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MSc Graduation Work:

"Effects of coagulation and operational flux on the membrane performance of an inline coagulation/ultrafiltration process for water treatment"

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Abstract:

The objective of the study was to investigate the effects of coagulation and operational flux on the membrane performance of an inline coagulation/ultrafiltration process for water treatment in the lab. A two-phase optimisation approach was adopted in order to achieve stepwise performance improvement using raw water (taken from one of Singapore's reservoirs) as a case study. "Phase I" focused on the simulation of the inline coagulation/UF process composed of coagulation in jar test followed by immediate filtration with 0.05um paper filter, while "Phase II" consisted of the operation of a bench scale hybrid inline coagulation/UF system equipped with a pressurized membrane module in laboratory.

The main focus area for "Phase I" was the identification of optimum alternative coagulant among aluminium chlorohydrate (ACH), polyaluminum chloride (PACl) and ferric chloride (FeCl3) compared to aluminium sulphate (alum). "Phase II" supplementary applied the previous findings of the selected coagulant and dosage in order to optimise the membrane performance during operation of a bench scale hybrid inline coagulation/ultrafiltration system. The experiments in "Phase II" included runs at different fluxes in the range of 72-146$Lm^{-2}h^{-1}$, for the determination of the fouling behaviour in terms of transmembrane pressure (TMP), fouling tendency and specific flux (K). The critical operational flux values were also estimated which might help in the determination of a "sustainable flux" under the operating conditions investigated.

It was found that for "Phase I" the optimum coagulant would be ACH in a dosage of 1.7mg (Al)/L, with a TOC removal efficiency (40%) comparable to alum (35-45%), good effluent turbidity and acceptable dissolved aluminium concentration <0.05mg/L without the need of pH pre-adjustment, while usage of lime for pH post-adjustment could be reduced. In "Phase II", from the elaboration of the results under different fluxes, the critical flux (J_{cs}) was roughly estimated around 20 $Lm^{-2}h^{-1}$, for the threshold flux (J_{thr}) a range around 90-125 $Lm^{-2}h^{-1}$ was selected, while for the critical flux for irreversibility (J_{ci}) and the "sustainable flux" non-quantified suggestions were made. Regarding the operational parameters, even though an exact flux has not been clearly proposed, the alternative of 94 $Lm^{-2}h^{-1}$ stood out as it resulted compared always with the flux of around 74 $Lm^{-2}h^{-1}$, to a 5% improvement in specific flux, 16% increase in the average TMP, while the fouling rate remained similar to lower fluxes at around 0.16bar/h with a backwashable component after 1.5h being at 70% and dropping to 65% for the first 3h. Recommendations for the final selection have been given as there are a plethora of subjective operational parameters that need to be taken into account.

Table of Contents

List of Figures

List of Tables

Acknowledgements

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Chapter 1: Introduction

The current thesis was the final graduation requirement for the completion of the Double MSc Programme in Hydraulic Engineering & Water Resources Management, commonly offered by National University of Singapore (NUS) and Delft University of Technology (TUD). The report was the outcome of laboratory and bench scale studies conducted using raw water from one of Singapore's reservoirs during 6 Feb-5 Aug 2013 under the authority of Singapore's Public Utilities Board (PUB) with supervision from both academic institutes.

1.1. Project Description

The project used acase study in order to cover different aspects involved in water treatment processes using membrane systems and in order to seek easily applicable solutions for limiting factors related to membrane fouling. Starting point was to understand the importance of pre-treatment for membrane processes, evaluate the limitations introduced to the system from membrane fouling and then determine the best strategy for the overall system improvement.

Fouling is of major concern in membrane systems used in water treatment, including ultrafiltration (Heijman, et al., 2007) (Laîné, et al., 2003) so its elimination is targeted. In an ideal case scenario the irreversible fouling would be sought to be avoided, but since this can't be feasible its minimization is required. An appropriate pre-treatment step before the membrane process, can results in more efficient operation, while operation in low fluxes can also lead to low fouling. That is why for the overall system improvement these two components should be in an optimum stage. The synergy of the two processes, like the integrated system used in the selected surface water treatment plant in Singapore, one of the few using this hybrid inline coagulation-UF process, proved to have better removal efficiencies combined with good membrane performance according to the literature.

As a conclusion of the above, for the elimination of membrane fouling and to achieve efficient performance with easily applicable solutions like shift of coagulants or different flux operation, a two-phase optimisation was selected.

The project structure follows also the same concept with the two phases elaborated separately in respective chapters.

- First the inline coagulation/UF system was tried to be simulated with lab studies in order to bring improvements by studying alternative coagulants compared to alum while maintaining always a high product water quality. The optimum dosage and the necessity or not of pH control were determined.
- Next step, after the alternative coagulant with the best potential and the optimum dosage range were identified, was the optimisation of the inline coagulation/UF membrane operation. Main driving force for this phase was the minimization of the membrane fouling with easily applicable solutions.

The outcomes of the two-phase optimisation were combined so that an optimum operation with high product water quality, low fouling and the highest possible flux conditions, could be suggested. The results of the current report may be used as a case study for future research, providing some data for the determination of the best operating flux conditions with the same configuration. Sustainability is an important component in water industry, so determining the optimum flux conditions that can balance the capital and operational costs linked to high production rates resulting from higher fluxes with low fouling operation linked to lower fluxes, is crucial.

1.2. Project Objectives

Main objective of this study was the minimisation of membrane fouling in hybrid coagulation/UF systems by applying easily optimized solutions. As these solutions can refer to either one of the integrated treatment processes of the hybrid system, the main objective of the project could be divided into two secondary objectives as following:

I. Optimization of pretreatment step by changing coagulant
   a. Understand and optimize the coagulation/flocculation process
   b. Determine the potential to propose an alternative (PACl/ACH) compared to Alum (based on lab test results)

II. Optimization of membrane operation in order to achieve higher fluxes
   a. Determine the operational optimum permeate flux that can bring further improvements in the overall performance of the UF system (based on lab bench scale operation results)

1.3. Research questions

1. What are the benefits of using PACl or ACH instead of Alum at an inline coagulation/UF system
2. How can the overall performance of an inline coagulation/UF drinking water plant can be improved by changing operational parameters like the permeate flux.
   a. What is the effect of higher fluxes to the product water quality, operation (membrane fouling) and cost of the system?
   b. What is the threshold flux up to which low-fouling operation can be achieved?
   c. Is it possible to determine a sustainable flux above the threshold flux where more fouling is allowed as a return for capital cost savings?

Chapter 2:
Background study

In this chapter the background information for the involved processes will be presented. As the project scope covers a combination of the pre-treatment processes with membrane processes in water treatment and the improvements that can be sought from different membrane operations, three sections are presented, one for each sub-process respectively.

In the first section (2.1), the possible pre-treatment methods will be elaborated and the selection of the inline coagulation will be justified. For the second section (2.2) the ultrafiltration membrane applications within water industry, their material properties, operation as well as recovery and maintenance will be described. The final section (2.3) expands further in the membrane operation part with a focus on the cost evaluation and the membrane performance, including also some key variables that can affect the system's performance. More details about the flux terminology will be given with some models and equations presented for the mathematical representation of these terms.

2.1. Pre-treatment for membrane processes in drinking water treatment

2.1.i. Need for pretreatment

One of the objectives of this study is understanding the fouling mechanisms involved in drinking water treatment and try minimizing them, since fouling cannot be completely removed. One of the techniques to mitigate fouling is through pre-treatment of raw water prior of the membrane filtration.

Water chemistry is an important parameter that affects the membrane fouling (Katsoufidou, et al., 2005), so the measures taken during pre-treatment, target in altering the raw water characteristics in order to achieve more efficient performance of the downstream filtration step(s). An important foulant is also natural organic matter (NOM) that can and should also be reduced during pre-treatment. The importance of removing the organic matter is not only justified due to the potential fouling effects on the membranes, but mainly because of the proven interaction with chlorine during subsequent disinfection steps (if chlorination is used as disinfection method) and the formation of disinfection by-products (DBPs) harmful for human health. Some of the treatment technologies applied for DBP precursors removal are: coagulation, precipitative softening, preoxidation, separation processes, GAC and PAC adsorption (USEPA, 1999).

According to (Huang, et al., 2009) pre-treatment can affect the physical, chemical and/or biological properties of the source water and can impact membrane filtration either by altering the contaminant size distributions, changing mutual affinities of contaminants or their affinities to membrane surfaces, and suppressing microbial growth or removing biodegradable contaminants. The major pre-treatments according to the same authors for full scale membrane filtration are coagulation, adsorption, pre-oxidation, prefiltration and some more recently applied ones, with the first being briefly discussed.

2.1.ii. Methods of pretreatment: Coagulation

Coagulation is a physicochemical treatment process widely applied as pre-treatment method for membrane filtration, mainly due to its low cost and ease of operation (Chen, et al., 2007). Its primary objective is the reduction of natural organic matter by increasing their size to a filterable level and reducing their affinity to membrane surfaces. In that way color, taste and odor removal is achieved, membrane fouling is alleviated by a shift from pore constriction and pore blockage to cake fouling (Huang, et al., 2009), while the potential of microbial growth caused by fraction of NOM is reduced. Action that also mitigates the detrimental effects of DBPs, for which NOM are precursors (Matilainen, et al., 2010).

It can include a combination of different steps like coagulation, flocculation, sedimentation, flotation rapid or membrane filtration. The sequence of the first three is an established technology for several years, while the combination of coagulation with membrane processes has been also studied intensively. Conventional coagulation as a pretreatment process for MF has been proved to enhance flux recovery compared to MF alone (Wiesner, et al., 1989), (Lahoussine-Tucard, et al., 1992). The same can count for the hydraulic membrane resistance, which is decreased. However, as presented in (Chen, et al., 2007) some phenomena related to NOM properties like hydrophobicity, hydrophylicity and molecular weight distribution didn't allow the mitigation of the fouling rate. Coagulation can remove more efficiently the hydrophobic fraction and the high molecular mass compounds of NOM, compared to the LMM and hydrophilic fractions (Matilainen, et al., 2010).

2.1.iii. Methods of pretreatment: Enhanced coagulation

If the removal efficiency of NOM exceeds some set requirements as presented in Table 1 the coagulation process can be referred as enhanced. Enhanced coagulation is another method of controlling NOM. According to (Uyak, et al., 2007) it is considered to have more effective results in the removal of the portion of NOM composed of large organic molecules with negative charged functional groups.

2.1.iv. Methods of pretreatment: Inline coagulation

Also if it is combined with membrane filtration the necessary contact time of flocculation is reduced to around 15-60s so the process can also be applied inline. In terms of water quality, pilot study focusing on the NOM removal using various NF and UF membranes for surface (lake) water treatment concluded in the suitability of a flocculation-filtration-NF system for drinking water production (Mijatović, et al., 2004). Using a coagulation/MF system for NOM removal (Leiknes, et al., 2004) also presented the efficiency in contaminants removal for NOM rich water sources in Norway, with potential on replacing the conventional direct filtration process. As far as other parameters are concerned, studies with a flocculation/UF system for drinking water production by (Hagmeyer, et al., 2001) had also revealed that residual Al could be minimized by pH control, while the plants stable operation by an optimum coagulant dose, making the whole procedure a potential replacement of the conventional treatment process plants.

Table 1. Required Removal of TOC by Enhanced Coagulation for plants using conventional treatment: Step 1 Removal %

Source water TOC (mg/L)	Source water alkalinity (mg/L as CaCO3)		
	0-60	>60-120	>120
>2.0-4.0	35	25	15
>4.0-8.0	45	35	25
>8.0	50	40	30

Adopted from (USEPA, 1999)

Furthermore, for tropical conditions, (Qin, et al., 2006) tested a coagulation/UF system under different operating conditions of backwash interval and permeate fluxes and identified high turbidity removal over 99%, with DOC removal ranging from 30.5-59.5% and concluded that the hybrid system could be incorporated into existing conventional processes replacing dual media filtration for drinking water production of improved quality. (Xia, et al., 2007) in their studies with inline coagulation/UF system for river water treatment identified the effect of coagulation on turbidity, DOC, UV removal as well as the effect to the membrane flux decline. Their conclusions showed that pre-treatment with coagulation increased DOC removal from 8.5% to 44.5% (for 14ppm Alum), UV254 removal having even higher percentages than DOC removal, while flux reduction from the same alum dosage was reduced from 69% to 21% (J/J_0=31% and 79% respectively). They also supported their results with the study of (Park, et al., 2002).

Additionally because of the presence of aggregates, precipitates of the coagulated water and some contaminants after destabilization, the membrane pore size is preferable to be smaller so that cake fouling would prevail over pore blockage. (Guigui, et al., 2002) concluded that the optimum coagulation conditions used for a conventional coagulation/settling process obtained with jar testing could be applied to the hybrid system and manage to reduce membrane fouling. In terms of membrane performance, the system which was an inside-out hollow fiber hybrid system, like the one currently applied in this study, responded positively to the coagulation with the permeation flux improving. Different flux and operating conditions were also studied by (Qin, et al., 2006) in a hybrid coagulation/UF system, with the results indicating lower trans-membrane pressures than the typical UF, while high normalized flux was achieved with low energy consumption

Other advantages of the inline coagulation are according to (Oh, et al., 2005) reduction in the coagulant dosage, reduction of the mixing time, the energy consumption, the head losses etc. Several other studies using low pressure membrane systems under dead end, cross flow or submerged, combined with pre-treatment by coagulation or flocculation in order to reduce and control fouling have been reported (Leiknes, et al., 2004), (Kim, et al., 2001), (Schäfer, et al., 2000) (Lahoussine-Turcaud, et al., 1990). Final advantage, important especially for densely populated countries like Singapore and the Netherlands, where there are space limitations, is the smaller footprints that hybrid plants can achieve compared to the conventional treatment plants. In the Netherlands there are several drinking water treatment facilities using ultrafiltration, while in Singapore there are only two plants with installed membrane technologies that are used for direct potable water production, with one of them studied in the current thesis.

2.1.v. Comparison of different methods

According to a review done by (Huang, et al., 2009) it was reported that it is reasonable to proceed to proper integration of different systems and combine the benefits that each one separately has. In the studies of (Lee, et al., 2000) and (Jacangelo, et al., 1994) pre-treatment with coagulation has been reported to increase the ability of a membrane systems to remove dissolved organic matter, whereas (Côté, et al., 1998) supported that coupling of pre-treatment with membranes can achieve better removal of both dissolved and particulate contaminants when MF membranes are linked with one conventional process like coagulation, oxidation, absorption or biological treatment. However, into consideration has to be taken that the capital cost will be increased if this decision will be made, even though the operational costs may reduce. So again there should be a selection of the different processes

that can be integrated to achieve the required water quality or membrane performance and followed by a cost evaluation of the new hybrid process.

Regarding the efficiency of different integration in the removal of specific parameters some examples are presented next for a better comparison. (Farahbakhsh, et al., 2002) evaluated in their study three low pressure membrane treatment plants for water production equipped with hollow fiber hydrophilic membranes (0.01-0.2μm) -similar to the one used in the current thesis- and concluded that for all of them chemical coagulation was more effective in DBP precursor removal and the reduction of membrane fouling rate, while powdered activated carbon addition, on the other hand, resulted in moderate removal of DBP precursors but increased the rate of membrane fouling.

(Matsui, et al., 2005) presented the benefits of coupling both the major pretreatment methods of coagulation with adsorption, where increased percentages for NOM removal were reported. In more details the NOM removal compared to S-PAC adsorption itself improved approximately 20-50%. In their studies however, (Berube, et al., 2002) found that adsorption prior to membrane treatment did not significantly increase the removal of organic material or trihalomethane (THM) precursors contained in the raw water, compared to membrane treatment alone.

As there can be a plethora of combinations of the different processes , from the “conventional” to more advanced like the ones recently discussed, the selection should be made based also on the main objective of the case study. Even for the same combination the results can be different as the feed conditions or the operational conditions selected may differ. As an example two inline coagulation UF systems from (Choi, et al., 2004) are presented. In the first case study (Gardner,MA) the main objective was to increase the permeate flux so as to obtain the desired plant production, with Alum and ACH coagulation tested at dosages less than 1mg (Al)/L. In general the ACH resulted in better performance than Alum, and both resulted in decreased hydraulic resistance and increased critical flux, which allowed the accomplishment of the objective and increased production. In the second case (Duncannon,PA) the primary target was the TOC removal, so ACH was used in a dose of 1.67mg (Al)/L and achieved the required TOC removal (35%) while in the mean time lead to a decreased resistance and improved fouling.

As a conclusion, the integration of different processes is possible to lead to improvements of the system operation, as it can combine the benefits of the different processes, with the advantages and disadvantages of the main processes summarized in Table 2. The required improvements based on which the selection will be made, can be subjective and depend on the objective in each case. However whatever the selection of the processes to be integrated would be, the common part is the cost which will be increased initially in terms of capital cost and there is a possibility to be reduced in terms of operational costs. So for the final selection other parameters including the cost need to be included.

Table 2. List of the mechanisms, effects, and applications of major pretreatments for membrane filtration

Pretreatment	Coagulation	Adsorption	Preoxidation	Prefiltration
Chemicals applied	Coagulants or flocculants at proper dose	Porous or nonporous adsorbents in suspension or fixed contractor	Gaseous or liquid oxidants	Granular media with/without coagulants, membranes
Dose effects	Under-, optimal, or overdose (optimal for enhanced coagulation)	Minimal effective dose if used as suspended particles	Minimal effective dose	None
Physical mechanisms	Increases the size of aquatic contaminants to filterable level	Binds small contaminants to adsorbents much larger than membrane pores	May cause dissociation of organic colloids into smaller sizes or the release of EPS by aquatic organisms	Removes coarse materials that may cause cake/gel layers formation on downstream membranes
Chemical mechanisms	Destabilizes contaminants to cause aggregation or adsorption on coagulant precipitates or membrane surfaces	Provides new interfaces to adsorb/accumulate substances detrimental to membrane performance	Oxidizes and/or partially decomposes NOM, possible mineralization if VUV used	Selectively removes contaminants or other particles that are sticky to filter media and downstream membranes
Biological mechanisms	Partially removes autochthonous NOM and hinder bacterial growth in feedwater or on membrane	May adsorb organic contaminants relevant to biofouling	Suppresses microbial growth	Partially removes microorganisms that can cause biofouling
Targeted contaminants	Viruses, humic/fulvic acids, proteins, polysaccharides with acidic groups, colloids smaller than membrane pores	Humic/fulvic acids, small natural organic acids, some DBPs, pesticides and other synthetic organic compounds	Viruses and organic contaminants with ozonation	Particulate and colloidal organic/inorganic substances, microbiota
Effect on membrane fouling	Reduces colloidal fouling and NOM fouling	May increase or decrease membrane fouling	May reduce biofouling and NOM fouling	May reduce fouling to different extents
Advantages	• Significantly improves LPM performance (less fouling and greater rejection)	• Increase the removal of DBPs and DBP precursors	• Reduces the occurrence of biofouling • Increases organic removal (ozonation)	• May reduce biofouling, colloidal fouling, and/or solids loading
Disadvantages	• Requires proper dose that can be difficult to meet if feedwater quality varies rapidly/significantly • May exacerbate fouling • Produce solid wastes • Ineffective in mitigating the fouling by hydrophilic neutral organics	• Possible exacerbation of LPM fouling • Difficulty in removing PAC powders from treatment facilities	• Formation of DBPs • May damage membranes incompatible with oxidants • May be ineffective in suppressing the growth of some microbiota resistant to oxidation	• Performance of prefilters may deteriorate and be difficult to recover • May require pretreatment (e.g., coagulation or preoxidation) to enhance the efficacy

Adapted from: (Huang, et al., 2009)

2.2. Membrane processes in drinking water treatment

As the current report deals with the studies of membrane system performance, it could be helpful to provide some background information regarding the membrane processes used in drinking water treatment in order to gain a better understanding. The information provided in the following sections include: (2.2.i) a brief review on the ultrafiltration process, its advantages as well as the characteristics of the UF membranes (2.2.ii) a more focused elaboration on the membrane fouling methods, causes and solutions, and finally (2.2.iii) information regarding the recovery of fouled membranes.

2.2.i. Ultrafiltration

From the individual membrane processes (MF/UF/NF/RO) ultrafiltration can be characterized as a "solids-liquid separation (filtration) process" which can act as a low pressure-driven barrier to suspended solids, bacteria, viruses, endoxins and other pathogens (GE, 2012). According to (Chen, et al., 2010) its pore size is not adequate to retain microsolutes (MWs<300) so osmotic pressure difference is not going to be produced, that is why low pressure is present during ultrafiltration.

Ultrafiltration became an attractive alternative for water treatment for various reasons. It can be fabricated by a majority of materials, namely cellulose acetate (CA), polyamide (PA), polysulfone (PS), polyether sulphone (PES), polycarbonate (PC), polyether imide (PEI), polyvinylidene fluoride (PVDF), polyacrilonitrile (PAN) and polymethyl methacrylate (PMMA). The operation parameters of four of those material are presented in Table 3, from where we can conclude that UF membranes can handle feeds within a wider pH and temperature range and can be fairly chlorine resistant.

Other than the material, membrane characteristics that are usually discussed are their degree of hydrophobicity (membrane character), their membrane module configuration and geometry and other various properties like the surface area, their pore size, internal diameter and outside diameter. Most of them can be selected based on their end applications.

The degree of hydrophobicity was discussed earlier and it was concluded that it is determined by the chemical structure of the material. Regarding the membrane and module configuration, ultrafiltration membranes can be in a flat sheet, hollow fiber or tubular configuration, while the modules could be plate and frame, immersed, hollow fiber contained in pressure vessels etc. Table 4 summarizes the membrane and module configurations including information for their applicability, while a brief comparison between four membrane and module configurations is given in Table 5. The advantages of hollow fiber membranes like its cleaning ease, the high recovery rate and a moderate need for pretreatment are highlighted. With regard to the pretreatment need aforementioned (General Electric Company, 2012) explained the need of some pretreatment process coupled with UF, so that higher reduction of the concentration of dissolved materials/contaminants would be achieved. Something that wouldn't have happened if there wasn't upstream a process which would increase the non-desirable materials' size to a filterable particulate one.

To sum up ultrafiltration membranes have become an attractive and promising process to satisfy the standards required for the production of large volumes of safe drinking water (Regula, et al., 2013) due to the low pressures required, the different materials that can be used and address the different feed water conditions of pH and temperature, their membrane and module configuration that can be also selectived for each case study and finally for their high efficiency, and the economic and environmental interests especially if preceeded by a pretreatment step capable to increase the dissolved organic matter into filterable level.

Table 3. Generic continuous operation parameters for different material UF membranes

Polymer type	Max Temp (oC)	Max Pressure (psig)	Optimum pH Range	Max Free Chlorine Continuous (ppm)
Cellulose Acetate (CA)	60	200	2-9	3
Polysulfone (PS)	100	200	0.5-13	25
Polyvinylidene fluoride (PVDF)	80	200	1-12	50
Polyacrylonitrile (PAN)	80	200	1-10	50

Source (Chung, 2012)

Table 4. Summary of membrane and module configurations

Membrane configuration	Module configuration Or operating method	Driving force	Pore size	Common Applications
Flat Sheet (FS)	Plate and frame (PF)	Pressure	MF/UF	WWT, EDI
	Immersed membranes	Vacuum	MF/UF	iMBR
	Spiral wound (SW)	Pressure	UF/RO	DS, PR
Hollow Fiber (HF)	Contained in pressure vessels	Pressure	MF/UF/RO	WT, PR, etc.
	Immersed module without pressure vessels	Vacuum	MF/UF	WT, iMBR
Tubular (TB)	Pressure filtration	Pressure	MF/UF	WWT, PR, sMBR
	Vacuum filtration with bubbling	Vacuum	MF/UF	sMBR

DS: Desalination, ED: Electrodialysis, PR: Process Recovery, WT: Water Treatment, WWT: Wastewater Treatment

Source: (Chung, 2012)

Table 5. Comparison of different membrane geometries

	Hollow Fiber (HF)	Flat Sheet (FS) Plate and frame	Flat Sheet (FS) Spiral wound	Tubular (TB)
Applicability				
RO/NF	yes	yes	>95%	yes
UF/MF	>95%	yes	yes	yes
Cleaning Ease	+++	-	+	+
Pre-Treatment need	+	+	-	+++
Recovery rate	+++	+	++	+
Module Size	++	+	++	-
Cost per m2	+++	+	+++	-

-: disadvantage, +++: obvious advantage

Source: (Degrémont Suez, 1991)

2.2.ii. Membrane Fouling

In systems using membrane technologies, membrane fouling still remains the main bottleneck for the process (Huisman, et al., 2000), (Sheikholeslami, 1999)), so a key towards more efficient performance is the determination of ways to achieve low fouling tendencies (Strathmann, 2001). As membrane fouling is also related to higher energy costs required to overcome the pressure drops and also other maintenance or running costs related to the higher cleaning frequency caused by membrane contamination (Regula, et al., 2013), its alleviation will lead to significant cost savings.

Based on the definition of fouling given by the International Union of Pure and Applied Chemistry: *"The process that results in an decrease in performance of a membrane, caused by the deposition of suspended or dissolved solids on the external membrane surface, on the membrane pores, or within the membrane pores"* (Koros, et al., 1996) we can already identify the 3 fouling mechanisms for a porous membrane, whose selective properties depend mainly on screening of the filtered species. These mechanisms are (Katsoufidou, et al., 2005):

- cake formation by the species rejected by the membrane
- pore blocking at the membrane surface, and
- pore constriction due to adsorption of filtered species within the membrane pores

The nature of each fouling mechanism varies, so the fouling can have different types. It can be surface fouling or internal fouling depending on the particle size and the membrane pore size. Surface fouling is caused by deposition of solid material on the membrane surface so it can be reversible and controlled with high turbulence (backwashing). Alternatively hydrophilic or charged membranes will minimize the adhesion of the colloids to the surface. As far as internal fouling is concerned it is more related to the adsorption of dissolved material into the membrane causing pore plugging, while it is generally irreversible and removed only by chemical cleaning (Chung, 2012). A schematic representation of fouling on an ultrafiltration membrane can be found in Figure 1

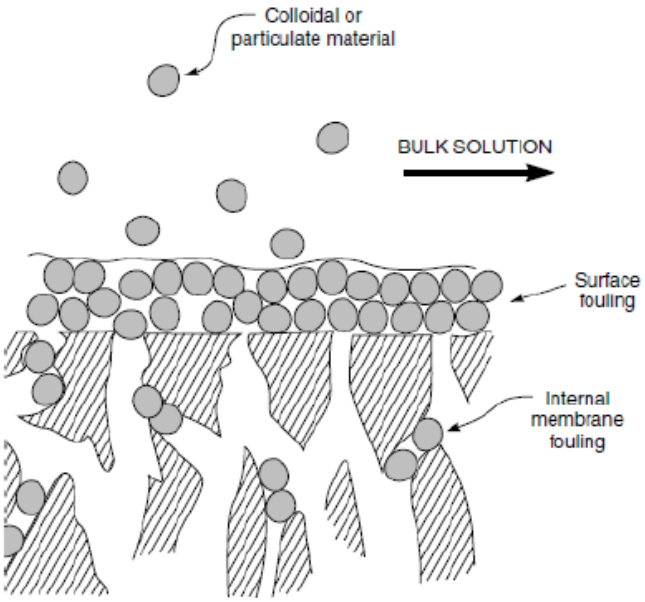

Figure 1. Schematic representation of fouling on an ultrafiltration membrane (adopted from: (Li, et al., 2008)

A final classification can be given based on the main foulants into:

- *colloidal fouling*, caused by particulate deposition of metal colloids and grouping of molecules of 10^{-5} to 10^{-7} cm diameter. It depends on both the particle relative size and the membrane pore size. They are usually hydrophobic so tend to cluster or group together to form colloidal particles that lowers the surface tension due to surface area exposure (Chung, 2012)
- *organic fouling* that is caused due to adsorption of organic molecules, some of them with hydrophobic regions (like proteins) (Chung, 2012). The NOM have been identified as a major foulant, along with polysaccharides -biopolymers-humic substances and LMM acids. For ceramic membranes organic fouling potential is lower even though more research was required in order to prove the relation relationship between polysaccharides and irreversible fouling (Hofs, et al., 2011).
- *scaling* caused due to precipitation of insoluble minerals, inorganic deposition of metal oxides, clays-silicates, alumina, ferric hydroxides and soluble salts;
- *biofouling* caused by microbial adhesion and bacterial, algal or fungal growth including biofilm formation due to TEP and EPS precursors like overgrowth of filamentous bacteria (Meng, et al., 2009).

Important factors that influence membrane fouling can be grouped into 3 categories according to the literature (Katsoufidou, et al., 2005), (Li, et al., 2008) (Chung, 2012). These categories are relevant to the bulk characteristics, the membrane and module characteristics and the operation conditions.

1. Bulk characteristics:
   In this group of factors influencing membrane fouling can be found the bulk components, the particle size distribution of the biosolids including the NOM characteristics, where it is generally suggested that hydrophilic fraction have a higher fouling tendency (Cho, et al., 2000), while in terms of MW distribution the larger molecular weight fractions caused more significant fouling (Lin, et al., 2000). Other factors are the water chemistry including the pH and the ionic character of the environment, as studies had revealed that decreasing the pH or increasing the ionic strength promotes the adsorption and the gel formation (Jones, et al., 2000) (Yuan, et al., 1999) (Jones, et al., 2001). Finally bulk viscosity and hydrophobicity can also affect the membrane fouling.
2. Membrane and module characteristics:
   From the membrane properties the ones affecting mainly the membrane fouling are the MWCO or the pore size and their shape. It has be found that looser membranes like MF is more probable to be affected by pore blockage and cake formation while for UF membranes where pore size distribution is smaller usually the reversible cake fouling prevails. According to (Chung, 2012) surface properties like the membrane hydrophilicity, charge and surface topography, also influence membrane fouling along with porosity. With studies supporting that hydrophilic membranes foul in a smaller degree while the flux reversibility increases (Crozes, et al., 1997). Finally according to the same author, the module geometry and dimensions play a role as well in membrane fouling.

3. Operating conditions:

   Regarding the factors influencing membrane fouling coming for the variation of the operating conditions (Li, et al., 2008) included the operating pressure, the different hydrodynamic conditions and the membrane cleaning condition as possible factors. More specifically the cross-flow velocity, the aeration rate, the flow and pulse rate as well as the relaxation time were studied while as far as the membrane cleaning is concerned the study focused on both physical and chemical cleaning and cleaning intervals.

As for the current study, the bulk characteristics and the membrane and module characteristics either remained the same or had been preselected, for the evaluation of the membrane fouling the factors of the last category could be studied. In an upcoming section (2.3.ii) the literature review on these factors expands, while also the final selection of the operational variable to be checked in the bench scale studies is justified.

After the classification of the factors that can influence the membrane fouling into three main categories of bulk characteristics, membrane and module characteristics and operating conditions, it can be expected also for the methods and techniques for its alleviation to be classified in similar way.

1. Bulk characteristics:

   Since the bulk characteristics can affect the membrane fouling, methods that control these parameters will mitigate the impacts to membrane fouling. In this case, effective pre-treatment as explained earlier in section (2.1) is the solution for alleviating membrane fouling.

2. Membrane and module characteristics:

   It is known that an effective strategy to suppress membrane fouling, especially irreversible fouling is to increase the hydrophilicity of membrane surface, which can be implemented by incorporating hydrophilic macromolecule modifiers (Katsoufidou, et al., 2005) in order to enhance the antifouling behavior of the membranes. (Chung, 2012) summarized the membrane surface modification techniques to the use of:

   1. Surfactants
   2. Coatings
   3. Chemical grafting
   4. Polymer blends and
   5. Plasma modification

   Each one of which had its advantages and limitations; with, for example, the treatment with water insoluble surfactant in order to enhance hydrophilicity, having the potential problem of contamination of the water product; or the plasma modification having the disadvantage of the high cost. Whereas from the other hand the application of membrane coatings, by depositioning a thin film of a different polymer or monomer-system in order to form a new surface via composite formation, showing high potential in developing new chemistry polymeric surfaces. Similarly high potential to the one of chemical grafting, which is the attachment of a low molecular weight active group (monomer) to polymeric membranes.

   To conclude with the techniques of this category, some examples from the literature are presented that support the improved properties of the modified membranes. (Wang, et al., 2006) in their study used pluronic polymer with PES and created a hydrophilic blend membrane with superior fouling-resistant ability. The total membrane fouling and irreversible membrane fouling decreased remarkably with an increase in PEO chain length and density at the PES-

Pluronic blend membranes surface, and excellent flux recovery property rendered the blend membranes with good recycling utilization. (Zhao, et al., 2013) used isocyanate-treated grapheme oxide (iGO) dispersed in organic solvent in order to fabricate modified iGO-PSf UF membranes which resulted in enhanced antifouling property due to improved hydrophilicity with more negative zeta potential and achieved to improve smoothness. (Fan, et al., 2008) used polyaniline nanofibers blended in polysulfone membranes which lead to improved permeability and slower flux decline rate, due to larger porosity and better hydrophilic properties. Finally, for their study (Rahimpour, et al., 2008) used TiO_2 nanoparticles and UV-irradiation in polyether-sulfone (PES) UF membrane for fouling improvement. The surface modified TiO_2-entrapped membrane showed slower flux reduction than PES while UV-irradiated TiO_2 entrapped membranes showed higher antifouling properties and higher initial flux compared to TiO2 entrapped.

3. Operating conditions:

   As for the last category, of the operational factors that influence the membrane fouling, that is going to be elaborated in section (2.3.ii), it can be suggested that through the appropriate process design and process control the impacts to membrane fouling can be controlled. As mentioned in (Rouaix, et al., 2006) strategies to alleviate membrane fouling can include improved hydrodynamic conditions (turbulent, non-steady, secondary flows and multiphase flow), while another category can include the process control that allows the frequency of the (clean in-place) CIP procedures to be reduced. A new method that uses vibratory shear (VSEP) for the mitigation of membrane fouling (Petala, et al., 2006) can be also suggested as an alternative example of process design that achieved improvements in term of membrane fouling.

2.2.iii. Membrane Cleaning

According to the literature membrane cleaning is performed in treatment systems using membrane processes when either the production flow rate drops to a limit value (if constant pressure is applied), or when the driving pressure required is increased in order to keep constant production. Some arithmetical examples for the case of RO plants are given in (Avlonitis, et al., 2003) there is a 10% decrease in the normalized permeate flow, a 10% increase in the driving pressure occurred in order to maintain constant production (other parameters kept same), or a 15% increase in the pressure differential between feed and reject flows. Two are the main categories of mechanisms in use for membrane cleaning and recovery. They include cleaning mechanisms involving physical or chemical methods. Main objective is to restore membrane properties that were affected due to fouling to a situation as close as possible to the initial. As presented earlier, different types of fouling occur, so different types of cleaning have been developed as well.

Physical Cleaning

Membrane cleaning can be performed either with the use of chemicals or not. The second category is going to be discussed under this section, with the main means used for cleaning being mechanical forces like turbulence. Several methods can be applied and can be grouped into 4 categories:

1. Hydraulic Flushing (Forward/Backward)
2. Air Scouring
3. Vibration
4. CO2 permeation

Two subcategories in hydraulic flushing can exist, depending on the direction of the flushing, "forward" or "backward". If the flushing is performed from the feed stream to the concentrate/waste stream along the membrane surface it is called forward flushing, otherwise if performed in a reverse flow direction from the permeate stream to the concentrate/waste stream through the membrane, backward flushing. In both cases the supplied flow rate or pressure are usually 2-2.5 times higher than the normal filtration flow rate or pressure. Due to the hydraulic gradient, turbulence is created and the accumulated foulants from the membrane surface and pores can be dislodged. The membrane fouling that can be removed with hydraulic flushing is characterised as backwashable reversible fouling, and mainly consist of the fouling due to cake formation. The frequency of hydraulic backwashing depends on the filtration backwashing pattern selected for the membrane system and other operational parameters.

Similar procedure as before, is applied also for air scouring, with the difference that flushing doesn't only occur with permeate, pure solvent or feed but with the introduction of air as well. Air bubbles moving through the pores and/or on the surface can carry away foulants attached there. The mixing of the two fluids will result in more turbulent streams.

Another category of physical cleaning is vibration, where pneumatic hammers or other type of vibrating devices can get attached to the filtration modules (not applicable in all cases) and provide the required motion in order to remove foulants from the membranes and reject them to the waste (reject) stream.

Finally CO2 back permeation, is a method only suitable for hollow fiber membrane configurations, as CO2 gas under high pressure enters the system from the permeate side of the membrane through internal fiber bores, and exits the system after passing through the fiber walls. The purpose remains the same, carrying away the lifted foulants. (Chian, et al.) Studies by Vitens and WE-consult showed that due to the increased solubility of CO2 compared to air, and the avoidance of air-locking as well as the chemicals introduced in water treatment systems for the membrane cleaning, this cleaning method can lead to increased membrane lifetimes and improved end-product quality results (Vitens N.V., 2012). The process time is also shorter than other methods of membrane recovery using chemicals, which leads to higher capacities and operation cost savings.

