62E-04 | 1 |
| 2014-10-21 12:51 | 1570 | 1.96 | -3.31E-04 | 2.15 | -1.62E-04 | 1 |
| 2014-10-21 12:56 | 1575 | 1.96 | -3.31E-04 | 2.16 | -1.62E-04 | 1 |
| 2014-10-21 13:01 | 1580 | 1.96 | -3.32E-04 | 2.16 | -1.62E-04 | 1 |
| 2014-10-21 13:06 | 1585 | 1.96 | -3.32E-04 | 2.18 | -1.62E-04 | 1 |
| 2014-10-21 13:11 | 1590 | 1.96 | -3.32E-04 | 2.16 | -1.62E-04 | 1 |
| 2014-10-21 13:16 | 1595 | 1.96 | -3.33E-04 | 2.16 | -1.62E-04 | 1 |
| 2014-10-21 13:21 | 1600 | 1.95 | -3.33E-04 | 2.16 | -1.62E-04 | 1 |
| 2014-10-21 13:26 | 1605 | 1.95 | -3.34E-04 | 2.17 | -1.62E-04 | 1 |
| 2014-10-21 13:31 | 1610 | 1.95 | -3.34E-04 | 2.16 | -1.62E-04 | 1 |
| 2014-10-21 13:36 | 1615 | 1.95 | -3.35E-04 | 2.15 | -1.63E-04 | 1 |
| 2014-10-21 13:41 | 1620 | 1.95 | -3.35E-04 | 2.16 | -1.63E-04 | 1 |
| 2014-10-21 13:46 | 1625 | 1.95 | -3.36E-04 | 2.16 | -1.63E-04 | 1 |
| 2014-10-21 13:51 | 1630 | 1.94 | -3.36E-04 | 2.16 | -1.63E-04 | 1 |
| 2014-10-21 13:56 | 1635 | 1.94 | -3.37E-04 | 2.14 | -1.63E-04 | 1 |
| 2014-10-21 14:01 | 1640 | 1.94 | -3.37E-04 | 2.15 | -1.63E-04 | 1 |
| 2014-10-21 14:06 | 1645 | 1.94 | -3.38E-04 | 2.15 | -1.63E-04 | 1 |
| 2014-10-21 14:11 | 1650 | 1.94 | -3.38E-04 | 2.16 | -1.63E-04 | 1 |
| 2014-10-21 14:16 | 1655 | 1.93 | -3.39E-04 | 2.14 | -1.63E-04 | 1 |
|                  |      |      |           |      |           |   |

| 2014-10-21 14:21 | 1660 | 1.93 | -3.39E-04 | 2.16 | -1.63E-04 | 1 |
|------------------|------|------|-----------|------|-----------|---|
| 2014-10-21 14:26 | 1665 | 1.93 | -3.39E-04 | 2.15 | -1.63E-04 | 1 |
| 2014-10-21 14:31 | 1670 | 1.93 | -3.40E-04 | 2.15 | -1.63E-04 | 1 |
| 2014-10-21 14:36 | 1675 | 1.93 | -3.40E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 14:41 | 1680 | 1.93 | -3.41E-04 | 2.15 | -1.64E-04 | 1 |
| 2014-10-21 14:46 | 1685 | 1.92 | -3.41E-04 | 2.15 | -1.64E-04 | 1 |
| 2014-10-21 14:51 | 1690 | 1.92 | -3.42E-04 | 2.16 | -1.64E-04 | 1 |
| 2014-10-21 14:56 | 1695 | 1.92 | -3.42E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 15:01 | 1700 | 1.92 | -3.43E-04 | 2.15 | -1.64E-04 | 1 |
| 2014-10-21 15:06 | 1705 | 1.92 | -3.43E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 15:11 | 1710 | 1.92 | -3.44E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 15:16 | 1715 | 1.92 | -3.44E-04 | 2.13 | -1.64E-04 | 1 |
| 2014-10-21 15:21 | 1720 | 1.92 | -3.45E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 15:26 | 1725 | 1.91 | -3.45E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 15:31 | 1730 | 1.91 | -3.46E-04 | 2.14 | -1.64E-04 | 1 |
| 2014-10-21 15:36 | 1735 | 1.91 | -3.46E-04 | 2.13 | -1.65E-04 | 1 |
| 2014-10-21 15:41 | 1740 | 1.90 | -3.47E-04 | 2.15 | -1.65E-04 | 1 |
| 2014-10-21 15:46 | 1745 | 1.91 | -3.47E-04 | 2.14 | -1.65E-04 | 1 |
| 2014-10-21 15:51 | 1750 | 1.91 | -3.47E-04 | 2.14 | -1.65E-04 | 1 |
| 2014-10-21 15:56 | 1755 | 1.90 | -3.48E-04 | 2.13 | -1.65E-04 | 1 |
| 2014-10-21 16:01 | 1760 | 1.90 | -3.48E-04 | 2.13 | -1.65E-04 | 1 |
| 2014-10-21 16:06 | 1765 | 1.90 | -3.49E-04 | 2.13 | -1.65E-04 | 1 |
| 2014-10-21 16:11 | 1770 | 1.89 | -3.49E-04 | 2.14 | -1.65E-04 | 1 |
| 2014-10-21 16:16 | 1775 | 1.89 | -3.50E-04 | 2.13 | -1.65E-04 | 1 |
| 2014-10-21 16:21 | 1780 | 1.89 | -3.50E-04 | 2.12 | -1.65E-04 | 1 |
| 2014-10-21 16:26 | 1785 | 1.89 | -3.51E-04 | 2.13 | -1.65E-04 | 1 |
| 2014-10-21 16:31 | 1790 | 1.89 | -3.51E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 16:36 | 1795 | 1.89 | -3.52E-04 | 2.14 | -1.66E-04 | 1 |
| 2014-10-21 16:41 | 1800 | 1.89 | -3.52E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 16:46 | 1805 | 1.88 | -3.53E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 16:51 | 1810 | 1.89 | -3.53E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 16:56 | 1815 | 1.88 | -3.54E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 17:01 | 1820 | 1.88 | -3.54E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 17:06 | 1825 | 1.87 | -3.54E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 17:11 | 1830 | 1.87 | -3.55E-04 | 2.13 | -1.66E-04 | 1 |
|                  |      |      |           |      |           |   |

| 2014-10-21 17:16 | 1835 | 1.87 | -3.55E-04 | 2.13 | -1.66E-04 | 1 |
|------------------|------|------|-----------|------|-----------|---|
| 2014-10-21 17:21 | 1840 | 1.87 | -3.56E-04 | 2.13 | -1.66E-04 | 1 |
| 2014-10-21 17:26 | 1845 | 1.87 | -3.56E-04 | 2.12 | -1.66E-04 | 1 |
| 2014-10-21 17:31 | 1850 | 1.87 | -3.57E-04 | 2.12 | -1.67E-04 | 1 |
| 2014-10-21 17:36 | 1855 | 1.87 | -3.57E-04 | 2.11 | -1.67E-04 | 1 |
| 2014-10-21 17:41 | 1860 | 1.88 | -3.58E-04 | 2.13 | -1.67E-04 | 1 |
| 2014-10-21 17:46 | 1865 | 1.86 | -3.58E-04 | 2.13 | -1.67E-04 | 1 |
| 2014-10-21 17:51 | 1870 | 1.86 | -3.59E-04 | 2.11 | -1.67E-04 | 1 |
| 2014-10-21 17:56 | 1875 | 1.86 | -3.59E-04 | 2.12 | -1.67E-04 | 1 |
| 2014-10-21 18:01 | 1880 | 1.86 | -3.60E-04 | 2.12 | -1.67E-04 | 1 |
| 2014-10-21 18:06 | 1885 | 1.85 | -3.60E-04 | 2.11 | -1.67E-04 | 1 |
| 2014-10-21 18:11 | 1890 | 1.85 | -3.61E-04 | 2.11 | -1.67E-04 | 1 |
| 2014-10-21 18:16 | 1895 | 1.85 | -3.61E-04 | 2.14 | -1.67E-04 | 1 |
| 2014-10-21 18:21 | 1900 | 1.85 | -3.62E-04 | 2.11 | -1.67E-04 | 1 |
| 2014-10-21 18:26 | 1905 | 1.84 | -3.62E-04 | 2.11 | -1.67E-04 | 1 |
| 2014-10-21 18:31 | 1910 | 1.85 | -3.62E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 18:36 | 1915 | 1.85 | -3.63E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 18:41 | 1920 | 1.84 | -3.63E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 18:46 | 1925 | 1.84 | -3.64E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 18:51 | 1930 | 1.84 | -3.64E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 18:56 | 1935 | 1.83 | -3.65E-04 | 2.10 | -1.68E-04 | 1 |
| 2014-10-21 19:01 | 1940 | 1.84 | -3.65E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 19:06 | 1945 | 1.83 | -3.66E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 19:11 | 1950 | 1.83 | -3.66E-04 | 2.10 | -1.68E-04 | 1 |
| 2014-10-21 19:16 | 1955 | 1.84 | -3.67E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 19:21 | 1960 | 1.82 | -3.67E-04 | 2.11 | -1.68E-04 | 1 |
| 2014-10-21 19:26 | 1965 | 1.82 | -3.68E-04 | 2.10 | -1.68E-04 | 1 |
| 2014-10-21 19:31 | 1970 | 1.82 | -3.68E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 19:36 | 1975 | 1.82 | -3.69E-04 | 2.09 | -1.69E-04 | 1 |
| 2014-10-21 19:41 | 1980 | 1.82 | -3.69E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 19:46 | 1985 | 1.81 | -3.69E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 19:51 | 1990 | 1.81 | -3.70E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 19:56 | 1995 | 1.81 | -3.70E-04 | 2.09 | -1.69E-04 | 1 |
| 2014-10-21 20:01 | 2000 | 1.81 | -3.71E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 20:06 | 2005 | 1.80 | -3.71E-04 | 2.10 | -1.69E-04 | 1 |
|                  |      |      |           |      |           |   |

| 2014 10 21 20 11 | 2010 | 1.00 | 2.725.04  | 2.10 | 1.600.04  |   |
|------------------|------|------|-----------|------|-----------|---|
| 2014-10-21 20:11 | 2010 | 1.80 | -3.72E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 20:16 | 2015 | 1.80 | -3.72E-04 | 2.08 | -1.69E-04 | 1 |
| 2014-10-21 20:21 | 2020 | 1.80 | -3.73E-04 | 2.09 | -1.69E-04 | 1 |
| 2014-10-21 20:26 | 2025 | 1.80 | -3.73E-04 | 2.10 | -1.69E-04 | 1 |
| 2014-10-21 20:31 | 2030 | 1.80 | -3.74E-04 | 2.09 | -1.70E-04 | 1 |
| 2014-10-21 20:36 | 2035 | 1.80 | -3.74E-04 | 2.09 | -1.70E-04 | 1 |
| 2014-10-21 20:41 | 2040 | 1.79 | -3.75E-04 | 2.09 | -1.70E-04 | 1 |
| 2014-10-21 20:46 | 2045 | 1.79 | -3.75E-04 | 2.09 | -1.70E-04 | 1 |
| 2014-10-21 20:51 | 2050 | 1.79 | -3.76E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 20:56 | 2055 | 1.79 | -3.76E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 21:01 | 2060 | 1.78 | -3.76E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 21:06 | 2065 | 1.78 | -3.77E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 21:11 | 2070 | 1.79 | -3.77E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 21:16 | 2075 | 1.78 | -3.78E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 21:21 | 2080 | 1.78 | -3.78E-04 | 2.08 | -1.70E-04 | 1 |
| 2014-10-21 21:26 | 2085 | 1.77 | -3.79E-04 | 2.07 | -1.71E-04 | 1 |
| 2014-10-21 21:31 | 2090 | 1.77 | -3.79E-04 | 2.09 | -1.71E-04 | 1 |
| 2014-10-21 21:36 | 2095 | 1.77 | -3.80E-04 | 2.08 | -1.71E-04 | 1 |
| 2014-10-21 21:41 | 2100 | 1.76 | -3.80E-04 | 2.08 | -1.71E-04 | 1 |
| 2014-10-21 21:46 | 2105 | 1.77 | -3.81E-04 | 2.07 | -1.71E-04 | 1 |
| 2014-10-21 21:51 | 2110 | 1.76 | -3.81E-04 | 2.08 | -1.71E-04 | 1 |
| 2014-10-21 21:56 | 2115 | 1.76 | -3.82E-04 | 2.08 | -1.71E-04 | 1 |
| 2014-10-21 22:01 | 2120 | 1.77 | -3.82E-04 | 2.08 | -1.71E-04 | 1 |
| 2014-10-21 22:06 | 2125 | 1.76 | -3.83E-04 | 2.07 | -1.71E-04 | 1 |
| 2014-10-21 22:11 | 2130 | 1.76 | -3.83E-04 | 2.06 | -1.71E-04 | 1 |
| 2014-10-21 22:16 | 2135 | 1.76 | -3.84E-04 | 2.08 | -1.71E-04 | 1 |
| 2014-10-21 22:21 | 2140 | 1.75 | -3.84E-04 | 2.07 | -1.71E-04 | 1 |
| 2014-10-21 22:26 | 2145 | 1.75 | -3.84E-04 | 2.08 | -1.72E-04 | 1 |
| 2014-10-21 22:31 | 2150 | 1.75 | -3.85E-04 | 2.08 | -1.72E-04 | 1 |
| 2014-10-21 22:36 | 2155 | 1.75 | -3.85E-04 | 2.07 | -1.72E-04 | 1 |
| 2014-10-21 22:41 | 2160 | 1.75 | -3.86E-04 | 2.07 | -1.72E-04 | 1 |
| 2014-10-21 22:46 | 2165 | 1.74 | -3.86E-04 | 2.07 | -1.72E-04 | 1 |
| 2014-10-21 22:51 | 2170 | 1.74 | -3.87E-04 | 2.07 | -1.72E-04 | 1 |
| 2014-10-21 22:56 | 2175 | 1.74 | -3.87E-04 | 2.06 | -1.72E-04 | 1 |
| 2014-10-21 23:01 | 2180 | 1.74 | -3.88E-04 | 2.06 | -1.72E-04 | 1 |
| <u> </u>         |      | 1    |           | I.   |           |   |

