EFFECTS OF OXIDANTS ON DRINKING WATER BIOFILTERS

by

Daniel Urfer-Frund

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ABSTRACT

Biological rapid filtration represents an important process step for the production of high quality drinking water. Bacteria attached to the filter media as biofilm use biodegradable organic matter (BOM) present in the filter influent as a source of carbon and energy. The decrease of the BOM levels through biofiltration is important with respect to the prevention of bacterial regrowth and related problems in the distribution system.

The research presented in this thesis examined the effects of different oxidants on the biological performance, i.e. removal of BOM, of biofilters. The investigated oxidants included hydrogen peroxide (H_2O_2), free and combined chlorine (Cl_2) and ozone (O_3). Experiments were performed at bench scale using several anthracite/sand filter columns, operated in parallel. The filter influent was dechlorinated tap water to which a cocktail containing BOM, N and P was added. The BOM cocktail contained four easily biodegradable components, i.e. acetate, formate, formaldehyde and glyoxal.

The inhibitory effects of the different oxidants on BOM removal in the filters varied over a relatively wide range. When continuously present in the filter influent, free Cl_2 had the strongest negative effect followed by combined Cl_2 and H_2O_2. In general, the presence of an oxidant residual in the biofilter effluent was more important than the bactericidal and oxidative strength of a given oxidant/disinfectant *per se*. The threshold concentration above which the removal of selected easily biodegradable BOM components was found to be inhibited was < 0.2 mg/L in the case of free Cl_2, 0.1-0.3 mg/L for combined Cl_2 and between 1 and 5 mg/L in the case of H_2O_2. The inhibition of BOM removal in the filters continuously dosed with an oxidant was likely the result of the suppressed growth of biomass in these filters.

The intermittent dosage of free Cl_2 to the influent of an anthracite/sand filter (~0.5 mg/L once per week for 6 hours) was found to have a substantial negative effect on the removal of BOM. The negative impact of free chlorinated backwash water (~1 mg/L Cl_2) on BOM removal was considerable, whereas the effect of chloraminated backwash water was negligible. The inhibitory effect of the periodic presence of ozone (~0.15 mg/L) in the influent of an anthracite/sand filter was minor, likely because O_3 rapidly disappeared in the filter as a result of its reaction with the anthracite.

A CT-approach similar to the traditional CT-approach used for disinfection was successfully used to compare the effects of different oxidants, when oxidants were continuously present in the filter influent. For the intermittent presence of the oxidants, the experimental results could not be entirely described with this CT-approach. The comparison between continuous vs. intermittent presence of oxidants in the biofilters showed that the mechanisms of BOM removal inhibition in the biofilters were likely different for these two conditions.

A new method for the measurement of active, i.e. substrate-degrading, biomass in biological drinking water filters was developed during this research. The method (biomass respiration potential method) is simple and requires only standard laboratory equipment.

Therefore, the method is of potential interest to the water industry and its further development should be pursued.

The investigation of mass transfer limitations for the removal of BOM in the control filter (no oxidant) indicated that BOM removal was likely not limited by external (to the biofilm) and internal (in the biofilm) mass transfer. The application of the mass transfer calculations to a broader range of biofiltration conditions suggested that BOM removal in such filters is likely generally limited by biodegradation kinetics, rather than mass transfer. These results are relevant in regards to the overall optimization of biological filtration for BOM removal, particularly in terms of future modeling.

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À Nathalie, Nina et Sora avec amour

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CHAPTER 1: INTRODUCTION, RESEARCH OBJECTIVES AND ORGANIZATION

INTRODUCTION

Over the last two decades biological rapid filtration of drinking water has become a widely used process step in many water treatment plants. The principal reason for this is the increased use of ozone (O_3) as a primary disinfectant instead of the traditionally performed addition of free chlorine (Cl_2) to the plant influent, referred to as prechlorination. This major change in water treatment practice was primarily caused by the discovery of the formation of harmful chlorinated disinfection by-products (DBPs), e.g. trihalomethanes (THMs) (Rook, 1974; Symons et al., 1975) and haloacetic acids (e.g. Miller and Uden, 1983; Reckhow and Singer, 1984; Reckhow et al., 1990), when free Cl_2 is added to water containing natural organic matter (NOM).

Ozonation of natural waters increases the biodegradable fraction of the NOM (e.g. Sontheimer et al., 1978; van der Kooij et al., 1982; Werner and Hambsch, 1986; Servais et al., 1987). Rittmann has proposed the generic term biodegradable organic matter (BOM) for the biodegradable portion of NOM (cf. Huck et al., 1991). As a result of the BOM increase upon ozonation, biological rapid filtration is often implemented following ozonation in order to decrease the BOM levels in the finished water and therefore reduce the risks of bacterial regrowth in the distribution system and control other water quality problems related to bacterial regrowth.

In biologically active filters, biodegradable electron donor substrates are oxidized through redox reactions catalyzed by bacterial enzymes. The bacteria which grow and gain energy as a result of these bioreactions, are attached to the filter media and form a biofilm. Such biofilms may contain matrix-enclosed bacterial microcolonies interspersed with less-dense regions of the matrix that include highly permeable water channels (Costerton et al., 1994). Dissolved oxygen usually serves as electron 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^-, dissolved H_2 and several reduced species of sulfur (Rittmann and Huck, 1989). This research focuses on the removal of BOM as it represents the biodegradable substrate of most relevance in North America (Huck, 1988).

A critical review of the different parameters and factors influencing the biological performance, i.e. BOM removal, of biological rapid filtration has been completed recently (Urfer et al., 1997). This review and previous work by the author and others identified the presence of oxidants in the influent and/or the backwash water of biofilters as an important factor with respect to the biological performance of such filters. The oxidants most likely present in biofilter influents either continuously or periodically are O_3, hydrogen peroxide (H_2O_2) and free Cl_2. In terms of the filter backwash water, the oxidants of concern are free and combined Cl_2. Because of the bactericidal impact of these oxidants/disinfectants on the biofilms of biologically active filters, the contact of water containing an oxidant with the biofilm attached to the filter media is expected to lead to a deterioration of the BOM removal capability of such filters. The extent of this deterioration depends on factors such as the bactericidal strength of the oxidant, oxidant concentration, reactivity of the oxidant with the filter media and the biomass, duration of contact between oxidant containing water and the biofilm, etc..

RESEARCH OBJECTIVES

The principal objective of this research is the evaluation and quantification of the effects of several oxidants on the biological performance, i.e. BOM removal, in biologically active drinking water filters. The oxidants which were investigated are the ones most likely to be present in full-scale biofilter influents, i.e. O_3, H_2O_2 and free Cl_2, and the backwash water of such filters, i.e. free and combined Cl_2. The experiments were performed using several laboratory scale glass filter columns operated in parallel. The filter influent consisted of dechlorinated tap water to which a BOM cocktail containing several easily biodegradable organic compounds was added. The different oxidants were dosed either to the influent of the biofilters or to the backwash water and one filter was routinely operated as control (no oxidant dosage). The following secondary objectives evolved during this research:

- the investigation of the removal mechanisms of hydrogen peroxide and ozone in the biofilters;
- the development and application of a method allowing the quantification of the active substrate-degrading biomass in biological filters; and
- the investigation of the relevance of external (to the biofilm) and internal (in the biofilm) mass transfer limitation of BOM degradation in the biofilters operated under the specific conditions of this research.

ORGANIZATION OF THESIS

Chapter 2 presents a condensed literature review providing relevant background information to the reader. This is followed by a detailed description of the experimental setup and the analytical methods which were used in this research (Chapter 3). Analytical

methods and experimental procedures which were specifically used in a given chapter are described in the 'Materials and Methods' section of the relevant chapter.

Chapters 4 to 6 contain the presentation and discussion of the experimental results obtained for the different oxidants. Chapter 4 presents the results of the experiments using hydrogen peroxide, Chapter 5 the results for chlorine and Chapter 6 the results for ozone and ozone combined with hydrogen peroxide. The results of Chapters 4 to 6 are integrated in Chapter 7, which provides a summary of the experimental results of the different experiments and an attempt to compare the different oxidants regarding their inhibitory effect on BOM removal in biofilters. The detailed results of experiments 4-6 are listed in Appendix B.

Finally, Chapter 8 presents the results of the assessment of mass transfer limitation of BOM removal under the specific experimental conditions. This chapter, although not directly related to the principal objective of this research, evolved during this study as a result of the attempt to further understand BOM degradation in drinking water biofilters and its limitations. The thesis ends with the presentation of the overall conclusions and recommendations for future research as well as for the water industry (Chapter 9).

CHAPTER 2: BACKGROUND

This chapter presents a condensed review of the literature relevant to this research. The chapter begins with a general introduction of biological treatment of drinking water. This is followed by a review of some principles and fundamentals of ozonation. Finally, the main part of the chapter addresses biological rapid filtration, which was the focus of this research.

BIOLOGICAL TREATMENT OF DRINKING WATER

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 (Huisman and Wood, 1975; Sontheimer, 1980; Cleasby, 1990; Hambsch, 1992). Although particle removal, i.e. in particular the removal of pathogenic microorganisms (Logsdon, 1990), rather than biological treatment was the principal treatment goal of SSF at that time, biological degradation of biodegradable substances occurred in these filters.

However, the beginning of biological drinking water treatment as an operational strategy is more recent and much of the emphasis on biological treatment followed the discovery of chlorinated DBPs, as mentioned earlier. A considerable contribution with respect to the initial development of biological water treatment has been provided by Sontheimer and colleagues (e.g. Sontheimer et al., 1978, Sontheimer, 1983; Sontheimer

and Hubele, 1986). The initial efforts of these researchers focused in particular on the biological removal of ammonia as a replacement for the traditionally performed breakpoint chlorination (Huck, 1988). In a thorough review of biological treatment of drinking water in Western Europe, Huck (1988) identified a variety of approaches in the different countries. In Germany and the Netherlands, biological treatment is often achieved through SSF, bank filtration or ground passage. If rapid filters and/or granular activated carbon (GAC) contactors are incorporated in the process, these are both typically installed following ozonation. In France on the other hand, biological treatment is traditionally performed in second stage GAC rapid filters, i.e. GAC filters following a first filtration step designed for particle removal (e.g. Bablon et al., 1988; Servais et al., 1991).

In most biological treatment steps the principal treatment goals are either removal of BOM and/or removal of ammonia (nitrification). In other applications biological processes have been successfully used for the removal of iron and manganese (Mouchet, 1992) and nitrate (NO_3^-). In the case of biological denitrification, processes using autotrophic bacteria have been used as well as procedures based on the utilization of NO_3^- by heterotrophic bacteria, requiring the addition of an organic substrate (Houel et al., 1982; Blecon et al., 1983; Böckle et al., 1984).

For additional information on biological water treatment in general and particularly its fundamental principles and historic development, the following reviews are suggested to the interested reader as they provide a large amount of relevant information (Rittmann and Snoeyink, 1984; Huck, 1988; Bouwer and Crowe, 1988; Rittmann and Huck, 1989, Rittmann, 1995a).

OZONATION

Following the discovery of the ubiquitous presence of chlorinated DBPs in the treated water of prechlorination plants, considerable research efforts have been made in

order to investigate alternative disinfectants, in particular O_3, and to enhance NOM removal prior to the addition of Cl_2. The recent research efforts in the field of ozone and related topics have been particularly intense in North America because ozonation, although common water treatment practice in certain Western European countries, is not yet a widely used process in North America. It can be expected that the use of O_3 as an alternative disinfectant will further increase in North America in the future, particularly if the US Environmental Protection Agency promulgates a regulation for *Cryptosporidum parvum* oocysts under the Enhanced Surface Water Treatment Rule. In fact, recent studies have demonstrated that free Cl_2 at practical dosage has essentially no effect on the inactivation of *Cryptosporidum parvum* (e.g. Finch et al., 1994). In addition, the CT-values required for the disinfection of *C. parvum* with O_3 may be up to one order of magnitude higher than what is currently practiced for the inactivation of *Giardia* cysts (Oppenheimer et al., 1997). Therefore, a potential future regulation of *Cryptosporidum* in drinking water will likely have a substantial impact on the water industry in North America and elsewhere.

The general trend in water treatment practice away from prechlorination towards the use of alternative primary disinfectants such as O_3 or the addition of Cl_2 later in the treatment process, e.g. following filtration, indirectly led and will lead to an increased interest in biological rapid filtration. As mentioned previously, ozonation leads to a considerable increase of the biodegradable fraction of the NOM which might lead to bacterial regrowth and related problems in the distribution system if ozonation is not followed by biofiltration (e.g. LeChevallier et al., 1992; 1996). Thus ozonation and biological filtration should be considered as a coupled process, rather than two independent process steps (Urfer et al., 1997). Relevant background information regarding ozonation of natural waters is provided in the following section.

Aqueous Chemistry of Ozone

Aqueous O_3 can react via two different pathways: the molecular ozone pathway, or the free radical pathway (Hoigné and Bader, 1976; 1977; Langlais et al., 1991). Ozone may either react directly with solutes, or decompose prior to its reaction with solutes. A schematic representation of the different reaction pathways of O_3 in natural waters is shown in Figure 2.1. Ozone decomposition is generally due to a chain reaction involving highly reactive hydroxyl radicals which become the important oxidants (Staehelin and Hoigné, 1985).

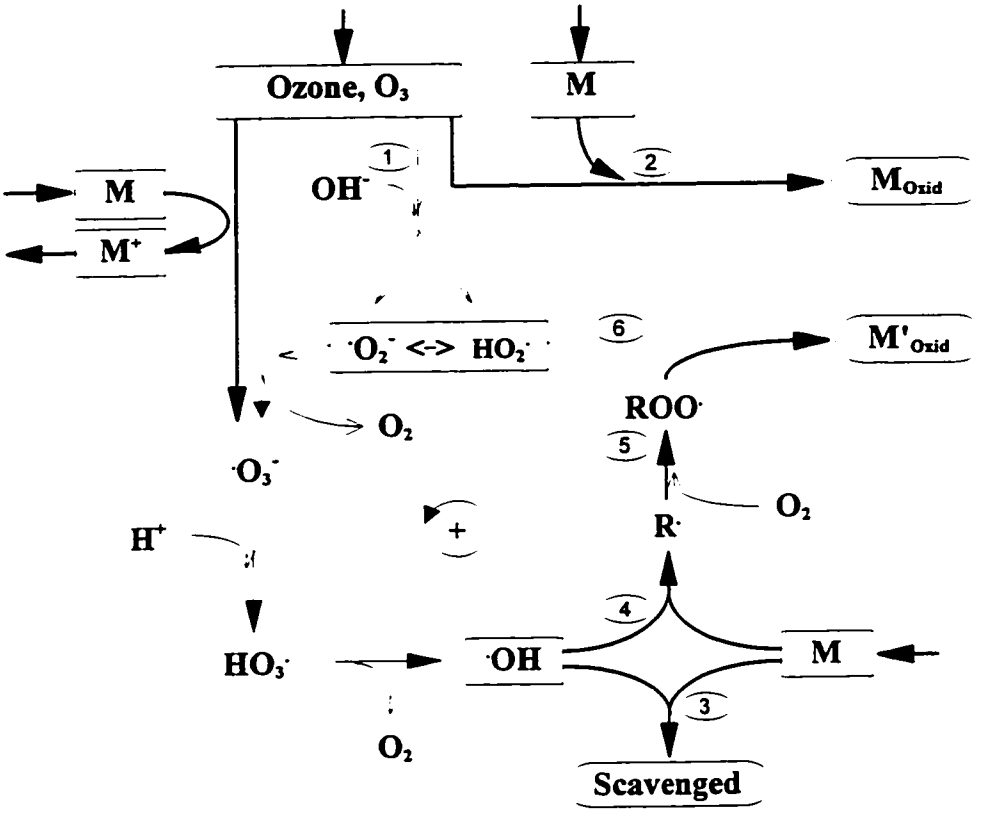

Figure 2.1: Reactions of aqueous ozone in natural waters (adapted from Staehelin and Hoigné, 1985)

An understanding of the different reaction pathways of O_3 is important because, depending on the treatment objectives, one or the other pathway may be relevant. In the case of disinfection, the direct reaction pathway of molecular O_3 (reaction 2 in Figure 2.1)

is relevant because the reaction of molecular O_3 with different constituents of natural waters is relatively selective and slow compared to the OH-radical pathway. In comparison, the OH-radicals react very fast with many types of dissolved species and are therefore scavenged before they encounter particles such as microorganisms (Hoigné and Bader, 1976). This has been demonstrated experimentally using *Giardia muris* cysts (Labatiuk et al., 1994). Also, the molecular O_3 pathway rather than the OH-radical pathway is important with regards to the oxidation of precursor material of chlorinated DBPs, as has been demonstrated by Reckhow et al., (1986) and Xiong (1990).

For the oxidation of certain micropollutants the kinetics of the direct reactions of molecular O_3 are too slow for practical processes, and therefore the reaction of the OH-radicals (reaction 4 in Figure 2.1) with such components is of importance (e.g. Hoigné and Bader, 1983a; Glaze et al., 1987; Paillard et al., 1988; Ferguson et al., 1990).

Ozone decomposition through the OH-radical pathway is initiated by hydroxide ions (reaction 1 in Figure 2.1). Therefore, the pH of the water is an important parameter in terms of O_3 decomposition kinetics (Stumm, 1954; Hoigné and Bader, 1976; Staehelin and Hoigné, 1985; Westerhoff et al., 1997). Lower pH-values of the water to be ozonated have a stabilizing effect on molecular O_3 as a result of the lower concentration of OH^-.

Regarding the reaction pathway which will be favored in a given water, alkalinity is another important parameter in addition to $[OH^-]$, because HCO_3^- and CO_3^{2-} act as scavengers (reaction 3 in Figure 2.1) of the OH-radicals (Hoigné and Bader, 1976). If the OH-radicals are not scavenged, they may react with other solutes (promoters) such as some organic compounds, e.g. formate and humic acids, to form organic radicals and finally O_2^- (reaction 6 in Figure 2.1) which then reacts further with additional O_3 (Staehelin and Hoigné, 1985). An increase in alkalinity therefore has a stabilizing effect on the presence of molecular ozone (e.g. Reckhow et al., 1986).

The rate of O_3 depletion in natural waters can generally be assumed as first order in O_3 concentration, at a given pH (Staehelin, 1983; Staehelin and Hoigné, 1985; Langlais et al., 1991; Guittonneau et al., 1992; Hoigné, 1994a; Jans and Hoigné, 1998). This appears to be particularly true for reactive cells of an ozone contactor (i.e. cells without O_3 addition), where the instantaneous ozone demand caused by substances readily oxidized by O_3 has been met in preceding cells, where gaseous O_3 is added to the water. Using California State Project Water, Coffey et al., (1995a) showed that a model using first-order kinetics for the O_3 decay was a good approximation for the observed decrease of the O_3 concentration in the reactive cells.

Colder water temperatures lead to a reduction of the O_3 decay rate constant at a given pH (Stumm, 1954, Hoigné, 1994b), in other words the natural O_3 decay is slower in cold waters. This is the result of the temperature dependency of the different reaction rates leading to O_3 decay, i.e. the rates of the direct reaction of aqueous O_3 with different solutes (Hoigné and Bader, 1983) and the rate of the hydroxide ion catalyzed decomposition of O_3 (Stumm, 1954).

Reaction of Ozone with NOM

The effects of ozonation on NOM include formation of hydroxyl, carbonyl, and carboxyl groups, increased polarity and hydrophilicity that decreases adsorbability, loss of double bonds and aromaticity, and a shift in the molecular weight distribution, resulting in an increased percentage of lower molecular weight compounds (e.g. Lienhard and Sontheimer, 1979; Reckhow and Singer, 1984; Amy et al., 1988; Glaze and Weinberg, 1993; Eighmy et al., 1993; Goel et al., 1995). Although some conflicting results exist regarding the net effect of ozone on the THM formation potential (THMFP) (Reckhow et al., 1986), numerous studies have shown that ozonation leads to a decrease of the THMFP (e.g. Reckhow and Singer, 1984; Reckhow et al., 1986; Amy et al., 1988; Xiong, 1990; Eighmy et al., 1993). This appears to be particularly true in waters with a relatively high

alkalinity where the direct reaction of molecular O_3 with the NOM is favored (Reckhow et al., 1986; Legube et al., 1989).

Andrews (1993) provides a comprehensive literature review on the formation of organic by-products upon ozonation. Ozonation of natural waters leads to the formation of numerous organic by-products, including carboxylic acids, aldehydes and aldo/keto acids (Xie and Reckhow, 1992; Reckhow et al., 1993; Andrews, 1993; Glaze and Weinberg, 1993; Andrews and Huck, 1994; García-Araya et al., 1995; Schechter and Singer, 1995; Najm and Krasner, 1995; Weinberg and Glaze, 1997). In general, these ozonation by-products are easily biodegradable components and good biological removals, i.e. >75%, are normally observed in biological rapid filters (Krasner et al., 1993; Swertfeger et al., 1993; Coffey et al., 1995b; Wang and Summers, 1996).

The combination of ozone O_3 and H_2O_2, commonly referred to as PEROXONE, leads to an increased production of highly reactive OH-radicals compared to O_3 alone (Staehelin and Hoigné, 1985; Glaze et al., 1987). The higher concentration of OH-radicals under PEROXONE conditions may lead to differences in the formation of BOM, both qualitatively and quantitatively, compared to O_3 alone.

The formation of biodegradable dissolved organic carbon (BDOC) has been observed to be equal or lower with PEROXONE compared to O_3 alone (Volk et al., 1993). Some of the formed BDOC appears to be further oxidized to carbon dioxide by OH-radicals. In other studies however, PEROXONE led to the formation of higher concentrations of assimilable organic carbon (AOC) compared to O_3 (McGuire et al., 1991; Hacker et al., 1994). A comparison of the formation of carboxylic acids by O_3 vs. O_3 followed by the addition of H_2O_2 did not show major differences for oxalate, acetate and formate (Griffini and Iozzelli, 1996). The formation of ketoacids, i.e. ketomalonic acid, pyruvic acid and glyoxylic acid, upon batch ozonation of fulvic acids was shown to be lower when H_2O_2 was present at a H_2O_2:O_3 ratio of 0.5 mole/mole compared to O_3 alone

(García-Araya et al., 1995). The somewhat conflicting results of these studies suggest that a more thorough understanding of the impacts of PEROXONE on BOM formation and downstream biological filters is required.

BIOLOGICAL RAPID FILTRATION

Although SSF, ground passage and bank filtration are important process steps in regards to the production of biologically stable water, the focus of this research was biological rapid filtration for BOM removal. Biological rapid filtration likely represents the process of choice for many new and retrofitted treatment plants containing a biological treatment step. Therefore the following sections of this chapter will focus on this particular aspect of biological treatment of drinking water. A critical review of biological rapid filtration has been completed recently (Urfer et al., 1997). The article provides a summary of the relevant aspects of biological rapid filtration.

Biofiltration has the potential to improve several water quality parameters which are not treatable by classical physico-chemical treatment processes. Most importantly, biofiltration leads to a decrease of the regrowth potential of the water prior to the distribution system. Additional benefits of biological rapid filtration include a reduction of chlorinated DBPs formed during secondary disinfection, reduction of chlorine demand and a decrease of the corrosion potential (Rittmann and Huck, 1989). Furthermore, biofiltration has the potential to control taste-and-odor causing compounds and other micropollutants of health and aesthetic concern (Lundgren et al., 1988; Manem and Rittmann, 1992; Rittmann, 1995b; Rittmann et al., 1995; Speitel and Segar, 1995).

Natural Organic Matter (NOM)

NOM is ubiquitous in natural waters (surface and groundwater) and consists of both humic and nonhumic components (e.g. Eighmy et al., 1993; Owen et al., 1993). Dissolved NOM is commonly quantified as dissolved organic carbon (DOC). Humic substances are

often responsible for the color of water and they normally represent 30-50% of the DOC of surface waters (Thurman and Malcolm, 1981) while their percentage of DOC is only about 15% in groundwater (Malcolm, 1990). Because humic substances precipitate in the presence of Ca^{2+} and Mg^{2+}, surface waters high in hardness usually contain relatively low levels of humic substances (Stumm and Morgan, 1981). By definition, humic substances represent the NOM fraction which is adsorbable on XAD-8 resins at a pH of 2 (Thurman and Malcolm, 1981). Based on their solubility in alkaline and acid solutions, humic substances are usually divided into three fractions: humic acid, which is soluble in alkaline solution but is precipitated by acidification; fulvic acid, which is soluble over the whole pH range; and humin, the fraction that cannot be extracted by acid or base (Stumm and Morgan, 1981). In surface waters the ratio between humic acids and fulvic acids is typically equal to about 1:9 (Malcolm, 1990). The non-humic fraction of the NOM consists of low molecular weight acids, neutral hydrophils, neutral hydrophobes, bases and contaminants (Malcolm, 1990). The non-humic NOM fraction usually contains substantially more easily biodegradable material than the humic fraction.

Biodegradable Organic Matter

The term biodegradable organic matter (BOM) is a surrogate expression for the biodegradable fraction of the NOM and is independent of the analytic method used for its quantification. The most commonly used methods for the quantification of BOM in drinking water are the measurement of assimilable organic carbon (AOC) (van der Kooij, 1982; 1989) and biodegradable dissolved organic carbon (BDOC) (Hascoët et al., 1986; Joret and Lévi, 1986; Servais et al., 1987; Frías et al., 1992). The different methods and approaches for the quantification of BOM have been thoroughly reviewed by Huck (1990) and others have compared and evaluated the different methods for the measurement of BOM in drinking waters (e.g. Kaplan, 1994; Woolschlager and Rittmann, 1995; Frías et al., 1995).

Although surrogate methods such as AOC and BDOC are useful, they both have some limitations. Therefore, much attention is currently focusing on quantifying the major chemical components and groups of components of BOM, some of which, i.e. ketoacids and aldehydes, have been proposed as surrogates for AOC (Krasner et al., 1993; Reckhow et al., 1993). The principal components and groups of components of BOM are amino acids, fatty and aromatic acids, carbohydrates, certain humic substances and where appropriate, organic ozonation by-products, e.g. aldehydes, carboxylic acids and aldo/keto acids (Andrews, 1993; Agbekodo et al., 1996; Merlet et al., 1996; Camper et al., 1998).

Although one of the most important issues regarding design and operation of biofilters, well-established criteria for acceptable BOM concentrations entering the distribution system in order to prevent bacterial regrowth are currently lacking (Urfer et al., 1997). van der Kooij recommended concentrations of 10 μg C_{eq}/L as the target AOC concentration in order to prevent regrowth of heterotrophic bacteria in non-chlorinated distribution systems (e.g. van der Kooij, 1990; van der Kooij, 1992). Others have shown that coliform regrowth in a free-chlorinated distribution system was low when AOC levels in the finished water were below 100 μg C_{eq}/L (LeChevallier et al., 1992; 1996). Using BDOC as a surrogate for BOM, Servais and colleagues have proposed a maximum BDOC concentration of about 0.15 mg/L in order to consider the water as biologically stable, i.e. water which does not support the growth of microorganisms to a significant extent (Rittmann and Snoeyink, 1984), in the absence of Cl_2 (Servais et al., 1995). However, the maximum allowable BOM concentration entering the distribution system is highly site specific and depends on numerous physical and chemical parameters of the water and the distribution system. In the absence of better information many engineers have chosen the reduction of post-ozonation AOC (or BDOC) levels to their pre-treatment levels as a treatment goal for BOM reduction in biofilters (Reckhow et al., 1993).

Microorganisms in Biological Rapid Filters

Much of the emphasis of biological rapid filters and the microbial ecosystems of such filters has been on bacteria, particularly heterotrophs and nitrifiers. 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 and LeChevallier (1990a) has cited several studies which reported the presence of fungi in GAC filters.

Heterotrophic bacteria readily attach to the media of biofilters (Hozalski and Bouwer, 1998) and they are present in very high numbers in such filters. Therefore, the metabolic activities of bacteria are principally responsible for the utilization of BOM in biofilters. Considering literature data of biomass measured as phospholipid (e.g. Wang et al., 1995; Miltner et al., 1995; Carlson et al., 1996a), the number of viable bacteria in the top part of such filters can be estimated between 10^9 and 10^{10} cells per cm^3 of filter, 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. Identified bacterial species in biological rapid filters include both Gram-negative and Gram-positive species, however Gram-negative bacteria appear to dominate (Eighmy et al., 1993; Norton and LeChevallier, 1996; Moll and Summers, 1997). In distribution systems the dosage of free Cl_2 led to a shift from predominantly Gram-negative in a non-chlorinated system towards increased levels of Gram-positive species (Norton and LeChevallier, 1996). Nevertheless, Moll and Summers (1997) have reported opposite trends for biofilters backwashed with chlorinated water. The dominant genera which have been identified in biologically active rapid filter include *Pseudomonas, Flavobacterium, Acinetobacter* and *Bacillus* (AWWA Committee Report, 1981; Rice and Robson, 1982;

Bouwer and Crowe, 1988, Eighmy et al., 1993; Norton and LeChevallier, 1996), some of which are opportunistic pathogens, e.g. *Pseudomonas*. The presence of coliforms in biologically equilibrated filters is unlikely because such pathogens are generally unable to compete with these relatively fast-growing bacteria (Camper et al., 1985; Bouwer and Crowe, 1988). However, several investigations have shown the presence of coliforms in GAC filters (LeChevallier, 1990a,b) and such bacteria may readily colonize virgin GAC filters. Therefore, the startup procedure of such filters is important (Camper et al., 1985) 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 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, e.g. nitrifiers, in the biofilm depends on the substrate concentrations, the biofilm thickness and external phenomena such as shearing and sloughing.

Kinetics of Bacterial Growth and Substrate Utilization

It is generally accepted that the rate of bacterial growth in growth limited systems can be adequately described by the following expression proposed by Monod (1942).

$$r_x = \frac{\mu_m * X * S}{K_S + S} \qquad (2.1)$$

where
- r_x: rate of bacterial growth, (M_x/L^3*T)
- μ_m: maximum specific growth rate, (T^{-1})
- X: concentration of microorganisms, (M_x/L^3)
- S: concentration of growth-limiting substrate, (M_s/L^3)
- K_S: half-velocity constant, substrate concentration at one-half the maximum growth rate, (M_s/L^3)

In a continuous-growth culture system, part of the substrate is converted to new cells and part of the substrate is oxidized to inorganic and organic end products. The

following relationship has been developed between the rate of growth and the rate of substrate utilization.

$$r_x = -Y * r_s \tag{2.2}$$

where: r_x: rate of bacterial growth, (M_x/L^3*T)
Y: maximum yield coefficient, M_x/ M_s)
r_s: rate of substrate utilization, (M_s/L^3*T)

If the expression for r_x in equation 2.1 is substituted in equation 2.2 and the term μ_m/Y is replaced by the term k (T^{-1}), defined as the maximum rate of substrate utilization per unit mass of microorganisms, the resulting expression for the rate of substrate utilization, r_s is (Metcalf and Eddy, 1991):

$$r_s = \frac{-k * X * S}{(K_S + S)} \tag{2.3}$$

At low substrate concentrations ($S<<K_S$), r_s is directly proportional to the substrate concentration S, i.e. the process is first order. As the concentration of S increases, the rate of substrate utilization increases less than proportionally and reaches a maximum ($S>>K_S$) where r_s is independent of S, i.e. the process is zero order, and some other factor (not substrate concentration) might be limiting (Schwarzenbach et al., 1993).

These two cases, i.e. $S<<K_S$ and $S>>K_S$, are important with respect to modeling BOM removal in drinking water rapid filters, because they represent a substantial simplification of equation 2.3. In fact, the analytical integration of the widely used steady-state biofilm model developed by Rittmann and McCarty (1980a) is impossible because of the non-linearity of equation 2.3 (Zhang and Huck, 1996a).

Huck and Anderson, (1992) and Huck et al., (1994) observed that filter influent BOM concentration and the amount of BOM removed in a given biofilter were directly proportional. Therefore they noted that the removal of BOM can be approximated by a first-order model. This suggested that BOM concentrations were substantially lower than K_S under the low substrate, i.e. oligotrophic, conditions of drinking water biofiltration. This

was supported by the work of Zhang (1996) and Zhang and Huck, (1996a,b) who estimated K_s values in the range of ~7-55 mg C_{eq}/L, considering AOC as a surrogate for the sole energy and carbon source. These values for K_s are substantially higher than common AOC filter influent concentrations.

However, other studies have estimated K_s values under oligotrophic conditions which are substantially lower than the estimates of Zhang (1996) and Zhang and Huck, (1996a,b). Rittmann et al., (1986) have estimated K_s values $\leq$ 0.1 mg/L of chemical oxygen demand (COD) in biofilm reactors fed with different organic substrates and they have noted that their estimations were in good agreement with other literature values. Nevertheless, if the data reported by Rittmann et al., (1986) are analyzed using plots of substrate concentration vs. observed rate of substrate removal, their K_s estimations are far below the concentrations at half of the maximum substrate removal rate (data not shown). Therefore, the K_s estimations from Rittmann et al., (1986) seem too low and they may have relatively large confidence intervals similarly to the estimations of Zhang (1996) and Zhang and Huck, (1996a,b).

Consequently, under low substrate conditions such as encountered in drinking waters, the issue of K_s estimations and reaction order of BOM removal in biological filters is not fully elucidated to date and further work seems to be necessary.

Impact of Filter Media

Because most of the earlier studies on biofiltration, particularly in Germany and France, have been conducted using GAC filters, biological rapid filtration has been traditionally associated with the use of GAC. However, as a result of the interest of retrofitting conventional treatment plants with ozone followed by the existing rapid filtration step, questions arise regarding the necessity of replacing the existing filter media (sand or anthracite/sand) with GAC in order to successfully operate biofiltration. The

selection of filter media is a central question when implementing biological filtration and is important because of its major cost implications (Urfer et al., 1997).

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). Little biogrowth occurs in the micropores of GAC, because their small diameter (1-100 nm) does not allow the penetration of bacteria which typically have a diameter of over 200 nm (AWWA Committee Report, 1981; Rice and Robson, 1982; Werner, 1982). Therefore, 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, if they contain media of comparable size. However, the irregular (macroporous) surface of GAC offers suitable bacterial attachment sites providing protection from shear stress. In addition, GAC has the ability to adsorb and remove potentially inhibitory chemicals and adsorb and retain slowly biodegradable components which can be biodegraded by the attached bacteria, leading to continuous bioregeneration of the GAC (Nayar and Sylvester, 1979; AWWA Committee Report, 1981; Li and DiGiano, 1983; Chang and Rittmann, 1987).

In general, anthracite/sand and GAC/sand filters provide similar average BOM removals (Urfer et al., 1997), and different studies have shown that biological rapid filtration can be successfully implemented in anthracite/sand filters. However, GAC/sand filters seem 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) and permit a faster reestablishment of BOM removal after periods out of service. GAC/sand often showed better DOC and total organic carbon (TOC) removals compared to anthracite/sand, possibly due to slow adsorption

processes or continuous bioregeneration. For biological NH_4^+ removal (nitrification), Bablon et al., (1988) showed that GAC/sand outperformed sand, particularly at low water temperatures and others indicated that a GAC filter containing wood-based GAC was a better support medium than coal-based GAC for biological nitrification (Merlet et al., 1992). For BOM removal however, minor differences have generally been reported between wood-based GAC and coal-based GACs (Urfer et al., 1997).

In general, optimized filter media selection for biofilters depends upon numerous site specific characteristics such as water quality (i.e. BOM composition, water temperature), and specific operational issues of the plant (Urfer et al., 1997). Therefore, for a given biofiltration application the choice of the ideal filter media configuration, requires a careful evaluation of the situation and potentially pilot-scale investigations.

Impact of Contact Time

Several researchers have demonstrated the important influence of contact time within 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). Contact time, usually expressed as empty bed contact time (EBCT), is a key design and operating variable and recent modeling efforts have provided additional justification for this experimentally observed finding. In practice, either filter depth or hydraulic loading can be changed to increase (or decrease) the EBCT.

As mentioned previously, Huck and colleagues have used a first-order approach to describe BOM removal in biofilters (Huck and Anderson, 1992; Huck et al., 1994). Consequently, increasing contact time (EBCT) will provide improved removals, but less than proportionally. The incremental benefit of using very long contact times is therefore small, which has been shown both theoretically and experimentally (Merlet et al., 1992; LeChevallier et al., 1992; Zhang and Huck, 1996a; Zhang, 1996).

Nevertheless, some researchers have observed an essentially linear increase of BDOC removal with increasing EBCT between 10 and 30 minutes (Servais et al., 1992), whereas others have observed no effect of EBCT on the removal of BOM (Price et al., 1993; 1994; Hozalski et al., 1995). These results are in conflict with the studies mentioned immediately above, although several reasons may be responsible for the somewhat unexpected findings of these investigations (cf. Urfer et al., 1997).

Zhang (1996) and Zhang and Huck, (1996a) have introduced the concept of dimensionless empty bed contact time, X* (equation 2.4). They have shown that at X* values ≥ 2.5, BOM removal is nearly complete, i.e. > 90% (Zhang and Huck, 1996a).

$$X^* = \theta / \left(\frac{\tau}{\alpha D_{eff}} \right) \qquad (2.4)$$

where
- X^*: dimensionless detention time, (-)
- θ: empty bed contact time, (T)
- τ: standard biofilm thickness dimension, $(K_s D_{eff}/kX_f)^{0.5}$, (L)
- α: specific biofilm surface area, (L^{-1})
- D_{eff}: substrate diffusivity in the biofilm, (L^2*T^{-1})
- X_f: cell density in the biofilm, (M_x*L^{-3})

The author has proposed including filter porosity (ε) into equation 2.4, in order to account for the "real contact time" between the water and the biofilm, rather than using the somewhat meaningless EBCT. Thus, equation 2.4 can be modified to equation 2.5:

$$X^{**} = \theta\varepsilon / \left(\frac{\tau}{\alpha D_{eff}} \right) \qquad (2.5)$$

Zhang (1996) noted that ($\tau/\alpha D_{eff}$) represents the standard time dimension for a biofilm to intercept (adsorb) substrate from the bulk liquid. Therefore, equation 2.5 represents the ratio of real contact time in a given biofilter, i.e. $\theta\varepsilon$, to standard time for a biofilm to intercept substrate, i.e. $\tau/\alpha D_{eff}$. Common porosity values in rapid filters are ~ 0.4 (Cleasby, 1990). Consequently, the introduction of porosity in equation 2.4 results in X**

values that are generally about a factor of 2.5 lower compared to X*. Therefore, analyzing the data from Zhang and Huck, (1996a) leads to the conclusion that BOM removal is nearly complete, i.e. > 90%, when X** is around 1. This means that BOM removal is nearly complete when the real contact time and the standard time for a biofilm to intercept substrate are about equal. This provides additional justification for the meaningfulness of the concept of X*. Huck (1997) has introduced the term biotime for X* and he extended the X* concept to distribution systems.

The contact time required in biological filters can vary over a substantial range, depending on the objectives. In general, longer contact times are required for the removal of chlorination by-product precursors and/or chlorine demand, compared to ozonation by-products and biological instability as measured by AOC (Prévost et al., 1990). Relatively good removals of ozonation by-products at EBCTs as short as 2-4 minutes have been reported, while the removals of BDOC, chlorine demand and chlorination by-products precursors require considerably longer EBCTs. In general, full scale biological rapid filters are designed for EBCTs below ~30 minutes.

Impact of Backwashing

Rapid filters (biologically operated or not) require periodic backwashing in order to reestablish their hydraulic capacity as well as their ability to collect particles. For successful operation of biofiltration the biomass level must be carefully managed during the filtration cycle and biomass losses during backwashing must be controlled. Therefore, optimized backwashing of biological single-stage filters, i.e. filters with the dual treatment goal of particle and BOM removal, necessitates carefully balancing the conflicting requirements of the backwashing process regarding the filter's function as particle collector and biological reactor.

Different investigations have emphasized the importance of backwashing on 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; Ahmad and Amirtharajah, 1995; Coffey et al., 1995b; Miltner et al., 1995; Prévost et al., 1995; Miltner et al., 1996). While certain treatment plants use non-chlorinated backwash water for their biological filters, others (particularly retrofitted plants) are operated with chlorinated backwash water.

For non-biological filters it has been shown that backwashing with water alone is an inherently ineffective process due to the limited collisions and abrasions among fluidized particles (Amirtharajah, 1978). A synthesis of more recent research on non-biological filters has established that the best removal of particles during backwashing is given by simultaneous use of air and water at subfluidization velocities to achieve collapse pulsing conditions (Amirtharajah et al. 1991; Amirtharajah, 1993). Ahmad and Amirtharajah (1995) indicated that backwashing with air scour, i.e. collapse pulsing conditions, was necessary to control long term headloss increases in biological filters. This was indirectly confirmed by data from others who observed an increase in clean bed headloss over time in biological filters backwashed without air-scour (Goldgrabe et al., (1993; Coffey et al., 1995b; 1996).

Servais et al. (1991) observed no major losses of biomass (as measured by ^{14}C-glucose oxidation) upon backwashing with air-scour. Similar findings for filters backwashed with and without air-scour were reported by others (Miltner et al., 1995; Wang 1995; Huck et al., 1998). However, others have found more significant losses of biomass during backwashing with (Lu and Huck, 1993) and without (Hozalski and Bouwer, 1998) air-scour.

In regards to BOM removal the available literature indicates that backwashing with non-chlorinated water does not impair the BOM removal capacity of biofilters immediately following backwash cycle (Miltner et al., 1995; Prévost et al., 1995; Carlson et al., 1996a; Coffey et al., 1996; Hozalski and Bouwer, 1998). In fact, several studies have shown that

BOM removal was slightly better immediately following backwashing (Prévost et al., 1995; Carlson et al., 1996a; Coffey et al., 1996). Prévost et al., (1995) advanced several hypotheses for this phenomenon including a decrease in the actual contact time due to floc loading and the effects of precipitated metals (coagulants) towards the end of a filter cycle.

Different studies have investigated the effects of chlorinated backwash water on biological rapid filters (Reckhow et al., 1992; Miltner et al., 1995; Miltner et al., 1996; Huck et al., 1998). There exist some conflicting results regarding the effects of chlorinated backwash water on biological performance, i.e. BOM removal, in biofilters. Some studies have demonstrated a relatively strong negative effect of the presence 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 (Miltner et al., 1995; 1996). Nevertheless, in other investigations the presence of free and combined Cl_2 in the backwash water of demonstration scale anthracite/sand and GAC/sand filters showed essentially no effect on BOM removal (Huck et al., 1998). The data from Miltner et al., (1996) showed that free Cl_2 in the backwash water (~1.6 mg Cl_2/L) had a stronger inhibitory effect on the removal of several BOM components and surrogates than did combined Cl_2 (~2 mg Cl_2/L).

Regarding the impact of Cl_2 in the backwash water of biological filters, the duration of the backwashing procedure, i.e. the period of Cl_2 exposure, is likely a relevant factor in addition to the Cl_2 concentration in the backwash water. These two factors, i.e. backwashing duration and [Cl_2] in the backwash water, could be quantified using a CT approach similar to the CT concept for disinfection. Thus vigorous backwashing for a short period of time, i.e. collapse pulsing followed by water wash, might be preferable to a long, less powerful backwashing procedure, i.e. water wash only, if the backwash water contains Cl_2 (Urfer et al., 1997).

In general, biological filters should be backwashed with chlorine-free water whenever this is economically feasible. In the absence of better information it is probably safe to include air-scour in the design of the filter backwashing procedure for such filters in order to control the potential increase of headloss over time.

Impact of Oxidants In Filter Influents

Although the presence of oxidants/disinfectants in the influent of biologically active filters represent an issue of concern regarding the biological performance of such filters, only very little literature is currently available.

In some cases, oxidant residuals, e.g. O_3, H_2O_2, Cl_2 and monochloramine (NH_2Cl), may be present at low levels in biofilter influents either continuously or intermittently. Because all of these oxidants are biocides at certain concentrations, their presence in biofilter influents will potentially have negative effects on the BOM-removal capability of biofilters. Biocides have a non-selective killing action on various microorganisms and such components therefore lack selective toxicity against different classes of microorganisms (Russell et al., 1997).

Regarding the influence of different oxidants on biofilms in biologically active filters, the filter medium is important: GAC decomposes Cl_2 and other oxidants through a redox reaction at the surface of the carbon, yielding carbon surface oxides which potentially serve as catalysts for the reaction (Sontheimer et al., 1988; Boere, 1991). Therefore, biological activity can be established in GAC filters even if the filter influent is chlorinated (Rice and Robson, 1982; DiGiano et al., 1992, LeChevallier et al., 1992). However, Cl_2 in the influent of GAC filters can lead to a structural deterioration of the GAC (Sontheimer et al., 1988). Additionally Cl_2 reacts with the GAC and different adsorbed organics, e.g. phenolic compounds and anilines, to form chlorinated organics not formed in the liquid phase (Snoeyink et al., 1981; McCreary et al., 1982; Voudrias et al.,

1985; Hwang et al., 1990). Therefore, the presence of Cl_2 in the influent of GAC filters should be avoided.

Hydrogen Peroxide

For advanced oxidation purposes, H_2O_2 is combined with O_3 (PEROXONE) or with ultraviolet (UV) light in order to promote the production of highly reactive OH-radicals (Staehelin and Hoigné, 1985; Glaze et al., 1987; Paillard et al., 1988; McGuire et al., 1991). In other cases H_2O_2 is dosed prior to the exit of a given ozone contactor in order to accelerate the natural O_3 decay prior to the following treatment steps (Griffini and Iozzelli, 1996; Schick et al., 1997). In certain waters H_2O_2 is formed as an oxidation by-product during ozonation (Staehelin and Hoigné, 1985; Xiong et al., 1992; Paillard, 1994; Weinberg and Glaze, 1997). Consequently, the influent of biological filters following ozonation/advanced oxidation is likely to contain residual concentrations of H_2O_2.

Hydrogen peroxide in high concentrations is bactericidal and similarly to hypochlorous acid (HOCl) the undissociated acid, i.e. H_2O_2, is a stronger biocide than the anion formed upon dissociation (Baldry, 1983). This is likely the result of the increased disinfectant permeability of the uncharged acid, i.e. H_2O_2 or HOCl, into the microorganisms (Jacangelo et al., 1987). However because of the high pK_a of hydrogen peroxide (pK_a = 11.6) this is not critical for drinking water applications where the pH normally varies between ~6-9. Alasri et al., (1992) showed that H_2O_2 was a relatively weak disinfectant because the inactivation of *Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa* with H_2O_2 required C*T-products about 3-4 orders of magnitude higher compared to free Cl_2. Baldry (1983) reported that H_2O_2 was bacteriostatic at concentrations above 0.15 mmole/L (5.1 mg/L) while others showed that H_2O_2 inhibited microbial growth in batch mixed cultures at concentrations of 3-30 mg/L (Pardieck et al., 1990). However, others have reported substantially higher H_2O_2 concentrations of 200-500 mg/L as the toxic limit for microorganisms (Lee et al., 1988). Goepfert et al. (1995) showed that the bactericidal activity of H_2O_2 on *E. coli* was low, however it was dramatically increased when H_2O_2 was combined with Cu^{2+}, probably as a result of the formation of free radicals, which acted as secondary disinfectants.

Numerous bacterial species can convert H_2O_2 to oxygen and water by the action of catalase and protect themselves by destroying external H_2O_2 (Campbell and Kimmick, 1966; Schlegel, 1977; Spain et al., 1989; Pardieck et al., 1990).

The effects of residual concentrations of H_2O_2 on the biological removal of BOM in biofilters is currently not well understood. In addition, the potential removal of H_2O_2 in biologically active filters is of importance because H_2O_2 in treated water is undesirable for several reasons, e.g. H_2O_2 residuals lead to Cl_2 consumption (Bader et al., 1988), and is regulated in certain cases, e.g. the limit of tolerance is 0.1 mg/L in tap water in Germany (Schick et al., 1997).

Chlorine

The continuous presence of free Cl_2 in the influent of the filtration step, such as is usually the case in conventional prechlorination plants, is known to prevent the establishment of a biofilm in such filters, particularly in anthracite/sand and sand filters. In certain biologically operated plants (no prechlorination) Cl_2 is periodically added ahead of sedimentation in order to control the excessive growth of certain microorganisms (e.g. algae) in uncovered sedimentation basins (Teefy, 1997). In such cases Cl_2 residuals are likely present in the influent of the filtration stage during the period of Cl_2-addition to the sedimentation basins.

McGuire et al., (1991) presented data indicating that chloramine residuals of approximately 1 mg/L in the influent of biological anthracite/sand filters inhibited the biological removal of aldehydes and AOC. In another investigation, concentrations of 3 mg/L of free and combined Cl_2 in the influent of a GAC filter had virtually no effect on the removal of AOC (LeChevallier et al., 1992). Free Cl_2 was rapidly reduced in the filter, whereas NH_2Cl was more stable and filter effluent NH_2Cl concentrations averaged 0.1 mg/L. There appear to exist major differences in the biocidal effects of free Cl_2 and NH_2Cl on biofilms, as NH_2Cl does not react with extracellular polysaccharides while free Cl_2

possibly does (LeChevallier et al., 1988). This may allow NH_2Cl to penetrate a biofilm and react with the microorganisms whereas free Cl_2 is consumed before it can fully penetrate the biofilm surface (LeChevallier et al., 1988; 1992; LeChevallier and Lowry, 1990). Different authors showed that the reaction rate of free Cl_2 with cellular biomass was fast enough that diffusion of Cl_2 into the biofilm became rate limiting (DeBeer et al., 1994; Chen and Stewart, 1996).

Ozone

Several authors have observed that the continuous presence of O_3 residuals of ~0.1-0.3 mg/L in the influent of pilot scale anthracite/sand filters inhibited bacterial development and therefore reduced biofiltration performance (Huck et al., 1991; Weinberg et al., 1993). In the case of GAC filters, the data from Weinberg and colleagues showed that the biological aldehyde removal in such filters seemed to be essentially unaffected by the presence of O_3 residuals in the filter influent, likely as a result of the rapid reduction of the O_3 on GAC. Kaur et al. (1991; 1992) showed that approximately 90% of a *Pseudomonas fluorescens* biofilm grown on a glass surface simulating a heat exchanger was removed due to exposure to 0.04 - 0.07 mg O_3/L for periods of 2 - 6 hours. In a recent publication, Jans and Hoigné (1998) have shown that the contact of ozonated water with GAC leads to the formation of OH-radicals, similarly to O_3 combined with H_2O_2 or UV. Based on these results, they suggested the combination of O_3 and GAC as a new advanced oxidation process (AOP).

SUMMARY

A relatively large amount of literature has been published in the field of drinking water biofiltration during the last two decades. This is primarily the indirect result of the recent awareness of the shortcomings of the traditionally used prechlorination for disinfection and/or treatment of ammonia, i.e. breakpoint chlorination. This led to an

increased interest in ozone as a primary disinfectant and indirectly to the investigation of biological filtration as a treatment step for the increased BOM levels in the effluent of ozonation.

The most fundamental process considerations of biological filtration at pseudo steady-state are relatively well established at the present time. These include the impacts of contact time within the biological filters, the effects of hydraulic loading and the impacts of filter media on biological performance, i.e. BOM removal. However, the influence of several other factors on the BOM removal capability of biofilters are not sufficiently understood at the present time. Such factors include the impacts of temperature, the effects of the presence of oxidants in the biofilters, the impacts of biofiltration on headloss buildup, the effects of different backwashing strategies, the morphological conditions of biofilms in drinking water biofilters and mass transfer limitations.

The future investigation of those issues appears to be necessary for the optimization of biofiltration considering the overall treatment goal of producing high quality drinking water at the consumer's tap. Also, an improved knowledge of those topics will allow the further development of mechanistic modeling in the field of BOM degradation in biofilters. In general, such research activities are important because biological rapid filtration is likely to become a more widely used process step in North America and elsewhere in the future.

CHAPTER 3: MATERIALS AND METHODS

This chapter provides detailed information on the experimental setup, the operational procedures and the analytical methods used throughout the experiments described in Chapters 4-6. Procedures and analytical methods which were specifically employed for a given experiment are described in the "Materials and Methods" section of the relevant chapter.

EXPERIMENTAL DESIGN

Experiments were performed at bench scale using a set of several parallel custom-made glass filter columns (Lasalle Scientific Inc. Guelph, ON). The effects of the different oxidants on BOM removal in the filters were investigated by comparing the biological performance of filters dosed with oxidants under various conditions, with a parallel filter which received no oxidant (control). For the purposes of this research and considering the duration of each experiment, this approach seemed more appropriate than a factorial type of experimental design. The experimental design in terms of filter operation and design, e.g. media depth, hydraulic loading, backwashing conditions, BOM influent concentrations, oxidant influent concentrations, etc., was generally intended to simulate full scale conditions as closely as possible.

In most cases the filter media used was anthracite over sand, because the negative effects of oxidants on BOM removal were expected to be more critical in such filters

compared to GAC/sand (cf. Chapter 2). The minimal duration of the experiments 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 (e.g. Servais et al., 1994). Five experiments were performed in total, a summary of the experimental conditions for each of these experiments is provided in Table 3.1.

Table 3.1: Summary of experimental conditions for the different experiments.

Experiment	No. of Filters, (media)	Oxidant, Conditions of Dosage	Duration (months)
H1	2, (A/S)[§]	H_2O_2, ~1 mg/L in influent continuously (F2)	4
H2	2, (A/S)	H_2O_2, ~5 mg/L in influent continuously (F2)	2
C1	4, (3 A/S and 1 GAC/S)[‡]	free Cl_2, ~0.5 mg/L in influent of A/S (F3) and GAC/S (F4) continuously, ~0.5 mg/L in A/S periodically (6 hours/week) (F2)	3
C2	4, (A/S)	free Cl_2, ~0.2 mg/L in influent of A/S continuously (F2), ~1 mg/L of free (F3) and combined (F4) Cl_2 in backwash water	3
O1	4, (A/S)	O_3, ~0.15 mg/L (F4) and H_2O_2, ~0.4 mg/L (F3) in influent periodically (1-2 times per week for ~1 hour)	2

[§] anthracite/sand filter
[‡] granular activated carbon/sand filter

FILTRATION APPARATUS

The filters were fed with dechlorinated tap water and were operated in the NSERC Chair laboratory at the University of Waterloo. All materials in contact with the water were either glass, stainless steel or inert fluorocarbons. The schematics of the experimental setup of the different experiments are shown in the "Materials and Methods" section of Chapters 4-6. The filters were held in a wooden frame, which was placed on and attached to a

laboratory bench. The filters were covered and insulated in order to prevent the growth of phototrophic organisms, e.g. algae, and to minimize temperature variations.

Dechlorination

Dechlorination of the tap water was achieved through upflow filtration of the water through GAC-containing standard glass chromatography columns (Kontes Chromaflex™, Vineland, NJ) with an internal diameter (ID) of 48 mm and 600 mm in length. These columns were filled with exhausted GAC (F-300, Calgon Corp., Pittsburgh, PA) from the top of a full-scale filter at the Mannheim water treatment plant in Kitchener, ON. At the time of GAC sampling the GAC filter had been in operation for about two years and therefore had had a throughput of considerably more than 40,000 bed volumes. Consequently the GAC's adsorptive capacity for NOM was likely exhausted. The EBCT of the water in the dechlorination columns was about 2 minutes in experiments H1, H2, C1 and C2 (cf. Table 3.1), whereas in experiment O1 an additional 2 minutes of EBCT was provided (cf. Chapter 6). The dechlorination filters were also covered with black insulation material in order to prevent phototrophic growth and control temperature fluctuations.

Filter Columns

The ID of the filter columns was 50 mm and was selected considering that wall effects can usually be minimized when the ratio of the column diameter to the media diameter is ≥ 50 (Lang, 1982). Therefore, with a media diameter of ~1 mm, an ID of 50 mm represented the minimal column diameter allowing the minimization of wall effects. A schematic of the filter columns is shown in Figure 3.1. A total of seven sampling ports allowed withdrawal of liquid and media samples at different depths within the filters (Figure 3.1).

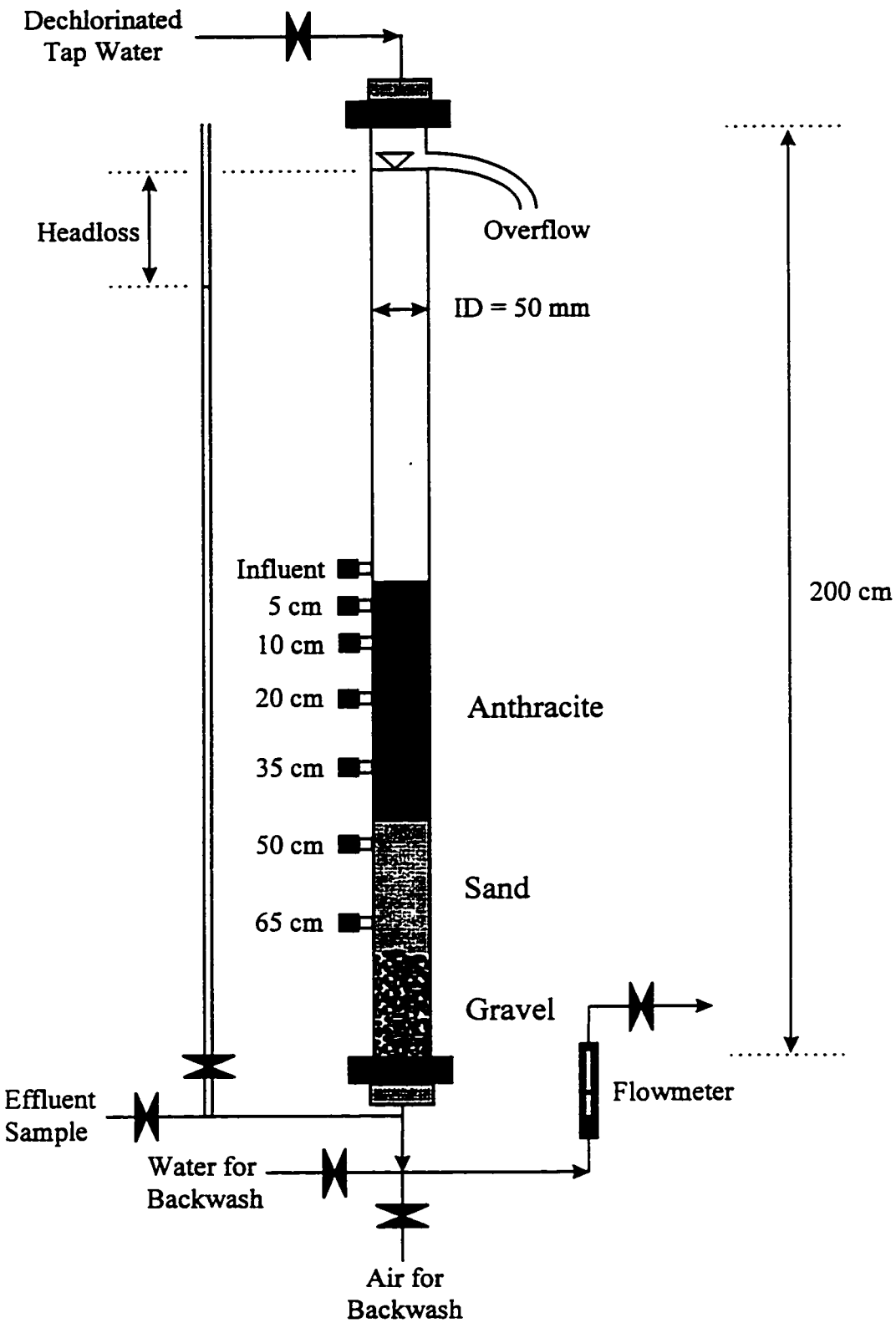

Figure 3.1: Schematic of filter column setup (not to scale)

Liquid sampling was performed by piercing the rubber septum of the screw cap of a given sampling port with the tip of a reusable 50 mL glass syringe (Becton Dickinson, Franklin Lakes, NJ), and liquid samples were drawn into the syringe. For the sampling of filter media, the filters were drained and the screw caps were opened and media was withdrawn with a small laboratory scoop.

Specifics of the filter media used in the different experiments are listed in Table 3.2. At the beginning of each experiment the used media from the previous experiment was removed from the filters, the filters were cleaned and new (biomass-free) media was placed into the columns. Media breakthrough was prevented by a support bed of approximately 200 mm of graduated gravel (Figure 3.1).

Table 3.2: Filter media specifics

Experiment	Media	Media Depths (mm)	Effective Size (mm)	Uniformity Coefficient (-)	Particle Density (g/cm^3)
H1	anthracite:	500	1-1.1	1.5	1.6
	sand:	250	0.45-0.5	1.4	2.6
H2	anthracite:	500	1-1.1	1.5	1.6
	sand:	250	0.45-0.5	1.4	2.6
C1	anthracite:	450	1-1.1	1.5	1.6
	GAC*:	450	0.8-1.0	2.1	0.86
	sand:	250	0.45-0.5	1.4	2.6
C2	anthracite:	450	1-1.1	1.5	1.6
	sand:	250	0.45-0.5	1.4	2.6
O1	anthracite:	450	1-1.1	1.5	1.6
	sand:	250	0.45-0.5	1.4	2.6

*Filtrasorb 300, Calgon Corp., Pittsburgh, PA, same GAC as used for dechlorination (exhausted), oven-dried before use at 100°C in order to inactivate biomass

In all experiments the filters were operated at a hydraulic loading of 7.5 m/h (3 gpm/ft^2) corresponding to a total EBCT of 6 minutes in experiments H1 and H2 and 5.6 minutes in experiments C1, C2 and O1. The hydraulic loading chosen (7.5 m/h) is in the common range of full scale rapid filters (Montgomery, 1985) and the resulting EBCT of 5.6-6.0 minutes in the filters is in the high range of what might be encountered in single-stage biological filters at full scale, i.e. filters with the dual treatment goal of particle and BOM removal. The hydraulic loading of the filters was adjusted using direct reading flowmeters (Gilmont® Instruments, Barrington, IL), as shown in Figure 3.1. The filters were operated in constant head, decreasing flow mode, although the decrease of the flow during a filter cycle, i.e. between two backwashes, was usually small (~10%) as a result of the absence of a significant amount of particles in the filter influent.

Backwash

Although backwashing would not have been necessary from the perspectives of headloss buildup or particle breakthrough, the filters were backwashed about twice per week on average. This was done in order to simulate the operation of full scale biofilters in practice as closely as possible. Each filter was backwashed with its own effluent in order to prevent the introduction of unfamiliar organisms (particularly bacteria) into the specific bacterial community of a given filter operated under specific conditions. The backwash water, i.e. filter effluent, was collected in 20 L glass carboys, which were usually filled immediately before backwash. Backwashing was performed manually and the procedure was identical during all experiments listed in Table 3.1. The procedure was as follows:

1. drain the filters until the water level reaches 5-10 cm above the top of the media;
2. air scour: water at subfluidization velocity (12 m/h, corresponding to 40% of the minimum fluidization velocity, v_{mf}) simultaneously with air (60 m/h) for 2.5

minutes, i.e. until the water level in the columns reached about 20 cm below the overflow (Figure 3.1);

3. water only at 54 m/h, in order to obtain a bed expansion of 40-50%, duration: 4 minutes.

This backwashing procedure required a water volume of approximately 10 L per filter. Water from the carboys was pumped through the filter columns with a peristaltic pump (Masterflex L/S, 600 rpm, Cole-Parmer, Vernon Hills, IL) using PharMed® tubing (Norton Co.). Air was provided from a tank containing oil-free pressurized air and the air flowrate was adjusted with a direct reading flowmeter (Gilmont® Instruments, Barrington, IL). The conditions for collapse pulsing backwashing were calculated based on the recommendations from Amirtharajah et al. (1991).

FEED WATER

The feed water of the filter columns was dechlorinated tap water to which a cocktail of BOM, nitrogen and phosphorus was added. The filters were therefore inoculated with the bacteria naturally present in this water. The tap water at the University of Waterloo is local groundwater, which is low in organics and high in alkalinity and hardness. This water normally did not contain measurable concentrations of aldehydes, however in several samples low concentrations of acetate and formate (20-30 μg/L) were measured.

During the course of this research a change in the tap water quality occurred, likely because the University of Waterloo received water from different sources before and after the change. The change occurred during experiment C2 and further details regarding the principal water quality parameters that were affected will be discussed in Chapter 5. Typical characteristics of the tap water before the water quality change were as follows: pH: 7.4-7.5, TOC: 1.0-1.1 mg/L, alkalinity: 300-325 mg/L as $CaCO_3$, hardness: 325-350 mg/L as $CaCO_3$, temperature: 12°C - 16°C, conductivity: 1300-1400 μS.

Organic carbon, nitrogen (as $NaNO_3$-N) and phosphorus (as K_2HPO_4-P) were dosed to the influent of the filters with a peristaltic pump (Masterflex L/S, 100 rpm, Cole-Parmer, Vernon Hills, IL) using PharMed® tubing. BOM, nitrogen and phosphorus were added at a ratio of C:N:P of 15:5:1 (w/w/w) in order to guarantee that organic carbon was the limiting nutrient (Metcalf and Eddy, 1991; Goel et al., 1995). Other essential components for microbial growth were assumed to be present in sufficient amounts in the tap water. The BOM and N/P solutions were prepared in autoclaved ultrapure water (Milli-Q, Millipore Corp., Bedford, MA) and were kept in previously autoclaved amber glass bottles. These bottles were equipped with 0.2 μm PTFE air filters (Gelman, Lot No. 5300) in order to prevent the introduction of bacteria from the air. The flowrate and the concentration of these feed solutions were adjusted such that the content of one bottle, i.e. 4 liters, was sufficient for one week of filter operation, when fresh solutions were prepared. The feed solutions were added to the filter influent just after the dechlorination GAC columns and ahead of a static in-line mixer (Koflo Co., Cary, IL).