Chemical Cleaning mechanisms

Since the properties of the fouled membranes like the flux, or its resistance, cannot be fully restored only with the use of backwashing or other physical cleaning methods, chemical cleaning is required. (Sheikholeslami, 1999). Chemical washing and chemical cleaning methods usually target on the weakening of the foulant-foulant or foulant-membrane forces present. For this purpose, chemical agents are used, depending on the chemical reactions required and the prevailing type of fouling. Some of the usual reactions carried out by the chemicals are peptization, saponification, solubilization, dispersion, chelation, sequestering and suspending, while the chemical agents involved can be alkalies (NaOH), acids (nitric, citric), surface-active agents, sequestering agents (EDTA), formulated cleaning agents, enzymes and disinfectants (H2O2) (Trägårdh, 1989). Some criteria for the selection of the appropriate chemicals are, their ability to loosen and dissolve foulants from the membrane surface, while at the same time keeping them in dispersed and soluble form. Their potential in achieving avoidance of fresh fouling is also important. Finally it is desirable not to interact with the membrane material in a way that can cause impacts to the membrane integrity (Rouaix, et al., 2006), to be chemically stable throughout the entire process and to be cost effective (Chian, et al.).

The procedure followed for the chemical washing of membranes is most of the time similar and should include both alkaline and acid cleanings to deal with organic and inorganic fouling respectively. For example NAOCl is used for the removal of organic foulants, while citric acid can be utilized to remove inorganic contaminants. Adequate rinsing steps before and after the different chemical cleaning steps should be allowed in order to avoid interference with each other that can lower their performance. For the same reason before the start of the chemical cleaning the dosed water have to be removed from the system, while after the end of the chemical cleaning a disinfection stage can be introduced.

Even though the membrane cleaning process is most of the time similar and may include the aforementioned steps, there are still some parameters that will differentiate the whole procedure. For example based on (Dudley, 1998) the frequency of cleaning will be determined by the rate of fouling, while the effectiveness of the membrane cleaning will be influenced by the following factors.

- Type of applied chemicals for cleaning
- Dosed cleaning agent volume, based on the size of the system
- Contact time with the agents and/or application or not of soaking of the membranes in the chemicals to aid cleaning
- Temperature, as warm temperatures will have positive effects in chemical cleaning
- Design of the cleaning circuit and operating parameters

Also ageing of the membranes due to the chemicals used is something that affects the frequency of the cleanings. Chemical concentrations used have to be low for frequent use, so careful planning needs to be decided for the interval of the more frequent and the less frequent chemical cleanings. In (Causserand, et al., 2008), an example of a membrane cleaning is given. The paper refers to a clean in place (CIP) method using detergents or chlorine at low concentrations in a less frequent scheme (daily/weekly) for the removal of the more persistent foulants. NaOCl dosages were ranging from 2-10ppm not applied in intervals more than every 30min, with the pH of water source, while at 20-400ppm once a week or less frequently, and at a pH=12.

Less frequent recovery chemical cleaning (up to 6months) can be applied since “chemical backwashing would not necessarily restore the original properties (flux) either (Sheikholeslami, 1999). This chemical cleaning is another clean-in-place (CIP) method for removal of the reversible organic or inorganic fouling and restoring the membranes to conditions similar to the initial. Longer cleaning with chlorine either in the form of Cl_2 or OCl^- can be used, at higher concentrations, or alternatively other alkaline or acidic solutions might be necessary (Causserand, et al., 2008). Based on a study of (Liikanen, et al., 2002) alkaline chelating cleaning agents were found to lead to an increase in membrane permeability by 100%, making them the most efficient in cleaning of the NF membranes used for filtration of treated surface water. Membrane manufacturers (ZENON Membrane Solutions, 2006) also reported that extensive “soaking of the membranes in a 10g/L citric solution followed by a soak in 1000ppm NaOCl restored” adequately “the membrane permeability”. The ageing result and the effect of NaOCl to UF polysulfone hollow fiber membranes were explored in (Regula, et al., 2013).

2.3. Improvement of membrane filtration operation

Achieving improvements of the membrane filtration operation could be subjective, as one could focus only on financial improvements (in terms of cost savings), while another could focus in improvements in terms of water quality or fouling tendency. In order to check how these two are related and thus make it easier to couple them in a common solution that will have potential overall improvements, the following sections are presented.

Firstly the possible costs linked to an inline coagulation/UF system are going to be presented and further elaborated. Studies from the literature showing possible effect of the performance to the cost will be sought. In a following section (2.3.ii) similar procedure will be followed for the effects of the hybrid system's operational parameters to the membrane performance, while sections (2.3.iii-2.3.iv) will focus more on the operational parameter of the permeate flux, with different manifestations for its critical values presented, as well as descriptions and mathematical expressions for their determination.

2.3.i. Cost evaluation of membrane system operation

A crucial parameter in almost all industrial applications is the cost, and drinking water treatment is not an exception. The components are capital costs and operational costs, with the former having a significant importance initially for new applications, while the later throughout the system's operational lifetime. The capital or investment costs are usually set before the commencement of the application and can consist of land costs, construction costs, equipment/membrane purchase costs and others depending on the treatment application. During operation from the other side the operational costs which consist from the membrane replacement and maintenance costs, the energy and chemical costs, can vary and thus be optimized.

For MF and UF systems even though less energy is required the principal operational costs are energy and membrane replacement (Blume, et al., 1995). The sources of energy consumption in membrane systems are related to the need of higher (or not so high) pressures for the filtration procedure. So the energy consuming equipment are the feed, permeate or backwash pumps, and in a lesser degree the chemical pumps used for the introduction of different chemical streams in the system (pH-control, coagulant, coagulant aids etc). Another source could be the blowers if air scouring is applied, while there might be also minor energy consumption sources from mixers or other monitoring equipment that can be ignored.

For the quantification simple equation can be used, summing up the individual energy requirements of the different pumps and multiplying with the electricity costs. A pump's energy consumption is dependent on the head that needs to be provided, so it is in other words pressure dependent. An expression for the determination of the specific energy consumption for filtration can be the following:

(Eq. 1) $$E = \frac{TMP_{ave} + P_{losses}}{3.6x10^6 \xi}$$ (Judd, et al., 2001)

Where E= the specific energy consumption in kWh/m^3

TMP_{ave}= the average TMP expected (Pa)

P_{losses}= the hydraulic pressure losses within the system (Pa)

ξ=the pump efficiency (%)

For other pumps, the pressure difference ΔP, which for filtration is the sum of the average TMP and the P_{losses}, is dependent on the differential head, fluid density and the gravity coefficient as ΔP= Hρg with the

specific energy consumption being again Ei= ΔP/3.6x10^{6}ξ. The total specific operational energy costs in S$/m^3 cost being ∑(Ei)xL where Ei the specific energy consumption of pump/component i in kWhm^{-3}, and L the electricity unit cost in S$/kWh.

Other than the principal operational costs per m^3, another operational cost component is the chemicals. The chemical costs could include the expenditure for their purchase as well as the treatment, handling and disposal of their waste streams (chemical sludge). If all these costs are summarizes per unit mass (S$/tonne) or per unit mole (S$/mole) (i.e. M), then the chemical costs could be M·c with c being the chemical mass (tonnes) or the chemical dosage (mM) required. The total specific operational costs will then be: Opex = ∑(Ei)xL + M·c in S$/m^3

The variability of the energy and the chemical costs can be easily correlated with the system itself and with its performance. As an example the selected operation mode can have a significant difference in the operating costs as according to (Blume, et al., 1995) UF systems operating in dead-end mode can have 10 times lower costs than the ones operating in cross-flow. The energy consumption could be reduced by achieving sub-critical membrane process operation, however this would lead to a need for larger membrane surface area. So the decrease in running costs would be partially off-set by increased investment cost (Bacchin, et al., 2006). According to (Kennedy, et al., 1998) reduced operational costs can be achieved by improving the performance of backwashing and reducing the frequency of chemical cleaning, which will also result in increased system efficiency.

In their report (Jamaluddin, et al., 1998) focus on the rate of flux decline on long term operations, which has to be assessed a priori, during the plant design phase and before the membrane selection, so that the possible productivity loss affecting the cost of water production will be avoided. (Fane, et al., 2005) presented also that one of the advantages to find subcritical fluxes in membrane systems, other than environmental sustainability (less chemical usage, lower energy consumption) and operational ease, is financial feasibility. Meaning that the drop in the capital costs from the reduction of membrane costs, in combination with sub critical operation that requires lower operational costs for cleaning etc will make the systems more attractive. In a review by (Laîné, et al., 2003) it is mentioned that the last years membrane processes became indeed more attractive, due to the more competitive prices that resulted also in low capital and operational cost, which are “inversely proportional to membrane hydraulic performance (permeate flux)”. Finally, if more environmental aspects are taken into account like the impact of the chemical usage that still remains the same for the environment whereas as far as energy usage is concerned renewable sources can be used, (Schäfer, et al., 2001) concluded that it might be cheaper to operate tighter pore size membranes with higher energy rather than MF or UF.

To sum up all the aforementioned information it can be concluded that operational costs are related with the system performance, which can be enhanced, with different methods that are going to be studied in the next section.

2.3.ii. Operational Parameters that affect membrane performance

The efficiency of membrane systems, which is highly related to membrane fouling, is mainly controlled by three sets of data, the bulk characteristics, the membrane and module characteristics and the operation conditions, introduced earlier in section 2.2.ii. As a result, if the target is the optimization of the system efficiency, some alterations to the variables included in those set of parameters should be proposed, in a way that the best performance will be identified. As for the most of those parameters

related to the feed characteristics or the membrane properties there isn't a lot of flexibility, the parameters that will be sought to be optimized will originate from the group of operating parameters. In that way the membrane performance and the overall system efficiency might be improved, in a sustainable environmental way without the introduction of additional chemicals to alter the water chemistry, or costly solutions like suggesting the replacement of membrane modules.

The possible operational variables that could have been changed in order to improve membrane fouling came from the hydrodynamic conditions' factors, as the experiments were preferred to be performed under constant flux and monitor the pressure rather than under constant pressure and monitor the flux. These possible variables are then:

- Filtration time
- Ceasing time
- Aeration intensity
- Flushing variations
- Permeate Flux

With the literature supporting that decreasing the filtration time or increasing the ratio of filtration time/ceasing time was favorable to enhance membrane permeability (Mo, et al., 2002), while with the use of 40layers S-PAC pre-coats prior the MF ceramic membranes (Hamad, et al., 2009) found that even for longer filtration times up to 4hrs the TMP increase was reduced by 10% compared to the reference 1hr filtration time experiments, meaning that both the reversible and the irreversible fouling could be controlled. As far as aeration intensity in concerned (Mo, et al., 2002) reported that the membrane permeability improved with the aeration intensity increasing up to the critical value of $4m^3/h$. While different studies with various kinds of UF membrane modules (hollow fiber (Laborie, et al., 1997), tubular (Cheng, et al., 1999)) showed enhancement of permeate flux with gas sparging.

Finally, for backwashing and flushing patterns, fouling studies had been done with (Decarolis, et al., 2001) demonstrating pilot findings with improved membrane productivity being achieved, with increasing backwashing with chlorine addition, due to biogrowth control and organic oxidation effects on foulants. In the same study the backwashing frequency was investigated and showed that there was flux enhancement when the time interval between backwashing events was decreased.

Since in our system most of the above mentioned parameters are fixed, we chose to investigate the relationship between fluxes and membrane fouling. Regarding the effect of permeate flux studies have concluded that operating flux is a key operational condition that control membrane performance (Laine, et al., 1991) with more quantitative results presented by (Decarolis, et al., 2001) where they conducted experiments using an inside-out, hollow fiber, PES UF pilot in dead-end operation, a set up similar to the one currently used in this thesis. They identified that membrane performance was observed to deteriorate faster as operating flux increased. Figure 2 was extracted from their study with the observations of the effect of operating flux to the normalized specific water flux Kw/Kw_0 being obvious, with the lower operating flux of 34LMH having much better performance than the higher operating flux of 102LMH. Similar study using wastewater as a feed for an MBR has been presented by (Jiang, et al., 2003) for shorter filtration durations and demonstrated in each operating flux tested (18-52-72LMH) the effect of pore blocking fouling with a rapid TMP increase and the cake filtration fouling that has linear TMP increase.

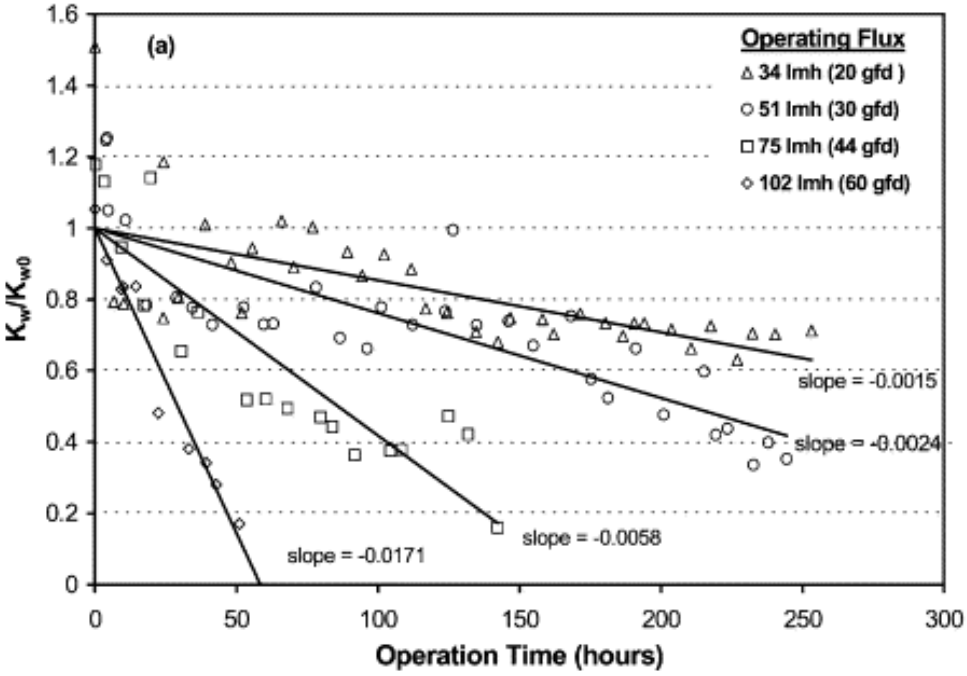

Figure 2. Effect of operating flux on UF membrane productivity: Normalized Kw (Kw/Kw0) vs. operation time for BWI of 20min, adopted from (Decarolis, et al., 2001)

It is also known that flux reduction is partially caused due to fouling and partially due to concentration polarization (Bacchin, et al., 2006). Fouling can be interpreted in the forms of adsorption of particles and solutes to the membrane, partial or full pore blockage, particle deposit growth or gel formation, as explained in previous sections. With concentration polarization there is accumulation of particles or solutes at an area close to the surface of the membranes that causes variation to the osmotic pressure (π) between the feed and the permeate. The osmotic pressure difference reduces the driving force of the filtration which is the transmembrane pressure (TMP) and thus the membrane flux is affected. Higher fluxes in that way will naturally lead to more particles accumulating and an earlier appearance of the phenomenon.

In order to confirm these relationships between these two parameters of flux and fouling, and in order to determine up to which flux a good performance can be achieved, some more information regarding the possible flux definitions need to be explained next.

2.3.iii. Flux Definitions:

Flux/Net Flux/Normalized Flux:

The measure of the flow rate Q at which the permeate passes through the membrane fibers per unit of the membrane surface area (A) is defined as flux. It can be expressed as J=Q/A in $L/m^2/h$ (LMH). If in that amount the losses of permeate product due to backwashing, maintenance cleans and recovery cleans are taken into account then net flux could be defined (ZENON Membrane Solutions, 2006).

Regarding the normalized flux definition, it depends on the parameters that affect the flux by changing the permeability of membrane to water. These parameters are temperature and pressure. A flow rate or a flux normalized for a standard temperature should be corrected using temperature

correction factor ($TCF=e^{K*[1/(273+t)-1/298]}$, where t is the temperature in ^{o}C, and $K=2700^{o}K$ for composite membranes). The temperature normalized flux is then $J_{Norm}=J_{actual}*(TCF_r/TCF_t)$, in LMH at t ^{o}C. Increase in temperature will increase the permeability and thus the permeate flow. Similarly an increase in the net driving pressure the production increases. The term net driving pressure (NDP) is linking all pressures involved in the membrane system, like applied pressure (Pf), pressure drop (ΔP_{fb}), osmotic pressure (P_{osm}), and permeate pressure (P_p), with the following equation ($NDP=P_f-1/2\Delta P_{fb}-P_{osm}-P_p$). (Nitto Denko/Hydranautics, 2001)

Limiting flux

A term that studied in 1970s in (Michaels, 1968) and (Porter, 1972) who defined it as the "maximum stationary permeation flux" achievable with increasing TMP while keeping the rest of the hydrodynamic conditions set. Later in (Wijmans, et al., 1984) the authors defined it as the flux that is independent of the membrane resistance and pressure differences, especially at high values of pressure differences. It is also a value that occurs independently of fouling and is explained by concentration polarization (Field, et al., 1995).

Critical flux

Based on (Bacchin, et al., 2006) the critical flux has been defined, throughout the years since it was first introduced as a term by Field, et al., 1995, either as the one "at which the flux-TMP curve starts to deviate from linearity" or the one for which the irreversible fouling appears and becomes noticeable. In literature it can be found as a strong form (J_{cs}), weak form (J_{cw}) or critical flux for irreversibility (J_{ci}).

The first two terms, which also relate to the first definition of critical flux, where initially presented by (Field, et al., 1995). If the flux-TMP relation of the membrane process is in the beginning the same as the one obtained from pure solvent filtration, then the strong form for the critical flux can be used. In that case as critical flux can be considered the value at which the TMP starts to deviate from the pure solvent flux-TMP line. In the second case, when there is assumed that there is some initial fouling, and the flux-TMP curve will always be below the one for the pure solvent, then the weak form for the critical flux can be used. The critical flux in this case is the flux value at which the flux-TMP curve is not any more linear.

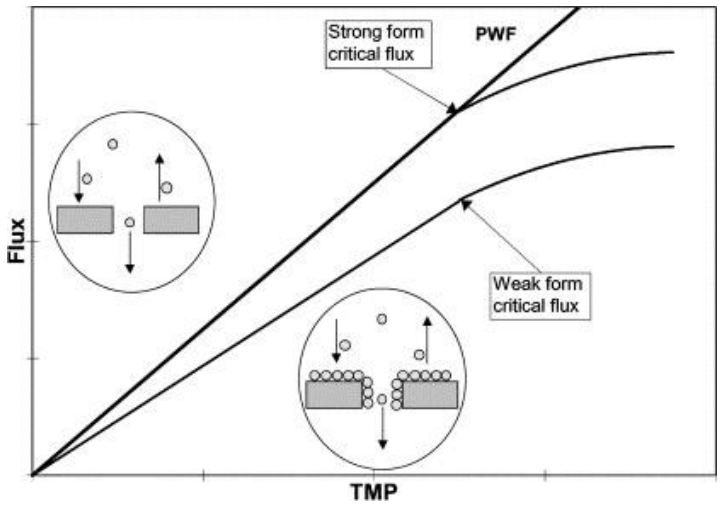

Figure 3. Schematic representation of a weak form and a strong form critical flux. Adopted from (Metsämuuronen, et al., 2002)

This linearity in the sub-critical region of the flux-TMP curve, is also related to a hysteresis effect for repeating cycles of variating fluxes. In more details, for repetition of variating fluxes within the subcritical region the TMP values will also repeat, and vice versa. If a flux above the critical flux will be applied and then restored to a lower value (even within the linear part of the curve), the TMP value in the first and second time will not be the same, with the latter being somewhat increased due to irreversible fouling that occurred above the subcritical region (Chen, et al., 1997).

The third term within the "critical fluxes" terminology, is a flux more related to the transition between dispersed solutes or particles and aggregates on the membrane, with the criterion of reversibility being used, in contrary to the two aforementioned situations describing only if deposition-non-deposition conditions existed (Bacchin, et al., 2006). In the same publication it is also observed that this transition to irreversible fouling can occur either at the strong or weak form of critical flux or at a higher flux. So the flux (J_{ci}) below which the trans-membrane pressure remains stable and additionally the fouling is reversible is defined as critical flux by (Defrance, et al., 1999) and it was explained through colloidal fouling, with a mass transfer equation linking the deposition rate to the hydrodynamic conditions by (Bacchin, et al., 1995).

For dead end filtration however the critical flux concept applied cannot be the same as the cross-flow one. Critical flux is difficult to be observed and instead a criticul filtered volume is used, under which a deposit will not appear on the membrane similarly to the cross flow filtration when critical flux for irreversibility is not exceeded (Bessiere, et al., 2005). Additional concerns were presented in (Le Clech, et al., 2003) where based on the claim that "clean water fluxes are rarely attained due to irreversible adsorption of components not removed other than by chemical cleaning" and that the weak form of critical flux "does not necessarily equate to the clean water flux" alternative manifestations should be proposed. (Howell, 1995) suggested that subcritical conditions should be determined based on the stable filtration operation, like constant permeability over time and not only the fluxes, while several others proposed different definitions for the sub-critical conditions based on the determination method, as summarized for various feedwaters in Table 6 that was extracted from (Le Clech, et al., 2003).

Table 6. Critical flux definitions, adopted from (Le Clech, et al., 2003)

Definition	Method of determinatio	Restriction	Reference
Stable operation for long period	Observation of TMP and flux behavior	Initial flux decline not take account	(Howell, 1995)
Transition between pressure-dependent and pressure-independent flux	Hydraulic tests (changes in TMP for different fluxes)	Short-term experiment	(Bouhabila, et al., 1998)
Inertial lift velocity (*V*IL)	Determination of *V*IL	Based on theoretical model	(Kwon, et al., 1998)
No material deposition	DOTM	Soluble deposition not visible	(Kwon, et al., 2000)
No material deposition	Mass balance	Soluble deposition not visible	(Shirato, et al., 1985)
Stable operation (constant specific flux) from the start-up	Flux-step method	Short-term experiment	(Cho, et al., 2002)
Limiting flux	Stepwise increase of TMP	Less fouling control	(Defrance, et al., 1999)

Threshold flux

Another term that was recently introduced within the group of critical fluxes is the threshold flux. As defined by (Field, et al., 2011) threshold flux is the value below which a low and near constant rate of fouling occurs, while exceedance will lead to markedly increase of the fouling rate. In more general terms the threshold flux can be taken to be the flux that divides a low fouling region from a high fouling region, so it is expected to be higher than the critical fluxes (strong and weak form). Similar definition including the low fouling and high fouling rates is given also by (Luo, et al., 2013) with a more detailed explanation given previously, that below the threshold flux, filtration resistance is independent of flux, with adsorption and reversible fouling almost stable, while above it is flux-dependent (Luo, et al., 2012).

Clearer view of the terms can be sought through the mathematical formulas given in section 2.3.iv. A simple model applicable for dead-end filtration is given in (Field, et al., 2011), that correlates the rate of permeability loss with the flux. The rate of permeability loss is related to the resistance increase and the rate of mass accumulation on the membranes. The foulants which can accumulate regardless of flux or not, are represented with two parameters in that model. These parameters can theoretically vary with the amount of foulants that accumulate for fluxes above the threshold flux. In their work (Hughes, et al., 2006) is using the "filter aid" and the "overclogging" situations in order to explain why this could be true, resulting in different values for the expected fluxes. In the first case the extra layer created by the accumulated cells can be an additional barrier to the material of high fouling impact to the membrane and thus increase the filter performance. However in the second case there might be deposition of specific material (fine particles, soluble components) that can clog the cake layer formed previously causing in that way more intense impacts to the membrane itself, that would have done if the cake layer wasn't present (Bacchin, et al., 2006).

Sustainable flux

Last term that is related to permeate fluxes is the sustainable flux. Again here there are different definitions but most of the authors are concluding that sustainable flux is a value affected by financial and operational parameters. As described by (Field, et al., 2011) it is the flux "at which a modest degree of fouling occurs, providing a compromise between capital expenditure and operating costs". As briefly seen in section 2.3.i capital costs are reduced when a plant is designed for high fluxes, due to lesser membrane modules needed. From the other hand, operating costs are reduced by limiting the energy and chemical costs required, which is true if the fouling rate is restricted. Under these optimum balanced costs a membrane system can operate for extended periods of time.

There are some similarities, between sustainable flux and other "critical fluxes", for example the concept of allowing some fouling to occur while operating a membrane system is similar to the threshold flux that makes the division between low and high fouling rates. The difference is that usually the economically sustainable flux will change with variable water quality, and will be different for different operation conditions that affect the operational costs like the aeration rate in aerobic MBRs while the critical flux will remain unchanged. Moreover the actual value of the sustainable flux can even change if operational costs, not directly relative to the membrane system, change as well; For example if the energy costs rise or if the capital costs or membrane costs decrease (Field, et al., 2011). Different membrane application will have probably different sustainable fluxes, as the sustainable fouling rate is also dependent on additional parameters like the filtration time and the grade of tolerance of the occurrence of fouling or not, depending on operational time.

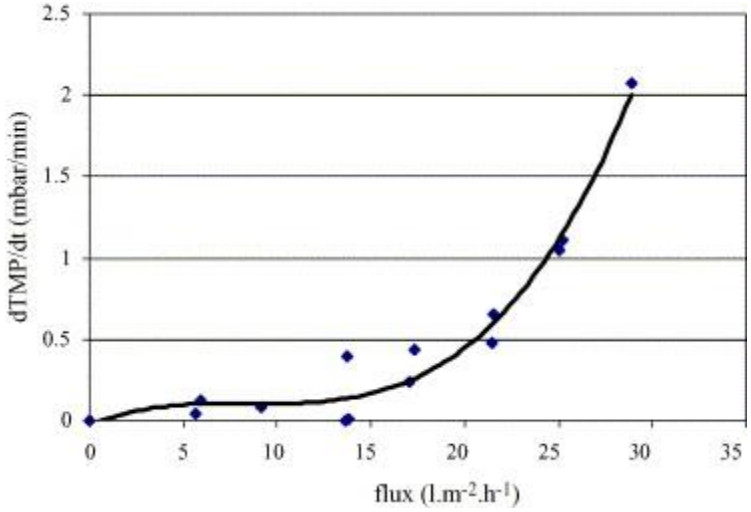

Figure 4. Fouling rate vs. flux. Adopted from (Bacchin, et al., 2006)

To sum up, due to the fact that these economical parameters and the cost evaluation toward sustainable operation can be somewhat subjective, it is difficult to have a set value of sustainable flux. It can be maybe righter to express the flux that is more likely to lead to enlonged operation with the minimum costs as an apparent sustainable flux. This should be the case also when the determination of such a flux value is done through experimental data that is not necessarily true also for a scale-up to the actual plant operation. (Hughes, et al., 2006)

2.3.iv. Determination of Flux: (Fouling equations)

For the determination of the permeate flux in membrane systems different mathematical models and expressions have been established. Some of them are the "gel layer model", the "osmotic pressure model" and the "resistance in-series model" that are explained later.

The "Gel layer model" as described by (Wijmans, et al., 1984) takes into account the solute concentration at the membrane surface (c_m) and tries to relate it to the bulk concentration which is much higher, the permeate flux and the mass transfer coefficient, as combined in equation (Eq. 2):

$$c_m = c_b \exp(J/k) \quad \text{(Eq. 2)}$$

Where c_m= concentration in the surface membrane

C_b= bulk concentration

J= the permeate flux and

k= the mass transfer coefficient

According to this relationship the concentration of the solute at the membrane surface increases rapidly with an increase in the permeate flux, until a value c_g , which is the concentration when the solution is no longer fluid. The gel layer formed at the surface of the membrane has a hydraulic resistance that reduces the permeate flux so that the limiting flux value can be calculated by equation (Eq. 3).

$$J_\infty = k \ln (c_g/c_b) \quad \text{(Eq. 3)}$$

If the gel concentration can be assumed constant, then (Eq. 3) can be rewritten as:

$$J_\infty = k \ln c_g - k \ln c_b \quad \text{(Eq. 4)}$$

So by plotting the J_∞ against the bulk concentration c_b the slope of the trend line (-k) will define the mass transfer coefficient, while extrapolation to the value of $J_\infty=0$ can determine the value of the gel concentration $\ln c_g$. This model can be used for correlating the experimental values of limiting fluxes.

However since the c_m concentration is much higher than the bulk concentration the osmotic pressure effects can be induced that need to be considered. The "Osmotic Pressure model" described in (Wijmans, et al., 1984) and presented next, attributes for this aspect by correlating the permeate flux with the applied and osmotic pressure differences and the membrane hydraulic resistance, as seen in (Eq. 5).

$$J = \frac{\Delta P - \Delta \pi}{R_m} \quad \text{(Eq. 5)}$$

Where J= the permeate flux and

ΔP = the applied pressure difference

$\Delta \pi$ = the osmotic pressure difference

R_m= the membrane resistance

The osmotic pressure difference can be determined by the concentration at the surface c_m, so when the applied pressure becomes higher, there will be an increase in the permeate flux, but after the concentration at the membrane surface becomes significant so is the osmotic pressure difference and thus the effect of the applied pressure difference is cancelled. So the mathematical description of the osmotic pressure model after using the equation to determine the osmotic pressure difference (Eq. 6) and after some derivations (Eq. 7) can be proposed.

$$\Delta \pi = \alpha c^n \quad \text{(Eq. 6)}$$

$$J = (k/n) \ln(\Delta P/(a c_b^n)) \quad \text{(Eq. 7)}$$

However since the particles filtered with UF or MF don't have most of the time significant osmotic pressure, compared to NF or RO the theory is not in many cases applicable to UF or MF. So another mathematical expression for the calculation of the flux reduction can be sought from a usually applied filtration law, an integral form of the Darcy's law, known as the "resistance-in-series model". As appended in (Bacchin, et al., 2006) and summarized here, the model links the permeate flux to various fouling situations according to the following equation:

$$J = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_{ads} + R_{rev} + R_{irrev})} \quad \text{(Eq. 8)}$$

Where: R_m= intrinsic membrane resistance

R_{ads}= resistance due to surface or pore adsorption (independently of flux), ,

R_{rev}= reversible fouling resulted from concentration polarisation layer with monolayer of adsorbed particles and solvents

R_{irrv}= irreversible fouling including pore plugging and cake formation that leads to growth of multiple layers of irreversible fouling that accelerates flux decline

The resistance-in-series model can be used also for the determination of permeate flux within different regions in the flux range (no fouling, low fouling, high fouling). First the strong form of the critical value will be used as a threshold value for the transition of one mathematic expression to another. As for fluxes lower than the critical flux no fouling is assumed the components of the resistances above and below that critical value change accordingly. Also due to low concentration of the solute the osmotic pressure difference can be still neglected. The next set of equations can describe their relationship:

(Eq. 9) $$J = \frac{\Delta P}{\mu R_m}$$, for $J<J_{cs}$

(Eq. 10) $$J = \frac{\Delta P}{\mu(R_m+(R_{rev}+R_{irrev}))}$$, for $J>J_{cs}$

If the weak form of critical flux is used the initial resistance due to surface or pore adsorption has to be counted, and thus the set of equations becomes:

(Eq. 11) $$J = \frac{\Delta P}{\mu(R_m+R_{ads})}$$, for $J<J_{cw}$

(Eq. 12) $$J = \frac{\Delta P}{\mu(R_m+(R_{ads}+R_{rev}+R_{irrev}))}$$, for $J>J_{cw}$

If the transition to the flux region of low and high fouling or reversible to irreversible fouling is to be made, then the critical flux for irreversibility can be used in the expression of the resistance-in-series model. For this case the osmotic pressure differences can no longer be neglected.

(Eq. 13) $$J = \frac{\Delta P-\Delta\pi}{\mu(R_m+R_{ads}+R_{rev})}$$, for $J<Jci$

(Eq. 14) $$J = \frac{\Delta P-\Delta\pi}{\mu(R_m+R_{ads}+R_{rev}+R_{irrev})}$$, for $J>J_{ci}$

For dead end mode, (Harmant, et al., 1996) presented a model that has been developed in order to couple the formation of the irreversible layers with both critical fluxes and critical values of the accumulated mass. The accumulated mass was related to either the filtered volume or a critical operation time, while the flux conditions remained constant during operations (Jönsson, et al., 1996).

As a short summarizing point of the above mentioned terms and mathematical expressions, and in order to have a better understanding an example of the threshold, critical (irreversibility) and limiting flux is given for the case of nanofiltration applications for dairy wastewater treatment (see Figure 5).

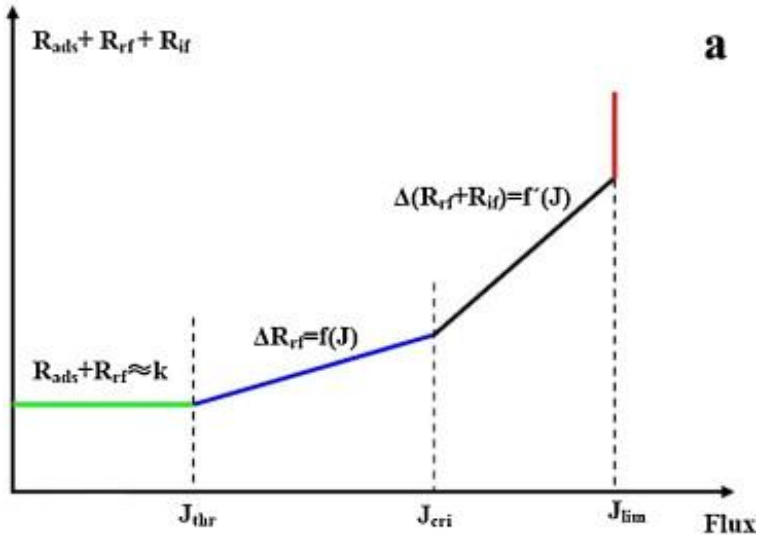

Figure 5. Schematic representation of threshold flux, critical flux for irreversibility and limiting flux for shear-enhanced NF process. Adopted by (Luo, et al., 2012)

Quantification of critical flux

Regarding the determination of the critical values of the permeate flux, based on the fouling behaviour, different methods can be used. (Bacchin, et al., 2006) in their review described the different methods which are summarised here in the 5 bullet points, while their advantages, disadvantages and application are shown in Table 7. For the current study the first and third methods were tried to be approached.

1. Interpretation of "flux-pressure" profiles
2. Flux stepping and Flux cycling
3. Direct Observation through the membrane (DOTM)
4. Mass balance
5. Fouling rate analysis

Table 7. Methods of measurement for critical flux: a comparison. Adopted from (Bacchin, et al., 2006)

Method	Advantages	Disadvantages	Form measured	Suitability
Flux-pressure profile: Deviation from linearity	Simplicity	Can be subjective. No link with reversibility	Strong (J_{cs}) and weak form (J_{cw})	Feeds with low osmotic pressure
Flux or pressure vs. time: Flux stepping	With up and down steps, fouling hysteresis found. Resistance should be determined for each step	Unlike flux cycling, points of transition to irreversibility can be missed	Strong (J_{cs}) and weak form (J_{cw})	Feeds with low osmotic pressure; if correction is to be made for osmotic pressure flux cycling is to be preferred
Flux or pressure vs. time: Flux cycling	Rigorous when allowance made for osmotic pressure	Time consuming and complex	All forms J_{cs}, J_{cw} and J_{ci}	All kinds of feed
Direct observation through the membrane (DOTM)	Direct observation of flux giving deposition. Potential for measuring Jci yet to be exploited	Limited to particulate feeds and membranes that are transparent when wet	Linkage to J_{cs}, J_{cw} and J_{ci} not obvious, but value determined is significant	Particulate feeds
Mass balance	Linked to a complementary parameter, the deposited mass	Need to be used in conjunction with another method	Linkage to J_{cs}, J_{cw} and J_{ci} not obvious, but value determined is significant	Particulate feeds
Determination by fouling rate analysis	If a flux for "low fouling" is not found then determination of dP/dt (under fixed fluxes) may identify a point of sustainable flux. Absolute "no fouling" corresponds to a critical flux	Can be subjective. No link with reversibility	Strong (J_{cs}) and weak form (J_{cw})	All kinds of feed

Chapter 3:
Materials & Methods

After the theoretical background has been established and before the actual experimental part is developed, the methodology followed has to be presented. The methodology includes both the materials used for the conduction of the experiments plus the methods and concepts applied. The materials used are similar for all processes and are presented first (Section 3.1). Then, as within the work scope of the current project there are two phases of optimization involving different methods and techniques, the chapter is divided into two parts (3.2.i & 3.2.ii). One will give the basic procedures of the laboratory studies (3.2.i) and the second the conceptual design and the philosophy of the bench scale study (3.2.ii). Additional information regarding material specifications or experimental procedures are also appended at the end of the report.

3.1. Materials

3.1.i. Raw water

The raw water used in both the experimental processes (lab studies and bench scale studies) was collected from one of the reservoirs in Singapore. The surface raw water characteristics are presented in Table 8. It can be noted that the water has low TOC and turbidity values. The water samples after collection were stored in jerry cans at room temperature of around 25oC, with the experiments conducted a few days after each collection. For the case of the bench scale studies the raw water used for the different runs was collected once and was stored in the 250L raw water feed tank again under the same temperature conditions while adequate mixing using four submersible aquarium jet pumps, was provided in order to keep the sample homogeneous for the different runs and prevent settling.

3.1.ii. Chemicals

As far as the chemicals utilized are concerned, during the coagulation process of “optimization phase I” four different coagulants were used. These coagulants were the reference Aluminum Sulphate solution (Alum), and the three alternative ones: Aluminum Chlorohydrate solution (ACH), Polyaluminum Chloride solution (PACl) and Ferric Chloride solution. The concentrations and analysis results are given in the specifications of Table 15 presented in APPENDIX II.