| 2014-10-21 23:06   2185   1.73   -3.88E-04   2.06   -1.72E-04   1   |                  |      |      |                        |      |           |   |
|---|------------------|------|------|------------------------|------|-----------|---|
| 2014-10-21 23:16   2195   1.73   -3.89E-04   2.06   -1.72E-04   1   | 2014-10-21 23:06 | 2185 | 1.73 | -3.88E-04              | 2.06 | -1.72E-04 | 1 |
| 2014-10-21 23:21   2200   1.73   -3.90E-04   2.07   -1.72E-04   1   | 2014-10-21 23:11 | 2190 | 1.74 | -3.89E-04              | 2.06 | -1.72E-04 | 1 |
| 2014-10-21 23:26   2205   1.73   -3.90E-04   2.06   -1.73E-04   1   | 2014-10-21 23:16 | 2195 | 1.73 | -3.89E-04              | 2.06 | -1.72E-04 | 1 |
| 2014-10-21 23:31   2210   1.72   -3.91E-04   2.07   -1.73E-04   1   | 2014-10-21 23:21 | 2200 | 1.73 | -3.90E-04              | 2.07 | -1.72E-04 | 1 |
| 2014-10-21 23:36   2215   1.73   -3.91E-04   2.06   -1.73E-04   1   | 2014-10-21 23:26 | 2205 | 1.73 | -3.90E-04              | 2.06 | -1.73E-04 | 1 |
| 2014-10-21 23:41   2220   1.72   -3.91E-04   2.05   -1.73E-04   1   | 2014-10-21 23:31 | 2210 | 1.72 | -3.91E-04              | 2.07 | -1.73E-04 | 1 |
| 2014-10-21 23:46         2225         1.72         -3.92E-04         2.05         -1.73E-04         1           2014-10-21 23:51         2230         1.72         -3.92E-04         2.05         -1.73E-04         1           2014-10-21 23:56         2235         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:01         2240         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:06         2245         1.72         -3.94E-04         2.06         -1.73E-04         1           2014-10-22 0:11         2250         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.04 </td <td>2014-10-21 23:36</td> <td>2215</td> <td>1.73</td> <td>-3.91E-04</td> <td>2.06</td> <td>-1.73E-04</td> <td>1</td> | 2014-10-21 23:36 | 2215 | 1.73 | -3.91E-04              | 2.06 | -1.73E-04 | 1 |
| 2014-10-21 23:51         2230         1.72         -3.92E-04         2.05         -1.73E-04         1           2014-10-21 23:56         2235         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:01         2240         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:06         2245         1.72         -3.94E-04         2.06         -1.73E-04         1           2014-10-22 0:11         2250         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04 <td>2014-10-21 23:41</td> <td>2220</td> <td>1.72</td> <td>-3.91E-04</td> <td>2.05</td> <td>-1.73E-04</td> <td>1</td>       | 2014-10-21 23:41 | 2220 | 1.72 | -3.91E-04              | 2.05 | -1.73E-04 | 1 |
| 2014-10-21 23:56         2235         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:01         2240         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:06         2245         1.72         -3.94E-04         2.06         -1.73E-04         1           2014-10-22 0:11         2250         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.95E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.04 <td>2014-10-21 23:46</td> <td>2225</td> <td>1.72</td> <td>-3.92E-04</td> <td>2.05</td> <td>-1.73E-04</td> <td>1</td>        | 2014-10-21 23:46 | 2225 | 1.72 | -3.92E-04              | 2.05 | -1.73E-04 | 1 |
| 2014-10-22 0:01         2240         1.72         -3.93E-04         2.06         -1.73E-04         1           2014-10-22 0:06         2245         1.72         -3.94E-04         2.06         -1.73E-04         1           2014-10-22 0:11         2250         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.95E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.05         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:41         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.99E-04         2.05  | 2014-10-21 23:51 | 2230 | 1.72 | -3.92E-04              | 2.05 | -1.73E-04 | 1 |
| 2014-10-22 0:06         2245         1.72         -3.94E-04         2.06         -1.73E-04         1           2014-10-22 0:11         2250         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.95E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.99E-04         2.04  | 2014-10-21 23:56 | 2235 | 1.72 | -3.93E-04              | 2.06 | -1.73E-04 | 1 |
| 2014-10-22 0:11         2250         1.71         -3.94E-04         2.05         -1.73E-04         1           2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.05         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.04  | 2014-10-22 0:01  | 2240 | 1.72 | -3.93E-04              | 2.06 | -1.73E-04 | 1 |
| 2014-10-22 0:16         2255         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.05         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04  | 2014-10-22 0:06  | 2245 | 1.72 | -3.94E-04              | 2.06 | -1.73E-04 | 1 |
| 2014-10-22 0:21         2260         1.71         -3.95E-04         2.05         -1.73E-04         1           2014-10-22 0:26         2265         1.71         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.05         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.05         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04  | 2014-10-22 0:11  | 2250 | 1.71 | -3.94E-04              | 2.05 | -1.73E-04 | 1 |
| 2014-10-22 0:26         2265         1.71         -3.96E-04         2.04         -1.74E-04         1           2014-10-22 0:31         2270         1.70         -3.96E-04         2.05         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.04  | 2014-10-22 0:16  | 2255 | 1.71 | -3.95E-04              | 2.05 | -1.73E-04 | 1 |
| 2014-10-22 0:31         2270         1.70         -3.96E-04         2.05         -1.74E-04         1           2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.05         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.04         -1.75E-04         1           2014-10-22 1:21         2320         1.68         -4.01E-04         2.04  | 2014-10-22 0:21  | 2260 | 1.71 | -3.95E-04              | 2.05 | -1.73E-04 | 1 |
| 2014-10-22 0:36         2275         1.70         -3.97E-04         2.04         -1.74E-04         1           2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.05         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.05         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.04         -1.75E-04         1           2014-10-22 1:26         2325         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:31         2330         1.68         -4.02E-04         2.04  | 2014-10-22 0:26  | 2265 | 1.71 | -3.96E-04              | 2.04 | -1.74E-04 | 1 |
| 2014-10-22 0:41         2280         1.69         -3.97E-04         2.05         -1.74E-04         1           2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.05         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.05         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:26         2325         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:31         2330         1.68         -4.02E-04         2.04         -1.75E-04         1           2014-10-22 1:36         2335         1.68         -4.02E-04         2.04  | 2014-10-22 0:31  | 2270 | 1.70 | -3.96E-04              | 2.05 | -1.74E-04 | 1 |
| 2014-10-22 0:46         2285         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 0:51         2290         1.70         -3.98E-04         2.05         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.05         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.05         -1.74E-04         1           2014-10-22 1:21         2320         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:26         2325         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:31         2330         1.68         -4.02E-04         2.04         -1.75E-04         1           2014-10-22 1:41         2340         1.68         -4.03E-04         2.04  | 2014-10-22 0:36  | 2275 | 1.70 | -3.97E-04              | 2.04 | -1.74E-04 | 1 |
| 2014-10-22 0:51         2290         1.70         -3.98E-04         2.05         -1.74E-04         1           2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.05         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.05         -1.74E-04         1           2014-10-22 1:21         2320         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:26         2325         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:31         2330         1.68         -4.02E-04         2.04         -1.75E-04         1           2014-10-22 1:36         2335         1.68         -4.02E-04         2.04         -1.75E-04         1           2014-10-22 1:41         2340         1.68         -4.03E-04         2.04  | 2014-10-22 0:41  | 2280 | 1.69 | -3.97E-04              | 2.05 | -1.74E-04 | 1 |
| 2014-10-22 0:56         2295         1.70         -3.98E-04         2.04         -1.74E-04         1           2014-10-22 1:01         2300         1.69         -3.99E-04         2.05         -1.74E-04         1           2014-10-22 1:06         2305         1.69         -3.99E-04         2.04         -1.74E-04         1           2014-10-22 1:11         2310         1.69         -4.00E-04         2.04         -1.74E-04         1           2014-10-22 1:16         2315         1.68         -4.00E-04         2.05         -1.74E-04         1           2014-10-22 1:21         2320         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:26         2325         1.68         -4.01E-04         2.04         -1.75E-04         1           2014-10-22 1:31         2330         1.68         -4.02E-04         2.04         -1.75E-04         1           2014-10-22 1:36         2335         1.68         -4.02E-04         2.04         -1.75E-04         1           2014-10-22 1:41         2340         1.68         -4.03E-04         2.04         -1.75E-04         1           2014-10-22 1:46         2345         1.68         -4.03E-04         2.04  | 2014-10-22 0:46  | 2285 | 1.70 | -3.98E-04              | 2.04 | -1.74E-04 | 1 |
| 2014-10-22 1:01       2300       1.69       -3.99E-04       2.05       -1.74E-04       1         2014-10-22 1:06       2305       1.69       -3.99E-04       2.04       -1.74E-04       1         2014-10-22 1:11       2310       1.69       -4.00E-04       2.04       -1.74E-04       1         2014-10-22 1:16       2315       1.68       -4.00E-04       2.05       -1.74E-04       1         2014-10-22 1:21       2320       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:26       2325       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:31       2330       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:36       2335       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:41       2340       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:46       2345       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:51       2350       1.67       -4.04E-04       2.04       -1.75E-04       1  | 2014-10-22 0:51  | 2290 | 1.70 | -3.98E-04              | 2.05 | -1.74E-04 | 1 |
| 2014-10-22 1:06       2305       1.69       -3.99E-04       2.04       -1.74E-04       1         2014-10-22 1:11       2310       1.69       -4.00E-04       2.04       -1.74E-04       1         2014-10-22 1:16       2315       1.68       -4.00E-04       2.05       -1.74E-04       1         2014-10-22 1:21       2320       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:26       2325       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:31       2330       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:36       2335       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:41       2340       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:46       2345       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:51       2350       1.67       -4.04E-04       2.04       -1.75E-04       1   | 2014-10-22 0:56  | 2295 | 1.70 | -3.98E-04              | 2.04 | -1.74E-04 | 1 |
| 2014-10-22 1:11       2310       1.69       -4.00E-04       2.04       -1.74E-04       1         2014-10-22 1:16       2315       1.68       -4.00E-04       2.05       -1.74E-04       1         2014-10-22 1:21       2320       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:26       2325       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:31       2330       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:36       2335       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:41       2340       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:46       2345       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:51       2350       1.67       -4.04E-04       2.04       -1.75E-04       1  | 2014-10-22 1:01  | 2300 | 1.69 | -3.99E-04              | 2.05 | -1.74E-04 | 1 |
| 2014-10-22 1:16       2315       1.68       -4.00E-04       2.05       -1.74E-04       1         2014-10-22 1:21       2320       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:26       2325       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:31       2330       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:36       2335       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:41       2340       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:46       2345       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:51       2350       1.67       -4.04E-04       2.04       -1.75E-04       1   | 2014-10-22 1:06  | 2305 | 1.69 | -3.99E-04              | 2.04 | -1.74E-04 | 1 |
| 2014-10-22 1:21       2320       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:26       2325       1.68       -4.01E-04       2.04       -1.75E-04       1         2014-10-22 1:31       2330       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:36       2335       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:41       2340       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:46       2345       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:51       2350       1.67       -4.04E-04       2.04       -1.75E-04       1  | 2014-10-22 1:11  | 2310 | 1.69 | -4.00E-04              | 2.04 | -1.74E-04 | 1 |
| 2014-10-22 1:26     2325     1.68     -4.01E-04     2.04     -1.75E-04     1       2014-10-22 1:31     2330     1.68     -4.02E-04     2.04     -1.75E-04     1       2014-10-22 1:36     2335     1.68     -4.02E-04     2.04     -1.75E-04     1       2014-10-22 1:41     2340     1.68     -4.03E-04     2.04     -1.75E-04     1       2014-10-22 1:46     2345     1.68     -4.03E-04     2.04     -1.75E-04     1       2014-10-22 1:51     2350     1.67     -4.04E-04     2.04     -1.75E-04     1   | 2014-10-22 1:16  | 2315 | 1.68 | -4.00E-04              | 2.05 | -1.74E-04 | 1 |
| 2014-10-22 1:31       2330       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:36       2335       1.68       -4.02E-04       2.04       -1.75E-04       1         2014-10-22 1:41       2340       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:46       2345       1.68       -4.03E-04       2.04       -1.75E-04       1         2014-10-22 1:51       2350       1.67       -4.04E-04       2.04       -1.75E-04       1  | 2014-10-22 1:21  | 2320 | 1.68 | -4.01E-04              | 2.04 | -1.75E-04 | 1 |
| 2014-10-22 1:36     2335     1.68     -4.02E-04     2.04     -1.75E-04     1       2014-10-22 1:41     2340     1.68     -4.03E-04     2.04     -1.75E-04     1       2014-10-22 1:46     2345     1.68     -4.03E-04     2.04     -1.75E-04     1       2014-10-22 1:51     2350     1.67     -4.04E-04     2.04     -1.75E-04     1   | 2014-10-22 1:26  | 2325 | 1.68 | -4.01E-04              | 2.04 | -1.75E-04 | 1 |
| 2014-10-22 1:41     2340     1.68     -4.03E-04     2.04     -1.75E-04     1       2014-10-22 1:46     2345     1.68     -4.03E-04     2.04     -1.75E-04     1       2014-10-22 1:51     2350     1.67     -4.04E-04     2.04     -1.75E-04     1  | 2014-10-22 1:31  | 2330 | 1.68 | $-4.0\overline{2E-04}$ | 2.04 | -1.75E-04 | 1 |
| 2014-10-22 1:46 2345 1.68 -4.03E-04 2.04 -1.75E-04 1<br>2014-10-22 1:51 2350 1.67 -4.04E-04 2.04 -1.75E-04 1  | 2014-10-22 1:36  | 2335 | 1.68 | -4.02E-04              | 2.04 | -1.75E-04 | 1 |
| 2014-10-22 1:51 2350 1.67 -4.04E-04 2.04 -1.75E-04 1  | 2014-10-22 1:41  | 2340 | 1.68 | -4.03E-04              | 2.04 | -1.75E-04 | 1 |
|   |                  | 2345 | 1.68 | -4.03E-04              | 2.04 | -1.75E-04 | 1 |
| 2014-10-22 1:56   2355   1.67   -4.04E-04   2.03   -1.75E-04   1  | 2014-10-22 1:51  | 2350 | 1.67 | -4.04E-04              | 2.04 |           | 1 |
|   | 2014-10-22 1:56  | 2355 | 1.67 | -4.04E-04              | 2.03 | -1.75E-04 | 1 |

