DRINKING WATER BIOFILTRATION: ASSESSING KEY FACTORS AND IMPROVING PROCESS EVALUATION

by

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ABSTRACT

Biodegradable organic matter (BOM) removal in drinking water biofilters can be affected by several factors. The factors investigated in this research were non-biological particles/ coagulant in the influent, chlorine in the backwash water, air scour during backwashing, anthracite/sand vs. GAC/sand media, and low (5 °C)/high (20 °C) temperature operation. Other investigations included: impact of biomass accumulation within a filter run; impact of empty contact time (EBCT); and impact of step increases in BOM concentration and hydraulic loading rate, and filter shutdown on biofilter performance. The research also included the evaluation of biomass respiration potential (BRP) as an alternative biomass measurement, the development of a simple experimentally-based approach for estimation of key bio-kinetic parameters, and the modeling of BOM removal in drinking water biofilters. Laboratory scale biofilters fed a cocktail of easily biodegradable compounds were used for this research.

Fractional factorial design experiments in blocks I and II (phases I and II) showed that the three main factors (chlorine in backwash, temperature and media type) and their two or three-factor interactions were significant in most cases. The temperature effect was more significant when chlorine was present in the backwash water. GAC filters were much more resistant to chlorinated water backwash than anthracite filters, as expected.

Further investigation of factors affecting drinking water biofiltration in phase III suggested that air scour, particle and coagulant effects were generally negligible although an air scour effect should be considered under unfavourable operating conditions (low temperature, chlorine, anthracite). Longer-term operation in phase III indicated that for easily biodegradable compounds (acetate, formate and formaldehyde), good removals were obtained after several months in the low temperature filter backwashed with chlorinated water (0.25 mg/L Cl_2). Glyoxal removal was more sensitive to unfavourable biofiltration conditions than acetate, formate and formaldehyde. EBCT was not as important in biofilters run at the high temperature as at the low temperature. BOM removal was not sensitive to the biomass accumulation during a filter run.

The concept of bed utilization (the ratio of the bed depth required for substantial BOM removal to the entire bed depth) was introduced in the study. It could allow for better evaluation of the factors affecting biofiltration.

Based on the experimental results in phases I, II and III, multiple linear regression models were developed to roughly predict BOM removal for various conditions at contact times similar to those used in this research.

Mature biofilm in biofilters was able to maintain or quickly recover good BOM removal when exposed to a sudden increase either in BOM concentration or hydraulic loading rate. The impact of filter shutdown (24-h period, filter drained) was minor, at least for removal of easily degradable BOM components.

The amount of biomass on the filter media was evaluated by BRP (biomass respiration potential) and the phospholipid method in parallel. A good linear relationship was found

between BRP and phospholipid biomass. The BRP method might be appropriate for routine use by treatment plant personnel due to its simpler and faster nature compared to other approaches.

The key bio-kinetic parameters (k and K_s) were estimated in a dedicated experiment in which the biomass from the filter media and the BOM from the filter influent were used. The experimental conditions here closely simulated biofilters. The estimated kinetic parameters were expected to be more robust than previous estimates by using other approaches.

Three biofilter models, based on the simplified biofilm model, Suidan and Wang's semi-empirical equation, and Sáez and Rittmann's revised solution, respectively, were applied to the modeling of acetate removal performance in biofilters in this study, by using the estimated bio-kinetic parameters (k and K_s) from the experimentally-based approach in this research. The modeling results indicated that these three models are all applicable to the modeling of drinking water biofilter performance and they all provided a good prediction for acetate removal in biofilters for the conditions evaluated. The very close performance of these three models was also verified by a general comparison of the three models based on the estimated parameters from this study. The simplified biofilter model is recommended for its simplicity. Typical modeling results of biofilm thickness distribution, acetate profiles along the depth of biofilters, and acetate concentration in the biofilm could give some insights into the biofilter performance. A series of generalized curves was established to compare the percent removal of different substrates under various operating conditions among studies.

A revised S_{min} (minimum substrate concentration that can maintain a single layer biofilm in biofilters) and critical dimensionless contact time $X^*_{critical}$ (beyond $X^*_{critical}$, little further removal is obtained) were proposed and evaluated in this study.

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LIST OF ABBREVIATIONS

ANOV	Analysis of variance
AOC	Assimilable organic carbon
BDOC	Biodegradable dissolved organic carbon
BOM	Biodegradable organic matter
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
GAC	Granular activated carbon
GC/ECD	Gas chromatography with electron capture detection
HPC	Heterotrophic plate count
HLR	Hydraulic loading rate
NOM	Natural organic matter
PFBHA	o-2,3,4,5,6-pentafluorobenzyl-hydroxylamine hydrochloride
RPM	Revolutions per minute
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TOC	Total organic carbon

LIST OF SYMBOLS

b	Overall biofilm decay rate coefficient (T^{-1})
b	First-order biofilm detachment rate coefficient (T^{-1})
D	Free liquid diffusivity ($L^2\ T^{-1}$)
D*	Dimensionless substrate diffusivity, $D^* = D/D_f$
D_f	Diffusivity in a biofilm ($L^2\ T^{-1}$)
D_H	Hydrodynamic dispersivity ($L^2\ T^{-1}$)
D_p	Particle diameter of packed-bed media (L)
f	The conversion factor
J	Substrate flux into a steady-state biofilm (J, $Ms\ L^{-2}\ T^{-1}$)
J*	Dimensionless substrate flux into a steady-state biofilm, $J^* = J\tau/KsD_f$
k	Maximum specific rate of substrate utilization (T^{-1})
k_d	Detachment rate coefficient (units depend the expression)
k_d'	Detachment rate coefficient ($ML^{-3}T^{-1}$)
k_d''	Detachment rate coefficient (ML^{-3})
K_s	Half velocity constant in Monod expression (MsL^{-3})
L	Thickness of effective diffusion layer (L)
L*	Dimensionless thickness of effective diffusion layer, $L^* = L/T$
L_f	Biofilm thickness (L)
L_f*	Dimensionless biofilm thickness, $L_f^* = L_f/\tau$
R_e	Reynolds number $Re = vdp\rho/\mu$
S_b	Bulk liquid concentration of substrate (MsL^{-3})
S_b*	Dimensionless bulk substrate concentration, $S_b^* = S_b/K_s$
S_C	Schmidt number, $S_C = \mu/(\rho D)$
S_e	Effluent concentration (MsL^{-3})
S_e*	Dimensionless effluent concentration, $S_e = S_e/K_s$
S_f	Substrate concentration within the biofilm (MsL^{-3})
S_f*	Dimensionless substrate concentration within the biofilm

S_i	Influent concentration (MsL^{-3})
S_i^*	Dimensionless influent concentration, $S_i^* = S_i/K_s$
S_{min}	Minimum substrate concentration for sustaining a steady-state biofilm (MsL^{-3}).
S_{min}^*	Dimensionless minimum substrate concentration, $S_{min}^* = S_{min}/K_s$
S_s	Substrate concentration at biofilm outer surface (MsL^{-3})
S_s^*	Dimensionless substrate concentration at biofilm outer surface, $S_s^* = S_s/K_s$
S_w	Substrate concentration at inner surface of the biofilm (MsL^{-3})
S_w^*	Dimensionless substrate concentration at substratum surface, $S_w^* = S_w/K_s$
v	Superficial flow velocity or hydraulic loading rate ($L\ T^{-1}$)
V	Volume of a biofilm reactor (L^3)
x	Longitudinal distance along packed-bed biofilm column (L)
X*	Dimensionless empty bed contact time
$X_{critical}^*$	Critical dimensionless empty bed contact time
X_f	Biofilm density (MxL^{-3})
Y	Biomass yield coefficient, Mx/Ms

Greek Letters

τ	Shear stress (NL^2), in Chapter 2
τ	Factor for dimensionless transformation, $\tau = (K_s D_f/kX_f)\,1/2$ (L), in Chapter 8
ε	Porosity of packed bed
α	Biofilm surface area in each unit volume of biofilm column (L^{-1})
μ_g	Specific growth rate (T^{-1})

CHAPTER 1: INTRODUCTION

1.1 PROBLEM STATEMENT

Biological filtration of drinking water is currently receiving increased attention as a result of more stringent water quality regulations and the wider use of ozone in drinking water treatment. Biological filtration is an effective strategy for reducing the amount of biodegradable organic matter (BOM) that can cause bacterial regrowth in the distribution system and contribute to disinfectant by-products following final disinfection. In North America, biological filtration is likely to occur along with particle removal in a single-stage filtration step.

BOM can be removed by biofilms attached to media in drinking water biofilters. Several factors may significantly influence the BOM removal performance in biofilters, and a number of significant interactions may exist among these factors (e.g. Urfer *et al.*, 1997). These factors include: presence/absence of non-biological particles in the influent, presence/absence of coagulant, presence/absence of chlorine in the backwash water, presence/absence of air scour during backwashing, anthracite/sand media vs. granular activated carbon (GAC)/sand media, and low/high temperature operation. In previous studies, these factors and their interactions have either not been well documented or not systematically investigated. In particular, literature addressing BOM removal performance at low temperatures is very limited. The effects of non-biological particles and coagulant can be used to evaluate the performance of single-stage and second-stage biofilters. The effects of chlorine in the backwash water and air scour during

backwashing can be used to assess the influence of backwash strategies. The effects of an occasional upset or perturbation of a biological filter (BOM steps, hydraulic loading steps and filter shutdown) on the performance of the biofilter can also provide some insight into biofilter operation control.

The estimated amount of biomass (as biofilm) present in a biological filter is a core concept in drinking water biofilter models (Zhang and Huck, 1996a; Wang *et al.*, 1995; Hozalski, 1996). Traditional biomass measurements are typically very time consuming (i.e. phospholipid or adenosine triphosphate (ATP) methods). Developing a simple alternative approach for biomass estimation is of practical use for water utilities.

The biomass respiration potential (BRP) concept for drinking water biofilters was originally proposed by Urfer (1998). The BRP test is based on the consumption of dissolved oxygen (DO) resulting from aerobic respiration of given BOM components in a water sample containing a given amount of biofilter media. Theoretically, it can be expected that a good relationship between biomass and BRP exists. BRP can be evaluated for use as a surrogate for biomass as measured by phospholipid or ATP.

Biofiltration kinetic parameter estimation is a difficult component of biofilm-based biofilter modeling. Previous researchers have either depended solely on experiments not specifically designed for parameter estimation (Zhang and Huck, 1996a), or on special experiments in which the conditions of real drinking water biofilters may not be well simulated (Hozalski, 1996; Hozalski and Bouwer, 1998). Establishing a simpler and more accurate method for the estimation of key kinetic parameters is helpful for the application of biofilm-based drinking water biofilter models.

Several drinking water biofilter models have been proposed to provide a framework for the interpretation and generalization of results, and to provide kinetic descriptions for the design and operation of drinking water biofilters (Billen *et al.*, 1992; Huck *et al.*, 1994; Wang and Summers, 1995; Zhang and Huck, 1996a; and Hozalski, 1996).

Rittmann and McCarty's steady-state biofilm model (Rittmann and McCarty, 1980) has been widely used to describe substrate removals in biofilm processes. Three types of solutions to this steady-state biofilm model have been developed: the analytical solution which assumes first order kinetics, the semi-empirical solution from Suidan and Wang (1985), and the pseudo-analytical solution from Sáez and Rittmann (1992). Zhang and Huck (1996a) applied the pseudo-analytical solution from Sáez and Rittmann (1992) to the plug flow biofilter model to describe assimilable organic carbon (AOC) removal in biofilters. The implementation and evaluation of the other two types of solutions to this steady-state biofilm model have not been addressed to date.

Rittmann and McCarty (1980) introduced the concept of S_{min} (minimum substrate concentration to support a monolayer biofilm). Except for some work by Zhang (1996) and Zhang and Huck (1996a), the revision of S_{min}, and the potential application of S_{min} in drinking water biofilters have not been discussed in current literature.

Zhang (1996) and Zhang and Huck (1996a) proposed the X* concept (biofilter dimensionless contact time). The X*, as a function of substrate and operating parameters, is helpful for interpreting the results from different investigators and allowing for prediction of removals under conditions which have not been tested. Therefore, it is necessary to develop a series of generalized curves (percent removal vs. X* in terms of different substrates) to provide such quantification.

This investigation examines a number of key factors affecting biofiltration, particularly at low temperature, evaluates an alternative approach for measuring biomass, and provides additional kinetic modeling development.

1.2 RESEARCH OBJECTIVES

The main objective of this research was to investigate key factors affecting the BOM removal performance of drinking water biofilters using laboratory experimentation and

computer modeling. Other investigations were conducted regarding the BRP method as a surrogate for phospholipid biomass, and bio-kinetic parameter estimation.

Specific objectives of this research are listed below:

- to investigate factors affecting drinking water biofiltration by using a fractional factorial design approach in order to describe the effects of factors and interactions quantitatively;
- to conduct further experimental investigation based on the initial results of a fractional factorial design experiment;
- to develop a multiple linear regression model for the prediction of BOM removal;
- to evaluate the BRP method as a surrogate for phospholipid biomass;
- to find a suitable experimental approach for the estimation of bio-kinetic parameters;
- to develop and evaluate steady-state biofilter models using three different solutions to the steady-state biofilm model;
- to propose a revised definition of S_{min} and explore further applications of the X^* concept.

1.3 ORGANIZATION OF THESIS

Chapter 2 presents a literature review regarding the relevant background information to this research. A detailed description of the overall experimental design and the analytical methods is then provided in Chapter 3. The specific experimental procedures and the analytical methods in a given chapter are described in the "Materials and Methods" section of the relevant chapter.

Fractional factorial design experimental results are discussed in Chapter 4. Further investigation of the significant factors and interactions determined are presented in Chapter 4, and additional experiments are described in Chapter 5. The investigation of BRP as a surrogate for phospholipid is presented in Chapter 6. Chapter 7 explores an experimental approach for biokinetic parameter estimation. The estimated parameters in

Chapter 7 were used in the modeling of BOM removal in Chapter 8, and other modeling issues such as S_{min} and X^* are also discussed in Chapter 8. The final chapter addresses the overall conclusions and recommendations for future research, as well as the potential industrial application of this research.

CHAPTER 2 BACKGROUND

This chapter presents background information relevant to this research. First, a general discussion of the principles and applications of drinking water biofiltration is presented. Then, the factors affecting drinking water biofiltration are evaluated, followed by a review of the conventional performance of biological filters, and currently available biomass estimation techniques for drinking water biofilters. Finally, this chapter concludes with a review of current approaches for modeling the removal of BOM (biodegradable organic matter) in biological filters.

2.1 PRINCIPLES AND APPLICATIONS OF DRINKING WATER BIOFILTRATION

2.1.1 Characteristics of BOM in Drinking Water

BOM, as a very general definition, cannot be measured by a standard method such as BOD_5 or COD. Although some parameters, such as assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC), are useful surrogates for BOM, each suffers from limitations (Huck, 1990; Kaplan *et al.*, 1994; Woolschlager and Rittmann, 1995). For this reason, attention is currently focusing on quantifying the major components of BOM such as humic substances, amino acids, carbohydrates, and where appropriate, ozonation by-products.

BOM components and concentrations may change during conventional water treatment processes. In raw water, the BOM mainly consists of NOM (natural organic matter) including humic acid, amino acids, carbohydrates etc. (Camper 1998). Coagulation/flocculation and sedimentation may reduce BOM to a certain extent, depending upon the source water characteristics and unit processes adopted (Weber and Jodella, 1985; Krasner *et al.*, 1996). After chlorination, BOM may experience some insignificant changes, with a slight increase in the AOC concentration (Van der Kooij, 1987).

However, since the adoption of alternative disinfection methods (other than chlorine), one common observation made with respect to BOM is related to the use of ozonation in the treatment scheme. It has been found that ozonation can enhance the biodegradability of organic matter, because it is thought that ozonation breaks down some of the refractory organics into easily degradable organics (Brunet *et al.*, 1983; Langlais *et al.*, 1991). Ozonation of aromatic compounds in humic substances results in ring cleavage and produces lower molecular weight hydroxyl, carbonyl, and carboxylic acids that are more easily degradable (Gilbert, 1983; Amy *et al.*, 1992; Goel *et al.*, 1995). Thus, as a result of the increase in BOM upon ozonation, biological activity in filters following ozonation is considerably enhanced (DeWaters and DiGiano, 1990).

Currently identified major organic ozonation by-products include carboxylic acids, aldehydes and aldo/keto acids (Xie and Reckhow, 1992; Andrews, 1993; Glaze and Weinberg, 1993; Andrews and Huck, 1994; Najm and Krasner, 1995; Weinberg and Glaze, 1997), which are all relatively easily biodegraded. Good removals, i.e. >75%, are normally observed in pilot or full-scale biofilters (Krasner *et al.*, 1993; Swertfeger *et al.*, 1993; Coffey *et al.*, 1996; Wang and Summers, 1996; Coffey *et al.*, 1999).

Coagulation/flocculation, sedimentation, and filtration processes can be effective for the treatment of humic substances, but may not be effective at removing the smaller, more biodegradable compounds, which are less likely to coagulate and settle (Sinsasbaugh *et al.*, 1986; Amy *et al.*, 1992). Thus, it is suggested that biofiltration should be used to remove ozonation by-products in drinking water treatment (Krasner *et al.* 1993; Urfer *et*

al., 1997). It should be noted that humic substances, which are largely non-biodegradable or only slowly biodegradable, were found to be bound to the biofilm matrix within biofilters. Thus, humic substances are also available for growth (Camper, 1998).

2.1.2 Biofilm Processes in Drinking Water Biofilters

General Concept and Principles of Biofilms

The key to any biological treatment process is the accumulation of a sufficiently large population of microorganisms (biomass immobilization) which can bring about the desired biodegradation of BOM. Biomass immobilization can be realized either by suspended biomass (i.e. acitvated sludge system) or by attached biomass (biofilm process). Biofilm processes are advantageous and are usually required when the concentration of growth substrates is low. Drinking water, with a very low concentration of BOM, is clearly one of these cases (Rittmann and Huck, 1989). Most of the biological processes in slow sand filtration, rapid sand filtration and biologically active granular activated carbon, are biofilm processes (Rittmann and Huck, 1989).

Figure 2-1 illustrates a conceptual representation of a biofilm. The configuration of a conceptual biofilm is homogenous with respect to biofilm components and bioactivity.

Biofilm formation is the net result of a number of processes including adsorption, desorption, attachment, detachment, microbial growth and endogenous decay (Characklis, 1990). Attachment is usually considered to be important during the initial development period and negligible during the dynamic steady-state period.

Biofilms are generally considered to be composed of two major components: microbial cells and EPS (extracellular polysaccharide material). The microbial species and their morphology, as well as the EPS composition largely determine the physical properties of the biofilm. Thus, the biofilm can be considered as an organic polymer gel with living microorganisms trapped within it.

Substrate (nutrients) to be used by the microorganisms within the biofilm must be transported by diffusion across the stagnant liquid layer into the biofilm matrix, since the only source of substrate is in the bulk liquid. Substrate utilization by the biofilm creates a substrate concentration gradient in the biofilm and a driving force for nutrient diffusion into the biofilm. BOM removal in biofilters is an aerobic bioreaction process. Dissolved oxygen diffusion and consumption take place simultaneously with BOM diffusion and degradation in biofilms.

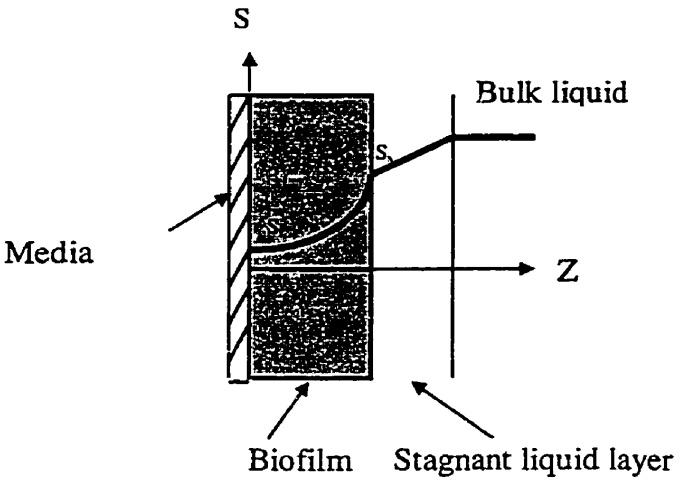

Figure 2-1: Conceptual biofilm configuration for biofilm model

(after Rittmann and McCarty, 1980)

In biologically active filters, biodegradable electron donor substrates are oxidized through redox reactions catalyzed by bacterial enzymes. Dissolved oxygen usually serves as the electronic acceptor for the biological oxidation of substrate in biofilters. The most relevant electron donor substrates in drinking water are BOM, NH_4^+, Fe^{2+}, Mn^{2+}, NO_2^-, dissoved H_2 and several reduced species of sulphur (Rittmann and Huck, 1989). Different bacteria are required for these electronic donor substrates. BOM degradation uses BOM

as both a carbon source and electron donor. In drinking water biofilters, the dissolved oxygen concentration is often 1 to 2 orders of magnitude higher than BOM. Therefore, oxygen is not normally the bioreaction rate limiting factor in drinking water biofilters.

Biofilm Configurations in Drinking Water Biofilters

Biofilms in drinking water biofilters are usually discontinuous or patchy (Langlais *et al.*, 1991; Lu and Huck, 1993). This can also be verified by preliminary estimation using available results of measured biomass in biofilters. For biofilters with non-biological particles in the influent, the biofilm configuration can be assumed to be of different forms. Ahmad and Amirtharajah (1998) represented an overlapping configuration (non-biological particles overlap biomass). There may be other assumptions: a homogenous mixture of biomass and non-biological particles or a configuration of biomass and non-biological particles distributed separately. The real biofilm morphology may be a combination of these two configurations.

Biofilm processes in drinking water biofilters can usually be divided into two stages: an initial biomass development period and a dynamic steady-state period, as shown in Figure 2.2.

During the initial biofilm development period, attachment may play an important role in the bacterial colonization of granular filters. The net results of attachment, growth, decay and detachment makes the biomass (biofilm) increase steadily in a more proportional way, depending on the operating conditions in biofilters (Hozalski, 1996).

In a pilot scale investigation, Servais *et al.* (1994) observed a nearly linear increase of biomass versus time, until an apparent steady-state was achieved after approximately three months. A possible reason for this is that the GAC adsorption in the early stage might enhance the biofilm formation, and then mitigate the biofilm formation rate in the later stage.

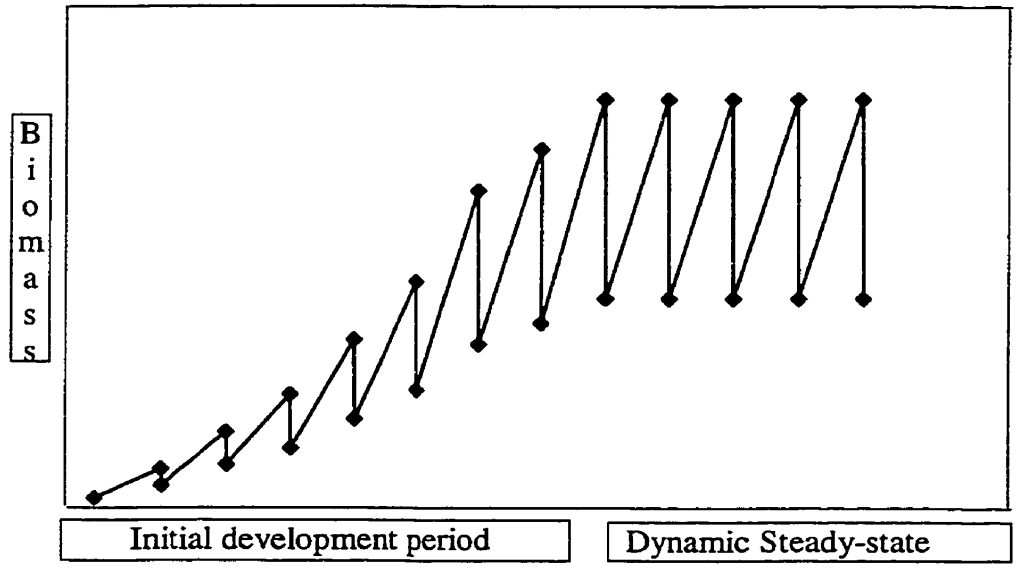

Figure 2.2: Conceptual biofilm processes in biofilters

During the dynamic steady-state period, biomass may be expected to change within a filter run (as shown in Figure 2.2). However, there are no changes with respect to different filter runs, assuming the influent of the filter is constant.

After backwashing, biomass was observed to be substantially reduced in a number of previous studies (Coffey *et al.*, 1995; Wang *et al.*, 1995 Ahmad and Amirtharajah, 1998). Servais *et al.* (1991) observed no major changes in biomass during backwashing, followed by an increase in biomass (replenishment) during the following filter run. This trend is illustrated in the sawtooth pattern in Figure 2.2. The biomass loss during backwash and the sawtooth pattern of biomass is not well documented to date. For second stage biofilters (GAC filters after sand or anthracite filters), backwashing is much less frequent because there is virtually no particle removal. The impact of biomass on BOM removal in biofilters will be reviewed later in this Chapter.

Microorganisms in Biofilms of Biological Filters

The low concentrations and multiple components of BOM in drinking water favour the growth of oligotrophic, heterotrophic bacteria known as oligotrophs. Oligotrophs are characterised as being able to survive and metabolically function when their substrate concentration is very low (Atlas and Bartha, 2000). If there are substantially high levels of ammonia in the source water, autotrophic bacteria (nitrifiers) may be the dominant bacteria. Bacteria are the dominant microorganisms in the microbial ecosystems of drinking water filters. However, different studies have shown that higher organisms, e.g., heterotrophic protozoans (Servais *et al.*, 1991) and annelids (Beaudet *et al.*, 1996) are present in biofilters. Kelley *et al.*, (1997) have discussed the significance of fungi and their potential importance in the production of off-tastes in distribution systems. Based on the results of that study, it can be expected that fungi are present in biological rapid filters. LeChevallier (1990a) has cited several studies which report the presence of fungi in GAC filters. Although the existence of the other microorganisms is probable, the metabolic activities of bacteria are principally responsible for the utilization of BOM in biofilters.

Based on several literature sources of biomass levels in biofilters reported as phospholipid, Urfer (1998) provided an estimation of the number of bacteria in the top part of filters. The biomass ranged between 10^9 to 10^{10} cells per cm^3 filter media, using conversion factors from Findlay *et al.*, (1989). These numbers are about an order of magnitude higher than those reported by Servais *et al.*, (1991) using different methods. The typical cell concentration in the bulk liquid of biofilters were reported in the range of 10^4 to 10^5 per mL (Servais *et al.*, 1991; Lu and Huck, 1993). Norton and LeChevallier (1999) indicated that suspended bacteria have little impact on biofilms. Thus, it is not unexpected that the number of cells in biofilms are much higher than that in the bulk liquid in biofilters.

Both Gram-negative and Gram-positive bacteria exist in biofilms of biofilters. However gram-negative bacteria appear to dominate (Eighmy *et al.*, 1993; Norton and

LeChevallier, 1996; Moll *et al.*, 1998). This is in agreement with results in natural water systems (Atlas and Bartha, 2000). Norton and LeChevallier (1999) found that prechlorination with free chlorine resulted in a dramatic shift in the composition of the bacterial population to predominately Gram-positive bacteria. Moll *et al.* (1998) observed changes in drinking water biofilter communities when different pre-treatment processes were used. Those researchers also found that biofilter microbial communities were differentiated as a function of filter depth, particularly for filters treating ozonated water.

The presence of pathogenic organisms in well developed biofilters is unlikely because pathogens are generally unable to compete with these fast-growing bacteria (Camper *et al.*, 1985; Bouwer and Crowe, 1988; Camper *et al.*, 1999). However, several investigations have shown the presence of coliforms in GAC filters (LeChevallier, 1990a,b) and other such bacteria may be able to colonize virgin GAC filters. Therefore, the start-up procedure of such filters is important (Camper *et al.*, 1985, 1999), in addition to secondary disinfection with chlorine or chloramines prior to the distribution system.

Several studies have investigated and modeled the interactions of heterotrophs and autotrophs (i.e. nitrifying bacteria) in biofilms (Kissel *et al.*, 1984; Wanner and Gujer, 1986; Rittmann and Manem, 1992). These studies generally predict that the distribution of heterotrophs and autotrophs, in the biofilm mainly depends on the BOM and ammonia concentrations. However, operation of biofilters (e.g., backwashing) can also affect their distribution (Morgenroth and Wilderer, 1999).

2.1.3 Applications of biofiltration in drinking water treatment

Biological treatment of drinking water has been used since the nineteenth century, when water utilities in the UK, Germany and elsewhere in Western Europe started to use slow sand filtration (SSF) and bank filtration for the treatment of surface water (Sontheimer, 1980; Huck, 1988; Cleasby, 1999). Although the SSF process was mainly used to remove pathogenic microorganisms and particles at that time, biological degradation of BOM also occurred in these filters. If rapid filters and/or GAC contactors are incorporated in

the process, these are nowadays often installed following ozonation (Huck, 1988). However, for many North American water utilities considering the biological retrofit of existing plants, or the construction of new biological filters, the most economical and attractive approach to implementing a biological process in drinking water treatment is to combine microbial activity with an existing physicochemical unit operation, rather than adding a completely separate biological filter. Thus, the objectives of both non-biological particle removal and BOM removal must be achieved in the same filter, referred to here as single stage biofiltration.

The initial efforts of biological drinking water treatment (e.g., Sontheimer *et al.*, 1978) focused in particular on the biological removal of ammonia, as a replacement for the traditionally performed breakpoint dechlorination (Huck, 1988). As a result of more stringent DBP (disinfection by-product) regulations and bacterial regrowth concerns, the DBP precursor removal is receiving increased attention. The biological removal of BOM to produce biologically stable water is an economical and attractive approach that has been investigated and practiced for at least two decades (e.g. Bouwer and Crowe, 1988; Huck *et al.*, 1991; LeChevallier *et al.*, 1992; Coffey *et al.*, 1995; Urfer *et al.*, 1998).

The present research and application focuses on the removal of BOM as it represents the biodegradable substrate of relevance in North America (Huck, 1988). In other applications, biological processes have been successfully used for the removal of iron and manganese (Mouchet, 1992; Schulz *et al*, 1999). More applications, such as the removal of taste and odor compounds and haloacids in biofilters, have been reported recently (Rittamann, 1995c; Singer *et al.*, 1999).

2.2 FACTORS AFFECTING DRINKING WATER BIOFILTRATION

Factors that may influence BOM removal performance in biofilters include: non-biological particles in the influent (single stage or second stage biofilters), backwash strategies (chlorine in the backwash water, air scour during backwashing), filter media,

and temperature. Significant interactions may exist among these factors and the possible significant interactions have not been well studied and documented.

2.2.1 Impact of non-biological particles in the filter influent

Although biofilteres operated as single or second stage have been studied during the last two decades, the variations in influent and media type make it difficulty to determine the influence of non-biological particle removal on biofilter BOM removal performance. Several investigations at pilot scale (LeChevallier *et al.*, 1992; Krasner *et al.*, 1993; Gloldgrabe *et al.*, 1993), laboratory scale (Ahmad and Amirtharajah, 1998) and full scale (Coffey *et al.*, 1995; 1996) have found that biological filters provided good removals of turbidity and BOM. This also indirectly indicates that particle removal does not impede the BOM removal in biofilters. Literature directly evaluating the impact of non-biological particle removal on biofilter BOM removal performance is limited.

2.2.2 Impact of Filter Media

The selection of filter media is a critical question when implementing biological filtration because of its major cost implications (Urfer *et al.*, 1997) and its BOM removal efficiency. Obviously, if there is no major difference in BOM removal between GAC and anthracite filters, it is not necessary to replace the existing filter media (sand or anthracite/sand) with GAC in order to successfully operate biofiltration in North America.

Due to a much larger surface area in GAC media (mainly from micropores with a small diameter ranging from 1 to 100 nm) compared to anthracite or sand media, GAC media adsorptive capacity is much higher than anthracite and sand media. However, the specific surface area (unit surface per unit volume of filter) available for biomass attachment is likely similar in magnitude in a sand or anthracite filter compared to a GAC filter, because the bacteria (more than 200 nm in diameter) can not penetrate the micropores of GAC (1-100 nm in diameter) (AWWA Committee Report, 1981; Rice and Robson, 1982).

Several investigations have compared adsorptive media (GAC) and non-adsorptive media (anthracite and sand) for biological BOM removal in parallel (e.g. LeChevallier *et al.*, 1992; Krasner *et al.*, 1993; Coffey *et al.*, 1995b; Wang *et al.*, 1995; Prévost *et al.*, 1995; Coffey *et al.*, 1996). It is expected that the BOM removal performance in GAC and anthracite/sand filters should be similar. However, the irregular (macroporous) surface of GAC offers more suitable bacterial attachment sites and may provide more protection from shear stress than that of anthracite or sand. In addition, the adsorption process occurring on GAC can provide a longer retention time in filters for slowly biodegradable components, and remove potentially inhibitory chemicals (Nayar and Sylvester, 1979; AWWA Committee Report, 1981; Li and DiGiano, 1983; Chang and Rittmann, 1987). Therefore, generally better BOM removal (especially for slowly biodegradable BOM) in GAC filters can be expected.

Urfer *et al.* (1997) reviewed different studies and concluded that anthracite/sand and GAC/sand filters provide similar average BOM removals. However, it is not unexpected that GAC/sand filters appear to provide better aldehyde removals at colder temperatures, and establish a BOM-removing biofilm more rapidly (Krasner *et al.*, 1993, Coffey *et al.*, 1995b). Also, GAC/sand filters provide increased protection against oxidant residuals in the filter influent (Rice and Robson, 1982; DiGiano *et al.*, 1992; Urfer, 1998), due to the reaction between GAC and oxidants. The biological capacity in GAC filters was more resistant to temporary perturbations and reductions in this capacity (Krasner *et al.*, 1993). GAC/sand often showed better DOC and total organic carbon (TOC) removals compared to anthracite/sand (Coffey *et al.*, 1995) and this might be due to adsorption processes. For biological ammonia removal (nitrification), Bablon *et al.* (1988) showed that GAC/sand outperformed sand, particularly at low water temperatures. Minor differences have generally been reported between wood-based GAC and coal-based GACs (Krasner *et al.*, 1993) and among microporous, mesoporous and macroporous GACs (Wang *et al.*, 1995).

In conclusion, biological rapid filtration can often be successfully implemented in anthracite/sand filters even though there are several advantages of GAC over anthracite.

To a certain extent, the above observations derived from various studies are dependent on the initial GAC state (exhausted or not), BOM components and concentrations in the influent, chemicals of potential inhibitory effect in the influent, operation period of the filters, EBCT and backwash strategies. One should be cautious when making general conclusions regarding biofilter capabilities, and operating conditions should always be considered.

In general, optimized filter media selection for biofilters depends upon numerous site specific characteristics such as water quality (i.e., BOM composition, chemicals of potential inhibitory effect in the influent, water temperature), specific operational issues of the plant (such as EBCT, backwashing strategies), and the treatment target for different BOM components (especially the treatment target of the slowly biodegradable BOM). Therefore, for a given biofiltration application, the choice of the ideal filter media configuration should incorporate the key design parameters EBCT, backwash strategies, influent water quality and the treatment target for various BOM components. A careful evaluation of the situation, and potential pilot-scale investigations, are therefore required.

2.2.3 Impact of Contact Time and Biodegradability of BOM

A number of researchers have demonstrated the important influence of empty bed contact time (EBCT) in biological rapid filters on BOM removal (e.g. Servais *et al.*, 1989; DeWaters and DiGiano, 1990; Huck *et al.*, 1994; Wang and Summers, 1995, 1996; Zhang and Huck, 1996a, Carlson and Amy, 1998). EBCT, which is hydraulic loading rate and media depth dependent, is a key design and operating variable. Different studies have demonstrated that, for a given EBCT, the removal of BOM is generally independent of hydraulic loading, in the range typically used in rapid filters or GAC contactors (Servais *et al.*, 1994; Wang and Summer, 1996; Carlson and Amy, 1998). This suggests that biomass that develops under different hydraulic loadings matches the BOM removal in biofilters (more biomass needs to be developed to remove more BOM flux at the same depth with higher hydraulic loadings).

In developing the steady-state biofilter model, Zhang (1996) and Zhang and Huck (1996a) proposed a dimensionless contact time, X^* ($EBCT^*$). X^* incorporates the biofilter contact time and surface area of the media, as well as the substrate diffusivity and biodegradation kinetic parameters. Those authors have shown that the percent removal of AOC increases with increasing X^*, but in a less than proportional way. The incremental benefit of using very long contact times is therefore small, which has been previously observed experimentally (LeChevallier *et al.*, 1992; Carlson and Amy, 1998).

However, Servais *et al.* (1992) have observed an essentially linear increase in BDOC removal with increasing EBCT between 10 and 30 minutes. Others have observed that the removal of BOM (as ozonated by-products) is independent of EBCT in the range of 4 to 20 minutes (Price *et al.*, 1993, 1994; Hozalski *et al.*, 1995). These results seem to be in conflict with the aforementioned studies; however, a good explanation can be given by using the proposed $X^*_{critical}$ (beyond $X^*_{critical}$, further removal achieves little improvement) or filter bed utilization (the ratio of bed depth exhibiting substantial BOM removal to the entire bed depth). Ozonation by-products are the main components of BOM in the biofilter influents of those studies, leading to a lower ratio of $X^*_{critical}/X^*$ (or bed utilization). After $X^*_{critical}$, no observable BOM can be achieved.

The EBCT required to remove the target BOM components in biological filters can vary over a substantial range (2 – 30 minutes), primarily depending on the biodegradability of the target BOM components. In general, longer contact times are required for the removal of TOC, BDOC and relatively slowly biodegradable BOM components, compared to the rapidly biodegradable portion of ozonation by-products and biological instability (as measured by AOC). A relatively good removal of ozonation by-products at EBCTs as short as 2-4 minutes has been reported (e.g., Urfer, 1998), while the removal of BDOC, chlorine demand and chlorination by-product precursors require considerably longer EBCTs. In general, full-scale biological rapid filters are designed for EBCTs below 30 minutes.

In general, the impact of EBCT or X* is affected by the biodegradability of BOM components. Therefore, one should be cautious while making conclusions about these impacts. Factor interactions also exist among influent BOM biodegradability, media and EBCT. When evaluating BOM removal in biofilters, these interactions should also be considered in these types of comparative evaluations.

2.2.4 Impact of Backwashing

The goal of backwashing biofilters is to remove biomass and non-biological particles, to restore headloss capacity, and to permit desired run times, while retaining a suitable amount of biomass to maintain a relatively stable BOM removal. The difference in the detachment of these groups of particles during backwashing, and the frequency of backwashing, will influence the optimization of backwashing strategies for biofilters as a particle collector and a biological reactor.

Drinking water biofilters are a type of submerged biofilm reactor. It is generally necessary to remove non-active biofilm and/or detached biofilm, in order to maintain a good bioactivity of the biomass in the biofilters, and prevent the media bed from clogging. Different investigations have emphasized the importance of backwashing on the long term performance of biological drinking water filters (Camper *et al.*, 1987; Graese *et al.*, 1987; Bouwer and Crowe, 1988; Bablon *et al.*, 1988; Servais *et al.*, 1991; Goldgrabe *et al.*, 1993; Coffey *et al.*, 1995b; Miltner *et al.*, 1995; Miltner *et al.*, 1996; Ahmad *et al.*, 1998; Ahmad and Aminharajah, 1998). While certain treatment plants use non-chlorinated backwash water for their biological filters, others (particularly retrofitted plants) are operated with chlorinated or chloraminated backwash water.

Backwashing with water alone is an inherently ineffective process for the removal of particles in non-biological filters, because of the limited collisions and abrasions among fluidized particles (Amirtharajah, 1978). Further studies have shown that the best removal of particles in non-biological filters during backwashing is obtained by the simultaneous use of air and water, at subfluidization velocities, to achieve collapse

pulsing conditions (Amirtharajah *et al.* 1991; Amirtharajah, 1993). Several authors have directly or indirectly shown that backwashing with air scour (collapse pulsing conditions) was necessary to control long term headloss increases in biological filters (Goldgrabe *et al.*, 1993; Ahmad and Amirtharajah, 1998).

Based on the measurement of the potential for bacterial activity under standard conditions, Servais *et al.* (1991) observed no substantial losses of biomass activities (as measured by the production of $^{14}CO_2$) before and after backwash. Moreover, despite the application of air scour, backwashing does not break the vertical stratification of the biomass. Huck *et al.* (1998) observed that the biomass at the top surface of filter media, in a full-scale plant, was not significantly decreased by backwashing for a GAC/sand filter or anthracite/sand filter. Miltner *et al.*, (1995) found a 15-25 percent biomass loss during backwash in most cases (measured by phospholipids). Others have found a more significant biomass loss of 50-60 percent in a pilot–scale experiment, when backwashing with air scour (Lu and Huck, 1993). In a bench scale experiment, Hozalski and Bouwer (1998) observed 20-40 percent removal during 10-min backwash without air scour.

In regards to the BOM removal before and after backwashing with non-chlorinated water, the available literature indicates that no major changes were observed (Miltner *et al.*, 1995; Carlson *et al.*, 1998; Coffey *et al.*, 1996; Hozalski and Bouwer, 1998). In fact, several studies have shown that the BOM removal was slightly enhanced immediately following backwashing (Prévost *et al.*, 1995; Carlson *et al.*, 1996a; Coffey *et al.*, 1996). Prévost suggested that backwashing was beneficial to the efficiency of biological filtration. The author proposed three hypotheses for the observed increase in BOM removal due to backwash: (1) effect of aluminium flocs on the activity of bacteria; (2) shorter actual contact time because of the non-biological particle accumulation; and, (3) increased diffusion resistance of BOM, nutrients and oxygen to biofilm.

With regard to the influence of chlorinated backwash water on BOM removal within a biological filter, there are conflicting results. Miltner *et al.* (1995; 1996) observed a relatively strong negative effect of free and combined Cl_2 (~1-2 mg/L) in the backwash

water of anthracite/sand filters on the removal of BOM. Particularly the less easily biodegradable fraction of BOM was affected. However, Huck *et al.* (1998) noted essentially no effect on BOM removal in the presence of free and combined Cl_2 in the backwash water of demonstration scale anthracite/sand and GAC/sand filters, after long term operation. Others also observed relatively good removals in anthracite/sand (Hacker *et al.*, 1994) and GAC/sand filters (Rechhow *et al.*, 1992), despite backwashing with chlorinated water. In another pilot study, Miltner *et al.* (1996) demonstrated the effect of the types of chlorine (free chlorine or combined chlorine) in the backwash water on BOM removal. Free chlorine (~1.6 mg/L) showed a stronger inhibition of the removal of several BOM components and surrogates compared to combined chlorine (2 mg/L).

These conflicting results may be caused by: (1) the media effect (GAC can mitigate chlorine effects); (2) the types of chlorine (free chlorine is a much stronger disinfectant than combined chlorine); (3) the acclimation effect (biofilm can develop chlorine resistance after a longer term operation); and, (4) the biofilter media bed utilization (the less easily biodegradable fraction of BOM is more sensitive to the biomass changes caused by backwash because of the higher media bed utilization for removal of that fraction).

BOM removal is not as sensitive to backwash events as might be expected, especially for non-refractory BOM components. More use of biofilms extending to greater depth in biofilters, and longer detention times after backwash, due to the detachment of non-biological and biological particles, may mitigate the effect of biomass loss caused by backwashing. It should be noted that the impact of backwashing is also affected by other factors due to the possible interactions between these factors.

2.2.5 Impact of temperature

Temperature is expected to be of importance in biofilter operation due to its effect on bacterial growth. Bacterial growth approximately doubles with every 10 °C increase in temperature (Atlas, 1997), and microbial nutritional requirements and activity vary

significantly with temperature (Madigan *et al.*, 2000). Therefore, it is expected that initial biofilm development and steady-state BOM removal may be enhanced at high temperatures. Literature regarding BOM removal performance at low temperatures is very limited (Moll *et al.*, 1999).

Coffey *et al.* (1995) observed that the time needed to reach steady-state removal of glyoxal was shorter at high temperatures than low temperatures, especially for A/S filters. The authors also demonstrated a difference in apparent steady-state glyoxal removal profiles at different temperatures (10 °C vs. 20-25 °C) in a GAC filter and A/S filter. The percent removal of glyoxal was increased from 76 to 87 percent in the GAC filter, and from 61 to 86 percent in the A/S filter at the higher temperature, when considering the glyoxal removal within the GAC or anthracite layers with an EBCT of 2.1 minutes. The temperature impacts were reduced, when considering the glyoxal removal within the entire GAC or anthracite filters with an EBCT of 4.7 minutes. Coffey *et al.* (1999) reported the temperature effects (3 °C vs. 25 °C) in a full-scale plant with ozonation. The oxalic acids removal was decreased from over 90 percent to non-detectable removal in an anthracite/sand filter, and to 50 percent in a GAC filter. Other authors also observed increased BOM removal at higher temperatures (Servais *et al.*, 1992; Prévost *et al.*, 1995).

Temperature has been shown to impact microbial community structure (Fonseca, *et al.*, 1999; Moll *et al.*, 1999). Higher temperatures favour the growth of Gram-positive bacteria and sulfate-reducing bacteria while Gram-negative and microeukaryotes preferred lower temperatures.

2.2.6 Impact of Biofilter Perturbation

Hydraulic or BOM concentration steps may affect BOM removal in biofilters, depending on whether the existing biofilm is capable of removing the altered BOM flux in the biofilter. Carlson *et al.* (1998) investigated the effect of hydraulic loading changes on the BOM removal of ozonated water in a pilot plant. The authors found that the same amount

of DOC was removed at the acclimation HLR and at a lower loading rate, but a much smaller amount was removed at a higher hydraulic loading rate. This suggests that the increased BOM flux surpassed the ability of the biomass to assimilate the available BOM.

Niquette *et al.* (1998) indicated that shutdown of biological filters promoted anaerobic conditions that reduced the density of fixed bacteria and the quality of water inside the filter. It was then suggested that the filter should be backwashed before being returned to normal operation. The results also suggested that BAC filters can withstand a shutdown of <24 h without impairing their capacity to remove DOC and ammonia. Huck *et al.* (1996) indicated that bringing pilot scale biological filters back on-line after a few days of being out of service can lead to the presence of elevated concentrations of endotoxins.

2.2.7 Interactions among Affecting Factors

It should be noted that interactions among effects of factors exist, while describing these effects qualitatively and/or quantitatively. $X^*_{critical}$ or bed utilization (mainly dependent on the biodegradability of BOM surrogates and EBCT) in this thesis may help to evaluate the impact of different factors from different studies, in the context of BOM removal in biofilters. One must be cautious while making conclusions about the impacts of affecting factors.

2.3 CONVENTIONAL PERFORMANCE OF BIOLOGICAL FILTERS

2.3.1 Turbidity and Particle Removal

Several investigations have generally indicated that biological filters provided similar removals of turbidity to conventional filters and reliably met current drinking water guidelines (LeChevallier *et al.*, 1992; Goldgrabe *et al.*, 1993; Krasner *et al.*, 1993; Coffey

et al, 1995; 1996; Amad and Amirtharajah, 1998; Zensius *et al.* 1998; Booth *et al.*, 1999). Goldgrabe *et al.* (1993) observed no measurable difference in effluent turbidities between non-biological (pre-chlorinated and backwash-chlorinated) and biological anthracite/sand filters in a pilot study. However, the non-biological filter consistently outperformed the biological filter in all particle size ranges examined (1-150 μm), yielding a 0.4-0.5 log better total particle removal. The researchers attributed the better performance of the conventional filter to either improved particle destabilization by pre-chlorination or no biological particle detachment in the conventional filers. Other pilot scale studies showed no difference in turbidity removal between biological GAC/sand and anthracite/sand filters with an average effluent turbidity of less than 0.2 NTU (LeChevallier *et al.*, 1992; Krasner *et al.*, 1993). In a bench scale study, the biofilter effluent at the end of a 48 hour filter run was always less than 0.4 NTU (Ahmad and Amirtharajah, 1998). At full-scale, biological filters produce an effluent tubidity below 0.1 NTU on average (Coffey *et al.*, 1995; 1996; Booth *et al.*, 1999).

2.3.2 Headloss Buildup in Biofilters

Biofilm development/accumulation over a period of operation may increase the clean bed headloss in biofilters due to clogging of media. Coffey *et al.* (1995) observed a major increase (~ 40%) in clean bed headloss in a biological GAC/sand filter backwashed without air-scour after a period of three months. Goldgrabe *et al.* (1993) found that the headloss build-up rate in a biological filter during a filter run was substantially faster than in two other non-biological filters, although the clean bed headloss was at the same level. After a 27 week acclimation period, about 102 and 86 hours were required to reach a terminal headloss of 60 inches in the non-biological filter and the biological filter, respectively. Ahmad and Amirtharajah (1998) indicated that air scour (collapse pulsing) backwashing can overcome the increase of headloss in successive filter runs experienced, when using water wash without air-scour.

2.4 BIOMASS ESTIMATION IN DRINKING WATER BIOFILTERS

The amount of biomass (as biofilm) present is a critical concept in drinking water biofilter models (Zhang (1996); Zhang and Huck, 1996a; Wang *et al.*, 1995; Hozalski, 1996). BOM removal performance can be evaluated in terms of biomass (biofilm) distribution in biofilters. The biomass distribution in the biofilters can be estimated from the biofilter modeling (Zhang (1996); Zhang and Huck, 1996a; Hozalski, 1996) or by the regression of the measured distribution (Wang *et al.*, 1995). However, it may be more robust to use the measured distribution in biofilter modeling. Thus, the techniques for biomass measurement in drinking water biofilters are of importance.

Several methods for the measurement of biomass in drinking water biofilters have been used, including the fairly common phospholipid method (Wang *et al.*, 1995, Miltner *et al.*, 1995; Coffey *et al.*, 1995; Carlson *et al.*, 1998; Urfer, 1998), the ^{14}C-glucose respiration method (Servais *et al.*, 1991; 1992), and the ATP method (Ahmad *et al.*, 1998). The application of those methods is not widely practiced due to their own limitations.

The phospholipid method (Findlay *et al.*, 1989) provides a measure of viable biomass and has been successfully applied to drinking water biofilters by researchers (Wang *et al.*, 1995, Miltner *et al.*, 1995; Coffey *et al.*, 1995; Carlson *et al*, 1998; Urfer, 1998). This test requires only standard laboratory equipment. However, the whole procedure is typically very time consuming and labour intensive. The phospholipid method measures the viable biomass, but it does not provide a measure of microbial activity (Findlay *et al.*, 1989).

The ^{14}C-glucose respiration method is based on the measurement of the production of $^{14}CO_2$ via the respiration of radio-labelled glucose, by the biomass in the media sample. This method provides a measurement of the organic substrate degradation potential (i. e., respiration) of the biomass, and has been used in drinking water biofilter evaluations (Servais *et al.*, 1991; 1992). Special laboratory equipment and security features are

required for this method, which may not be applicable in most water utilities. One drawback to this method is that free glucose (unbound) may not be a true representation of the BOM components present in drinking water influents. Acetate may be a more appropriate indicator than glucose, since it is a common organic ozonation product (Andrews and Huck, 1994; Gagnon *et al.*, 1997). The measurement of the metabolic activity of a microbial community by the incorporation of ^{14}C–acetate into cellular lipids has been used by White and colleagues (White *et al.*, 1977; Vestal and White, 1989). Wang (1995) has successfully applied the ^{14}C–acetate method for the analysis of the microbial activity of biomass in drinking water biofilters.

Adenosine triphosphate (ATP) is present in a relatively constant proportion in all living cells, and is typically not present in detritus or dead cells. The ATP method provides a measurement of cellular ATP of the sample biomass, and has been used for the measurement of biomass in drinking water biofilters (Ahmad *et al.*, 1998). In this method, cellular ATP is extracted before being subjected to a bioluminescent reaction. The ATP content is then determined by the luciferine-luciferase reaction with an ATP bioluminescent assay kit. The ATP method provides a measurement of the viable biomass. However, one of the drawbacks of this method is the requirement of special instruments.

These aforementioned methods for biomass measurementare typically very time consuming (i.e., the phospholipid method) or dependent on special instrumentation (the ATP method and the ^{14}C-glucose/acetate respiration method). Therefore, the development of a simple alternative approach for biomass estimation is of practical use for water utilities.

Respirometric techniques, such as the measurement of the rate of oxygen consumption, are commonly used for the estimation of microbial metabolism (Metcalf and Eddy, 1991; Atlas and Bartha, 2000). This approach has also been applied in the estimation of biodegradation kinetic parameters in activated sludge (Ellis *et al.*, 1996). The respiration of low substrate concentrations can be quantified, due to the high sensitivity of the DO

(dissolved oxygen) measurement. The high sensitivity of the DO measurement allows for the enhancement of these kinds of applications.

The biomass respiration potential concept for drinking water biofilters was originally proposed by Urfer (1998). The BRP test is based on the consumption of dissolved oxygen (DO) resulting from aerobic respiration of BOM in a water sample containing a given amount of biofilter media. Urfer (1998) used the BOM components he spiked to his laboratory biofilters. He found that the pseudo steady-state concentration profiles of substrate (as a function of filter depth) were similar to those of active biomass represented as BRP in a BRP investigation using about 1-8 g of media in 300 mL BOD-bottles, with a biodegradation time of 5 h. However, a linear relationship between phospholipid biomass and BRP was not observed in that study.

Moll *et al.* (1998) applied phospholipid fatty acid (PLFA) profiles, sole carbon source utilization profiles, and DNA fingerprinting to determine changes in drinking water biofilter communities when different treatment processes and /or operational changes were being used in the treatment plant. This approach might help the understanding of BOM removal mechanisms and kinetics under a variety of operating conditions.

2.5 MODELING BOM REMOVAL IN BIOFILTERS

BOM is removed in biofilters by biofilm type processes. Bacterial attachment on filter media (similar principles to particle removal) in biofilters plays an important part in the initial development of a biofilm. The BOM removal attributable to suspended bacteria has been assumed to be insignificant due to the low influent suspended cell concentrations and the short hydraulic residence time in the filter (Rittmann, 1982b). Biofilm is the key concept in biofilm-based drinking water biofilter models, and biofilm models play an important role in the simulation of BOM removal in biofilter models. BOM removal in biofilters can be modeled by the incorporation of a biofilm model into a bioreactor model. In drinking water biofilters with typical hydraulic loading rates, a plug-

flow bioreactor model can be used for the modeling of biofilters (Zhang and Huck, 1996a). The estimation of parameters used in biofilter models can impact the application of these models.

2.5.1 Bacterial Attachment and Non-biological Particle Removal

In the initial development period of biofilm in biofilters, bacterial attachment plays an important role in the accumulation of bacteria. A net accumulation of biomass will develop with respect to time until a dynamic steady-state biofilm is achieved. Both BOM and non-biological particle removal occurs in first stage biofilters.

The particle removal mechanisms of transport, attachment, and detachment are described using two different approaches: (1) phenomenological theories and (2) trajectory theories. The phenomenological approach to filtration has developed from attempts to describe changes in either concentration or mass of particles in the influent water:

$$C = C_0 e^{-\lambda z} \tag{2.1}$$

Where, λ is the filter coefficient. The principle of trajectory analysis is to view a granular bed as an assembly of collectors, and to determine the extent of particle deposition on the collectors, as the suspension flows past these collectors.

The removal of suspended particles by a one-dimensional clean-bed filter can be described by the following equation (Yao *et al.*, 1971):

$$N_e / N_i = e^{-[1.5(1-\varepsilon)\alpha\eta(L/d)]} \tag{2.2}$$

where, N_i is influent particle concentration; N_e is effluent particle concentration; L is the bed depth; d is media diameter; ε is porosity; η is single collector efficiency; and α denotes collision efficiency, or (number of collision producing attachment)/(total collisions). Single collector efficiency (η) and collision efficiency (α) are two important parameters that need to be estimated.

Rajagopalan and Tien (1976) utilized Happel's sphere-in-cell model and included the effects of hydrodynamic retardation, electrical double layer, and London-van der Waals forces to obtain the following empirical correlation for η:

$$\eta = A_s N_{Lo}^{1/8} N_R^{15/8} + .00338 A_s N_G^{1.2} N_R^{-0.4} + 4 A_s^{1/3} N_{Pe}^{15/8} \qquad (2.3)$$

Where, N_R is the ratio of suspended particle size to collector size and indicates the importance of interception; N_G reflects the gravity effects; N_{Lo} accounts for van der Waals interactions, and N_{Pe} expresses the role of diffusion. A_s denotes Happel's field factor. These parameters are given by: $N_R = a_p / a_s$; $N_G = 2a_p^2 (\rho_p - \rho) g / [9\mu U]$; $N_{Lo} = H/[9\pi\mu a_p^2 U]$; $N_{Pe} = 2Ua_s / D_{BM}$; $A_s = 2(1-p^5)/(2-3p+3p^5-2p^6)$, $p = (1-\varepsilon)^{1/3}$; D_{BM} (Brownian diffusion coefficient) $= kt/[6\pi\mu a_p]$. In these definitions, a_p and a_s are the radii of the suspended particles and the media grains, respectively, μ and ρ denote the viscosity and density of the water, U represents the approach velocity, g is the gravitational acceleration, ρ_p is the density of the suspended particles, and H is the Hamaker constant. Another important parameter in the clean-bed filtration model is the collision efficiency (α). This can be obtained from the literature or by specially designed experiments.

All of the models discussed above assume particle destabilization, such that there is no repulsive potential between particles and collectors. Experimental data have indicated that the actual collection efficiency, under a repulsive double layer, exhibits a gradual decline (Amirtharajah, 1988). These experimental data indicate the limitations of trajectory analysis, and also emphasize the need of adequate chemical pretreatment prior to filtration, to achieve maximum particle removal.

Non-biological particle removal in biofilters, and bacterial attachment on the media surface in biofilters, could be modeled approximately by the clean-bed filtration model which is based on the trajectory theories. Different investigations have been conducted to obtain the key parameters for the application of the above clean-bed filtration model to bacterial attachment on the media surface in biofilters (Harvey and Garabedian, 1991;

Martin *et al*, 1992; Hozalski, 1996). The clean-bed filtration model has been used to evaluate the biofilm accumulation in a biofilter during the initial developing period (Hozalski, 1996).

2.5.2 Biofilm Models

For a well-developed biofilm, substrate utilization and biofilm growth, decay and detachment in biofilters are the most important phenomena.

Substrate Diffusion-Biodegradation in Biofilms

The substrate flux from the bulk liquid, across the stagnant diffusion layer, and into the biofilm where the substrate is degraded, can be described by Fick's second law:

$$J = D(S\text{-}S_s)/L \tag{2.4}$$

Where, D = molecular diffusivity of the substrate in the liquid (L^2/T), S = concentration of substrate in the bulk liquid (M_s/L^3), S_s = substrate concentration at the biofilm surface (M_s/L^3), L = diffusion layer thickness (L).

In the biofilm, the processes of molecular diffusion and substrate utilization occur simultaneously and their rates are described by:

$$D_f \frac{d^2 S_f}{dz^2} = \frac{k S_f X_f}{K_s + S_f} \tag{2.5}$$

where, S_f = substrate concentration in the biofilm (M_s/L^3), D_f = molecular diffusivity in the biofilm (L^2/T), z = direction normal to the biofilm surface (L), k = maximum rate of substrate utilization ($M_s/(M_s T)$), X_f = bacteria density in the biofilm ($M_s s/L^3$), and K_s = Monod half -velocity coefficient (M_s/L^3).

Biomass detachment without backwashing

Biofilm processes are complicated, and the following main processes are included: bacterial attachment, substrate utilization and biofilm growth, decay and detachment. The biofilm (biomass) growth rate is proportional to the substrate flux into the biofilm by a microbial yield coefficient Y (M_x/M_s). Biofilm decay is proportional to the amount of biomass by a decay coefficient b having units of T^{-1}.

Biofilm detachment can be a complex process, and is important for the maintenance of a suitable amount of biofilm in a biofilter system. Detachment mechanisms include: (1) erosion, (2) abrasion, (3) sloughing and (4) grazing or predation (Rittmann, 1989). Erosion is the continuous removal of small particles of biofilm, which is the most common mechanism of detachment in biofilm processes (Peyton and Characklis, 1993). Although the rate coefficient of erosion is affected by many factors, the fluid shear is believed to be the most significant. Therefore, biofilm erosion is often called shear loss. Abrasion occurs when particles collide with the biofilm and scrape cells off the surface, such as during backwashing of bioreactors. Sloughing is the process by which relatively large sections of the biofilm are lost. Grazing or predation losses are due to the harvesting of the biofilm by larger organisms such as protozoa, worms, snails and insects. In full-scale biofilm reactors, detachment is due to a combination of different processes, and depends on the operation of the biofilter. It can be expected that erosion (during a filter run) and abrasion (during backwashing) are two important mechanisms of biofilm detachment in drinking water biofilters. Current understanding of detachment processes is limited due to their complexity.

A summary of reported biofilm detachment rate expressions is included in Table 2.1.

Most of the biofilm detachment models developed have been concentrated on erosion processes caused by shear stress (models 1 to 7 in Table 2.1). Constant biofilm thickness was assumed in those biofilm detachment models. Thus, they may not be applicable in predicting biomass removal by backwashing, because of the much more vigorous shear stress and abrasion in backwashing than during steady-state operation conditions.

Stewart (1993) developed a general mathematical framework for modeling biofilm detachment. The author introduced a conceptual model, such that biofilm detachment is equal to the product of a detachment frequency and a detachment particle mass. The author also confirms the complexity of modeling biofilm detachment processes in the paper.

Morgenroth and Wilderer (1999) proposed the concept of dynamic variations with a constant average thickness over time for biofilms in biofilters (model 8 in Table 2.1). The authors assumed that the biofilm detachment rate is negligible during operation, and is proportional to the increase in biofilm thickness in a filter run during backwashing.

In general, the biofilm detachment rate is a function of biofilm thickness, the biofilm growth rate and other physical factors which are dependent upon operational conditions, such as shear stress and intensity of abrasion. The influence of these physical factors on the biofilm detachment rate is even less understood.

Non-biological Particles and Biomass Detachment during Backwashing

Amirtharajah (1978) developed a semi-empirical correlation for determining the shear stress on the surface of filter media during water only backwashing. In more recent research, Amirtharajah (1993) indicated that collapse-pulsing (a particular combination of simultaneous air and subfluidization water flows) can create significant abrasions between filter grains. The optimal backwashing conditions in water only and air scour systems can be determined by semi-empirical correlations.

The mechanisms and kinetics for the removal of attached biofilm are similar to those of non-biological particles. However, recent research from Ahmad and Amirtharajah (1998) indicates that biological particles are held with greater force than non-biological particles.

Table 2.1: Summary of Reported Detachment Rate Expressions

(adapted from Peyton and Characklis, 1993; Morgenroth and Wilderer, 1999)

No.	Detachment rate expression (ML^{-2}/T)	Reference
1	$k_d X_f L_f$	Kreikenbohm and Stephan (1985); Chang and Rittmann (1987); Rittmann (1989)
2	$k_d (X_f L_f)^2$	Bryers (1984); Trulear and Characklis (1982)
3	$k_d X_f L_f^2$	Wanner and Gujer (1986)
4	$k_d X_f \tau$	Bakke *et al.* (1990)
5	$k_d X_f \tau^{0.58}$	Rittmann (1982b)
6	$L_f(k_d' + k_d'' \mu_g)$	Speitel and DiGiano (1987)
7	$k_d \mu_{g(ave)} X_f L_f^2$	Peyton and Characklis (1993)
8	0 during operation; kd ($L_f - L_{base\ thickness}$) during backwashing	Morgenroth and Wilderer, (1999)

Where, k_d = detachment rate coefficient (units depend on the expression)

k_d' = detachment rate coefficient ($M L^{-3} T^{-1}$)

k_d'' = detachment rate coefficient ($M L^{-3}$)

μ_g = specific growth rate (T^{-1})

$\mu_{g(ave)}$ = average specific growth rate (T^{-1})

τ = shear stress (NL^{-2})

The optimal backwashing condition using air scour or water only can be established to achieve the best removal of non-biological particles and biofilms. However, the amount of biomass detached during backwashing, or the biomass residual immediately after backwashing, has not been addressed properly in the literature.

Hozalski (1996) assumed a constant percent removal for biomass during backwashing in biofilm models, based on bench scale experimental results using two model bacteria (*Pseudomonas aeruginosa* and *Klebsiella pneumoniae*). No substantial BOM removal changes due to the biomass detachment caused by filter backwashing were predicted as long as no significant biomass loss occurred during backwashing.

Based on mathematical simulations, Morgenrorth and Wilderer (1999) investigated the influence of non-steady-state detachment mechanisms (backwashing and sloughing events) on microbial competition in biofilms. It was concluded that the application of the steady-state biofilm model (i.e., constant biofilm thickness in a filter run), when predicting the performance of systems with large fluctuations of the biofilm thickness over time, (e.g., biofilter backwashing), may be misleading.

The concentration and biodegradability of BOM, the hydraulic loading rate, the backwash strategies, and the media configurations will impact the changes in biofilm (amount and distribution) in biofilters. A biofilm model incorporating the aforementioned factors, is of critical importance for the application of biofilter models. However, as previously disscussed, limited relevant research is available because of the complexity of the phenomena, and further research is needed for a more complete understanding.

2.5.3 Development of Biofilter Models

In recent years, attempts have been made to model the removal of BOM either in an integrated form (e. g. AOC, BDOC) or as specific components in biofilters. As described above, drinking water biofiltration can be considered as a process of biofilms which are attached to the surface of the media. Therefore, all biofilter models are based on biofilm models to a great extent.

Rittmann and McCarty (1980) proposed a steady-state biofilm model. However, this model can not be solved explicitly, because of the second-order non-linear differential equation in the model. By simplifying the model to either first-order or zero-order kinetics, analytical solutions can be provided to the diffusion-with-bioreaction equation. Suidan and Wang (1985) developed a semi-empirical solution to Rittmann and McCarty's steady-state biofilm model. Sáez and Rittmann (1988) provided a pseudo-analytical solution (an approximate analytical solution) to the steady-state biofilm model and subsequently published a revised solution (Sáez and Rittmann, 1992). A steady-state biofilter model based on the revised biofilm model pseudo-analytical solution (regression from the numerical solution), was presented by Zhang (1996) and Zhang and Huck (1996a).

Multi-species steady-state biofilm models with similar structures have been developed by dividing biomass into subgroups, either in terms of biofilm composition (autotrophs and heterotrophs and inert materials) or according to biodegradation kinetics of different substrates (Rittmann and Manem, 1992; Wanner and Gujer, 1986). In these models, biomass growth was always balanced with detachment, resulting in constant biofilm thickness simulations. These types of steady-state biofilm models become more sophisticated, since more parameters are required to describe the biofilm. The implementation of these biofilm models to biofilter models is thus becoming much more difficult.

Other researchers (Wang, 1995; Wang and Summers, 1995) modeled drinking water biofiltration by assuming a full penetration biofilm model (substrate concentration inside the biofilm is homogeneous), using the regressed biomass (biofilm) profile from the measured data in real biofilters. Although this model is of more practical use, the biofilm profile suffers from site-specificity and BOM-specificity.

All of the models discussed above address steady-state conditions. Drinking water biofilters may be considered pseudo steady-state while considering the backwashing of the biofilters during steady-state operation. Steady-state biofilter modeling is useful in

predicting the long term performance of a biologically active filter, which is important to water utilities. However, steady-state biofilter models can neither predict the BOM removal performance of biofilters in the initial period of biofilm development, nor the possible sawtooth pattern throughout the filter cycle. By considering biomass accumulation in the initial period of biofilm development, biomass loss during backwashing and its gradual replenishment during the subsequent filter cycle, Hozalski (1996) developed a non-steady-state biofilter model to address non-steady-state BOM removal performance. A constant percent removal of biomass in the entire depth of the biofilter bed during backwashing was assumed in this model, which may not adequately represent the biomass detachment during backwashing (the modeling results showed a slow decrease for the overall BOM removal over a number of filter cycles).

The establishment of a good model for the description of biomass detachment during backwashing and in filter runs is crucial to non-steady-state biofilter models. However, it is extremely difficult to provide an applicable kinetic description for biomass detachment during backwash and filter runs because of the complex nature of the biomass detachment phenomena and the limit of current techniques for biomass measurement.

The models which have been discussed previously, provide important process insights for drinking water biofilters. However, they are relatively complex and cannot be directly used by utilities. A simple linear regression model has been developed to evaluate the BOM removal performance in biofilters (Huck and Anderson (1992); Huck *et al.*, 1994). This model illustrates that the amount of BOM removed in a given biofilter is approximately proportional to the influent concentration. This also means that a biofilter at apparent steady-state will essentially achieve a constant percent removal at a given EBCT and temperature. This relationship has been shown to hold for the removal of AOC, BDOC, THMFP, chlorine demand and carboxylic acids (Huck *et al.*, 1994; Gagnon *et al.*, 1997).

In developing the steady-state biofilm model, Rittmann and McCarty (1980) proposed a definition for S_{min} (the minimum substrate concentration capable of sustaining a steady-

state biofilm). It is based on the assumption of first-order biofilm decay and detachment. Zhang (1996) developed a generalized definition of S_{min}, to accommmodate many possible biofilm detachment mechanisms. Parameters in this generalized S_{min} related to biofilm detachment mechanisms could be very difficult to quantify, if not impossible Zhang (1996) therefore suggested that S_{min} should be estimated *in situ* instead of by parameter estimation.

In developing the steady-state biofilter model, Zhang (1996) and Zhang and Huck (1996a) proposed a dimensionless contact time, X^* (X^* is described in detail in Chapter 8). X^* incorporates biofilter contact time and surface area of the media, as well as the substrate diffusivity and biodegradation kinetic parameters. This parameter allows for the comparison of removal performance among different studies. Huck (1999) explored the use of X^* to evaluate humic substance removals as a function of operating parameters, and showed that it is a good indicator of BOM removal.

2.5.4 Estimation of Biokinetic Parameters in Biofilter Models

Most of the aforementioned models are Monod type biokinetics dependent. Therefore, the key parameters (k and K_s) play an important role in the application of these biofilter models. These biokinetic parameters can be obtained by empirical data (Billen *et al.*, 1992), by parameter estimation from model validation (Zhang (1996) and Zhang and Huck, 1996a), by parameter estimation from independent experiments (Hozalski, 1996), or by parameter estimation from dependent experiments (Wang, 1995). By using BOM (as AOC) removal data in biofilters, Zhang and Huck (1996a) used parameter estimation techniques to obtain the model parameters. However, these estimates are less robust because of the requirement of four estimated parameters (k, K_s, D_f and S_{min}). Hozalski (1996) estimated key model parameters from experiments, using the growth of *Pseudomonas aeruginosa* on acetate. The estimated parameters are also limited when applied to practical biofilters for BOM removal, because of the bacteria-specific limitation. By using a bioreactor with biomass from real biofilter media and with a high recycle flow rate, Wang (1995) showed a kinetic parameter estimation approach in terms

of DOC removal. One drawback for this estimation approach is the requirement of a carefully controlled steady-state operating system. Improved biokinetic parameter estimation techniques would greatly facilitate the successful application of biofilter models.

2.6 SUMMARY

A considerable amount of research has been performed in the field of drinking water biofiltration during the last two decades, due to the wider use of ozone and increasing requirements to remove the increased BOM level in the effluent of ozonation.

The individual effects of important factors that affect performance (e.g., media, temperature and backwash strategies) are relatively well addressed at the present time. However, in previous studies, these factors and their interactions have not been well evaluated in an integrated way. In particular, literature addressing BOM removal performance at low temperatures is very limited.

Currently available methods for biomass estimation (i.e. phospholipid or ATP methods) are limited to some extent, due to their common disadvantage of being very time consuming. A good relationship between biomass and BRP can be expected. BRP can therefore be evaluated for use as a surrogate for biomass as measured by phospholipid or ATP.