For the final part, in “optimization phase II” the optimum coagulant selected (ACH) was used, from the same stock source, in a concentration adjusted by the dosing pump capacity and the required dosing rate. Additional to coagulants, chemicals for the membrane cleaning were used as well. Citric Acid ($C_6H_8O_7$) in a concentration of 2000ppm was prepared and sodium hypochlorite (NaOCl) of concentration 500ppm was required.

Table 8. Raw water quality

Parameters	pH	Colour	Conductivity	Turbidity	TOC	Tot.Alkalinity	Chloride
Units	-	Hazen	µS/cm	NTU	mg/L	mg/L	mg/L
Avg.Values	6.82	14	215	1.2	2.7	19	33

3.1.iii. Membranes and supplementary equipment

Regarding the consumables of the filtration step simulated in the lab, a vacuum pump, filter housing and 0.05µm membrane filter papers were mainly used. If analyses for parameters in dissolved state like dissolved organic carbon, dissolved aluminium or iron were necessary, 0.45µm syringe filters mounted on 10mL disposable syringes were utilized. Other consumables for the lab studies mainly consisted of test tubes and plastic bottles for sample collection. For the bench scale studies, other than the chemicals, the membrane module used can be listed as a necessary piece of equipment. For reference purpose APPENDIX II gives some general and technical specifications of the chemicals and consumables.

3.2. Methods

Prerequisites for the optimization of treatment processes are first the understanding of the concept behind them and then the identification of the most suitable way for their simulation. For the "hybrid inline coagulation- UF" process, the concept is quite simple, even though a bit different from the conventional method of coagulation/flocculation.

The differences between the two methods lie on the fact that for the coagulation of the raw water with the dosed chemicals, the reaction time is less and occurs inline and not in a separate tank. Similarly is the flocculation, where there is no discreet step (tank) for that. Moreover the mixing required is provided by the turbulence created in the pipeline or with static mixers instead of rapid tank mixers. Finally the dosed water is supplied to the membrane tanks for filtration while in the conventional process usually is supplied to single-medium/multi-media filter beds. The similarities between the two processes are that the same coagulants can be used if they are proven to be beneficial for the process improvement and that backwashing is needed in both systems but in different intervals.

In general a simple procedure that could be used to describe the concept behind the hybrid inline coagulation-flocculation system is the following:

1. Coagulants are dosed inline to the raw water to be treated, along with other chemicals that might be required i.e. acidic/basic solutions for pH control.
2. Coagulated/Dosed water is supplied to membrane tanks from where it will be filtered using either positive or negative pressure, in order to produce the final permeate water.
3. Hydraulic backwashing with the produced permeate will occur in frequent intervals between the filtration cycles to remove the reversible (cake) fouling.
4. Chemical backwashing with sodium hypochlorite and/or sodium hypochlorite and citric acid ($NaOCl/C_6H_8O_7$) can be initiated in less frequent intervals for removal of non-backwashable reversible fouling.

Table 9. Overview of optimization process

	Treatment Process	Simulation Method		Operation
	Hybrid (Inline Coagulation/UF)	Modified Jar Test	Filtration through 0.05µm filter paper	Bench scale hybrid system
Target:	Understand the process	Optimize pretreatment		Optimize operation

Next step after understanding the concept of the process is its simulation in the lab (optimization phase I) with appropriate methods, while the final step will be to test the membrane operation and optimize its performance (optimization phase II). In the following sections the methods explained earlier, for the simulation of the inline coagulation/UF process in the lab and the bench scale UF system provided by NUS (supported by EWI funding), are going to be described. For the lab study mainly steps 1 and 2 are applicable as there is no need for backwashing or membrane recovery, while for the bench scale system all steps can be applicable.

3.2.i. Optimization phase I: Pretreatment

An overview of the optimization process is presented in Table 9, where the methods used for the simulation of the hybrid system in the lab are also shown. The inline coagulation was simulated using a modified jar test procedure where only the rapid mixing (at 180rpm for 1minute) was applied after the coagulant dosing. Then the dosed water sample was filtered using a 0.05μm MF-Milipore™ Membrane filter paper, to simulate the UF filtration step (for a more detailed description of the procedure refer to APPENDIX I).

The filtrate was considered product water (quality-wise) and was compared for the optimization purposes to both the raw water quality as well as with the water quality of other batches' filtrates. The samples were compared based on the effect of the coagulants to dosed water pH, TOC removal efficiency, product water turbidity and total aluminum concentration of the product water.

3.2.ii. Optimization phase II: Membrane Operation

For the phase II of the optimization a bench scale pilot was used that followed a quite simple concept. For the holistic description of the pilot both the conceptual design and the philosophy behind the design for the determination of the appropriate parameters of the operation, are going to be presented in the following sections.

Conceptual Design

To describe the conceptual design of the system the schematic in Figure 6 can be found useful. As it is observed and described in a previous section there are five main sub-processes involved in the process, the coagulation, the pH control, the filtration, the backwashing and the CIP process.

The concept can be similar to the general concept behind the hybrid inline coagulation-flocculation system that was described earlier, with some adjustment and more details based on the current pilot:

1. ACH was used as coagulant which was dosed inline in constant dose to the raw water for treatment, without any other chemicals that might be required in different cases for pH control
2. Coagulated/Dosed water was supplied to the membrane module , which was operated in dead end mode, and from where it was filtered using a feed pump providing positive head, in order to produce the final permeate water
3. Hydraulic backwashing with the produced permeate occurred in frequent intervals of 15min between the filtration cycles in order to remove the reversible (cake) fouling.
4. Cleaning –in-place was applied at the end of every constant flux operation, by soaking in 500ppm sodium hypochlorite (NaOCl) followed by soaking in 2000ppm citric acid ($C_6H_8O_7$) in order to remove the non-backwashable reversible fouling and restore the membrane module's properties.

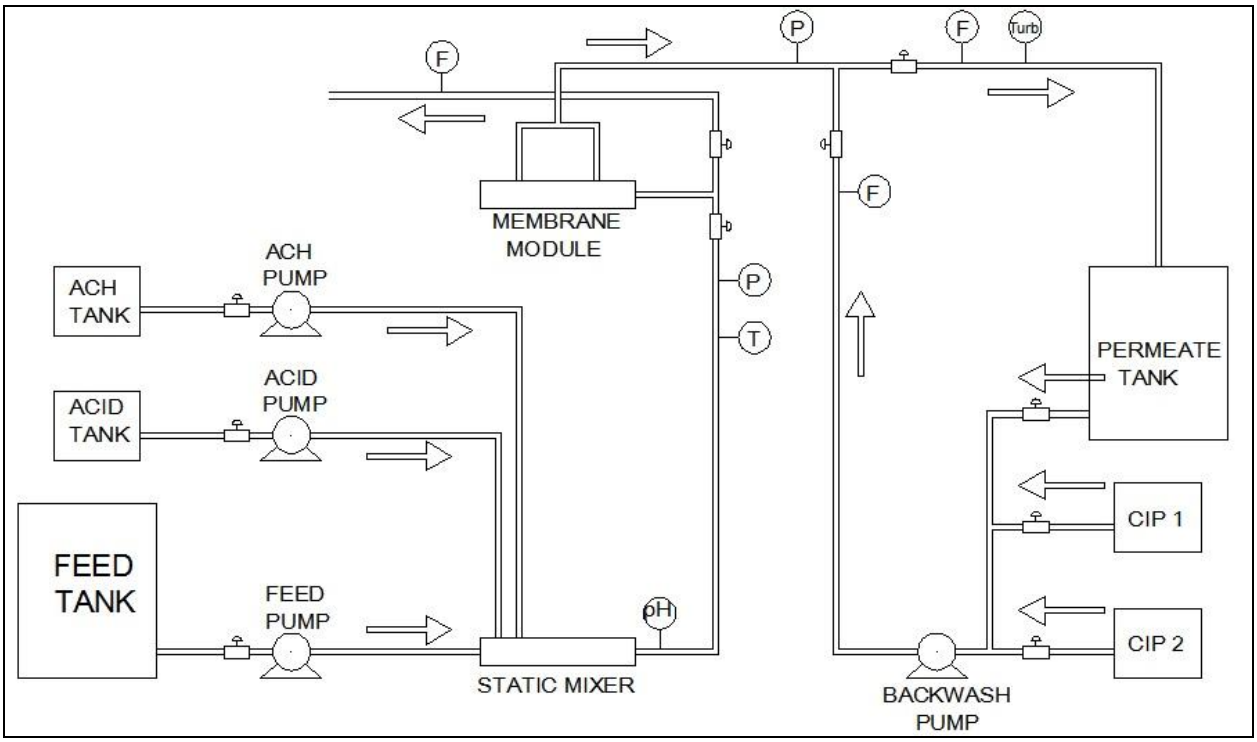

Figure 6. Schematic of hybrid coagulation/UF bench scale system

Philosophy of the design

For the determination of the variables and constants that are required for the system setup the parameters interacting with each other in the separate processes were divided and summarized in Table 10.

The constant parameters could be either fixed, or had to be defined. For example the fixed constants were the capacities of the installed pumps ($Q_{i,min}$, $Q_{i,max}$), the membrane module surface area (A), the volumes of the tanks used ($V_{i,max}$, V_{module}) and the coagulation dosage that has been already optimized.

The constant parameters that had to be selected were the permeate operating fluxes (J_i) based on the pump capacities, the chemical concentrations (C_i) so that the tank volumes would be adequate to store the required chemicals, and some other parameters like the backwashing operating time (t_{BW}).

Finally the variables included the feed flow rate (Q_{Feed}), in order to achieve the predefined fluxes (J_i), the filtration time (t_{Filt}) that had to be also determined based on the filtered volume (V_F), the coagulant flow rate (Q_{ACH}) that was variable in order to achieve every time the required dosage and finally the backwashing flowrate (Q_{BW}) that had to be 2-2.5 higher than the feed flow rate Q_{Feed}.

Table 10. Summary of constants and variables used for the set-up of hte bench scale pilot

Sub-process	Constants (Fixed)	Constants (Predefined)	Variables
Filtration	Q_{min}, Q_{max}, A, V_{mod}, V_{max}	J	$Q_{Feed}=f(J)$, $t_{Filt}=f(V_F)$
pH control	Q_{min}, Q_{max}, V_{max}	$C_{Acid/Base}$	
Coagulation	Q_{min}, Q_{max}, V_{max}, Dosage	C_{ACH}	$Q_{ACH}=f(dosage)$
Backwashing	Q_{min}, Q_{max}, V_{max},V_{mod},V_{tub}	t_{BW}	$Q_{BW}=f(Q_{Feed})$
CIP	Q_{min}, Q_{max}, V_{max}	C_{Citric}, C_{NaOCl}	

Chapter 4: Results

Under this chapter the available results will be presented and elaborated. The data sources vary for each phase that tried to be optimized, based on the respective objectives. "Optimization phase I" results consist mainly of the outcomes of the laboratory measurements conducted for the evaluation of the most potentially feasible pre-treatment coagulant for the hybrid inline coagulation/UF system, which was selected based primarily on the filtrate water quality achieved in every scenario. From the other hand the "Optimization phase II" results cover more the operational parameters with respect to fouling rate, and include in a lesser grade some water quality results. The main focus will be on the TMP profiles and the productivity in terms of specific water flux (K_w), while also information that can help later the determination of the critical fluxes will be presented. Finally the hydraulic resistances of the membrane process will be tried to be explained through the received results.

Most of the upcoming graphs and plots are either the summaries or averaged values of the data acquired, while the full analytical data results are available in the appendices.

4.1. Optimization Phase I: Pre-treatment results

In the following sections (4.1.i.a -d) the graphical representation of the results for the measured water quality parameters are summarized, with the required justification, comments and preliminary conclusions for the lab studies.

4.1.i. Water Quality parameters

a. Parameter: Dosed water and filtrate pH

From Figure 7a it is shown that pH is not affected a lot by the variations in the ACH or PACl dosages. Dosed water pH values are close to the raw water pH, with small increments or decrements in the range of 0.1-0.2 being observed. At the plot, the one-point-Alum pH values are shown as adjusted near 6.0. Different Alum dosage is needed every time for the raw water pH to be corrected to 6.0-6.1.

The pH difference of dosed water using the alternative coagulants compared to that of adjusted pH when using alum, is also in some degree carried over to the filtrate pH (Figure 7b) which can introduce potential savings in terms of lime cost. A preliminary lime study on the lab filtrates showed that the amount of lime needed for the post adjustment of filtrate pH to 8.0-8.1 was 48% less, meaning that the chemical costs of pH post-treatment will be already halved. Additional chemical cost savings will be introduced also if the chosen optimized coagulant dosage has lower price compared to alum, if the required dosage is lower than the one for aluminium sulphate.

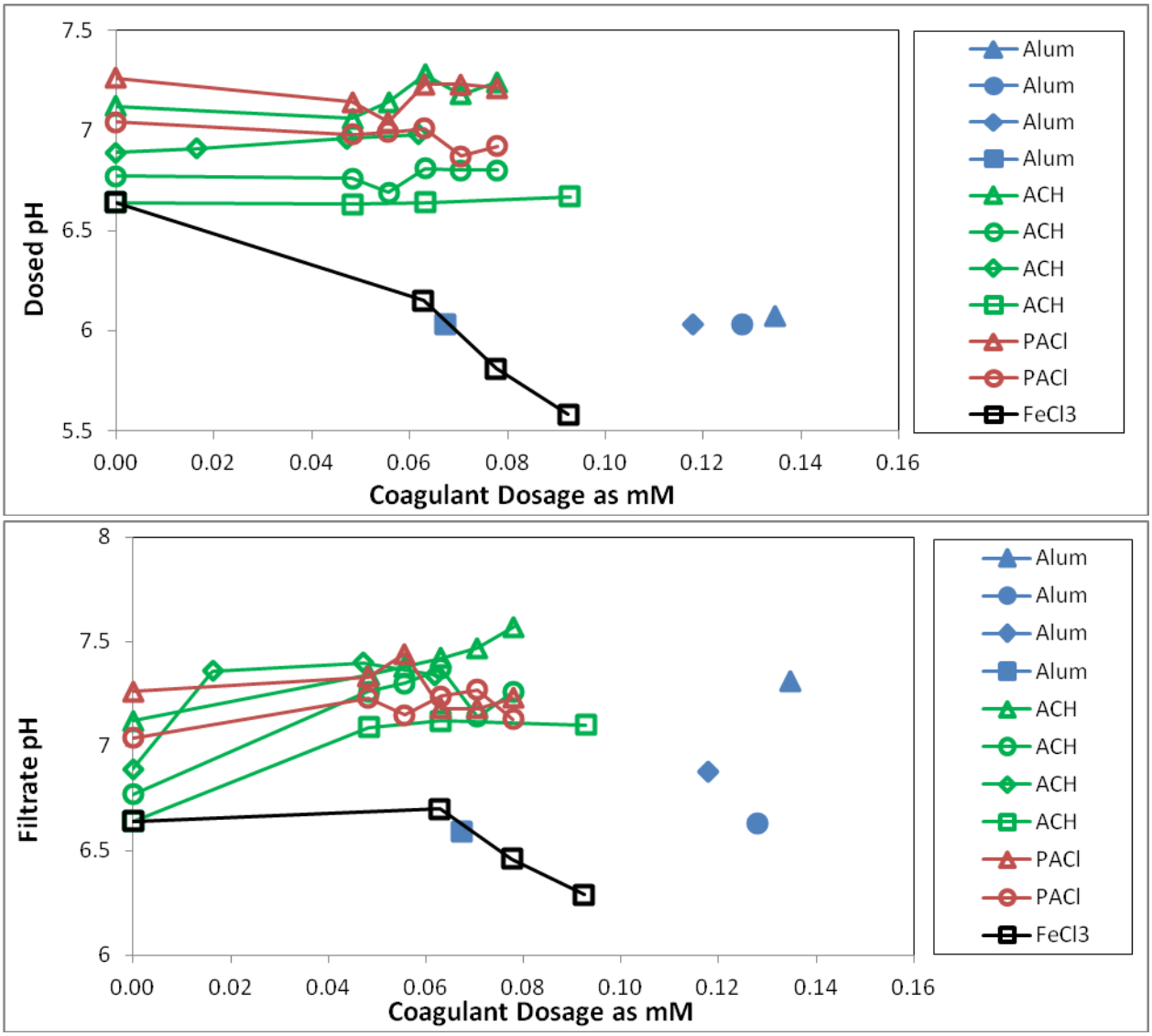

Figure 7. Summary plot: a. Dosed water pH vs coagulant dosage as mM (top), b. Filtrate pH vs. coagulant dosage as mM (bottom) Blue=Alum, Green=ACH, Red=PACl, Black=FeCl3

b. Parameter: TOC

For the interpretation of the TOC results, both absolute and relative values (removal efficiencies %) are used. In terms of absolute values in all cases but the last (Figure 8) the filtrate TOC of the reference coagulant (alum) gave the best results. As a first observation of the jar test results the new tested coagulants achieve satisfying values as presented from the relative removal percentages.

Some preliminary conclusions drawn from the plots of Figure 8 are that:

- The TOC removal efficiency achieved by the Alum dosing (35-45%), can be comparable to the one achieved if ACH is used in the inline coagulation process (30-40%)
- TOC removal efficiency of ACH confirmed with jar test results
- The dosages required are lower if ACH is used as coagulant for comparable TOC removal efficiencies
- PACl has much lower TOC removal efficiency ranging around 20%
- FeCl3 has higher TOC removal efficiency ranging also around 40%

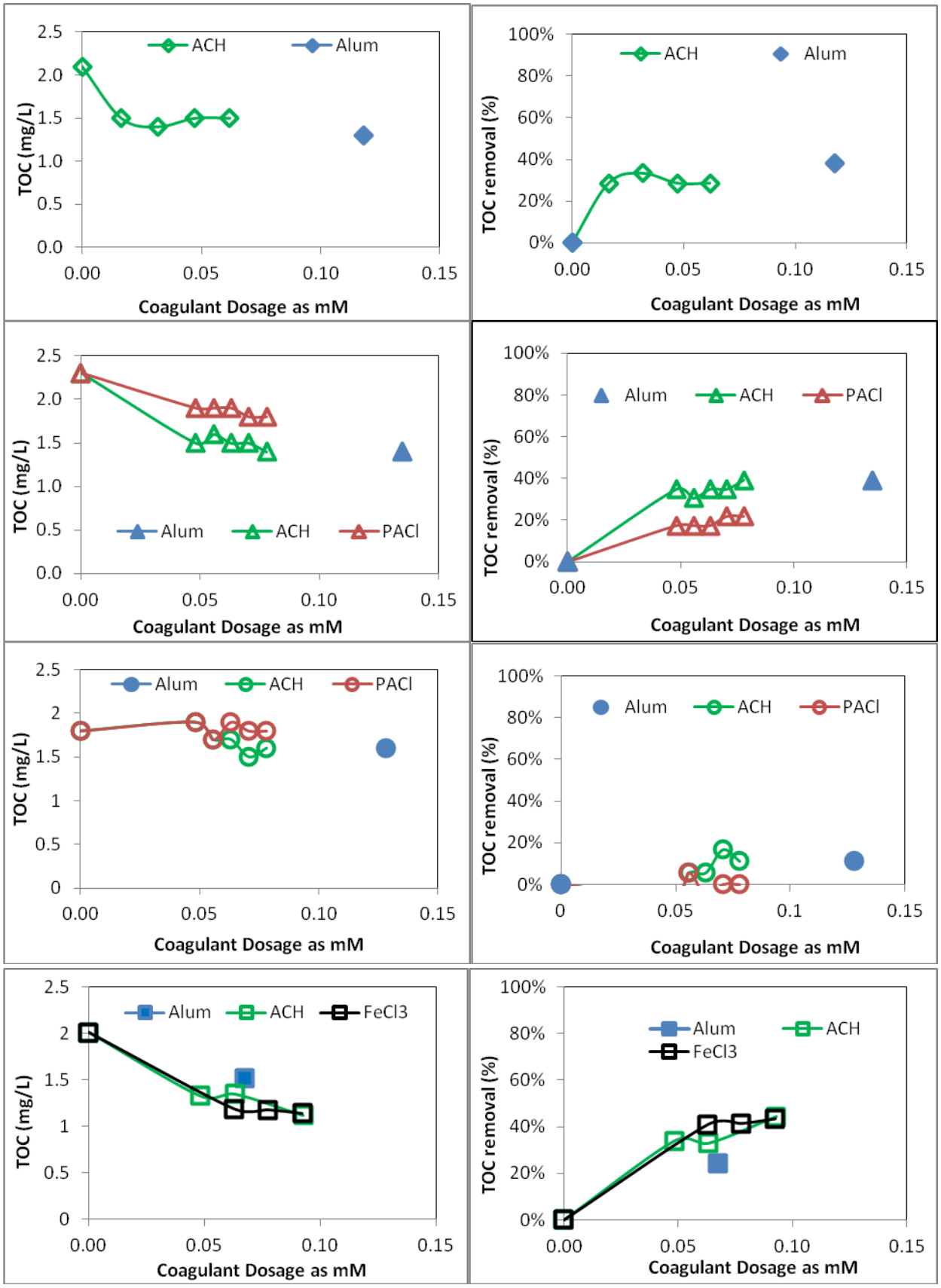

Figure 8. Summary plot: TOC & TOC removal efficiencies vs. coagulant dosage as mM
Blue=Alum, Green=ACH, Red=PACl, Black=FeCl3

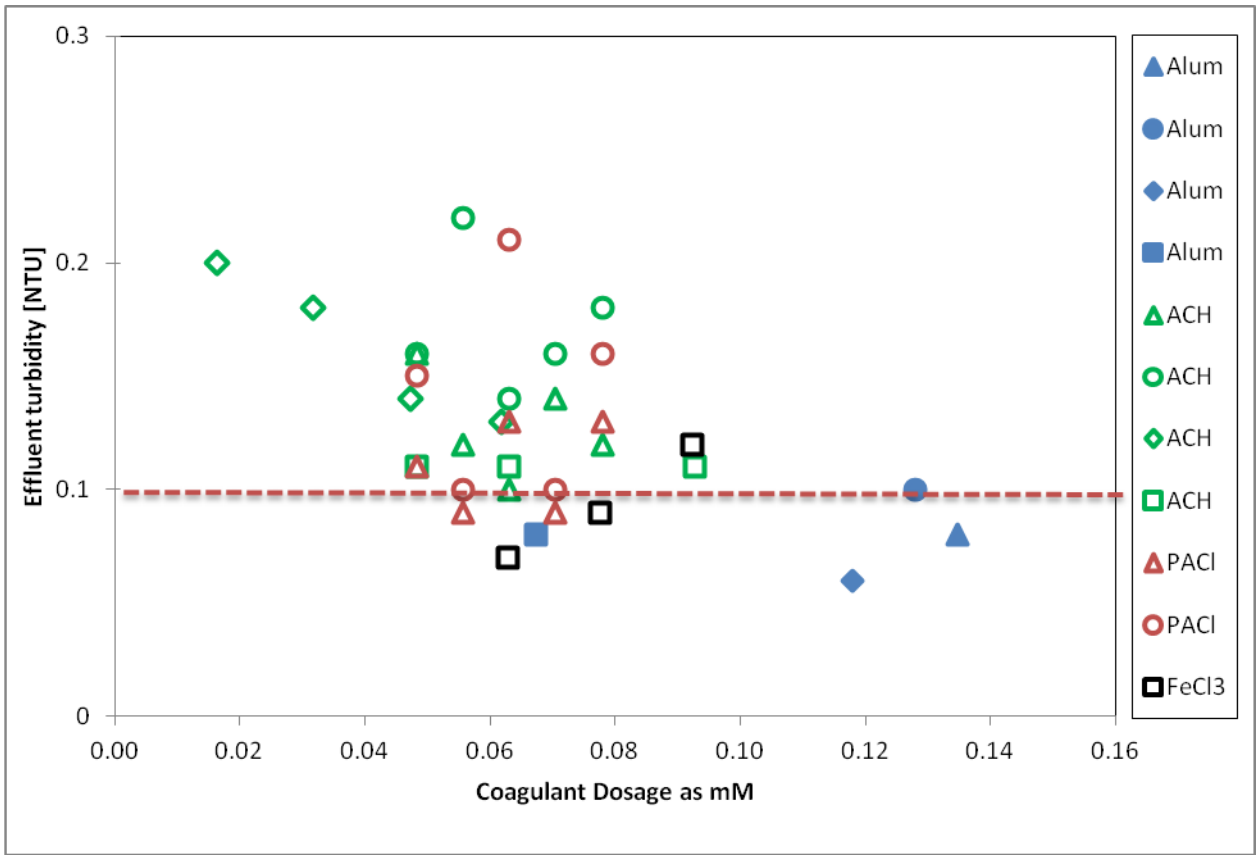

Figure 9. Summary plot: Effluent turbidity vs coagulant dosage as mM
Blue=Alum, Green=ACH, Red=PACl, Black=FeCl3

c. *Parameter: Filtrate turbidity*

Based on the jar test results, in a brief observation almost all samples show low filtrate product water turbidity ranging between (0.09-0.20NTU). As observed in Figure 9 the reference coagulant (alum) has satisfactory results with filtrate turbidity lower than the set threshold value of 0.10NTU. From the other alternative coagulants, PACl is the one that is comparable in terms of turbidity removal as well as FeCl3, while ACH shows slightly higher values. However the UF membranes at the larger scale are expected to be able to achieve high turbidity removal efficiencies, with absolute turbidity values lower than 0.10NTU.

d. *Parameter: Aluminium concentration*

The graph of aluminium concentration (Figure 10) show that based on the jar tests, almost all values are within the internal PUB limit of 0.05mg/L. It is also easily observable that since the dosed water pH doesn't vary significantly when the new coagulants are dosed, the aluminum concentration –which is affected by the pH- ranges within smaller spans of ±0.01 mg/L. Generally, PACl reflected to lower residual aluminum concentrations, comparable to the control coagulant (alum). ACH had a wider range of results for the parameter of aluminum concentration at the filtrates, based always on jar tests.

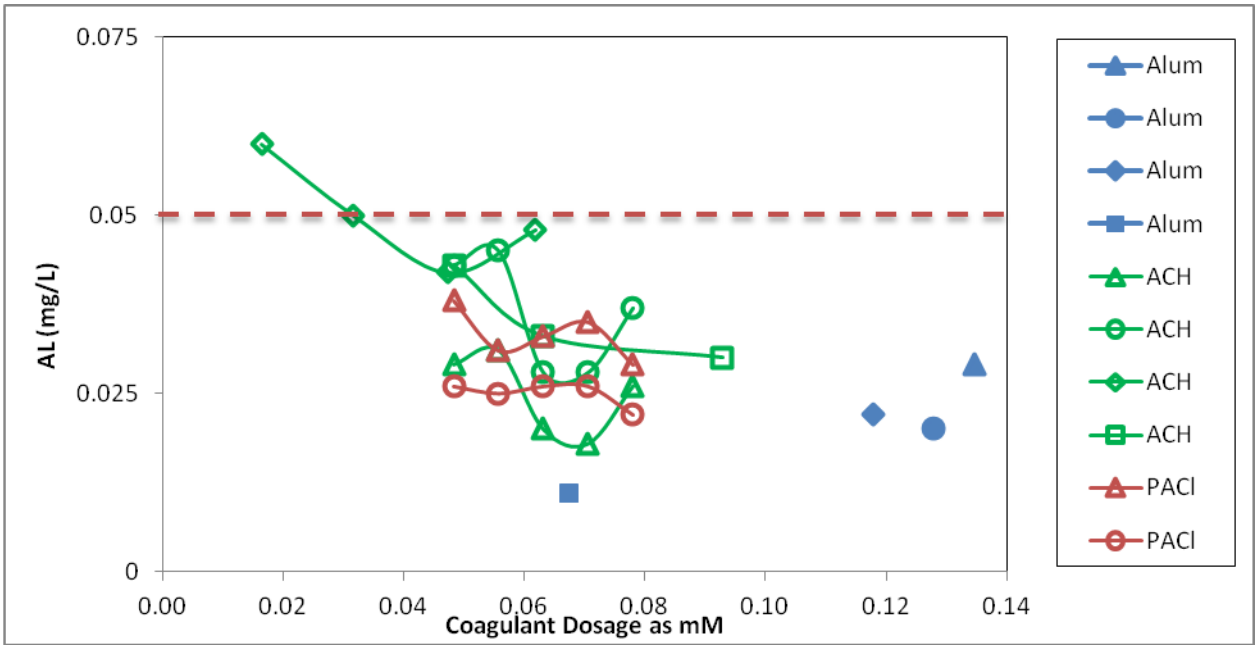

Figure 10. Summary plot: Aluminum concentration after filtration vs. coagulant dosage as mM Blue=Alum, Green=ACH, Red=PACl

4.2. Optimization Phase II: Membrane Operation

The phase II of the optimization process mainly focuses on the membrane performance concluded by elaboration of the TMP and specific flux profiles, in order to understand the rate of TMP increase or the productivity losses, as well as the increase of the hydraulic resistance of the membrane module. All these results can be used for the determination of the effect of the operating flux to the membrane fouling. Critical values for the fluxes can be set as well. In order to comply with the water quality limits some plots with the results of the filtrate will also be presented.

4.2.i. Water quality parameters:

In accordance with the previous chapter with the laboratory results, a series of water samples was also taken during the bench scale pilot operation for the determination of the filtrate water quality. Other than the parameters of pH and turbidity, that were monitored online, TOC, total aluminium concentration, UV254, colour, TDS and conductivity were also measured. Average values of the results are presented next while some summary graphs are plotted for reference.

TOC results as summarized in Figure 12, show TOC removal efficiency around 30%, while all the dissolved aluminium concentrations where within the limit of 0.05mg/L (Figure 13). pH was monitored online continuously without any significant changes observed as the coagulant dosage was kept the same and the batch of raw water was homogenous. Turbidity was monitored online intermittently, but it shouldn't be an issue for membrane filtrates as the membrane acts as the barrier achieving high turbidity removal. For colour removal the principle is the same with no problems observed for its elimination. UV absorbance was kept within a limited range between 0.023-0.028., translated to specific UV adsorbance (SUVA) range of 1.4-1.8L/mg.m. Since the range is below 2L/mg.m the dominant group of NOM fractions is most probable non-humic substances. Finally for TDS and conductivity as well there are not any significant variations by changing operating fluxes.

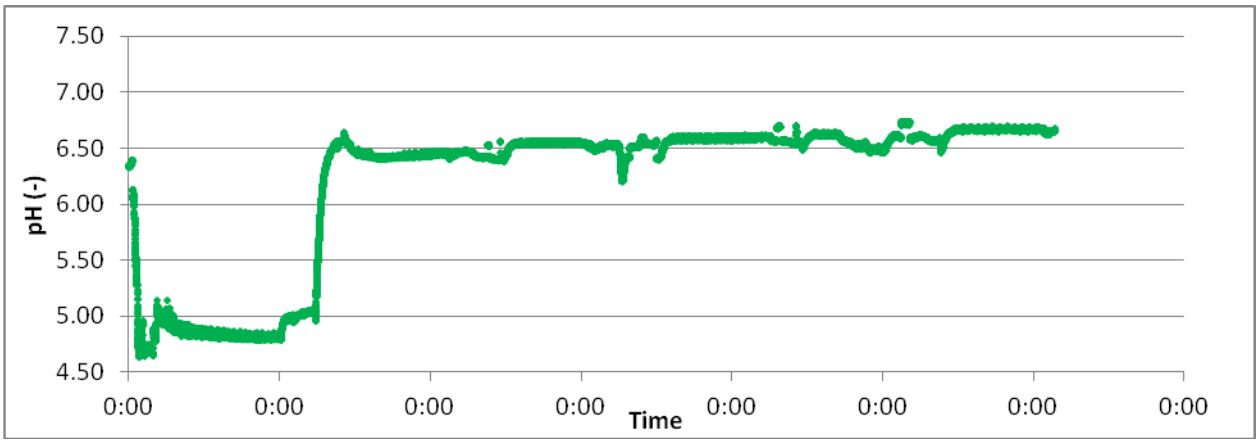

Figure 11. pH profile for all tested fluxes

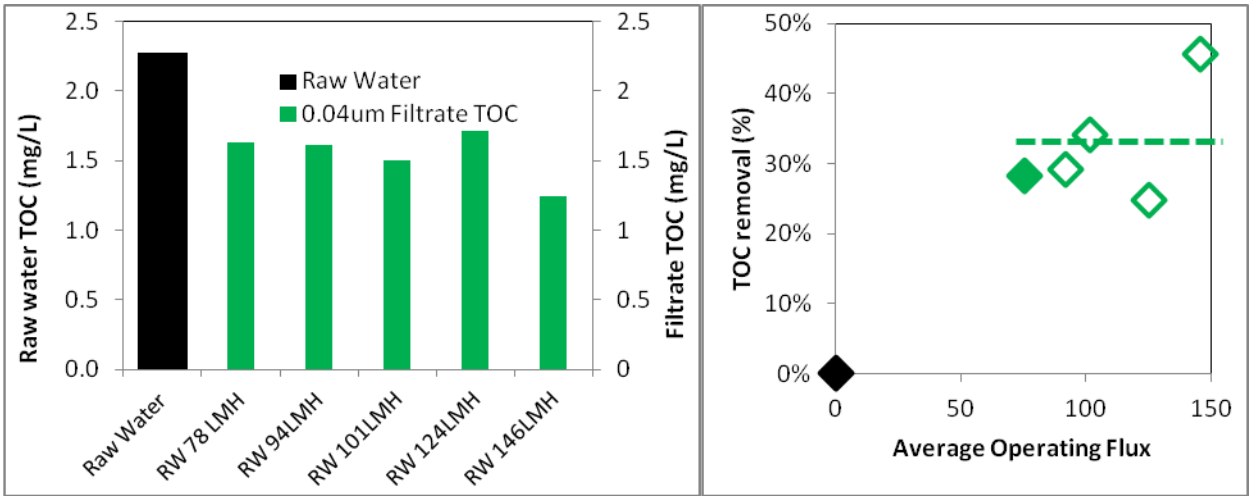

Figure 12. Summary plot: TOC & TOC removal efficiencies vs. operational flux for the optimum ACH dosage

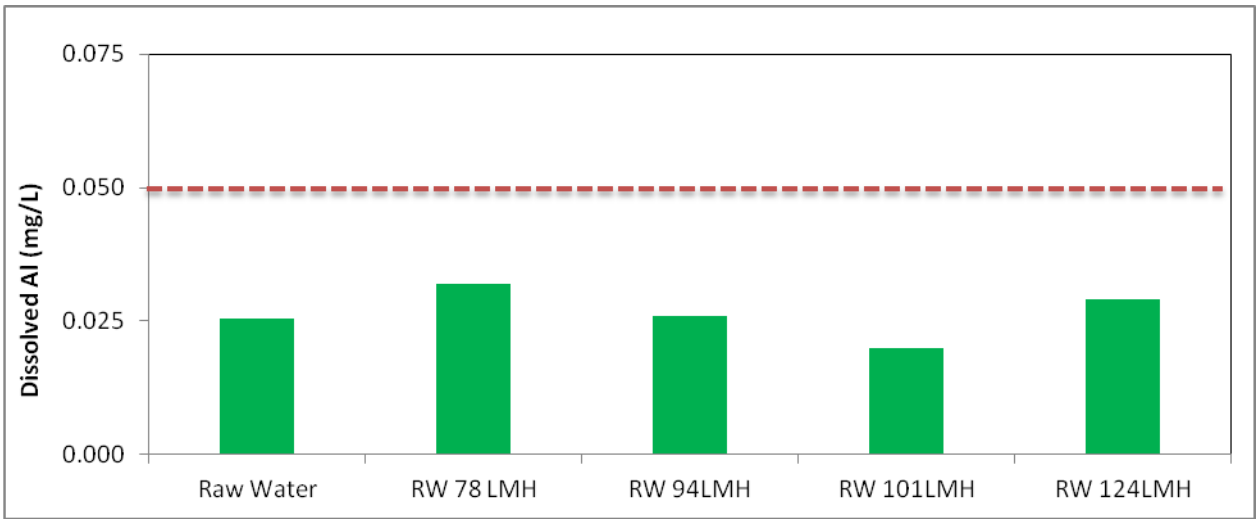

Figure 13. Aluminum concentration of the filtrates (0.04um) for different flux operations (used coagulant: ACH)

4.2.ii. Membrane Performance:

The current section consists of the results of all the operational parameters, which were either monitored or calculated for the batch experiments in the bench scale pilot plant. Of main focus were primarily the trans-membrane pressure (TMP) profiles, including plots of absolute values and relative rates of change with time. Secondarily there was focus on the productivity parameters expresses as the specific flux or permeance normalized over pressure, again with absolute and relative values for comparison purposes. These results will lead to conclusions for the fouling behavior and whether or not it is affected by the operational flux variations. As a reference for the comparison, operation with a pure solvent (deionized water) will be used under set reference operating conditions for the treatment of the same raw surface water.

a. Trans-membrane Pressure (TMP) Profiles

In the experimental set-up of the bench scale UF system the transmembrane pressure wasn't directly monitored, but it instead could be easily calculated. Since there where installed pressure sensors before and after the membrane module, TMP was determined for every time step by substracting the effluent side pressure (P_e) from the feed side pressure (P_f), or $TMP=P_f-P_e$. The timeseries of TMP for the various fluxes tested are presented in APPENDIX III (Figure 30 & Figure 31).