| 2014-10-22 2:01   2360   1.67  |                 |      |      |           |      |           |   |
|--|-----------------|------|------|-----------|------|-----------|---|
| 2014-10-22 2:11   2370   | 2014-10-22 2:01 | 2360 | 1.67 | -4.05E-04 | 2.03 | -1.75E-04 | 1 |
| 2014-10-22 2:16   2375   1.66  | 2014-10-22 2:06 | 2365 | 1.66 | -4.05E-04 | 2.03 | -1.75E-04 | 1 |
| 2014-10-22 2:21   2380   | 2014-10-22 2:11 | 2370 | 1.67 | -4.06E-04 | 2.03 | -1.75E-04 | 1 |
| 2014-10-22 2:26  | 2014-10-22 2:16 | 2375 | 1.66 | -4.06E-04 | 2.04 | -1.75E-04 | 1 |
| 2014-10-22 2:31   2390   | 2014-10-22 2:21 | 2380 | 1.66 | -4.06E-04 | 2.03 | -1.76E-04 | 1 |
| 2014-10-22 2:36  | 2014-10-22 2:26 | 2385 | 1.66 | -4.07E-04 | 2.03 | -1.76E-04 | 1 |
| 2014-10-22 2:41  | 2014-10-22 2:31 | 2390 | 1.66 | -4.07E-04 | 2.03 | -1.76E-04 | 1 |
| 2014-10-22 2:46  | 2014-10-22 2:36 | 2395 | 1.66 | -4.08E-04 | 2.03 | -1.76E-04 | 1 |
| 2014-10-22 2:51  | 2014-10-22 2:41 | 2400 | 1.65 | -4.08E-04 | 2.03 | -1.76E-04 | 1 |
| 2014-10-22 2:56         2415         1.65         -4.10E-04         2.02         -1.76E-04         1           2014-10-22 3:01         2420         1.64         -4.10E-04         2.02         -1.76E-04         1           2014-10-22 3:06         2425         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:11         2430         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:16         2435         1.64         -4.12E-04         2.02         -1.76E-04         1           2014-10-22 3:21         2440         1.63         -4.12E-04         2.02         -1.77E-04         1           2014-10-22 3:26         2445         1.63         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.15E-04         2.00 | 2014-10-22 2:46 | 2405 | 1.65 | -4.09E-04 | 2.03 | -1.76E-04 | 1 |
| 2014-10-22 3:01         2420         1.64         -4.10E-04         2.02         -1.76E-04         1           2014-10-22 3:06         2425         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:11         2430         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:16         2435         1.64         -4.12E-04         2.02         -1.76E-04         1           2014-10-22 3:21         2440         1.63         -4.12E-04         2.02         -1.77E-04         1           2014-10-22 3:26         2445         1.63         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:41         2465         1.63         -4.15E-04         2.01 | 2014-10-22 2:51 | 2410 | 1.64 | -4.09E-04 | 2.02 | -1.76E-04 | 1 |
| 2014-10-22 3:06         2425         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:11         2430         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:16         2435         1.64         -4.12E-04         2.02         -1.76E-04         1           2014-10-22 3:21         2440         1.63         -4.12E-04         2.02         -1.77E-04         1           2014-10-22 3:26         2445         1.63         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.15E-04         2.01 | 2014-10-22 2:56 | 2415 | 1.65 | -4.10E-04 | 2.02 | -1.76E-04 | 1 |
| 2014-10-22 3:11         2430         1.64         -4.11E-04         2.02         -1.76E-04         1           2014-10-22 3:16         2435         1.64         -4.12E-04         2.02         -1.76E-04         1           2014-10-22 3:21         2440         1.63         -4.12E-04         2.02         -1.77E-04         1           2014-10-22 3:26         2445         1.63         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01 | 2014-10-22 3:01 | 2420 | 1.64 | -4.10E-04 | 2.02 | -1.76E-04 | 1 |
| 2014-10-22 3:16  | 2014-10-22 3:06 | 2425 | 1.64 | -4.11E-04 | 2.02 | -1.76E-04 | 1 |
| 2014-10-22 3:21         2440         1.63         -4.12E-04         2.02         -1.77E-04         1           2014-10-22 3:26         2445         1.63         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01 | 2014-10-22 3:11 | 2430 | 1.64 | -4.11E-04 | 2.02 | -1.76E-04 | 1 |
| 2014-10-22 3:26         2445         1.63         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01         -1.77E-04         1           2014-10-22 4:26         2505         1.61         -4.18E-04         2.01 | 2014-10-22 3:16 | 2435 | 1.64 | -4.12E-04 | 2.02 | -1.76E-04 | 1 |
| 2014-10-22 3:31         2450         1.63         -4.13E-04         2.01         -1.77E-04         1           2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01         -1.77E-04         1           2014-10-22 4:16         2495         1.61         -4.17E-04         2.00         -1.77E-04         1           2014-10-22 4:26         2505         1.61         -4.18E-04         2.00 | 2014-10-22 3:21 | 2440 | 1.63 | -4.12E-04 | 2.02 | -1.77E-04 | 1 |
| 2014-10-22 3:36         2455         1.64         -4.13E-04         2.02         -1.77E-04         1           2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01         -1.77E-04         1           2014-10-22 4:16         2495         1.61         -4.17E-04         2.00         -1.77E-04         1           2014-10-22 4:26         2505         1.61         -4.18E-04         2.01         -1.78E-04         1           2014-10-22 4:31         2510         1.61         -4.19E-04         2.00 | 2014-10-22 3:26 | 2445 | 1.63 | -4.13E-04 | 2.02 | -1.77E-04 | 1 |
| 2014-10-22 3:41         2460         1.63         -4.14E-04         2.01         -1.77E-04         1           2014-10-22 3:46         2465         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01         -1.77E-04         1           2014-10-22 4:16         2495         1.61         -4.17E-04         2.00         -1.77E-04         1           2014-10-22 4:26         2505         1.61         -4.18E-04         2.01         -1.78E-04         1           2014-10-22 4:31         2510         1.61         -4.19E-04         2.00         -1.78E-04         1           2014-10-22 4:41         2520         1.61         -4.19E-04         2.01 | 2014-10-22 3:31 | 2450 | 1.63 | -4.13E-04 | 2.01 | -1.77E-04 | 1 |
| 2014-10-22 3:46         2465         1.63         -4.14E-04         2.00         -1.77E-04         1           2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01         -1.77E-04         1           2014-10-22 4:16         2495         1.61         -4.17E-04         2.00         -1.77E-04         1           2014-10-22 4:26         2505         1.61         -4.18E-04         2.01         -1.78E-04         1           2014-10-22 4:31         2510         1.61         -4.19E-04         2.00         -1.78E-04         1           2014-10-22 4:36         2515         1.61         -4.19E-04         2.01         -1.78E-04         1           2014-10-22 4:46         2525         1.60         -4.20E-04         2.01 | 2014-10-22 3:36 | 2455 | 1.64 | -4.13E-04 | 2.02 | -1.77E-04 | 1 |
| 2014-10-22 3:51         2470         1.62         -4.15E-04         2.01         -1.77E-04         1           2014-10-22 3:56         2475         1.62         -4.15E-04         2.00         -1.77E-04         1           2014-10-22 4:01         2480         1.62         -4.16E-04         2.01         -1.77E-04         1           2014-10-22 4:06         2485         1.62         -4.16E-04         2.02         -1.77E-04         1           2014-10-22 4:11         2490         1.62         -4.17E-04         2.01         -1.77E-04         1           2014-10-22 4:16         2495         1.61         -4.17E-04         2.00         -1.77E-04         1           2014-10-22 4:21         2500         1.61         -4.18E-04         2.01         -1.78E-04         1           2014-10-22 4:26         2505         1.61         -4.18E-04         2.00         -1.78E-04         1           2014-10-22 4:31         2510         1.61         -4.19E-04         2.00         -1.78E-04         1           2014-10-22 4:36         2515         1.61         -4.19E-04         2.01         -1.78E-04         1           2014-10-22 4:46         2525         1.60         -4.20E-04         2.01 | 2014-10-22 3:41 | 2460 | 1.63 | -4.14E-04 | 2.01 | -1.77E-04 | 1 |
| 2014-10-22 3:56       2475       1.62       -4.15E-04       2.00       -1.77E-04       1         2014-10-22 4:01       2480       1.62       -4.16E-04       2.01       -1.77E-04       1         2014-10-22 4:06       2485       1.62       -4.16E-04       2.02       -1.77E-04       1         2014-10-22 4:11       2490       1.62       -4.17E-04       2.01       -1.77E-04       1         2014-10-22 4:16       2495       1.61       -4.17E-04       2.00       -1.77E-04       1         2014-10-22 4:21       2500       1.61       -4.18E-04       2.01       -1.78E-04       1         2014-10-22 4:26       2505       1.61       -4.18E-04       2.00       -1.78E-04       1         2014-10-22 4:31       2510       1.61       -4.19E-04       2.00       -1.78E-04       1         2014-10-22 4:36       2515       1.61       -4.19E-04       2.01       -1.78E-04       1         2014-10-22 4:41       2520       1.60       -4.20E-04       2.01       -1.78E-04       1         2014-10-22 4:46       2525       1.60       -4.20E-04       2.00       -1.78E-04       1   | 2014-10-22 3:46 | 2465 | 1.63 | -4.14E-04 | 2.00 | -1.77E-04 | 1 |
| 2014-10-22 4:01       2480       1.62       -4.16E-04       2.01       -1.77E-04       1         2014-10-22 4:06       2485       1.62       -4.16E-04       2.02       -1.77E-04       1         2014-10-22 4:11       2490       1.62       -4.17E-04       2.01       -1.77E-04       1         2014-10-22 4:16       2495       1.61       -4.17E-04       2.00       -1.77E-04       1         2014-10-22 4:21       2500       1.61       -4.18E-04       2.01       -1.78E-04       1         2014-10-22 4:26       2505       1.61       -4.18E-04       2.00       -1.78E-04       1         2014-10-22 4:31       2510       1.61       -4.19E-04       2.00       -1.78E-04       1         2014-10-22 4:36       2515       1.61       -4.19E-04       2.01       -1.78E-04       1         2014-10-22 4:41       2520       1.60       -4.20E-04       2.01       -1.78E-04       1         2014-10-22 4:46       2525       1.60       -4.20E-04       2.00       -1.78E-04       1  | 2014-10-22 3:51 | 2470 | 1.62 | -4.15E-04 | 2.01 | -1.77E-04 | 1 |
| 2014-10-22 4:06       2485       1.62       -4.16E-04       2.02       -1.77E-04       1         2014-10-22 4:11       2490       1.62       -4.17E-04       2.01       -1.77E-04       1         2014-10-22 4:16       2495       1.61       -4.17E-04       2.00       -1.77E-04       1         2014-10-22 4:21       2500       1.61       -4.18E-04       2.01       -1.78E-04       1         2014-10-22 4:26       2505       1.61       -4.18E-04       2.00       -1.78E-04       1         2014-10-22 4:31       2510       1.61       -4.19E-04       2.00       -1.78E-04       1         2014-10-22 4:36       2515       1.61       -4.19E-04       2.01       -1.78E-04       1         2014-10-22 4:41       2520       1.60       -4.20E-04       2.01       -1.78E-04       1         2014-10-22 4:46       2525       1.60       -4.20E-04       2.00       -1.78E-04       1   | 2014-10-22 3:56 | 2475 | 1.62 | -4.15E-04 | 2.00 | -1.77E-04 | 1 |
| 2014-10-22 4:11       2490       1.62       -4.17E-04       2.01       -1.77E-04       1         2014-10-22 4:16       2495       1.61       -4.17E-04       2.00       -1.77E-04       1         2014-10-22 4:21       2500       1.61       -4.18E-04       2.01       -1.78E-04       1         2014-10-22 4:26       2505       1.61       -4.18E-04       2.00       -1.78E-04       1         2014-10-22 4:31       2510       1.61       -4.19E-04       2.00       -1.78E-04       1         2014-10-22 4:36       2515       1.61       -4.19E-04       2.01       -1.78E-04       1         2014-10-22 4:41       2520       1.60       -4.20E-04       2.01       -1.78E-04       1         2014-10-22 4:46       2525       1.60       -4.20E-04       2.00       -1.78E-04       1  | 2014-10-22 4:01 | 2480 | 1.62 | -4.16E-04 | 2.01 | -1.77E-04 | 1 |
| 2014-10-22 4:16       2495       1.61       -4.17E-04       2.00       -1.77E-04       1         2014-10-22 4:21       2500       1.61       -4.18E-04       2.01       -1.78E-04       1         2014-10-22 4:26       2505       1.61       -4.18E-04       2.00       -1.78E-04       1         2014-10-22 4:31       2510       1.61       -4.19E-04       2.00       -1.78E-04       1         2014-10-22 4:36       2515       1.61       -4.19E-04       2.01       -1.78E-04       1         2014-10-22 4:41       2520       1.60       -4.20E-04       2.01       -1.78E-04       1         2014-10-22 4:46       2525       1.60       -4.20E-04       2.00       -1.78E-04       1   | 2014-10-22 4:06 | 2485 | 1.62 | -4.16E-04 | 2.02 | -1.77E-04 | 1 |
| 2014-10-22 4:21     2500     1.61     -4.18E-04     2.01     -1.78E-04     1       2014-10-22 4:26     2505     1.61     -4.18E-04     2.00     -1.78E-04     1       2014-10-22 4:31     2510     1.61     -4.19E-04     2.00     -1.78E-04     1       2014-10-22 4:36     2515     1.61     -4.19E-04     2.01     -1.78E-04     1       2014-10-22 4:41     2520     1.60     -4.20E-04     2.01     -1.78E-04     1       2014-10-22 4:46     2525     1.60     -4.20E-04     2.00     -1.78E-04     1  | 2014-10-22 4:11 | 2490 | 1.62 | -4.17E-04 | 2.01 | -1.77E-04 | 1 |
| 2014-10-22 4:26       2505       1.61       -4.18E-04       2.00       -1.78E-04       1         2014-10-22 4:31       2510       1.61       -4.19E-04       2.00       -1.78E-04       1         2014-10-22 4:36       2515       1.61       -4.19E-04       2.01       -1.78E-04       1         2014-10-22 4:41       2520       1.60       -4.20E-04       2.01       -1.78E-04       1         2014-10-22 4:46       2525       1.60       -4.20E-04       2.00       -1.78E-04       1   | 2014-10-22 4:16 | 2495 | 1.61 | -4.17E-04 | 2.00 | -1.77E-04 | 1 |
| 2014-10-22 4:31     2510     1.61     -4.19E-04     2.00     -1.78E-04     1       2014-10-22 4:36     2515     1.61     -4.19E-04     2.01     -1.78E-04     1       2014-10-22 4:41     2520     1.60     -4.20E-04     2.01     -1.78E-04     1       2014-10-22 4:46     2525     1.60     -4.20E-04     2.00     -1.78E-04     1  | 2014-10-22 4:21 | 2500 | 1.61 | -4.18E-04 | 2.01 | -1.78E-04 | 1 |
| 2014-10-22 4:36     2515     1.61     -4.19E-04     2.01     -1.78E-04     1       2014-10-22 4:41     2520     1.60     -4.20E-04     2.01     -1.78E-04     1       2014-10-22 4:46     2525     1.60     -4.20E-04     2.00     -1.78E-04     1   | 2014-10-22 4:26 | 2505 | 1.61 | -4.18E-04 | 2.00 | -1.78E-04 | 1 |
| 2014-10-22 4:41 2520 1.60 -4.20E-04 2.01 -1.78E-04 1<br>2014-10-22 4:46 2525 1.60 -4.20E-04 2.00 -1.78E-04 1   | 2014-10-22 4:31 | 2510 | 1.61 | -4.19E-04 | 2.00 | -1.78E-04 | 1 |
| 2014-10-22 4:46  | 2014-10-22 4:36 | 2515 | 1.61 | -4.19E-04 | 2.01 | -1.78E-04 | 1 |
|  | 2014-10-22 4:41 | 2520 | 1.60 | -4.20E-04 | 2.01 | -1.78E-04 | 1 |
| 2014-10-22 4:51 2530 1.60 -4.20E-04 2.00 -1.78E-04 1   | 2014-10-22 4:46 | 2525 | 1.60 | -4.20E-04 | 2.00 | -1.78E-04 | 1 |
|  | 2014-10-22 4:51 | 2530 | 1.60 | -4.20E-04 | 2.00 | -1.78E-04 | 1 |