BOM-COCKTAIL

The BOM cocktail was largely based on ozonation by-products because ozonation and biofiltration are closely related processes, as mentioned previously, and because the presence of H_2O_2 and O_3 residuals in biofilter influents is relevant if biofiltration follows ozonation. For reasons of comparison between the different experiments and oxidants, the BOM cocktail was identical for all five experiments. The cocktail contained four components (two aldehydes and two carboxylic acids), which are common ozonation by-products (e.g. Glaze and Weinberg, 1993; Gagnon et al., 1997). For aldehydes, formaldehyde and glyoxal were chosen, as these two components represent a relatively easily biodegradable and a less readily biodegradable aldehyde (Krasner et al., 1993) respectively. For carboxylic acids, formate and acetate were selected because they seem to be formed in largest yields upon ozonation together with oxalate (Griffini and Iozzelli,

1996; Gagnon et al., 1997). Oxalate was not included in the BOM cocktail, because at the time these experiments were performed the analytical method used for the quantification of carboxylic acids (Peldszus et al., 1996) did not permit the quantification of oxalate. The target concentrations of the different BOM components in the influent of the filters were: formaldehyde 100 µg/L, glyoxal 30 µg/L, formate 400 µg/L and acetate 300 µg/L. Those concentrations are in the high range of what is usually observed following ozonation. The addition of the BOM cocktail at these concentrations yielded a target BDOC filter influent concentration of 0.28 mg/L.

The choice of relatively easily biodegradable substances, i.e. carboxylic acids and aldehydes, is considered to represent a best case approach for the assessment of the inhibitory effects of oxidants on BOM removal in biofilters. If a given oxidant concentration were to inhibit the removal of carboxylic acids and aldehydes in a major way, it could be hypothesized that the effect of that oxidant concentration on the removal of less rapidly biodegradable components, such as those quantified by BDOC measurements for example, would be even more pronounced.

ANALYTICAL METHODS

All analyses were performed in the laboratory of the NSERC Chair in Water Treatment at the University of Waterloo.

Nonpurgeable Organic Carbon and UV Absorbance

Nonpurgeable organic carbon (NPOC) or TOC was measured using a Xertex Dohrmann DC-180 Total Carbon Analyzer. The method used (5310 C Total Organic Carbon/ Persulfate Oxidation Method) was as described in APHA, AWWA, WEF (1992). Each result was the average of two determinations. NPOC samples were analyzed by Lillian Liao or Valerie Goodfellow. UV absorbance at 254 nm was determined on a UV spectrophotometer (HP 8453, Hewlett-Packard, Palo Alto, CA) in a 1 cm quartz cell without any sample preparation. The instrument was zeroed with ultrapure (Milli-Q) water.

Carboxylic Acids

Carboxylic acids were analyzed by ion chromatography as described by Peldszus et al. (1996). Water samples were directly injected into the ion chromatograph without any sample preparation step. A high capacity anion exchange column (AS 10, 250 * 4 mm ID, Dionex, Sunnyvale, CA) was used followed by conductivity detection. The method detection limits (MDLs) for the different organic acids are between 1 and 5 μg/L (Peldszus et al., 1996). Immediately after sampling 0.1% (v/v) of chloroform was added to the water sample in order to prevent bacterial decomposition of the carboxylic acids during storage. This allowed sample storage of up to 2 weeks at 4°C without substantial losses of carboxylic acids. The basic method (Peldszus et al., 1996) provides good separation of several organic acids. This method has recently been improved in order to quantitatively determine oxalate, which is commonly formed during ozonation, in addition to the other organic acids (Peldszus et al., 1998). For further information regarding the determination of carboxylic acids the interested reader may consult Peldszus et al. (1996; 1998).

Aldehydes

The analysis of aldehydes was performed using the standard GC/ECD method (Sclimenti et al., 1990; APHA, AWWA, WEF, 1995) with minor modifications. Samples were collected in 20 mL EPA vials containing 1 mL of o-2,3,4,5,6-pentafluorobenzyl-hydroxylamine (PFBHA) (6 mg/mL) and derivatized overnight at room temperature to form oxime derivatives. These vials also contained mercuric chloride ($HgCl_2$), which was used to prevent bacterial decomposition of aldehydes and ammonium chloride (NH_4Cl_2) used to convert potentially present free Cl_2 to chloramines. The derivatives were extracted from the water with hexane, washed with 0.1 M H_2SO_4 and the organic solvent was transferred to vials containing ~20 mg Na_2SO_4. These vials were stored in the freezer at -20°C until analysis. The aldehyde samples were analyzed by GC/ECD (HP 5890 series II,

Hewlett-Packard, Sunnyvale, CA). The MDLs for formaldehyde, acetaldehyde, glyoxal and methyl-glyoxal were determined in our lab previously and were in the range of 1-2 μg/L.

Theoretical Oxygen Demand

The theoretical oxygen demand (ThOD) was used as an index parameter for the summation of the acetate, formate formaldehyde and glyoxal data. The chemical oxygen demand is an estimator of the energy available for the metabolic needs of the substrate degrading bacteria (Stumm and Morgan, 1981). Therefore, the ThOD is likely a more appropriate surrogate for the summation of different organic components than organic carbon on a weight basis, i.e. μg organic C/L. The ThOD of each component was calculated based on the following stoichiometric equations and the total ThOD was computed as the sum of the ThOD of each component.

Acetate: $$CH_3COO^- + H^+ + 2O_2 \Rightarrow 2CO_2 + 2H_2O \quad (3.1)$$

Formate: $$HCOO^- + H^+ + 0.5O_2 \Rightarrow CO_2 + H_2O \quad (3.2)$$

Formaldehyde: $$H_2CO + O_2 \Rightarrow CO_2 + H_2O \quad (3.3)$$

Glyoxal: $$H_2C_2O_2 + 1.5O_2 \Rightarrow 2CO_2 + H_2O \quad (3.4)$$

Based on equations 3.1-3.4 and considering that oxygen consumption is directly related to energy gain by the aerobic bacteria (Stumm and Morgan, 1981), the degradation of equal amounts (on a weight basis) of acetate, formaldehyde and glyoxal will lead to an energy gain about a factor of 2-3 higher compared to formate.

In the case of BOM component measurements it is therefore important to account for the differences in the energy gain associated with the bacterial degradation of different components. As an example, the significance of a finished water concentration of 50 μg/L of acetate or oxalate is substantially different from a bacterial regrowth point of view. This is nicely illustrated by data reported by van der Kooij (1990), which show maximum heterotrophic plate counts (HPC) as a function of acetate and oxalate concentrations. For identical concentrations of these two components the data indicate that the maximum HPC

counts are over a factor of four higher for acetate compared to oxalate. This is directly related to the fact that the ThOD of acetate is over a factor of five higher than that of oxalate.

Viable Biomass

Biomass in the filters was measured using the phospholipid method (Findlay et al., 1989). This method was initially developed for the measurement of biomass in sediments (e.g. White et al., 1979) and has been recently adapted and used for the measurement of biomass in biologically active filters (e.g. Wang et al., 1995; Miltner et al., 1995; Carlson et al., 1996; Moll and Summers, 1997). The method quantifies the amount of phosphate contained in the phospholipid of a given sample of biomass. All cells contain phospholipids in their membranes (Vestal and White, 1989) and the phospholipids are found in relatively constant amounts in bacterial cells occurring in nature (White, 1993). Because the phospholipids are not stored but are turned over relatively rapidly during metabolism, they represent the viable biomass (White et al., 1979). The analytical procedure used for the measurement of phospholipid biomass is shown in Figure 3.2.

For the extraction of the lipids, the biomass sample was exposed to a single-phase mixture of chloroform, methanol and water followed by the addition of additional chloroform and water in order to separate the phases as originally described by Bligh and Dyer, (1959). This method allows the separation of all the lipids from the non-lipids in that the total lipid fraction will be found in the chloroform layer, whereas the more polar proteins, nucleic acids, cell walls and other components remain in the methanol-water phase (Bligh and Dyer, 1959; Vestal and White, 1989).

The extraction was followed by the digestion of the phospholipids in order to yield phosphate, which was quantified using a photometric method described by van Veldhoven and Mannaerts (1987). Phosphate was quantified at a wavelength of 610 nm in a 1 cm quartz cell using a spectrophotometer (HP 8453, Hewlett-Packard, Palo Alto, CA).

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), 5 mL 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_2O) 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 on heating plate

QUANTIFICATION

10. Let cool then add 0.2 mL of ammonium molybdate solution (2.5% $(NH_4)_6Mo_7O_{24}$-$4H_2O$ 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

⇓

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

⇓

12. 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

A calibration curve established with inorganic phosphate, i.e. K_2HPO_4, was used to convert absorbance at 610 nm to nmole P. The calibration curve, which is shown in Appendix A, was linear in the range from 0 to 40 nmole P. The use of K_2HPO_4 instead of a phospholipid containing substance for the establishment of the calibration curve was thought to be acceptable because it has been demonstrated that the phospholipid method allowed the quantitative recovery of the phosphate contained in such substances (Findlay et al., 1989). Others have also used inorganic phosphate for the establishment of calibration curves for this method (e.g. Wang 1995; Moll 1996). Following extraction, the media samples were oven-dried at 100° C overnight and weighed in order to express the results as nmole lipid P/g of media. Apparent filter density values from the literature were used to convert nmole lipid P/g of media to nmole lipid P/cm^3 of filter. The following densities were used for these conversion: 0.43 g/cm^3 for GAC, 0.8 g/cm^3 for anthracite and 1.5 g/cm^3 for sand. The amount of biomass per unit volume of filter may be a more meaningful parameter for filter performance than the amount of biomass per mass of media (Urfer et al., 1997).

Hydrogen Peroxide

Hydrogen peroxide was analyzed using the method of Bader et al., (1988). For this photometric method N,N-diethyl-p-phenylenediamine (DPD) is oxidized by hydrogen peroxide using horseradish peroxidase (POD) as a catalyst. The formed radical cation $DPD^{\cdot+}$ has a fairly stable color which is measured at 551 nm. The method is very specific and sensitive, allowing the measurements of low concentrations of H_2O_2 (low µg/L range).

Briefly, 2.7 mL of sample, 0.3 mL of phosphate buffer (0.5 M Na_2HPO_4 and 0.5 M NaH_2PO_4) were added directly into a 1 cm quartz cell using Eppendorf® pipettes. To this, 50 µL of DPD reagent (10 mg/mL of 0.1 n H_2SO_4) and 50 µL of POD solution (110 units/mL DI water) were added in rapid succession. Absorbance at 551 nm was measured in a spectrophotometer (HP 8453, Hewlett-Packard, Palo Alto, CA) exactly 60 seconds following the addition of POD. The absorbance (at 551 nm) of the sample containing all

reagents except POD was measured and considered for the calculation of the absorbance of the H_2O_2-containing sample.

A calibration curve was established using laboratory grade hydrogen peroxide (BDH Inc., Toronto, ON) diluted in Milli-Q water. The concentration of the H_2O_2 stock solution was determined by titration with $KMnO_4$. As a secondary method, the UV absorption of H_2O_2 at 240 nm ($M = 40\ M^{-1}cm^{-1}$) was used for the analysis of the stock solution (Bader et al., 1988). The calibration curve, which is shown in Appendix A, was linear up to a concentration of ~2 mg/L of H_2O_2. Samples containing H_2O_2 concentrations above 2 mg/L were diluted with Milli-Q water using Eppendorf® pipettes. The error associated with this procedure was verified several times by diluting a H_2O_2 standard of 5 mg/L by a factor of three, followed by the photometric determination of the H_2O_2 concentration. It was found that the error was small. Therefore it was concluded that the dilution procedure was acceptable for the purposes of this research.

Chlorine

Free and total chlorine were measured with a commercially available colorimetric method (Hach Company, Loveland, CO) based on the DPD-method (APHA, AWWA, WEF, 1992). In parallel and particularly for filter influent and effluent samples, the standard amperometric titration method was used (APHA, AWWA, WEF, 1992). In general, the results obtained with the two methods were in good agreement.

Dissolved Oxygen

Dissolved oxygen (DO) was measured with a common DO-probe (ATI Orion, model 835, ATI Orion, Boston MA). Water samples were collected headspace-free in BOD-bottles and DO was directly measured in these bottles. During the measurement the water sample was continuously stirred and the DO-value was recorded after a stabilization period of 2-3 minutes.

Headloss

Total headloss through the filter bed was quantified using a glass tube connected to the effluent of the filters (Figure 3.1). Total headloss was determined as the difference between the water level in the glass tube under static conditions (no flow through the filter) and the level under the specific flow conditions of the filter. Headloss measurements were usually performed immediately before backwash, i.e. terminal headloss, and immediately following backwash, i.e. clean bed headloss. Throughout this thesis, results of headloss are expressed as cm of water.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

This section summarizes the QA/QC measures which were taken in order to ensure the quality of the data presented in Chapters 4-6.

Carboxylic Acids

Samples for the quantification of carboxylic acids were handled with great care as the contact of samples with the skin was shown to lead to considerable contamination, particularly with respect to acetate. Latex gloves were always worn during sampling and sample preparation for quantification in the IC. In order to prevent contamination in the dishwasher, all sample vials used for carboxylic acids were washed using a special program which did not contain acid rinse with acetic acid. In addition, these vials were always rinsed two times with Milli-Q water immediately prior to sampling. A large majority of carboxylic acid samples was sampled in duplicate. The average acetate and formate concentrations of such duplicate determinations generally had a low variability. This is shown by the error bars (± 1 standard deviation) in the different graphs showing carboxylic acid data throughout this thesis.

Method blanks and standards in DI and/or in tap water were included in each sample run. Standards were prepared from a 100 mg/L stock solutions. Usually, 200 µg/L standards were prepared because this concentration was about in the middle of the concentration range of the samples. The standard contained (in order of elution):

hydroxybutyrate, acetate, glycolate, butyrate, formate, pyruvate and ketobutyrate. One standard every ten samples was included in the sample runs and the replicate analysis of the acid concentrations in the standard were generally very similar.

Aldehydes

The PFBHA used for the derivatization of the aldehydes was prepared fresh before each sampling of aldehydes. All samples were normally collected in duplicate. It was found that variabilities were low for duplicate formaldehyde samples, however, a much higher variability was usually observed for glyoxal. Glyoxal concentrations were determined by adding the area counts of the two glyoxal isomers, i.e. glyoxal-E and glyoxal-Z, and concentrations were calculated based on a calibration curve. The reasons for the high variability of the glyoxal results is not currently understood. Because of the scatter in the glyoxal data, the aldehyde results throughout this thesis emphasize the formaldehyde results. Because glyoxal was dosed to the filter influent at relatively low concentrations (target = 30 μg/L) compared to the other BOM components, this was considered of no major importance.

Standards containing formaldehyde and glyoxal were analyzed during each sample run at a frequency of one standard every ten samples. Two standards were usually prepared, i.e. 50 μg/L and 100 μg/L, in DI-water. The hexane used for the extraction of the derivatized aldehydes contained 100 μg/L of dibromopropane, which served as internal standard.

Viable Biomass

Special care was taken to assure the quality of the biomass results. All biomass samples were taken in duplicate and the variability of such duplicate samples was in general low, i.e. coefficient of variability (CV) between 5 and 10%, considering the

potential natural variability in the amount of biomass at a given filter depth (e.g. Carlson and Amy, 1995).

The use of clean, i.e. phosphate-free, glassware, represents a factor of particular importance regarding the measurement of biomass with the phospholipid method. Therefore, new glassware was used for the phospholipid analysis and this glassware was used only for this purpose. Sampling vials were washed manually with a phosphate-free laboratory detergent (Extran 3000) and extensively rinsed with tap water (10x) followed by Milli-Q water (10x). These procedures usually led to the absence of phosphate contaminated glassware.

Blanks, i.e. biomass-free media, were analyzed on several occasions and the results were comparable with the results reported by others (Wang 1995). Standards of inorganic phosphate (K_2HPO_4) were periodically analyzed in parallel with the samples in order to verify the quantification step.

Hydrogen Peroxide

Hydrogen peroxide samples were periodically analyzed in duplicate and the results of such measurements always showed a low variability, i.e. CVs were usually < 5%. Hydrogen peroxide standards were periodically analyzed in parallel with the samples in order to verify the quantification step.

Based on 9 replicate measurements of a sample with a low H_2O_2 concentration, the MDL was estimated as 2.9*standard deviation = 3 µg/L (8 degrees of freedom) (APHA, AWWA, WEF, 1995).

Chlorine

Chlorine samples were periodically analyzed in duplicate using the photometric method (Hach Company, Loveland, CO) and CVs of such determinations were between 5 and 10%. The MDL of this method was determined by the replicate measurement (n=13) of a sample at a Cl_2-concentration close to the anticipated MDL. Using this approach, the

MDL was estimated as 2.7 times the standard deviation (APHA, AWWA, WEF, 1995) resulting in 0.03 mg Cl_2/L with 12 degrees of freedom.

CHAPTER 4: EFFECTS OF HYDROGEN PEROXIDE RESIDUALS ON BIOFILTER PERFORMANCE*

INTRODUCTION

Ozonation and biological rapid filtration are two closely related processes, as has been discussed in some detail in Chapter 2. In advanced oxidation processes (AOPs), hydrogen peroxide is combined with ozone (PEROXONE) or with ultraviolet (UV) light in order to promote the production of highly reactive hydroxyl radicals (e.g. Glaze et al., 1987). In other applications H_2O_2 is dosed prior to the effluent of a given ozone contactor in order to accelerate ozone decay prior to the following treatment steps, e.g. biofiltration (Griffini and Iozzelli, 1996). In addition, H_2O_2 is formed as an ozonation by-product in many types of water (e.g. Staehelin and Hoigné, 1985; Paillard, 1994). Glaze et al. (1987) have observed reasonable oxidation rates of trichloroethylene using H_2O_2 with UV radiation, but hydrogen peroxide accumulated to unacceptable concentrations (about 2 mg/L) in the reactor effluent. Based on these results they concluded that H_2O_2/UV was

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unlikely to be a practical process for drinking water treatment until the problem of the high H_2O_2 residuals was solved.

Consequently, ozonation/AOP effluents may contain residual concentrations of H_2O_2 in certain cases and if biofiltration follows such process steps, H_2O_2 residuals would be present in the influent of the biofilters. Hydrogen peroxide is a biocide at certain concentrations, as discussed in Chapter 2. Therefore, knowledge of the potentially negative effects of H_2O_2-residuals in biofilter influents represents an issue of concern regarding biofiltration performance, i.e. BOM removal. In addition, the potential removal of H_2O_2 in biologically active filters is of importance because H_2O_2 in treated water is undesirable for several reasons and is regulated in certain cases, as mentioned in Chapter 2.

In this chapter the results of experiments H1 and H2 (Table 3.1) are reported and discussed.

OBJECTIVES

The overall objective of the experimental work described in this chapter was the investigation of the potential negative effects of H_2O_2 residuals in the influents of anthracite/sand filters on the removal of easily biodegradable BOM components. Specific goals of the study included:

- to determine the H_2O_2 concentration range for which the removal of selected easily biodegradable BOM components was substantially inhibited when H_2O_2 was present continuously in the biofilter influent;
- to assess the potential removal of H_2O_2 in the biofilters and to hypothesize the removal mechanism;
- to study the effects of H_2O_2 residuals in biofilter influents on the accumulation of viable biomass in the filters and

- to evaluate the time required for the establishment of a biofilm capable of degrading specific easily biodegradable organic ozonation by-products.

MATERIALS AND METHODS

Filtration Setup

Detailed information regarding the filtration setup has been provided in Chapter 3. For both experiments discussed in this chapter, i.e. H1 and H2 (Table 3.1), two filter columns were operated in parallel, filter 1 served as control and filter 2 received ~1 mg/L of H_2O_2 continuously (H1) and ~5 mg/L of H_2O_2 continuously (H2). Except for the presence of H_2O_2 residuals in filter 2, both filter columns were operated identically. A schematic of the filtration setup for the two experiments is shown in Figure 4.1. A filter influent concentration of ~1 mg/L of H_2O_2 (experiment H1) was selected as being in the range of the probable maximum value that would be encountered in full scale plants using PEROXONE. The target influent H_2O_2 concentration in experiment H2, i.e. ~5 mg/L, is high for typical drinking water conditions, however such levels may be encountered in the effluent of AOPs such as UV/H_2O_2 (Glaze et al., 1987; Andrews et al., 1995).

In order to investigate the possibility of a chemical reaction between H_2O_2 and filter media, the two filter columns were emptied at the end of experiment H1 and refilled with media for a brief experiment. Filter 1 was filled with fresh (biomass-free) anthracite/sand and filter 2 was filled with exhausted GAC (same GAC as used in the dechlorination columns, cf. Chapter 3) over sand with identical media depths as filter 1. Prior to the experiment, the GAC was oven dried at 105°C for 24 hours in order to eliminate any biomass. Both columns were operated at a hydraulic loading of 7.5 m/h and were dosed with H_2O_2 yielding an influent concentration of approximately 1 mg/L. Sampling was performed about 5 hours after the start of the experiment.

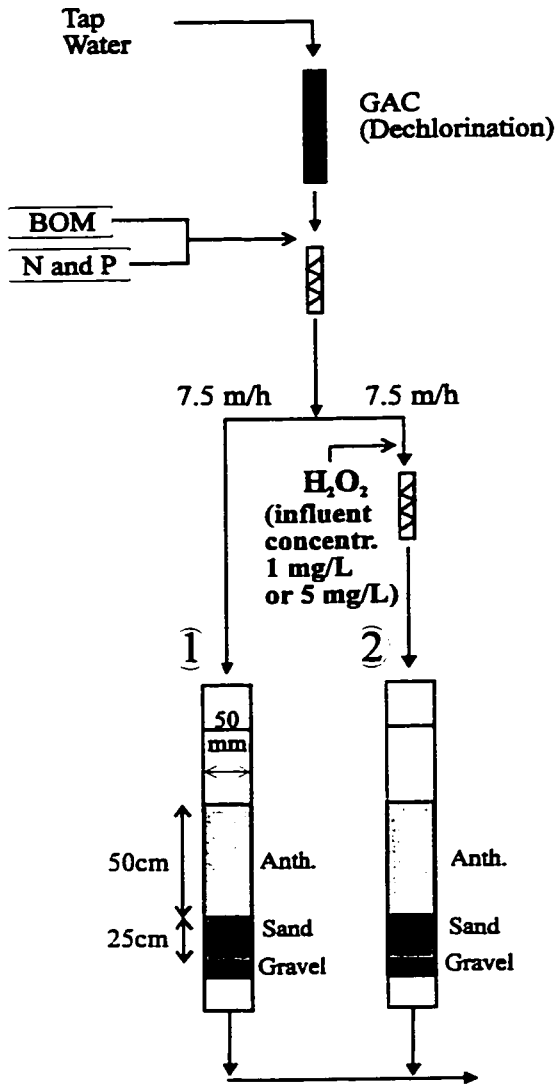

Figure 4.1: Experimental setup for experiments H1 and H2

Analytical Methods

The analytical methods for carboxylic acids, aldehydes, ThOD and phospholipid biomass have been described in detail in Chapter 3. No aldehyde and biomass data are available for experiment H1, therefore the results of this experiment focus on the biological degradation of carboxylic acids and the removal of H_2O_2 in the biofilters.

RESULTS AND DISCUSSION

Error bars shown in the figures of this chapter represent ± 1 standard deviation of duplicate samples unless otherwise noted.

Experiment H1

Operation of the filters was started on May 7, 1996 (Day 0). Nutrients (BOM, N and P) as well as H_2O_2 (for filter 2 only) were added to the column influent water from the beginning of the experiment in order to assess the effects of H_2O_2 on the establishment of a BOM-removing biofilm.

Removal of BOM Components

Figures 4.2 and 4.3 represent the concentrations of acetate and formate vs. EBCT in filter 1, which served as control filter (no H_2O_2 added). Because of time constraints, these samples were not routinely analyzed in duplicate and therefore no error bars are shown in these figures. Replicate samples were occasionally analyzed and yielded in general a reasonable coefficient of variation (CV) of approximately 20% for the data shown in Figures 4.2 and 4.3.

As can be observed by comparing Figures 4.2 and 4.3, the concentration profiles of acetate and formate through the filters showed major differences. However, for both components relatively good total removals (at an EBCT of 6 minutes) were obtained during the whole course of the experiment. Both acetate and formate were well removed within a few days of startup of the experiment, e.g. day 8 sampling shown in Figures 4.2 and 4.3, suggesting that a microbial population degrading these substances was established quickly within this filter. The concentration of formate decreased more or less exponentially within the filter bed for all the sample dates (Figure 4.3). Acetate showed a very different pattern, in fact the acetate concentration was observed to increase substantially within the filter for several samples (Figure 4.2).

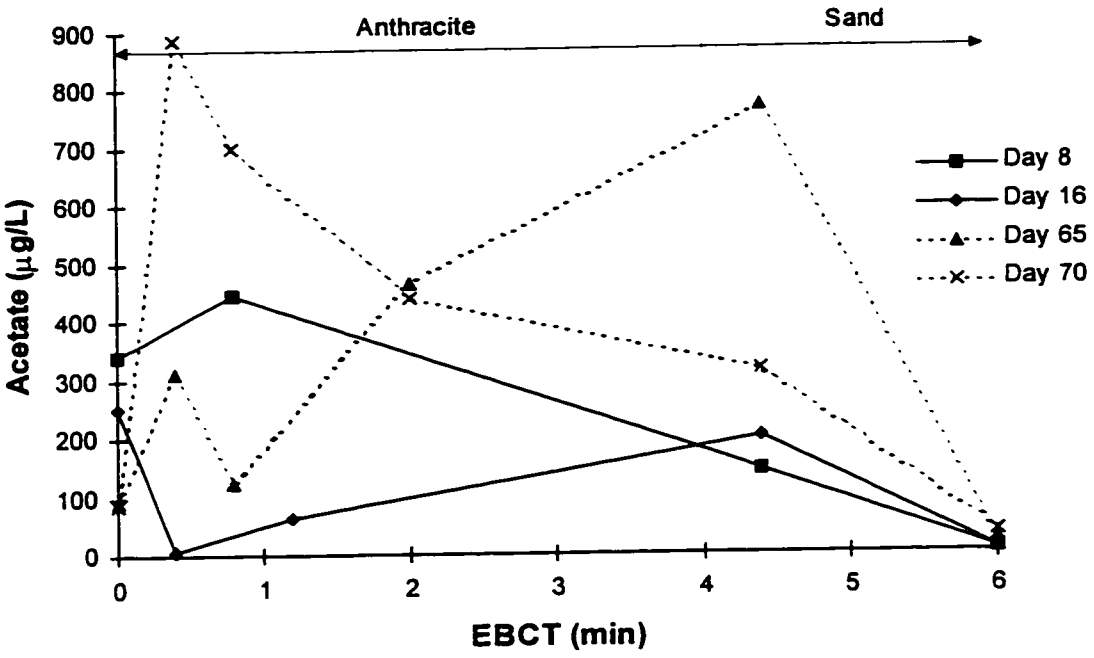

Figure 4.2: Concentrations of acetate vs. EBCT in filter 1 (control)

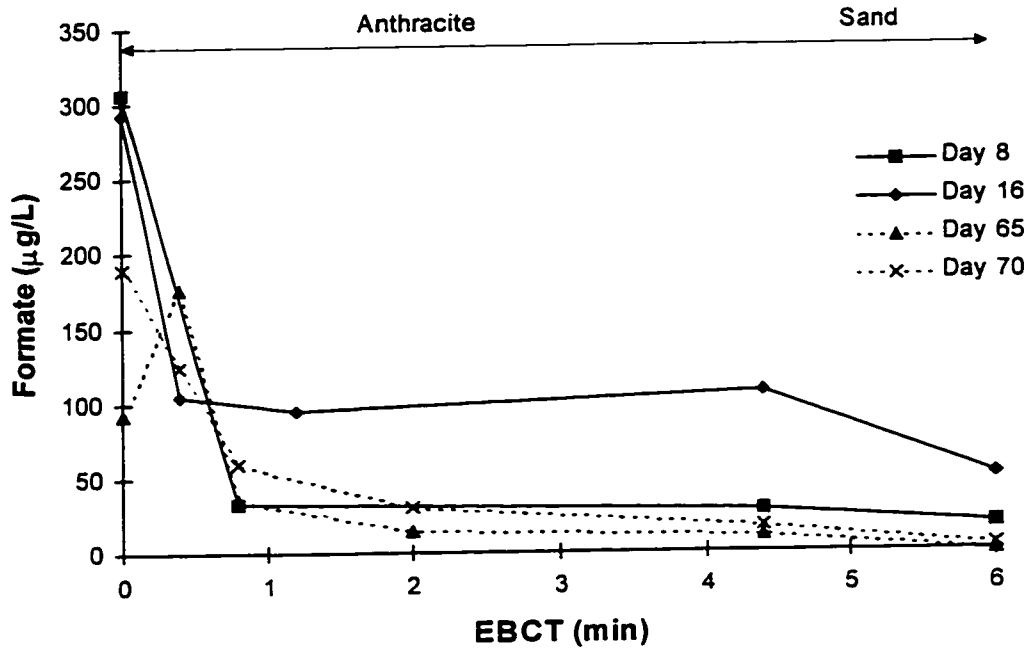

Figure 4.3: Concentrations of formate vs. EBCT in filter 1 (control)

Hypothetically, microbial formation of acetate as a product of the degradation of other biodegradable substances as proposed by Booth et al., (1995) might be a reason for the observed increases of acetate. Contamination of the samples might be a possibility as well. As mentioned in Chapter 3, carboxylic acid samples could be easily contaminated with acetate during sampling and sample preparation. The fact that acetate profiles such as the ones shown in Figure 4.2 were not obtained in later experiments, i.e. H2, C1, C2 and O1 (Chapters 4-6), suggests that sample contamination might have been the reason for the observed increases of the acetate concentration in the filter (Figure 4.2).

Figure 4.4 represents the percentage removal of acetate for the two parallel filters (filters 1 and 2) vs. time since startup of the experiment. No major difference in the total removal of acetate was observed between filter 1 and filter 2 suggesting that the presence of approximately 1 mg/L of H_2O_2 in the influent of filter 2 did not have a major impact on the biological removal of acetate. Interestingly the percentage removal of acetate seemed to decrease with time since startup. Initially essentially total acetate removal was achieved in both filters, however after approximately 70 days of filter operation the total removal decreased to about 60 to 70% for both filters. This observation seems consistent with full scale data on the removal of carboxylic acids in biological filters at pseudo steady-state, which suggested that acetate was not totally removed in biofilters operated at very high EBCTs of about 30 minutes (Gagnon et al., 1997). Again, microbial formation of acetate as a microbial product of the degradation of other organic substances (Booth et al., 1995) might be a reason for this.

For formate the figure showing percentage removal versus time since startup for filter 2 (Figure 4.5) was quite different compared to acetate.

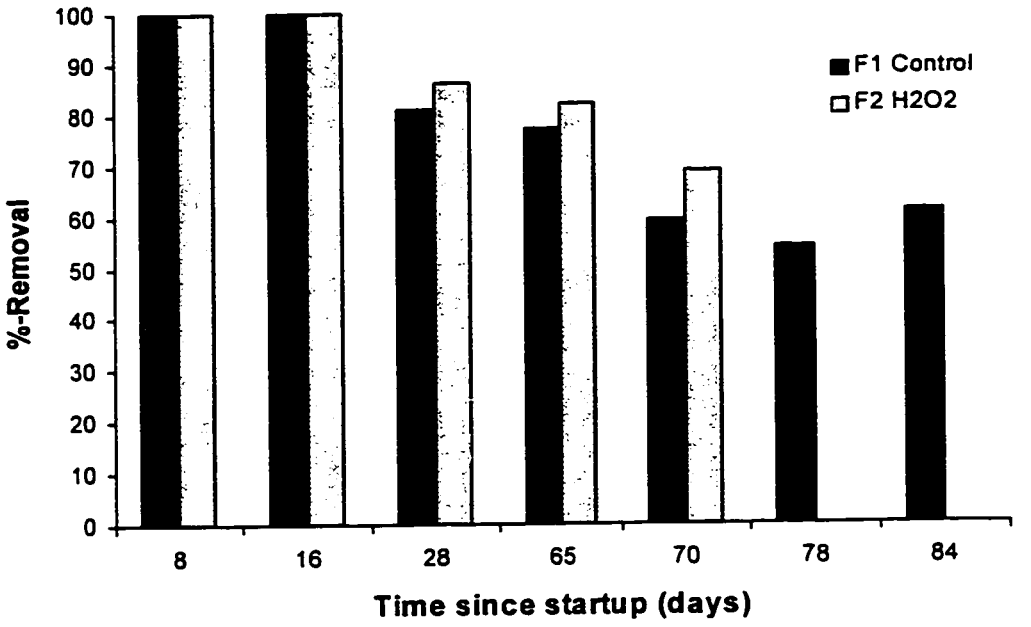

Figure 4.4: Percentage removal of acetate (EBCT = 6 minutes) for filters 1 and 2 vs. time since startup (no data available for filter 2 on days 78 and 84)

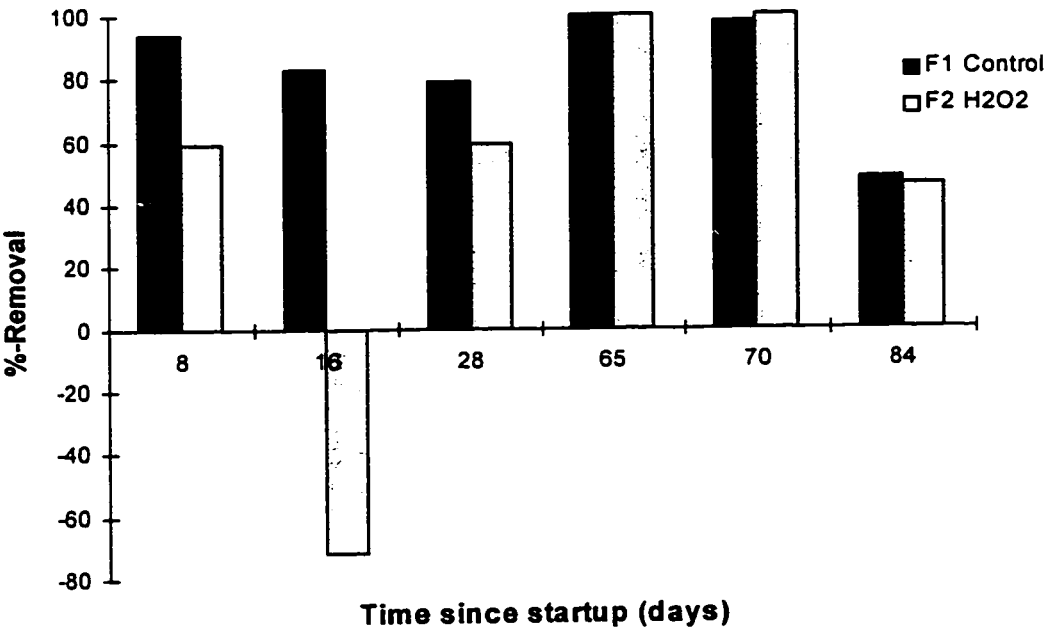

Figure 4.5: Percentage removal of formate (EBCT = 6 minutes) for filters 1 and 2 vs. time since startup

Similarly to acetate, the control filter (filter 1) provided very good removals of formate from the very beginning of the experiment (day 8). However, this was not the case for the filter with hydrogen peroxide in the influent (filter 2). In fact as can be seen in Figure 4.5, the percentage removal of formate in filter 2 was measurably lower compared to filter 1 during approximately the first month of the experiment. Therefore, the presence of H_2O_2 at ~1 mg/L in the influent of filter 2 had a measurably stronger inhibitory effect on the removal of formate compared to acetate during the first month of filter operation.

In later samples (2-3 months after startup), filters 1 and 2 showed essentially identical percentage removals of formate (Figure 4.5). Consequently, H_2O_2 at concentrations of ~1 mg/L in the influent partially inhibited the biological removal of formate during the early phase (about one month) of biological acclimatization. However, after two months of biological operation of the filters, the H_2O_2 had no measurable effect and the biological removals of formate were similar in both filters. This is further illustrated in Figure 4.6, which shows formate concentration profiles through filters 1 and 2 on day 65 following startup.

In order to assess the possible reaction of H_2O_2 with carboxylic acids and aldehydes, two sets of influent samples from filter 2 (i.e. containing H_2O_2) were analyzed. For the first set, 0.12% (v/v) of a 5% solution of bovine catalase was added to the sample immediately after sampling, in order to quench the H_2O_2. In the second set of samples the catalase solution was added after allowing a time for reaction with the H_2O_2 of 10 minutes. Comparison of the results of the two sets of samples (data not shown) indicated that there was no measurable difference in the concentrations of acetate, formate and formaldehyde between the two sets. Thus there was no significant chemical reaction occurring between H_2O_2 and these components within the time frame relevant for the filters.

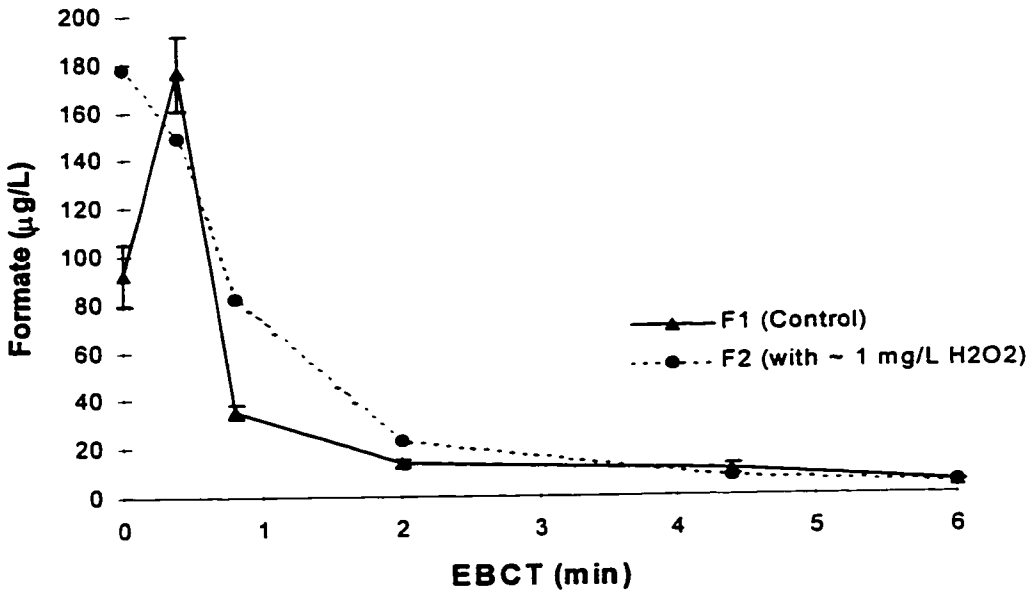

Figure 4.6: Formate concentration profiles on day 65 following startup, no replication in filter 2

Removal of Hydrogen Peroxide

Figure 4.7 represents the removal pattern of hydrogen peroxide in filter 2. At the beginning of the experiment, i.e. new, biomass-free media in the filter, essentially no removal of H_2O_2 occurred through the filter. After about 1 month of biological operation, H_2O_2 was rapidly removed and within 2 to 3 minutes of EBCT the H_2O_2 concentration was below the MDL. Observed decreases of the concentration of hydrogen peroxide in biologically active anthracite/sand filters (Figure 4.7) therefore appear to be due to a reaction of H_2O_2 with the biomass or with catalase produced by certain bacterial species or with some inorganic species, e.g. ferric iron (cf. Chapter 6), deposited on the filter media during the course of filter operation. Others have reported substantial decreases of hydrogen peroxide concentrations through biologically active filters (McGuire et al., 1991;

Weinberg and Glaze, 1997), although H_2O_2 filter influent concentrations were lower in those studies, i.e. ~0.03-0.20 mg/L.

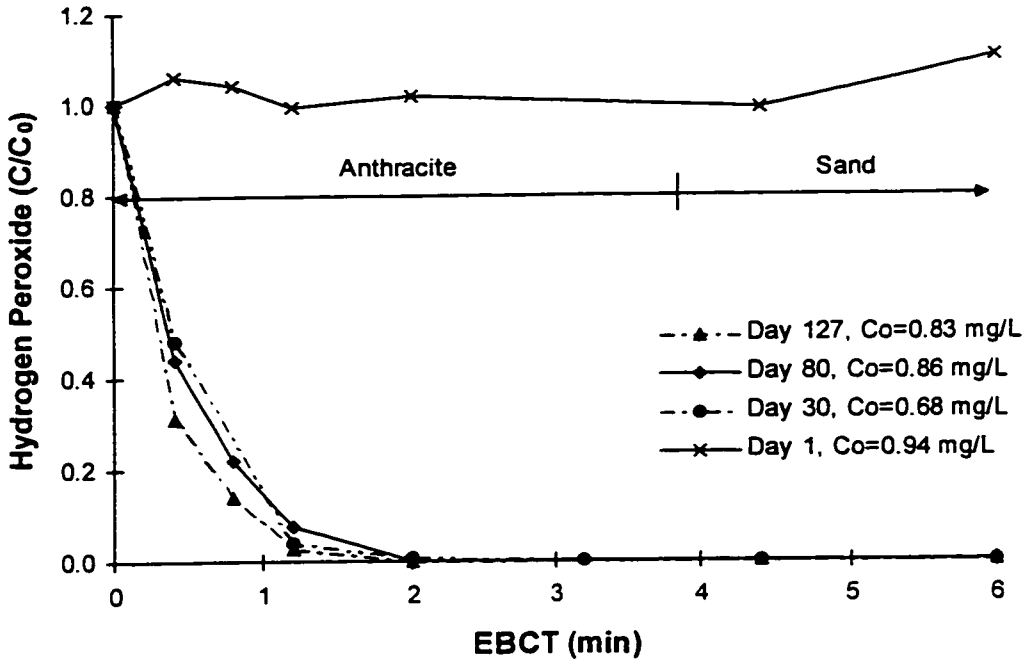

Figure 4.7: Removal of hydrogen peroxide in filter 2

Data from experiment H2 (discussed later) indicated that it takes less than 1 month for the H_2O_2 removal to become established, however for experiment H1, no H_2O_2 measurements were performed between days 0 and 30. After the first month of operation, the removal pattern only changed in a minor way until the end of the experiment on day 127 (Figure 4.7).

Figure 4.8 shows the results of the brief experiment with non-biological filters. As mentioned earlier, no measurable decrease of the H_2O_2 concentration was observed in the anthracite/sand filter containing new media and the filter influent and effluent H_2O_2 concentrations were essentially identical. For GAC/sand a major decrease of the H_2O_2 concentration was observed in the filter, as was expected based on the literature

(Sontheimer et al., 1988). However, the H_2O_2 removal in the non-biological GAC/sand filter was less than that observed in a biologically active anthracite/sand filter (Figure 4.7).

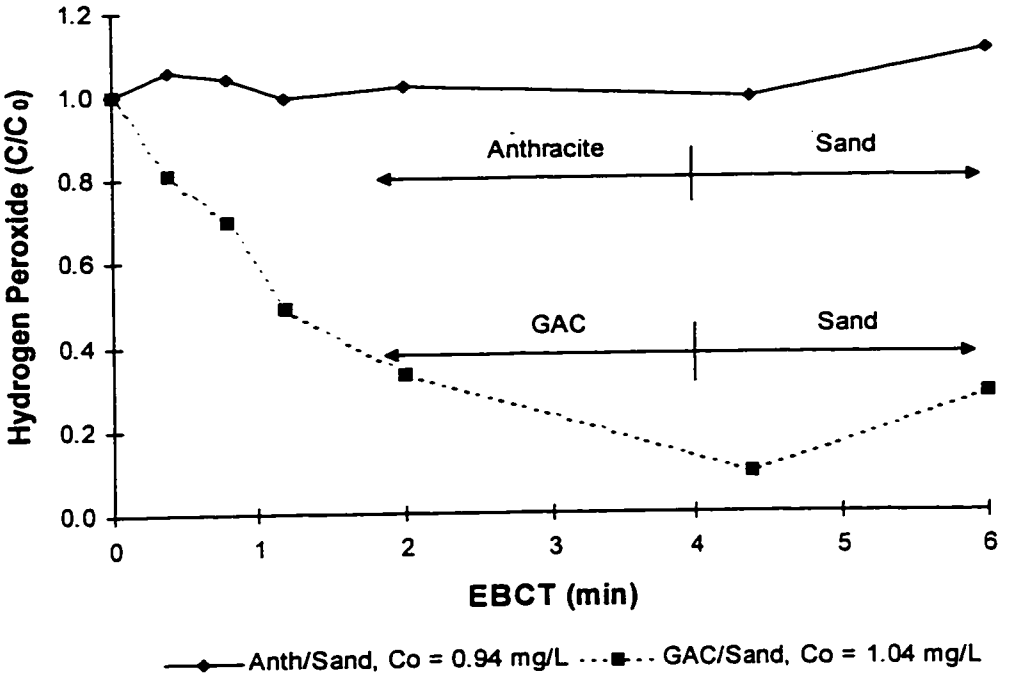

Figure 4.8: Removal of hydrogen peroxide in non-biological filters

The purpose of the experiment shown in Figure 4.9 was to assess the possible adaptation of a microbial population to the continuous presence of H_2O_2. The figure shows the removals of H_2O_2 in filter 2 (which always received H_2O_2) after 127 days of biological operation, and in filter 1 which did not receive hydrogen peroxide during the period prior to day 127 when H_2O_2 started to be dosed (for about 24 hours) to the influent of this filter. Figure 4.9 shows that although filter 1 was operated biologically for about 4 months, the filter did not remove H_2O_2 as well as filter 2, which was adapted to the presence of H_2O_2. This may be due to the increased growth of catalase-producing bacteria in filter 2 as a result of the continuous presence of H_2O_2, or differences in the amount of inorganic chemicals, i.e. ferric iron, present in the two filters. If the addition of H_2O_2 to the influent

of filter 1 was continued for a longer period of time (several days), it is possible that the removal of hydrogen peroxide in this filter would have been similar compared to filter 2.

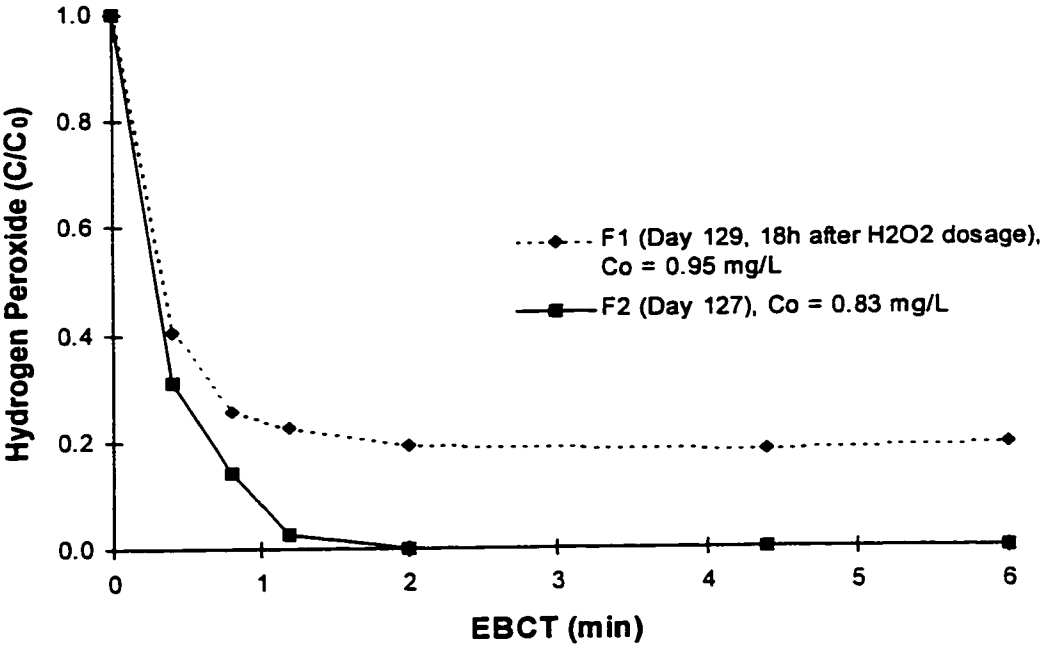

Figure 4.9: Removal of hydrogen peroxide in biological filters (continuous presence of H_2O_2 vs. periodic presence)

The results shown in Figure 4.9 may be significant for the operation of full scale filters as they suggest measurable differences in the H_2O_2-removal capability of biological filters depending on whether H_2O_2 is present continuously in the filter influent or just periodically. For treatment plants using AOPs or O_3 alone prior to biological filters, fluctuations of water quality parameters affecting the oxidation process will result in more or less significant changes in the H_2O_2 concentration in the biofilter influent (oxidation effluent). Such changes might have a negative impact on the H_2O_2-removal capability of the biofilters in certain cases.

Experiment H2

Experiment H2 was started on October 9, 1996 (day 0) and lasted for approximately two months. The experimental design of this experiment was identical to experiment H1 except that the target H_2O_2 concentration in the influent of filter 2 was 5 mg/L instead of 1 mg/L.

Removal of BOM Components

Upon startup of experiment H2, the establishment of the biological removal capability for acetate and formate in the control filter (filter 1) required about 10 and 20 days of filter operation respectively (Figures 4.10 and 4.11).

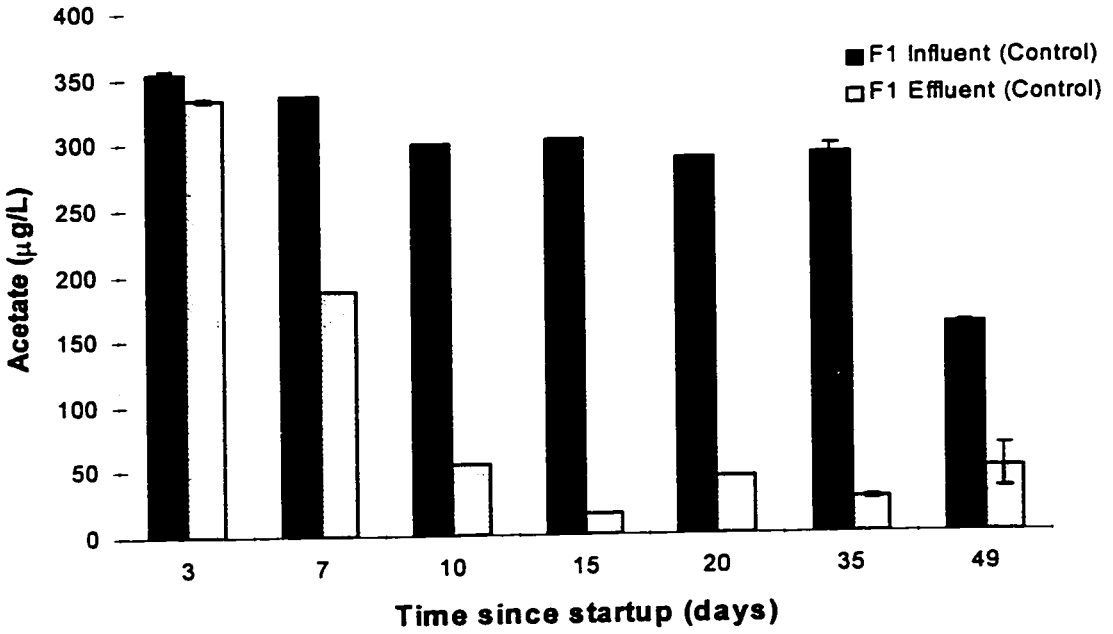

Figure 4.10: Concentrations of acetate in filter 1 (control) vs. time of filter operation

The fact that the removal of acetate was established faster than that of formate is probably related to differences in the utilization of these two components by different bacterial species and related issues. Acetate can be metabolized by a wide range of heterotrophic bacterial species and is used as the calibration substance for the widely used

AOC test (van der Kooij, 1982). Therefore, a sufficient number of bacteria able to metabolize acetate was potentially present earlier in the control filter compared to formate degrading bacteria. However, this remains speculation and further investigation of the cause of this observation was outside the scope of this research.

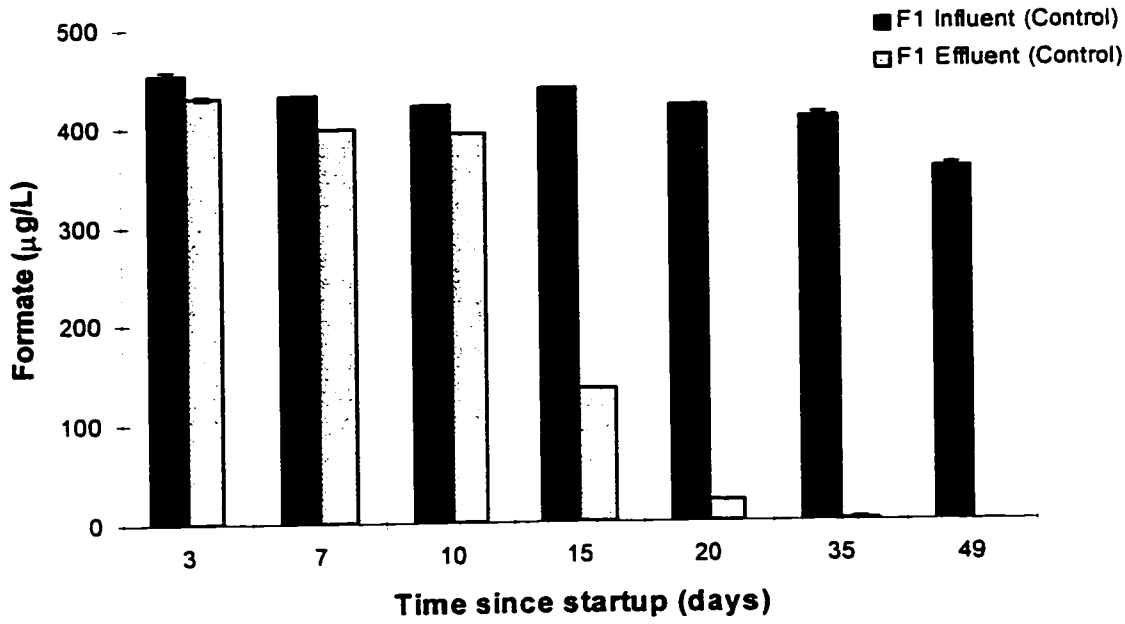

Figure 4.11: Concentrations of formate in filter 1 (control) vs. time of filter operation

In the filter with approximately 5 mg H_2O_2/L in the influent (filter 2), the removal of acetate and formate was substantially inhibited as shown in Figures 4.12 and 4.13. These two figures show the concentrations of acetate (Figure 4.12) and formate (4.13) in filter 2 over time. No acetate and formate data are available for days 3 and 7. The reason for this is that the relatively high concentrations of H_2O_2 (~5 mg/L) in the samples from filter 2 interfered with the quantitative determination of acetate and formate in the IC. Following this discovery, H_2O_2 present in the samples from filter 2 was quenched with 0.25% (v/v) of a 5% solution of bovine catalase in order to circumvent this problem.

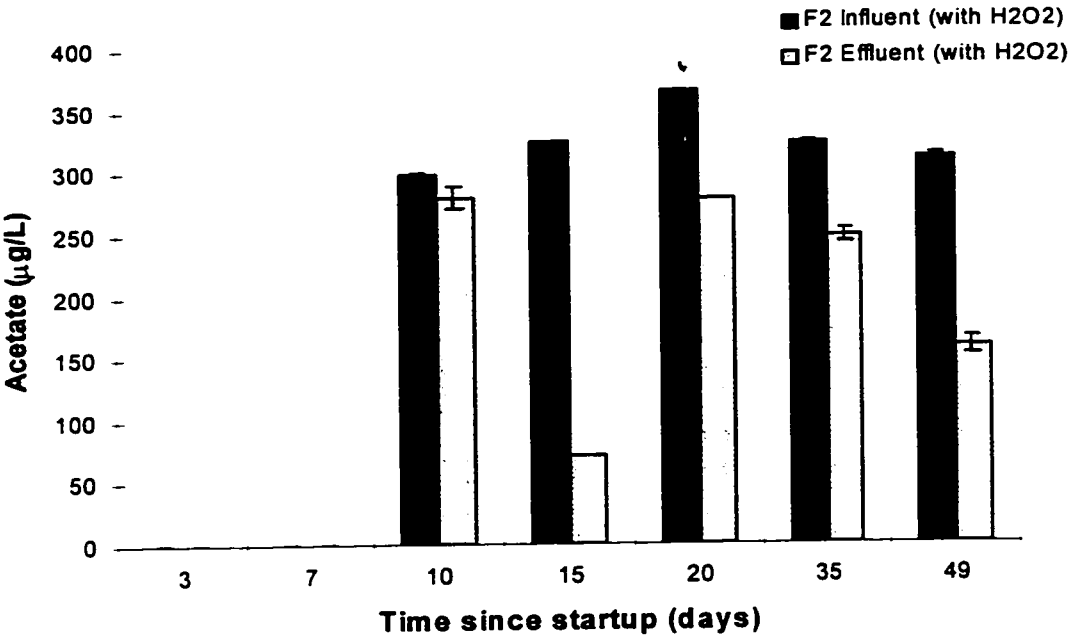

Figure 4.12: Concentrations of acetate in filter 2 (~5 mg/L H_2O_2 in the influent) vs. time of filter operation

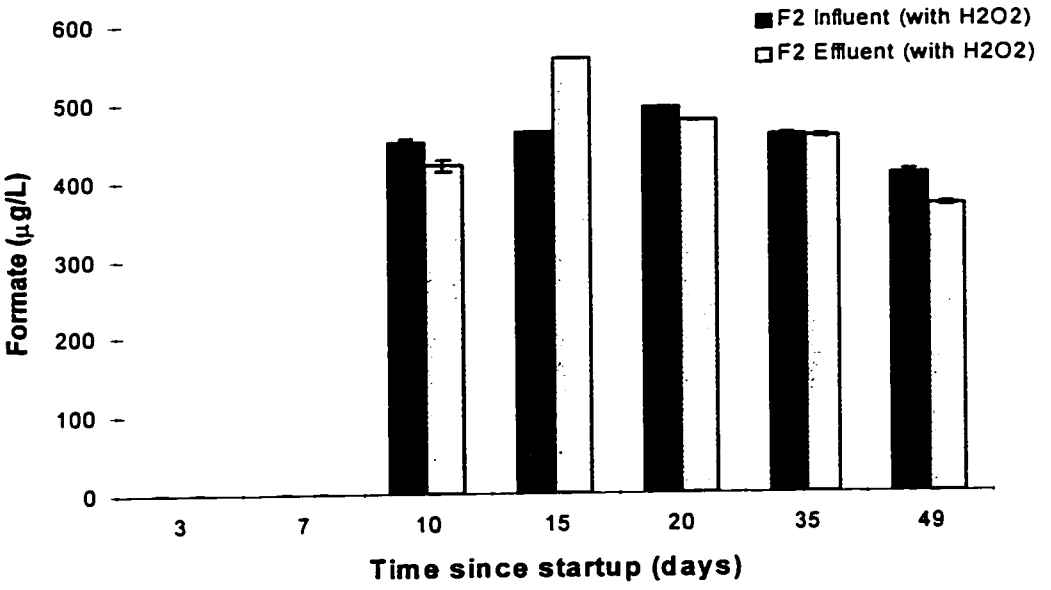

Figure 4.13: Concentrations of formate in filter 2 (~5 mg/L H_2O_2 in the influent) vs. time of filter operation

Comparing the acetate and formate results in the control filter (Figures 4.10 and 4.11) with the results in filter 2 (Figures 4.12 and 4.13) shows that the presence of ~5 mg H_2O_2/L in the influent of this filter had a substantial negative effect on the biological removal of these two components. In the case of biological formate degradation the inhibition caused by the presence of H_2O_2 at the specific conditions was essentially total, whereas removals of acetate in filter 2 were partially but not totally inhibited. This is consistent with the observations made during the first month of experiment H1, which showed that formate degradation was more strongly inhibited by the presence of H_2O_2 than was acetate degradation. Again, the differences in the effects of the presence of H_2O_2 might be related to the different bacterial species responsible for acetate and/or formate degradation and in differences in the response of these bacteria to the presence of an oxidant, i.e. hydrogen peroxide.

The substantial inhibition of formate removal in filter 2 is further illustrated in Figure 4.14, which compares formate concentration profiles in filters 1 and 2 on day 35 after startup. Profiles for acetate were similar, although the inhibition was less pronounced as mentioned previously (acetate concentration profile not shown).

Figure 4.15 shows a similar plot as 4.14 but for formaldehyde (sampling days 37 and 50). The results of both sampling days shown in Figure 4.15 were similar, suggesting that the filters were at some sort of pseudo steady-state regarding the biodegradation of formaldehyde. The control filter (filter 1) showed a rapid decrease of the formaldehyde concentration and the levels were below detection limit after about 2 to 3 minutes of EBCT. The pattern of the formaldehyde concentration in the control filter (filter 1) was similar to the pattern of formate in this filter, suggesting that the biodegradation kinetics for these two components were similar under the specific conditions of these experiments.

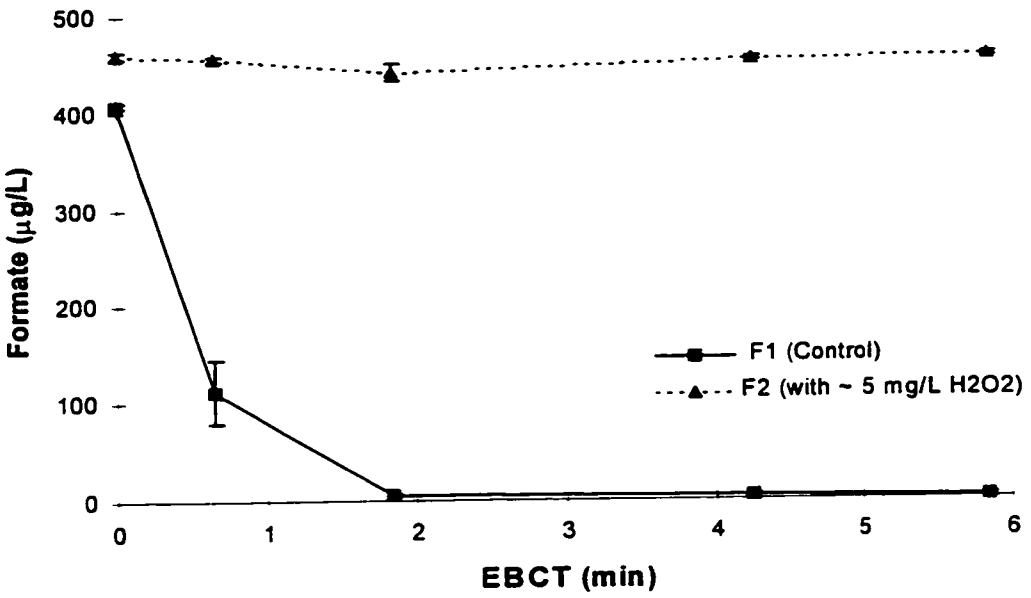

Figure 4.14: Formate concentration profiles in filters 1 and 2 on day 35 following startup

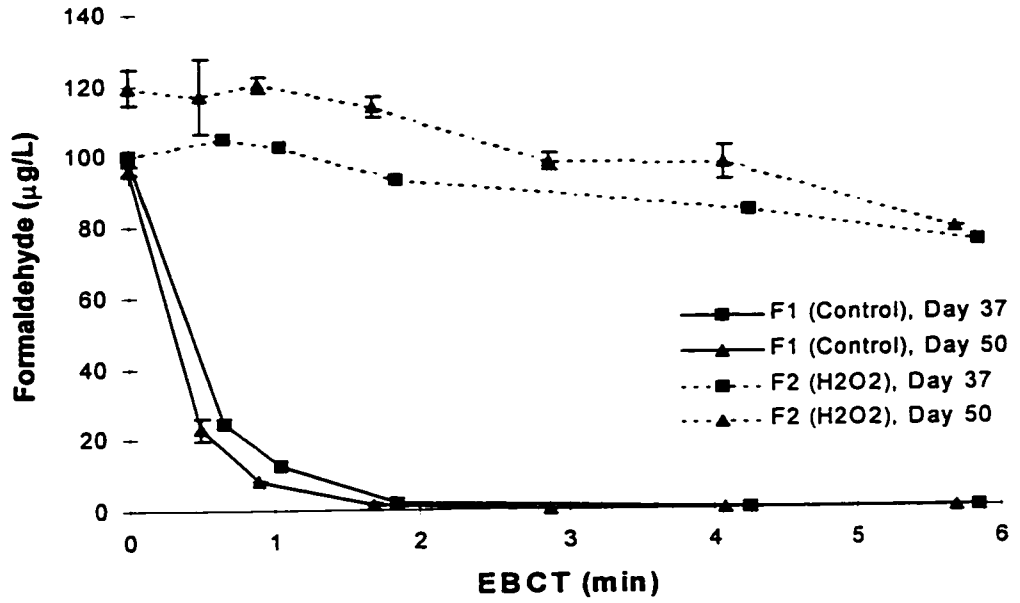

Figure 4.15: Formaldehyde concentration profiles in filter 1 (control) and filter 2 (~5 mg H_2O_2/L in the influent) on days 37 and 50 following startup, no replication for day 37 sample.

Formaldehyde degradation in the control filter was well approximated by a first order model as illustrated in Figure 4.16. The first order rate constants calculated for the samples from days 37 and 50 were 2.1 min^{-1} and 2.4 min^{-1} respectively. A similar observation was made during experiment C2 (Chapter 5), where the formaldehyde concentration in filter 1 on day 93 following startup could be described by an exponential function as well (data not shown). In this case, the first order rate constant was 2.1 min^{-1}.