A more detailed and concise representation of the TMP for every filtration cycle for all the tested scenarios is given in the box and whisker plots of Figure 32, Figure 33 and Figure 34. In those plots the box gives the range of the 50% of the observed values, with the three horizontal lines indicating the value of the 1st (25%) percentile, the median and the 3rd (75%) percentile. The length of the whiskers refers to the observed values till the maximum and minimum values. Outliers have to be excluded in order to keep the length into reasonable ranges, so the top and bottom 1% of the observed values are excluded. The average values of the maximum, 3rd percentile, median, 1st percentile and minimum from all filtration cycles will be used to create the box and whisker diagram for each tested operating flux which are summarized in Figure 14.

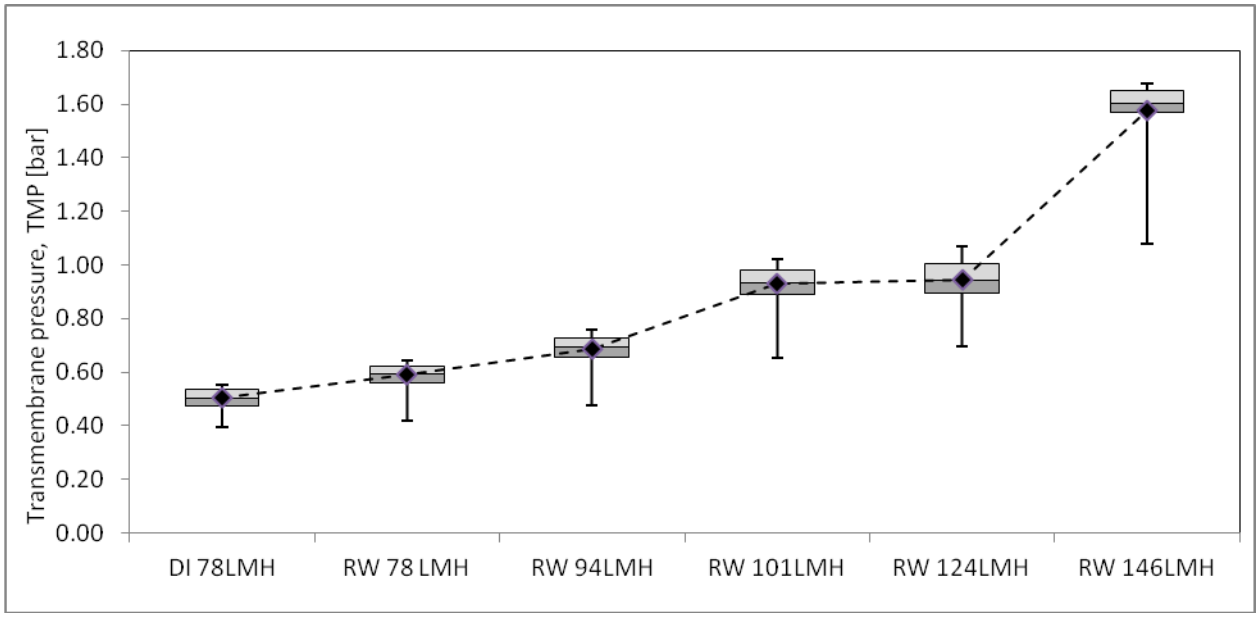

Figure 14. Summary of average TMP values for different flux operations
Box=Range of 50% of the values, Top/Bottom Whiskers=Max/Min value observed excluding outliers (99%-1%), Dotted line: Average values

Additional to the aforementioned values in Figure 32, Figure 33, Figure 34, the average value of each filtration cycle is also plotted and finally connected with the dotted line in order to create the average TMP profile vs. time for each operating flux. The average TMP profiles of all the measured fluxes are then summarized in one graph (Figure 15) for comparison purposes and further elaboration.

From both plots (Figure 14 & Figure 15) it can be observed that an initial TMP around 0.50bar is established for the pure solvent (DI) filtration at 78L/m^2-hr (LMH), while there is a slight increase to 0.58bar when raw surface water is filtered under similar flux conditions (74LMH). Noticeable is also that there is gradual increase of the trans-membrane pressure with increasing operating fluxes. Doubling of the operation flux leads to 2.7 times higher TMP, which can be translated to higher operating costs.

The TMP increase is also an indicator of membrane fouling, as for constant flux operation the accumulated cake layer and/or the worsening of pore blockage add extra resistance to the initial membrane resistance and thus increase the feed side pressure needed for the continuation of the filtration process. Therefore in order to understand better the fouling tendecy of the membrane process, the TMP increase and the hydraulic resistance are studied next.

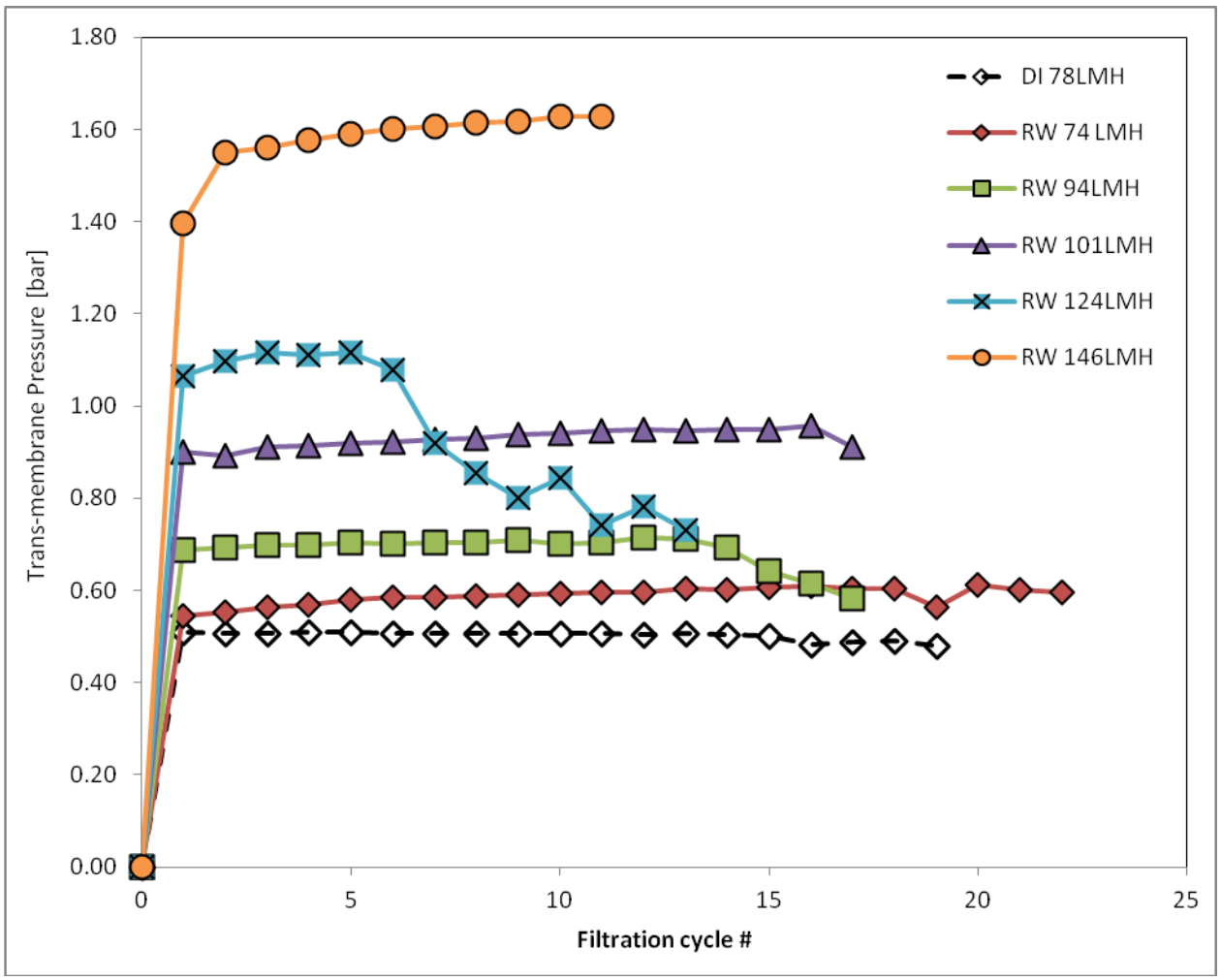

Figure 15. Average TMP profiles under different flux operations vs time (15min filtration cycle)

b. Fouling tendency- Rate of TMP change

The rate of TMP increase is an important parameter for the evaluation of the fouling behaviour of the different applied scenarios. For the determination of the fouling tendency, the TMP values for each 5sec timestep were plotted against the lapsed time and were analysed for every filtration cycle and operational flux as seen in Figure 35-37 (Appendix III). Trendlines were added, with the slope indicating the increase rate of trans-membrane pressure between two consecutive hydraulic backwashes. Where some fluctuations and TMP decline were observed like for the operational flux of 124LMH due to minor leakages,the results were discarded and the filtration cycles were excluded from further elaboration. The results per 15-minute filtration cycle are plot in Figure 16 with the average values of the fouling rates per operational flux given in Table 11 while a summary of the full results of the fouling rates of each cycle that was run under different operational flux can be retrieved from Table 20 in APPENDIX III.

As expected and observed in Figure 16, the higher fouling rate occurs for the highest operational flux tested (i.e 144 L/m^{2}h) with an initial rate around 0.87bar/h later stabilising at around 0.60bar/h. In a descending average fouling rate order the other operational fluxes were 126 L/m^{2}h, 108 L/m^{2}h and 74 L/m^{2}h, while the lowest fouling rate for filtration of raw water was on average for the operational flux of 90 L/m^{2}h. The lowest fouling rate was initially 0.42bar/h, stabilising later at ca. 0.16bar/h.

In a trial to correlate the fouling rate and operational flux (Figure 17) it is concluded that for approximately a 50% increase in operational flux (72 to 108 L/m^{2}h) the fouling rate increased by 68% while for a 100% increase it more than tripled. Noticeable is also that for a slightly higher flux (at 94 L/m^{2}h) the fouling rate remained to a similar range.

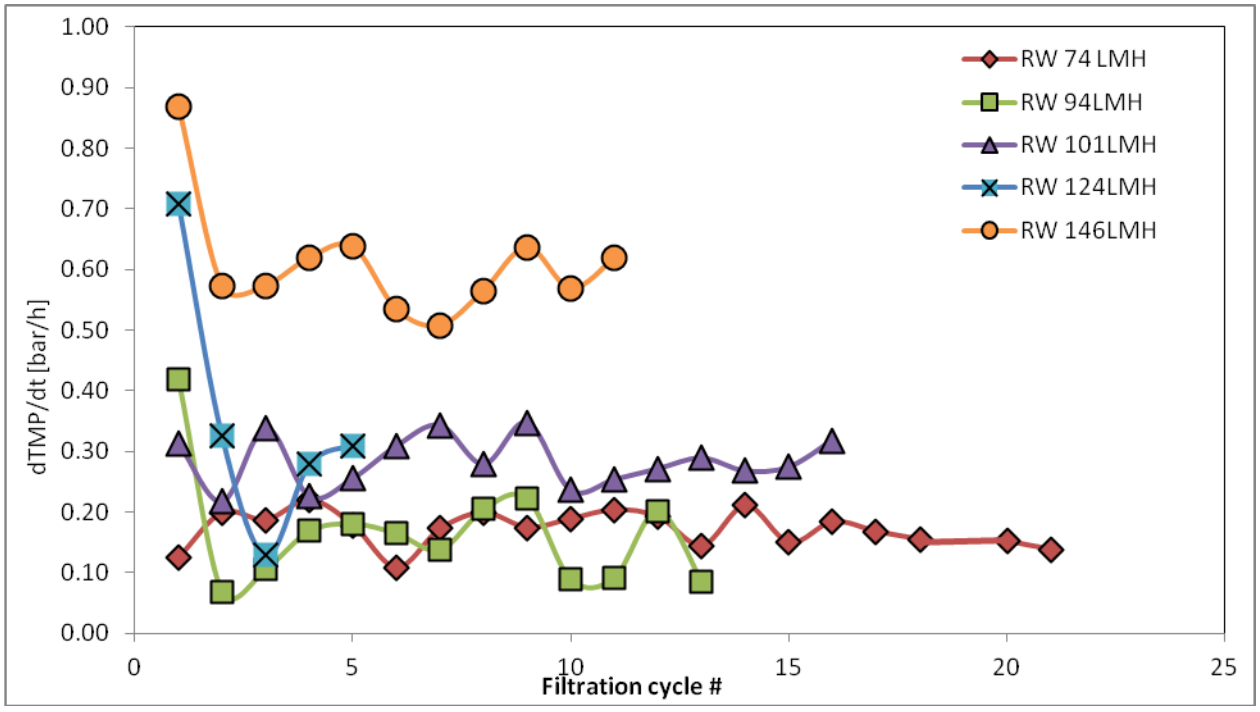

Figure 16. Fouling rate profiles for tested fluxes

Table 11. Fouling rate of each operational flux

Operating flux	DI (74LMH)	RW 74LMH	90LMH	108LMH	126LMH	144LMH
	bar/h	bar/h	bar/h	bar/h	bar/h	bar/h
Average fouling rate	0.032	0.182	0.164	0.283	0.350	0.609

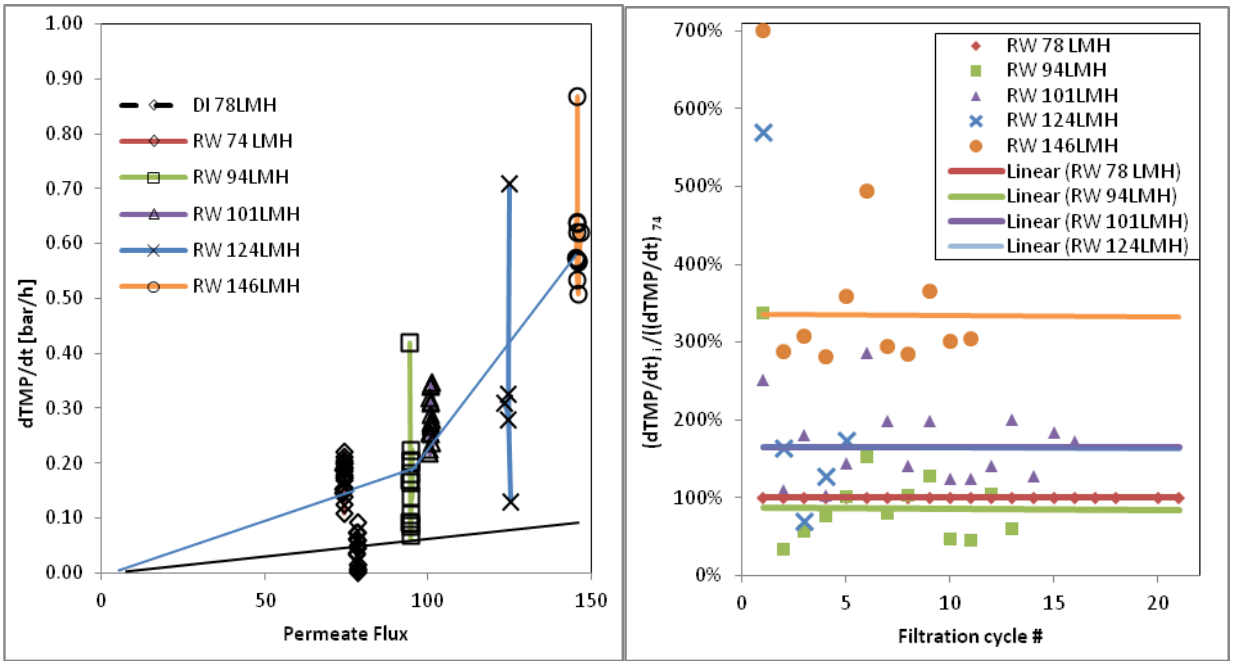

Figure 17. Correlation of fouling rate to operational flux (left:absolute, right: relative to 74LMH)

c. *Evaluation of backwashing*

Hydraulic backwashing is a crucial component for membrane cleaning. It acts towards the removal of the accumulated cake layer that contributes to the TMP increase. After the hydraulic backwash, the TMP is partially recovered but still a non-backwashable component could be present. The determination of the fouling components was based on (Quintanilla, 2005) and calculated using equations (Eq. 15) and (Eq. 16):

$$BW_i = TMPf_i - TMPb_i \quad \text{(Eq. 15)}$$

Where: BW_i = the backwashable component of fouling in terms of TMP after a hydraulic backwashing at the end of filtration cycle i

TMP_{fi} = the trans-membrane pressure at the end of filtration cycle i

TMP_{bi} = the trans-membrane pressure after the hydraulic backwashing of filtration cycle i

$$nBW_i = TMPb_i - TMP_0 \quad \text{(Eq. 16)}$$

Where: nBW_i = the non-backwashable component of fouling in terms of TMP after a hydraulic backwashing at the end of filtration cycle i

TMP_{bi}= the trans-membrane pressure after the hydraulic backwashing of filtration cycle i

TMP_0 = the trans-membrane pressure at the beginning of filtration

The results for the different operational fluxes are appended in Figure 38 to Figure 40 where a detailed distribution for the backwashable and non-backwashable fouling after every filtration cycle can be sought for each operating flux tested. A summary of the results in presented in the plot of Figure 18, with the graph showing the backwashable fouling component in every filtration cycle. It can be observed that as the filtration process continues the backwashable component reduces. Based on Table 12 it is

observed that during the first 5 filtration cycles (75min) membrane fouling can be backwashed at around 70%, while after the first 10 filtration cycles (3h) at around 65%.

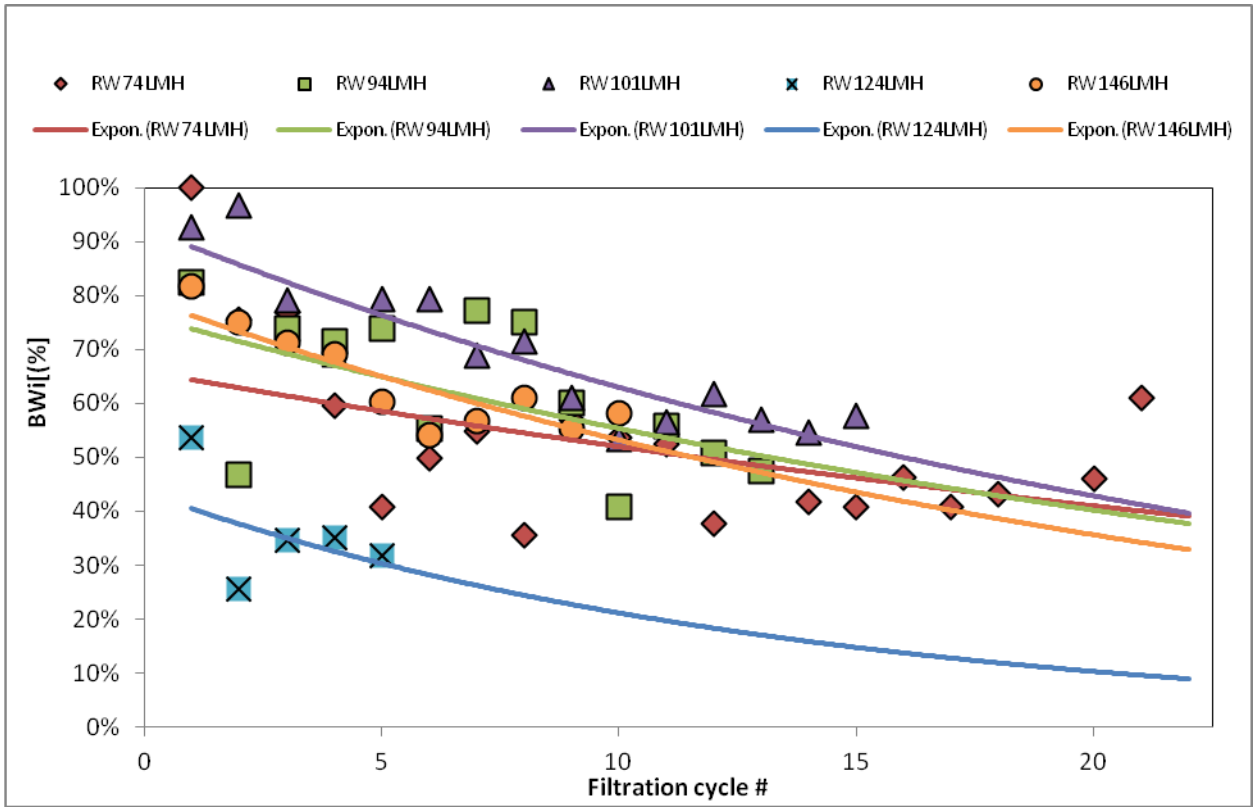

Figure 18. Backwashable component of fouling for tested fluxes

Table 12. Average values of the backwashable fouling component (in %) for the first 5 (Avg5) and the first 10 cycles (Avg10)

Operational Flux	RW74LMH	RW94LMH	RW101LMH	RW124LMH	RW146LMH
Avg_5	71%	70%	83%	36%	71%
Avg_{10}	60%	66%	75%	-	64%

d. Temperature corrected specific flux - Permeance

Specific flux (K) or permeability (Lp) or permeance (Lp/ℓ) are all terms related, one way or another, to the filtrate productivity. Productivity of membrane processes is highly dependent on environmental conditions changes (temperature, pressure), that is why it has to be normalized or corrected over pressure or temperature if the flux itself hasn't been previously corrected as mentioned in section 2.3.iii. For our case the temperature correction is applied at the specific flux. "Specific flux" is usually called the pressure normalized flux (J/TMP), sometimes called permeability which for dense membranes is an inherent membrane, thickness independent, property. However if permeability is divided with the membrane thickness (ℓ) it gives the actual flux or permeance which is the thickness dependent parameter that can be used for easier comparison with specific fluxes of other membranes.

For the conducted experiments, since the thickness of the selective layer of the hollow fiber membranes used is not confirmed, the results for the specific flux are given in terms of permeance. The permeance values (Ki) were calculated from the monitored TMP and flux results using the following equation:

$$\text{(Eq. 17)} \quad L_p = \frac{Q \cdot l}{A \cdot T\ MP} \rightarrow K_i = \frac{L_P}{l} = \frac{Q}{A \cdot TMP} = \frac{J \cdot e^{(-0.0239(T-20))}}{TMP}$$

The results of every 5sec timestep were edited similarly to the TMP results presented earlier. The specific fluxes averaged over the whole duration of each operation under constant fluxes were then plotted in Figure 19, while the profiles that contributed towards the production of the summary plot are presented in APPENDIX III (Figure 41-Figure 45). As the fluxes (J) were kept constant and temperature T was controlled to room temperature (25^{o}C) the K_{wi} profiles vs. time are similar to the reverse of the TMP profiles and they are thus appended as well in APPENDIX III (Figure 46). However the normalized specific flux profiles with regard to DI specific flux and the reference flux scenario (74LMH) are presented in Figure 20 and Figure 21.

From these plots the absolute and relative specific flux losses can be determined which as expected get higher as the operational fluxes increase. For instance with regard to the pure water specific flux at 20^{o}C which is around 140LMH/bar, the reference raw water specific flux at the same temperature and for similar flux conditions drops to 113LMH/bar, 18% lower than the pure water specific flux. A 100% increase on top of the reference flux will lead to the lowest specific flux observed at around 83LMH/bar. All the other tested fluxes but one,lead to specific fluxes within this range of 83-113LMH/bar, while only for the flux of 94LMH the permeability was higher than the reference (RW@74LMH) at around 120LMH/bar, but still lower than the pure water specific flux.

In relative numbers, compared to the reference (Figure 21) the maximum permeance drop for the increased flux (144LMH), can be translated to a specific flux loss of more than ¼ of the initial average permeance (Kw_{144}=0.72Kw_{74}). Accordingly with the TMP calculations presented in the previous section and as mentioned before for the flux of 94LMH the specific flux at 20oC was found increased by 5% compared to the refernce raw water specific flux.

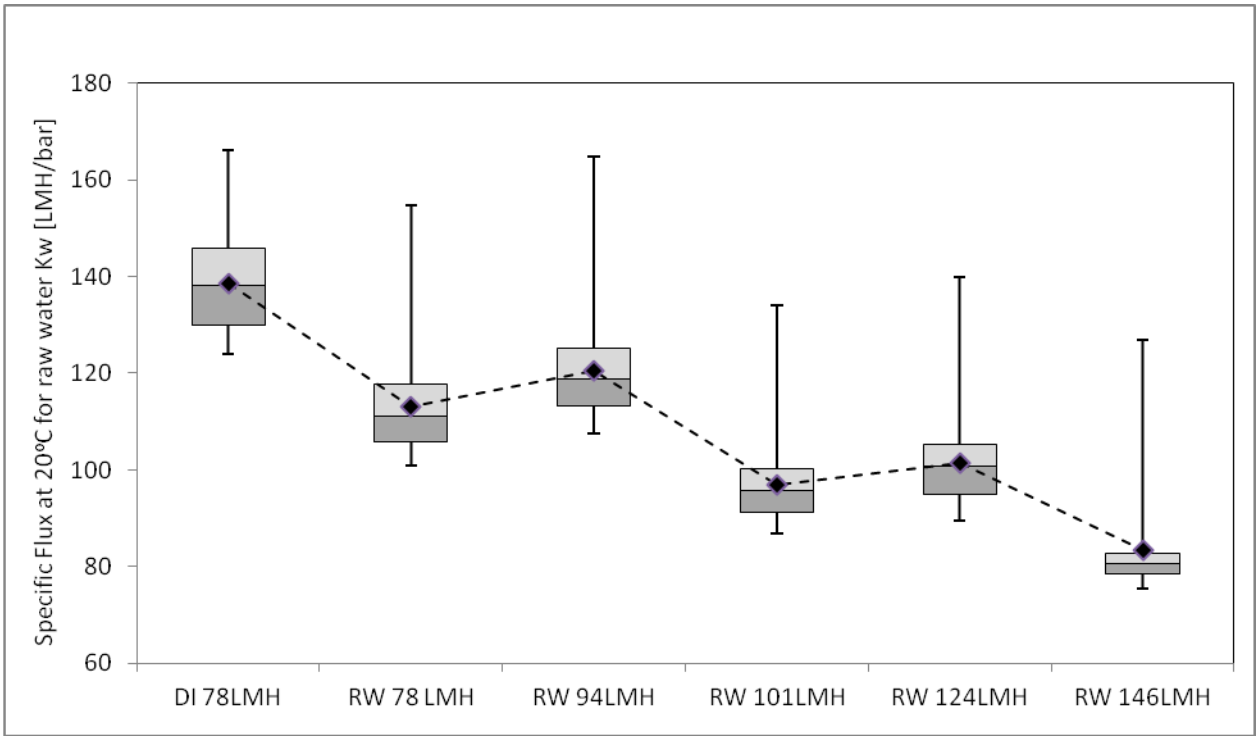

Figure 19. Summary of average specific flux (permeance) values for different flux operations
Box=Range of 50% of the values,Top/Bottom Whiskers=Max/Min value observed excluding outliers (99%-1%),Dotted line: Average values

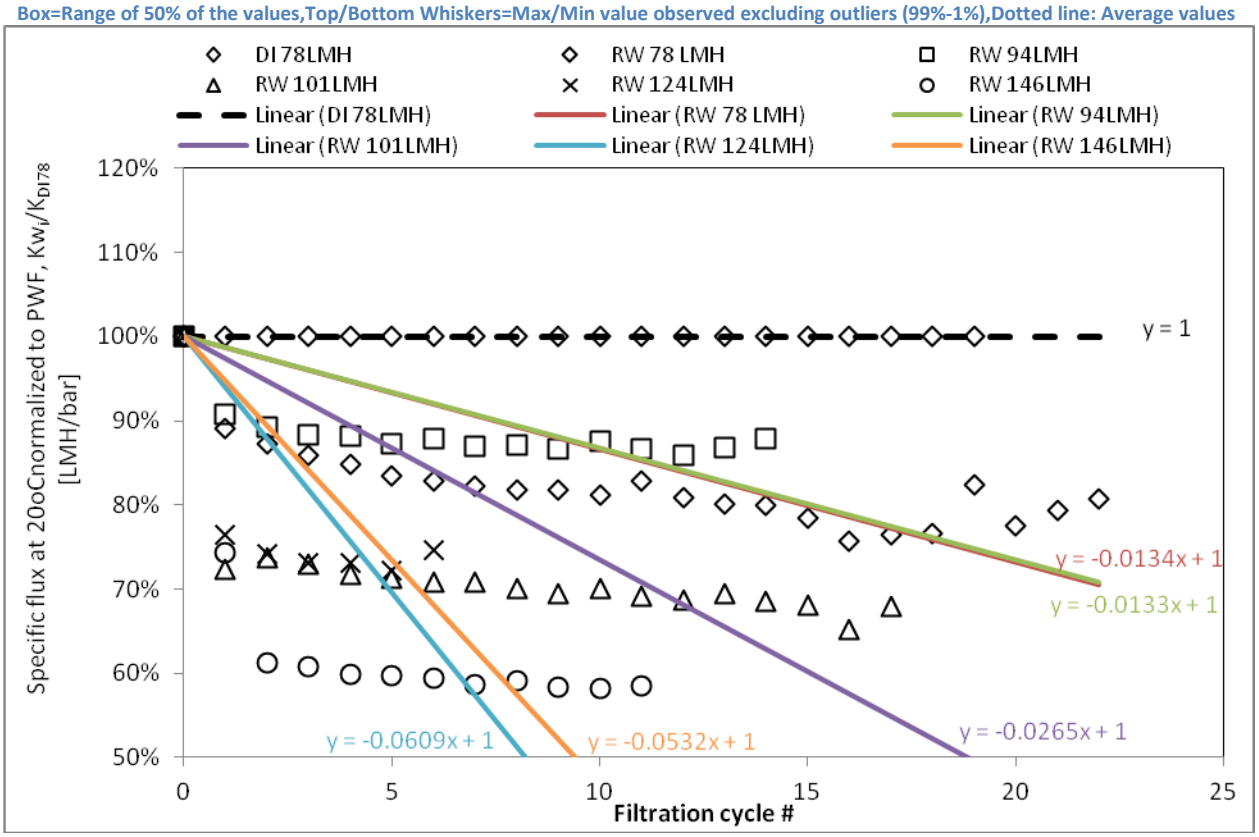

Figure 20.Relative profiles of the average specific flux normalized with the DI water avg permeance for each filtration cycle

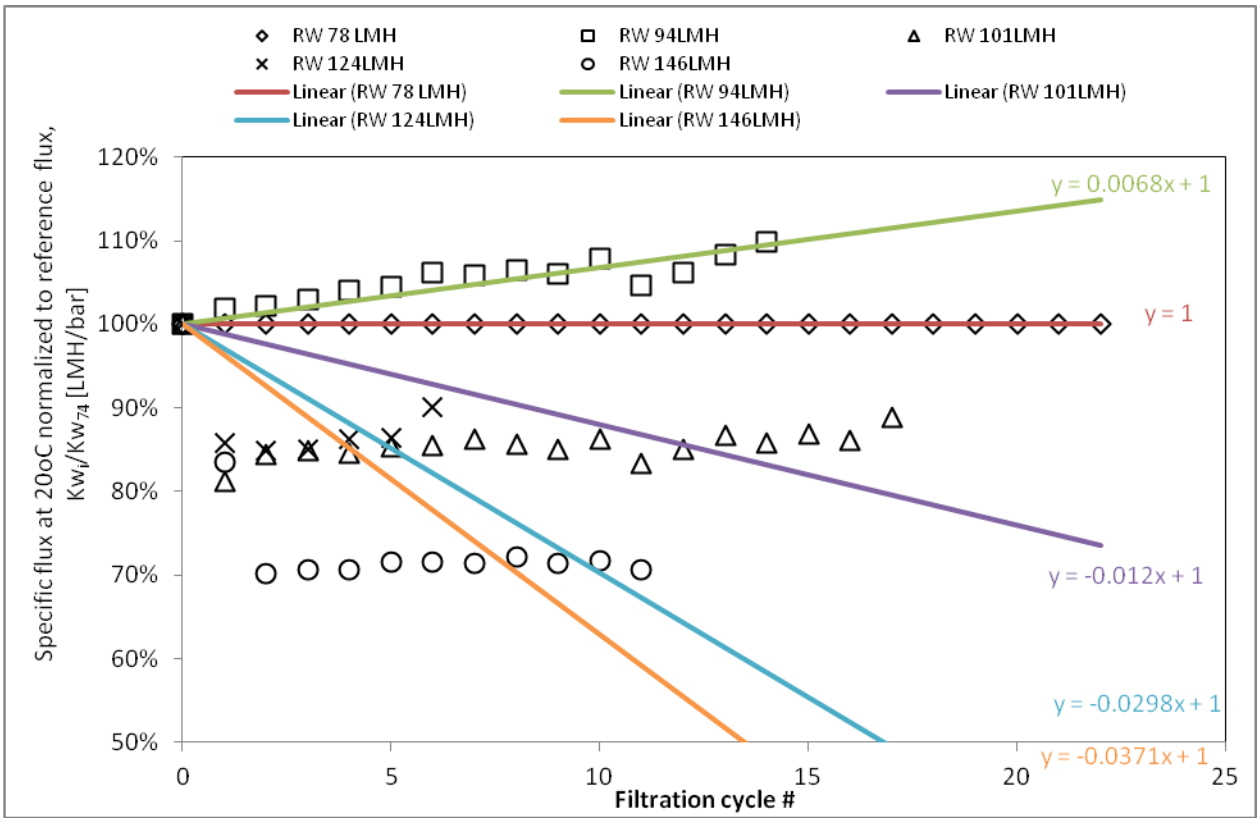

Figure 21. Relative profiles of the average specific flux normalized with the reference condition's (RW 74LMH) average permeance for each filtration cycle

e. Hydraulic Resistance

For the identification of the critical flux values sometimes the TMP profiles alone are not adequate, and the help of resistance profiles need to be sought. As described in earlier sections (2.3.iv) flux and pressure profiles can be related with the different components of hydraulic resistance (clean membrane resistance, initial resitance due to adsorption, reversible and irreversible fouling resistances) using various mathematical expressions. However their sum which is the total resistance (R_T) can be calculated at each timestep, based on Darcy's law as following:

$$R_T(m^{-1}) = \frac{TMP\ (Pa)}{\mu\ (Pa.s).J(\frac{m}{s})} \quad \text{(Eq. 18)}$$

Where:

TMP = the observed transmembrane pressure in Pa (1bar=10^5Pa)

μ= the dynamic viscosity of the fluid in Pa.s ($8.9*10^{-4}$Pa·s for water at 25°C)

J= the permeate flux in m.s^{-1} (1LMH=1L/m2.hr = 10^{-3} m^3 /m^2.3600s=$2.7*10^{-7}$ m/s)

As the flux is fixed during the constant flux batch experiments and water temperature is controlled to room temperature, the resistance profiles vs. time are similar to the TMP profiles. For this reason they are appended with other auxiliary plots in APPENDIX III (Figure 51-Figure 53). However averaged values extracted for each flux were used and the boxplot of Figure 22 was created. For the DI water filtration the observed resistance can be translated to the clean membrane resistance (R_m), as there should be no other component of hydraulic resistance present yet. It is also observed that the resistance increases with the operating flux increase. The maximum average total hydraulic resistance is for the highest

operating flux of 146LMH. As a result the higher fouling resistance R_f (including the reversible and irreversible components) is also observed for the highest flux.

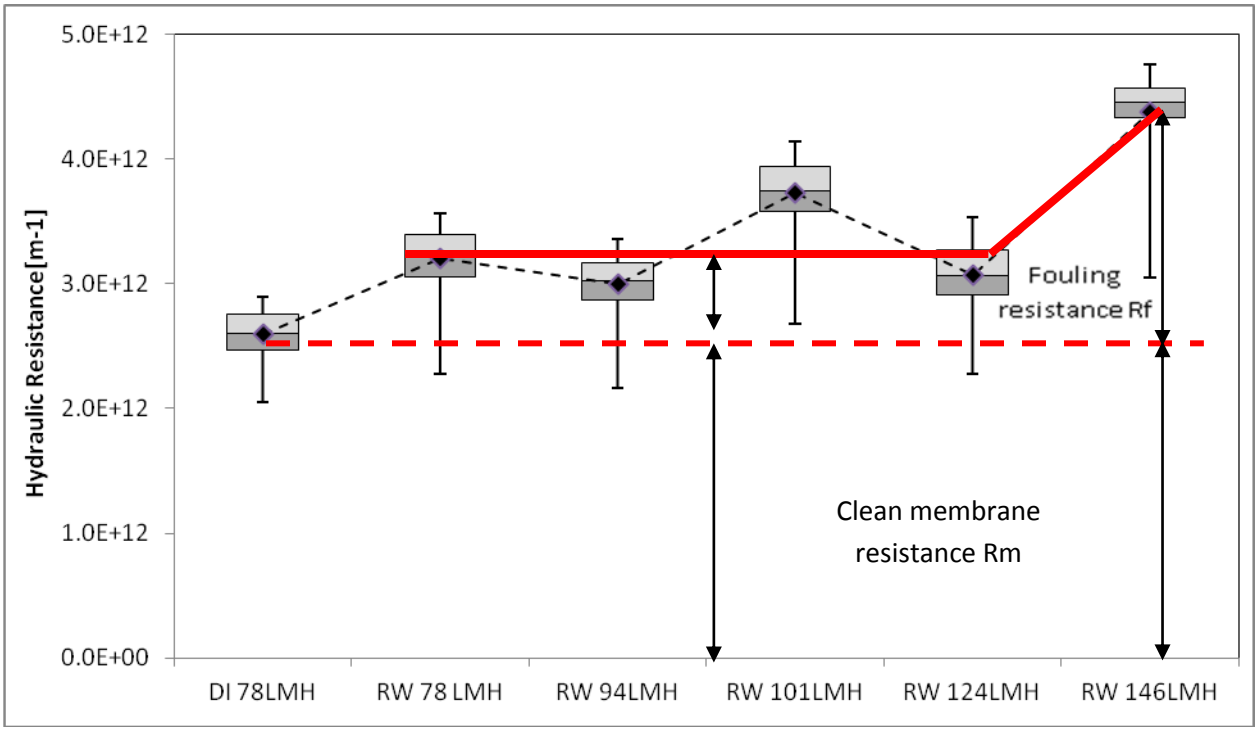

Figure 22. Summary of average total hydraulic resistance values for different flux operations
Box=Range of 50% of the values, Top/Bottom Whiskers=Max/Min value observed excluding outliers (99%-1%)
Dotted line= Average values, Dashed line= clean membrane resistance, Solid line= fouling resistance

4.2.iii. Determination of fluxes

One of the objectives for the phase II optimization was the determination of critical values for the operating flux that can divide the operating flux range to different regions, a no fouling region, a low fouling rate region and a high fouling rate region. As elaborated in section 2.3 there are many definitions on the different critical values for the operational fluxes. Later the findings for three of them, the critical flux, the threshold flux and the critical flux for irreversibility, are going to be explained respectively.

a. Critical flux (strong-weak form)

In the following section the definition of "critical flux" will be used for the separation of the "no fouling" and "low fouling rate" regions. It will be then the value under which no fouling has been yet present. Practically, it means that the specific flux still has the same value as the pure water flux (PWF) and the flow is only affected by the clean membrane resistance R_m as given by (Eq. 5) in section 2.3.iv.