| 2014-10-22 4:56 | 2535 | 1.59 | -4.21E-04 | 2.01 | -1.78E-04 | 1 |
|-----------------|------|------|-----------|------|-----------|---|
| 2014-10-22 5:01 | 2540 | 1.60 | -4.21E-04 | 2.00 | -1.78E-04 | 1 |
| 2014-10-22 5:06 | 2545 | 1.60 | -4.22E-04 | 2.00 | -1.78E-04 | 1 |
| 2014-10-22 5:11 | 2550 | 1.59 | -4.22E-04 | 2.00 | -1.78E-04 | 1 |
| 2014-10-22 5:16 | 2555 | 1.59 | -4.23E-04 | 2.00 | -1.78E-04 | 1 |
| 2014-10-22 5:21 | 2560 | 1.58 | -4.23E-04 | 2.00 | -1.79E-04 | 1 |
| 2014-10-22 5:26 | 2565 | 1.58 | -4.24E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 5:31 | 2570 | 1.58 | -4.24E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 5:36 | 2575 | 1.58 | -4.25E-04 | 2.00 | -1.79E-04 | 1 |
| 2014-10-22 5:41 | 2580 | 1.58 | -4.25E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 5:46 | 2585 | 1.57 | -4.26E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 5:51 | 2590 | 1.58 | -4.26E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 5:56 | 2595 | 1.57 | -4.27E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 6:01 | 2600 | 1.57 | -4.27E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 6:06 | 2605 | 1.57 | -4.28E-04 | 1.99 | -1.79E-04 | 1 |
| 2014-10-22 6:11 | 2610 | 1.56 | -4.28E-04 | 1.98 | -1.79E-04 | 1 |
| 2014-10-22 6:16 | 2615 | 1.56 | -4.28E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:21 | 2620 | 1.56 | -4.29E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:26 | 2625 | 1.56 | -4.29E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:31 | 2630 | 1.56 | -4.30E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:36 | 2635 | 1.55 | -4.30E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:41 | 2640 | 1.56 | -4.31E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:46 | 2645 | 1.55 | -4.31E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:51 | 2650 | 1.55 | -4.32E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 6:56 | 2655 | 1.54 | -4.32E-04 | 1.97 | -1.80E-04 | 1 |
| 2014-10-22 7:01 | 2660 | 1.54 | -4.33E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 7:06 | 2665 | 1.54 | -4.33E-04 | 1.98 | -1.80E-04 | 1 |
| 2014-10-22 7:11 | 2670 | 1.54 | -4.34E-04 | 1.97 | -1.80E-04 | 1 |
| 2014-10-22 7:16 | 2675 | 1.54 | -4.34E-04 | 1.98 | -1.81E-04 | 1 |
| 2014-10-22 7:21 | 2680 | 1.53 | -4.35E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 7:26 | 2685 | 1.53 | -4.35E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 7:31 | 2690 | 1.53 | -4.35E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 7:36 | 2695 | 1.53 | -4.36E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 7:41 | 2700 | 1.53 | -4.36E-04 | 1.96 | -1.81E-04 | 1 |
| 2014-10-22 7:46 | 2705 | 1.53 | -4.37E-04 | 1.97 | -1.81E-04 | 1 |
|                 |      |      |           | -    |           |   |