The evaluation and further development of the pseudo steady-state biofilter models will allow for the optimization of biofiltation processes and the better understanding of biofiltration mechanisms. The development of a more robust approach for key biokinetic parameter (k and K_s) estimates, the revision of S_{min}, and the further exploration of X*, will enhance the application of steady-state biofilter models.

CHAPTER 3: MATERIALS AND METHODS

The overall experimental design, biofilter systems and analytical methods used in this research are described in detail in this chapter. Procedures specifically employed for a given experiment are included in the "Materials and Methods" section of each of the following individual experimental chapters.

3.1 OVERALL EXPERIMENTAL DESIGN

Drinking water biofiltration experiments in this research were divided into three phases. A 2_{IV}^{6-2} fractional factorial design experiment was conducted in phase I (block I) and phase II (block II). The initial 2_{IV}^{6-2} fractional factorial design experiment was terminated after the first two of four blocks, due in part to the difficulty associated with running biofilters in constant mode with inline static mixers for the simulation of coagulation and flocculation, but primarily due to the fact that some experimental factors were found to have relatively minor effects. By assuming that particle/coagulant and air scour effects were negligible, the experiments from phases I and II could be analyzed as a 2^3 factorial design. The main factors were chlorine backwash, temperature and media. All main effects and interactions were analyzed quantitatively. Additional experiments were carried out in phase III, in order to assess the assumptions made from phase I and II, and to further investigate significant factors and interactions. Other experiments, including the BRP test and the bio-kinetic parameter estimation tests, were also included in phase III.

The minimum duration of the experiments in phases I, II and III was two months, because information from the literature suggested that the period to reach pseudo steady-state conditions in biofilters following startup was relatively long and in the order of a couple of months (e.g. Servais *et al.*, 1994).

3.1.1 Fractional Factorial Design Experiment

A two-level 2_{IV}^{6-2} fractional factorial design was designed initially to investigate the significant factors and interactions in this study. The factors investigated include: presence/absence of non-biological particles in the influent (kaolinite clay, dosage 1.5 mg/L), presence/absence of coagulants in the influent (aluminium sulphate, dosage 3 mg/L), presence/absence of chlorine in backwashing water (free chlorine residual 0.5 mg/L), presence/absence of air scour in backwashing, anthracite/sand media vs. GAC/sand media, and low (5 °C)/high (20 °C) temperature operation. The details of the 2_{IV}^{6-2} fractional factorial design are listed in Table 4.1 in Chapter 4.

3.1.2 Additional Experiments

Significant effects and interactions were evaluated from the first two blocks of the fractional factorial design experimental results, by assuming that particle/coagulant and air scour effects were negligible. This is the most critical assumption made in the experimental investigations within phases I and II.

Based on the literature review in Chapter 2, this assumption was supported by most of the previous studies. However, this assumption was substantiated by further experimental work.

Further experimental exploration of the significant factors and interactions identified in phases I and II were performed to enhance the understanding of these significant factors and their interactions.

In addition, an evaluation of the BRP and the phospholipid biomass was conducted. The simple and fast BRP method was evaluated for use as a surrogate for the phospholipid biomass method. Experiments for bio-kinetic parameter estimation were also performed in phase III. At the end of phase III experiments, the influences of biofilter perturbation (e.g. BOM concentration, hydraulic loading rate and shut down) were investigated.

For detailed experimental procedures of the above mentioned experiments, please refer to individual chapters of experimental results.

3.2 BIOFILTER SYSTEMS

3.2.1 Biofiltration Apparatus

Experiments were performed at bench-scale using four parallel, custom-made glass columns. The experimental set-up is shown in Figure 3.1.

In phases I and II, experiments were performed with two 19.6 cm^2 (ID: 5 cm) anthracite/sand filters (anthracite layer thickness: 45 cm, effective size = 1.1 mm, sand layer thickness: 25 cm, effective size = 0.48 mm) and two granular activated carbon (GAC) filters (GAC layer thickness: 45 cm, effective size = 0.9 mm, sand layer thickness: 25 cm, effective size = 0.48 mm) operated in parallel. In phase III, four anthracite/sand filters were employed. Each filter had eight sampling ports, the uppermost of which served as the filter influent sample port. The lowest of which (under the gravel) served as the filter effluent. The other six sampling ports were located below the top media at depths of 5, 10, 20, 35, 50 and 65 cm, respectively.

Wall effects can usually be minimized when the ratio of the column diameter to the media diameter is greater than 50 (Lang, 1982). Therefore, with a media diameter of about 1 mm, an internal diameter of 50 mm represented the minimal column diameter to minimize wall effects.

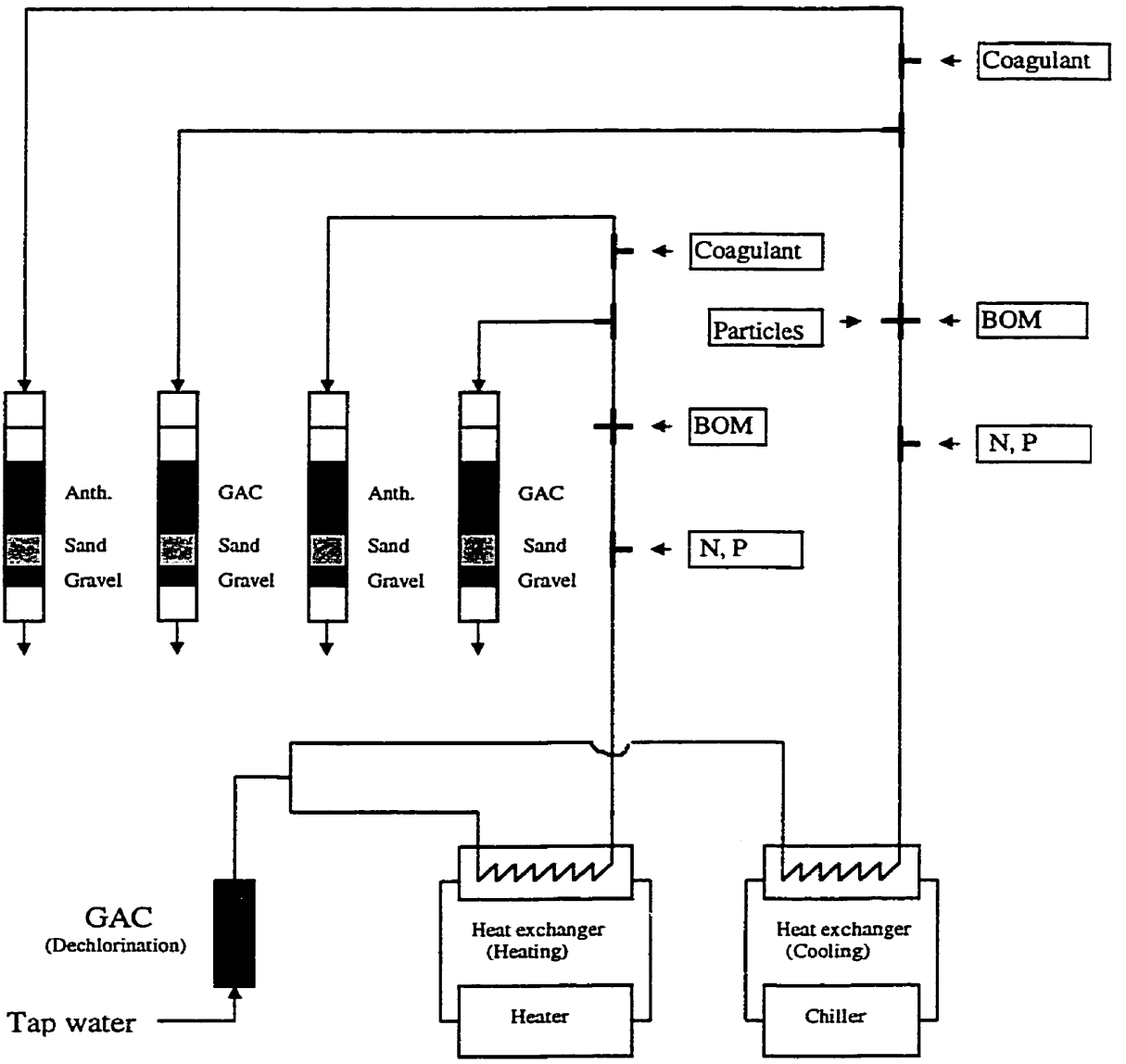

Figure 3.1: Schematic of biofilter system

Four pre-filter GAC columns (two in series for high and low temperature influents) were used for the dechlorination of the source tap water (Kontes Chromaflex™, Vineland, NJ; ID = 4.8 cm, Length = 60cm). In most cases, the chlorine residual was below 0.07 mg/L).

The GAC media (F-300, Calgon Corp., Pittsburgh, PA) in the GAC filters or in the pre-filter GAC columns had been exhausted in terms of BOM removal since it had been in use in a full-scale filter for over two years. The GAC media was oven-dried (105 °C, overnight) before putting it into use to inactivate the biological component of the media.

In experiments with the feeding of non-biological particles and coagulants, custom-made stainless steel static mixers (Koflo Co, Cary, IL; ID =1/4 inch.; Length = 14 inch.), with a Gt value of 680 (in the lower range of jet injection blending: 700 –1000), were used for rapid mixing. The rest of the tube leading to the filters with similar Gt (a lower G value), was used to simulate flocculation. The destabilized particles present in filter influents and the flocs formed during the above processes were used to simulate the particles after sedimentation in full-scale plants.

The filter influent water was temperature controlled. Two filter influent lines were heated to the high temperature (20 °C) through a custom-made stainless steel heat exchanger with appropriate capacity in a recirculating heater (Model Lauda RM6; GmbH and Co., Germany). The two other filter influent lines were cooled to the low temperature (5 °C) through a similar custom-made stainless steel heat exchanger with the corresponding appropriate capacity in a recirculating chiller (Model 1175, Polyscience).

In addition, all materials in contact with the water were either glass, stainless steel or inert fluorocarbons. The filter and pre-filter GAC column walls were covered with black insulation materials in order to prevent the growth of phototrophic organisms, and to minimize the water temperature fluctuations in the filters.

The filter hydraulic loading rate was measured and controlled using a pre-calibrated flow meter (Gilmont® Instruments, Barrington, IL), with a valve on the effluent line.

3.2.2 Biofilter Influent

The filter influent was dechlorinated tap water to which concentrated solutions of targeted BOM components, nutrients and particles/coagulants (if applicable) were added.

Tap Water in the Filter Influent

The tap water used in the filter influent was mainly from local groundwater, which is low in organics and high in alkalinity and hardness. Some typical water quality parameters include: pH: 7.4-7.5; alkalinity: 300-325 mg/L as Ca CO_3; hardness: 325-350 mg/L as Ca CO_3; TOC: 1.0-1.1 mg/L; conductivity: 1300-1400 μS; temperature: 12 –16 °C. Because of the low organic source water and GAC/BAC pretreatment, the filter source water BOM target components were normally at very low or non-detectable levels compared to the concentration attained by addition. Ammonia in the influent was generally lower than 0.1 mg/L. Nitrification is negligible in comparison with the aerobic biodegradation of BOM in biofilters.

During a short period in experimental phase III, a change of tap water sources occurred from "groundwater only" to a blend of groundwater and treated surface water from the Mannheim WTP. There were some relatively major changes in the total chlorine residual (from below 0.08 mg/L to 0.3 mg/L), pH (from 7.4-7.5 to 7.0-7.1), TOC (from 1.0-1.1 to 1.5-1.6 mg/L), conductivity (from 1300-1400 μS to 750 μS). The effect of this brief change on biofilter operation was the reduced BOM removal in biofilters operated under unfavourable conditions.

BOM in the filter influent

The choice of BOM target components was largely based on ozonation by-products, because ozonation and biofiltration are closely related processes (as mentioned in

Chapter 2). Four typical ozonation products chosen as the targeted BOM components in a previous bench-scale biofiltration experiment (Urfer, 1998) were used in this research. For the aldehyde component, formaldehyde and glyoxal were chosen, as relatively easily biodegradable and less readily biodegradable aldehydes, respectively (Krasner *et al.*, 1993; Urfer, 1998). For the carboxylic acid component, formate and acetate were chosen, because they appear to be formed in the largest yield upon ozonation (Gagnon *et al.*, 1997), together with oxalate. The same targeted BOM components and concentrations were adopted in this research. The targeted concentrations of the BOM components in the filter influent were: formaldehyde 100 μg/L; glyoxal 30 μg/L; formate 400 μg/L and acetate 300 μg/L. These are concentrations of whole compounds rather than the concentrations as carbon. These concentrations are in the high range of what is usually observed following ozonation (e.g. Glaze and Weinberg, 1993; Griffini and Iozzelli, 1996; Gagnon *et al.*, 1997).

Nutrients in the filter influent

A typical empirical formula for a bacterial cell, C_{55} $H_{77}O_{22}N_{11}P$ (Metcalf and Eddy, 1991), indicates a C:N:P ratio of 21:5:1 (w/w/w). Urfer (1998) chose a C:N:P ratio of 15:5:1 (w/w/w) to guarantee that the organic carbon was the limiting nutrient. The same C:N:P ratio was used in this biofiltration study. Sodium nitrate ($NaNO_3$) and potassium phosphate (K_2HPO_4) were used as the sources of nitrogen and phosphorus, respectively.

Particles and coagulants in the filter influent

Kaolinite was used as the surrogate for non-biological particles in the filter influent. A dosage of 1.5 mg/L was adopted in this study, which is in the typical particle concentration range of 1- 4 mg/L (Montgomery, 1985). Aluminum sulphate ($Al_2(SO_4)_2.18H_2O$) was chosen as the coagulant, due to its wide use in North America. The optimized dosage of the coagulant at 3 mg/L was determined by a jar-test experiment.

When applied, kaolinite and aluminum sulphate were dosed to the filter influent using a peristaltic pump (Model 7518-10, Masterflex L/S, Cole-Parmer, Vernon Hills, IL) using PharMed® tubing (L/S™ 13).

3.2.3 Biofilter Operation Module

BOM, nutrients and particle/coagulant feeding

BOM, nutrients, kaolinite particles and aluminum sulphate coagulant were prepared with autoclaved Milli-Q water (Millipore Corp., Bedford, MA) and kept in their own previously autoclaved amber glass bottles. The 0.2 µm PTFE air filters (Gelman, Lot No. 5300) were used to prevent contamination from surrounding air. The source bottles for kaolinite were continuously stirred (Barn Stead/Thermolyne, Model S46725, Iowa, US), to keep the kaolinite particles suspended in the feeding bottles. The concentrations and the flow rate of the feed solutions were set according to the targeted concentrations and resulted in a feeding rate of about 3 liters per week (3.5 liter stock solution in 4 liter bottles). These feed solutions were pumped using peristaltic pumps (Model 7518-10, Masterflex L/S, Cole-Parmer, Vernon Hills, IL) and PharMed® tubing.

Biofilter Operation in a Filter Run

The four biofilters were operated at 7.5 m/h in a constant rate mode, corresponding to a total EBCT of 5.6 minutes, excluding the gravel layer.

The filter hydraulic loading rate was controlled by a valve on the effluent line. Valve adjustment during a filter run was necessary to maintain constant rate operation, especially when dosing kaolinite.

Biofilter backwash

As mentioned in Chapter 2, a compromise in backwash frequency had to be made to meet the conflicting requirements of backwashing for biofilters with particles in the influent (a couple of days) and biofilters without particles in the influent (a couple of weeks). As a compromise biofilters were backwashed every other day. This frequency was chosen in order to simulate the operation of full-scale first-stage biofilters in practice as closely as possible.

Each filter was backwashed with its own effluent water (chlorine/or chloramine was added if applicable), either by water only or with air scour. The backwash water was collected in 20 L glass carboys just before the backwash events.

The procedure for water only backwashing included: (1) draining of the filters until the water level was 5-10 cm above the top of the media, (2) start backwashing at 50 m/h (increase the water flow rate to 50m/h in one minute in order to avoid possible media loss).

The procedure for backwashing with air scour was as follows: (1) draining of the filters until the water level was 5-10 cm above the top of the media, (2) "Collapse pulsing" backwash (Amirtharajah *et al.*, 1991): water at 40% of the fluidization velocity, (i.e. 12 m/h), and simultaneously with air 50 m/h (at standard pressure and temperature) for 2.5 minutes. (3) Water only at 50 m/h for 4 minutes, in order to achieve a bed expansion of 35-45%.

Backwash water was pumped from the carboys (about 10L of 12 L collected filter effluent was consumed during backwashing), with a peristaltic pump (Model 7553-70, Masterflex L/S, Cole-Parmer, Vernon Hills, IL) using PharMed® tubing. Air was provided from a tank containing pressured air. The air flow rate was measured using a flow rate meter (Gilmont® Instruments, Barrington, IL).

Sampling during Operation

Liquid sampling was collected using sampling beakers by piercing (punching) the sample port rubber septum with a stainless steel needle. For the sampling of filter media, the filters were drained and the media was withdrawn with a small re-shaped laboratory scoop. Acid free gloves were worn during sampling in order to avoid possible contamination.

3.3 ANALYTICAL METHODS

3.3.1 Microbial Analyses

HPC

The Standard Plate Count method (APHA-AWWA-WEF, 1998) was used to enumerate viable culturable heterotrophic bacteria in aqueous samples from the biofilter influent, effluent and backwashing effluent. The results from plate counts are expressed in colony forming units (CFU) per unit volume. The term colony forming units is used because a colony on an agar plate can result from a single cell or a multi-cellular aggregate of bacteria. Heterotrophic plate count (HPC) bacteria were enumerated using a spread plate procedure with R2A agar, incubated at room temperature for seven days (APHA-AWWA-WEF, 1998).

Phospholipid Biomass

Phospholipids are contained within membranes of living cells. The amount of biomass can be quantified by measuring the organically bound phosphorus (phospholipids) according to a method described by Findlay *et al.* (1989). The organically bound phosphorus is extracted and then digested to inorganic phosphate followed by colorimetric quantification. The phospholipid biomass method has been used previously for the measurement of biomass in biofilters (e.g. Wang and Summers, 1995; Coffey *et al.*, 1995; Carlson *et al*, 1998; Urfer, 1998).

The analytical procedure previously used (Urfer, 1998), and adopted in this study for the measurement of phospholipid biomass in filter media is described in Figure 3.2. It is based on the method described by Findlay *et al.* (1989).

EXTRACTION

1. Transfer between 0. 1 and 1 g of media to a 20-mL EPA vial (the amount of sampled media must yield an amount of lipid phosphate < 40 nmol)

⇓

2. Add 1.8 mL of DI (Milli-Q), 5mL of methanol and 2.5 mL of chloroform in this order (the final solution must be single-phase)

⇓

3. Mix at low speed on a shaker table for about 10 minutes, let stand overnight for extraction

⇓

4. Add 2.5 mL of chloroform and 2.5 mL DI in this order, let stand for phase separation for about 30 minutes

⇓

5. Remove upper layer (MeOH-H_20) with pasteur pipette (to waste)

6. Transfer lower layer (chloroform) to Hach® vial (used for COD-measurement) with pasteur pipette

⇓

7. Remove solvent (chloroform) under a stream of nitrogen

DIGESTION

8. Add 1.1 mL of potassium persulfate solution (5% potassium persulfate in 0.36 N sulfuric acid)

⇓

9. close vial tightly and digest @ 95-100 °C overnight in an oven

QUANTIFICATION

10. Let cool, then add 0.2 mL of ammonium molybdate solution (2.5% $(NH_4)_6Mo_7O_{24}$-$4H_20$ in 5.72 N sulfuric acid), wait 10 minutes

⇓

11. Add 0.9 mL of malachite green solution (0.011% malachite green in 0.111% polyvinyl alcohol solution), wait 30 minutes

⇓

12. Measure absorbance @ 610 nm, use reagent blank (potassium persulfate, ammonium molybdate and malachite green) to zero the instrument

⇓

13. Convert to nmole of lipid phosphate using a standard curve established using inorganic phosphate (K_2HPO_4)

Figure 3.2: Analytical procedure used for the measurement of phospholipid biomass (after Urfer, 1998)

The amount of biomass was reported as nmol lipid-P/g dry filter media or nmol lipid-P/cm^3 filter media.

As was found by Carlson and Amy (1998), duplicate measurements from single extraction were repeatable, however, results from duplicate sample media produced more variability. To avoid excessive media consumption, duplicate samples of media were not routinely taken.

3.3.2 Chemical Analyses

Carboxylic Acids

Carboxylic acids were analyzed by ion chromatography as described by Peldszus *et al.*, (1996). Immediately after sampling 0.1% (v/v) of chloroform was added to the water sample as a preservative. For analysis, water samples were injected directly into the ion chromatograph without a sample preparation step. A high capacity anion exchange column (AS 10, 250 *4mm ID, Dionex, Sunnyvale, CA) was used followed by conductivity detection. The method detection limit for the organic acids is between 1 and 5 µg/L. The method provides good separation of a number of acids.

Aldehydes

As described by Sclimenti *et al.* (1990), aldehydes were analyzed using direct aqueous derivatization of the carbonyl compounds with PFBHA (o-2,3,4,5,6-pentafluorobenzyl-

hydroxylamine) to form oxime derivatives. The derivatives were extracted from the water with hexane and analyzed by GC and ECD (HP 5890 Series II, Hewlett-Packard, Sunnyvale, CA). The method detection limit for formaldehyde, acetaldehyde, glyoxal and methyl-glyoxal is between 1-2 μg/L.

Chlorine

Free chlorine was determined by the amperometric method described in Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WEF, 1992).

Dissolved Oxygen

Dissolved oxygen (DO) was measured using an Orion Dissolved Oxygen Meter (Model 835 and Orion DO Probe 08310, Boston, MA). Water samples were collected headspace-free in BOD-bottles and measured directly in these BOD-bottles.

3.3.3 Physical Analyses

Turbidity

Turbidity was measured by using a turbidimeter (2100P Turbidimeter, Hach®, Colorado, USA).

Headloss

Headloss in the biofilter was measured by comparing the water level difference between two glass tubes connected to the desired pressure-measuring ports in biofilters.

3.4 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

QA/QC measures were taken in order to ensure the quality of the experimental results presented in Chapters 4 to 7. These QA/QC measures were described in Appendix A.

CHAPTER 4: INVESTIGATION OF FACTORS AFFECTING DRINKING WATER BIOFILTRATION PROCESSES: A FRACTIONAL FACTORIAL DESIGN APPROACH

4.1 INTRODUCTION

BOM can be removed by biofilms attached to media in drinking water biofilters. Several factors may significantly influence BOM removal performance in biofilters, and significant interactions may exist among these factors. These factors include: BOM characteristics and concentrations in the influent of biofilters, seasonal water temperature variations, the type of media (anthracite/sand media vs. GAC/sand media), characteristics (coagulated or not) and concentrations of non-biological particles in the influent of biofilters, presence/absence of chlorine in the backwash water, presence/absence of air scour during backwashing, frequency of backwashing, empty bed contact time (EBCT) and hydraulic loading rate (HLR). Some of these factors (media, backwashing conditions, EBCT/HLR, particle/coagulant) can be controlled to a greater extent than others (such as water temperature and BOM components).

Media type, EBCT and HLR are the typical filter design parameters. The presence or absence of air scour in the backwash process is a design choice; but in current practice air is normally included in the backwash procedure for filters used for particle removal. The use of air scour as a more rigorous backwash procedure can help to prevent the over accumulation of non-biological particles in biofilters, especially when a high particle flux exists. The use of air scour is also used for the control of biomass over-growth in biofilters. Ideally, chlorine should not be present in the backwash water because of its

potential inhibitory effects on the development of biofilms in biofilters. However, free chlorine may be present in the backwash water, if the water for backwashing is obtained from a clearwell to which these disinfectants are added. In addition, in certain full scale plants, chlorine is added periodically to the backwash water of biofilters in order to control headloss buildup, likely due to the excessive buildup of biomass within the biofilter (Huck *et al.*, 1998). Biofiltration can be practiced in second stage rapid GAC filters (common in Europe) or in single stage filters (common in North America). The characteristics and concentrations of non-biological particles in the filter influent are dependent on the raw water quality and pre-treatment processes (i.e. coagulation/flocculation/sedimentation processes, or the coagulation/flocculation process for direct filtration). The accumulation of non-biological particles in biofilters may affect the morphology of the biofilm in biofilters, and consequently impact BOM removal. Therefore, this potential accumulation may affect the frequency and type of backwash process. BOM components and concentrations in the filter influent are dependent on the raw water quality and any ozonation process used in the previous treatment steps. Ozonation by-products can enhance biofiltration processes to a greater extent because of the formation of low molecular weight easily biodegradable organic compounds. Temperature is of importance due to its effect on bacterial growth. Temperature may also affect particle and BOM removal in previous treatment processes (such as coagulation and flocculation).

Previous studies have demonstrated that media, temperature, and chlorine backwash are three important factors affecting drinking water biofiltration processes (refer to section 2.2). The effects of these factors and the potential significant interactions have not been compared quantitatively in previous studies. In particular, literature regarding BOM removal performance at low temperatures is very limited (Fonseca *et al.*, 1999).

In this study two-level fractional factorial designs were used to investigate the significant factors and interactions. Two-level fractional factorial designs are often of great value at an early stage of an investigation, when it is good practice to use a preliminary experimental effort to screen a large number of factors, rather than investigate a smaller

number (which may or may not include the important ones) thoroughly. These designs may be used as building blocks so that the degree of complexity of the finally constructed design can match the sophistication of the problem. The significant factors and their interactions can be investigated in detail in later experiments.

4.2 OBJECTIVES

The overall objective of the experiments described in this chapter is the investigation of the significant factors affecting drinking water biofiltration by using a fractional factorial design approach. Specific goals of this part of the study are:

- to describe the effects of factors and interactions quantitatively;
- to determine the statistically significant factors and interactions;
- to develop a multiple linear regression model for the prediction of BOM removal and
- to gain some insights into further experimental investigation.

4.3 EXPERIMENTAL DESIGN

In these biofiltration experiments, a 2_{IV}^{6-2} fractional factorial design in four blocks of four runs was performed to establish the significant factor(s) and interaction(s) influencing biofilter performance, as described in Table 4.1.

The system variables include different backwashing conditions (presence/absence of air scour; presence/absence of chlorine); the presence/absence of non-biological particles in the influent; filter media (GAC/sand or anthracite/sand); the presence/absence of coagulant in the influent, and temperature (low or high). An EBCT effect was investigated in experiments conducted within the fractional factorial design experiment. HLR (hydraulic loading rate) effects were studied in phase III (described in the next Chapter) since it is a relatively stable parameter in filter operation and related to EBCT. The frequency of backwash, which is dependent on the headloss accumulation of the

biofilter and /or the effluent turbidity levels, may also influence the biofiltration performance. A filter run can last for days with non-biological particles in the influent and for weeks without non-biological particles in the influent. Therefore the frequency of backwash could not be treated as an independent variable in the fractional factorial design because it would depend on whether or not a particular filter had non-biological particles in its influent. Therefore, all biofilters were backwashed every other day in this study.

Table 4.1: Fractional Factorial Design Experiment of Biofiltration: 2_{IV}^{6-2} Design in Four Blocks of Four Runs

Variable	-	+
A Presence of non-biological particles in influent	Yes	No
B Air scour in backwash	Yes	No
C Chlorinated water in backwash	Yes	No
D Temperature	Low	High
E Filter media (=**ABC**)	Anthracite/sand	GAC/sand
F Coagulant (=**CDE**)	Yes	No

2_{IV}^{6-2} design			Block variable		Design rearranged in four blocks				
Run	**A B C D E F**		B_1(AC)	B_2(AD)	Block	**A B C D E F**		B_1(AC)	B_2(AD)	Run
					I	+ - - - + -		-	-	2
1	- - - - - -		+	+		+ + - - - +		-	-	4
2	+ - - - + -		-	-		- - + + + -		-	-	13
3	- + - - + +		+	+		- + + + - +		-	-	15
4	+ + - - - +		-	-						
5	- - + - + +		-	+	II	- - + - + +		-	+	5
6	+ - + - - +		+	-		- + + - - -		-	+	7
7	- + + - - -		-	+		+ - - + + +		-	+	10
8	+ + + - + -		+	-		+ + - + - -		-	+	12
9	- - - + - +		+	-						
10	+ - - + + +		-	+	III	+ - + - - +		+	-	6
11	- + - + + -		+	-		+ + + - + -		+	-	8
12	+ + - + - -		-	+		- - - + - +		+	-	9
13	- - + + + -		-	-		- + - + + -		+	-	11
14	+ - + + - -		+	+						
15	- + + + - +		-	-	IV	- - - - - -		+	+	1
16	+ + + + + +		+	+		- + - - + +		+	+	3
						+ - + + - -		+	+	14
						+ + + + + +		+	+	16

All fractional factorial design variables and other biofilter operation parameters were assigned typical values in accordance with available reported results in the literature. The six variables **A, B, C, D, E** and **F** in Table 4.1 were defined as follows: Non-biological particles in the influent (kaolinite clay, dosage 1.5 mg/L), the presence/absence of air scour in the backwash process, the presence/absence of chlorine in the backwash water (free chlorine residual 0.5 mg/L), low (5 °C)/high (20 °C) temperature conditions, anthracite/sand media vs. GAC/sand filter, and the presence/absence of coagulants in the influent (aluminium sulphate, dosage 3 mg/L; determined by jar test).

If it is assumed that interactions **AC** and **AD** are negligible, then the **AC** and **AD** interactions can be used as blocking factors for the four blocks of four runs each.

A design of resolution IV does not confound main effects and two-factor interactions with each other, but does confound two-factor interactions with other two-factor interactions. For this design the confounding pattern for two-factor interactions is: **AB = CE, AC = BE, AD = EF, AE = CD = EF, AF = DE, BD = CF, BF = CD.** Higher order interactions are assumed negligible.

The response is the percentage removal of specific BOM components in biofilters.

For a complete description of the filtration apparatus and analytical methods used in this study, please refer to Chapter 3.

Other experiments, including the evaluation of biomass and BOM distribution in biofilters, HPC levels in the influent, effluent and backwash discharge, and headloss in the filter bed were also conducted during block I and II experiments. These experimental results are discussed in Chapter 5.

As mentioned in Chapter 3, the 2_{IV}^{6-2} fractional factorial design experiment was terminated after finishing the first two of four blocks. The operating conditions of the eight completed runs in blocks I and II are summarised in Table 4.2.

Table 4.2: Filter Operating Conditions in Blocks I and II

	Filter	Media	Chlorine in BW	Temperature (°C)	Air scour in BW	Non-biol. Particles	Coagulant
Block I	F1	Anthr.	No	20	No	Yes	No
	F2	GAC	No	20	Air	Yes	Yes
	F3	Anthr.	Chlorine	5	No	No	No
	F4	GAC	Chlorine	5	Air	No	Yes
Block II	F1	Anthr.	Chlorine	20	Air	Yes	No
	F2	GAC	Chlorine	20	No	Yes	Yes
	F3	Anthr.	No	5	Air	No	No
	F4	GAC	No	5	No	No	Yes

4.4 RESULTS AND DISCUSSION

4.4.1 BOM removal in blocks I and II

BOM removal during the entire period of operation

BOM removal during the entire period of operation in blocks I and II (also referred to as phases I and II) is depicted in Figures 4.1 to 4.8 (Filter influent/effluent concentrations are tabulated in Appendix A).

In general, about 20 to 40 days were needed for the biofilters to reach steady-state BOM removal (Figures 4.1 to 4.8). More time was required for biofilters operated at low temperature or those biofilters backwashed with chlorinated water (F3, F4 in blocks I and II; F1 in block II), to reach steady-state BOM removal. Less time was needed for GAC than for anthracite biofilters to reach steady-state BOM removal (F2 and F4 in blocks I and II). A number of other operating parameters (e.g. media, the specific BOM component being considered) also affected the time needed to reach steady-state BOM removal to various extents.

The removal fluctuations of glyoxal during the whole operational period were greater than for other BOM components, indicating that glyoxal was more sensitive to biofiltration operation conditions.

In comparison to block I experiments, strong initial BOM removal was found in block II biofilters, especially for GAC biofilters. This might be due to the fact that biofilter media in block II was autoclaved and oven dried instead of autoclaved only as in block I. The oven drying process may enhance the desorption of adsorbed compounds on the media, and initial adsorption may have occurred in the initial starting period of block II.

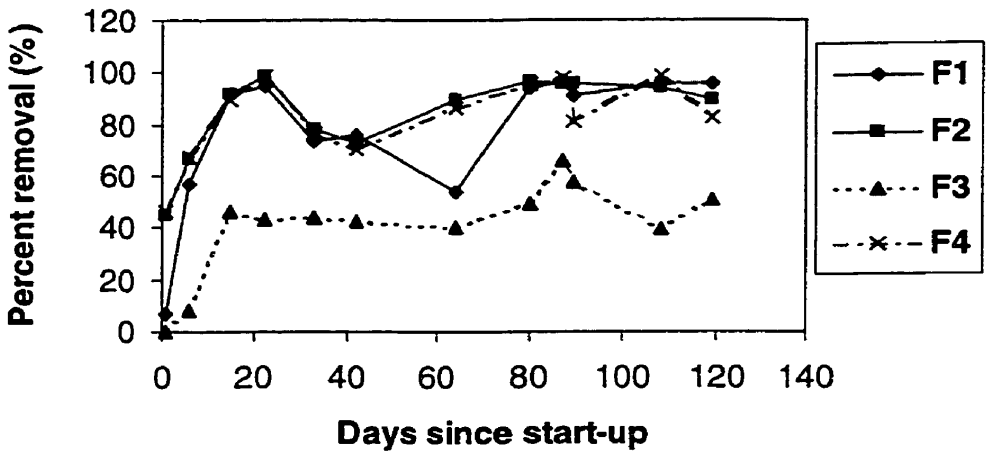

Figure 4.1: Acetate removal in filters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

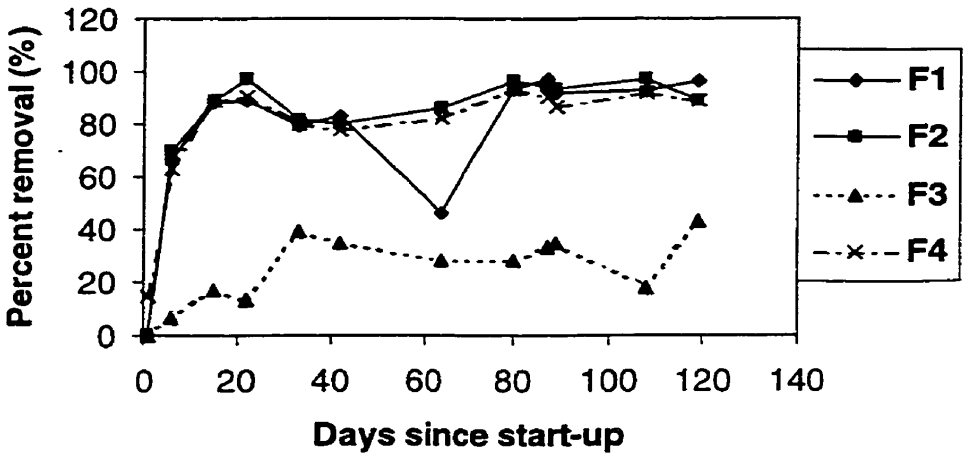

Figure 4.2: Formate removal in filters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

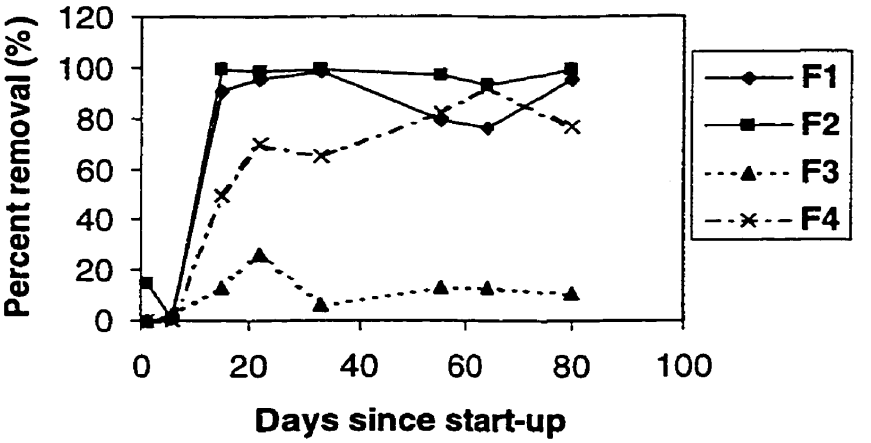

Figure 4.3: Formaldehyde removal in filters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

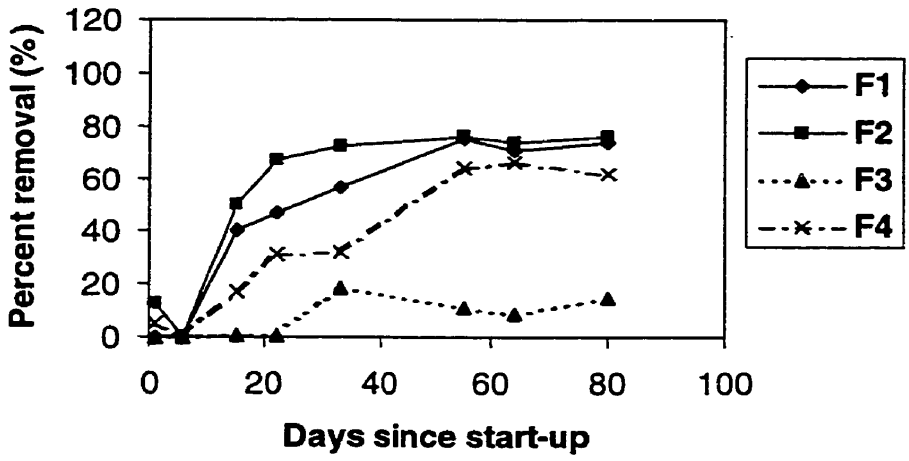

Figure 4.4: Glyoxal removal in filters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

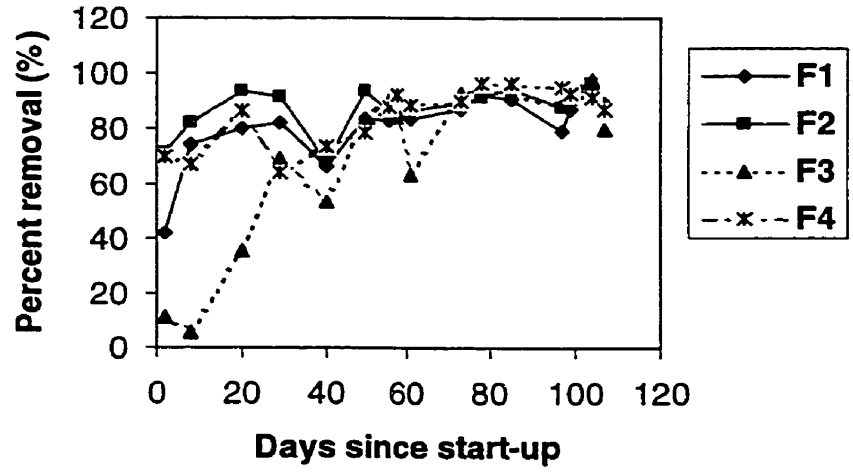

Figure 4.5: Acetate removal in filters (block II)

F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

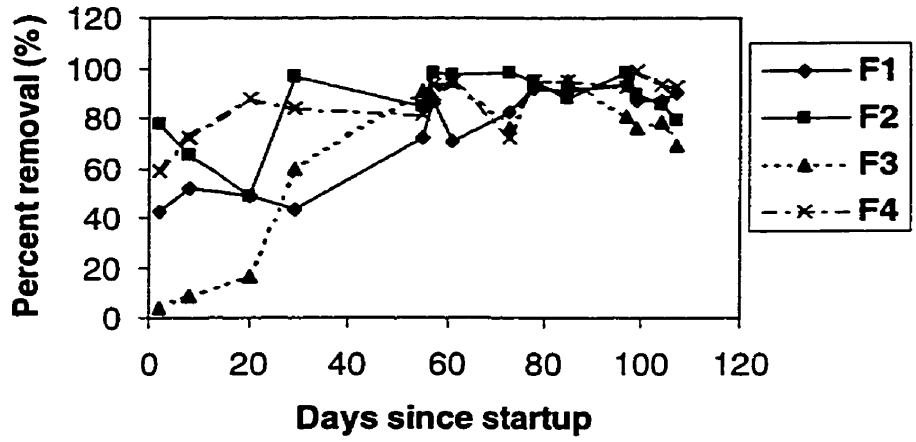

Figure 4.6: Formate removal in filters (block II)

F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

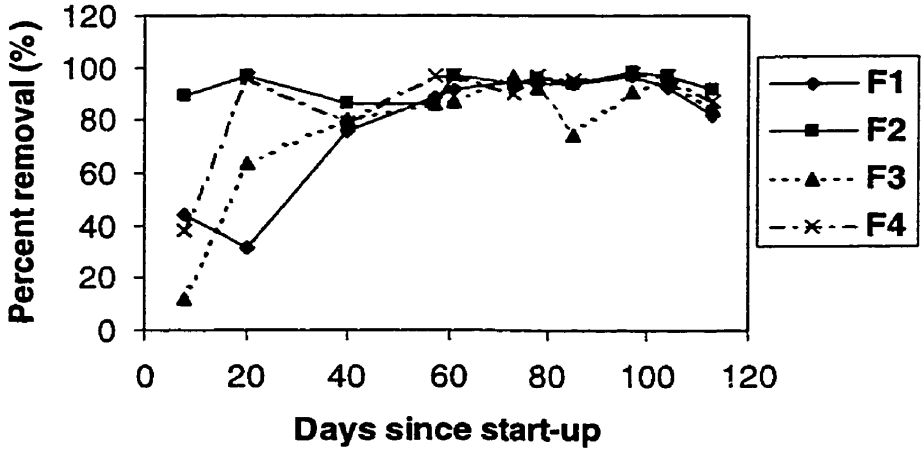

Figure 4.7: Formaldehyde removal in filters (block II)

F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

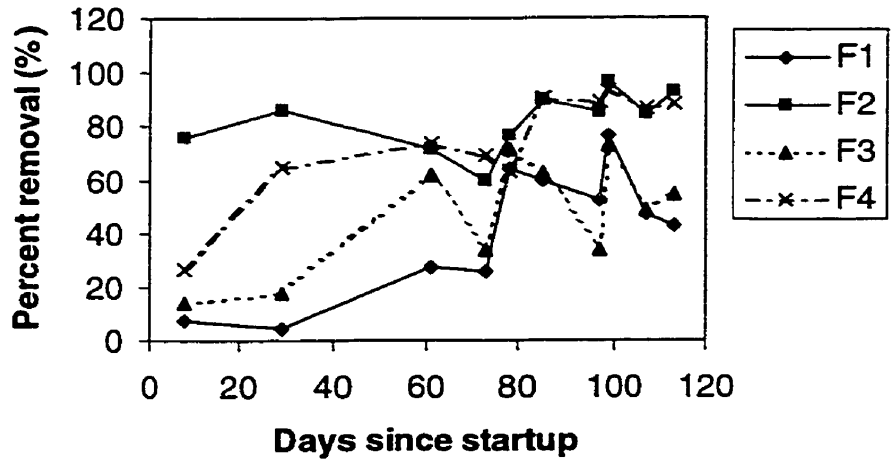

Figure 4.8: Glyoxal removal in filters (block II)

F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

BOM removal during pseudo steady-state in blocks I and II

Average BOM removal during pseudo steady-state in blocks I and II (also referred to as phase I and II) is depicted in Figures 4.9 to 4.12.

Pseudo steady-state was defined as 40 days after the start-up of the filter operation. In this research, BOM removal in most cases (except for glyoxal removal in block II) reached pseudo steady-state in 40 days.

In both blocks I and II, glyoxal removal in the filters was lower than for other BOM components, and more than 85 % removal of acetate, formate and formaldehyde was obtained in all filters except Filter 3. BOM removal in Filter 3 in block I (Figure 4.10) was considerably lower than in the other three filters, due to "worst case" operating conditions (low temperature, chlorine backwash, anthracite media).

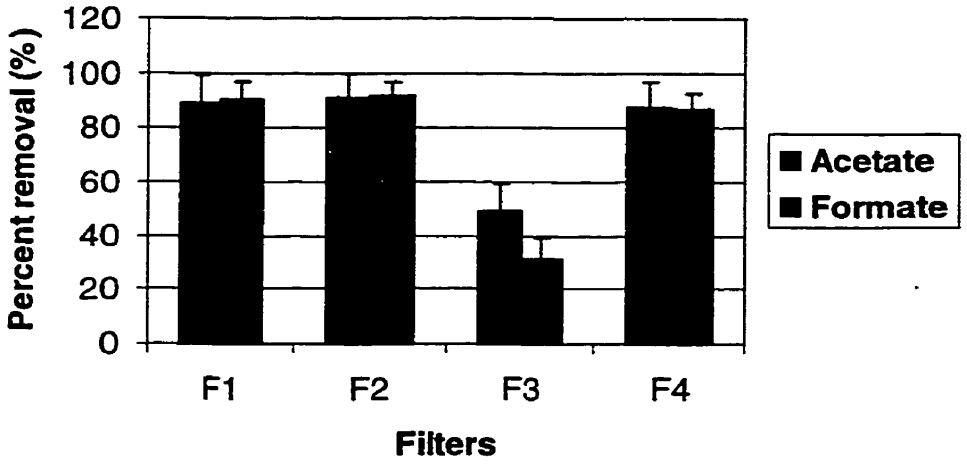

Figure 4.9: Pseudo steady-state removal of carboxylic acids in filters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

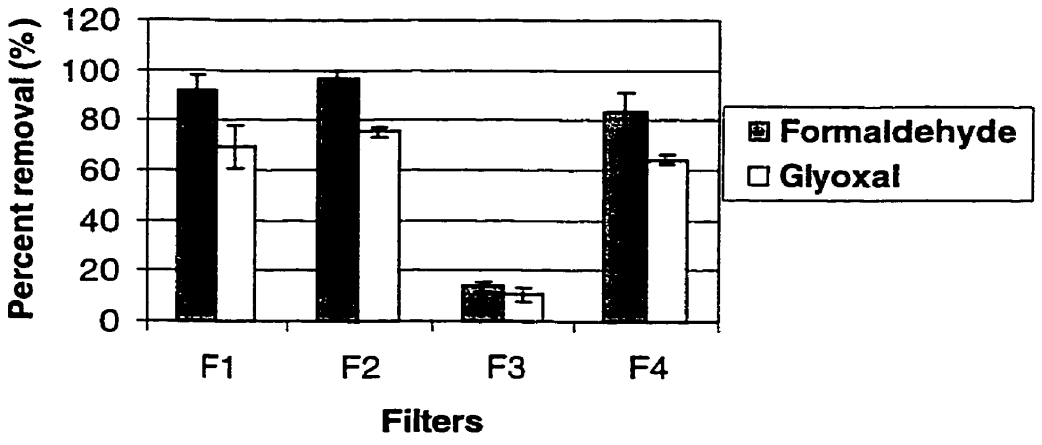

Figure 4.10: Pseudo steady-state removal of aldehydes in filters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

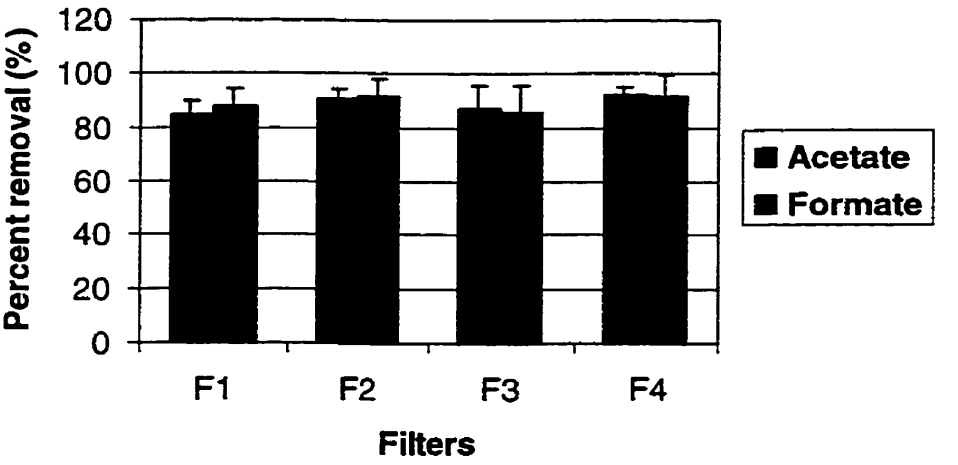

Figure 4.11: Pseudo steady-state removal of carboxylic acids in filters (block II)

F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

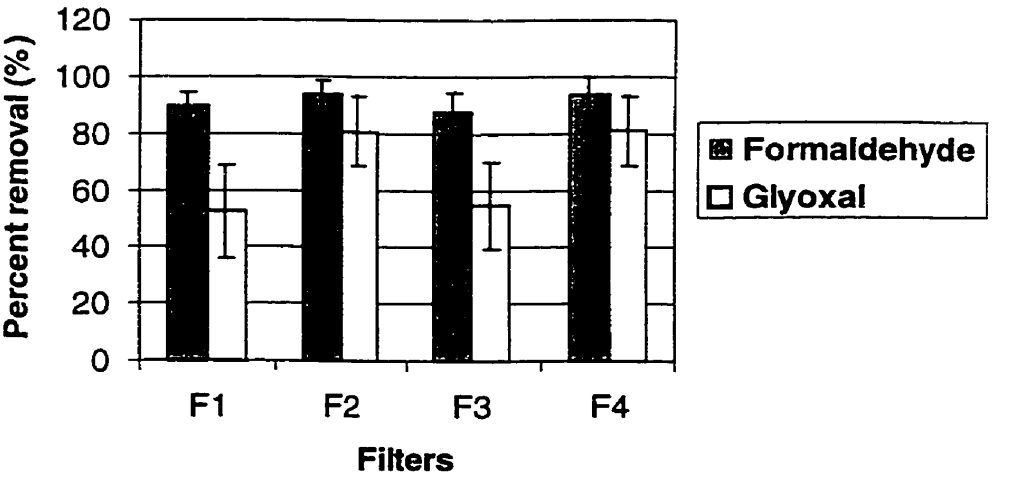

Figure 4.12: Pseudo steady-state removal of aldehydes in filters (block II)

F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

BOM removal performance: relationship to chlorinated backwash water

Chlorinated backwash water showed essentially no effect on BOM removal in either anthracite Filter 1 or GAC Filter 2 (no chlorine in the backwash water and high temperature in block I vs. chlorine in the backwash water at 0.5 mg/L and high temperature in block II). This observation is in agreement with full-scale results (Huck *et al.*, 1998). However, in a similar bench scale biofiltration experiment, Urfer (1998) observed a substantial negative effect of chlorinated backwash water on BOM removal in anthracite/sand and GAC/sand filters when the chlorine level was at about 1 mg/L. A stronger inhibitory effect has been reported while the chlorine level is at about 1.6 mg/L (Miltner *et al.*, 1996). BOM removal in Filter 3 (chlorine in the backwash water at 0.5 mg/L; low temperature; block I) showed a detrimental effect on BOM removal. The chlorine effect is also related to specific BOM components, for example, glyoxal (a less readily biodegradable aldehyde) showed a significant difference: 11% removal for chlorine (0.5 mg/L) in the backwash water (Figure 4.10) vs. 55% for no chlorine in the backwash water (Figure 4.12). The study conducted by Miltner *et al.* (1995), showed more of a difference: 21 % removal for chlorine in the backwash water (~ 1 mg/L) vs. 97% for no chlorine in the backwash water. In the present research, GAC filters were able to tolerate chlorinated backwash water even when operated at the low temperature (Figures 4.9 and 4.10).

Therefore, it might be concluded that a chlorine effect is related to chlorine dosage, temperature, media and BOM components. It seems that there is an interaction between chorine, temperature and media.

In block II, there was no chlorine in the backwash water of Filter 3, and BOM removals were much better (Figures 4.5 to 4.8). This result suggests that backwashing with chlorine substantially impacts BOM removal in anthracite filters operated at low temperature. However, as explained later in this Chapter, GAC filters were able to tolerate chlorinated backwash water even when operated at the low temperature (Figures 4.9 and 4.10). The impact of chlorine backwash was not as significant in filters operated

at high temperatures in terms of easily degradable BOM components such as acetate, formate and formaldehyde (Figures 4.9 to 4.12).

The distribution of chlorine residuals in the expanded media bed of the biofilters can be used to gauge the extent of chlorine disinfection of the biofilms in the biofilters. Figure 4.13 shows the distribution of chlorine residual in two biofilters during backwashing. There was no measurable difference in the chlorine residual in the gravel and sand layers between the GAC filter (F2) and the anthracite filter (F1). However, chlorine residual in the GAC media (the upper layer in the GAC filter) was considerably lower than 0.1 mg/L, in comparison to 0.25 mg/L in the anthracite media (the upper layer in the anthracite filter). By considering the fact that most of the biomass was in the upper layer of the media bed, it was concluded that the extent of chlorine disinfection in GAC filters was significantly lower than that in anthracite filters. The GAC media was able to mitigate the effect of chlorine in biofilters because the activated carbon can react with free chlorine (Snoeyink, 1981). This reduces the effect of free chlorine on BOM removal in GAC filters.

The distribution of chlorine/chloramine residual in the expanded bed of the two biofilters from phase III (refer to Chapter 5), is shown in Figure 4.14. The distribution of the chlorine/chloramine residual in the anthracite biofilters is similar to that in Figure 4.13. However, except at the very top of the bed, measurably less chloramine than free chlorine was consumed. More chlorine demand (consumption) was exerted in GAC /sand filters (Figure 4.13). In a similar bench scale biofiltration experiment, Urfer (1998) found that the free chlorine and combined chlorine demand in anthracite/sand filters were 0.56 mg/L and 0.45 mg/L respectively when the chlorine levels in the backwash water were at about 1mg/L.

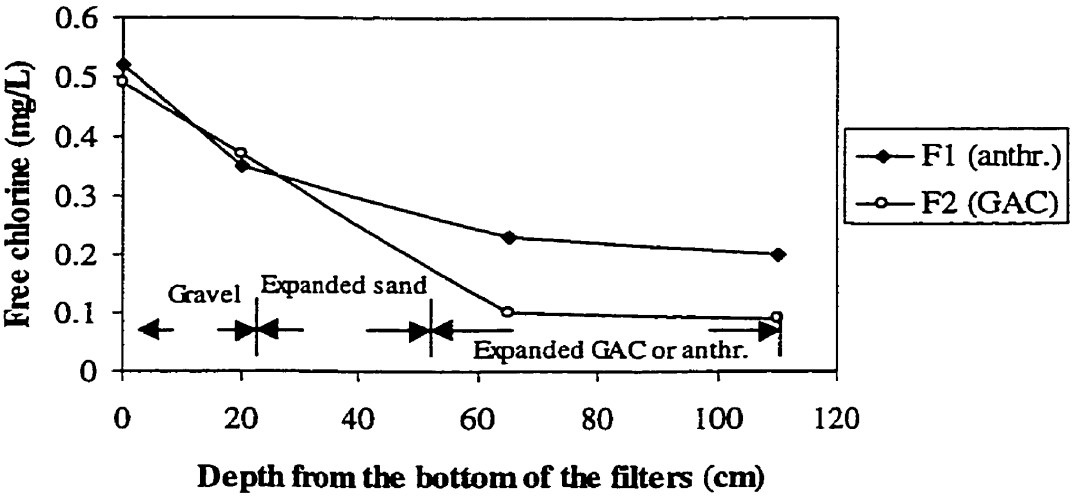

Figure 4.13: Chlorine residual in the expanded bed of biofilters (day 50, Block II)
F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.)

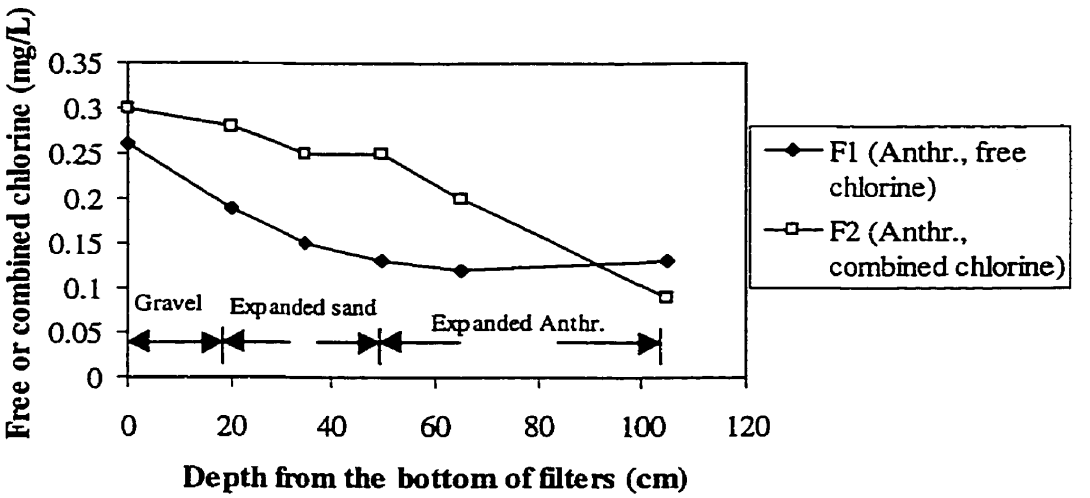

Figure 4.14: Chlorine residual in the expanded bed of biofilters (day 100, phase III)
F1 (Anthr., chlorine, high temp.); F2 (Anthr., chloramine, high temp.)

BOM removal performance: relationship to temperature

In regards to the temperature effect, it seems that there is an interaction between EBCT and temperature, in addition to the just mentioned interaction of chlorine and temperature. The time to reach steady state BOM removal (especially for the less readily biodegradable BOM) was shorter at 20 °C than at 5 °C (Figures 4.1 to 4.8). This observation is in agreement with the results from Coffey *et al.* (1995). BOM removal was slightly higher at 20 °C than at 5 °C when the negative effect of chlorine on BOM removal (Figures 4.9 and 4.12) is taken into account. This chlorine effect is greater for the anthracite filters, as just discussed. A greater removal at higher temperature would be expected from the data by other researchers (Servais *et al.* 1992; Prévost *et al*, 1995; Coffey *et al.*, 1995; Fonseca *et al.*, 1999). Interactions involving chlorine, temperature and media are discussed later in the Chapter.

BOM removal patterns in the biofilters were related to the different temperatures. Because of the available EBCT in the biofilters at the normal hydraulic loading rate and filter bed depth, the theoretically expected temperature effect was "mitigated" to a certain extent. The reason why temperature effect was not so significant for the easily biodegradable compounds studied in this research is likely the fact that measurable BOM removal occurred in the entire filter bed at lower temperatures, whereas it occurred only in the top layer of the filter bed at higher temperatures (refer to Figures 5.5 – 5.8 in Chapter 5). The temperature effect is also affected by chlorine in the backwash water, media and the biodegradability of the BOM compounds. In general, the temperature effect is more significant under unfavourable conditions (chlorine in the backwash water; anthracite media; refractory BOM components) (refer to Figures 5.5 – 5.8 in Chapter 5).

BOM removal performance: relationship to media

In regards to the media effect, GAC filters were able to tolerate chlorinated backwash water by neutralizing the disinfection effect of free chlorine. GAC filters enhanced the removal of less readily biodegradable substances (glyoxal) in comparison to the anthracite filters (Figures 4.10 and 4.12). Similar findings from a full-scale study were reported by Coffey *et al.* (1995). In that full-scale biofiltration testing, at 10-13 °C, the

anthracite/sand filter and GAC/sand filter removed 45 and 70 percent, respectively, of the glyoxal at an EBCT of 2.1 min. However, in terms of overall BDOC removal, another full scale investigation (Huck *et al.*, 1998) showed no difference between GAC and anthracite, except perhaps at temperatures below 10 °C.

The results from blocks I and II suggest that GAC media is needed in order to maintain good removal of all BOM components investigated at both low and high temperature when chlorine backwash is used. The results also demonstrate that a good BOM removal can be achieved at both high and low temperatures if there is no chlorine in the backwash water. Glyoxal as a recalcitrant BOM component is more sensitive to chlorine backwash, and to achieve a good removal, the backwash water should not be chlorinated.

Based on the experimental results, it can be concluded that chlorine in the backwash water, temperature and media are three important factors affecting BOM removal in biofilters.

BOM removal performance: relationship to biomass

Total biomass changes with time in block I are shown in Figure 4.15. The trends of biomass development generally matched those of BOM removal in the different filters. However, the biomass in GAC filters (F2 and F4) was substantially higher than in anthracite filters (F1 and F3). This was in agreement with the results found in a pilot study with ozonated water by Wang *et al.* (1995). This means that GAC media can hold more biomass than anthracite media. BOM removal in the anthracite filter run at the high temperature (F1) with less biomass was close to that in GAC filters run at either low or high temperature with more biomass. One possible explanation is that there may have been more pronounced biomass stratification in GAC filters than in the anthracite filter and therefore less efficiency of biomass in the GAC filters. In addition, biomass in Filter 3 ("the worst case") was considerably lower than in the other three filters and the BOM removal in Filter 3 was also substantially lower than in the other three filters.

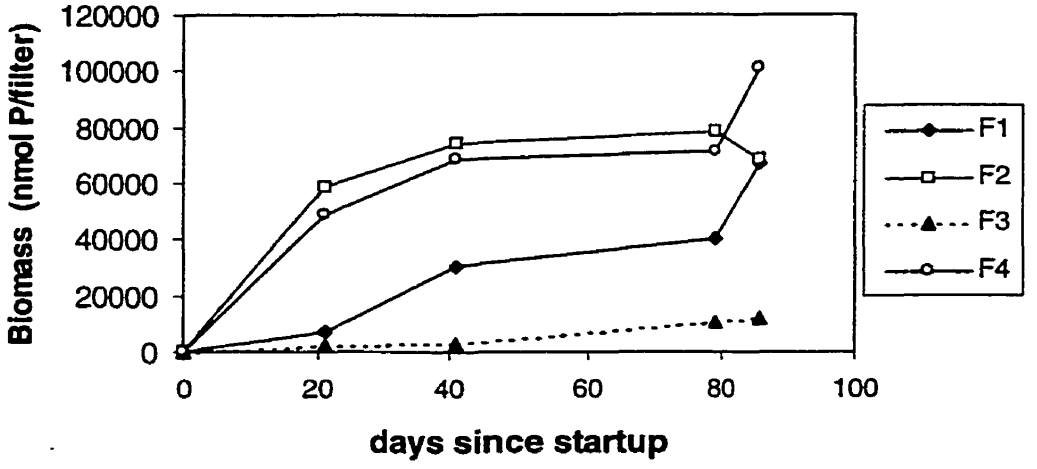

Figure 4.15 : Changes of the total amount of biomass in biofilters (block I)

F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

Correlations between the BOM (as acetate and glyoxal) removal and the phospholipid biomass are presented in Figures 4.16 and 4.17. The data are total biomass from all filters in block I, measured on various days. In general, higher levels of biomass are beneficial to both easily biodegradable BOM (acetate) and refractory BOM (glyoxal) removals. However, it appears that the phospholipid biomass measurement may not be sensitive enough to indicate biofilter performance (Figures 4.16 and 4.17) due to the poor correlation between the BOM removal and the phospholipid biomass. For acetate, and for most glyoxal data points, it would appear that once biomass exceeds a certain level it has no effect on removal. This lack of direct correlation between BOM removal and biomass

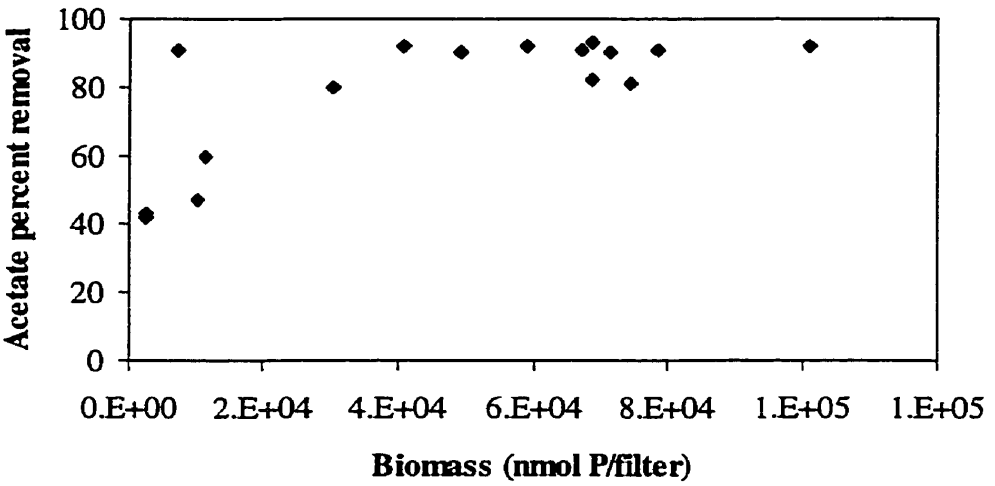

Figure 4.16: Acetate percent removal vs. Biomass in filters (block I)

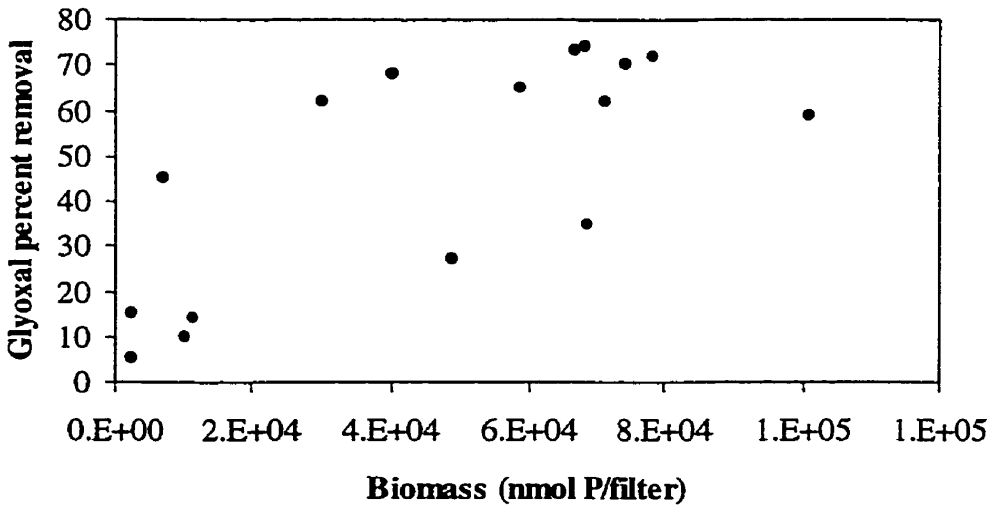

Figure 4.17: Glyoxal percent removal vs. Biomass in filters (block I)

levels is supported by results from a full-scale study (Huck *et al.*, 1998). This lack of correlation is likely due to the following two main reasons: First, BOM removal is related to not only the amount of biomass but also its distribution in biofilters, which is a complicated biofilm phenomenon and will be discussed in Chapter 8. Second, as mentioned previously, the phospholipid method measures viable biomass, but it does not provide a measurement of microbial activity, thus, phospholipid biomass may not directly represent the biodegradation capacity of the measured biomass.

Biomass distribution and BOM removal patterns in biofilters are also affected by temperature. Biomass and BOM removal patterns are discussed in detail in Chapter 5.

4.4.2 Effects/interactions of affecting factors

As mentioned in Chapter 3, previous studies suggest that the effects of factors A (particles), B (air scour) and F (coagulant) are not important. By assuming that these factors have minor effects (this is substantiated further by the experimental results in Chapter 5), the layout of the 8 finished runs in blocks I and II is a full 2^3 design of factor C (chlorine in backwash water), D (temperature) and E (media). All three factors and their interactions can then be analyzed without confounding effects.

The layout of the 2^3 design of the 8 finished runs is given in Table 4.3. For a detailed description of factors C, D and E, refer to Table 4.1.

Pseudo steady-state BOM removal in filters for the finished 8 runs are summarised in Table 4.4.

Based on Tables 4.3 and 4.4, calculated effects and interactions are given in Table 4.5 (Box *et al.*, 1978). All these effects and interactions will be used to evaluate the significant factors and interactions in the following section.

Table 4.3: Layout of 2^3 Design of completed 8 Runs

Run	C (Chlorine)	D (Temp)	E (Media)	CD	CE	DE	CDE
2 (F4, block I)	-1	-1	1	1	-1	-1	1
4 (F3, block I)	-1	-1	-1	1	1	1	-1
13 (F2, block I)	1	1	1	1	1	1	1
15 (F1, block I)	1	1	-1	1	-1	-1	-1
6 (F3, block II)	1	-1	-1	-1	-1	1	1
8 (F4, block II)	1	-1	1	-1	1	-1	-1
9 (F1, block II)	-1	1	-1	-1	1	-1	1
11 (F2, block II)	-1	1	1	-1	-1	1	-1

Table 4.4: Pseudo Steady-state BOM Percent Removal in Filters

Run	Acetate		Formate		Formaldehyde		Glyoxal	
	(Avg.)	(Sdev)	(Avg.)	(Sdev)	(Avg.)	(Sdev)	(Avg.)	(Sdev)
(F4, I)	87	10	87	6	85	8	64	2
(F3, I)	49	10	31	8	14	2	11	3
(F2, I)	91	9	92	5	96	3	75	2
(F1, I)	89	10	91	7	92	6	69	8
(F3, II)	87	9	86	10	87	7	55	15
(F4, II)	92	3	91	8	94	7	81	12
(F1, II)	85	5	88	7	90	5	54	16
(F2, II)	90	4	92	7	94	5	81	12

Note: I = Block I; II = Block II; Avg. = average; Sdev = standard deviation;

Table 4.5: Effects/interactions in Terms of BOM Removal

BOM component	C (Chlorine)	D (Temp)	E (Media)	CD	CE	DE	CDE
Acetate	11.6	10.0	12.5	-9.4	-9.1	-8.9	7.4
Formate	15.4	16.5	16.6	-14.0	-13.3	-13.9	11.6
Formaldehyde	22.3	23.3	21.1	-19.5	-16.0	-17.0	16.0
Glyoxal	17.8	17.2	27.9	-12.8	-12.0	-11.6	1.7

The main effects of C, D, and E were somewhat higher than their interactions. However, the effects and interactions (except the CDE interaction for glyoxal) are of the same magnitude, therefore these three factors and their interactions might all be significant. For a given substrate, the differences among the three main effects are minor except for glyoxal. Fomaldehyde removal seems to be most sensitive to the three factors, and acetate removal least sensitive.

4.4.3 Evaluation of significant effects/interactions

A normal probability plot can be used to detect the significant factors and interactions when the experimental error is not available. Significant effects and interactions can also be evaluated by the F-test if the error of experiments can be estimated. Both these approaches were used to assess the significant factors and interactions in this study. Significant interactions were further evaluated by pictorial representation. A better understanding of significant effects/interactions was achieved by doing this combination of analyses.

Evaluation of significant effects/interactions by normal probability plots

The relationship between effects and the expected normal value are shown in Figures 4.18 to 4.21. The detailed calculations of expected normal values are given in Tables B-1 to B- 4 in Appendix B.

Taking Figure 4.18 as an example, if a straight line is drawn to fit the CD, CE, DE and CDE interactions, the effects of C, D and E can be considered as significant factors. Another less likely possibility is to fit a straight line among effects of C, D and E, then the interactions of CD, CE, DE and CDE can be considered as significant interactions. Similar conclusions can be obtained in other scenarios.

In general, the normal probability plots demonstrate a complicated significance relationship among factors and interactions. The main effects and their interactions might be all significant because of the sophisticated relationships that exist.