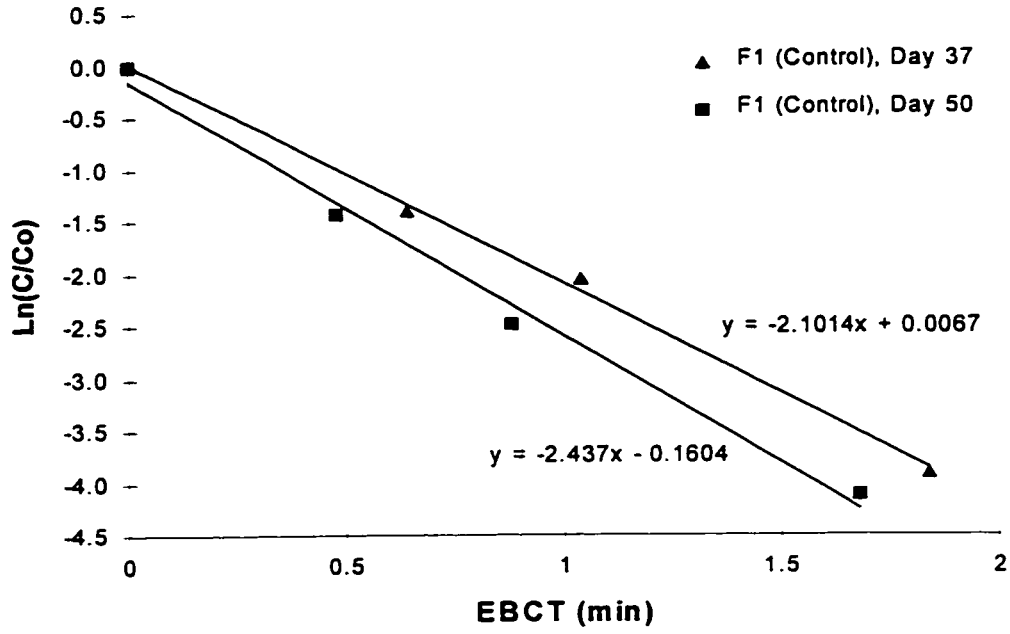

Figure 4.16: First order model for the degradation of formaldehyde in filter 1 (control)

First order rate constants of 2.1 to 2.4 min^{-1} translate to a half life of formaldehyde in the control filter of between 17 and 20 seconds of EBCT, or 8-9 seconds of real contact time, assuming a porosity of the anthracite of 0.45. These results are in agreement with observations from others, indicating that formaldehyde is readily biodegradable in biofilters (e.g. Krasner et al., 1993; Coffey et al., 1995b).

The results for formaldehyde in the filter with ~5 mg/L of H_2O_2 in the influent (filter 2) were similar to those for acetate (data not shown). Similarly to acetate and unlike

formate, formaldehyde was degraded to a minor extent in filter 2, despite the presence of hydrogen peroxide in the influent of this filter (Figure 4.15).

Biomass

The distribution of viable biomass measured as phospholipid is shown in Figure 4.17 for the control filter (filter 1) and in Figure 4.18 for the filter receiving 5 mg/L of H_2O_2 (filter 2). In order to facilitate comparison, Figures 4.17 and 4.18 have the same scale for the y-axis.

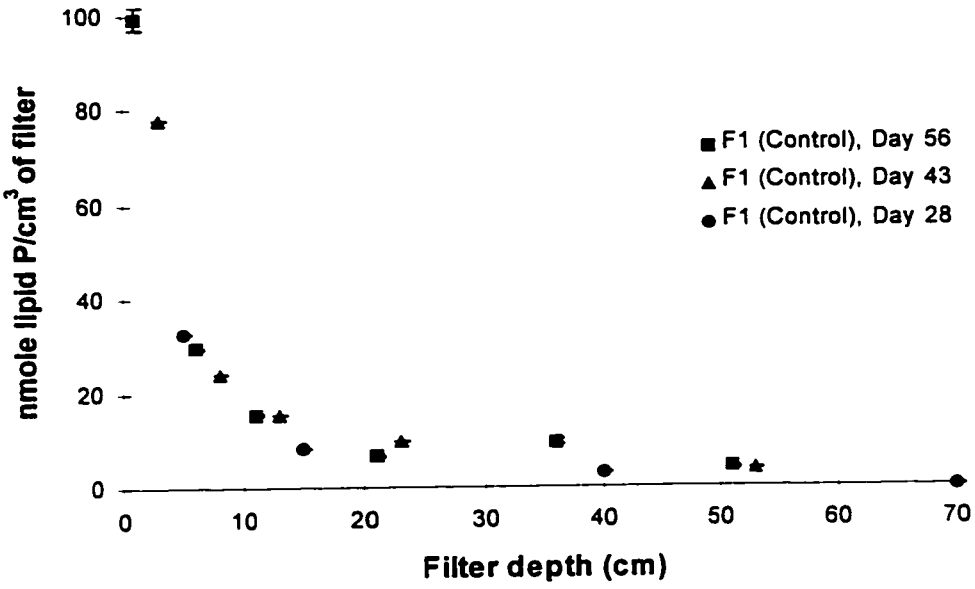

Figure 4.17: Viable biomass (phospholipid) in filter 1 (control)

Viable biomass (measured as phospholipid) in the control filter showed a very pronounced stratification with depth (Figure 4.17). Others have reported similar phospholipid biomass profiles in pilot scale filters (Wang, 1995; Carlson and Amy, 1995; Carlson et al., 1996a; Moll and Summers, 1997). Such a biomass stratification may be expected based on the results of substrate removal in the biofilters. In fact, most of the BOM removal occurred in the top 0-20 cm of the control filter as shown in Figures 4.14

and 4.15, whereas deeper in the filter bed BOM concentrations were very low. Therefore, it can be expected that most of the biomass is present at the top of the biofilters. It is likely that biomass profiles in biological filters generally depend on the BOM composition of the influent water. In cases where relatively easily biodegradable components are the major fraction of the filter influent BOM (such as in the case of this research), a relatively pronounced biomass stratification can be expected, although this also depends on the EBCT and temperature. On the other hand, if the BOM in the filter influent is less readily biodegradable, the stratification of biomass is likely less pronounced. In full scale studies different authors have reported a relatively minor biomass stratification with depth (Servais et al., 1991; Huck et al., 1998), although a large amount of full scale data is not currently available. The relationships between biomass and substrate removal are further discussed in Chapter 6.

In filter 2, the amount of viable biomass was considerably lower than in filter 1 as shown in Figure 4.18.

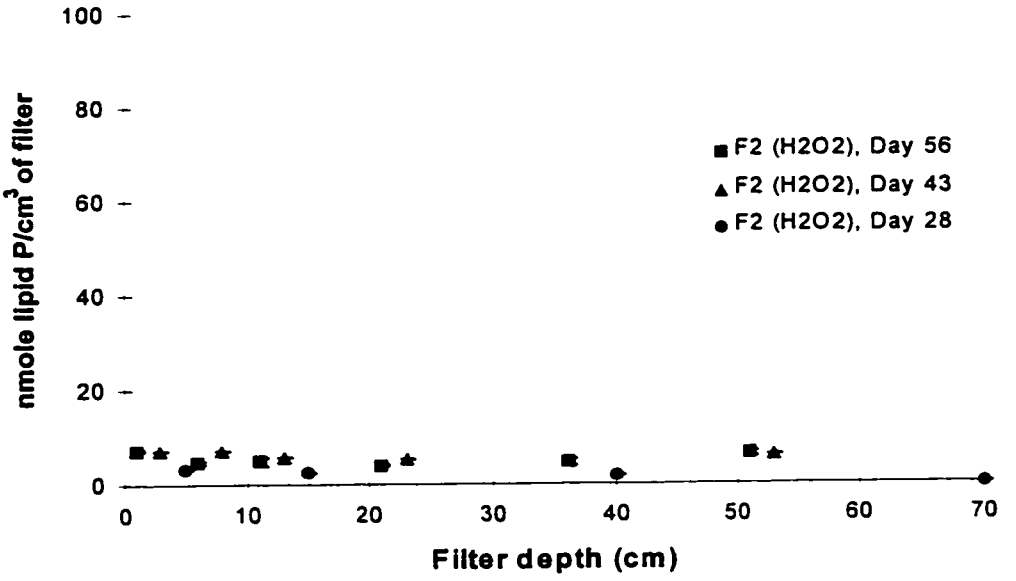

Figure 4.18: Viable biomass in filter 2 (~ 5 mg/L of H_2O_2 in influent)

This indicates that the presence of ~5 mg/L of H_2O_2 in the influent of filter 2 led to a major inhibition of the growth of viable biomass. The amount of biomass was essentially constant with depth in filter 2, and was between 4 and 8 nmole lipid P/cm^3 of filter (Figure 4.18). The average amount of viable biomass in filter 2 was equal to 5.3 nmole lipid P/cm^3 of filter.

The substantially lower amount of viable biomass in filter 2 is consistent with the results of substrate removal in this filter which have been presented earlier. Therefore it can be concluded that the continuous presence of ~5 mg/L of hydrogen peroxide in the influent of a lab scale anthracite/sand filter had a major negative effect on the removal of selected easily biodegradable components as well as on the accumulation of viable biomass.

Based on literature information presented in Chapter 2, this finding might be somewhat surprising. As mentioned in Chapter 2, some authors have proposed H_2O_2 concentrations of 200-500 mg/L as the toxic limit for microorganisms in the sub-surface (Lee et al., 1988). Others have reported successful biodegradation of benzene, toluene, ethylbenzene and xylenes (BTEX) in contaminated aquifer material when laboratory columns containing a sample of the contaminated material were fed with a BTEX solution which also contained 110 mg/L of H_2O_2 (Anid et al., 1993). The results of that study suggest that substantially higher H_2O_2 concentrations than the one employed in this experiment, i.e. 5 mg/L, did not have a toxic effect on the BTEX degrading bacteria, under the specific conditions of that investigation.

One explanation for this difference might be the substantially lower organic substrate concentration relevant in drinking water filters (and used in this research) and the much thinner biofilms associated with such oligotrophic conditions. In addition, because H_2O_2 was continuously fed to the influent of filter 2 from the very beginning of the experiment, the bacteriostatic activity of H_2O_2 rather than its bactericidal activity may be relevant. As mentioned in Chapter 2, Baldry (1983) reported that H_2O_2 was bacteriostatic at

concentrations above ~5 mg/L. Ibrahim and Schlegel, (1980a) reported that the presence of ~0.3-3.0 mg/L H_2O_2 in growth media substantially inhibited the synthetic processes in bacterial cells. They noted that the toxicity mechanism of low H_2O_2 concentrations was likely the formation of reaction products between H_2O_2 and the medium (substrates, metabolites and heavy metals), which are far more toxic than H_2O_2 itself.

The impacts of H_2O_2 were further analyzed using the formaldehyde data from day 50 (Figure 4.15) and the biomass results shown in Figures 4.17 and 4.18. Based on these biomass results, accumulated amounts of biomass were calculated for the two filters. Because of the fact that the formaldehyde removal in filter 1 was essentially complete after an EBCT of 1.7 minutes (Figure 4.15), i.e. at a filter depth of 21 cm, the calculations considered only the first 21 cm of the two filters. For filter 2, a constant amount of biomass of 5.3 nmole lipid P/cm^3 of filter was considered, yielding an accumulated value of 111 nmole lipid P in a filter core of 21 cm of depth with a 1 cm^2 surface. For filter 1 (the control), the accumulated amount of biomass was obtained by linearly extrapolating the values between the different sample points. This yielded an accumulated value in filter 1 of 600 nmole lipid P in a filter core of 21 cm of depth with a 1 cm^2 surface.

Using the accumulated amount of biomass in the first 21 cm of each filter and the amount of formaldehyde which was removed in this part of each filter, i.e. influent formaldehyde concentration minus concentration at 21 cm, the amount removed was normalized by the accumulated amount of viable biomass:

$$\Delta_X = \frac{(S_{in} - S_{21cm})}{X_{acc}} \qquad (4.1)$$

where:

Δ_X:	observed, normalized amount removed (μg formaldehyde/L*nmole lipid P)
S_{in}, S_{21cm}:	influent formaldehyde concentration and formaldehyde concentration at 21 cm within the filter (μg formaldehyde/L)
X_{acc}:	accumulated amount of biomass in a filter core with a surface of 1 cm^2 and a depth of 21 cm (nmole lipid P)

The approach described in equation 4.1 is useful because it allows normalization of the amount of substrate removed, considering the substantial differences in the accumulated amount of viable biomass for the different filters. The calculations yielded an observed, normalized amount removed in the first 21 cm of the bed of 0.16 μg formaldehyde/L *nmole lipid P for filter 1 (the control), whereas filter 2 (with ~5 mg H_2O_2/L in the influent) yielded a substantially lower amount of 0.05 μg formaldehyde/L*nmole lipid P. Thus the control filter (filter 1) showed an observed, normalized amount removed about 3 times higher compared to the filter with H_2O_2 (filter 2). This suggests not only that the presence of approximately 5 mg H_2O_2/L in the influent of filter 2 led to a major inhibition of the growth of viable biomass, but also that the biomass present in filter 2 appeared to have lower specific degradation capabilities for formaldehyde compared to filter 1.

However, biomass measurements with the phospholipid method may not accurately quantify the amount of active (substrate degrading) biomass as will be further discussed in Chapter 6.

Removal of Hydrogen Peroxide

Figure 4.19 shows the normalized concentration profiles of hydrogen peroxide through filter 2 on several sampling dates. Shortly after startup of the experiment (day 2) the hydrogen peroxide concentration did not decrease to a measurable extent within the filter bed, confirming the results of experiment H1, which showed that no physical or chemical reactions occurred between the H_2O_2 and new anthracite or sand. After about a week of operation (day 8) the H_2O_2 concentration was slightly decreased within the filter, whereas in later samples the decrease was substantial, as can be seen examining the curves for days 31 and 52 in Figure 4.19. Figure 4.20 represents influent and effluent H_2O_2 concentrations of filter 2 during the entire experiment.

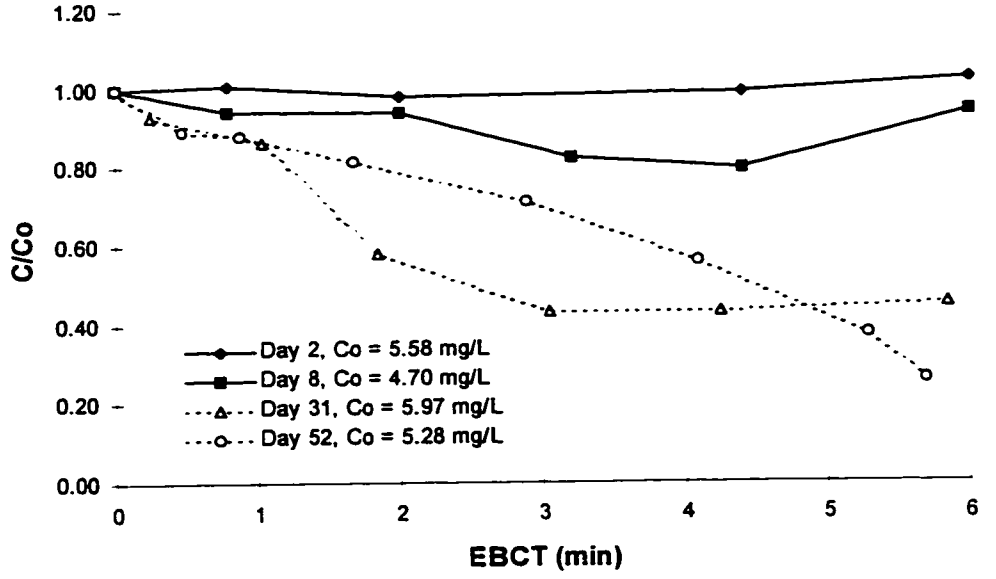

Figure 4.19: Normalized concentration profiles of hydrogen peroxide in filter 2 on several sampling dates

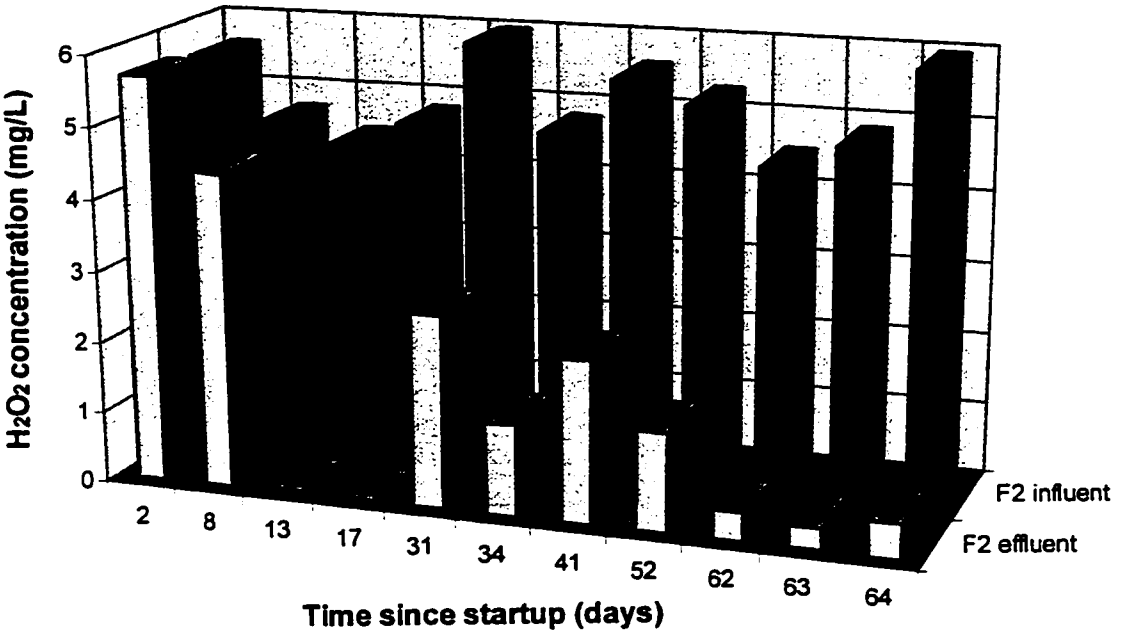

Figure 4.20: Hydrogen peroxide concentrations in filter 2

The variability of the data shown in Figures 4.19 (compare days 31 and 52) and 4.20 indicates that the removal of H_2O_2 in filter 2 might not have reached steady-state conditions during the term of this experiment, i.e. two months. On sampling days 13 and 17 the removal of H_2O_2 in filter 2 was essentially total. Interestingly, the acetate effluent concentration in filter 2 was substantially lower on sampling day 15 compared to the other sampling dates (Figure 4.12). This suggests that the absence of H_2O_2 in the effluent of filter 2 for a relatively short period of time led to a rapid improvement of the biological removal of acetate in this filter. Formate did not respond in this manner (Figure 4.13), likely because of the fact that the establishment of formate removal capacity was observed to require considerably more time compared to acetate.

The decrease of H_2O_2 within filter 2 was possibly caused by the presence of catalase-producing bacteria in this filter. Certain bacteria contain intracellular catalase, an enzyme which catalyzes the decomposition of H_2O_2 to oxygen and water (Schlegel, 1977; Ibrahim and Schlegel, 1980a,b; Pardieck et al., 1990), and therefore protects the bacteria from the effects of hydrogen peroxide (Campbell and Kimmick, 1966).

$$2H_2O_2 \xrightarrow{Catalase} O_2 + 2H_2O \qquad (4.2)$$

Other inorganic substances such as iron and manganese oxides (Colodette et al., 1988; Spain et al., 1989; Pardieck et al., 1990; McGuire et al., 1991) can serve as catalysts instead of catalase in equation 4.2. According to equation 4.2, the decomposition of 1 mg H_2O_2/L yields 0.47 mg O_2/L.

The hypothesis of the catalytic destruction of H_2O_2 according to equation 4.2 was supported by the measurement of a major increase in dissolved oxygen in the effluent of filter 2 as shown in Figure 4.21 for sampling day 59. The increase of dissolved oxygen in filter 2 on day 59 was equal to 1.83 mg O_2/L corresponding to a calculated decomposition of 3.9 mg H_2O_2/L (equation 4.2). This is in good agreement with the measured decrease of

the hydrogen peroxide concentration of 3.9 and 4.1 mg H_2O_2/L on sampling days 52 and 62 respectively.

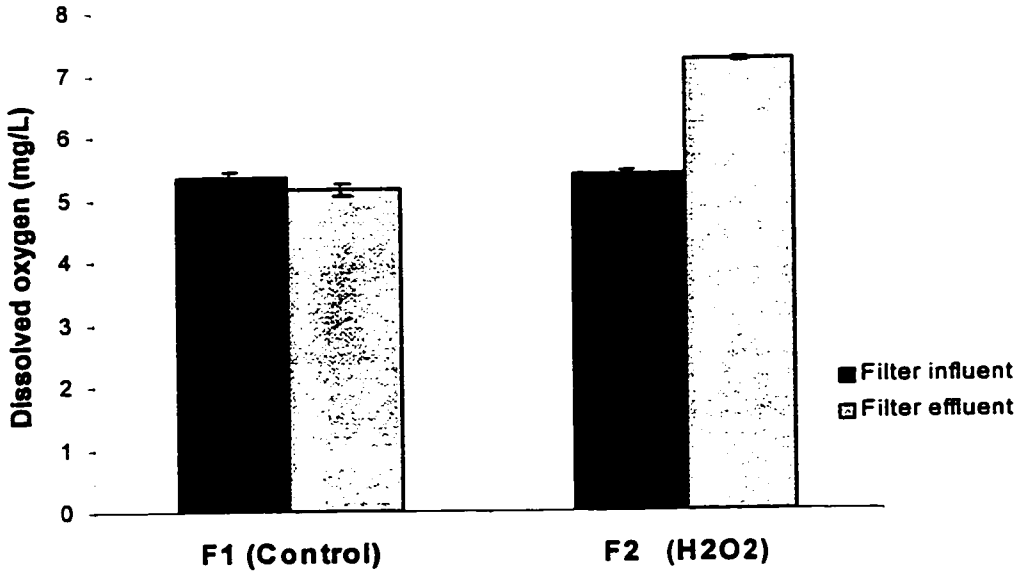

Figure 4.21: Concentrations of dissolved oxygen in filter 1 (control) and filter 2 (~5 mg H_2O_2/L in the influent) on day 59 after startup

On day 60 following startup the hydraulic loading of filter 2 was changed from 7.5 m/h to 3.75 m/h, in order to assess the potential impacts of this change on the removal of H_2O_2. The increase of the EBCT at the lower hydraulic loading was expected to lead to an increase of the amount of H_2O_2 removed, if the H_2O_2 removal mechanism was limited by the kinetics of the reaction. Figure 4.22 shows that the amount of H_2O_2 removed did not substantially change in the samples analyzed following the decrease of the hydraulic loading. However, the data in Figure 4.22 show a trend indicating that the amount of H_2O_2 removed might have increased following the decrease of the hydraulic loading. Unfortunately, experiment H2 had to be stopped on day 64. Also, H_2O_2 removals were already relatively high before the decrease in the hydraulic loading and a potential change

in the amount of H_2O_2 removed following the decrease in the hydraulic loading may therefore be difficult to observe.

The data in Figures 4.20 and 4.22 also suggest that some different phenomena may have occurred during days 13 and 17. On these sampling dates the removal of H_2O_2 was essentially total, as mentioned previously. The reasons for the somewhat different performance of filter 2 regarding H_2O_2 removal on days 13 and 17 is not currently understood.

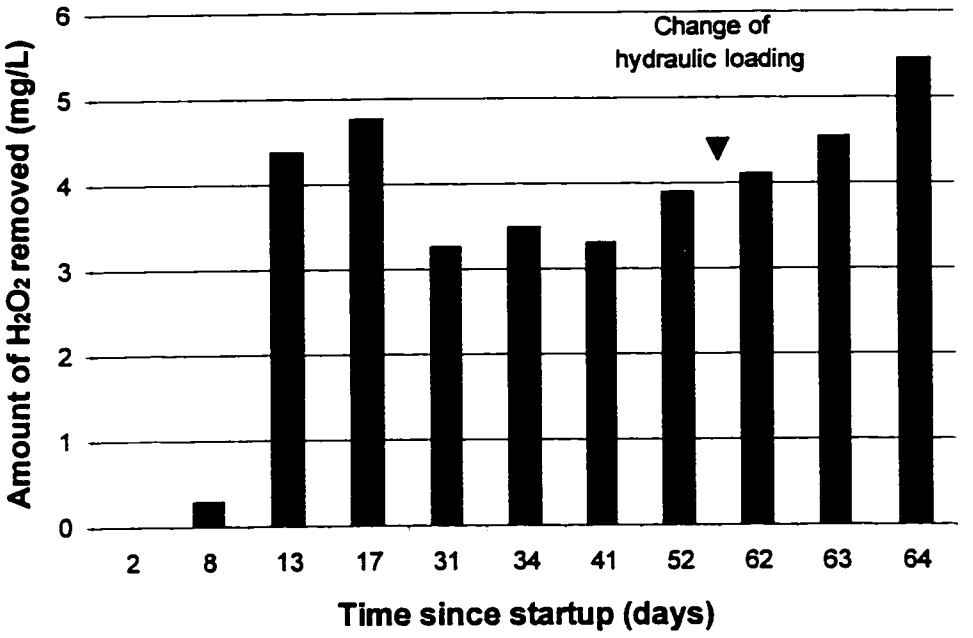

Figure 4.22: Amount of hydrogen peroxide removed in filter 2

Statistically, the average amount of H_2O_2 removed was not different ($\alpha = 0.05$) at a hydraulic loading of 7.5 m/h (sampling days 13,17, 31, 34, 41 and 52) compared to 3.75 m/h (sampling days 62, 63 and 64). However filter 2 had possibly not reached steady-state conditions regarding its H_2O_2 removal capability, both before and after the change in the hydraulic loading, as mentioned previously.

CONCLUSIONS

The results obtained during two lab scale experiments (H1 and H2) investigating the effects of hydrogen peroxide in the influent of biological anthracite/sand filters allow the following principal conclusions to be drawn:

- The continuous presence of ~1 mg/L of H_2O_2 did not lead to a major inhibition of the biological removal of acetate and formate in a laboratory scale anthracite/sand drinking water biofilter. However, when the influent concentration was increased to 5 mg H_2O_2/L, a substantial inhibition of the biological degradation of acetate, formate and formaldehyde occurred. Because these components are known to be readily biodegradable, the inhibitory effect of the hydrogen peroxide would probably be stronger for more slowly biodegradable organic components.
- Under the specific conditions which were tested, the critical hydrogen peroxide concentration, i.e. the concentration above which the biological performance (BOM removal) of biofilters will be substantially impaired, appears to be somewhere between 1 and 5 mg/L.
- The growth of viable biomass (measured as phospholipid) was observed to be substantially inhibited as a result of the presence of ~5 mg/L of H_2O_2 in the influent of an anthracite/sand filter. However, a measurable amount of biomass was present throughout the filter.
- Hydrogen peroxide at filter influent concentrations of ~1 mg/L was essentially totally removed after about 2-3 minutes of EBCT. At a filter influent H_2O_2 concentration of ~5 mg/L, the removal of H_2O_2 through the filter bed was only partial and H_2O_2 residuals of up to 1-2 mg/L were measured in the filter effluent. These results suggest that biologically active filters represent a promising process to prevent the presence of undesired H_2O_2 residuals in the finished water.

- The H_2O_2 removal was possibly the result of the presence of catalase-producing bacteria attached to the filter media. The measurement of a substantial increase of the dissolved oxygen concentration through the filter receiving H_2O_2 supports the hypothesis of a catalase-H_2O_2 reaction. However, inorganic species, e.g. ferric iron, could have served as catalysts for the H_2O_2-decomposition instead of catalase.

In addition, the following secondary conclusions can be drawn:

- Upon startup of the biofilters containing biomass-free media (anthracite/sand) the establishment of biological acetate removal required measurably less time compared to formate. This is potentially the result of the fact that acetate represents an organic component which can be metabolized by a large number of microbial species.
- The inhibitory effect of H_2O_2 on the biological removal of formate was consistently stronger compared to acetate. Again, the reason might be that the amount of bacteria surviving the presence of H_2O_2 preferably metabolize acetate compared to formate. This might be related to the substantially higher gain of energy associated with the oxidation of acetate.
- The biomass present in the filter receiving H_2O_2 at ~5 mg/L had a lower specific (biomass normalized) degradation capability for formaldehyde compared to the biomass in the control filter. This suggests that the H_2O_2 may also have had a negative impact on the metabolic properties of the cells using formaldehyde as a source of carbon and energy.
- A measurable difference in the H_2O_2-removal ability of biological filters was observed depending on whether H_2O_2 was present continuously or just periodically (less than 24 hours). Biological anthracite/sand filters receiving H_2O_2 continuously seem to reliably remove H_2O_2 within a relatively short EBCT, whereas this might not be the case if H_2O_2 is only periodically present in the biofilter influent.

CHAPTER 5: A STUDY ON THE EFFECTS OF FREE AND COMBINED Cl_2 IN THE INFLUENT AND BACKWASH WATER OF BIOFILTERS*

INTRODUCTION

Conventional (non-biological) surface water treatment practice may involve the dosage of free Cl_2 to the raw water (prechlorination), an operational strategy generally leading to the presence of Cl_2 residuals throughout the treatment plant. As a result of the presence of Cl_2 residuals through filtration, the filters in such plants are usually non-biological unless the filter media consists of GAC (e.g. LeChevallier et al., 1992). Nevertheless, the presence of free Cl_2 in the influent of GAC filters does not represent an optimized treatment strategy for reasons given in Chapter 2.

Free Cl_2 and monochloramine (where sufficiently long contact times are available) are commonly used disinfectants for the inactivation of pathogenic microorganisms such as bacteria, viruses and *Giardia* cysts. In addition, these chemicals are used throughout the world as secondary disinfectants added to the water prior to the distribution system in order to control bacterial regrowth. It can be expected that the use of combined Cl_2 instead of

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free Cl_2 as a secondary disinfectant will increase in North America, mostly as a result of the more stringent regulations of chlorinated DBPs in the future. In addition, some researchers have made a strong case regarding the improved control of distribution system biofilms with monochloramine instead of free Cl_2, mostly as a result of the limited reactiveness of NH_2Cl with demand-causing compounds in biofilms (LeChevallier et al., 1988; 1992; 1993; 1996; LeChevallier and Lowry, 1990).

Although it is expected that the contact between biofilms and Cl_2-containing water will harm such biofilms as a result of the bactericidal properties of Cl_2, it may not always be possible to avoid the presence of Cl_2 residuals in full scale biofilters. Such residuals would occur in the influent of biofilters either intermittently or continuously at low levels, or in the backwash water.

Even though filters in treatment plants using prechlorination are usually considered to be non-biological, it can be expected that biological BOM removal will occur in such filters despite the presence of Cl_2, if the Cl_2 concentration in the biofilter influent is below a certain threshold level. In practice, biologically operated plants (no prechlorination) might require the periodic addition of Cl_2 prior to sedimentation in order to control the excessive growth of phototrophic microorganisms, e.g. algae, in uncovered sedimentation basins. In such cases a Cl_2 residual is likely to be present in the influent of the filtration stage during the period of Cl_2-addition to the sedimentation basins.

Because of the potential negative effects of Cl_2 in the backwash water on the biofilms in biologically active filters, Cl_2 should ideally not be present in the backwash water of such filters. However, free Cl_2 or NH_2Cl residuals may be present in the backwash water, if the water for backwashing is provided from a clearwell to which these disinfectants are added. Therefore, chlorine in the backwash water is of particular relevance in the case of "biologically" retrofitted plants. Furthermore, in certain full scale plants Cl_2

is added periodically to the backwash water of biofilters in order to control headloss buildup, likely caused by the excessive growth of biomass (Huck et al., 1998).

OBJECTIVES

The principal objective of the research reported in this chapter was to investigate the effects of free and combined Cl_2 in biofilter influents and the backwash water on the removal of selected easily biodegradable BOM components and the accumulation of viable biomass in such filters. Secondary objectives of the study included:

- to assess the differences between GAC/sand and anthracite/sand media regarding BOM removal when Cl_2 was present in the influent of such filters;
- to study the dynamic behavior of BOM removal in anthracite/sand biofilters which are intermittently dosed with Cl_2 either in the filter influent or in the backwash water;
- to apply UV_{285} analysis to biological filters as a tool to address the potential formation of soluble microbial products (SMPs) in the biofilters operated under the specific conditions of these experiments;
- to investigate headloss buildup in the biofilters operated under the particular conditions of these experiments, i.e. negligible amount of particles in the filter influent.

MATERIALS AND METHODS

Filtration Setup

The filtration setup, media specifics, feed water and the conditions of BOM addition have been described in detail in Chapter 3. Prior to the experiments with chlorine (experiments C1 and C2) reported in this chapter, the experimental setup was completed by adding two parallel filters to the setup used in experiments H1 and H2 (Chapter 4). The

filter setup as well as the conditions of oxidant (chlorine) dosage for experiments C1 and C2 are shown in Figures 5.1 and 5.2.

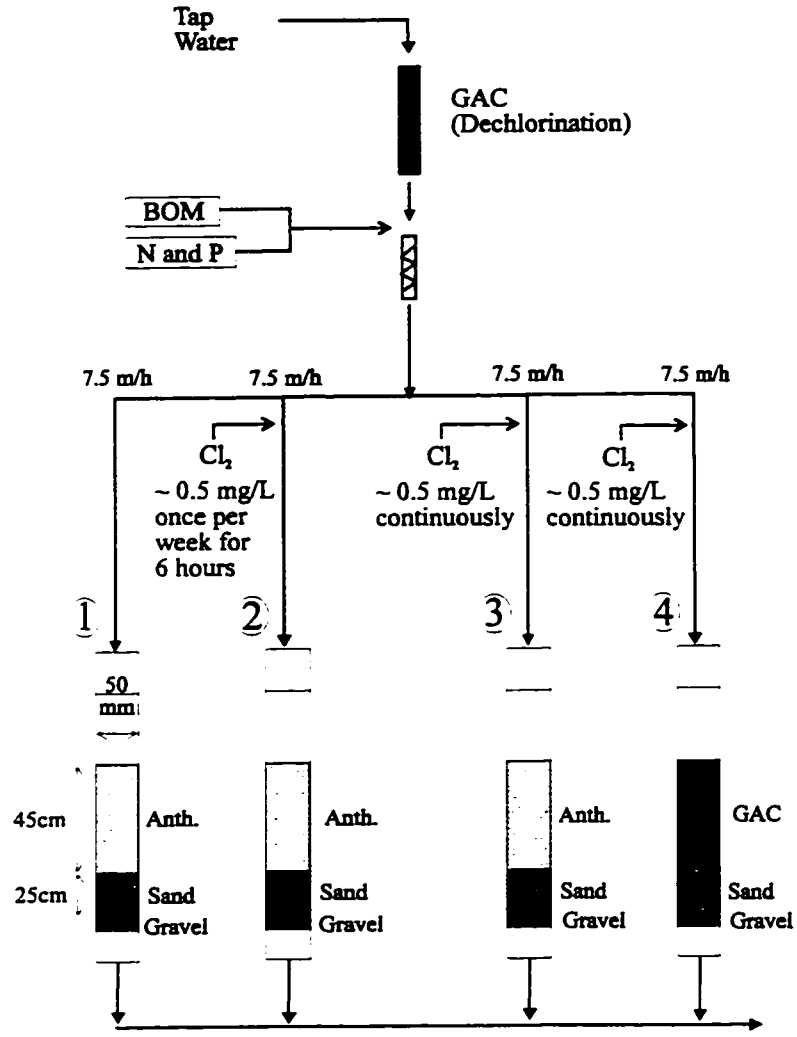

Figure 5.1: Experimental setup of experiment C1

Chlorine Dosage

In experiment C1 free chlorine (diluted, commercially available bleach) was continuously dosed to the influents of filters 3 and 4 at a target influent concentration of 0.5 mg Cl_2/L. This concentration was chosen because it is in the range of commonly

encountered Cl_2 concentrations in full scale plants. Therefore, this concentration appeared to represent an appropriate starting point for the study of the effects of the continuous presence of free Cl_2 in biofilter influents, which were essentially uninvestigated at the beginning of this experiment. Filter 2 received the same influent concentration (0.5 mg/L Cl_2) periodically, i.e. once per week for a period of 6 hours. The operating conditions of filter 2 were chosen in order to simulate the effects of the periodic chlorination of open-air sedimentation basins such as practiced at certain full-scale plants (Teefy, 1997). In general, the actual Cl_2 concentrations in the filter influents were relatively close to the target.

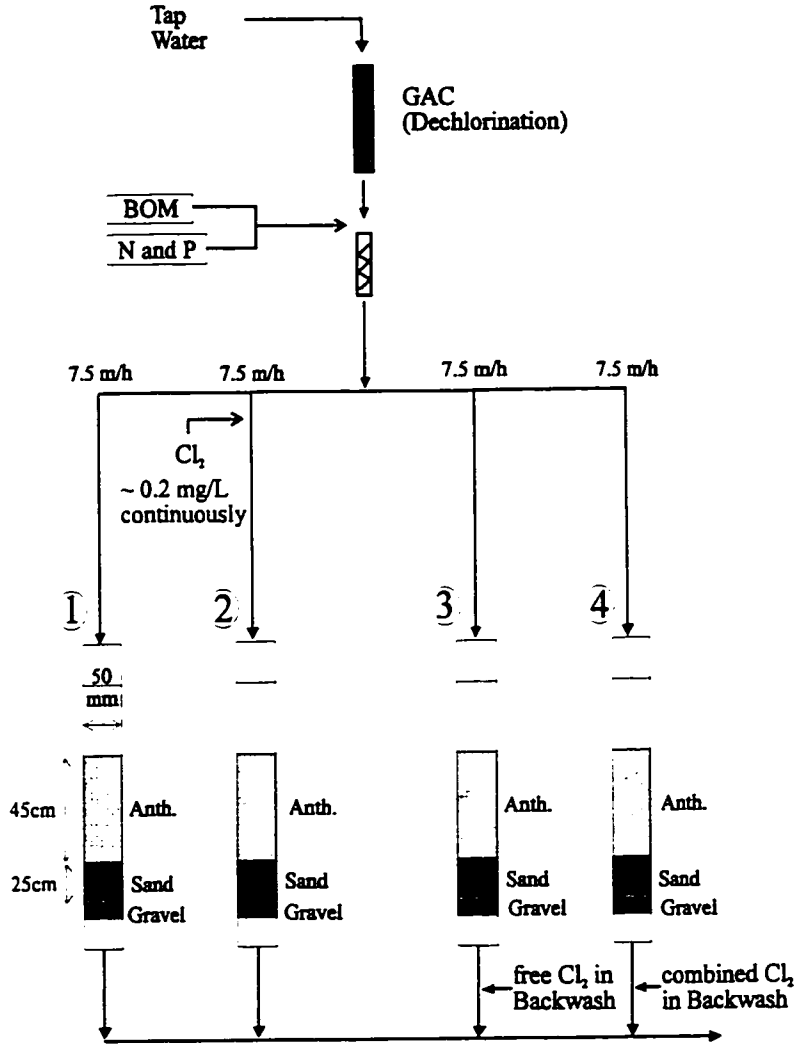

Figure 5.2: Experimental setup of experiment C2

Filter 1 served as control and received no Cl_2. During experiment C1 the feed water temperature was between 12 and 15°C and the pH was 7.4. This pH-value is close to the pK_a of the ionization of hypochlorous acid (HOCl), i.e. $pK_a = 7.54$, and free Cl_2 in filters 2, 3 and 4 was therefore present in about equal proportions as HOCl and hypochlorite (OCl^-). The equilibrium between hypochlorous acid and hypochlorite is of importance because HOCl is a much stronger disinfectant compared to OCl^-, likely as a result of the increased disinfectant permeability of the uncharged HOCl into the microorganisms (Jacangelo et al., 1987), as already mentioned in Chapter 2.

In experiment C2, free Cl_2 was continuously dosed to the influent of filter 2 at a target influent concentration of 0.2 mg Cl_2/L. This concentration was chosen as a result of the major negative effect on BOM removal observed at a filter influent concentration of 0.5 mg Cl_2/L (cf. Results and Discussion). Filters 3 and 4 were backwashed with chlorinated water at a concentration of ~1 mg Cl_2/L. Filter 3 was backwashed with free chlorinated water and filter 4 with chloraminated water. The Cl_2 concentrations in the backwash water of filters 3 and 4 were chosen because they are in the common range of chlorine levels in the backwash water of full scale filters.

Chloramines were formed by adding corresponding amounts of an ammonia solution (NH_4Cl) followed by diluted, commercially available bleach at a ratio of Cl_2:NH_4-N of 3:1 (w:w) to the carboy containing the backwash water for filter 4. This Cl_2:NH_4-N ratio leads to the predominant formation of monochloramine and is in the range of common full scale chloramination practice (Montgomery, 1985). Filter influent temperatures during experiment C2 ranged from 13 to 16°C.

As already mentioned in Chapter 3, a change of the tap water quality occurred during experiment C2. The major water quality parameters which were affected by this change were Cl_2 residual, pH, TOC and conductivity. The Cl_2 residual increased from < 0.1 mg/L before the change to ~0.5 mg/L combined Cl_2, the pH dropped from 7.4-7.5 to 7.0-

7.1, TOC increased from 1.0-1.1 mg/L to 1.5-1.6 mg/L and conductivity decreased from 1300-1400 μS to ~700 μS. The cause of this change was likely the fact that the University of Waterloo was receiving a blend of groundwater and treated surface water from the Mannheim WTP following the change whereas groundwater was the only source before the change.

Analytical Methods

The analytical methods for carboxylic acids, aldehydes, TOC, ThOD, phospholipid biomass, chlorine and headloss have been presented in Chapter 3.

UV absorbance at 285 nm

The bacteria present in biofilms oxidize BOM through bioreactions, transforming BOM to either cell mass, carbon dioxide or microbial products. Namkung and Rittmann (1986) have shown the significance of the formation of soluble microbial products (SMPs) in biofilters, regarding the concentration of organic carbon in the filter effluent. They reported that SMPs were mostly high-molecular-weight compounds, potentially including polysaccharides, proteins, RNA, exocellular enzymes and cell fragments. Different researchers have used UV absorbance at 285 nm (UV_{285}) to characterize NOM in water, specifically the fraction referred to by these authors as refractory organic matter (ROM) (Buffle et al., 1982; Zumstein and Buffle, 1989; Krasner et al., 1996). ROM is composed of humic substances which are stable by-products resulting from bacterial decomposition of a wide number of biochemical compounds (Zumstein and Buffle, 1989). The choice of 285 nm as the wavelength for the quantification of ROM is somewhat arbitrary because of the absence of well characterized absorbance bands in the UV spectral band (Buffle et al., 1982). However, because UV_{285} has been used by several researchers for the characterization of NOM, absorbance measurements reported in this chapter were made at 285 nm instead of the more commonly used 254 nm. Carlson et al., (1996b) have used

specific UV absorbance (SUVA) measurements through a biofilter in order to assess SMP formation. They observed a steady increase of SUVA through the filter and noted that this implied an increasing concentration of larger, more aromatic or proteinaceous compounds as a result of SMP production (Carlson et al., 1996b). However, because SUVA is equal to the ratio of UV_{254} to DOC, biodegradation of BOM, which in general has a low UV absorbance, is expected to lead to an increase of the SUVA. Therefore, SUVA measurements are likely not the optimized tool in order to quantify SMP formation.

Recent studies using annular reactors (ARs), which simulate BOM degradation and bacterial growth in distribution systems, showed that UV_{285} increased from the influent of the first of three ARs operated in series, to the effluent of the third (Gagnon, 1997). The reason for this observed increase in UV_{285} was likely the result of the formation of SMPs (Gagnon, 1997).

UV_{285} was analyzed on a UV spectrophotometer (HP 8453, Hewlett-Packard) in a 5 cm glass cell without any sample preparation (no filtration). The instrument was zeroed with ultrapure (Milli-Q) water. Four replicates of each sample were usually analyzed.

RESULTS AND DISCUSSION

Error bars shown in the figures of this chapter represent ± 1 standard deviation of duplicate samples unless otherwise noted.

Experiment C1

The date of startup of experiment C1 was March 18, 1997 and the experiment lasted for 3 months.

Removal of BOM Components

Figure 5.3 shows the concentration of formate through filters 1, 3 and 4 on day 8 following startup. The results obtained in filter 2 are not shown in Figure 5.3 because the

periodic addition of Cl_2 to the influent of this filter led to highly dynamic conditions with respect to BOM removal. Therefore, BOM removal in filter 2 was found to be strongly dependent on sampling time, i.e. elapsed time since last Cl_2 dosage. This will be further discussed later in this section. The data for acetate on day 8 were very similar compared to formate (Figure 5.3) however they are not shown here.

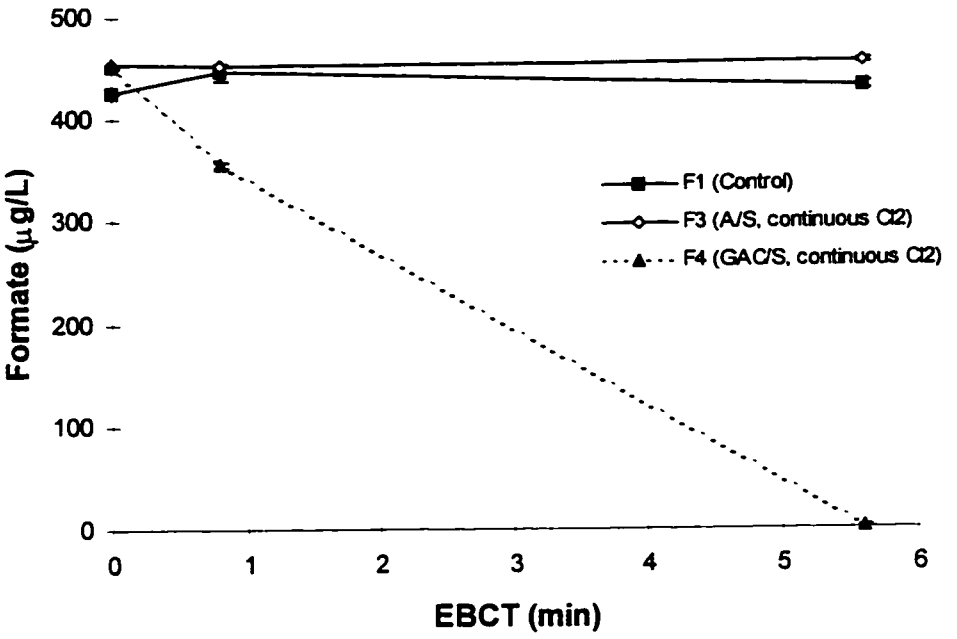

Figure 5.3: Concentration of formate through filters 1, 3 and 4 on day 8 following startup

The control filter (F1), and the anthracite/sand filter with the continuous dosage of Cl_2 to the influent (F3), did not show a measurable decrease of the concentration of formate through the filter, after 8 days of operation (Figure 5.3). In filter 4, which is the GAC/sand filter with Cl_2 in the influent continuously, formate was essentially totally removed through the filter after 8 days, most likely as a result of biodegradation.

Adsorption of formate in the GAC/sand filter seems unlikely because: 1) the GAC's adsorptive capacity was exhausted and 2) formate is a small and polar molecule which is not easily adsorbable on GAC. Therefore, biological formate removal capability was more

rapidly established in the GAC/sand filter (despite the presence of Cl_2 in the influent) compared to the control anthracite/sand filter (F1). This observation is in agreement with pilot and full scale results from the literature, suggesting that biological activity can be established more rapidly in GAC/sand filters compared to anthracite/sand (A/S) (Krasner et al., 1993; Coffey et al., 1995a). This is likely the result of differences in the surface structure of these media, i.e. GAC and anthracite. In fact, the rough and macroporous structure of GAC offers suitable attachment sites for bacteria present in the bulk water.

The fact that adsorption played a minor role in the removal of organics in F4 was supported by the similar patterns of TOC removal through filters 1 (anthracite/sand) and 4 (GAC/sand) as shown in Figure 5.4.

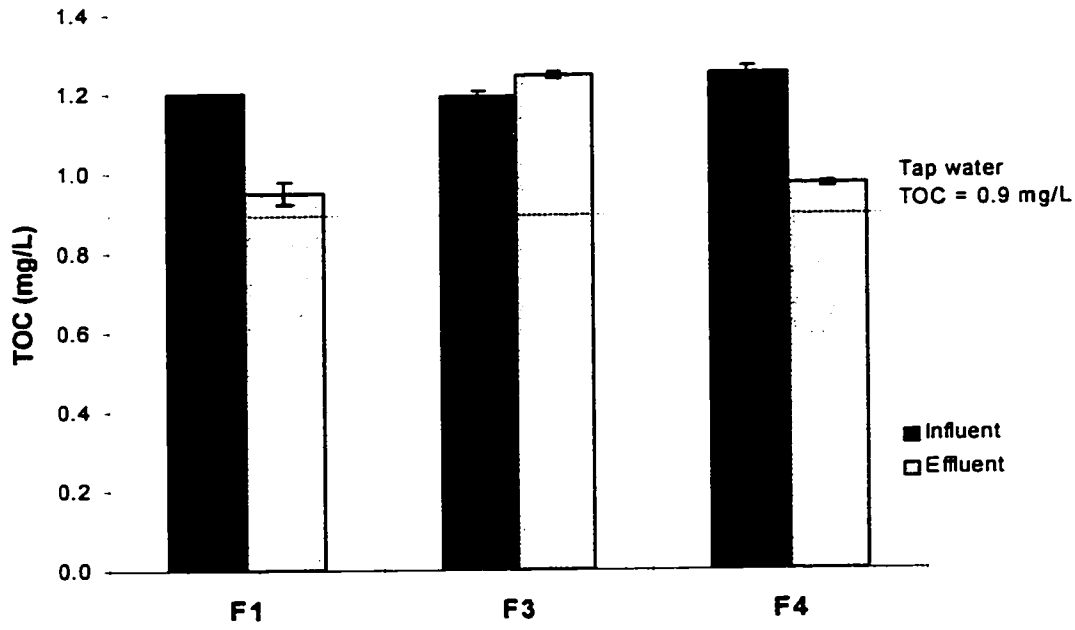

Figure 5.4: Removal of total organic carbon (TOC) through the different filters on day 50 following startup

In this figure the effluent of both filters, i.e. F1 and F4, had essentially identical TOC concentrations, suggesting that adsorption of organics on GAC played a negligible role during this investigation. In addition, Figure 5.4 shows that the dosage of the BOM-

cocktail to the tap water led to an increase of about 0.3 mg/L of organic carbon, which corresponds well to the target (0.28 mg C/L).

Figure 5.5 shows a similar plot as Figure 5.3 but for formaldehyde on day 22 following startup. Again, the data for filter 2 are not shown in Figure 5.5. After 22 days of operation, formaldehyde was essentially totally degraded in the control filter (F1) and the GAC/sand (F4) filter with 0.5 mg/L of Cl_2 in the influent (Figure 5.5). The anthracite/sand filter with 0.5 mg/L of Cl_2 in the influent (F3) did not show an appreciable decrease of the formaldehyde concentration as a result of the presence of chlorine under the specific conditions (Figure 5.5).

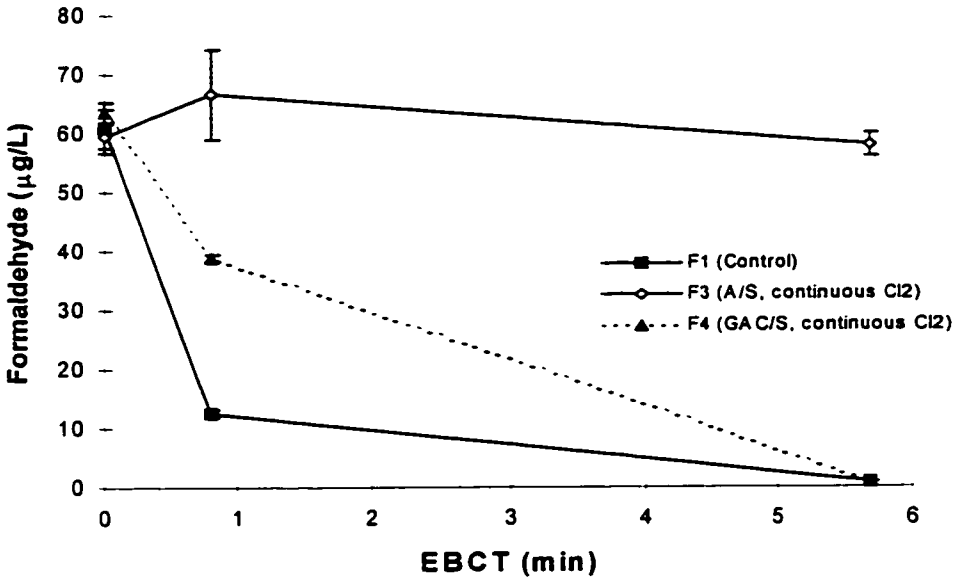

Figure 5.5: Concentration of formaldehyde through filters 1, 3 and 4 on day 22 following startup

The inhibitory effect of the continuous presence of 0.5 mg/L of Cl_2 in the influent of the anthracite sand filter (F3) on the removal of selected easily biodegradable components is further illustrated in Figures 5.6 for acetate and 5.7 for formate.

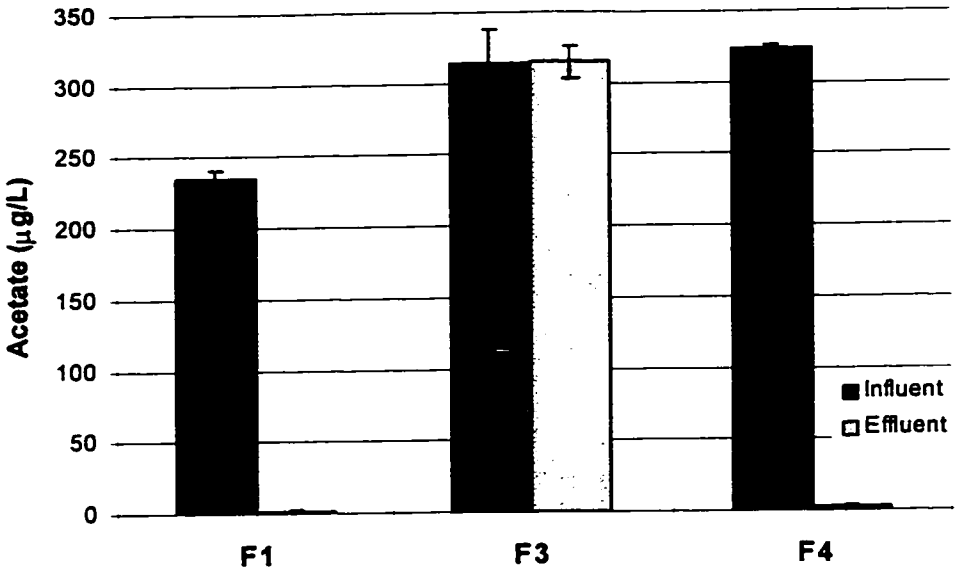

Figure 5.6: Concentrations of acetate in the influent and effluent of the different filters on day 49 following startup

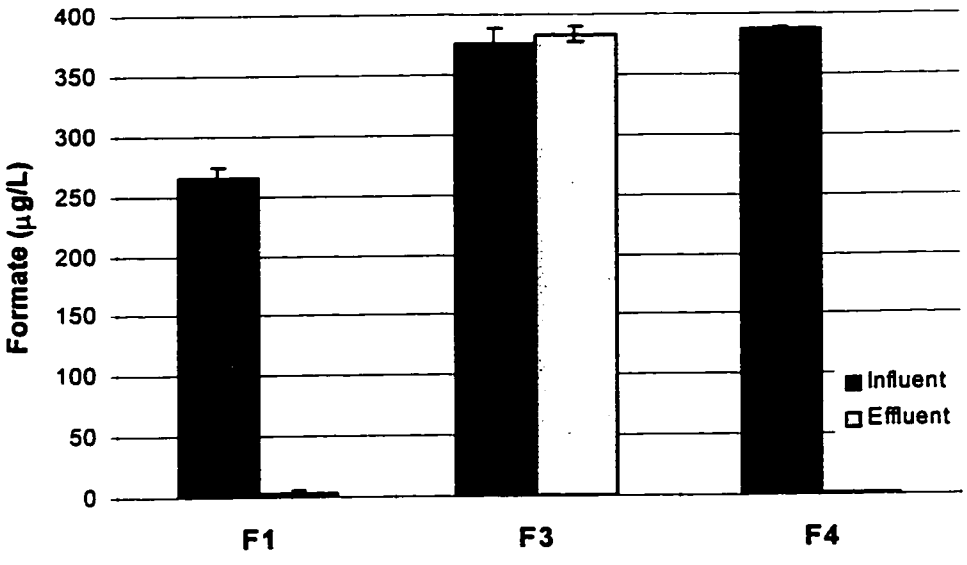

Figure 5.7: Concentrations of formate in the influent and effluent of the different filters on day 49 following startup

These figures show data from day 49 following startup. In both figures influent and effluent concentrations of acetate and formate in filter 3 are essentially identical, whereas these substances were very well degraded in filters 1 (control) and 4 (GAC/sand with chlorine). The reason for the lower influent concentration of acetate and formate in filter 1 compared to the other two filters (Figures 5.6 and 5.7) is not totally understood, although biodegradation prior to the filter media, i.e. biofilm formation on the glass wall above the media might be an explanation. Note that filters 3 and 4 did have a chlorine residual in the filter influent and the growth of a biofilm on the glass surface of these filters is therefore expected to be inhibited.

As a result of the continuous presence of a free Cl_2 residual in the influent, filter 3 did not show a measurable removal of acetate, formate and formaldehyde during the course of this experiment (Figures 5.3, 5.5, 5.6 and 5.7). This observation is confirmed by the measurement of virtually identical influent and effluent TOC concentrations in this filter as shown in Figure 5.4. Consequently under the tested conditions, the presence of approximately 0.5 mg/L free Cl_2 in the influent of the anthracite/sand filter totally inhibited the capacity of this filter to establish biological degradation of several easily biodegradable substances.

In the GAC/sand filter (F4) the continuous presence of ~0.5 mg Cl_2/L in the influent did not prevent the biological removal of formaldehyde (Figure 5.5), acetate (Figure 5.6) and formate (Figures 5.3 and 5.7) in this filter.

The reason for this is the rapid decrease of the Cl_2 residual in the GAC filter bed as a result of the chemical reduction of Cl_2 at the surface of the GAC, as illustrated in Figure 5.8. This figure further shows that the free Cl_2 concentrations in the influent and effluent of filter 3 were essentially identical, indicating that the filter's "chlorine demand" was negligible. The slight increase of the Cl_2 concentration from F3-influent to F3-effluent was likely the result of experimental imprecision. In filter 2 (the periodically chlorinated

anthracite/sand filter) a substantial decrease of the Cl_2 concentration was observed through the filter, particularly at the beginning of the 6-hour chlorination period. This decrease was likely the result of the reaction of Cl_2 with the biomass present in this filter.

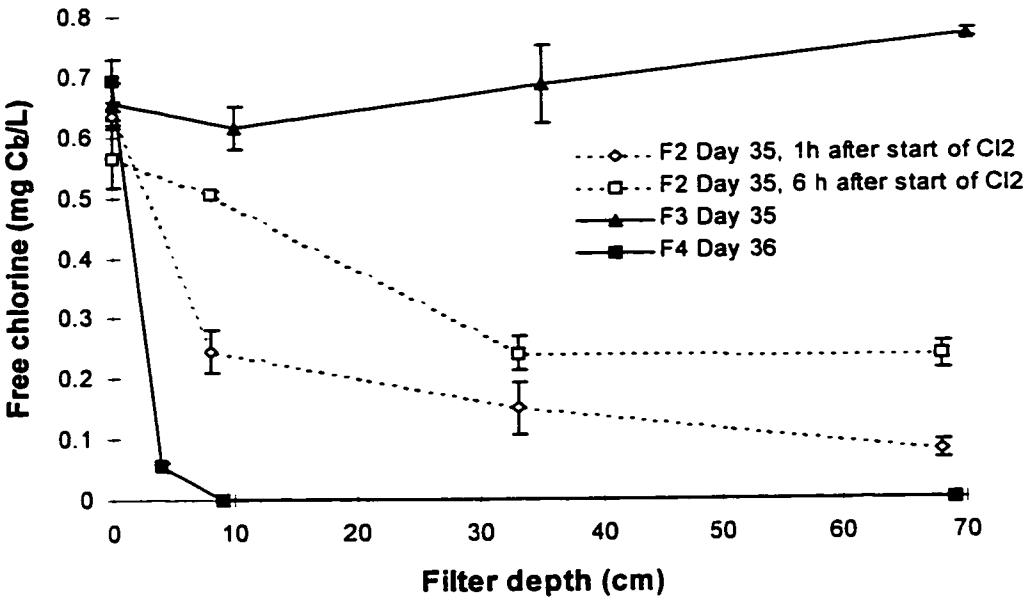

Figure 5.8: Free chlorine concentrations through filters 2, 3 and 4 on days 35/36 following startup

These results confirm that GAC/sand and GAC filters can operate biologically, i.e. degrade BOM, despite the presence of a free chlorine residual in the influent, as has been reported by others (e.g. DiGiano et al., 1992; LeChevallier et al., 1992). However as mentioned earlier, the presence of free Cl_2 in the influent of GAC filters is undesirable because of the formation of different chlorinated organics, and this operational mode is therefore not recommended. The GAC/sand filter was included in this investigation for comparative purposes.

An assessment of the effects of the periodic dosage of chlorine to the influent of a biologically active anthracite/sand filter is shown in Figures 5.9 and 5.10.

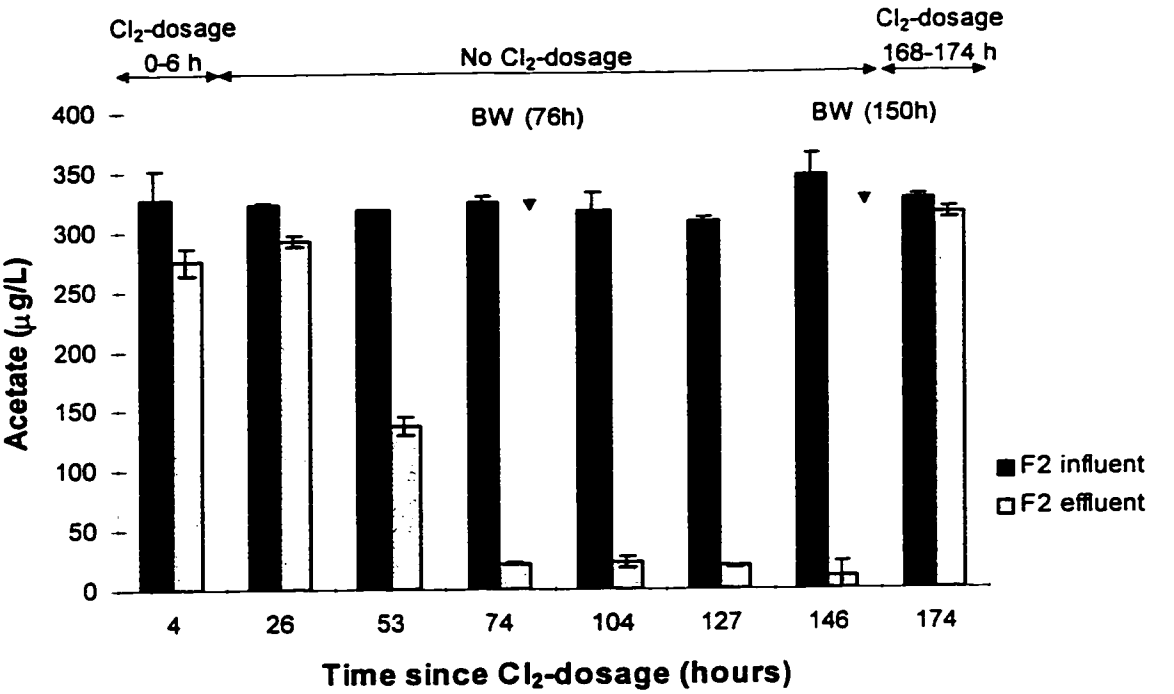

Figure 5.9: Removal of acetate in the periodically chlorinated filter (filter 2) over a period of one week, i.e. one chlorination cycle

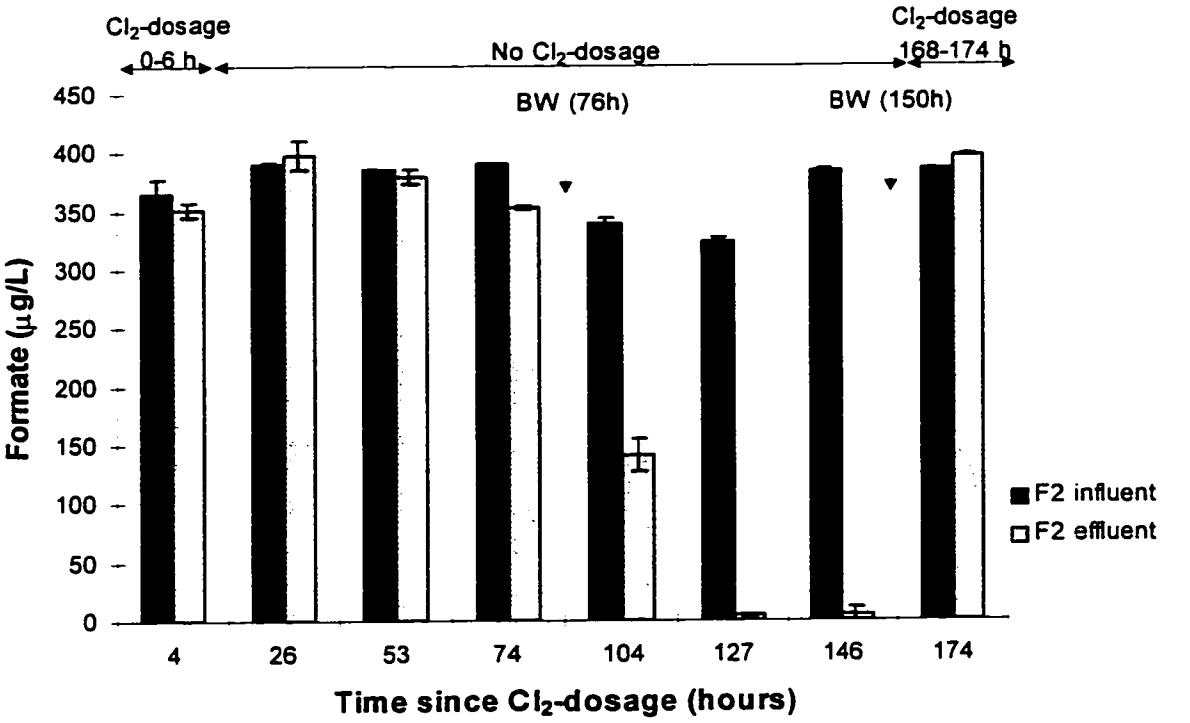

Figure 5.10: Removal of formate in the periodically chlorinated filter (filter 2) over a period of one week, i.e. one chlorination cycle

Both of these figures show influent and effluent concentrations of acetate (Figure 5.9) and formate (Figure 5.10) in filter 2 during the period of one chlorination cycle (days 49-56 following startup). Because of time constraints, only one chlorination cycle could be analyzed in detail during this experiment (Figures 5.9 and 5.10).