The means for the determination of the critical flux were the flux-pressure profiles created using the average values for the permeate fluxes and TMP. As there were some limitations by the pilot scale system's capacity that didn't allow to check low fluxes near the expected, from the literature critical value range [(Bacchin, et al., 1995): suggested from calculations for flux of small particles in the order of 0.1μm the range 3.6-36LMH which equals to 1-10μm/s], we could only proceed to a rough estimation, based on the back-projection of the trend of the polynomial curve created to fit the higher experimental values. As seen in Figure 23 and also confirmed by the trend curves' equations for the pure water flux and the raw water filtration [J=156.83(TMP) and $J=-42.94(TMP)^2+160.44(TMP)$], the linear part of the

flux-TMP profile for the raw water filtration that matches the pure water flux stops around the value of 20LMH, which will be selected as the critical flux (strong form) (J_{cs}).

b. Threshold flux

The next critical value that was tried to be identified was the threshold flux which is the turning point from the low fouling rate region of fluxes to a higher fouling rate region. It has also physical meaning as explained earlier (2.3.iii) that below this value there is no additional fouling resistance, which remains nearly stable and independent of the operating flux. Therefore, flux-TMP profiles and the hydraulic resistances were utilised in the comparison for the final determination of a possible threshold value.

The flux-pressure profile of Figure 23, used previously for the critical flux, could also be used for the determination of the threshold flux, but this time the checked parameter being the slopes of the fitting curve. In other words it was tried to check the specific flux variations and the rate of TMP increase in terms of the applied flux. Figure 24 might be a more appropriate plot for the determination of the threshold flux. It was observed that within our tested flux range, the first point of slope change (specific flux: dJ/dTMP) is around 90LMH while a second one occurs above 120LMH. The rate of TMP increase (dTMP/dt) was constant around 23mbar/min (for fluxes up to 90LMH), slightly increased to 31mbar/min (for fluxes from 90 to 120LMH) and then rises rapidly to over 50mbar/min (fluxes >120LMH). Additionally from Figure 22 some hint for the hydraulic resistance can be made, as the fouling resistance (R_f) increases more rapidly after the tested operating flux of 124LMH.

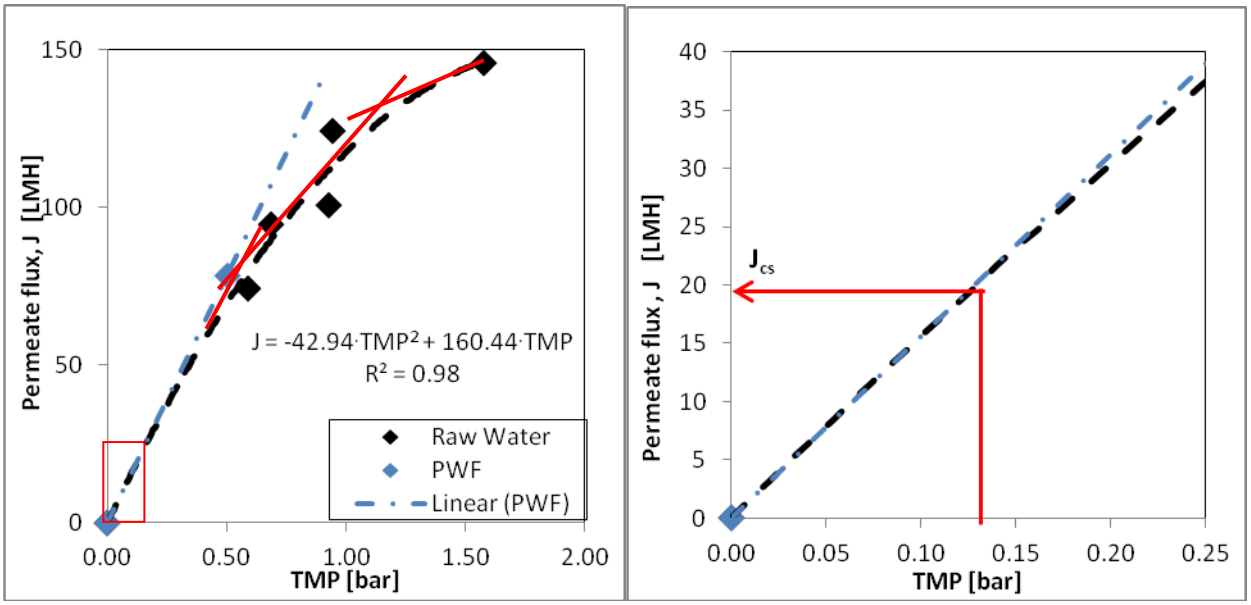

Figure 23. Average values of TMP vs. the operating flux

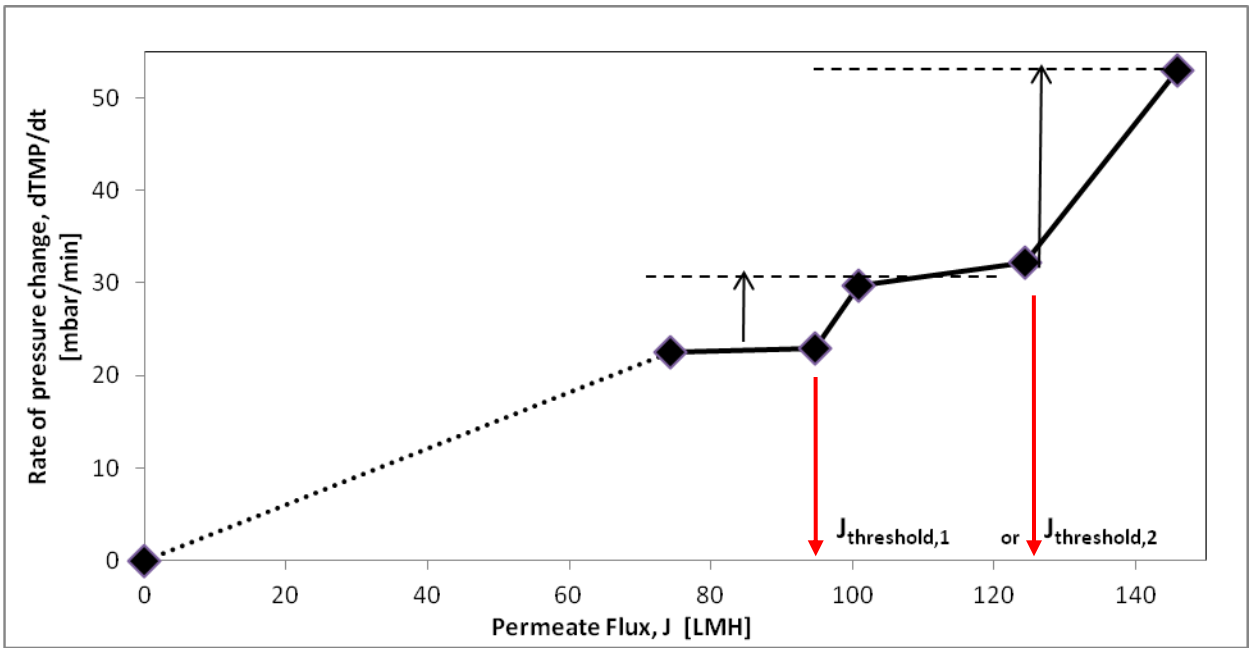

Figure 24. Average rate of TMP changes vs. the operating flux

c. *Critical flux (irreversibility)*

Regarding the critical flux for irreversibility (J_{ci}), an exact determination wasn't achieved, but instead a check if the critical flux for irreversibility has been exceeded or not, could be performed. The confirmation was retrieved by checking the reversibility of the "TMP-flux" profiles for the respective cases before and after a filtration at the higher suspected flux had been completed. If that higher flux is below the J_{ci}, the TMP profiles should be similar because either the fouling rate would be low or the fouling itself would be reversible. To achieve that, a flux stepping process has to be selected. Based on the literature for flux stepping, two alternatives were evaluated and a final selection was made.

As indicated in the literature, flux stepping methods could include a series of steps with only increasing steps (Wu, et al., 1999), (Kwon, et al., 2000), a series of steps where every increased flux step is preceded by a lower flux step (flux cycling) (Mänttäri, et al., 2000), (Espinasse, et al., 2002) or a series of only increased followed by a series of only decreasing steps (Chen, et al., 1997), (Gésan-Guiziou, et al., 1999) , (Le Clech, et al., 2003). For the second cases either a minimum flux step has to be applied in order to ensure it is in the subcritical region of fluxes, or the flux of the immediate previous step. So since in our case, there were limited capabilities for achieving low operating fluxes due to the system design, it was decided not to proceed with this flux stepping alternative. Instead the method of flux stepping that is performed in an increasing and then a decreasing sequential order similar to the publications of the third group was selected.

The results of the TMP values and the fluxes can be found in the plot of Figure 28, from where it is observable that in most of the cases the TMP profiles in the repeated runs have higher values, an indication that the critical flux for irreversibility might have been exceeded. For further validation of the results, the pressure hysteresis effect was studied and the hydraulic resistance values were compared.

Among others, (Chen, et al., 1997) has elaborated on the hysteresis effect of the pressure profiles and found, that for subcritical flux conditions the hysteresis of TMP in ultrafiltration can be negligible. From the other hand, when higher fluxes were used due to transition from concentration polarization to cake formation, the pressure had a period of instability for increasing and decreasing fluxes with significant hysteresis. In our case the instability in the pressure profiles can be detected in Figure 28, while the significance of hysteresis can be also evaluated from Figure 25 and Figure 26. In the former figure that was created with the average values for each operation under a constant flux, it can be seen that the “increasing flux operation” runs show more stable transitions to higher fluxes, also supported by the TMP values shown in details in Figure 48 -Figure 50. In contrary, the decreasing sequence segment shows more instability. If the point representing the operation under 126LMH for the repeating cycle of operations (as mentioned earlier, it showed some abnormalities) is excluded, the trend line drawn (thinner dashed line) reveals that the TMP was higher than that of the increasing cycle (wider dashed line) by an average of approximately 0.15bar.

Similar to Figure 25 is Figure 26, with the difference that it was drawn in more details using the initial and the final TMP values (with some exceptions) for filtration under the specified constant fluxes. Noticeable is that for the “increasing” branch, TMP shows limited variations under each operation for almost all fluxes but the last (146LMH). In the “decreasing” segment these variations are more significant as seen from the overall lower TMP values of flux 126LMH and the wider TMP ranges of flux 77LMH. The flux-TMP loop was then closed using arrows following the route of the connected calculated points. Again the flux of 126LMH was excluded for this procedure.

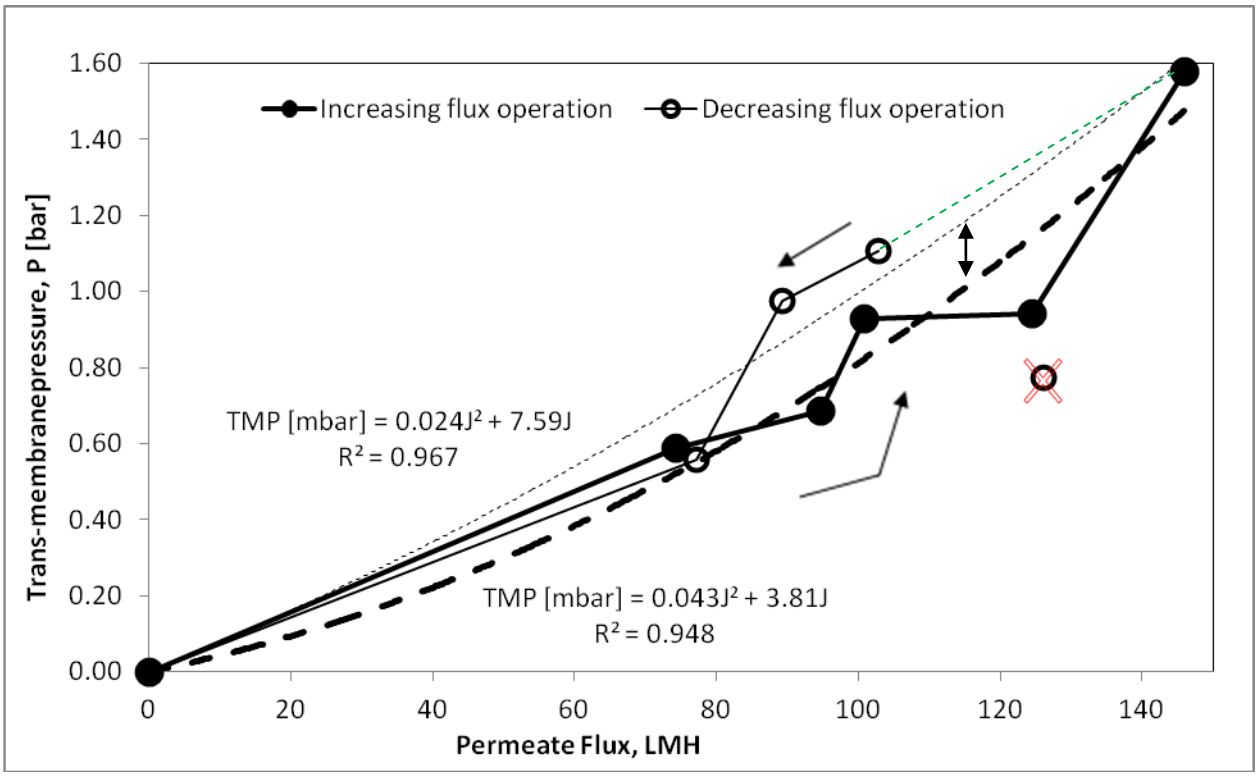

Figure 25. Evaluation of the pressure hysteresis: Average TMP values vs. operational flux for increasing (filled) and decreasing flux operations (empty markers)

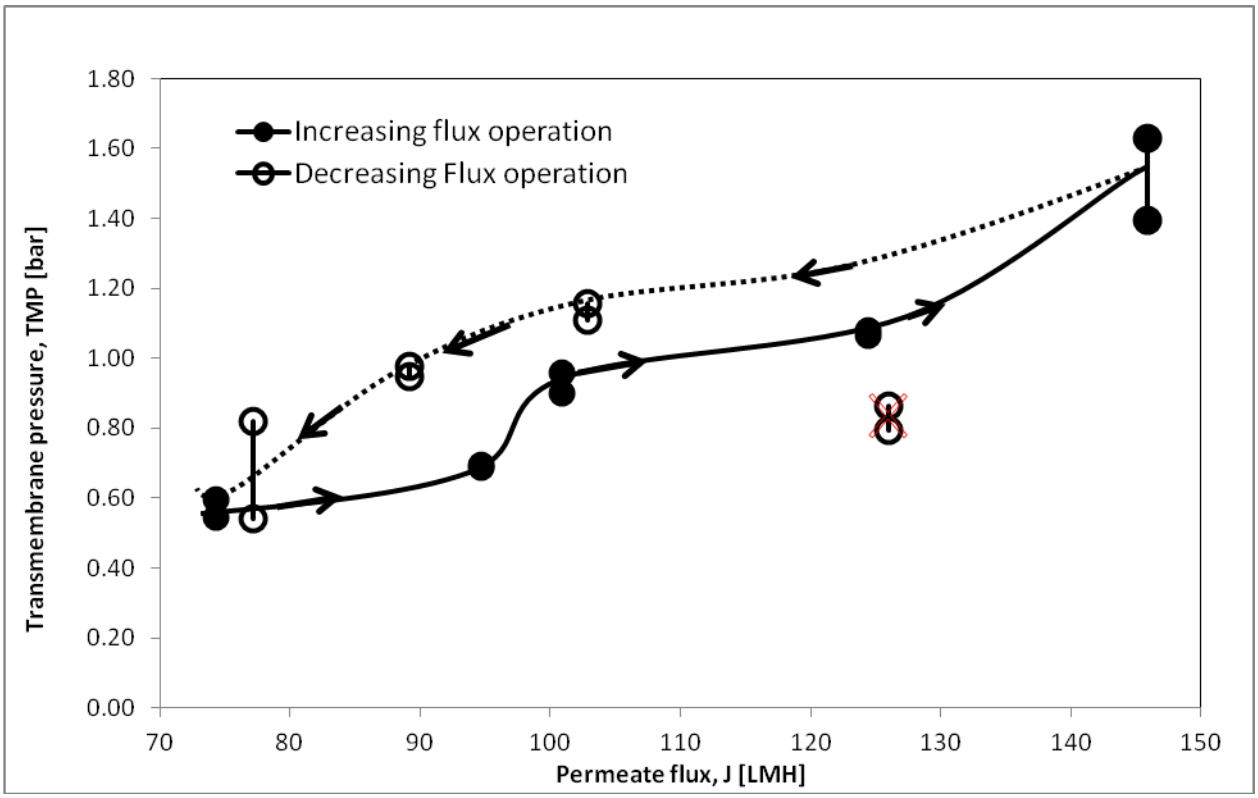

Figure 26. Evaluation of the pressure hysteresis: Initial and final TMP values vs. operational flux for increasing (filled) and decreasing flux operations (empty markers)

Additional to the TMP profiles for the decision of the initiation of irreversible fouling or not, hydraulic resistances were used. Figure 27 and Figure 29 compare the total hydraulic resistance R_T for each flux operation before and after the highest flux operation has been tested. In most of the cases, hydraulic resistance during the second run was higher. Here as well, exception was the operation under the flux of 126LMH that presented some abnormalities, which again is not going to be considered for further elaboration. Some disturbances were also present for the reference operation with raw water at 77LMH. More details regarding the differences between the runs can be sought from the following figures (Figure 27, Figure 29) and from Table 13 with the relative percentages. The highest operating flux tested was 146LMH, and lacks relative differences as it was only repeated once.

Table 13. Relative differences in the hydraulic resistance before and after possible exceedance of the critical conditions

Operation	DI@78LMH	RW@78LMH	RW@90LMH	RW@108LMH	RW@126LMH	RW@144LMH
Flux Difference $(J_{aft}-J_{bef})/J_{bef}$	-1%	+4%	-6%	+2%	+1%	-
Hydr. Resistance Difference $(R_{aft}-R_{bef})/R_{bef}$	+42%	-8%	+47%	+16%	-19%	-

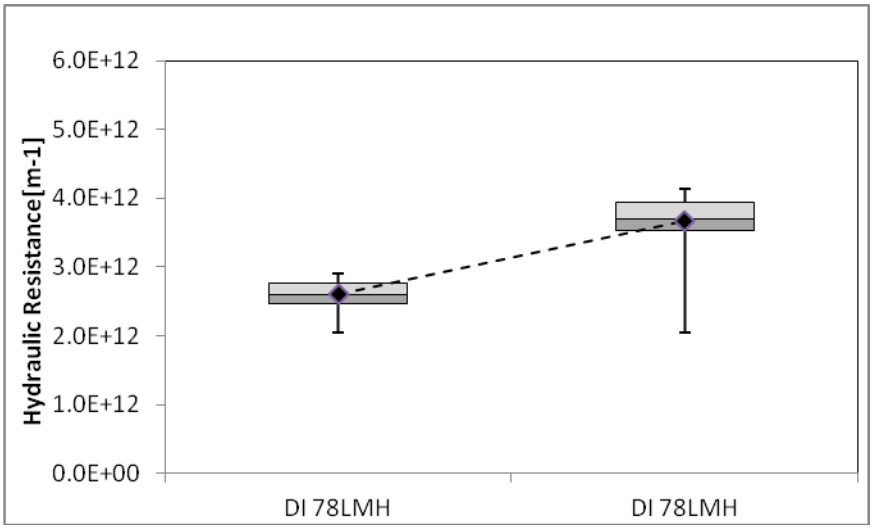

Figure 27. Comparison of total hydraulic resistance before and after operation at supercritical fluxes

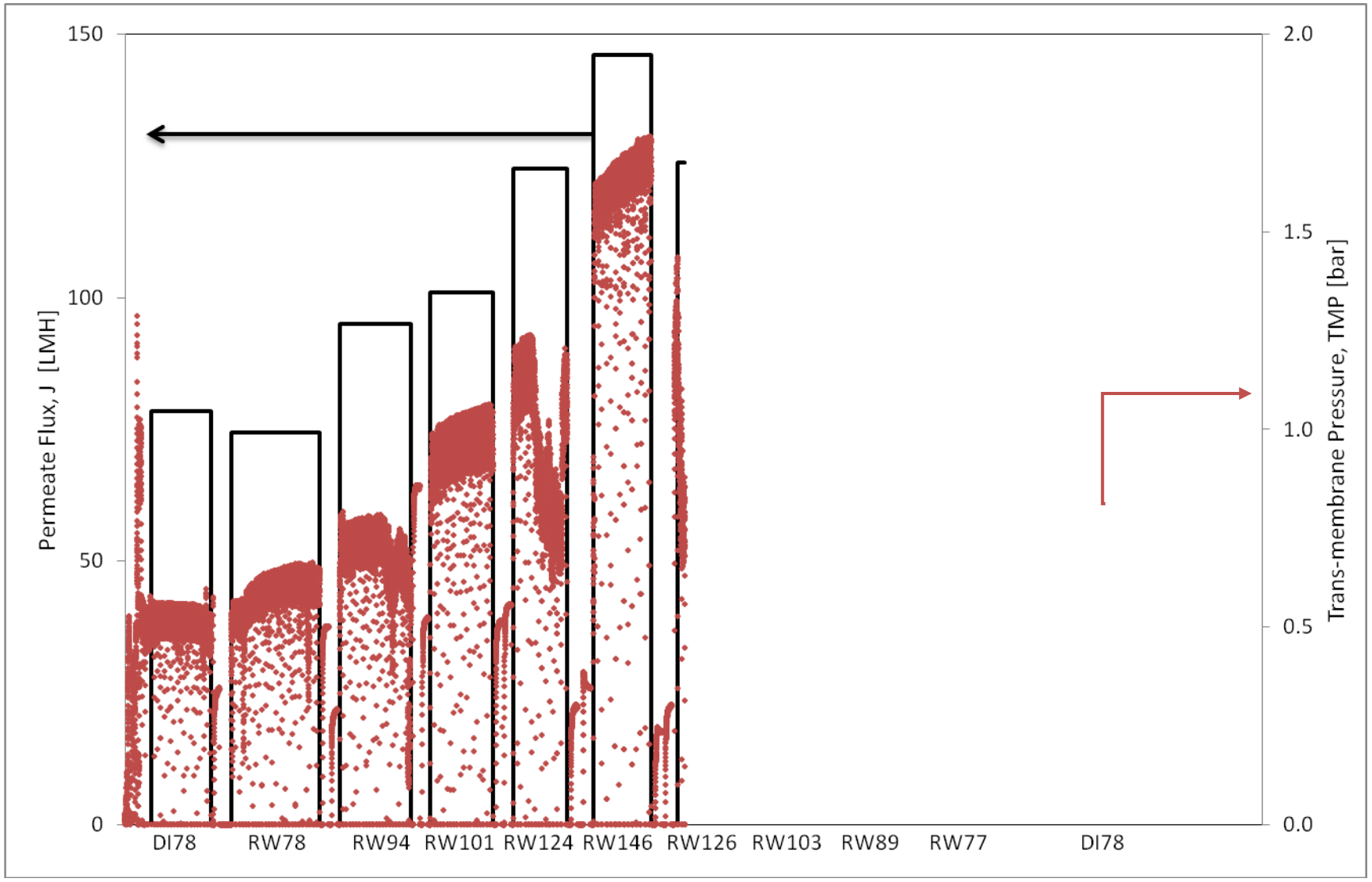

Figure 28. Summary plot of TMP and operating fluxes as applied in an increasing and decreasing order

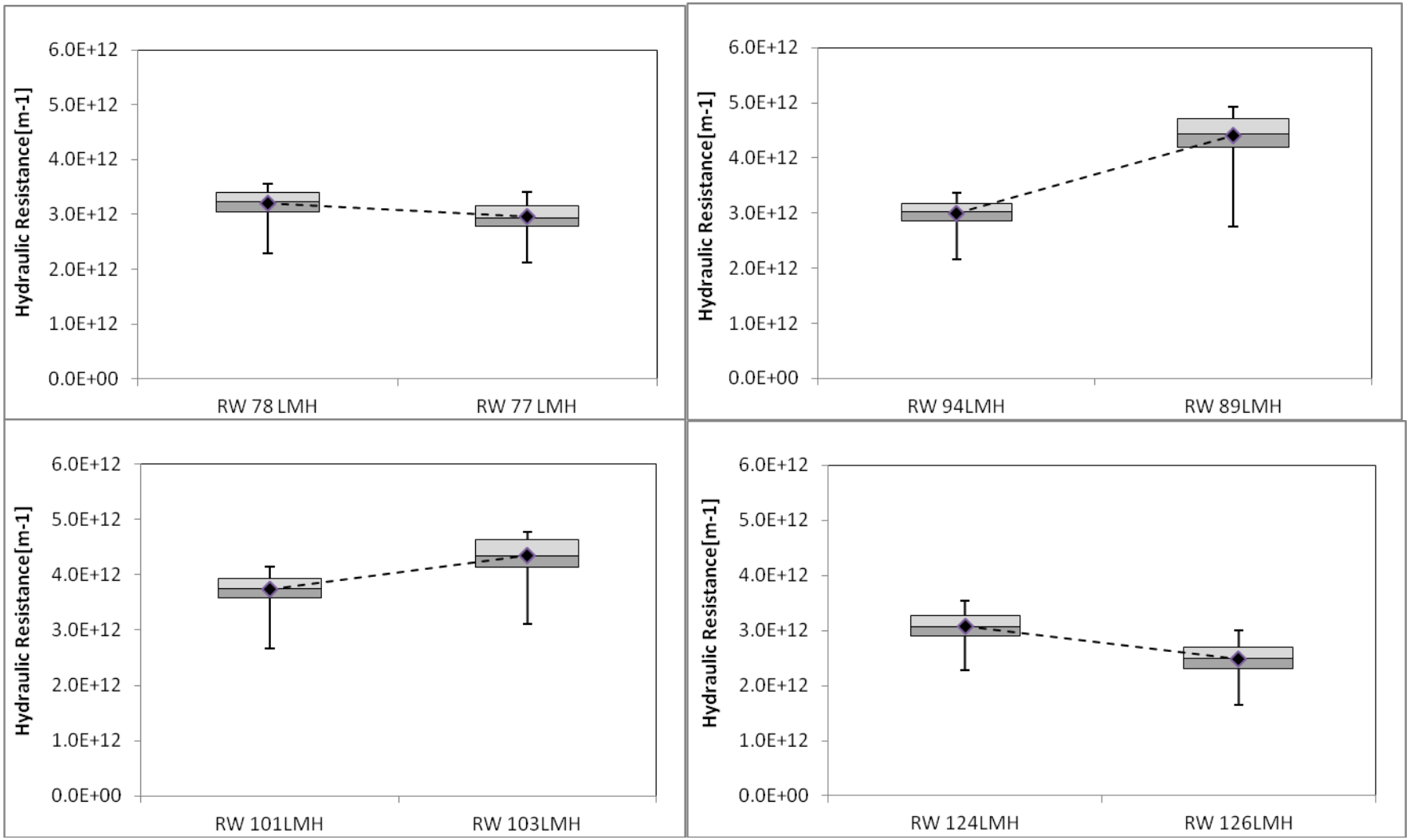

Figure 29. Comparison of total hydraulic resistance before and after operation at supercritical fluxes

Chapter 5: Discussion

For the simulation of the membrane performance in the lab, the means used were mainly jar tests conducted with aluminium chlorohydrate (ACH), polyaluminum chloride (PACl) or ferric chloride (FeCl3). The acquired data revealed potential advantages of the alternative coagulants compared to aluminium sulphate (alum). The water quality was the main concern at this phase so the results included comparisons of the different chemicals in terms of organic carbon removal (TOC), dissolved aluminium, pH and turbidity.

The first alternative coagulant tested on grounds of lab experiments was ACH, which showed sufficient TOC removal efficiencies up to 40%, comparable efficacy for TOC removal (35-45%) with respect to alum. Lower relative equivalent dosages as Al were achieved, approximately 56% of the initially required (in terms of Al) when using alum. Aluminium concentration at the product filtrate was below the limit of 0.05mg/L, without the need to control the pH as required with alum. Regarding PACl, the potential seems to be less , as the TOC removal efficiencies achieved was on average around 20%. As far as total aluminium concentration is concerned, the returned results were within the range of 0.00-0.05mg/L, again for pH values not much different than the feed water pH. Ferric chloride, the last tested coagulant, was only checked in order to have an indication of its performance for future studies. The achieved filtrate water quality was acceptable.

From the optimisation of the membrane performance (Phase II), some interesting results could also be obtained, regarding mainly the operational changes in parameters like TMP and specific flux. Also some optimum values of the permeate flux can be considered for the improved operation. The relation of TMP to the operational fluxes (J_i)could be found with the absolute initial TMP of pure water being around 0.50bar for operation under 78$Lm^{-2}h^{-1}$, while there was slightly increased to 0.58bar when raw surface water was filtered after pre-treatment under similar flux conditions (74$Lm^{-2}h^{-1}$). Noticeable was also the fact that the increase of the trans-membrane pressure is not linear but more rapid with increasing operating fluxes, as doubling of the operation flux (J_i) from 74$Lm^{-2}h^{-1}$ to 146$Lm^{-2}h^{-1}$ lead to a 2.7 times higher TMP.

In terms of the rate of TMP increase, interesting was that a limited TMP change rate was observed when flux was increased from 74LMH to 94LMH compared to a 68% increase in the TMP change rate that was a result of a 50% increase in the operational flux (74-108LMH). The same result when the operational flux was increased by 100% was over 300%, rising on average from 0.18bar/h to 0.61bar/h. The pure solvent TMP change rate had low TMP change rates as expected with an average around 30mbar/h.

The effect of backwashing was also part of the evaluation of the membrane performance with almost a constant backwashable fouling component around 70% after five 15-minute-cycle operations for all operational fluxes that dropped to around 65% when averaged for the first ten 15-minute-cycle operations.

The next operational parameter that was investigated was the specific flux (K_w). The absolute and relative specific flux losses determined were, as expected from the literature, getting more significant with the increase of the operational fluxes (J_i). For instance with regard to the pure water specific flux at 20°C (Kw_{DI}) which was around 140LMH/bar, the raw water specific flux at the same temperature (for similar flux and feedwater conditions) (Kw_{74}) dropped to 113LMH/bar, 18% lower than the pure water specific flux (Kw_{DI}). A 100% increase on top of that base flux lead to the lowest specific flux observed, at around 83LMH/bar, while all the other tested fluxes but one,lead to specific fluxes within this range of 83-113LMH/bar. Only the flux of 94$Lm^{-2}h^{-1}$ revealed a higher permeance compared to 74LMH at around 120LMH/bar, but still lower than the pure water specific flux as expected.

Finally, the critical values of the operational flux needed for the division to a no fouling region, a low fouling one and a higher irreversible fouling region, could be roughly estimated. The critical flux was estimated to lie in the vicinity of 20$Lm^{-2}h^{-1}$ with the threshold flux selected based on the criterion of the transition from flux independent TMP increase to flux dependent TMP rates. It was found to lie most probably around 90$Lm^{-2}h^{-1}$. However if the criterion of constant hydraulic resistance is used it might be even higher but not more than 124$Lm^{-2}h^{-1}$. Fluxes in that order of range might be more operationally feasible, however for an even better understanding of the fouling behaviour a third critical value was tried to be identified. That value was the critical value for irreversibility, an indication of which was achieved based on the reversibility of TMP profiles, the pressure hysteresis and the comparison of the hydraulic resistances before and after the exposure to a probable super-critical flux. Since the TMP profiles in the repeated flux operations, after the suspected supercritical flux operation, were mostly higher than their respective previous ones, the flux of 146$Lm^{-2}h^{-1}$ can be assumed supercritical.

Chapter 6: Conclusions

The conclusions from the study of effects of coagulation and operational flux on the membrane performance of an inline coagulation/ultrafiltration process for water treatment in laboratory can be drawn as follows.

1. ACH was selected as the optimum coagulant among ACH, PACl, FeCl3 and alum for the membrane process with potential benefits of less lime usage for pH post-adjustment and reduced sludge yield.
2. ACH dosage of 17.4mg/L was selected without compromising the water quality to study the effect of operational flux on the membrane fouling.
3. The operating flux has a significant impact on the membrane fouling. The TMP increased by 16% to 270% when the flux was increased from 94 $Lm^{-2}h^{-1}$ and 144 $Lm^{-}{}_{2}h^{-1}$ respectively compared to the selected baseline of 74 $Lm^{-2}h^{-1}$
4. The critical flux (J_{cs}) was estimated around 20 $Lm^{-2}h^{-1}$ and the threshold flux (J_{thr}) was in a range of 90-125 $Lm^{-2}h^{-1}$. However, the quantified critical flux for irreversibility (J_{ci}) and "sustainable flux" could not be made.
5. The backwashable component of fouling increased with an increase in TMP, however, the relative ratio remained stable with around 30% of fouling being non-back washable.

Chapter 7: Recommendations

As the aforementioned conclusions were only based on experimental data and bench scale study in the lab using a pressurized UF module, it would be interesting to be considered for further testing on bench scale or even scale up in future pilot plant studies. The continuation of the studies could use the findings and the proposed solutions of either the phase I optimisation, the membrane performance optimisation or the combination of both in order to achieve a more detailed and concrete proposal.

Additional recommendation for the study could be the identification of the critical fluxes that couldn't be determined due to some system technical limitations, in order to confirm or amend the calculated findings. For this purpose a different method of flux stepping could be checked, like the one with the series of increased and decreased fluxes, instead of the one used in the current study. However if further bench studies are performed the new feed and operation conditions should be considered before the final comparison.

Even further elaboration, with more practical rather than research benefits might be sought, by trying to identify what could be an ideal optimisation function for the maximisation of the profits when a sustainable flux is applied. The parameters mentioned and of course more, subject to the case study, can be used for these means. A holistic approach for the proposal including all kind of different operational (and not only) constraints could be selected. For example the optimization function should be maximising the profit of the operation, while the constrains should come from the operational costs of the chemical cleaning, the energy requirements, the capital costs of membrane replacement if and whether will be required, the price of the product filtrate and other operational parameters like the plant's redundancy that might need to be reduced in order to achieve higher fluxes (standby pumps might need to operate more frequently, additional storage might need to be reduced, more frequent chemical deliveries might increase the plant's dependency on suppliers etc). All the above have to be selected carefully and studied maybe in a smaller scale, even though the scale up and the transition to the actual plant might bring different parameters as the configuration of an actual membrane plant may differ from lab bench scale systems. The degree of acceptance that will help selecting the maximum sustainable flux is something that has to be proposed carefully.

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APPENDIX I. Coagulation and filtration procedures simulating the inline-coagulation/UF process

The procedure for coagulation experiment is as following:

Steps 1 to 7, 9, skip step 8 and 10 for baseline experiment. Steps 1 to 8, 10 are applicable for pretesting experiment.

1) Before the experiment, test the conductivity, TDS, pH, turbidity of the raw water sample.
2) Clean the paddles of the jar test apparatus with a dry tissue.
3) Prepare and adjust the pipettes to the required volume of coagulant, polymer, lime or acid. Select a series of dosage so that the first beaker will represent under-treatment and the last beaker will represent overtreatment. E.g.: Alum dose 20ppm to 45ppm.
4) Pour 1L/(2L on site) of raw water sample into each of the 6 beakers.
5) Place the beakers in the jar test apparatus and lower the stirring paddles into the first beaker (200mL mark).
6) Start the jar test machine at a speed of 180 revolutions per minutes (rpm).
7) Add in the first coagulant dose into the first beaker and stir for 1 minute. Shake the coagulant bottle until the solution is homogenous before pipetting.
8) For pretesting, add in lime or acid in small increments to increase or decrease the pH to 6 through pH probe measurement. Shake the lime/acid bottle until the solution is homogenous before pipetting.
9) Repeat steps 5 to 7 for the remaining beakers subsequently for baseline.
10) Repeat steps 5 to 8 for the remaining beakers subsequently for pretesting.