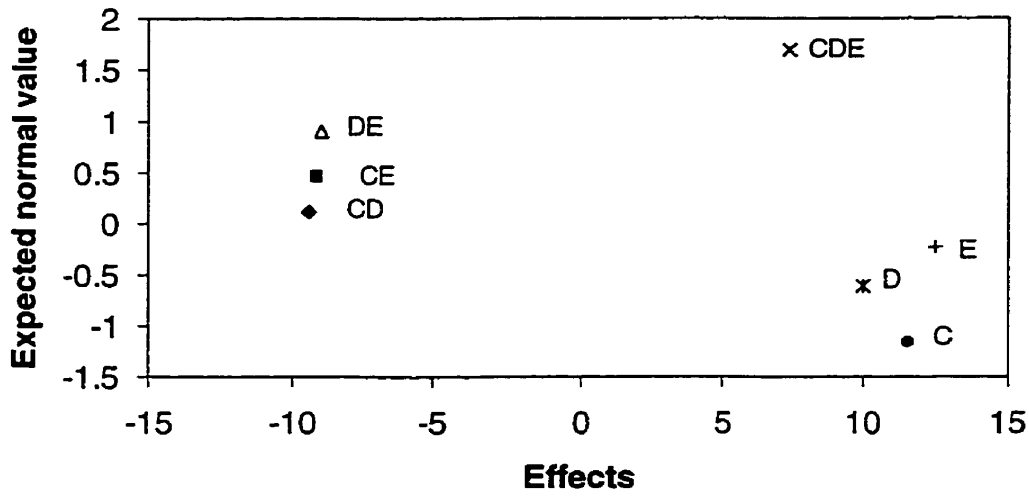

Figure 4.18: Normal probability plot in terms of acetate removal

(C: Chlorine; D: Temperature; E: Media)

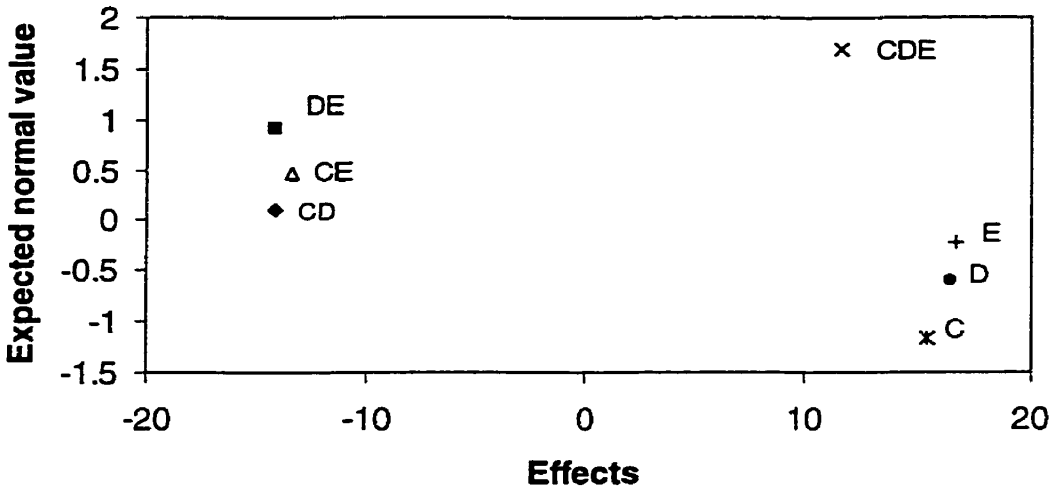

Figure 4.19: Normal probability plot in terms of formate removal

(C: Chlorine; D: Temperature; E: Media)

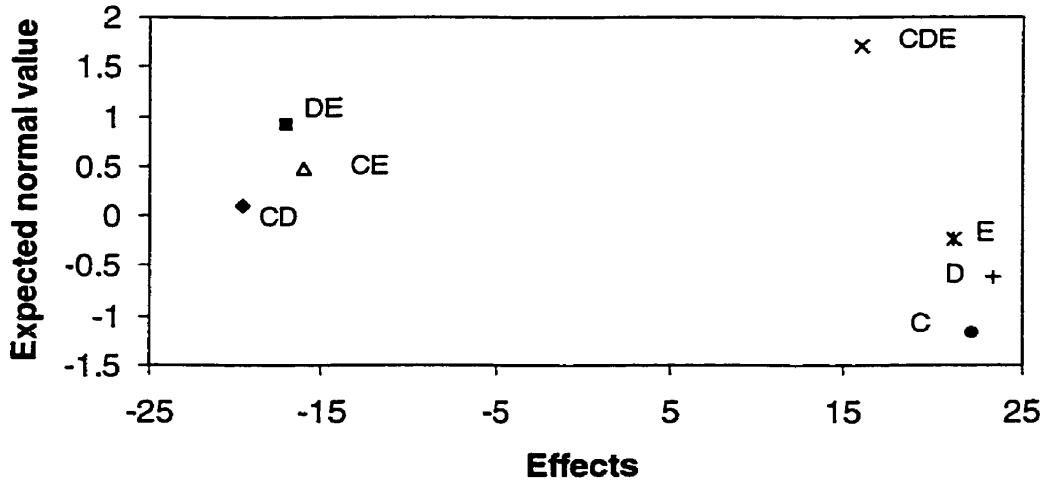

Figure 4.20: Normal probability plot in terms of formaldehyde removal

(C: Chlorine; D: Temperature; E: Media)

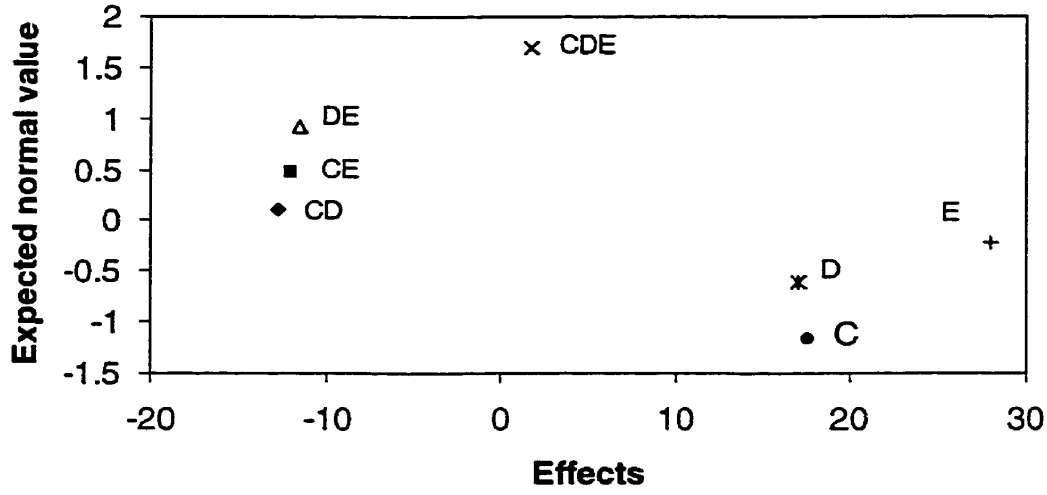

Figure 4.21: Normal probability plot in terms of glyoxal removal

(C: Chlorine; D: Temperature; E: Media)

Evaluation of significant effects/interactions by using F-test

Significant effects and interactions can also be evaluated using the F-test if the error of experiments is available. A formal error estimation can not be performed due to lack of repeated experiments in the experimental design. An approximate error, however, can be estimated by assuming that chlorine backwash does not impair the BOM removal in GAC biofilters. This assumption is reasonable based on the data already presented. A lack of effect is expected because GAC can react with free chlorine in the backwash water, mitigating the negative effects of chlorine on the biofilter performance.

The experimental errors were calculated by pooling the errors from GAC filters operated at high and low temperatures in blocks I and II. The standard deviation for F2 (GAC, high temperature) was obtained by considering the average BOM removal in F2 in blocks I and II as replicates. Similarly, the standard deviation for F4 (GAC, low temperature) was calculated by considering the average BOM removal in F4 in blocks I and II as replicates. Finally the experimental error was estimated by pooling the variances from both F2 and F4 (equal degrees of freedom).

Error estimation in terms of BOM removal in the GAC filters is listed in Table 4.6. Based on the estimated errors, the F- test at a 95% confidence level was performed and the results are given in Tables 4.7 to 4.10.

Table 4.6: Error Estimation in Terms of BOM Removal in GAC Filters

		Acetate	Formate	Formaldehyde	Glyoxal
BOM removal in F2 (%)	Block I	90.9	91.5	96.3	75.3
	Block II	90.4	91.8	93.5	80.7
BOM removal in F4 (%)	Block I	87.3	86.9	83.7	64.0
	Block II	91.8	91.4	93.5	80.8
SDEV (F2)		0.368	0.212	2.02	3.79
SDEV (F4)		3.20	3.20	6.96	11.9
SDEV (pool)		2.28	2.27	5.13	8.84

Table 4.7: F-test in Terms of Acetate Removal

	Effect	SS	df	MS	Fobs.	Significance
C (Chlorine)	11.58	268.3	1	268.3	51.6	Yes
D (Temp.)	10.02	200.7	1	200.7	38.6	Yes
E (Media)	12.48	311.6	1	311.6	59.9	Yes
CD	-9.43	177.9	1	177.9	34.2	Yes
CE	-9.07	164.4	1	164.4	31.6	Yes
DE	-8.93	159.6	1	159.6	30.7	Yes
CDE	7.42	110.0	1	110.0	21.2	Yes
Error			2	5.2		

Note: $F_{1,2,0.05} = 18.51$

Table 4.8: F-test in Terms of Formate Removal

	Effect	SS	df	MS	Fobs.	Significance
C (Chlorine)	15.4	473.2	1	473.2	91.9	Yes
D (Temp.)	16.5	542.4	1	542.4	105.3	Yes
E (Media)	16.6	553.3	1	553.3	107.5	Yes
CD	-14.0	393.8	1	393.8	76.5	Yes
CE	-13.3	352.1	1	352.1	68.4	Yes
DE	-14.0	391.0	1	391.0	76.0	Yes
CDE	11.6	269.9	1	269.9	52.4	Yes
Error			2	5.1		

Table 4.9: F-test in Terms of Formaldehyde Removal

	Effect	SS	df	MS	Fobs.	Significance
C (Chlorine)	22.3	990.1	1	990.1	36.2	Yes
D (Temp.)	23.3	1085.8	1	1085.8	39.7	Yes
E (Media)	21.1	886.2	1	886.2	32.4	Yes
CD	-19.5	760.5	1	760.5	27.8	Yes
CE	-16.0	508.8	1	508.8	18.6	Yes
DE	-17.0	578.0	1	578.0	21.1	Yes
CDE	16.0	512.0	1	512.0	18.7	Yes
Error			2	26.3		

Table 4.10: F-test in Terms of Glyoxal Removal

	Effect	SS	df	MS	Fobs.	Significance
C (Chlorine)	17.8	631.4	1	631.4	8.1	No
D (Temp.)	17.2	590.5	1	590.5	7.6	No
E (Media)	27.9	1557.1	1	1557.1	19.9	Yes
CD	-12.8	330.1	1	330.1	4.2	No
CE	-12.0	289.3	1	289.3	3.7	No
DE	-11.6	270.2	1	270.2	3.5	No
CDE	1.7	6.1	1	6.1	0.1	No
Error			2	78.1		

The F-test results show that all the effects and interactions are significant for acetate, formate and formaldehyde removal. However, the scenario of F–test conclusions is different for glyoxal removal. The error of the estimated glyoxal removal is much higher than that of other BOM components and the ability of the F–test to detect significant differences is closely related to the experimental errors. MS values in the F-test for glyoxal removal, are of the same magnitude as for other BOM components (except for the three-factor interaction CDE). The general lack of significance of main effects and interactions for glyoxal removal is mainly due to the larger fluctuations in glyoxal removal.

Pictorial illustration of the significant effects/interactions

Complicated interactions were observed both in the probability plots and the F-tests. These complex interactions are also further illustrated pictorially.

Significant interactions in terms of acetate removal are shown pictorially in Figures 4.22 to 4.23. The lines joining the points show trends to aid the reader, and do not necessarily imply a linear relationship.

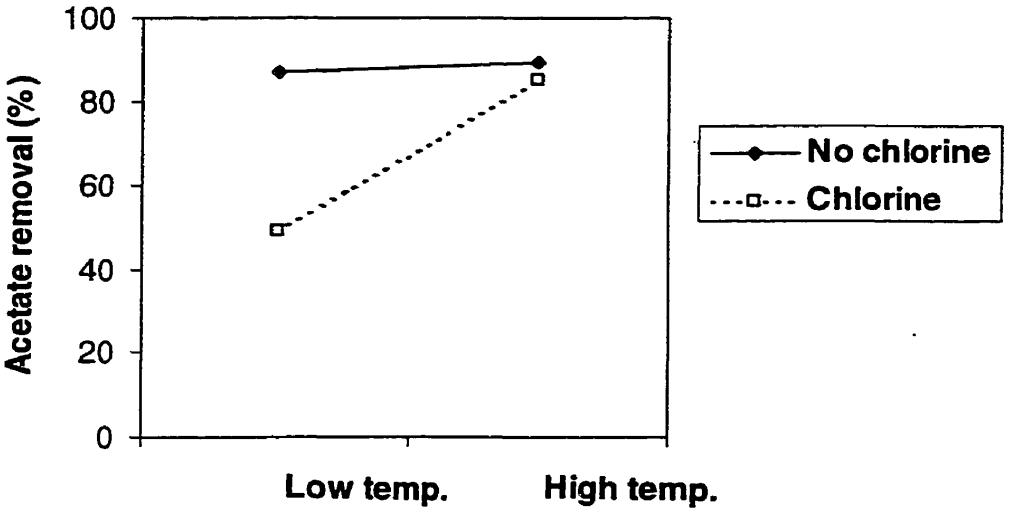

Figure 4.22: C D (chlorine and temperature) interactions for acetate removal (anthracite media)

In anthracite media filters (Figure 4.22), the temperature factor was significant when chlorine existed in the backwash water. Acetate removal received a little improvement as the temperature increased when chlorine was not in the backwash water. However, acetate removal increased significantly as the temperature increased when chlorine was in the backwash water.

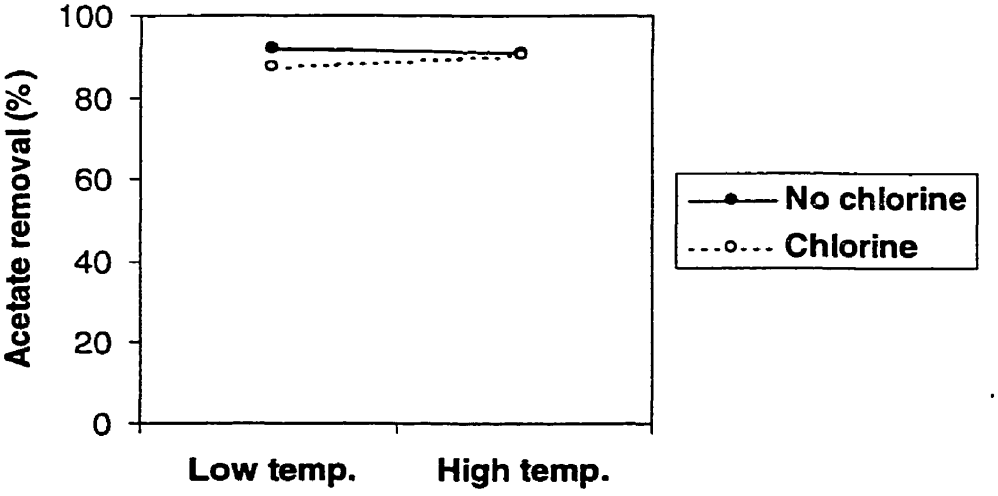

Figure 4.23: CD (chlorine and temperature) interactions for acetate removal (GAC media)

In GAC media filters (Figure 4.23), the CD interaction (temperature and chlorine) was minor. The increase of temperature did not improve the acetate removal significantly in GAC biofilters backwashed with or without chlorine in the backwash water.

Similar conclusions were obtained for formate and formaldehyde removal. These interactions are shown in Figures 4.24 to 4.27.

Glyoxal is a special component in the BOM cocktail. Different BOM removal behaviours were found in Figures 4.28 and 4.29 than for the other substrates. High temperature was generally beneficial to glyoxal removal in either the chlorine or non-chlorine cases. In anthracite filters, the temperature effect was more significant when chlorine existed in the backwash water. In GAC filters, however, the temperature effect was not as significant when chlorine existed in the backwash water.

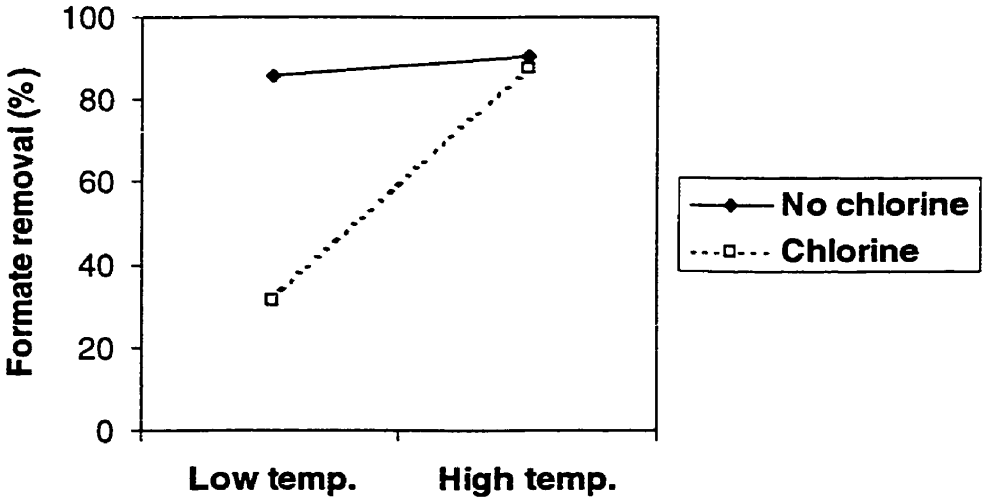

Figure 4.24: CD (chlorine and temperature) interactions for formate removal (anthracite media)

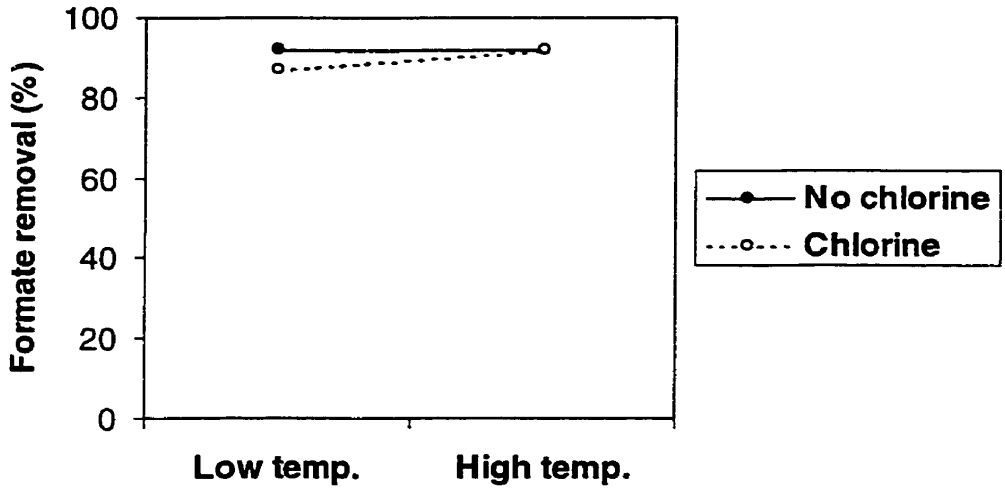

Figure 4.25: CD (chlorine and temperature) interactions for formate removal (GAC media)

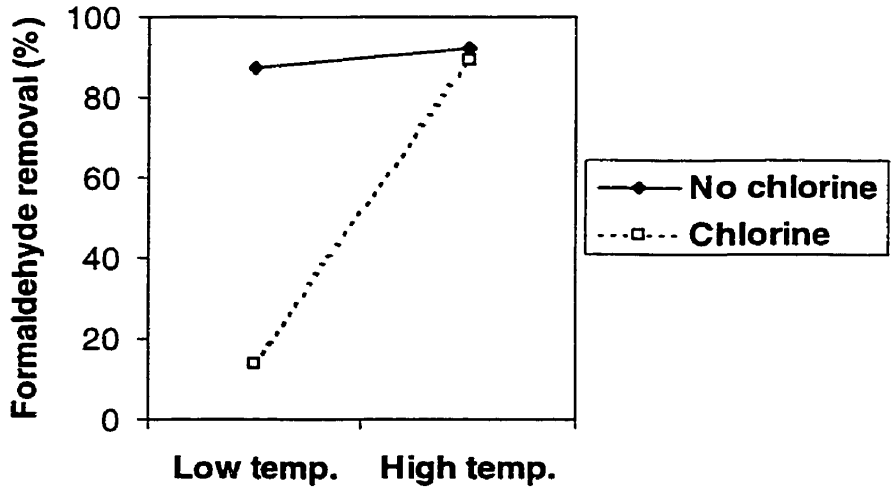

Figure 4.26: CD (chlorine and temperature) interactions for formaldehyde removal (anthracite media)

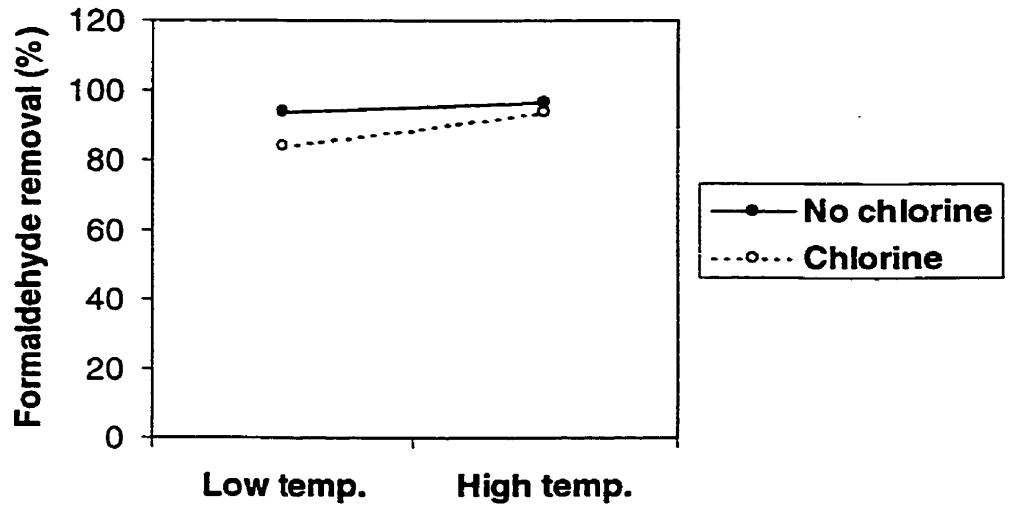

Figure 4.27: CD (chlorine and temperature) interactions for formaldehyde removal (GAC media)

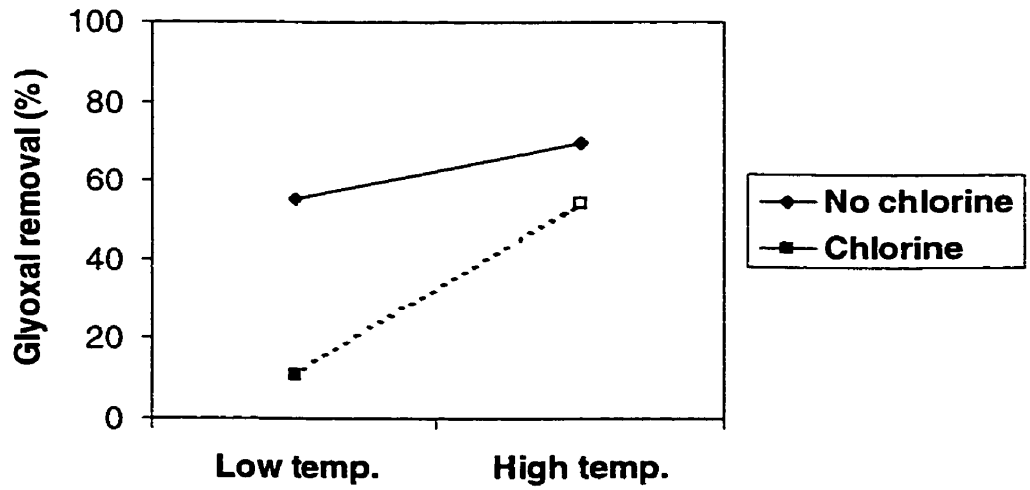

Figure 4.28: CD (chlorine and temperature) interactions for glyoxal removal (anthracite media)

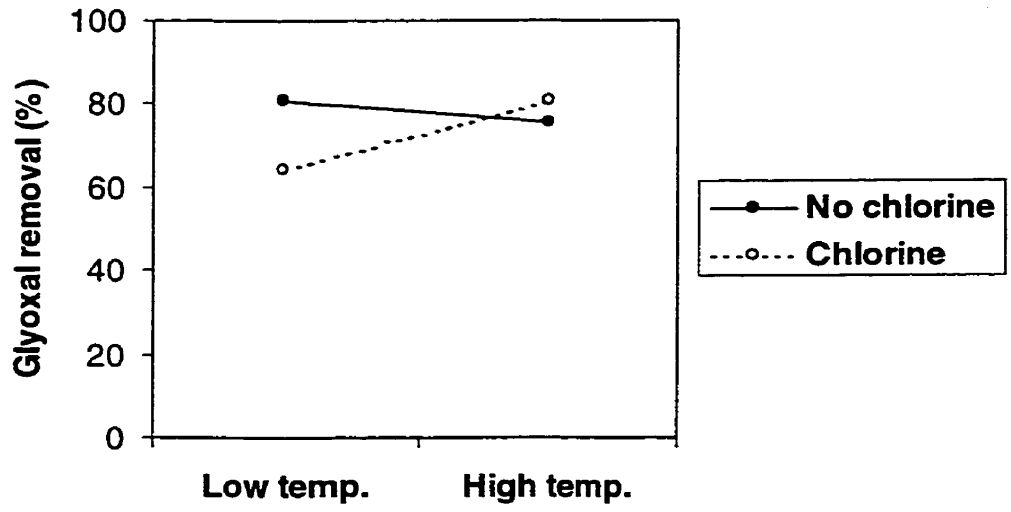

Figure 4.29: CD (chlorine and temperature) interactions for glyoxal removal (GAC media)

4.3.4 Multiple linear regression models

By assuming that the effects of factors A (particles), F (coagulant) and B (air scour) are minor, multiple linear regression models for factors C, D, E and their interactions, in terms of steady-state BOM removal, can be obtained using linear regression techniques (e.g., Rawlings, 1988).

Source data for multiple regression models includes BOM removal and assigned values for factors C (chlorine in the backwash water), D (temperature) and E (media) and their interactions in phases I, II and III (F1/F2/F3/F4) (Phase III will be discussed in Chapter 5). The factor C in phase III was assigned a value of 0 because the chlorine dosage in the backwash water was 0.25 mg/L, which was in the middle of the two levels of the variable used in phases I and II (0 mg/L: 1, 0.5mg/L: -1). Similarly, the factor C in the case of chloramine (dosage: 0.25 mg/L) in the backwash water was assigned a value of 0.99, by

assuming that the disinfection efficiency of free chlorine is 100 times that of chloramine (refer to Appendix C). This assumption was based on the effectiveness of inactivation of specific microorganisms (Montgomery, 1985). Effectively this means that a dosage 0.25 mg/L chloramine had essentially the same coded value as a dose of 0 mg/L free chlorine (0.99 vs. 1.0, respectively).

General form of multiple linear regression models

The general form of multiple linear regression models is described in equation 4.1:

$$Y = X*\beta + \varepsilon \qquad (4.1)$$

Where, Y is the matrix of predicted values; X denotes the matrix of assigned values of the variables; β represents the matrix of coefficients; and ε is the error (the difference between measured and predicted values).

The detail of the model regression process is given in Appendix C.

The regressed models are listed in equations (4.2) to (4.5). The variables are expressed as their coded values. For the coded values of chlorine in the backwash water (Cl_2), temperature (T) and media, please refer to Table 4.1.

Model for acetate: Based on steady-state acetate removal

$$Y_i = 81.6 + 5.3[Cl_2]_i + 5.8[T]_i + 8.5\,[Media]_i - 4.9[Cl_2*T]_i - 4.0[Cl_2*Media]_i - 5.3[T*Media]_i + 3.9[Cl_2*T*Media]_i + error \qquad (4.2)$$

Model for formate: Based on steady-state formate removal

$$Y_i = 80.8 + 7.6[Cl_2]_i + 8.5[T]_i + 9.6\,[Media]_i - 7.2[Cl_2*T]_i - 6.5[Cl_2*Media]_i - 7.3[T*Media]_i + 6.0[Cl_2*T*Media]_i + error \qquad (4.3)$$

Model for formaldehyde: Based on steady-state formaldehyde removal

$$Y_i = 82.0 + 11.1\,[Cl_2]_i + 11.2\,[T]_i + 9.8\,[Media]_i - 9.8[Cl_2 * T]_i - 7.9[Cl_2 * Media]_i - 8.1[T * Media]_i + 8.0[Cl_2 * T * Media]_i + error \quad (4.4)$$

Model for glyoxal: Based on steady-state glyoxal removal

$$Y_i = 62.3 + 11.3[Cl_2]_i + 11.3[T]_i + 12.9[Media]_i - 5.6\,[Cl_2 * T]_i - 8.4[Cl_2 * Media]_i - 8.5[T * Media]_i + 0.0[Cl_2 * T * Media]_i + error \quad (4.5)$$

The overall regression significance tests are given in Tables C.4 to C.7 of Appendix C. At a 95% confidence level, the overall regression is significant for formate ($F_{observed} = 27.9$ vs. $F_{7,4,0.05\ table} = 6.09$) and formaldehyde ($F_{observed} = 91.4$ vs. $F_{7,4,0.05\ table} = 6.09$) removal, but not significant for acetate ($F_{observed} = 5.3$ vs. $F_{7,4,0.05\ table} = 6.09$) and glyoxal ($F_{observed} = 5.9$ vs. $F_{7,4,0.05\ table} = 6.09$) removal. However, the overall regression F-values for acetate and glyoxal removal were very close to the significance level.

Residual plots are also shown in Appendix C (Figures C.1 to C.4). There were no significant patterns missed in the model. The largest residual occurred when the percent removal was low, which was the case in F3. BOM removal in F3 as the "worst case" scenario in all phases was relatively unstable compared to other filters.

In general, the multiple regression models can be used to roughly predict BOM removal for given circumstances (various operating conditions).

Model interpretation

In addition to their use of predicting BOM percent removal at given operating conditions, these models can also be used to evaluate the importance of various factors in drinking water biofiltration.

The media is one of the important design parameters in drinking water biofiltration. It can be separated from the other parameters by substituting the assigned value of negative 1

for anthracite media and a value of positive 1 for GAC media. The model described in equations 4.2 can then be simplified into equations 4.6 and 4.7:

Acetate removal in anthracite filters:

$$Y_i = 73.1 + 9.3[Cl_2]_i + 11.1[T]_i - 8.8[Cl_2 * T]_i + \text{error} \quad (4.6)$$

Acetate removal in GAC filters:

$$Y_i = 90.1 + 1.3[Cl_2]_i + 0.5[T]_i - 1.0[Cl_2 * T]_i + \text{error} \quad (4.7)$$

In anthracite filters, acetate removal is influenced by factor C (chlorine in the backwash water), D (temperature) and their interaction CD as shown by the relatively large coefficients of C, D and CD in equation 4.6. Backwashing with chlorine substantially impacted BOM removal in anthracite filters operated at the low temperature (C = -1, D = -1). In GAC filters, however, acetate removal is approximately independent of factor C, D and their interaction CD because of the much smaller coefficients of C, D and CD in equation 4.7.

Similarly, the models 4.3, 4.4 and 4.5 can be simplified to equations 4.8/4.9, 4.10/4.11 and 4.12/4.13, respectively:

Formate removal in anthracite filters:

$$Y_i = 71.2 + 14.1[Cl_2]_i + 15.8[T]_i - 13.2[Cl_2 * T]_i + \text{error} \quad (4.8)$$

Formate removal in GAC filters:

$$Y_i = 90.4 + 1.1[Cl_2]_i + 1.2[T]_i - 1.2[Cl_2 * T]_i + \text{error} \quad (4.9)$$

Formaldehyde removal in anthracite filters:

$$Y_i = 72.2 + 19.0[Cl_2]_i + 19.3[T]_i - 17.8[Cl_2 * T]_i + \text{error} \quad (4.10)$$

Formaldehyde removal in GAC filters:

$$Y_i = 91.8 + 3.2[Cl_2]_i + 3.1[T]_i - 1.8[Cl_2 * T]_i + \text{error} \quad (4.11)$$

Glyoxal removal in anthracite filters:

$$Y_i = 49.4 + 19.7[Cl_2]_i + 19.8[T]_i - 5.6[Cl_2 * T]_i + \text{error} \quad (4.12)$$

Glyoxal removal in GAC filters:

$$Y_i = 75.2 + 2.9[Cl_2]_i + 2.8[T]_i - 5.6[Cl_2 * T]_i + \text{error} \quad (4.13)$$

The impacts of factors C (chlorine in the backwash water), D (temperature) and their interaction CD on the removal of formate, formaldehyde and glyoxal were similar to those on the removal of acetate. The interaction CD may affect glyoxal removal in GAC filters to a certain extent (equation 4.13). The relatively larger coefficients (in comparison to the constant) in equation 4.12 indicate that glyoxal removal was more sensitive to unfavourable conditions than were the other BOM components.

4.5 CONCLUSIONS

Conclusions from BOM removal in the initial periods for phases (blocks) I and II include the following:

- Biofilters reached steady-state BOM removal in about one month, depending on their operating conditions.
- Less time was required to reach steady-state for GAC biofilters backwashed with non-chlorinated water and run at high temperature.

The following major conclusions were drawn from steady-state BOM removal experimental results in phases I and II, and they were also illustrated in multiple linear regression BOM removal models for anthracite and GAC filters (except for the last conclusion in this section).

- GAC filters were able to tolerate chlorine backwash, even operated at low temperature (5 °C). Good BOM removal was achieved in GAC filters regardless of the unfavourable operating conditions (such as low temperature and chlorine backwash).

- In anthracite media filters, however, the temperature effect was significant when chlorine existed in the backwash water. Backwashing with chlorine substantially impacted BOM removal in anthracite filters operated at low temperature (5 °C).
- Glyoxal as a special component in the BOM cocktail was more sensitive to the changes of operating conditions in biofilters.
- High temperature was more beneficial to recalcitrant BOM component (such as glyoxal) removal than to more easily degradable BOM component removal.
- The higher levels of phospholipid biomass generally mean the better BOM removal, however, the capacity of BOM removal is not proportional to the amount of phospholipid biomass in biofilters.

Based on the analysis of probability plots, F-tests and pictorial interactions, the following important findings and conclusions were drawn:

- All of the effects (media, temperature and chlorine in the backwash) and their interactions were significant (except for some cases of glyoxal removal).
- Complicated interactions existed among the three factors.

The multiple linear regression models developed in this research can be used to approximately predict BOM removal in filters under different operating conditions, by assigning a value to each variable according to the definition of the variables.

The following operating conditions are recommended for water utilities for the operation of biofilters:

- In biofilters with GAC media, backwashing without chlorine is recommended but not mandatory, to achieve good BOM removal. Backwashing without chlorine and high temperature (20 °C) can help to increase the removal of recalcitrant components (such as glyoxal).
- In biofilters with anthracite media, backwashing without chlorine is strongly recommended, since chlorine can reduce recalcitrant BOM component removal significantly, especially at low temperature (5 °C). High temperature (20 °C) can enhance the removal of recalcitrant components.

The significant interactions among anthracite media, chlorine backwash and temperature are worthy of further investigation.

All significance tests in this study were based on the assumption that factors A (particles), F (coagulant) and B (air scour) had minor effects. It is necessary to assess this assumption with further experiments. This is one of the objectives of the next chapter.

CHAPTER 5: FURTHER EVALUATION OF FACTORS AFFECTING DRINKING WATER BIOFILTRATION PROCESSES

5.1 INTRODUCTION

Based on the assumption that the effects of air scour, particles and coagulant are minor, significant effects and interactions were evaluated from factorial design experiments in Chapter 4. As described in Chapter 2, the reasonableness of the assumption was supported by most of the previous studies. However, it was considered important to assess these assumptions by further experimental work. This was an important objective of this Chapter.

Different factors affecting BOM removal performance in bioflilters have been described in Chapter 2. Deeper insights into the mechanisms of biofiltration processes, and optimization of the design and operation of biofilters, can be expected from a comprehensive evaluation of these factors.

Experimental results from Chapter 4 indicate that temperature, chlorine backwash and media are significant factors. A typical significant interaction was temperature and chlorine backwash in anthracite filters. As mentioned in Chapter 2, different studies have examined the individual significant factors, and they have been well discussed in a

critical review paper (Urfer *et al.*, 1998). However, the investigation of significant two or three-factor interactions is very limited. Thus an additional important objective of this chapter was to examine the important chlorinated backwash water/temperature interactions observed in Chapter 4. For this reason, only anthracite filters were used in the work described in this chapter.

The impact of EBCT on BOM removal in biofilters was not evaluated directly in the fractional factorial design experiments (Chapter 4), because this is a special variable for which several levels (at different depths) can be examined. EBCT is related to both the depth of media and the hydraulic loading rate in biofilters. EBCT impacts were investigated in all three phases of the experiments and discussed in this chapter.

The concept of bed utilization in biofilters (the ratio or portion of media bed in which there is substantial BOM removal) introduced in this chapter can be used to evaluate in a deeper way the factors affecting BOM removal. The concept of bed utilization in biofilters is useful for the design and operation of biofilters.

BOM removal in a biofilter run may be affected by the event of backwashing (Hozalski, 1996). For single stage biofilters, backwashing is used to remove non-biological particles and biomass. Backwashing can remove part of the biomass in biofilters and this biomass may be disinfected/inactivated by chlorine or chloramine in the backwash water. The removal and disinfection of biofilms on the biofilter media during periodic backwashing of biofilters, and the refreshment of biomass following a cleaning event, may affect the BOM removal performance in a filter run. However, a full-scale biofiltration study by Huck *et al.* (1998) showed that backwashing may not be a major effect on BOM removal in a biofilter run. Further modeling by Hozalski *et al.* (1998) also indicated that backwashing with up to 40%-50% biomass loss would not significantly affect BOM removal in the following filter run. The effect of backwashing on BOM removal in a biofilter run was also evaluated in this chapter.

Hydraulic loading rate steps (and /or BOM steps) may affect BOM removal performance in biofilters (Carlson *et al.*, 1998). The BOM concentration in filter influents and hydraulic loading rate affect the BOM loading to a biofilter. The response of BOM removal to rapid BOM changes (such as could occur in highly variable source water) or hydraulic loading rate steps is largely dependent on the removal capacity of the existing biofilm in the biofilters. However, the longer term BOM and/or hydraulic loading rate steps will lead to a new pseudo steady-state of the biofilters under new operating conditions. The time to reach a new pseudo steady-state BOM removal profile and biomass distribution in biofilters will be dependent on the changes in BOM influent concentration or hydraulic loading rate. By examining BOM and hydraulic changes, the results in this chapter are helpful for predicting the influences of BOM concentration and hydraulic loading rate steps on BOM removal performance in biofilters.

Temporary shutdown of biological filters may also impact the BOM removal performance. Niquette *et al.* (1998) indicated that shutdown of biological filters promoted anaerobic conditions that reduced the density of fixed bacteria and the quality of water inside the filter. Huck *et al.* (1996) observed elevated concentrations of endotoxins when bringing pilot scale biological filters back on-line after a few days of being out of service. It is of importance for both biofilter design and operation to investigate the impacts of regular maintenance and emergency shutdown of biofilters. Those are also addressed in this Chapter.

5.2 OBJECTIVES

The specific objectives of the research described in this chapter are:

- to evaluate the assumption that air scour, particle and coagulant effects are minor;
- to further investigate the observed significant interaction of temperature and chlorine backwash;
- to evaluate the EBCT effect on BOM removal performance in biofilters;

- to assess the impacts of BOM /HLR steps and filter shutdown on BOM removal performance in biofilters (evaluated in short term experiments at the end of this phase);
- to collect and interpret information regarding the effects of biofilm detachment/disinfection during backwash and biomass accumulation on BOM removal in a filter run;
- to evaluate the effects of longer term operation on biofilter BOM removal performance.

5.3 EXPERIMENTAL DESIGN

Table 5.1 summarises experiments in phase III. The design of these experiments is based on the aforementioned objectives.

Four anthracite filters were used in these experiments. Filters 1 and 2 were operated at high temperature (20 °C), and Filters 3 and 4 at low temperature (5 °C). Chlorine or chloramine was added to the backwash water at a dosage of 0.25 mg/L as free chlorine or combined chlorine (as monochloramine). To provide additional information, this dosage was half that used in Chapter 4. Also it will be recalled that chloramine was not included in Chapter 4 (phase I and II experiments). When added, the dosages of particles and coagulant in phase III were the same as in phases I and II (particle at 2 mg/L; coagulant at 3 mg/L). The same hydraulic loading rate and air scour procedure were practised in phase III as in phases I and II (refer to Chapter 3).

Phase III was divided into four periods as described in Table 5.1. Periods I to III were mainly designed to assess the assumption that the effects of particle, coagulant and air scour on BOM removal in biofilters are minor. The impacts of EBCT and filter backwash on BOM removal were investigated during the entire phase III. The influences of a BOM

step (100 % increase from the normal influent concentration), an HLR step (50% increase from the normal hydraulic loading) and filter shutdown on BOM removal performance were carried out in period IV, after all pseudo steady-state experiments had been completed.

Table 5.1: Experimental Design in Phase III

Period	Filter	Media	Temperature*	Backwash	Particle/coagulant
IA (day 0 – 157)	F1	Anthracite	High	Chlorine + air	No
	F2	Anthracite	High	Chloramine + air	No
	F3	Anthracite	Low	Chlorine + air	No
	F4	Anthracite	Low	Chloramine + air	No
II (day 158 - 197)	F1	Anthracite	High	Chlorine	No
	F2	Anthracite	High	Chloramine	No
	F3	Anthracite	Low	Chlorine	No
	F4	Anthracite	Low	Chloramine	No
IB (day 198 - 230)	F1	Anthracite	High	Chlorine + air	No
	F2	Anthracite	High	Chloramine + air	No
	F3	Anthracite	Low	Chlorine + air	No
	F4	Anthracite	Low	Chloramine + air	No
III (day 231 - 245)	F1	Anthracite	High	Chlorine + air	Particle
	F2	Anthracite	High	Chloramine + air	Particle/coagulant
	F3	Anthracite	Low	Chlorine + air	Particle/coagulant
	F4	Anthracite	Low	Chloramine + air	Particle
IC (day 245 - 318)	F1	Anthracite	High	Chlorine + air	No
	F2	Anthracite	High	Chloramine + air	No
	F3	Anthracite	Low	Chlorine + air	No
	F4	Anthracite	Low	Chloramine + air	No

*High =20 °C, Low = 5 °C

The air scour effect was evaluated by comparing steady-state BOM removal in period IA (with air scour) to period II (without air scour). After period II, the filter operation was switched back to the starting conditions (period IB) to re-establish the baseline. Particle and coagulant effects were then assessed by making a comparison between period IB (day 198-230) and period III (day 231 – 245).

After period III, filter operation was switched back to the starting period I (as in Table 5.1, IC). In this period, the effects of BOM/HLR steps and filter shutdown were investigated. Filters were switched back to period IC conditions for at least one week for the refreshment of the original pseudo steady-state, before starting the tests of each operating scenario. One week was considered sufficient for biofilters to become restored to the original pseudo steady-state since the effect of particle/coagulant on BOM removal from previous studies was negligible (refer to Chapter 2).

For a detailed description of filtration apparatus and analytical methods (BOM, biomass, HPC) in this study, please refer to Chapter 3.

As mentioned before, the impacts of EBCT and filter backwash on BOM removal were investigated in phases I, II and III through the entire experimental investigations. All these results are presented in this chapter.

5.4 RESULTS AND DISCUSSION

BOM (as acetate, formate, formaldehyde and glyoxal) removal results in phase III are presented in Figures 5.1 to 5.4 (actual influent and effluent concentrations are tabulated in Appendix D). The effects of HLR/BOM steps and shutdown on BOM removal performance were investigated during the period IC (after 245 days).

5.4.1 Overall evaluation of biofilter performance in longer term operation

Biofilters in phase III were operated for more than 300 days before shutdown. Longer term effects on biomass accumulation characteristics and BOM removal could therefore be assessed.

In general, the BOM removal in biofilters operated at high temperature reached a pseudo steady-state faster than the biofilters run at low temperature. More time was required to achieve the pseudo steady-state in biofilters with chlorine in the backwash water than with chloramine in the backwash water, especially when the biofilters were operated at low temperature (i.e. the effect of chlorine was more pronounced at the lower temperature). This also indicates that more time is needed for biomass to develop and acclimate to low temperature or to chlorine in the backwash water.

The number of days to reach pseudo steady-state BOM removal in phase III are listed in Table 5.2. All values were obtained by inspection. For comparison, the number of days for anthracite filters in phases I and II are included in the table. A shorter period of time was required to achieve the pseudo steady-state BOM removal in the biofilters operated at the high temperature than at the low temperature. Less time was needed for the biofilters to reach the pseudo steady-state BOM removal in terms of easily degradable BOM (acetate, formate and formaldehyde: Figures 5.1, 5.2 and 5.3) than less easily degradable BOM (glyoxal: Figure 5.4). It was difficult to define the pseudo steady-state removal of glyoxal in F3 due to the low percent removal level. A longer period of time was required for chlorine than for chloramine backwashed filters in terms of easily degradable BOM at low temperature, and a longer period of time was required at the low than at the high temperature in terms of less easily degradable BOM (glyoxal).

The number of days required to reach the pseudo steady-state BOM removal was influenced by filter media, temperature, chlorinated backwash water and the biodegradability of the BOM components. A longer period of time was required for biofilters to reach pseudo steady-state BOM removal under unfavourable conditions (e.g.

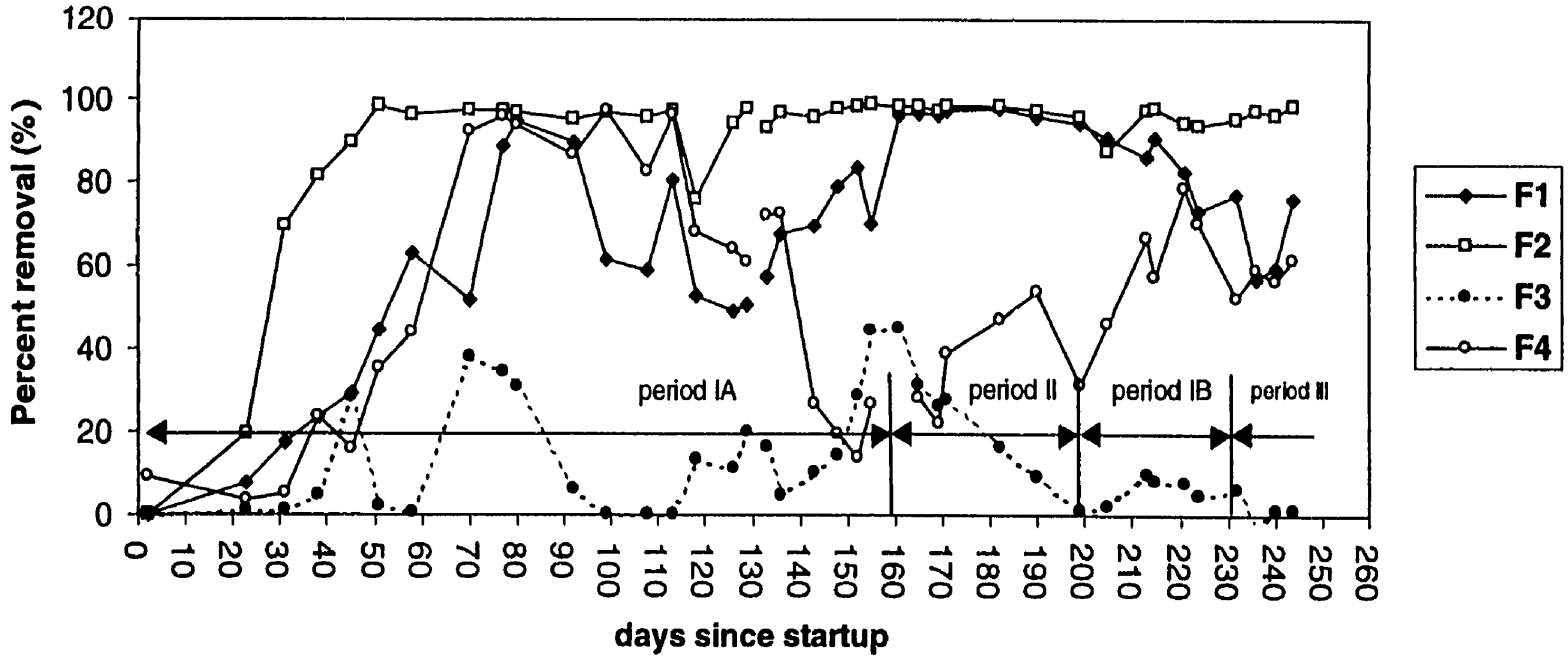

Figure 5.4: Glyoxal removal in biofilters during phase III

F1 (anthracite, chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

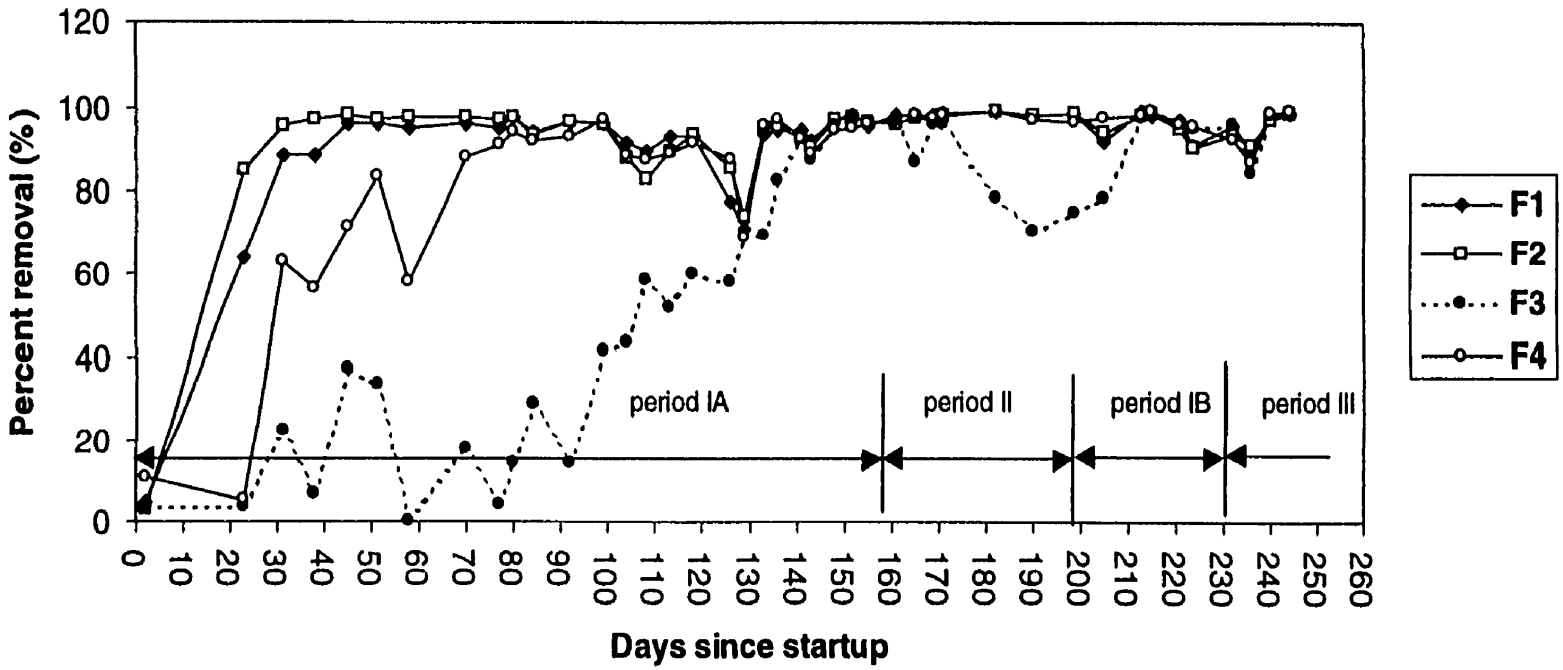

Figure 5.3: Formaldehyde removal in biofilters during phase III

F1 (anthracite, chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

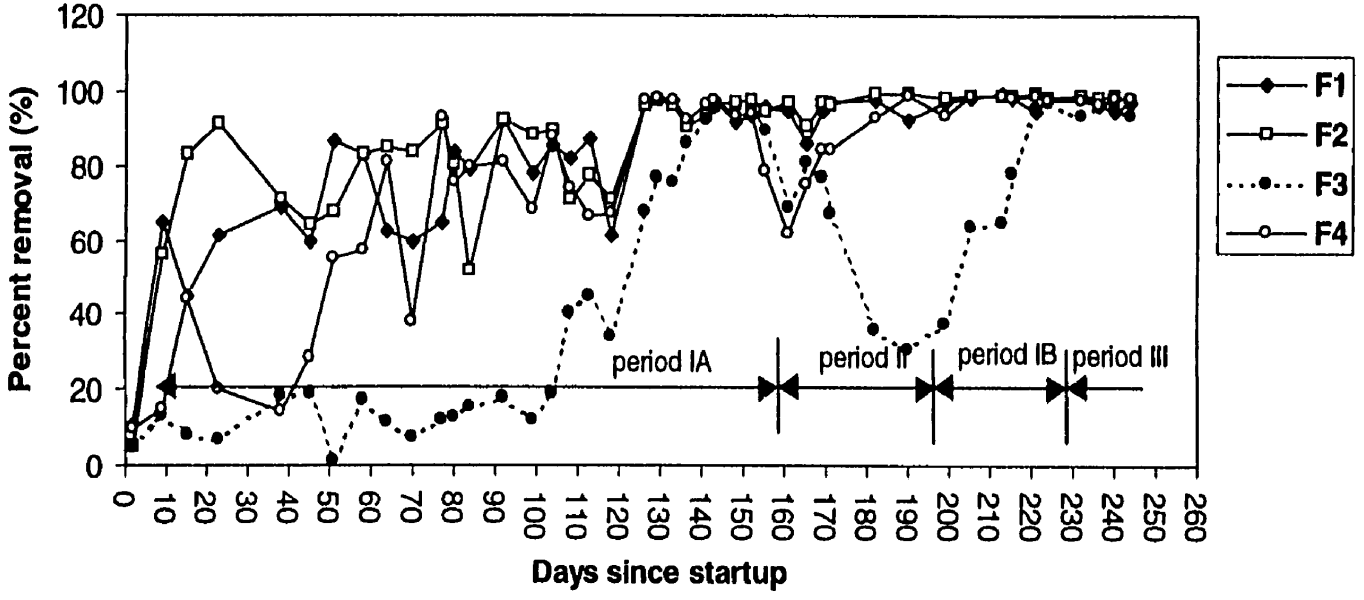

Figure 5.2: Formate removal in biofilters during phase III

F1 (anthracite, chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

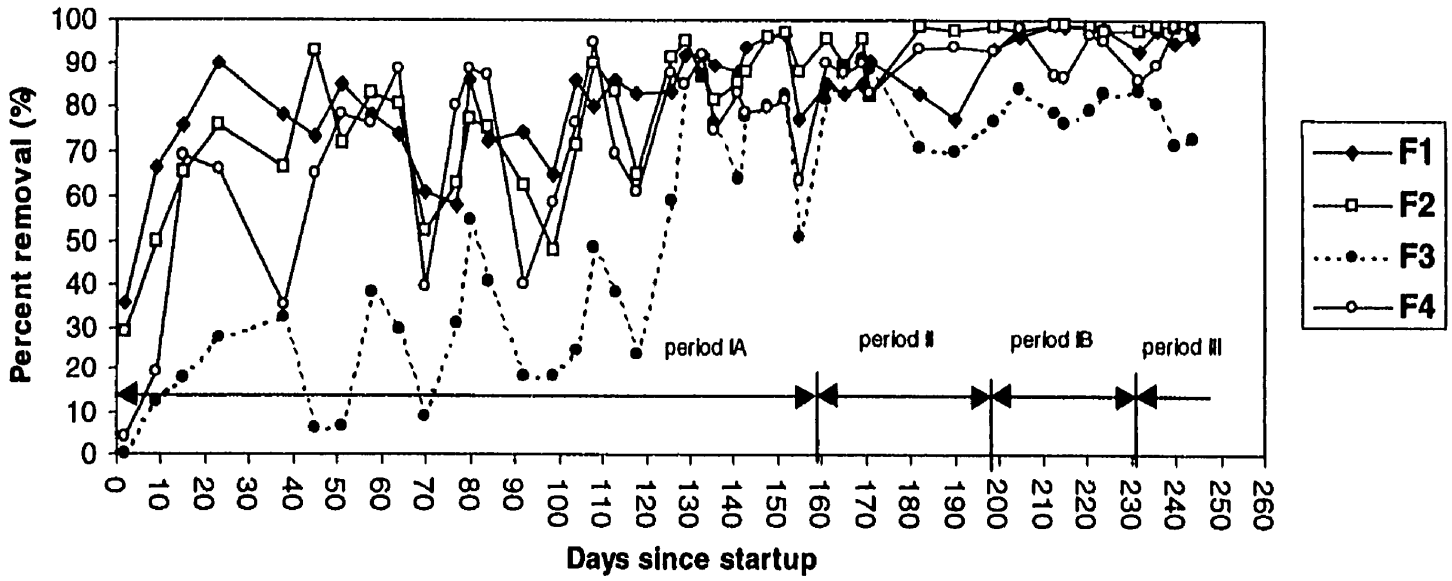

Figure 5.1: Acetate removal in biofilters during phase III

F1 (anthracite, chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

Table 5.2: Number of Days to Reach Pseudo Steady-state BOM Removal in Anthracite/sand Biofilters (by inspection)

Phase	BOM	F1	F2	F3	F4
I	Easily biodegradable	~20	~20	~20-40	~20-30
	Less biodegradable	~40	~40	NA	~60
II	Easily biodegradable	20-50	20-50	~60	20-60
	Less biodegradable	~80	~30	NA	40-80
III	Easily biodegradable	30-40	30-40	~140	50-80
	Less biodegradable	~80	~30	NA	~80

Phase I: F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

Phase II: F1 (Anthr., chlorine, high temp.); F2 (GAC, chlorine, high temp.); F3 (Anthr., no chlorine, low temp.); F4 (GAC, no chlorine, low temp.)

Phase III: F1 (anthracite, chlorine, high temp.); F2 (anthracite, chloramine, high temp.); F3 (anthracite, chlorine, low temp.); F4 (anthracite, chloramine, low temp.)

NA: not available

anthracite media, low temperature, chlorine in the backwash water, less easily biodegradable BOM components) than under favourable conditions (e.g. GAC media, high temperature, no chlorine in the backwash water, easily biodegradable BOM components). In general, a period of 20-40 days was needed for biofilters operated at higher temperatures in terms of the easily biodegradable BOM component removal. This was in a similar range of that from a full-scale study (ozonated filter influent, filter backwashed with chlorinated water) reported by Coffey et al. (1995). Hozalski (1996) predicted a substantially shorter time (less than 10 days) to reach pseudo steady-state BOM removal in his model by assuming a constant biomass loss during backwashing and no chlorine in the backwash water. For biofilters operated at lower temperatures in terms of the easily biodegradable BOM component removal, approximately 20-60 days is needed; A greater variance of time was observed for biofilters in terms of less biodegradable BOM components (e.g., glyoxal).

For biofilters operated at the low temperature, more time was needed to reach the pseudo steady-state BOM removal in phase III than in phases I and II. This may be due to general higher chlorine residual in the filter influent in phase III caused by the tap water source changes (more surface water in the tap water).

Although all filters operated were subjected to unfavourable operating conditions such as chlorine/chloramine in the backwash water, the biomass and BOM removal in biofilters operated at low temperature were more sensitive to chlorine residual fluctuations in the filter influents (around day 190 in Figures 5.2 and 5.3, the chlorine residual during that time was close to 0.1 mg/L, higher than the normal level of much less than 0.1 mg/L in total, the laboratory tap-water was monitored for these relatively infrequent fluctuations).

Results (Figure 5.4) indicate that glyoxal removals were more sensitive than those of other BOM components. This is in agreement with the results from other studies (Booth, 1998; Urfer, 1998 and Coffey *et al.*, 1995). In the present study, it was found that glyoxal removal is sensitive to unfavourable operating conditions such as low temperature and chlorine in the backwash water. Good glyoxal removal was not achieved, even after 280 days, in biofilters operated at low temperature with chlorine in the backwash water. Thus, chlorine in the backwash water had a detrimental effect on the removal of "recalcitrant" BOM components. "Steady-state" glyoxal removal in F4 (low temperature, chloramine backwash) was subject to fluctuations during the entire operating period of phase III (Figure 5.4). A possible explanation is that the biomass in biofilters operated at low temperature is not as robust as that developed at high temperature.

Acetate, formate and formaldehyde removals in Filter 3 (low temperature, chlorine in the backwash water) were lower than in the other three filters in the first four months (~130 days). After longer term operation (>130 days), however, acetate, formate and formaldehyde removals in Filter 3 reached a similar level to that of the other filters during the remainder of period IA (Figures 5.1 to 5.3). In general, there was no major difference for acetate, formate and formaldehyde removal in all filters except for filter F3, although filter F4 took longer to reach pseudo steady-state. This means that similar

acetate, formate and formaldehyde removals can be achieved, even in filters operated at low temperature and backwashed with chloraminated water. However, the removal pattern within the biofilters might be different due to the fact that a greater depth of the bed (corresponding to a higher bed utilization) may be used for BOM removal in biofilters operated under unfavourable conditions such as low temperature and/or chlorine in the backwash water. This suggests that it might be inappropriate to evaluate the impacts of significant factors on BOM removal performance by only using the effluent concentrations of biofilters. It is also of importance to include the BOM removal profiles as a function of depth. This may be helpful in explaining why the conclusions obtained from different studies, as reviewed in Chapter 2, might be different.

Chloramine in the backwash water (0.25 mg/L) did not substantially impact BOM removal in biofilters operated at both high and low temperatures. This is likely because chloramine as a disinfectant for bacteria is much weaker than chlorine (e.g., wolf *et al.*, 1984). In contrast to this general conclusion, if the bacteria are attached on reactive media such as GAC or iron pipes, chloramine might show more effective inactivation of biofilm organisms than chlorine (LeChevallier *et al.*, 1990; LeChevallier *et al.*, 1992). This phenomenon is due to the consumption of the chlorine by the chemical reactions occurring between media and free chlorine.

In biofilters operated at high temperature, chlorine in the backwash water did not seem to affect the removal of "easily biodegradable" BOM components (acetate, formate and formaldehyde) (Figures 5.1 to 5.3), but it impacted the removal of recalcitrant BOM components (glyoxal) to some extent (Figure 5.4).

In biofilters run at low temperature, chlorine in the backwash water impacted the time to reach steady-state BOM removal (for acetate, formate, and formaldehyde), the steady-state removal level (for acetate, F3), the steady-state removal fluctuations (formate, formaldehyde, F3), and the removal level of "recalcitrant" BOM components (glyoxal, F3).

Mature biofilms were developed in biofilters after long term operation (e.g. >200 days). These biofilms showed a substantial resistance to unfavourable operating conditions. For example, biofilms were able to withstand the filter shutdown, BOM/HLR steps without losing significant BOM removal capacity (refer to sections 5.4.5 and 5.4.6 in this chapter).

BOM removal in the last 32 days of Period IA was used to represent the pseudo steady-state performance in this period. The length of time for BOM removal performance in other periods was similar.

The same operating conditions applied to period IA and IB (period IB was used to re-establish baseline prior to proceeding to period III). In most cases, there were no significant differences for BOM removal between period IA and IB (refer to Appendix D).

5.4.2 Effects of air scour/particle/coagulant

The evaluation of air scour and particle/coagulant effects was performed by comparing the BOM removal in period IA and period II, and period IB and period III, respectively. In period II air scour was discontinued (Table 5.1) while in period III particles or particles and coagulants were added to each filter.

Effect of air scour

The average pseudo steady-state BOM removal in period IA and II is listed in Table 5.3. The t-test results (the 5% significance level, two-sided test) are summarised in Table 5.4. The detailed t-test results can be found in Appendix E. For certain components in some filters, removals were not considered to be at pseudo steady-state. Although the t-tests were performed, these comparisons are denoted an asterisk in the table.

At the high temperature, results of the t-test at 5% significance level in Table 5.4 demonstrate that air scour effects are not significant or barely significant in terms of easily biodegradable BOM component removal. However, the less easily degradable BOM (glyoxal) removal is influenced by air scour in filters backwashed with chlorinated water.

At the low temperature, results of the t-test at 5% significance level in Table 5.4 show a complicated conclusions: air scour effects are significant in terms of BOM removal in biofilters backwashed with chloramine (a much weaker disinfectant). BOM removal in filter 3 and glyoxal removal in filter 4 was fluctuating state (not at pseudo steady-state), therefore, the results of the t-test in Table 5.4 under those circumstances were not so useful.

The results in this study are similar to those reported in previous studies (e. g. Miltner *et al.*, 1995; Coffey *et al.*, 1996; Carlson *et al.*, 1998; Hozalski and Bouwer, 1998). It is more likely that air scour affects BOM removal in biofilters run at low temperature and backwashed with chlorinated water. In those "worst case" scenarios, the amount of biomass in biofilters is crucial to BOM removal performance, and vigorous biomass detachment caused by backwashing might affect BOM removal to a larger extent. However, the BOMremoval results in Filter 3 did not demonstrate such a difference.

Table 5.3: The Average Pseudo Steady-State BOM Removal in Period IA and II(%)*

		Period IA (day 133-157)				Period II (day 158-197)			
		F1	F2	F3	F4	F1	F2	F3	F4
Aetate	Avg.	90.2	88.9	73.9	78.9	83.8	92.6	81.7	89.4
	Std. Dev.	6.7	5.7	12.4	8.6	4.2	5.8	9.4	4.0
Formate	Avg.	95.6	95.4	89.7	93.0	93.9	96.8	60.1	83.1
	Std. Dev.	2.4	2.5	6.9	6.5	4.3	3.0	21.7	12.8
Formaldehyde	Avg.	95.5	95.3	88.9	94.8	98.7	98.1	87.8	98.6
	Std. Dev.	6.6	4.1	14.5	3.5	0.5	0.9	11.3	0.7
Glyoxal	Avg.	65.8	96.9	18.8	44.5	96.8	98.2	25.7	37.8
	Std. Dev.	12.7	2.0	12.5	25.0	0.8	0.5	12.3	13.0

* Air scour discontinued in period II

Table 5.4: t –test of Significance for Air Scour Effects on BOM Removal (5% significance level)

		Acetate	Formate	Formaldehyde	Glyoxal
F1 (20°C/Cl_2[#])	t_{table}	2.20	2.33	2.43	2.57
	$t_{observed}$	2.01	0.86	1.28	6.00
	Significance	No	No	No	Yes*
F2 (20°C/NH_2Cl[$])	t_{table}	2.20	2.20	2.39	2.51
	$t_{observed}$	1.15	0.91	1.77	1.60
	Significance	No	No	No	No
F3 (5°C/Cl_2)	t_{table}	2.20	2.20	2.20	2.23
	$t_{observed}$	1.25	3.44	0.15	0.97
	Significance	No	Yes*	No*	No*
F4 (5°C/NH_2Cl)	t_{table}	2.27	2.20	2.39	2.23
	$t_{observed}$	2.90	1.79	2.75	0.54
	Significance	Yes	No	Yes	No*

Cl_2[#]: Chlorine in the backwash water; NH_2Cl[$]: Chloramine in the backwash water.

Yes*/No*: BOM removal not at pseudo steady-state.

In regard to backwash effects for different BOM components, it seems that the less easily degradable BOM (e.g. glyoxal) is more sensitive to the unfavourable backwash conditions. A markedly higher value of $t_{observed}$ than that of t_{table} was observed in Filter 1 (chlorine in the backwash water) in terms of glyoxal removal. This influence was not observed in Filter 3 due to the non-steady-state and very low percent removal of glyoxal.

In regard to the assumption in Chapter 4 that the effect of air scour is not significant, it holds for easily biodegradable BOM component removal at higher temperatures. It seems that air scour effects are not negligible in unfavourable conditions (such as lower temperatures). However it will be recalled that chloramine were not used in Chapter 4. Therefore only the results for F1 and F3 in table 5.4 apply directly to Chapter 4.

Effect of particles/coagulants

The average pseudo steady-state BOM removals in Periods IB and III are summarized in Table 5.5.

Table 5.5: The Average Pseudo Steady-State BOM Removal in Periods IB and III (%)

		Period IB (day 199-231)				Period III (day 232-244)			
		F1	F2	F3	F4	F1	F2	F3	F4
Acetate	Avg.	97.2	98.2	79.5	92.6	95.1	98.1	76.9	92.9
	Std.	2.3	0.7	3.1	4.9	2.1	0.5	5.9	6.5
Formate	Avg.	97.7	98.9	72.9	97.7	97.0	98.4	95.0	97.8
	Std.	1.5	0.4	22.4	2.0	1.6	0.5	1.5	1.0
Formaldehyde	Avg.	96.5	96.2	90.5	97.6	96.0	95.6	94.9	94.7
	Std.	3.6	3.3	10.8	1.4	4.1	3.4	6.7	5.7
Glyoxal	Avg.	86.3	94.6	5.6	58.3	67.3	97.0	1.2	57.0
	Std.	7.8	3.7	3.5	17.4	10.9	1.3	3.9	4.0

It can be expected that the particle /coagulant might minimally affect the morphology of the biofilm in biofilters, and then impact BOM removal in biofilters to a measurable or non-measurable extent. Results of a t-test at 5% significance level in Table 5.6 indicate that particle and coagulant effects are not significant in all cases except one case (refer to Appendix E). This result was supported indirectly by pilot scale (LeChevallier *et al.*, 1992; Krasner *et al.*, 1993; Goldgrabe *et al.*, 1993), lab scale (Ahmad and Amirtharajah, 1998) and full scale (Coffey *et al.*, 1995; 1996) studies.

Table 5.6: t –test of Significance of Particle and Coagulant

		Acetate	Formate	Formaldehyde	Glyoxal
F1	t_{table}	2.31	2.31	2.45	2.57
	$t_{observed}$	1.42	0.70	0.20	3.01
	significance	No	No	No	Yes
F2	t_{table}	2.31	2.55	2.31	2.31
	$t_{observed}$	0.37	1.58	0.31	1.19
	significance	No	No	No	No
F3	t_{table}	2.31	2.57	2.31	2.31
	$t_{observed}$	0.92	2.39	0.79	1.85
	significance	No	No*	No	No*
F4	t_{table}	2.53	2.45	3.10	2.31
	$t_{observed}$	0.08	0.13	0.99	0.17
	significance	No	No	No	No*

This result means that the impact of particle and coagulant on BOM removal is negligible.

Assessment of the assumptions made in Chapter 4

The important assumption was made in Chapter 4 that factors A (particle), B (air scour) and F (coagulant) have minor effects. Based on this assumption, all three factors and their interactions were analyzed using the finished experimental results. Based on the aforementioned experimental results, it can be concluded that the effects of particles/coagulants are negligible and the effects of air scour are minor at favourable biofiltration conditions (e.g. at higher temperatures, for easily biodegradable BOM component removal). However, it seems that air scour effects should be considered in unfavourable conditions (such as lower temperatures, chloramine in the backwash water).