As already mentioned, the periodic addition (once per week for a period of 6 hours) of 0.5 mg/L of free Cl_2 to the influent of filter 2 led to non-steady state conditions with regards to the removal of acetate and formate in this filter (Figures 5.9 and 5.10). Hozalski (1996) has emphasized the importance of such dynamic conditions in biofilters and presented a non-steady state biofiltration model predicting the dynamic behavior of BOM removal in biofilters caused by biomass loss during backwashing. The results in Figures 5.9 and 5.10 confirm that BOM removal in biological filters can be a highly dynamic process, however in this case not caused by biomass loss during backwash but biomass inactivation caused by the periodic presence of an oxidant.

Figures 5.9 and 5.10 clearly show that the periodic addition of ~0.5 mg/L of free Cl_2 to the influent of this filter substantially impaired its removal capacity for acetate and formate. Following the periodic chlorination the re-establishment of BOM removal required about 60 to 70 hours for acetate and 110 to 120 hours for formate, under the specific conditions of this experiment. The fact that the re-establishment of the capability to remove acetate required less time compared to formate is consistent with observations made during the startup of experiment H2 (Chapter 4).

The data in Figures 5.9 and 5.10 indicate that the periodic chlorination of biological anthracite/sand filters might seriously impair the overall biological performance, i.e. BOM-removal, of such filters. This may be particularly true for the removal of more slowly biodegradable organics. As already mentioned in Chapter 3, the use of relatively easily biodegradable components in the BOM cocktail of this research, e.g. acetate and formate, represents a best case approach in regards of the inhibitory effects of oxidants, i.e. Cl_2, on

BOM removal. For utilities which operate their filters biologically and periodically use free Cl_2 for the control of algae growth in the sedimentation basins or for other purposes, it might be advisable to assess the impacts of this operational strategy on the biological performance of the specific filters. The prevention of the presence of Cl_2 in the influent of the biofilters could be readily achieved by the temporary addition of a reduced inorganic chemical, e.g. sodium bisulfite, to the filter influent during the presence of Cl_2.

UV absorbance at 285nm

The interest in measuring UV_{285} through the biofilters evolved during the experimental work presented in Chapter 4. UV_{285} was measured during this experiment (C1) and the second chlorine experiment (C2). The results were generally similar, however, only the UV_{285} results from experiment C1 are discussed in this thesis.

On several occasions a substantial increase of the UV absorbance at 285 nm was observed through the filter bed of the biologically active filters. As an example, Figure 5.11 shows the change in UV_{285} through filter 1 (A/S, control) and filter 3 (A/S, 0.5 mg/L Cl_2 in influent continuously) on day 65 following startup. The data in Figure 5.11 are shown as the difference in UV_{285} of samples within the filter bed compared to the UV_{285} of the filter influent sample. For a better understanding of the results in this figure, the dashed horizontal line through zero represents no change in UV_{285} through the filter bed.

No significant change in UV_{285} occurred through the filter bed of the non-biological anthracite/sand filter (F3). In filter 1 (anthracite/sand, control) however, a significant increase of UV_{285} was observed through the filter bed. This suggests that the increase in UV_{285} observed in filter 1 was related to the filter's biological activity, because no significant change in UV_{285} was observed through the non-biological filter (F3), which otherwise was designed and operated identically to filter 1. Therefore, it is thought that the increase in UV_{285} through filter 1 was the result of the formation of SMPs in this filter,

although the potentially increased amount of light-scattering bio-particles, i.e. cells and cell fragments, in the water of filter 1 may be an alternative explanation.

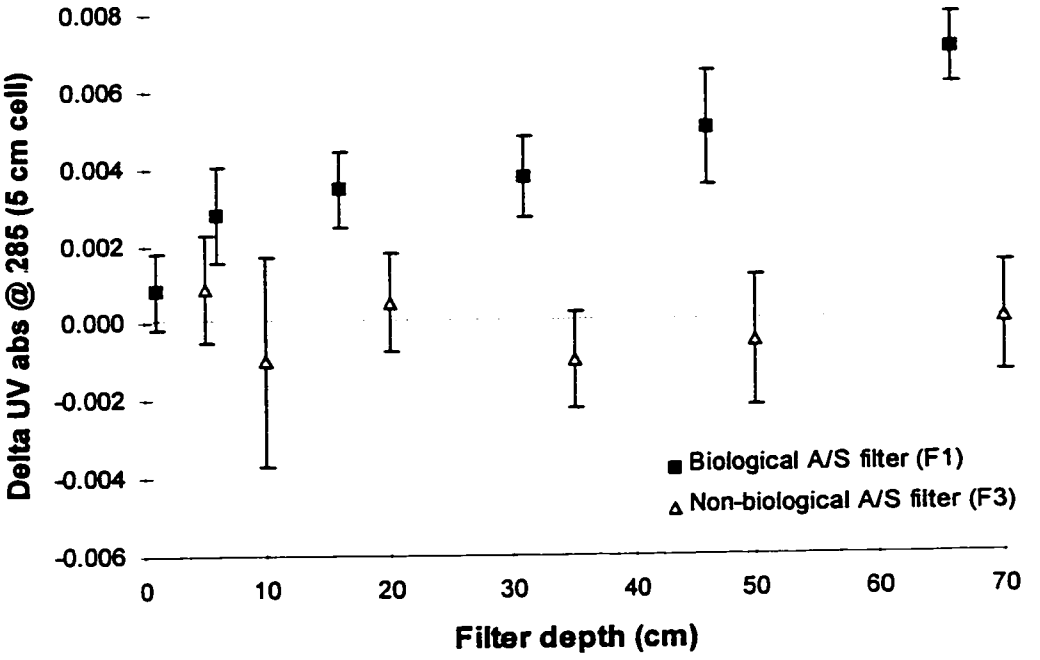

Figure 5.11: Change of UV_{285} through filters 1 and 3 on day 65 following startup, error bars represent 95% confidence intervals

Namkung and Rittmann (1986) have modeled the formation of SMPs in a completely-mixed biofilm reactor as the sum of utilization-associated SMP (P_1) and biomass-associated SMP (P_2):

$$P = P_1 + P_2 = k_1 \frac{YJA}{Q} + k_2 \frac{X_f L_f A}{Q} \qquad (5.1)$$

where:

P:	total SMP concentration (M_s/L^3)
k_1:	net utilization-associated SMP formation constant (M_s/M_x)
k_2:	net biomass-associated SMP formation constant (M_s/M_x*T)
Y:	true yield coefficient (M_x/M_s)
JA:	total substrate flux into the biofilm (M_s/T)
X_fL_fA:	total biofilm mass in the reactor (M_x)
Q:	flowrate (L^3/T)

If equation 5.1 is multiplied by Q, the resulting equation is an expression for the SMP production per unit of time. According to equation 5.1, the total SMP concentration is inversely proportional to flowrate, Q. Therefore, it is expected that a short-term decrease of flowrate would lead to a substantial increase of the SMP concentration. In fact, if the change in the flowrate is only of short duration, the total biofilm mass in the reactor, i.e. $X_f L_f A$, can be assumed to remain constant. Therefore, the decrease in flowrate is expected to lead to an inversely proportional increase in the formation of biomass-associated SMPs (cf. equation 5.1).

On the other hand, the total substrate flux into the biofilm (JA) in the expression for utilization-associated SMP (P_1) will decrease proportionally to flowrate, if substrate flux into the biofilm is assumed to be approximately equal to the organic loading of the filter. However, this is a somewhat approximate assumption. Nevertheless, it can be expected that a short-term change in flowrate will affect P_2 in a major way and likely to a lesser extent P_1.

On day 91 following startup, UV_{285} through the control filter (F1) was measured before and 2 hours after a decrease of the filter's hydraulic loading from 7.5 to 2.5 m/h. The results of this test are shown in Figure 5.12. A significant difference in the increase of UV_{285} through the filter was observed as a function of the hydraulic loading. At the lower hydraulic loading, a significantly higher increase in UV_{285} was observed through the filter. Based on equation 5.1 and what has been said immediately above, this suggests that under the conditions of this experiment and considering the assumptions which were made, the biomass-associated SMP fraction, i.e. P_2, represented a substantial part of the total amount of SMPs produced in the biofilter.

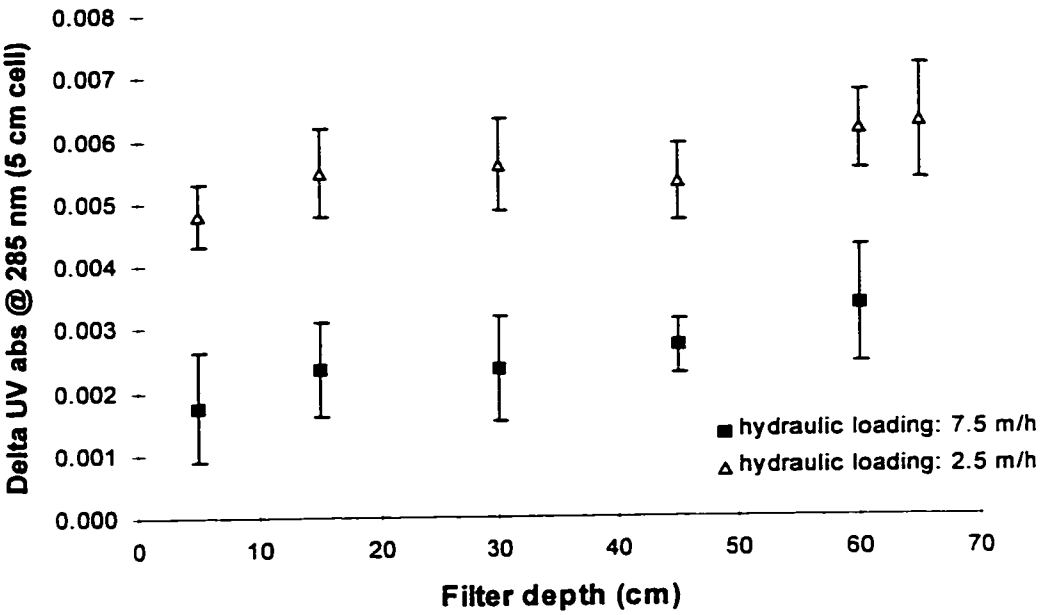

Figure 5.12: Change of UV_{285} through the control filter on day 91 following startup, error bars represent 95% confidence intervals

In summary, the results presented in this section suggest that the measurement of UV absorbance may represent a useful tool for the monitoring of the formation of SMPs in biofilters under low substrate (oligotrophic) conditions typically encountered in drinking water biofiltration. However, this is only possible in waters where the NOM fraction which is quantified by UV absorbance has a low or ideally no biodegradability. Otherwise removal and formation of UV absorbing organics might occur in parallel in a given biofilter and a distinction of the different processes becomes impossible.

Biomass

Figure 5.13 presents data of viable biomass measured as phospholipid at three different depths, top (1-2 cm), middle (31-32 cm) and bottom (61-62 cm) on day 70 following startup. In filter 2, media was sampled just prior to the 6-hour dosage of free chlorine.

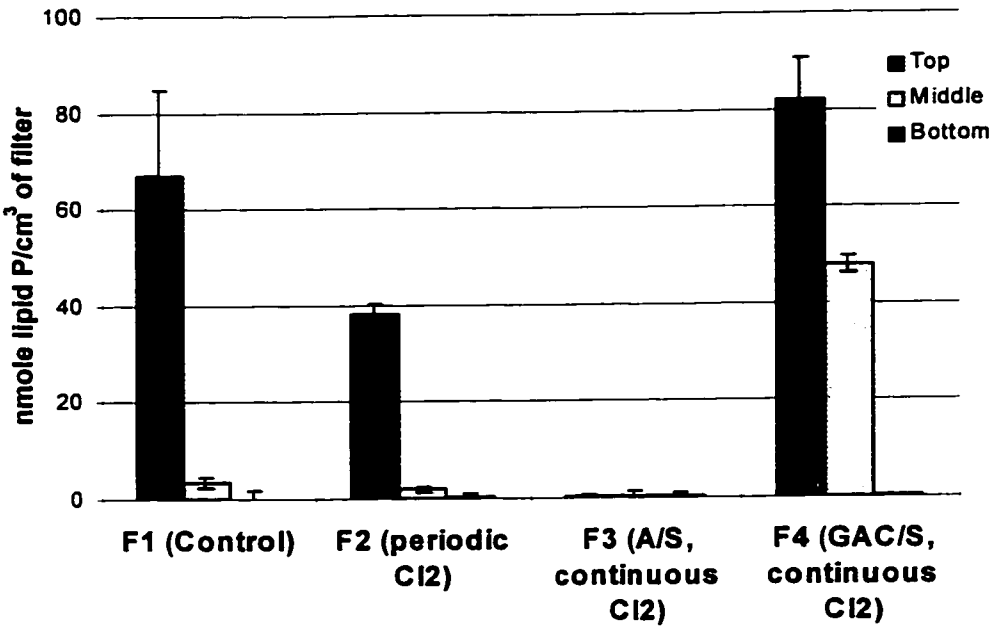

Figure 5.13: Total amount of viable biomass (measured as phospholipid) in the filters at three different depths on day 70 following startup

Figure 5.13 shows that filter 3 did not contain a measurable amount of viable biomass attached to the media, confirming the acetate, formate and TOC data, which showed no decrease of the concentration of these parameters through this filter. Filters 1 and 4 showed similar amounts of biomass per unit volume of filter at the top, however, filter 4 (GAC/sand) contained substantially more biomass in the middle compared to filter 1 (A/S). The reasons for this difference are not fully understood, although a flatter BOM concentration profile in the GAC/sand filter (F4) compared to the control filter (F1) might be an explanation for this observation. A flatter BOM profile in filter 4 has been observed in the case of formaldehyde (Figure 5.5). This is possibly the result of the partial inhibition of BOM removal/biomass growth in the top part of this filter due to the presence of Cl_2. This would lead to higher substrate concentrations deeper in the filter and therefore to a higher amount of biomass in the lower parts of the filter. However, the data are insufficient

to draw more definite conclusions. The relationship between substrate concentration profiles and biomass distribution will be further discussed in Chapter 6.

The biomass profile in the control filter (F1) showed a pronounced stratification with most of the biomass present in the top part of the filter. This is in agreement with biomass results obtained in the control filter during experiment H2 (Chapter 4). Filter 2 had an appreciable amount of viable biomass at the top, however, as a result of the dynamic conditions of the removal of acetate and formate in this filter (Figures 5.9 and 5.10) the amount of biomass in a periodically chlorinated anthracite/sand filter is likely highly dynamic and strongly depends on the time of sampling. Lower levels of biomass can be expected when sampling is performed earlier in the chlorination cycle.

Headloss

Total headloss was measured in all four filters and the emphasis was on the headloss immediately before backwash, referred to here as terminal headloss, and the headloss just after backwash, referred to here as clean bed headloss. In the case of clean bed headloss, the data indicate no substantial change during the whole duration of the study (Figure 5.14).

Figure 5.14 shows that filters 1 and 3, which contained identical media, had similar values of total clean bed headloss throughout the study, despite the fact that filter 1 was biologically active and filter 3 was not. This suggests that backwashing using air scour at collapse pulsing conditions maintained the clean bed headloss of a biologically active filter (F1) at a similar level compared to a non-biological filter (F3). Hence, the presence of biomass attached to the filter media as biofilm did not lead to an increase of the clean bed headloss under the tested conditions, i.e. filter influent (tap water) with a very low concentration of particles.

The same trend as for the biologically active anthracite/sand filter (F1), i.e. no increase of the clean bed headloss over time, was observed for the biologically active

GAC/sand filter (F4) (Figure 5.14) and the periodically chlorinated filter (F2) (data not shown in Figure 5.14).

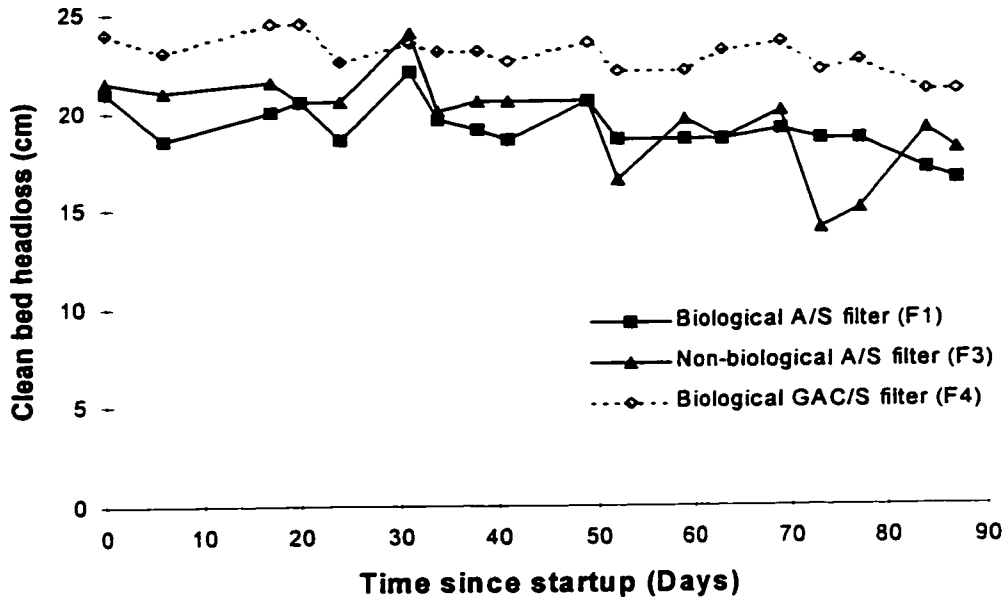

Figure 5.14: Clean bed headloss in the different filters over the entire duration of experiment C1

Different authors have reported opposite trends, i.e. an increase of clean bed headloss in biofilters with time, however for filters backwashed without air scour (Goldgrabe et al., 1993; Coffey et al., 1995b; 1996). Consequently, in the absence of pilot scale or other data, the design of full scale biofilters including air scour in the backwashing procedure might be a safe option in regards of headloss control in such filters.

Regarding the buildup of headloss during the filter cycle, it was observed that the headloss increase during a filter cycle, which lasted about 3-4 days on average, was minimal. As an example, Figure 5.15 shows a comparison between the clean bed headloss and the terminal headloss for the control filter (F1).

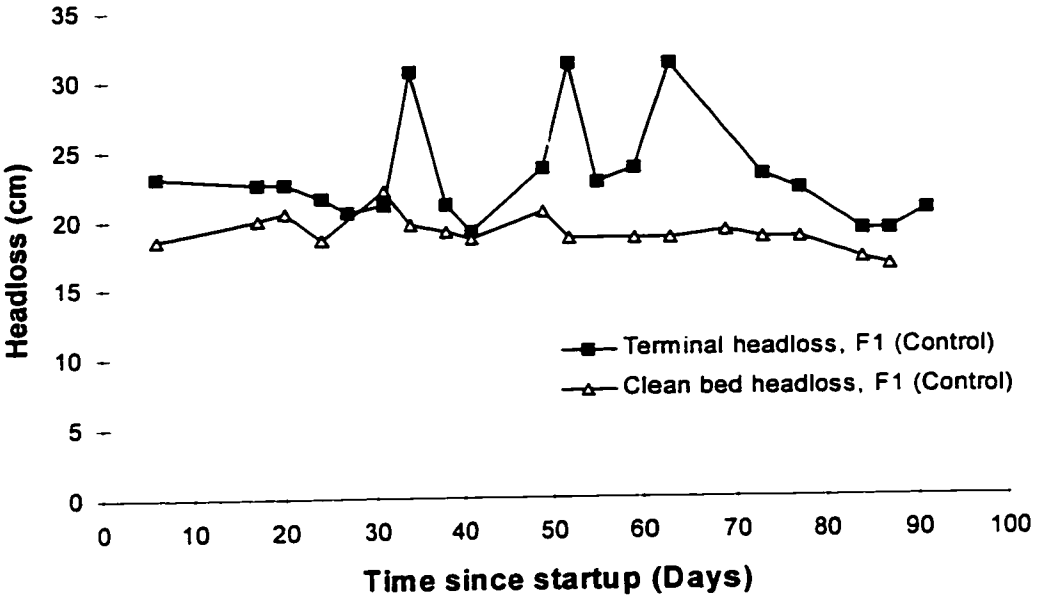

Figure 5.15: Comparison of clean bed and terminal headloss in the control filter (F1) over the entire duration of experiment C1

The headloss increase during the filter cycle was < 5 cm for most measurements. In the case of the terminal headloss data-points which are just above 30 cm (Figure 5.15), air-binding occurred towards the end of the filter cycle. This led to an unusually high value for the terminal headloss in those cases. The occurrence of air binding will be further discussed in the second part of this chapter in conjunction with the discussion of the results of experiment C2.

Experiment C2

Experiment C2 was started on August 18, 1997. The experimental setup of this experiment is shown in Figure 5.2. Briefly, filter 2 (A/S) received ~0.2 mg/L free Cl_2 continuously and filters 3 and 4 (A/S) were backwashed with free chlorinated and chloraminated water, respectively (~1 mg/L Cl_2). Filter 1 (A/S) served as control (no oxidant).

As already mentioned in the "Materials and Methods" section of this chapter a change in the tap water quality occurred during experiment C2. The change occurred on approximately day 30 following startup. Following the change of water quality, the tap water usually had a combined Cl_2 residual of about 0.5 mg/L. This concentration decreased to about 0.1 mg/L following the GAC dechlorination columns. Therefore, in the samples of day 30 and later, the filter influents of F1, F3 and F4 contained about 0.1 mg/L of combined Cl_2 in the influent. In the case of F2, the water quality change led to a switch from free Cl_2 (~0.2 mg/L) to combined Cl_2 (~0.3 mg/L) in the influent of this filter. Later in the experiment, i.e. day 88 following startup, the Cl_2 dosage to the influent of F2 was increased in order to obtain a free Cl_2 residual again. This chlorine addition mode was maintained until the end of experiment C2.

Removal of BOM Components

Figures 5.16 and 5.17 show the removals of acetate and formate respectively over time following startup. These figures also show the conditions regarding Cl_2 concentration and form (free or combined) in the influent of F2 during the entire experiments. The filters which were backwashed with chlorinated water, i.e. F3 and F4, showed a pronounced dynamic BOM removal pattern as a function of time since the last backwash. The BOM results collected in these filters are therefore not shown in Figures 5.16 and 5.17 and will be discussed later in this section.

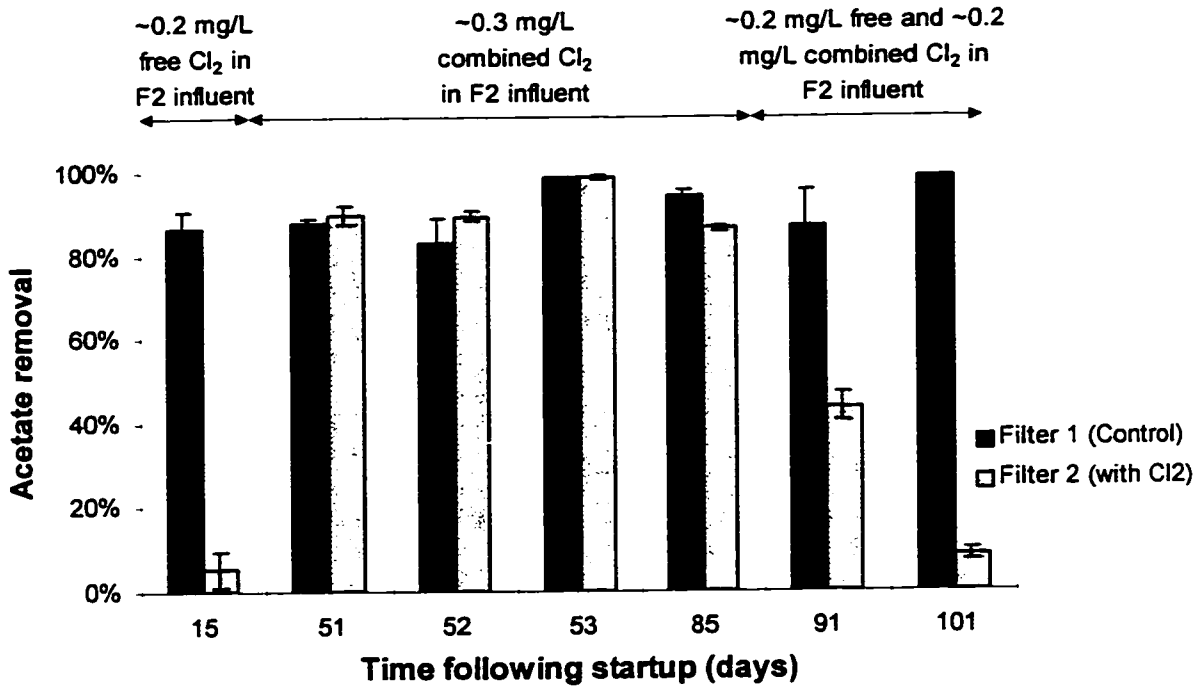

Figure 5.16: Removal of acetate in filters 1 and 2 during experiment C2

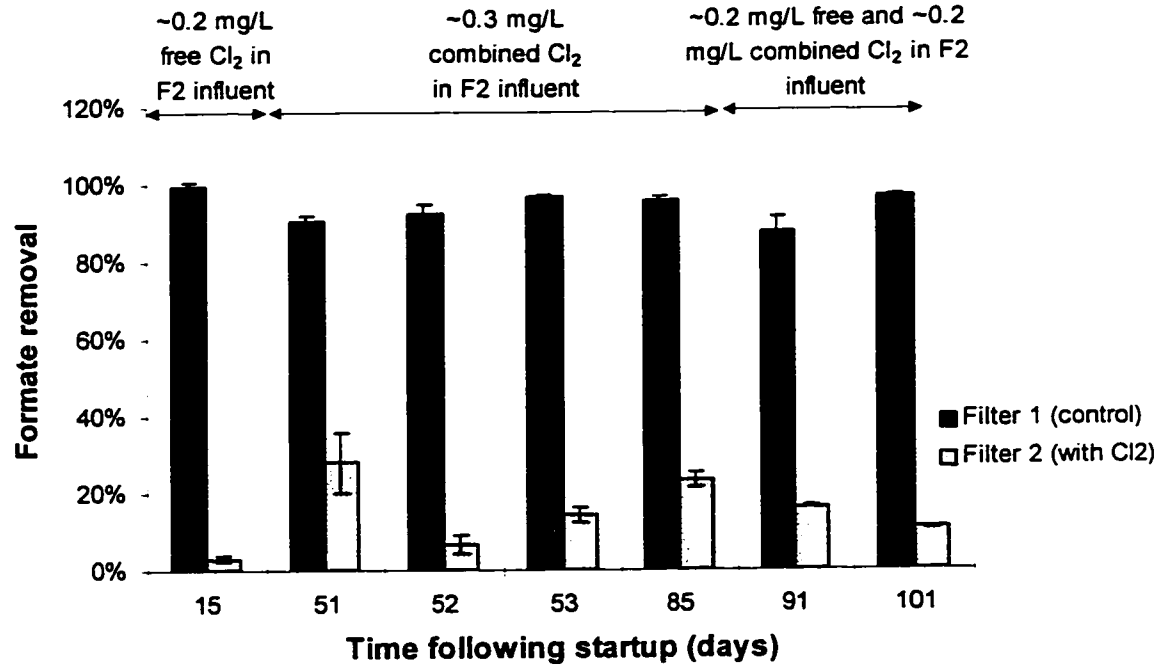

Figure 5.17: Removal of formate in filters 1 and 2 during experiment C2

The results for filter 1 in Figures 5.16 and 5.17 suggest that the appearance of a combined Cl_2 residual of about 0.1 mg/L Cl_2 in the influent of filter 1 on approximately day 30 did not lead to a measurable inhibition of the removals of acetate and formate in samples collected subsequently.

This suggests that in the case of an existing biofilm, biological degradation of acetate and formate continued to occur in filter 1 despite the appearance of ~0.1 mg/L combined Cl_2 in the influent of this filter. A low but measurable combined Cl_2 residual was usually measured in the effluent of filter 1, i.e. ~0.03 mg/L. These data imply that the threshold combined Cl_2 concentration above which biological degradation of easily biodegradable components (such as the ones used in this research) is inhibited, is greater than 0.1 mg/L. In addition, the fact that a combined Cl_2 residual was usually observed in the effluent of filter 1 during the time period when about 0.1 mg/L combined Cl_2 was present in the filter influent confirms the low reactivity of combined Cl_2 with biofilm components, noted by LeChevallier and colleagues (e.g. LeChevallier et al., 1988).

In the case of filter 2, the presence of ~ 0.2 mg/L of free Cl_2 in the filter influent did substantially inhibit the removals of acetate and formate (Figures 5.16 and 5.17). This can be observed by examining the data points of days 15, 91 and 101 in Figures 5.16 and 5.17. The same observation, i.e. substantial inhibition of biological removal, was made for formaldehyde on day 93 following startup (data not shown).

During the presence of a combined Cl_2 residual of 0.3 mg/L in the influent of F2, i.e. days 30-88, the degradation of acetate and formate were affected differently. While biological formate degradation continued to be suppressed in filter 2 in a major way (Figure 5.17), the removal of acetate was not inhibited by the presence of combined Cl_2 at 0.3 mg/L in the influent of F2 (Figure 5.16).

Thus under the specific conditions of this experiment, biological formate removal was observed to be inhibited at a combined Cl_2 influent concentration of 0.3 mg/L.

Therefore, considering what has been said earlier in relation to the results in filter 1, the combined Cl_2 concentration in the filter influent at which removal of easily biodegradable BOM components will be inhibited appears to be between 0.1 mg/L and 0.3 mg/L. As already mentioned, McGuire et al., (1991) have observed essentially no AOC removal in pilot scale anthracite/sand filters when the filter influent contained 1 mg/L of combined Cl_2. These results are consistent with what was observed in this research in that they suggested that the threshold combined Cl_2 concentration at which biological degradation of easily biodegradable components is inhibited is < 1 mg/L.

Figures 5.18 and 5.19 show the removal of acetate and formate respectively during one filter cycle, i.e. between two backwashes.

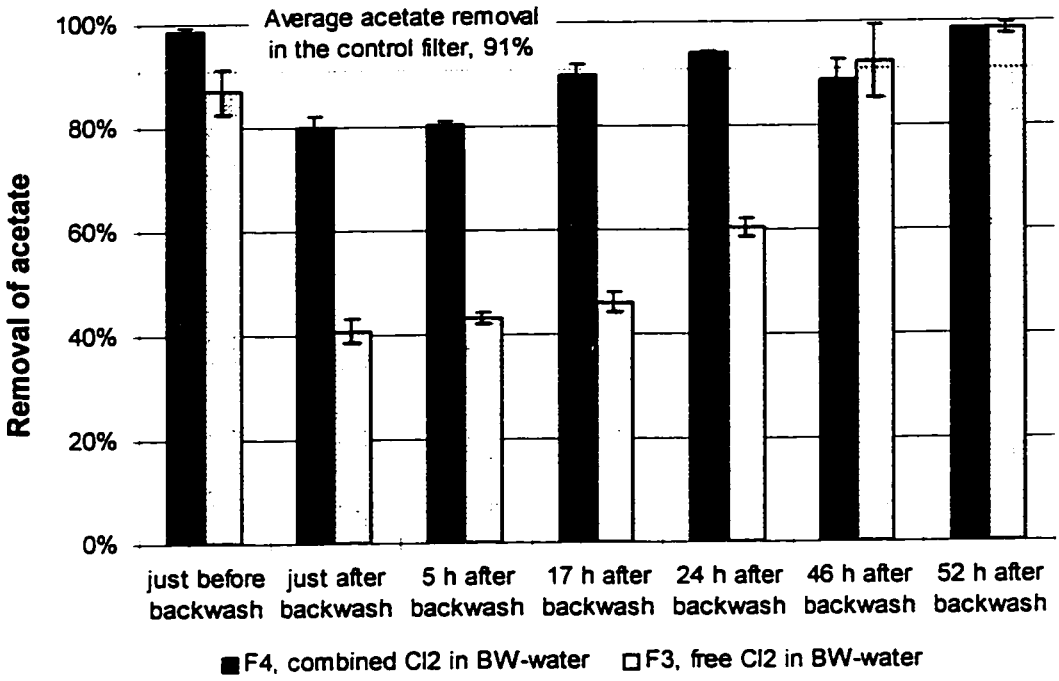

Figure 5.18: Removal of acetate in the filter containing Cl_2 in the backwash water (F3 and F4) during one filter cycle

The samples shown in these figures were not collected during one specific filter cycle but during different cycles at the specific times following backwash. For reasons of

comparison, the dashed horizontal lines in Figures 5.18 and 5.19 show the average removal of the specific carboxylic acid in the control filter (F1). In the control filter the removal of acetate and formate was unaffected by backwashing (data not shown).

Figure 5.18 shows that free Cl_2 in the backwash water (F3) affected the removal of acetate substantially more than did combined Cl_2 (F4), although Cl_2 concentrations were about equal, i.e. ~1 mg/L Cl_2. Acetate removal in filter 4 only slightly decreased following backwash and for most of the filter cycle acetate removal in filter 4 was comparable to the control filter. For filter 3 however, the suppression of acetate removal was substantial and a recovery time between 24-46 hours was required to reestablish biological acetate degradation.

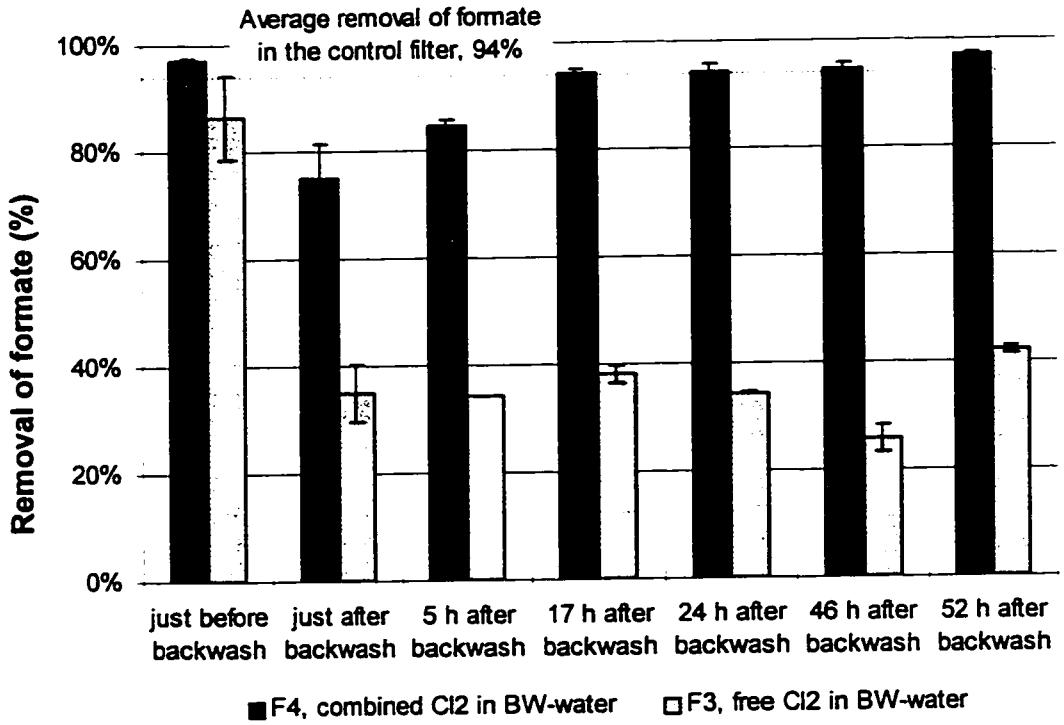

Figure 5.19: Removal of formate in the filter containing Cl_2 in the backwash water (F3 and F4) during one filter cycle

The results for formate (Figure 5.19) were similar compared to acetate with the exception that the inhibitory effect on formate removal in filter 3 (free Cl_2 in backwash water) was even stronger than for acetate. As shown in Figure 5.19, formate removal was not reestablished in filter 3 even after 52 hours following backwash. The reason why the filter 3 sample "just before BW" in Figure 5.19 showed a good removal of formate was likely the fact that this sample was collected at the end of a particularly long filter cycle, i.e. 6 days. The fact that the inhibition of formate removal in the free chlorinated filter (F3) was stronger compared to acetate removal is consistent with what has been observed in experiments H1, H2 and C1.

The results presented in Figures 5.18 and 5.19 suggest that backwashing with free chlorinated water (~1 mg/L Cl_2) has a substantial negative effect on the biological performance, i.e. removal of easily biodegradable BOM components, of biological anthracite/sand filters. This is consistent with pilot scale results presented by others (Miltner et al., 1995, Wang et al., 1995; Miltner et al., 1996). However, in an extensive study at demonstration scale, Huck et al., (1998) have observed a negligible effect of chlorinated backwash water (both as free Cl_2 and NH_2Cl) on the removal of BOM in anthracite/sand and GAC/sand filters. The reasons for these observed differences in the effect of chlorinated backwash water on BOM removal are not currently understood.

Figure 5.20 shows the calculated theoretical oxygen demand (ThOD) decrease through the different filters using aldehyde and carboxylic acid data from days 93 and 101 respectively, in conjunction with the measured dissolved oxygen consumption on day 98. The samples for carboxylic acids (day 101) and aldehydes (day 93) were collected about 2 days following backwashing and the DO-measurement of day 98 was also performed 2 days following backwash. Therefore, it seemed acceptable to compare these data, although they were not collected/measured on the same day.

The ThOD was calculated based on the redox reactions 3.1-3.4, shown in Chapter 3. The data in Figure 5.20 demonstrate that the measurement of the consumption of dissolved oxygen through the filters provides a reasonable approximation for the removal of BOM in the different filters.

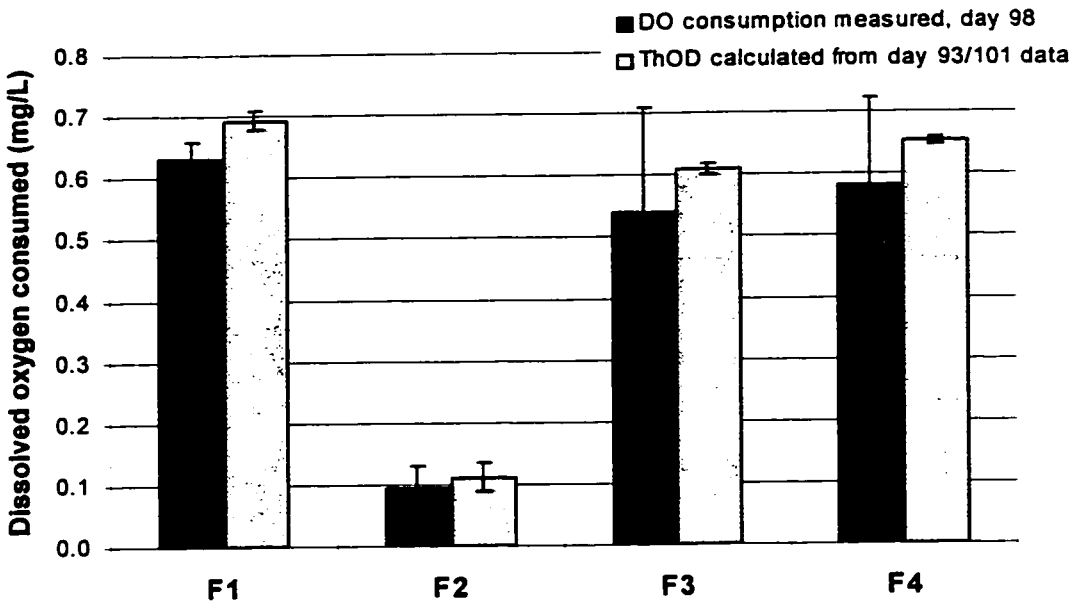

Figure 5.20: Comparison of dissolved oxygen decrease through the filters with the calculated ThOD of the consumed substrate

The DO-consumption measurement in F2 clearly indicates a major inhibition of BOM removal compared to the remaining filters. This suggests that DO-measurements represent a readily available tool for approximate assessments of BOM removal in biofilters. The applications potential of DO consumption measurements through biofilters are further discussed in Chapter 6.

Biomass

Figure 5.21 shows viable biomass, measured as phospholipid, at a filter depth of 4 cm before and after backwash on day 99 following startup. Each biomass measurement

shown in Figure 5.21 was performed in duplicate and error bars in this figure show standard deviations. The results in Figure 5.21 suggest that backwashing using air scour under collapse pulsing conditions led to an appreciable loss of biomass in the filters, i.e. average decrease of 52% in filters 1, 3 and 4. However, replication was insufficient in order to perform a statistical significance test of the biomass loss upon backwashing. The very low level of viable biomass in filter 2 on day 99 following startup is in agreement with the low percentage removals of acetate and formate observed in this filter (Figures 5.16, 5.17 and 5.20).

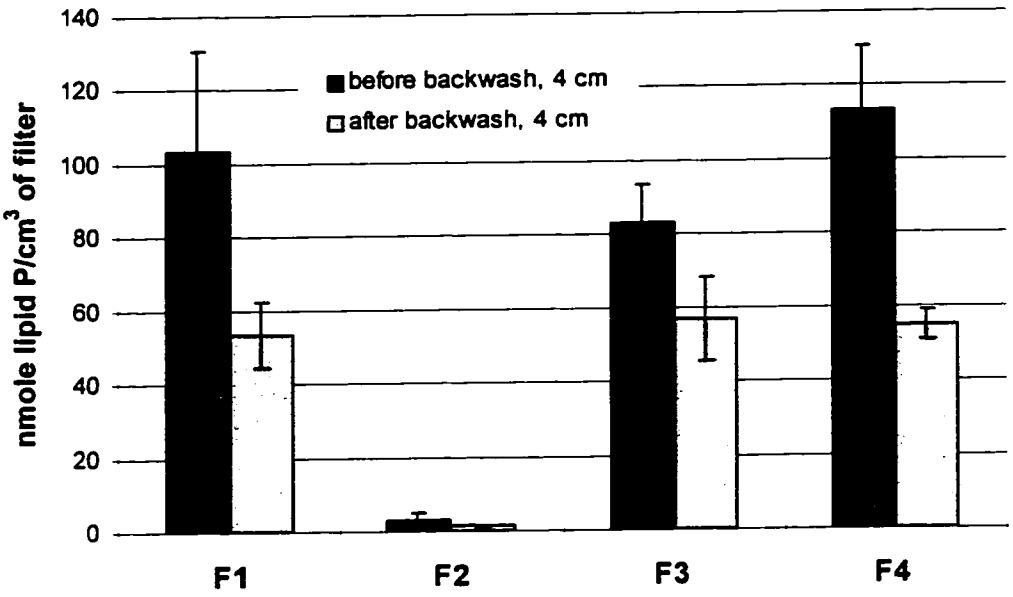

Figure 5.21: Viable biomass at a filter depth of 4 cm before and after backwash on day 99 following startup

It is noteworthy that biomass levels in filters 1 and 3 at a filter depth of 4 cm were similar following backwashing (Figure 5.21), although acetate and formate removal in filter 3 (free Cl_2 in backwash water) was observed to be substantially inhibited upon backwashing (Figures 5.18 and 5.19). This suggests that the measurement of the amount of viable biomass as phospholipid might not adequately quantify the substrate removal

capability of a given biofilter, as mentioned previously by the author and others (Miltner et al., 1996; Urfer et al., 1997).

The data for filters 1, 3 and 4 in Figure 5.21 were further analyzed in order to estimate the number of bacteria removed during backwashing. The data of filter 2 were excluded for this calculation because this filter contained essentially no biomass at 4 cm. At 4 cm filter depth, the average amount of biomass (phospholipid) removed as a result of backwashing was equal to 45 nmole lipid P/cm^3 of filter. Assuming that 100 nmole lipid P correspond to $3.4*10^9$ cells (Findlay et al., 1989), the number of bacteria removed per cm^3 of filter at the specific depth can be calculated as $1.5*10^9$ cells. In a bench scale investigation, Hozalski and Bouwer (1998) have estimated the average amount of HPC bacteria removed during backwashing (water wash only) as ~ $2*10^7$ cfu/cm^3 of filter. This estimation is about two orders of magnitude lower compared to what was calculated in this research. Three factors may be principally responsible for this difference: 1) the results from Hozalski and Bouwer (1998) represent an average for the entire filter whereas in this research only the removal at a filter depth of 4 cm was estimated. As shown in experiments H2 and C1, the amount of biomass at 4 cm is substantially higher compared to the average amount of biomass in the biofilters. 2) In this study the backwashing procedure included air scour while in the study from Hozalski and Bouwer the filters were backwashed with water only. As already mentioned previously (Chapter 2), Amirtharajah (1978) showed that backwashing with water alone was an ineffective process for the removal of accumulated particles from filters. 3) Hozalski and Bouwer (1998) used HPC bacteria as the method to quantify biomass, whereas viable biomass (phospholipid) was used in this research. HPC counts quantify the culturable bacteria under the specific conditions of the test, and HPC counts can therefore be expected to underestimate the actual amount of bacteria (e.g. Yu and McFeters, 1994).

Chlorine Removal through the Filters

In the continuously chlorinated filter (F2) a low Cl_2 residual (~0.10-0.15 mg/L) was always measurable in the filter effluent under the different Cl_2-dosage conditions described previously.

For the filters backwashed with chlorinated water, Figures 5.22 and 5.23 show Cl_2 concentrations in the overflowing backwash water of filters 3 and 4 during backwashing on day 84 following startup. Figure 5.22 shows that the free Cl_2 concentration in the overflow water increased continuously until the end of the backwashing procedure, i.e. 220 seconds after the start of overflow.

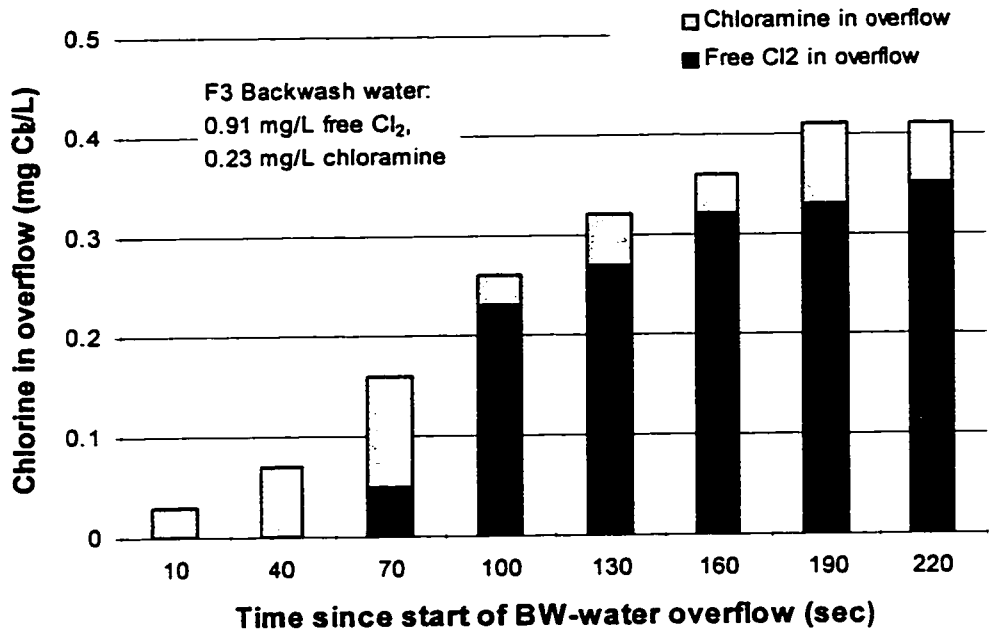

Figure 5.22: Chlorine in the overflow of filter 3 during backwash on day 84 following startup

The difference between the free Cl_2 concentration of the backwash water on day 84, i.e. 0.91 mg/L Cl_2, and the free Cl_2 concentration of the filter overflow at the end of backwashing, i.e. 0.35 mg/L Cl_2, indicates that the free chlorine demand of filter 3 at the end of backwashing was equal to about 0.56 mg/L Cl_2.

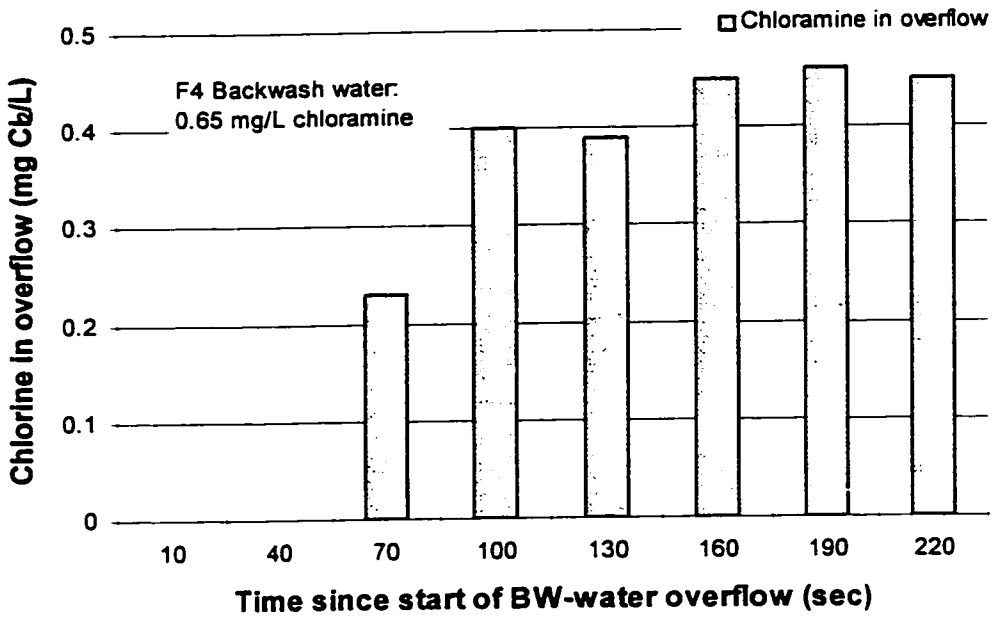

Figure 5.23: Chlorine in the overflow of filter 4 during backwash on day 84 following startup

In the case of filter 4, backwashed with chloraminated water, the combined Cl_2 concentration in the backwash water on day 84 was 0.65 mg/L, which was substantially below target for reasons which are not clear. Figure 5.23 shows that the combined Cl_2 concentration in the overflow water at the end of backwashing was equal to 0.45 mg/L. Thus the combined chlorine demand of filter 4 at the end of backwashing was equal to about 0.20 mg/L Cl_2. This is almost a factor of three lower compared to the free chlorine demand of filter 3.

Because the amount of viable biomass in filters 3 and 4 was found to be similar at 4 cm (Figure 5.21), the differences between the free and the combined chlorine demand of these filters suggest that free Cl_2 was reacting more readily with the biomass during backwash compared to combined Cl_2. This supports the better BOM removal in the chloraminated filter (F4) and is in agreement with results from LeChevallier and colleagues, as mentioned previously (e.g. LeChevallier et al., 1988).

Headloss

Clean bed and terminal headloss were measured for the four filters throughout experiment C2, similarly to experiment C1. For all the filters no increase of the clean bed headloss was observed during the entire duration of experiment C2 (data not shown). This is in agreement with the results of experiment C1, which indicated that under the specific conditions of this experiment biological filtration did not lead to a change in the clean bed headloss of the filters.

Figure 5.24 shows the terminal headloss, i.e. headloss just prior to backwashing, of filters 1 (control) and 2 (continuous Cl_2) over time.

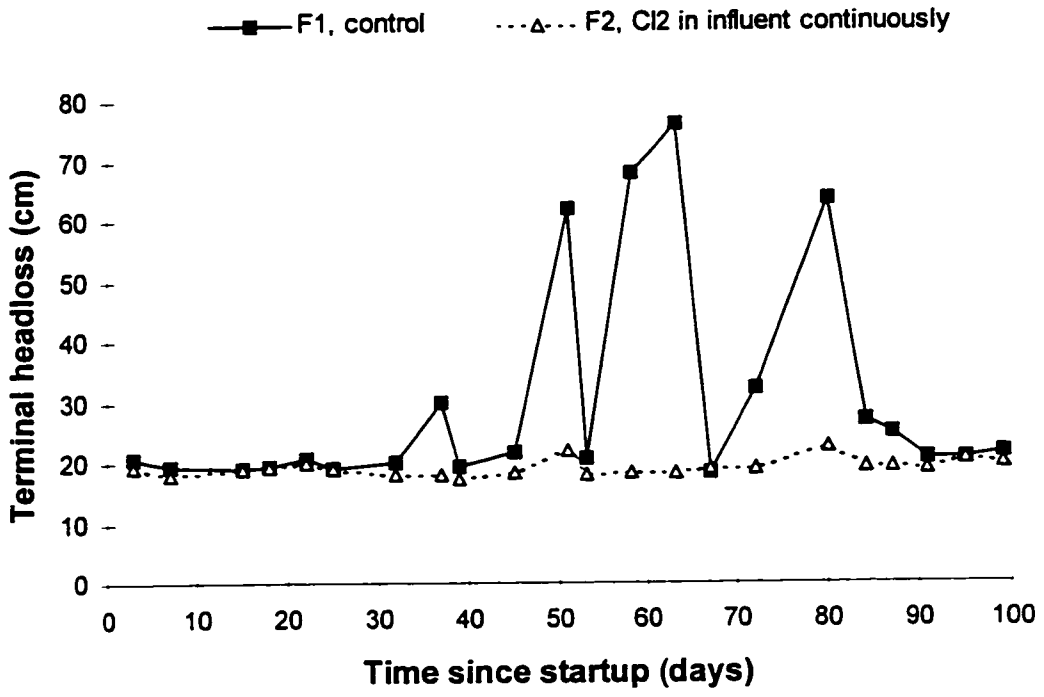

Figure 5.24: Terminal headloss in filters 1 (biological) and 2 (non-biological) over time (experiment C2)

Figure 5.24 shows that terminal headloss in filter 2, which was essentially non-biological, did not change substantially during the experimental duration. However, in the case of filter 1 (control) a substantial increase in the terminal headloss was observed on

several occasions during the second half of the experiment. Similar increases in terminal headloss were observed in filters 3 and 4 (data not shown). The increase of the terminal headloss in the biologically active filters, i.e. filters 1, 3 and 4, was likely the result of substantial air-binding, which was observed to occur in these filters towards the end of the filter cycles. In the non-biologically active filter (F2) however, air-binding did not occur.

The concentrations of dissolved oxygen were measured on several occasions. The results of these measurements indicated that DO levels in the influents of filters 1 and 2 were similar and were substantially below the DO concentration of saturation. Thus, it was concluded that air binding in the biological filter (F1) was not the result of dissolved oxygen degassing. An alternative hypothesis was that differences in the formation of CO_2 as an end product of microbial substrate utilization might have been responsible for the distinct development of air binding in filters 1 and 2. However, at the pH of the filter influent, i.e. 7.0-7.1, the CO_2 formed as a product of microbial substrate degradation is quickly transformed to HCO_3^-. Therefore, the presence of gas bubbles in filter 1 was most likely not the result of carbon dioxide formation.

Consequently, the reason for the observed difference in air-binding occurrence between a biological (F1) and a non-biological filter (F2) is not understood at the present time.

CONCLUSIONS

The results of experiments C1 and C2 led to the following principal conclusions:

- When chlorine was continuously present as free Cl_2 in the influent of an anthracite/sand filter (temperature = 13-16°C), concentrations of ~0.2 mg/L Cl_2 in the filter influent led to a substantial suppression of BOM removal. Therefore, the threshold free Cl_2 concentration above which the removal of easily biodegradable BOM components is inhibited is below 0.2 mg/L Cl_2.

- In the case of the continuous presence of combined Cl_2 in the influent of an anthracite/sand filter (temperature = 13-16°C), the threshold combined Cl_2 concentration above which the removal of selected easily biodegradable BOM components was found to be inhibited was between 0.1 and 0.3 mg/L Cl_2. At lower water temperatures this threshold concentration would probably be even lower.
- The periodic presence of free chlorine (0.5 mg/L Cl_2 for 6 hours once per week) in the influent of anthracite/sand filter led to a substantial negative effect on the biological removals of acetate and formate during approximately 3-5 days following the addition of chlorine.
- Chlorinated backwash water (~1 mg/L Cl_2) was found to considerably impair the removals of acetate and formate, particularly if the chlorine in the backwash water was present as free Cl_2.
- Free chlorine had a stronger negative effect on BOM removal compared to combined chlorine. This was true when chlorine was continuously present in the filter influent as well as when chlorine was present in the backwash water.
- Measurement of the depletion of dissolved oxygen through the biofilters was demonstrated to represent a readily available method for the approximate prediction of BOM removal in such filters.

In addition, the following secondary conclusions can be drawn:

- Backwashing using air scour did not impair the biological removal of acetate and formate when the backwash water did not contain chlorine.
- The continuous presence of ~0.5 mg/L free Cl_2 in the influent of a GAC/sand filter had essentially no effect on the biological performance of this filter. This was the result of the rapid reduction of the chlorine in the GAC filter bed. However, the presence of

chlorine in the influent of GAC filters should be avoided, for reasons mentioned previously.

- Under the specific conditions of this research, the use of UV measurements at 285 nm was found to represent a useful tool for the assessment of the formation of soluble microbial products in biofilters. It was shown that UV_{285} increased through a biologically active filter, potentially as a result of SMP formation.
- Under the specific conditions of these experiments, i.e. "particle-free" and coagulant-free water used as filter influent and backwashing including air scour, clean bed headloss did not increase over time as a result of biomass growth in the biologically active filters.
- In the second experiment reported in this chapter a major increase in terminal headloss due to air binding was observed in the biologically active anthracite/sand filters. In a non-biologically active filter however, air binding did not occur. The reasons for this difference are presently unknown.

CHAPTER 6: A STUDY OF THE IMPACTS OF PERIODIC OZONE RESIDUALS ON BIOLOGICALLY ACTIVE FILTERS

INTRODUCTION

Because of the major increase in the BOM concentration upon ozonation discussed in Chapter 2, ozonation is often followed by biological filtration in order to reduce the BOM concentration prior to the distribution system. In full scale biofilters, measurable ozone residuals would typically not be permitted in the influent because this could lead to harmful O_3 concentrations in the ambient air of filter buildings. However, for enclosed (e.g. pressure and many pilot/lab scale filters) and open air filters this restriction does not exist, and therefore O_3 residuals might be present in the influent (Urfer et al., 1997).

The periodic presence of O_3 residuals in ozonation contactor effluents may be expected for waters with highly variable water quality during the year. As already discussed in Chapter 2, particularly important water quality parameters affecting the rate of O_3 decay in natural waters are pH, concentration and characteristics of the organic matter, water temperature and alkalinity, i.e. HCO_3^-/CO_3^{2-} concentration (Stumm, 1954; Hoigné and Bader, 1976; Bose et al., 1994). In certain raw waters used as a source for drinking water some of these parameters are relatively variable over time. Consequently, the rate of O_3 decay undergoes considerable fluctuations in such waters and O_3 residuals may be encountered in the ozonation contactor effluent during periods of low O_3 decay rates. If

ozonation is followed by biofiltration such residuals would be present in the biofilter influent.

If ozone residual concentrations are present in the effluent of a given ozone contactor, i.e. biofilter influent, several approaches are possible to prevent their reaching the filters. As mentioned in Chapter 2, ozone decay in natural water is generally first-order in O_3 concentration. Therefore, an increase of the residence time in the ozone contactor will lead to decreased O_3 concentration in the contactor effluent. This could be either achieved by lowering the flow rate or by increasing the ozone contactor volume, however, both of these options are unfeasible in many full scale plants. An alternative option to prevent the presence of O_3 residuals in the ozone contactor effluent is the dosage of different chemicals which react with the ozone and thus lead to its depletion. Chemicals used for this purpose in drinking water applications include reduced sulfur components, e.g. bisulfite (Thompson and St. John, 1996) and hydrogen peroxide (Thompson and St. John, 1996; Griffini and Iozzelli, 1996, Schick et al., 1997).

Reduced inorganic components are oxidized through the direct reaction with aqueous ozone leading to ozone consumption (reaction 2 in Figure 2.1). Hydrogen peroxide in its deprotonated form (peroxide ion, HO_2^-) reacts with ozone similarly to the hydroxide ion (OH^-) (reaction 1 in Figure 2.1) as an initiator of the free radical ozone decomposition pathway (Staehelin, 1983). Above a pH of 5 the presence of H_2O_2 leads to a considerable acceleration of the ozone decay (Staehelin, 1983). At a given pH, given O_3 concentration and in the presence of an OH-radical scavenger (e.g. HCO_3^-), the rate of ozone decay is first order in H_2O_2 concentration (equation 6.1, adapted from Staehelin, 1983).

$$(d[O_3]/dt)_{pH} = -k[O_3]^1[H_2O_2]^1 \qquad (6.1)$$

Consequently, an increase of the H_2O_2 dosage to waters containing aqueous ozone is expected to lead to increased rates of the natural ozone decay. Compared to the addition

of reduced inorganic components, e.g. bisulfite, as ozone quenchers, the addition of H_2O_2 has the advantage of promoting the formation of highly reactive OH-radicals and therefore provide some advanced oxidation (Glaze et al., 1987, Ferguson et al., 1990). Jans and Hoigné, (1998) have suggested that the addition of H_2O_2 could be replaced by the contact of O_3-containing water with GAC, which apparently leads to the formation of OH-radicals similarly to O_3/H_2O_2 (Jans and Hoigné, 1998).

OBJECTIVES

The objectives of experiment O1 described in this chapter were:

- to collect and interpret information regarding the effects of the periodic presence of O_3 residuals in the influent of a lab scale anthracite/sand filter on the biological performance, i.e. removal of easily biodegradable BOM components, of the filter;
- to assess the feasibility of O_3 decay acceleration through the addition of H_2O_2 prior to the biofilter influent and to study the impacts and the removal of the periodically present H_2O_2 in the influent of an anthracite/sand filter;
- to develop and test a new and simple method for the measurement of active, i.e. substrate degrading, biomass in biologically active filters.

MATERIALS AND METHODS

Filtration Apparatus

The lab scale filtration apparatus which was used in this experiment has been described in detail in Chapter 3. As a result of the presence of combined chlorine in the tap water mentioned in Chapter 5, two additional GAC dechlorination columns were added for this experiment. They were filled with exhausted GAC from the Mannheim WTP and were installed following the two existing GAC columns. Thus the dechlorination apparatus for this experiment consisted of two parallel streams, each containing two 60 cm long GAC

columns (ID = 4.8 cm) in series. Figure 6.1 represents a schematic of the operational mode of the filtration apparatus during experiment O1.

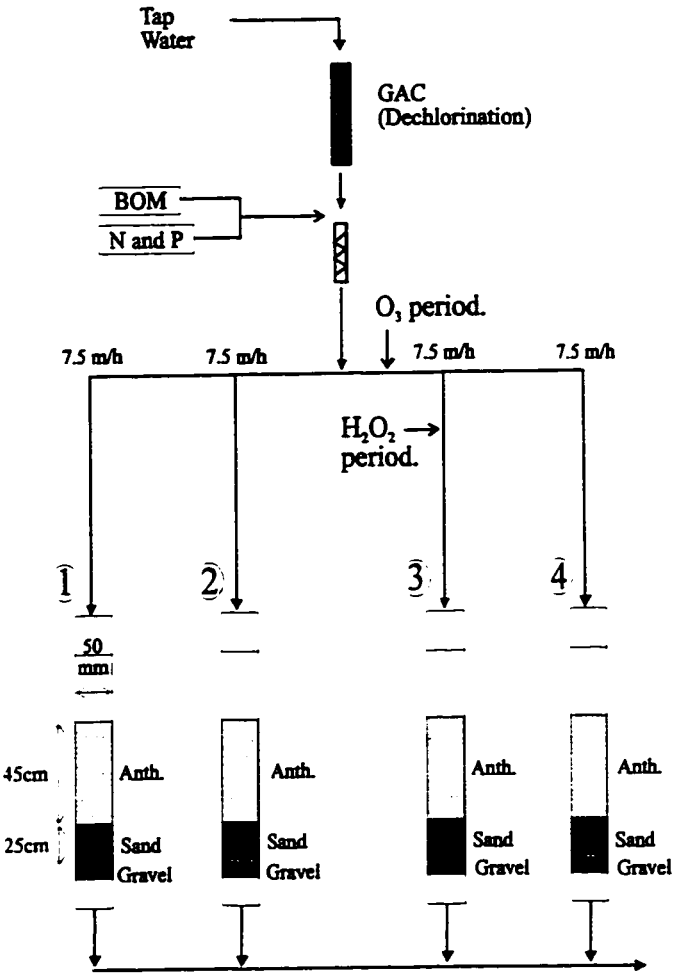

Figure 6.1: Schematic of the filtration apparatus setup and the experimental design

Two filters (filters 1 and 2) were operated as controls, i.e. no oxidant in the influent. The reason for this was that filter 2 was explicitly used for the testing of the new biomass method. Ozone was dosed to the influent of filters 3 and 4 for a period of approximately one hour about 1-2 times per week. Filter 3 received additionally hydrogen peroxide during each ozone dosage period. Filter influent O_3 and H_2O_2 concentrations are presented in the 'Results and Discussion' section.

Ozone Production

Ozone was produced with a laboratory scale corona discharge ozone generator (Hankin, Ozotec™, Type S, Model 2), which was water cooled. The ozone generator was fed with dried and oil-free air (dew point ≤ - 60°C). The ozonated air was bubbled through a small, water jacketed ozone contactor (volume of 3.5 L) containing DI water (Milli-Q, Millipore Corp., Bedford, MA). The ozone contactor was cooled by pumping ice water through the water jacket in a closed loop. The O_3 concentration of the contactor off-gas was continuously monitored in a UV-analyzer (Ozometer™, Hankin Ozone), ozone concentrations in the off-gas ranged between 35-40 mg/L.

Milli-Q water (3.5 L) was ozonated in batch mode for about 2-4 hours resulting O_3 concentration in the stock solution of ~8-12 mg/L. The temperature of the stock solution at the end of the ozonation process was 8-10°C. The stock solution was kept in an amber glass bottle which was ice cooled during the pumping of the solution to the influents of filters 3 and 4.