Cleaning and Flushing membrane filter

11) Clean the filter housing and 2xfiltrate bottle (filter cleaning, filtrate collection) with D.I water (3x).
12) Assemble the filter housing to the filtrate bottle (filter cleaning).
13) Place the 0.05µm membrane filter on the filter housing and ensure everything is tightened.
14) Connect the vacuum pump rubber hose to the filter housing and cover the other end with the rubber plug.
15) Start the vacuum pump and wait for a few seconds for equilibration.
16) Add 400ml of D.I water over through the membrane filter for cleaning.
17) Stop the vacuum pump and detach the plug and rubber hose from the filter housing.
18) Detach the filter housing (with the membrane filter intact) from the filtrate bottle (filter cleaning).
19) Pour away the filtered D.I water from the filtrate bottle (filter cleaning).
20) Assemble the filter housing to the filtrate bottle (filtrate collection).
21) Connect the vacuum pump rubber hose to the filter housing and cover the other end with the rubber plug.
22) Start the vacuum pump and wait for a few seconds for equilibration.

For coagulation after baseline and pretesting

23) Repeat steps 1 to 6.
24) If pretesting has been done, add in the required lime or acid dosage into the first beaker. Shake the lime/acid bottle until the solution is homogenous before pipetting.
25) Add in the first coagulant dose into the first beaker and allow the stirring to take place for 1 minute. Shake the coagulant bottle until the solution is homogenous before pipetting.

Filtration

26) Pipette the dosed water for 0.05µm filtration.
27) Pipette 50ml of the dosed water over through the membrane filter for flushing.
28) Stop the vacuum pump and detach the plug and rubber hose from the filter housing.
29) Detach the filter housing (with the membrane filter intact) from the filtrate bottle (filtrate collection).
30) Swirl the filtrate bottle (filtrate collection) with the filtrate to flush the bottle.
31) Pour away the flushed filtrate from the filtrate bottle (filtrate collection).

32) Assemble back the filter housing to the filtrate bottle (filtrate collection).
33) Connect the vacuum pump rubber hose to the filter housing and cover the other end with the rubber plug.
34) Start the vacuum pump and wait for a few seconds for equilibration.
35) Carry on with the actual 0.05µm filtration.
36) Stop the vacuum pump and detach the plug and rubber hose from the filter housing.
37) Detach the filter housing (with the membrane filter intact) from the filtrate bottle (filtrate collection).
38) Clean 2 x centrifuge tube with D.I water and flush it with 10ml of 0.05 µm filtrate.
39) Collect 2x50ml of 0.05µm filtrate to measure TOC (DOC) & total residual aluminum concentration.
40) Use the remaining 0.05 µm filtrate to measure conductivity, TDS, pH, temperature, turbidity and other parameters deem necessary.
41) Repeat steps 11 to 40 for the remaining beakers subsequently.

APPENDIX II. Test designs and specifications (chemicals-membranes)

During the study period, a number of experiments were completed to simulate an inline coagulation/UF water treatment process. The experiments followed set procedures with different coagulants being dosed at each batch. The sets and batches, with some additional information are shown in Table 14.

Table 14. Design and additional details of experimental sets and batches conducted

Set 1:	Batch 1: "Setting the alum baseline with pH adjusted to 6.0" ▪ Alum dosage: 2.80mg/L as Al
	Batch 2: "Testing the effect of ACH on UPR raw water " ▪ ACH dosages: 0.44/ 0.85/1.27/1.67 mg/L as Al
Set 2:	Batch 1: "Setting the alum baseline with pH adjusted to 6.0" ▪ Alum dosage: 3.20mg/L as Al
	Batch 2: "Testing the effect of ACH on UPR raw water" ▪ ACH dosages: 1.30/ 1.50/ 1.70/ 1.90/ 2.10 mg/L as Al
	Batch 3: "Testing the effect of PACl on UPR raw water " ▪ PACl dosages: 1.30/ 1.50/1.70/1.90/ 2.10 mg/L as Al
Set 3:	Batch 1: "Setting the alum baseline with pH adjusted to 6.0" ▪ Alum dosage: 3.04 mg/L as Al
	Batch 2: "Testing the effect of ACH on UPR raw water " ▪ ACH dosages: 1.30/ 1.50/ 1.70/ 1.90/ 2.10 mg/L as Al
	Batch 3: "Testing the effect of PACl on UPR raw water " ▪ PACl dosages: 1.30/ 1.50/ 1.70/ 1.90/ 2.10 mg/L as Al
Set 4:	Batch 1: "Setting the alum baseline with pH adjusted to 6.0" ▪ Alum dosage: 1.60 mg/L as Al
	Batch 2: "Testing the effect of ACH on UPR raw water " ▪ ACH dosages: 1.30/ 1.70/ 2.50 mg/L as Al
	Batch 4: "Testing the effect of FeCl3 on UPR raw water " ▪ FeCl3 dosages: 3.55/ 4.38/ 5.22 mg/L as Fe ▪ FeCl3 dosages: 1.70/ 2.10/ 2.50 mg/L as equivalent Al

Table 15. Specifications of the chemicals used in jar tests of "optimization phase I"

Item	Design conc. of stock solution (g/L)	Actual conc from lab. Analysis (g/L)	State & Conc. of origin solution	Formula	Molecular weight (g/mol)	Prepare stoke solution method
Alum	20 g/L as Alum (1.82 g/L as Al)	1.60g/L as Al 8.95g/L as $SO4^{2-}$	Solid	$Al_2(SO_4)_3{\cdot}14H_2O$	594	dissolve 20g of alum in water to make 1L
PACl	1.5 g/L as Al	1.32 g/L as Al 2.8 g/L as Cl	Liquid 16% w/w Al_2O_3	-	-	transfer 17.69g or 13.5mL origin PACl solution to 1L volumetric flask and dilute to volume
ACH	1.5 g/L as Al	1.21 g/L as Al 1.3 g/L as Cl	Liquid 23% w/w Al2O3	-	-	transfer 12.35g ACH to 1L volumetric flask and dilute to volume
$FeCl_3$	5 g/L as Fe	5.27 g/L as Fe	Solid	$FeCl_3{\cdot}6H_2O$	270.5	dissolve 24.15g of $FeCl_3{\cdot}6H_2O$ in water to make 1L

Table 16. Index for transition between volume added and coagulant dosage

Chemical used	Procedure	From Volume added → ppm as coagulant	From Volume added → ppm as Al/Fe
Alum	Pretesting/1L jar test	1mL=20 ppm	1mL=1.6 ppm as Al
	2L jar test	1mL=10 ppm	1mL=0.8 ppm as Al
PACl	Pretesting/1L jar test	1mL=17.7 ppm	1mL=1.32 ppm as Al
	2L jar test	1mL=8.85 ppm	1mL=0.66 ppm as Al
ACH	Pretesting/1L jar test	1mL=12.35 ppm	1mL=1.21 ppm as Al
	2L jar test	1mL=6.18 ppm	1mL=0.61 ppm as Al
FeCl3	Pretesting/1L jar test	1mL=24.15 ppm	1mL=5.27 ppm as Fe
	2L jar test	1mL=12.07 ppm	1mL=2.64 ppm as Fe

For the transition from the required dosage as ppm to volume in mL that needs to be dosed during the lab studies, we used (based on Table 15) the following formula:

Required dosage in ppm (coagulant/Al/Fe)=(concentration x volume added)/jar volume

Where: **Alum:** conc.20g/L as alum, equiv. 1.82g/L as Al (Lab result=1.60g/L as Al)

PACl: conc. 17.7g/L as PACl liquid 16%, equiv. 1.5g/L as Al (Lab result=1.32g/L as Al)

ACH: conc. 12.35g/L as ACH, equiv. 1.5g/L as Al (Lab result=1.21g/L as Al)

FeCl3: conc. 24.15g/L as FeCl3, equiv. 5g/L as Fe (Lab result=5.27g/L as Fe)

Since a comparison of the different coagulants has to be made in a common axis, a single unit has to be chosen. Therefore the dosages, for both aluminum based and iron based coagulants, can be translated into molar dosages by dividing with the molecular weight of the coagulant/Al/Fe. So if the dosages are expressed in ppm as Al for example, they will be divided by 27 in order to reflect to dosages as mM. (See Table 17)

Other than the chemicals utilized for the experiments, other consumables like membrane filters were used. The specifications of this supplementary material used in the lab tests are presented in Table 18, while the membrane module characteristics, used during the bench scale studies are presented next.

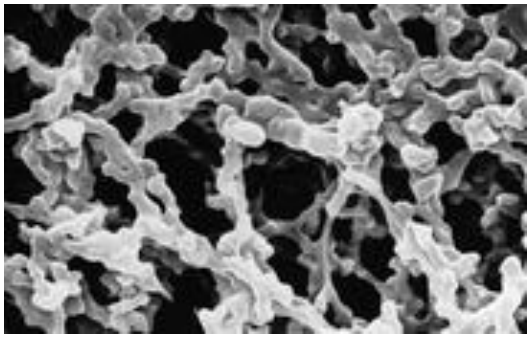
The module consists of 65 hollow fiber Polysulfone membranes with the following geometric characteristics, it has an Inside-out flow direction and can be operated under “dead end” or “cross flow“ regime.

- Outside diameter, OD=1.3mm
- Internal diameter, ID=0.7mm
- Length, L= 35cm
- Area, A= 65x($\pi \cdot D \cdot L$) = 0.05m2 (feed side=lumen side, D=ID)

Table 17. Index for transition between dosage as ppm and as mM

Chemical used	From ppm as coagulant → ppm as mM	From ppm as Al/Fe → ppm as mM
Alum	1ppm=1/594 ppm	1ppm as Al=1/27 ppm as mM
PACl	1ppm=1/361.2 ppm	1ppm as Al=1/27 ppm as mM
ACH	1ppm=1/275 ppm	1ppm as Al=1/27 ppm as mM
FeCl3	1ppm=1/162.5 ppm	1ppm as Fe=1/56 ppm as mM

Table 18. Specifications of membrane filters used for the simulation of the hybrid inline coagulation/UF system



MF-Millipore™ Membrane Filters

Biologically inert mixtures of cellulose acetate and cellulose nitrate have made MF-Millipore membrane filters one of the most widely used membranes in analytical and research applications.

MF-Millipore filters without Triton® surfactant contain minimum amounts of wetting agent and have a lower water extractable content than standard MF-Millipore filters.

General Specifications	Technical Specifications
Color: white or black **Surface:** plain or gridded **Wettability**: hydrophilic **Sterilization**: by autoclave (121 °C at 1 bar), EO **Operating temperature**: 55 °C max **Protein binding:** 150 µg/ cm^2 **Bacterial endotoxins:** 8.0 EU/mL **Gravimetric extractables:** < 1.0% Source: (EMD Milipore Corporation, 2013)	**Description:** MF-Millipore Membrane, mixed cellulose esters, Hydrophilic, 0.05 µm, 25 mm, white, plain **Chemistry:** Mixed Cellulose Esters **Filter Type:** Screen filter **Maximum Operating Temperature, °C:** 75 **Pore Size (µm):** 0.05 **Wettability:** Hydrophilic **Filter Diameter (mm):** 25 **Filter Surface:** Plain **Thickness, µm:** 105 **Air Flow Rate, L/min x cm^2:** 0.25 **Water Flow Rate, mL/min x cm^2:** 0.74 **Bubble Point at 23 °C:** ≥17.6 bar, air with water **Porosity %:** 72

APPENDIX III. Full results of bench scale study

The current appendix consists of the results of all the parameters, which were either monitored or calculated for the varying runs in the bench scale pilot plant. The averaged water quality parameters are summarized in Table 19, while the operational parameters follow. Of main focus will be primarily the TMP profiles, including absolute values and relative rates of change with time and secondarily the productivity parameters expressed as the specific flux or permeance normalized over pressure again with absolute and relative values for comparison purposes. These results will lead to conclusions for the fouling behavior and whether or not it is affected by the operational flux variations. As a reference for the comparison, operation with a pure solvent (deionized water) will be used, as well as the operating flux of 74LMH using raw surface water.

Water quality

The batch experiments for the bench scale system operation in the lab used the same water source as the one used for the simulation of the inline coagulation/UF process. The collected water used at different flux operations was from the same batch. Some of the water quality characteristics were tested for reference purposes, even though water quality is not supposed to greatly vary by altering the operational conditions. Among the parameters tested were TOC, total aluminum concentration, turbidity, pH, total dissolved solids, conductivity and UV absorbance. The average values from the different runs are summarized in Table 19. An average TOC removal efficiency of around 30%, similar to the lab experiments was observed, while the aluminum concentration at the filtrate was near 0.03mg/L.

Trans-membrane pressure – TMP

The TMP profiles of Figure 30 and Figure 31 that were obtained by plotting the 5sec-timestep TMP values calculated from the bench pilot monitoring data, can be summarised into the box and whisker plots of Figure 32-Figure 34. The box and whisker plots were used in order to extract the average TMP profiles presented in Figure 15. The same plots can be used as a base for the determination of the fouling tendency as described in a next section. From visual interpretation some abnormalities might be noticed. An example is for raw water filtration under the operating flux of 124LMH where due to minor leakages the TMP profile after the first 6 of the total 11 cycles starts declining, making the determination of the TMP increase rate (dTMP/dt) more complicated, as explained in the next section.

Table 19. Average water quality characteristics of bench scale system operation samples

	Avg Oper. Flux $L/m^2/h$	Avg TOC mg/L	TOC removal %	Avg SUVA	Avg Tot.Al mg/L	Avg Turbidity NTU	Avg pH	Avg TDS	Avg Cond µS/cm
Raw Water		2.3							
RW 78 LMH	75.7	1.6	28%	1.53	0.026	0.215	6.83	149.9	235.2
RW 94LMH	92.0	1.6	29%	1.58	0.032	0.185	7.01	150.4	236.7
RW 101LMH	101.8	1.5	34%	1.72	0.026	0.170	6.82	151.9	238.8
RW 124LMH	125.2	1.7	25%	1.36	0.020	0.110	6.73	151.3	237.3
RW 146LMH	145.9	1.2	46%	1.85	0.029	0.260	6.98	154.2	242.5

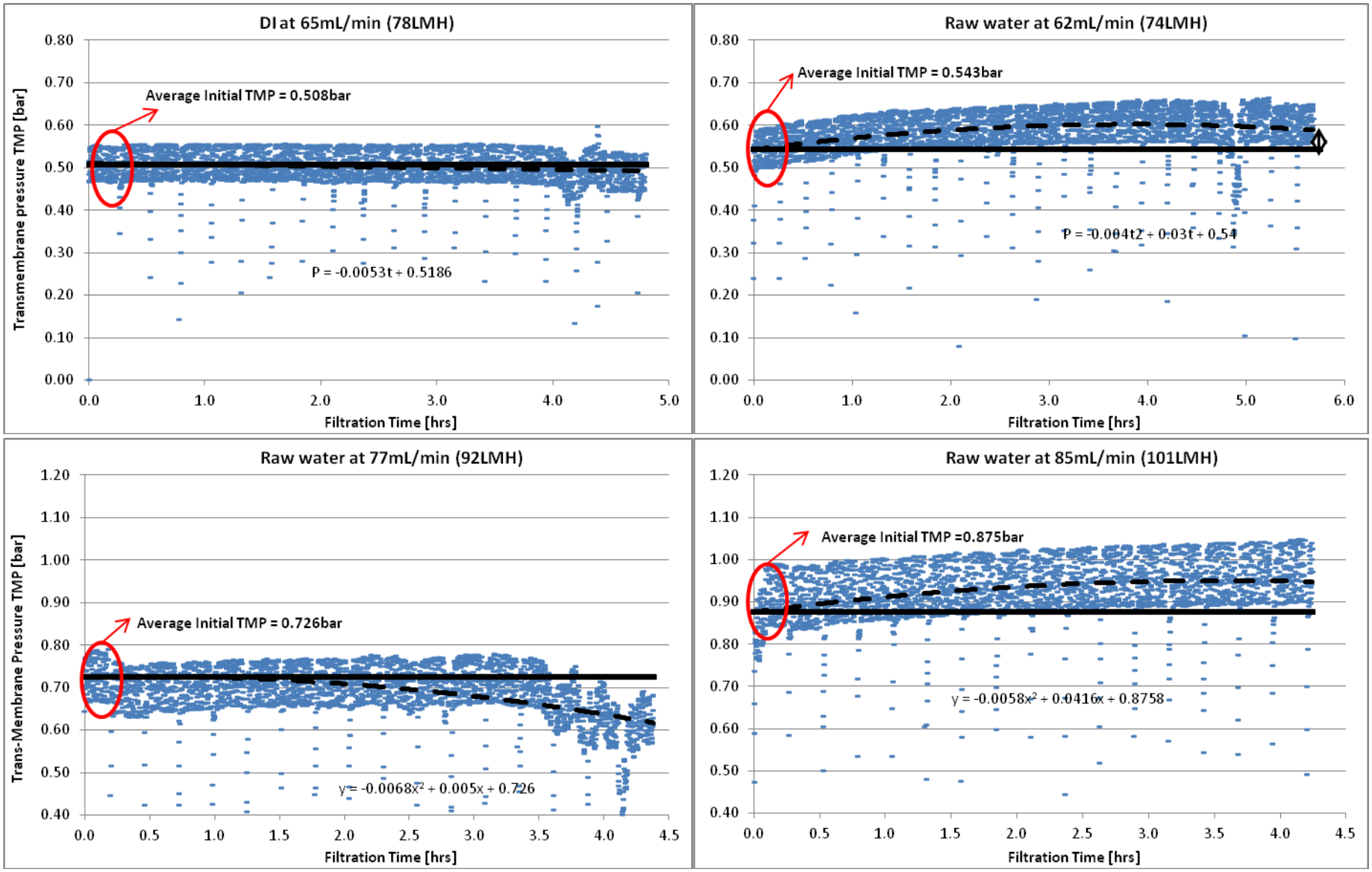
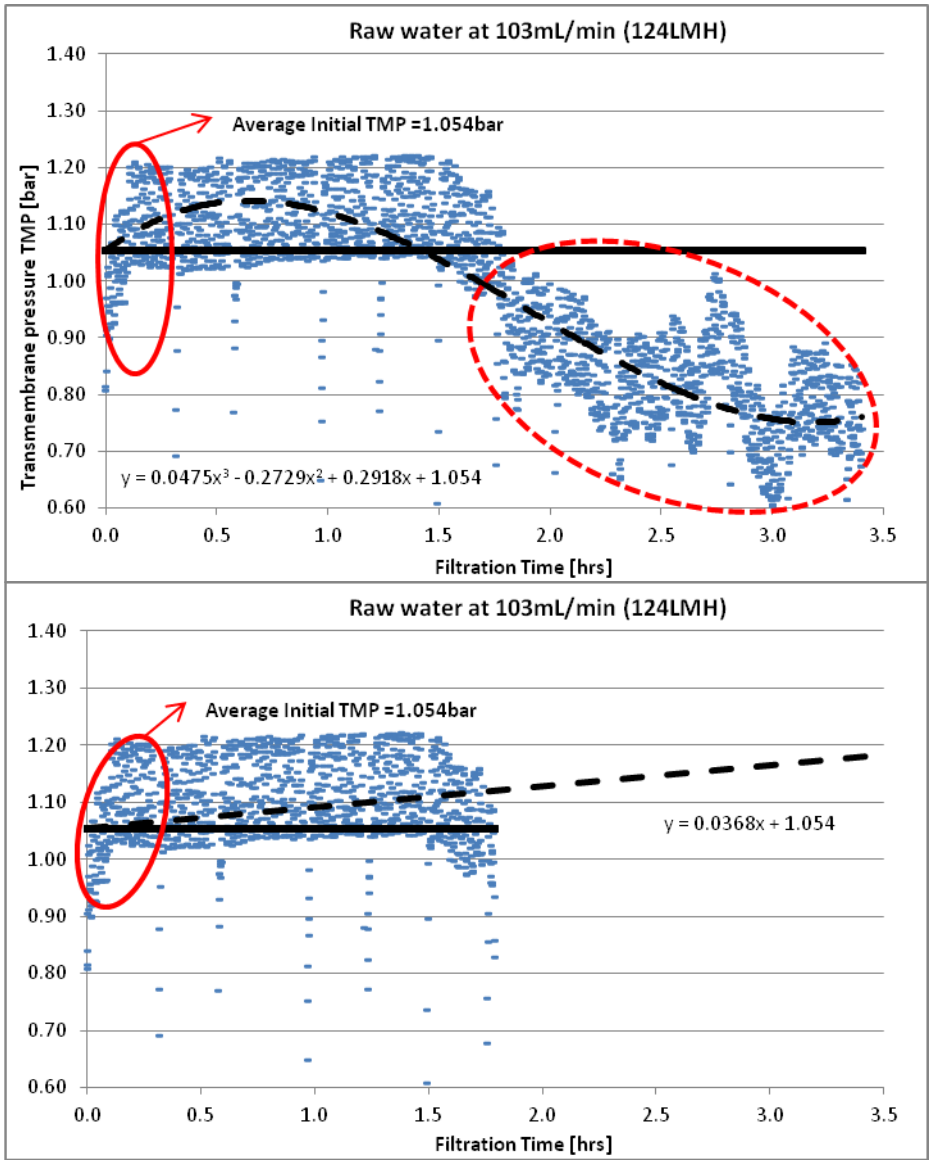


Figure 30. TMP profiles vs. time for various fluxes.
Top row: DI@78LMH (left), RW@74LMH (right), Bottom row: RW@92LMH (left), RW@101LMH (right)


Raw water at 103mL/min (124LMH)
Average Initial TMP =1.054bar
Transmembrane pressure TMP [bar]
y = 0.0475x³ - 0.2729x² + 0.2918x + 1.054
Filtration Time [hrs]
Raw water at 103mL/min (124LMH)
Average Initial TMP =1.054bar
y = 0.0368x + 1.054
Filtration Time [hrs]

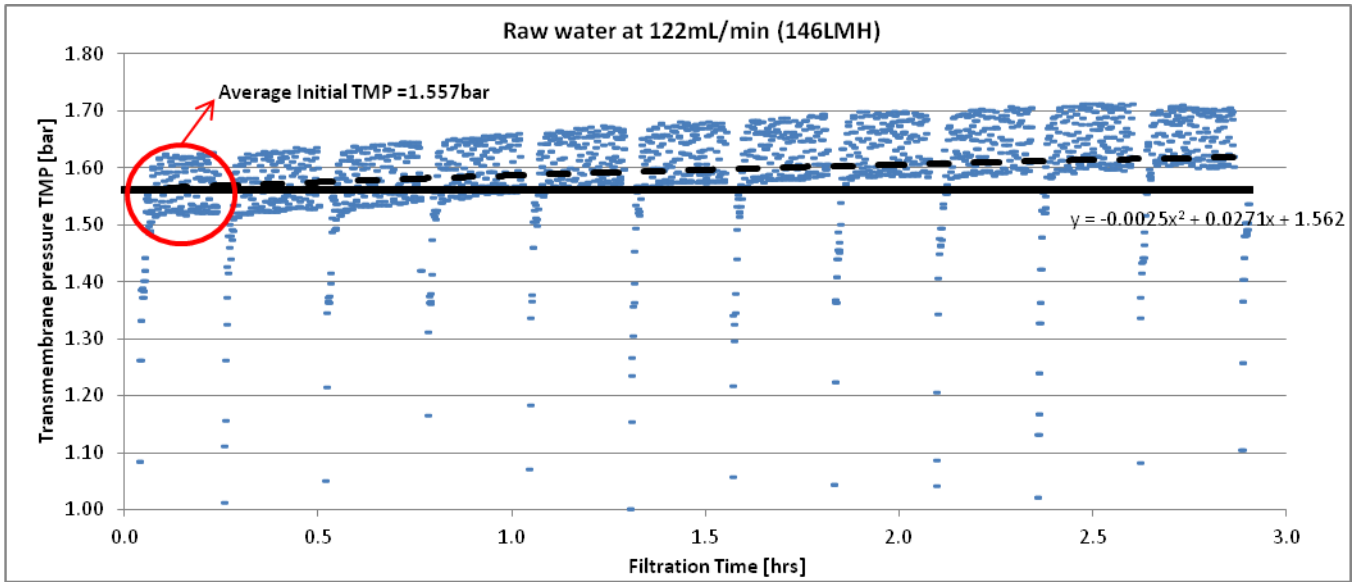


Figure 31. TMP profiles vs. time for various fluxes.
Top row: RW@124LMH (left), RW@124LMH-corrected (right), Bottom row: RW@146LMH

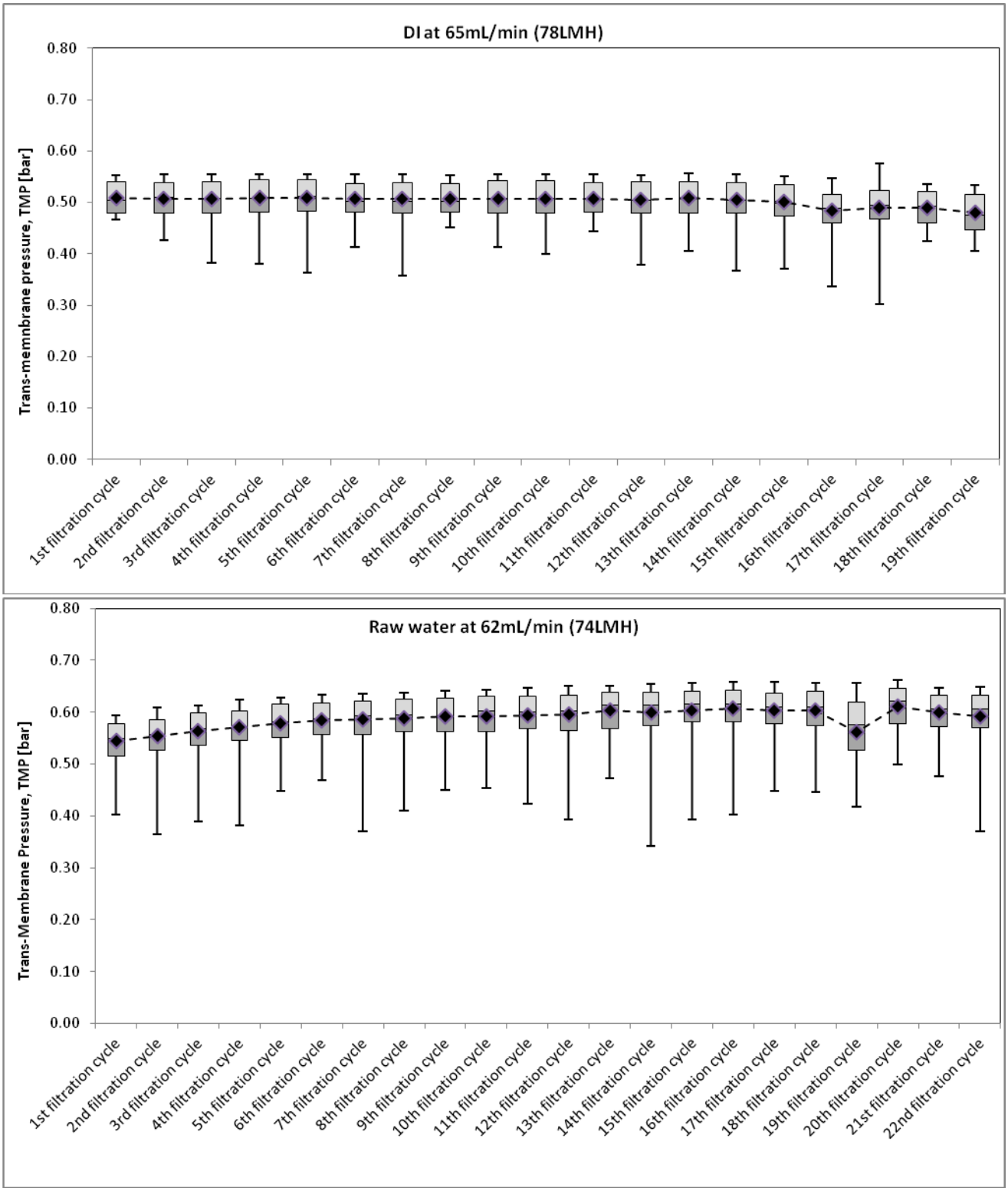


Figure 32. Box and whisker plots: TMP profiles for filtration of DI at 78LMH (top) and raw water at 74LMH (bottom)

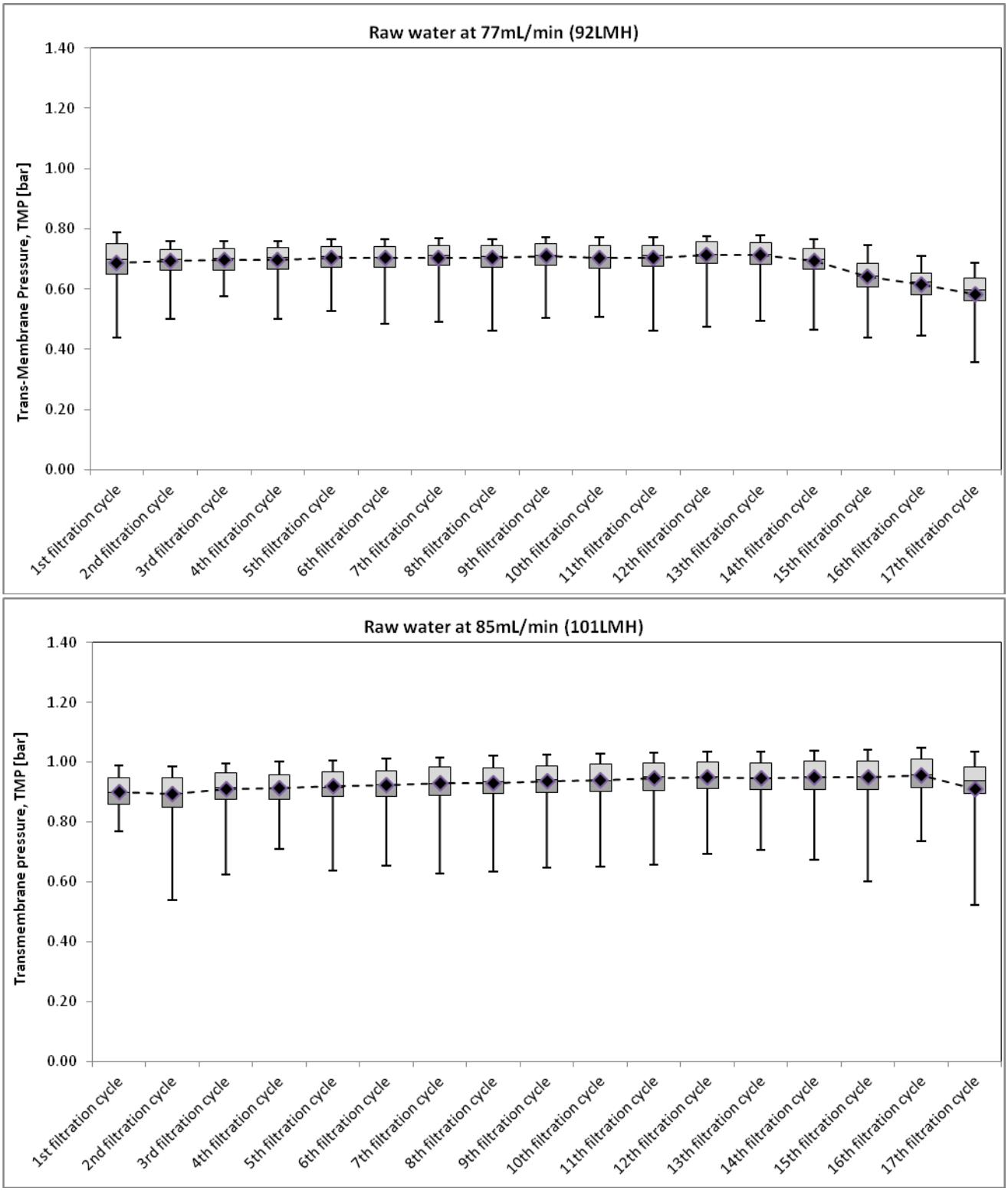


Figure 33. Box and whisker plots: TMP profiles for filtration of raw water at 92LMH (top) and 101LMH (bottom)

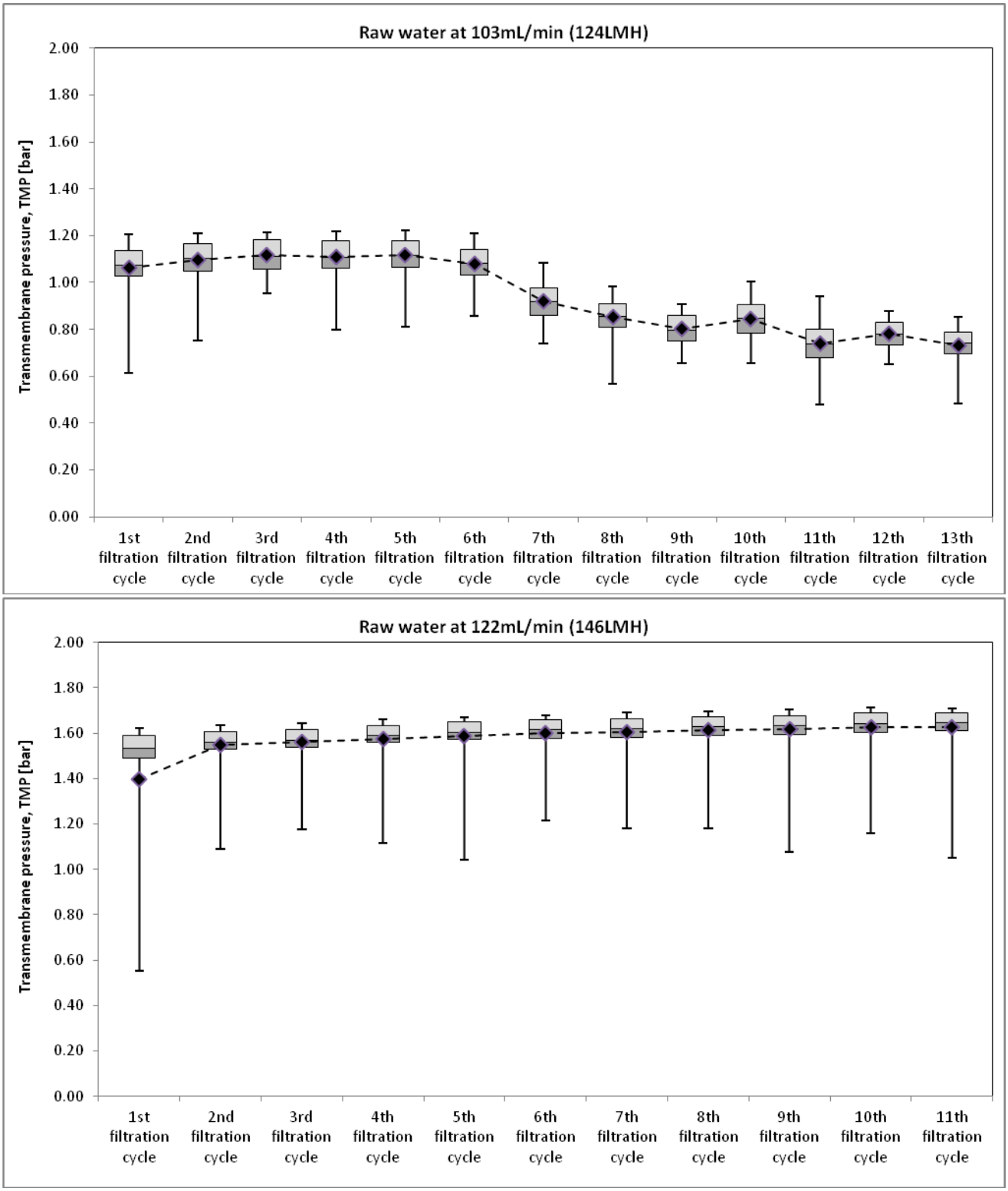


Figure 34.Box and whisker plots: TMP profiles for filtration of raw water at 124LMH (top) and 146LMH (bottom)

Fouling Tendency - Rate of TMP change – dTMP/dt

As the TMP profiles presented previously refer to absolute values, a parameter that uses relative values which can be used for the comparison of the different operational conditions is required. This parameter is the fouling tendency or the rate of TMP change. It can be extracted from the plots in Figure 35 - Figure 37 and be used to compare the evolution of the fouling process under different scenarios.

It was determined for every filtration cycle, using the values of the monitored TMP, and elaborating their profiles with the slope of the drawn trendlines representing each filtration cycle's TMP rise. Adopting a standard bachwash interval (BWI) of 15min and due to the various operational fluxes tested, in order to keep the filtered volume constant, different number of filtration cycles was introduced for each experiment.

As briefly explained earlier there were some cases where the profiles deviated from the expected trends or values resulting to their exclusion from further elaboration. An example would be the case of raw water filtration under an operational flux of 124LMH, where after 6 cycles of filtration (or 1.5h) minor leakages disturbed the ascending TMP profile by causing pressure loss. Other individual cases were also identified and excluded based also on common sense criteria.