| 2014-10-22 7:51  |                  |      |      |           |      |           |   |
|--|------------------|------|------|-----------|------|-----------|---|
| 2014-10-22 8:01   2720   1.51   -4.38E-04   1.97   -1.81E-04   1   2014-10-22 8:06   2725   1.51   -4.39E-04   1.97   -1.81E-04   1   2014-10-22 8:16   2735   1.51   -4.39E-04   1.97   -1.81E-04   1   2014-10-22 8:16   2735   1.51   -4.40E-04   1.97   -1.82E-04   1   2014-10-22 8:21   2740   1.50   -4.40E-04   1.96   -1.82E-04   1   2014-10-22 8:26   2745   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:36   2755   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:36   2755   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 10:11   2850   2.41   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:16   2855   2.40   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:26   2865   2.37   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:36   2865   2.37   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:36   2875   2.37   -2.15E-04   2.39   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 10:56   2895   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 10:56   2895   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 11:01   2900   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:36   2925   2.33   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11: | 2014-10-22 7:51  | 2710 | 1.52 | -4.37E-04 | 1.96 | -1.81E-04 | 1 |
| 2014-10-22 8:06   2725   1.51  | 2014-10-22 7:56  | 2715 | 1.52 | -4.38E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 8:11   2730   | 2014-10-22 8:01  | 2720 | 1.51 | -4.38E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 8:16   2735   1.51   -4.40E-04   1.97   -1.82E-04   1   2014-10-22 8:21   2740   1.50   -4.40E-04   1.96   -1.82E-04   1   2014-10-22 8:26   2745   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:31   2750   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:36   2755   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 10:11   2850   2.41   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:16   2855   2.40   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:21   2860   2.39   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:22   2865   2.37   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:31   2870   2.38   -2.15E-04   2.39   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.83E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.40   -1.83E-04   2   2014-10-22 10:51   2890   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 10:56   2895   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 11:01   2900   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2905   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2905   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.37   -1.84E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.37   -1.84E-04   2   2014-10-22 | 2014-10-22 8:06  | 2725 | 1.51 | -4.39E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 8:21   2740   1.50   -4.40E-04   1.96   -1.82E-04   1   2014-10-22 8:26   2745   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:31   2750   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:36   2755   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:36   2755   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 10:11   2850   2.41   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:16   2855   2.40   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:21   2860   2.39   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:26   2865   2.37   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:31   2870   2.38   -2.15E-04   2.39   -1.82E-04   2   2014-10-22 10:36   2875   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.40   -1.83E-04   2   2014-10-22 10:51   2890   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 10:56   2895   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 11:01   2900   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2905   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2905   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.38   -1.84E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.38   -1.84E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.38   -1.84E-04   2   2014-10-22 11:31   2930   2.34   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.18E-04   2.35   -1.84E-04   2   2014-10-22 | 2014-10-22 8:11  | 2730 | 1.51 | -4.39E-04 | 1.97 | -1.81E-04 | 1 |
| 2014-10-22 8:26  | 2014-10-22 8:16  | 2735 | 1.51 | -4.40E-04 | 1.97 | -1.82E-04 | 1 |
| 2014-10-22 8:31   2750   1.50   -4.41E-04   1.96   -1.82E-04   1   2014-10-22 8:36   2755   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 10:11   2850   2.41   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:16   2855   2.40   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:21   2860   2.39   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:26   2865   2.37   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:31   2870   2.38   -2.15E-04   2.39   -1.82E-04   2   2014-10-22 10:36   2875   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.83E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.40   -1.83E-04   2   2014-10-22 10:51   2890   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 10:56   2895   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 11:01   2900   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2905   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2915   2.35   -2.16E-04   2.38   -1.84E-04   2   2014-10-22 11:16   2925   2.32   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:36   2935   2.34   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.38   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.35   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.18E-04   2.35   -1.84E-04   2   2014-10-22 11:56   2955   2.33   -2.18E-04   2.35   -1.85E-04   2   2014-10- | 2014-10-22 8:21  | 2740 | 1.50 | -4.40E-04 | 1.96 | -1.82E-04 | 1 |
| 2014-10-22 8:36   2755   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 8:41   2760   1.50   -4.42E-04   1.96   -1.82E-04   1   2014-10-22 10:11   2850   2.41   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:16   2855   2.40   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:21   2860   2.39   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:26   2865   2.37   -2.14E-04   2.40   -1.82E-04   2   2014-10-22 10:31   2870   2.38   -2.15E-04   2.39   -1.82E-04   2   2014-10-22 10:36   2875   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:41   2880   2.37   -2.15E-04   2.40   -1.82E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.40   -1.83E-04   2   2014-10-22 10:46   2885   2.37   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 10:56   2895   2.36   -2.15E-04   2.38   -1.83E-04   2   2014-10-22 11:01   2900   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:10   2900   2.35   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2905   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:16   2915   2.33   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:26   2925   2.34   -2.16E-04   2.38   -1.83E-04   2   2014-10-22 11:26   2925   2.32   -2.17E-04   2.38   -1.83E-04   2   2014-10-22 11:31   2930   2.34   -2.16E-04   2.37   -1.84E-04   2   2014-10-22 11:31   2930   2.34   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:41   2940   2.33   -2.17E-04   2.38   -1.84E-04   2   2014-10-22 11:41   2940   2.33   -2.17E-04   2.38   -1.84E-04   2   2014-10-22 11:41   2940   2.33   -2.17E-04   2.38   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.38   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.37   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.17E-04   2.35   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.18E-04   2.35   -1.84E-04   2   2014-10-22 11:46   2945   2.33   -2.18E-04   2.35   -1.84E-04   2   2014-1 | 2014-10-22 8:26  | 2745 | 1.50 | -4.41E-04 | 1.96 | -1.82E-04 | 1 |
| 2014-10-22 8:41         2760         1.50         -4.42E-04         1.96         -1.82E-04         1           2014-10-22 10:11         2850         2.41         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:16         2855         2.40         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:21         2860         2.39         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:26         2865         2.37         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:31         2870         2.38         -2.15E-04         2.39         -1.82E-04         2           2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04 <td< td=""><td>2014-10-22 8:31</td><td>2750</td><td>1.50</td><td>-4.41E-04</td><td>1.96</td><td>-1.82E-04</td><td>1</td></td<>   | 2014-10-22 8:31  | 2750 | 1.50 | -4.41E-04 | 1.96 | -1.82E-04 | 1 |
| 2014-10-22 10:11         2850         2.41         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:16         2855         2.40         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:21         2860         2.39         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:26         2865         2.37         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:31         2870         2.38         -2.15E-04         2.39         -1.82E-04         2           2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04 <t< td=""><td>2014-10-22 8:36</td><td>2755</td><td>1.50</td><td>-4.42E-04</td><td>1.96</td><td>-1.82E-04</td><td>1</td></t<>  | 2014-10-22 8:36  | 2755 | 1.50 | -4.42E-04 | 1.96 | -1.82E-04 | 1 |
| 2014-10-22 10:16         2855         2.40         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:21         2860         2.39         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:26         2865         2.37         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:31         2870         2.38         -2.15E-04         2.39         -1.82E-04         2           2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.33         -2.16E-04 <t< td=""><td>2014-10-22 8:41</td><td>2760</td><td>1.50</td><td>-4.42E-04</td><td>1.96</td><td>-1.82E-04</td><td>1</td></t<>  | 2014-10-22 8:41  | 2760 | 1.50 | -4.42E-04 | 1.96 | -1.82E-04 | 1 |
| 2014-10-22 10:21         2860         2.39         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:26         2865         2.37         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:31         2870         2.38         -2.15E-04         2.39         -1.82E-04         2           2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:10         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04 <t< td=""><td>2014-10-22 10:11</td><td>2850</td><td>2.41</td><td>-2.14E-04</td><td>2.40</td><td>-1.82E-04</td><td>2</td></t<>   | 2014-10-22 10:11 | 2850 | 2.41 | -2.14E-04 | 2.40 | -1.82E-04 | 2 |
| 2014-10-22 10:26         2865         2.37         -2.14E-04         2.40         -1.82E-04         2           2014-10-22 10:31         2870         2.38         -2.15E-04         2.39         -1.82E-04         2           2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.36         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04 <t< td=""><td>2014-10-22 10:16</td><td>2855</td><td>2.40</td><td>-2.14E-04</td><td>2.40</td><td>-1.82E-04</td><td>2</td></t<>   | 2014-10-22 10:16 | 2855 | 2.40 | -2.14E-04 | 2.40 | -1.82E-04 | 2 |
| 2014-10-22 10:31         2870         2.38         -2.15E-04         2.39         -1.82E-04         2           2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04 <t< td=""><td>2014-10-22 10:21</td><td>2860</td><td>2.39</td><td>-2.14E-04</td><td>2.40</td><td>-1.82E-04</td><td>2</td></t<>   | 2014-10-22 10:21 | 2860 | 2.39 | -2.14E-04 | 2.40 | -1.82E-04 | 2 |
| 2014-10-22 10:36         2875         2.37         -2.15E-04         2.40         -1.82E-04         2           2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:12         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.38         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04 <t< td=""><td>2014-10-22 10:26</td><td>2865</td><td>2.37</td><td>-2.14E-04</td><td>2.40</td><td>-1.82E-04</td><td>2</td></t<>   | 2014-10-22 10:26 | 2865 | 2.37 | -2.14E-04 | 2.40 | -1.82E-04 | 2 |
| 2014-10-22 10:41         2880         2.37         -2.15E-04         2.40         -1.83E-04         2           2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.38         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04 <t< td=""><td>2014-10-22 10:31</td><td>2870</td><td>2.38</td><td>-2.15E-04</td><td>2.39</td><td>-1.82E-04</td><td>2</td></t<>   | 2014-10-22 10:31 | 2870 | 2.38 | -2.15E-04 | 2.39 | -1.82E-04 | 2 |
| 2014-10-22 10:46         2885         2.37         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.36         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.38         -1.84E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04 <t< td=""><td>2014-10-22 10:36</td><td>2875</td><td>2.37</td><td>-2.15E-04</td><td>2.40</td><td>-1.82E-04</td><td>2</td></t<>   | 2014-10-22 10:36 | 2875 | 2.37 | -2.15E-04 | 2.40 | -1.82E-04 | 2 |
| 2014-10-22 10:51         2890         2.36         -2.15E-04         2.39         -1.83E-04         2           2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.36         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:41         2940         2.33         -2.17E-04 <t< td=""><td>2014-10-22 10:41</td><td>2880</td><td>2.37</td><td>-2.15E-04</td><td>2.40</td><td>-1.83E-04</td><td>2</td></t<>   | 2014-10-22 10:41 | 2880 | 2.37 | -2.15E-04 | 2.40 | -1.83E-04 | 2 |
| 2014-10-22 10:56         2895         2.36         -2.15E-04         2.38         -1.83E-04         2           2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.36         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:41         2940         2.33         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:46         2945         2.33         -2.17E-04 <t< td=""><td>2014-10-22 10:46</td><td>2885</td><td>2.37</td><td>-2.15E-04</td><td>2.38</td><td>-1.83E-04</td><td>2</td></t<>   | 2014-10-22 10:46 | 2885 | 2.37 | -2.15E-04 | 2.38 | -1.83E-04 | 2 |
| 2014-10-22 11:01         2900         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:06         2905         2.34         -2.16E-04         2.36         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:41         2940         2.33         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:46         2945         2.33         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:51         2950         2.33         -2.18E-04 <t< td=""><td>2014-10-22 10:51</td><td>2890</td><td>2.36</td><td>-2.15E-04</td><td>2.39</td><td>-1.83E-04</td><td>2</td></t<>   | 2014-10-22 10:51 | 2890 | 2.36 | -2.15E-04 | 2.39 | -1.83E-04 | 2 |
| 2014-10-22 11:06         2905         2.34         -2.16E-04         2.36         -1.83E-04         2           2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:41         2940         2.33         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:46         2945         2.33         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:51         2950         2.33         -2.18E-04         2.35         -1.84E-04         2           2014-10-22 11:56         2955         2.33         -2.18E-04 <t< td=""><td>2014-10-22 10:56</td><td>2895</td><td>2.36</td><td>-2.15E-04</td><td>2.38</td><td>-1.83E-04</td><td>2</td></t<>   | 2014-10-22 10:56 | 2895 | 2.36 | -2.15E-04 | 2.38 | -1.83E-04 | 2 |
| 2014-10-22 11:11         2910         2.33         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:41         2940         2.33         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:46         2945         2.33         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:51         2950         2.33         -2.18E-04         2.35         -1.84E-04         2           2014-10-22 11:56         2955         2.33         -2.18E-04         2.34         -1.85E-04         2           2014-10-22 12:01         2960         2.33         -2.18E-04 <t< td=""><td>2014-10-22 11:01</td><td>2900</td><td>2.35</td><td>-2.16E-04</td><td>2.38</td><td>-1.83E-04</td><td>2</td></t<>   | 2014-10-22 11:01 | 2900 | 2.35 | -2.16E-04 | 2.38 | -1.83E-04 | 2 |
| 2014-10-22 11:16         2915         2.35         -2.16E-04         2.38         -1.83E-04         2           2014-10-22 11:21         2920         2.34         -2.16E-04         2.39         -1.84E-04         2           2014-10-22 11:26         2925         2.32         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:31         2930         2.34         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:36         2935         2.34         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:41         2940         2.33         -2.17E-04         2.38         -1.84E-04         2           2014-10-22 11:46         2945         2.33         -2.17E-04         2.37         -1.84E-04         2           2014-10-22 11:51         2950         2.33         -2.18E-04         2.35         -1.84E-04         2           2014-10-22 11:56         2955         2.33         -2.18E-04         2.34         -1.85E-04         2           2014-10-22 12:01         2960         2.33         -2.18E-04         2.37         -1.85E-04         2  | 2014-10-22 11:06 | 2905 | 2.34 | -2.16E-04 | 2.36 | -1.83E-04 | 2 |
| 2014-10-22 11:21       2920       2.34       -2.16E-04       2.39       -1.84E-04       2         2014-10-22 11:26       2925       2.32       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:31       2930       2.34       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:36       2935       2.34       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:41       2940       2.33       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:46       2945       2.33       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:51       2950       2.33       -2.18E-04       2.35       -1.84E-04       2         2014-10-22 11:56       2955       2.33       -2.18E-04       2.34       -1.85E-04       2         2014-10-22 12:01       2960       2.33       -2.18E-04       2.37       -1.85E-04       2  | 2014-10-22 11:11 | 2910 | 2.33 | -2.16E-04 | 2.38 | -1.83E-04 | 2 |
| 2014-10-22 11:26       2925       2.32       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:31       2930       2.34       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:36       2935       2.34       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:41       2940       2.33       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:46       2945       2.33       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:51       2950       2.33       -2.18E-04       2.35       -1.84E-04       2         2014-10-22 11:56       2955       2.33       -2.18E-04       2.34       -1.85E-04       2         2014-10-22 12:01       2960       2.33       -2.18E-04       2.37       -1.85E-04       2  | 2014-10-22 11:16 | 2915 | 2.35 | -2.16E-04 | 2.38 | -1.83E-04 | 2 |
| 2014-10-22 11:31       2930       2.34       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:36       2935       2.34       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:41       2940       2.33       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:46       2945       2.33       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:51       2950       2.33       -2.18E-04       2.35       -1.84E-04       2         2014-10-22 11:56       2955       2.33       -2.18E-04       2.34       -1.85E-04       2         2014-10-22 12:01       2960       2.33       -2.18E-04       2.37       -1.85E-04       2  | 2014-10-22 11:21 | 2920 | 2.34 | -2.16E-04 | 2.39 | -1.84E-04 | 2 |
| 2014-10-22 11:36       2935       2.34       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:41       2940       2.33       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:46       2945       2.33       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:51       2950       2.33       -2.18E-04       2.35       -1.84E-04       2         2014-10-22 11:56       2955       2.33       -2.18E-04       2.34       -1.85E-04       2         2014-10-22 12:01       2960       2.33       -2.18E-04       2.37       -1.85E-04       2  | 2014-10-22 11:26 | 2925 | 2.32 | -2.17E-04 | 2.37 | -1.84E-04 | 2 |
| 2014-10-22 11:41       2940       2.33       -2.17E-04       2.38       -1.84E-04       2         2014-10-22 11:46       2945       2.33       -2.17E-04       2.37       -1.84E-04       2         2014-10-22 11:51       2950       2.33       -2.18E-04       2.35       -1.84E-04       2         2014-10-22 11:56       2955       2.33       -2.18E-04       2.34       -1.85E-04       2         2014-10-22 12:01       2960       2.33       -2.18E-04       2.37       -1.85E-04       2  | 2014-10-22 11:31 | 2930 | 2.34 | -2.17E-04 | 2.37 | -1.84E-04 | 2 |
| 2014-10-22 11:46     2945     2.33     -2.17E-04     2.37     -1.84E-04     2       2014-10-22 11:51     2950     2.33     -2.18E-04     2.35     -1.84E-04     2       2014-10-22 11:56     2955     2.33     -2.18E-04     2.34     -1.85E-04     2       2014-10-22 12:01     2960     2.33     -2.18E-04     2.37     -1.85E-04     2  | 2014-10-22 11:36 | 2935 | 2.34 | -2.17E-04 | 2.38 | -1.84E-04 | 2 |
| 2014-10-22 11:51       2950       2.33       -2.18E-04       2.35       -1.84E-04       2         2014-10-22 11:56       2955       2.33       -2.18E-04       2.34       -1.85E-04       2         2014-10-22 12:01       2960       2.33       -2.18E-04       2.37       -1.85E-04       2  | 2014-10-22 11:41 | 2940 | 2.33 | -2.17E-04 | 2.38 | -1.84E-04 | 2 |
| 2014-10-22 11:56     2955     2.33     -2.18E-04     2.34     -1.85E-04     2       2014-10-22 12:01     2960     2.33     -2.18E-04     2.37     -1.85E-04     2  | 2014-10-22 11:46 | 2945 | 2.33 | -2.17E-04 | 2.37 | -1.84E-04 | 2 |
| 2014-10-22 12:01 2960 2.33 -2.18E-04 2.37 -1.85E-04 2  | 2014-10-22 11:51 | 2950 | 2.33 | -2.18E-04 | 2.35 | -1.84E-04 | 2 |
|  | 2014-10-22 11:56 | 2955 | 2.33 | -2.18E-04 | 2.34 | -1.85E-04 | 2 |
| 2014-10-22 12:06 2965 2.32 -2.18E-04 2.35 -1.85E-04 2  | 2014-10-22 12:01 | 2960 | 2.33 | -2.18E-04 | 2.37 | -1.85E-04 | 2 |
|  | 2014-10-22 12:06 | 2965 | 2.32 | -2.18E-04 | 2.35 | -1.85E-04 | 2 |