Ozone Decay Tests

Batch ozone decay tests were performed using dechlorinated tap water, i.e. filter influent, in order to assess ozone decay kinetics in the presence/absence of H_2O_2 at different H_2O_2:O_3 ratios in this water. A schematic of the experimental setup for these tests is shown in Figure 6.2. All glassware was made ozone-demand free by adding ozonated DI water at a high concentration to the glassware and allow sufficient time for potential reactions between the ozone and the glassware (glassware contamination). Relevant water quality parameters for ozone decay studies have been listed by Hoigné (1994b). Table 6.1 provides selected water quality parameters of the tap water used for the ozone decay tests.

For these tests, 3.6 L of dechlorinated tap water was placed in the continuously stirred reactor and 400 mL of a concentrated ozone stock solution was added. When the 400 mL of ozone stock solution were added to the reactor, time was set to zero. Samples

for the measurement of O_3 concentrations were withdrawn from the reactor at predetermined time intervals. Samples were collected in 50 mL beakers and were immediately reacted with the indigo blue reagent contained in the accuvac vials (Hach Company, Loveland CO 80539).

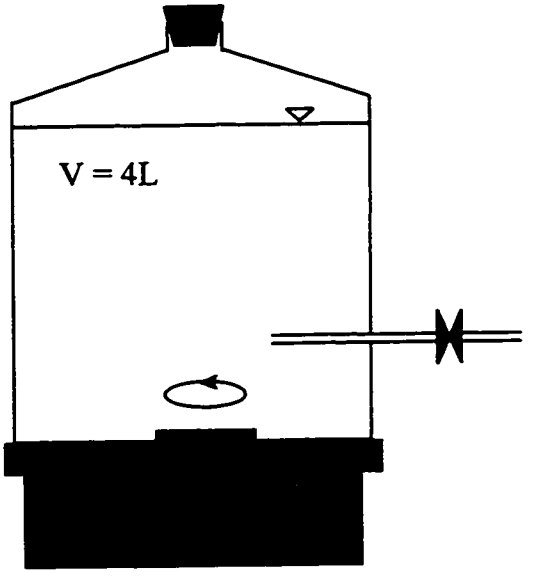

Figure 6.2: Apparatus used for the study of the ozone decay and the rate of the ozone-filter media reactions

Table 6.1: Water quality parameters of tap water used during ozone decay tests

Parameter	**Range**	**Units**
pH	7.0 - 7.1	(-)
Temperature	16 - 19	(°C)
TOC	1.2 - 1.6	(mg/L)
UV_{254}	~ 0.02	(cm^{-1})
SUVA	~ 1.3	(L/mg*m)
Alkalinity	300 - 325	(mg/L as $CaCO_3$)
Hardness	325 - 350	(mg/L as $CaCO_3$)
Conductivity	700 - 800	(μS)

Hydrogen peroxide was added to the reactor during several tests. Predetermined volumes of H_2O_2 from a stock solution (3.15 g/L) were added to the reactor with an Eppendorf® pipette.

Analytical Methods

The analytical methods for carboxylic acids, aldehydes, theoretical oxygen demand and phospholipid biomass have been described in detail in Chapter 3.

Ozone

Ozone concentrations were determined with a commercially available kit (Hach accuvac method, Hach Company, Loveland CO 80539), which is based on the classical indigo method (Bader and Hoigné, 1981). As a partial result of an extensive study on disinfection with ozone at full scale, Coffey et al., (1995a) have reported good agreement between the accuvac and the indigo method. Ozone in the stock solution was quantified on a UV spectrophotometer (HP 8453, Hewlett-Packard, Palo Alto, CA 94304) by measuring the absorbance of ozone at 258 nm in a 1 cm quartz cell. A molar absorptivity of 2900 $M^{-1}cm^{-1}$ was used (Bader and Hoigné, 1981) to convert absorbance to mg O_3/L.

Catalase Activity

Catalase activity of the filter biomass was tested on several occasions during this experiment using a standard test procedure (Gerhardt et al., 1994) with minor modifications. A small amount of filter media (~10-20 grains) was sampled from the drained filters with a sterile scoop into an empty Petri dish. From the Petri dish the grains were directly placed onto a plate containing microbiological medium lacking blood, i.e. R2A agar (BBL Products, Becton Dickinson Microbiology Systems, Cockeysville, MD). The use of medium which does not contain blood is important for this test because blood contains catalase activity unless the blood has been heated (Gerhardt et al., 1994). The plates were incubated in the dark at room temperature for four days. After four days of

incubation bacterial colonies had grown all around the filter grains. A few drops of H_2O_2 at a concentration of 3% were added to the colonies with a pasteur pipette and catalase activity was tested by observing the presence/absence of bubble formation, i.e. oxygen formation.

Biomass Respiration Potential (BRP) Method

BACKGROUND

A new method for the measurement of biomass attached to biofilter media was developed during the course of this experiment. The objective was to develop a simple and rapid method requiring only basic laboratory equipment. Such a method represents a useful tool for water utilities which are operating their filters biologically. The two most commonly used methods for the measurement of biomass or biomass activity in drinking water biofilters are the phospholipid method (Findlay et al., 1989; Wang et al., 1995) and the ^{14}C-glucose respiration method (Servais et al., 1991; 1992).

The phospholipid method, which has been described in Chapter 3, is relatively simple and requires only standard laboratory equipment, however, the whole procedure is very labor intensive. In addition, although the method measures viable biomass, it does not provide a measure of microbial activity. In the case of biofiltration studies, the microbial activity feature of most interest is the substrate degradation potential of the biomass present.

The method developed by Servais and colleagues is based on the measurement of the production of $^{14}CO_2$ by respiration of radio-labeled glucose, which is added to the media sample at a saturating concentration (Servais et al., 1991). Although this method provides a measure of the organic substrate degradation potential, i.e. respiration, of the biomass, the laboratory equipment and security features required for the analysis of radio-labeled substances may not be available in most water utilities. Also, free glucose (unbound) may not represent a component which is normally present in drinking water

biofilter influents. Glucose can be degraded by numerous species of heterotrophic bacteria (Hambsch, 1992) and has been identified as polysaccharide- and humic-bound in surface and groundwaters (Merlet et al., 1996; Labouyrie-Rouillier et al., 1996).

White and colleagues have used the incorporation of ^{14}C-acetate into cellular lipids to measure the metabolic activity of a microbial community (White et al., 1977; Vestal and White, 1989). Acetate may represent a more appropriate substrate than glucose, because acetate is a common organic ozonation by-product (Andrews, 1993; Andrews and Huck, 1994; Gagnon et al., 1997) and therefore often present in biofilter influents. Wang (1995) has successfully applied the ^{14}C-acetate method for the analysis of the microbial activity of biomass in drinking water biofilters.

PROCEDURE

The developed biomass respiration potential (BRP) method is based on the consumption of dissolved oxygen (DO) resulting from the aerobic respiration of several BOM components in a water sample containing a certain amount of biofilter media. The presence of anaerobic bacteria was ignored in the test because the amount of substrate degraded by potentially present anaerobic bacteria is likely minor compared to their aerobic counterparts. Respirometric techniques such as the measurement of the rates of oxygen consumption are commonly used methods for the estimation of microbial metabolism (Atlas and Bartha, 1993). They have been used for a number of applications including the study of the impacts of organic content and particle size in sediments on oxygen uptake (Hargrave, 1972) and the estimation of biodegradation kinetic parameters in activated sludge (Ellis et al., 1996). These authors have noted the high sensitivity of DO measurements allowing the quantification of the respiration of low substrate concentrations.

The procedure which was developed for the BRP method is shown in Figure 6.3. The tests were performed in standard BOD bottles which were autoclaved and oven-dried

at 100°C overnight prior to use. The water added to the BOD bottles (steps 4 and 7 in Figure 6.3) was dechlorinated tap water (filter overflow) which was autoclaved prior to use. The use of dechlorinated tap water was thought to be most representative, because it represents the water which was used as filter influent in the experiment. Measurements of DO, i.e. steps 5 and 9 in Figure 6.3, were performed with a DO-probe (ATI Orion, model 835, ATI Orion, Boston MA). The N, P and BOM sources used in the test (step 6 in Figure 6.3) were the same as used in the experiment.

1. Sampling of media from the drained filter into a weighing dish

⇓

2. determine wet weight of media sample on a scale

⇓

3. place media in empty BOD bottle (previously autoclaved)

⇓

4. add dechlorinated tap water (previously autoclaved) to BOD bottle

⇓

5. measure dissolved oxygen concentration with DO-probe

⇓

6. add N, P and BOM (Time = 0)

⇓

7. fill BOD bottle headspace free, close with glass stopper (previously autoclaved)

⇓

8. place BOD bottles on shaker table (medium speed) for 5 hours

⇓

9. measure dissolved oxygen concentration with DO-probe

Figure 6.3: Procedure for the measurement of active biomass as biomass respiration potential (BRP)

For BOM, acetate, formate, formaldehyde and glyoxal were added to the BOD bottles in order to yield a final concentration of 1.5 mg/L for each component. This corresponds to a total concentration of biodegradable carbon of 2.2 mg C/L. If all of the

biodegradable carbon is degraded during the 5-hour incubation period, the calculated (stoichiometric) decrease in DO is equal to ~5 mg O_2/L. Nitrogen (as $NaNO_3$-N) and phosphorus (as K_2HPO_4-P) were added to the water in order to yield a C:N:P ratio of 15:5:1 (w/w/w), representing carbon limited conditions. The calculation of carbon limiting conditions was based on an empirical formula for a bacterial cell, $C_{55}H_{77}O_{22}N_{11}P$ (Metcalf and Eddy, 1991; Goel et al., 1995). Other nutrients necessary for microbial metabolism were assumed to be present in sufficient amounts in the dechlorinated tap water.

The incubation period of 5 hours was chosen because it allowed the addition of reasonable amounts of filter media (~1-8 g, wet weight) to the BOD bottles resulting in an accurately measurable DO depletion during the 5-hour incubation period, i.e. ~0.2-4.0 mg O_2/L consumed. In addition, this procedure allowed completion of BRP biomass measurements in one day. Media sampling and sample preparation were normally completed in the morning, allowing the measurement of the final DO concentration in the samples in the late afternoon.

The results of the BRP test were calculated as the oxygen consumption during 5 hours per unit volume of filter, i.e. mg O_2/L*cm^3 of filter. The weight of the wet media was multiplied by a factor of 0.89 in order to obtain dry weight. The factor of 0.89 was obtained by weighing several media samples before and after drying in the oven at 100° C (factor = 0.8888, SDEV = 0.0098, n = 4). The dry media weights were converted to filter volumes using the apparent densities of anthracite (0.8 g/cm^3) and sand (1.5 g/cm^3). The analysis of an autoclaved anthracite sample showed that the change in the DO concentration during the 5 hour period was very small in the absence of active biomass. For the sterile anthracite sample a BRP value of 0.007 mg O_2/L/cm^3 of filter (SDEV = 0.004, n = 2) was obtained. This value is almost an order of magnitude lower than the results obtained in the lower part of the control filter (filter 2) on day 63 following startup (results discussed later). This indicates a relatively good sensitivity for the BRP method. The average coefficient of

variation (CV) of duplicate samples was 14.5%. Given that there is likely some natural heterogeneity in the distribution of biomass at a given filter depth and considering that there is some obvious variability in the ratio of wet weight to dry weight between the different media samples, the reproducibility of the method appears to be reasonably good.

Because the BRP method is based on the oxygen consumption potential of a given media sample as a result of BOM degradation, the results of this method provide an indication of the substrate removal capability of a given media sample. In biofiltration studies it is often necessary to assess the impacts of a given operational procedure, e.g. chlorinated backwash water, on the filter biomass. Because organic substrate removal is often the principal goal of biofiltration, a measurement of the substrate degradation potential of the biomass, e.g. DO consumption, provides information on the impact of a given operational procedure regarding the main function (from an engineering point of view) of the biomass, i.e. substrate removal.

Consequently, as a result of its simplicity and because of what has been said immediately above, the BRP method represents a promising tool for biofiltration research and its development should be pursued. BRP results are presented in the following section of this chapter.

RESULTS AND DISCUSSION

Ozone Decay with and without Hydrogen Peroxide

Experiment O1 was started on January 8, 1998 and lasted for nine weeks. Several measurements of free and total Cl_2 showed that the passage of the tap water through the GAC columns successfully prevented the presence of Cl_2 residuals in the filter influents. The filter influent water temperature during the whole experiment was 10-13°C.

Batch tests of ozone decay in the dechlorinated tap water were performed with and without the addition of H_2O_2, in order to obtain information on the efficiency of O_3 decay

acceleration by H_2O_2. Although the mechanism of O_3 decay acceleration by H_2O_2 has been well described mechanistically (Staehelin, 1983), the author is not aware of experimental data comparing the rates of natural O_3 decay with and without the addition of H_2O_2. Figure 6.4 shows the natural ozone decay results in the absence of H_2O_2 for two different batch tests. For tests 1 and 2 shown in Figure 6.4, ozone dosages were 1 mg/L and 0.7 mg/L respectively. The data were reasonably approximated with a first-order expression (Figure 6.4), coefficients of determination (R^2) were equal to 0.95 and 0.98. First-order kinetics for the overall ozone decay are in agreement with the literature (cf. Chapter 2).

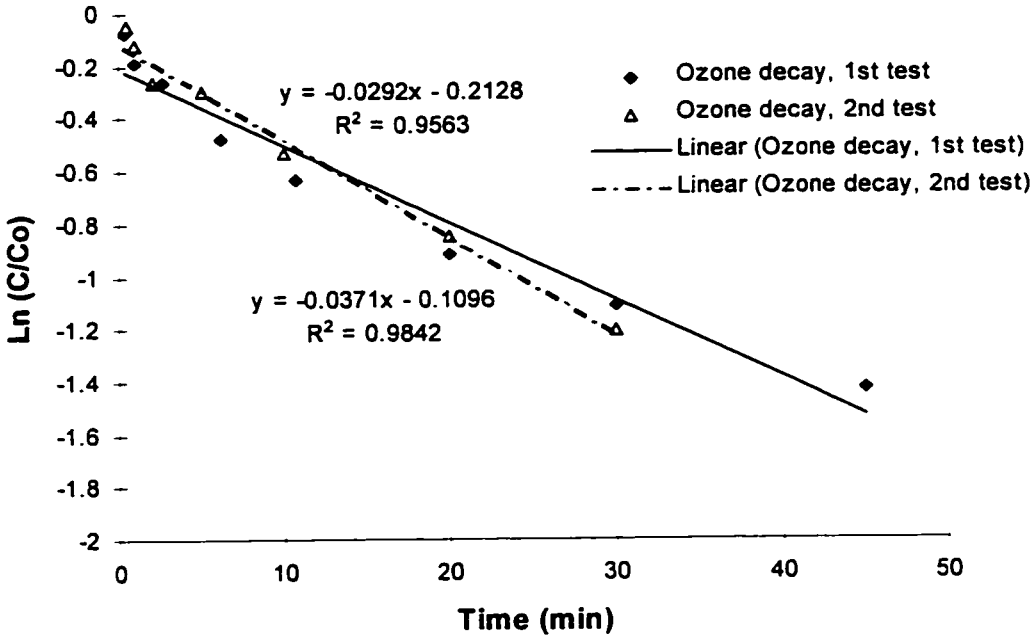

Figure 6.4: Kinetics of natural ozone decay in dechlorinated tap water

The first-order rate constants for the two tests were 0.029 and 0.037 min^{-1}, resulting in an ozone concentration half life of 19 and 24 minutes. These half lifes are in the range of what has been reported in the case of good quality groundwaters, i.e. 20-60 minutes (Hoigné, 1994a). The relatively slow O_3 decomposition observed for the water tested in this experiment can be explained by the moderate to high alkalinity of the water (300-325 mg/L as $CaCO_3$). As discussed in Chapter 2, HCO_3^- serves as OH-radical scavenger and

therefore stabilizes molecular ozone. In addition, the water had a low specific UV absorbance (SUVA) of ~1.3 L/mg*m, indicating a particularly low content of humic substances (Edzwald and Van Benschoten, 1990; Edzwald, 1993), which represent the organic fraction with the highest reactivity towards ozone (Bose et al., 1994).

The addition of H_2O_2, either at the beginning of the batch test or after 6 minutes of test duration, led to a considerable acceleration of the natural O_3 decay. This is shown in Figure 6.5 for the addition of H_2O_2 at the beginning of the batch test and in Figure 6.6 for the case of H_2O_2-addition at 6 minutes following the start of the test. The addition of H_2O_2 following a certain period of ozone contact time corresponds to a full scale scenario where ozone in its molecular form is used as a disinfectant, followed by an advanced oxidation/ozone decay acceleration step. On the other hand, the addition of H_2O_2 at the beginning of a given ozone contactor corresponds to "traditional" advanced oxidation treatment with O_3/H_2O_2 (PEROXONE) (e.g. McGuire et al., 1991; Karimi et al., 1997).

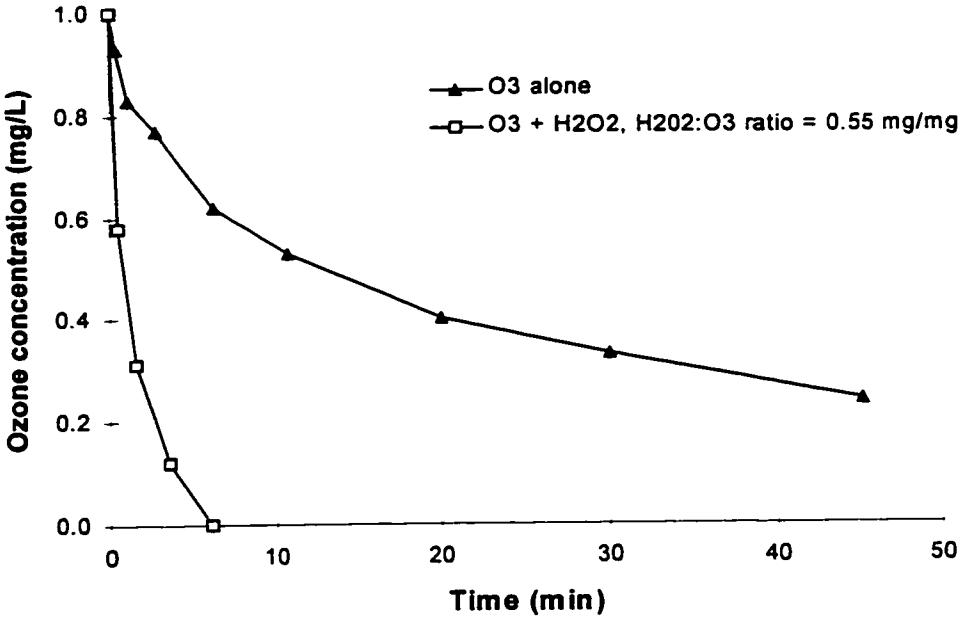

Figure 6.5: Ozone decay in dechlorinated tap water with and without H_2O_2

Figure 6.5 shows that in the test where H_2O_2 was dosed at a H_2O_2:O_3 ratio of 0.55 (w:w), the depletion of the ozone required about 5-6 minutes. In comparison, in the test where no H_2O_2 was added the O_3 concentrations was still > 0.2 mg/L after 45 minutes (Figure 6.5). These results indicate that although the addition of H_2O_2 to the specific water tested did not lead to an immediate consumption of the ozone, natural O_3 decay was considerably accelerated.

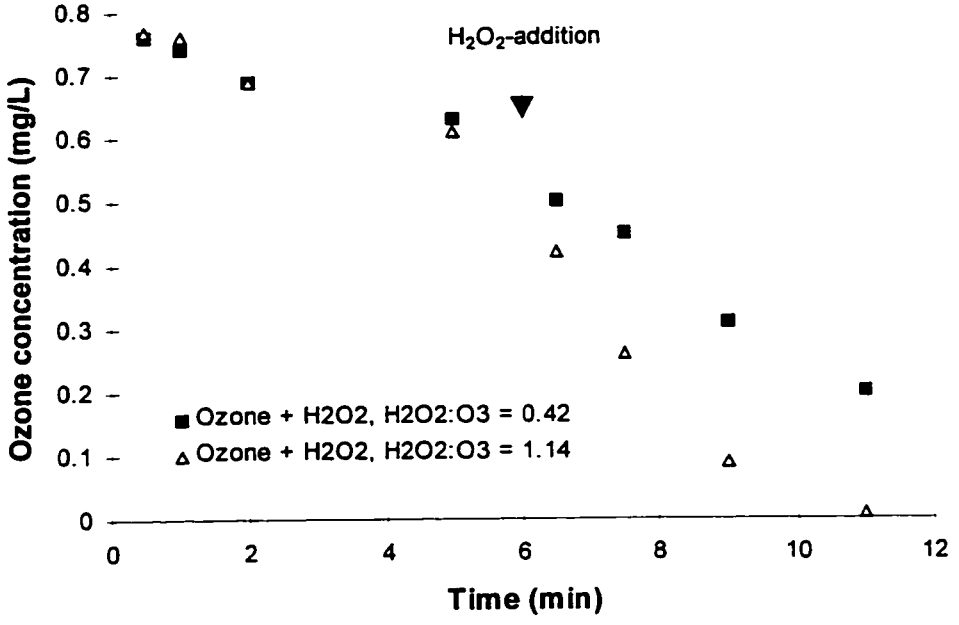

Figure 6.6: Ozone decay at different H_2O_2:O_3 ratios

The results in Figure 6.6 show that an increase in the H_2O_2:O_3 ratio leads to an acceleration of the ozone decay, as anticipated (Staehelin, 1983). For the test using a H_2O_2:O_3 ratio of 1.14 (w:w), the total depletion of the O_3 concentration of about 0.6 mg/L required 5-6 minutes of reaction time. Higher H_2O_2:O_3 ratios would likely lead to even faster O_3 depletion. For comparison, in the test where no H_2O_2 was added the O_3 concentration was still > 0.2 mg/L after 30 minutes of reaction time (data not shown in Figure 6.6). Therefore, the addition of H_2O_2 as an ozone decay accelerator appears to

represent a feasible operational mode for full scale ozonation systems, if adequate contact time is provided following the point of H_2O_2-addition. However, because ozone chemistry is highly dependent on specific water quality parameters, O_3 decay acceleration with H_2O_2 should be tested for each water to be treated in such a manner.

In O_3/H_2O_2 applications either as an AOP or for O_3 decay acceleration, the control of H_2O_2 residuals in the finished water must be considered because such residuals are undesired, as previously noted. Results from an advanced oxidation study with PEROXONE showed that H_2O_2 residuals in the ozone contactor effluent increased with increasing H_2O_2:O_3 ratios (McGuire et al., 1991). Biofiltration following PEROXONE led to a major decrease of the H_2O_2 levels and biofilter effluent H_2O_2 concentrations were consistently below 0.02 mg/L (McGuire et al., 1991). The removal of H_2O_2 in biofilters has been extensively discussed in Chapter 4, and biofiltration represents a useful process step to prevent the presence of undesirable H_2O_2 residuals in the finished water of plants which add H_2O_2 either as ozone decay accelerator or for advanced oxidation.

During the experiment discussed in this chapter, H_2O_2 was added to the influent of filter 3 during each 1-hour period of O_3 addition to the influents of filters 3 and 4. Hydrogen peroxide was dosed to the top of filter 3 at a H_2O_2:O_3 ratio of approximately 1:1 (w:w). The hydraulic residence time of the water from the point of H_2O_2-addition to the top of the filter media was equal to 9.5 minutes. This reaction time was sufficient to prevent the presence of O_3 residuals above 0.02 mg/L in the influent of filter 3. This is shown together with the O_3 concentrations in the influent of filter 4 in Figure 6.7.

Ozone concentrations in the influent of filter 4 were somewhat variable. Reasons for this include the variability in the concentration of the ozone stock solution of different batches and changes in the water quality of the filter influent. Another ozone addition event not shown in Figure 6.7 occurred on day 26, however O_3 residuals were not analyzed on day 26. On day 50 following startup (not shown in Figure 6.7), ozone was dosed only to the

influent of filter 4 in order to investigate higher O_3 concentrations in the influent of this filter.

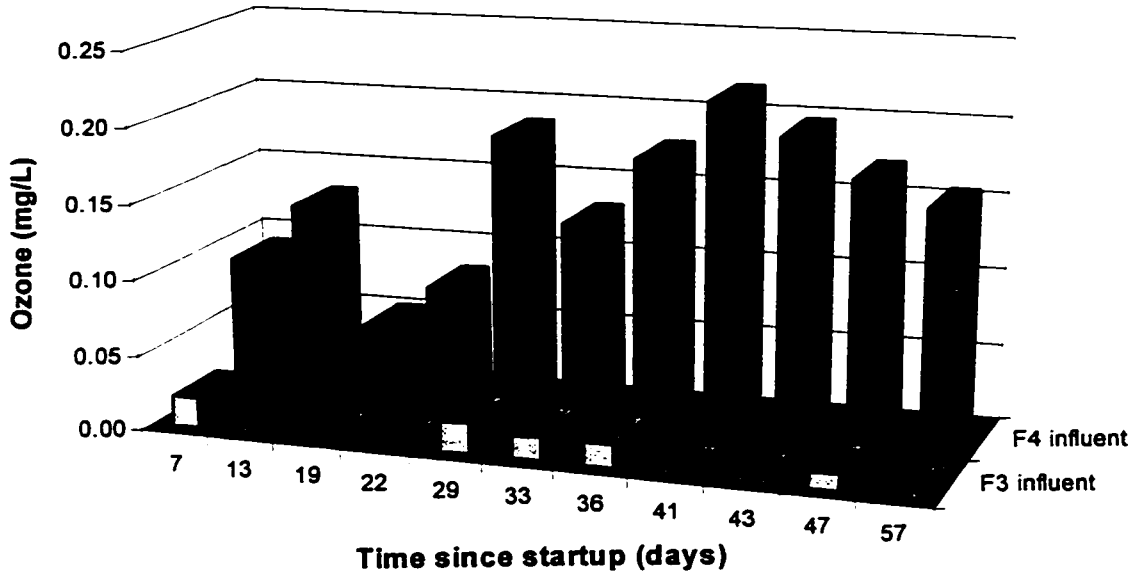

Figure 6.7: Ozone concentrations in the influents of filters 3 and 4

The O_3 (and H_2O_2) addition frequency was about once per week for a period of one hour during the first three weeks of the experiment. Because this did not exhibit a measurable effect on BOM removal in filter 4 (results discussed later), the frequency was increased to about twice per week for a period of one hour for the rest of the experiment.

Removal of BOM Components

Acetate and Formate

The establishment of biological acetate and formate removal in the control filter (F1) containing new media required about 10 and 20 days, respectively, of biological operation of the filter (data not shown). This is in agreement with results reported in

Chapters 4 and 5, which demonstrated that biological acetate removal was established more quickly following startup of a biomass-free filter compared to formate.

Acetate and formate concentrations in the influents of F3 and F4 measured during O_3/H_2O_2 addition on day 19, i.e. ~295 μg/L for acetate and ~355 μg/L for formate, were similar to concentrations measured in the absence of O_3/H_2O_2 dosage on days 14 and 22 (data not shown). This was particularly true for acetate. This indicates that under the specific conditions, O_3 and O_3 followed by H_2O_2 did not substantially react with acetate and formate. Similar results from a full-scale investigation have been reported by Griffini and Iozzelli, (1996). Hoigné and Bader, (1983a,b) have reported very low reaction rates for acetate and formaldehyde with molecular O_3, however, they measured substantially higher reaction rates in the case of formate. Possibly, the relatively low ozone dosage on day 19 (O_3 concentration of ~0.05 mg/L in influent of F4) was not sufficient to substantially oxidize formate during the 10-minute reaction time between ozone addition and the filter influent. The results collected during O_3/H_2O_2 dosage on day 19 also suggest that acetate and formate formation from the oxidation of the background NOM present in the tap water was minor, although formation and degradation could have occurred simultaneously in the case of formate.

The periodic presence of hydrogen peroxide (filter 3) and ozone (filter 4) residuals in the influents of the filters did not show a measurable inhibition of the removal of acetate and formate after about one month of filter operation (Figures 6.8 and 6.9). Error bars in these and the following figures in this chapter represent ± 1 standard deviation of duplicate samples unless otherwise stated. Both figures show percentage removals of the two components during a typical O_3/H_2O_2 addition cycle, i.e. days 33-36 following startup. The O_3 concentrations in the influent of F4 during the O_3/H_2O_2 additions on days 33 and 36 are shown in Figure 6.7. The presence of H_2O_2 esiduals in the influent of F3 is discussed later in this section, H_2O_2 residuals in the influent of F3 were in the range of 0.5 mg/L.

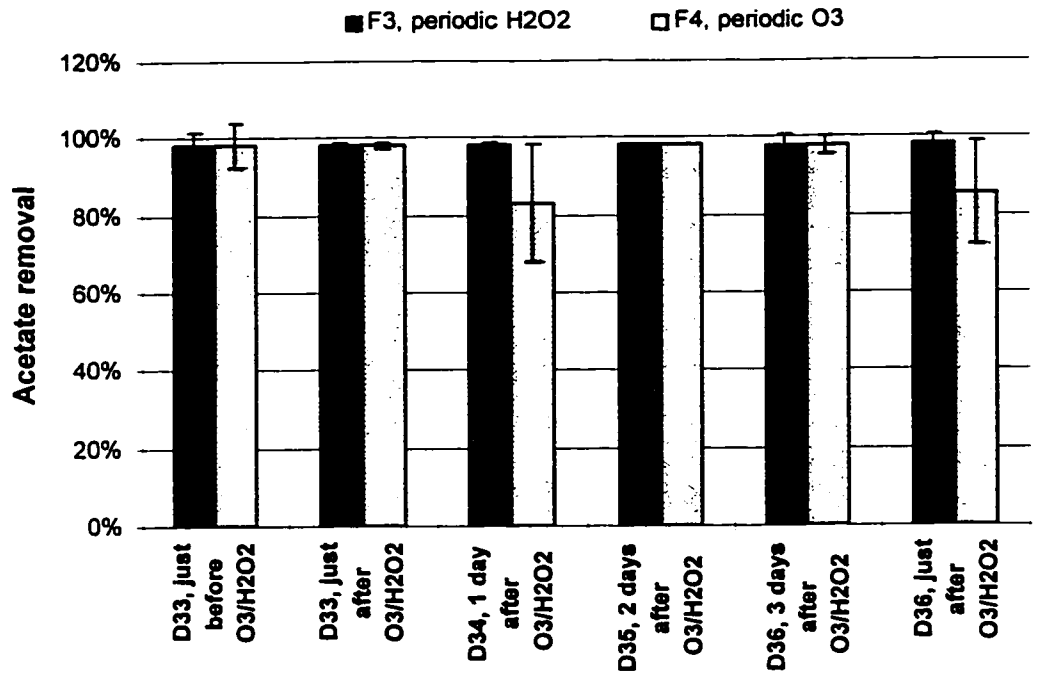

Figure 6.8: Removal of acetate during one O_3/H_2O_2 addition cycle (days 33-36 following startup)

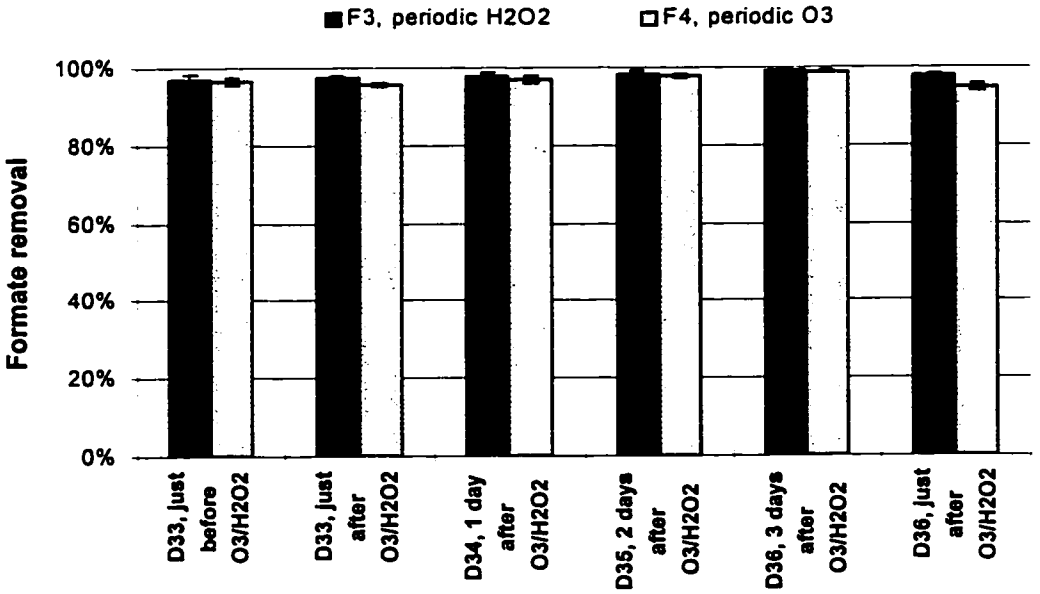

Figure 6.9: Removal of formate during one O_3/H_2O_2 addition cycle (days 33-36 following startup)

The filter receiving H_2O_2 periodically at an influent concentration of ~0.5 mg/L (F3) showed acetate and formate removals >95% in all the samples (Figures 6.8 and 6.9). Therefore, the periodic presence of H_2O_2 under these specific conditions had no measurable effect on the removals of these components. These results are in agreement with the data reported in Chapter 4, where it was shown that higher H_2O_2 concentration (~1 mg/L) fed continuously to an identical filter did not show a measurable effect on the removals of acetate and formate at pseudo steady-state.

In the filter receiving O_3 periodically (F4) at influent concentrations of ~0.1-0.2 mg/L, the removal of acetate and formate was not inhibited as a result of the periodic presence of O_3 in the filter influent. This is shown in Figure 6.8 for acetate and 6.9 for formate.

The removals of formate in filter 3 and 4 before and after the addition of O_3/H_2O_2 are further analyzed in Figures 6.10 and 6.11. Both figures show formate concentration profiles through filters 3 (Figure 6.10) and 4 (Figure 6.11), before and after the periodic dosage of O_3/H_2O_2 on day 33 following startup. The results obtained in the control filter (F1) are shown in both figures for reasons of comparison. Results for acetate were similar to formate, however acetate data are not shown here.

Figure 6.10 shows that the periodic presence of H_2O_2 in the filter influent of filter 3 had essentially no effect on the formate concentration profile through this filter and the formate concentration profiles in filter 3 were similar compared to the control filter. In filter 4, the formate data shown in Figure 6.11 indicate slightly slower formate removal in the top part of this filter following the periodic addition of ozone. Considering the entire filter however, formate concentration profiles before and after the periodic dosage of ozone were very similar and essentially identical to the control filter (F1).

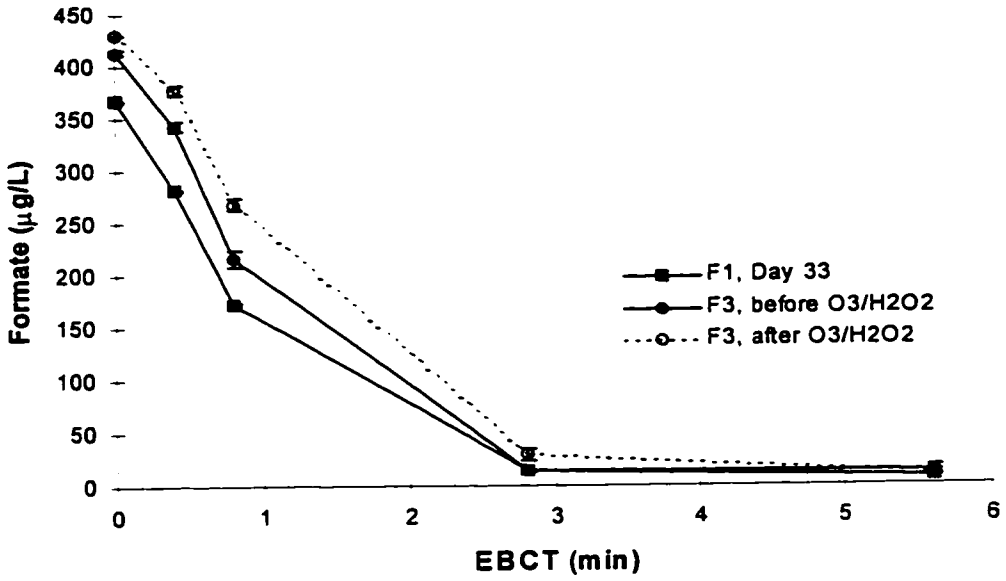

Figure 6.10: Formate concentration profiles on day 33 in filters 1 and 3, before and after the addition of O_3/H_2O_2

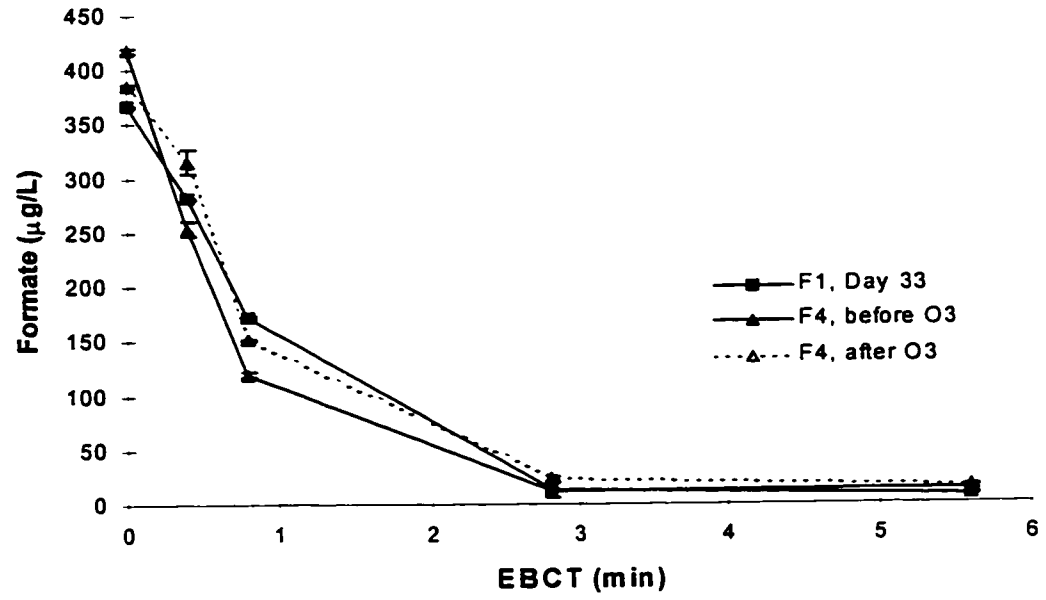

Figure 6.11: Formate concentration profiles on day 33 in filters 1 and 4, before and after the addition of O_3

Formaldehyde and Glyoxal

The removals of formaldehyde and glyoxal showed a slightly different behavior compared to acetate and formate, particularly in filter 3 (periodic H_2O_2). However, only one sampling before and after O_3/H_2O_2 was performed during this experiment. The results are shown in Figure 6.12.

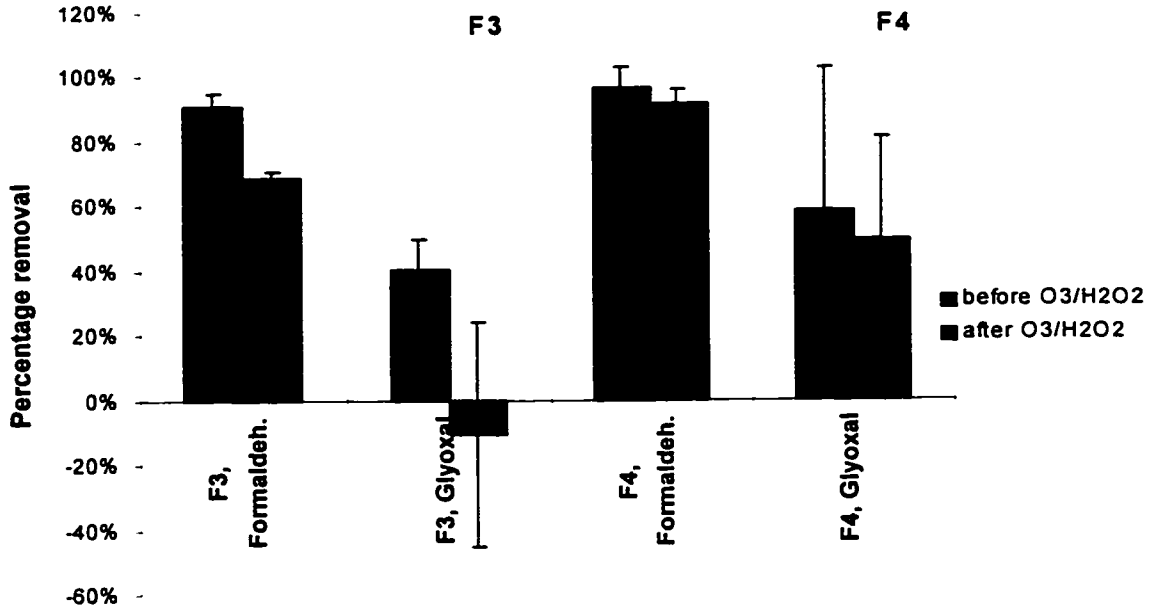

Figure 6.12: Removals of formaldehyde and glyoxal in F3 (periodic H_2O_2) and F4 (periodic O_3) on day 33

The results for filter 3 in Figure 6.12 suggest that formaldehyde and glyoxal removals were slightly lower following the 1-hour dosage of H_2O_2. Nevertheless, in the case of glyoxal, standard deviations of replicate samples were very high for reasons which are not clear. The formaldehyde results in filter 4 were in agreement with the acetate and formate results discussed previously, i.e. no measurable removal inhibition due to the periodic presence of O_3.

The absence of an inhibitory effect of the periodic presence of O_3 in the influent of filter 4 on the biological removal of the easily biodegradable components measured in this

study was somewhat unexpected. Ozone is known to be a very strong disinfectant and oxidant, e.g. CT-values for the inactivation of *Giardia* cysts are about two orders of magnitude lower for O_3 than for free Cl_2 (Malcolm Pirnie Inc. and HDR Inc., 1991). Based on the relatively strong effect on the removals of acetate and formate caused by the periodic addition of free Cl_2 (~0.5 mg/L for a period of 6 hours) to the influent of a biofilter (cf. Chapter 5), it was expected that O_3 at a lower concentration and for a shorter period of time might show an appreciable negative effect on the biological removals of these BOM components.

The reason for the lack of a measurable effect of the ozone on the biological degradation of several easily biodegradable BOM components was the very rapid consumption of O_3 in the filter bed. On several occasions, i.e. days 29, 33, 41 and 43, ozone residuals were determined in filter 4 at a filter depth of 4 cm. The measured O_3 residuals at 4 cm were 0.00-0.02 mg/L (O_3 influent concentrations for these days are shown in Figure 6.7). Therefore, most of the biomass in filter 4 actually never came in contact with O_3. The rapid decrease of the O_3 concentration in filter 4 was either the result of the reaction of O_3 with the biomass, including extracellular polysaccharides, and/or with the anthracite.

The O_3 concentration decrease in filter 4 was further examined on day 50 following startup when O_3 was added to filter 4 only. On day 50 the O_3 influent concentration in filter 4 was 0.5-0.6 mg/L and the concentration decreased to 0.05-0.10 mg/L at a filter depth of 4 cm. To examine the potential reaction of the O_3 with the anthracite, the media of filter 4 was replaced with new (biomass-free) media on day 60 following startup, as mentioned previously. On day 61, ozone was again added to filter 4 only, at an O_3 influent concentration of ~0.6 mg/L. A similar O_3 concentration decrease was measured compared to what was observed in the biologically active filter 4 on day 50. Therefore, it seemed that

the principal reason for the O_3 concentration decrease in filter 4 was the result of the reaction between O_3 and the anthracite.

This was further tested in batch tests using the apparatus shown in Figure 6.2. A volume of 125 cm^3 of new media (sand, anthracite and GAC, F-400) was placed in the continuously stirred reactor containing 2 L of deionized (Milli-Q) water. A volume of 100 mL of a concentrated ozone stock solution was added (ozone dose = 0.35 mg/L) and the O_3 decay was observed over time and compared with the decay in a control (no media addition). The results of these tests are shown in Figure 6.13.

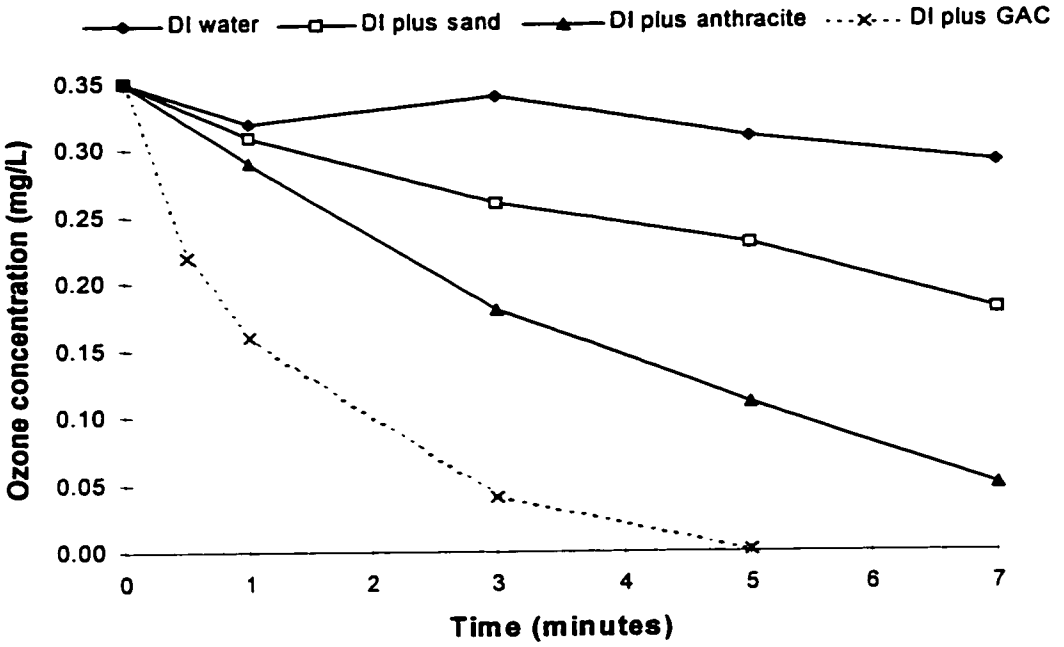

Figure 6.13: Ozone - filter media reaction tests

The curves shown in Figure 6.13 indicate that all of the filter media tested reacted with the ozone in the order of reactivity GAC > anthracite > sand. The relatively rapid reaction between O_3 and GAC was expected based on the literature (Sontheimer et al., 1988; Boere, 1991). Figure 6.13 shows that O_3 was also relatively quickly consumed in the presence of new anthracite and more slowly when new sand was present in the reactor.

Ozone decomposition in the presence of GAC could be approximated by a first-order equation ($R^2 = 0.997$), whereas for anthracite and sand a zero order equation was a better approximation of the experimental data.

It can be expected that the O_3 removal capabilities of anthracite and sand filters might be relatively rapidly exhausted compared to GAC, as the reactive sites of anthracite and sand media with O_3 may be relatively quickly oxidized. This would be particularly true in filters receiving O_3 continuously. Huck et al., (1991) have observed low but measurable O_3 concentrations in the effluent of a pilot scale anthracite/sand filter which received O_3 continuously at concentrations < 0.3 mg/L. In the case of the present study it must be remembered that O_3 was dosed only for a period of about 15 hours in total (during the whole experiment). Therefore, it is possible that the ozone reactive sites in the anthracite media were not yet exhausted (oxidized) and were still reacting with O_3, which might have been responsible for the rapid O_3 decomposition in filter 4. Based on this, it would be necessary to undertake additional studies where O_3 is present for longer periods of time in the filter influent of anthracite/sand filters, in order to further assess the effects and the significance of O_3 residuals on BOM removal in such filters. Due to time constraints, the conduct of such investigations was not possible during this research.

Dissolved Oxygen

On several occasions, dissolved oxygen (DO) was measured in the influent and effluent of the different filters in order to indirectly assess organic substrate removal through the depletion of the electron acceptor of the bioreactions, i.e. O_2. Figure 6.14 compares the measured DO-decrease on day 32 following startup through the different filters with the ThOD calculated based on the removals of the carboxylic acids and the aldehydes on day 33. Figure 6.14 shows that the values of the calculated ThOD-decrease and the measured DO-depletion were relatively close except maybe for filter 1.

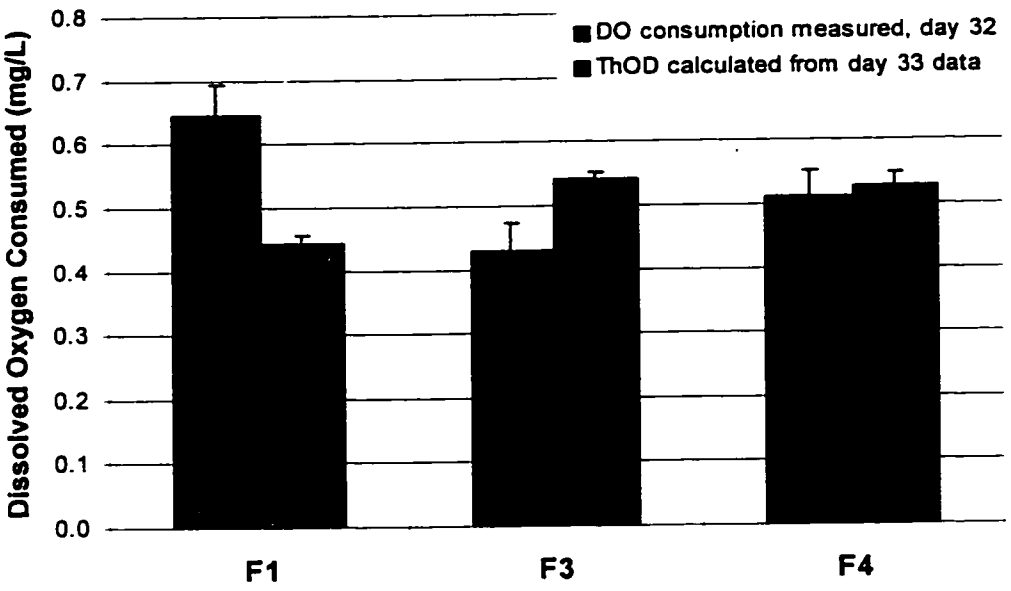

Figure 6.14: Comparison of dissolved oxygen measurement with the calculated theoretical oxygen demand (ThOD) of the substrate

This suggests that measurements of the oxygen depletion through biofilters represent a useful (and particularly a simple) way of roughly assessing the biological performance (BOM removal) of such filters, as already mentioned in Chapter 5. This may be of particular interest to full scale plants which operate their filters biologically and which do not have the analytical equipment/capacities to routinely perform AOC/BDOC tests or to analyze specific BOM components.

Also, measurements of DO-depletion through biofilters are relatively sensitive indicators of BOM degradation. The filter influent organic substrate concentrations which were used for these experiments were not particularly high, i.e. < 0.3 mg C/L, compared to full scale biofilters, which in many cases follow ozonation. Kaplan et al., (1994) have reported a median BDOC concentration of 0.3 mg/L in an extensive survey of BOM in North American surface waters and numerous studies have demonstrated the substantial increase of BOM levels upon ozonation (cf. Chapter 2).

Despite the low to moderate BOM concentrations in the filter influents of this experiment, it was possible to indirectly approximate the biodegradation of the BOM components in the filters through DO-measurements (Figure 6.14). Therefore, for certain full scale situations carefully performed measurements of DO-depletion through biofilters represent an easy and sensitive tool for an approximate assessment of BOM removals in such filters.

Measurements of dissolved oxygen are particularly useful to study the non-steady-state (dynamic) behavior of biofilters. Such investigations are very labor intensive because they require a large number of samples. Hozalski (1996) has stressed the importance of the non-steady-state behavior of biofilters. Examples of operational strategies potentially leading to dynamic conditions regarding BOM removal in biofilters are the periodic presence of oxidants in the influent (cf. Chapter 5), vigorous backwashing leading to high losses of biomass, Cl_2 in the backwash water (cf. Chapter 5), etc. The author believes that the measurement of DO-consumption through a given biofilter represents a useful tool to perform a preliminary assessment of the impacts of such events and operational strategies on BOM removal. Note that such measurements should consider the potential presence of ammonia (NH_4^+) in the biofilter influent, because the biological oxidation, i.e. nitrification, of NH_4^+ leads to a significant depletion of DO, i.e. 4.54 mg/L O_2 per mg/L NH_4^+-N (e.g. Metcalf and Eddy, 1991).

Biomass

Both biomass methods (the phospholipid and the developed BRP method) were used during this experiment. Figures 6.15 and 6.16 represent phospholipid and BRP results collected on days 53 and 54 following startup respectively. Because of time constraints only one sampling session for phospholipid biomass, i.e. day 53 sample, was performed during this experiment.

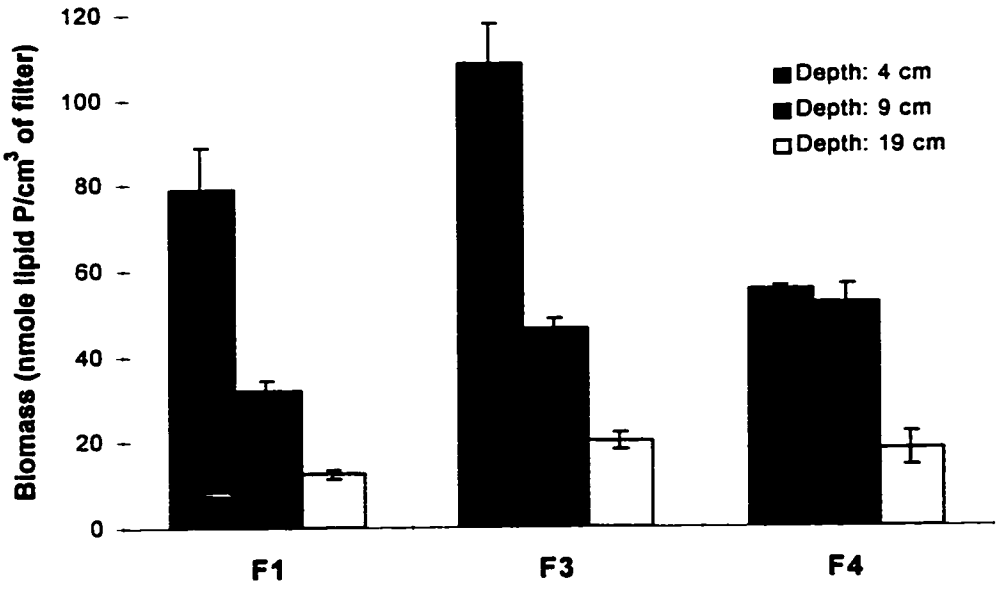

Figure 6.15: Biomass measured as phospholipid on day 53 following startup

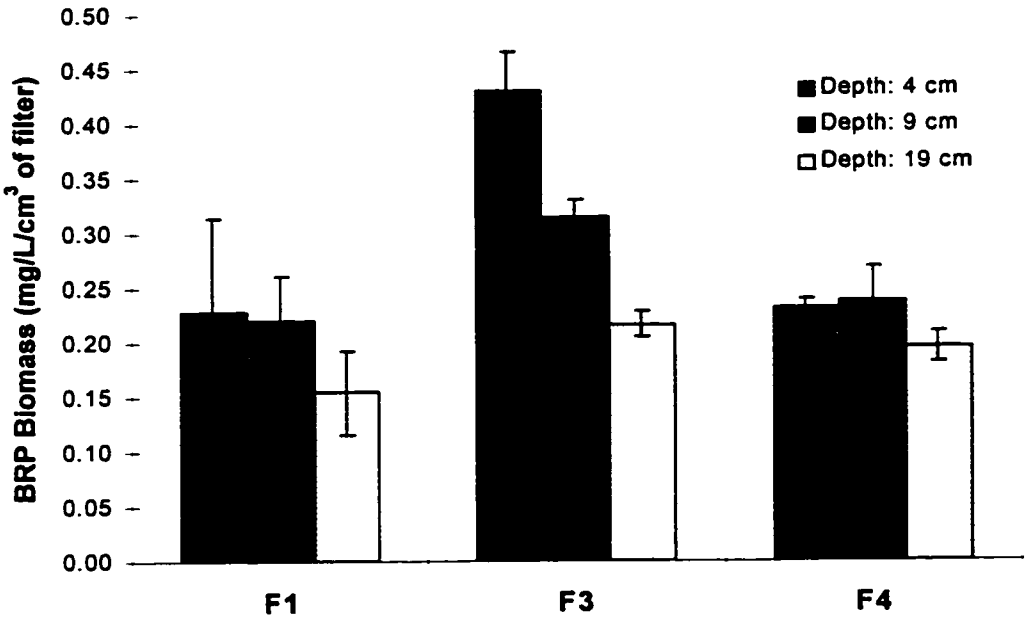

Figure 6.16: Biomass respiration potential (BRP) measured on day 54 following startup

Overall, the filters periodically receiving H_2O_2 (filter 3) and O_3 (filter 4) had similar amounts of viable biomass compared to the control filter (Figure 6.15). This is in agreement with the BOM removal data, which indicated a negligible effect of these oxidants on acetate, formate and formaldehyde removal under the specific conditions of this experiment. Filter 4 had a lower amount of viable biomass (phospholipid) at 4 cm compared to the two other filters, possibly as a result of the periodic addition of O_3 to the influent of this filter.

The results of the BRP measurements showed some important differences compared to the phospholipid results (Figure 6.16). Overall, the BRP stratification was less pronounced compared to the phospholipid results. Again, in the case of filter 4 this might be the result of the periodic presence of O_3 in the influent of this filter. Filter 3 contained the highest amount of active (substrate degrading) biomass, in particular at a filter depth of 4 cm. The reason for this is not currently understood.

In an attempt to further analyze the biomass data shown in Figures 6.15 and 6.16, normalized biomass activity was calculated as the ratio of active, i.e. substrate degrading, biomass (BRP) to viable biomass (phospholipid) using the data of Figures 6.15 and 6.16. Wang (1995) has used a similar approach using the rate of ^{14}C-acetate incorporation into cellular lipids (Vestal and White, 1989) as an indicator of biomass activity. The results of the normalized biomass activity are shown in Figure 6.17. The most striking pattern of the data (shown in Figure 6.17) is the reverse stratification with filter depth of biomass activity per unit amount of viable biomass. The results in Figure 6.17 show that normalized biomass activity tended to increase with filter depth between 4 and 19 cm, suggesting that the biomass located deeper in the biofilter was more active with respect to substrate removal. This might be explained by the fact that the concentrations of the easily biodegradable substances which were fed to the influent of the filters decreased rapidly within the filters, as shown earlier. Therefore, the bacteria present deeper in the biofilters

where easily biodegradable substrate concentrations are low might be in a state of environmental stress, i.e. starvation, and thus responding with high substrate degradation (DO consumption) per unit amount of biomass during the BRP test. An alternative explanation might be that the biomass at the top of the filter is composed of an outer active, i.e. substrate-degrading, layer of bacteria, whereas bacteria located deeper in the biofilm might be less active, although viable. Deeper in the filter where the biofilm is much thinner, the occurrence of this phenomenon is less likely.

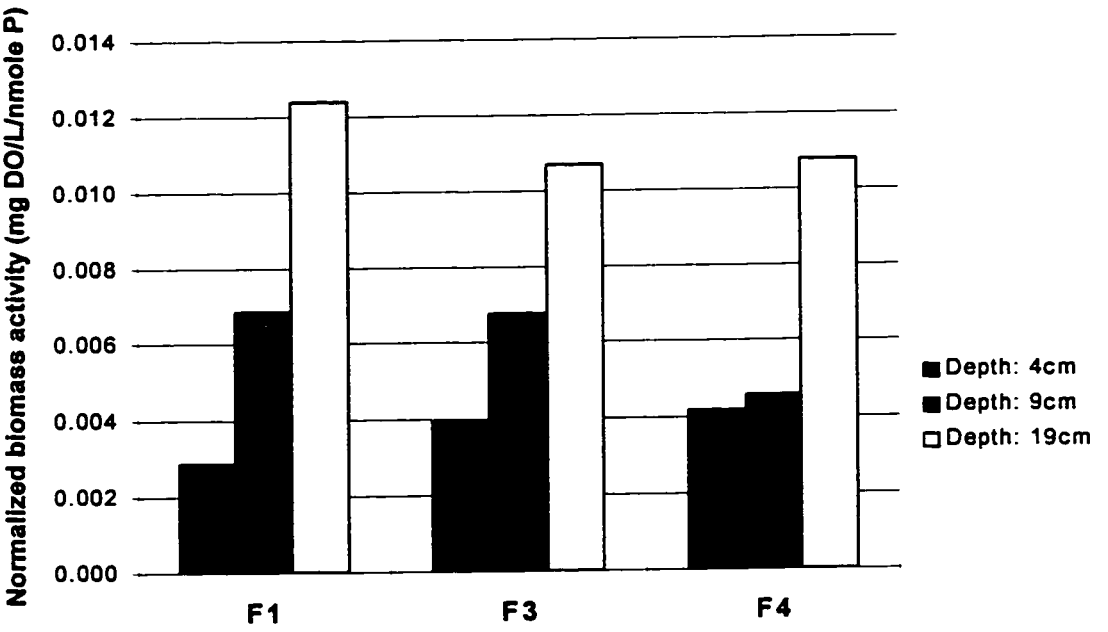

Figure 6.17: Normalized biomass activity expressed as the ratio between BRP and phospholipid biomass in the control filter (filter 2) on days 53/54 following startup

Wang (1995) reported increased biomass activity per unit amount of viable biomass (phospholipid) in bench-scale filters which contained new media at the beginning of a biofiltration test (duration of 2 months) compared to bioacclimated filters containing media from a biologically active filter. Those results indicated that the microbial activity of biomass measured as phospholipid changes as a function of biofilter operation time.

Figure 6.18 represents two BRP biomass profiles (days 41 and 63 following startup) in the control filter (filter 2). The figure shows that the amount of BRP biomass in the top part of the filter increased between days 41 and 63 indicating that the biofilter was not at steady-state after 41 days with regard to the amount of active substrate-degrading biomass.

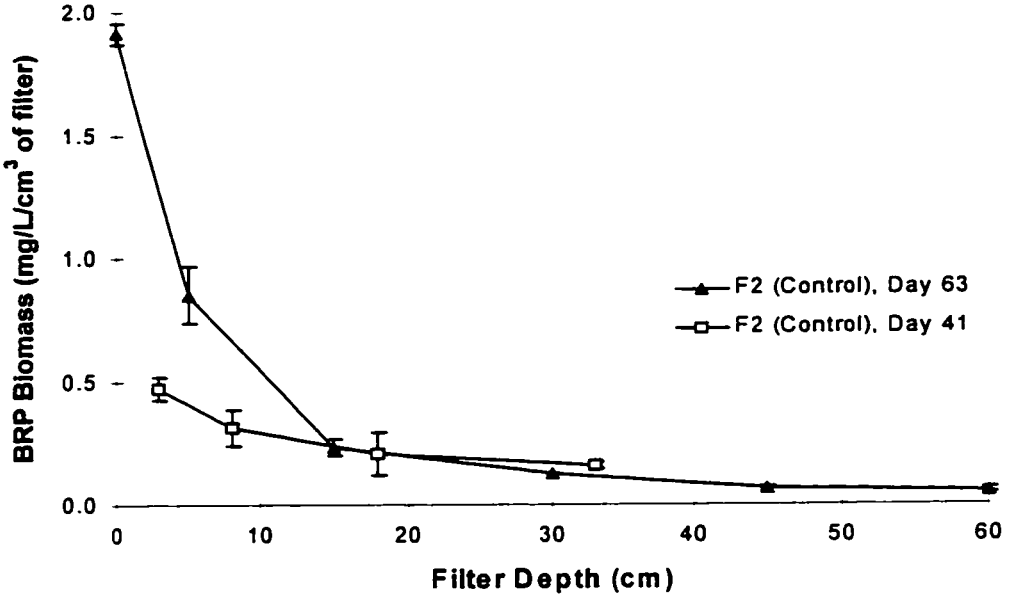

Figure 6.18: Biomass activity (measured as biomass respiration potential, BRP) profiles through filter 2 (control)

The BRP profile on day 63 shows a relatively pronounced stratification, less pronounced, however, compared to phospholipid biomass (cf. Chapters 4 and 5).

When biomass activity was calculated per unit amount of viable biomass for the data in Figure 6.18, i.e. ratio of BRP and phospholipid biomass, stratification was again reversed. Figure 6.19 shows the results obtained by using the BRP biomass data from day 63 (Figure 6.18) in combination with phospholipid data collected in the control filter (filter 1) on day 64 of experiment C2. Although the data shown in Figure 6.19 were collected during two distinct experiments, they should be comparable because the control filter was operated under exactly the same conditions in all the experiments.

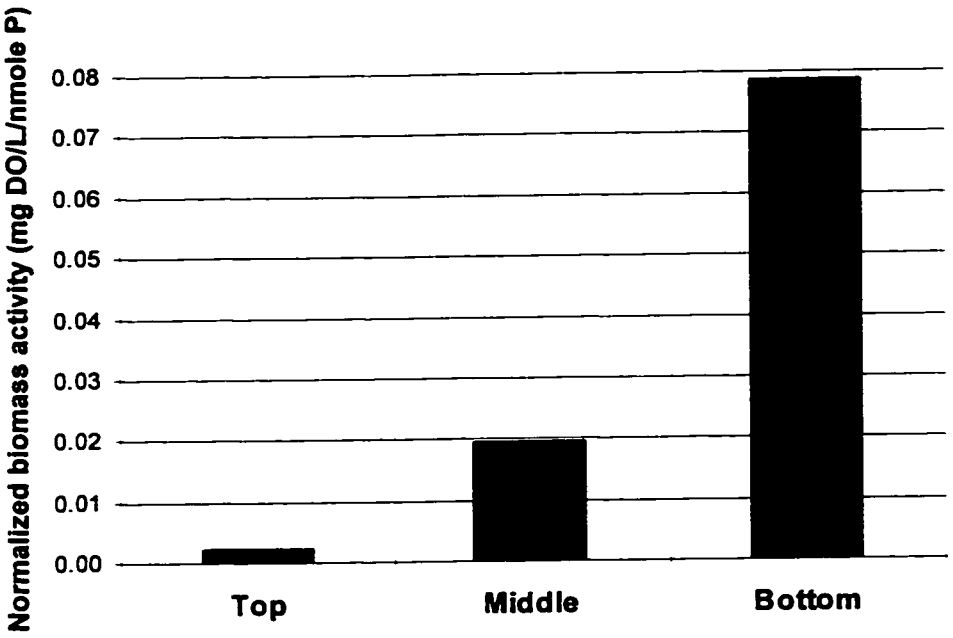

Figure 6.19: Biomass activity expressed as the ratio between BRP biomass and phospholipid biomass in the control filter on days 63/64 following startup

Figure 6.19 shows the normalized biomass activity results for the filter top (0 cm) middle (35 cm) and bottom (65 cm). The biomass activity per unit amount of viable biomass increased substantially with biofilter depths confirming the data shown in Figure 6.17. The values shown in Figure 6.19 are in good agreement with the data in Figure 6.17. At a depth of 4 cm, the control filter (F1) in Figure 6.17 yielded a biomass activity per unit amount of viable biomass of $2.9*10^{-3}$ mg DO/L per nmole P, whereas the biomass sample at the top of F1 in Figure 6.19 yielded $2.4*10^{-3}$ mg DO/L per nmole P.