Table 20. Fouling rate of each operational flux

	DI (74LMH)	74LMH		90LMH		108LMH		126LMH		144LMH	
Cycle	Fouling Rate	Fouling Rate	%	Fouling Rate	%	Fouling Rate	%	Fouling Rate	%	Fouling Rate	%
	bar/h	bar/h		bar/h		bar/h		bar/h		bar/h	
1	-0.007	0.124	100%	0.418	100%	0.312	100%	0.708	100%	0.869	100%
2	0.062	0.199	160%	0.067	16%	0.217	70%	0.325	46%	0.572	66%
3	0.072	0.187	151%	0.106	25%	0.338	108%	0.129	18%	0.574	66%
4	0.006	0.221	178%	0.168	40%	0.226	72%	0.279	39%	0.619	71%
5	0.049	0.178	143%	0.181	43%	0.256	82%	0.309	44%	0.638	73%
6	0.032	0.108	87%	0.164	39%	0.308	99%			0.534	61%
7	0.060	0.173	139%	0.138	33%	0.342	110%			0.508	58%
8	0.015	0.199	160%	0.204	49%	0.279	89%			0.565	65%
9	-0.005	0.174	141%	0.222	53%	0.347	111%			0.637	73%
10	0.036	0.189	152%	0.089	21%	0.236	76%			0.568	65%
11	-0.007	0.204	164%	0.092	22%	0.254	81%			0.620	71%
12	0.045	0.192	155%	0.202	48%	0.271	87%				
13	0.073	0.144	116%	0.086	20%	0.289	93%				
14	0.003	0.211	170%			0.268	86%				
15	0.006	0.149	120%			0.274	88%				
16		0.184	148%			0.318	102%				
17	0.092	0.168	135%								
18	0.015	0.155	124%								
19											
20		0.152	122%								
21		0.138	111%								

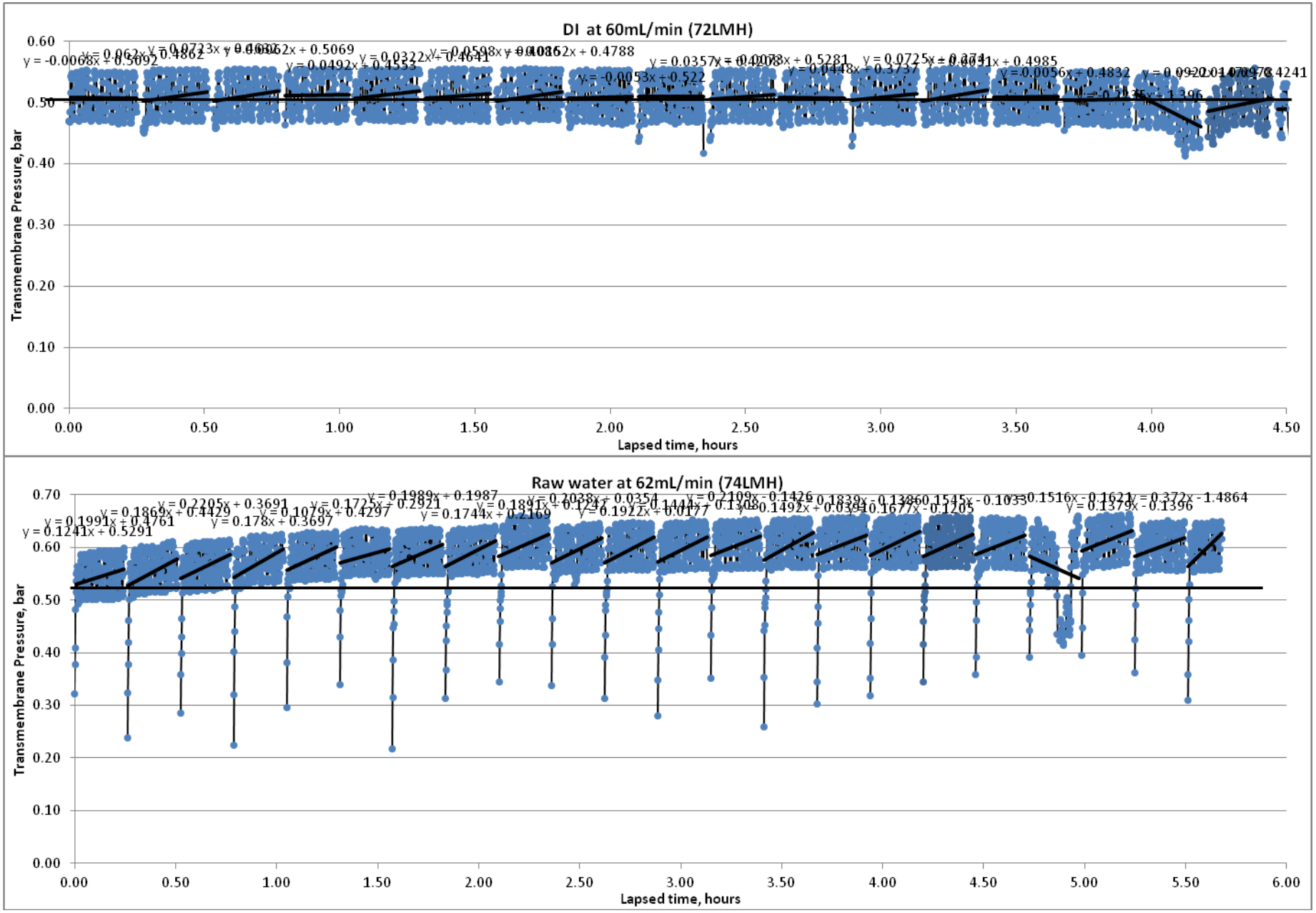


Figure 35. Evaluation of hydraulic backwashing for the operating fluxes of DI72LMH (top) and RW74LMH (bottom)

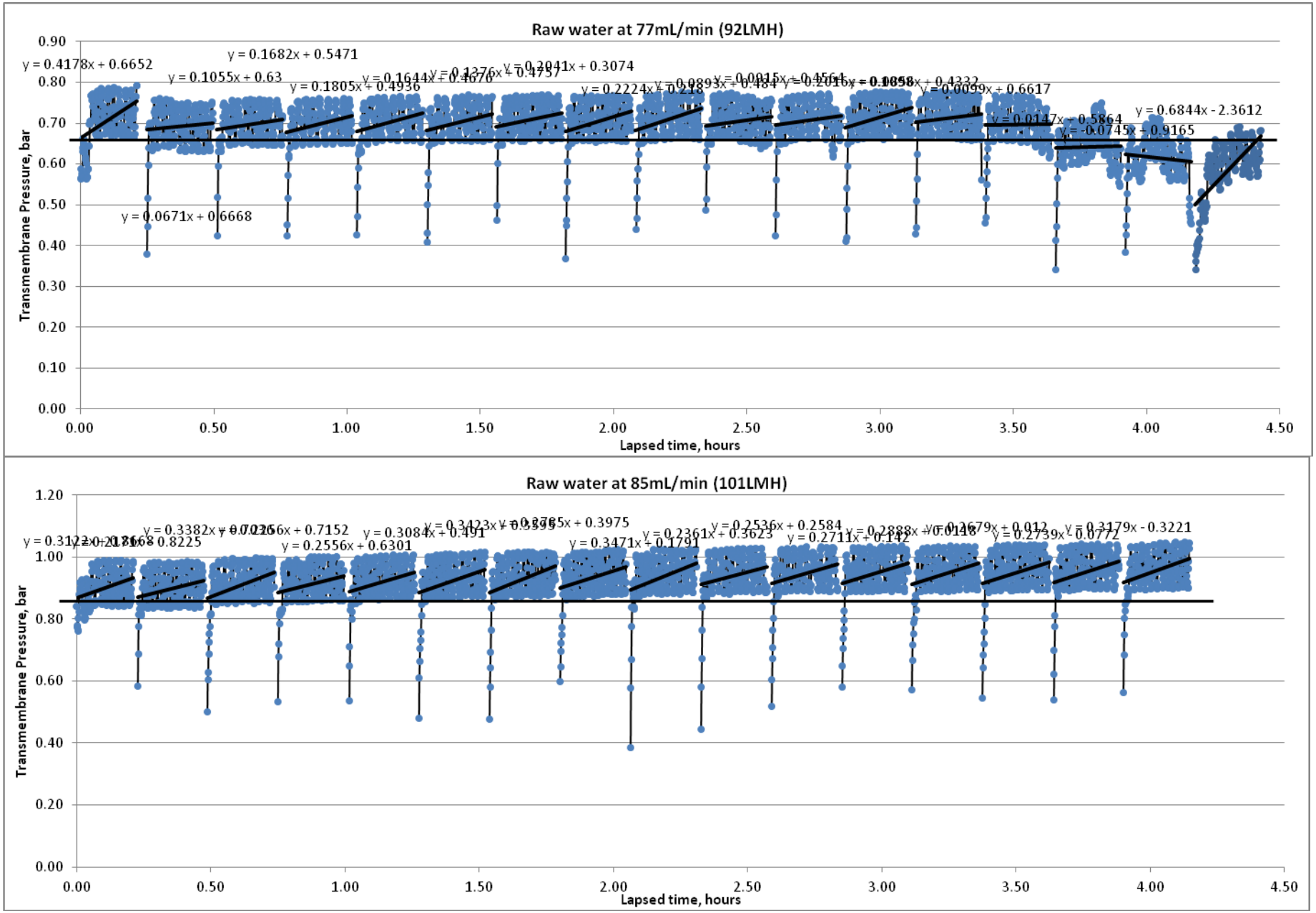


Figure 36. Evaluation of hydraulic backwashing for the operating fluxes of 94LMH (top) and 108LMH (bottom)

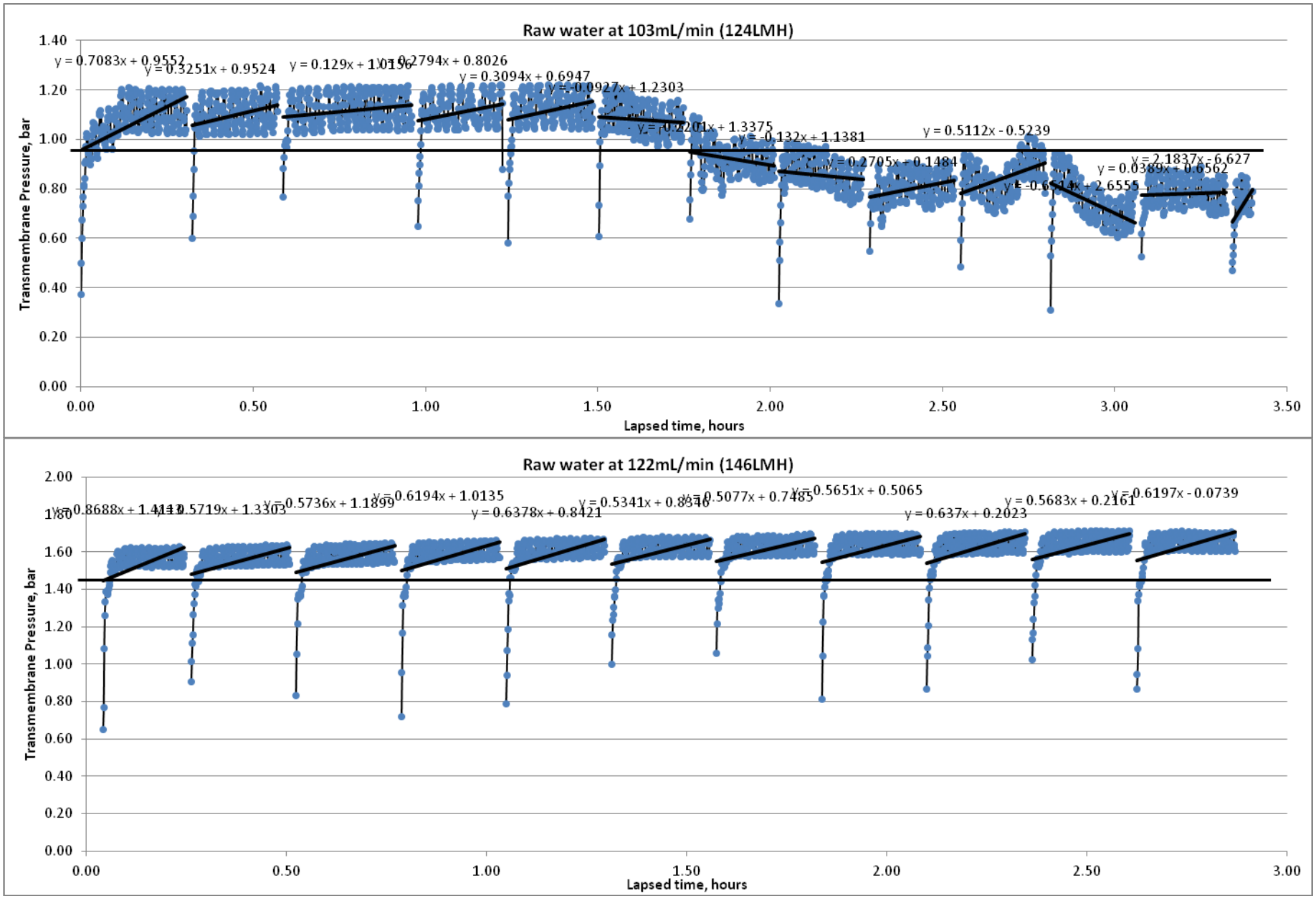


Figure 37. Evaluation of hydraulic backwashing for the operating fluxes of 126LMH (top) and 144LMH (bottom)

Determination of fouling types

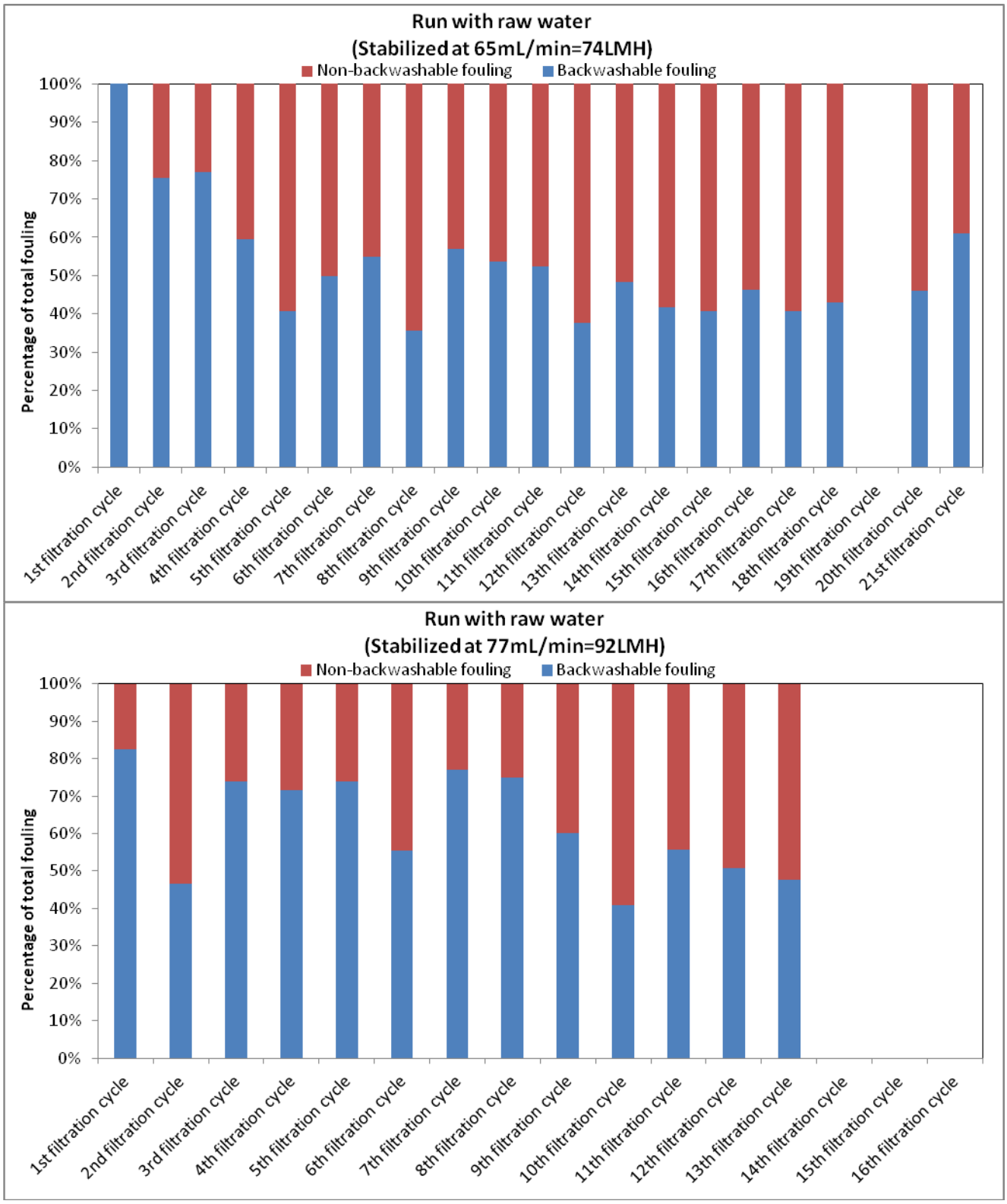


Figure 38. Backwashable and non-backwashable fouling distribution per filtration cycle for the operational fluxes of 74LMH (top) and 92LMH (bottom)

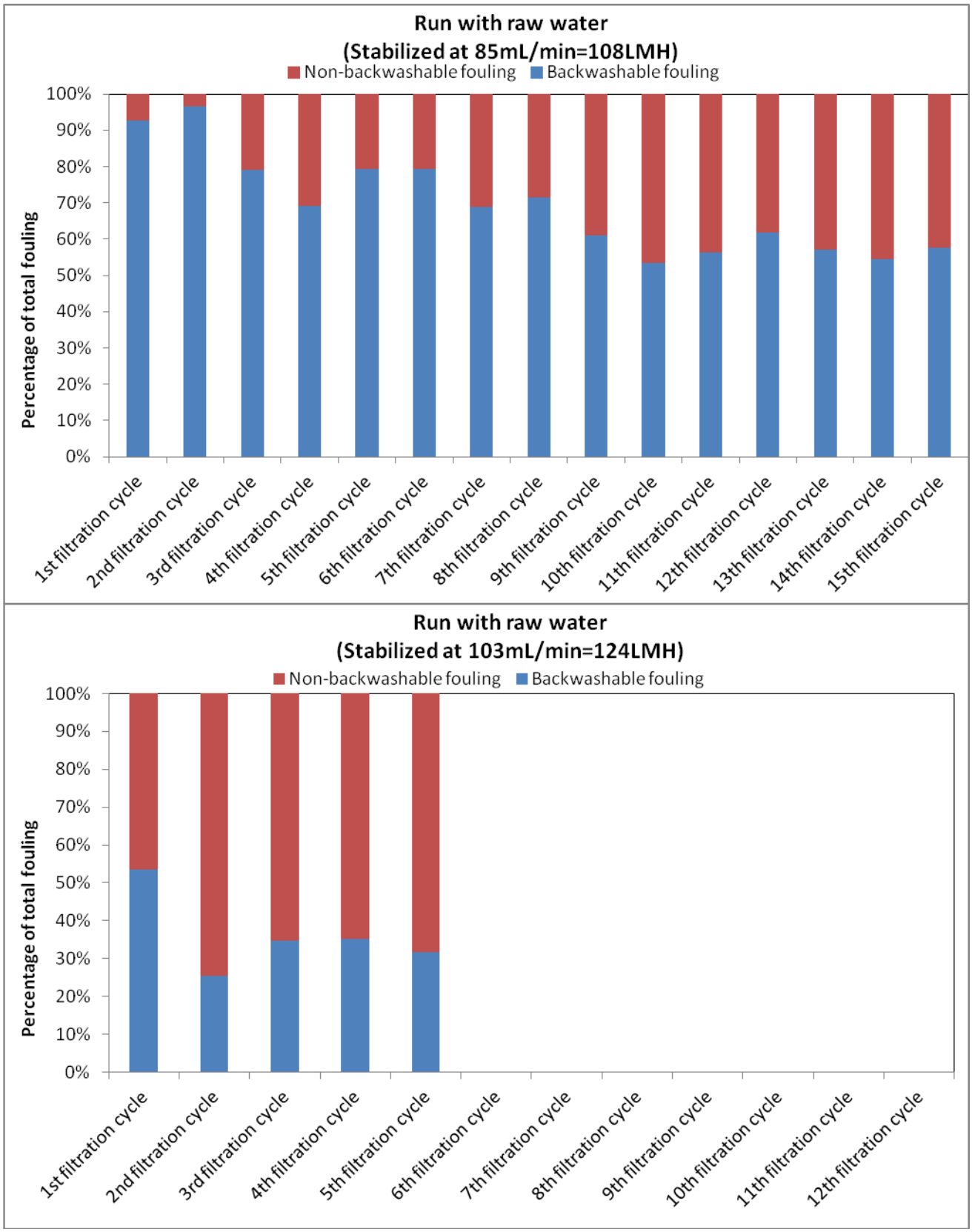


Figure 39. Backwashable and non-backwashable fouling distribution per filtration cycle for the operational fluxes of 108LMH (top) and 124LMH (bottom)

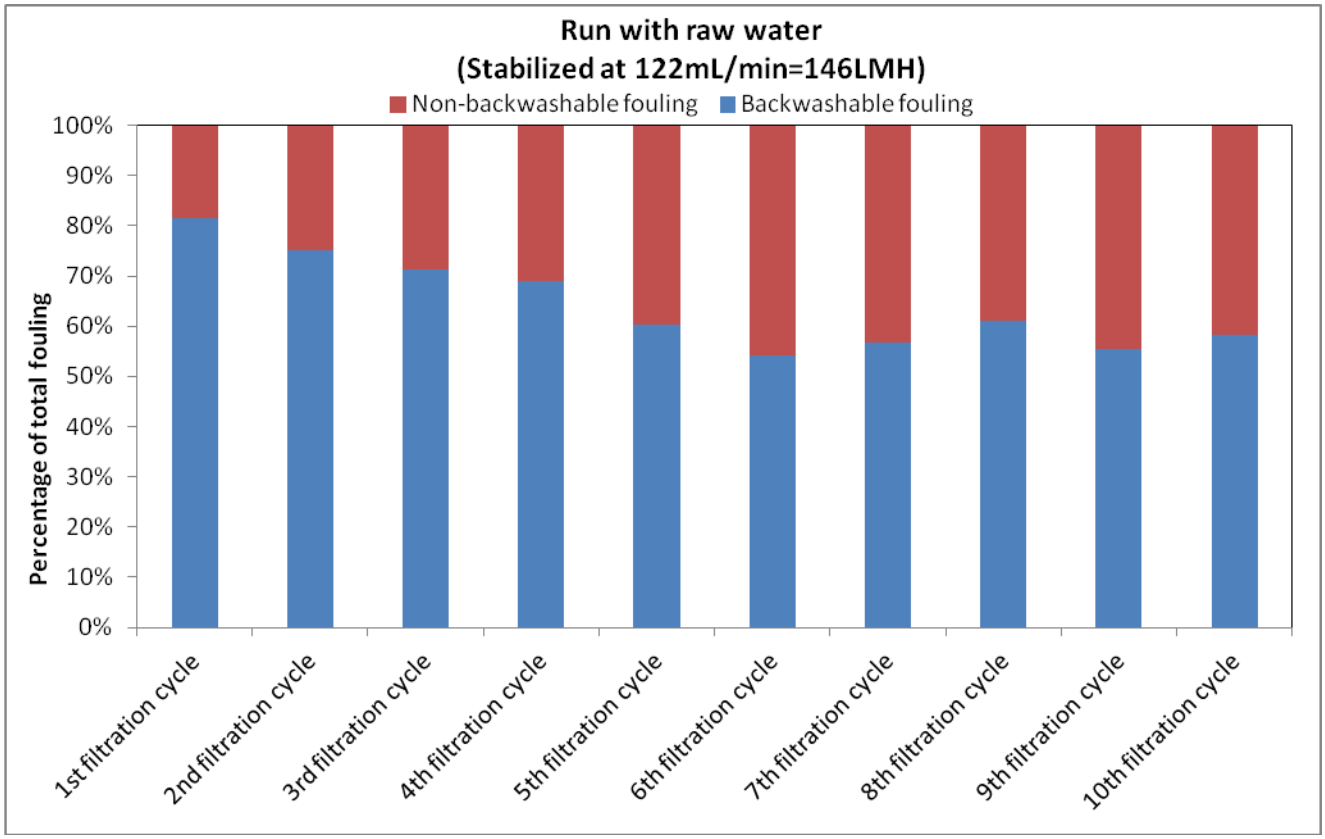


Figure 40. Backwashable and non-backwashable fouling distribution per filtration cycle for the operational flux of 146LMH

Specific Flux – Permeance – K

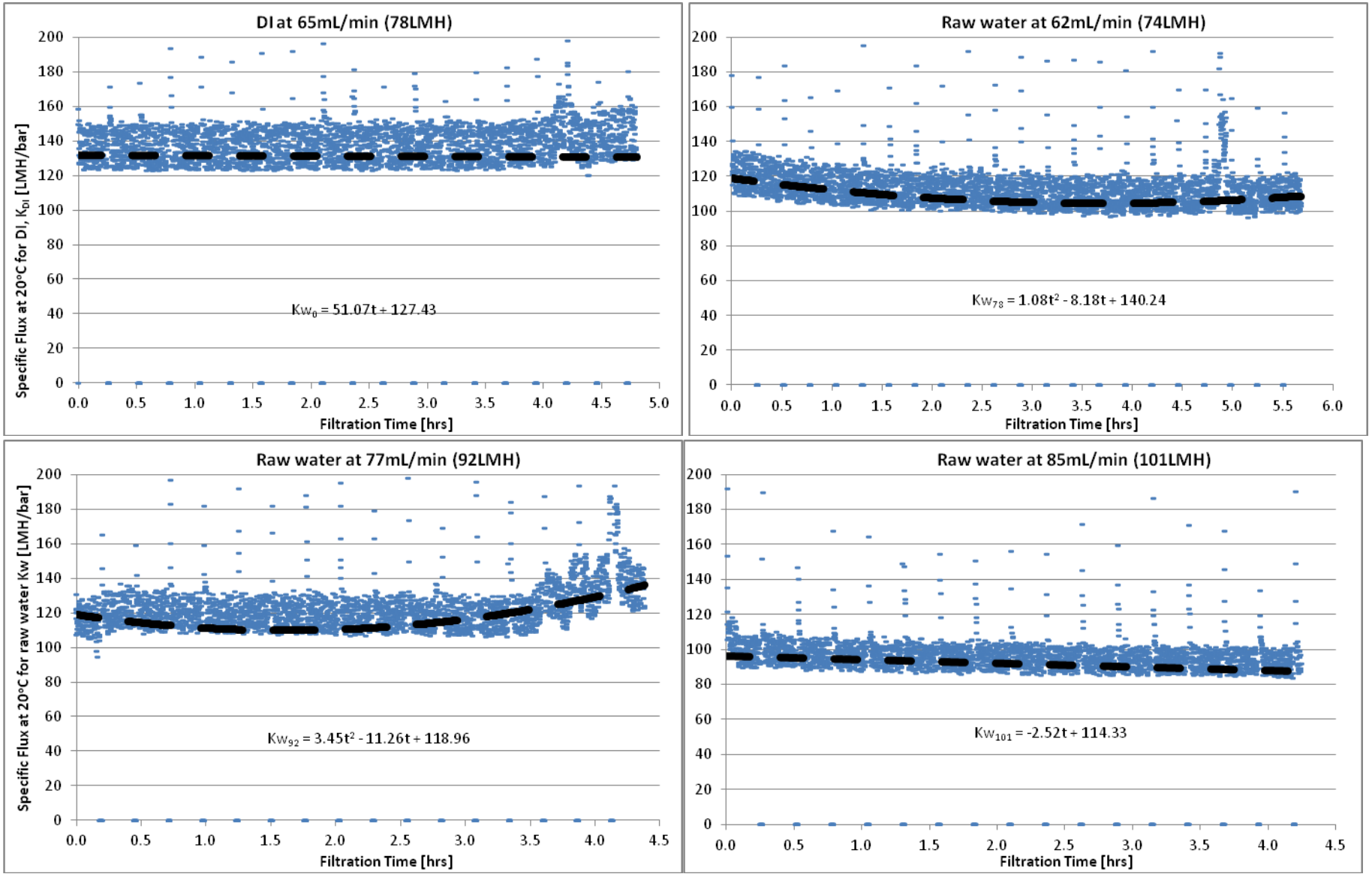


Figure 41. Temperature corrected specific flux (permeability) profiles vs. time for various fluxes.
Top row: DI@78LMH (left), RW@74LMH (right), Bottom row: RW@92LMH (left), RW@101LMH (right)

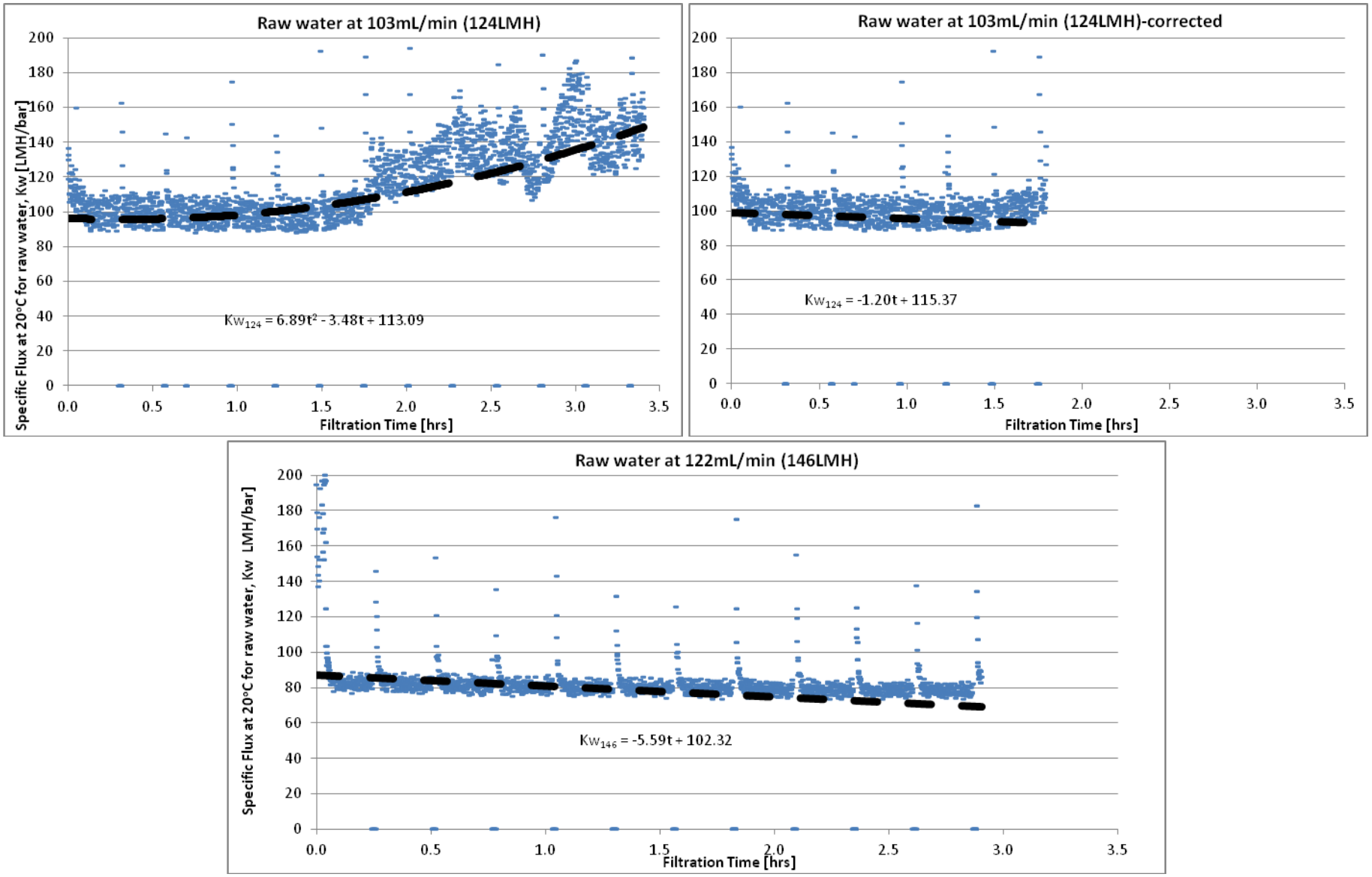


Figure 42. Temperature corrected specific flux profiles vs. time for various fluxes.
Top row: RW@124LMH (left), RW@124LMH-corrected (right), Bottom row: RW@146LMH

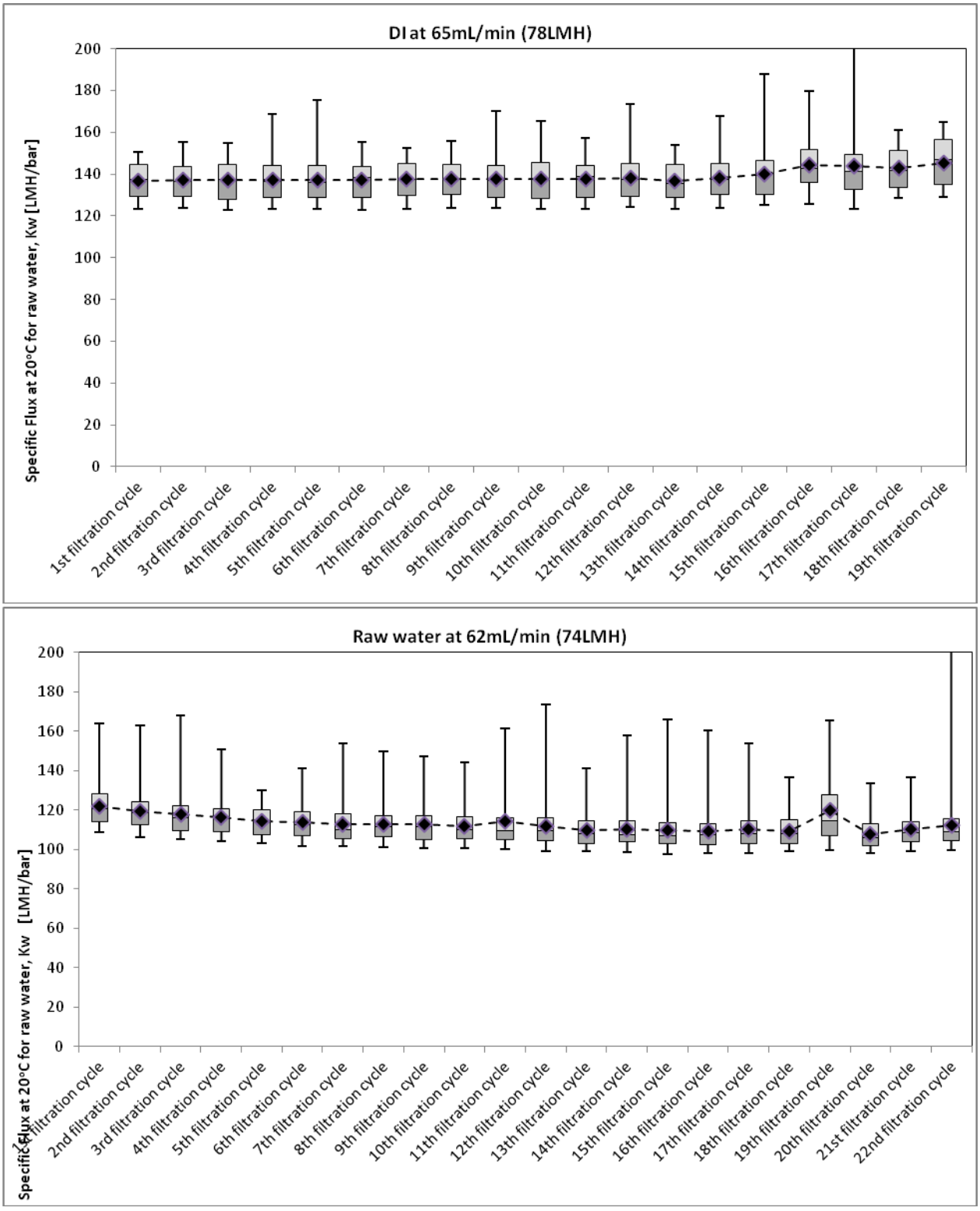


Figure 43. Box and whisker plots: Temperature corrected specific flux for filtration of DI at 78LMH (top) and raw water at 74LMH (bottom)