| 2 | -1.85E-04 | 2.36 | -2.18E-04                             | 2.33 | 2970                                  | 2014-10-22 12:11                      |
|---|-----------|------|---------------------------------------|------|---------------------------------------|---------------------------------------|
| 2 | -1.85E-04 | 2.37 | -2.19E-04                             | 2.34 | 2975                                  | 2014-10-22 12:16                      |
| 2 | -1.85E-04 | 2.35 | -2.19E-04                             | 2.32 | 2980                                  | 2014-10-22 12:21                      |
| 2 | -1.85E-04 | 2.37 | -2.19E-04                             | 2.32 | 2985                                  | 2014-10-22 12:26                      |
| 2 | -1.85E-04 | 2.34 | -2.19E-04                             | 2.33 | 2990                                  | 2014-10-22 12:31                      |
| 2 | -1.86E-04 | 2.35 | -2.19E-04                             | 2.32 | 2995                                  | 2014-10-22 12:36                      |
| 2 | -1.86E-04 | 2.35 | -2.20E-04                             | 2.31 | 3000                                  | 2014-10-22 12:41                      |
| 2 | -1.86E-04 | 2.37 | -2.20E-04                             | 2.32 | 3005                                  | 2014-10-22 12:46                      |
| 2 | -1.86E-04 | 2.36 | -2.20E-04                             | 2.32 | 3010                                  | 2014-10-22 12:51                      |
| 2 | -1.86E-04 | 2.38 | -2.20E-04                             | 2.32 | 3015                                  | 2014-10-22 12:56                      |
| 2 | -1.86E-04 | 2.37 | -2.20E-04                             | 2.30 | 3020                                  | 2014-10-22 13:01                      |
| 2 | -1.86E-04 | 2.34 | -2.20E-04                             | 2.32 | 3025                                  | 2014-10-22 13:06                      |
| 2 | -1.86E-04 | 2.36 | -2.21E-04                             | 2.32 | 3030                                  | 2014-10-22 13:11                      |
| 2 | -1.87E-04 | 2.36 | -2.21E-04                             | 2.31 | 3035                                  | 2014-10-22 13:16                      |
| 2 | -1.87E-04 | 2.34 | -2.21E-04                             | 2.32 | 3040                                  | 2014-10-22 13:21                      |
| 2 | -1.87E-04 | 2.33 | -2.21E-04                             | 2.30 | 3045                                  | 2014-10-22 13:26                      |
| 2 | -1.87E-04 | 2.36 | -2.21E-04                             | 2.31 | 3050                                  | 2014-10-22 13:31                      |
| 2 | -1.87E-04 | 2.34 | -2.22E-04                             | 2.31 | 3055                                  | 2014-10-22 13:36                      |
| 2 | -1.87E-04 | 2.33 | -2.22E-04                             | 2.31 | 3060                                  | 2014-10-22 13:41                      |
| 2 | -1.87E-04 | 2.34 | -2.22E-04                             | 2.30 | 3065                                  | 2014-10-22 13:46                      |
| 2 | -1.88E-04 | 2.36 | -2.22E-04                             | 2.31 | 3070                                  | 2014-10-22 13:51                      |
| 2 | -1.88E-04 | 2.33 | -2.22E-04                             | 2.30 | 3075                                  | 2014-10-22 13:56                      |
| 2 | -1.88E-04 | 2.33 | -2.23E-04                             | 2.30 | 3080                                  | 2014-10-22 14:01                      |
| 2 | -1.88E-04 | 2.32 | -2.23E-04                             | 2.30 | 3085                                  | 2014-10-22 14:06                      |
| 2 | -1.88E-04 | 2.36 | -2.23E-04                             | 2.30 | 3090                                  | 2014-10-22 14:11                      |
| 2 | -1.88E-04 | 2.36 | -2.23E-04                             | 2.30 | 3095                                  | 2014-10-22 14:16                      |
| 2 | -1.88E-04 | 2.35 | -2.23E-04                             | 2.30 | 3100                                  | 2014-10-22 14:21                      |
| 2 | -1.88E-04 | 2.34 | -2.24E-04                             | 2.30 | 3105                                  | 2014-10-22 14:26                      |
| 2 | -1.89E-04 | 2.35 | -2.24E-04                             | 2.30 | 3110                                  | 2014-10-22 14:31                      |
| 2 | -1.89E-04 | 2.35 | -2.24E-04                             | 2.30 | 3115                                  | 2014-10-22 14:36                      |
| 2 | -1.89E-04 | 2.32 | -2.24E-04                             | 2.30 | 3120                                  | 2014-10-22 14:41                      |
| 2 | -1.89E-04 | 2.36 | -2.24E-04                             | 2.29 | 3125                                  | 2014-10-22 14:46                      |
| 2 | -1.89E-04 | 2.32 | -2.25E-04                             | 2.29 | 3130                                  | 2014-10-22 14:51                      |
| 2 | -1.89E-04 | 2.32 | -2.25E-04                             | 2.29 | 3135                                  | 2014-10-22 14:56                      |
| 2 | -1.89E-04 | 2.32 | -2.25E-04                             | 2.29 | 3140                                  | 2014-10-22 15:01                      |
|   |           |      | · · · · · · · · · · · · · · · · · · · |      | · · · · · · · · · · · · · · · · · · · | · · · · · · · · · · · · · · · · · · · |

| 2014-10-2 | 2 15:06 | 3145 | 2.29 | -2.25E-04 | 2.35 | -1.89E-04 | 2 |
|-----------|---------|------|------|-----------|------|-----------|---|
| 2014-10-2 | 2 15:11 | 3150 | 2.29 | -2.25E-04 | 2.35 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:16 | 3155 | 2.29 | -2.25E-04 | 2.31 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:21 | 3160 | 2.29 | -2.26E-04 | 2.34 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:26 | 3165 | 2.28 | -2.26E-04 | 2.34 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:31 | 3170 | 2.28 | -2.26E-04 | 2.35 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:36 | 3175 | 2.28 | -2.26E-04 | 2.30 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:41 | 3180 | 2.28 | -2.26E-04 | 2.33 | -1.90E-04 | 2 |
| 2014-10-2 | 2 15:46 | 3185 | 2.29 | -2.27E-04 | 2.31 | -1.91E-04 | 2 |
| 2014-10-2 | 2 15:51 | 3190 | 2.28 | -2.27E-04 | 2.31 | -1.91E-04 | 2 |
| 2014-10-2 | 2 15:56 | 3195 | 2.28 | -2.27E-04 | 2.33 | -1.91E-04 | 2 |
| 2014-10-2 | 2 16:01 | 3200 | 2.27 | -2.27E-04 | 2.34 | -1.91E-04 | 2 |
| 2014-10-2 | 2 16:06 | 3205 | 2.28 | -2.27E-04 | 2.34 | -1.91E-04 | 2 |
| 2014-10-2 | 2 16:11 | 3210 | 2.27 | -2.28E-04 | 2.30 | -1.91E-04 | 2 |
| 2014-10-2 | 2 16:16 | 3215 | 2.28 | -2.28E-04 | 2.29 | -1.91E-04 | 2 |
| 2014-10-2 | 2 16:21 | 3220 | 2.27 | -2.28E-04 | 2.31 | -1.91E-04 | 2 |
| 2014-10-2 | 2 16:26 | 3225 | 2.27 | -2.28E-04 | 2.33 | -1.92E-04 | 2 |
| 2014-10-2 | 2 16:31 | 3230 | 2.27 | -2.28E-04 | 2.30 | -1.92E-04 | 2 |
| 2014-10-2 | 2 16:36 | 3235 | 2.27 | -2.29E-04 | 2.31 | -1.92E-04 | 2 |
| 2014-10-2 | 2 16:41 | 3240 | 2.27 | -2.29E-04 | 2.32 | -1.92E-04 | 2 |
| 2014-10-2 | 2 16:46 | 3245 | 2.26 | -2.29E-04 | 2.33 | -1.92E-04 | 2 |
| 2014-10-2 | 2 16:51 | 3250 | 2.27 | -2.29E-04 | 2.33 | -1.92E-04 | 2 |
| 2014-10-2 | 2 16:56 | 3255 | 2.27 | -2.29E-04 | 2.30 | -1.92E-04 | 2 |
| 2014-10-2 | 2 17:01 | 3260 | 2.27 | -2.30E-04 | 2.32 | -1.92E-04 | 2 |
| 2014-10-2 | 2 17:06 | 3265 | 2.26 | -2.30E-04 | 2.31 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:11 | 3270 | 2.27 | -2.30E-04 | 2.29 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:16 | 3275 | 2.26 | -2.30E-04 | 2.32 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:21 | 3280 | 2.26 | -2.30E-04 | 2.29 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:26 | 3285 | 2.26 | -2.30E-04 | 2.31 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:31 | 3290 | 2.24 | -2.31E-04 | 2.32 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:36 | 3295 | 2.25 | -2.31E-04 | 2.29 | -1.93E-04 | 2 |
| 2014-10-2 | 2 17:41 | 3300 | 2.26 | -2.31E-04 | 2.32 | -1.94E-04 | 2 |
| 2014-10-2 | 2 17:46 | 3305 | 2.26 | -2.31E-04 | 2.32 | -1.94E-04 | 2 |
| 2014-10-2 | 2 17:51 | 3310 | 2.25 | -2.31E-04 | 2.29 | -1.94E-04 | 2 |
| 2014-10-2 | 2 17:56 | 3315 | 2.25 | -2.32E-04 | 2.31 | -1.94E-04 | 2 |
|           |         |      |      |           |      |           |   |