The results of Figures 6.17 and 6.19 indicate that biomass activity in terms of BOM degrading biomass per unit amount of viable biomass is strongly dependent on filter depth. The very pronounced stratification of phospholipid biomass in biofilters observed in this and other studies (Wang, 1995; Carlson et al., 1996a; Moll and Summers, 1997) leads to the conclusion that most of the biomass is present in the first 25% of filter depth. However,

the results shown in Figures 6.17 and 6.19 indicate that biomass activity (in terms of BOM degradation potential) per unit amount of viable biomass was substantially lower for the biomass in the top part compared to biomass located deeper in the biofilter. Because of this, the author believes that phospholipid biomass results, despite their usefulness for the overall understanding of biological filtration, may not adequately quantify the active biomass in regards to substrate removal. Consequently phospholipid biomass measurement may not represent the optimal method for the purpose of BOM removal modeling in biofilters.

Figure 6.20 shows pseudo steady-state concentration profiles of substrate (represented as ThOD) and active biomass represented as BRP biomass. The BRP results are from day 63 following startup (Figure 6.18) and the acetate, formate and formaldehyde data used to calculate the ThOD are from days 35, 49 and 50 of experiment H2, respectively.

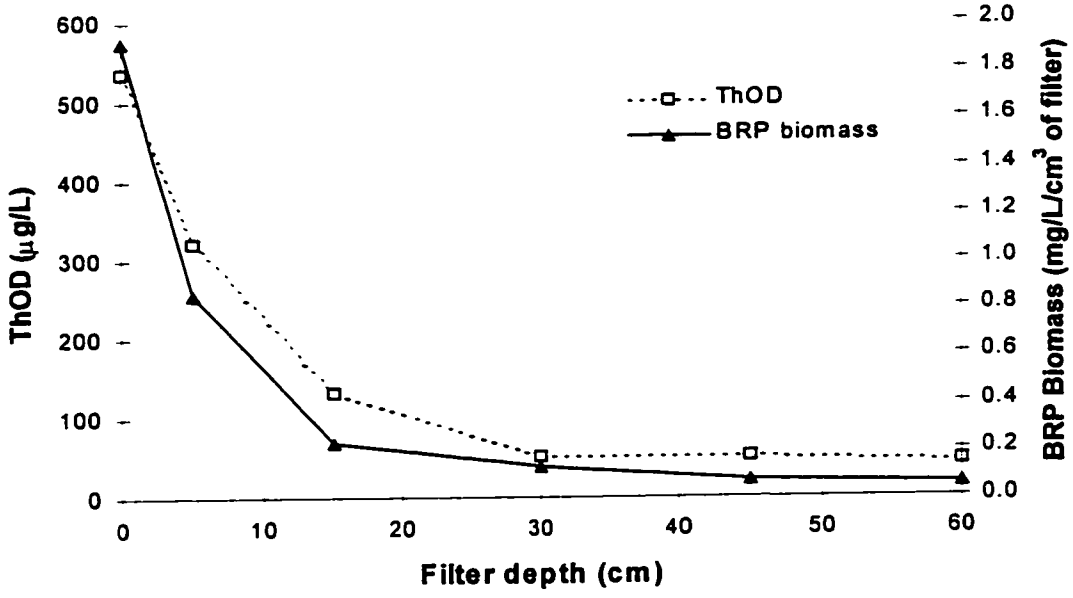

Figure 6.20: Concentration profiles of ThOD and active biomass (measured as BRP) in the control filter

No glyoxal data were used for the calculation of the ThOD, because glyoxal concentrations were always low and somewhat inconsistent as mentioned previously. BOM results from experiment H2 were used because no formaldehyde profiles were measured in the current experiment (O1). The ThOD is assumed to represent a surrogate for the growth limiting substrate for bacterial growth. This is probably a reasonable assumption based on what has been mentioned in Chapter 3.

The results in Figure 6.20 show that substrate concentration and biomass activity quantified as BRP are highly correlated (coefficient of determination R^2 of linear regression = 0.98, not shown). The similarity between the profiles of the growth limiting substrate, i.e. ThOD, and biomass activity is not surprising from the standpoint that these two parameters are directly related through the yield factor (equation 2.2 in Chapter 2). Consequently, the data shown in Figure 6.20 suggest that the BRP method is effectively quantifying the amount of substrate-degrading activity.

Removal of Hydrogen Peroxide

As mentioned earlier, the dosage of H_2O_2 as an ozone decay accelerator will likely lead to the presence of H_2O_2 residuals in the influent of subsequent treatment steps, e.g. biofiltration, particularly if H_2O_2:O_3 ratios are substantially above the stoichiometric ratio of 0.35 (w:w). This was confirmed in this experiment. Figure 6.21 shows the measured H_2O_2 concentrations in the influent and effluent of filter 3.

Hydrogen peroxide influent concentrations were between 0.35 and 0.60 mg/L and these concentrations substantially decreased through the filter.

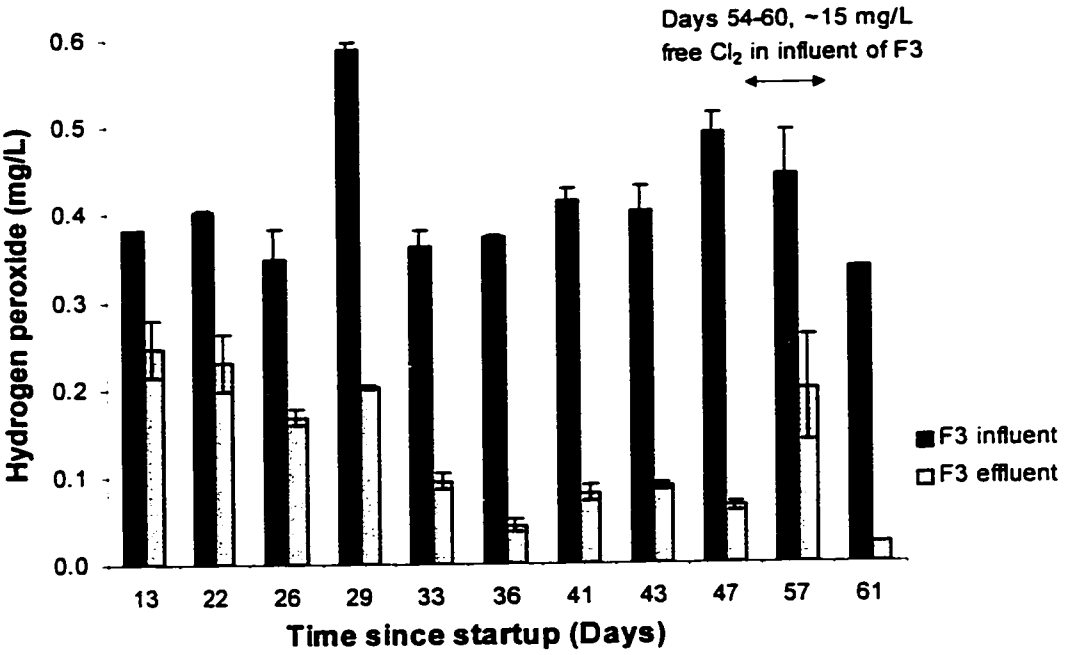

Figure 6.21: Hydrogen peroxide concentrations in the influent and effluent of filter 3

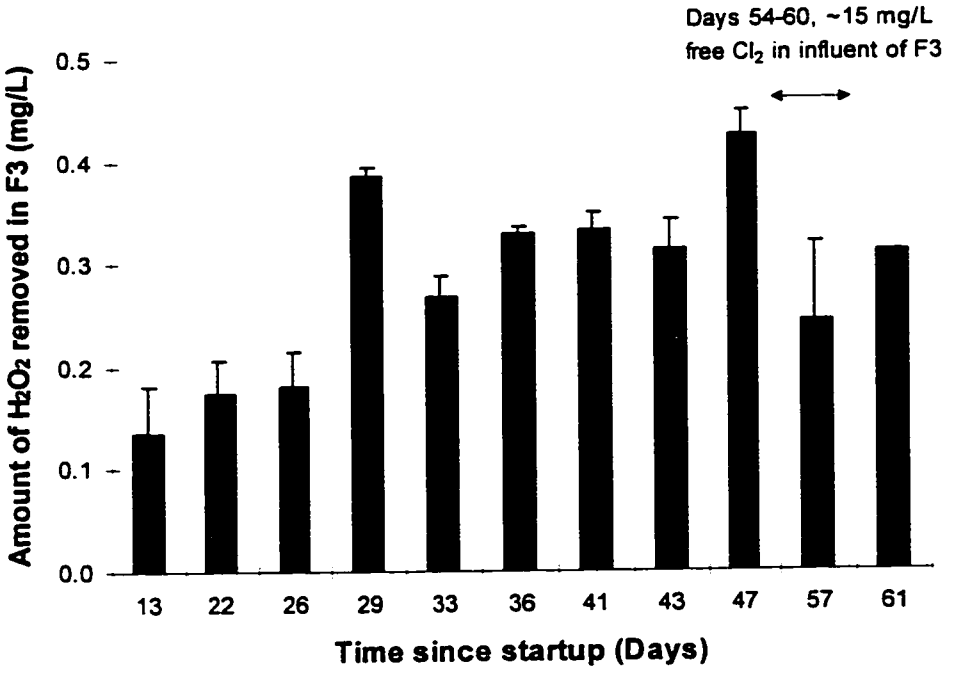

Figure 6.22: Amount of hydrogen peroxide removed in filter 3

However, the H_2O_2 concentration in the effluent did not decrease to below the MDL as was the case in experiment H1 where H_2O_2 was fed continuously at an influent concentration of ~1 mg/L (Chapter 4). Figure 6.22, which represents the amount of H_2O_2 removed through filter 3, suggests that after about 30 days following startup the removal of H_2O_2 was at some sort of steady-state.

In order to elucidate the H_2O_2 removal mechanism in filter 3, catalase activity of the filter biomass was tested on several occasions using the approach described earlier in this chapter. Catalase is an intracellular enzyme (Ibrahim and Schlegel, 1980a) contained in many Gram-negative and Gram-positive bacteria. Catalase activity testing represents a standard microbiological test for the characterization of bacterial species. The biomass samples withdrawn from filter 3 and incubated on R2A agar were all catalase positive. Therefore, these results are in agreement with the potential H_2O_2 removal mechanism through catalase producing bacteria. The same observation, i.e. catalase positive reaction, was made for a biomass sample from the control filter (filter 1), which never received H_2O_2.

Further testing of the potential H_2O_2 removal mechanism through catalase producing bacteria was done by disinfecting filter 3 with free Cl_2 at an influent concentration of about 15 mg/L for a period of one week (days 54-60). Following this period, filter 3 was no longer biologically active. This was inferred from the absence of a DO-decrease through the filter (data not shown). Had substrate degradation been taking place, such a DO-decrease would have been observed. Hydrogen peroxide measurements on days 57 and 61 indicated that H_2O_2 was still removed in filter 3, despite the absence of viable biomass (Figures 6.21 and 6.22). The amount of H_2O_2 removed following the disinfection of filter 3 was not substantially different compared to before disinfection. These results suggested that the removal of H_2O_2 during this experiment where H_2O_2 was present periodically in the filter influent did not, or only to a minor extent, occur as a result

of enzymatic activity of the bacteria, i.e. catalase activity. Therefore, the H_2O_2 removal in filter 3 was related to the maturation of the filter but not with respect to its biological activity. Note that results shown in Chapter 4 demonstrated that a filter containing new and biomass-free media had essentially no H_2O_2 removal capability.

To further investigate H_2O_2 removal, the media of filter 4 was replaced with new media on day 60 following startup and H_2O_2 was dosed to the influents of both filters, i.e F3 (used media, disinfected) and F4 (new media, biomass-free) for several hours. The differences in the H_2O_2 removal between filters 3 and 4 are shown in Figure 6.23 for two tests using different filter influent H_2O_2 concentrations.

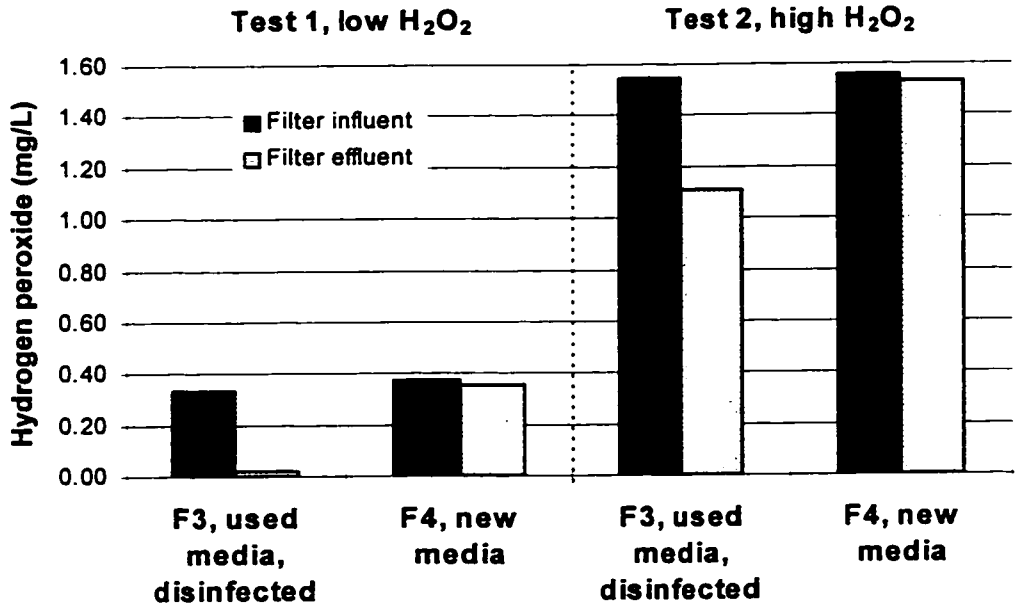

Figure 6.23: Hydrogen peroxide removal in used (and disinfected) filter media vs. new filter media

The new media (filter 4) did not lead to a measurable decrease of the H_2O_2 concentration, what is consistent with results reported in Chapter 4. However, filter 3 showed a clear decrease of the H_2O_2 concentration during both tests, despite the fact that the filter was not biologically active. Consequently, the H_2O_2 removal in filter 3 was likely

caused by a chemical reaction, which occurred in the filter only after a certain period of operation.

Several components can catalyze the decomposition of H_2O_2 to oxygen and water, including manganese and copper oxides (Snoeyink and Jenkins, 1980; Colodette et al., 1988) and ferric iron (Fe^{3+}) (Spain et al., 1989; McGuire et al., 1991; Ravikumar and Gurol, 1994). The reaction of H_2O_2 with ferrous iron (Fe^{2+}) known as Fenton's Reagent leads to the production of OH-radicals (e.g. McGuire et al., 1991).

Iron was likely present in the filter influent water because the fluoro-carbon feed lines were stained with a rusty color after a certain period of operation. The origin of this color may have been the deposition of iron oxides, e.g. ferric iron, and the same deposits on the filter media may have been responsible for the observed decomposition of H_2O_2 through filter 3 in this experiment.

Headloss

Headloss was measured in all four filters during this experiment. Figure 6.24 shows clean bed (immediately after backwash) as well as terminal (immediately before backwash) headloss in filter 1 (control). The other three filters showed very similar behaviors compared to filter 1 (data not shown).

Clean bed headloss did not increase during the course of the experiment, confirming the results reported in Chapter 5. This suggests that under the specific conditions of the experiment (i.e. low to moderate BOM concentrations in the filter influents, no particles in the filter influents, backwash using air scour) the growth of a biofilm on the filter media did not cause a measurable increase in the clean bed headloss. Terminal headloss did not increase substantially during the experiment, although in the last couple of data points shown in Figure 6.24 a trend towards an increase of the values can be observed. Similarly to what was mentioned in Chapter 5, air binding was likely the cause of this increase. The phenomenon of excessive air binding in biofilters reported in Chapter

5 was not observed during this experiment, possibly because the experiment had to be stopped after two months of operation and air binding was observed to occur in biofilters only after about two months of operation (cf. Chapter 5).

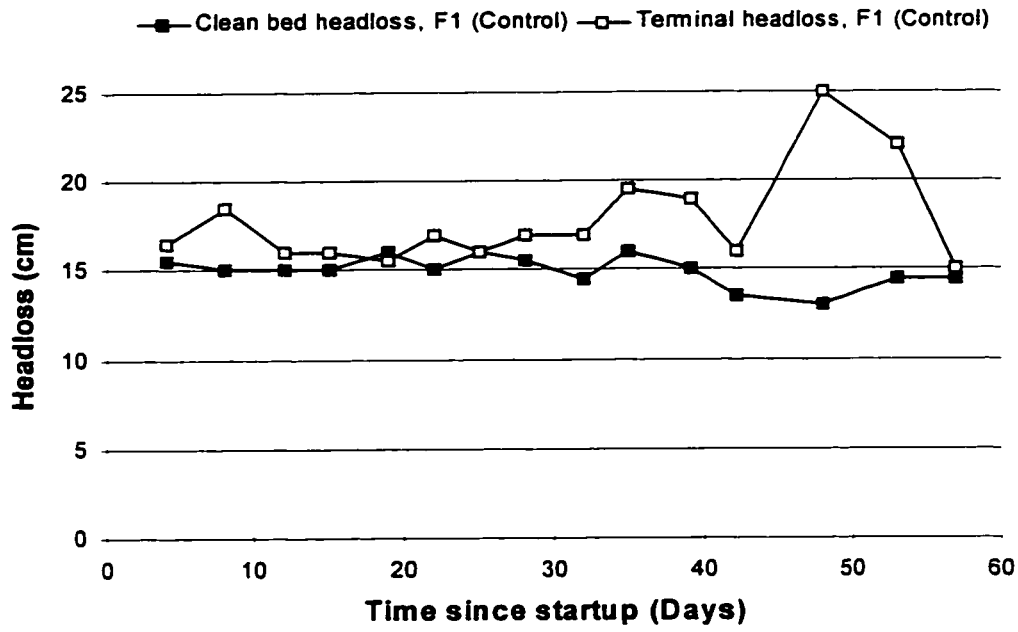

Figure 6.24: Headloss in filter 1 during the entire experiment

CONCLUSIONS

The following principal conclusions were drawn based on the experimental results presented in this chapter:

- The periodic presence of O_3 (1-2 hours per week) at concentrations between 0.1 and 0.2 mg/L in the influent of an anthracite/sand filter had a negligible effect on the biological removals of several easily biodegradable components. The amount of viable biomass and biomass activity in this filter was similar to a control filter (no oxidant dosage), supporting the negligible effect of the ozone regarding substrate removal.

- The irrelevant effect of O_3 on the biological performance of the filter under the specific conditions of this experiment was likely the result of the rapid decrease of the O_3 concentration in the first few centimeters of the filter bed. The rapid disappearance of the O_3 in the filter was caused by the reaction of O_3 with the anthracite media.
- The intermittent presence of H_2O_2 residuals (0.4-0.6 mg/L) in the influent of an anthracite/sand filter had a minor effect on the biological removals of acetate, formate and formaldehyde. This is consistent with the results obtained when H_2O_2 was dosed continuously to the influent of a biofilter at a concentration of ~1 mg/L (experiment H1, Chapter 4). The following chapter (Chapter 7) presents a summary and comparison of the effects of the different oxidants, i.e. H_2O_2, O_3 and Cl_2 on the biological performance of anthracite/sand biofilters.
- A new method for the measurement of biomass activity, i.e. substrate degradation potential, was developed and applied for the measurement of biomass activity in the biofilters. The new method (biomass respiration potential, BRP) was shown to be applicable to the measurement of biomass activity in drinking water biofilters.
- Calculated ratios of BRP to phospholipid biomass showed that biomass activity per unit amount of viable biomass strongly increases with biofilter depth under the tested conditions. Therefore, the phospholipid method is likely not the appropriate method for BOM degradation modeling in biofilters because it provides a measurement of the amount of viable biomass rather than the amount of biomass which is actively degrading organic substrate (BOM).
- The similarity of the profiles of ThOD and BRP through the control filter suggests that the BRP method provides a quantification of the BOM degradation potential of the present biomass.

In addition, the results presented in this chapter led to the following secondary conclusions:

- Under the specific conditions of this experiment, O_3 decay acceleration was successfully accomplished by adding hydrogen peroxide at a H_2O_2:O_3 ratio of approximately 1:1 (w:w) to the influent of a biofilter containing O_3. A reaction time of about 9.5 minutes from the point of H_2O_2-addition to the filter influent was sufficient in order to consistently obtain O_3 concentrations $\leq$ 0.02 mg/L in the filter influent. In parallel batch tests it was demonstrated that for the specific water tested, the rate of O_3 decay increased with increasing H_2O_2:O_3 ratios.
- The periodic dosage of H_2O_2 as an O_3 decay accelerator led to the presence of H_2O_2 residuals in the filter influent. Although these residuals decreased substantially through the filter bed, residual H_2O_2 concentrations were measurable in the filter effluent.
- The principal H_2O_2 removal mechanism in this experiment, where H_2O_2 was periodically present in the filter influent, appeared to be the reaction of H_2O_2 with deposits in the filter, possibly ferric iron. The "biological" H_2O_2 removal mechanism through the catalytic decomposition of H_2O_2 by catalase appeared to be of minor importance in this experiment.
- Measurements of the decrease of dissolved oxygen (DO) through the biofilters were successfully used to approximate BOM removal. Measurements of DO-consumption through biofilters should be reemphasized as a simple method for an approximate assessment of the biological performance, i.e. BOM removal, of drinking water biofilters.

CHAPTER 7: COMPARISON AND INTEGRATION OF THE RESULTS FOR DIFFERENT OXIDANTS

INTRODUCTION

In Chapters 4-6, the experimental results obtained for the different oxidants, dosed to the biofilters under various conditions of concentration and duration were presented and discussed. Based on literature information (e.g. Baldry, 1983; LeChevallier et al., 1988; Pardieck et al., 1990; Huck et al., 1991), the negative effects of the investigated oxidants/disinfectants, i.e. H_2O_2, free Cl_2, combined Cl_2 and O_3, on BOM removal in the biofilters were expected to be substantially different. Such differences were anticipated mostly as a result of the distinct bactericidal strength of the oxidants/disinfectants and their different reactivity with biomass constituents and filter media. This chapter presents a summary of the experimental data as well as a comparison of the effects of the different oxidants on BOM removal in the biologically active filters.

OBJECTIVES

The objective of this chapter is to compare the effects of the different oxidants/disinfectants at different concentrations and to quantify the extent of substrate removal inhibition for each oxidant. Specific objectives included comparison and discussion of the results obtained for the different oxidants/disinfectants dosed to the

influent or backwash water of the biofilters under various conditions, using a common basis similar to the CT concept used in disinfection. In addition, it was attempted to provide some more fundamental explanations for the experimental results.

APPROACH

Biofilter CT-Concept

The results of the five experiments, i.e. H1, H2, C1, C2 and O1 (cf. Table 3.1), were analyzed using a CT-approach similar to the traditional CT-approach used for disinfection. The two CT-approaches are schematically represented in Figure 7.1, parts A and B.

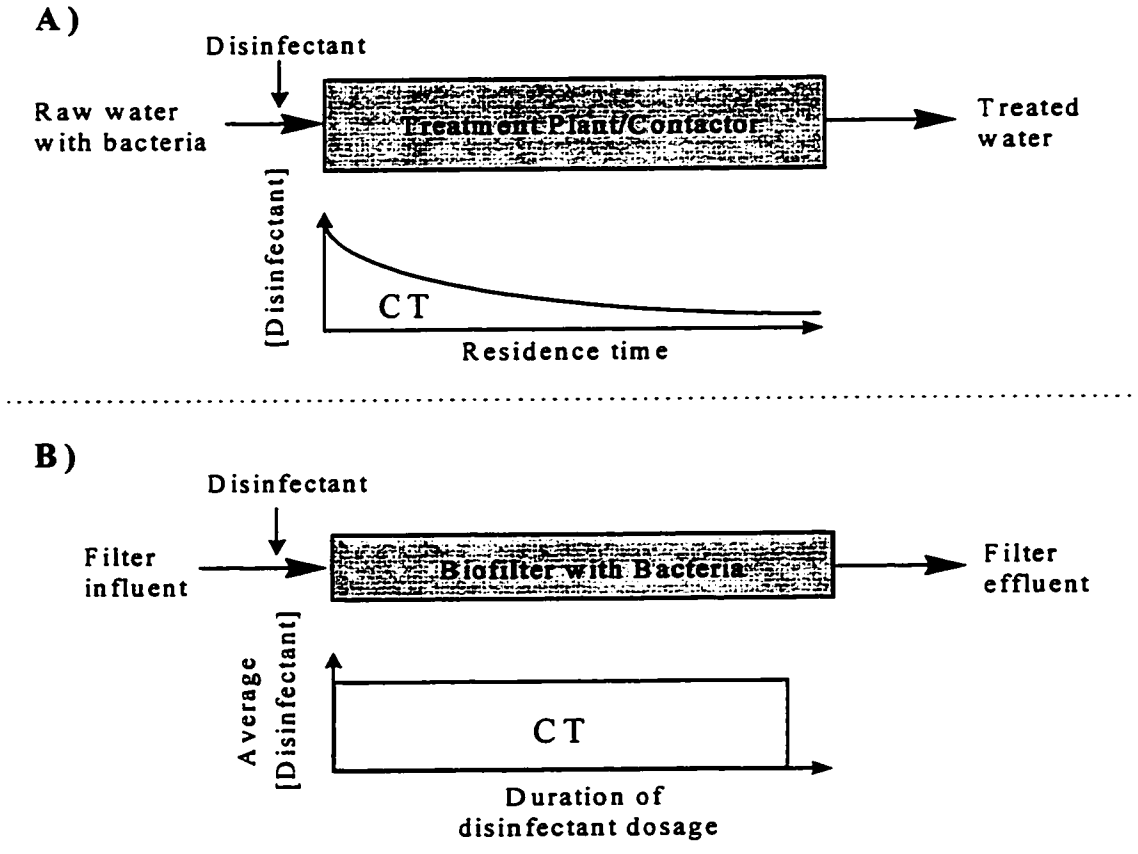

Figure 7.1: Application concepts of the CT approach in treatment plants (A) and biofilters (B)

Because disinfectant residuals were applied continuously to biofilter influents in many cases and time (T) would be infinity in this case, the data were normalized by calculating all CT-products based on a period of 1 week, i.e. 168 hours. The relevant oxidant concentration, C was calculated as the average of the filter influent and effluent oxidant concentration. Consequently, no CT products were calculated in cases where the oxidant residual in the filter effluent was below detection limit.

As an example, the continuous presence of 0.4 mg/L of free Cl_2 in the filter influent (0.2 mg Cl_2/L effluent residual) yields a CT-product of 0.3 mg/L*168 h = 50 mg*h/L on a weekly basis. Although other more sophisticated methods could perhaps be developed for comparing intermittent to continuously applied oxidants, this normalized CT-approach provides a simple comparative tool.

RESULTS AND DISCUSSION

Summary of Substrate Removal

For all the experiments listed in Table 3.1, at least one filter (F1) was always operated as a control (no oxidant dosage). The average BOM removal in the control filter (Figure 7.2) was calculated considering the data of all the experiments listed in Table 3.1. The data in Figure 7.2 served as reference BOM removal performance (no oxidant dosage) for the assessment of the relative suppression of BOM removal capability of the different oxidants.

The calculation of the average BOM removal in the control filter (F1) using the data from all experiments was possible because in each experiment this filter was operated under identical conditions with respect to filter media, hydraulic loading, BOM influent concentration, etc. The data for glyoxal are not included in Figure 7.2, because glyoxal filter influent concentrations were generally low (< 20 μg/L) and duplicate samples usually showed a relatively large variability, as mentioned previously.

Figure 7.2 shows that the average removals of acetate, formate and formaldehyde in the control filter (EBCT = 5.6-6.0 minutes) at pseudo steady-state were between 90 and 95%. The average removals of the three components are not statistically different at the 5% significance level. In the case of acetate and formate, the average removals are statistically different (α = 0.05) from 100%, i.e. total removal, whereas for formaldehyde this difference is not statistically significant (α = 0.05).

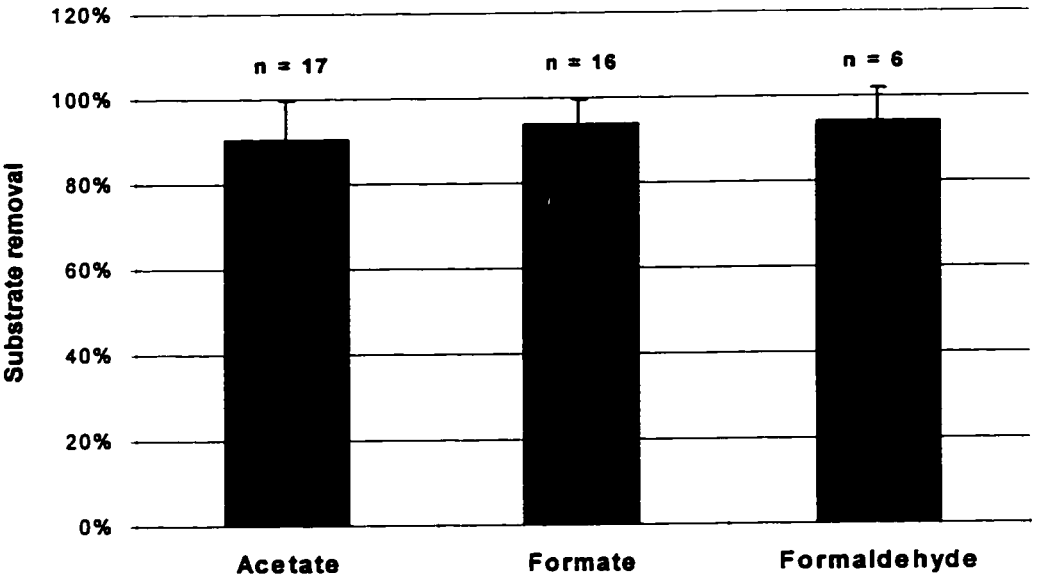

Figure 7.2: Average substrate removal in the control filter (F1) at pseudo steady-state

Filter influent concentrations for acetate, formate and formaldehyde were usually 250-350 µg/L, 350-450 µg/L and 70-100 µg/L, respectively. Using average filter influent concentrations of 300 µg/L for acetate, 400 µg/L for formate and 85 µg/L for formaldehyde, the average percentage removals shown in Figure 7.2 translate to average filter effluent concentrations of about 28 µg/L (acetate), 25 µg/L (formate) and 5 µg/L (formaldehyde). These effluent concentrations indicate that although removals of the easily biodegradable components shown in Figure 7.2 were > 90%, the total BOM effluent concentration was above the level of 10 µg C_{eq}/L proposed by van der Kooij as the target

AOC concentration in order to prevent regrowth of heterotrophic bacteria in non-chlorinated distribution systems (e.g. van der Kooij, 1992). These results suggest that in order to consistently achieve such low levels of BOM, i.e. AOC of 10 μg C_{eq}/L, at full scale, relatively long EBCTs, i.e. considerably greater than 6 minutes, or an additional biological treatment step, e.g. ground passage, would be required.

Figure 7.3 summarizes the substrate removal results for the experiments with hydrogen peroxide (H1 and H2). As discussed in Chapter 4, BOM removal inhibition was minor at a continuous H_2O_2 concentration of ~1 mg/L in the filter influent (H1) whereas at ~5 mg/L H_2O_2 in the filter influent (H2), the suppression of the BOM removal capability was major, particularly in the case of formate.

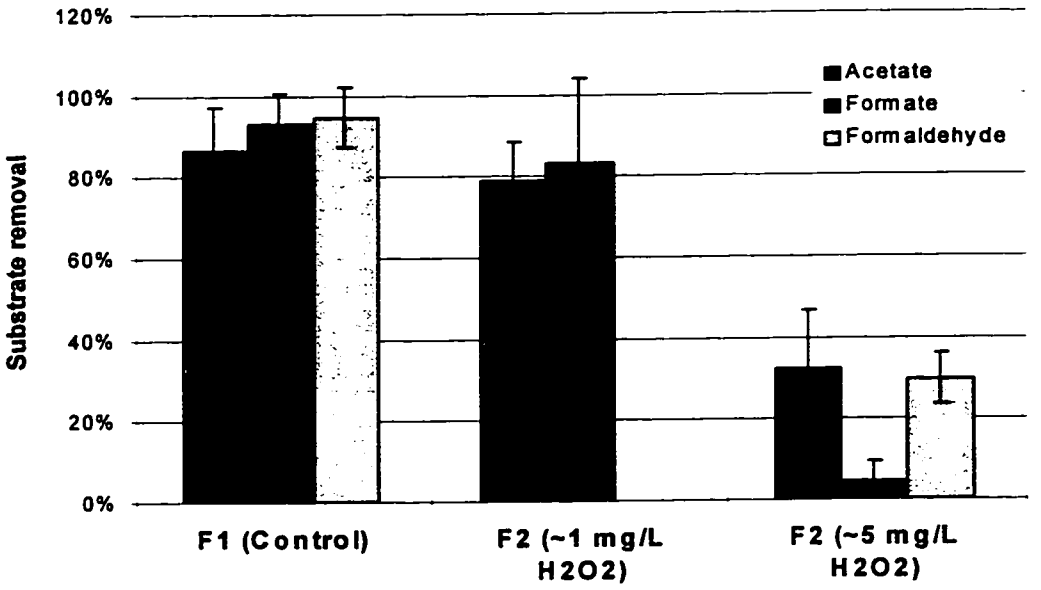

Figure 7.3: Summary of acetate, formate and formaldehyde removal during the experiments with hydrogen peroxide (Chapter 4), no formaldehyde data for F2, ~1 mg/L H_2O_2

The results obtained for free and combined chlorine are summarized in Figures 7.4 (free Cl_2) and 7.5 (combined Cl_2).

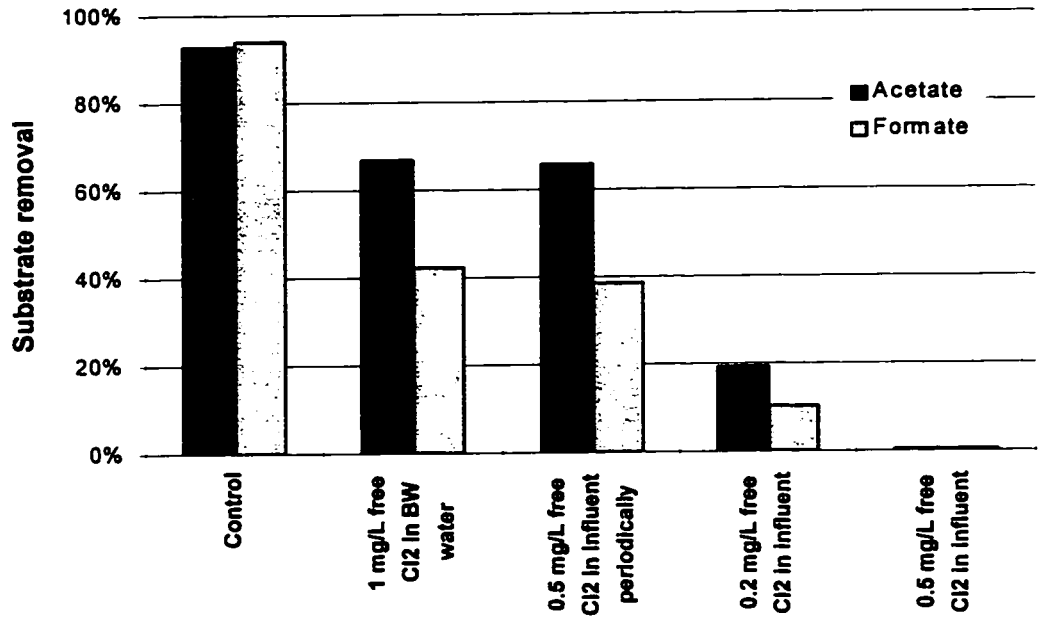

Figure 7.4: Summary of acetate and formate removal under the different conditions of free Cl_2 dosage (experiments C1 and C2, Chapter 5)

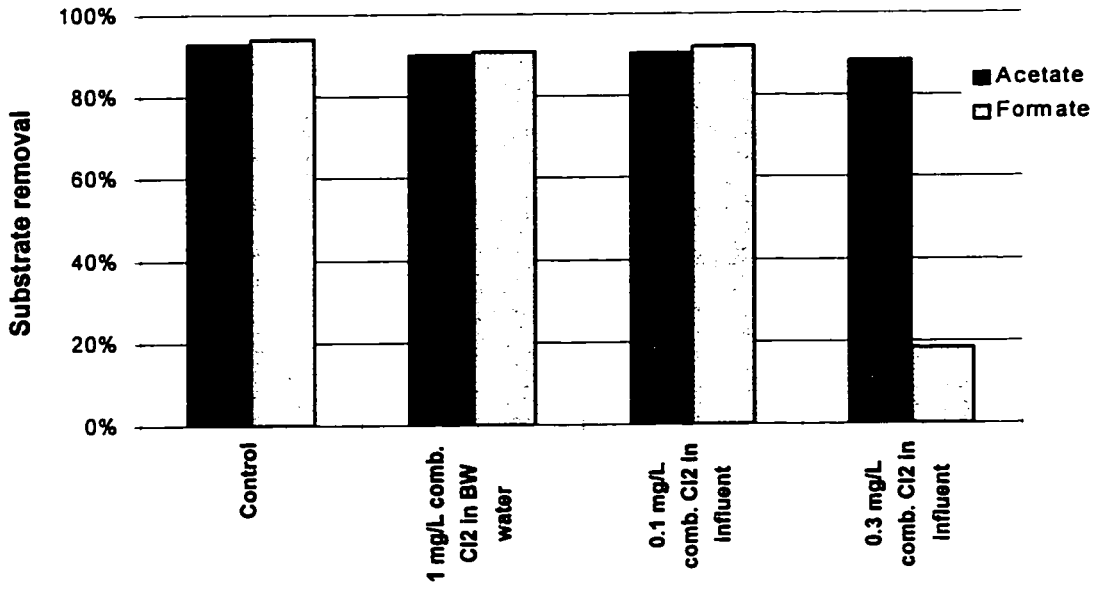

Figure 7.5: Summary of acetate and formate removal under the different conditions of combined Cl_2 dosage (experiments C1 and C2, Chapter 5)

Because some of the biofilters showed a pronounced non steady-state behavior as a result of the intermittent dosage of chlorine, the average substrate removal for the different filters shown in Figures 7.4 and 7.5 are represented without error bars.

The results in Figures 7.4 and 7.5 clearly show that the inhibition of biological formate removal under given chlorine dosage conditions was consistently stronger than for acetate. As already mentioned in Chapters 4 and 5, this is potentially related to differences in the biodegradation kinetics between these substances, the preferred use of acetate by the specific bacterial population in the biofilters or to differences in the oxidant sensitivity of the microbial populations responsible for acetate and formate degradation.

CT Products

Continuous Dosage of Oxidants

The results of the normalized CT calculations for the continuous presence of oxidants in the filter influents are summarized in Table 7.1. The results of the GAC/sand filter with ~0.5 mg/L free Cl_2 in the influent continuously are not shown in Table 7.1, because of the rapid reaction of Cl_2 with the GAC, resulting a negligible effect on BOM removal (cf. experiment C1, Chapter 5).

In the case of the continuous presence of an oxidant/disinfectant in the filter influent, the bacteriostatic properties (inhibition of bacterial growth or activity) of a given oxidant are likely most relevant, whereas for the intermittent dosage of an oxidant to the biofilters, the bactericidal strength (kill of bacteria) of the oxidant is of importance.

The effects of free Cl_2 and combined Cl_2 on the suppression of the biological removals of acetate and formate are compared in Figure 7.6. Figure 7.6 indicates that free Cl_2 had a stronger inhibitory effect on BOM removal compared to combined Cl_2, when these oxidants were continuously present in the filter influent.

Table 7.1: CT-products, average substrate removal and relative substrate removal suppression for the continuous dosage of oxidants in the biofilter influents

	Oxidant	Filter, (conditions of oxidant dosage) experiment	CT-product‡ (mg*h/L)	Average substrate removal (%)	Relative suppression of substrate removal (%)
1	-	1, (no oxidant) H1, H2, C1, C2 and O1	-	Acetate: 91% Formate: 94% Formald.: 94%	--
2	H_2O_2	2, (~1 mg/L H_2O_2 in influent continuously) H1	NA[S]	Acetate: 79% Formate: 83%	Acetate: 13% Formate: 11%
3	H_2O_2	2, (~5 mg/L H_2O_2 in influent continuously) H2	613	Acetate: 32% Formate: 5% Formald.: 30%	Acetate: 64% Formate: 95% Formald.: 68%
4	Cl_2	1, (~0.1 mg/L comb. Cl_2 in influent continuously) C2	12	Acetate: 90% Formate: 92%	Acetate: 0% Formate: 2%
5	Cl_2	2, (~0.3 mg/L comb. Cl_2 in influent continuously) C2	42	Acetate: 89% Formate: 19%	Acetate: 2% Formate: 80%
6	Cl_2	2, (~0.2 mg/L free Cl_2 in influent continuously) C2	22	Acetate: 19% Formate: 10%	Acetate: 79% Formate: 89%
7	Cl_2	3, (~0.5 mg/L free Cl_2 in influent continuously) C1	84	Acetate: 1% Formate: 1% Formald.: 3%	Acetate: 99% Formate: 99% Formald.: 97%

‡ CT- product normalized on a weekly basis
NA[S]: no oxidant residual was measurable in the filter effluent, therefore no CT product was calculated.

This finding is in agreement with the substantially stronger bactericidal effect of free chlorine on planktonic bacteria (e.g. Malcolm Pirnie, Inc. and HDR Engineering, Inc., 1991). However, in the case of biofilms, several researchers have reported improved control of such films in distribution systems with combined chlorine, particularly in the

case of iron pipes (LeChevallier et al., 1988; 1992; 1993; 1996; LeChevallier and Lowry, 1990).

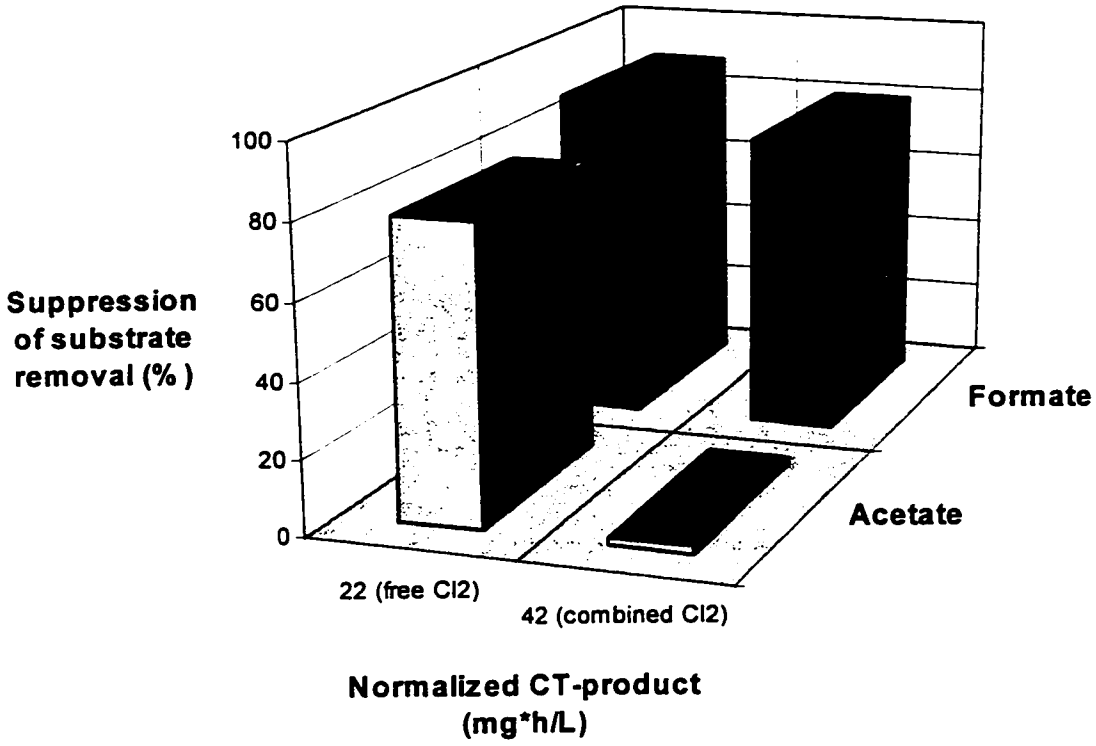

Figure 7.6: Relative suppression of substrate removal of free Cl_2 vs. combined Cl_2

It must be kept in mind that suppression of BOM degradation in the biofilm by the presence of oxidants was the principal response parameter of interest in this research. In distribution system studies however, the presence of bacteria (particularly coliforms and HPCs) in the bulk liquid and biofilms attached to the pipe walls is often the parameter of primary interest. The response of these parameters, i.e. BOM degradation potential and culturable bacteria, to the presence of different oxidants, e.g. free and combined Cl_2, seems to be substantially different based on results from Stewart et al., (1994). These authors showed that in the case of the exposure of biofilms to ~4 mg/L of monochloramine for a period of 1 hour, HPCs decreased by about 3 orders of magnitude, whereas substrate (glucose) consumption rate decreased only by ~15% during the same period.

Comparing substrate removal suppression (lines 3, 6 and 7 in Table 7.1) with the amount of viable biomass (cf. Chapters 4 and 5) in the filters continuously dosed with H_2O_2 or free Cl_2 shows that these two parameters were correlated. In all of these cases (lines 3, 6 and 7 in Table 7.1), the removal of acetate and formate was substantially suppressed and viable biomass (phospholipid) levels in these filters were very low (Figures 4.18, 5.13 and 5.21 in Chapters 4 and 5).

However, in the case of the presence of free Cl_2 in the backwash water (discussed in more detail later in this section), no obvious correlation between substrate removal and biomass growth suppression was observed. This suggests that the mechanism of BOM-removal suppression was different in the case of the continuous presence of an oxidant, e.g. H_2O_2 and free Cl_2, compared to the presence of free Cl_2 in the backwash water. The continuous presence of an oxidant in the filter influent seemed to essentially inhibit the growth of viable biomass as a result of the bacteriostatic strength of the relevant oxidant. However, when free chlorine was present in the backwash water, the metabolic functions responsible for BOM degradation appeared to be inhibited, because an amount of viable biomass (phospholipid) similar to the control filter was still present following Cl_2 addition.

The results in Table 7.1 further indicate that under the specific conditions of this research, combined chlorine (line 5 in Table 7.1) was likely a stronger biocide with regards to acetate and formate degradation capability of the biofilms, compared to hydrogen peroxide (line 3 in Table 7.1). Overall, the strength of the different biocides (oxidants) on the inhibition of the removal of acetate and formate was: free chlorine > combined chlorine > hydrogen peroxide, when these oxidants were continuously present in the filter influent. As noted in Chapter 6, the results for ozone are insufficient to draw conclusions regarding the effects of the continuous presence of this oxidant in biofilter influents.

The results of the study conducted by Huck et al., (1991) suggested that the presence of an ozone residual (~0.3 mg/L) in the influent of an anthracite/sand filter (F4 in

that study) led to a partial suppression of biological AOC removal. Comparing the AOC removal in that filter with the results obtained in an identical filter (F2 in that study) without an ozone residual in the influent showed that suppression of AOC removal in F4 in the Huck et al. study averaged 40% as a result of the ozone. Using the previously discussed CT approach, an ozone CT of ~25 mg*h/L can be calculated for their filter 4. However, an ozone residual was not continuously measurable in the filter effluent and therefore the CT calculation above might be an overestimation. However, these results suggest that the negative effects of ozone residuals in influents of anthracite/sand filters on BOM removal might be substantial, if such residuals are present continuously. As mentioned in Chapter 6, additional work would be required to further investigate the effects of continuously present ozone residuals on the removal of BOM in biofilters.

Periodic Addition of Oxidants

The CT results for the intermittent oxidant dosage to the biofilters (Table 7.2) indicate that the experimental results could not be entirely described with this simplified approach. As an example, in the filter dosed with ~0.5 mg/L free Cl_2 intermittently (F2 in experiment C1) and the filter backwashed with ~1 mg/L free Cl_2 (F3 in experiment C2), the specific CT products were equal to 2.0 and 0.2 mg*h/L, respectively (lines 3 and 4, Table 7.2). However, the relative acetate and formate removal capability of these filters was suppressed to approximately the same extent (lines 3 and 4, Table 7.2).

This suggests that in the case of the periodic addition of an oxidant to biofilters, the kinetics of the reestablishment of the BOM removal capability following the addition of an oxidant and the time interval between each oxidant addition are of importance, as suggested by the modeling work of Stewart et al., (1996). These parameters are not accounted for in the simplified CT-approach.

The work of Stewart and colleagues suggested that optimized biofilm control, i.e. maximum biofilm suppression, was achieved when intervals between pulses of biocide

addition were equal to the time at which minimum biofilm thickness is reached (TMT), following a periodic oxidant dosage. In the computer simulations shown in Stewart et al., (1996), TMT was equal to about 20 hours, using specific model input values. Those results suggest that the suppression of biofilm growth (and BOM removal) is likely higher if the interval between biocide addition is relatively short (about 1 day).

Table 7.2: CT-products, average substrate removal and relative substrate removal suppression for the intermittent addition of oxidants to the biofilters

	Oxidant	**Filter, (conditions of oxidant dosage) experiment**	**CT-product‡ (mg*h/L)**	**Average substrate removal (%)**	**Relative suppression of substrate removal (%)**
1	-	1, (no oxidant) H1, H2, C1, C2 and O1	-	Acetate: 91% Formate: 94% Formald.: 94%	--
2	Cl_2	4, (~1 mg/L combined Cl_2 in backwash water) C2	0.2	Acetate: 90% Formate: 91%	Acetate: 0% Formate: 3%
3	Cl_2	3, (~1 mg/L free Cl_2 in backwash water), C2	0.2	Acetate: 67% Formate: 42%	Acetate: 26% Formate: 55%
4	Cl_2	2, (~0.5 mg/L free Cl_2 once per week for 6 hours) C1	2	Acetate: 66% Formate: 38%	Acetate 28% Formate: 59%
5	H_2O_2	3, (~0.5 mg/L H_2O_2 twice per week for 1 hour) O1	0.5	Acetate: 90% Formate: 98%	Acetate: 1% Formate: 0%
6	O_3	4, (~0.15 mg/L O_3 twice per week for 1 hour) O1	$NA^{\$}$	Acetate: 94% Formate: 97%	Acetate: 0% Formate: 0%

‡ CT- product normalized on a weekly basis
$NA^{\$}$: no oxidant residual was measurable in the filter effluent, therefore no CT product was calculated.

This might be an explanation for the similar suppression of the average acetate and formate removals in the filter backwashed with free chlorinated water and the filter which

received free Cl_2 in the influent intermittently, despite CT products varying by an order of magnitude (lines 3 and 4, Table 7.2). Although the duration of Cl_2-addition was substantially higher in the filter with free Cl_2 in the influent intermittently, the time interval between each Cl_2-addition was about twice as long in this filter compared to the filter backwashed with free chlorinated water.

Thus, in regards to the periodic addition of oxidants to the biofilters, the recovery time to reestablish BOM removal represents an important parameter. In Chapter 4 it was shown that the establishment of BOM removal in the initially biomass-free control filter (F1), required about 10 days (240 hours) for acetate and 20 days (480 hours) in the case of formate (experiment H2). In the periodically free-chlorinated filter (line 4 in Table 7.2), the recovery of acetate removal following Cl_2 dosage required ~65 hours, whereas ~115 hours were necessary to reestablish formate removal. In the filter backwashed with free chlorinated water (line 3 in Table 7.2) acetate removal recovered after ~46 hours following backwash and formate required between 52 and 144 hours.

The modeling work of Hozalski and Bouwer (in: Huck et al., 1998) indicates that the time to establish BOM removal in biofilters is a strong function of temperature and of biodegradation kinetics. In the current research the time required to (re)establish acetate removal following startup or a biofiltration challenge through chlorine addition was always about a factor of two lower than for formate. This is likely related to the slower biodegradation kinetics, i.e. lower maximum utilization rate k, of formate compared to acetate (Hozalski and Bouwer, in: Huck et al., 1998). The fact that the time for acetate and formate removal recovery was substantially lower during the chlorine challenges (lines 3 and 4 in Table 7.2) compared to startup, indicates that these events did not lead to a total kill of the biomass. The intermittent contact of chlorinated water with the bacteria present in the biofilm rather led to a partial kill and/or impairment of the metabolic functions of the bacterial biomass. The similar results of viable biomass (phospholipid) measured in the

control filter and the filters backwashed with chlorinated water (cf. Figure 5.21, Chapter 5) suggest that impairment of the physiological activities of the specific bacterial population was the reason for the decreased substrate removals in these filters, rather than kill of a fraction of the bacterial biomass.

This might be an explanation for observed differences in the effects of chlorinated backwash water on BOM removal in biofilters. As mentioned in Chapter 5, Huck et al., (1998) have observed negligible effects of chlorinated backwash water on the biological performance of demonstration scale biofilters. On the other hand, the results of the present research and results from others (e.g. Miltner et al., 1995, 1996) indicate a considerable negative effect of chlorinated backwash water on BOM removal, particularly in the case of free Cl_2. Potentially, the specific bacterial biomass present in the biofilters of the different studies was different, particularly regarding the injury of the physiological activities of the specific biomass by the presence of Cl_2 in the backwash water. However, this remains speculation and additional work would be required to further investigate this. Nevertheless, the differences in the effects of chlorinated backwash water on BOM removal observed in the above-mentioned studies, suggest that such effects may be depending on site specific characteristics of the filter influent water (e.g. BOM composition) and the biomass in the filters. Therefore, definite conclusions with respect to the significance of chlorinated backwash water on the biological performance of biofilters might not be possible at the present time. Site specific investigations (pilot tests) may be necessary to address the significance of the negative effects of Cl_2 in the backwash water in a given biofiltration situation.

Yu and McFeters, (1994) have used several approaches to study the effects of free chlorine and monochloramine on the physiological activities of *Klebsiella pneumoniae* biofilms. They demonstrated that RNA turnover rate quantified by the bacterial uptake of uridine was substantially less affected by the exposure to chlorine and monochloramine

than were conventional plate counts. Based on these results those authors concluded that microbiological tests relying on the comprehensive integrity of cellular physiology (e.g. plate counts) are more susceptible to biocides than are tests quantifying discrete physiological processes, e.g. incorporation of uridine (Yu and McFeters, 1994).

In another study, Huang et al., (1995) showed that respiratory activity within biofilms grown in an AR was not uniformly affected by the presence of 2 mg/L monochloramine (2-hour dosage), but greater respiratory activity persisted deep in the biofilm than near the biofilm-bulk fluid interface. Mass transport of monochloramine and/or growth-limiting substrate into the biofilm were thought to be responsible for these observed spatial differences in the effects of monochloramine exposure on respiratory activity (Huang et al., 1995).

The results of those investigations, i.e. Yu and McFeters, 1994 and Huang et al., 1995, suggest that the effects of biocides, e.g. free and combined Cl_2, are manifold and are influenced by several physico-chemical parameters of a given system. As will be shown in Chapter 8, the biofilms in the filters of this research were relatively thin, i.e. < ~20 μm, whereas the biofilms investigated in the studies mentioned immediately above generally had a thickness in the range of 100-200 μm. In addition, those biofilms were generally grown in ARs using high substrate concentrations, i.e. ~20 mg/L of glucose. Such differences in the biofilm physiology are likely important with regard to the direct comparison of the results of these studies with the oligotrophic conditions relevant in drinking water biofiltration, e.g. this research.

CONCLUSIONS

Summarizing and integrating the experimental results of this research leads to the following conclusions:

- The comparison of the experimental results obtained for the continuous presence of the different oxidants in the influent of anthracite/sand filters showed that the effect of different oxidants on the relative suppression of BOM removal varied over a considerable range. Free Cl_2 had the strongest negative effect followed by combined Cl_2 and H_2O_2. The experimental results for ozone are incomplete regarding the effects of the continuous presence of O_3 residuals in biofilter influents. Literature data indicate that the inhibitory effect of O_3 residuals in the influent of anthracite/sand filters on BOM removal is relatively strong, when O_3 residuals are continuously present in the filter influent.
- A clear relationship between the amount of viable biomass (phospholipid) and BOM removal (suppression) was observed in the filters receiving an oxidant continuously, i.e. no viable biomass - no BOM removal. For the periodic presence of free Cl_2 in the biofilters, this relationship was not observed. This suggests that the mechanisms of the suppression of BOM degradation were different when oxidants were present continuously compared to their periodic presence in biofilters. In the case of the periodic dosage of free Cl_2 to the biofilters, the metabolic functions responsible for BOM degradation seemed to be partially impaired, but the biomass was still viable, i.e. quantifiable with the phospholipid method.
- The use of the normalized CT concept represents a useful tool for comparing the effects of different, continuously present oxidants on BOM removal. The application of the CT concept to biofilters receiving oxidants intermittently however, showed that this approach was unable to describe certain experimental results. This is likely related to

the fact that the concept does not account for the time period between oxidant addition pulses, which is an important factor regarding biofilm control and related BOM removal.

- Regarding the relative suppression of BOM removal capability, the presence of a disinfectant residual in the filter *effluent* appeared to be more important than the bactericidal and/or bacteriostatic strength of the disinfectant *per se*.
- Biological acetate, formate and formaldehyde removals in the control anthracite/sand filter (no oxidant), operated at an EBCT of 5.6-6.0 minutes and a water temperature of ~11-17°C, were between 90 and 95%. The average formaldehyde removal was not statistically different from total removal (100%), whereas this difference was statistically significant in the case of acetate and formate.
- Under the conditions of this research, the inhibitory effect of a given oxidant, i.e. H_2O_2, free and combined Cl_2, dosed to the filters either continuously or intermittently, was consistently stronger for formate removal compared to acetate removal. This is potentially the result of slower biodegradation kinetics of formate compared to acetate, the presence of different microbial subpopulations responsible for acetate and formate degradation and differences in the oxidant sensitivity of these subpopulations.
- A difference in the biodegradation kinetics of acetate and formate may be expected based on the substantially higher gain of energy associated with the bacterial enzyme-catalyzed oxidation of acetate.
- The fact, that the (re)establishment of acetate removal following startup or a temporary chlorine addition challenge generally required about half the time compared to formate is in support of the existence of differences in the bacterial subpopulations responsible for acetate and formate degradation and the preferred utilization of acetate.

CHAPTER 8: AN INVESTIGATION OF MASS TRANSFER LIMITATIONS IN BIOFILTERS

INTRODUCTION

Mass transfer limitations are important aspects in many scientific and engineering disciplines and the assessment of their relevance in a given system is necessary in order to determine whether a given process is limited by the rate of reaction or the rate of mass transfer, e.g. diffusion. The case where mass transfer limitations are found to be irrelevant leads to a considerable simplification of the mechanistic modeling of the relevant process.

In the case of drinking water biofiltration, different authors have shown that contact time and not hydraulic loading is the key parameter for biological BOM removal and that for a given EBCT, removal of BOM is independent of hydraulic loading, in the range typically used in rapid filters or GAC contactors (Sontheimer and Hubele, 1987; Servais et al., 1994; Wang, 1995; Carlson and Amy, 1995; Wang and Summers, 1996). These results suggested that under typical drinking water conditions biological removal of BOM is not limited by external mass transfer, i.e. mass transfer from the bulk liquid through the mass-transfer boundary layer to the surface of the biofilm. Based on a kinetic modeling approach for AOC removal in biological filters, Zhang and Huck (1996a) drew similar conclusions.

The widely accepted modeling work of Rittmann and McCarty (1980a,b) considers molecular diffusion as the only means of mass transport to and in the biofilm, i.e. not

advection. Therefore and in order to be general, many (more recent) models based on the work of Rittmann and McCarty (1980a) consider molecular diffusion to and in the biofilm in order to model the removal of BOM in drinking water biofilters (e.g. Hozalski 1996; Zhang, 1996).

The recent use of more sophisticated techniques for the observation of biofilms, e.g. confocal scanning laser microscopy, has shown that, at least under some conditions, such films are composed of locally isolated cell clusters interspersed with less dense highly permeable water channels (e.g. Costerton et al., 1994; DeBeer et al., 1994; Lewandowski et al., 1995; Yang and Lewandowski, 1995; DeBeer et al., 1996). These results led to the conclusions that an exact mathematical description of mass transport within biofilm systems may not be possible and that simplifying assumptions are needed for purely practical purposes (Lewandowski et al., 1995). Such assumptions had to be made for the calculations of mass transfer limitation presented in this chapter.

Different authors have developed parameters which relate reaction rate and mass transfer, allowing assessment of whether a given process is limited by reaction or mass transfer (e.g. Weisz, 1973), and such parameters are used in numerous scientific disciplines (e.g. Weisz, 1973; Karel et al., 1985; Bailey and Ollis, 1986; Xu et al., 1996).

OBJECTIVES

The principal objective of the work presented in this chapter was to investigate mass transfer limitations, both external (to the biofilm) and internal (in the biofilm), of BOM degradation in the biofilters operated under the conditions reported in Chapters 4-6. An additional objective was to extend the results obtained under the particular conditions of this research to a broader range of biofiltration situations.

APPROACH

Biofilm Concept

For the calculations of mass transfer resistance it was assumed that the degradation of BOM occurred through substrate uptake by the bacteria present in the biofilm attached to the filter media. The role of suspended bacteria in the bulk liquid was neglected because several studies have shown that under drinking water biofilm conditions the importance of the suspended bacteria is negligible, particularly in the case of high specific surface area reactors such as biofilters (e.g. Hozalski 1996; Gagnon 1997; Gagnon et al., 1998). A biofilm is a layer of microorganisms in an aquatic environment held together in a matrix of extracellular polymeric substances (EPS) attached to a substratum (van der Wende and Characklis, 1990). Biofilms have traditionally been assumed to be a homogenous layer of bacteria, i.e. constant cell density, X_f and a locally uniform thickness, L_f, attached to an inert surface, i.e. the substratum (e.g. Rittmann and McCarty, 1980a). However as mentioned previously, recent studies have emphasized the heterogeneity of biofilms (e.g. Costerton et al., 1994; Lewandowski et al., 1995). Therefore, several simplifying assumptions had to be made for the calculations presented in this chapter.

It was assumed herein that the biofilm coverage of the filter media under pseudo steady-state conditions was equal to 50%, whereas the remaining 50% of the surface was considered uncovered. This assumption was made based on results from De Beer et al., (1996), who observed a biofilm coverage of ~50% in a biofilm grown on the surface of a polycarbonate closed channel flow cell. The percentage of biofilm coverage is important because it directly affects the calculation of the biofilm thickness, L_f, which is probably the most important parameter used in the calculations of mass transfer resistance, presented later in this chapter.

A conceptual schematic of the biofilm system considered for the calculations of mass transfer limitations is shown in Figure 8.1.

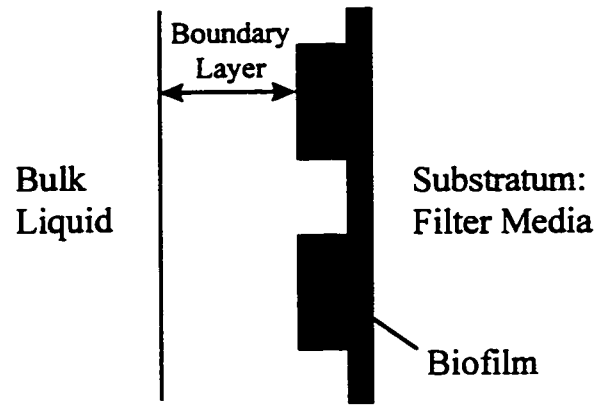

Figure 8.1: Conceptual biofilm representation for the calculation of mass transfer resistance

The mass transfer boundary layer was assumed parallel to the surface of the substratum, i.e. filter media, although the conceptual biofilm consisted of biofilm clusters with uncovered surfaces in-between (Figure 8.1). The fact that the mass transfer boundary layer is parallel to the substratum surface is a function of the flow velocity (DeBeer et al., 1996). Those authors showed that in the case of low flow velocities, i.e. ~0.008 m/s, the mass transfer boundary layer is parallel to the substratum surface despite the presence of cell clusters with a thickness of ~ 100 μm. In the present research flow velocity in the voids of the filter was equal to about 0.005 m/s. Therefore, the assumption of a mass boundary layer which is parallel to the surface of the substratum is reasonable.

Based on the results from De Beer et al., (1996), molecular diffusion was assumed to be the predominant mass transfer mechanism within the biofilm and the potential existence of interstitial voids leading to convective mass transport in the biofilm was ignored. Neglecting potential convective mass transport represents a conservative assumption regarding the significance of mass transfer limitations.