5.4.3 Biofilter bed utilization (impact of EBCT)

The concept of biofilter bed utilization is introduced here to reflect how effectively the filter bed is used to remove BOM, and the BOM removal loading at different depths of the filter media (or at different EBCT). Biofilter bed utilization (or EBCT effect) was investigated in several selected cases through the three experimental phases.

Biofilter bed utilization vs. BOM removal profiles in biofilters

Some typical results regarding BOM removal in the filters are shown in Figures 5.5 to 5.8.

In the biofilters run at high temperature (F1 and F2), most of the easily biodegradable BOM components (such as acetate, formate and formaldehyde) were removed in less than 1.2 minutes EBCT (corresponding to the first 15 cm of the filter media at 7.5 m/h). A similar conclusion was obtained for the biofilter operated at low temperature, and backwashed with chloramine in the backwash water (F4). BOM removal improved only a little if at all with increasing EBCT after the initial period. The biofilter media efficiency

in these filters is low in terms of easily biodegradable BOM components because much of the filter media (the lower layers of the filter bed) was not used efficiently for BOM removal (F1, F2 and F4 in Figures 5.5, 5.6 and 5.7). A longer EBCT (2.8 min or 35 cm depth of media) was needed to obtain a relatively stable effluent of a more recalcitrant BOM component (glyoxal) in biofilters run at the high temperature (F1 and F2 in Figure 5.8). Biofilter media efficiency was higher in terms of recalcitrant BOM components because more filter media was used efficiently for BOM removal (F1 and F2 in Figure 5.8). The entire filter bed was used to remove glyoxal in the biofilters run at low temperature (F3 and F4 in Figure 5.8). In general, the entire biofilter bed was also used for BOM removal in Filter 3, which was run at low temperature and backwashed with chlorinated water (Figures 5.5 to 5.8).

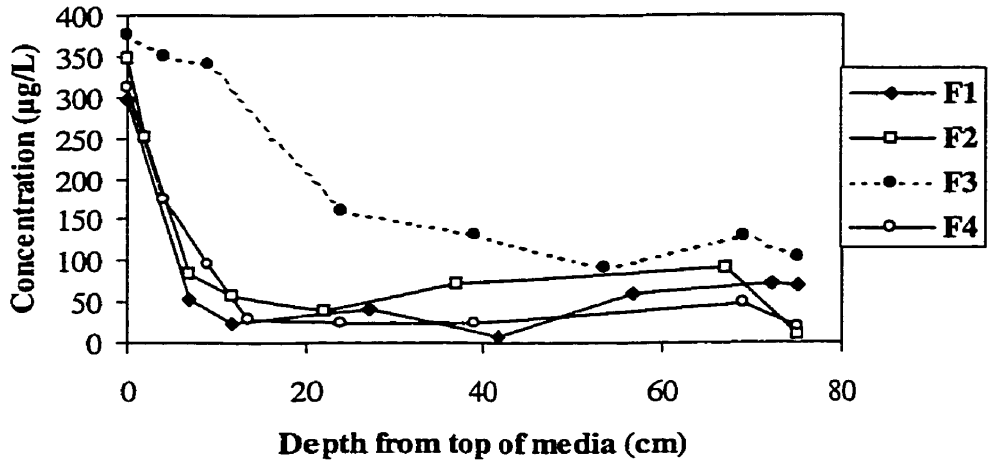

Figure 5.5: Acetate removal in biofilters (day190, phase III)

F1 (anthracite, free chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, free chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

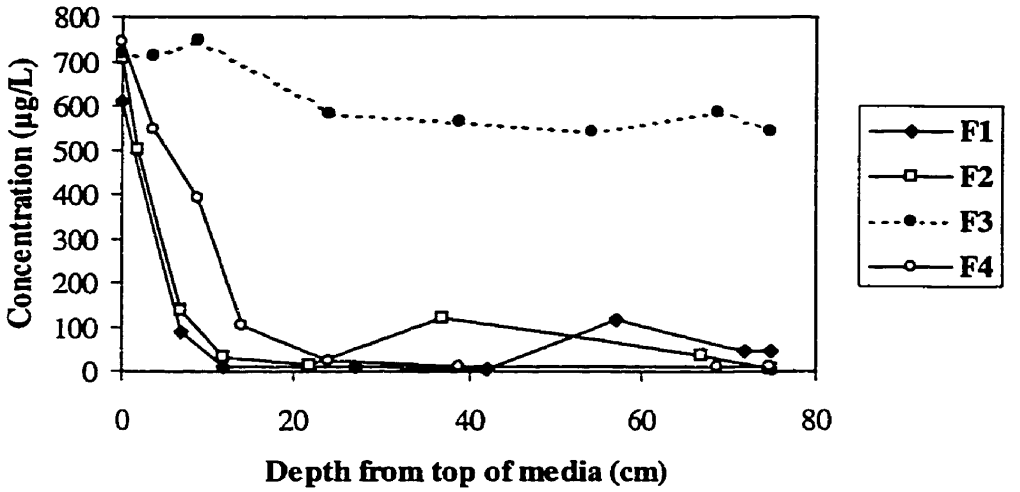

Figure 5.6: Formate removal in biofilters (day190, phase III)

F1 (anthracite, free chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, free chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

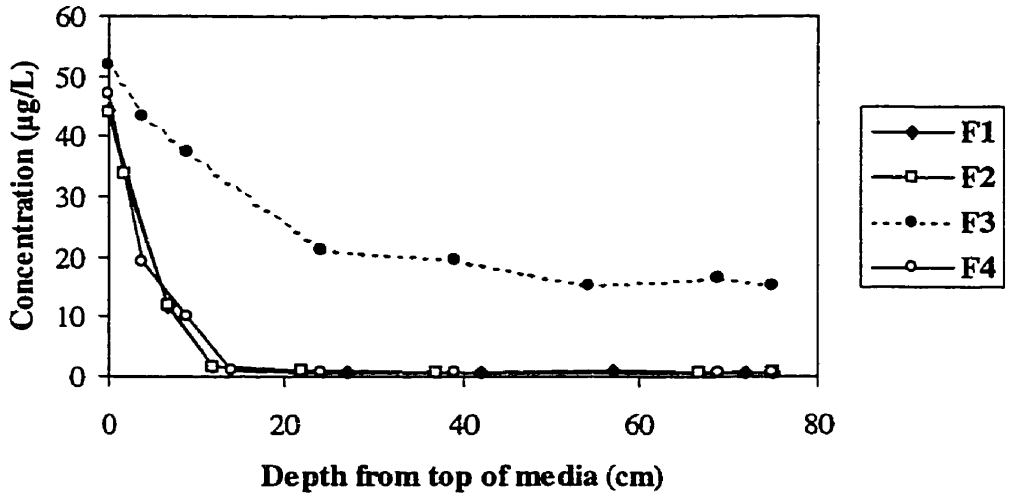

Figure 5.7: Formaldehyde removal in biofilters (day190, phase III)

F1 (anthracite, free chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, free chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

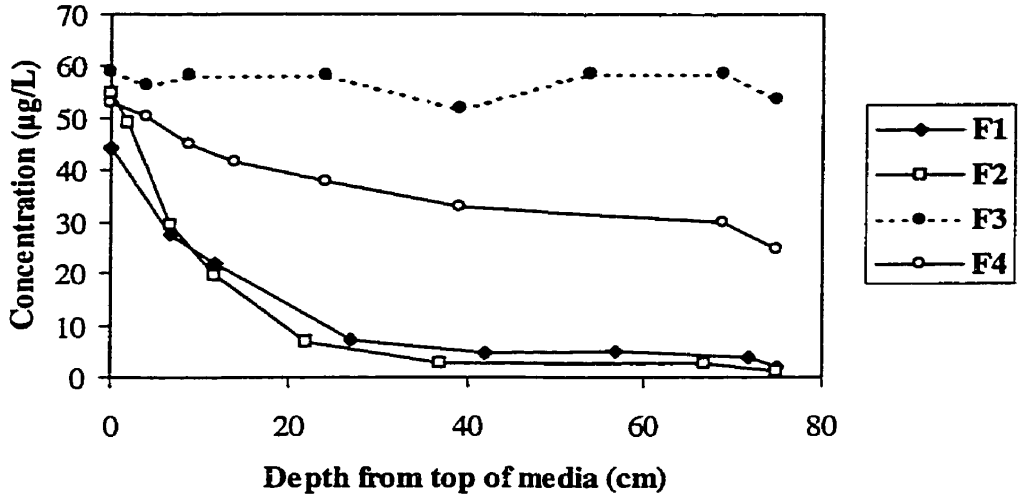

Figure 5.8: Glyoxal removal in biofilters (day190, phase III)

F1 (anthracite, free chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, free chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

BOM removal patterns in the biofilters may experience changes. Figure 5.9 represents the changes in the formate removal pattern in Filter 3 of phase III (day 190 for the lower percent removal case; and day 276 for the higher percent removal case). Bed utilization was similar in each case: the entire filter bed was used efficiently in the biofilter on both days with different percent removals.

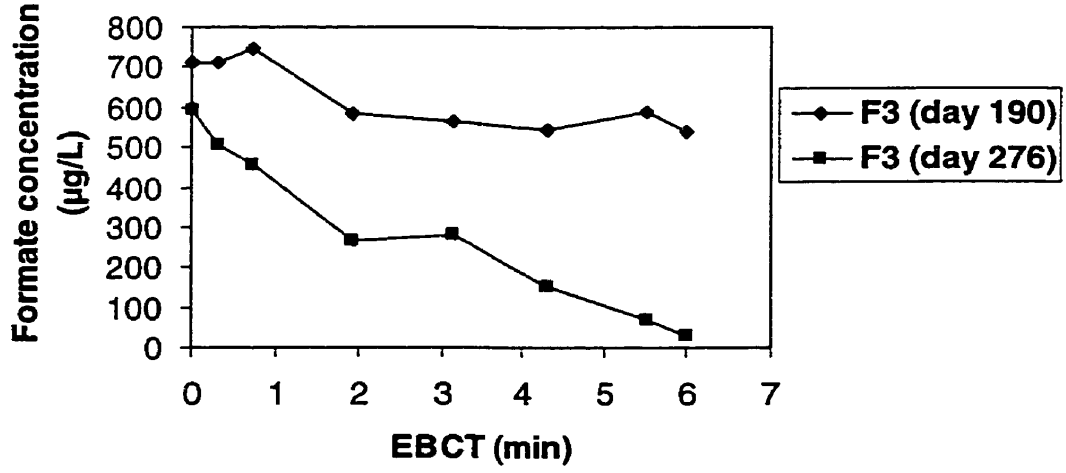

Figure 5.9: Formate removal pattern in biofilters (phase III)

Figure 5.10 represents the relationship between acetate removal and EBCT or X^* at two different hydraulic loading rates in Filter 1 of phase III. EBCT represents the contact time of BOM with media. EBCT is determined by the filter bed depth and the filter hydraulic loading rate (EBCT = filter depth/HLR). X^* is the dimensionless contact time as described in Chapter 8 ($X^* = (EBCT)\ \alpha(X_f k D_f / K_s)^{1/2}$). The parameters required for the estimation of the X^* can be found in Table 8.1 of Chapter 8. For the same biofilter with different HLRs, X^* is proportional to the EBCT.

Similar BOM removal for the same EBCT was observed in Filter 1 operated at two different hydraulic loading rates (Figure 5.10). This result was in agreement with that from a pilot study (Carlson *et al.*, 1998).

As mentioned in Chapter 2, Zhang and Huck (1996a) suggest that X^* is a better parameter for the comparison of BOM removal among biofilters (e.g. different media, operating conditions). For the same biofilter, the same trend of BOM removal should be obtained by using either EBCT or X^* as shown in Figure 5.10. The trend of BOM removal vs. X^* in the present study is similar to the modeling results from Zhang and Huck (1996a). Those authors suggested that removals should increase with increasing X^* up to about a value of $X^*=3$, and thereafter there would be little additional removal. The experimental results in Figure 5.10 support this, and suggest the usefulness of X^* as a biofilter design parameter.

Biofilter bed utilization vs. biomass profiles in biofilters

Similar to the BOM profile, biomass profiles in biofilters can also be used to evaluate the biofilter bed utilization. For the biofilters operated at the high temperature (or the low temperature but backwashed with chloramine in the backwash water), most biomass (measured as phospholipid) was in the upper layers of filter media (Filters 1, 2 and 4 in. Figure 5.11). For the biofilter run at low temperature and backwashed with chlorinated water, there was less biomass overall and no pronounced changes in the biomass profile with depth (Filter 3 in Figure 5.11).

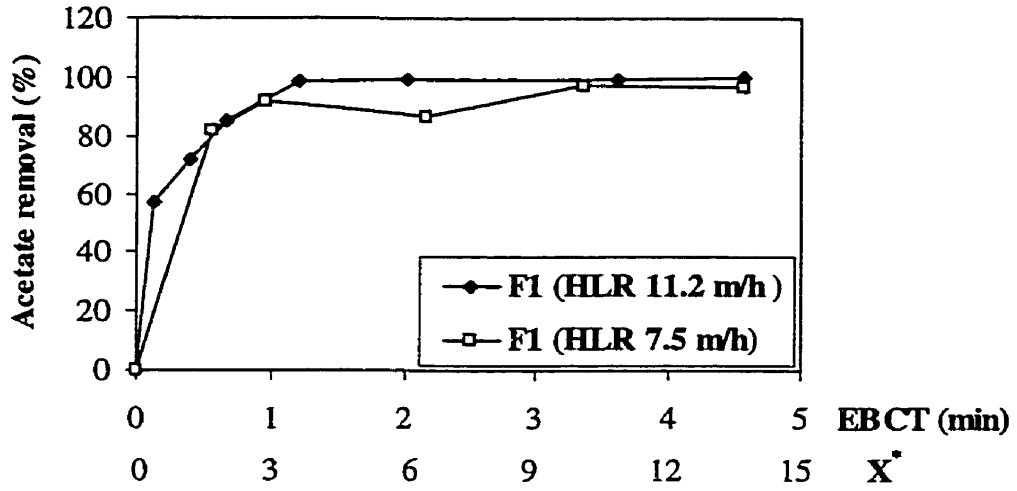

Figure 5.10: Acetate removal vs. EBCT or X^*
(day 190@ 7.5 m/h; day 318 @ 11.2 m/h, phase III)

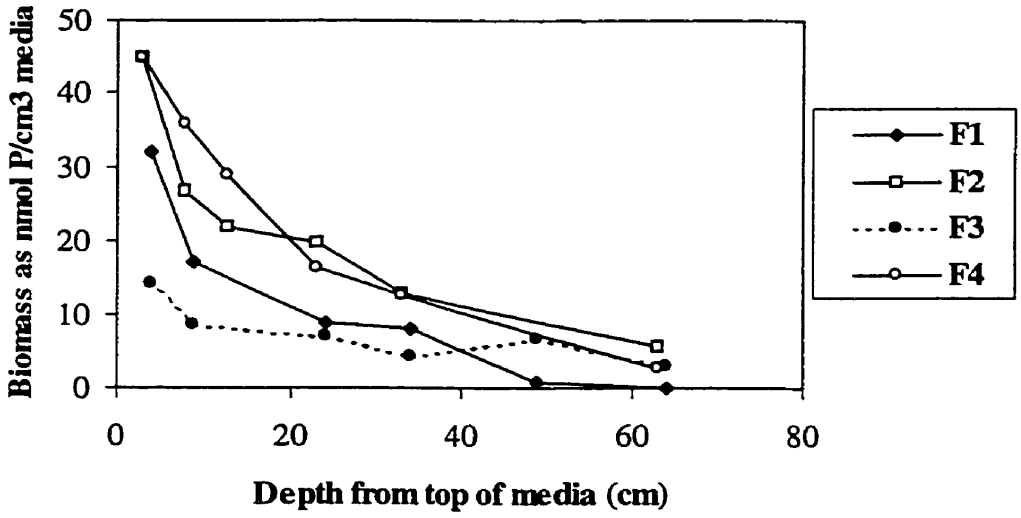

Figure 5.11: Biomass in biofilters (day 87, phase III)

In general, it was found in the present study that biomass in biofilters operated under favourable conditions (high temperature, no chlorine in the backwash water) had a pronounced stratification similar to that reported from most previous studies (e.g. Coffey *et al.*, 1995; Carlson *et al.*, 1998; Urfer, 1998). However, the biomass profile in biofilters run under unfavourable conditions (low temperature, chlorine in the backwash water) was less pronounced than under favourable conditions. This is in agreement with results from a full-scale GAC biofilter using preozonation (Servais *et al.*, 1992), although that filter should have experienced favourable conditions. Therefore, it is concluded that biofilter bed utilization is higher in biofilters operated under unfavourable conditions than under favourable conditions. This of course does not mean that BOM removals are higher. It does suggest however, that in principle, biofilters should be designed to exhibit full bed utilization for the most recalcitrant target compound under the most unfavourable conditions they will experience.

BOM removal vs. biomass profiles in biofilters

In comparison to the BOM removal profile in the biofilters (Figures 5.5 to 5.8), a basically similar trend was found with the biomass profiles in the biofilters (Figure 5.11). This means that BOM removal in the biofilters is roughly proportional to the biomass that exists. This result is supported by some studies (Servais *et al.*, 1992; Wang *et al.*, 1995; Miltner *et al.*, 1995; Coffey *et al.*, 1995; Booth, 1998). However, Urfer (1998) found that phospholipid biomass might not adequately quantify the active biomass with regard to substrate removal. That author suggested the use of BRP (biomass respiration potential) as a better method for quantifying substrate-degrading biomass. BRP is investigated extensively in Chapter 6.

5.4.4 BOM removal and biomass changes during a filter run

Figure 5.12 represents the total biomass in each biofilter during a filter run of block I (phase I). No duplicate was available due to the large numbers of biomass samples at one time and the very time consuming procedure for biomass measurements. There were essentially no changes of total biomass within a given biofilter in a filter run. Much less

biomass was found in Filter 3, which had the "worst " operating conditions in phase I (anthracite media, low temperature and chlorine in the backwash water).

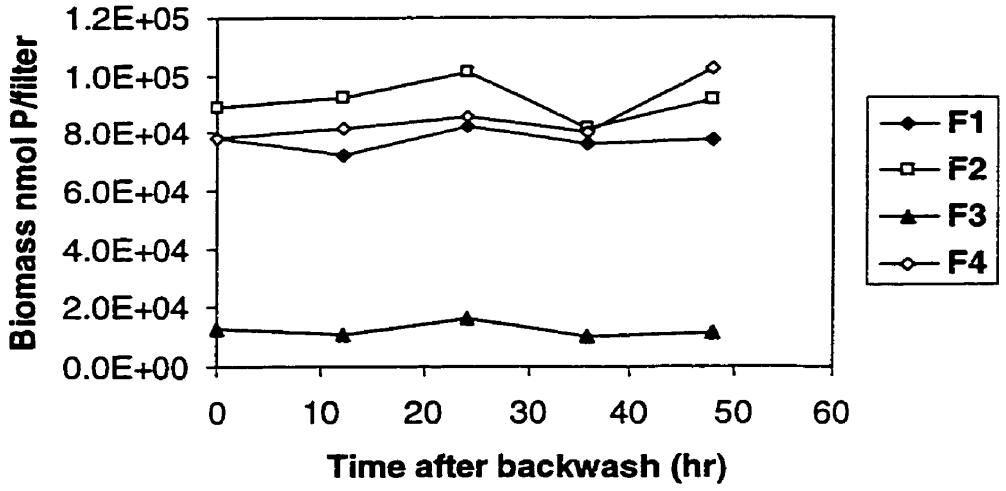

Figure 5.12: Biomass changes in a filter run (day 84, phase I)
F1 (Anthr., no chlorine, high temp.); F2 (GAC, no chlorine, high temp.); F3 (Anthr., chlorine, low temp.); F4 (GAC, chlorine, low temp.)

The difference in BOM removal in terms of formate and glyoxal (similar results for acetate and fomaldehyde removals) is less than 13% before and after backwash (phase III, day 260; Figures 5.13 to 5.16). The operating conditions for the filters on day 260 of phase III were the same as those in period IA/IB (anthracite; chlorine or chloramine in the backwash water, air scour).

The biomass profiles for Filter 4 on day 260 from phase III before and after backwash are presented in Figure 5.17. A pronounced stratification was observed both before and after backwash. Biomass loss during backwash could be calculated by integration from Figure 5.17, and the phospholipid biomass loss due to backwash was about 19%. This supports conclusions from major previous studies as indicated in Chapter 2 (e.g., Huck *et al.*, 1998: in the range of 15% - 50% in a full-scale biofilter). Biomass loss was also estimated in terms of HPCs levels in backwash discharge by using a bacteria formula: C_{55}

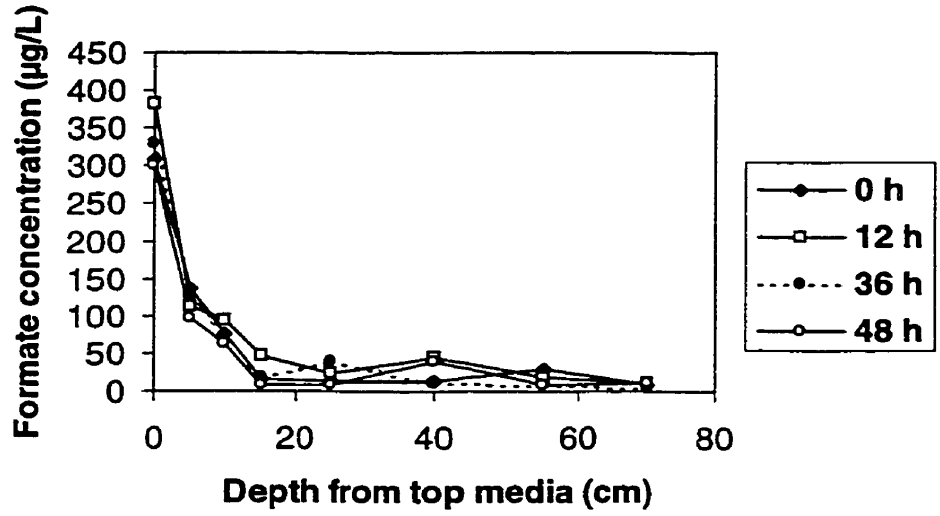

Figure 5.13: Formate removal during a filter run (F1, day 260, phase III)

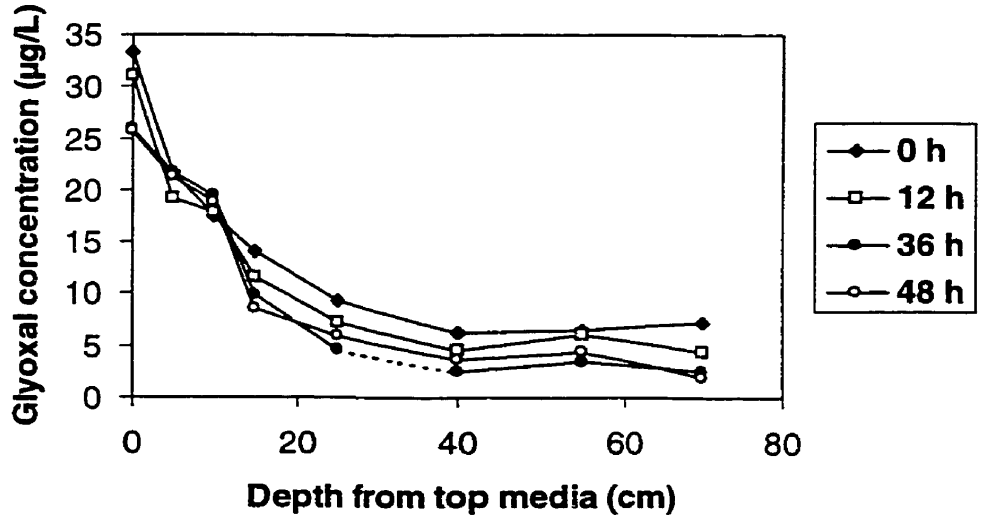

Figure 5.14: Glyoxal removal during a filter run (F1, day 260, phase III)

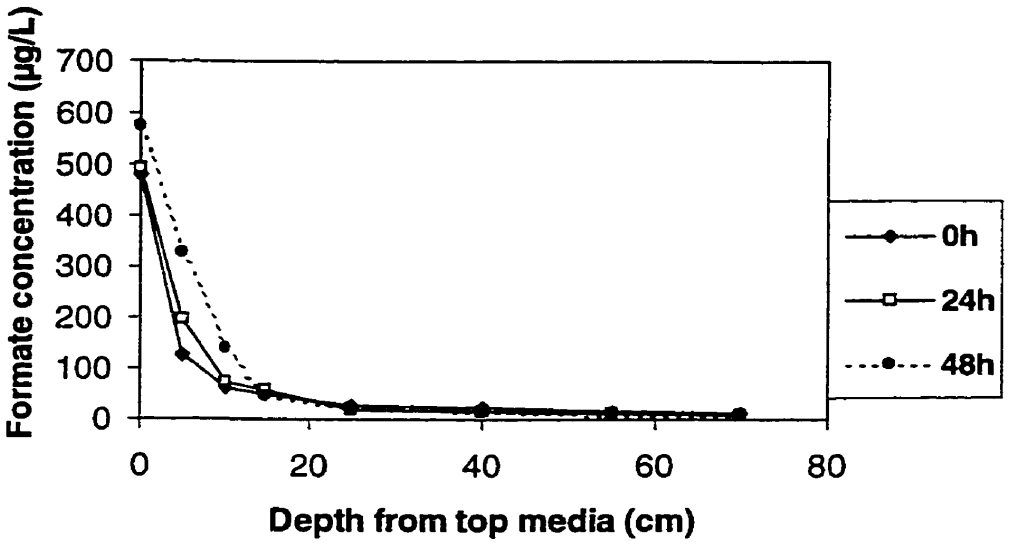

Figure 5.15: Formate removal during a filter run (F4, day 260, phase III)

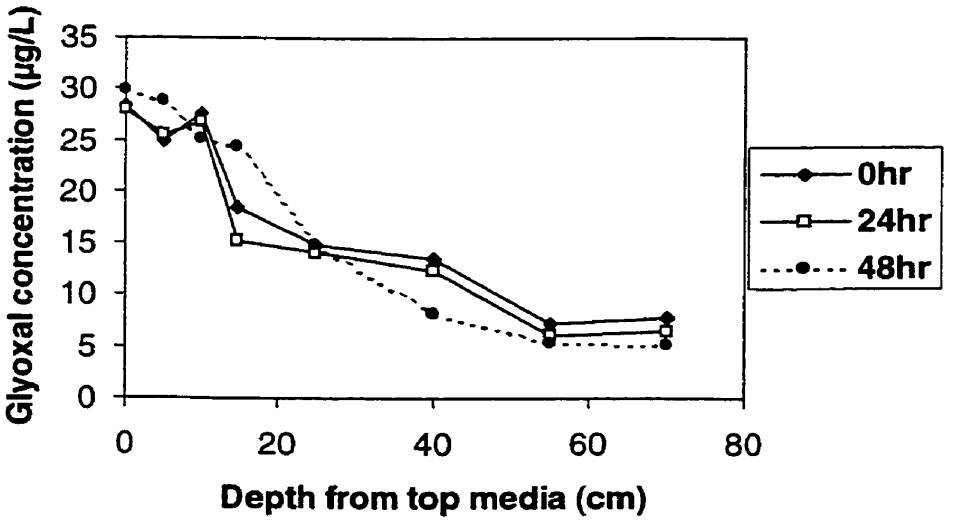

Figure 5.16: Glyoxal removal during a filter run (F4, day 260, phase III)

$H_{77}O_{22}N_{11}P$ (Metcalf and Eddy, 1991) (refer to Appendix F). A biomass loss of 3% ~ 41% was estimated based on HPCs levels in the backwash discharge. Both of these estimates are very approximate because of errors in the phospholipid method and HPC sampling and measurements.

Biomass loss during a filter run can be estimated by using the information on HPC difference between the filter influent and effluent. Based on the calculation in Appendix G which describes biomass loss due to detachment during a filter run and discharge in a backwash event, it was concluded that the biomass loss by detachment during a filter run could be at a similar level to that by the backwash discharge.

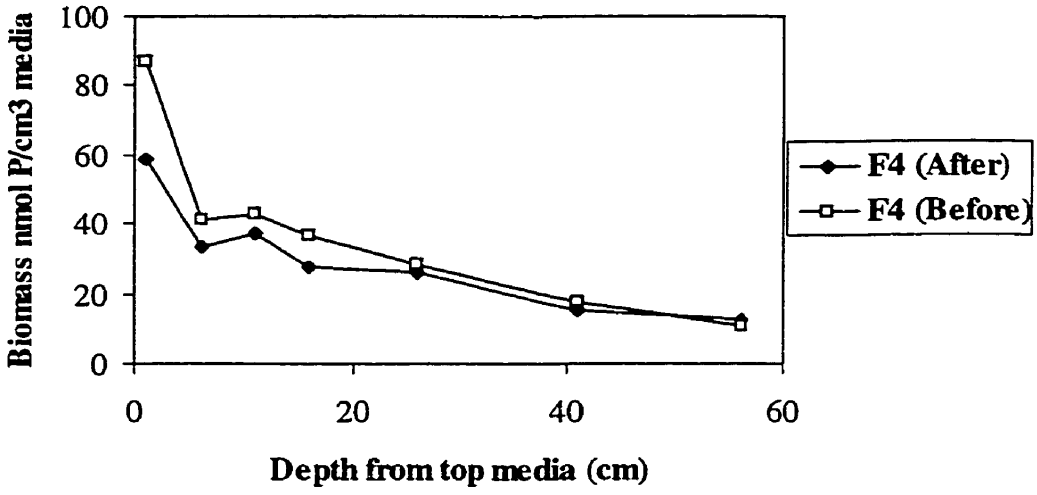

Figure 5.17: Biomass changes before /after backwash (day 260 of period IC, F4, Phase III, air scour)

Similar to the findings in phase I (block I), there were no substantial changes in BOM removal during a filter run. BOM removal was not sensitive to backwash and the biomass changes in a filter run. Biomass removed during backwash did not substantially interfere with the BOM removal in the following filter run. This might be due to the deeper bed removal pattern in the initial period of a filter run. These results are supported by most of the previous studies (e.g., Huck *et al.*, 1998; Hozalski *et al*, 1998).

5.4.5 Impact of hydraulic loading rate and BOM steps

The rapid and long-term effects of hydraulic loading rate and BOM steps on BOM removal performance were investigated in period IC of phase III. The effects of instantaneous hydraulic loading rate step increase were investigated in all four filters from the baseline. BOM instantaneous step increase was conducted in all four filters after re-establishing the base line for one week. Longer term effects of HLR step increase in F1 and F3 and BOM step increase in F2 and F4 were investigated at the same time after re-establishing the baseline from the BOM instantaneous step increase.

The effects of instantaneous hydraulic loading steps on BOM removal performance in biofilters are presented in Figures 5.18 to 5.21. The measurement was taken half an hour after the instantaneous hydraulic loading steps.

In response to the instantaneous HLR steps (50% increase), a similar BOM removal response was observed in the biofilters run at high temperature (F1 and F2) and the biofilter run at low temperature with chloramine (F4) in the backwash water. For all parameters except glyoxal, there was essentially no change in removal in these three filters as a result of the sudden increase in hydraulic loading. There was a decrease in the BOM removal in the biofilter run at low temperature and backwashed with chlorinated water (F3). Glyoxal removal was sensitive to HLR steps in biofilters operated at low temperature and biofilters run at high temperature and backwashed with chlorinated water (F3, F4 and F1 in Figure 5.21). The percent removal in F1, F3 and F4 decreased from 96%, 1.2% and 93% to 73%, 0.8% and 75%, respectively. Carlson *et al.* (1998) reported that no major difference in DOC removal was observed in a pilot plant when increasing HLR from 5.0 m/h to 9.7 m/h, but markedly less removal occurred when the HLR was increased to an extremely high level of 17.5 m/h. This indicates that well developed biomass can endure a sudden increase in HLR to a certain extent, depending on the operating conditions and the biodegradability of the BOM. Either the HLR or the BOM steps means an increase of BOM flux to biofilm. A well developed biofilm can use its potential capacity to degrade BOM in a more effective way. It is likely that the glyoxal

removal was decreased because of the lower biodegradation rate of this more recalcitrant BOM component. This can also be evaluated by the biofilter modelling shown in Chapter 8.

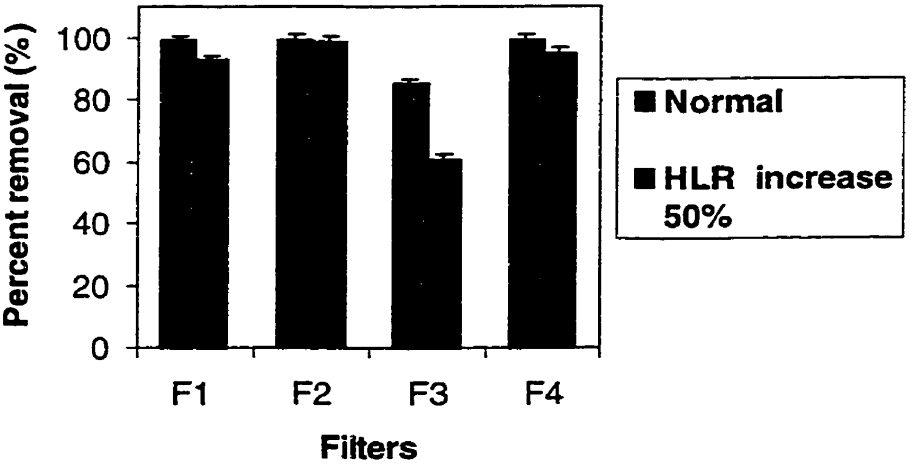

Figure 5.18: Instantaneous HLR effects in terms of acetate removal

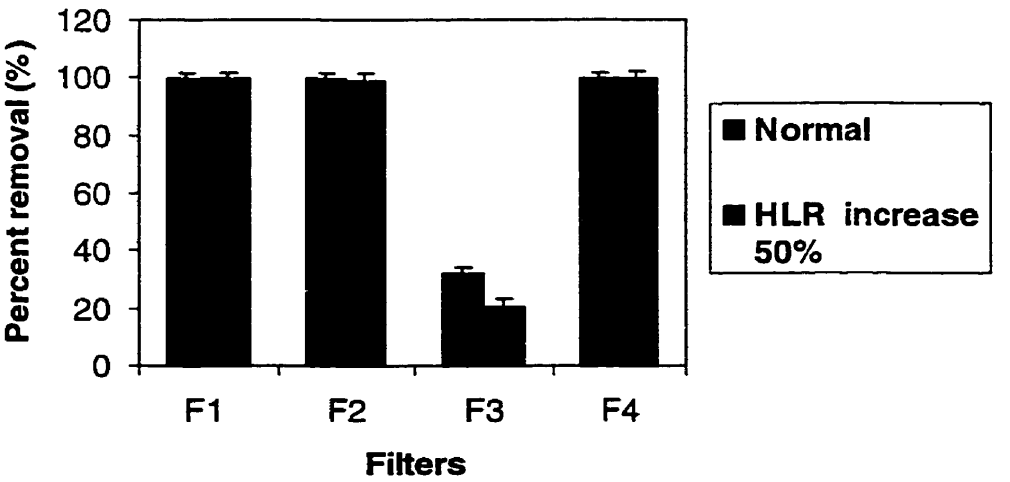

Figure 5.19: Instantaneous HLR effects in terms of formate removal

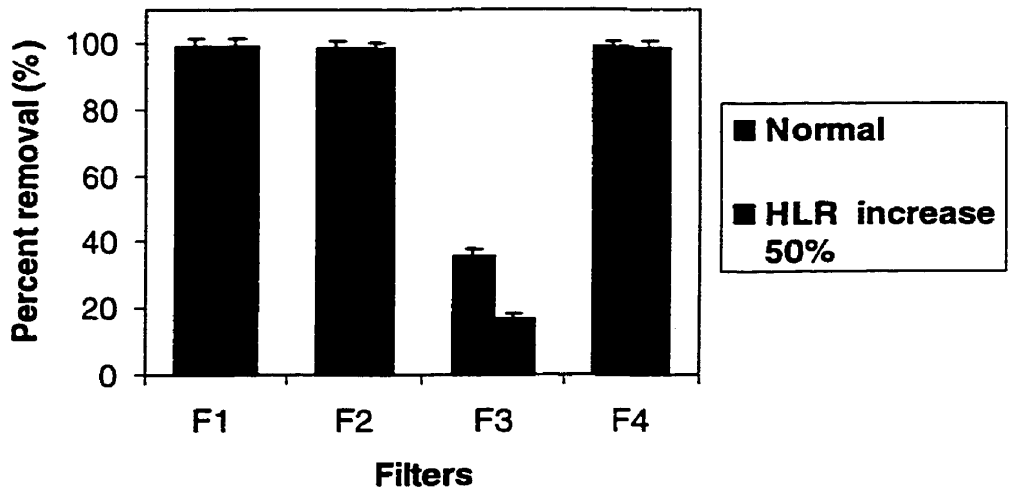

Figure 5.20: Instantaneous HLR effects in terms of formaldehyde removal

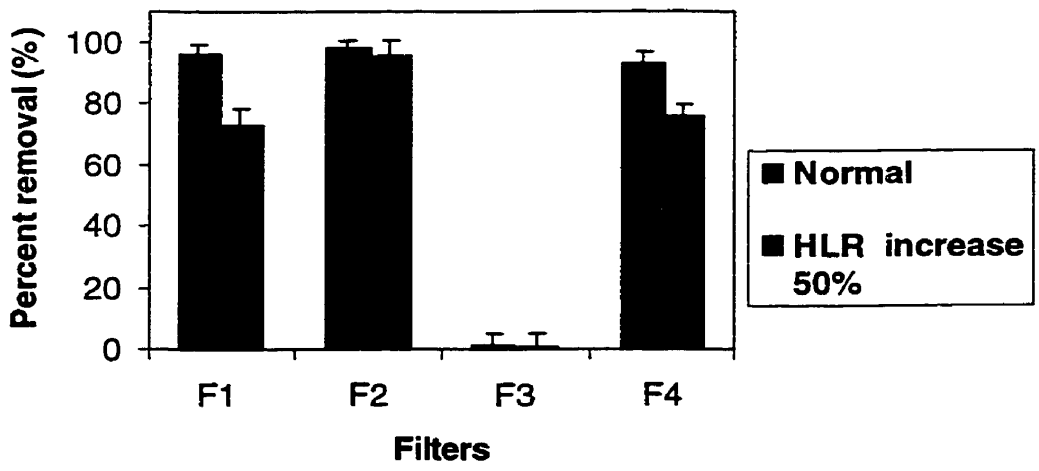

Figure 5.21: Instantaneous HLR effects in terms of glyoxal removal

The error bars shown in Figures 5.18 to 5.21 represent standard deviation form the mean. It is evident that the reproducibility of BOM (as acetate, formate, formaldehyde and glyoxal) measurements, was generally lower than 5%.

The effects of an instantaneous BOM step increase on BOM removals are shown in Figures 5.22 to 5.25. Measurements were taken half an hour following increase. Results from the instantaneous BOM steps were similar to those obtained from the instantaneous HLR steps. Removal of acetate, formate and formaldehyde decreased in the worst case Filter 3, whereas removal of glyoxal, the most sensitive BOM component, was impacted in all filters except in the "best case" Filter 2. The increased BOM steps can enhance the use of biofilm in deeper depth of a filter bed, so that a similar BOM removal can be maintained. The glyoxal removal was decreased because of the requirement of longer time for biodegradation of this more recalcitrant BOM component.

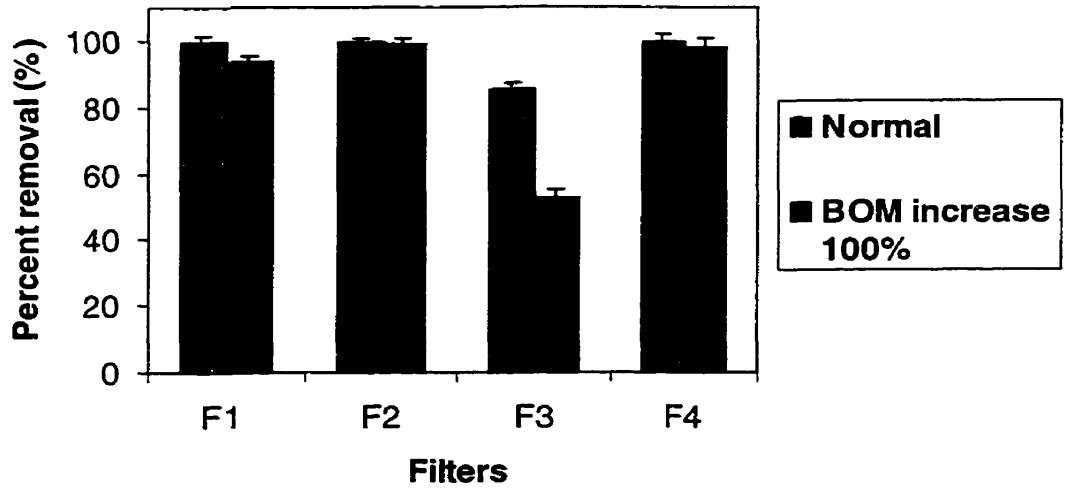

Figure 5.22: Effects of instantaneous BOM steps in terms of acetate removal

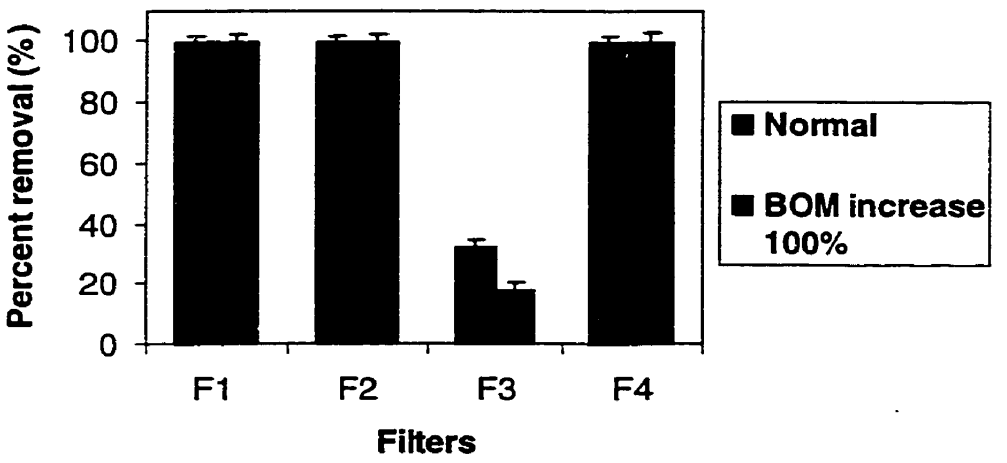

Figure 5.23: Effects of instantaneous BOM steps in terms of formate removal

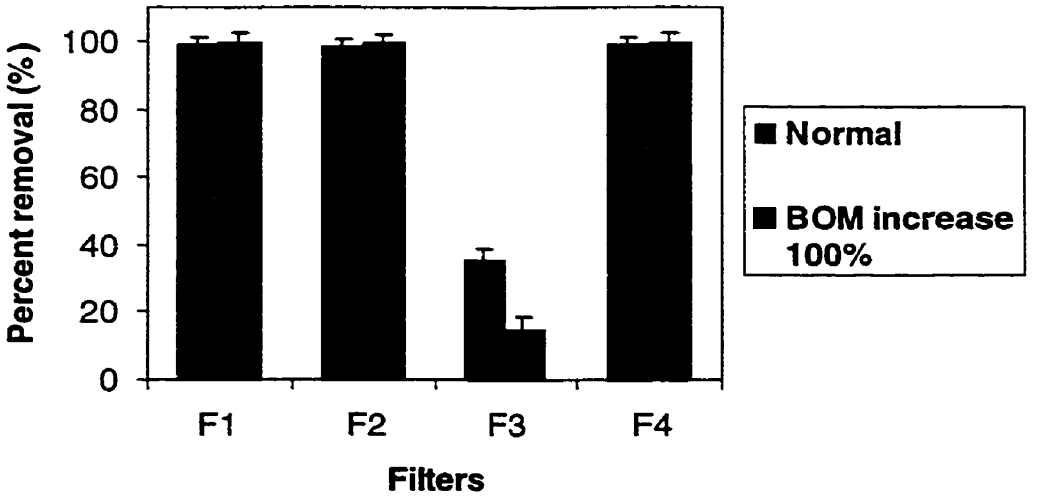

Figure 5.24: Effects of instantaneous BOM steps in terms of formaldehyde removal

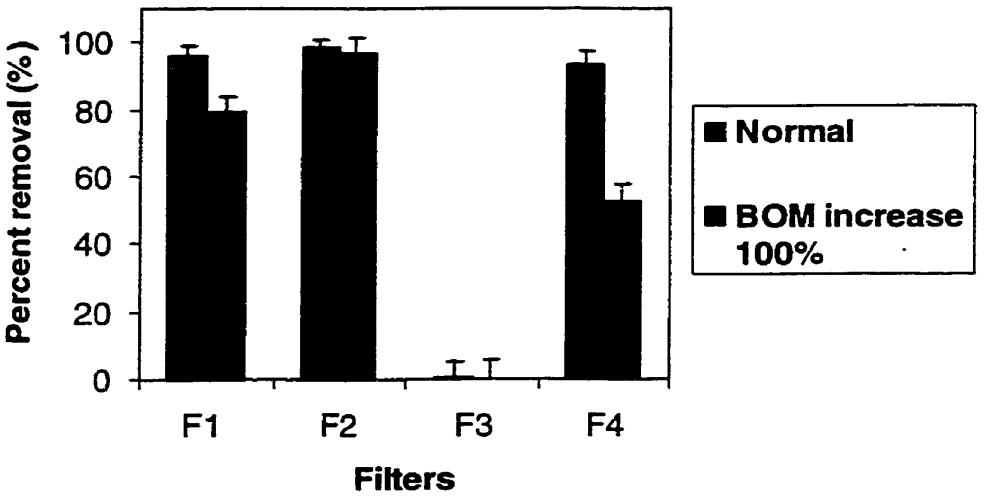

Figure 5.25: Effects of instantaneous BOM steps in terms of glyoxal removal

Longer term impacts of HLR on BOM removal in biofilters were investigated in Filters 1 and 3. Figures 5.26 to 5.29 represent BOM removal for a period up to about two weeks after the HLR step. BOM removal in Filter 1 achieved a similar level to that obtained with the normal HLR after about 2-3 days for easily biodegradable BOM components (acetate, formate and formaldehyde) and about two weeks for less easily biodegradable BOM components (glyoxal). BOM removal in Filter 3 was more susceptible to longer term effects of the HLR changes. For example, more time might be required for Filter 3 to restore the BOM removal level to that before HLR steps. It might be possible that BOM removal in Filter 3 in the new pseudo steady-state is lower than that in the old pseudo steady-state. As a matter of fact, the pseudo steady-state BOM removal in Filter 3 is not so "stable".

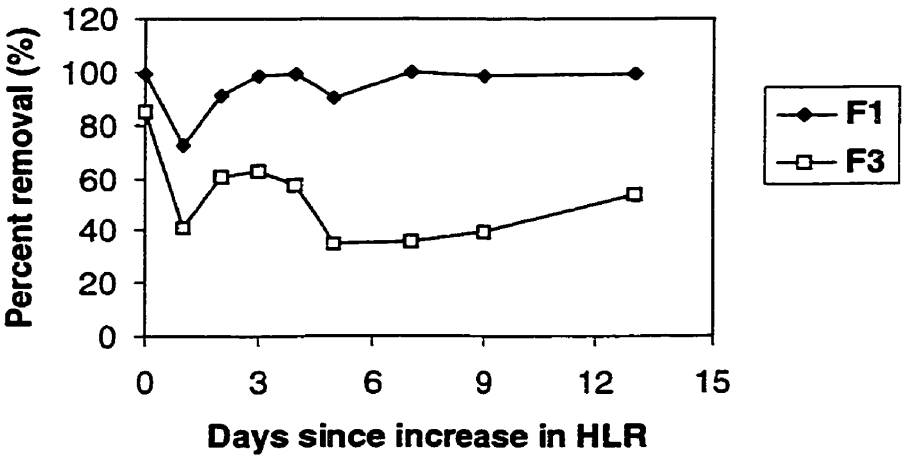

Figure 5.26: Longer term effects of HLR step increase in terms of acetate removal F1 (anthracite, chlorine, 20 °C); F3 (anthracite, free chlorine, 5 °C)

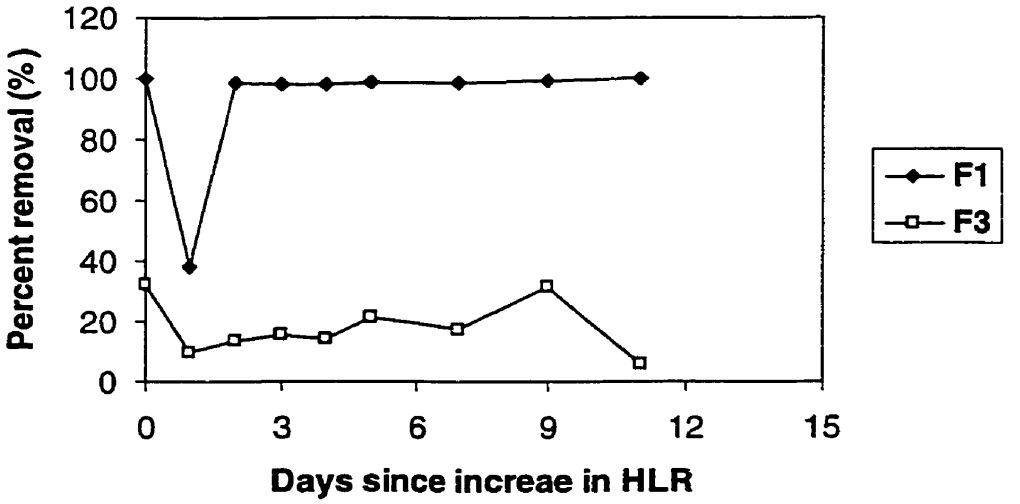

Figure 5.27: Longer term effects of HLR step increase in terms of formate removal F1 (anthracite, chlorine, 20 °C); F3 (anthracite, free chlorine, 5 °C)

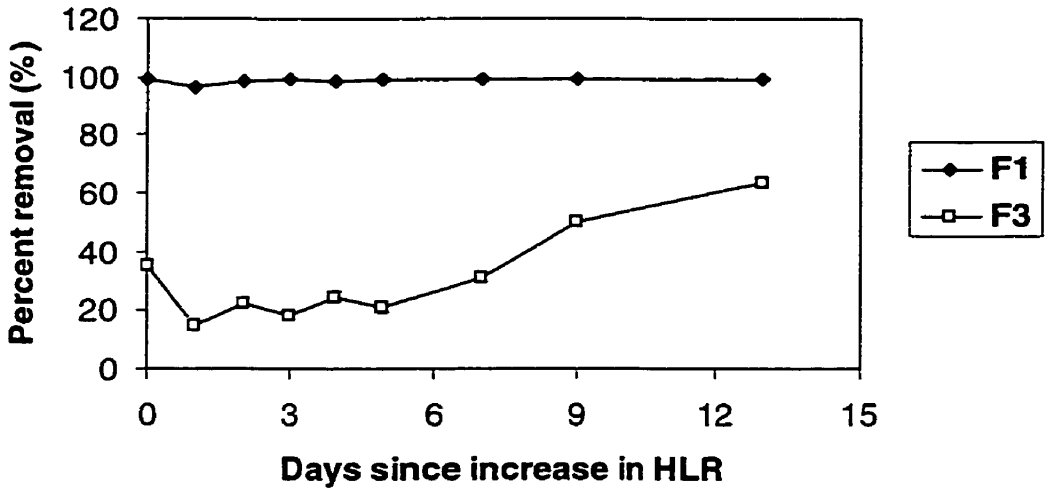

Figure 5.28: Longer term effects of HLR step increase in terms of formaldehyde removal F1 (anthracite, chlorine, 20 °C); F3 (anthracite, free chlorine, 5 °C)

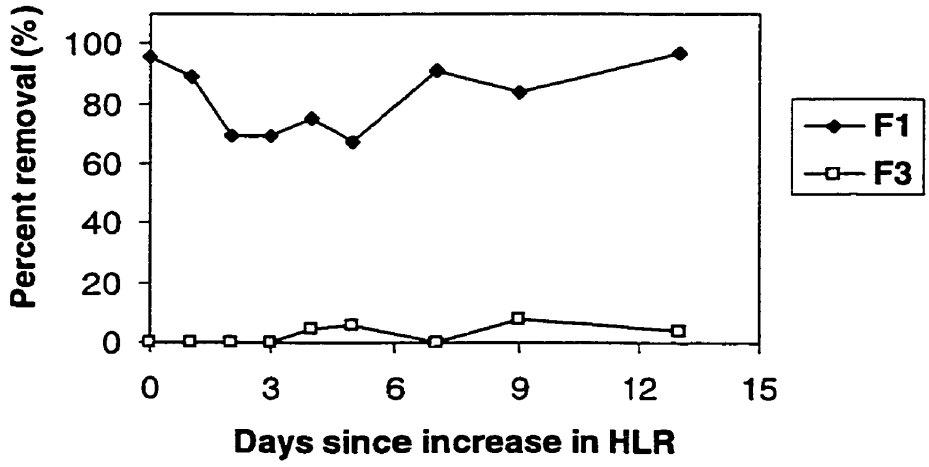

Figure 5.29: Longer term effects of HLR step increase in terms of glyoxal removal F1 (anthracite, chlorine, 20 °C); F3 (anthracite, free chlorine, 5 °C)

Longer term impacts of a BOM step on BOM removal in biofilters were investigated in Filters 2 and 4. Figures 5.30 to 5.34 show the BOM removal after the BOM step increase. The reproducibility of the BOM removal data for the longer-term impacts were similar to that for the instantaneous impacts. There is no discernible effect for formate and formaldehyde removal in Filters 2 and 4 (Figures 5.31 and 5.32). The acetate and glyoxal removal achieved a similar level to that at normal BOM conditions after about 6 days (Figure 5.30) in Filters 2 and 4. Glyoxal removal in Filter 4 (Figure 5.33) reached a new pseudo steady-state at a lower level (decrease from 87% to 78% in F4). There was no measurable changes in F2, except for a slight decrease during the first 3 days. The good tolerance to the BOM longer steps in Filters 2 and 4 may be due to the more favourable backwash condition in Filters 2 and 4 (chloramine in the backwash water) than in Filters 1 and 3.

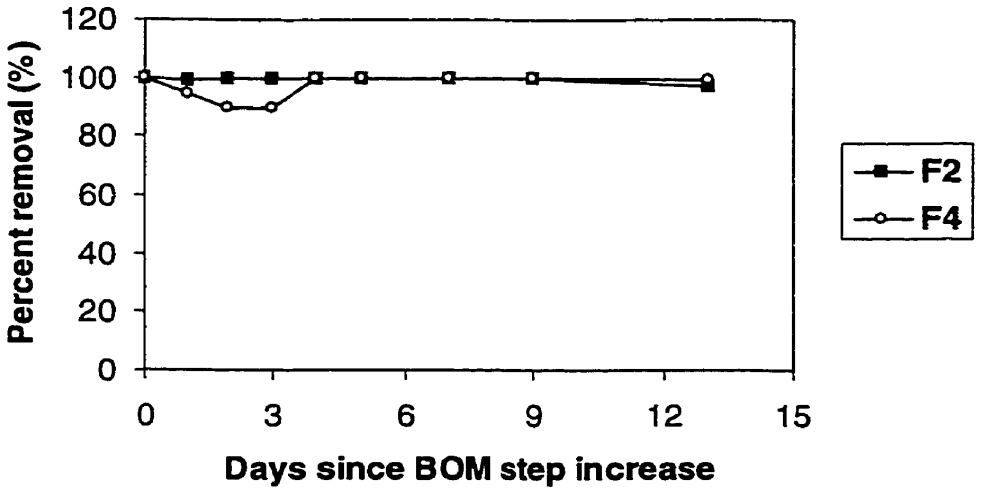

Figure 5.30: Longer term effects of BOM step increase in terms of acetate removal F2 (anthracite, chloramine, 20°C); F4 (anthracite, chloramine, 5 °C)

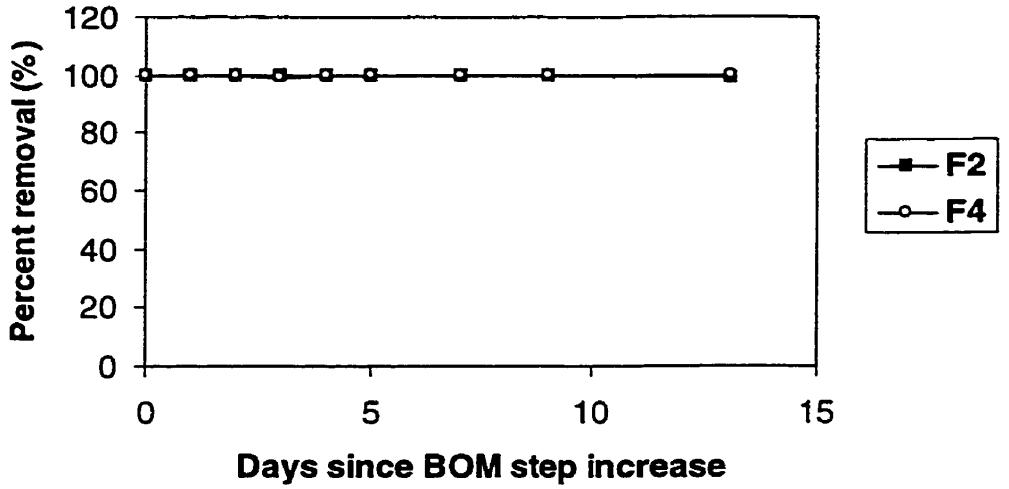

Figure 5.31: Longer term effects of BOM step increase in terms of formate removal
F2 (anthracite, chloramine, 20°C); F4 (anthracite, chloramine, 5 °C)

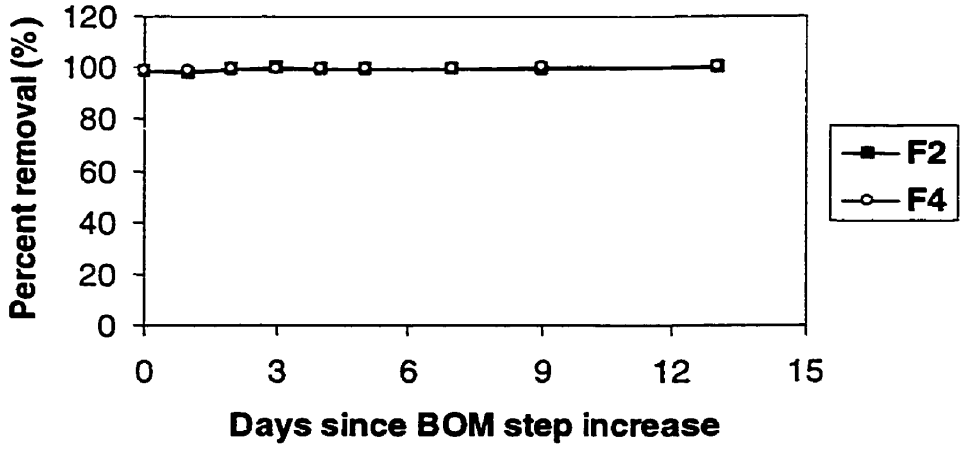

Figure 5.32: Longer term effects of BOM step increase in terms of formaldehyde removal
F2 (anthracite, chloramine, 20°C); F4 (anthracite, chloramine, 5 °C)

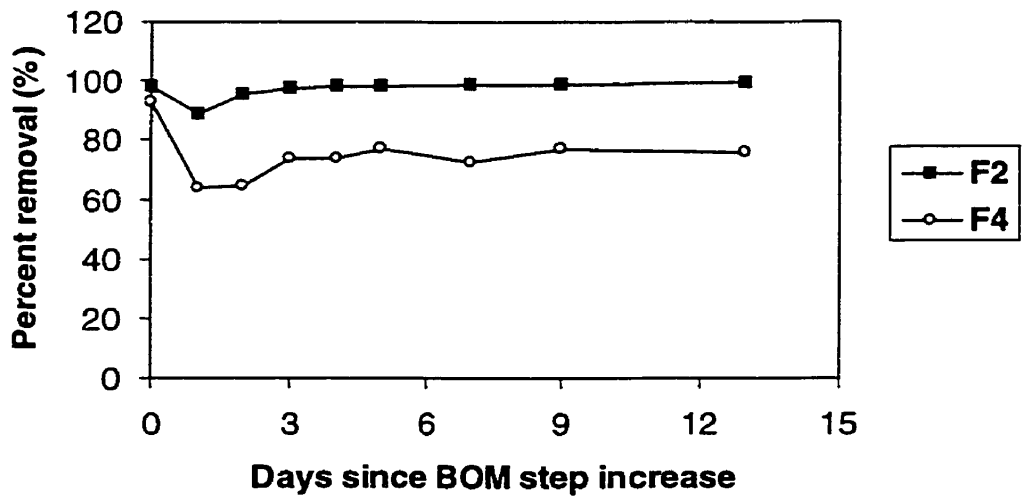

Figure 5.33: Longer term effects of BOM step increase in terms of glyoxal removal F2 (anthracite, chloramine, 20°C); F4 (anthracite, chloramine, 5 °C)

After a longer period of operation following the HLR or BOM step increase (14 days), the biofilters developed a new BOM removal profile. BOM (as acetate and glyoxal) removal profiles after 14 days are shown in Figures 5.34 and 5.35. The BOM removal (as acetate and glyoxal) trends shown in these figures can be evaluated by comparing them to those in Figures 5.15 and 5.16. Formate and formaldehyde removal profiles in the biofilters were similar to acetate removal.

Following the HLR or BOM steps, approximately 20 cm of bed media (or EBCT = 1.6 min) was efficiently used to remove easily degradable BOM components such as acetate, formate and formaldehyde in biofilters run at high temperature or at low temperature with chloramine backwash. More than 60 cm of bed media (or 4.8 min) was needed to get a relatively stable effluent for easily degradable BOM removal in biofilters run at low

temperature and backwashed with chlorine in the backwash water. For recalcitrant components such as glyoxal, the entire filter bed was used in biofilters run both at high and low temperatures for removal (Figure 5.35).

Thus, in longer-term operation (14 days) following either a BOM step or an HLR step, the use of top 20 cm of the bed for removal of easily biodegradable BOM component lead to a higher biofilter bed utilization, in comparison with the normal operating conditions, where about 15 cm of the bed was used. The biofilters were therefore able to endure the HLR/BOM steps without losing BOM removal capacity, by using biofilms present deeper in the bed.

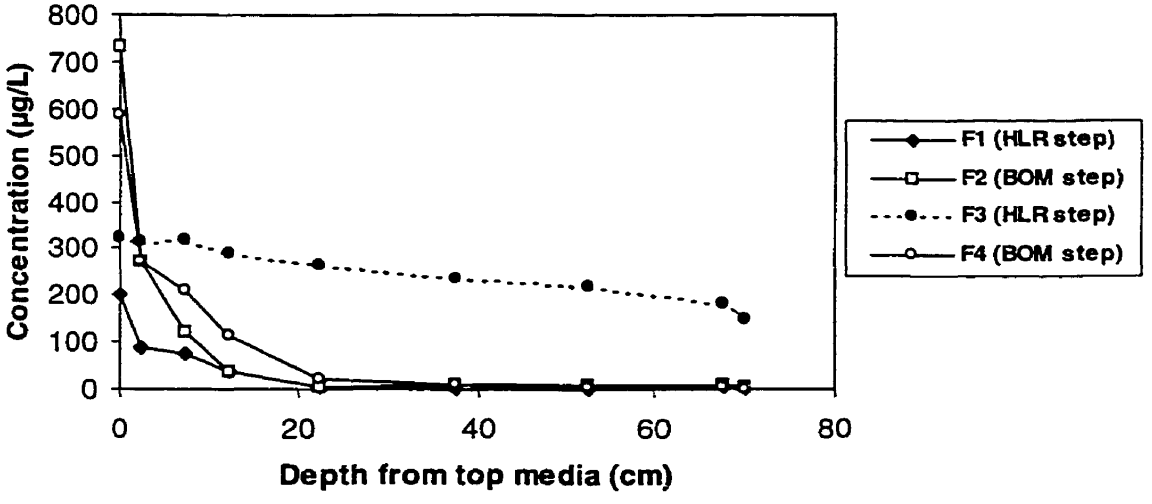

Figure 5.34: Acetate removal profile in biofilters (day 318, phase III)

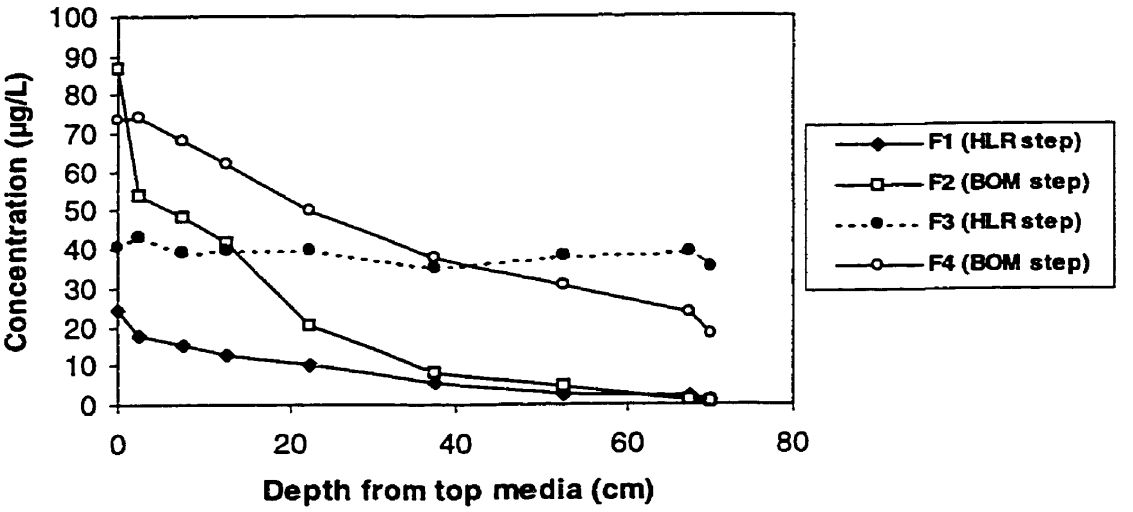

Figure 5.35: Glyoxal removal profile in biofilters (day 318, phase III)

5.4.6 Impact of biofilter shut down on biofilter performance

Filter shut down effects were investigated in the final stage of period IC in phase III. Filters were shut down and drained for 24 h, and then restarted. BOM removal samples were taken 0.5 h and 24 h after filter restart. BOM removal results before and after 24 h filter shut down demonstrated that the biofilms within the four biofilters were mature and strong enough to suffer the unfavourable influences of filter shut down (Figures 5.36, 5.37). Therefore, it is suggested the regular shut down maintenance of biofilters would not impact the BOM removal performance, at least for easily biodegradable compounds. The formaldehyde and glyoxal removal could not be measured due to the repair of the instrument. Shut down impact of not draining was not investigated in this study. A full-scale study conducted by Huck *et al.* (1998) did not show any appreciable degradation in effluent quality in GAC/sand filters following the 72 h out-of-service period with no draining, however, the anthracite/sand filter did exhibit a slight decrease in the removal

of BOM compounds such as oxalate, formaldehyde, glyoxal and DOC. Niquette *et al.* (1998) indicated that shutdown of biological filters (not draining) promoted anaerobic conditions that reduced the density of fixed bacteria and the quality of water inside the filter. The results also suggested that BAC filters could withstand a shutdown of <24 h without impairing their capacity to remove DOC and ammonia.

Thus, it is suggested that during the filter shut down it should be drained if it is possible, if not, the filter should be backwashed before being returned to normal operation. The filter media, operating conditions and biodegradability of BOM compounds could impact biofilter performance following restart to various extents.

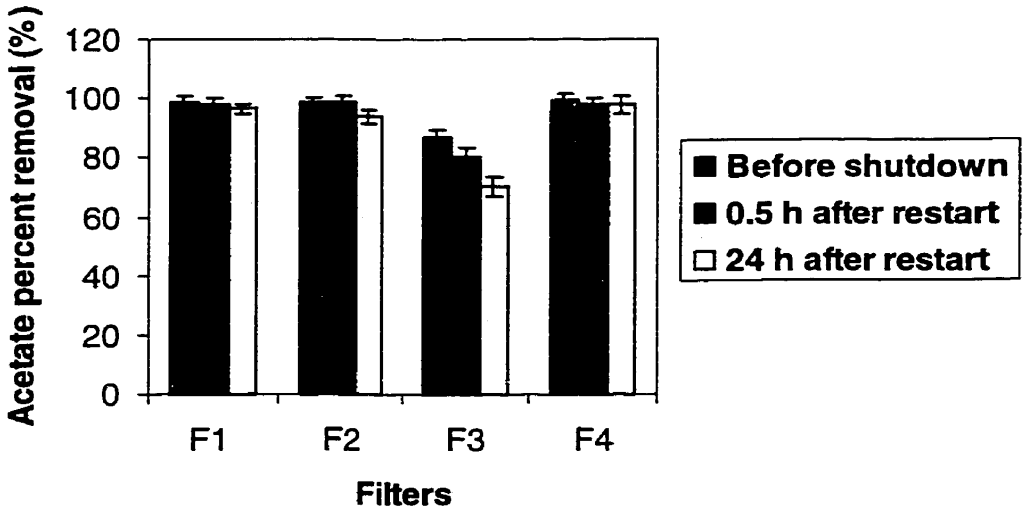

Figure 5.36: Impacts of biofilter shutdown in terms of acetate removal

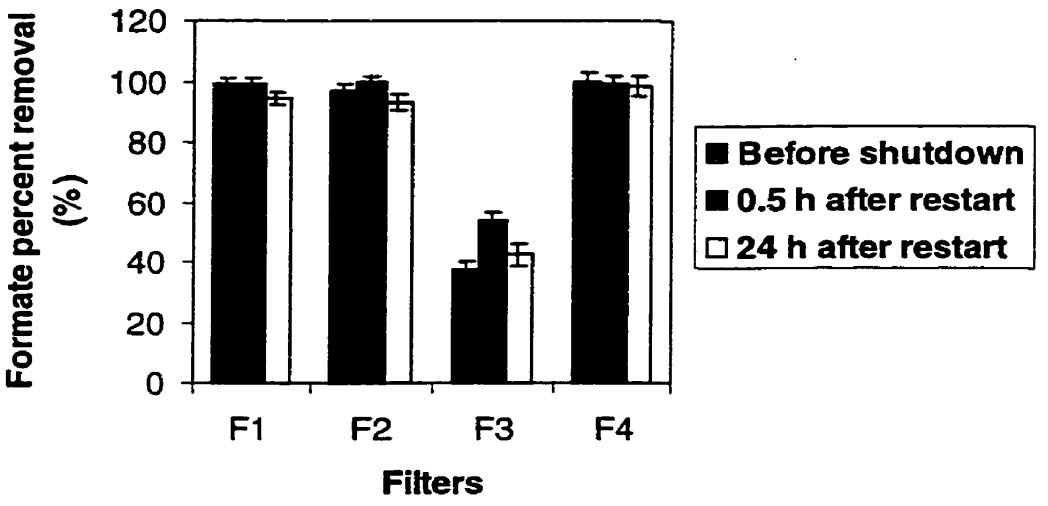

Figure 5.37: Impacts of biofilter shutdown in terms of formate removal

5.4.7 Biofilter conventional performance

Headloss

The experimental results in this study can provide some insights into biofilter design and operation. The relevant experimental results include: headloss accumulation in a filter run and headloss build-up in long-term operation (115 days in phases I and II; 300 days in phase III), the effects of chlorine/chloramine in the backwash water, the effects of air scour, particle removal loading in biofilters, effects of temperature, and unfavourable operating conditions (i.e. steps and shutdown).