| 4 2 | -1.94E-04 | 2.28 | -2.32E-04 | 2.25 | 3320 | 2014-10-22 18:01 |
|-----|-----------|------|-----------|------|------|------------------|
| 4 2 | -1.94E-04 | 2.29 | -2.32E-04 | 2.25 | 3325 | 2014-10-22 18:06 |
| 4 2 | -1.94E-04 | 2.31 | -2.32E-04 | 2.24 | 3330 | 2014-10-22 18:11 |
| 4 2 | -1.94E-04 | 2.31 | -2.32E-04 | 2.25 | 3335 | 2014-10-22 18:16 |
| 4 2 | -1.95E-04 | 2.28 | -2.33E-04 | 2.26 | 3340 | 2014-10-22 18:21 |
| 4 2 | -1.95E-04 | 2.30 | -2.33E-04 | 2.25 | 3345 | 2014-10-22 18:26 |
| 4 2 | -1.95E-04 | 2.28 | -2.33E-04 | 2.25 | 3350 | 2014-10-22 18:31 |
| 4 2 | -1.95E-04 | 2.31 | -2.33E-04 | 2.24 | 3355 | 2014-10-22 18:36 |
| 4 2 | -1.95E-04 | 2.27 | -2.33E-04 | 2.23 | 3360 | 2014-10-22 18:41 |
| 4 2 | -1.95E-04 | 2.29 | -2.34E-04 | 2.24 | 3365 | 2014-10-22 18:46 |
| 4 2 | -1.95E-04 | 2.31 | -2.34E-04 | 2.24 | 3370 | 2014-10-22 18:51 |
| 4 2 | -1.96E-04 | 2.29 | -2.34E-04 | 2.23 | 3375 | 2014-10-22 18:56 |
| 4 2 | -1.96E-04 | 2.29 | -2.34E-04 | 2.24 | 3380 | 2014-10-22 19:01 |
| 4 2 | -1.96E-04 | 2.29 | -2.34E-04 | 2.24 | 3385 | 2014-10-22 19:06 |
| 4 2 | -1.96E-04 | 2.26 | -2.35E-04 | 2.24 | 3390 | 2014-10-22 19:11 |
| 4 2 | -1.96E-04 | 2.30 | -2.35E-04 | 2.24 | 3395 | 2014-10-22 19:16 |
| 4 2 | -1.96E-04 | 2.29 | -2.35E-04 | 2.23 | 3400 | 2014-10-22 19:21 |
| 4 2 | -1.96E-04 | 2.29 | -2.35E-04 | 2.23 | 3405 | 2014-10-22 19:26 |
| 4 2 | -1.96E-04 | 2.28 | -2.35E-04 | 2.24 | 3410 | 2014-10-22 19:31 |
| 4 2 | -1.97E-04 | 2.28 | -2.35E-04 | 2.23 | 3415 | 2014-10-22 19:36 |
| 4 2 | -1.97E-04 | 2.30 | -2.36E-04 | 2.23 | 3420 | 2014-10-22 19:41 |
| 4 2 | -1.97E-04 | 2.30 | -2.36E-04 | 2.23 | 3425 | 2014-10-22 19:46 |
| 4 2 | -1.97E-04 | 2.27 | -2.36E-04 | 2.25 | 3430 | 2014-10-22 19:51 |
| 4 2 | -1.97E-04 | 2.27 | -2.36E-04 | 2.23 | 3435 | 2014-10-22 19:56 |
| 4 2 | -1.97E-04 | 2.26 | -2.36E-04 | 2.23 | 3440 | 2014-10-22 20:01 |
| 4 2 | -1.97E-04 | 2.29 | -2.37E-04 | 2.23 | 3445 | 2014-10-22 20:06 |
| 4 2 | -1.97E-04 | 2.26 | -2.37E-04 | 2.22 | 3450 | 2014-10-22 20:11 |
| 4 2 | -1.98E-04 | 2.25 | -2.37E-04 | 2.22 | 3455 | 2014-10-22 20:16 |
| 4 2 | -1.98E-04 | 2.27 | -2.37E-04 | 2.23 | 3460 | 2014-10-22 20:21 |
|     | -1.98E-04 | 2.29 | -2.37E-04 | 2.22 | 3465 | 2014-10-22 20:26 |
| 4 2 | -1.98E-04 | 2.25 | -2.38E-04 | 2.22 | 3470 | 2014-10-22 20:31 |
| 4 2 | -1.98E-04 | 2.29 | -2.38E-04 | 2.22 | 3475 | 2014-10-22 20:36 |
|     | -1.98E-04 | 2.29 | -2.38E-04 | 2.22 | 3480 | 2014-10-22 20:41 |
| 4 2 | -1.98E-04 | 2.29 | -2.38E-04 | 2.22 | 3485 | 2014-10-22 20:46 |
| 4 2 | -1.99E-04 | 2.26 | -2.38E-04 | 2.21 | 3490 | 2014-10-22 20:51 |
| •   |           |      | l l       |      |      |                  |

| 2 | -1.99E-04 | 2.25 | -2.39E-04 | 2.22 | 3495 | 2014-10-22 20:56 |
|---|-----------|------|-----------|------|------|------------------|
| 2 | -1.99E-04 | 2.29 | -2.39E-04 | 2.21 | 3500 | 2014-10-22 21:01 |
| 2 | -1.99E-04 | 2.28 | -2.39E-04 | 2.21 | 3505 | 2014-10-22 21:06 |
| 2 | -1.99E-04 | 2.29 | -2.39E-04 | 2.21 | 3510 | 2014-10-22 21:11 |
|   | -1.99E-04 | 2.25 | -2.39E-04 | 2.21 | 3515 | 2014-10-22 21:16 |
| 2 | -1.99E-04 | 2.29 | -2.40E-04 | 2.21 | 3520 | 2014-10-22 21:21 |
| 2 | -1.99E-04 | 2.25 | -2.40E-04 | 2.21 | 3525 | 2014-10-22 21:26 |
| 2 | -2.00E-04 | 2.24 | -2.40E-04 | 2.21 | 3530 | 2014-10-22 21:31 |
| 2 | -2.00E-04 | 2.28 | -2.40E-04 | 2.21 | 3535 | 2014-10-22 21:36 |
| 2 | -2.00E-04 | 2.24 | -2.40E-04 | 2.21 | 3540 | 2014-10-22 21:41 |
| 2 | -2.00E-04 | 2.25 | -2.40E-04 | 2.20 | 3545 | 2014-10-22 21:46 |
| 2 | -2.00E-04 | 2.25 | -2.41E-04 | 2.20 | 3550 | 2014-10-22 21:51 |
| 2 | -2.00E-04 | 2.26 | -2.41E-04 | 2.20 | 3555 | 2014-10-22 21:56 |
| 2 | -2.00E-04 | 2.24 | -2.41E-04 | 2.20 | 3560 | 2014-10-22 22:01 |
| 2 | -2.00E-04 | 2.25 | -2.41E-04 | 2.20 | 3565 | 2014-10-22 22:06 |
| 2 | -2.01E-04 | 2.24 | -2.41E-04 | 2.20 | 3570 | 2014-10-22 22:11 |
| 2 | -2.01E-04 | 2.28 | -2.42E-04 | 2.20 | 3575 | 2014-10-22 22:16 |
| 2 | -2.01E-04 | 2.25 | -2.42E-04 | 2.20 | 3580 | 2014-10-22 22:21 |
| 2 | -2.01E-04 | 2.26 | -2.42E-04 | 2.19 | 3585 | 2014-10-22 22:26 |
| 2 | -2.01E-04 | 2.26 | -2.42E-04 | 2.19 | 3590 | 2014-10-22 22:31 |
| 2 | -2.01E-04 | 2.23 | -2.42E-04 | 2.18 | 3595 | 2014-10-22 22:36 |
| 2 | -2.01E-04 | 2.23 | -2.43E-04 | 2.20 | 3600 | 2014-10-22 22:41 |
| 2 | -2.02E-04 | 2.25 | -2.43E-04 | 2.19 | 3605 | 2014-10-22 22:46 |
| 2 | -2.02E-04 | 2.25 | -2.43E-04 | 2.19 | 3610 | 2014-10-22 22:51 |
| 2 | -2.02E-04 | 2.23 | -2.43E-04 | 2.18 | 3615 | 2014-10-22 22:56 |
| 2 | -2.02E-04 | 2.22 | -2.43E-04 | 2.18 | 3620 | 2014-10-22 23:01 |
| 2 | -2.02E-04 | 2.25 | -2.44E-04 | 2.18 | 3625 | 2014-10-22 23:06 |
| 2 | -2.02E-04 | 2.24 | -2.44E-04 | 2.18 | 3630 | 2014-10-22 23:11 |
| 2 | -2.02E-04 | 2.25 | -2.44E-04 | 2.18 | 3635 | 2014-10-22 23:16 |
|   | -2.02E-04 | 2.25 | -2.44E-04 | 2.19 | 3640 | 2014-10-22 23:21 |
| 2 | -2.03E-04 | 2.23 | -2.44E-04 | 2.18 | 3645 | 2014-10-22 23:26 |
| 2 | -2.03E-04 | 2.23 | -2.45E-04 | 2.18 | 3650 | 2014-10-22 23:31 |
| 2 | -2.03E-04 | 2.22 | -2.45E-04 | 2.18 | 3655 | 2014-10-22 23:36 |
| 2 | -2.03E-04 | 2.24 | -2.45E-04 | 2.17 | 3660 | 2014-10-22 23:41 |
| 2 | -2.03E-04 | 2.23 | -2.45E-04 | 2.17 | 3665 | 2014-10-22 23:46 |
|   |           |      |           |      |      |                  |

| 201 | 4-10-22 23:51  | 3670 | 2.17 | -2.45E-04 | 2.24 | -2.03E-04 | 2 |
|-----|----------------|------|------|-----------|------|-----------|---|
| 201 | 4-10-22 23:56  | 3675 | 2.17 | -2.45E-04 | 2.24 | -2.03E-04 | 2 |
| 20  | 014-10-23 0:01 | 3680 | 2.17 | -2.46E-04 | 2.24 | -2.03E-04 | 2 |
| 20  | 014-10-23 0:06 | 3685 | 2.17 | -2.46E-04 | 2.24 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:11 | 3690 | 2.17 | -2.46E-04 | 2.25 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:16 | 3695 | 2.17 | -2.46E-04 | 2.24 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:21 | 3700 | 2.16 | -2.46E-04 | 2.22 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:26 | 3705 | 2.17 | -2.47E-04 | 2.22 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:31 | 3710 | 2.17 | -2.47E-04 | 2.23 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:36 | 3715 | 2.16 | -2.47E-04 | 2.21 | -2.04E-04 | 2 |
| 20  | 014-10-23 0:41 | 3720 | 2.15 | -2.47E-04 | 2.21 | -2.05E-04 | 2 |
| 20  | 014-10-23 0:46 | 3725 | 2.16 | -2.47E-04 | 2.21 | -2.05E-04 | 2 |
| 20  | 014-10-23 0:51 | 3730 | 2.15 | -2.48E-04 | 2.23 | -2.05E-04 | 2 |
| 20  | 014-10-23 0:56 | 3735 | 2.15 | -2.48E-04 | 2.21 | -2.05E-04 | 2 |
| 20  | 014-10-23 1:01 | 3740 | 2.15 | -2.48E-04 | 2.21 | -2.05E-04 | 2 |
| 20  | 014-10-23 1:06 | 3745 | 2.15 | -2.48E-04 | 2.20 | -2.05E-04 | 2 |
| 20  | 014-10-23 1:11 | 3750 | 2.15 | -2.48E-04 | 2.20 | -2.05E-04 | 2 |
| 20  | 014-10-23 1:16 | 3755 | 2.15 | -2.49E-04 | 2.22 | -2.05E-04 | 2 |
| 20  | 014-10-23 1:21 | 3760 | 2.15 | -2.49E-04 | 2.23 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:26 | 3765 | 2.15 | -2.49E-04 | 2.21 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:31 | 3770 | 2.15 | -2.49E-04 | 2.22 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:36 | 3775 | 2.15 | -2.49E-04 | 2.23 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:41 | 3780 | 2.15 | -2.50E-04 | 2.22 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:46 | 3785 | 2.14 | -2.50E-04 | 2.20 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:51 | 3790 | 2.14 | -2.50E-04 | 2.21 | -2.06E-04 | 2 |
| 20  | 014-10-23 1:56 | 3795 | 2.14 | -2.50E-04 | 2.22 | -2.06E-04 | 2 |
| 20  | 014-10-23 2:01 | 3800 | 2.14 | -2.50E-04 | 2.19 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:06 | 3805 | 2.14 | -2.50E-04 | 2.19 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:11 | 3810 | 2.13 | -2.51E-04 | 2.20 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:16 | 3815 | 2.13 | -2.51E-04 | 2.21 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:21 | 3820 | 2.14 | -2.51E-04 | 2.20 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:26 | 3825 | 2.14 | -2.51E-04 | 2.18 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:31 | 3830 | 2.13 | -2.51E-04 | 2.19 | -2.07E-04 | 2 |
| 20  | 014-10-23 2:36 | 3835 | 2.13 | -2.52E-04 | 2.20 | -2.08E-04 | 2 |
| 20  | 014-10-23 2:41 | 3840 | 2.13 | -2.52E-04 | 2.18 | -2.08E-04 | 2 |
|     |                |      |      |           |      |           |   |