Calculation of Mass Transfer Resistance

The relative rates of reaction, i.e. BOM degradation, and diffusion within the biofilm were evaluated by calculating the dimensionless modulus Φ, which only contains observable parameters (Weisz 1973; Karel et al., 1985; Bailey and Ollis, 1986; Blanch and Clark, 1996):

$$\Phi = \frac{R_{obs} * L_f^{\,2}}{D_{eff} * S_b} \tag{8.1}$$

where: R_{obs}: overall rate of BOM removal, (M_s/L^3*T)
L_f: biofilm thickness (L)
D_{eff}: effective BOM diffusivity in the biofilm (L^2/T)
S_b: BOM concentration in the bulk liquid (M_s/L^3)

The principal advantage of the modulus, Φ is that it can be calculated without the knowledge of the intrinsic kinetic parameters or the specific reaction order. If Φ is ≥ 3, the system can be considered as limited by internal mass transfer, i.e. diffusion. On the other hand if Φ is ≤ 0.3, reaction rather than internal mass transfer is limiting (Weisz 1973; Bailey and Ollis, 1986).

The influence of external mass transfer was evaluated by calculating the dimensionless ratio of the observable modulus, Φ, and the Biot number, N_{Bi} defined as (Bailey and Ollis, 1986, p. 219):

$$N_{Bi} = \frac{k_s * L_f}{D_{eff}} \tag{8.2}$$

where: k_s: external mass transfer coefficient (L/T)

If Φ/N_{Bi} is « 1, the influence of external film resistance is negligible (Bailey and Ollis, 1986). The ratio of Φ/N_{Bi} is identical to the definition of an observable external modulus, Ω, according to Karel et al., (1985).

Calculation/Estimation of Parameters

Based on equations 8.1 and 8.2, several parameters have to be calculated/estimated in order to calculate Φ and N_{Bi}. These parameters include the observed removal rate R_{obs}, the biofilm thickness, L_f, the substrate diffusivity in the biofilm, D_{eff} and the external mass transfer coefficient, k_s. The methodology used for the estimation/calculation of each of these parameters is presented in the following section.

Observed Removal Rate, Robs

The biofilters operated under the specific conditions of this research showed a hydraulic behavior close to a plug-flow reactor. This is shown in Figure 8.2, which presents the results of a tracer test using a step input of a concentrated solution of sodium chloride to the influent of filter 2. Conductivity was used as the response variable because of the simplicity of the measurement. Conductivity was measured with a laboratory conductivity meter (CO 150, Model 50150, Hach Company, Loveland CO). The tracer test shown in Figure 8.2 was performed between experiments C2 and O1.

The sodium chloride solution had a conductivity of 63.5 mS which is about 2 orders of magnitude higher than the conductivity of the tap water, i.e ~0.7 mS. The results in Figure 8.2 indicate that the hydraulic behavior of the filter operated at a hydraulic loading of 7.5 m/h was close to a plug flow reactor. This is in agreement with results from Zhang (1996), who calculated axial Peclet numbers in pilot scale filters in the range of 8000 and concluded that the filters could be regarded as plug-flow reactors. Using the continuous-stirred tank reactor (CSTR) in series model (e.g. Levenspiel, 1972), the experimental data were well approximated by a model consisting of 35 CSTRs in series (Figure 8.2). Considering the total media depth of 70 cm in the filters this is conceptually equivalent to one CSTR every 2 cm of filter depth.

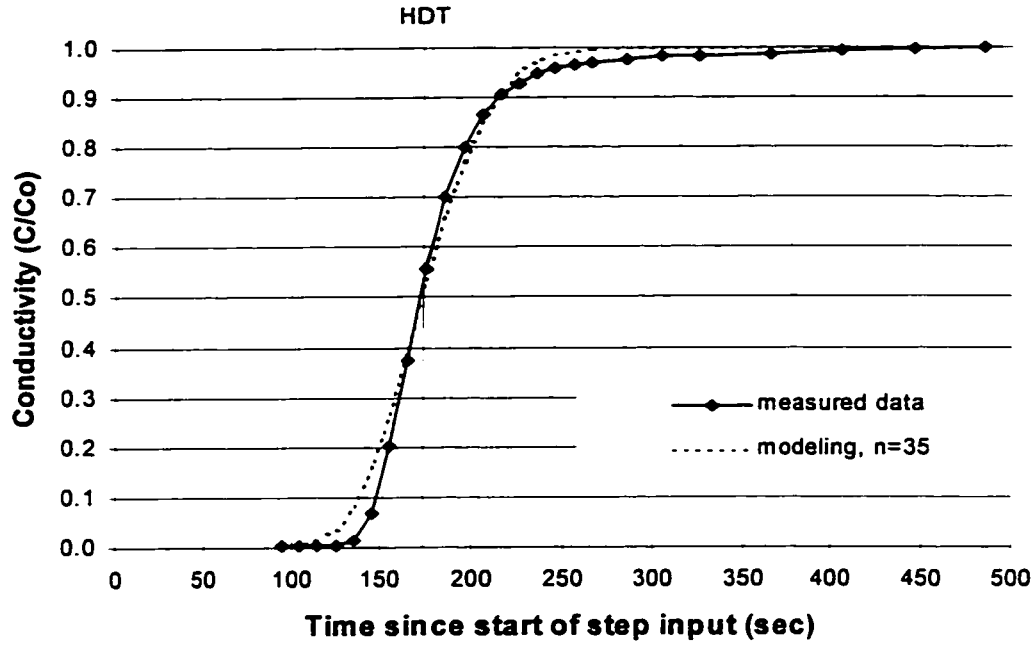

Figure 8.2: Results of tracer test in the filter columns

Because mass transfer resistance (if any) is expected to occur in situations where biofilm thickness is high, the emphasis of the calculations was on the top part of the control filter (F1), because biofilm thickness is highest at the top, as will be shown later in this section. Consequently, the observed BOM removal rate, R_{obs} was calculated considering the first conceptual CSTR in the filter, i.e. 0-2 cm filter depth. Acetate, formate and formaldehyde data from days 35, 49 and 50 of experiment H2 were used to calculate the ThOD profile in filter 1 (control) at pseudo steady-state. The resulting profile in the top part of the filter is shown in Figure 8.3.

Using the data shown in Figure 8.3, the observed removal rate in the top part of the filter (the first conceptual CSTR) can be approximated as:

$$R_{obs} = \frac{S_{in} - S_{2cm}}{HDT} \tag{8.3}$$

where: S_{in}, S_{2cm}: influent ThOD concentration and ThOD concentration at a filter depth of 2 cm, respectively (M_s/L^3)

HDT: hydraulic detention time in the filter section from 0-2 cm, HDT = EBCT*porosity, assumed porosity = 0.45

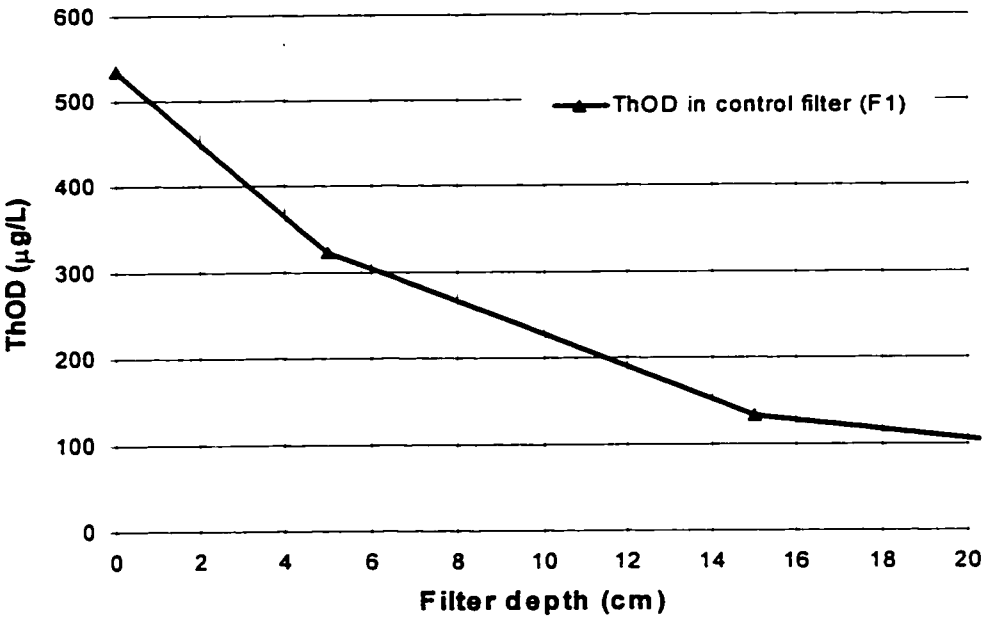

Figure 8.3: ThOD profile in the top part of the control filter (F1) at pseudo steady-state

Biofilm Thickness, Lf

In order to calculate the biofilm thickness, L_f it was first necessary to estimate the average media diameter. On day 64 following startup of experiment C2, media samples were collected at different depths in filter 1 (control). The media was weighed (dry weight) and the number of filter grains was manually determined. Assuming spherical particles and considering the density of the filter media, i.e. 1.6 g/cm^3 for anthracite and 2.6 g/cm^3 for sand, the average media diameter, d_m was estimated. The results of this procedure are shown in Figure 8.4.

Figure 8.4 shows that the filter had a relatively pronounced stratification regarding anthracite media diameter, with the smallest media at the top of the filter. This is the result

of the routinely performed backwashing, which is expected to distribute the media as a function of diameter as shown in Figure 8.4, i.e. the smallest media in the top part.

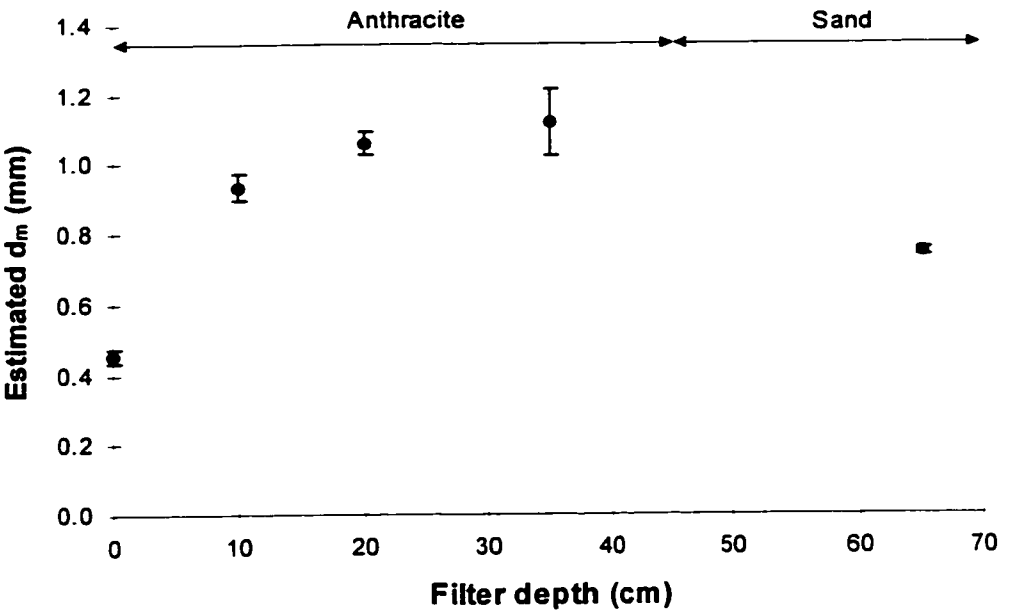

Figure 8.4: Estimation of the average media diameter, d_m as a function of filter depth in filter 1 on day 64 following startup (experiment C2)

The media characteristics provided by the manufacturer (Table 3.2) yield d_{60}-values of 1.6 mm and 0.7 mm for anthracite and sand respectively. For anthracite this d_{60}-value is about 50% higher than the average estimated d_m in Figure 8.4. This is likely the result of the over-simplified assumption of spherical anthracite particles in the estimations of d_m shown in Figure 8.4. For sand however, the estimated d_m at 65 cm (Figure 8.4) corresponded fairly well with the d_{60}-value given by the manufacturer, i.e. 0.7 mm. Literature data indicate that sand has a substantially higher sphericity compared to anthracite (Cleasby, 1990). Therefore the assumption of spherical particles is expected to affect the d_m-estimations of anthracite more than for sand.

The d_m estimations shown in Figure 8.4 were used to calculate the specific surface of the media at the different filter depths as follows (e.g. Zhang and Huck, 1996a):

$$\alpha = \frac{1.2 * 6 * (1 - \varepsilon)}{d_m} \qquad (8.4)$$

where:
- α: specific surface area (L^{-1})
- 1.2: factor to account for non-sphericity of media (-)
- ε: porosity (-)
- d_m: average estimated particle diameter (L)

Zhang and Huck (1996a) used a factor of 1.5 to account for the non-sphericity of the media. In this research a value of 1.2 was used, because this value is more conservative in the sense that it leads to a higher calculated amount of biomass per unit amount of media surface and therefore ultimately to a higher estimate of L_f.

Using the estimates of the specific surface in combination with the biomass (phospholipid) results obtained in the control filter on day 64 following startup of experiment C2, the amount of biomass per cm^2 of media surface was calculated. As mentioned previously, a biofilm coverage of 50% was assumed for this conversion. Biomass measurements expressed as nmole lipid P/cm^3 were converted to μg C/cm^3 using a conversion factor from Findlay et al., (1989), i.e. 191.7 μg C per 100 nmole of phospholipid. Finally, biofilm thickness, L_f was calculated by dividing the amount of biomass per unit surface by the biofilm density, X_f. For X_f a value of 15,540 μg C/cm^3 was used, a value calculated from X_f estimations from a biofiltration study by Rittmann et al. (1986). Similar X_f-values have been used by those authors in previous work (e.g. Rittmann and McCarty, 1980b).

BOM Diffusivity in the Biofilm, Deff

The organic cocktail in the filter influent consisted of acetate, formate, formaldehyde and glyoxal. All of these components have similar diffusivities in water (Schwarzenbach et al., 1993, p. 196). Hozalski (in: Huck et al., 1998) used a diffusivity in the biofilm of $7.3*10^{-10}$ m^2/s for acetate at a temperature of 12.5°C. Others have proposed similar values for acetate, i.e. $9.9*10^{-10}$ m^2/s (Rittmann et al., 1986). For the investigation

of mass transfer limitations in annular reactors (ARs), Gagnon (1997) used a diffusion coefficient of 10^{-10} m^2/s for a BOM cocktail similar to what was used in this research. A BOM diffusivity in the biofilm of $3*10^{-10}$ m^2/s was used in this research. This value represents a conservative approach in the sense that it is almost half an order of magnitude below the values proposed by Hozalski and Rittmann and co-workers for acetate (Rittmann et al., 1986; Hozalski, in: Huck et al., 1998).

External Mass Transfer Coefficient, ks

The external mass transfer coefficient, k_s was estimated with commonly used empirical calculations for packed bed reactors (Sontheimer et al., 1988). Such calculations use the Reynolds (Re) and the Schmidt (Sc) numbers as well as empirical constants in order to calculate the dimensionless Sherwood number (Sh) (equations 8.5-8.8). The Sherwood number is the dimensionless expression of the external mass transfer coefficient, k_s.

$$\mathrm{Re} = \frac{d_p * u}{\nu} \tag{8.5}$$

$$Sc = \frac{\nu}{D_L} \tag{8.6}$$

$$Sh = \frac{k_s * d_p}{D_L} \tag{8.7}$$

$$Sh = A + B * \mathrm{Re}^m * Sc^n \tag{8.8}$$

where:

d_p:	particle diameter (L)
u:	interstitial velocity (L/T)
ν:	kinetic viscosity of water (L^2/T)
D_L:	BOM diffusion coefficient in water (L^2/T)
k_s:	external mass transfer coefficient (L/T)
A, B, n and m:	empirical constants (from: Gnielinski, 1978, in Sontheimer et al., 1988, p. 274)

Sontheimer et al. (1988) showed that such empirical estimations of k_s were in general lower than experimentally determined values. Therefore, such k_s-estimations represent a conservative approach. For the purpose of the present calculations, the mass transfer coefficient, k_s was assumed to be constant, both horizontally and vertically, although this represents an oversimplification according to the results of Yang and Lewandowski (1995).

RESULTS AND DISCUSSION

Parameter Estimations

Biofilm Thickness, Lf

Figure 8.5 shows the results of the biofilm thickness estimations in conjunction with the results of viable biomass in filter 1 on day 64 of experiment C2. The biomass results in Figure 8.5 indicate a very pronounced biomass stratification with a particularly high biomass value at the very top of the control filter (F1), i.e. ~800 nmole P/cm^3 of filter. Similarly high values were measured in filters 3 and 4 (data not shown). Such biomass stratifications are the result of increased substrate degradation in the top part of the control filter and the fact that biomass-coated media grains have a lower total density. Therefore biomass-coated media grains tend to be accumulated at the top of biofilters following fluidization, i.e. backwash with water, (Hozalski, 1996), although the significance of this phenomenon is a function of the biofilm thickness.

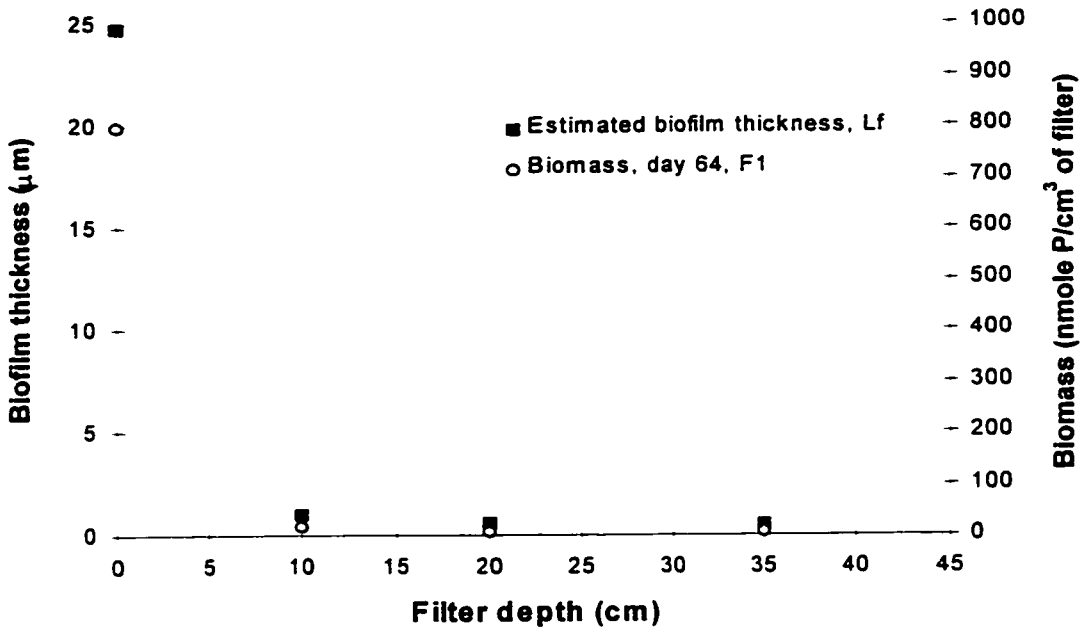

Figure 8.5: Viable biomass in the control filter (F1) on day 64 following startup of experiment C2 and estimated biofilm thickness, L_f

Because of the relatively high amount of biomass at the top, the L_f-estimations based on these values can be considered as conservative. As a comparison, Wang et al. (1995) have measured biomass levels (phospholipid) of about 100-200 nmole P/cm^3 of filter at the top of several pilot scale filters (cf. Urfer et al., 1997) and others have reported similar values (e.g. Carlson and Amy, 1995; Moll and Summers, 1997; Huck et al., 1998).

The estimations shown in Figure 8.5 indicate that biofilm thickness, L_f in the top part of the filter, i.e. 0-2 cm of filter depth, was equal to about 20 μm. This value was used for the calculations of mass transfer limitation of BOM degradation in the top part of the control filter.

External Mass Transfer Coefficient, ks

In packed bed reactors such as rapid filters, the mass transfer coefficient, k_s is a function of engineered parameters, i.e. hydraulic loading, particle diameter and porosity, as

well as water quality and substrate characteristics, i.e. viscosity and substrate diffusivity. Figure 8.6 represents the dependency of k_s as a function of the two engineered factors, media diameter and hydraulic loading.

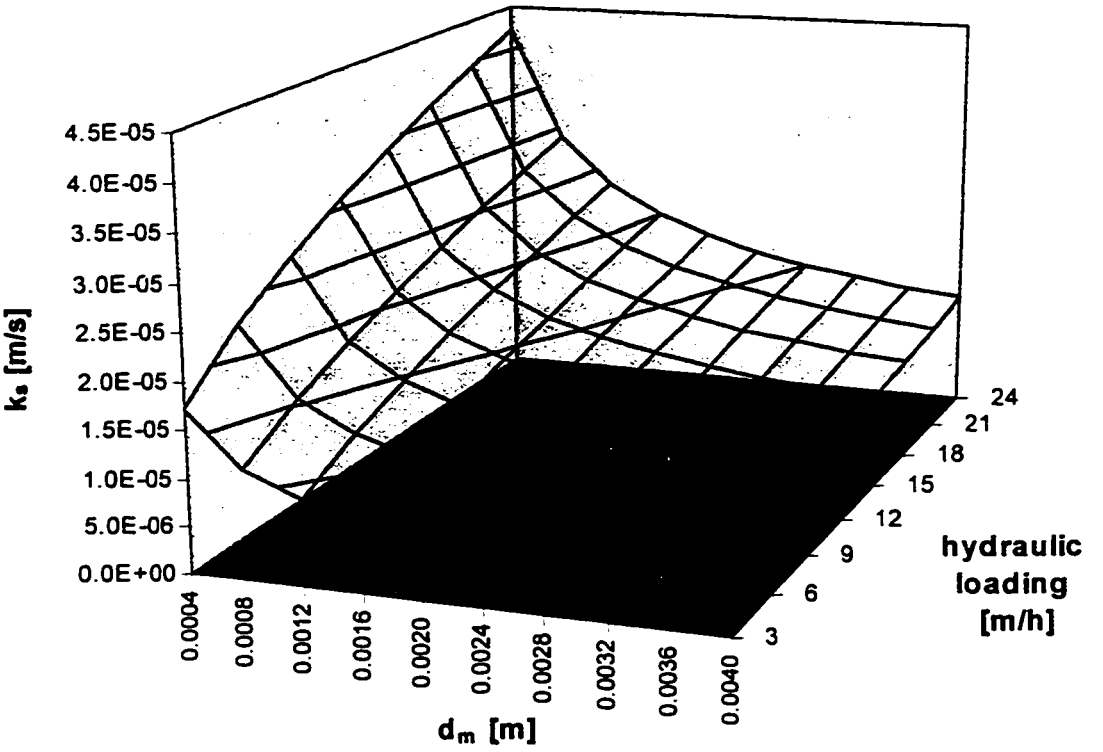

Figure 8.6: Calculated mass transfer coefficient, k_s, as a function of media diameter and hydraulic loading; diffusivity: $4.05*10^{-10}$ m^2/s, temperature: 15°C, porosity: 0.45

Figure 8.6 shows that under the specific conditions of substrate diffusivity and temperature considered for these calculations, mass transfer coefficients for biological rapid filters are generally $\geq 10^{-5}$ m/s, considering commonly used media diameters and hydraulic loadings. The diffusivity of BOM in water used in the calculations in Figure 8.6, i.e. $4.05*10^{-10}$ m^2/s, is about 30% higher compared to the considered diffusivity of BOM in the biofilm, i.e. $3*10^{-10}$ m^2/s. This is reasonable considering the results reported by others (e.g. Rittmann et al., 1986; Westrin and Axelsson, 1991). Considering the values of diffusivity as a function of molecular mass shown in Schwarzenbach et al. (1993), a BOM

diffusivity in water in the range of $4*10^{-10}$ m^2/s can be considered as a conservative estimate.

Based on modeling of DOC removal in biologically active filters, Wang (1995) noted that external mass transfer was not the rate limiting step for DOC removal when mass transfer coefficients were above $5*10^{-5}$ m/s. Considering the hydraulic loading used in this research, i.e. 7.5 m/h, and a particle diameter at the top of the filter of 0.6 mm (Figure 8.4), k_s can be estimated as $2*10^{-5}$ m/s in the top part of the filter. This k_s-value will decrease deeper in the anthracite as media diameter increases. However, based on the results shown in Figure 8.6, k_s is not likely to decrease below $1*10^{-5}$ m/s.

Figure 8.7 shows the calculated mass transfer coefficient, k_s as a function of the "environmental" parameters, i.e. substrate diffusivity, D_L and water temperature.

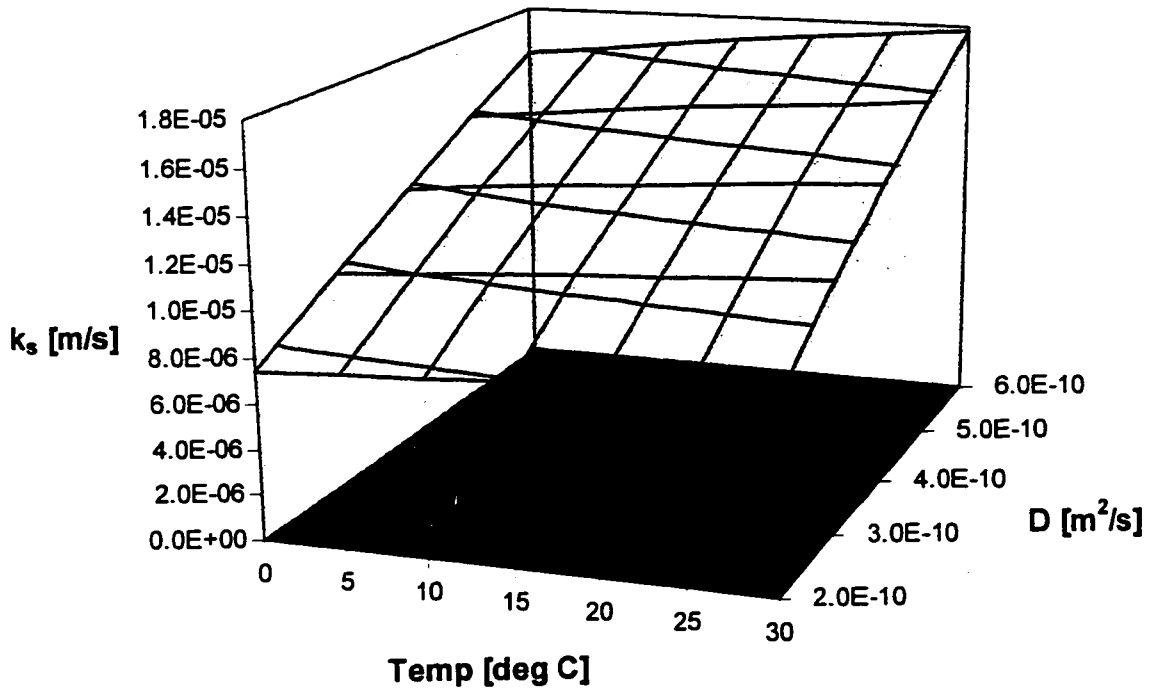

Figure 8.7: Calculated mass transfer coefficient, k_s, as a function of diffusivity and temperature; media diameter d_m: 2 mm, hydraulic loading: 12 m/h, porosity: 0.45

The results in Figure 8.7 indicate that water temperature, which influences the viscosity, has a minor impact on the calculated mass transfer coefficient, whereas the influence of substrate diffusivity is more important. The impact of temperature on substrate diffusivity was ignored for the calculations shown in Figure 8.7.

Mass Transfer Limitations

According to the results shown immediately above and considering the values and approaches previously mentioned in this chapter (cf. 'Calculation/Estimation of Parameters'), the following input parameters were used for the calculation of mass transfer limitation in the top part of the control filter operated under the specific conditions of this research:

observed substrate removal rate, R_{obs}:	19.8 μg O_2/L*s
biofilm thickness at a filter depth of 0-2 cm, L_f:	20 μm
substrate diffusivity in the biofilm, D_{eff}:	$3*10^{-10}$ m^2/s
substrate concentration in the bulk liquid, $S_b=S_{2cm}$:	450 μg O_2/L
mass transfer coefficient, k_s:	$2*10^{-5}$ m/s

The calculations of internal mass transfer limitation in the top part of the control filter yielded an observable modulus, Φ, of 0.06. This indicates that BOM removal in the very top of the control filter where biofilm thickness is highest was not limited by internal mass transfer, i.e. diffusion, but rather by biodegradation kinetics. The calculation of the ratio of the observable modulus, Φ and the Biot number, N_{Bi} yielded a value of Φ/N_{Bi} of 0.04. This suggests that external mass transfer played a negligible role in the overall removal rate of BOM under the specific conditions which were considered for these calculations. This is consistent with experimental observations from various authors, as mentioned previously in this chapter.

When mass transfer limitation was calculated deeper in the filter bed, the results indicated that mass transfer was even less important compared to the top of the filter, as

anticipated. Considering the substrate removal at 20 cm filter depth (Figure 8.3) as well as L_f-estimations at this depth (Figure 8.5), the dimensionless modulus Φ yielded a value of 0.0001 and Φ/N_{Bi} was equal to 0.0013. These numbers are considerably lower than the values indicating internal and external mass transfer limitations.

Because biofilm coverage has a direct impact on the estimate of the biofilm thickness, L_f, biofilm coverage is an important parameter, as mentioned previously in this chapter. For the calculations discussed immediately above, a biofilm coverage of 50% was assumed. Considering a biofilm coverage of 30% or lower leads to internal mass transfer limitations in the very top part of the control filter (Φ = ~0.3). However, for most of the filter internal mass transfer is not limiting the overall removal of BOM, even if such a low biofilm coverage is assumed. Considering a biofilm coverage > 50% leads to lower values of Φ and Φ/N_{Bi} compared to a 50% coverage, indicating reaction limited conditions in the entire filter.

Consequently, under the particular conditions of this research and considering the various simplifying assumptions made, BOM removal in the control filter was reaction limited and external and internal mass transfer limitations appeared to be of negligible importance. This was also the case in the very top part of this filter (filter depth of 0-2 cm), where mass transfer limitations are most likely to occur. Studying mass transfer limitation of bacterial growth and substrate utilization in a simulated distribution system (ARs), Gagnon (1997) came to similar conclusions.

In an attempt to apply such mass transfer calculations to a broader range of conditions, Figure 8.8 shows the dimensionless modulus, Φ, as a function of the biofilm thickness, L_f and the observed removal rate, R_{obs}. These two parameters were considered because they are likely the ones with the broadest range under different conditions of biological rapid filtration. In addition, biofilm thickness, L_f is of particular importance in the calculation of Φ, because Φ is proportional to the square of L_f (equation 8.1). The

remaining parameters affecting Φ (equation 8.1), i.e. substrate diffusivity in the biofilm, D_{eff} and substrate concentration in the bulk liquid, S_b are expected to vary to a more minor extent under various conditions of drinking water biofiltration.

Figure 8.8 shows that internal mass transfer is the limiting factor for BOM degradation, i.e. $\Phi \geq 0.3$, only in cases where the biofilm thickness is ≥ 40 μm and the observed removal rate is ≥ 15 μg O_2/L*s.

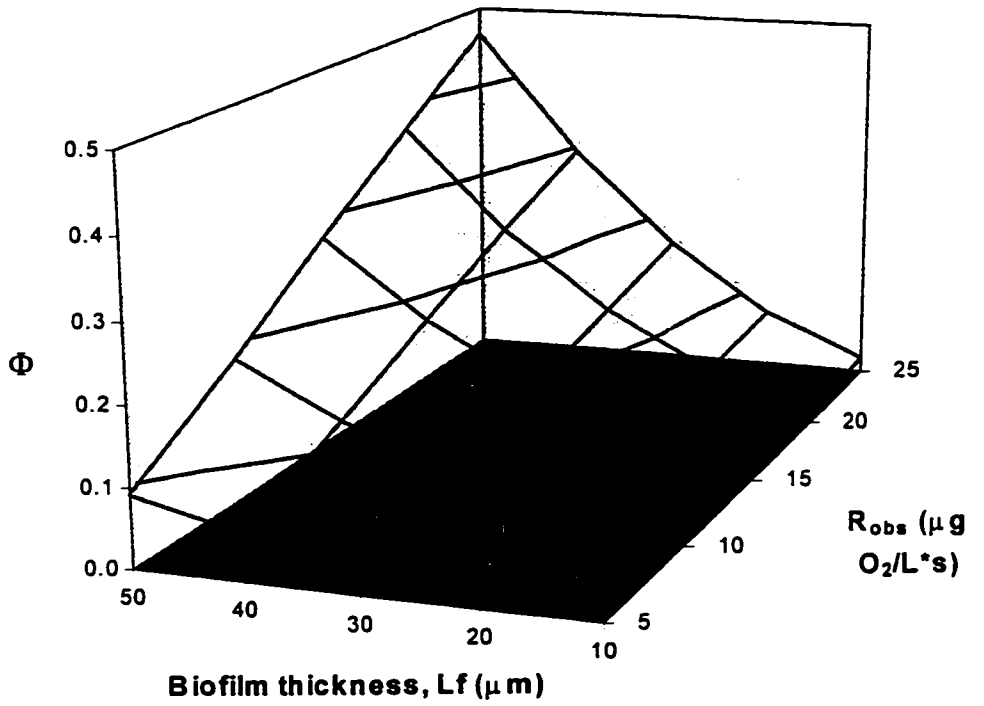

Figure 8.8: Dimensionless modulus, Φ, as a function of biofilm thickness and observed removal rate; S_b: 450 μg O_2/L, D_{eff}: $3*10^{-10}$ m^2/s

In granular filters the pore size is approximately equal to 0.07-0.1 times the particle diameter (Amirtharajah 1988). Therefore, assuming a typical particle diameter in granular filters of 1 mm, the pore size is 70-100 μm. Therefore, in the absence of estimations or measurements of L_f, it is likely not reasonable to assume that the biofilm thickness, L_f in such filters is in excess of about 50 μm. Considering a particularly high amount of biomass (~800 nmole P/cm^3 of filter) and a biofilm coverage of 50%, L_f-estimations in this research

were in the range of 20 μm at the top of the control filter (F1) and decreased very rapidly deeper in the filter. Based on these results and considerations, biofilms attached to the media of drinking water biofilters likely have a thickness below 40 μm in most cases.

Regarding the observed substrate removal rate, R_{obs} it should be kept in mind that R_{obs}-values of 15 μg O_2/L*s and higher are relatively high numbers. As an example, considering a constant rate of substrate removal of 15 μg O_2/L*s in the entire bed of a biofilter, a ThOD influent concentration of 1 mg O_2/L would be degraded in about 2 minutes of EBCT, corresponding to a rather fast removal. Therefore, it is likely that such high R_{obs}-values will only occur in the very top part of biofilters, where the easily biodegradable BOM components are degraded, e.g. this research. Deeper in the biofilters, substantially lower values of R_{obs} are expected.

As a comparison, using data from biofiltration experiments in complete-mix biofilm reactors (Rittmann et al., 1986; Zhang and Huck 1996b), R_{obs}-values for acetate of 4.7 μg/L*s were calculated for the data from Rittmann et al., (1986). In the case of the AOC results from Zhang and Huck (1996b), a maximum value for the observed AOC removal rate of 6.3 μg C_{eq}/L*s was calculated.

In summary, the limitation of BOM removal in biologically active filters by internal mass transfer, i.e. diffusion in the biofilm, is not expected to play a major role. In particular cases where the BOM in the filter influent consists of very easily biodegradable substances at high concentrations, internal mass transfer limitations might occur in the very top part of such filters. However, for most of the biofilter bed, internal mass transfer is expected to be negligible in terms of BOM degradation under drinking water biofiltration conditions.

Figure 8.9 shows the ratio of Φ/N_{Bi} as a function of the biofilm thickness, L_f, and the observable BOM removal rate, R_{obs}. As mentioned previously, Φ/N_{Bi} indicates external diffusion control as $\Phi/N_{Bi} \rightarrow 1$ and kinetic control for $\Phi/N_{Bi} \ll 1$.

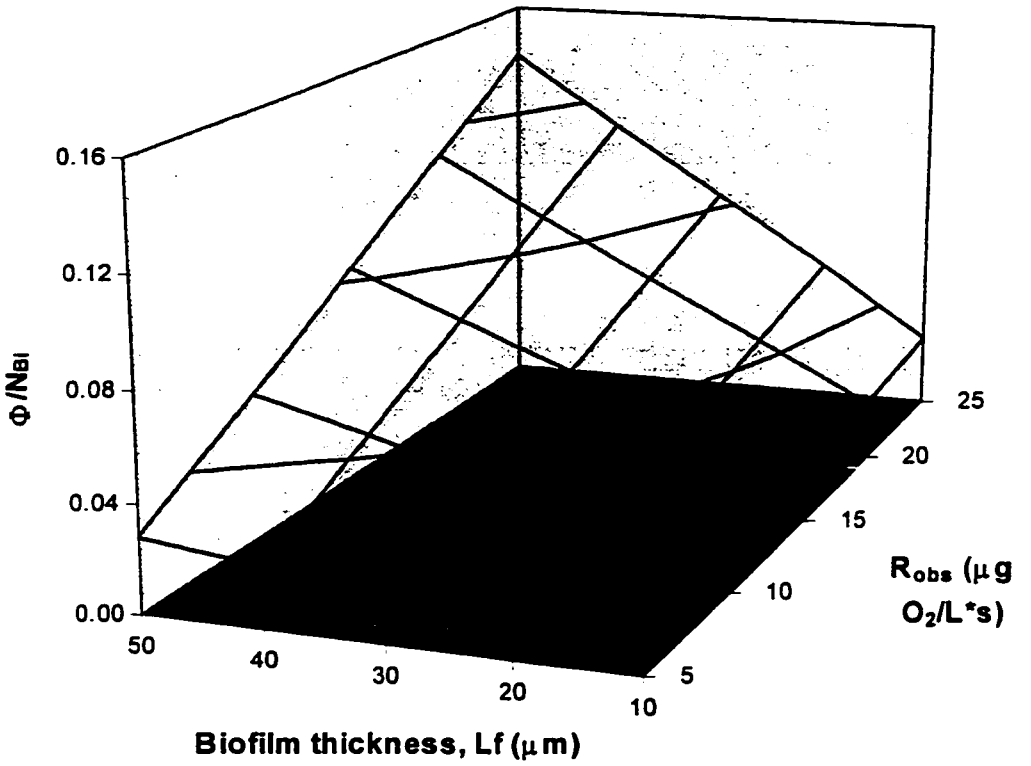

Figure 8.9: Φ/N_{Bi} as a function of biofilm thickness and observed removal rate; S_b: 450 μg O_2/L, D_{eff}: $3*10^{-10}$ m^2/s, k_s: $2*10^{-5}$ m/s

The results shown in Figure 8.9 suggest that BOM degradation in biological drinking water filters is likely not limited by external mass transfer under the conditions of these calculations. As mentioned earlier, this finding is in agreement with empirical results from various authors who reported that for a given EBCT, BOM removal was independent of hydraulic loading. The hydraulic loading influences the external mass transfer coefficient, k_s (Figure 8.6) and an increase in k_s is therefore expected to lead to improved BOM removal rates if external mass transfer is the limiting factor of the process.

CONCLUSIONS

The results presented in this chapter lead to the following conclusions:

- Under the specific operational conditions of the control filter (F1) and considering the simplifying assumptions made, internal (in the biofilm) and external (to the biofilm) mass transfer were shown to be of minor importance regarding the removal of several easily biodegradable BOM components in this filter.
- The calculations of the observable modulus Φ and the Biot number, N_{Bi} showed that this was also the case in the very top part of the control filter, where mass transfer limitations are mostly expected as a result of the high value of the biofilm thickness, L_f.
- The biofilm thickness, L_f was estimated using biomass results obtained with the phospholipid method and conversion factors from the literature. The results indicated that L_f was equal to 20-25 μm in the top part of the control filter and L_f decreased very rapidly deeper in the filter.
- Considering the biofilm thickness estimations in this research as well as physical characteristics of granular filters, i.e. pore sizes, L_f is likely $\leq$ ~50 μm under typical drinking water biofiltration conditions.
- Semi-empirical calculations for the estimation of the BOM external mass transfer coefficient, k_s suggested that under typical drinking water rapid filtration conditions, k_s is $\geq 10^{-5}$ m/s.
- The application of the mass transfer calculations to a broader range of biofiltration conditions in terms of substrate biodegradability (BOM removal rate) and biofilm thickness indicated, that biological removal of BOM in rapid filters is likely not limited by internal and external mass transfer, in many cases.
- The point raised immediately above is important regarding the future application and development of mechanistic models for the prediction of BOM removal in biofilters.

More fundamental measurements of mass transfer limitations in drinking water filter biofilms might be required to confirm the findings of this research.

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

This research investigated the effects of the presence of oxidants, i.e. hydrogen peroxide, free and combined chlorine and ozone, on the biological performance, i.e. BOM removal, of biological rapid filters. Experiments were performed at bench scale using several parallel filter columns. Dechlorinated tap water, to which a cocktail containing BOM, N and P was added, served as filter influent. Oxidants were added to the influent or the backwash water of selected filters and one filter was always operated as a control (no oxidant).

CONCLUSIONS

The following conclusions can be drawn regarding the effects of different oxidants on biologically active drinking water filters:

1. The continuous or intermittent presence of the different oxidants in the influent or the backwash water of anthracite/sand filters was generally found to represent an important factor regarding the overall biological performance, i.e. BOM removal, of such filters. When continuously present in the filter influent, free Cl_2 had the strongest inhibitory effect on the removal of selected easily biodegradable BOM components, followed by combined Cl_2 and H_2O_2.

2. For the continuous presence of oxidants in the influent of anthracite/sand filters, the critical oxidant concentration, i.e. the concentration above which the biological performance (BOM removal) of anthracite/sand biofilters is substantially impaired, was found to be < 0.2 mg/L for free Cl_2, ~0.3 mg/L for combined Cl_2 and between 1 and 5 mg/L for hydrogen peroxide. At water temperatures lower than the ones investigated in this research, i.e. ~10-15°C, these critical concentrations are expected to be lower, because of the slower biodegradation/growth kinetics at lower water temperatures.
3. The periodic presence of free Cl_2 in the influent of an anthracite/sand filter (~0.5 mg/L Cl_2 once per week for 6 hours) was found to have a substantial negative effect on the biological performance of this filter.
4. Chlorine in the backwash water at a concentration of ~1 mg/L Cl_2 had a substantial negative effect on acetate and formate removal when the chlorine was present as free Cl_2. However, for combined Cl_2 the effect was negligible. In the control filter (no oxidant), backwashing using air scour had no measurable effect on the biological removals of acetate and formate immediately following backwash.
5. A normalized CT concept was successfully used for the comparison of the effects of different, continuously present oxidants on BOM removal. In the case of biofilters receiving oxidants intermittently however, the application of the CT concept showed that this approach was unable to describe certain experimental results This indicates that the mechanisms of BOM removal inhibition were different for the continuous presence of oxidants compared to their intermittent presence.
6. An obvious relationship between the amount of viable biomass (phospholipid) and BOM removal suppression was observed in the filters receiving an oxidant continuously, i.e. no viable biomass - no BOM removal. For the periodic presence of free Cl_2 in the biofilters, this relationship was not observed. This is in support of the

different mechanisms of BOM removal suppression when oxidants were present continuously compared to their periodic presence in biofilters.

7. In the case of a GAC/sand filter, it was demonstrated that the continuous presence of ~0.5 mg/L free Cl_2 in the filter influent had no measurable effect on the biological performance, i.e. BOM removal, of this filter. This was the result of the rapid reaction of free chlorine with the GAC surface. However, for reasons mentioned previously in this thesis, the presence of free Cl_2 in the influent of GAC filters should be prevented.
8. In terms of the relative suppression of BOM removal capability, the presence of a disinfectant residual in the filter *effluent* appeared to be more important than the bactericidal and/or bacteriostatic strength of the disinfectant *per se*. Therefore, the oxidant quenching ability of the filter media is an important parameter.
9. The substantial decrease of the hydrogen peroxide concentrations in the biofilters continuously dosed with ~1 mg/L and ~5 mg/L H_2O_2 in the influent suggested that biofilters represent a promising treatment step to prevent the presence of undesired H_2O_2 residuals in the finished water. The decrease of the H_2O_2 concentration through the filters was likely the result of the catalytic destruction of H_2O_2 to oxygen and water. The bacterial enzyme catalase potentially served as catalyst for this reaction, however inorganic substances could have served as catalyst as well, e.g. ferric iron.
10. The periodic presence of ozone residuals (~0.15 mg/L twice per week for 1 hour) in the influent of an anthracite/sand filter had a negligible effect on the removals of the different BOM components. This was likely the result of the rapid disappearance of the ozone within the filter, presumably as a result of the reaction of ozone with the anthracite. However, the experimental results for ozone are insufficient to draw definite conclusions regarding the effects of O_3 residuals on biofiltration performance.
11. Hydrogen peroxide was successfully used as an accelerator of the natural O_3 decay in order to prevent the presence of O_3 residuals in the influent of a biofilter, when

sufficient contact time was available between the point of H_2O_2-addition and the filter influent. This operational mode led to the intermittent presence of H_2O_2 residuals (~0.5 mg/L) in the biofilter influent, however this did not affect biofiltration performance.

In addition, the following conclusions, which are not directly related to the principal objective of this research, can be drawn:

1. Mass transfer calculations using the dimensionless Thiele modulus and the Biot number indicated that BOM removal in the control filter was not limited by external mass transfer (to the biofilm) and internal mass transfer (in the biofilm). The application of the calculations to a broader range of biofiltration conditions suggested that BOM removal in biological drinking water filters is likely limited by biodegradation kinetics and not mass transfer, in many cases.
2. A new method for the quantification of biomass activity was developed during this research, i.e. biomass respiration potential (BRP) method. The BRP method is based on the consumption of dissolved oxygen resulting from the aerobic respiration of several BOM components in a water sample containing a certain amount of biofilter media. The method was successfully used in this research and the results suggested that this method quantifies the active, i.e. substrate-degrading, biomass more adequately that the phospholipid method.
3. The comparison of the depletion of the electron acceptor of the bioreactions, i.e. dissolved oxygen (DO), through the different filters with the decrease of the theoretical oxygen demand (ThOD), showed that the measured DO-consumption through the biofilters corresponded relatively well with the calculated ThOD decrease. This suggested that carefully performed DO-measurements may serve as an approximation for BOM removal in biofilters. This is of particular interest because of the relative simplicity of DO-measurements.

4. The time period required to (re)establish biological acetate removal in the filters following startup or a biofiltration challenge with chlorine was consistently shorter compared to the time required for formate removal to (re)start. This suggested differences in the microbial subpopulations responsible for acetate and formate removal.

5. Under the specific conditions of this research, measurements of UV absorbance at 258 nm showed that this parameter significantly increased through a biologically active anthracite/sand filter. The increase of UV_{258} was likely the result of the formation of soluble microbial products in this filter.

6. Clean bed headloss in the biologically active anthracite/sand filters was observed to be constant during the different experiments. This suggested that under the specific conditions of these experiments, i.e. "particle-free" and coagulant-free water used as filter influent and backwashing with air scour, clean bed headloss did not increase over time as a result of biofilm growth in these filters.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Further work is required regarding the effects of continuously present ozone residuals in the influent of biological anthracite/sand filters. Based on the results of this research and literature information, such residuals are expected to have a substantial negative effect on the removal of BOM in such filters.
2. The development of the biomass respiration potential (BRP) method should be pursued. Because of the simplicity of the BRP method and the fact that it indirectly quantifies the substrate degradation potential of the biomass, this method is of potential interest to the water industry.
3. A better understanding of the relationships between the amount of biomass and substrate removal appears to be necessary. The utilization of the BRP method may be

useful in this context. A more thorough comprehension of the relationships between biomass accumulation and substrate removal may ultimately lead to some alternative process considerations for optimized biofiltration.

4. Because many mechanistic biofiltration models have been initially developed for waste water applications where biofilms are usually relatively thick, these models consider molecular diffusion to and in the biofilm in order to model BOM degradation. In drinking water biofiltration however, biofilms are typically thin and patchy and the results presented in this thesis suggested that external and internal mass transfer limitations of BOM removal in drinking water biofilters are likely of a more minor importance. This important point requires additional research in order to further understand the relevance of mass transfer limitations of BOM removal in drinking water biofilters.
5. Existing biofiltration models should be extended/adapted in order to address the effects of oxidants on BOM removal in drinking water filters. The data presented in this thesis may serve as a starting point for this purpose. Modeling may substantially contribute to the future development of treatment strategies allowing to minimize the negative effects of oxidants on biofilter performance.
6. The role of biofilm coated media in the buildup of headloss in biologically active filters should be further investigated. The results of this research showed that the biofilm itself is likely not responsible for increased headloss buildup in biofilters, reported in the literature. However, in this research the biofilters were fed with "particle-free" and coagulant-free water. Therefore, the simultaneous presence of biofilms and particles/coagulants in biofilters potentially has a synergistic effect on headloss buildup in such filters.
7. The effects of advanced oxidation processes such as O_3/H_2O_2 and UV/H_2O_2 on the formation of BOM and the impacts of this on downstream biofiltration should be

investigated in more detail, because the relevant literature information is somewhat conflicting.

RECOMMENDATIONS FOR THE WATER INDUSTRY

The experiments for this research were performed in bench scale biofilters. However, based on the results obtained the following recommendations for the water industry are possible:

1. The results of this research showed that oxidant residuals have an important negative effect on the BOM removal capabilities of anthracite/sand biofilters. For a given biofiltration situation, it is recommended to carefully evaluate the possibilities of the contact of the biofilters with water containing an oxidant and the impacts this may have on BOM removal.
2. In general, the contact of biofilters with oxidant-containing water, particularly free chlorinated water, should be prevented. If for various reasons free Cl_2 has to be temporarily used in treatment steps ahead of biofiltration, it is recommended to dose a chlorine quencher, e.g. bisulfite, prior to the biofilters in order to protect the biofilm from the effects of the chlorine.
3. The use of chlorinated backwash water for biofilters is generally not recommended, particularly if the backwash water contains free Cl_2. If for different reasons the presence of chlorine in the backwash water can not be avoided, it is advisable to evaluate the effects of this on BOM removal. If a substantial suppression of BOM removal resulting from the chlorine in the backwash is observed, the temporary dosage of a chlorine quencher to the backwash water might be feasible, as well.
4. Biologically active anthracite/sand filters led to a substantial decrease of H_2O_2 concentrations when H_2O_2 was continuously present in the filter influent. Therefore,

biofilters following advanced oxidation processes such as UV/H_2O_2 may serve as a reliable process step in order to prevent undesired H_2O_2 residuals in the finished water.

5. The use of hydrogen peroxide as an accelerator of the natural ozone decay is feasible if sufficient contact time is available between the point of H_2O_2-addition and the point where the aqueous ozone is expected to have disappeared, e.g. ozone contactor effluent or biofilter influent. For each specific water, bench scale tests of ozone decay acceleration with H_2O_2 should be performed, if such treatment was to be implemented at full scale.
6. The use of carefully performed DO-measurements in the influent and effluent of biofilters is recommended as an approximation for BOM removal in such filters. Such measurements may be particularly useful for the evaluation of different, parallel biofiltration treatments and in cases where measurements of BOM surrogates, i.e. AOC and BDOC, or specific BOM components are unfeasible. In addition, DO-measurements may be useful for the assessment of the impacts of process upsets, e.g. temporary presence of an oxidant or filter shutdown, on the biological performance of biofilters.

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APPENDIX A

Calibration Curves

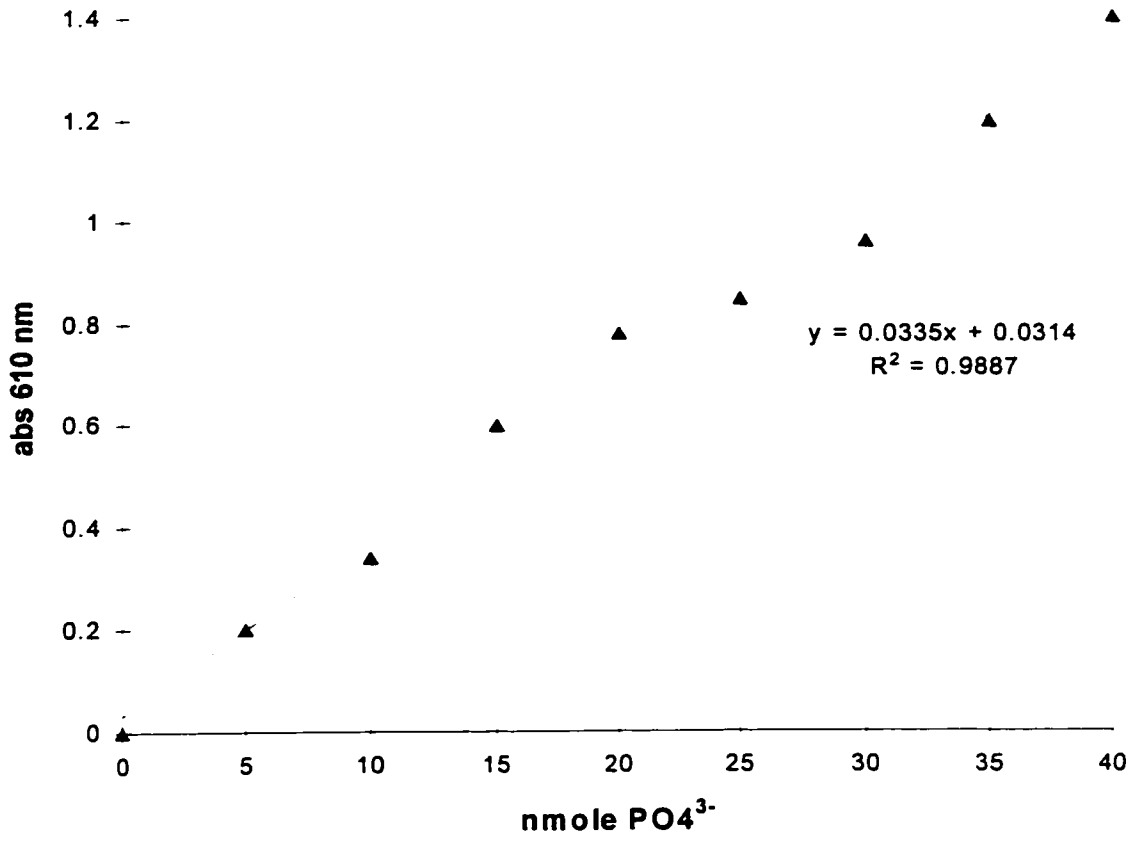


Figure A1: Calibration curve used to convert absorbance @ 610 nm to nmole of phosphate (for phospholipid biomass measurements)

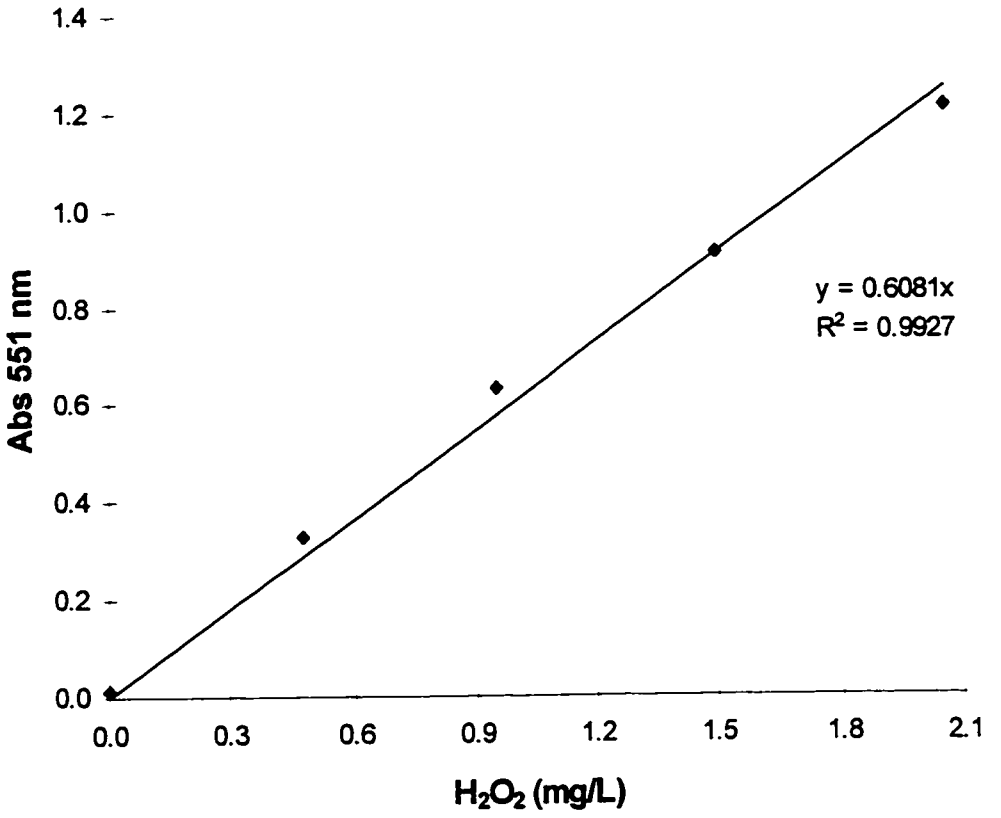


Figure A2: Calibration curve used to convert absorbance @ 551 nm to mg/L of hydrogen peroxide

APPENDIX B

Experimental Results

EXPERIMENT H1

Carboxylic Acids

Experimental results from May 15, 1996 (Day 8)

Sample	EBCT (min)	Acetate (ug/L)	Acetate C/Co	Formate (ug/L)	Formate C/Co
F1 influent	0	339	1.00	306	1
F1 10 cm	0.8	444	1.31	33	0.11
F1 55 cm	4.4	144	0.42	28	0.09
F1 effluent	6	5	0.015	18	0.059
F2 influent	0	566	1.00	432	1.00
F2 10 cm	0.8	397	0.70	348	0.81
F2 55 cm	4.4	93	0.16	223	0.52
F2 effluent	6	5	0.009	178	0.412

Experimental results from May 23, 1996 (Day 16)

Sample	EBCT (min)	Acetate (ug/L)	Acetate C/Co	Formate (ug/L)	Formate C/Co
F1 influent	0	252	1.00	293	1.00
F1 5 cm	0.4	6	0.02	104	0.35
F1 15 cm	1.2	64	0.25	95	0.32
F1 55 cm	4.4	200	0.79	107	0.37
F1 effluent	6	5	0.020	51	0.174
F2 influent	0	219	1.00	250	1.00
F2 5 cm	0.4	495	2.26	568	2.27
F2 15 cm	1.2	270	1.23	447	1.79
F2 55 cm	4.4	0	0.00	405	1.62
F2 effluent	6	0	0.00	429	1.72

Experimental results from July 11, 1996 (Day 65)

Sample	EBCT min	Acetate (ug/L) 1st repl	Acetate (ug/L) 2nd repl	Acetate avg	std dev	Acetate C/Co	Formate (ug/L) 1st repl	Formate (ug/L) 2nd repl	Formate avg	std dev	Formate C/Co
F1 influent	0	96	87	92	6	1.00	83	101	92	13	1.00
F1 5 cm	0.4	293	333	313	28	3.42	165	187	176	16	1.91
F1 10 cm	0.8	115	132	124	12	1.35	33	37	35	3	0.38
F1 25 cm	2	448	479	464	22	5.07	13	15	14	1	0.15
F1 55 cm	4.4	760	782	771	16	8.43	9	12	11	2	0.11
F1 effluent	6	14	29	22	11	0.235	5	5	5	0	0.054
F2 influent	0	163				1.00	178				1.00
F2 5 cm	0.4	517				3.17	149				0.84
F2 10 cm	0.8	574				3.52	82				0.46
F2 25 cm	2	462				2.83	23				0.13
F2 55 cm	4.4	433				2.66	8				0.04
F2 effluent	6	29				0.178	5				0.028

Experimental results from July 16, 1996 (Day 70)

Sample	EBCT min	Acetate (ug/L) 1st repl	Acetate (ug/L) 2nd repl	Acetate avg	Acetate std dev	Acetate C/Co	Formate (ug/L) 1st repl	Formate (ug/L) 2nd repl	Formate avg	Formate std dev	Formate C/Co
F1 influent	0	87		87		1.00	190		190		1.00
F1 5 cm	0.4	887		887		10.20	124		124		0.65
F1 10 cm	0.8	701		701		8.06	60		60		0.32
F1 25 cm	2	440		440		5.06	30		30		0.16
F1 55 cm	4.4	316		316		3.63	17		17		0.09
F1 effluent	6	36		36		0.41	4		4		0.021
F2 influent	0	121				1.00	71				1.00
F2 5 cm	0.4	336				2.78	167				2.35
F2 10 cm	0.8	296				2.45	61				0.86
F2 25 cm	2	149				1.23	4				0.06
F2 55 cm	4.4	231				1.91	19				0.27
F2 effluent	6	38				0.314	5				0.070

Experimental results from July 30, 1996 (Day 84)

With Chloroform

Sample	EBCT (min)	Acetate (ug/L)	Acetate C/Co	Formate (ug/L)	Formate C/Co
F1 influent	0	237	1.61	471	1.62
F1 10 cm	0.8	391	2.66	187	0.64
F1 40 cm	3.2	186	1.27	190	0.65
F1 70 cm	5.6	258	1.76	198	0.68
F1 effluent	6	57	0.39	151	0.52
F2 influent	0	445	1.11	427	1.08
F2 10 cm	0.8	128	0.32	261	0.66
F2 40 cm	3.2	154	0.38	407	1.03
F2 70 cm	5.6	1000	2.49	355	0.90
F2 effluent	6	388	0.97	215	0.54

Hydrogen Peroxide

June 6, 1996 (day 30) sampling

Sample	EBCT min	Abs 551 nm	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.11464	7.05E-03	3	0.68	1.00	
F2 5cm	0.4	6.38E-02	4.98E-03	3	0.33	0.48	
F2 15cm	1.2	3.94E-02	1.45E-02	1	0.03	0.04	
F2 25cm	2	2.58E-02	9.91E-03	1	0.01	0.01	
F2 40cm	3.2	1.78E-02			0.00	0.00	
F2 55cm	4.4	1.74E-02			0.00	0.00	
F2 effl	6	2.70E-02			0.00	0.00	
F1 infl		1.99E-02			0.00		
Calib check		0.16053	3.89E-03	1	0.34		target 0.315 mg/L

July 26, 1996 Sampling (Day 80)

soso walks

Sample	EBCT min	Abs 551 nm	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.19715	4.72E-03	2	0.86	1.00	
F2 5cm	0.4	0.1802	9.71E-03	1	0.38	0.44	
F2 10 cm	0.8	9.89E-02	6.25E-03	1	0.19	0.22	
F2 15cm	1.2	5.32E-02	1.21E-02	1	0.07	0.08	
F2 25cm	2	1.95E-02	1.00E-02	1	0.00	0.00	
F2 40cm	3.2				0.00	0.00	
F2 55cm	4.4				0.00	0.00	
F2 effl	6				0.00	0.00	
Calib check		0.1493	6.99E-04	1	**0.323**		target 0.315 mg/L

September 11, 1996 Sampling (Day 127)

Sample	EBCT min	Abs 551 nm	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.1352	5.86E-03	3	0.83	1.00	
F2 5cm	0.4	5.48E-02	5.22E-03	3	0.26	0.31	
F2 10 cm	0.8	6.94E-02	6.92E-03	1	0.12	0.14	
F2 15cm	1.2	3.02E-02	6.92E-03	1	0.02	0.03	
F2 25cm	2	1.25E-02	6.92E-03	1	0.00	0.00	
F2 55cm	4.4	8.54E-03	6.92E-03	1	0.00	0.00	
F2 effl	6	6.92E-03	6.92E-03	1	0.00	0.00	
Calib check		0.1521	9.67E-03	1	**0.309**		**target 0.315 mg/L**

September 13, 1996 (Day 129)

Sample	EBCT min	Abs 551 nm	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F1 infl	0	0.1479	1.79E-03	3	0.95	1.00	H2O2 dosage for 18 h prior to sampling
F1 5cm	0.4	0.0676	3.98E-04	3	0.39	0.40	
F1 10 cm	0.8	0.1162	8.48E-04	1	0.24	0.26	
F1 15cm	1.2	0.1047	1.68E-03	1	0.21	0.23	
F1 25cm	2	0.0915	1.68E-03	1	0.18	0.19	
F1 55cm	4.4	0.0876	1.68E-03	1	0.17	0.18	
F1 effl	6	0.0918	1.68E-03	1	0.18	0.19	
F1 infl	0	0.1284	1.68E-03	3	0.81	1.00	H2O2 dosage for 23 h prior to sampling
F1 10 cm	0.8	0.1245	1.68E-03	1	0.26	0.32	
F1 25cm	2	0.0976	1.68E-03	1	0.20	0.24	
F1 55cm	4.4	0.0875	1.68E-03	1	0.17	0.21	
F1 effl	6	0.0968	1.68E-03	1	0.20	0.24	
Calib check		8.89E-02	3.70E-03	1	**0.172**		**target 0.157 mg/L**

Fresh media comparison, Oct 3, 1996

Sample	EBCT min	Abs 551 nm	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
A/S infl	0	0.151	7.09E-03	3	0.94	1.00	Sampling ~ 5 hours after the filters were brought online
A/S 5cm	0.4	0.1586	7.05E-03	3	0.99	1.06	
A/S 10 cm	0.8	0.156	7.08E-03	3	0.97	1.04	
A/S 15cm	1.2	0.1501	7.08E-03	3	0.93	0.99	
A/S 25cm	2	0.1531	7.08E-03	3	0.95	1.02	
A/S 55cm	4.4	0.1493	7.08E-03	3	0.92	0.99	
A/S effl	6	0.164	7.08E-03	3	1.03	1.10	
GAC infl	0	0.165	7.11E-03	3	1.04	1.00	**GAC, F300 exhausted**
GAC 5cm	0.4	0.1376	7.08E-03	3	0.84	0.81	
GAC 10 cm	0.8	0.1211	7.08E-03	3	0.72	0.70	
GAC 15cm	1.2	0.0913	7.08E-03	3	0.51	0.49	
GAC 25cm	2	0.0681	7.08E-03	3	0.34	0.33	
GAC 55cm	4.4	0.0345	7.08E-03	3	0.10	0.10	
GAC effl	6	0.0611	7.08E-03	3	0.29	0.28	

EXPERIMENT H2

Carboxylic Acids

Experimental results from October 11, 1996 sample (Day 3)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
F1 influent	0	355	352	353.5	2.12	1.000	456	452	454	2.83	1.000
F1 10 cm	0.8	389		389	#DIV/0!	1.100	465		465	#DIV/0!	1.020
F1 25 cm	2	373		373	#DIV/0!	1.055	442		442	#DIV/0!	0.969
F1 55 cm	4.4	332		332	#DIV/0!	0.939	421		421	#DIV/0!	0.923
F1 effluent	6	334	332	333	1.41	0.942	431	429	430	1.41	0.945
F2 influent	0			#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	#DIV/0!
F2 10 cm	0.8	Data were impossi		#DIV/0!	#DIV/0!	######	Data were impossil		#DIV/0!	#DIV/0!	#VALUE!
F2 40 cm	3.2	to integrate		#DIV/0!	#DIV/0!	######	to integrate		#DIV/0!	#DIV/0!	#VALUE!
F2 70 cm	5.6			#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	#DIV/0!
F2 effluent	6			#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	#DIV/0!