Initial headloss (headloss after backwash) development in the biofilters during blocks I/II (phase I/II) is shown in Figures 5.38 and 5.39. There were no substantial increases in initial headloss in the biofilters during either block I or II. The initial headloss fluctuations in block I (Figure 5.38) might be due to the fact that the backwash operation in block I may not have been well controlled to some extent.

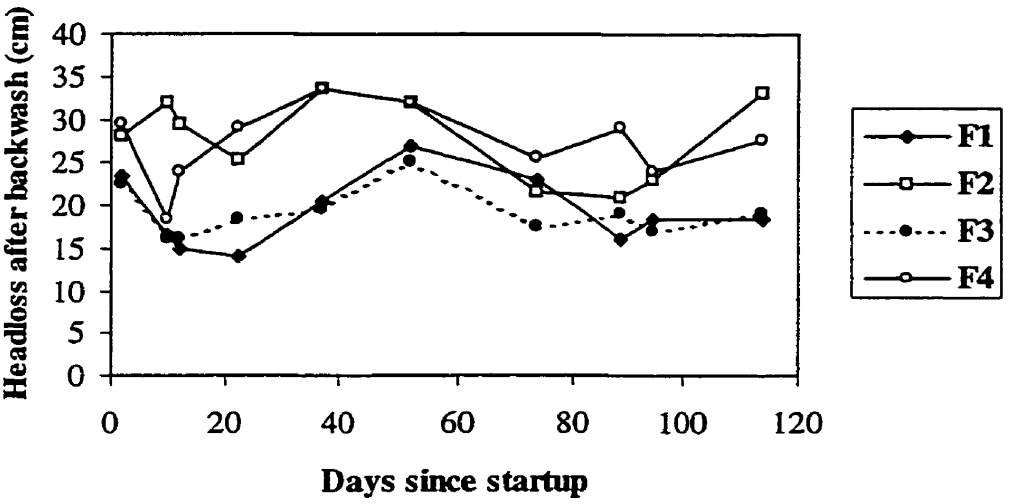

Figure 5.38: Initial headloss development in block I

F1 (Anthr., no chlorine, high temp., particle, no coagulant, water only); F2 (GAC, no chlorine, high temp., particle, coagulant, air scour); F3 (Anthr., chlorine, low temp., no particle, no coagulant, water only); F4 (GAC, chlorine, low temp., no particle, no coagulant, air scour)

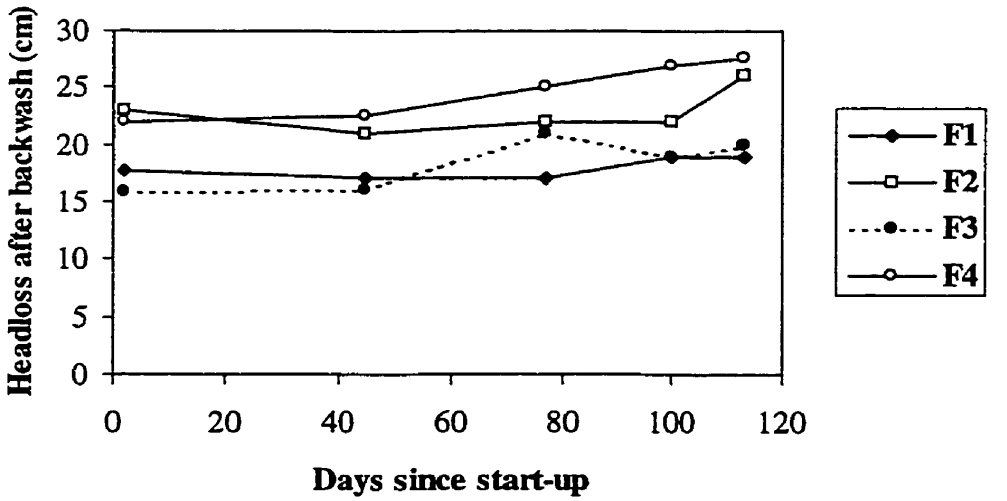

Figure 5.39: Initial headloss development in block II

F1 (Anthr., chlorine, high temp., particle, no coagulant, air scour); F2 (GAC, chlorine, high temp., particle, coagulant, water only); F3 (Anthr., chlorine, low temp., no particle, no coagulant, air scour); F4 (GAC, chlorine, low temp., no particle, coagulant, water only)

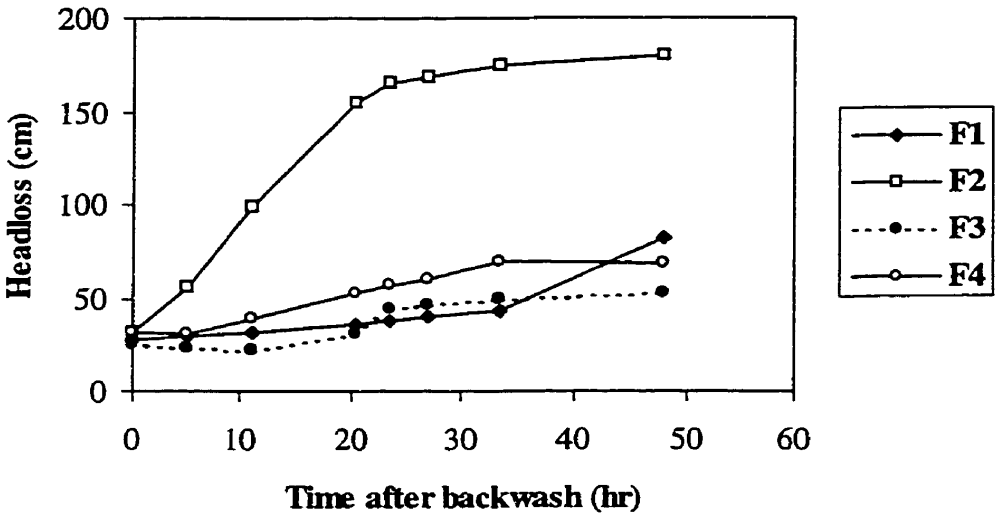

Figure 5:40: Head loss accumulation in a filter run (day 65, block I)

F1 (Anthr., no chlorine, high temp., particle, no coagulant, water only); F2 (GAC, no chlorine, high temp., particle, coagulant, air scour); F3 (Anthr., chlorine, low temp., no particle, no coagulant, water only); F4 (GAC, chlorine, high temp., no particle, coagulant, air scour)

No substantial initial headloss accumulation occurred in biofilters whether backwashed with or without air scour (even for the case F1 in block I: no air scour, no chlorine in the backwash water) in the present study. This is in agreement with a pilot study conducted by Goldgrabe *et al.* (1993). However, Coffey *et al.* (1995) observed a major increase (~ 40%) in clean bed headloss in a biological GAC/sand filter backwashed without air-scour (no chlorine in the backwash water) after a period of three months. However, from a biofilter operation perspective, the use of air scour is recommended for ease of backwash operation.

Headloss accumulation during a filter run in each filter (day 65, block I) is shown in Figure 5.40. The accumulation rate in Filter 2 (with both particles and coagulant) was substantially greater than in the other three filters. This is due to the fact that the particles were destabilized and removed well in Filter 2.

Particle removal in biofilters

During the three phases of experiments, when kaolinite was added to the influent, the turbidity in the filter influent was in the range of 1 – 2 NTU and the effluent was in the range of 0.2 – 0.4 NTU. The effluent turbidity level in the present study was close to the value of 0.4 NTU in a pilot scale biofilter reported by Goldgrabe *et al.* (1993). A lower turbidity level (<0.1 NTU), which is comparable to those produced by full-scale conventional treatment plants (i.e. typically ~0.1 NTU), was achieved in a full-scale biofilter (Coffey *et al.*, 1995). The poorer effluent turbidity at bench or pilot scale biofilters may be attributable to the filter "wall effect" or non-optimized coagulation/flocculation processes. Particle removal in biofilters was not substantially impacted by BOM removal. The turbidity was slightly higher immediately following a backwash, and the filter ripening period, with respect to particle counts, was somewhat longer in biofilters (Booth et al., 1999).

Bacteria levels in the biofilter influent and effluent

There was no significant difference between HPC levels in the filter influent and the effluent at a 5% significance level. However, the HPC levels in the effluent of the biofilters were generally higher than in the influent (average: $4.7*10^4$ vs. $1.9*10^4$, n = 27, in Appendix G). These results are similar to those from Servais *et al.* (1992). Those authors found that bacteria were more numerous in the outflow (~10^5 CFU/ml) than in the inflow (10^4~10^5 CFU/ml) of a full-scale GAC biofilter in the Choisy-le-Roi plant. A much greater difference was seen by Lu and Huck (1993), who reported that the HPCs in the effluent of filters receiving ozonated water were consistently substantially higher than the HPCs in the influent (10^4 vs. 10^2 CFU/ml). This may be due to the fact that a pre-ozonation process can reduce the influent HPC level by ozone disinfection.

One concern for the operation of biofilters is whether the detached biofilms will affect the particle concentration in the effluent. Based on the experimental results from this study, an approximate estimation indicated that the concentration (by weight) of non-biological particles in the filtration effluent is more than 196 times higher than that of biological particles (as bacteria) (refer to Appendix H). Therefore, the contribution of turbidity

caused by increased biological particles (as bacteria) in the biofiltration effluent is negligible. More stringent turbidity or particle count requirements will not limit the use of biofiltration. Therefore biofiltration should not have a major negative impact on turbidity or particle counts in the finished water.

5.5 CONCLUSIONS

The following principal conclusion regarding the effects of particle/coagulant and air scour on BOM removal was drawn from t-test results in different periods of phase III:

- Air scour effects were generally not significant under favourable conditions (at a 5% significance level), although the air scour effects may need to be considered under unfavourable conditions (low temperature, primarily chloramine). Particle and coagulant effects were not significant (at a 5% significance level).

Major conclusions from BOM removal under various circumstances in phase III are:

- In general, the BOM removal in biofilters operated at high temperature (even low temperature with chloramine backwash) reached a dynamic steady-state faster than in biofilters run at low temperature with chlorine in the backwash water.
- Glyoxal was more sensitive than other BOM components to unfavourable operating conditions, such as low temperature and chlorine in the backwash water.
- The interaction of temperature and chlorine was still significant when using chlorine in the backwash water at a dosage of 0.25 mg/L. Chlorine in the backwash water (at a dosage of 0.25 mg/L) could affect all BOM component removal in biofilters run at low temperatures, but it only impacted recalcitrant BOM component (as glyoxal) removal in biofilters operated at high temperature. Chloramine at a dosage of 0.25 mg/L in the backwash water did not impact BOM removal in biofilters operated at high and low temperatures.

- EBCT (or X^*) is a good indicator for BOM removal in biofilters. Similar removals were observed within the same EBCT (or X^*) when the biofilters were run at different HLRs. EBCT (or X^*) can be used as a design parameter for biofilters.
- Biofilter media utilization (the extent to which the entire bed depth contributes to removals) was dependent on the biofilter operating conditions and the biodegradability of BOM components. In general, biofilter media utilization was low under favourable conditions (easily biodegradable BOM components; high temperature, backwashed with chloramine in the backwash water) and biofilter media utilization was high under unfavourable conditions (recalcitrant BOM components; low temperature and backwashed with chlorine in the backwash water).
- In general, there were no major changes in BOM removal duirng a filter run. BOM removal was not sensitive to biomass changes in a filter run. Biomass removed during backwash (<50%) did not substantially interfere with the BOM removal in the following filter run.
- Instantaneous effects of HLR and BOM steps on BOM removal were similar: BOM removal (as acetate, formate formaldehyde and glyoxal) in Filter 3 (the "worst case" scenario) was decreased. The recalcitrant BOM components (glyoxal) removal was impacted in all filters except in Filter 2 (the "best case" scenario).
- BOM removal could be restored to the original level after about 1 to 10 days of operation of BOM or HLR steps, depending on biofilter operating conditions and the biodegradability of BOM components.
- BOM removal results before and after filter shutdown demonstrated that the biofilms on the four biofilters were mature and strong enough to withstand the unfavourable influences of filter shutdown, at least for easily biodegradable BOM compounds.
- Particle removal in biofilters is not substantially affected by the BOM removal, and the turbidity caused by increased bacteria concentration (measured by HPC count) in the biofiltration effluent is relatively negligible.

The following conclusions related to biofilter operation can be derived from the experimental results in this Chapter:

- The use of air scour is recommended for the ease of the backwash operation in biofilters for both particle and BOM removal, although it may impact the less easily biodegradable BOM compound removal to a certain extent, under unfavourable conditions.
- A similar BOM removal can be expected in either single stage or second stage biofilters because the effect of particles and coagulant in the filter influent is negligible with respect to BOM removal in biofilters.
- Chlorine is not recommended for filter backwash, except for the control of biomass build-up in a vigorous biofiltration process.
- Biofiltration can be performed efficiently when the temperature is above 5 °C and no chlorine is present in the backwash water.
- HLR/BOM steps and regular biofilter maintenance should not have a major impact on biofilter performance.
- Particle removal in biofilters is not substantially affected by the BOM removal, and the turbidity caused by increased bacteria concentration (measured by HPC count) in the biofiltration effluent is relatively negligible.

CHAPTER 6: EVALUATION OF AN ALTERNATIVE BIOMASS TEST: BRP

6.1 INTRODUCTION

The amount of biomass (as biofilm) present is a critical concept in drinking water biofilter models (Zhang and Huck, 1996a; Wang *et al.*, 1995; Hozalski, 1996). BOM removal performance can be evaluated in terms of biomass (biofilms) distribution in biofilters. The biomass distribution in the biofilters can be estimated from the biofilter modeling itself (Zhang and Huck, 1996a; Hozalski, 1996) or by regression of the measured distribution (Wang *et al.*, 1995). However, it may be more robust to use the measured distribution in biofilter modeling.

Several methods for the measurement of biomass have been used. Some of the more common, include the phospholipid method (Findlay *et al.*, 1989; Wang *et al.*, 1995, Coffey *et al.*, 1995; Carlson *et al.*, 1998; Urfer, 1998), the ^{14}C-glucose respiration method (Servais *et al.*, 1991; 1992), and the ATP method (Ahmad *et al.*, 1998). This Chapter discusses the further development of a new method, biomass respiration potential (BRP), originally introduced by Urfer (1998).

6.2 BACKGROUND

The amount of living biomass on the filter media can be quantified by determining its phospholipid content using the method of Findlay *et al.* (1989). The phospholipid

method, which has been described in detail in Chapter 3, requires only standard laboratory equipment. However, the whole procedure is typically very time consuming and labour intensive. The phospholipid method measures the viable biomass, but it does not provide a measure of microbial activity.

The ^{14}C-glucose respiration method is based on the measurement of the production of $^{14}CO_2$ from the respiration of radio-labelled glucose by the biomass in the media sample. This method provides a measurement of the organic substrate degradation potential (i.e. respiration) of the biomass. Special laboratory equipment and security features are required for this method, which may not be applicable in most water utilities. One drawback to this method is that free glucose (unbound) may not be a true representation of the BOM components present in drinking water influents. Acetate may be a more appropriate indicator than glucose, since it is a common organic ozonation product (e.g. Andrews and Huck, 1994; Gagnon *et al.*, 1997). The measurement of the metabolic activity of a microbial community by the incorporation of ^{14}C–acetate into cellular lipids has been used by White and colleagues (White *et al.*, 1977; Vestal and White, 1989). Wang (1995) has successfully applied the ^{14}C–acetate method for the analysis of the microbial activity of biomass in drinking water biofilters (Wang, 1995).

Adenosine triphosphate (ATP) is present in a relatively constant proportion within all living cells, and is typically not present in detritus or dead cells. The ATP method is a measurement of cellular ATP of biomass in the media sample. In this method, cellular ATP is extracted before being subjected to a bioluminescent reaction. The ATP content is then determined by the luciferine-luciferase reaction with an ATP bioluminescent assay kit. ATP methods provide a measurement of the viable biomass. However, one of the drawbacks of this method is the requirement of special instruments. The other is the difficulty to convert ATP measurements to the amount of biomass since the ATP yield may increase when the concentration of sodium acetate is increased (Stanfield *et al.*, 1987).

These aforementioned methods for biomass measurement are either typically very time consuming (i.e. the phospholipid) or dependent on special instrumentation (the ATP method and the ^{14}C-glucose respiration method). Developing a simple alternative approach for biomass estimation is, therefore, of practical use for water utilities.

Respirometric techniques such as the measurement of the rates of oxygen consumption are commonly used for the estimation of microbial metabolism (e.g. Atlas and Bartha, 2000; Metcalf and Eddy, 1991). This application has also been used in the estimation of biodegradation kinetic parameters in activated sludge (e.g. Ellis *et al.*, 1996). Instrumentation is of high sensitivity for DO (dissolved oxygen) measurements, and allows for the enhancement of these applications.

The biomass respiration potential (BRP) concept for drinking water biofilters was originally proposed by Urfer (1998). The BRP test is based on the consumption of dissolved oxygen (DO) resulting from aerobic respiration of several BOM components in a water sample containing a given amount of biofilter media. Urfer (1998) found that the trend of pseudo steady-state substrate concentration profiles was similar to that of active biomass represented as BRP. In his study, Urfer used about 1-8 g of media in 300 mL BOD-bottles, with a biodegradation time of 5 h.

Theoretically, by carefully choosing the appropriate experimental conditions, a good relationship between biomass as measured by BRP and biomass measured any other way can be expected. BRP can be evaluated for use as a surrogate for biomass as measured by phospholipid, ATP or ^{14}C-glucose respiration. However, this expected "good" relationship between phospholipid biomass and BRP biomass was not observed in Urfer's study (1998).

In the current research, one specifically designed exploratory experiment was carried out to develop a simple and fast alternative biomass measurement. The BRP method was evaluated for use as a surrogate for phospholipid biomass. In the current study, a larger amount of media (about 5 - 30 g media in 300 mL BOD-bottles) and shorter

biodegradation time (1 - 2 h instead of 5 h) were evaluated, in comparison to the original BRP method investigations (Urfer, 1998). The BRP test conditions with more media and shorter time can be expected to avoid substantial changes of biomass and BOM concentrations during the BRP test. The theoretical background for the BRP test is discussed later in this Chapter.

6.3 OBJECTIVES

The overall objective of this component of the research is to evaluate the BRP method as a surrogate for phospholipid biomass. The specific objectives described in this Chapter are the following:

- to find suitable conditions for the BRP test;
- to establish a relationship (possibly linear) between BRP and phospholipid biomass;
- to investigate the effect of temperature on BRP tests; and
- to provide some theoretical explanations as to the existing relationship between BRP and phospholipid biomass.

6.4 MATERIALS AND METHODS

6.4.1 Operating conditions of bioreactors for BRP test

Standard BOD bottles were used as bioreactors for the BRP test. These standard BOD bottles (300 mL in volume) were autoclaved and oven-dried at 100°C overnight prior to use.

Tap water was dechlorinated (by GAC filter in this study) and then autoclaved prior to use. The dechlorinated and autoclaved tap water was then used to make BOM and nutrient cocktails in the bioreactors for the BRP test. In the BRP test, the BOM and nutrient target concentrations were three times that in the filter influents. Therefore, the

target concentrations of BOM as acetate, formate, formaldehyde and glyoxal in the bioreactors were 900, 1200, 300 and 90 μg/L, respectively. The choice of those concentrations of BOM components is in an effort to allow for a measurable BOM degradation rate (as DO change) and to cause no major concentration shock on bacteria attached on the media.

Biomass in the bioreactors for the BRP test was from the filter media (the biofilm attached on the media) at different depths of the biofilters. The filter was rinsed with dechlorinated water prior to the BRP test sampling to limit the effect of background N, P and BOM on the measurement of phospholipid biomass and BRP biomass.

Bioreactions in the bioreactors for the BRP test were performed at the same temperatures as those in the filters (either 20 °C or 5 °C in this study). The temperature in the bioreactors was controlled by using a temperature-controlled water bath shaker (Gyrotory Water Bath Shaker, Model G76, New Brunswick Scientific Co, Inc. Edoson, N. J. USA). The bioreactors were shaken at a medium speed (~90 rpm) in an effort to maintain a non-diffusion-controlled bioreaction condition.

In the current study, shorter biodegradation times (1 and /or 2 h instead of 5 h) were chosen, in comparison to the original BRP investigations by Urfer (1998). Shorter bioreaction periods were expected to minimize major changes in both biomass and BOM concentrations in the bioreactors. These major changes could affect the accuracy of the BRP as a biomass surrogate. A 5-h BRP test was also performed in some cases, to show the impact of longer incubation times on the BRP test.

A larger amount of media (about 5 - 30 g instead of 1 – 8 g media in 300 mL BOD-bottles) was used, in comparison to the original BRP investigations by Urfer (1998). Larger amount of media from the lower layer of filter bed (less biomass on the media) than that from the upper layer of filter media bed (more biomass on the media) was used in order to observe significant DO changes in the BRP test from both top and bottom media samples.

Investigations of BRP and phospholipid biomass tests were performed during phase III. Media for BRP and phospholipid biomass tests were sampled from different depths of the biofilters. These results are discussed first. The conceptual optimization of conditions for the BRP test is then discussed to allow for a better understanding of appropriate conditions for the BRP test.

For the operating conditions in the four biofilters of phase III, please refer to Chapter 5. For the measurements of DO and phospholipid biomass, please refer to Chapter 3.

6.4.2 Procedures for the BRP test

The procedure for the BRP test is simple and easy to perform. Figure 6.1 describes the procedure for the measurement of active biomass as BRP. The procedure is similar to that described by Urfer (1998).

Sample media from different depth of the filter bed in the drained and rinsed filter

⇓

Weigh the wet media samples on a scale

⇓

Place the media in empty bottles (previously autoclaved)

⇓

Add dechlorinated tap water (previously autoclaved) to BOD bottles

⇓

Measure dissolved oxygen with DO-probe

⇓

Add BOM and N, P into BOD bottles (Start time)

⇓

Fill BOD bottle headspace free with tap water (previously autoclaved), close with glass stoppers

⇓

Place BOD bottles on a shaker table submerged in water bath (medium speed, temperature controlled) for 1 h

⇓

Measure the dissolved oxygen concentration with DO-probe at 1 h

⇓

Put BOD bottles on shaker table submerged in water bath again for another 1h (optional)

⇓

Measure the dissolved oxygen concentration with DO-probe at 2 h (optional)

Figure 6.1: Procedure for the BRP test

6.5 RESULTS AND DISCUSSION

The results of the BRP test are shown in Appendix I.

A preliminary experiment was performed to choose an appropriate time period for the BRP test. Three BRP tests (1h, 2h and 5 h) and phospholipid biomass were investigated in Filter 1 (day 63 in phase III). A typical result for BRP and phospholipid biomass test from F1 is illustrated in Figure 6.2.

The phospholipid biomass profile was similar to that described in Chapter 5. There was a pronounced stratification for the phospholipid biomass in the biofilter. BRP (1h) and BRP (2h) profiles are close to that of phospholipid biomass. A substantially less pronounced stratification for the BRP (5h) was observed, and this might be due to the following reasons: (1) bioreaction rate (i. e. oxygen consumption rate) in bioreactors after a couple of hours may be reduced due to the lowered BOM concentration; (2) some inhibitory effects caused by bacterial metabolic products may occur in bioreactors for the BRP test when the amount of phospholipid biomass is higher and the bioreaction time period is longer. On the other hand, this kind of an inhibitory effect was relatively negligible because of the lower concentration of bacterial metabolic products when the

biomass is lower on the media; (3) the possible major increase of biomass during a longer BRP test may enhance the processes in (1) and (2); (4) the bioactivity of biomass at the top and bottom media may be different (Servais *et al.*, 1992).

The BRP (5h) profile from this study is similar to that of Urfer's findings (1998). Urfer (1998) found that the ratio of BRP (5h) to phospholipid biomass was significantly higher for the bottom media (with less biomass) than for the top media (with more biomass). A larger relative error for the measurement of low concentrations of biomass may contribute to this trend, however the more substantially reduced BOM concentration and the more substantially accumulated metabolic products during a longer BRP test period may also contribute to this trend.

Based on the results from the BRP tests shown in Figure 6.2, the BRP (1h) and BRP (2h) may be considered suitable times for the BRP test. Further experimental work was performed during phase III to investigate the BRP (1h) and BRP (2h) as surrogates for the phospholipid biomass method. These experiments are included in Table 6.1. The experimental results of the BRP and the phospholipid biomass are given in Appendix I.

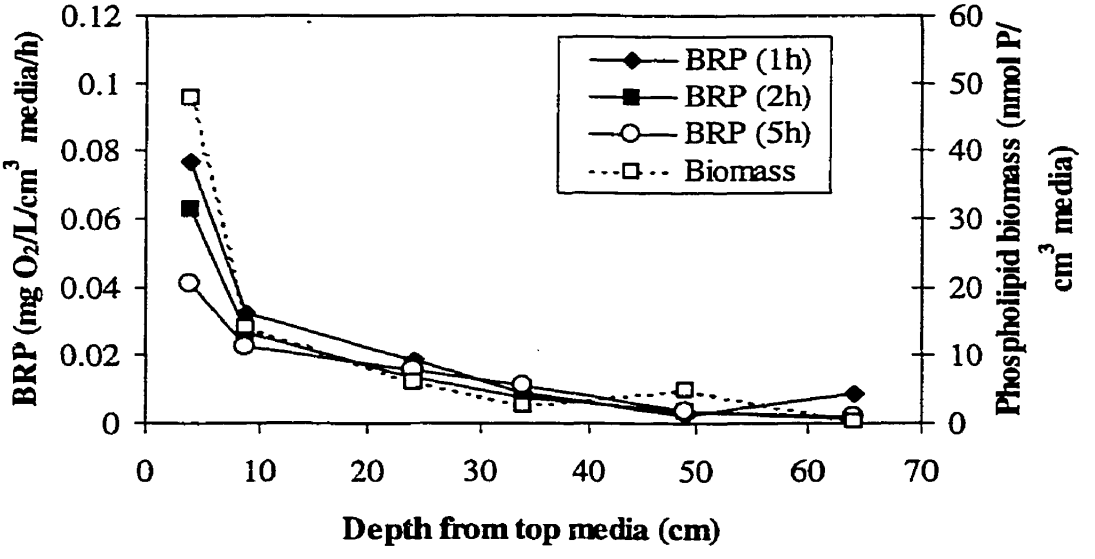

Figure 6.2: Time effects on BRP vs. phospholipid biomass

The level of significance of the correlation of the BRP and the phospholipid biomass given by the correlation coefficient is the same as the level of significance of the slope of the regression line (Kennedy and Neville, 1986). The correlation between the BRP (1h)/BRP (2h) and the phospholipid biomass in a single filter was established by linear regression. The square of coefficient R, the coefficient R and the significance of the correlation for different filters and sampling days are summarised in Table 6.1.

Table 6.1: The Relationship Between BRP (1h) and Phospholipid Biomass in Single Filter

Filter	F1			F2			F3			F4		
Sampling day#	63	85	286	78	87	288	63	85	286	78	87	288
R^2 (1h)	.93	.90	.92	.65	.75	.80	.30	.63	.83	.97	.83	.92
R^2 (2h)	.95	.97	.93	.83	.83	.93	.49	.57	.82	.98	.77	.91
R (1h)	.96	.95	.96	.81	.87	.89	.55	.80	.91	.98	.91	.96
R (2h)	.97	.98	.96	.91	.91	.96	.70	.75	.90	.99	.88	.95
Significant (1h)*	Yes/ Yes	Yes/ Yes	Yes/ Yes	Yes/ No	Yes/ No	Yes/ No	No/ No	No/ No	Yes/ No	Yes/ Yes	Yes/ No	Yes/ Yes
Significant (2h)*	Yes/ Yes	Yes/ Yes	Yes/ Yes	Yes/ No	Yes/ No	Yes/ Yes	No/ No	No/ No	Yes/ No	Yes/ Yes	Yes/ No	Yes/ Yes

* At 5 percent/1 percent level of significance, degrees of freedom $\nu = 6 - 2 = 4$, $R_{4,0.05} = 0.811$, $R_{4,0.01} = 0.917$

Days since start-up

In most cases (except for F3), there was a good correlation between the BRP (1h)/BRP (2h) and the phospholipid biomass in a single filter. As noted in Chapter 5, the values of phospholipid biomass in F3 are significantly lower than in other filters, and are therefore more sensitive to the errors from measurements of the phospholipid biomass. This is considered to be the reason for the poor relationship between the BRP and the phospholipid biomass in Filter 3.

In a given experiment, the correlation coefficient (R^2) between BRP and phospholipid biomass was similar, regardless of whether BRP was measured over one or two hours. This may be due to the fact that experimental errors from the measurements of the phospholipid biomass are the same for a single filter in the same batch experiment.

Biofilm which developed in biofilters operated at different operating conditions may have different behaviours with regards to the BRP test and the phospholipid biomass. By pooling the data from different days of measurement for each filter, the correlation between the BRP (1h) and the phospholipid biomass can be evaluated in Figures 6.3 to 6.6. The same scales were used in those Figures to facilitate visual comparison. In each filter, the regression is based on 18 measurements from 3 days of measurement at 6 different sampling points in each biofilter. Although the regression are shown in these

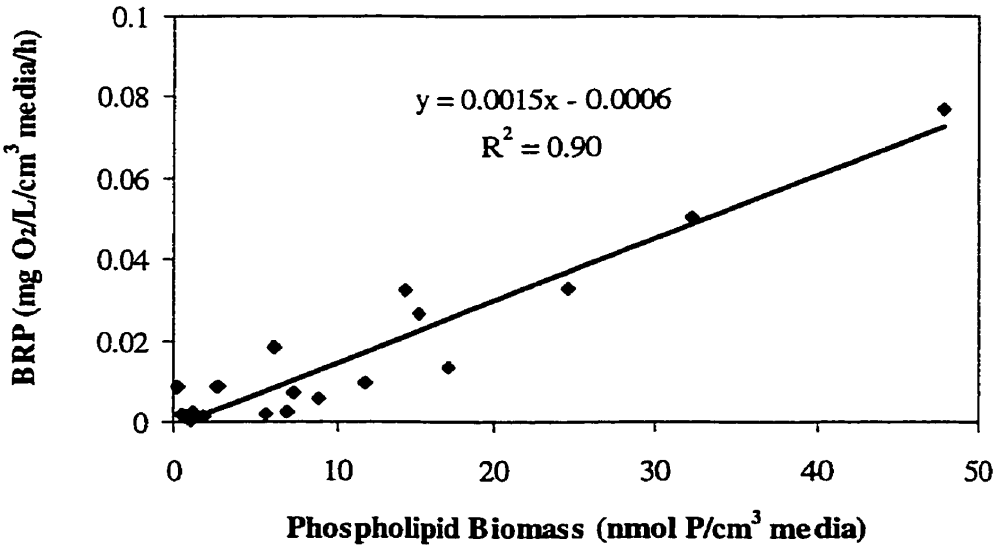

Figure 6.3: BRP (1h) vs. phospholipid biomass in Filter 1 (phase III)

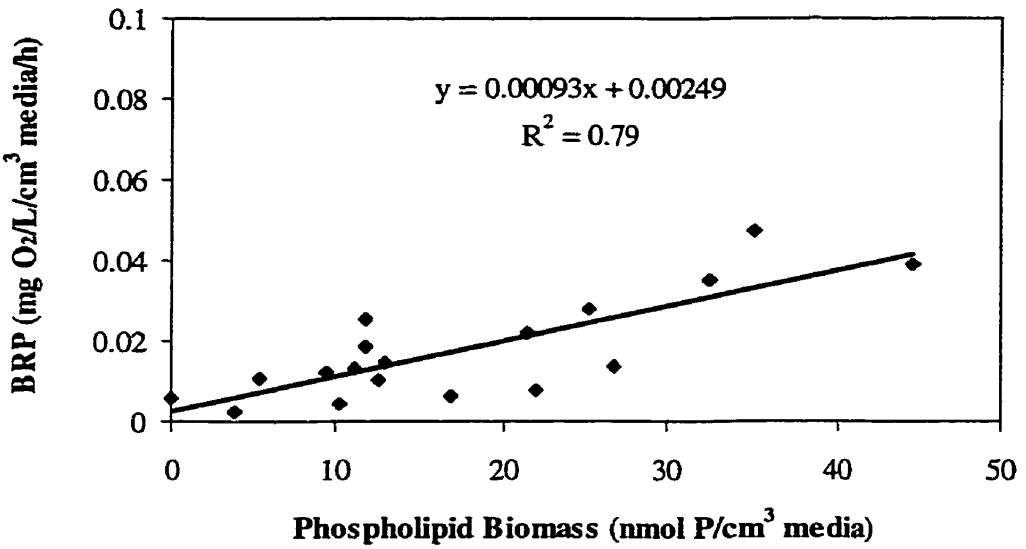

Figure 6.4: BRP (1h) vs. phospholipid biomass in Filter 2 (phase III)

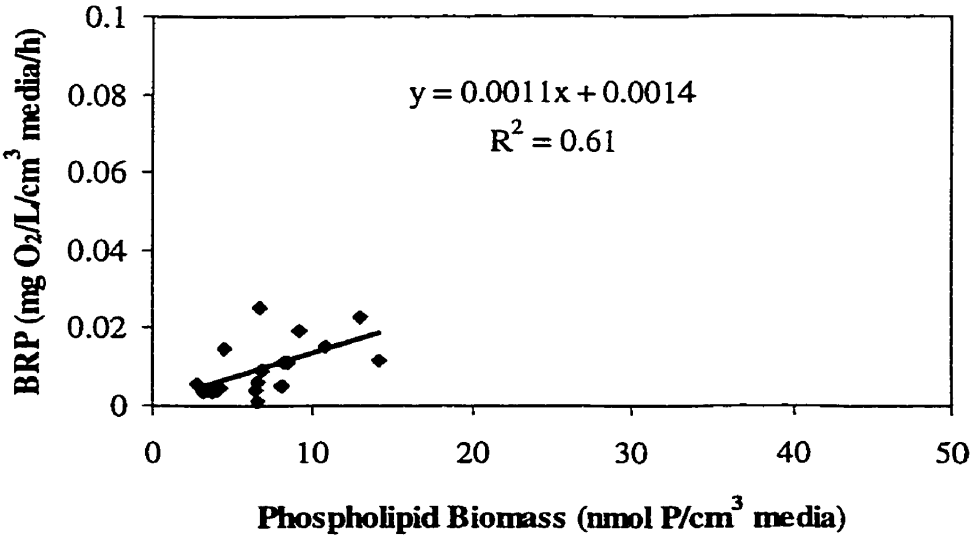

Figure 6.5: BRP (1h) vs. phospholipid biomass in Filter 3 (phase III)

figures, in fact one of the key assumptions for regression (namely that the independent variable is error-free) is not satisfied.

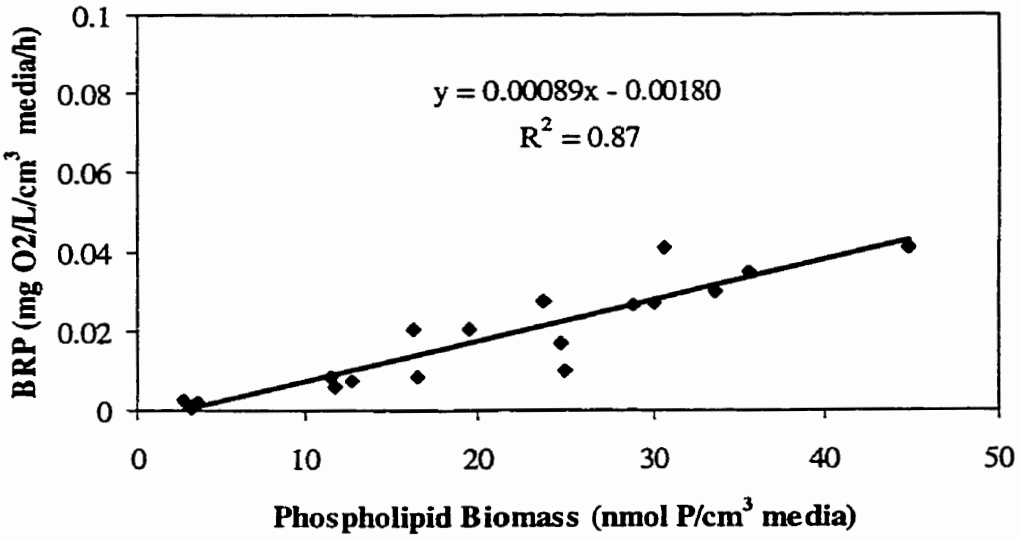

Figure 6.6: BRP (1h) vs. phospholipid biomass in Filter 4 (phase III)

Regressions from all four filters are significant at a 1% significance level ($R_{16,0.01} = 0.59$, therefore $R^2 = 0.35$). It is concluded that there is a good correlation between BRP (1h) and phospholipid biomass.

A more scattered pattern of the linear relationship was found in Filter 3. This might be due to the fact that the biomass level in Filter 3 is substantially lower than in the other three filters, and the relative errors for phospholipid biomass (errors include variations in biomass levels from one media to another) are higher in Filter 3 than in the other three filters.

In comparing BRP (1h) vs. BRP (2h) (the procedure for BRP (1h) and BRP (2h) tests shown in Figure 6.1), the differences between BRP (1h) and BRP (2h) in Filter 1 and

Filter 4 are presented in Figures 6.7 and 6.8 by using the regressed equations. It is difficult to give confidence intervals for the predicted BRP values in Figures 6.7 and 6.8 because relatively large errors (not negligible) occur in the measurement of phospholipid biomass. BRP (1h) levels are generally higher than BRP (2h) levels. A similar trend was observed in the other two filters. The differences become greater as the biomass levels increase. The differences between the BRP (1h) and BRP (2h) are between 0 – 25 %, depending on the biomass levels and the particular biofilters in the BRP tests. The higher levels of BRP (1h) might be due to a higher bioreaction rate (with higher BOM concentration) and possibly a lower inhibitory effect (with lower bacterial metabolic products), in comparison with the BRP (2h) test.

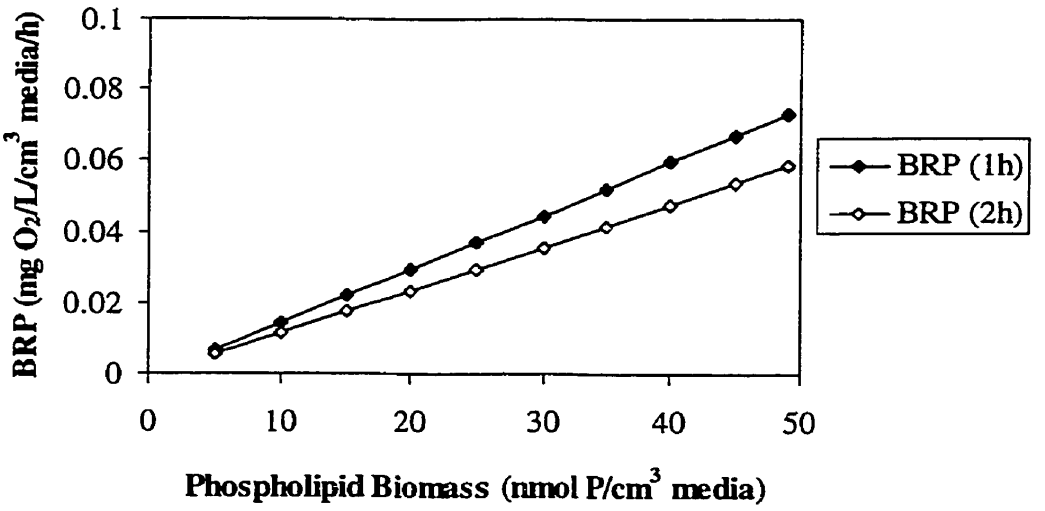

Figure 6.7: Predicted values of BRP(1h) and BRP(2h) vs. Phospholipid biomass in Filter 1 of phase III

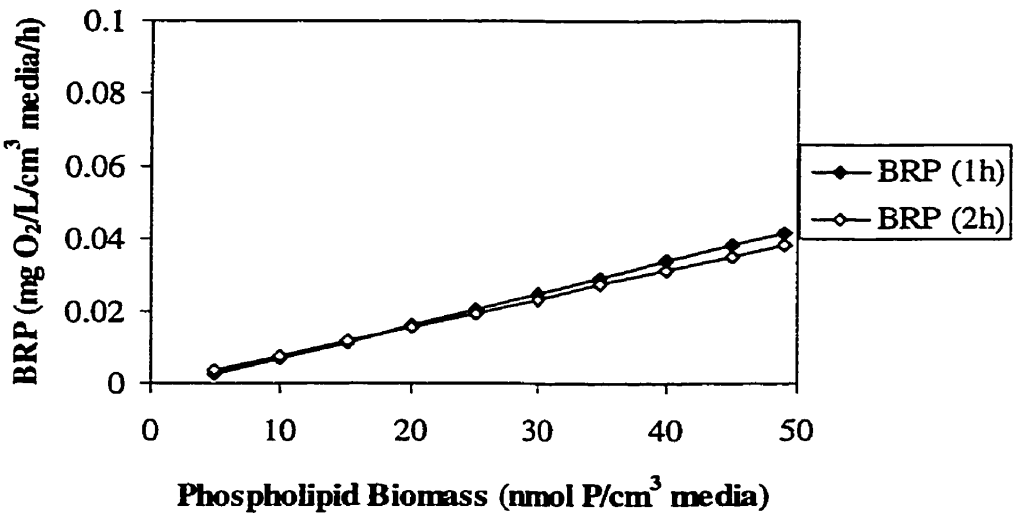

Figure 6.8: Predicted values of BRP(1h) and BRP(2h) vs. Phospholipid biomass in Filter 4 of phase III

The relationship of BRP vs. phospholipid biomass for different filters is presented in Figure 6.9. BRP levels in F1 (backwashed with chlorinated water; high temperature) are generally higher than those backwashed with chloraminated water (F2 and F4 in Figure 6.9). A possible explanation is that the chlorine acclimated (during backwash) biomass might have a higher bioreaction potential than chloraminated (during backwash) biomass in the BRP test. Irobi (1997) observed a difference in bacterial species in bench-scale annular reactors modelling a drinking water distribution ecosystem (with chlorine or with chloramine). In the presence of chlorine slightly more Gram positive bacteria were recovered while the selection patterns in chloraminated reactors showed a slight preponderance of Gram negative bacteria (Irobi, 1997). Generally higher BRP levels were observed in filters operated at high temperature than in filters operated at low temperature (F1 vs. F3; and F2 vs. F4 in Figure 6.9), although the difference between F2 and F4 is minor. The higher temperature can increase the bioreaction rate in the BRP test, thereby increasing the BRP values.

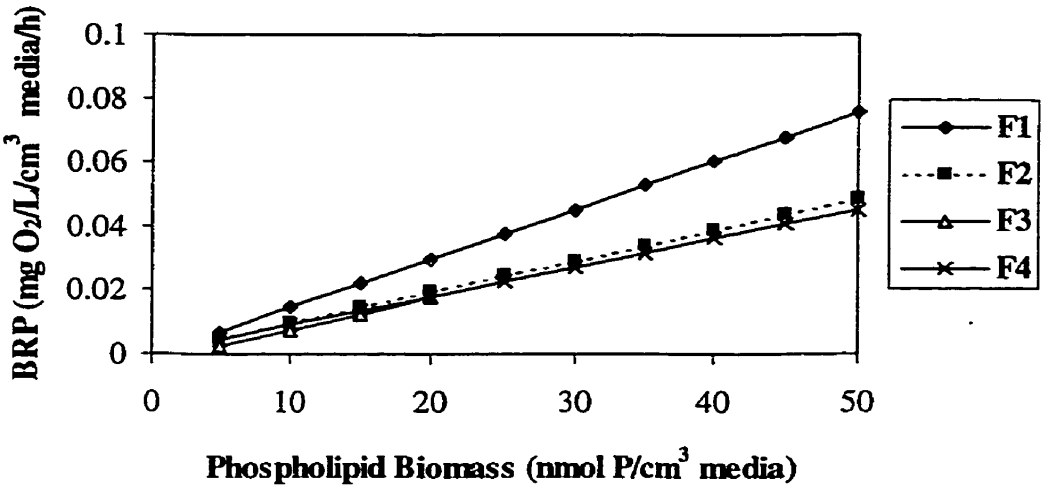

Figure 6.9: Comparison of regression equations for BRP(1h) vs. phospholipid biomass in four filters (phase III)

F1 (anthracite, chlorine, 20 °C); F2 (anthracite, chloramine, 20°C); F3 (anthracite, free chlorine, 5 °C); F4 (anthracite, chloramine, 5 °C)

Theoretically, BRP should be temperature dependent because higher bioreaction rates are expected in bioreactors for BRP tests run at higher temperatures. Based on pooled data from all experiments, the relationship between BRP (1h) and phospholipid biomass is presented in Figures 6.10 and 6.11. In each case, the regression is based on 36 measurements. The analyses of R values indicate that the overall regressions are significant at the 5% level. The R^2 value at low temperature (0.79) falls between R^2 values for F3 (0.61 in Figure 6.5) and F4 (0.87 in Figure 6.6). Similarly, the R^2 value at high temperature (0.80) falls between R^2 values for F2 (0.79 in Figure 6.4) and F1 (0.90).

By using a similar approach to the regression equations shown in Figures 6.10 and 6.11, the temperature effect on the BRP vs. the phospholipid biomass relationship can be illustrated in Figure 6.12. As expected, the BRP level at high temperatures is higher than that at low temperatures, for the same phospholipid biomass value.

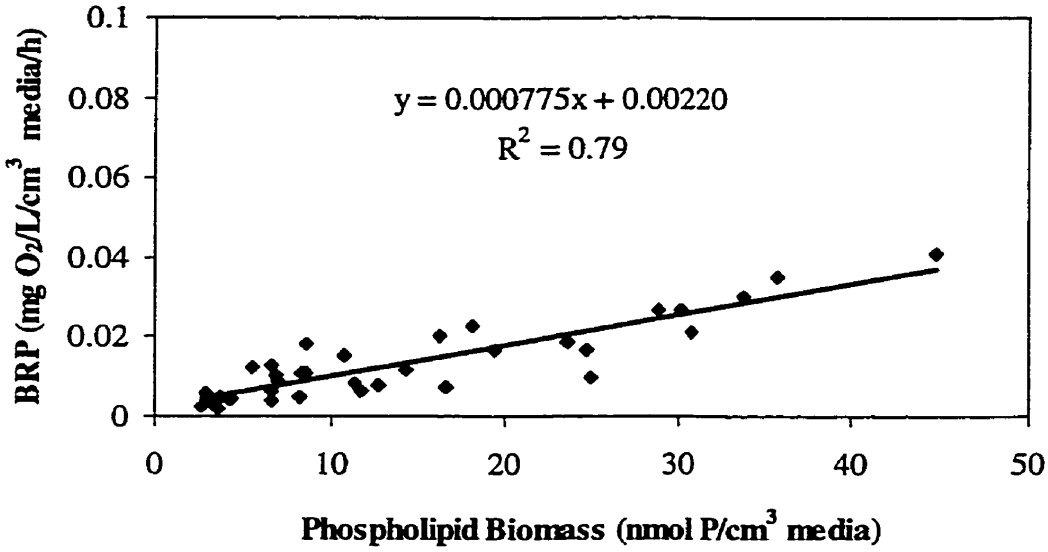

Figure 6.10: BRP (1h) vs. phospholipid biomass at low temperature (5 °C, phase III)

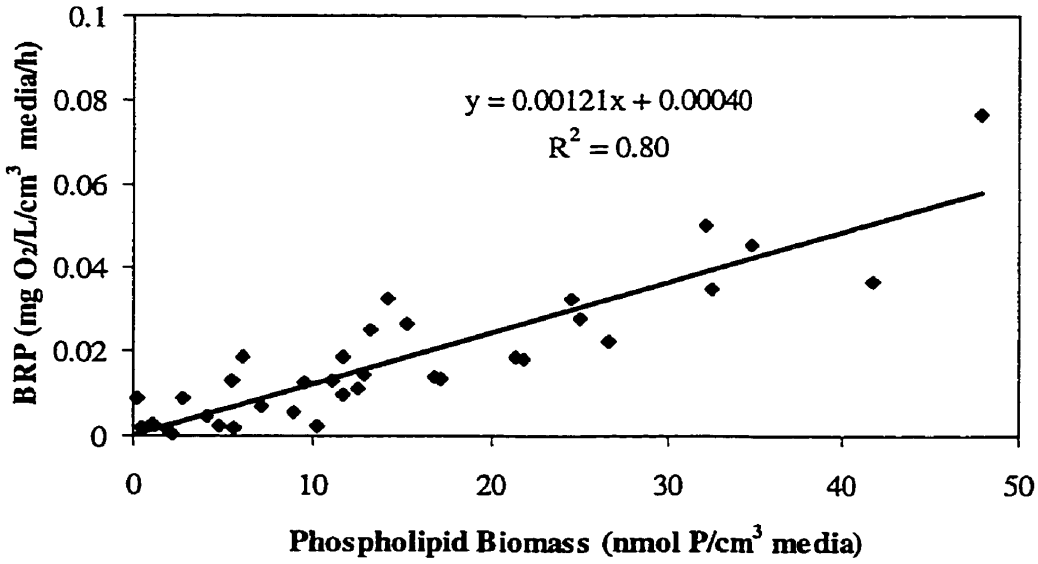

Figure 6.11: BRP (1h) vs. phospholipid biomass at high temperature (20 °C, phase III)

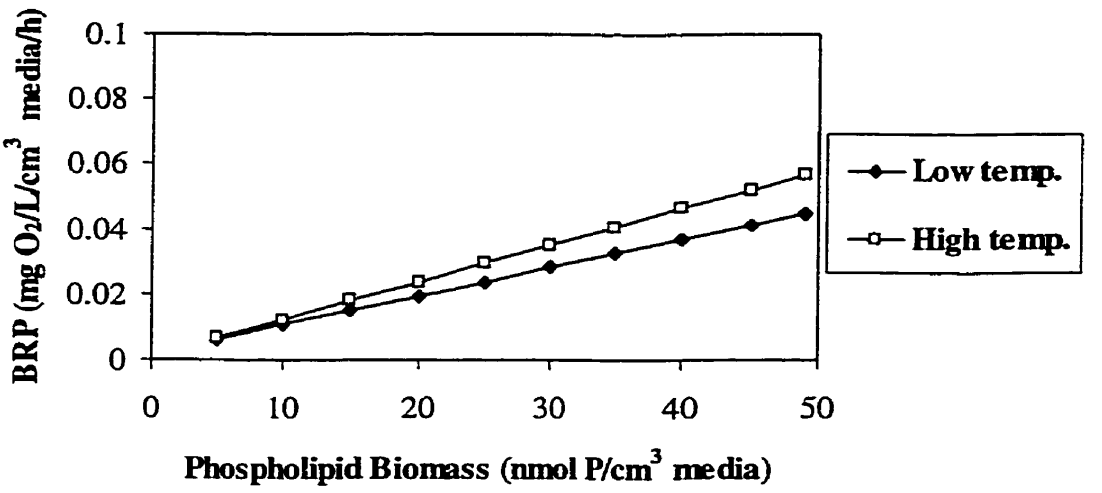

Figure 6.12: Temperature effects on BRP vs. phospholipid biomass (phase III)

The temperature dependence of the BRP tests is important in assessing the amount of biomass in the biofilters. Temperature influences the metabolic activities of microbial populations, and for engineering purposes the effect of temperature on the reaction rate of a biological process is usually expressed in the following empirical form (Metcalf and Eddy, 1991):

$$r_T = r_{20}\,\theta^{(T-20)} \qquad (6.1)$$

where, r_T is the reaction rate; r_{20} denotes the reaction rate at 20 °C; θ represents the temperature-activity coefficient and T is the temperature (°C).

The effect of temperature on BRP tests is essentially the same as the effect of temperature on the reaction rate of a biological process. A similar equation can be used to describe the effect of temperature on BRP tests:

$$BRP_{(T)} = BRP_{(20)}\,\theta^{(T-20)} \qquad (6.2)$$

Where, $BRP_{(T)}$ is the BRP value at temperature T °C, and $BRP_{(20)}$ denotes the BRP value at 20 °C.

The temperature-activity coefficient θ was estimated to be 1.014, by using the data provided in Figure 6.12. This value is close to the lower range of trickling filters (1.02 – 1.08) in wastewater treatment (Metcalf and Eddy, 1991).

The relationship between BRP (as mg O_2/L/cm^3 media/h) and phospholipid biomass (as nmol P/cm^3 media) at 20 °C as depicted in Figure 6.11 has the following equation:

$$BRP_{(20)} \text{ (predicted)} = 0.00121 * \text{Phospholipid biomass} + 0.00040 + \text{error} \qquad (6.3)$$

Equation 6.3 can be transformed into the following form:

$$\text{Phospholipid biomass} = 826 * BRP - 0.33 + \text{error} \qquad (6.4)$$

Because neither the BRP nor the phospholipid biomass measurements used as the independent variable in the regression are error-free. Calculation of a confidence interval for predicted phospholipid biomass values is complicated and was not performed.

By substituting equation 6.2 into equation 6.4, the phospholipid biomass (as nmol P/cm^3 media) at any given temperature can be estimated, in terms of the measured $BRP_{(T)}$, in equation 6.6:

$$\text{Phospholipid biomass}_{(T)} = 826 * BRP_{(T)}\, 1.014^{(20-T)} - 0.33 \qquad (6.5)$$

Similarly to equation 6.5, based on the relationship between BRP (as mg O_2/L/cm^3 media/h) and phospholipid biomass (as nmol P/cm^3 media) at 5 °C as depicted in Figure 6.10, equation 6.6 can also be used to estimate the phospholipid biomass at any given temperature, in terms of the measured $BRP_{(T)}$:

$$\text{Phospholipid biomass}_{(T)} = 1.29 * 10^3\, BRP_{(T)}\, 1.014^{(5-T)} - 2.8 \qquad (6.6)$$

Both equations 6.5 and 6.6 can be used to estimate the phospholipid biomass at any given temperature, in terms of the measured $BRP_{(T)}$. However, equation 6.6 is recommended for use at higher temperatures and equation 6.7 at lower temperatures, in order to minimize errors in estimated phospholipid biomass. For reasons discussed above, confidence intervals for these predictiions were not determined.

6.5 OPTIMIZATION OF THE CONDITIONS FOR BRP TESTS

The appropriate conditions for the BRP test are crucial to the establishment of a good correlation between the BRP and the phospholipid biomass.

The BRP test is performed in a batch bioreactor. A certain amount of biomass on the media and a substrate (BOM) cocktail of a desired concentration are put into a closed bioreactor. There is no mass transfer between the bioreactor and the ambient environment. The dissolved oxygen mass balance in the bioreactor can be described by equation 6.7, according to the principle of aerobic biodegradation of BOM in a batch bioreactor (Metcalf and Eddy, 1991; Grady and Lim, 1980).

[DO depletion rate in bioreactor] = [DO consumption rate by substrate (BOM) oxidation] – 1.42 [Microorganism production rate] + 1.42 [Microorganism decay rate]

$$-\frac{dO_2}{dt}V = -\frac{dS}{dt}Vf - 1.42\frac{dX}{dt}V + 1.42XVk_d \qquad (6.7)$$

Where, O_2, S and X express the concentrations of oxygen, substrate and biomass in the bioreactor (ML^{-3}), respectively; V is the volume of the bioreactor (L^3); f denotes the conversion factor for converting substrate carbon to dissolved oxygen requirement; k_d represents the endogenous decay coefficient (T^{-1}). 1.42 is the coefficient for converting bacteria to dissolved oxygen requirement.

Based on the Monod model, the rate of substrate utilization can be expressed as in equation 6.8 (Metcalf and Eddy, 1991):

$$\frac{dS}{dt} = \frac{-kXS}{K_s + S} \tag{6.8}$$

The rate of biomass growth is proportional to the rate of substrate utilization, as expressed in equation 6.9:

$$\frac{dX}{dt} = -Y\frac{dS}{dt} \tag{6.9}$$

Where, k is the maximum utilization rate of the substrate (T^{-1}); K_s is Michaelis-Menten half-velocity constant (ML^{-3}); Y is the yield coefficient (M_x/M_s).

Substituting equations 6.8 and 6.9 into 6.7 yields:

$$-\frac{dO_2}{dt} = [1.42k_d - (1.42Y - f)\frac{kS}{K_s + S}]X \tag{6.10}$$

In a BRP test, dO_2/dt can be approximately considered to be constant for a given BRP test, if there are no major changes in the coefficient of X and X itself in equation 6.10. A good linear relationship (i.e. dO_2/dt can be approximately considered to be proportional to the biomass concentrations in different BRP tests can be expected if the coefficient of X and in equation 6.10 are approximately constant during the BRP tests.

The endogenous decay coefficient (k_d), the conversion factor for converting substrate carbon to the dissolved oxygen requirement (f), the yield coefficient (Y), the maximum utilization rate of the substrate (k) and the Michaelis-Menten half-velocity constant (K_s) can be considered constant in the BRP test. Therefore, the coefficient of X is dependent on substrate utilization kinetics in the Michaelis-Menten equation (i. e. S dependent). At low substrate concentrations ($S<<K_s$), the coefficient of X is proportional to the substrate concentration S. As the concentration of S increases, the coefficient of X increases less

than proportionally and reaches a maximum ($S >> K_s$), where the coefficient of X is independent of S. Therefore, if choosing a high initial substrate concentration S_o ($S_o >> K_s$), the coefficient of X is expected to be proportional to the biomass concentration in the BRP test. It is also expected that no significant changes in the concentration of S occur during the BRP test because of the higher level of S in the bioreactor for the BRP test.

An overly high initial concentration of substrate (S_o) may impair the bioreaction rate in the BRP test because the bacteria (as biomass) might experience a sudden change in substrate concentration. The appropriate initial concentration of substrate in the BRP test can be determined in a specific experiment similar to the BRP test (not done in the present study). In such an experiment, about the same amount of biomass media as in BRP test, from the same depth of the biofilter, would be added to several BRP test bottles. The initial substrate concentrations (S_1, S_2, ... S_n) in these BRP test bottles varies from low to very high levels ($S_n >> K_s$). The substrate concentration in each BRP test bottle would be measured at 1 h. The dS/dt vs. S relationship would be plotted in a curve. An optimized substrate concentration $S_{opt.(BRP)}$ at which the rate of substrate utilization just reaches a maximum and the rate of substrate utilization is independent of S, could then be determined.

Any biomass changes between the start and the end of the BRP test may also impact the linear relationship between the BRP and phosholipid biomass because of the difficulty of defining the biomass concentration. No significant changes in biomass concentration during the BRP test are allowed, in order to obtain a good linear relationship between the BRP and the phosholipid biomass to be obtained. This can be optimized by using a shorter bioreaction time and a larger amount of biomass in the BRP test, as was done in this research compared to the original work of Urfer (1998).

In the present research, about 5 – 30 grams of filter media was recommended for the BRP test. The actual amounts of biomass media used in the measurement were adjusted as a function of filter depth, in order to maintain a relatively consistent concentration of biomass and relatively consistent DO changes in the BRP test bottles. It is recommended

that a smaller amount of filter media be used for biomass samples taken from the upper-layer media (more biomass on the media) in biofilters. Conversely, a larger amount of filter media is required for biomass samples taken from the lower layer media (less biomass on the media) in biofilters.

Theoretically, a shorter time period for BRP tests should give a better linear relationship between BRP and phospholipid biomass, as long as the response in DO changes is readable and the bioreaction lag time is negligible. Based on the experimental results in the current study, the time period of 1 to 2 h is recommended. However, additional work to confirm and refine this would be warranted.

Bacteria (as biomass) might experience a shock from higher substrate concentrations when starting the BRP test, especially for the biomass from the media at lower depth of filters (S_o or $S_{opt.(BRP)}$ is independent of the biomass concentration on the media). This shock of biomass can be minimized by using a substrate concentration as low as possible (S_o is a little larger than $S_{opt.(BRP)}$). Choosing the representative components of BOM and the percentage of each component in accordance with the influent of biofilters will also limit the potential shock.

The response of DO in the range of 0.1-0.6 mg/L observed in this research can be accurately measured, and at the same time other BRP test conditions were suitable to establish a good linear relationship between the BRP and phospholipid biomass.

6.6 CONCLUSIONS

Overall conclusions from the investigation of the BRP test as a surrogate for phospholipid biomass in phase III are described as the following:

- The BRP test is a good surrogate for the phospholipid biomass, and might also be a good surrogate for other kinds of biomass tests such as the ATP method.

- The BRP test might find a potential use by water utilities because it is simple and fast.
- The temperature dependence of the BRP test is important in assessing the amount of biomass in biofilters. The estimated temperature-activity coefficient (θ =1.014) can be used to estimate the equivalent biomass from the results of the BRP test at any given temperature.
- The existence of an approximately linear relationship between BRP and phospholipid biomass is supported theoretically if the test conditions are well defined.

In order to obtain a good linear relationship between BRP and phospholipid biomass, the following conditions for the BRP test are recommended:

- BOM components and concentrations: using the "recipe" of BOM components in the influents of biofilters; the concentrations of BOM components can be determined by a specially designed experiment as described previously in this Chapter.
- Amount of media: about 5 – 30 grams. The amount of biomass media should be adjusted according to the biomass concentration per volume of biomass media, in order to maintain a relatively consistent concentration of biomass and relatively consistent DO changes in the BRP test bottles.
- Time period: 1 – 2 h.
- Temperature: The same temperature as in the biofilters should be used in order to minimize the unfavourable influences on the BRP test caused by sudden changes in temperature.

CHAPTER 7: ESTIMATION OF BIOKINETIC PARAMETERS

7.1 INTRODUCTION

Several drinking water biofilter models have been proposed to provide a framework for the interpretation and generalization of results and to provide some kinetic description for the design and operation of drinking water biofilters (Billen *et al.*, 1992; Huck *et al.*, 1994; Wang and Summers, 1995; Zhang, 1996; Zhang and Huck, 1996a; and Hozalski, 1996). Huck *et al.* (1994) presented a simple first-order regression model for BOM removal performance in terms of AOC removal in the filters vs. AOC in the influent, which is bio-kinetic parameter independent. The other aforementioned models are Monod type bio-kinetics dependent. Therefore, the key parameters (k and K_s) in the Monod formulation play an important role in the application of these models. As described in Chapter 3, these biokinetic parameters can be obtained by using empirical data (Billen *et al.*, 1992), by parameter estimation from model validation (Zhang, 1996; Zhang and Huck, 1996a), by parameter estimation from independent experiments (Hozalski, 1996), or by parameter estimation from dependent experiments (Wang, 1995). A simpler and more representative approach to estimate the key bio-kinetic parameters (k, K_s) for BOM removal in practical biofilters is needed to describe biofiltration processes more accurately.

7.2 OBJECTIVES

The overall objective of the component of the research described in this chapter is to estimate the biokinetic parameters (K_s and k) using a simple and fast approach. The specific objectives of this Chapter are described as the following:

- to find a suitable experimental approach for the estimation of biokinetic parameters;
- to estimate the biokinetic parameters by appropriate techniques;
- to investigate the effect of temperature on the estimated biokinetic parameters;
- to evaluate the competitive effects of different BOM components on the estimated parameters.

7.3 MATERIALS AND METHODS

7.3.1 Operating conditions of bioreactors for the k and K_s test

Standard BOD bottles were used as bioreactors for the k and K_s test. These standard BOD bottles (300 mL in volume) were autoclaved and oven-dried at 100°C overnight prior to use.

Tap water was dechlorinated (by GAC filters in this study) and then autoclaved prior to use to ensure no effect from background contamination. The dechlorinated and autoclaved tap water was then used to make BOM and nutrient cocktails in the bioreactors for the k and K_s test. In the k and K_s test, the BOM and nutrient target concentrations vary from a low level ($S_{low} << K_s$) to a high level ($S_{high} >> K_s$). The ratio of relative concentrations of BOM as acetate, formate, formaldehyde and glyoxal in the bioreactors for the k/K_s test, are the same as in the filter influents (4:3:1:0.3 by weight) to minimize the effect of substrate changes on bacterial metabolism. Nitrogen (as $NaNO_3$-N) and phosphorus (as K_2HPO_4-P) were added to the water to yield a ratio of 15:5:1 (C:N:P by w/w/w),

representing carbon limited conditions. The BOM concentrations in the k and K_s test ranges from 0.3 to 3 times the target BOM concentration in the filter influent. The target BOM concentrations as acetate, formate, formaldehyde and glyoxal in the filter influent were 300 µg/L, 400 µg/L, 100 µg/L and 30 µg/L, respectively.

Biomass in the bioreactors for the k and K_s test was taken from the upper-layer media (the biofilm attached on the media) in the biofilters. The filter was rinsed with dechlorinated water prior to the k and K_s test sampling to reduce the residual effect of N, P and BOM on the measurement of phospholipid biomass.

Bioreactions in the BOD bottles for the k and K_s test were performed at the same temperatures as those in the filters (either 20 °C or 5 °C in this study) to minimize the effect of temperature "shock" on the bacteria. The temperature in the bioreactors was controlled by using a temperature-adjustable water bath shaker (Gyrotory Water Bath Shaker, Model G76, New Brunswick Scientific Co, Inc. Edoson, N. J. USA). The bioreactors were shaken at a medium speed (~90 rpm) in an effort to eliminate diffusion-controlled reaction conditions since the parameter estimation is based on this assumption. Based on the operating conditions (typical design criteria) in drinking water biofilters, Urfer (1998) concluded that bioreaction was not likely diffusion-controlled. It is easy to check that the condition for BOM diffusion in the stagnant layer is more favourable in the k and K_s test than that in drinking water biofilters.

A good combination of media amount and biodegradation time period can optimize the accuracy of the k and K_s estimation. In the current study, a 1h biodegradation time period and about 20 - 30 g of media (in 300 mL BOD-bottles) were chosen since this combination can result in measurable BOM changes and avoid a major biomass change in the bioreactors. The major biomass change change in the bioreactors could have affected the accuracy of the k and K_s estimation.

The k and K_s tests and the phospholipid biomass measurements were performed during Period IB and IC in phase III. The operating conditions during period IB and IC are the

same (refer to Table 5.1 in Chapter 5). For the measurements of DO and phospholipid biomass, please refer to Chapter 3.

7.3.2 Procedures for the k and K_s test

The procedure for the k and K_s test is simple and easy to perform. Figure 7.1 describes the procedure, which is similar to the BRP test described in Chapter 6.

Sample media from the upper-layer media in drained and rinsed filter

⇓

Weigh the wet media sample on a scale

⇓

Place the media in an empty bottle (previously autoclaved)

⇓

Add the target concentrations of BOM/N, P in dechlorinated tap water (previously autoclaved) and fill BOD bottle headspace free, close with the glass stopper (start time)

⇓

Place BOD bottle on shaker table submerged in water bath (medium speed, temperature controlled) for 1 h

⇓

Measure the BOM concentration

Figure 7.1: Procedure for the k and K_s test

7.3.3 Techniques for the estimation of k and K_s parameters

When Monod type kinetics are used to interpret substrate utilization, the rate of substrate utilization can be expressed by equation 7.1 (which is same as the equation 6.7).

$$\frac{dS}{dt} = \frac{-kXS}{K_s + S} \tag{7.1}$$

Rearranging equation 7.1, and defining V^* as the specific substrate utilization rate, yields:

$$V^* = -\frac{1}{X}\frac{dS}{dt} = \frac{kS}{K_s + S} \tag{7.2}$$

Where, V^* is the specific substrate utilization rate (T^{-1}).

In equation 7.2, $\frac{dS}{dt}$ and the S are approximated as $\frac{S_0 - S_e}{t}$ and $\frac{S_0 + S_e}{2}$, respectively.

Where, S_0 is the initial substrate concentration (ML^{-3}), S_e denotes the end substrate concentration (ML^{-3}), and t represents the time period for the k/K_s test.

In equation 7.2, S is an independent variable and V^* is a dependent variable. k and K_s are to be estimated.

The parameters of k and K_s can be estimated by non-linear regression (using the Gauss-Newton method). The non-linear regression is based on the minimization of the sum of squares of the difference between predicted and measured specific substrate utilization rates (Bard, 1974):

$$\text{Min} \sum_{i=1}^{n} (V^*_{i(predicted)} - V^*_{i(measured)})^2 \tag{7.3}$$

The choice of initial values of k and K_s in regression is based on the available modeling or experimental results. In some cases, the transformation of independent and /or dependent variables may facilitate the estimation of parameters. Equation 7.2 can be rearranged into the following form:

$$\frac{1}{V^*} = \frac{K_s}{k}\frac{1}{S} + \frac{1}{k} \tag{7.4}$$

When the term $\frac{1}{V^*}$ is plotted versus the $\frac{1}{S}$, a linear relationship is obtained. Therefore the parameters of k and K_s can be estimated by simple linear regression. The linear regression is based on the minimization of the sum of squares of the difference between reciprocals of predicted and measured specific substrate utilization rates:

$$\text{Min} \sum_{i=1}^{n} \left(\frac{1}{V^*_{i(predicted)}} - \frac{1}{V^*_{i(measured)}}\right)^2 \tag{7.5}$$

For the data being considered here, non-linear regression provided a better fit when higher scatter in the V^* values occurred at lower values of S, and vice versa, linear regression provided a better fit when higher scatter in the V^* values occurred at higher values of S. For these data, non-linear regression was used in almost all cases.

7.4 RESULTS AND DISCUSSION

Three experiments to determine the k and K_s and measure phospholipid biomass were carried out during phase III on days 205, 280 and 294, respectively. Media samples were taken from four filters in each experiment. The results of these k and K_s tests (substrate utilization rate, and biomass) are shown in Appendix J and also plotted later in this Chapter. The applicability of the techniques for k and K_s parameter estimation was evaluated. The k and K_s parameters in different scenarios were then estimated. Temperature effects on k estimation were assessed. The 95% joint confidence region for k and K_s in terms of different BOM components were depicted in order to give a general range for the estimated parameters and indicate the extent of correlation in the estimates. Competitive effects of BOM components were preliminarily evaluated in terms of the enzyme-reaction patterns.

7.4.1 Estimation of k and Ks parameters

To perform the estimation of k and K_s parameters, the three sets of experimental results from the same filter are pooled. The estimated k and K_s parameters in the four filters are listed in Table 7.1. Most of the parameters were estimated by non-linear regression.

Table 7.1: The Estimated k and K_s Parameters in Four Anthracite Filters

BOM	Parameters	F1	F2	F3	F4
Acetate	k (1/h)	0.15	0.24	0.14	0.11
	K_s (μg/L)	460	1260	4530	929
Formate	k (1/h)	0.18	0.25	0.082	0.29
	K_s (μg/L)	563	1680	1890	2100
Formaldehyde	k (1/h)	0.037	0.013*	0.011	0.00097*
	K_s (μg/L)	144	69.5*	230	193*
Glyoxal	k (1/h)	0.011	0.0023	0.0038	0.0016
	K_s (μg/L)	127	13.0	292	35.3

Note: * k and K_s estimated by linear regression;
F1 (anthracite, chlorine, 20 °C); F2 (anthracite, chloramine, 20°C);
F3 (anthracite, chlorine, 5°C); F4 (anthracite, chloramine, 5°C).

The maximum utilization rates of the substrate (k) in filters run at the higher temperature (20°C, F1 and F2) are generally higher than in filters run at the low temperature (5°C, F3 and F4). This is in agreement with the effect of temperature on bioreaction rates. The maximum utilization rates of the substrate for acids are generally higher, by at least an order of magnitude, than for aldehydes, which is indirectly supported by the acids/aldehydes removal results from this research and others (Coffey *et al.*, 1995). This also means that acids are perhaps easier to metabolize than aldehydes.

Table 7.2: Estimated k and K_s Parameters From Different Studies

Study	k (1/h)	K_s (μg/L)	k / K_s (μg/(L.h))
Metcalf and Eddy (1991)	0.21	53000*	4.0E-6
Zhang and Huck (1996a)	0.37	7600#	4.7E-5
Hozalski (1996)	0.27	470	5.8E-4
Rittmann (1986)	0.0046	16.9	2.7E-4
van der Kooij et al. (1982)	0.02	70.3	2.8E-4
Present study (20 °C)	0.15 - 0.24	460 -1260	1.9E-4 – 3.2E-4

Note: * converted from BOD_5; # converted from AOC.