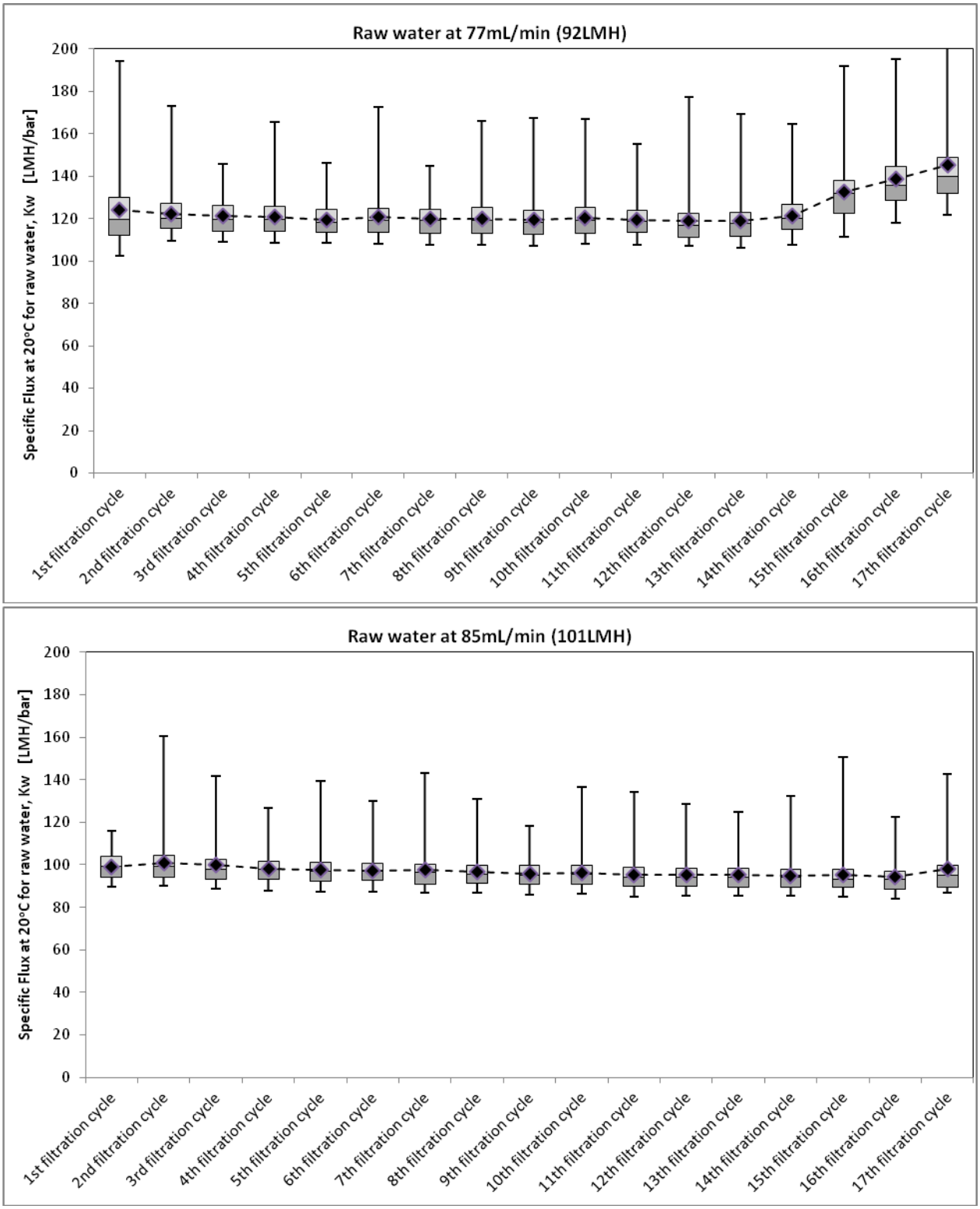


Figure 44. Box and whisker plots: Temperature corrected specific flux for filtration of raw water at 92LMH (top) and 101LMH (bottom)

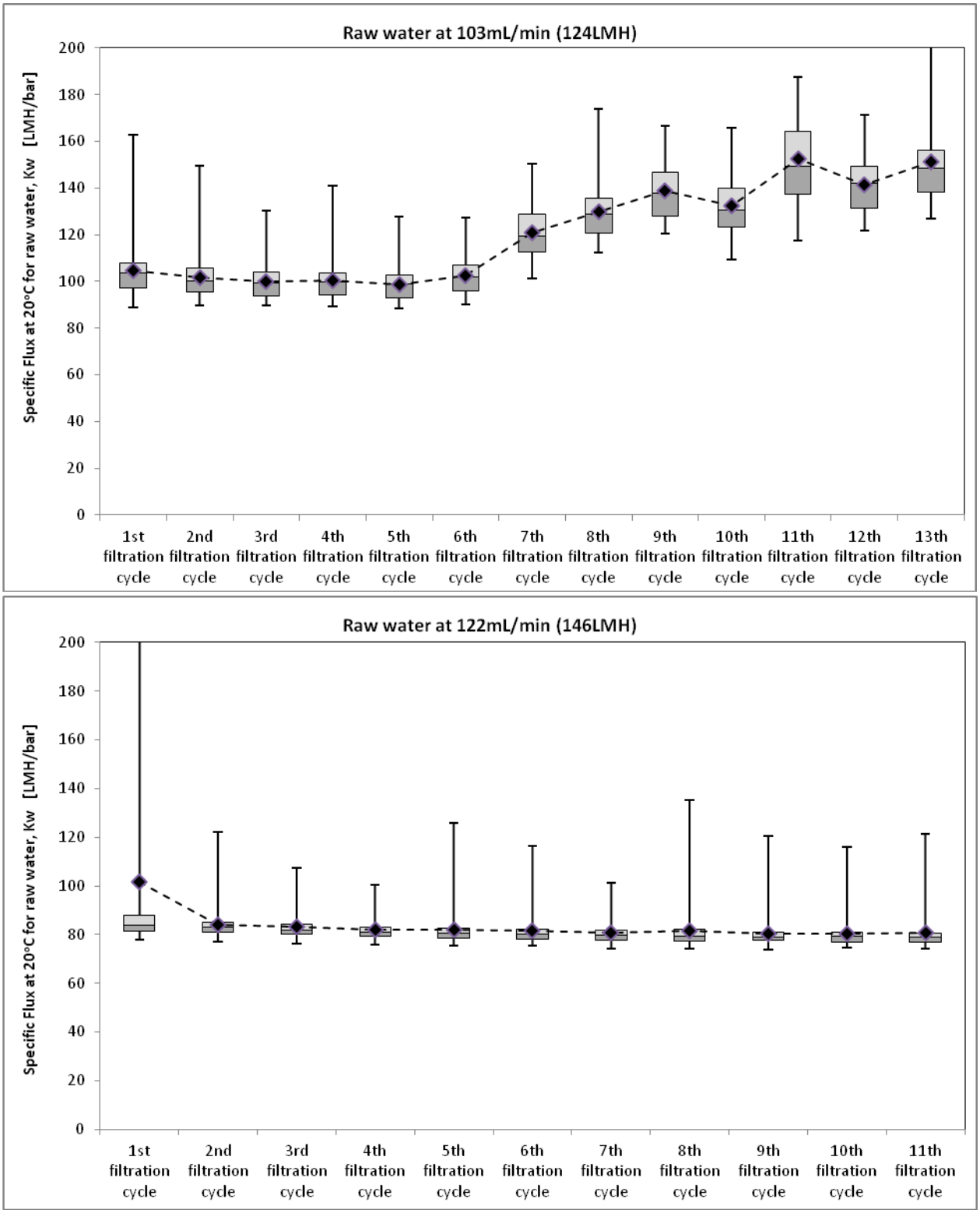


Figure 45. Box and whisker plots: Temperature corrected specific flux for filtration raw water at 124LMH (top) and 146LMH (bottom)

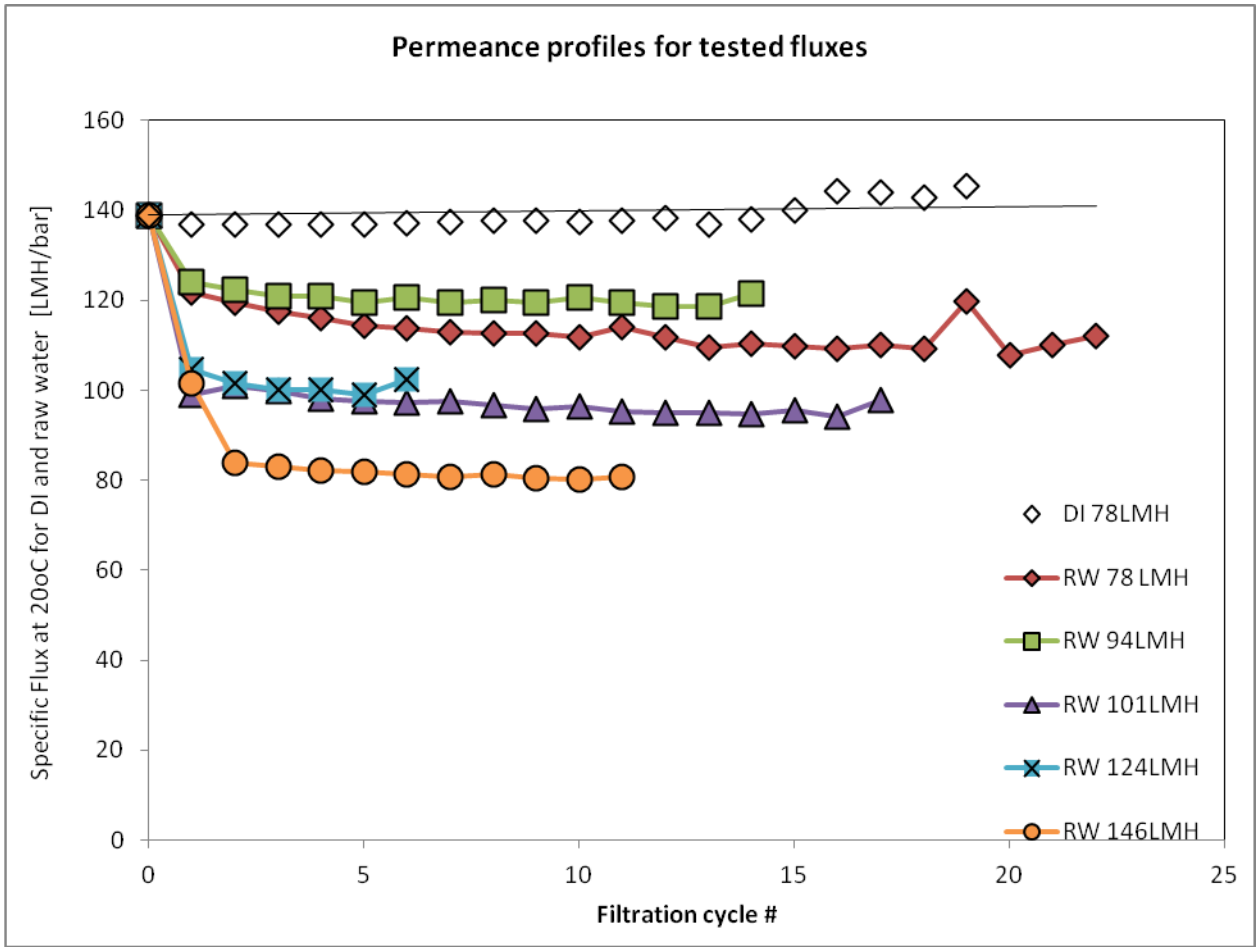


Figure 46. Average temperature corrected specific flux profiles under different flux operations vs time (15min filtration cycle)

Total Hydraulic Resistance – R_T

The determination of the hydraulic resistances will be performed with the interpretation of the TMP profiles and especially focus on the transition to another operating condition of higher flux. The TMP of the tested fluxes are presented in Figure 47 while the details of the transition during the back wash to the higher subsequent operating flux are provided in Figure 48 - Figure 50. The hydraulic resistance can be calculated based on the fluxes and the TMP profiles, using Darcy's law. The boxplots in Figure 51 to Figure 53 can then be created. Their averaged values from each filtration cycle per operational flux are used to summarize the boxplots in one figure as seen in section 4.2.ii.e (Figure 22).

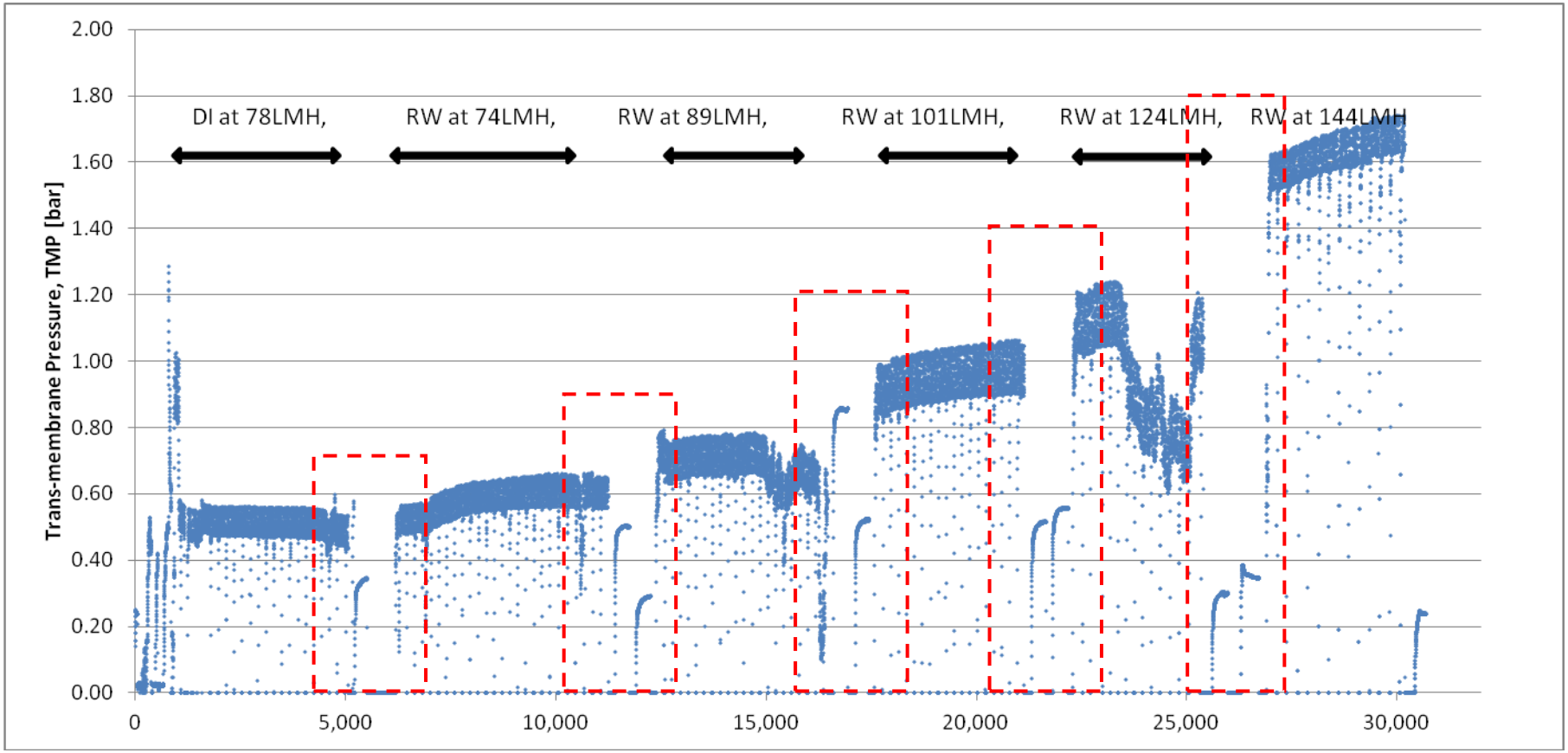


Figure 47. TMP profiles of the tested fluxes, including DI78, RW74, RW89, RW101, RW124 and RW146LMH

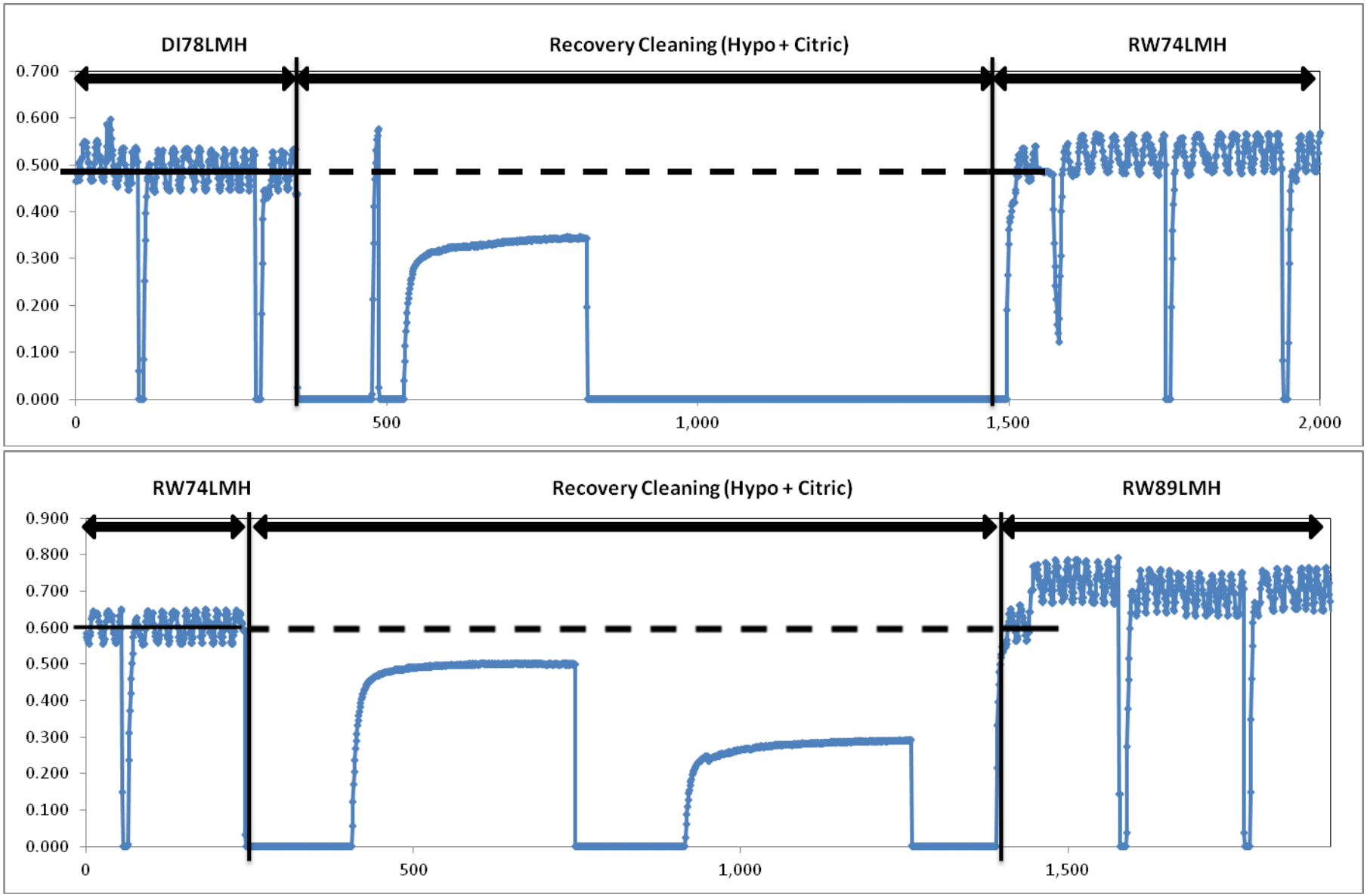


Figure 48. Detail of the TMP transition after changing the operating flux.
Top: transition from DI filtration at 78LMH to raw water filtration at 74LMH. Bottom: transition from raw water filtration at 74LMH to 89LMH

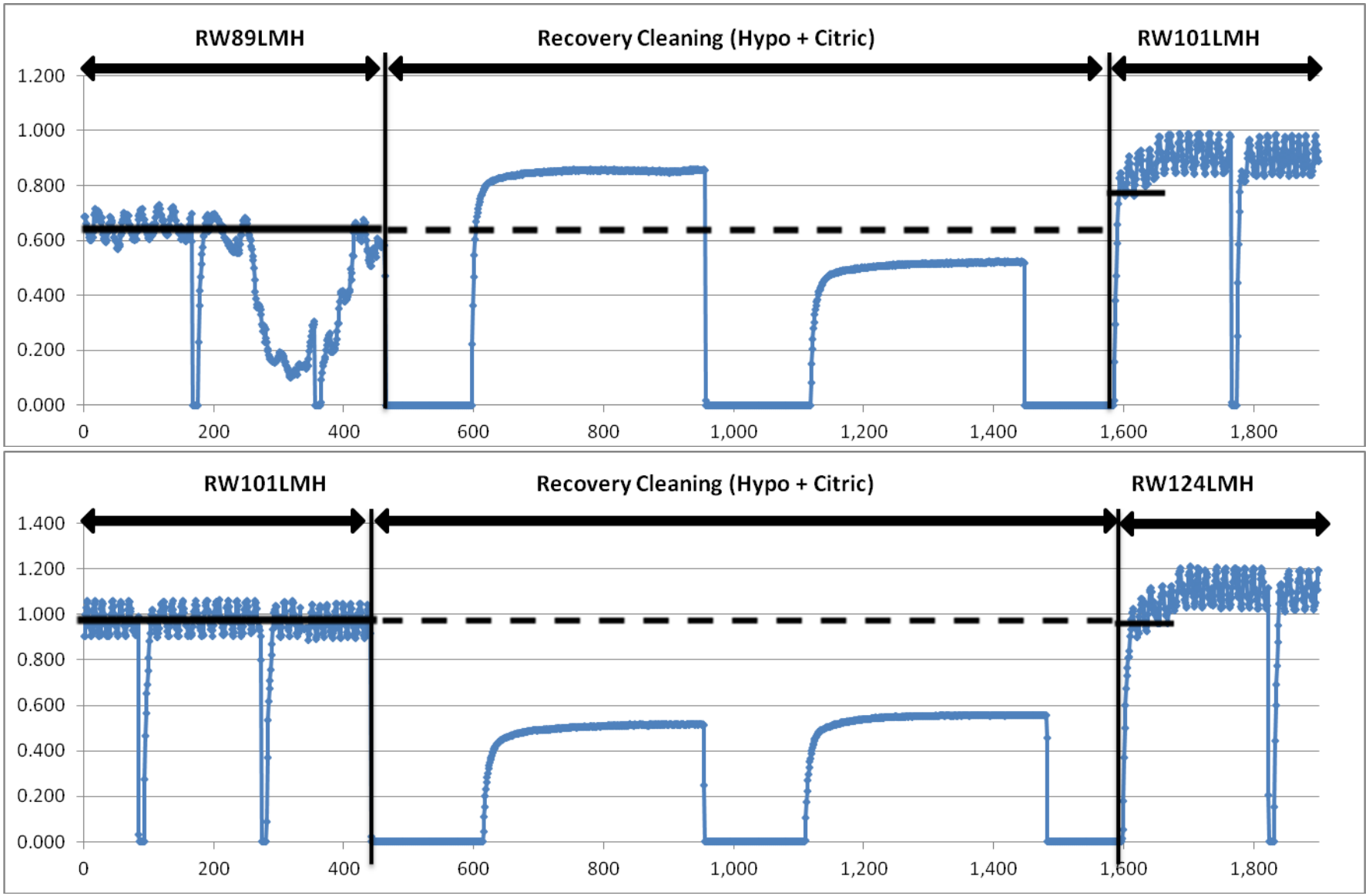


Figure 49. Detail of the TMP transition after changing the operating flux.
Top: transition from raw water filtration at 89LMH to raw water filtration at 101LMH. Bottom: transition from raw water filtration at 101LMH to 124LMH

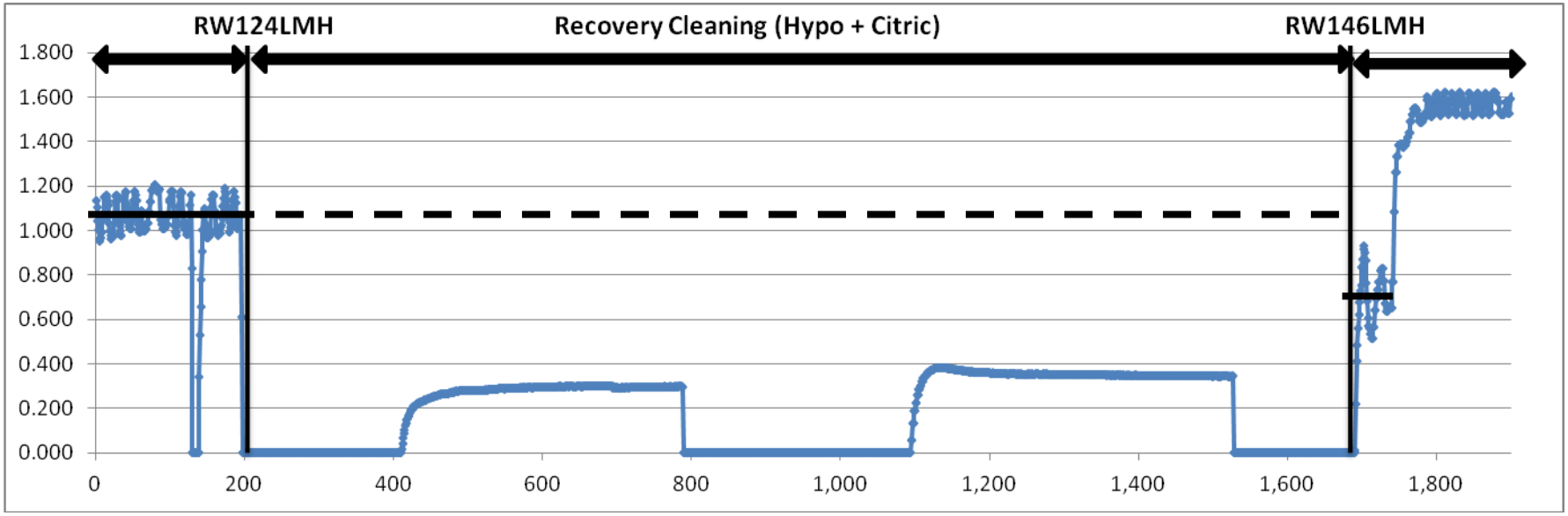


Figure 50. Detail of the TMP transition after changing the operating flux.
Transition from raw water filtration at 124LMH to raw water filtration at 146LMH

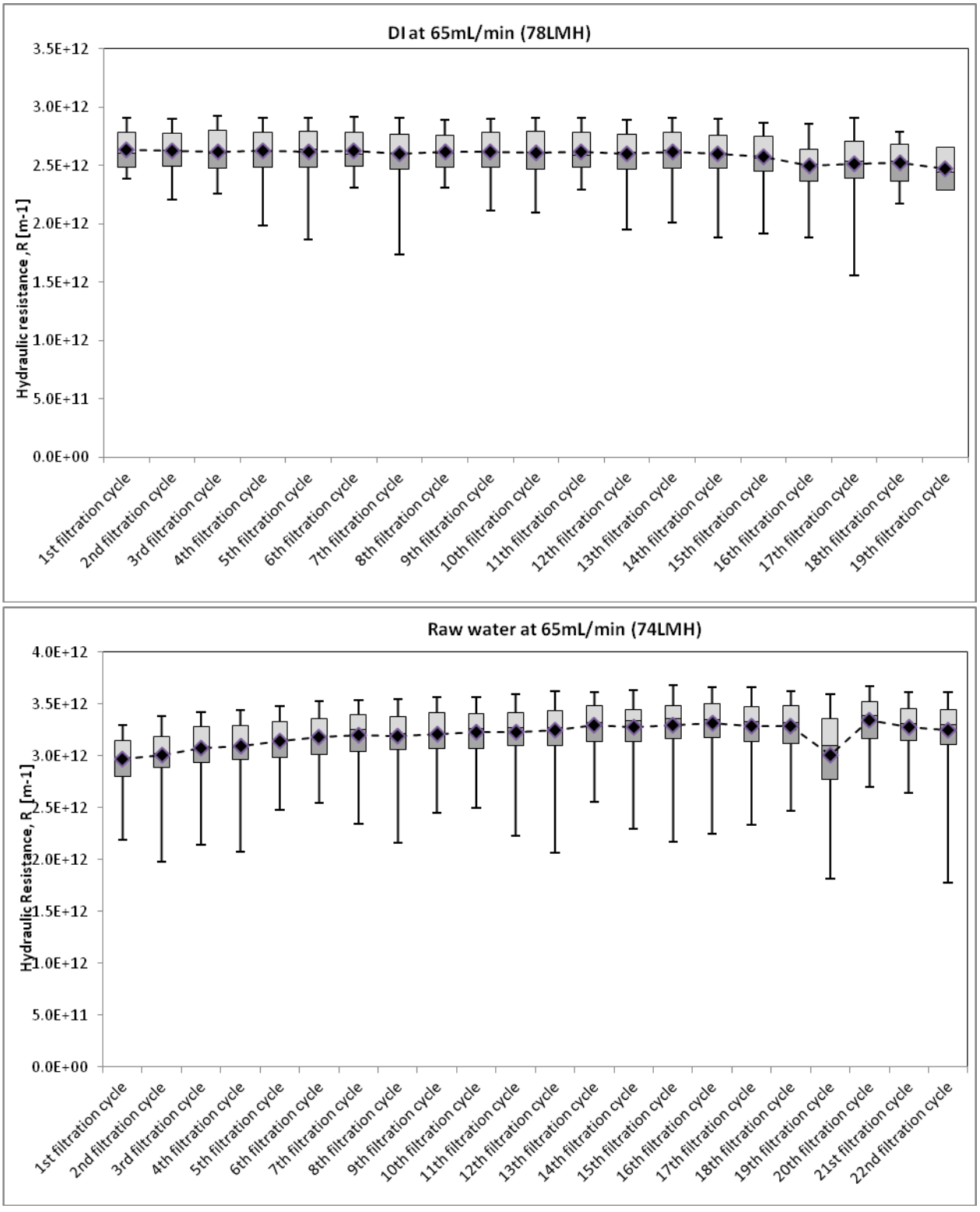


Figure 51. Box and whisker plots: Total Hydraulic resistance for filtration of DI at 78LMH (top) and raw water at 74LMH (bottom)

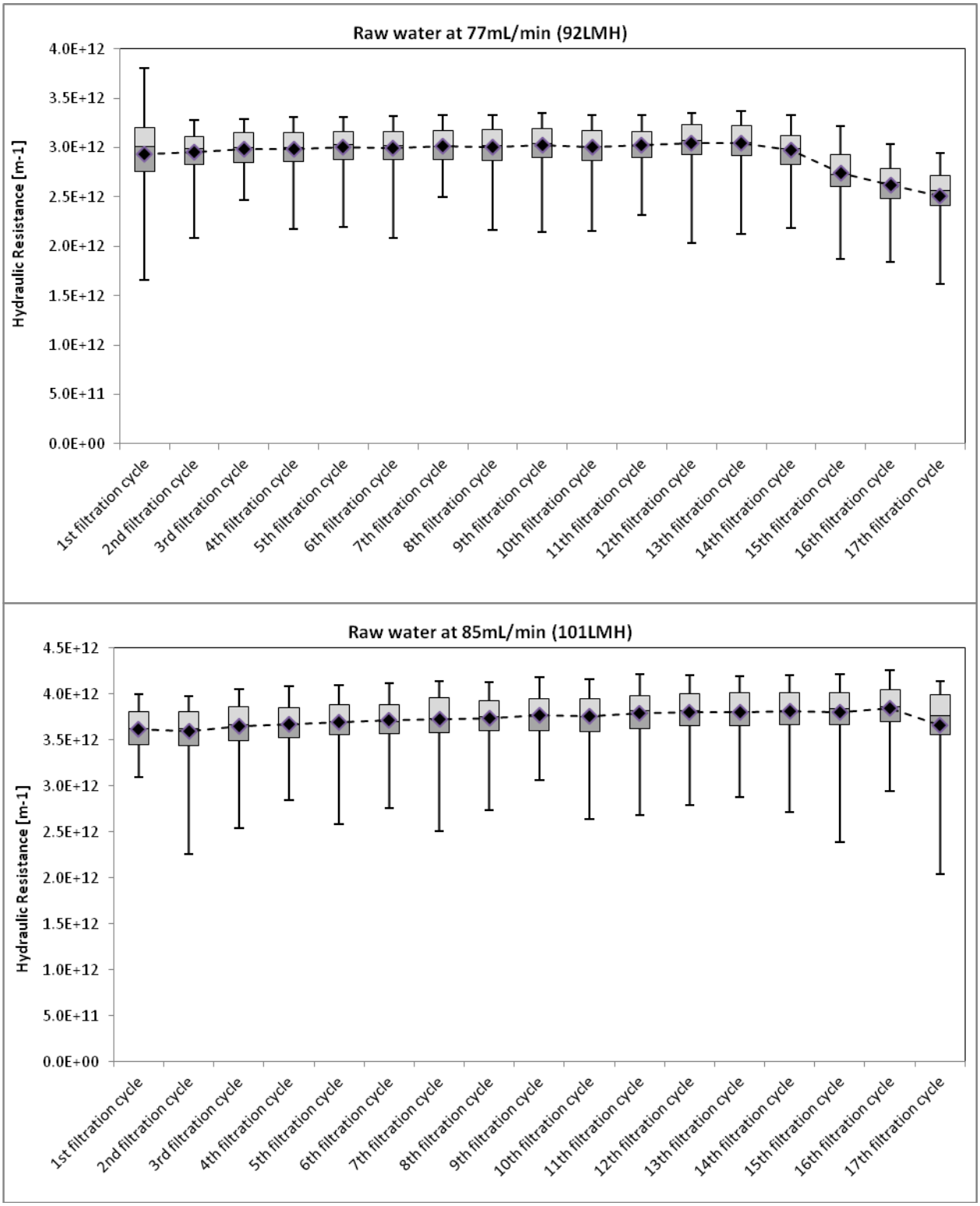


Figure 52. Box and whisker plots: Total hydraulic resistance for filtration of raw water at 92LMH (top) and 101LMH (bottom)

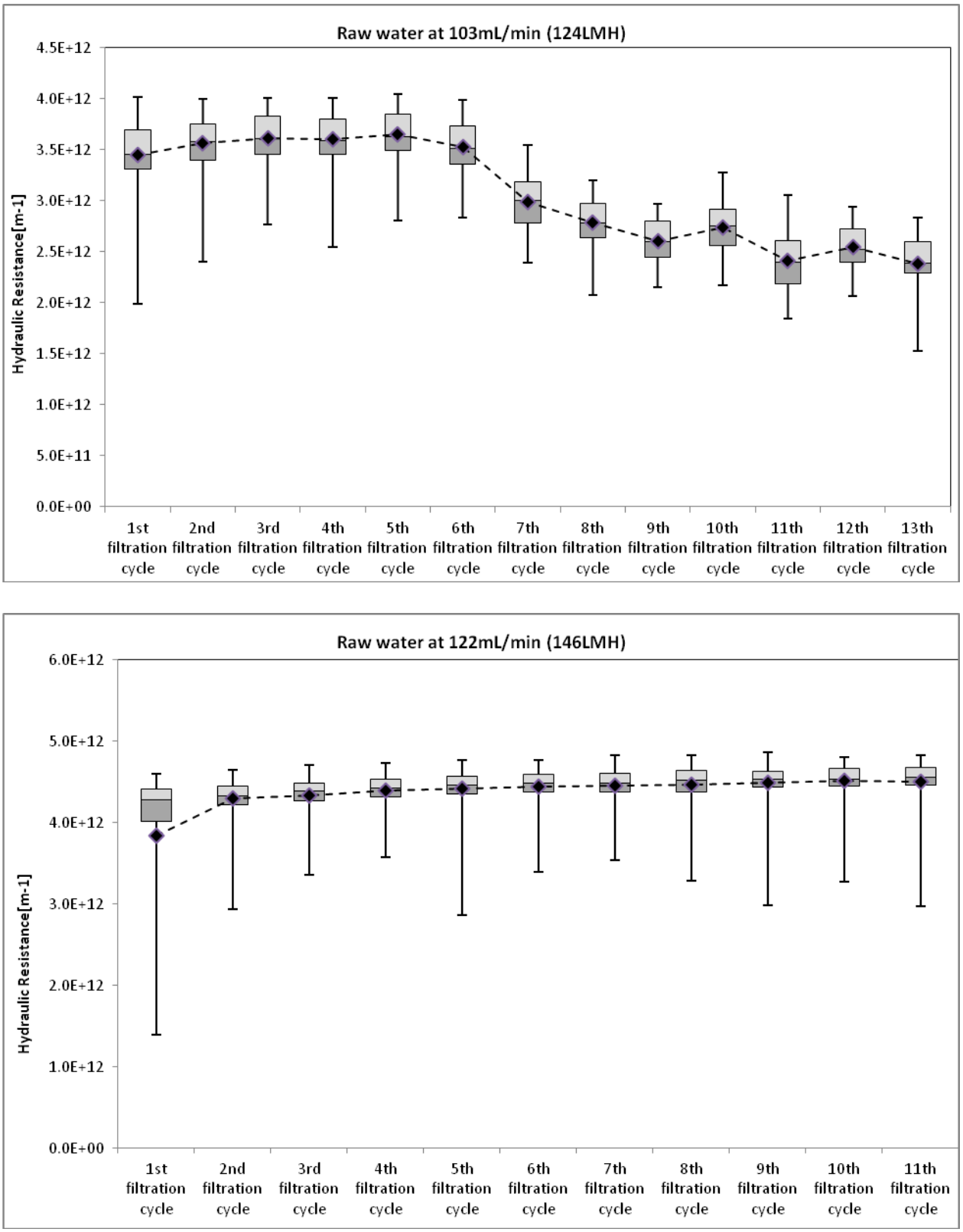


Figure 53. Box and whisker plots: Total hydraulic resistance for filtration of raw water at 124LMH (top) and 146LMH (bottom)