| 2 | -2.08E-04                             | 2.18 | -2.52E-04                             | 2.13 | 3845 | 2014-10-23 2:46                       |
|---|---------------------------------------|------|---------------------------------------|------|------|---------------------------------------|
| 2 | -2.08E-04                             | 2.18 | -2.52E-04                             | 2.13 | 3850 | 2014-10-23 2:51                       |
| 2 | -2.08E-04                             | 2.19 | -2.52E-04                             | 2.12 | 3855 | 2014-10-23 2:56                       |
| 2 | -2.08E-04                             | 2.20 | -2.53E-04                             | 2.12 | 3860 | 2014-10-23 3:01                       |
| 2 | -2.08E-04                             | 2.18 | -2.53E-04                             | 2.13 | 3865 | 2014-10-23 3:06                       |
| 2 | -2.08E-04                             | 2.18 | -2.53E-04                             | 2.13 | 3870 | 2014-10-23 3:11                       |
| 2 | -2.09E-04                             | 2.20 | -2.53E-04                             | 2.12 | 3875 | 2014-10-23 3:16                       |
| 2 | -2.09E-04                             | 2.19 | -2.53E-04                             | 2.12 | 3880 | 2014-10-23 3:21                       |
| 2 | -2.09E-04                             | 2.18 | -2.54E-04                             | 2.12 | 3885 | 2014-10-23 3:26                       |
| 2 | -2.09E-04                             | 2.21 | -2.54E-04                             | 2.12 | 3890 | 2014-10-23 3:31                       |
| 2 | -2.09E-04                             | 2.17 | -2.54E-04                             | 2.11 | 3895 | 2014-10-23 3:36                       |
| 2 | -2.09E-04                             | 2.17 | -2.54E-04                             | 2.12 | 3900 | 2014-10-23 3:41                       |
| 2 | -2.09E-04                             | 2.17 | -2.54E-04                             | 2.11 | 3905 | 2014-10-23 3:46                       |
| 2 | -2.09E-04                             | 2.19 | -2.55E-04                             | 2.11 | 3910 | 2014-10-23 3:51                       |
| 2 | -2.10E-04                             | 2.17 | -2.55E-04                             | 2.11 | 3915 | 2014-10-23 3:56                       |
| 2 | -2.10E-04                             | 2.17 | -2.55E-04                             | 2.11 | 3920 | 2014-10-23 4:01                       |
| 2 | -2.10E-04                             | 2.18 | -2.55E-04                             | 2.11 | 3925 | 2014-10-23 4:06                       |
| 2 | -2.10E-04                             | 2.18 | -2.55E-04                             | 2.10 | 3930 | 2014-10-23 4:11                       |
| 2 | -2.10E-04                             | 2.17 | -2.56E-04                             | 2.11 | 3935 | 2014-10-23 4:16                       |
| 2 | -2.10E-04                             | 2.18 | -2.56E-04                             | 2.10 | 3940 | 2014-10-23 4:21                       |
| 2 | -2.10E-04                             | 2.17 | -2.56E-04                             | 2.10 | 3945 | 2014-10-23 4:26                       |
| 2 | -2.11E-04                             | 2.16 | -2.56E-04                             | 2.09 | 3950 | 2014-10-23 4:31                       |
| 2 | -2.11E-04                             | 2.20 | -2.56E-04                             | 2.10 | 3955 | 2014-10-23 4:36                       |
| 2 | -2.11E-04                             | 2.16 | -2.56E-04                             | 2.12 | 3960 | 2014-10-23 4:41                       |
| 2 | -2.11E-04                             | 2.16 | -2.57E-04                             | 2.10 | 3965 | 2014-10-23 4:46                       |
| 2 | -2.11E-04                             | 2.16 | -2.57E-04                             | 2.10 | 3970 | 2014-10-23 4:51                       |
| 2 | -2.11E-04                             | 2.20 | -2.57E-04                             | 2.09 | 3975 | 2014-10-23 4:56                       |
| 2 | -2.11E-04                             | 2.17 | -2.57E-04                             | 2.09 | 3980 | 2014-10-23 5:01                       |
| 2 | -2.11E-04                             | 2.17 | -2.57E-04                             | 2.09 | 3985 | 2014-10-23 5:06                       |
| 2 | -2.12E-04                             | 2.17 | -2.58E-04                             | 2.09 | 3990 | 2014-10-23 5:11                       |
| 2 | -2.12E-04                             | 2.16 | -2.58E-04                             | 2.09 | 3995 | 2014-10-23 5:16                       |
| 2 | -2.12E-04                             | 2.16 | -2.58E-04                             | 2.09 | 4000 | 2014-10-23 5:21                       |
| 2 | -2.12E-04                             | 2.16 | -2.58E-04                             | 2.09 | 4005 | 2014-10-23 5:26                       |
| 2 | -2.12E-04                             | 2.16 | -2.58E-04                             | 2.08 | 4010 | 2014-10-23 5:31                       |
| 2 | -2.12E-04                             | 2.16 | -2.59E-04                             | 2.08 | 4015 | 2014-10-23 5:36                       |
|   | · · · · · · · · · · · · · · · · · · · |      | · · · · · · · · · · · · · · · · · · · |      |      | · · · · · · · · · · · · · · · · · · · |

| 2014-10-23 5:41 | 4020 | 2.08 | -2.59E-04 | 2.15 | -2.12E-04 | 2 |
|-----------------|------|------|-----------|------|-----------|---|
| 2014-10-23 5:46 | 4025 | 2.08 | -2.59E-04 | 2.16 | -2.13E-04 | 2 |
| 2014-10-23 5:51 | 4030 | 2.07 | -2.59E-04 | 2.16 | -2.13E-04 | 2 |
| 2014-10-23 5:56 | 4035 | 2.09 | -2.59E-04 | 2.15 | -2.13E-04 | 2 |
| 2014-10-23 6:01 | 4040 | 2.08 | -2.60E-04 | 2.15 | -2.13E-04 | 2 |
| 2014-10-23 6:06 | 4045 | 2.07 | -2.60E-04 | 2.16 | -2.13E-04 | 2 |
| 2014-10-23 6:11 | 4050 | 2.07 | -2.60E-04 | 2.14 | -2.13E-04 | 2 |
| 2014-10-23 6:16 | 4055 | 2.07 | -2.60E-04 | 2.15 | -2.13E-04 | 2 |
| 2014-10-23 6:21 | 4060 | 2.07 | -2.60E-04 | 2.16 | -2.13E-04 | 2 |
| 2014-10-23 6:26 | 4065 | 2.07 | -2.61E-04 | 2.15 | -2.14E-04 | 2 |
| 2014-10-23 6:31 | 4070 | 2.07 | -2.61E-04 | 2.14 | -2.14E-04 | 2 |
| 2014-10-23 6:36 | 4075 | 2.07 | -2.61E-04 | 2.15 | -2.14E-04 | 2 |
| 2014-10-23 6:41 | 4080 | 2.07 | -2.61E-04 | 2.14 | -2.14E-04 | 2 |
| 2014-10-23 6:46 | 4085 | 2.07 | -2.61E-04 | 2.16 | -2.14E-04 | 2 |
| 2014-10-23 6:51 | 4090 | 2.06 | -2.61E-04 | 2.14 | -2.14E-04 | 2 |
| 2014-10-23 6:56 | 4095 | 2.06 | -2.62E-04 | 2.14 | -2.14E-04 | 2 |
| 2014-10-23 7:01 | 4100 | 2.06 | -2.62E-04 | 2.14 | -2.14E-04 | 2 |
| 2014-10-23 7:06 | 4105 | 2.06 | -2.62E-04 | 2.14 | -2.15E-04 | 2 |
| 2014-10-23 7:11 | 4110 | 2.06 | -2.62E-04 | 2.13 | -2.15E-04 | 2 |
| 2014-10-23 7:16 | 4115 | 2.05 | -2.62E-04 | 2.13 | -2.15E-04 | 2 |
| 2014-10-23 7:21 | 4120 | 2.05 | -2.63E-04 | 2.14 | -2.15E-04 | 2 |
| 2014-10-23 7:26 | 4125 | 2.05 | -2.63E-04 | 2.12 | -2.15E-04 | 2 |
| 2014-10-23 7:31 | 4130 | 2.05 | -2.63E-04 | 2.12 | -2.15E-04 | 2 |
| 2014-10-23 7:36 | 4135 | 2.05 | -2.63E-04 | 2.13 | -2.15E-04 | 2 |
| 2014-10-23 7:41 | 4140 | 2.05 | -2.63E-04 | 2.13 | -2.16E-04 | 2 |
| 2014-10-23 7:46 | 4145 | 2.04 | -2.64E-04 | 2.13 | -2.16E-04 | 2 |
| 2014-10-23 7:51 | 4150 | 2.05 | -2.64E-04 | 2.12 | -2.16E-04 | 2 |
| 2014-10-23 7:56 | 4155 | 2.05 | -2.64E-04 | 2.14 | -2.16E-04 | 2 |
| 2014-10-23 8:01 | 4160 | 2.06 | -2.64E-04 | 2.13 | -2.16E-04 | 2 |
| 2014-10-23 8:06 | 4165 | 2.04 | -2.64E-04 | 2.13 | -2.16E-04 | 2 |
| 2014-10-23 8:11 | 4170 | 2.04 | -2.65E-04 | 2.12 | -2.16E-04 | 2 |
| 2014-10-23 8:16 | 4175 | 2.03 | -2.65E-04 | 2.12 | -2.16E-04 | 2 |
| 2014-10-23 8:21 | 4180 | 2.03 | -2.65E-04 | 2.12 | -2.17E-04 | 2 |
| 2014-10-23 8:26 | 4185 | 2.04 | -2.65E-04 | 2.12 | -2.17E-04 | 2 |
| 2014-10-23 8:31 | 4190 | 2.03 | -2.65E-04 | 2.12 | -2.17E-04 | 2 |
|                 |      |      |           |      |           |   |

| 2 | -2.17E-04 | 2.11 | -2.66E-04 | 2.03 | 4195 | 2014-10-23 8:36 |
|---|-----------|------|-----------|------|------|-----------------|
| 2 | -2.17E-04 | 2.12 | -2.66E-04 | 2.03 | 4200 | 2014-10-23 8:41 |
| 2 | -2.17E-04 | 2.12 | -2.66E-04 | 2.02 | 4205 | 2014-10-23 8:46 |
| 2 | -2.17E-04 | 2.11 | -2.66E-04 | 2.03 | 4210 | 2014-10-23 8:51 |
| 2 | -2.17E-04 | 2.11 | -2.66E-04 | 2.03 | 4215 | 2014-10-23 8:56 |
| 2 | -2.18E-04 | 2.10 | -2.66E-04 | 2.03 | 4220 | 2014-10-23 9:01 |
| 2 | -2.18E-04 | 2.17 | -2.67E-04 | 2.03 | 4225 | 2014-10-23 9:06 |
| 2 | -2.18E-04 | 2.13 | -2.67E-04 | 2.03 | 4230 | 2014-10-23 9:11 |
| 2 | -2.18E-04 | 2.11 | -2.67E-04 | 2.03 | 4235 | 2014-10-23 9:16 |
| 2 | -2.18E-04 | 2.11 | -2.67E-04 | 2.02 | 4240 | 2014-10-23 9:21 |
| 2 | -2.18E-04 | 2.10 | -2.67E-04 | 2.02 | 4245 | 2014-10-23 9:26 |
| 2 | -2.18E-04 | 2.69 | -2.68E-04 | 2.65 | 4250 | 2014-10-23 9:31 |
| 2 | -2.19E-04 | 2.70 | -2.68E-04 | 2.67 | 4255 | 2014-10-23 9:36 |