The estimated parameters of k and K_s for acetate from the current study are compared with that from other research in Table 7.2. The estimated k value in this study agrees well with those from Metcalf and Eddy (1991), Zhang and Huck (1996a) and Hozalski (1996). However, it is more than one magnitude higher than those estimated from oligotrophic conditions (van der Kooij *et al.*, 1982; Rittmann *et al.*, 1986). There is a larger difference among different studies for K_s. The estimated K_s from the present study and from Hozalski (1996) are substantially lower than from Metcalf and Eddy (1991) and Zhang and Huck (1996a), and higher than from van der Kooij *et al.* (1982) and Rittmann (1986). This might be due to the fact that the K_s parameters from this research and Hozalski (1996) are estimated from experiments independently, compared to the K_s parameters from wastewater (Rittmann and McCarty, 1980) and from model fitting in terms of AOC removal in filters (Zhang and Huck, 1996a). In general, K_s in wastewater is higher than in drinking water because of the higher nutrient levels in wastewater.

The value of k/K_s represents the increasing rate of the substrate utilization with respect to the substrate concentration for a given substrate and biomass concentration. Therefore, it is also useful to make a comparison of k/Ks among studies other than the individual k and K_s values. The value of k/K_s in the present study agrees well with those from Hozalski (1996), van der Kooij *et al.* (1982) and Rittmann *et al.* (1986). The values of k/K_s from Zhang and Huck' modeling fitting (1996a) and Metcalf and Eddy (1991) are one

magnitude, two magnitudes lower than in this research, respectively. One possible explanation for the low value of k/K_s in wastewater is the less condensed biomass in the activated sludge system than in drinking water biofiilters. It should be noted that relatively high correlation exists between k and K_s. Therefore, it might be more meaningful to compare both the k and K_s values.

As a typical example, the residual plot ($V^*_{predicted} - V^*_{measured}$ vs. S) for the pooled formate data in Filter 1 is depicted in Figure 7.2. The random appearance of the residual plot suggests that the model form is adequate. Residual plots in other cases (not shown) also support this conclusion. Therefore, the Monod type kinetic model is applicable to the modeling of BOM removal in biofilters. Use of the model is discussed in Chapter 8.

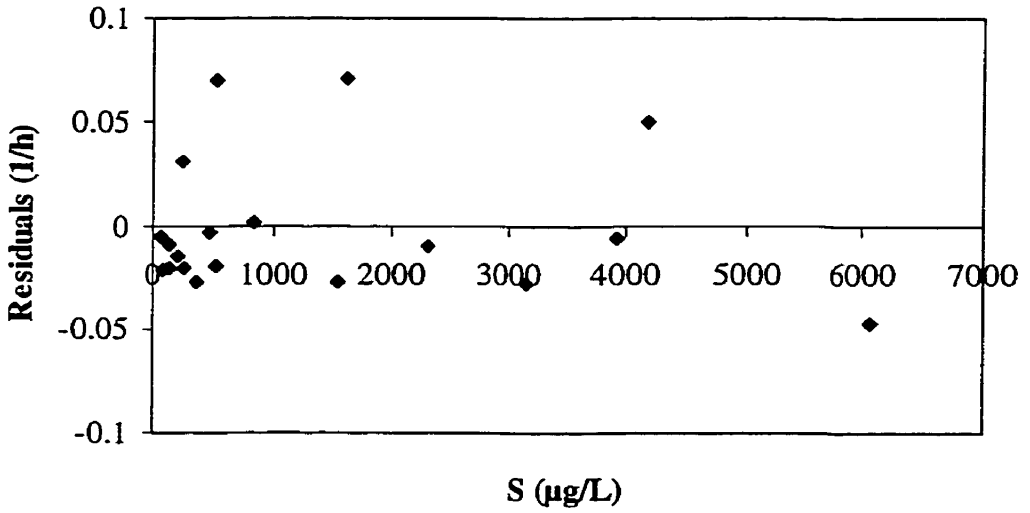

Figure 7.2: Residuals vs. formate concentration in Filter 1

7.4.2 Temperature effects on the estimation of parameters k and K_s

Theoretically, parameters k and K_s are much more influenced by temperature and BOM components than by the filter backwash procedure. These parameters can therefore be estimated by pooling the data from various experiments, based on temperature (i.e. F1 and F2 high temperature, 20°C; F3 and F4 low temperature, 5°C).

The prameters k and K_s were estimated using non-linear regression for acetate, formate, formaldehyde and glyoxal at both high temperature and the low temperature. The results are presented in Table 7.3 and the observed and predicted V^* values as a function of S are shown in Figures J.1 to J.8 (Appendix H). As an example, acetate at high temperature was shown in Figure 7.3. Joint confidence regions for k and K_s will be discussed in the next section.

The data for the k and K_s estimation were from three sets of experiments. To a certain extent, errors from biomass and BOM measurements might contribute to the observed scatter in Figures J.1 to J.8 (Appendix J). In general, less scatter data was observed for acids (Figures J.1, J.2, J.5 and J.6) and more scatter for aldehydes (Figures J.3, J.4, J.7 and J.8). One possible reason for this could be that the lower concentration of aldehydes in the k and K_s test might cause higher relative measuring errors.

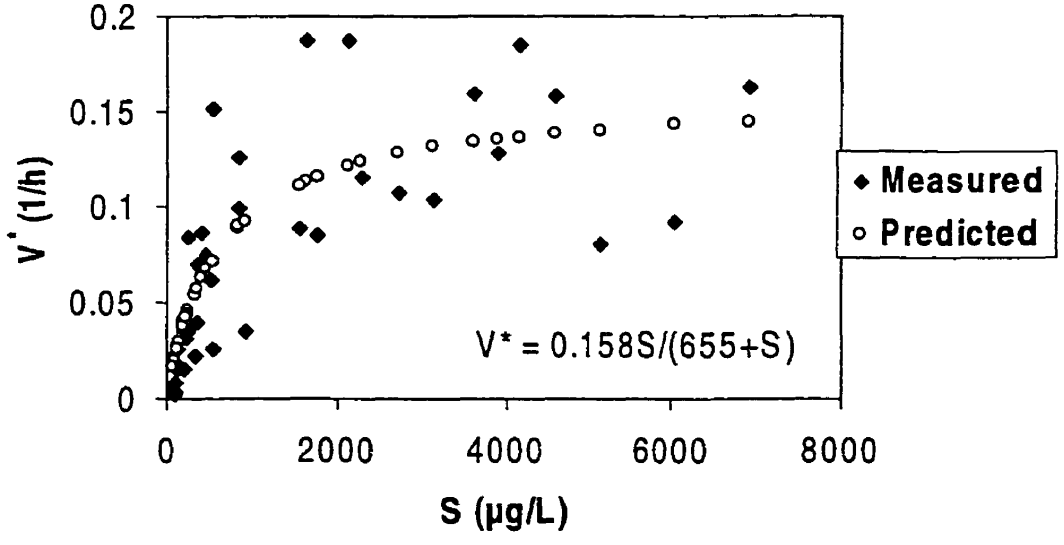

Figure 7.3: k and K_s estimation at the high temperature (20°C) (acetate)

Theoretically it is expected that the maximum utilization rate of the substrate (k) is increased at higher temperatures because the metabolic activities of microbial populations are more rapid. The temperature dependence of the maximum substrate utilization rate (k) is important in assessing biofiltration processes in the biofilters. The effect of temperature on the maximum substrate utilization rate of the substrate (k) is usually expressed in the following form (Metcalf and Eddy, 1991):

$$k_T = k_{20}\,\theta^{(T-20)} \qquad (7.6)$$

Where, k_T is the maximum substrate utilization rate at T °C; k_{20} denotes the maximum substrate utilization rate at 20 °C; and θ represents the temperature-activity coefficient.

By using the regression results at two different temperatures in Table 7.3, the values of k at other temperatures can be calculated using equation 7.6 with the estimated θ values in Table 7.3.

Table 7.3: Summary of the Temperature Effect on the Parameter k

BOM	k		Estimated temperature effect
	5 °C	20 °C	θ
Acetate	0.107	0.158	1.026
Formate	0.163	0.214	1.018
Formaldehyde	0.0144	0.0186	1.017
Glyoxal	0.0032	0.0048	1.028

The estimated θ values for BOM components are between 1.02 – 1.03, which is in the lower range for trickling filters (1.02-1.08) used in wastewater treatment (Metcalf and Eddy, 1991). This might be due to the difference of the bacterial populations grown on the media of drinking water and wastewater biofilters. In wastewater biofilters, the microorganisms which are accustomed to seeing a higher level of BOM are selected, and

similarly, in drinking water biofilters, microorganisms which are accustomed to seeing lower levels of BOM are selected.

7.4.3 Joint confidence regions for k and Ks

The 95% joint confidence regions (JCRs) for k and Ks at both low and high temperatures, in terms of acetate, formate, formaldehyde and glyoxal removal, are depicted in Figures J.9 to J.16 in Appendix J. As examples, the JCRs for acetate and glyoxal at high temperature are shown in Figures 7.4 and 7.5. The JCR gives more information than the individual confidence intervals by showing the extent of correlation between the estimated parameters.

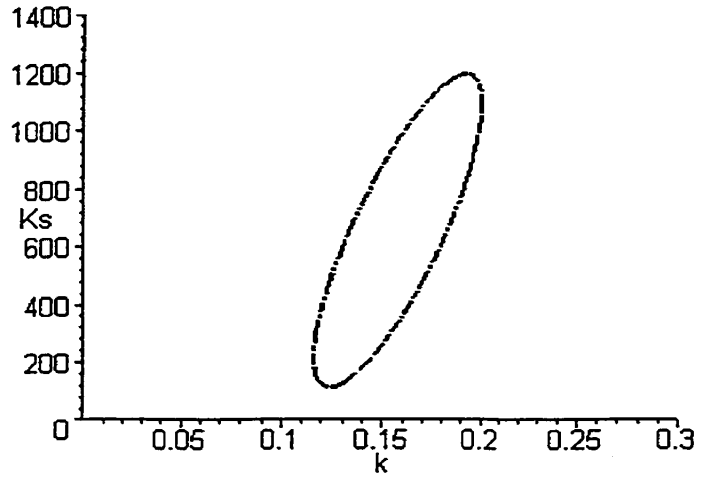

Figure 7.4: The 95% elliptical joint confidence contour for k and Ks (Acetate, high temperature, 20°C)

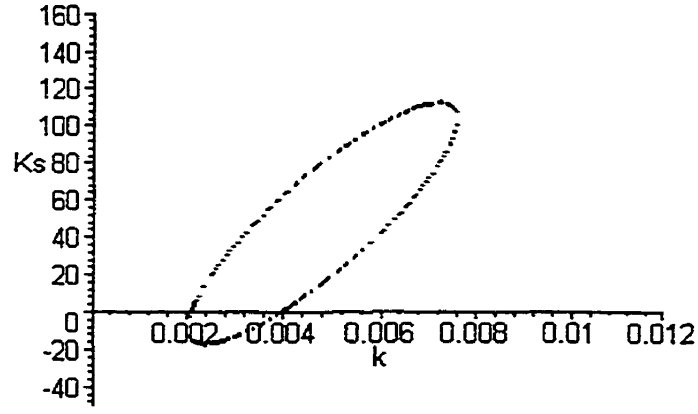

Figure 7.5: The 95% elliptical joint confidence contour for k and Ks (Glyoxal, high temperature, 20°C)

In general, k was more precisely estimated than K_s. Elliptical contours for acids (Figures J.9 and J.10) are generally "better" (smaller contour area) than for aldehydes (Figures J.13 and J.14) because the range of k contained within the 95% confidence level is smaller. Similarly, elliptical contours at the high temperature (Figures J.9 to J.12) are generally "better" (smaller contour area) than at the low temperature (Figures J.13 to J.16).

All JCRs for aldehydes (Figures J.11, J.12, J.15 and J 1.6) include negative values for K_s values, which is related to the more scattered data (V* vs. S in Figures J.3, J.4, J.7 and J.8). The acetate JCR at low temperature also indicate negative values for Ks and the glyoxal JCR at low temperature includes a small proportion of negative values of k.

Based on the JCRs, the individual 95% confidence intervals k and K_s for acetate (20 °C) would be about ± 25% and about ±100%, respectively, whereas the individual 95% confidence intervals k and K_s for glyoxal (20 °C) would be about ±50% and about ±130%, respectively. It seems that JCRs for less easily biodegradable BOM components (e.g. glyoxal) are larger than those for easily biodegradable BOM components (e.g. acetate). The more precise estimates for k are expected because there was more data and less scatter in the convex part of the V* vs. S curves.

7.4.4 Competitive effects of BOM components on k and Ks estimation

The kinetic parameters estimated in this study are based on the four BOM components (acetate, formate, formaldehyde and glyoxal) and their relative concentrations. Therefore, they are applicable for this type of biofiltration influent. Significant changes in BOM components and their relative concentrations might require some adjustments of these estimated parameters, due to the different enzyme-reaction mechanisms.

Two ideal scenarios can be used to evaluate the effects of enzyme-reaction mechanisms on the estimation of kinetic parameters:

Scenario I: Each BOM component uses its own enzyme, and no competitive effect exists. The estimated kinetic parameters can be applied in any case without any adjustments.

Scenario II: Each BOM component uses the same enzyme, and a "full" competitive effect exists. If only one BOM component i (i = 1, 2, 3, 4) exists in the influent of biofilters, the real $k_{i(real)}$ value should fall in the range of k_i to the sum of k_i (i = 1, 2, 3, 4). Similarly, the real $Ks_{i\,(real)}$ value should fall in the range of Ks_i to the sum of Ks_i (i = 1, 2, 3, 4).

The real case of kinetic parameters should fall between scenarios I and II. Further investigations are needed to evaluate the enzyme competition effects on the estimation of kinetic parameters.

7.5 CONCLUSIONS

Overall conclusions from the investigation of the k and K_s test in phase III are described as the following:

- The approach for k and K_s estimation presented in this research is simpler than the classical approach and more robust than the pure modelling approach.
- The temperature dependence of the maximum utilization rate of the substrate k is important in assessing biofiltration processes in biofilters. The estimated temperature-activity coefficients (θ =1.026, 1.018, 1.017 and 1.028, for acetate, formate, formaldehyde and glyoxal, respectively) can be used to estimate the maximum utilization rate of the substrate k at any given temperature.
- Non-linear regression (Gauss-Newton method) is recommended for the estimation of k and K_s parameters in most cases.
- Enzyme-reaction patterns affect the estimation and application of bio-kinetic parameters in multi-substrate systems. Further work is needed to evaluate the competitive effects on the estimation of bio-kinetic parameters.

In order to obtain a good estimation of the k and K_s bio-kinetic parameters, the following conditions are recommended:

- Test conditions: Amount of biomass media: about 10 – 30 grams. Time period for the test: 1 h. The amount of media should be adjusted according to the biomass concentration per volume of media, in order to obtain a measurable change of BOM concentration in the k and K_s test bottles.
- Biomass measurement: The phospholipid biomass measurement is used in this research. The BRP test developed in Chapter 6, a surrogate of the phospholipid biomass, can also be used for the estimation of biomass concentrations used for parameter estimation.
- Temperature for the k and K_s test: The same temperature as in the biofilters should be used in order to minimize the "bacteria shock" caused by sudden changes of temperature.

CHAPTER 8: MODELING BOM REMOVAL IN DRINKING WATER BIOFILTERS

8.1 INTRODUCTION

Despite the fact that numerous engineered or natural biological water treatment facilities are in operation, the design and operation of these facilities are still mainly based on empirical data. It will be helpful to provide some biological kinetic description for the design and operation of these bioactive facilities. In the last decade, attempts have been made to model the removal of BOM or specific components in drinking water biofilters, to provide a framework for the interpretation and generalization of results, which currently suffer from site-specificity.

In a biofilm process, there is simultaneous diffusion with reaction. Thus, a diffusion-with-bioreaction model proposed by Atkinson and Daoud (1968) has been widely used in modeling biofilm processes. Rittmann and McCarty (1980) later proposed a steady-state biofilm model, however, this model can not be solved explicitly because of the second-order non-linear differential equation in the model. By simplifying the model to either first-order or zero-order kinetics, analytical solutions can be provided to the diffusion-with-bioreaction equation. Suidan and Wang (1985) developed a semi-empirical equation to Rittmann and McCarty's steady-state biofilm model. Sáez and Rittmann (1988) provided a pseudo-analytical solution (an approximate "analytical" solution which is regressed from numerical solutions to the second-order non-linear differential equation) to the steady-state biofilm model and subsequently published a revised solution (Sáez and

Rittmann, 1992). A steady-state biofilter model based on the revised biofilm model pseudo-analytical solution was presented by Zhang and Huck (1996a). Since drinking water biofilters may be considered pseudo steady-state, modeling is useful in predicting the long term performance of a biologically active filter, which is important to water utilities.

Based on the steady-state biofilm model, several multispecies biofilm models with generally similar structures have been developed (Kissel *et al.*, 1984; Wanner and Gujer, 1986; Rittmann and Manem, 1992). Those authors considered the various component of biofilm (i.e., heterotorophs, autotrophs and inert materials) and biofilm detachment mechanisms (i.e., shear and sloughing). These types of biofilm models become more sophisticated than single species models, since more parameters are required to describe the biofilm models, and the incorporation of these biofilm models in biofilter models becomes much more difficult.

Other researchers (Wang, 1995; Wang and Summers, 1995) modeled drinking water biolfiltration by assuming a full penetration biofilm model, using the regressed biomass (biofilm) profile from the measured data in real biofilters. This model suffers from site-specificity and BOM-specificity since it is based on the biofilm profile in the given biofilters.

All of the models discussed above address steady-state conditions. Steady-state biofilter models can neither predict the BOM removal performance of biofilters in the initial period of biofilm development nor the possible sawtooth pattern throughout the filter cycle proposed by Hozalski (1996) and Huck *et al.* (1998). By considering the biomass accumulation in the initial period of biofilm development, the biomass loss during backwashing and its gradual replenishment during the subsequent filter cycle, Hozalski (1996) developed a non-steady-state biofilter model to address non-steady-state BOM removal performance. A constant percent removal of biomass in the entire depth of the biofilter bed during backwashing was assumed in this model, which might not accurately represent the actual biomass detachment during backwashing (the modeling results

showed a slow decrease for the overall BOM removal over time). The establishment of a good model for the description of biomass detachment during backwashing and during a filter run is crucial for non-steady-state biofilter models. However, it is extremely difficult to provide an applicable kinetic description for the biomass detachment during backwashing and filter runs because of the complex nature of biomass detachment phenomena and the limits of current techniques for biomass measurement.

The models which have been discussed previously provide important process insights for drinking water biofilters. However, they are relatively complex and cannot be directly used by utilities. A simple linear regression model has been developed to evaluate the BOM removal performance in biofilters (Huck *et al.*, 1994). This model showed that the amount of BOM removed in a given biofilter was approximately proportional to the influent concentration, i.e. the process was first-order. This also means that a biofilter at apparent steady-state will essentially achieve a constant percentage removal at a given EBCT and temperature. This relationship has been shown to hold for AOC, BDOC, THMFP, chlorine demand and carboxylic acids (Huck *et al.*, 1994; Gagnon *et al.*, 1997; Carlson *et al.*, 1998). Zhang (1996) and Zhang and Huck (1996a) have provided a theoretical basis for first order removals.

In developing the steady-state biofilm model, Rittmann and McCarty (1980) proposed a definition for S_{min}, the minimum substrate concentration capable of sustaining a steady-state biofilm. It is based on the assumption of first-order biofilm decay and detachment. Zhang (1996) developed a generalized definition of S_{min} to accommodate many possible biofilm detachment mechanisms. Parameters in this generalized S_{min} relating to biofilm detachment mechanisms could be very difficult if not impossible to quantify. Zhang (1996) recommended S_{min} be treated as additional biofilm kinetic parameter and estimated in *situ*.

In developing the steady-state biofilter model, Zhang (1996) and Zhang and Huck (1996a) proposed a dimensionless contact time, X^* ($X^* = (EBCT)\ \alpha(X_f k D_f / K_s)^{1/2}$). X^* incorporates biofilter contact time and surface area of the media, as well as substrate

diffusivity and biodegradation kinetic parameters. Zhang (1996) and Zhang and Huck (1996a) illustrated that the percentage removal of AOC increased convexly with increasing X^*, and little further removal was achieved beyond a certain X^*. The X^* index allows removal performance comparisons of the same substrate among studies. Huck (1999) explored the use of X^* to evaluate humic substance removals as a function of operating parameters. The generalized relationships (percent removal vs. X^*) for different substrates are dependent on their kinetic parameters. Therefore, it would be very useful to develop a series of generalized relationships which include kinetic parameters to compare removals of different substrates in the same or different studies.

In this chapter, three steady-state drinking biofilter models, which are based on a simplified biofilm model, Suidan and Wang's semi-empirical equation, and Sáez and Rittmann's revised solution, are proposed and used to model the BOM removal performance in biofilters. A general comparison is carried out for these three biofilter models. A comprehensive S_{min} expression that considers biofilter operating conditions is also developed and evaluated. In addition, further development using the X^* concept is carried out.

8.2 OBJECTIVES

The overall objective of the work described in this chapter is to develop and evaluate steady-state biofilter models. The specific objectives of this Chapter are:

- to develop and evaluate steady-state biofilter models using three different solutions to the steady-state biofilm model;
- to propose a revised definition of S_{min};
- to develop a series of generalized relationships between percent removals, X^* and substrate kinetic parameters;
- to model the BOM removal performance and biofilm distribution in biofilters, and
- to relate bed utilization to S_{min} and $X^*_{critical}$.

8.3 STEADY-STATE BIOFILTER MODELS

8.3.1 Framework for biofilter models

Usually, the hydraulic loading rates for filters in drinking water treatment processes are typically in the range of 4 m/h to 15 m/h (Montgomery, 1985). The effect of axial hydrodynamic dispersion in drinking water biofilters is negligible (Zhang and Huck, 1996a; Booth, 1998). Therefore, the filters in drinking water treatment processes can be considered as plug-flow bioreactors.

Biofilms (fixed biomass) play a much more important role than the suspended bacteria (suspended biomass) for the BOM removal in drinking water biofilters (refer to Appendix K). The BOM removal caused by the suspended bacteria is, therefore, negligible.

Based on the steady-state biofilm model (Rittmann and McCarty, 1980) and the plug flow packed biofilm column model (Bailey and Ollis, 1986), the general form of the steady-state biofilter model (a transformation of the form from Zhang and Huck (1996a)) can be described in equation (8.1) (detailed derivation of the following equation was described in Appendix L):

$$\int_{J_o^*}^{J_s^*} \frac{d(S_s^* + \frac{L^*}{D^*} J^*)}{J^*} = \frac{\alpha D_f}{v\tau} X = X^* \qquad (8.1)$$

Where, $L^* = L/\tau$; $J^* = J\tau/(K_s D_f)$; $D^* = D/D_f$; $X^* = (EBCT)\ \alpha(X_f k D_f/K_s)^{1/2}$; $S_s^* = S_s/K_s$; $\tau = (\frac{K_s D_f}{X_f k})^{\frac{1}{2}}$; $J = D(S_b - S_s)/L$; $EBCT = x/v$

S_b and S_s are the substrate concentrations in the bulk liquid and on the surface of the biofilm (ML^{-3}), respectively; D_f and D denote the diffusitivity of the substrate in the

biofilm and in the liquid, respectively (L^2T^{-1}); k is the maximum utilization rate of the substrate (T^{-1}); K_s is Michaeles-Menten's half-velocity constant (ML^{-3}); X_f is the biofilm density within the biofilm (ML^{-3}); Y is the yield coefficient (M_x/M_s); b denotes the overall biofilm decay rate coefficient (T^{-1}); L denotes the thickness of the effective diffusion layer (L); α is the biofilm surface area in each unit volume of the biofilter (L^{-1}); J is the flux of substrate into the biofilm ($ML^{-2}T^{-1}$); υ is the superficial flow rate or hydraulic loading rate (LT^{-1}). J_o^* is the dimensionless flux of substrate into the biofilm at the inlet (top) of the biofilter ($ML^{-2}T^{-1}$); J_x^* is the dimensionless flux of substrate into the biofilm at any depth x; x denotes the effective length (media depth, excluding any support gravel) of the biofilter (L); and X^* is the dimensionless contact time.

Various solutions to the steady-state biofilm model (J^* vs. S_s^*), can be applied to the above biofilter model (equation (8.1)). However, the primary difficulty in applying the steady-state biofilm model is that no analytical solution is available to the second-order differential equation because of the non-linearity of the Monod-type reaction term. The solution to the steady-state biofilm model can be either in analytical form by simplification or in semi-empirical form. Three biofilter models based on three types of solutions to the steady-state biofilm model are discussed below.

8.3.2 Biofilter model A: Based on the analytical solution to the steady-state biofilm model (approximate first-order substrate degradation rate)

Compared to wastewater biofilms, the concentration of substrate is very low in drinking water biofilters. The bacteria are in an oligotrophic state (i.e. nutrient stressed). An analytical solution to Rittmann and McCarty's steady-state biofilm model (equation 2.5 in Chapter 2) could be obtained by assuming

$$K_s >> S_f \qquad \text{or} \quad S_f^* << 1$$

Where, $S_f^* = S_f/K_s$; S_f is the substrate concentrations inside the biofilm (ML^{-3}). Under these conditions, the reaction is essentially first order.

If S_f^* is defined as S_f/K_s, then $S_f^* << 1$, and the following analytical solution to Rittmann and McCarty's steady-state biofilm model can be obtained:

$$S_s^* = J^* / \tanh(J^* Yk/b) \tag{8.2}$$

Where, b denotes the decay and detachment coefficient of biofilm (T^{-1}).

Substituting equation (8.2) into equation (8.1) yields,

$$\int_{J_o^*}^{J_x^*} \frac{\tanh(J^*Yk/b) - J^*Yk/\{b[ch(J^*Yk/b)]^2\}}{[\tanh(J^*Yk/b)]^2 J^*} dJ^* + \frac{L^*}{D^*} \ln \frac{J_x^*}{J_o^*} = -X^* \tag{8.3}$$

Where, $ch(x) = (e^x + e^{-x})/2$

8.3.3 Biofilter model B: Based on Suidan and Wang's semi-empirical solution to steady-state biofilm model

Suidan and Wang (1985) obtained the following semi-empirical equation by using numerical integration and regression:

$$S_s^* = \frac{0.5J^{*2} + J^*[1 + (\frac{J^*}{3.4})^{1.19}]^{-0.61}}{\tanh[J^*(Yk/b - 1)]} \tag{8.4}$$

Substituting equation (8.4) into equation (8.1) yields,

$$\int_{J_o^*}^{J_x^*} \frac{\{J^* + [1+(J^*/3.4)^{1.19}]^{-.61} - 0.169[1+(J^*/3.4)^{1.19}]^{-1.61} J^{*1.19}\} \tanh[J^*(Yk/b-1)] - B}{\{\tanh[J^*(Yk/b-1)]\}^2 J^*}$$

$$+ \frac{L^*}{D^*} \ln \frac{J_x^*}{J_o^*} = -X \frac{\alpha D_f}{\upsilon \tau} = -X^* \tag{8.5}$$

Where, $B=\{ch[J^*(Yk/b-1)]\}^{-2}(Yk/b-1)\{0.5J^{*2}+J^*[1+(J^*/3.4)^{1.19}]^{-0.61}\}$

8.3.4 Biofilter model C: Based on Sáez and Rittmann's pseudo analytical solution to the steady-state biofilm model

Based on a pseudo-analytical solution to the steady-state biofilm model (Sáez and Rittmann, 1992) (equation 8.6), Zhang and Huck (1996a) proposed a biofilter model (equation 8.7):

$$J^* = \{2[S_s^* - \ln(1+S_s^*)]\}^{1/2} \times \tanh[\gamma(S_s^*/S_{min}^* - 1)\beta] \qquad (8.6)$$

$$\int_{S_0^*}^{S_s^*} \frac{dS_s^*}{\{2[S_s^* - \ln(1+S_s^*)]\}^{1/2} \tanh[\gamma(S_s^*/S_{min}^* - 1)^{\beta}]} dJ^* + \frac{L^*}{D^*} \ln \frac{J_s^*}{J_o^*} = -X^* \qquad (8.7)$$

Where, $S_{min}^* = S_{min}/K_s$; $\gamma = 1.557-0.4117\tanh(\log S_{min}^*)$; $\beta = 0.5035-0.0257\tanh(\log S_{min}^*)$

8.3.5 Detachment Submodel

The three aforementioned biofilter models (models A, B and C) are based on the assumption that biofilm loss (decay and detachment) is proportional to the thickness of the biofilm (first-order detachment kinetics). About half of the studies listed in Table 2.1 in Chapter 2 support the hypothesis that the biofilm losses can be expressed as a first-order loss term in terms of the biofilm thickness. The first-order biofilm loss model is considered more applicable to biofilms with lower thickness (Rittmann, 1982). In drinking water biofilters, the biofilm thickness is low because of the low nutrient levels. Biofilm thickness was estimated to be less than 30 μm in most cases by converting the measured biomass into biofilm thickness (Urfer, 1998) and by modeling estimation (Hozalski, 1996). This thickness is much lower than that in biofilters for wastewater treatment. Thus, it appears that the first-order biofilm loss model might be generally

appropriate for drinking water biofilters. In reality, biofilms often have a complex structure consisting of microbial cell clusters (Beer *et al.*, 1994) and thin biofilms in drinking water biofilters are often patchy in nature (e.g. Lu and Huck (1993); Urfer (1998)). However for modeling purposes, a uniform thickness is normally assumed.

With the advancement of the understanding of biofilm detachment mechanisms and kinetic descriptions and of experimental techniques, more accurate biofilm detachment models will likely be developed. Further modification of the above mentioned analytical and pseudoanalytical solutions to the steady-state biofilm model would almost certainly be required to accommodate biofilm loss kinetics.

8.4 DEFINITION OF S_{min} IN BIOFILTER MODELS

Rittmann and McCarty (1980) introduced the concept of S_{min}, which is defined as the bulk substrate concentration below which the substrate flux can not support the existing monolayer biofilm and the existing monolayer biofilm will decay or disappear.

By assuming that:

(1) there is no diffusion limitation in the bulk liquid and the monolayer biofilm, in other words, $S_b \approx S_s \approx S_f$

(2) biofilm detachment is negligible

Rittmann and McCarty (1980) provided the following expression of S_{min}:

$$S_{min} \approx S_{min\text{-}s} = bK_s/(Yk\text{-}b) \qquad (8.8)$$

Where, $S_{min\text{-}s}$ is the substrate concentration on the surface of the media (ML^{-3}).

However, biofilm detachment is not negligible in many situations (Peyton and Characklis, 1993). Therfore, S_{min} should account for both endogenous decay and biofilm detachment.

As noted previously, the biofilm detachment rate can be considered to be proportional to the thickness of the biofilm due to the low levels of biofilm thickness in drinking water biofilters. For the scenario of S_{min}, the biofilm thickness is definitely low because of the assumption of monolayer biofilm. By substituting an overall coefficient b′, which combines both biofilm decay (b) and detachment (b_{det}), in equation (8.8) with $b' = b$, S_{min} can account for both biofilm decay and first-order detachment.

$$S_{min} \approx S_{min\text{-}s} = b' K_s/(Yk - b') \qquad (8.9)$$

As discussed previously, the parameters required for Zhang's (1996) generalized definition of S_{min} are not measurable in practice.

Therefore, based on the original definition of S_{min} from Rittmann and McCarty, a revised expression for S_{min} is developed herein, assuming that detachment is proportional to biofilm thickness. As discussed above, this new S_{min} should be applicable for the thin biofilms in drinking water biofilters.

Both the diffusion gradients in the bulk liquid and in the biofilm, which are ignored in the original definition of S_{min} by Rittmann and McCarty, are considered in this revised expression of S_{min}. The revised S_{min} reflects not only the kinetic parameters of the biofilm process (such as k, K_s, b, Y, X_f, D, and D_f) but also the characteristic size of the bacteria, δ (say the diameter of a bacterium or a colony of bacteria), and the operating conditions of the biofilm process (media size d_p and filter hydraulic loading rate υ which can affect the thickness of the effective diffusion layer L). The revised definition of S_{min} is given in equation 8.10.

$$S_{min} = (\tanh(\delta/\tau))^{-1} \left(\frac{K_s X_f}{kD_f}\right)^{1/2} b\delta/Y + \frac{L}{D}\frac{b}{Y} X_f \delta \quad (8.10)$$

Equation (8.10) is derived by combining the following three equations:

$$J = \frac{D}{L}(S_{min} - S_{min\text{-}s}) \quad (8.11)$$

$$J = \frac{D_f}{\tau} S_{min\text{-}s} (\tanh(\delta/\tau)) \quad (8.12)$$

$$YJ = bX_f \delta \quad (8.13)$$

The first and third equations can be obtained from Fick's first law and a mass balance. The second equation is derived from the analytical solution of the steady-state biofilm model by assuming $K_s >> S_{min}$, which is a reasonable assumption. The last equation addresses the biofilm balance for the steady-state biofilm.

With the expected advancement of biofilm thickness measurement techniques, it is anticipated that S_{min} could be measured directly in-*situ*, because the substrate concentration in biofilters at a certain depth where monolayer biofilm exists can be considered S_{min}. The S_{min} measured in-*situ* and the further understanding of biofilm detachment mechanisms and their kinetic description, could then be used to calibrate the S_{min} estimation model presented in equations 8.9 and 8.10.

8.5 MODELING APPROACH

Data used to evaluate the aforementioned biofilter models were obtained from Filter1 in period IB of phase III (refer to Chapter 5). Filter1 is an anthracite/sand filter (anthracite layer thickness: 45cm, effective size =1.05mm, sand layer thickness: 25 cm, effective size = 0.48mm) operated at 7.5 m/h.

In the present investigation, the specific surface area (α) of the media can be calculated directly for a given bed porosity (ε) and particle diameter (d_p) by assuming that the particles are exactly spherical. Based on the visual estimates of biofilm coverage on the media of drinking water biofilters (Lu and Huck, 1993), a 75% coverage of the media surface was assigned. In a similar manner to that of Zhang and Huck (1996a), the estimation of the thickness of the effective liquid diffusion layer, L, was calculated using Gnieliski's correlation (Roberts et al., 1985) as described in equation 8.14:

$$L = \frac{d_p}{(2+0.644R^{1/2}Sc^{1/3})[1+1.5(1-\varepsilon)]} \qquad (8.14)$$

where Sc is the Schmidt number ($\mu/\rho D$), with ρ denoting density of water (ML^{-3}), and μ representing the dynamic viscosity of water ($ML^{-1}T^{-1}$). R is the Reynolds number ($vd_p\rho/\mu$).

Model kinetic parameters k and K_s were estimated independently by the specially designed experiments described in Chapter 7. S_{min} and D (diffusivity) were estimated in biofilter model C. For biofilter models A and B, the parameter Y/b can be calculated from the estimated S_{min} by using equation (8). D/D_f was assigned 1.1 (Hozalski, 1996).

The method of least squares is the most widely used parameter estimation procedure. However, this method has optimal statistical properties only when the errors of the observations are uniformly randomized and normally distributed (Bard, 1974). The filter effluent BOM levels during the steady-state may change from several µg/L to several tens of µg/L. The BOM measurement procedure involves dilutions, the relative errors of measured BOM data can be more important the absolute errors. A logarithmic transformation of the BOM data can be considered to be more appropriate.

An alternative to the method of least squares is the sum of absolute residuals (SAR) (Robinson, 1985; Bard, 1974). In the present study, a weighting coefficient (W_i) was used

for minimization to reduce the influence of the worst observations (Robinson, 1985). The objective function then becomes:

$$\text{Min } \sum W_i \text{ ABS } (\ln S_{b\text{-observed}} - \ln S_{b\text{-modeling}}) \qquad (8.15)$$

Where, $W_i = (1-u_i^2)^2$

The u_i values are defined as $(\ln S_{b\text{-observed}} - \ln S_{b\text{-modeling}})/c$, where c is a "robustness constant". By using $W_i ABS(\ln S_{b\text{-observed}} - \ln S_{b\text{-modeling}})$ instead of $ABS(\ln S_{b\text{-observed}} - \ln S_{b\text{-modeling}})$, the impact of the data having the greatest scatter is minimized. Mosteller and Tukey (1977) suggested that a value of c for equal to six times the sum of the absolute values of the $(\ln S_{b\text{-observed}} - \ln S_{b\text{-modeling}})$ divided by the numbers of observations.

FORTRAN programs for the modeling work were attached in Appendix M.

8.6 RESULTS AND DISCUSSION

8.6.1 Parameter estimates

Kinetic parameter estimation was performed using acetate removal data in Filter 1 (anthracite/sand, 20°C) in period IB of phase III. The estimated and calculated parameters for Filter 1 are listed in Table 1.

Confidence intervals were not estimated for the parameters in Table 1 because of the mathematical complexity.

Table 8.1: Estimated/Calculated Parameters for Filter 1 (Anthracite/Sand, 20°C)

Filter	k (1/s)	K_s (mg/m^3)	S_{min} (mg/m^3)	D (m^2/s)	SD (D/D_f)	X_f (mg/m^3)	Y/b (s)
Filter 1	4.4E-5	650	10.1	1.8E-10	1.1	3.5E+7	1.5E6

Note: k and K_s are estimated in Chapter 7; S_{min} and D are estimated in the biofilter model; Other parameters are assigned (SD = 1.1 (Zhang and Huck (1996a); X_f = 3.5e+7 mg/m^3 (Rittmann and McCarty (1980)); The Y/b was calculated from the estimated parameters k, K_s and S_{min}.

The estimated parameters of k and K_s for acetate from this study were compared with that from other research in Table 7.2 in Chapter 7. The estimated k value in this study agrees well with those from Metcalf and Eddy (1991), Zhang and Huck (1996a) and Holzaski (1996). However, it is more than one magnitude higher than those estimated for oligotrophic conditions (van der Kooij *et al.*, 1982; Rittmann, 1986). There is a larger difference among different studies for K_s. The estimated K_s from this study and from Hozalski are substantially lower than that from Metcalf and Eddy (1991) and Zhang and Huck (1996a), and higher than that from van der Kooij *et al.* (1982) and Rittmann (1986). This might be due to the fact that the K_s parameters from this research and Hozalski were estimated from experiments independently, the K_s parameter provided by Rittmann and McCarty (1991) was estimated from wastewater, and that given by Zhang and Huck (1996a) was obtained by model fitting of AOC removal in drinking water biofilters. In general, K_s in wastewater is higher than in drinking water because of the higher nutrient levels in wastewater. It should be noted that the correlation of k and K_s (as shown in Chapter 7) affects these comparisons to a certain extent.

The estimated S_{min} from this study (Table 8.1) is close to that (4.5 – 10 mg/m^3) reported by Zhang and Huck (1996a) for AOC.

The Y/b (1.5E6 s) estimated in this study (Table 8.1) by model fitting is about one magnitude lower than that (1.1E7) from model fitting by Zhang and Huck (1996a), and

higher than that (4.9E5) experimentally estimated from Hozalski (1996) and that (8.6E5) given empirically by Metcalf and Eddy (1991). Y/b reflects the ratio of biomass production and loss in biofilters. The Y/b values from this study and the value from Zhang and Huck (1996a) are considerably larger than that in the wastewater case. Higher Y/b indicates the higher requirement for maintenance of biomass. This would be expected in the oligotrophic conditions in this study and especially in the study of Zhang and Huck (1996a). It is not clear why the value of Y/b estimated by Hozalski (1996) is lower. The assumption that one cell equals to one CFU may contribute to this lower value of Y/b. The another possible explanation is that the value of Y/b was estimated in an experiment using a single species *P. aeruginosa* growth on acetate, rather than the naturally developed bacteria in drinking water biofilters.

The D value estimated from this study is a little lower than that (4.3E-10) from Zhang and Huck (1996a), however, it is almost one magnitude lower than that (1.21E-9) from other values quoted in the literature (Perry and Green, 1984).

The large range of the estimated/empirical single parameters from different studies makes it difficult to compare the estimated parameters quantitatively. It is also likely that there are mathematical difficulties in obtaining reliable single parameter estimates from data sets not designed for this purpose, because of the inherent correlation among parameters in the model. It should also be mentioned that the first-order biomass (biofilm) loss model applied in these three biofilter models might not represent the real case in biofilters.

8.6.2 BOM removal in biofilters

The steady-state biofilm and steady-state biofilter models are based on the premise that biofilters have reached a pseudo steady-state with respect to their influent BOM concentrations. In practice some fluctuation in influent concentrations occurs. Comparisons between measured and modeled acetate removals in Filter 1 (period IB, phase III) are shown in Figures 8.1 and 8.2. It will be recalled that this was an anthracite

filter operated at high temperature (20 °C) and backwashed with chlorinated water (0.25 mg/L).

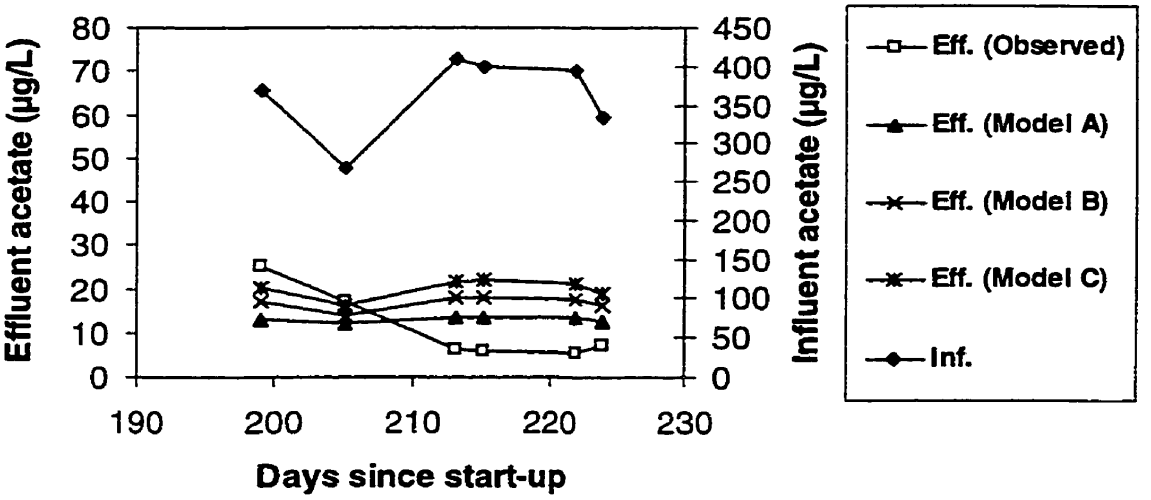

Figure 8.1: Influent and effluent (observed and predicted) acetate in Filter 1 (period IB, phase III)

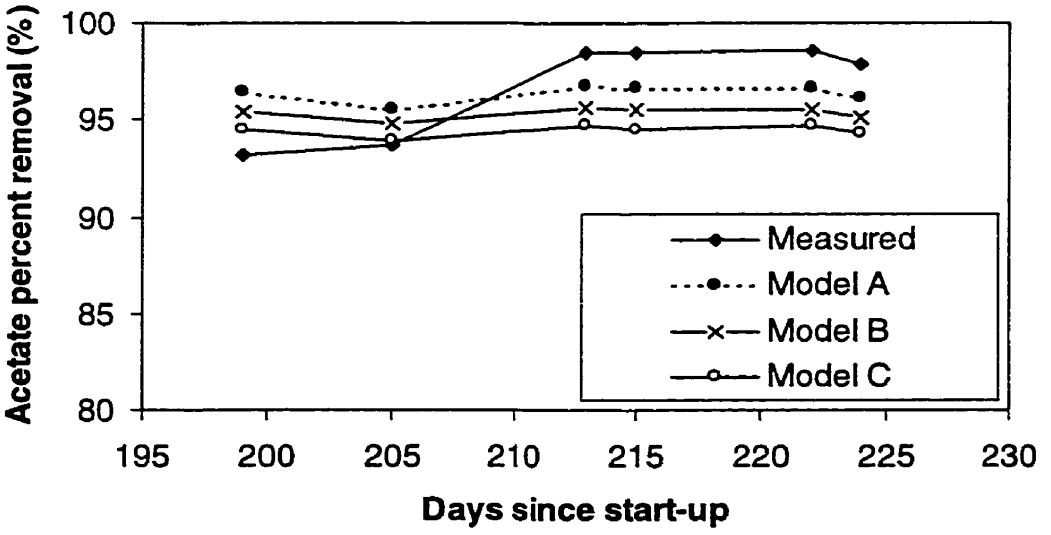

Figure 8.2: Acetate percent removal in Filter 1 (period IB, phase III)

Figure 8.1 shows that there is good fit between measured and modeled effluent profiles during this period. Figure 8.2 demonstrates a similar trend in terms of percent removal during the same period. The models appear to underestimate the effluent acetate levels initially when the measured effluent acetate concentrations are higher, and overestimate the effluent acetate levels later in the period, when the measured effluent acetate concentrations are lower.

The results from models A, B and C are very close. In fact, models B and C are derived from different regression solutions to the steady-state biofilm model, and should exhibit similar behaviour. Models B and C can be simplified to model A when $K_s >> S_f$ (S_f is the substrate concentration in biofilms). The behaviour of these three biofilter models in drinking water biofiltration is also verified and evaluated later in this Chapter in the section, "General comparison of models A, B and C".

8.6.3 Biofilm thickness and BOM profiles in biofilters

The models (models A, B and C) and the estimated model parameters (Table 8.1) can be used to predict both biofilm thickness and BOM profiles in biofilters. As an example, the modeled biofilm thickness in Filter 1 (Anthracite media; 20 °C; chlorine in the backwash water 0.25 mg/L; influent concentration: 369 μg/L) is shown in Figure 8.3.

Figure 8.3 shows that most of the biomass accumulates in the upper layers of the biofilter. A similar trend of biomass profiles measured in this study can be found in Figures 5.11 and 5.13 in Chapter 5. Other investigations from bench-scale biofilters (Urfer, 1998; Booth, 1998), pilot biofilters (Wang *et al.*, 1995; Carson and Amy, 1998) and full-scale biofilters (Coffey *et al.*, 1995) also demonstrated a similar trend to the above modeling results. No actually measured biomass thickness is available in the literature, because of the limit of current experimental methodologies. The predicted biofilm thickness in the upper parts of the filter is at or above higher end of the range (0 –

30 μm) estimated from measured phospholipid biomass (Urfer, 1998) or from biofilter modelling (Hozalski, 1996). The predicted biofilm thickness also suggested that the first-order biofilm detachment model is more adequate for the lower part of the filter (biofilm thickness < 30 μm) than for the higher parts of the filters (biofilm thickness >30 μm).

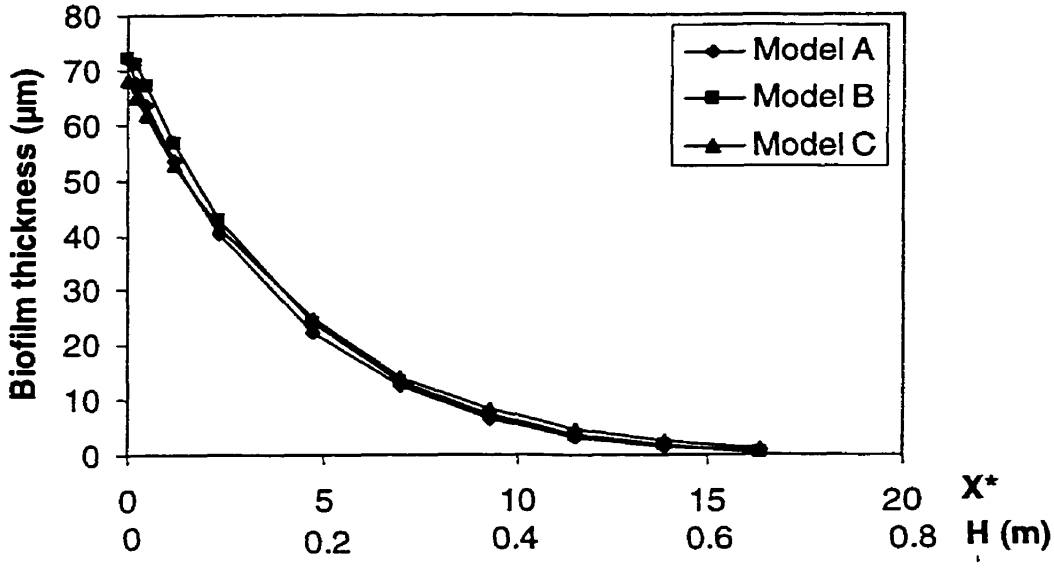

Figure 8.3: Calculated biofilm thickness distribution with depth in Filter 1

Modeled acetate concentration profiles in the anthracite/sand biofilter are depicted in Figure 8.4, for the same conditions as for the biofilm thickness modeling (Figure 8.3). Most of the acetate was predicted to be removed in the upper layers of the media in the biofilters. A similar trend of BOM profiles measured in this study can be found in Figures 5.5, 5.6 and 5.7 in Chapter 5. The measured substrate profiles in drinking water biofilters from other studies showed similar trends (e. g. Servais et al., 1992; Urfer, 1998; Booth, 1998).

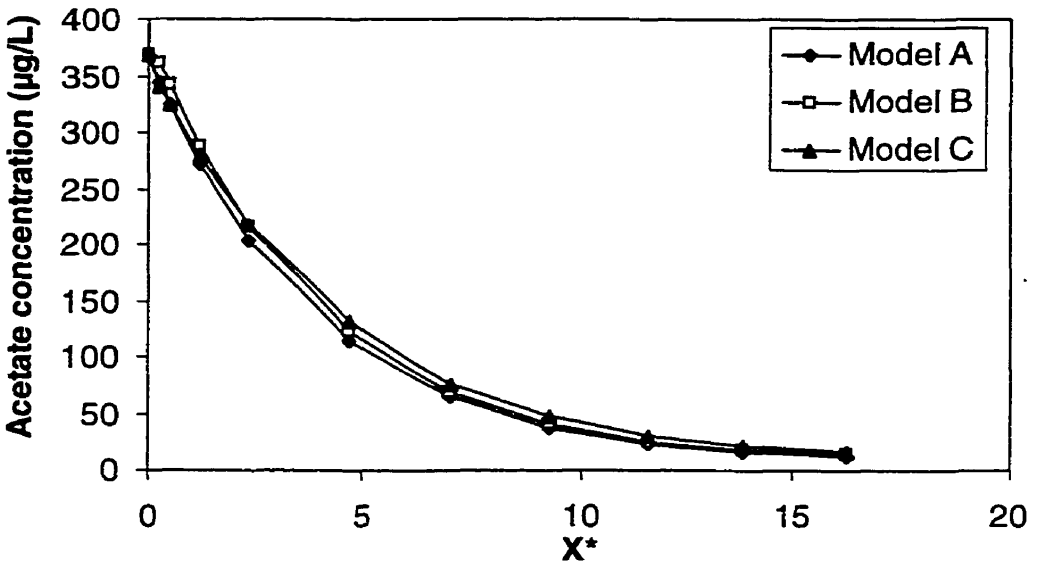

Figure 8.4: Predicted acetate concentration profiles in Filter 1

Figures 8.3 and 8.4 show that for the representative conditions selected, the differences in models A, B and C are negligible in predicting the profiles of acetate and biofilm thickness in biofilters.

By using the modeling results from model A and plotting acetate concentration and biofilm thickness profiles in biofilters, a good relationship between acetate concentration and biofilm thickness was found and is shown in Figure 8.5. This means that the acetate removal in biofilters can be approximately described either as first-order with respect to concentration or as first-order with respect to biofilm thickness. As mentioned previously, the estimated diffusion coefficient D is significantly lower than the normal value from the literature. This could indicate a "deep" biofilm in biofilters. Within a deep biofilm, substrate concentration decreases asymptotically to zero. Therefore, the contribution (per unite mass or volume of biofilm) of a thick biofilm to the biodegradation of substrates would be less than for a thin biofilm.

Based on the results of methylglyoxal and pyruvate removal in bench-scale biofilters, Booth (1998) argued that substrate removal in biofilters was inherently zero-order with respect to the substrate concentration, but could be approximately described as first-order relationship with respect to the biomass in biofilters. This first-order removal pattern is in agreement with the modeling results in this research.

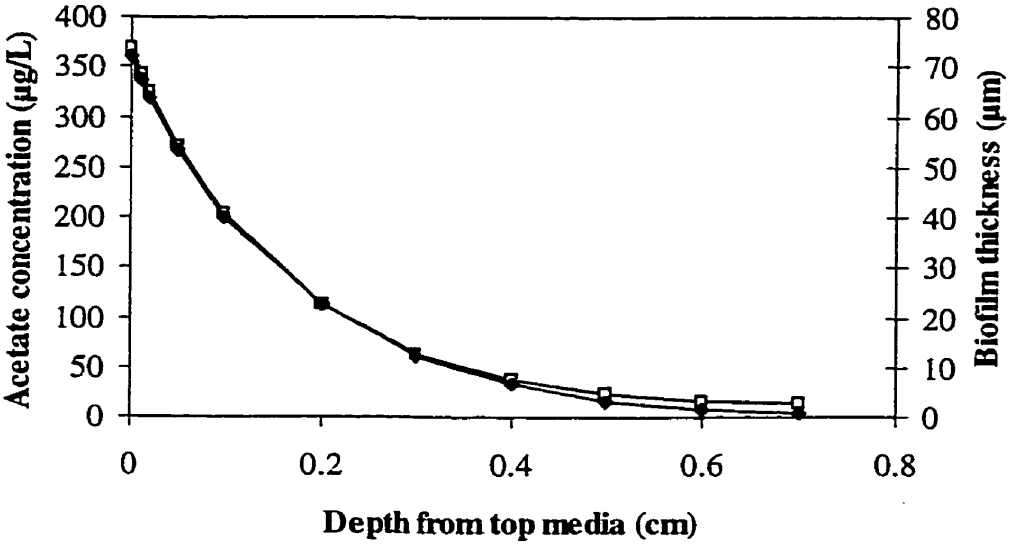

Figure 8.5: Calculated acetate concentration profile vs. biofilm thickness profile

8.6.4 General comparison of biofilter models A, B, and C

A general comparison of biofilter models A, B, and C can be performed by evaluating S_s^* (dimensionless substrate concentration at the biofilm surface) vs. J^*(dimensionless substrate flux to the biofilm) Figure 8.6 provides this general comparison using parameters estimated in this research (Table 8.1, acetate). The relationships of S_s^* vs. J^* in Model A, B and C have been shown in equations 8.2, 8.4 and 8.6, respectively. Figure 8.6 shows dimensionless substrate concentration at the biofilm surface as a function of dimensionless substrate flux to the biofilm. To a large extent, the BOM removal from

bulk liquid (dependent on the flux) vs. BOM concentration in bulk liquid (dependent on S_s^*) can be evaluated using the relationships of J^* vs. S_s^*.

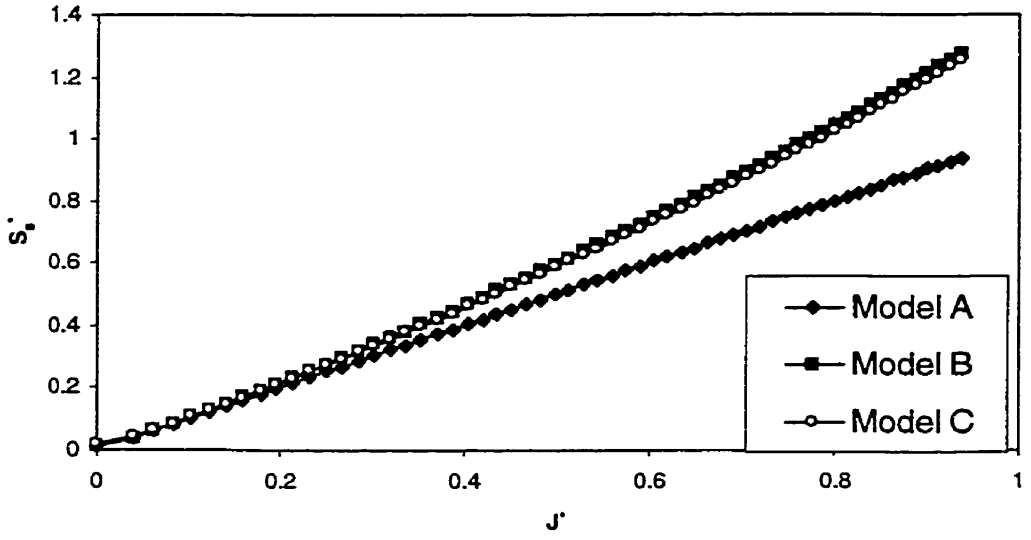

Figure 8.6: S_s^* vs. J^* in terms of models A, B and C

Biofilter models B and C are consistent over a wide range of predicted J^* values (the overlapping upper lines in Figures 8.6). The relative error is less than 2% for all cases. However, the difference between model A and model B or C increases as the substrate concentration increases. Model A gives an essentially liner relationship whereas models B and C give a relationship that is convex upwards.

The difference between model A and model B or C is less than 10 % only in the low S_s^* range ($S_s^* < 19.5S_{min}^*$ using parameters in this research). Generally, S_s^* would be less than $20S_{min}^*$ (i.e. $S_b < 20\ S_{min}$ approximately) for drinking water biofiltration. Based on estimates of S_{min} in the next section, S_b, the bulk BOM concentration would need to be

less than about 200-300 μg/L, which would be true for many cases. Therefore, model A can be considered as a good approximation to model B or model C, in drinking water biofiltration.

Based on the good agreement between observed and predicted values in Figures 8.1 and 8.2 and the similar results shown for all three models in Figures 8.3 and 8.4, it is likely that all three models are applicable for the modeling of drinking water biofiltration performance. Models B and C should be used for modeling higher substrate concentrations (above 300 μg/L). Because the actual testing of the models with experimental data has been limited, all models should be tested using a range of data sets (when these might be available) to verify their general applicability.

The fact that Figure 8.6 is essentially linear indicates that dimensionless substrate (acetate) removal (J^*) is approximately proportional to the dimensionless substrate concentration on the surface of the biofilm (S_s^*). This also means that the acetate removal in biofilters is essentially proportional to the acetate concentration in bulk liquid, which is the case for the first-order biofilter model proposed by Huck *et al.*(1994).

It should be noted that sophisticated multiple substrate effects are present, similar as mentioned in k and K_s estimation discussed in Chapter 7.

8.6.5 S_{min}

The new S_{min} expression (equation 8.10), which includes both kinetic parameters and biofilter operating parameters, is more complicated than the original one proposed by Rittmann and McCarty (1980). Based on parameters estimated from this research (Table 8.1), the new can be calculated using equation 8.10. The relative difference in S_{min} obtained using these two expressions is 25% (10.1 μg/L by Rittmann and McCarty (1980); 13.7 μg/L by this study).

The values of S_{min} estimated from this research and Rittmann and McCarty (1980) are close to the middle of the range of typical effluent acetate concentrations in this study (5 –25 μg/L). S_{min} can be approximately considered as the BOM residual sent to the distribution system. Therefore, both of the Rittmann and McCartyand the revised S_{min} expressions are applicable from an engineering perspective.

It is not economical to reduce the BOM concentration to a level below S_{min} in biofilters. Biofilter bed utilization, discussed in Chapter 5 can approximately be defined as the ratio of the bed depth needed to reduce the BOM from the influent level to S_{min} over the total bed depth. S_{min} occurs around $X^*_{critical}$ (where no substantial further BOM removal occurs) in biofilters. Below S_{min}, no substantial BOM removal would occur in biofilters or distribution systems, and this is why biomass can still grow after a long period of time in distribution systems. Hypothetically, it would be possible to calculate S_{min} for different distribution system conditions.

8.6.6 X^*

X^*, as mentioned previously, can be used as a better independent variable than simple EBCT to evaluate the performance of different kinds of biofilters under different operating conditions. Theoretically, as long as X^* is the same, different combinations of hydraulic loading rates, column depth, and media size would achieve the same removal for the same BOM. Results from this study (Figure 5.10 in Chapter 5) supported this hypothesis. In Figure 5.10, similar acetate removals at the same EBCT (or X^*) were observed in Filter 1 while operated at different HLRs. This finding was also supported by the results of a pilot study reported by Servais *et al.* (1992).

As previously mentioned, BOM removals are dependent on both substrate and operating parameters. The X^* allows comparisons of removal performance for the same substrate among studies because the left sides of the equation (8.3), (8.5) and (8.7) are substrate characteristic (i.e. substrate kinetics) dependent. The removal performances of different

substrates can not be assessed using the same generalized relationship between percent removal and X^* because of the different kinetics.

By using the parameters estimated in this study, generalized curves for percent removals vs. X^* are developed in Figure 8.7 for different k/K_s values. The k/K_s value for acetate is used as a reference. As described in Chapter 7, the value of k/K_s quantifies the change of bioreaction rate with respect to substrate concentration when the substrate concentration is significantly lower than K_s. Therefore, it should be noted that, unlike k, the value k/K_s is not a direct indicator of the substrate biodegradability. However, it is useful to make generalized curves (percent removals vs. X^*) in terms of different values of k/K_s to explore the nature of this relationship.

Figure 8.7 shows that acetate removal performance in biofilters increases with increasing X^*, but in a less-than-proportional way. This trend agrees well with that shown by Zhang (1996) and Zhang and Huck (1996a), who also noted that beyond a certain X^*, little further removal would be expected. It might be helpful to describe BOM removal performance by defining a critical X^* ($X^*_{critical}$). Beyond the $X^*_{critical}$, further measurable removals with increasing X^* would not be expected.

The curve convexity is dependent on the biokinetic parameters of the substrate. The values of $X^*_{critical}$ for higher k/K_s values are higher than that for lower k/K_s values. This also means that more dimensionless contact time is needed to achieve an approximately complete removal (down to S_{min}) in biofilters for substrates with a higher k/K_s level. However in terms of actual contact time (EBCT), no substantial differences are required to reach same percent removal for substrates with different k/K_s values (calculation based on Figure 8.7, not shown). This also means that actual EBCTs needed to reach a given percent removal are not sensitive to substrates with different k/K_s values. It should be noted that X^* also includes α, the biofilter specific surface area, which is inversely related to media diameter. Thus, in principle EBCT and /or media diameter can be changed to achieve given or required X^*.

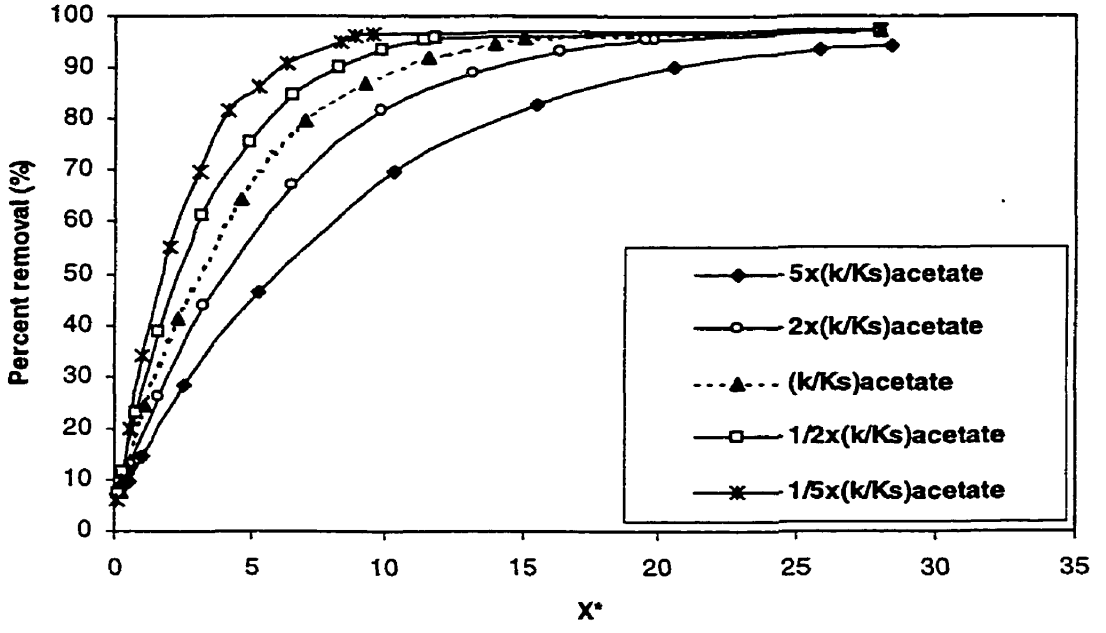

Figure 8.7: Generalized curves for percent removals vs. X^*

Based on the estimation of k/K_s in Chapters 7, the k/K_s values with respect to different substrates are calculated and shown in Table 8.2.

Table 8.2: k/K_s Values (mg /m^3/h) for Different Substrates in Biofilters

Substrate	Acetate ×E-4	Formate ×E-4	Formaldehyde ×E-4	Glyoxal ×E-4
F1	3.3	3.2	2.5	0.83
F2	1.9	1.5	1.8	1.7
F3	0.31	0.43	0.46	0.13
F4	1.2	1.3	0.05	0.45

In most cases of this study, k/K_s values are generally higher for more easily biodegradable substrates than for less easily biodegradable substrates. However, the difference in k/K_s values is not as big as that in k values (the k values are shown in Table 7.1 of Chapter 7).

Based on the definition of $X^*_{critical}$, the values of $X^*_{critical}$ in terms of k/K_s levels were estimated from Figure 8.7 and listed in Table 8.3.

Table 8.3: $X^*_{critical}$ vs. k/K_s Levels

k/K_s levels	1/5 × acetate	½ × acetate	acetate	2 × acetate	5 × acetate
$X^*_{critical}$	8	12	14	19	27

Figure 8.7 would be useful as a framework to quantify substrate (with similar K_s to acetate) removals as a function of k/K_s values of substrate and operating parameters of biofilters.

Table 8.4: X^* (at different k/K_s Levels) in Terms of Several Filter Media Designs[1]

Filter type	Depth (m)	Effective size (mm)	α (m^{-1})	Flowrate (m/h)	X^* (X^*/X^*_c) (acetate)	X^* (X^*/X^*_c) (1/5 x acetate)	X^* (X^*/X^*_c) (5 x acetate)
Sand	0.55	0.5	7200	5	40.6 (2.9)	18.2 (2.3)	90.8 (3.3)
Dual media	0.40 (anthr.)	1.0	3600	10	20.3 (1.4)	9.1 (1.1)	45.3 (1.7)
	0.35 (sand)	0.5	7200				
Deep-bed monomedia	1.1	1.0	3600	15	13.6 (0.97)	6.1 (0.76)	30.4 (1.1)

[1] Based on the filter operating conditions from Huck (1999); A 75% coverage of biofilm on the media surface was assumed; The "1/5x" means 1/5 times the acetate k/K_s level.

Bed utilization (whether the bed is over-designed or under-designed) can be evaluated by comparing the actual X^* in biofilters in Table 8.4 with the critical values in Table 8.3.

Sand and dual media biofilters are over-designed to various extents for substrates with 1/5 to 5 times the acetate k/K_s level. This is indicated in Table 8.4 by the fact that the ratio X^* / X^*_c is always greater than unity for these filters. The deep-bed monomedia biofilter is slightly over-designed for substrates with 5 times the acetate k/K_s level because X^* / X^*_c is less than 1. However, it is under-designed for substrates having k/K_s equal to that for acetate or 1/5 that for acetate. This means that the deep-bed monomedia biofilter is under-designed for substrates with lower k/K_s levels. This suggests that except for deep bed monomedia biofilters (large media) at lower k/K_s levels, X^* for all filters in Table 8.4 is high enough that removals are not sensitive to it.

As mentioned in the S_{min} section, the S_{min} occurs around $X^*_{critical}$ (where no substantial further BOM removal occurs) in biofilters. Below S_{min} (or beyond $X^*_{critical}$), no substantial BOM removal would occur in biofilters or distribution systems, and filter bed utilization reaches a maximum.

8.7 CONCLUSIONS

- Both actual modeling results and a general comparison of the models showed that the simplified model (first order) is a good approximation for the two more complicated models B, and C, in the modeling of drinking water biofiltration. Therefore, the simplified first order model is recommended for the modeling of drinking water biofiltration processes.
- Suidan and Wang's (1985) semi-empirical solution and Sáez Rittmann's (1992) pseudo-analytical solution to the steady-state biofilm model are very close in a wide range of influent substrate concentrations according to the estimated parameters in this study.
- The trend of estimated distribution of biofilm thickness is similar to the measured profiles in this study and other research.
- The estimated acetate profile agrees well with the measured one in this research.

- The difference between the original and the revised S_{min} developed in this research is around 25%, depending on the operating conditions and the estimated kinetic parameters. Because S_{min} is in the range of 10μg/L, a 25% difference is only a few μg/L. Therefore, both S_{min} expressions are therefore applicable from a practical engineering viewpoint.
- The S_{min} occurs around $X^*_{critical}$ in biofilters. Below S_{min}, no substantial BOM removal would occur in biofilters or distribution systems. It is not economically efficient to reduce the BOM to a level below S_{min} in biofilters.
- $X^*_{critical}$ is an important parameter in evaluating the filter bed utilization (i.e. the filter is over-designed or under-designed in terms of BOM removal).
- The generalized curves for percent removals vs. X^* can be used to evaluate BOM removals as a function of the k/K_s level of a given substrate and operating parameters in biofilters.
- Suggested further work includes: generalized curves for percent removals vs. X^* as a function of the values of individual k and K_s for a given substrate and operating parameters in biofilters; implementation of the biofilm detachment model in biofilter models; consideration of the morphology of the biofilm in the biofilter models; consideration of the competitive and inhibitory effects of substrates; and the improvement of parameter estimation.

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

This research included the examination of factors affecting BOM removal in biofilters and their interactions, the evaluation of biomass respiration potential (BRP) as an alternative biomass measurement, the development of a new approach for bio-kinetic parameter estimation, the evaluation of a revised S_{min} in biofilters, the assessment of dimensionless empty bed contact time (X^*) in biofilters, the introduction of the concept of bed utilization, and the application of steady-state biofilm models to drinking water biofilters. Other investigations within the overall research included: impacts of biomass accumulation during a filter run; impact of EBCT; impacts of longer term operation of biofilters; and impacts of step increases in BOM concentration, hydraulic loading rate and filter shutdown on biofilter performance. The investigations were conducted using laboratory scale biofilters fed synthetic water containing easily biodegradable components.

9.1 CONCLUSIONS

The following conclusions can be drawn regarding the investigation of factors affecting drinking water biofiltration:

- Biofilters reached pseudo steady-state BOM removal in approximately one month, depending on their operating conditions. Less time was required to reach pseudo

steady-state for GAC biofilters backwashed with non-chlorinated water and run at high temperature (20 °C).

- GAC filters were able to tolerate chlorine backwash (free chlorine 0.5 mg/L), even operated at low temperature (5 °C). In anthracite media filters, however, the temperature effect was measurable when chlorine was present in backwash water (even dosed at 0.25 mg/L). Backwashing with chlorine substantially impaired the BOM removal capacity in the anthracite filters operated at low temperature (5 °C). In practice, biomass may develop a resistance to chlorinated water (0.25 mg/L) after a longer period of operation (4-5 months) and the adverse effect on BOM removal may be reduced. Chloramine in the backwash water (0.25 mg/L) did not impact BOM removal in biofilters operated at high or low temperatures.
- Glyoxal as a specific component in the BOM cocktail was more sensitive than acetate, formate and formaldehyde to the unfavourable operating conditions such as low temperature and chlorinated water backwash in biofilters. Chlorine in the backwash water (at a concentration as low as 0.25 mg/L) showed impacts on glyoxal removal in biofilters, run at both low (5 °C) and high temperatures (20 °C).
- Statistical analyses showed that, at a 5% significance level, the three factors media, temperature and chlorine in the backwash water and their interactions were significant (except for some cases of glyoxal removal). Complicated interactions existed among these three factors. Air scour effects may be important under unfavourable conditions, and particle and coagulant effects were not significant.
- The multiple linear regression models developed in this research can be used to approximately predict BOM removal in filters under different operating conditions for roughly the same EBCT investigated in this study.
- Particle removal efficiency in biofilters was not substantially affected by the BOM removal, although the detached biomass in the filter effluent make minor contributions to the turbidity in the filter effluent.
- Biofilter bed utilization (the ratio of the bed depth required for substantial BOM removal to the entire bed depth) was dependent on the biofilter operating conditions and the BOM components. In general, biofilter bed utilization was low (i.e. only a portion of the bed was required) under favourable conditions (easily biodegradable

BOM components, high temperature, no chlorine in the backwash water), and biofilter bed utilization was high under unfavourable conditions (recalcitrant BOM components, low temperature and chlorine in the backwash water). These experimental results are also supported by the modeling results in this research ($X^*_{actual\ (acetate)} < X^*_{critical\ (acetate)}$ and $X^*_{actual\ (glyoxal)} < X^*_{critical\ (glyoxal)}$).

- EBCT (or X*) is a good indicator for BOM removal in biofilters. Similar removals were observed for the same EBCT (or X*) when the biofilters were run at different HLRs. This also agrees with the modeling results in this study.
- In general, there were no major changes in BOM removal within a given filter run. BOM removal was not sensitive to biomass changes during a filter run. Biomass removed during backwash did not substantially impact the BOM removal in the following filter run.
- Instantaneous effects of HLR and BOM steps on BOM removal were similar: BOM removal (as acetate, formate, formaldehyde and glyoxal) in Filter 3 (the "worst case" scenario) was negatively impacted. The recalcitrant BOM component (glyoxal) removal was negatively impacted in all filters except in Filter 2 (the "best case" scenario).
- BOM removal results before and after filter shutdown (24 hours, filter drained) demonstrated that the biofilms on the four biofilters were mature and strong enough to endure the unfavourable influences of filter shutdown. Mature biofilters were able to suffer the HLR/BOM steps without losing BOM removal capacity at least for easily biodegradable BOM, by using biofilms deeper in the filter bed.

Conclusions from BRP as an alternative biomass measurement are described as the following:

- A strong linear relationship between BRP and phospholipid biomass was observed in this research. The proposed simpler and faster BRP approach for biomass estimation may be appropriate for routine use by treatment personnel.
- The temperature dependence of the BRP test is important in assessing the amount of biomass in biofilters. The estimated temperature-activity coefficient (θ =1.02) can be

used to approximate the equivalent biomass from the results of the BRP test at any given temperature.

- The existence of an approximately linear relationship between BRP and phospholipid biomass can be explained theoretically if the BRP test conditions are well defined.

The major conclusions in terms of bio-kinetic parameter estimation from the specifically designed experiment are discussed below:

- The approach for k and K_s estimation presented in this research is simpler than the classical approach and more robust than the pure modeling approach. Drinking water biofilter modeling may be facilitated by the more accurately estimated key model parameters (k and K_s).

- The maximum utilization rate of the substrate k is temperature dependent and the estimated temperature-activity coefficients (θ =1.026, 1.018, 1.017 and 1.028, for acetate, formate, formaldehyde and glyoxal, respectively) can be used to estimate the maximum utilization rate of the substrate k at any given temperature.

- Enzyme-reaction patterns could affect the estimation and application of bio-kinetic parameters.

The important findings and conclusions from the modeling portion of this investigation include the following:

- Both the modeling results and a general comparison of the models showed that the simplified model (first order assumption) is a good approximation for the two more complicated models B, and C in terms of the modeling of drinking water biofiltration. Therefore, the simplified model is recommended for the modeling of drinking water biofiltration processes.
- Suidan and Wang's (1985) semi-empirical solution and Sáez and Rittmann's (1992) pseudo-analytical solution to the steady-state biofilm model are very close in a wide

range of influent substrate concentrations according to the estimated parameters in this study.

- The trend of estimated distribution of biofilm thickness with filter depth is similar to the measured distribution in this study and other research. The estimated acetate profile agrees well with the measured one in the research findings.
- The difference between the original and the revised S_{min} developed in this research is around 25%, depending on the operating conditions and the estimated kinetic parameters. Both S_{min} expressions are therefore applicable from a practical engineering viewpoint.
- S_{min} occurs around $X^*_{critical}$ in biofilters. Below S_{min} (or for X^* greater than $X^*_{critical}$), no substantial BOM removal would occur in biofilters or distribution systems. Therefore, it is not economically efficient to reduce BOM to a level below S_{min} in biofilters. S_{min} may be different for different systems.
- $X^*_{critical}$ is an important parameter in evaluating the filter bed utilization (i.e. whether the filter is over-designed or under-designed in terms of BOM removal).
- The generalized curves (percent removals vs. X^*) can be used to evaluate BOM removals as a function of the k/Ks level of a given substrate and operating parameters in biofilters.
- The concept of bed utilization may help the understanding of the effects of the factors affecting drinking water biofiltration.

9.2 RECOMMENDATIONS FOR FUTURE RESEARCH

- Further work is required regarding the effects of chlorine in the backwash water and air scour during backwashing.
- The contribution of detached biomass to the effluent turbidity needs to be addressed, with the use of particle count data.
- Direct or more efficient indirect biomass measurement methodologies, in addition to the ones mentioned and performed in this research, should be pursued because

biomass quantification is of critical importance to the understanding of BOM biodegradation processes.

- BRP test conditions need to be optimized through further investigation.
- Enzyme-reaction patterns affect the estimation and application of bio-kinetic parameters. Further work is needed to evaluate the competitive effects on the estimation of bio-kinetic parameters.
- The development of a universal biofilm model capable of describing the biofilm process (biomass accumulation in the initial development period, biomass changes in a filter run in the pseudo steady-state period, biomass responses to BOM or HLR steps) would be useful in evaluating BOM removal performance.
- The implementation of such a biofilm model in a dynamic steady-state biofilter model is of importance.
- Additional investigations into the biofilm physical structure (morphology of the biofilm) and the microbial community in drinking water biofilters can allow for a better understanding of biofiltration mechanisms.
- Consideration of the competitive and inhibitory effects of substrates is required in future studies.

9.3 RECOMMENDATIONS FOR THE WATER INDUSTRY

Based on the experimental and modeling results from these bench scale biofilters, the following recommendations for the water industry are made:

- The use of air scour in backwash is recommended for ease of the backwash operation in biofilters, for both particle and BOM removal.
- Either single stage or second stage biofilters can be used for BOM removal, since the particle removal has only a small effect on BOM removal in biofilters.
- Chlorine is not recommended for use in filter backwash, except for the control of biomass build-up in a very active biofiltration process. In GAC biofilters, chlorine-

free BW can enhance the removal of recalcitrant components (such as glyoxal). In biofilters with anthracite media, chlorine-free BW is strongly recommended, since chlorine can reduce recalcitrant BOM component removal substantially, especially at low temperature (5 °C).

- Unfavourable conditions such as HLR, BOM steps and relatively brief filter shutdown (<24 hours, filter drained) will not substantially impact BOM removal in biofilters with well-developed biofilms. Therefore, regular biofilter maintenance should have little impact on overall biofilter performance.
- The results of online DO testing can be used as an indicator of BOM removal in biofilters.
- In general, the typical filter design for particle removal in water facilities is over-designed for the removal of relatively readily biodegradable BOM components.

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APPENDIX A:

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) FILTER INFLUENT/EFFLUENT DURING BLOCKS I AND II

QA/QC

QA/QC measures regarding carboxylic acids, aldehydes and phospholipid biomass are discussed below.

Carboxylic acids

Great care was taken for carboxylic acids analysis due to the potential contamination from sampling vials, sampling process, and sample preparation for quantification in the IC. The sampling vials were washed using a special program with no acetate rinse. Latex gloves were always worn during sampling and sample preparation to avoid the contamination from the skin. Carboxylic samples were usually sampled in duplicate and the variability were low (refer to different graphs showing the error bars).

Method blanks and internal standards in DI and /or in tap water were included in each sample run to check if the instrument was in good condition. One standard every ten samples was included in the sample queue and the concentrations of the replicates were generally very similar. The fresh standards were prepared every week (by dilution from the standards with higher concentrations) to ensure no major degradation of the standards.

Aldehydes

Methods blanks (tap water) and internal standards in DI water were included in each sample run. It was found that variabilities were very low for duplicate formaldehyde sample (coefficient of variability less than 5% in most cases). However, a relatively higher variability was usually observed for glyoxal.

Phospholipid biomass

It is of importance to avoid the potential contamination during sampling. Phosphate-free sampling glass vials were prepared using a cleaning process with a phosphate-free laboratory detergent. Prior to phospholipid biomass media sampling, the biofilters were first drained and then rinsed with phosphate-free influent (no nutrient was fed during rinsing) because the residual of phosphate from the nutrient component potassium phosphate in the filter influent during normal filter operation may affect the accuracy of the measurement. It was found that duplicate measurements from single extraction were repeatable, however, results from sample media produced more variability.

A typical calibration curve used to convert absorbance @610 nm to nmole of phosphate is shown in Figure A-1.

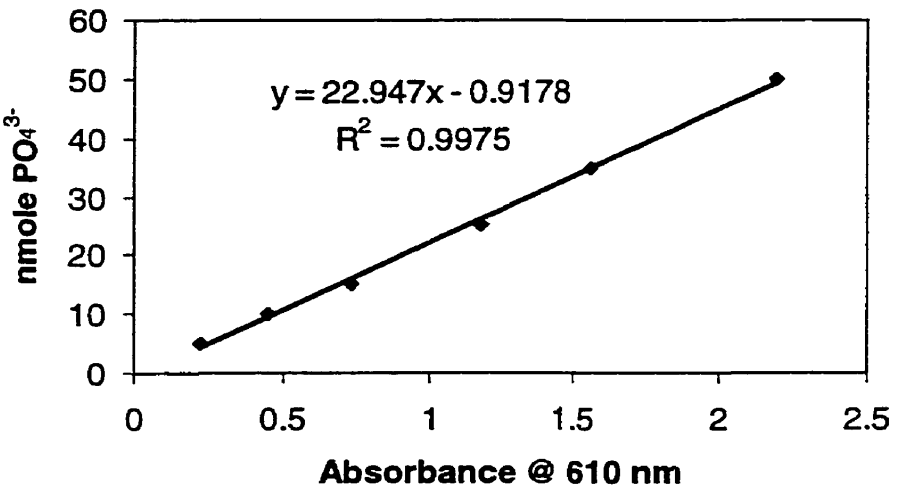

Figure A-1: Calibration curve used to convert absorbance @610 nm to nmole of phosphate

Block I Experimental Results (µg/L)

Days		Acetate Influent	Effluent	formate Influent	Effluent	Formaldehyde Influent	Effluent	Glyoxal Influent	Effluent
1	F1	540	500	538	589	107	112	28.5	30.9
	F2	570	313	590	670	118	100	32.2	28
	F3	533	541	572	699	115	171	30.5	32.9
	F4	612	330	700	590	123	167	33.4	31.7
6	F1	307	132	459	151	87.1	86	20.7	24.0
	F2	317	104	403	120	90.5	90	14.2	15.1
	F3	390	359	518	481	91.2	89	22.9	27.5
	F4	372	120	500	184	80.2	97.3	22.5	26.9
15	F1	399	33	414	49	98	9.8	36.2	21.7
	F2	405	34	385	43	99	0.99	29.2	13.7
	F3	745	326	648	537	113	98.5	34.8	31.3
	F4	789	50.8	497	55	115	58.4	39	32.3
22	F1	262	13	286	30.9	108.6	5.3	19.4	10.3

	F2	283	2.9	453	12.3	100.1	2.4	17.4	5.7
	F3	732	344	630	548	114.9	85	17.8	17
	F4	870	8.7	692	67.2	118.3	36	17.8	12.2
33	F1	289	75.1	265	54	54.8	0.7	33.2	14.3
	F2	286	60.4	312	58	58.9	0.6	33.4	9.4
	F3	404	227	443	270	80.8	75.9	33	26.7
	F4	381	87.6	416	89.2	80.8	28.3	35.3	24.0
42	F1	531	127.4	567	96.4	60.4	12.7	29.9	7.5
	F2	500	136.0	438	87.6				
	F3	493	284.5	483	315.9				
	F4	578	167.6	604	132.9				
55	F1					59.4	1.8	33.3	8.0
	F2					88.3	76.8	35.9	32.0
	F3					96.8	17.4	35.6	12.8
	F4								
64	F1	122	56.0	191	103.1	57	12.0	19.7	4.9
	F2	173	17.3	242	33.9	53	1.6	18.1	4.3
	F3	240	144.0	451	324.7	85	74.0	20.5	18.2
	F4	279	37.1	449	80.8	82	14.8	20.3	7.3
80	F1	512	30.4	584	40.9	130	31.2	37.9	11.0
	F2	440	15	482	19.3	96	6.7	28.4	7.4
	F3	485	247	557	401.6	120	104.4	31.4	28.6
	F4	616	26.7	624	43.7	150	12.0	50.9	17.3
87	F1	329	10.9	533	16.0				
	F2	382	15.3	482	28.9				
	F3	467	158.8	577	386.6				
	F4	432	8.2	531	53.1				
89	F1	301	27.1	462	37.0				
	F2	329	13.2	440	28.2				
	F3	359	150.8	516	334.9				
	F4	388	73.7	525	71.4				
108	F1	657	30.2	424	30.1				
	F2	239	14.3	434	12.2				
	F3	492	299.1	551	451.8				
	F4	511	7.2	557	44.6				
119	F1	401	16.8	701	25.9				
	F2	400	40.8	606	67.3				
	F3	427	209.2	628	358.6				
	F4	418	71.1	613	66.2				

Block II Experimental Results (µg/L)

		Acetate		formate		Formald.		Glyoxal	
Days		Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
2	F1	356	205	538	312				
	F2	346	100	541	127				
	F3	446	394	671	643				
	F4	436	130	464	192				
8	F1	480	125	610	293	88	49	35	32.5
	F2	399	72	640	222	85.8	9	22	5.3
	F3	441	416	679	622	106.1	93	32.2	27.7
	F4	513	168	952	268	132	102	59.3	43.5
20	F1	336	67	750	385				
	F2	341	22.8	558	286				
	F3	415	266	720	601				
	F4	330	46	99	12				
29	F1	512	92	648	366	86.1	58.8	27.4	26.2
	F2	534	47	671	338	83.6	2.45	28.2	3.9
	F3	512	158	640	256	76.8	27.9	26.3	21.6
	F4	582	208	693	110	73.6	3.15	28.8	10.1
40	F1	634	213			79.8	18.4		
	F2	738	237			63.7	8.6		
	F3	516	240			96.7	19.2		
	F4	582	154			78.3	16.7		
49	F1	447	72.5						
	F2	452	30.5						
	F3	268	44.8						
	F4	282	61						
55	F1	416	72.5	765	214				
	F2	478	69.9	564	118				
	F3	439	44.8	480	42				
	F4	464	55	537	99				
57	F1	435	65.7	590	76	60.8	6.9	12.8	8
	F2	389	31.3	469	61	60.2	8.4	12	3.4
	F3	441	68.4	506	60	64.4	9	15.1	5.75
	F4	483	36.5	511	33.5	90.3	3.05	17.2	4.55
61	F1	482	78.3	558	97.2	65.2	5.4	6.7	5
	F2	417	56.8	464	79	73.7	2.5	5.5	2.2
	F3	602	220	607	146	38.3	4.9	4.1	2.7
	F4	603	67.9	794	220	88.1	2.6	8.1	2.5
73	F1	324	41.3	484	38	31.3	1.8	18.5	6.7
	F2	371	39.6	496	11.6	51.5	3.2	23.9	5.6
	F3	380	26.1	518	26	91.8	2.7	22.5	6.4
	F4	446	46.1	552	28.7	21	2.1	7.6	2.8
78	F1	271	20.6	417	38.3	37.3	2.35	16.7	6.8
	F2	440	36.5	658	33	54.5	2	26.8	2.65
	F3	425	22.9	627	31.7	55.4	4.45	25.4	9.5
	F4	410	15.5	601	31.5	71.5	2.45	23.8	2.3

85	F1	378	34.85	615	42.9	40.1	2.4	17.6	8.45
	F2	323	17.65	692	25	29.5	1.95	14.3	2.1
	F3	414	30.4	583	116	36.6	9.4	18.9	12.5
	F4	443	17.3	583.4	45.35	46.4	2.3	19.9	2.15
97	F1	314	65	440	25.8	62.7	2	14.8	3.45
	F2	352	42	439	9.1	65	1	15.9	0.6
	F3	453	52.8	424	87	92.7	8.9	18.3	5
	F4	410	19.4	429	35	73.1	1.7	16.1	1.05
99	F1	269	33.7	406	52.6				
	F2	405	36.4	590	60.7				
	F3	379	28.9	459	110				
	F4	388	27.8	523	5.8				
104	F1	222	11.3	327	43	33.3	2.5	7.8	4.1
	F2	369	4.3	477	68.7	56	1.9	13.7	2.1
	F3	465	9.4	502	110	73.9	3.6	16.4	8.4
	F4	388	32.3	432	28.8	57.3	2	13.2	1.7
107	F1	351	38.3	452	42.8				
	F2	401	55.6	416	85.6				
	F3	424	84.9	423	131				
	F4	597	76.1	630	49				
113	F1					65	12	15	8.6
	F2					81	7	19	1.5
	F3					85	14	20	9.2
	F4					76	9.9	22	2.5

APPENDIX B:

ANALYSIS OF SIGNIFICANCE TEST BY NORMAL PROBABILITY PLOT

Table B-1: Analysis of significance test by normal probability plot (in terms of acetate removal)

i	effect	P	F(z)	Effect	Expected normal values 'z'
1	C	0.131	0.369	11.58	-1.18
2	D	0.251	0.249	10.02	-0.61
3	E	0.368	0.132	12.48	-0.23
4	CD	0.468	-0.032	-9.43	0.11
5	CE	0.682	0.182	-9.07	0.47
6	DE	0.818	0.318	-8.93	0.91
7	CDE	0.955	0.455	7.42	1.7

Table B-2: Analysis of significance test by normal probability plot (in terms of formate removal)

i	effect	P	F(z)	Effect	Expected normal values 'z'
1	C	0.131	0.369	15.38	-1.18
2	D	0.251	0.249	16.47	-0.61
3	E	0.368	0.132	16.63	-0.23
4	CD	0.468	-0.032	-14.03	0.11
5	CE	0.682	0.182	-13.27	0.47
6	DE	0.818	0.318	-13.98	0.91
7	CDE	0.955	0.455	11.62	1.7

Table B-3: Analysis of significance test by normal probability plot (in terms of formaldehyde removal)

i	effect	P	F(z)	Effect	Expected normal values 'z'
1	C	0.131	0.369	22.3	-1.18
2	D	0.251	0.249	23.3	-0.61
3	E	0.368	0.132	21.1	-0.23
4	CD	0.468	-0.032	-19.5	0.11
5	CE	0.682	0.182	-16.0	0.47
6	DE	0.818	0.318	-17.0	0.91
7	CDE	0.955	0.455	16.0	1.7

Table B-4: Analysis of significance test by normal probability plot (in terms of glyoxal removal)

i	effect	P	F(z)	Effect	Expected normal values 'z'
1	C	0.131	0.369	17.8	-1.18
2	D	0.251	0.249	17.2	-0.61
3	E	0.368	0.132	27.9	-0.23
4	CD	0.468	-0.032	-12.8	0.11
5	CE	0.114	-0.386	-12.0	0.47
6	DE	1.247	0.747	-11.6	0.91
7	CDE	1.367	0.867	1.7	1.7

APPENDIX C:

THE OVERALL REGRESSION TESTS

$Y_{predicted} = X^* \beta$

Parameters β can be obtained by the following equation:

$\beta = (X^T*X)^{-1}*X^T*Y_{measured}$

Table C.1: Components of Matrix X

Run	Cl_2 C	Temp D	Media E	CD	CE	DE	CDE
2 (F4, block I)	-1	-1	1	1	-1	-1	1
4 (F3, block I)	-1	-1	-1	1	1	1	-1
13 (F2, block I)	1	1	1	1	1	1	1
15 (F1, block I)	1	1	-1	1	-1	-1	-1
6 (F3, block II)	1	-1	-1	-1	-1	1	1
8 (F4,block II)	1	-1	1	-1	1	-1	-1
9 (F1, block II)	-1	1	-1	-1	1	-1	1
11 (F2, block II)	-1	1	1	-1	-1	1	-1
Phase III (F1)	0	1	-1	0	0	-1	0
Phase III (F2)	0.99	1	-1	0.99	-0.99	-1	-0.99
Phase III (F3)	0	-1	-1	0	0	1	0
Phase III (F4)	0.99	-1	-1	-0.99	-0.99	1	0.99

Note: Assuming Cl_2=100*chloramine in terms of the disinfection effect (Montgomery, 1985)

Table C.2: Measured BOM percent removal ($Y_{measured}$)

Run	Acetate	Formate	Formaldehyde	Glyoxal
2 (F4, block I)	87.3	86.9	83.7	64.0
4 (F3, block I)	49.4	31.4	13.7	10.7
13 (F2, block I)	90.9	91.5	96.3	75.3
15 (F1, block I)	89.0	90.5	92.2	69.3
6 (F3, block II)	86.9	85.7	87.4	55.1
8 (F4,block II)	91.8	91.4	93.5	80.8
9 (F1, block II)	85.2	87.5	89.5	54.1
11 (F2, block II)	90.4	91.8	93.5	80.7
Phase III (F1)	81.2	83.9	93.0	71.0
Phase III (F2)	82.1	86.8	92.6	96.1
Phase III (F3)	51.2	48.9	57.8	17.1
Phase III (F4)	78.4	82.7	89.3	61.1

Table C.3: Estimated β values in the multiple linear regression models

Acetate	Formate	Formaldehyde	Glyoxal
81.6	80.8	82.0	62.3
5.3	7.6	11.1	11.3
5.8	8.5	11.2	11.3
8.5	9.6	9.8	12.9
-4.9	-7.2	-9.8	-5.6
-4.0	-6.5	-7.9	-8.4
-5.3	-7.3	-8.1	-8.5
3.9	6.0	8.0	0.0

Table C.4: ANOVA table for overall regression significance test in terms of acetate removal

Source	SS	df	MS	$F_{observed}$	$F_{7,4,.05}$
Regression	2.15E+03	7	3.07E+02	5.3	6.09
residual	232	4	5.80E+01		
Total	2.38E+03	11			

Table C.5: ANOVA table for overall regression significance test in terms of formate removal

Source	SS	df	MS	$F_{observed}$	$F_{7,4,.05}$
Regression	3.99E+03	7	5.70E+02	27.9	6.09
residual	81.7	4	2.04E+01		
Total	4.07E+03	11			

Table C.6: ANOVA table for overall regression significance test in terms of formaldehyde removal

Source	SS	df	MS	$F_{observed}$	$F_{7,4,.05}$
Regression	6.11E+03	7	8.73E+02	91.4	6.09
residual	3.82E+01	4	9.55E+00		
Total	6.15E+03	11			

Table C.7: ANOVA table for overall regression significance test in terms of glyoxal removal

Source	SS	df	MS	$F_{observed}$	$F_{7,4,.05}$
Regression	2.15E+03	7	3.07E+02	5.3	6.09
residual	232	4	5.80E+01		
Total	2.38E+03	11			

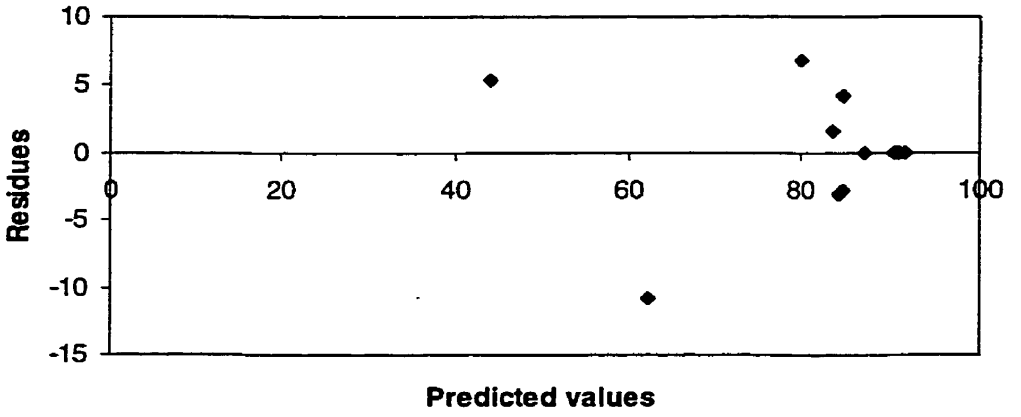

Figure C.1: Residues plot in terms of acetate removal

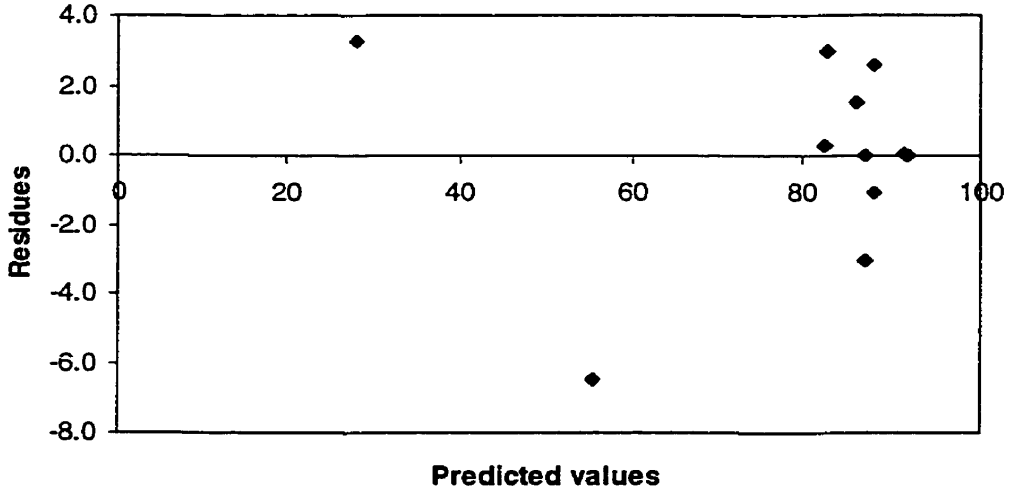

Figure C.2: Residues plot in terms of formate removal

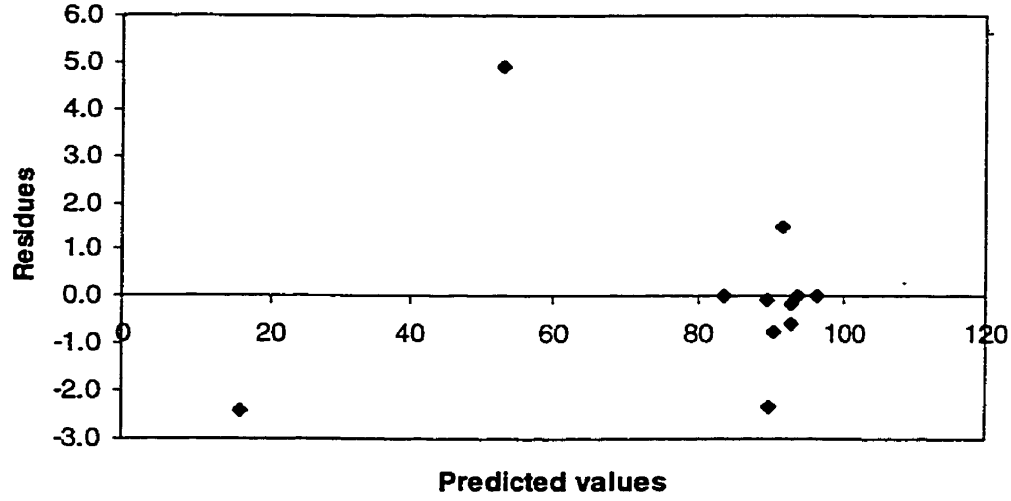

Figure C.3: Residues plot in terms of formaldehyde removal

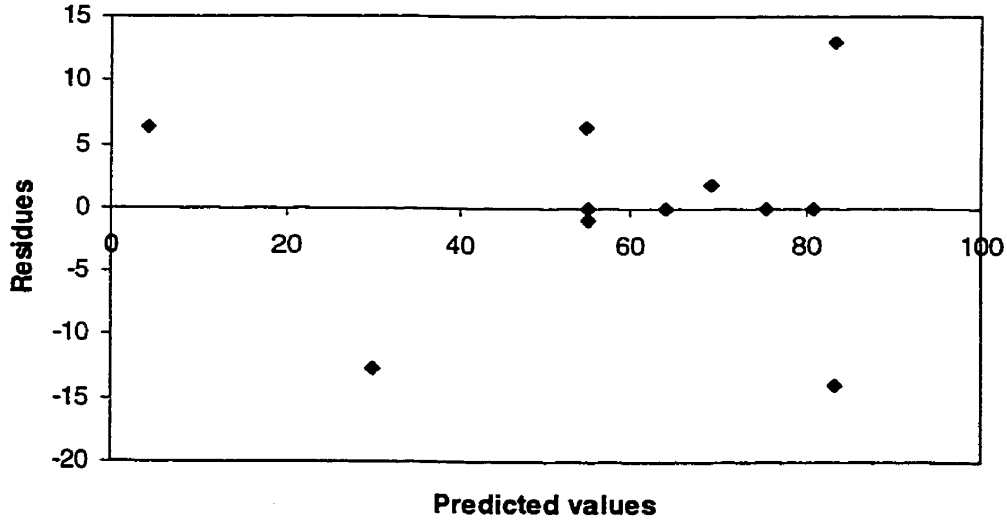

Figure C.4: Residues plot in terms of glyoxal removal

Appendix D:

BOM REMOVAL in Phase III

Day		Acetate (µg/L) Inf.	Eff.	Formate (µg/L) Inf.	Eff.	Formaldehyde (µg/L) Inf.	Eff.	Glyoxal (µg/L) Inf.	Eff.
2	F1	368	237	490	437	97.9	93.7	35.4	36.9
	F2	393	359	447	424	95.3	92.6	34.4	36.1
	F3	375	377	485	464	95.9	92.6	34.4	35.6
	F4	395	379	516	465	89.3	88.7	36.8	33.5
9	F1	210	71.4	262	91.6	71.7	10.75	21.1	30.15
	F2	230	115	277	121	71.6	4.45	27.6	127.95
	F3	204	179	485	421				
	F4	152	122.8	136	116				
15	F1	184	44.5	281	155	83.2	12.3	78.8	26.45
	F2	196	107	258	43.1	80.8	0.595	76.7	19.35
	F3	300	247	395	364	127	114.5	58.7	23.85
	F4	267	82.9	382	214	160	111	55.2	22.75
23	F1	213	22	225	86.0	97.1	35.1	19.1	17.65
	F2	123	30	177	15.1	95.6	14.05	18.2	14.7
	F3	217	158	236	219.8	113	109	13.3	13.2
	F4	165	56	243	193.9	111	105.5	19.9	19.2
31	F1	115.5	66.9	144.9	25.8	73.4	8.1	33.1	27.4
	F2	109.2	22.5	137.1	26.7	71.9	2.8	30.7	9.45
	F3	147.3	109.8	241.2	194.7	101.7	79.1	34.4	41.55
	F4	147.6	34.2	285.3	183.6	103	38.5	33.7	36.3
38	F1	270.3	92.8	305.6	95.0	89.8	9.95	41.8	32
	F2	275.0	148.0	225.9	64.3	78.7	2	40.9	7.4
	F3	350.0	237.5	279.6	227.8	106.3	99.3	35.3	33.65
	F4	362.5	234.4	325.9	279.6	103.8	45.6	37.8	28.9
45	F1	298	79	415	165	126.6	4.15	59.4	42.15
	F2	250	18	356	127	125.7	1.55	58.7	6.05
	F3	248	234	342	277	117.4	73.9	62	44.65
	F4	293	103	488	352	111	31.75	63.1	53.05
52	F1	313	47	366	48	100.9	3.5	56.9	31.55
	F2	309	88	340	108	107.5	2.6	67	1
	F3	230	215	386	382	106.8	70.6	57.2	56.1
	F4	307	68	323	143	113.8	18.35	64.4	41.6
58	F1	315	69	448	74	88.5	3.8	50	18.5
	F2	322	55	375	62	90.5	1.95	45.4	1.7
	F3	357	222	360	298	93.4	103.1	45.6	45.4
	F4	346	82	352	149	96.5	40.8	38.4	21.5
64	F1	214	56	285	170				
	F2	200	39	295	44				
	F3	203	143	286	253				
	F4	264	31	382	72				
70	F1	304	118	317	128	84.5	2.87	29	14.1

	F2	317	152	381	61	73.9	1.48	37.4	1
	F3	445	405	563	521	76.8	63.2	22.4	13.95
	F4	295	178	546	341	76.5	9.1	21.1	1.6
77	F1	369	154	680	236	75.9	3.6	44.8	4.9
	F2	217	80	456	38	71.9	1.8	41	1
	F3	266	184	558	491	68.9	66.2	37	24.4
	F4	242	48.7	635	44	78	6.6	25.1	1
80	F1	447	63	524	83	96.5	1.9	40.9	2
	F2	443	101	537	103	90.1	1.94	38.9	1.2
	F3	463	211	593	518	56.2	48.1	28.7	19.9
	F4	452	53.7	573	138	61.6	3.27	32.2	1.9
84	F1	282	79	600	124	84.5	4.65		
	F2	291	72	333	160	68.5	4.3		
	F3	336	199	448	379	85.5	60.6		
	F4	458	60	502	102	89.8	6.8		
92	F1	805	208.9	609	44.5	54.6	1.7	21.9	2.2
	F2	760	286.3	864	66.3	61.5	1.9	23.5	1
	F3	750	616	800	660	70.8	60.5	29	27.2
	F4	779	469	724	135	80.5	5.2	33.2	4.4
99	F1	435	152	570	123	52.3	1.7	27.8	10.8
	F2	399	209	592	69	44.4	1.55	40.6	1.2
	F3	323	265	498	439	62.1	36.35	39	39.5
	F4	348	144	460	144	66.1	1.6	39.1	1.05
104	F1	500.0	70.2	549.0	78.2	59.7	4.7		
	F2	479.0	138.0	523.0	54.9	33.2	3.85		
	F3	578.0	438.0	692.0	560.0	58.8	33.4		
	F4	549.0	130.0	629.0	77.0	59.4	6.7		
108	F1	250	50	514	91	51.9	5.2	36.6	15.1
	F2	221	23	409	118	35.2	5.9	42.6	1.8
	F3	370	191	577	346	43.5	18.3	31.6	31.8
	F4	385	20	540	138	49.8	6.1	32.9	5.6
113	F1	494	70.1	603	78	46.3	3	28.1	5.4
	F2	573	95.7	617	139	36	3.6	34	0.85
	F3	484	300	527	292	54.2	26.35	33.4	35.1
	F4	353	108	435	144	42.1	4.55	29.2	1
118	F1	752	129	805	310	89.1	5.75	59.7	28.2
	F2	689	243	845	240	61.7	3.7	59.0	14.0
	F3	735	560	749	499	72.5	29.05	56.0	48.7
	F4	782	306	821	268	75.1	6	60.3	19.3
129	F1	400	33.5	550.0	10.7				
	F2	396	18.5	550.0	11.2				
	F3	387	59.45	536.0	124.0				
	F4	410	61	576.0	9.3				
133	F1	399	34	510	12.7	40	2.1	29.1	12.4
	F2	396	53	557	18.35	33.2	1.6	31.6	2.1
	F3	449	59	627	151.65	43.6	13.4	30.6	25.5
	F4	457	38	649	16.55	61.7	2.3	42.8	12.1
141	F1	429	52.2	621	22.35	28.3	1.4		
	F2	345	50	630	38.4	18.8	1.35		
	F3	316	114.5	627	46.8	21.3	1.545		

	F4	320	54	622	21.7	20.4	1.39		
143	F1	300	19	617	15.55	28.5	2.1	27.5	8.45
	F2	326	40	527	17.05	25.8	2.4	23.7	0.9
	F3	309	69.7	598	27.95	24.6	3	23.2	20.8
	F4	233	50.55	643	14.9	22.5	2.4	20.4	14.95
148	F1	344	14	676	56	20.6	0.5	35.4	7.3
	F2	321	12	629	17	18.5	0.47	36.1	0.665
	F3	306	61.8	601	46	17.9	0.76	24.8	21.2
	F4	312	64	611	38	18.1	0.9	28.3	22.75
152	F1	396	14	868	56	33.6	0.55	42.3	6.95
	F2	407	12	693	17	20.3	0.44	34.6	0.47
	F3	353	61.8	653	35.4	24.5	0.625	28.4	20.3
	F4	341	64	652	38	21.9	0.98	26.5	22.8
155	F1	204	47	259	10.6	20.6	0.8	26.2	7.9
	F2	464	56	712	35	23	0.74	44	0.44
	F3	138.6	68	531	66.1	30.4	0.96	32.2	17.9
	F4	140	51	714	150	27.6	0.92	40.7	1.445
161	F1	247	37.25	831	42	51.3	0.68	32.8	0.47
	F2	313	13.1	734	18.4	30.6	1.035	37.6	20.75
	F3	330	59.9	705	220	41.4	1.15		
	F4	325	33.85	783	210				
165	F1	269	45.9	735	103	52.7	0.875	45.1	1.375
	F2	302	31.9	599	52	47.4	0.88	45.5	0.77
	F3	316	34.2	670	125	62.8	7.99	46.6	32.2
	F4	329	41.6	687	168	77.9	1.05	52.2	37.5
169	F1	247	37.25	734	39.65	37.8	0.625	46.4	1.68
	F2	313	13.1	831	22.55	26.3	0.6	52.7	1.275
	F3	330	30.8	705	161	31.6	1.05	51.8	38.4
	F4	325	33.8	789	122.5	31.6	0.565	48.8	38.15
171	F1	330	32.8	735	20.75	76.1	0.585	52	1.3
	F2	293	52	598	22.1	36.2	0.54	38.7	0.595
	F3	370	43.55	670	219.45	52.7	1.72	41.5	30.15
	F4	311	53.25	687	107.5	52.4	0.625	44.5	27.25
182	F1	408	68.8	803	17.3	74.7	0.385	14.1	0.305
	F2	447	5.7	830	5.65	81.2	0.515	16.9	0.21
	F3	428	125.5	810	520.5	73.8	15.8	13.6	11.4
	F4	393	26.25	786	53.85	57.6	0.29	12.3	6.535
190	F1	298	68.4	607	45.5	44.2	1.87	44.4	0.72
	F2	347	9.1	708	3.6	54.9	1.23	44.1	0.68
	F3	375	114	776	542	59.2	17.5	58.0	52.1
	F4	311	19.6	744	10.2	53	24.7	51.7	30.1
199	F1	369	25.4	678	19.25	52.8	0.39	46.8	2.5
	F2	440	7.35	689	10.8	51.4	0.5	50.3	2.1
	F3	320	74.4	651	409	53.4	13.4	48.4	47.9
	F4	390	28.9	673	41.95	62.5	1.715	49.1	33.9
205	F1	169	7	564	11.1	7.9	0.59	29.4	2.745
	F2	171	4.5	483	5.1	8.47	0.465	34.9	4.235
	F3	267	43.35	506	181.5	16.5	3.545	39.9	39
	F4	324	6.95	593	7.25	27.5	0.53	51.4	27.7

213	F1	510	5.25	800	5.05	58.4	0.335	43.3	6
	F2	463	4.55	689	6.25	43.5	0.605	38.5	0.9
	F3	566	122.5	785	271.5	83.1	1.03	44.4	40
	F4	548	71.75	798	8.95	64.8	0.97	47.3	16
215	F1	400	5.5	771	12.8	32.2	0.44	37.9	3.45
	F2	361	3.81	707	7.85	31.6	0.28	37.1	0.76
	F3	506	120	733	158.5	84.4	0.525	42.4	39
	F4	409	55.75	762	14.65	56.9	0.265	43.2	18.45
221	F1	395	5.5	518	25.8	43.7	1.1	29.1	4.98
	F2	344	5.1	485	2.85	18.1	0.85	17.8	0.95
	F3	436	91.35	511	23.2	58.5	1.9	25.3	23.35
	F4	423	15	615	7.95	32.1	1.15	38.7	8.2
224	F1	333	7	483	7.15	11.66	1	19.1	5.195
	F2	310	8.3	458	7.15	10.9	1	16.8	1.05
	F3	390	67	477	14.05	22.2	1	21.8	20.75
	F4	410	19.7	553	12.6	24.1	1	28.4	8.49
232	F1	435	32.5	652	5.85	26.9	1.1	31	7.08
	F2	305	7.5	417	5.7	18.9	1.1	18.5	0.839
	F3	440	74	490	32.1	35.5	1.15	25.2	23.6
	F4	389	55.5	477	11.3	15.4	1.1	22.1	10.6
236	F1	356	9.05	532	17.5	10.7	1.05	53.4	23.25
	F2	236	4	420	6.4	11.7	1	45.9	1.15
	F3	405	78.5	538	20.75	6.6	1	77	79.5
	F4	412	45.05	573	20.25	8.4	1.05	86.5	35.7
240	F1	318	17.4	449	21.9	30.2	0.455	30.3	12.3
	F2	386	5	589	7	19	0.5	24.6	0.88
	F3	319	91.5	457	16.05	36.5	0.455	29.9	29.65
	F4	418	5.55	626	9.2	30.7	0.345	35.2	15.5
244	F1	279	11.05	578	16.2	30	0.23	34.2	8.1
	F2	299	6.4	503	11.8	29.5	0.225	35.6	0.545
	F3	310	85	453	27.5	39.8	0.375	29.1	28.8
	F4	359	7.3	646	9.9	62.6	0.22	50.6	19.55

Appendix E

t-TEST FOR AIR SCOUR, PARTICLE AND COAGULANT EFFECTS

E1: (air scour effect)

Acetate

	Period IA (day 133-158)				Period II (day 158-198)			
	F1	F2	F3	F4	F1	F2	F3	F4
	91.5	86.6	86.9	91.7	84.9	95.8	81.7	89.6
	89.2	81.5	76.2	74.8	82.9	89.4	89.2	87.4
	87.8	85.5	63.8	83.1	84.9	95.8	90.7	89.6
	93.7	87.7	77.4	78.3	90.1	82.3	88.2	82.9
	95.9	96.3	79.8	79.5	83.1	95.1	70.7	93.3
	96.5	97.1	82.5	81.2	77.0	97.4	69.6	93.7
	77.0	87.9	50.9	63.6				
Avg.	90.2	88.9	73.9	78.9	83.8	92.6	81.7	89.4
Std.	6.68	5.70	12.41	8.56	4.21	5.78	9.45	4.02
n	7	7	7	7	6	6	6	6
F/Fobserved	OK	OK	OK	NO				
df	11	11	11	8.8				
T(0.25,13)	2.2	2.2	2.2	2.27				
Tobserved.	2.02	-1.16	-1.25	-2.90				

Formate

	Period IA (day 133-158)				Period II (day 158-198)			
	F1	F2	F3	F4	F1	F2	F3	F4
	97.5	96.7	75.8	97.4	95.0	97.4	68.9	73.2
	92.4	90.7	86.1	92.4	86.0	91.1	81.1	75.5
	96.4	93.9	92.5	96.5	94.6	97.3	77.2	84.5
	97.5	96.8	95.3	97.7	97.2	96.3	67.2	84.4
	91.7	97.3	94.1	93.8	97.8	99.3		93.1
	93.5	97.5	94.6	94.2	92.5	99.5		98.6
	95.9	95.1	89.7	79.0				
Avg.	95.6	95.4	89.7	93.0	93.9	96.8	60.1	84.9
Std.	2.40	2.46	6.94	6.49	4.29	3.05	21.7	9.82
n	7	7	7	7	6	6	6	6
F/Fobserved	NO	OK	OK	OK				
df	7.6	11	9	11				
T(0.25,13)	2.33	2.2	2.2	2.2				
Tobserved.	0.86	-0.91	3.44	1.79				

Formaldehyde

	Period IA (day 133-158)				Period II (day 158-198)			
	F1	F2	F3	F4	F1	F2	F3	F4
	94.2	95.3	69.2	96.1	98.7	96.6	97.2	
	94.8	96.1	82.6	97.7	98.3	98.1	87.3	98.7
	95.1	92.8	92.7	93.2	98.3	97.7	96.7	98.2
	92.6	90.7	87.8	89.3	99.2	98.5	96.7	98.8
	97.6	97.5	95.8	95.0	99.5	99.4	78.6	99.5
	98.4	97.8	97.4	95.5	98.4	98.5	70.4	97.6
	96.1	96.8	96.8	96.7				
Avg.	95.5	95.3	88.9	94.8	98.7	98.1	87.8	98.6
Std.	6.61	4.14	14.50	3.52	0.50	0.92	11.27	0.70
n	7	7	7	7	6	6	6	5
F/Fobserved	NO	NO	OK	NO				
df	6.1	6.7	11	6.7				
T(0.25,13)	2.43	2.39	2.2	2.39				
Tobserved.	-1.28	-1.77	0.15	-2.75				

Glyoxal

	Period IA (day 133-158)				Period II (day 158-198)			
	F1	F2	F3	F4	F1	F2	F3	F4
	57.2	93.6	16.5	71.8	96.4	98.6	44.8	
	67.2	97.0	4.7	72.4	97.0	98.3	30.9	28.2
	69.3	96.2	10.3	26.7	96.4	97.6	25.9	21.8
	79.4	98.2	14.5	19.6	97.5	98.5	27.3	38.8
	83.6	98.6	28.5	14.0	97.8	98.8	16.2	46.9
	70.0	99.0	44.4	26.3	95.8	97.8	9.1	53.4
Avg.	65.8	96.9	18.8	44.5	96.8	98.2	25.7	37.8
Std.	12.65	2.03	12.54	24.99	0.77	0.47	12.33	12.99
n	6	6	6	6	6	6	6	5
F/Fobserved	NO	NO	OK	OK				
df	5.0	5.5	10	10				
T(0.25,13)	2.57	2.51	2.23	2.23				
Tobserved.	-6.00	-1.61	-0.97	0.54				

E2: Particle/coagulant effect

Acetate

	Period IB (day 199-231)				Period III (day 232-244)			
	F1	F2	F3	F4	F1	F2	F3	F4
	93.1	98.3	76.8	92.6	92.5	97.5	83.2	85.7
	95.9	97.4	83.8	97.9	97.5	98.3	80.6	89.1
	99.0	99.0	78.4	86.9	94.5	98.7	71.3	98.7
	98.6	98.9	76.3	86.4	96.0	97.9	72.6	98.0
	98.6	98.5	79.0	96.5				
	97.9	97.3	82.8	95.2				
	97.2	98.2	79.5	92.6	95.1	98.1	76.9	92.9
	2.29	0.75	3.12	4.91	2.11	0.51	5.86	6.46
	6	6	6	6	4	4	4	4
F/Fobserved	OK	NO	OK	NO				
df	8	8.0	8	5.3				
$t_{(0.25,13)}$	2.31	2.45	2.31	2.53				
$t_{observed}$	1.42	0.37	0.92	-0.08				

Formate

	Period III (day 232-244)				Period IB (day 199-231)			
	F1	F2	F3	F4	F1	F2	F3	F4
	99.1	98.6	93.4	97.6	97.2	98.4	37.2	93.8
	96.7	98.5	96.1	96.5	98.0	98.9	64.1	98.8
	95.1	98.8	96.5	98.5	99.4	99.1	65.4	98.9
	97.2	97.7	93.9	98.5	98.3	98.9	78.4	98.1
					95.0	99.4	95.5	98.7
					98.5	98.4	97.1	97.7
	97.0	98.4	95.0	97.8	97.7	98.9	72.9	97.7
	1.64	0.51	1.54	0.96	1.51	0.38	22.49	1.96
	4	4	4	4	6	6	6	6
F/Fobserved	OK	NO	NO	NO				
df	8	5.2	4.1	7.6				
$t_{(0.25,13)}$	2.31	2.55	2.57	2.45				
$t_{observed}$	-0.70	-1.58	2.39	0.13				

Formaldehyde

	Period III (day 232-244)				Period IB (day 199-231)			
	F1	F2	F3	F4	F1	F2	F3	F4
	95.9	94.2	96.8	92.9	99.3	99.0	74.9	97.3
	90.2	91.5	84.8	87.5	92.5	94.5	78.5	98.1
	98.5	97.4	98.8	98.9	99.4	98.6	97.8	98.5
	99.2	99.2	99.1	99.6	98.6	99.1	99.4	99.5
					97.5	95.3	96.8	96.4
					91.4	90.8	95.5	95.9
	96.0	95.6	94.9	94.7	96.5	96.2	90.5	97.6
	4.10	3.44	6.75	5.69	3.56	3.31	10.80	1.37
	4	4	4	4	6	6	6	6
F/Fobserved	NO	OK	NO	NO				
df	5.9	8	8.0	3.2				
$t_{(0.25,13)}$	2.45	2.31	2.31	3.10				
$t_{observed}$	-0.20	-0.31	0.79	-0.99				

Glyoxal

	Period III (day 232-244)				Period IB (day 199-231)			
	F1	F2	F3	F4	F1	F2	F3	F4
	77.2	95.5	6.3	52.0	94.7	95.9	1.0	31.1
	56.5	97.5	-3.2	58.7	90.7	87.9	2.3	46.1
	59.4	96.4	0.8	56.0	86.1	97.7	9.9	66.2
	76.3	98.5	1.0	61.4	90.9	98.0	8.0	57.3
					82.9	94.7	7.7	78.8
					72.8	93.8	4.8	70.1
	67.3	97.0	1.2	57.0	86.3	94.6	5.6	58.3
	10.93	1.30	3.93	3.99	7.80	3.70	3.51	17.40
	4	4	4	4	6	6	6	6
F/Fobserved	NO	OK	OK	NO				
df	5.0	8	8	8				
$t_{(0.25,13)}$	2.57	2.31	2.31	2.31				
$t_{observed}$	-3.01	1.19	-1.85	-0.17				

Appendix F:

BIOMASS LOSS ESTIMATE DURING BACKWASH USING HPC DATA

Biomass loss during backwash can be estimated by the HPC in the backwash discharge:

The following assumptions were made to estimate the percent biomass loss caused by backwash:

Detached bacteria (or bacteria column) size in diameter: 1 – 1.5 μm; Bacteria density X_f = 3.5 mg/cm^3; Bacteria formula: $C_{55}H_{77}O_{22}N_{11}P$ (Metcalf and Eddy, 1991); The average biomass level in biofilters are 20 nmol P/cm^3 media; HPC level in backwash discharge: 1E6 - 4 E6).

Detached biomass in backwash dischage (as nmol P):

(1 ~ 4)E6 #/ml*10 L* 10E3 ml/L*3.14/6[(1~1.5)E-6m]^3*10E6 cm^3/m^3*35 mg/cm^3* 1E6ng/mg*1274ng/nmol = (8.5 ~ 115)E2 nmolP/filter backwash

Average biomass in biofilters (as nmol P):

20 nmol P/cm^3 * 3.14/4* (5 cm)^2 *70 cm = 2.8 E4 nmol P /filter

Therefore, the detached biomass is about 3% ~ 41% of total biomass. It is needed to note that this is very approximate estimation due to the values of so many parameters are assumed.

Appendix G:

BIOMASS DETACHMENT DURING A FILTER RUN VS. DURING BACKWASH

Based on the filter operating conditions in the present study, the ratio of product water to the entire filtered water in a filter run is estimated as 98.6%. The other 1.4% was consumed during backwash.

Biomass detachment during backwash = 1.4% * (1 ~ 4 E6) #/ml = (1.4 ~ 5.6) E4 #/ml

Biomass detachment during a filter run = 98.6% *($4.7E4_{Eff.} - 1.9E4_{Inf}$) = 2.8 E4 #/ml

Therefore, the biomass detached during backwash could be at the similar level with that detached by the filter effluent flush-out during a filter run.

Filter influent/effluent HPC data (four filters in blocks I and II):

Inf. (E4)	2.5	1.15	1.66	1.42	0.3	7.6	6.1	1.4	3.7
Eff.(E4)	1.5	3.9	1.5	1.3	1.8	9.5	9.8	2.6	6.1
Inf. (E4)	0.81	1.39	0.9	0.38	1.11	1.7	1.2	5.6	5.5
Eff.(E4)	1.76	3.4	3.9	2.1	11.2	4.7	3.7	9.5	10.3
Inf. (E4)	1.81	0.4	0.44	0.2	1.28	1.3	0.4	1.81	1
Eff.(E4)	2.3	1.7	1	1.1	6	3.3	2.4	15.3	6

Appendix H:

EFFECTS OF BIOLOGICAL PARTICLES (BACTERIA) ON FILTER EFFLUENT TURBIDITY

The contribution of the bacteria in the filter effluent to the turbidity can be estimated according to the HPCs in the filter effluent.

Particle concentration was assumed in the range of 0.1 – 0.3 mg/L (~ 0.1 –0.3 NTU).

The biological particle (bacteria) concentration by weight was estimated as follows (assume: bacteria size: 1 –2 μm; Bacteria density: 3.5 mg/cm^3; Filter effluent HPC: 4.7 *E4):

Bacteria (mg/L) = 4.7E4 #/ml * 1E3 ml/L * 3.14/6 * [(1~2)E-6]3 *1e3 L/m3 835 mg/L * 1E3 cm3/L = (1.5 ~ 5.1)E-4

Therefore, the concentration of non-biological particles is 196-200 times that of biological particles (bacteria).

Appendix I:

BRP TEST RESULTS

BRP vs. Phospholipid Biomass (F1, day 63 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	9.7789	2.3727	6.79	6.26	5.92	47.8	0.07657	0.06285
9	9.9565	2.3581	6.79	6.56	6.41	14.2	0.03239	0.02676
24	10.4468	2.3615	6.79	6.65	6.59	6.1	0.01853	0.01323
34	11.0248	2.3417	6.79	6.72	6.67	2.7	0.00863	0.00739
49	13.9915	2.3386	6.79	6.77	6.74	6.8	0.00256	0.00320
64	13.3394	2.3469	6.79	6.74	6.78	0	0.00873	0.00088

Note: W1= wet weight (dish +media); W2 = wet weight (dish); wet weight of anthracite =1.09 g/cm^3; wet weight of sand =1.92 g/cm^3

BRP vs. Phospholipid Biomass (F2, day 78 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr)
4	12.7515	2.5643	7.73	7.36	7.24	44.8	0.03886	0.02573
9	11.0844	2.52	7.73	7.62	7.5	26.7	0.01374	0.01437
14	12.4011	2.4999	7.73	7.66	7.56	21.9	0.00756	0.00919
24	14.6326	2.5	7.73	7.66	7.6	16.8	0.00617	0.00573
34	13.496	2.5149	7.73	7.58	7.5	12.9	0.01462	0.01121
64	18.5417	2.4398	7.73	7.64	7.62	5.5	0.01073	0.00656

Note: W1= wet weight (dish +media); W2 = wet weight (dish); wet weight of anthracite =1.09 g/cm^3; wet weight of sand =1.92 g/cm^3

BRP vs. Phospholipid Biomass (F3, day 63 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	10.0956	2.3745	9.24	9.1	8.94	9.3	0.01940	0.02079
9	11.12	2.473	9.24	9.12	9	4.6	0.01485	0.01485
24	12.5035	2.4332	9.24	9.23	9.14	6.7	0.00106	0.00531
34	12.5477	2.3771	9.24	9	8.99	6.9	0.02525	0.01315
49	15.7	2.3218	9.24	9.2	9.12	4.3	0.00446	0.00668
64	13.7874	2.323	9.24	9.22	9.2	3.8	0.00335	0.00335

BRP vs. Phospholipid Biomass (F4, day 78 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	11.626	2.4933	10.18	9.8	9.53	44.8	0.04452	0.03808
9	12.8864	2.4697	10.18	9.82	9.58	35.7	0.03698	0.03082
14	11.747	2.4644	10.18	9.93	9.75	24.3	0.02882	0.02478
24	13.0189	2.4808	10.18	9.98	9.82	16.2	0.02031	0.01828
34	15.3463	2.746	10.18	10.06	9.91	12.7	0.01019	0.01146
64	17.3365	2.5188	10.18	10.16	10.08	2.7	0.00259	0.00648

BRP vs. Phospholipid Biomass (F1, day 85 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	13.9637	2.4723	7.02	6.44	6.28	32.2	0.05401	0.03445
9	14.1681	2.4574	7.02	6.85	6.69	17.2	0.01553	0.01508
24	13.7615	2.5441	7.02	6.93	6.79	8.9	0.00858	0.01097
34	15.0065	2.5072	7.02	6.99	6.89	7.9	0.00257	0.00556
49	22.0566	2.4483	7.02	6.99	6.96	0	0.00228	0.00228
64	24.108	2.4622	7.02	7.02	7	0	0.00000	0.00089

BRP vs. Phospholipid Biomass (F2, day 87 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	14.0318	2.5071	6.04	5.53	5.3	35.1	0.0474	0.0344
9	15.5569	2.4831	6.04	5.77	5.65	21.4	0.0221	0.0160
14	16.3676	2.4828	6.04	5.87	5.73	11.1	0.0131	0.0119
24	16.1621	2.4772	6.04	5.91	5.78	12.5	0.0102	0.0102
34	15.0604	2.4614	6.04	5.99	5.88	10.2	0.0042	0.0068
64	22.7819	2.4394	6.04	5.98	5.85	0	0.0057	0.0090

BRP vs. Phospholipid Biomass (F3, day 85 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	16.1635	2.5042	9.13	8.98	8.85	14.2	0.01175	0.01097
9	18.2015	2.5789	9.08	8.92	8.78	8.6	0.01096	0.01027
24	17.94	2.417	9.06	8.93	8.79	7	0.00896	0.00931
34	17.7864	2.4665	9.04	8.98	8.78	4.2	0.00419	0.00908
49	24.659	2.4104	9.04	8.98	8.84	6.6	0.00402	0.00670
64	22.5704	2.4308	9.09	9.03	8.98	2.9	0.00572	0.00524

BRP vs. Phospholipid Biomass (F4, day 87 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	13.6025	2.492	9.71	9.4	8.96	33.8	0.02985	0.03611
9	14.8801	2.4919	9.71	9.4	9.06	30.1	0.02678	0.02807
14	16.5946	2.5207	9.72	9.5	9.18	24.6	0.01673	0.02053
24	19.5079	2.4757	9.71	9.55	9.38	24.9	0.01005	0.01037
34	18.007	2.4806	9.72	9.63	9.53	11.7	0.00620	0.00655
64	20.044	2.4275	9.74	9.72	9.65	3.6	0.00218	0.00490

BRP vs. Phospholipid Biomass (F1, day 286 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	89.68	61.87	5.03	4.18	3.7	24.7	0.03270	0.02559
9	108.28	82.61	5.03	4.39	4.12	15.2	0.02668	0.01897
24	98.34	62.64	5.03	4.7	4.55	11.7	0.00989	0.00719
34	96.85	65.12	5.03	4.82	4.81	7.2	0.00708	0.00371
49	133.36	75.27	5.03	5.01	5	1.1	0.00051	0.00038
64	143.34	91.19	5.03	4.99	4.96	1.9	0.00147	0.00129

BRP vs. Phospholipid Biomass (F2, day 288 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	103.64	69.96	7.92	6.82	6.15	32.5	0.03495	0.02812
9	115.45	80.29	7.92	7.01	6.43	25.1	0.02769	0.02267
14	111.83	76.77	7.92	7.09	6.89	11.7	0.02533	0.01572
24	115.47	76.86	7.92	7.25	7.04	11.7	0.01857	0.01219
34	109.47	72.21	7.92	7.49	7.24	9.5	0.01235	0.00976
64	142.13	85.59	7.92	7.78	7.74	4	0.00265	0.00170

BRP vs. Phospholipid Biomass (F3, day 286 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	110.14	72.91	8.37	7.58	7.29	12.9	0.02270	0.01552
9	103.86	71.58	8.37	7.91	7.78	10.8	0.01525	0.00978
24	105.83	67.55	8.37	7.98	7.86	8.3	0.01090	0.00713
34	125.27	75.74	8.37	8.14	8.08	8.2	0.00497	0.00313
49	155.69	105.07	8.37	8.16	8.1	6.7	0.00618	0.00397
64	197.64	134.16	8.37	8.26	8.24	3.3	0.00333	0.00197

BRP vs. Phospholipid Biomass (F4, day 288 since start-up in phase III)

Depth cm	W1 g	W2 g	DO(0hr) mg/L	DO(1hr) mg/L	DO(2hr) mg/L	Biomass nmolP/cm^3 media	BRP(1hr) mgDO/L/(cm^3 media)/h	BRP(2hr) mgDO/L/(cm^3 media)/h
4	109.78	60.41	10.18	8.29	7.89	30.7	0.04096	0.02482
9	105.39	63.19	10.18	9.11	8.59	23.6	0.02713	0.02016
14	107.4	64.92	10.18	9.38	9.1	19.4	0.02015	0.01360
24	107.86	64.4	10.18	9.83	9.6	16.5	0.00862	0.00714
34	114.1	68.99	10.18	9.82	9.6	11.4	0.00854	0.00688
64	154.48	89.86	10.18	10.16	9.99	3.2	0.00059	0.00282

Appendix J:

EXPERIMENTAL RESULTS OF BIO-KINETIC PARMETER ESTIMATION AND PARAMETER ESTIMATION EXAMPLES

k and Ks estimation (F2, day 205 in phase III)

BOM Conc. Levels		Low	middle low	Nomal	middle high	high
Weight of media (g)		21.85	22.2721	23.5319	24.3584	27.2559
Volume (cm^3)		20.421	20.815	21.992	22.765	25.473
Biomass(g)	45.6nmol/cm^3media					
BOM conc. @ o hr	Acetate	115	162	362	619	960
	Formate	46.8	140	377	874	1187
	Formaldehyde	16.2	36.3	78.5	157.7	200
	glyoxal	11.3	19.5	38.3	42.8	66
BOM conc. @ 1 hr	Acetate	90	30	45	46.7	118.5
	Formate	24.9	12.9	26.4	24.9	23.7
	Formaldehyde	0.41	0.35	0.44	0.38	0.43
	glyoxal	1.35	1.05	1.29	7.8	14.1
dS/dt in bulk liquid (0-1 hr)	Acetate	25.0	132.0	317.0	572.3	841.5
	Formate	21.9	127.1	350.6	849.1	1163.3
	Formaldehyde	15.8	36.0	78.1	157.3	199.6
	glyoxal	10.0	18.5	37.0	35.0	51.9
ds/dt*Vbottle/Weight of bacteria						
	Acetate	0.001865	0.009664	0.021967	0.038312	0.050344
	Formate	0.001634	0.009306	0.024295	0.056842	0.069596
	Formaldehyde	0.001178	0.002632	0.005409	0.010532	0.01194
	glyoxal	0.0007425	0.001351	0.002565	0.002343	0.003105
S (0-1 hr)	Acetate	102.5	96.0	203.5	332.9	539.3
	Formate	35.85	76.5	201.7	449.5	605.4
	Formaldehyde	8.305	18.3	39.5	79.0	100.2
	glyoxal	6.325	10.3	19.8	25.3	40.1

k and Ks estimation (F4, day 205 in phase III)

BOM Conc. Levels		Low	middle low	Nomal	middle high	high
Weight of media (g)		20.7805	18.6049	19.8986	20.6406	21.7065
Volume (cm^3)		19.421	17.388	18.597	19.290	20.286
Biomass(g)	45nmol/cm^3media					
DO changes (optional)						
BOM conc. @ c hr	Acetate	193.4	276.5	474.6	860.4	1047
	Formate	180	229.6	490.8	1063	1434
	Formaldehyde	17.2	36.5	88.9	176.9	240
	glyoxal	12.5	21	42.1	87.3	110
BOM conc. @ 1 hr	Acetate	168.8	202	324	592	836
	Formate	76	146	354.8	759	992
	Formaldehyde	0.39	0.95	31.3	114.2	164.1
	glyoxal	10	16.4	35.2	73	90
dS/dt in bulk liquid (0-1 hr)	Acetate	24.6	74.5	150.6	268.4	211.0
	Formate	104.0	83.6	136.0	304.0	442.0
	Formaldehyde	16.8	35.6	57.6	62.7	75.9
	glyoxal	2.5	4.6	6.9	14.3	20.0
ds/dt*Vbottle/Weight of bacteria						
		0.00196	0.00662	0.01251	0.02149	0.01606
		0.00827	0.00742	0.01129	0.02434	0.03365
		0.00134	0.00316	0.00478	0.00502	0.00578
		0.00020	0.00041	0.00057	0.00114	0.00152
S (0-1 hr)	Acetate	181.1	239.3	399.3	726.2	941.5
	Formate	128	187.8	422.8	911.0	1213.0
	Formaldehyde	8.795	18.7	60.1	145.6	202.1
	glyoxal	11.25	18.7	38.7	80.2	100.0

k and Ks estimation (F1, day 205 in phase III)

Conc. Levels		Low	middle low	Nomal	middle high	high
Weight of media (g)		25.014	21.9919	23.0735	26.1186	23.363
Volume (cm^3)		23.378	20.553	21.564	24.410	21.835
Biomass(g)	25.3nmol/cm^3media					
DO changes (optional)						
BOM conc. @ o hr	Acetate	150	240	382	600	879
	Formate	132	232	461	946	1372
	Formaldehyde	15.1	25.8	55.1	115.7	150.7
	glyoxal	13.1	18.2	32.4	62.4	90.8
BOM conc. @ 1 hr	Acetate	5	30.1	58.7	138	192.3
	Formate	10.1	11.5	14.2	31.5	284
	Formaldehyde	0.31	0.45	1.4	1.38	18.2
	glyoxal	4.2	8.84	19.2	37.7	60.6
dS/dt in bulk liquid (0-1 hr)	Acetate	145.0	209.9	323.3	462.0	686.7
	Formate	121.9	220.5	446.8	914.5	1088.0
	Formaldehyde	14.8	25.4	53.7	114.3	132.5
	glyoxal	8.9	9.4	13.2	24.7	30.2
ds/dt*Vbottle/Weight of bacteria						
		0.0170367	0.02805	0.041180	0.05198	0.0863
		0.01432	0.02946	0.056911	0.1029	0.1368
		0.001737	0.003387	0.00684	0.01286	0.0166
		0.00104	0.001250	0.001681	0.002779	0.00379
S (0-1 hr)	**Acetate**	77.5	135.1	220.4	369.0	535.7
	Formate	71.05	121.8	237.6	488.8	828.0
	Formaldehyde	7.705	13.1	28.3	58.5	84.5
	glyoxal	8.65	13.5	25.8	50.1	75.7

k and Ks estimation (F3, day 205 in phase III)

Conc. Levels		Low	middle low	Nomal	middle high	high
Weight of media (g)		24.6192	21.36	18.6774	21.3989	22.0601
Volume (cm^3)		23.009	19.963	17.456	19.999	20.617
Biomass(g)	20.9nmol/cm^3media					
DO changes (optional)						
BOM conc. @ o hr	Acetate	175	288	517	770	1100
	Formate	169	304	587	1088	1595
	Formaldehyde	17.6	34	63.8	129.6	168.2
	glyoxal	14.6	25.4	40.6	72.2	105.1
BOM conc. @ 1 hr	Acetate	166	260	440	640	900
	Formate	147	249	506	962	1423
	Formaldehyde	14.1	26.4	55.6	111.3	152
	glyoxal	14.3	24.6	39.7	71	103.6
dS/dt in bulk liquid (0-1 hr)	Acetate	9.0	28.0	77.0	130.0	200.0
	Formate	22.0	55.0	81.0	126.0	172.0
	Formaldehyde	3.5	7.6	8.2	18.3	16.2
	glyoxal	0.3	0.8	0.9	1.2	1.5
ds/dt*Vbottle/Weight of bacteria						
	Acetate	0.00130	0.00466	0.01467	0.02161	0.03226
	Formate	0.00318	0.00916	0.01543	0.02095	0.02774
	Formaldehyde	0.00051	0.00127	0.00156	0.00304	0.00261
	glyoxal	0.00004	0.00013	0.00017	0.00020	0.00024
S (0-1 hr)	Acetate	170.5	274.0	478.5	705.0	1000.0
	Formate	158	276.5	546.5	1025.0	1509.0
	Formaldehyde	15.85	30.2	59.7	120.5	160.1
	glyoxal	14.45	25.0	40.2	71.6	104.4

k and Ks estimation (F1, day 280 in phase III)

Conc. Levels		1(low)	2	3	4	5	6	7(high)
Weight of media (g)		17.51	19.13	19.93	20.13	16.41	17.29	14.85
Volume (cm^3)		16.364	17.879	18.626	18.813	15.336	16.159	13.879
Biomass conc.	26.1nmol/cm^3media							
BOM conc. @ o hr	Acetate	103	206	412	824	1236	2472	4944
	Formate	142	284	568	1136	1704	3408	6816
	Formaldehyde	15.025	30.05	60.1	120.2	180.3	360.6	721.2
	glyoxal	8.025	16.05	32.1	64.2	96.3	192.6	385.2
BOM conc. @ 1 hr	Acetate	81.5	88.3	122	144	440	766.5	3400
	Formate	14.7	16.5	12.4	210	772	1359	5216
	Formaldehyde	0.47	2.66	1.03	2.03	94.2	116.7	547.6
	glyoxal	5.42	12	20.9	43.5	73.8	118.5	341
dS/dt in bulk liquid (0-1 hr)	Acetate	21.5	117.7	290.0	680.0	796.0	1705.5	1544.0
	Formate	127.3	267.5	555.6	926.0	932.0	2049.0	1600.0
	Formaldehyde	14.6	27.4	59.1	118.2	86.1	243.9	173.6
	glyoxal	2.6	4.1	11.2	20.7	22.5	74.1	44.2
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.003498	0.017528	0.041455	0.096238	0.138193	0.281021	0.296212
	Formate	0.020712	0.039837	0.079421	0.131054	0.161804	0.337621	0.306956
	Formaldehyde	0.002368	0.004079	0.008444	0.016724	0.014948	0.040188	0.033305
	glyoxal	0.000424	0.000603	0.001601	0.00293	0.003906	0.01221	0.00848
S (0-1 hr)	Acetate	92.3	147.2	267.0	484.0	838.0	1619.3	4172.0
	Formate	78.4	150.3	290.2	673.0	1238.0	2383.5	6016.0
	Formaldehyde	7.7	16.4	30.6	61.1	137.3	238.7	634.4
	glyoxal	6.7	14.0	26.5	53.9	85.1	155.6	363.1

k and Ks estimation (F3, day 280 in phase III)

Conc. Levels		1	2	3	4	5	6	7
Weight of media (g)		13.84	17.65	13.23	16.3	16.04	13.91	18.59
Volume (cm^3)		12.935	16.495	12.364	15.234	14.991	13.000	17.374
Biomass conc.	36.7nmol/cm^3media							
BOM conc. @ o hr	Acetate	104.5	209	418	836	1254	2508	5016
	Formate	142	284	568	1136	1704	3408	6816
	Formaldehyde	16.3	32.6	65.2	130.4	195.6	391.2	782.4
	glyoxal	8.775	17.55	35.1	70.2	105.3	210.6	421.2
BOM conc. @ 1 hr	Acetate	99	188	267	496	904	2010	4568
	Formate	79.1	147.5	265	780.5	1298	2643	6189
	Formaldehyde	6.45	12.8	31.2	88.2	153.8	286.8	680
	glyoxal	8.42	17	26.9	59.9	95	192	403
dS/dt in bulk liquid (0-1 hr)	Acetate	5.5	21.0	151.0	340.0	350.0	498.0	448.0
	Formate	62.9	136.5	303.0	355.5	406.0	765.0	627.0
	Formaldehyde	9.9	19.8	34.0	42.2	41.8	104.4	102.4
	glyoxal	0.4	0.6	8.2	10.3	10.3	18.6	18.2

ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.00081	0.00241	0.02312	0.04226	0.04421	0.07254	0.04883
	Formate	0.00919	0.01564	0.04633	0.04412	0.05120	0.11125	0.06822
	Formaldehyde	0.00144	0.00227	0.00521	0.00525	0.00528	0.01521	0.01116
	glyoxal	0.00005	0.00006	0.00126	0.00128	0.00130	0.00271	0.00198

S (0-1 hr)								
	Acetate	101.8	198.5	342.5	666.0	1079.0	2259.0	4792.0
	Formate	110.6	215.8	416.5	958.3	1501.0	3025.5	6502.5
	Formaldehyde	11.4	22.7	48.2	109.3	174.7	339.0	731.2
	glyoxal	8.6	17.3	31.0	65.1	100.2	201.3	412.1

k and Ks estimation (F2, day 280 in phase III)

Conc. Levels		1	2	3	4	5	6	7
Weight of media (g)		16.02	17.77	17.29	12.36	14.89	11.09	19.67
Volume (cm^3)		14.972	16.607	16.159	11.551	13.916	10.364	18.383
Biomass conc.	24.4nmol/cm^3media							
BOM conc. @ o hr	Acetate	98	196	392	784	1176	2352	6272
	Formate	117.5	235	470	940	1410	2820	7520
	Formaldehyde	6.125	12.25	24.5	49	73.5	147	392
	glyoxal	5.1	10.2	20.4	40.8	61.2	122.4	326.4
BOM conc. @ 1 hr	Acetate	65	74	109	131	244	1360	4470
	Formate	6.1	3.7	18.9	262.5	350	2092	5469
	Formaldehyde	1.49	1.12	1.16	11.6	8.4	105.8	331
	glyoxal	4.21	4.03	7.93	29.7	33.4	111.6	307.2
dS/dt in bulk liquid (0-1 hr)	Acetate	33.0	122.0	283.0	653.0	932.0	992.0	1802.0
	Formate	111.4	231.3	451.1	677.5	1060.0	728.0	2051.0
	Formaldehyde	4.6	11.1	23.3	37.4	65.1	41.2	61.0
	glyoxal	0.9	6.2	12.5	11.1	27.8	10.8	19.2
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.004453	0.01484	0.03538	0.114198	0.135296	0.19335	0.198023
	Formate	0.015031	0.028135	0.056395	0.118483	0.153878	0.141894	0.225385
	Formaldehyde	0.000625	0.001354	0.002918	0.006541	0.00945	0.00803	0.006703
	glyoxal	0.00012	0.000751	0.001559	0.001941	0.004036	0.002105	0.00211
S (0-1 hr)	Acetate	81.5	135.0	250.5	457.5	710.0	1856.0	5371.0
	Formate	61.8	119.4	244.5	601.3	880.0	2456.0	6494.5
	Formaldehyde	3.8	6.7	12.8	30.3	41.0	126.4	361.5
	glyoxal	4.7	7.1	14.2	35.3	47.3	117.0	316.8

k and Ks estimation (F4, day 280 in phase III)

Conc. Levels		1	2	3	4	5	6	7
Weight of media (g)		13.84	17.65	13.23	16.3	16.04	14.74	18.59
Volume (cm^3)		12.935	16.495	12.364	15.234	14.991	13.776	17.374
Biomass conc.	29.9nmol/cm^3media							
BOM conc. @ o hr	Acetate	90.5	181	362	724	1086	2172	4344
	Formate	108.75	217.5	435	870	1305	2610	5220
	Formaldehyde	6.125	12.25	24.5	49	73.5	147	
	glyoxal	5.1	10.2	20.4	40.8	61.2	122.4	
BOM conc. @ 1 hr	Acetate	79	167.5	123	258.5	374	728	2550
	Formate	10.7	130	117	175	199	672	3894
	Formaldehyde	1.38	0.97	0.92	4.14	5.6	60.1	
	glyoxal	4.85	12.2	12.9	28.56	84	107.48	
dS/dt in bulk liquid (0-1 hr)	Acetate	11.5	13.5	239.0	465.5	712.0	1444.0	1794.0
	Formate	98.1	87.5	318.0	695.0	1106.0	1938.0	1326.0
	Formaldehyde	4.7	11.3	23.6	44.9	67.9	86.9	0.0
	glyoxal	0.3	-2.0	7.5	12.2	-22.8	14.9	0.0
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.002066	0.001902	0.044925	0.071021	0.110389	0.243625	0.239991
	Formate	0.017618	0.012329	0.059775	0.106035	0.171476	0.32697	0.177385
	Formaldehyde	0.000853	0.001589	0.004432	0.006844	0.010527	0.014661	
	glyoxal	4.49E-05	-0.000282	0.00141	0.001867	-0.003535	0.002517	
S (0-1 hr)	Acetate	84.8	174.3	242.5	491.3	730.0	1450.0	3447.0
	Formate	59.7	173.8	276.0	522.5	752.0	1641.0	4557.0
	Formaldehyde	3.8	6.6	12.7	26.6	39.6	103.6	0.0
	glyoxal	5.0	11.2	16.7	34.7	72.6	114.9	0.0

k and Ks estimation (F1, day 288 in phase III)

Conc. Levels		1	2	3	4	5	6	7
Weight of media (g)		15.41	15.23	18.46	16.43	17.18	19.05	25.31
Volume (cm^3)		14.402	14.234	17.252	15.355	16.056	17.804	23.654
Biomass conc.	20.1nmol/cm^3media							
BOM conc. @ o hr	Acetate	540	1080	2160	3240	4320	5400	8100
	Formate	585	1170	2340	3510	4680	5850	8775
	Formaldehyde							
	glyoxal							
BOM conc. @ 1 hr	Acetate	74	227.4	1260	2040	2920	3590	5745
	Formate	192.3	602	1636	2550	3568	4500	7275
	Formaldehyde							
	glyoxal							
dS/dt in bulk liquid (0-1 hr)	Acetate	466.0	852.6	900.0	1200.0	1400.0	1810.0	2355.0
	Formate	392.7	568.0	704.0	960.0	1112.0	1350.0	1500.0
	Formaldehyde							
	glyoxal							
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.111869	0.207096	0.180359	0.270191	0.301461	0.351488	0.344212
	Formate	0.094273	0.137967	0.141081	0.216153	0.239447	0.26216	0.219243
	Formaldehyde							
	glyoxal							
S (0-1 hr)	Acetate	307.0	653.7	1710.0	2640.0	3620.0	4495.0	6922.5
	Formate	388.7	886.0	1988.0	3030.0	4124.0	5175.0	8025.0
	Formaldehyde							
	glyoxal							

k and Ks estimation (F3, day 288 in phase III)

Conc. Levels		(1) Low	2	3	4	5	6	7
Weight of media (g)		14.87	14.49	14.57	16.62	17.86	13.53	15.86
Volume (cm^3)		13.897	13.542	13.617	15.533	16.692	12.645	14.822
Biomass conc.	32.9nmol/cm^3media							
BOM conc. @ o hr	Acetate	566	1132	2264	3396	4528	5660	8490
	Formate	550	1100	2200	3300	4400	5500	8250
	Formaldehyde							
	glyoxal							
BOM conc. @ 1 hr	Acetate	489	944	2009	2698	3612	4796	7401
	Formate	489	1072	2000	2436	3541	4911	7690
	Formaldehyde							
	glyoxal							
dS/dt in bulk liquid (0-1 hr)	Acetate	77.0	188.0	255.0	698.0	916.0	864.0	1089.0
	Formate	61.0	28.0	200.0	864.0	859.0	589.0	560.0
	Formaldehyde							
	glyoxal							
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.011703	0.029324	0.039556	0.094919	0.115915	0.144325	0.155186
	Formate	0.009271	0.004367	0.031024	0.117492	0.108702	0.098389	0.079802
	Formaldehyde							
	glyoxal							
S (0-1 hr)	Acetate	527.5	1038.0	2136.5	3047.0	4070.0	5228.0	7945.5
	Formate	519.5	1086.0	2100.0	2868.0	3970.5	5205.5	7970.0
	Formaldehyde							
	glyoxal							

k and Ks estimation (F2, day 288 in phase III)

Conc. Levels		1	2	3	4	5	6	7
Weight of media (g)		12.03	12.63	15.73	12.91	12.33	12.94	17.58
Volume (cm^3)		11.243	11.804	14.701	12.065	11.523	12.093	16.430
Biomass conc.	20.3nmol/cm^3media							
BOM conc. @ o hr	Acetate	540	1080	2160	3240	4320	5400	8100
	Formate	568	1136	2272	3408	4544	5680	8520
	Formaldehyde							
	glyoxal							
BOM conc. @ 1 hr	Acetate	256	854	1583	2546	3360	4310	6525
	Formate	350	842	1608	2658	3512	4490	6765
	Formaldehyde							
	glyoxal							
dS/dt in bulk liquid (0-1 hr)	Acetate	284.0	226.0	577.0	694.0	960.0	1090.0	1575.0
	Formate	218.0	294.0	664.0	750.0	1032.0	1190.0	1755.0
	Formaldehyde							
	glyoxal							
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.086473	0.065544	0.134361	0.196907	0.285191	0.308545	0.328162
	Formate	0.066377	0.085265	0.15462	0.212795	0.30658	0.336852	0.365667
	Formaldehyde							
	glyoxal							
S (0-1 hr)	Acetate	398.0	967.0	1871.5	2893.0	3840.0	4855.0	7312.5
	Formate	459.0	989.0	1940.0	3033.0	4028.0	5085.0	7642.5
	Formaldehyde							
	glyoxal							

k and Ks estimation (F4, day 288 in phase III)

Conc. Levels		1	2	3	4	5	6	7
Weight of media (g)		11.18	11.99	12.94	13.08	12.73	11.55	11.2
Volume (cm^3)		10.449	11.206	12.093	12.224	11.897	10.794	10.467
Biomass conc.	28.1nmol/cm^3media							
BOM conc. @ o hr	Acetate	487	974	1948	2922	3896	4870	7305
	Formate	550	1100	2200	3300	4400	5500	8250
	Formaldehyde							
	glyoxal							
BOM conc. @ 1 hr	Acetate	220	814	1720	2454	3256	4310	6930
	Formate	209	610	1440	2226	3000	4170	6825
	Formaldehyde							
	glyoxal							
dS/dt in bulk liquid (0-1 hr)	Acetate	267.0	160.0	228.0	468.0	640.0	560.0	375.0
	Formate	341.0	490.0	760.0	1074.0	1400.0	1330.0	1425.0
	Formaldehyde							
	glyoxal							
ds/dt*Vbottle/Weight of bacteria								
	Acetate	0.06320	0.03531	0.04662	0.09468	0.13304	0.12830	0.08860
	Formate	0.08071	0.10814	0.15542	0.21728	0.29102	0.30471	0.33668
	Formaldehyde							
	glyoxal							
S (0-1 hr)	Acetate	353.5	894.0	1834.0	2688.0	3576.0	4590.0	7117.5
	Formate	379.5	855.0	1820.0	2763.0	3700.0	4835.0	7537.5
	Formaldehyde							
	glyoxal							

Acetate (high temperature: F1 and F2)

Xi	Yi	k (1/h)	Ks	Matrix X Dk	Matrix X DKs	Ycalc.	W	S(r)
77.5	0.017037	0.28	1000	0.071926	-1.87E-05	0.020139	-0.003102	9.63E-06
135.05	0.025501	0.28	1000	0.118982	-2.94E-05	0.033315	-0.007814	6.11E-05
220.35	0.034317	0.28	1000	0.180563	-4.14E-05	0.050558	-0.01624	0.000264
369	0.03999	0.28	1000	0.26954	-5.51E-05	0.075471	-0.035481	0.001259
535.65	0.061704	0.28	1000	0.34881	-6.36E-05	0.097667	-0.035963	0.001293
92.25	0.003498	0.28	1000	0.084459	-2.17E-05	0.023648	-0.02015	0.000406
147.15	0.015935	0.28	1000	0.128274	-3.13E-05	0.035917	-0.019982	0.000399
267	0.034546	0.28	1000	0.210734	-4.66E-05	0.059006	-0.02446	0.000598
484	0.074029	0.28	1000	0.326146	-6.15E-05	0.091321	-0.017291	0.000299
838	0.098709	0.28	1000	0.45593	-6.95E-05	0.127661	-0.028951	0.000838
1619.25	0.187348	0.28	1000	0.618211	-6.61E-05	0.173099	0.014248	0.000203
4172	0.185133	0.28	1000	0.806651	-4.37E-05	0.225862	-0.04073	0.001659
249.5	0.084262	0.28	1000	0.19968	-4.47E-05	0.05591	0.028352	0.000804
538.7	0.151229	0.28	1000	0.350101	-6.37E-05	0.098028	0.053201	0.00283
1542	0.088175	0.28	1000	0.606609	-6.68E-05	0.169851	-0.081675	0.006671
2295	0.114831	0.28	1000	0.69651	-5.92E-05	0.195023	-0.080192	0.006431
3160	0.103358	0.28	1000	0.759615	-5.11E-05	0.212692	-0.109334	0.011954
3920	0.128167	0.28	1000	0.796748	-4.53E-05	0.223089	-0.094923	0.00901
6060	0.092082	0.28	1000	0.858357	-3.4E-05	0.24034	-0.148258	0.02198
102.5	0.001866	0.28	1000	0.092971	-2.36E-05	0.026032	-0.024166	0.000584
96	0.007987	0.28	1000	0.087591	-2.24E-05	0.024526	-0.016538	0.000274
203.5	0.015255	0.28	1000	0.16909	-3.93E-05	0.047345	-0.03209	0.00103
332.85	0.02267	0.28	1000	0.249728	-5.25E-05	0.069924	-0.047254	0.002233
539.25	0.025686	0.28	1000	0.350333	-6.37E-05	0.098093	-0.072407	0.005243
77.75	0.004851	0.28	1000	0.072141	-1.87E-05	0.020199	-0.015349	0.000236
127.5	0.015165	0.28	1000	0.113082	-2.81E-05	0.031663	-0.016498	0.000272
235.5	0.030967	0.28	1000	0.190611	-4.32E-05	0.053371	-0.022404	0.000502
427.5	0.086513	0.28	1000	0.299475	-5.87E-05	0.083853	0.00266	7.08E-06
846	0.125721	0.28	1000	0.458288	-6.95E-05	0.128321	-0.002599	6.76E-06
2128	0.18759	0.28	1000	0.680307	-6.09E-05	0.190486	-0.002896	8.38E-06
5131	0.080006	0.28	1000	0.836894	-3.82E-05	0.23433	-0.154325	0.023816
371.5	0.070335	0.28	1000	0.270871	-5.53E-05	0.075844	-0.005509	3.03E-05
914	0.034802	0.28	1000	0.477534	-6.99E-05	0.13371	-0.098907	0.009783
1765.5	0.084995	0.28	1000	0.638402	-6.46E-05	0.178752	-0.093758	0.008791
2734	0.106681	0.28	1000	0.732191	-5.49E-05	0.205013	-0.098332	0.009669
3628	0.159231	0.28	1000	0.783924	-4.74E-05	0.219499	-0.060267	0.003632
4590	0.158519	0.28	1000	0.821109	-4.11E-05	0.229911	-0.071392	0.005097
6915	0.162518	0.28	1000	0.873658	-3.09E-05	0.244624	-0.082106	0.006741

Iteration (1): $(X^{*}X)^{-1}X^{*}W$ = -0.1292

-318.0079

New k 0.1508

New Ks 681.9921

Xi	Yi	k (1/h)	Ks	Matrix X Dk	Matrix X DKs	Ycalc.	W	S(r)
77.5	0.017037	0.151	682	0.102041	-2.03E-05	0.015408	0.001629	2.65E-06
135.05	0.025501	0.151	682	0.16529	-3.05E-05	0.024959	0.000542	2.94E-07
220.35	0.034317	0.151	682	0.244196	-4.09E-05	0.036874	-0.002556	6.53E-06
369	0.03999	0.151	682	0.351094	-5.04E-05	0.053015	-0.013025	0.00017
535.65	0.061704	0.151	682	0.439905	-5.46E-05	0.066426	-0.004722	2.23E-05
92.25	0.003498	0.151	682	0.119148	-2.32E-05	0.017991	-0.014493	0.00021
147.15	0.015935	0.151	682	0.177471	-3.23E-05	0.026798	-0.010863	0.000118
267	0.034546	0.151	682	0.281349	-4.48E-05	0.042484	-0.007938	6.3E-05
484	0.074029	0.151	682	0.415094	-5.38E-05	0.062679	0.01135	0.000129
838	0.098709	0.151	682	0.551316	-5.48E-05	0.083249	0.015461	0.000239
1619.25	0.187348	0.151	682	0.703639	-4.62E-05	0.10625	0.081098	0.006577
4172	0.185133	0.151	682	0.859497	-2.67E-05	0.129784	0.055349	0.003063
249.5	0.084262	0.151	682	0.267848	-4.34E-05	0.040445	0.043817	0.00192
538.7	0.151229	0.151	682	0.441304	-5.46E-05	0.066637	0.084592	0.007156
1542	0.088175	0.151	682	0.693345	-4.71E-05	0.104695	-0.01652	0.000273
2295	0.114831	0.151	682	0.77091	-3.91E-05	0.116407	-0.001576	2.48E-06
3160	0.103358	0.151	682	0.822488	-3.23E-05	0.124196	-0.020838	0.000434
3920	0.128167	0.151	682	0.851804	-2.79E-05	0.128622	-0.000455	2.07E-07
6060	0.092082	0.151	682	0.898843	-2.01E-05	0.135725	-0.043643	0.001905
102.5	0.001866	0.151	682	0.130656	-2.51E-05	0.019729	-0.017863	0.000319
96	0.007987	0.151	682	0.123393	-2.39E-05	0.018632	-0.010645	0.000113
203.5	0.015255	0.151	682	0.229814	-3.92E-05	0.034702	-0.019447	0.000378
332.85	0.02267	0.151	682	0.32798	-4.88E-05	0.049525	-0.026855	0.000721
539.25	0.025686	0.151	682	0.441556	-5.46E-05	0.066675	-0.040989	0.00168
77.75	0.004851	0.151	682	0.102336	-2.03E-05	0.015453	-0.010602	0.000112
127.5	0.015165	0.151	682	0.157505	-2.94E-05	0.023783	-0.008618	7.43E-05
235.5	0.030967	0.151	682	0.256676	-4.22E-05	0.038758	-0.007791	6.07E-05
427.5	0.086513	0.151	682	0.385309	-5.24E-05	0.058182	0.028332	0.000803
846	0.125721	0.151	682	0.553665	-5.47E-05	0.083603	0.042118	0.001774
2128	0.18759	0.151	682	0.757295	-4.07E-05	0.114352	0.073239	0.005364
5131	0.080006	0.151	682	0.882677	-2.29E-05	0.133284	-0.053279	0.002839
371.5	0.070335	0.151	682	0.352634	-5.05E-05	0.053248	0.017088	0.000292
914	0.034802	0.151	682	0.572682	-5.42E-05	0.086475	-0.051673	0.00267
1765.5	0.084995	0.151	682	0.721348	-4.45E-05	0.108924	-0.023929	0.000573
2734	0.106681	0.151	682	0.800351	-3.54E-05	0.120853	-0.014172	0.000201
3628	0.159231	0.151	682	0.841763	-2.95E-05	0.127106	0.032125	0.001032
4590	0.158519	0.151	682	0.870637	-2.49E-05	0.131466	0.027053	0.000732
6915	0.162518	0.151	682	0.910228	-1.81E-05	0.137444	0.025074	0.000629

Iteration (1): $(X^*X)^{-1}X^*W$ = 0.007

-35.435

New k 0.158

New Ks 646.565

Xi	Yi	k (1/h)	Ks	Matrix X Dk	Matrix X DKs	Ycalc.	W	S(r)
77.5	0.017037	0.158	646	0.107118	-2.34E-05	0.016925	0.000112	1.26E-08
135.05	0.025501	0.158	646	0.172908	-3.5E-05	0.02732	-0.001818	3.31E-06
220.35	0.034317	0.158	646	0.254343	-4.64E-05	0.040186	-0.005869	3.44E-05
369	0.03999	0.158	646	0.363547	-5.66E-05	0.05744	-0.01745	0.000305
535.65	0.061704	0.158	646	0.453307	-6.06E-05	0.071622	-0.009919	9.84E-05
92.25	0.003498	0.158	646	0.124958	-2.67E-05	0.019743	-0.016245	0.000264
147.15	0.015935	0.158	646	0.185526	-3.7E-05	0.029313	-0.013378	0.000179
267	0.034546	0.158	646	0.292442	-5.06E-05	0.046206	-0.01166	0.000136
484	0.074029	0.158	646	0.428319	-5.99E-05	0.067674	0.006355	4.04E-05
838	0.098709	0.158	646	0.56469	-6.01E-05	0.089221	0.009488	9E-05
1619.25	0.187348	0.158	646	0.714822	-4.99E-05	0.112942	0.074406	0.005536
4172	0.185133	0.158	646	0.865919	-2.84E-05	0.136815	0.048318	0.002335
249.5	0.084262	0.158	646	0.278615	-4.92E-05	0.044021	0.040241	0.001619
538.7	0.151229	0.158	646	0.454714	-6.06E-05	0.071845	0.079385	0.006302
1542	0.088175	0.158	646	0.704753	-5.09E-05	0.111351	-0.023176	0.000537
2295	0.114831	0.158	646	0.780347	-4.19E-05	0.123295	-0.008464	7.16E-05
3160	0.103358	0.158	646	0.830268	-3.45E-05	0.131182	-0.027824	0.000774
3920	0.128167	0.158	646	0.858519	-2.97E-05	0.135646	-0.007479	5.59E-05
6060	0.092082	0.158	646	0.903668	-2.13E-05	0.14278	-0.050697	0.00257
102.5	0.001866	0.158	646	0.136941	-2.89E-05	0.021637	-0.019771	0.000391
96	0.007987	0.158	646	0.12938	-2.75E-05	0.020442	-0.012455	0.000155
203.5	0.015255	0.158	646	0.239553	-4.46E-05	0.037849	-0.022595	0.000511
332.85	0.02267	0.158	646	0.340042	-5.49E-05	0.053727	-0.031057	0.000965
539.25	0.025686	0.158	646	0.454967	-6.06E-05	0.071885	-0.046199	0.002134
77.75	0.004851	0.158	646	0.107427	-2.35E-05	0.016973	-0.012123	0.000147
127.5	0.015165	0.158	646	0.164835	-3.37E-05	0.026044	-0.010879	0.000118
235.5	0.030967	0.158	646	0.267158	-4.79E-05	0.042211	-0.011244	0.000126
427.5	0.086513	0.158	646	0.39823	-5.86E-05	0.06292	0.023593	0.000557
846	0.125721	0.158	646	0.567024	-6E-05	0.08959	0.036131	0.001305
2128	0.18759	0.158	646	0.767123	-4.37E-05	0.121205	0.066385	0.004407
5131	0.080006	0.158	646	0.888177	-2.43E-05	0.140332	-0.060326	0.003639
371.5	0.070335	0.158	646	0.365111	-5.67E-05	0.057687	0.012648	0.00016
914	0.034802	0.158	646	0.585897	-5.93E-05	0.092572	-0.05777	0.003337
1765.5	0.084995	0.158	646	0.732117	-4.8E-05	0.115674	-0.03068	0.000941
2734	0.106681	0.158	646	0.808876	-3.78E-05	0.127802	-0.021121	0.000446
3628	0.159231	0.158	646	0.848854	-3.14E-05	0.134119	0.025113	0.000631
4590	0.158519	0.158	646	0.876623	-2.65E-05	0.138506	0.020012	0.0004
6915	0.162518	0.158	646	0.914562	-1.91E-05	0.144501	0.018018	0.000325

Iteration (1): $(X^TX)^{-1}X^TW$ =			0.0004
			9.005
Results	**k**	**0.1584**	
	Ks	**655.005**	

The observed and predicted V* values as a function of S

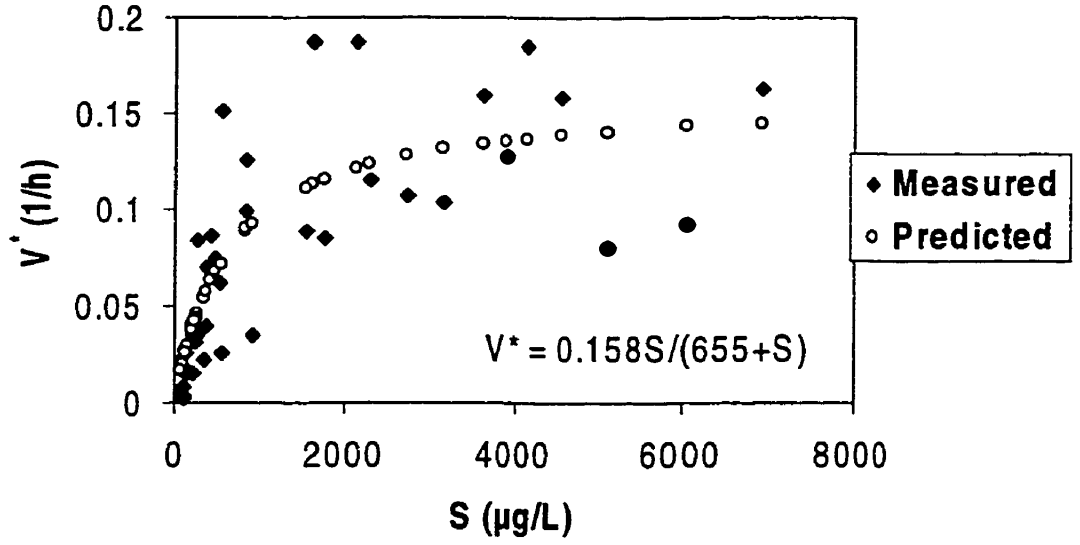

Figure J.1: k and K_s estimation at the high temperature (20°C) (acetate)

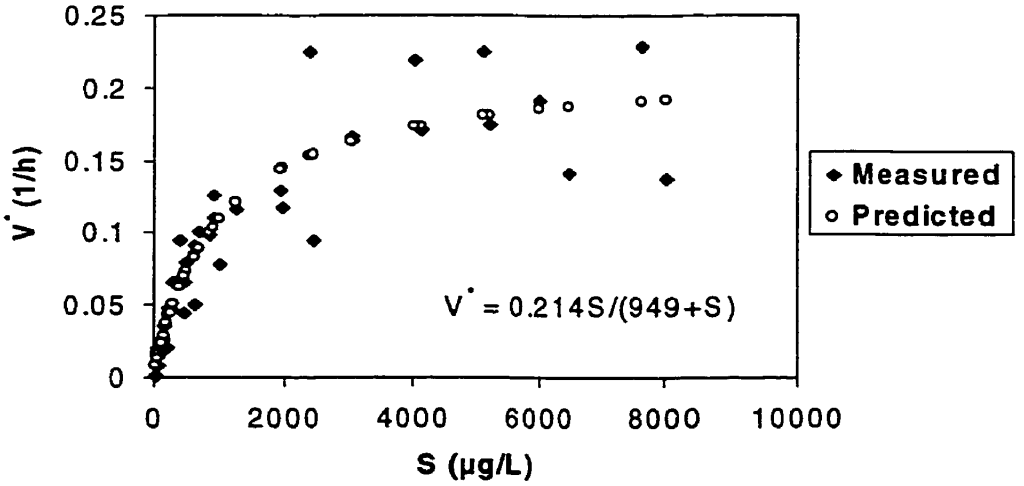

Figure J.2: k and K_s estimation at the high temperature (20°C) (formate)

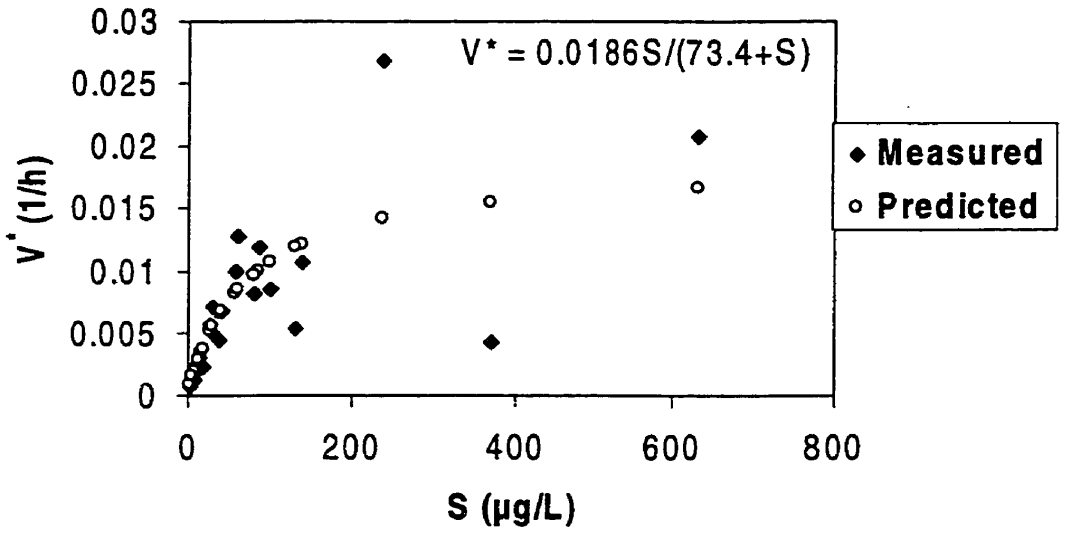

Figure J.3: k and K_s estimation at the high temperature (20°C) (formaldehyde)

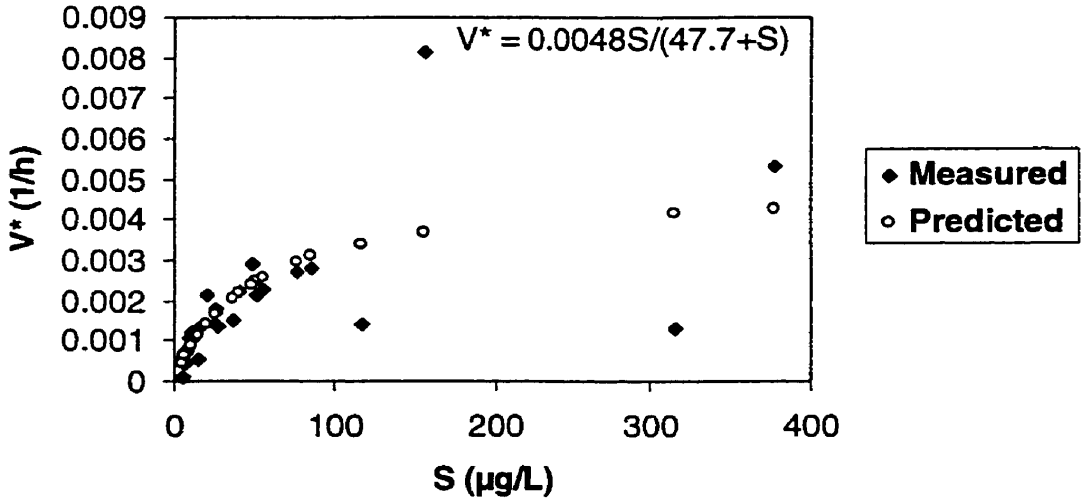

Figure J.4: k and K_s estimation at the high temperature (20°C) (glyoxal)

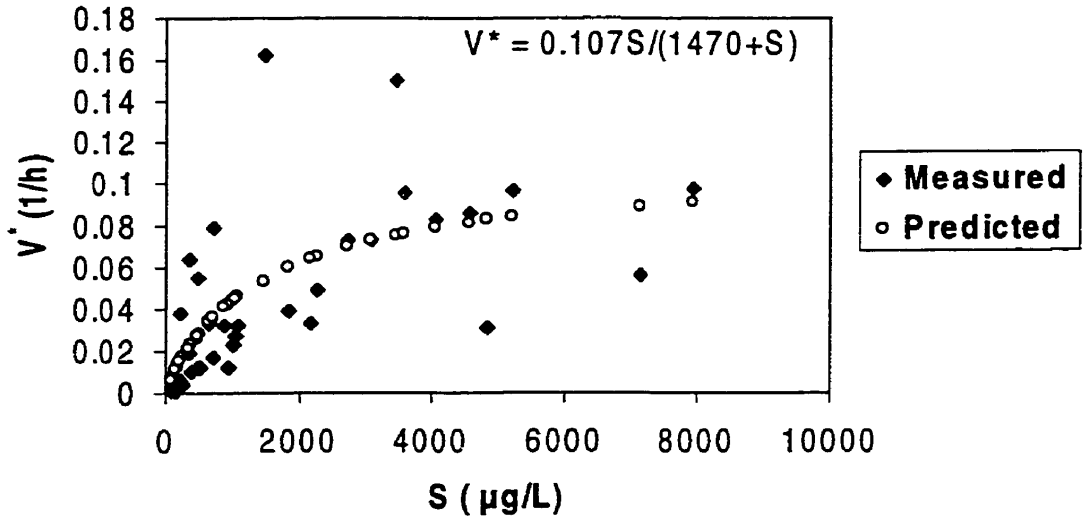

Figure J.5: k and K_s estimation at the low temperature (5°C) (acetate)

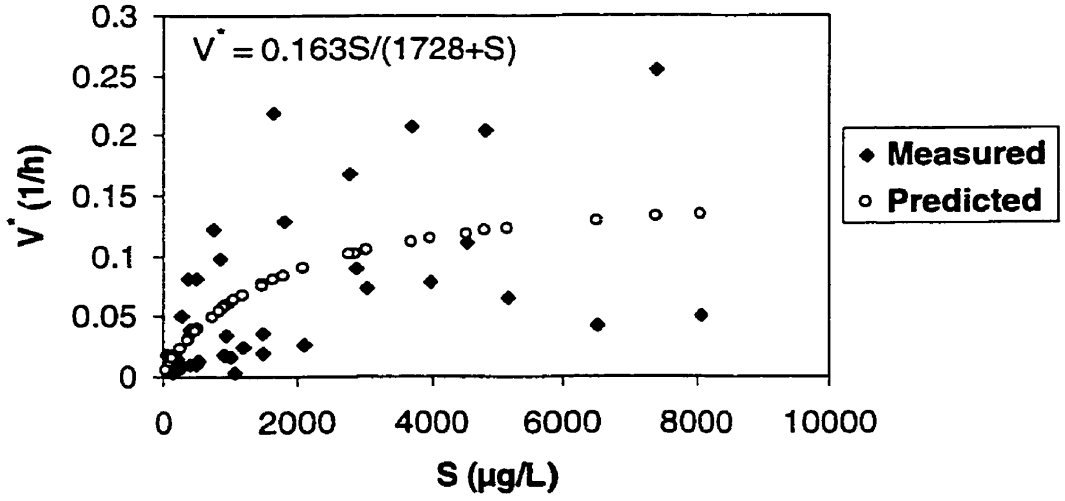

Figure J.6: k and K_s estimation at the low temperature (5°C) (formate)

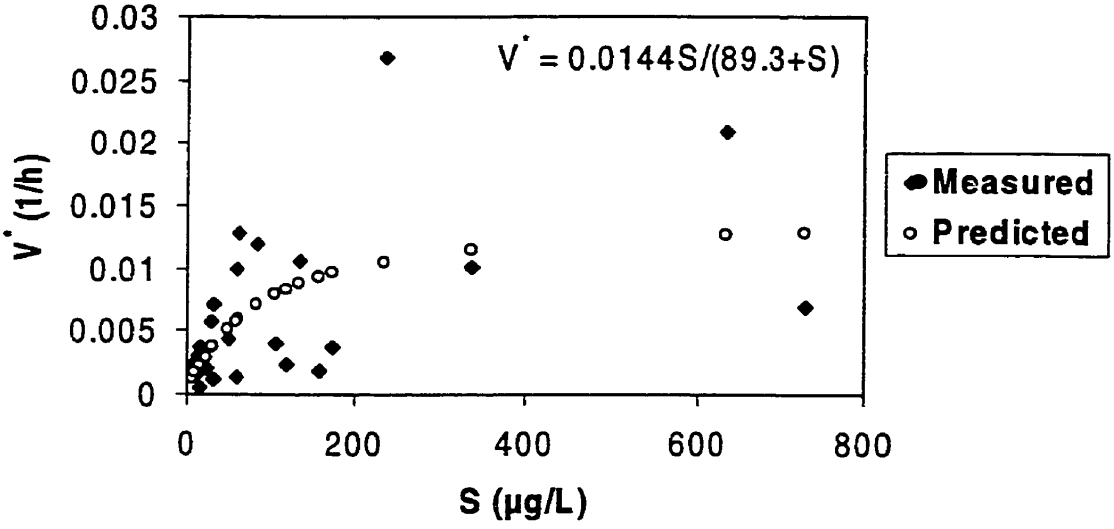

Figure J.7: k and K_s estimation at the low temperature (5°C) (formaldehyde)

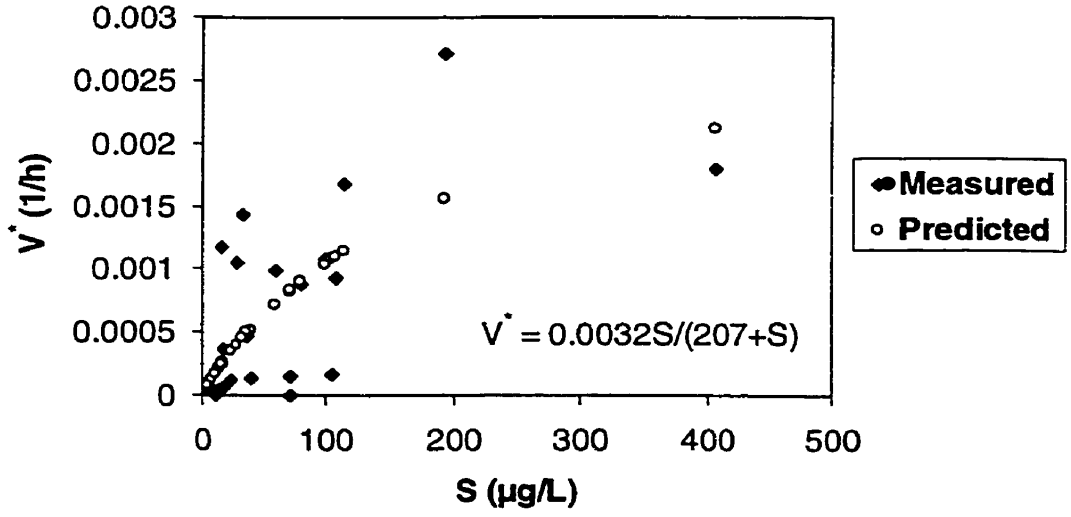

Figure J.8: k and K_s estimation at the low temperature (5°C) (glyoxal)

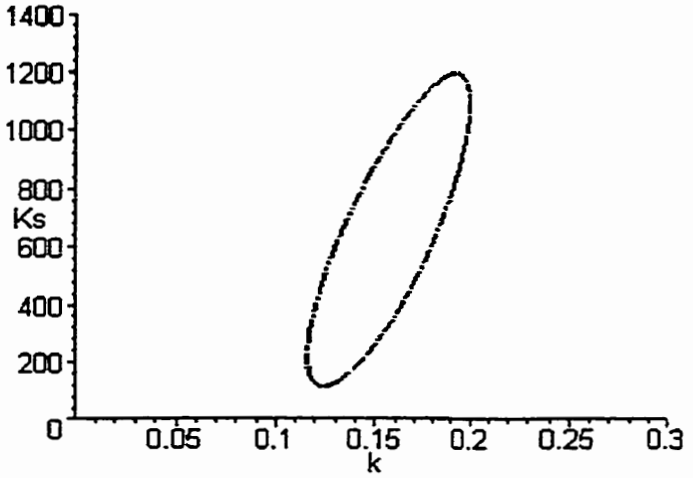

Figure J.9: The 95% elliptical joint confidence contour for k and Ks (Acetate, high temperature, 20°C)

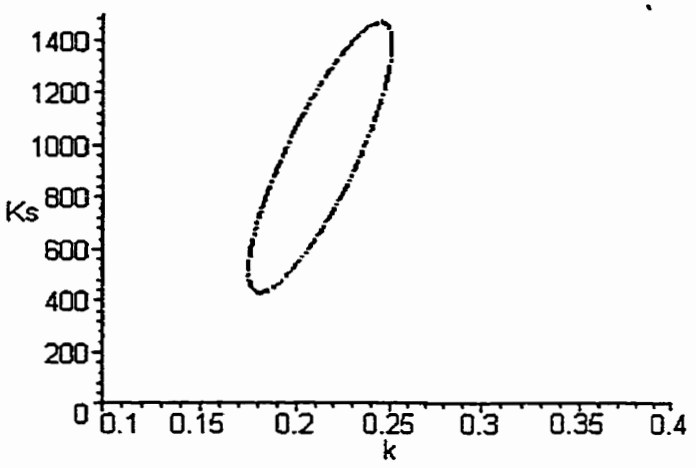

Figure J.10: The 95% elliptical joint confidence contour for k and Ks (Formate, high temperature, 20°C)

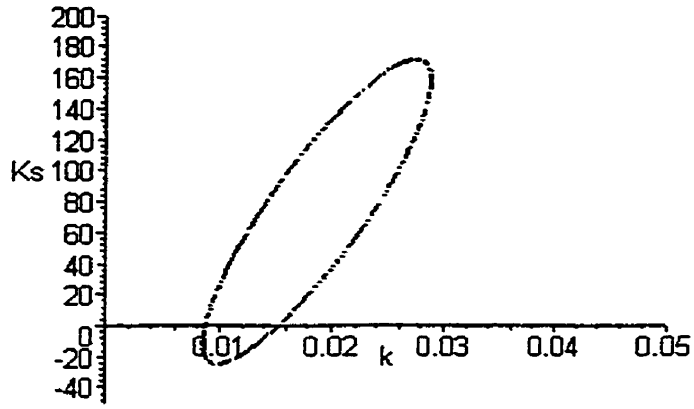

Figure J.11: The 95% elliptical joint confidence contour for k and Ks (Formaldehyde, high temperature; 20°C)

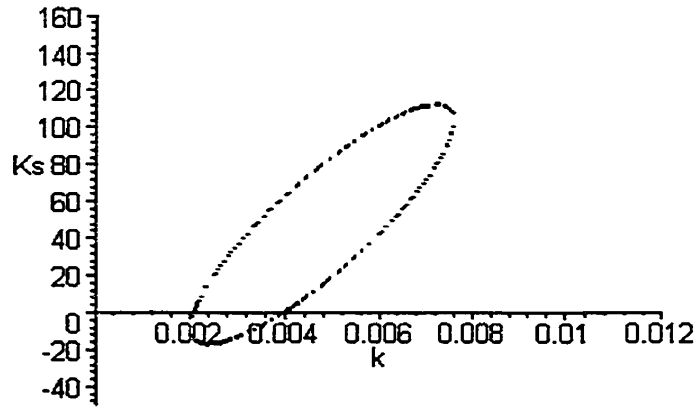

Figure J.12: The 95% elliptical joint confidence contour for k and Ks (Glyoxal, high temperature, 20°C)

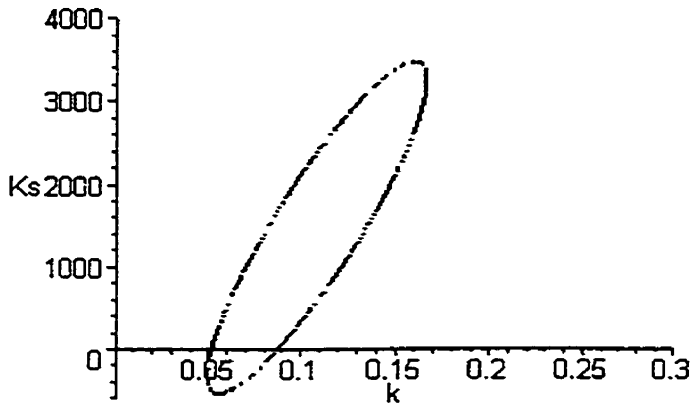

Figure J.13: The 95% elliptical joint confidence contour for k and Ks (Acetate, low temperature, 5°C)

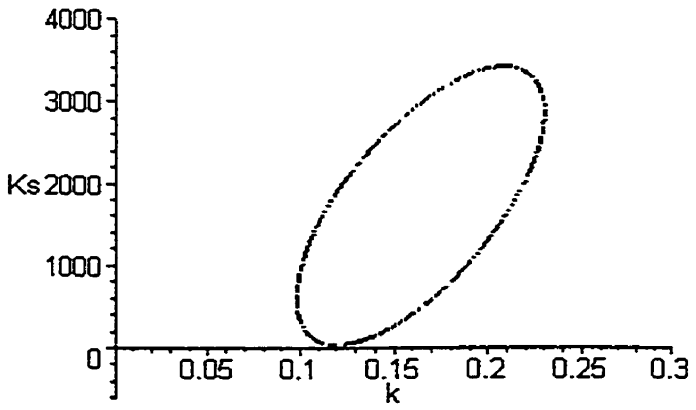

Figure J.14: The 95% elliptical joint confidence contour for k and Ks (Formate, low temperature, 5°C)

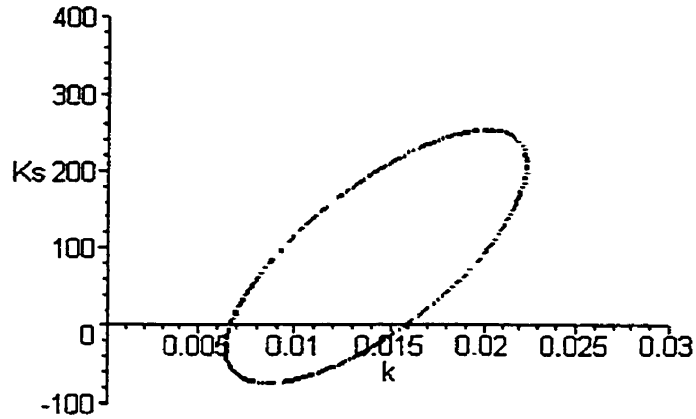

Figure J.15: The 95% elliptical joint confidence contour for k and Ks (Formaldehyde, low temperature, 5°C)

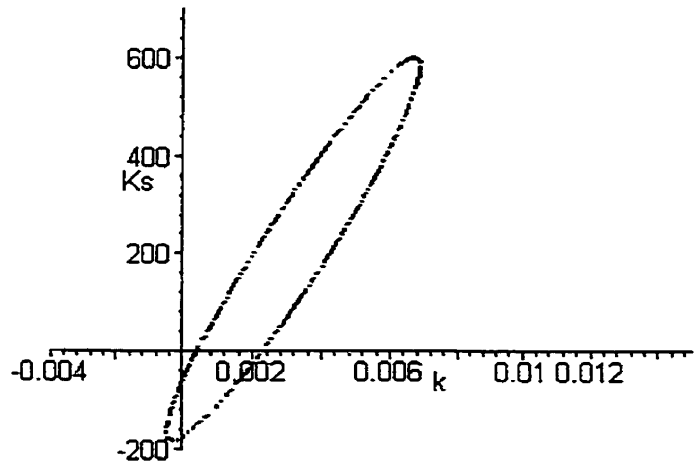

Figure J.16: The 95% elliptical joint confidence contour for k and Ks (Glyoxal, low temperature, 5°C)

Appendix K:

FIXED BACTERIA (BIOFILM) VS. SUSPENDED BACTERIA IN BIOFILTERS

The following estimation are based on assumptions: (1) average bacteria in bulk water in biofilters: ~10^4 #/cm^3; (2) average phospholipid biomass in biofilters: ~10 nmol/cm^3 media; (3) filter bed porosity: 0.4; (4) average bacteria size : 1μm; (5) bacteria density: 35 mg/cm^3

Total biomass (suspended) in biofilters = ~10^4 #/cm^3 *the volume of the filter bed (V) * 0.4*3.14/6*$(1*10^{-6})^3$*10^6cm3/m^3*35mg/cm^3 = V*7.3*10^{-8} mg

Total bimass (fixed as biofilm) = V*10nmolP/cm^3 3.7*10^{-3} mg bacteria/nmolP = V*3.7*10^{-2} mg

Therefore, the suspended bacteria in biofilters are negligible compared to the fixed bacteria as biofilm.

Appendix L

DEVELOPMENT OF X^* IN STEADY-STATE BIOFILTER MODELS

The derivation of X* was described in Zhang (1996) and Zhang and Huck (1996a).

Under steady-state conditions, the mass balance in a small segment (dx) of a packed biofilm column can be described in equation L-1 (Bailey and Ollis, 1986)

$$\upsilon \frac{dS_b}{dx} - D_H \frac{d^2 S_b}{dx^2} + \alpha J = 0 \qquad \text{(L-1)}$$

where υ is the superficial flow rate or hydraulic loading rate (LT^{-1}); x denotes the effective length (media depth, excluding any support gravel) of the biofilter (L); D_H is the hydrodynamic dispervity (L^2T^{-1}); S_b is the substrate concentrations in the bulk liquid (ML^{-3}); α is the biofilm surface area in each unit volume of the biofilter (L^{-1}).

The hydraulic loading rates for the biofilters in drinking water treatment are generally high and the effect of axial hydrodynamic dispersion is negligible (refer to the calculation from Zhang (1996)). Therefore, equation L-1 can be simplified as

$$\upsilon \frac{dS_b}{dx} + \alpha J = 0 \qquad \text{(L-2)}$$

Mass balance in steady-state biofilm model proposed by Rittmann and McCarty (1980) is described in equation L-3

$$S_b^* = S_s^* + J^* L^* / D^* \qquad \text{(L-3)}$$

Where, $L^* = L/\tau$; $J^* = J\tau/(K_s D_f)$; $D^* = D/D_f$; $S_s^* = S_s/K_s$; $\tau = \left(\frac{K_s D_f}{X_f k}\right)^{\frac{1}{2}}$.

D_f and D denote the diffusitivity of the substrate in the biofilm and in the liquid, respectively (L^2T^{-1}); k is the maximum utilization rate of the substrate (T^{-1}); K_s is Michaeles-Menten's half-velocity constant (ML^{-3}); X_f is the biofilm density within the biofilm (ML^{-3}); L denotes the thickness of the effective diffusion layer (L); and J is the flux of substrate into the biofilm ($ML^{-2}T^{-1}$).

By substituting equation L-3 into equation L-2, the EBCT (x/v) required to achieve a specific substrate flux (J) can be determined as follows

$$\frac{\tau}{\alpha D_f}\int_{J_o^*}^{J_x^*}\frac{d(S_s^* + \frac{L^*}{D^*}J^*)}{J^*} = \frac{x}{v} \qquad \text{(L-4)}$$

Rewriting equation L-4 and defining X* as in the left side of equation L-5

$$\int_{J_o^*}^{J_x^*}\frac{d(S_s^* + \frac{L^*}{D^*}J^*)}{J^*} = \frac{\alpha D_f}{v\tau}x = X^* \qquad \text{(L-5)}$$

J_o^* is the dimensionless flux of substrate into the biofilm at the inlet (top) of the biofilter ($ML^{-2}T^{-1}$); J_x^* is the dimensionless flux of substrate into the biofilm at any depth x; and X^* is the dimensionless contact time.

Appendix M:

FORTRAN PROGRAMS FOR MODELING IN CHAPTER 8

```
WATFOR-77 V3.1 Copyright WATCOM Systems Inc. 1984,1989  00/05/28
13:32:36

Options: list,disk,warnings,edit,xtype,terminal,logio,check,arraycheck

      1          PROGRAM MAIN 1
      2          DIMENSION ASBI(6),ASE(6),ASEC(6),SEC(6)
      3          COMMON /C1/ ASBI,ASE

      4          DATA XFK/5.14E2/,ASMIN/3.6/,D/1.8E-10/,RKS/206./
      5          SD=1.1
      6          VIS=1.22E-3
        c        DO 40 K=80,100,1
        c        ASMIN=K*2
      7          RSMIN=ASMIN/RKS
      8          CALL SAR(XFK,RSMIN,D,RKS,SD,VIS,SEC,R)
      9          DO 30 I=1,6
     10          ASEC(I)=SEC(I)*RKS
     11          WRITE(*,100) ASBI(I),ASE(I),ASEC(I)
     12  100     FORMAT(1X,'ASBI=',F7.2,1X,'ASE=',F7.2,1X,'SEC=,'F7.2)
     13  30      CONTINUE
     14  40      write(*,*) 'Rsar(', K ,')=',r
     15          END
        C

     16          SUBROUTINE SAR(XFK,SMIN,D,RKS,SD,VIS,SEC,WR)
     17          DIMENSION ASBI(6),ASE(6),SBI(6),SE(6),SEC(6),U(6)
     18          COMMON /C1/ASBI,ASE
     19          COMMON /C2/DP,E,H,V
     20          external rj,finte
     21          A=.75*1.*(1.0-E)*6.0/DP
     22          RE=DP*1000.0*V/VIS
     23          SC=VIS/(1000.0*D)
     24          AL=DP/((2.0+.644*RE**.5*SC**(1.0/3.0))*(1.0+1.5*(1.0-
E)))
     25          T=SQRT(RKS*D/(SD*XFK))
     26          RL=AL/T
        c         write (*,*) 'rl=',rl
     27          X=H*A*D/(V*T*SD)
     28          WRITE(*,*) 'sX=  ',X
     29          R=0
     30          DO 10 I=1,6
     31          SBI(I)=ASBI(I)/RKS
     32          SE(I)=ASE(I)/RKS
     33          CALL ROOT(SBI(I),SMIN,SD,RL,SSI)

     34          RJI=RJ(SSI,SMIN)
        c        ESMIN=SMIN+1.0E-3*SMIN
        c
XMIN=FINTE(SMIN,SSI,ESMIN,RJ)+RL*LOG(RJI/RJ(ESMIN,SMIN))/SD
        c        IF (XMIN.GT.X) THEN
        c        ELSE
        c        SEC(I)=SMIN
        c        GOTO 5
```

```
c       END IF
35      DO 20 J=998,1,-1
36      SSX=J*SSI/1000.0
37      XINTE=FINTE(SMIN,SSx,SSi)+RL*LOG(RJI/RJ(SSX,SMIN))/SD
38      IF (ABS((XINTE-X)/XINTE).GT.0.01) THEN
39      ELSE IF(J.EQ.2) THEN
40      WRITE(*,*) 'INTEGRATE PROCESS NOT CONVERGENT'
41      PAUSE

42      ELSE
43      GOTO 3
44      END IF
45   20 CONTINUE
46   3  ALfmin=RJ(SSX,SMIN)*(1.+SMIN)/SMIN*T
47      ALfmax=RJI*(1.+SMIN)/SMIN*T
48      WRITE(*,*) 'ALfmax=',ALFmax, 'ALfmin=',ALfmin
49      PAUSE
50      SEC(I)=SSX+RL*RJ(SSX,SMIN)/SD
51   5  R=R+ABS(LOG(SE(I))-LOG(SEC(I)))
52   10 CONTINUE
53      WR=0
54      DO 30 I=1,6
55      U(I)=ABS(LOG(SE(I))-LOG(SEC(I)))/(6.0*R/8.)
56      WR=WR+(1.0-U(I)**2)**2*ABS(LOG(SE(I))-LOG(SEC(I)))
57 30   CONTINUE
58      END
c

59      SUBROUTINE ROOT(SB,SMIN,SD,RL,SS)
60      external rj
61      do 10 i=999,1,-1
62      XX=smin+(sb-smin)*i/1000
c        XX=SB-(SB*.1)
c        DO 10 I=1,500
c        write (*,*) 'xx=',xx,'smin=',smin
63      SS=SB-RJ(xX,SMIN)*RL/SD
c        write(*,*) 'i=',i
64      IF (ABS((SS-XX)/XX).GT.5.E-2) THEN
c       XX=SS
c       WRITE (*,*) ' SS=', SS, '  XX=  ',XX
65      ELSE
66      GOTO 20
67      END IF
68   10 CONTINUE
69      IF (I.EQ.1) THEN
70      WRITE(*,*) 'ROOT SEARCH NOT CONVERGENT'
71      PAUSE
72      ELSE
73      END IF
74   20 RETURN
75      END
c

76      FUNCTION FINTE(SMIN,A,B)
77      external rj
78      REAL NEW ,OLD
79      N=2
```

```
      80          H=ABS(A-B)/N
      81          TWO=0.0
      82          FOUR=1./RJ(A+H,SMIN)
      83          S=1./RJ(A,SMIN)+1./RJ(B,SMIN)
      84          NEW=H*(S+4.0*FOUR)/3.0
      85    10    CONTINUE
      86          N=N*2
      87          T=A+H
      88          H=ABS(A-B)/N
      89          TWO=TWO+FOUR
      90          FOUR=0.0
      91          DO 20 I=1,N/2
      92          FOUR=FOUR+1./RJ(T,SMIN)
      93          T=T+H+H
      94     20   CONTINUE
      95          OLD=NEW
      96          NEW=H*(S+2.0*TWO+4.0*FOUR)/3.0
      97          IF (ABS((OLD-NEW)/OLD).LT.1E-2.OR.N.GT.500) THEN
      98          ELSE
      99          GOTO 10
     100          END IF
     101          FINTE=NEW
     102          END
          C
          c       FUNCTION RJ1(SS,SMIN)
          c       rj1=sqrt(2.0*(ss-alog(1.0+ss))-2.0*(smin-
alog(1.0+smin)))
          c       RETURN
          c       END
          C

     103          BLOCK DATA INIT1
     104          DIMENSION ASBI(6),ASE(6)
     105          COMMON /C1/ ASBI,ASE
     106          DATA ASBI/369.,269.,410.,400.,395.,333./
                $    ,ASE/25.,17.,6.,5.5,5.5,7./
     107          END
          C

     108          BLOCK DATA INIT2
     109          COMMON /C2/ DP,E,H,V
     110          DATA DP,E,H,V/1.05E-3,.20,0.01,2.1e-3/
     111          END


     112          FUNCTION RJ(SS,SMIN)
     113          RJ=SQRT(2.0*(SS-ALOG(1.0+SS)))*TANH((1.557-
0.4117*TANH(ALOG10(
                $     SMIN)))*(SS/SMIN-1.0)**(0.5035-
0.0257*TANH(ALOG10(SMIN))))
     114          END
```

```
6>sX=                  0.3298996
6>ALfmax=          2.0234080E-004ALfmin=          1.8756410E-004
6>ALfmax=          1.4844050E-004ALfmin=          1.3742860E-004
6>ALfmax=          2.2368800E-004ALfmin=          2.0752450E-004
6>ALfmax=          2.1856060E-004ALfmin=          2.0272770E-004
6>ALfmax=          2.1524600E-004ALfmin=          1.9962770E-004
6>ALfmax=          1.8250630E-004ALfmin=          1.6920830E-004
6> ASBI= 369.00 ASE=  25.00 SEC=, 331.97
6> ASBI= 269.00 ASE=  17.00 SEC=, 240.99
6> ASBI= 410.00 ASE=   6.00 SEC=, 368.66
6> ASBI= 400.00 ASE=   5.50 SEC=, 359.82
6> ASBI= 395.00 ASE=   5.50 SEC=, 354.11
6> ASBI= 333.00 ASE=   7.00 SEC=, 298.47
6>Rsar(    ????????)=              19.1765900

Compile time:                      00.16  Execution time:
13.29
Size of object code:                3082  Number of extensions:
2
Size of local data area(s):         1568  Number of warnings:
0
Size of global data area:            184  Number of errors:
0
Object/Dynamic bytes free: 313920/46094  Statements Executed:      55156
```

```
WATFOR-77 V3.1 Copyright WATCOM Systems Inc. 1984,1989  00/05/28
13:10:24

Options: list,disk,warnings,edit,xtype,terminal,logio,check,arraycheck


       1          PROGRAM MAIN 1
       2          DIMENSION ASBI(6),ASE(6),ASEC(6),SEC(6),YBB(20)
       3          COMMON /C1/ ASBI,ASE
       4          ND=6
       5          DATA YB/1.5e6/,RK/4.4E-5/,RKS/650/,D/1.8E-10/,SD/1.1/
             $    XF/3.5E7/
       6          VIS=1.0E-3
         c        DO 40 K=1,20
         c        YBB(K)=1e+5+.1e+5*k
         c        YB=YBB(K)
       7          CALL SAR(YB,RK,RKS,D,SD,XF,VIS,ND,SEC,R)
       8          DO 30 I=1,ND
       9          ASEC(I)=SEC(I)*RKS
      10          WRITE(*,100) ASBI(I),ASE(I),ASEC(I)
      11   100    FORMAT(1X,'ASBI=',F7.2,1X,'ASE=',F7.2,1X,' ASEC=,'F7.2)
      12   30     CONTINUE
      13   40     WRITE(*,*) 'RSAR=',R
      14          END
         C

*WRN* VA-05 YBB is an unreferenced symbol
      15          SUBROUTINE SAR(YB,RK,RKS,D,SD,XF,VIS,ND,SEC,WR)

      16          DIMENSION ASBI(6),ASE(6),SBI(6),SE(6),SEC(6),U(6)
      17          COMMON /C1/ASBI,ASE
      18          COMMON /C2/DP1,E1,H1,V1,co1
         C         COMMON /C3/DP2,E2,H2,V2,co2
      19          DATA DELTA/0.98e-6/
      20          T=SQRT(RKS*D/(SD*XF*RK))
      21          CALL
SLSX(RK,RKS,D,SD,XF,VIS,DP1,E1,H1,V1,co1,AL1,SL1,SX1)
         C         CALL
SLSX(RK,RKS,D,SD,XF,VIS,DP2,E2,H2,V2,co2,AL2,SL2,SX2)
         C        write(*,*) 'al=',al1,al2
      22          COEFF=1./SQRT(1.-(cosh(DELTA/T))**(-2))
      23
SMIN=COEFF*(RKS*XF/(RK*D/SD))**.5*DELTA/YB+AL1*XF*DELTA/(D*YB)
      24          WRITE(*,*) 'SMIN=',SMIN
         C        pause
      25          SSMIN=SMIN/RKS
      26          R=0
      27          DO 10 I=1,ND
         C         M=1
      28          SL=SL1
      29          SX=SX1
      30          WRITE(*,*) 'SX=   ',SX
      31          SBI(I)=ASBI(I)/RKS
```

```
      32          SE(I)=ASE(I)/RKS
      33          SBII=SBI(I)
      34        6 CALL ROOT(YB,RK,RKS,D,SD,XF,SL,SBII,SJI)
      35          WRITE(*,*) 'SJI=',SJI
         C        INPUT ORIGINAL SJX BY CHOOSING A REASONABLE J

      36          DO 20 J=1,50000,1
      37          SJX=J*SJI/50000
      38          IF (J.EQ.1) THEN
      39          XINTE1=VINTE(YB,RK,SJX,SJI)
      40          XINTE=XINTE1+SL*LOG(SJI/SJX)/SD
      41          ELSE
      42          XINTE1=XINTE1-SJI/50000.*(FJINTE1(YB,RK,(J-
1)*SJI/50000.)
             $    +FJINTE1(YB,RK,J*SJI/50000.))/2.
      43          XINTE2=SL*LOG(SJI/SJX)/SD
      44          XINTE=XINTE1+XINTE2
      45          END IF
         C        write(*,*) 'sx= ',sx,
         C     $  '  xinte1=',xinte1,'  xinte2=',sl*log(sji/sjx)/sd
         C        PAUSE
         C        END IF
      46          IF (ABS((XINTE-SX)/XINTE).LT.1.E-2) THEN
         C        WRITE(*,*) 'sx=',sx, 'xinte=',xinte
      47          GOTO 3
      48          ELSE IF(J.EQ.50000) THEN
      49          WRITE(*,*) 'INTEGRATE PROCESS NOT CONVERGENT'
         C        write(*,*) 'sx=',sx,'xinte=',xinte
      50          PAUSE
      51          ELSE
      52          END IF
      53     20   CONTINUE
      54      3   RLFMAX=T*SJI*YB*RK
      55          RLFMIN=T*SJX*YB*RK
      56          WRITE(*,*) 'RLFMAX=',RLFMAX,'RLFMIN=',RLFMIN
      57          pause
      58          WRITE(*,*) 'SJI=',SJI,'SJX=',SJX
         C        SSX=SJX/TANH(SJX*YB*RK)
      59          SSX=(0.5*SJX**2+SJX*(1.+(SJX/3.4)**1.19)**(-0.61))/
             $    (TANH(SJX*(YB*RK-1.0)))

      60          ssi=sji/tanh(sji*yb*rk)
         C         write(*,*) 'ssi=',ssi
         C         write(*,*) 'ssx=',ssx
         C         pause
      61          SEC(I)=SSX+SL*SJX/SD
      62          write (*,*) 'Ase=',SEC(I)*RKS
      63          pause

      64          SBII=SEC(I)
         C         SL=SL2
         C         SX=SX2
         C         M=M-1
         C         IF(M.EQ.0) THEN
         C         GOTO  6
         C         ELSE
         C         END IF
```

```
      11    R=R+ABS(LOG(SE(I))-LOG(SEC(I)))
      10    CONTINUE
            WR=0
            DO 30 I=1,ND
            U(I)=ABS(LOG(SE(I))-LOG(SEC(I)))/(6.0*R/ND)
            WR=WR+(1.0-U(I)**2)**2*ABS(LOG(SE(I))-LOG(SEC(I)))
   30       CONTINUE
            END
C

            SUBROUTINE ROOT(YB,RK,RKS,D,SD,XF,SL,SB,SJ)
C           INPUT TRIAL-ERROR ORIGINAL AJ
            DATA AJO/6.E-4/

            DO 10 I=1,10000,1
            AJ=AJO*I/100
C           AJ=AJO
            OOSJ=AJ*SQRT(SD/(RKS*D*XF*RK))
C           DO 10 I=1,1000,1

C           SJ=SB*SD/SL-SD/SL*OOSJ/TANH(OOSJ*YB*RK)
            SJ=SB*SD/SL-
SD/SL*((.5*OOSJ**2+OOSJ*(1.+(OOSJ/3.4)**1.19)
     $      **(-.61))/TANH(OOSJ*(YB*RK-1.)))
C           WRITE(*,*) 'SJTRIAL=',SJ
            IF (ABS((SJ-OOSJ)/OOSJ).GT.1.E-2) THEN
C           OOSJ=SJ
            ELSE
            GOTO 20
            END IF
            IF (I.EQ.10000)THEN
            WRITE(*,*) 'ROOT SEARCH NOT CONVERGENT'
            pause
            ELSE
            END IF
      10    CONTINUE
      20    SJ=OOSJ
C           WRITE (*,*)'I=',I
C           PAUSE
            RETURN
            END
C

            FUNCTION VINTE(YB,RK,A,B)
            REAL NEW ,OLD
            N=2
            H=ABS(A-B)/N
            TWO=0.0
            FOUR=FJINTE1(YB,RK,A+H)
            S=FJINTE1(YB,RK,A)+FJINTE1(YB,RK,B)
            NEW=H*(S+4.0*FOUR)/3.0
      10    CONTINUE
            N=N*2
            T=A+H
            H=ABS(A-B)/N
            TWO=TWO+FOUR
            FOUR=0.0
```

```
106           DO 20 I=1,N/2
107           FOUR=FOUR+FJINTE1(YB,RK,T)
108           T=T+H+H
109      20   CONTINUE
110           OLD=NEW
111           NEW=H*(S+2.0*TWO+4.0*FOUR)/3.0
112           IF (ABS((OLD-NEW)/OLD).LT.1E-3.OR.N.GT.500) THEN
113           ELSE
114           GOTO 10
115           END IF
116           VINTE=NEW
117           END
      C
118           FUNCTION FJINTE1(YB,RK,SJ)
119           FJINTE1=(TANH(SJ*YB*RK)-SJ*YB*RK/((COSH(SJ*YB*RK))**2))
             $  /(SJ*(TANH(SJ*YB*RK))**2)
120           END


121           SUBROUTINE
SLSX(RK,RKS,D,SD,XF,VIS,DP,E,H,V,co,AL,SL,SX)
122           A=0.75*co*1.*(1.0-E)*6.0/DP
123           RE=DP*1000.0*V/VIS
124           SC=VIS/(1000.0*D)
125           AL=DP/((2.0+.644*RE**.5*SC**(1.0/3.0))*(1.0+1.5*(1.0-
E)))
126           T=SQRT(RKS*D/(SD*XF*RK))
127           SL=AL/T
      C       WRITE (*,*) 'A=',A
128           SX=H*A*D/(V*T*SD)
129           END


130           BLOCK DATA INIT1
131           DIMENSION ASBI(6),ASE(6)
132           COMMON /C1/ ASBI,ASE
133           DATA ASBI/369.,269.,410.,400.,395.,333./
             $    ,ASE/25.,17.,6.1,6.0,5.5,7.0/
134           END
      C
135           BLOCK DATA INIT2
136           COMMON /C2/ DP1,E1,H1,V1,co1
137           DATA DP1,E1,H1,V1,co1/1.05E-3,.42,0.01,2.1e-3,1.0/
138           END

      C        BLOCK DATA INIT3
      C        COMMON /C3/ DP2,E2,H2,V2,co2
      C        DATA DP2,E2,H2,V2,co2/.48E-3,.50,0.20,2.1e-3,1.0/
      C        END

      C      FUNCTION FJINTE1(YB,RK,SJ)
      C       FJINTE1=((SJ+(1.+(SJ/3.4)**1.19)**(-.61)-
.169*(1.+(SJ/3.4)**
      C     $  1.19)**(-1.61)*SJ**1.19)*TANH(SJ*(YB*RK-1.))-
1./(COSH(SJ*(YB*
```

```
      C    $  RK-1.)))**2*(YB*RK-
1.)*(.5*SJ**2+SJ*(1.+(SJ/3.4)**1.19)**
      C    $  (-.61)))/((TANH(SJ*(YB*RK-1.)))**2*SJ)
      C       END


6>SMIN=              13.6608300
6>SX=                 0.2330642
6>SJI=               0.1312660
6>RLFMAX=          7.2000000E-005RLFMIN=          6.7484160E-005
6>SJI=               0.1312660SJX=               0.1230330
6>Ase=             343.3515000
6>SX=                 0.2330642
6>SJI=               0.0961055
6>RLFMAX=          5.2714280E-005RLFMIN=          4.9522960E-005
6>SJI=               0.0961055SJX=               0.0902873
6>Ase=             251.2141000
6>SX=                 0.2330642
6>SJI=               0.1457991
6>RLFMAX=          7.9971430E-005RLFMIN=          7.4893240E-005
6>SJI=               0.1457991SJX=               0.1365408
6>Ase=             381.5143000
6>SX=                 0.2330642
6>SJI=               0.1420486
6>RLFMAX=          7.7914290E-005RLFMIN=          7.2982320E-005
6>SJI=               0.1420486SJX=               0.1330569
6>Ase=             371.6628000
6>SX=                 0.2330642
6>SJI=               0.1406422
6>RLFMAX=          7.7142850E-005RLFMIN=          7.2265890E-005
6>SJI=               0.1406422SJX=               0.1317508
6>Ase=             367.9710000
6>SX=                 0.2330642
6>SJI=               0.1186082
6>RLFMAX=          6.5057140E-005RLFMIN=          6.1028800E-005
6>SJI=               0.1186082SJX=               0.1112640
6>Ase=             310.1750000
6> ASBI= 369.00 ASE=  25.00  ASEC=, 343.35
6> ASBI= 269.00 ASE=  17.00  ASEC=, 251.21
6> ASBI= 410.00 ASE=   6.10  ASEC=, 381.51
6> ASBI= 400.00 ASE=   6.00  ASEC=, 371.66
6> ASBI= 395.00 ASE=   5.50  ASEC=, 367.97
6> ASBI= 333.00 ASE=   7.00  ASEC=, 310.17
6>RSAR=             20.2706900

Compile time:                     00.16  Execution time:
01:15.20
Size of object code:               4274  Number of extensions:
3
Size of local data area(s):        2025  Number of warnings:
1
Size of global data area:           268  Number of errors:
0
Object/Dynamic bytes free:  310572/46094  Statements Executed:
4810355
```