Experimental results from October 15, 1996 sample (Day 7)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
F1 influent	0	336		336	#DIV/0!	1.000	432		432	#DIV/0!	1.000
F1 10 cm	0.8	393		393	#DIV/0!	1.170	444		444	#DIV/0!	1.028
F1 25 cm	2	283		283	#DIV/0!	0.842	404		404	#DIV/0!	0.935
F1 55 cm	4.4	239		239	#DIV/0!	0.711	422		422	#DIV/0!	0.977
F1 effluent	6	187		187	#DIV/0!	0.557	397		397	#DIV/0!	0.919
F2 influent	0			#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	#DIV/0!
F2 10 cm	0.8	Data were impossi		#DIV/0!	#DIV/0!	######	Data were impossil		#DIV/0!	#DIV/0!	#VALUE!
F2 40 cm	3.2	to integrate		#DIV/0!	#DIV/0!	######	to integrate		#DIV/0!	#DIV/0!	#VALUE!
F2 70 cm	5.6			#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	#DIV/0!
F2 effluent	6			#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	#DIV/0!

Experimental results from October 18, 1996 sample (Day 10)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
F1 influent	0	299		299	#DIV/0!	1.000	422		422	#DIV/0!	1.000
F1 effluent	6	55		55	#DIV/0!	0.184	393		393	#DIV/0!	0.931
F2 influent	0	296	298	297	1.41	1.000	445	453	449	5.66	1.000
F2 effluent	6	285	273	279	8.49	0.963	425	414	419.5	7.78	0.955

Experimental results from October 23, 1996 sample (Day 15)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
F1 influent	0	301		301	#DIV/0!	1.000	437		437	#DIV/0!	1.000
F1 10 cm	0.8	462		462	#DIV/0!	1.535	232		232	#DIV/0!	0.531
F1 25 cm	2	126		126	#DIV/0!	0.419	183		183	#DIV/0!	0.419
F1 55 cm	4.4	53		53	#DIV/0!	0.176	141		141	#DIV/0!	0.323
F1 effluent	6	16		16	#DIV/0!	0.053	134		134	#DIV/0!	0.307
F2 influent	0	324		324	#DIV/0!	1.000	463		463	#DIV/0!	1.000
F2 10 cm	0.8	133		133	#DIV/0!	0.410	484		484	#DIV/0!	1.045
F2 25 cm	2	41		41	#DIV/0!	0.127	517		517	#DIV/0!	1.117
F2 55 cm	4.4	50		50	#DIV/0!	0.154	546		546	#DIV/0!	1.179
F2 effluent	6	71		71	#DIV/0!	0.219	557		557	#DIV/0!	1.203

Experimental results from October 28, 1996 sample (Day 20)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
F1 influent	0	287		287	#DIV/0!	1.000	420		420	#DIV/0!	1.000
F1 10 cm	0.8	444		444	#DIV/0!	1.547	619		619	#DIV/0!	1.474
F1 25 cm	2	66		66	#DIV/0!	0.230	72		72	#DIV/0!	0.171
F1 55 cm	4.4	58		58	#DIV/0!	0.202	56		56	#DIV/0!	0.133
F1 effluent	6	44		44	#DIV/0!	0.153	22		22	#DIV/0!	0.052
F2 influent	0	365		365	#DIV/0!	1.000	494		494	#DIV/0!	1.000
F2 10 cm	0.8	382		382	#DIV/0!	1.047	554		554	#DIV/0!	1.121
F2 25 cm	2	392		392	#DIV/0!	1.074	913		913	#DIV/0!	1.848
F2 55 cm	4.4	292		292	#DIV/0!	0.800	476		476	#DIV/0!	0.964
F2 effluent	6	277		277	#DIV/0!	0.759	477		477	#DIV/0!	0.966

Experimental results from November 12, 1996 sample (Day 35)

Sample	Depth cm	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
Tap water			16.1		16.1	#DIV/0!	0.056	32		32	#DIV/0!	
std 250ug/L			271.2	267	269.1	2.97	0.929	209	198	203.5	7.78	
F1 influent	0	0	285.1	294.1	289.6	6.36	1.000	405.4	409	407.2	2.55	1.000
F1 8 cm	8	0.64	187.8	111.4	149.6	54.02	0.517	134.4	88.6	111.5	32.39	0.274
F1 23 cm	23	1.84	41.9	38.9	40.4	2.12	0.140	7.1	3.9	5.5	2.26	0.014
F1 53 cm	53	4.24	51.3	47	49.15	3.04	0.170	4.7	3.8	4.25	0.64	0.010
F1 effluent	73	5.84	26.9	25.2	26.05	1.20	0.090	0.1	2.4	1.25	1.63	0.003
F2 influent	0	0	323.3	322.1	322.7	0.85	1.000	459.8	455.4	457.6	3.11	1.000
F2 8 cm	8	0.64	338.5	349	343.75	7.42	1.065	455.5	451.2	453.35	3.04	0.991
F2 23 cm	23	1.84	325.1	318.5	321.8	4.67	0.997	440.2	453.8	447	9.62	0.977
F2 53 cm	53	4.24	288.7	285.7	287.2	2.12	0.890	453.1	450.7	451.9	1.70	0.988
F2 effluent	73	5.84	250.9	242.8	246.85	5.73	0.765	454.6	456.9	455.75	1.63	0.996

Experimental results from November 26, 1996 sample (Day 49)

Sample	Depth cm	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
Tap water			335		335	#DIV/0!	2.104	309		309	#DIV/0!	
std 250ug/L			177	255	216.0	55.15	1.356	195	202	198.5	4.95	
F1 influent	0	0	158.1	160.4	159.25	1.63	1.000	357.3	354.1	355.7	2.26	1.000
F1 6 cm	6	0.48	109.1	179.2	144.15	49.57	0.905	111.3	164	137.65	37.26	0.387
F1 11 cm	11	0.88	99.8	76.8	88.3	16.26	0.554	95.1	42.1	68.6	37.48	0.193
F1 21 cm	21	1.68	99.8	110.6	105.2	7.64	0.661	32.6	31.9	32.25	0.49	0.091
F1 36 cm	36	2.88	62	51.3	56.65	7.57	0.356	0.53	3.1	1.815	1.82	0.005
F1 51 cm	51	4.08	60.4	48.7	54.55	8.27	0.343	4.6	1.4	3	2.26	0.008
F1 effluent	71	5.68	61.1	37.7	49.4	16.55	0.310	0.7	0.7	0.7	0.00	0.002
F2 influent	0	0	307.7	312.1	309.9	3.11	1.000	406.7	410.6	408.65	2.76	1.000
F2 6 cm	6	0.48	326.6	315.5	321.05	7.85	1.036	404.9	397.2	401.05	5.44	0.981
F2 11 cm	11	0.88	289.7	276.8	283.25	9.12	0.914	396.7	393.4	395.05	2.33	0.967
F2 21 cm	21	1.68	246.7	226.4	236.55	14.35	0.763	401.1	402.3	401.7	0.85	0.983
F2 36 cm	36	2.88	219.9	235.4	227.65	10.96	0.735	405.5	415.1	410.3	6.79	1.004
F2 51 cm	51	4.08	168.2	199.9	184.05	22.42	0.594	383.8	389.9	386.85	4.31	0.947
F2 effluent	71	5.68	162.8	153.4	158.1	6.65	0.510	369.5	367	368.25	1.77	0.901

Aldehydes

Aldehyde Sample October 23 1996, Day 15

Sample	EBCT	Formaldehyde					Glyoxal				
		1st repl.	2nd repl.	Avg.	Sdev	C/Co	1st repl.	2nd repl.	Avg.	Sdev	C/Co
	min	ug/L	ug/L	ug/L	ug/L		ug/L	ug/L	ug/L	ug/L	
F1 infl	0	110.8	113.3	112.1	1.77	1.00	7.7	BDL	7.7	#DIV/0!	1.00
F1 10 cm	0.8	40.0		40.0	#DIV/0!	0.36	3.3		3.3	#DIV/0!	0.43
F1 25 cm	2	23.3		23.3	#DIV/0!	0.21	2.8		2.8	#DIV/0!	0.37
F1 55 cm	4.4	11.2		11.2	#DIV/0!	0.10	1.0		1.0	#DIV/0!	0.13
F1 effl	6	15.9	15.4	15.7	0.35	0.14	BDL	6.2	6.2	#DIV/0!	0.81
F2 infl	0	129.2	129.2	129.2	0.00	1.00	45.0	35.3	40.2	6.84	1.00
F2 10 cm	0.8	117.2		117.2	#DIV/0!	0.91	21.1		21.1	#DIV/0!	0.52
F2 25 cm	2	77.9		77.9	#DIV/0!	0.60	34.2		34.2	#DIV/0!	0.85
F2 55 cm	4.4	38.8		38.8	#DIV/0!	0.30	34.6		34.6	#DIV/0!	0.86
F2 effl	6	29.0		29.0	#DIV/0!	0.22	34.9		34.9	#DIV/0!	0.87

Aldehyde Sample November 14, 1996 (Day 37)

Sample	EBCT	Formaldehyde					Glyoxal				
		1st repl.	2nd repl.	Avg.	Sdev	Ln(C/Co)	1st repl.	2nd repl.	Avg.	Sdev	C/Co
	min	ug/L	ug/L	ug/L	ug/L		ug/L	ug/L	ug/L	ug/L	
F1 infl	0	99.2		99.2	#DIV/0!	0.00			#DIV/0!	#DIV/0!	#DIV/0!
F1 8 cm	0.64	24.2		24.2	#DIV/0!	-1.41			#DIV/0!	#DIV/0!	#DIV/0!
F1 13 cm	1.04	12.7		12.7	#DIV/0!	-2.06			#DIV/0!	#DIV/0!	#DIV/0!
F1 23 cm	1.84	2.0		2.0	#DIV/0!	-3.90			#DIV/0!	#DIV/0!	#DIV/0!
F1 53 cm	4.24	0.0		0.0	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F1 effl	5.84	0.0		0.0	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F2 infl	0	100.4		100.4	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F2 8 cm	0.64	105.1		105.1	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F2 13 cm	1.04	102.6		102.6	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F2 23 cm	1.84	93.2		93.2	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F2 53 cm	4.24	83.8		83.8	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!
F2 effl	5.84	75.0		75.0	#DIV/0!				#DIV/0!	#DIV/0!	#DIV/0!

Aldehyde Sample November 27, 1996 (Day 50)

Sample	EBCT	Formaldehyde					Glyoxal				
		1st repl.	2nd repl.	Avg.	Sdev	Ln(C/Co)	1st repl.	2nd repl.	Avg.	Sdev	C/Co
	min	ug/L	ug/L	ug/L	ug/L		ug/L	ug/L	ug/L	ug/L	
F1 infl	0	96.7	95.1	95.9	1.18	0.00	2.2	BDL	2.2	#DIV/0!	1.00
F1 6 cm	0.48	25.0	20.7	22.8	3.06	-1.44	BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F1 11 cm	0.88	8.0	8.0	8.0	0.00	-2.48	BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F1 21 cm	1.68	1.7	1.4	1.5	0.18	-4.13	6.2	BDL	6.2	#DIV/0!	2.85
F1 36 cm	2.88	0	0	0.0	0.00		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F1 51 cm	4.08	0	0	0.0	0.00		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F1 effl	5.68	0	0	0.0	0.00		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F2 infl	0	115.9	123.3	119.6	5.24		BDL	9.7	9.7	#DIV/0!	1.00
F2 6 cm	0.48	124.7	109.7	117.2	10.61		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F2 11 cm	0.88	121.7	118.5	120.1	2.30		BDL	17.0	17.0	#DIV/0!	1.76
F2 21 cm	1.68	115.8	111.7	113.8	2.89		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F2 36 cm	2.88	99.4	96.2	97.8	2.30		BDL	6.4	6.4	#DIV/0!	0.66
F2 51 cm	4.08	93.9	100.6	97.2	4.71		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F2 effl	5.68	78.8	78.7	78.7	0.12		BDL	BDL	#DIV/0!	#DIV/0!	#DIV/0!
F2 infl + 6 min		126.8	119.3	123.1	5.30		BDL	2.4	2.4	#DIV/0!	

Biomass (phospholipid method)

Phospholipid results, Nov 5, 1996 (Day 28)

Sample	Depth cm	Abs 610nm	nmoles PO4	Weight Media g	nmoles PO4/ g of media	Average nmoles PO4/ g of media	SDEV nmoles PO4/ g of media	Average nmoles PO4/ cm3 of filter	SDEV nmoles PO4/ cm3 of filter
F1 5cm 1st		0.9042	26.1	0.611	42.6				
F1 5cm 2nd	5	0.8055	23.1	0.594	38.9	**40.8**	2.64	**32.6**	2.12
F1 15cm 1st		0.288	7.7	0.825	9.3				
F1 15cm 2nd	15	0.2351	6.1	0.554	11.0	**10.1**	1.20	**8.1**	0.96
F1 40cm 1st		0.1071	2.3	0.734	3.1				
F1 40cm 2nd	40	0.1699	4.1	0.919	4.5	**3.8**	1.00	**3.0**	0.80
F1 70cm 1st		0.0287	-0.1	1.306	-0.1				
F1 70cm 2nd	70	0.0190	-0.4	1.201	-0.3	**0.1**	0.18	**0.2**	0.26
F2 5cm 1st		0.0908	1.77	0.467	3.80				
F2 5cm 2nd	5	0.1408	3.27	0.699	4.67	**4.24**	0.62	**3.4**	0.49
F2 15cm 1st		0.1434	3.34	0.95	3.52				
F2 15cm 2nd	15	0.1205	2.66	0.887	3.00	**3.26**	0.37	**2.6**	0.29
F2 40cm 1st		0.0885	1.70	0.84	2.03				
F2 40cm 2nd	40	0.0922	1.82	0.889	2.04	**2.04**	0.01	**1.6**	0.01
F2 70cm 1st		-0.0021	-1.00	1.064	-0.94				
F2 70cm 2nd	70	-0.0367	-2.03	0.827	-2.46	**0.00**	1.07	**0.0**	1.61

Phospholipid results, Nov 20, 1996 (Day 43)

Sample	Depth cm	Abs 610 nm	nmoles PO4	Weight Media g	nmoles PO4/ g of media	Average nmoles PO4/ g of media	SDEV nmoles PO4/ g of media	Average nmoles PO4/ cm3 of filter	SDEV nmoles PO4/ cm3 of filter
Anth blank 1st		0.232	6.0	1.054	5.7	**5.7**			
Anth blank 2nd		NA		1.141	NA	**NA**	#DIV/0!		
Sand blank 1st		0.09701	2.0	1.055	1.9	**1.9**			
Sand blank 2nd		0.283	7.5	1.109	6.8	**6.8**	3.48		
F1 3cm 1st		1.07	31.0	0.393	78.9				
F1 3cm 2nd	3	0.915	26.4	0.344	76.7	**77.8**	1.56	**62.2**	1.25
F1 8cm 1st		0.4318	12.0	0.498	24.0				
F1 8cm 2nd	8	0.4601	12.8	0.54	23.7	**23.9**	0.21	**19.1**	0.17
F1 13cm 1st		0.4524	12.6	0.757	16.6				
F1 13cm 2nd	13	0.3289	8.9	0.616	14.4	**15.5**	1.54	**12.4**	1.24
F1 23cm 1st		0.3594	9.8	0.976	10.0				
F1 23cm 2nd	23	0.3189	8.6	0.88	9.8	**9.9**	0.20	**7.9**	0.16
F1 53cm 1st		0.1386	3.2	0.752	4.3				
F1 53cm 2nd	53	0.0969	2.0	0.662	3.0	**3.6**	0.92	**5.4**	1.38
F2 3cm 1st		0.2048	5.18	0.634	8.16				
F2 3cm 2nd	3	0.2398	6.22	0.643	9.68	**8.92**	1.07	**7.1**	0.85
F2 8cm 1st		0.2957	7.89	0.909	8.68				
F2 8cm 2nd	8	0.2154	5.49	0.621	8.85	**8.76**	0.12	**7.0**	0.09
F2 13cm 1st		0.2624	6.90	0.954	7.23				
F2 13cm 2nd	13	0.1950	4.88	0.733	6.66	**6.95**	0.40	**5.6**	0.32
F2 23cm 1st		0.2476	6.45	0.92	7.01				
F2 23cm 2nd	23	0.2403	6.24	0.95	6.56	**6.79**	0.32	**5.4**	0.25
F2 53cm 1st		0.1556	3.71	1.01	3.67				
F2 53cm 2nd	53	0.1789	4.40	1.02	4.32	**3.99**	0.46	**6.0**	0.69

Phospholipid results, Dec 3, 1996 (Day 56)

Sample	Depth cm	Abs 610 nm	nmoles PO4	Weight Media g	nmoles PO4/ g of media	Average nmoles PO4/ g of media	STDEV nmoles PO4/ g of media	Coeff. of variation %	nmoles PO4/ cm3 of filter	Average nmoles PO4/ cm3 of filter	STDEV nmoles PO4/ cm3 of filter
GAC effl. 1st		2.005	58.9	0.6119	96.3				77.0		
GAC effl. 2nd		1.43	41.7	0.7607	54.9	75.6	29.27	38.7%	43.9	60.5	23.42
F1 1cm 1st		1.124	32.6	0.2574	122.0				97.6		
F1 1cm 2nd	1	1.818	53.3	0.4215	126.5	124.3	3.22	2.6%	101.2	99.4	2.58
F1 6cm 1st		0.7236	20.7	0.5545	36.6				29.3		
F1 6cm 2nd	6	0.6198	17.6	0.4749	37.0	36.8	0.27	0.7%	29.6	29.4	0.22
F1 11cm 1st		0.4405	12.2	0.6399	19.1				15.3		
F1 11cm 2nd	11	0.4628	12.6	0.6425	19.6	19.3	0.35	1.8%	15.7	15.5	0.28
F1 21cm 1st		0.2475	6.5	0.795	8.1				6.5		
F1 21cm 2nd	21	0.2474	6.4	0.766	8.4	8.3	0.21	2.6%	6.7	6.6	0.17
F1 36cm 1st		0.4446	12.3	1.0364	11.3				9.0		
F1 36cm 2nd	36	0.4045	11.1	0.9108	12.2	11.7	0.69	5.9%	9.8	9.4	0.55
F1 51cm 1st		0.1185	2.6	0.945	2.8				4.1		
F1 51cm 2nd	51	0.1392	3.2	1.2907	2.5	2.6	0.18	7.0%	3.7	3.9	0.27
F2 1cm 1st		0.2045	5.17	0.5482	9.43				7.5		
F2 1cm 2nd	1	0.2202	5.64	0.6353	8.87	9.15	0.39	4.3%	7.1	7.3	0.31
F2 6cm 1st		0.1933	4.83	0.8018	6.03				4.8		
F2 6cm 2nd	6	0.1619	3.90	0.6945	5.61	5.82	0.30	5.1%	4.5	4.7	0.24
F2 11cm 1st		0.2362	6.08	0.883	6.89				5.5		
F2 11cm 2nd	11	0.1850	4.59	0.8581	5.34	6.12	1.09	17.9%	4.3	4.9	0.87
F2 21cm 1st		0.2091	5.30	1.0425	5.09				4.1		
F2 21cm 2nd	21	0.1908	4.76	0.9992	4.76	4.93	0.23	4.7%	3.8	3.9	0.18
F2 36cm 1st		0.2479	6.46	1.0251	6.30				5.0		
F2 36cm 2nd	36	0.2105	5.35	1.0257	5.21	5.76	0.78	13.5%	4.2	4.6	0.62
F2 51cm 1st		0.2160	5.51	1.2214	4.51				6.8		
F2 51cm 2nd	51	0.2348	6.07	1.555	3.90	4.21	0.43	10.2%	5.9	6.3	0.64

Hydrogen Peroxide

October 10, 1996 (Day 2)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	1.1620	1.1540	1.1580	0.0057	0.0337	3	5.58	1.00	
F2 10 cm	0.8	1.1570	1.1620	1.1595	0.0035	0.0266	3	5.63	1.01	
F2 25 cm	2	1.1340	1.1200	1.1270	0.0099	0.0269	3	5.46	0.98	
F2 55 cm	4.4	1.1260	1.1440	1.1350	0.0127	0.0245	3	5.51	0.99	
F2 effl	6	1.1710	1.1670	1.1690	0.0028	0.0261	3	5.68	1.02	

October 16, 1996 (Day 8)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.9850	0.9750	0.9800	0.0071	0.0273	3	4.70	1.00	
F2 10 cm	0.8	0.9230	0.9130	0.9180	0.0071	0.0202	3	4.42	0.94	
F2 25 cm	2	0.9170	0.9250	0.9210	0.0057	0.0247	3	4.41	0.94	
F2 40 cm	3.2	0.8380	0.8260	0.8320	0.0085	0.0398	3	3.87	0.82	
F2 55 cm	4.4	0.7870	0.7930	0.7900	0.0042	0.0255	3	3.73	0.79	
F2 effl	6	0.9250	0.9170	0.9210	0.0057	0.0244	3	4.41	0.94	
F1 infl	0	0.0413		0.0413	#DIV/0!	2.77E-02	1	BDL		

October 21, 1996 (Day 13)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.9260	0.9240	0.9250	0.0014	0.0254	3	4.43	1.00	
F2 10 cm	0.8	0.5670	0.5650	0.5660	0.0014	0.0206	3	2.60	0.59	
F2 25 cm	2	0.2810	0.2840	0.2825	0.0021	0.0222	3	1.13	0.26	
F2 40 cm	3.2	0.2880	0.2890	0.2885	0.0007	0.0222	1	0.39	0.09	
F2 55 cm	4.4	0.1180	0.1160	0.1170	0.0014	0.0222	1	0.09	0.02	
F2 effl	6	0.0910	0.0890	0.0900	0.0014	0.0222	1	0.05	0.01	
Calib check		1.062		1.0620		0.0206	3	5.16	5.04 mg/L	

October 25, 1996 (Day 17)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.9970	0.9890	0.9930	0.0057	0.0247	3	4.78	1.00	
F2 10 cm	0.8	0.2670	0.2600	0.2635	0.0049	0.025	3	1.02	0.21	
F2 25 cm	2	0.1220	0.1210	0.1215	0.0007	0.025	1	0.10	0.02	
F2 40 cm	3.2	0.0621	0.0639	0.0630	0.0013	0.025	1	BDL	0.00	
F2 55 cm	4.4	0.0452		0.0452	#DIV/0!	0.025	1	BDL	0.00	
F2 effl	6	0.0455		0.0455	#DIV/0!	0.025	1	BDL	0.00	
Calib check		1.062		1.0620		0.0206	3	5.16	Target: 5.04 mg/L	

November 8, 1996 (Day 31)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	1.2275	1.2220	1.2248	0.0039	0.026	3	5.97	1.00	
F2 3 cm	0.24	1.1400		1.1400	#DIV/0!	0.025	3	5.54	0.93	
F2 13cm	1.04	1.0660		1.0660	#DIV/0!	0.025	3	5.16	0.86	
F2 23 cm	1.84	0.7362		0.7362	#DIV/0!	0.025	3	3.46	0.58	
F2 38 cm	3.04	0.5663		0.5663	#DIV/0!	0.025	3	2.58	0.43	
F2 53 cm	4.24	0.5661		0.5661	#DIV/0!	0.025	3	2.58	0.43	
F2 effl	5.84	0.5882		0.5882	#DIV/0!	0.025	3	2.69	0.45	
Calib check		1.2554		1.2554		0.03798	1	2.02	2.05 mg/L	

November 11, 1996 (Day 34)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0.9936	0.9959	0.9948	0.0016	0.027	3	4.78	1.00	
F2 7 cm	0.56	0.9532	0.9487	0.9510	0.0032	0.027	3	4.55	0.95	
F2 12cm	0.96	0.7609	0.7604	0.7607	0.0004	0.027	3	3.57	0.75	
F2 22 cm	1.76	0.5807	0.5738	0.5773	0.0049	0.027	3	2.63	0.55	
F2 37 cm	2.96	0.3765	0.3744	0.3755	0.0015	0.027	3	1.59	0.33	
F2 52 cm	4.16	0.3124	0.3095	0.3110	0.0021	0.027	3	1.25	0.26	
F2 effl	5.76	0.3152	0.3174	0.3163	0.0016	0.027	3	1.28	0.27	
Calib check		1.2004		1.2004		0.0258	1	1.95	2.05 mg/L	

November 18, 1996 (Day 41)

Sample	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	1.1520	1.1450	1.1485	0.0049	0.024	3	5.58	1.00	
F2 7 cm	0.56	0.6571	0.6701	0.6636	0.0092	0.024	3	3.08	0.55	
F2 12cm	0.96	0.7429	0.7373	0.7401	0.0040	0.024	3	3.48	0.62	
F2 22 cm	1.76	0.7721	0.7719	0.7720	0.0001	0.024	3	3.64	0.65	
F2 37 cm	2.96	0.7073	0.7075	0.7074	0.0001	0.024	3	3.31	0.59	
F2 52 cm	4.16	0.7868	0.7826	0.7847	0.0030	0.024	3	3.71	0.66	
F2 67 cm	5.36	0.6110	0.6060	0.6085	0.0035	0.024	3	2.80	0.50	
F2 effl	5.76	0.5048	0.5040	0.5044	0.0006	0.024	3	2.26	0.41	
Calib check		1.2462		1.2462		0.037	1	2.01	2.05 mg/L	

November 29, 1996 (Day 52)

Sample	Filter depth cm	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0	1.0893	1.0900	1.0897	0.0005	0.025	3	5.28	1.00	
F2 6 cm	6	0.48	0.9875	0.9744	0.9810	0.0093	0.025	3	4.72	0.89	
F2 11cm	11	0.88	0.9652	0.9644	0.9648	0.0006	0.025	3	4.63	0.88	
F2 21 cm	21	1.68	0.9008	0.8987	0.8998	0.0015	0.025	3	4.30	0.81	
F2 36 cm	36	2.88	0.7925	0.7926	0.7926	0.0001	0.025	3	3.75	0.71	
F2 51 cm	51	4.08	0.6377	0.6396	0.6387	0.0013	0.025	3	2.95	0.56	
F2 66 cm	66	5.28	0.4485	0.4453	0.4469	0.0023	0.025	3	1.96	0.37	
F2 effl	71	5.68	0.3294	0.3341	0.3318	0.0033	0.025	3	1.37	0.26	
Calib check			1.2727	1.27E+00	1.2736		0.025	1	2.08	Target: 2.05 mg/L	

December 9, 1996 (Day 62)

Hydraulic loading of Filter 2: 3.75 m/h since December 6, 1996

Sample	Filter depth cm	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0	0.9405	0.9395	0.9400	0.0007	0.025	3	4.51	1.00	
F2 10 cm	10	1.6	0.8076	0.8085	0.8081	0.0006	0.025	3	3.83	0.85	
F2 20 cm	20	3.2	0.6890	0.6803	0.6847	0.0062	0.025	3	3.19	0.71	
F2 35 cm	35	5.6	0.5414	0.5417	0.5416	0.0002	0.025	3	2.45	0.54	
F2 50 cm	50	8	0.3853	0.3856	0.3855	0.0002	0.025	3	1.65	0.37	
F2 effl	70	11.2	0.2904	0.2913	0.2909	0.0006	0.025	1	0.39	0.09	
Calib check			1.2667	1.2596	1.2632		0.025	1	2.06	Target: 2.05 mg/L	

December 11, 1996 (Day 64)

Hydraulic loading of Filter 2: 3.75 m/h since December 6, 1996

Sample	Filter depth cm	EBCT min	Abs 551 nm 1st repl	Abs 551 nm 2nd repl	Abs 551 nm avg	Abs 551 nm stdev	Abs 551 nm Blank	Dilution factor	H2O2-conc. mg/L	C/Co	Comments
F2 infl	0	0	1.2142	1.2172	1.2157	0.0021	0.025	3	5.93	1.00	
F2 10 cm	10	1.6	1.1133	1.1047	1.1090	0.0061	0.025	3	5.38	0.91	
F2 20 cm	20	3.2	0.9685	0.9499	0.9592	0.0132	0.025	3	4.60	0.78	
F2 35 cm	35	5.6	0.7802	0.7796	0.7799	0.0004	0.025	3	3.68	0.62	
F2 50 cm	50	8	0.5935	0.5906	0.5921	0.0021	0.025	3	2.71	0.46	
F2 65 cm	65	10.4	0.6189	0.6177	0.6183	0.0008	0.025	1	0.95	0.16	
F2 effl	70	11.2	0.3465	0.3448	0.3457	0.0012	0.025	1	0.48	0.08	
Calib check			1.2413	1.2596	1.2505		0.025	1	2.04	Target: 2.05 mg/L	

EXPERIMENT C1

Carboxylic Acids

Experimental results from March 26, 1997 sample (Day 8)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate 3rd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate 3rd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
Tap water		7	9		8	1.41	0.023	20	20		20	0.00	
std 100ug/L		188	200	204	197.3	8.33	0.570	238	251	249	246.0	7.00	
F1 influent	0	358	334		346	16.97	1.000	427	427		427	0.00	1.000
F1 10 cm	0.8	440	378		409	43.84	1.182	452	440		446	8.49	1.044
F1 effluent	5.6	318	322		320	2.83	0.925	427	433		430	4.24	1.007
F2 influent	0	335	333		334	1.41	1.000	441	442		441.5	0.71	1.000
F2 10 cm	0.8	359	351		355	5.66	1.063	450	448		449	1.41	1.017
F2 effluent	5.6	345	356		350.5	7.78	1.049	457	464		460.5	4.95	1.043
F3 influent	0	351	349		350	1.41	1.012	453	454		453.5	0.71	1.062
F3 10 cm	0.8	349	365		357	11.31	1.032	452			452	#DIV/0!	1.059
F3 effluent	5.6	348	356		352	5.66	1.017	452	455		453.5	2.12	1.062
F4 influent	0	350	351		350.5	0.71	1.049	451	452		451.5	0.71	1.023
F4 10 cm	0.8	292	303		297.5	7.78	0.891	358	354		356	2.83	0.806
F4 effluent	5.6	31	27		29	2.83	0.087	2	BDL		2	#DIV/0!	0.005

Experimental results from May 06, 1997 sample (Day 49)

	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
	std 250ug/L				#DIV/0!	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!	
F1	F1 influent	0	239	232	235.5	4.95	1.000	259	271	265	8.49	1.000
F1	F1 effluent	5.68	2	1	1.5	0.71	0.006	5	1	3	2.83	0.011
F2	F2 influent	0	344	310	327	24.04	1.000	374	355	364.5	13.44	1.000
F2	F2 effluent	5.68	283	267	275	11.31	0.841	346	355	350.5	6.36	0.962
F3	F3 influent	0	312	315	313.5	2.12	1.331	374	377	375.5	2.12	1.000
F3	F3 effluent	5.68	316	314	315	1.41	1.005	383	383	383	0.00	1.020
F4	F4 influent	0	324	323	323.5	0.71	0.989	384	390	387	4.24	1.000
F4	F4 effluent	5.68	1	3	2	1.41	0.006	2	2	2	0.00	0.005

Experimental results for F2 during a week (Days 49 - 56)

Sample	Time since Cl2 start hours	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate 3rd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate 3rd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co
std 250ug/L		188	200	204	197.3	8.33	#REF!	238	251	249	246.0	7.00	
F2 influent	4	344	310		327.0	24.04	1.000	374	355		364.5	13.44	1.000
F2 effluent	4	283	267		275.0	11.31	0.841	346	355		350.5	6.36	0.962
F2 influent	26	323	321		322	1.41	1.000	391	389		390	1.41	1.000
F2 effluent	26	289	295		292	4.24	0.907	406	389		397.5	12.02	1.019
F2 influent	53	317	318		317.5	0.71	1.000	385	385		385	0.00	1.000
F2 effluent	53	142	132		137	7.07	0.431	383	374		378.5	6.36	0.983
F2 influent	74	327	322		324.5	3.54	1.000	390	389		389.5	0.71	1.000
F2 effluent	74	21	22		21.5	0.71	0.066	352	354		353	1.41	0.906
F2 influent	104	327	306		316.5	14.85	1.000	342	335		338.5	4.95	1.000
F2 effluent	104	26	19		22.5	4.95	0.071	151	131		141	14.14	0.417
F2 influent	127	305	309		307	2.83	1.000	321	326		323.5	3.54	1.000
F2 effluent	127	20	19		19.5	0.71	0.064	4	5		4.5	0.71	0.014
F2 influent	146	334	358		346	16.97	1.000	385	382		383.5	2.12	1.000
F2 effluent	146	1	19		10	12.73	0.029	1	9		5	5.66	0.013
F2 influent	174	327	323		325	2.83	1.000	385	385		385	0.00	1.000
F2 effluent	174	310	316		313	4.24	0.963	396	397		396.5	0.71	1.030

Aldehydes

Experimental results from April 9, 1997 sample (Day 22)

Filter	Sample	EBCT min	Formald. 1st repl (ug/L)	Formald. 2nd repl (ug/L)	Formald. average (ug/L)	Formald. sdev (ug/L)	Formald. C/Co	Glyoxal 1st repl Area glyoxE	Glyoxal 1st repl Area glyoxZ	Glyoxal 1st repl ug/L	Glyoxal 2nd repl Area glyoxE	Glyoxal 2nd repl Area glyoxZ	Glyoxal 2nd repl (ug/L)	Glyoxal average (ug/L)	Glyoxal sdev (ug/L)	Glyoxal C/Co
F1	Influent	0	63.2	58.4	60.8	3.36	1.000	38,584	89189	5.55	28029	70685	4.59	5.07	0.68	1.000
F1	10cm	0.8	12.9	12.2	12.5	0.53	0.205	22600	50725	3.75	10720	24086	2.47	3.11	0.90	0.613
F1	Effluent	5.68	0.8	0.8	0.8	0.00	0.013	13132	32863	2.84	14918	35756	3.00	2.92	0.11	0.576
F2	Influent	0	56.0	63.2	59.6	5.13	1.000	12910	30609	2.76	28915	75520	4.78	3.77	1.43	1.000
F2	10cm	0.8	60.2	58.3	59.2	1.30	0.994	23945	61289	4.14	21660	56999	3.92	4.03	0.15	1.070
F2	Effluent	5.68	51.1	49.9	50.5	0.82	0.847	25295	63291	4.25	16311	42044	3.25	3.75	0.71	0.995
F3	Influent	0	57.5	61.2	59.3	2.59	1.000	33983	82331	5.17	25882	67853	4.42	4.80	0.53	0.946
F3	10cm	0.8	71.9	61.2	66.5	7.60	1.121	25265	61283	4.19	21355	53365	3.79	3.99	0.28	0.787
F3	Effluent	5.68	56.5	59.2	57.9	1.94	0.975	31428	78277	4.95	31839	79914	5.02	4.99	0.05	0.984
F4	Influent	0	62.2	64.7	63.5	1.77	1.000	37169	94686	5.69	32160	74322	4.85	5.27	0.59	1.397
F4	10cm	0.8	39.2	38.6	38.9	0.47	0.613	23691	59445	4.04	24453	63450	4.23	4.14	0.14	1.097
F4	Effluent	5.68	0.8	0.8	0.8	0.00	0.013	17113	47666	3.46	19171	50963	3.64	3.55	0.13	0.943

Biomass (phospholipid method)

Biomass results from May 27, 1997 (Day 70)

Filter	Sample	Depth cm	Abs 610nm 1st	media weight (g) 1st	nmol/g media 1st	nmol/cm3 fil. 1st	Abs 610nm 2nd	media weight (g) 2nd	nmol/g media 2nd	nmol/cm3 fil. 2nd	nmol/cm3 fil. Average	nmol/cm3 fil. STDEV
F1 (Control)	F1 1cm	1	0.442	0.179	68.48	54.78	0.617	0.176	99.32	79.46	67.12	17.46
F1 (Control)	F1 6cm	6	0.224	0.27	21.29	17.04	0.307	0.259	31.77	25.41	21.22	5.92
F1 (Control)	F1 16cm	16	0.113	0.378	6.44	5.16	0.141	0.357	8.92	7.13	6.14	1.40
F1 (Control)	F1 31cm	31	8.36E-02	0.445	3.50	2.80	0.101	0.4	5.19	4.16	3.48	0.95
F1 (Control)	F1 46cm	46	5.29E-02	0.585	1.10	1.65	2.03E-02	0.402	-0.82	-1.24	0.21	2.04
F1 (Control)	F1 61cm	61	2.37E-02	0.588	-0.39	-0.59	1.20E-03	0.466	-1.82	-2.73	0.05	1.51
F2 (periodic	F2 2cm	2	0.341	0.187	49.42	39.54	0.305	0.178	45.89	36.71	38.12	2.00
F2 (periodic	F2 32cm	32	5.71E-02	0.405	1.89	1.51	7.85E-02	0.466	2.89	2.31	1.91	0.57
F2 (periodic	F2 62cm	62	1.16E-02	0.725	-0.81	-1.22	2.51E-02	0.696	-0.28	-0.42	0.50	0.57
F3 (AS, con	F3 4cm	4	6.28E-04	0.38	-2.42	-1.93	-5.62E-03	0.32	-3.45	-2.76	0.20	0.59
F3 (AS, con	F3 34cm	34	-8.84E-03	0.313	-3.84	-3.07	-9.70E-03	0.54	-2.27	-1.82	0.40	0.89
F3 (AS, con	F3 64cm	64	-1.18E-02	0.548	-2.35	-3.53	-4.95E-03	0.638	-1.70	-2.55	0.30	0.89
F4 (GAC S	F4 2cm	2	8.46E-01	0.138	176.21	75.77	0.766	0.107	204.94	88.13	81.95	8.74
F4 (GAC S	F4 32cm	32	7.50E-01	0.198	108.34	46.59	0.777	0.195	114.14	49.08	47.83	1.76
F4 (GAC S	F4 62cm	62	9.39E-03	0.466	-1.41	-2.11	5.15E-03	0.554	-1.41	-2.12	0.30	0.00

Chlorine Residuals

Free chlorine profiles, April 22 1997 (Day 35)

Sample	Filter depth cm	Free Cl2 1st (mg/L)	Free Cl2 2nd (mg/L)	Free Cl2 Avg (mg/L)	Free Cl2 sdev (mg/L)	CV (%)	Remarks
F2 infl	0	0.63	0.64	0.635	0.007	1.1%	1h after start of Cl2
F2 8 cm	8	0.27	0.22	0.245	0.035	14.4%	1h after start of Cl2
F2 33 cm	33	0.12	0.18	0.15	0.042	28.3%	1h after start of Cl2
F2 effl	68	0.07	0.09	0.08	0.014	17.7%	1h after start of Cl2
F2 infl	0	0.53	0.6	0.565	0.049	8.8%	6h after start of Cl2
F2 8 cm	8	0.51	0.5	0.505	0.007	1.4%	6h after start of Cl2
F2 33 cm	33	0.26	0.22	0.24	0.028	11.8%	6h after start of Cl2
F2 effl	68	0.22	0.25	0.235	0.021	9.0%	6h after start of Cl2
F3 infl	0	0.63	0.68	0.655	0.035	5.4%	
F3 10cm	10	0.64	0.59	0.615	0.035	5.7%	
F3 35cm	35	0.64	0.73	0.685	0.064	9.3%	
F3 effl	70	0.76	0.77	0.765	0.007	0.9%	
F4 infl	0	0.72	0.67	0.695	0.035	5.1%	
F4 4cm	4	0.06	0.05	0.055	0.007	12.9%	
F3 9cm	9	0.001	0.001	0.001	0.000	0.0%	BDL (det. limit = 0.03 mg/L)
F3 effl	69	0.001	0.001	0.001	0.000	0.0%	BDL (det. limit = 0.03 mg/L)
				Average:		**8.2%**	

EXPERIMENT C2

Carboxylic Acids

Experimental results from September 2, 1997 sample (Day 15)

Sample	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %removal	Acetate %removal SDEV	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %removal	Formate %removal SDEV
Tap water					#DIV/0!	#DIV/0!	#DIV/0!		22.4		22.4	#DIV/0!		
Before BW														
F1	F1 influent	0	312.1	303.2	307.65	6.29			370.0	366.1	368.05	2.76		
F1	F1 effluent	5.6	53.0	28.7	40.85	17.18	87%	4.2%	2.0	0.1	1.05	1.34	99.7%	0.6%
F2	F2 influent	0	294.6	328.7	311.65	24.11			402.3	398.6	400.45	2.62		
F2	F2 effluent	5.6	296.8	293.7	295.25	2.19	5%	5.5%	390.1	386.7	388.4	2.40	3%	0.6%
F3	F3 influent	0	270.0	304.9	287.45	24.68			336.9	352.1	344.5	10.75		
F3	F3 effluent	5.6	48.6	22.0	35.3	18.81	88%	7.6%	2.8	2.5	2.65	0.21	99%	2.2%
F4	F4 influent	0	280.9	281.2	281.05	0.21			340.3	345.8	343.05	3.89		
F4	F4 effluent	5.6	33.4	55.2	44.3	15.41	84%	3.9%	7.9	32.2	20.05	17.18	94%	3.6%
After BW														
F1	F1 influent	0	298.4	326.5	312.45	19.87			326.4	338.3	332.35	8.41		
F1	F1 effluent	5.6	2	2	2	0.00	99%	4.5%	0.4	0.7	0.55	0.21	100%	1.8%
F2	F2 influent	0	349.2	355.3	352.75	5.02			394.1	407.0	400.55	9.12		
F2	F2 effluent	5.6	332.6	357.1	344.85	17.32	2%	3.6%	390.0	406.5	398.25	11.67	1%	2.6%
F3	F3 influent	0	271.5	283.9	277.7	8.77			322.9	332.7	327.8	6.93		
F3	F3 effluent	5.6	190.4	172.7	181.55	12.52	35%	3.9%	103.1	105.7	104.4	1.84	68%	1.5%
F4	F4 influent	0	290.5	253.9	272.2	25.88			328.1	297.3	312.7	21.78		
F4	F4 effluent	5.6	189.4	181.2	185.3	5.80	32%	6.9%	185.0	98.5	141.75	61.16	55%	14.7%

Experimental results from October 8, 1997 sample (Day 51)

Sample	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate %-removal SDEV	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate %-removal SDEV
Tap water					#DIV/0!	#DIV/0!	#DIV/0!		22.4		22.4	#DIV/0!		
Before BW														
F1	F1 influent	0	309.4	306.5	307.95	2.05			375.6	368	371.8	5.37		
F1	F1 effluent	5.6	37.5	35.7	36.6	1.27	88.1%	0.5%	32.7	38	35.35	3.75	90.5%	1.2%
F2	F2 influent	0	325.5	342.9	334.2	12.30			403.9	489.9	446.9	60.81		
F2	F2 effluent	5.6	37.2	32.4	34.8	3.39	90%	2.3%	328.4	315.5	321.95	9.12	28%	7.8%
F3	F3 influent	0	321.8	337.5	329.65	11.10			394.6	369.3	376.95	10.82		
F3	F3 effluent	5.6	30.1	55.5	43.3	18.67	87%	4.5%	17.4	84.8	51.1	47.65	86%	7.8%
F4	F4 influent	0	324.8	316.9	320.85	5.59			393.8	392.8	393.3	0.71		
F4	F4 effluent	5.6	5	5	5	0.00	98%	0.9%	10.3	11.5	10.9	0.85	97%	0.2%
After BW														
F1	F1 influent	0	327.3	329.5	328.4	1.55			352.9	366	359.45	9.26		
F1	F1 effluent	5.6	58.4	49.4	53.9	6.36	84%	1.2%	45.8	59.8	52.8	9.90	85%	2.7%
F2	F2 influent	0	352.1	360.4	356.25	5.87			413.9	437.1	425.5	16.40		
F2	F2 effluent	5.6	75.8	73.7	74.75	1.48	79%	1.0%	341.9	335.1	338.5	4.81	20%	2.5%
F3	F3 influent	0	341.5	342.6	342.05	0.78			357.7	380.6	374.15	9.12		
F3	F3 effluent	5.6	191.7	213.3	202.5	15.27	41%	2.3%	221.8	265.5	243.65	30.90	35%	5.3%
F4	F4 influent	0	340.3	333.3	336.8	4.95			353.5	360.1	361.8	2.40		
F4	F4 effluent	5.6	60.9	73.5	67.2	8.91	80%	2.1%	60.2	119.8	90	42.14	75%	6.2%

Experimental results from October 9, 1997 sample (Day 52)
(17 hours after BW)

Sample	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
	Tap water				#DIV/0!	#DIV/0!					#DIV/0!	#DIV/0!		
F1	F1 influent	0	230.8	231.8	231.3	0.71			317.7	304.1	310.9	9.62		
F1	F1 effluent	5.6	58	20.5	39.25	26.52	83.0%	6%	25.9	20.5	23.2	3.82	92.5%	2%
F2	F2 influent	0	251.1	255.7	253.4	3.25			322	337.7	329.85	11.10		
F2	F2 effluent	5.6	28.4	25.5	26.95	2.05	89%	1%	304.7	310.3	307.5	3.96	7%	2%
F3	F3 influent	0	270.2	255.6	262.9	10.32			341.5	328.5	335	9.19		
F3	F3 effluent	5.6	141.2	142.1	141.65	0.64	46%	2%	205.8	209.1	207.45	2.33	38%	2%
F4	F4 influent	0	248.1	253.7	250.9	3.96			315.9	321.7	318.8	4.10		
F4	F4 effluent	5.6	20.4	31.5	25.95	7.85	90%	2%	17.7	18.6	18.15	0.64	94%	1%

Experimental results from October 10, 1997 sample (Day 53)
(46 hours after BW)

Sample	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %removal	Acetate SDEV %removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %removal	Formate SDEV %removal
	Tap water				#DIV/0!	#DIV/0!					#DIV/0!	#DIV/0!		
F1	F1 influent	0	349.2	347.8	348.5	0.99			392.7	394.8	393.75	1.48		
F1	F1 10 cm	0.8	5	5	5	0.00			47.7	43.0	45.35	3.32		
F1	F1 20 cm	1.6	45	5	25	28.28			32.7	18.9	25.8	9.76		
F1	F1 effluent	5.6	5	5	5	0.00	98.6%	0%	12.8	12.7	12.75	0.07	96.8%	0%
F2	F2 influent	0	376.7	383.6	380.15	4.88			408.1	428.0	418.05	14.07		
F2	F2 effluent	5.6	5	5	5	0.00	99%	1%	360.6	357.4	359	2.26	14%	2%
F3	F3 influent	0	360.2	385.8	373	18.10			385.8	394.2	390	5.94		
F3	F3 effluent	5.6	5	53.6	29.3	34.37	92%	7%	299.2	280.7	289.95	13.08	26%	2%
F4	F4 influent	0	358.9	368.9	363.9	7.07			380.5	383.6	382.05	2.19		
F4	F4 effluent	5.6	24.9	57.9	41.4	23.33	89%	4%	17.3	22.8	20.05	3.89	95%	1%

Experimental results from November 11, 1997 sample (Day 85)
(24 hours after BW)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Acetate %removal	Acetate %removal SDEV	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co	Formate %removal	Formate %removal SDEV
Tap water		12.3		12.3	#DIV/0!	0.041			22.4		22.4	#DIV/0!			
F1 influent	0	297.8	300.8	299.3	2.12	1.000			423.4	423.9	423.65	0.35	1.000		
F1 4 cm	0.32	133.6	138.5	136.05	3.46	0.455			224.7	222	223.35	1.91	0.527		
F1 9 cm	0.72	69.5	68	68.75	1.06	0.230			158.3	157.2	157.75	0.78	0.372		
F1 effluent	5.52	21.1	13.1	17.1	5.65	0.057	94.3%	1.3%	24.5	12.8	18.65	8.27	0.044	95.6%	1.0%
F2 influent	0	326.8	328.8	327.8	1.41	1.000			441.1	447.9	445	2.69	1.000		
F2 5 cm	0.4	314.1	321.4	317.75	5.16	1.052			443.4	452.3	447.85	6.29	1.057		
F2 10 cm	0.8	298.8	304.9	301.85	4.31	0.921			436.5	440.4	438.45	2.76	0.983		
F2 effluent	5.6	42.4	46.9	44.65	3.18	0.135	86.4%	0.7%	351.1	332.9	342	12.87	0.767	23.3%	1.7%
F3 influent	0	306.5	319.3	312.9	9.05	1.045			423.7	422.5	423.1	0.85	0.999		
F3 5 cm	0.4	218	247.4	232.7	20.79	0.777			306.4	300.4	303.4	4.24	0.716		
F3 10 cm	0.8	201.3	199.9	200.6	0.99	0.670			235.7	294.1	294.9	1.13	0.696		
F3 effluent	5.6	125.1	122.6	123.85	1.77	0.414	60.4%	1.7%	278.5	276.2	277.35	1.63	0.655	34.4%	0.3%
F4 influent	0	301.2	303.4	302.3	1.55	0.922			420.9	423	421.95	1.48	0.946		
F4 5 cm	0.4	214.5	171.7	193.1	30.26	0.645			252.2	249.1	250.65	2.19	0.592		
F4 10 cm	0.8	75	92.7	83.85	12.52	0.255			88.3	102.7	95.5	10.18	0.214		
F4 effluent	5.6	17.1	18.6	17.85	1.06	0.054	94.1%	0.4%	16.4	31.7	24.05	10.82	0.054	94.3%	1.5%

Experimental results from November 17, 1997 sample (Day 91)
(5 hours after BW)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Acetate %removal	Acetate %removal SDEV	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co	Formate %removal	Formate %removal SDEV
Tap water		9.3		9.3	#DIV/0!	0.031			23.2		23.2	#DIV/0!			
F1 influent	0	298.5	301.8	300.15	2.33	1.000			415.5	417.9	416.7	1.70	1.000		
F1 effluent	5.52	74.2	5	39.6	48.93	0.132	86.8%	8.5%	73.3	30	51.65	30.62	0.124	87.6%	3.9%
F2 influent	0	318.7	316.3	317.5	1.70	1.000			426.7	426.1	426.4	0.42	1.000		
F2 5 cm	0.4	313.5	317.1	315.3	2.55	1.050			429.3	432.1	430.7	1.98	1.034		
F2 10 cm	0.8	313.5	323.2	318.35	6.86	1.003			431.3	434.7	433	2.40	1.015		
F2 effluent	5.6	193.2	165.4	179.3	19.66	0.565	43.5%	3.4%	358.2	354.5	356.35	2.62	0.836	16.4%	0.4%
F3 influent	0	311	304.3	307.65	4.74	1.025			415.8	415.7	415.75	0.07	0.998		
F3 effluent	5.6	175.8	173.1	174.45	1.91	0.581	43.3%	1.1%	272.6	273.5	273.05	0.64	0.655	34.3%	0.1%
F4 influent	0	312.5	317	314.75	3.18	0.991			408.8	413.6	411.2	3.39	0.964		
F4 effluent	5.6	60.6	62.9	61.75	1.63	0.194	80.4%	0.8%	59.1	67.9	63.5	6.22	0.149	84.6%	1.2%

Experimental results from November 27, 1997 sample (Day 101)
(62 hours after BW)

Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate C/Co	Acetate %removal	Acetate %removal SDEV	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate C/Co	Formate %removal	Formate %removal SDEV
Tap water				#DIV/0!	#DIV/0!	#DIV/0!					#DIV/0!	#DIV/0!			
F1 influent	0	345.9	348.7	347.3	1.98	1.000			422.6	425.8	424.2	2.26	1.000		
F1 effluent	5.52	5	5	5	0.00	0.014	98.6%	0.3%	15.2	13.6	14.4	1.13	0.034	96.6%	0.4%
F2 influent	0	366.9	374.2	370.55	5.16	1.000			443.3	445	444.15	1.20	1.000		
F2 effluent	5.6	336.6	341.8	339.2	3.68	0.915	8.5%	1.2%	395.4	396.7	396.05	0.92	0.892	10.8%	0.2%
F3 influent	0	338.6	348.4	343.5	6.93	0.989			419.2	423.7	421.45	3.18	0.994		
F3 effluent	5.6	5	5	5	0.00	0.014	98.5%	1.0%	242.2	245.5	243.85	2.33	0.575	42.1%	0.7%
F4 influent	0	329.1	327.7	328.4	0.99	0.886			402.5	405.9	404.2	2.40	0.910		
F4 effluent	5.6	5	5	5	0.00	0.013	98.5%	0.2%	10.7	12.4	11.55	1.20	0.026	97.1%	0.4%

Aldehydes

Experimental results from Nov 19, 1997 sample (Day 93)
2 Days after backwash

Filter	Sample	EBCT min	Formald. 1st repl (ug/L)	Formald. 2nd repl (ug/L)	Formald. average (ug/L)	Formald. sdev (ug/L)	Formald. C/Co	Glyoxal 1st repl Area glyoxalE	Glyoxal 1st repl Area glyoxalZ	Glyoxal 1st repl ug/L	Glyoxal 2nd repl Area glyoxalE	Glyoxal 2nd repl Area glyoxalZ	Glyoxal 2nd repl (ug/L)	Glyoxal average (ug/L)	Glyoxal sdev (ug/L)	Glyoxal C/Co
F1	Influent	0	168.4	154.7	161.5	9.72	1.000	198,453	764,365	33.49	108,284	346,216	16.58	25.04	11.98	1.000
F1	5cm	0.4	76.9	79.0	78.0	1.47	0.483	59,267	293,931	13.29	492,897	1,555,133	69.47	41.38	39.72	1.653
F1	10cm	0.8	24.2	36.4	30.3	8.66	0.188	26,483	180,234	8.43	58,382	319,482	14.04	11.24	3.96	0.449
F1	Effluent	5.6	1.5	1.5	1.5	0.00	0.009	0	163,365	7.00	19,635	181,608	8.25	7.62	0.89	0.304
F2	Influent	0	157.9	154.1	156.0	2.71	1.000	168,803	608,846	27.36	403,070	1,341,980	59.42	43.39	22.67	1.000
F2	5cm	0.4	147.7	159.4	153.5	8.31	0.950	103,279	452,950	20.02	169,974	682,041	29.82	24.92	6.93	0.995
F2	10cm	0.8	145.5	159.1	152.3	9.60	0.976	140,985	584,604	25.63	108,186	492,364	21.42	23.53	2.98	0.542
F2	Effluent	5.6	122.8	106.8	114.8	11.31	0.736	149,761	637,003	27.66	70,001	374,167	16.30	21.98	8.03	0.507
F3	Influent	0	162.2	163.6	162.9	0.94	1.009	459,446	1,465,004	65.37	462,984	1,489,059	66.28	65.83	0.65	2.629
F3	5cm	0.4	108.0	93.9	101.0	9.98	0.625	105,341	464,309	24.24	35,514	205,983	9.58	16.91	10.36	0.675
F3	10cm	0.8	105.6	103.3	104.5	1.59	0.647	256,638	983,760	42.03	335,864	1,171,147	51.53	46.78	6.72	1.869
F3	Effluent	5.6	28.5	31.1	29.8	1.83	0.184	47,207	285,036	11.93	46,733	281,808	12.47	12.20	0.38	0.487
F4	Influent	0	148.9	152.6	148.7	4.01	0.960	153,583	661,660	28.60	109,688	498,580	21.74	25.17	4.85	0.560
F4	5cm	0.4	114.8	105.4	110.1	6.66	0.682	0	653,070	23.23	63,684	335,918	14.83	19.03	5.94	0.760
F4	10cm	0.8	63.7	66.6	65.2	2.00	0.418	111,442	552,039	23.57	0	388,572	14.46	19.02	6.44	0.438
F4	Effluent	5.6	1.5	1.5	1.5	0.00	0.010	24,469	178,315	8.30	0	177,504	7.46	7.88	0.59	0.182

Dissolved Oxygen

Dissolved Oxygen DO, Nov. 24, 1997 (Day 98)

3 days following backwash

	Sample	DO mg/L 1st	DO mg/L 2nd	Average mg/L	SDEV mg/L
F1	F1 influent	7.19	7.38		
F1	F1 effluent	6.58	6.73		
F1	delta	0.61	0.65	0.63	0.028
F2	F2 influent	8.09	8.00		
F2	F2 effluent	7.97	7.93		
F2	delta	0.12	0.07	0.10	0.035
F3	F3 influent	7.57	7.83		
F3	F3 effluent	7.15	7.17		
F3	delta	0.42	0.66	0.54	0.170
F4	F4 influent	7.54	7.74		
F4	F4 effluent	7.06	7.06		
F4	delta	0.48	0.68	0.58	0.141

Biomass (Phospholipid)

Biomass results from Oct 21 1997 (Day 64)

Filter		Sample	Depth cm	Abs 610nm 1st	media weight (g) 1st	nmole/g media 1st	nmole/cm3 fil. 1st	Abs 610nm 2nd	media weight (g) 2nd	nmole/g media 2nd	nmole/cm3 fil. 2nd	nmole/cm3 fil. Average	nmole/cm3 fil. SDEV
F1	(Control)	F1 Top	0.01	0.892	0.029	885.87	708.69	0.923	0.024	1103.98	867.18	787.94	128.21
F1	(Control)	F1 10cm	10	0.097	0.088	18.90	15.12	0.104	0.105	20.64	16.51	15.82	0.99
F1	(Control)	F1 20cm	20	0.117	0.281	9.09	7.28	0.116	0.26	9.71	7.77	7.52	0.35
F1	(Control)	F1 35cm	35	0.100	0.275	7.43	5.94	0.072	0.232	5.17	4.14	5.04	1.27
F1	(Control)	F1 65cm	65	0.037	0.327	0.47	0.70	0.037	0.396	0.45	0.68	0.69	0.01
F2	(cont. CO2)	F2 Top	0.01	0.120	0.087	30.40	24.32	0.110	0.037	63.42	50.74	37.53	18.68
F2	(cont. CO2)	F2 10cm	10	0.092	0.325	5.53	4.42		0.305			4.42	#DIV/0!
F2	(cont. CO2)	F2 65cm	65	0.025	0.416	-0.48	-0.72	0.026	0.641	-0.28	-0.39	0.50	0.23
F3	(free CO2 in B/V)	F3 Top	0.01	1.281	0.026	1411.74	1129.39	0.953	0.025	1112.38	889.90	1009.65	169.34
F3	(free CO2 in B/V)	F3 10cm	10	0.050	0.118	4.61	3.69	0.059	0.133	6.11	4.89	4.29	0.85
F3	(free CO2 in B/V)	F3 65cm	65	0.033	0.591	0.09	0.14	0.031	0.504	-0.05	-0.07	0.03	0.15
F4	(comb. CO2 in B/V)	F4 Top	0.01	0.984	0.032	888.64	710.91	0.957	0.018	921.42	737.13	724.02	18.54
F4	(comb. CO2 in B/V)	F4 10cm	10	0.092	0.185	9.79	7.83	0.114	0.177	13.93	11.15	9.49	2.34
F4	(comb. CO2 in B/V)	F4 65cm	65	0.024	0.494	-0.48	-0.72	0.020	0.419	-0.84	-1.26	0.30	0.39

Biomass results from Nov 25, 1997 (Day 99)

Filter		Sample	Depth cm	Abs 610nm 1st	media weight (g) 1st	nmole/g media 1st	nmole/cm3 fil. 1st	Abs 610nm 2nd	media weight (g) 2nd	nmole/g media 2nd	nmole/cm3 fil. 2nd	nmole/cm3 fil. Average
F1	(Control) before B/V	F1 4 cm	4	0.5847	0.158	104.54	83.63	0.6171	0.114	153.37	122.70	103.16
F1	(Control) after B/V	F1 4 cm	4	0.4445	0.209	59.00	47.20	0.5457	0.205	74.67	59.74	53.47
F2	(cont. CO2) before B/V	F2 4 cm	4	0.0921	0.341	5.31	4.25	0.0554	0.395	1.88	1.51	2.88
F2	(cont. CO2) after B/V	F2 4 cm	4	0.0537	0.435	1.53	1.23	0.0552	0.42	1.69	1.35	1.29
F3	(free CO2 in B/V) bef. B/V	F3 4 cm	4	0.6115	0.183	94.63	75.70	0.8776	0.223	113.27	90.62	83.16
F3	(free CO2 in B/V) aft. B/V	F3 4 cm	4	0.6952	0.324	61.16	48.93	0.4720	0.182	81.19	64.95	56.94
F4	(comb. CO2 in B/V) bef. B/V	F4 4 cm	4	0.9763	0.224	125.92	100.74	1.2373	0.241	158.80	125.44	113.09
F4	(comb. CO2 in B/V) aft. B/V	F4 4 cm	4	0.4819	0.186	72.30	57.84	0.7908	0.348	65.14	52.11	54.98

EXPERIMENT O1

Carboxylic Acids

Experimental results from Jan 21, 1998 sample (Day 13)

Sample		EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
std 250ug/L			242.9	258.6	250.8	11.10	#REF!		129.1	131.1	130.1	1.41		
(Just before O3/H2O2)														
F1	F1 influent	0	282.3	276.7	279.5	3.96			401.8	399	400.4	1.98		
F1	F1 effluent	5.6	52.6	29.2	40.9	16.55	85.37%	3.67%	405.1	375.6	390.35	20.86	2.51%	2.85%
F3	F3 influent	0	286.1	294.2	290.15	5.73			410.9	410.8	410.85	0.07		
F3	F3 effluent	5.6	5	64.9	34.95	42.36	87.95%	8.29%	451.5	506.6	479.05	38.96	-16.60%	4.75%
F4	F4 influent	0	286.5	284.8	285.65	1.20			416.5	411.9	414.2	3.25		
F4	F4 effluent	5.6	5	30.7	17.85	18.17	93.75%	3.39%	397.1	394.5	395.8	1.84	4.44%	0.61%

Experimental results from Jan 22, 1998 sample (Day 14)

Sample		EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
22h after O3, O3/H2O2 addition														
F3	F3 influent	0	269.6	264.3	266.95	3.75			360.6	359.7	360.15	0.64		
F3	F3 effluent	5.6	5	5	5	0.00	98.13%	0.70%	374.9	368.8	371.85	4.31	-3.25%	0.69%
F4	F4 influent	0	274.2	281.8	278	5.37			370.4	374	372.2	2.55		
F4	F4 effluent	5.6	5	5	5	0.00	98.20%	0.97%	284.1	256.7	270.4	19.37	27.35%	2.94%

Experimental results from Jan 27, 1998 sample (Day 19)

Sample		EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
During O3, O3/H2O2 addition														
F3	F3 influent	0	313.2	293.4	303.3	14.00			334.5	364.9	349.7	21.50		
F3	F3 effluent	5.6	128.1	121.4	124.75	4.74	58.87%	3.09%	277.3	266	271.65	7.99	22.32%	4.22%
F4	F4 influent	0	291.1	293.2	292.15	1.48			357.4	365.8	361.6	5.94		
F4	F4 effluent	5.6	43.5	48	45.75	3.18	84.34%	0.80%	153.2	148.2	150.7	3.54	58.32%	1.31%

Experimental results from Jan 30, 1998 sample (Day 22)

	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
Before O3, O3/H2O2														
F1	F1 influent	0	294.5	300.6	297.55	4.31			399.4	409.4	404.4	7.07		
F1	F1 effluent	5.6	5	5	5	0.00	98.32%	0.72%	65	71.6	68.3	4.67	83.11%	1.45%
F3	F3 influent	0	314.4	319.1	316.75	3.32			418	427	422.5	6.36		
F3	F3 effluent	5.6	42.4	39.8	41.1	1.84	87.02%	0.81%	307	312	309.5	3.54	26.75%	1.17%
F4	F4 influent	0	303.6	307.9	305.75	3.04			419.6	418.4	419.0	0.85		
F4	F4 effluent	5.6	5	5	5	0.00	98.36%	0.50%	51.8	41.8	46.8	7.07	88.83%	0.95%
After O3, O3/H2O2														
F3	F3 influent	0	315.1	313.9	314.5	0.85			425.9	415	420.45	7.71		
F3	F3 effluent	5.6	115.7	107.2	111.45	6.01	64.56%	1.09%	294.6	290.2	292.4	3.11	30.46%	1.29%
F4	F4 influent	0	327.1	332.4	329.75	3.75			433.3	458.4	445.85	17.75		
F4	F4 effluent	5.6	5	5	5	0.00	98.48%	0.57%	52.6	55.2	53.9	1.84	87.91%	2.20%

Experimental results from Feb 10, 1998 sample (Day 33)

	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
Before O3, O3/H2O2														
F1	F1 influent	0	214.2	229.5	221.85	10.82			366.1	367	366.55	0.64		
F1	F1 5cm	0.4	168.5	171.3	169.9	1.98			279.9	281.6	280.75	1.20		
F1	F1 10cm	0.8	89.9	92.4	91.15	1.77			172.6	170.8	171.7	1.27		
F1	F1 35cm	2.8	5	5	5	0.00			13.6	13.7	13.65	0.07		
F1	F1 effluent	5.6	5	5	5	0.00	97.75%	4.88%	7.6	8.7	8.15	0.78	97.78%	0.27%
F3	F3 influent	0	303.5	289	296.25	10.25			411.3	415	413.15	2.62		
F3	F3 5cm	0.4	232.1	227.1	229.6	3.54			345.2	338.5	341.85	4.74		
F3	F3 10cm	0.8	138.1	145.8	141.95	5.44			209.8	221.4	215.6	8.20		
F3	F3 35cm	2.8	5	5	5	0.00			12.3	14.4	13.35	1.48		
F3	F3 effluent	5.6	5	5	5	0.00	98.31%	3.46%	16.1	9.3	12.7	4.81	96.93%	1.32%
F4	F4 influent	0	295.7	272.9	284.3	16.12			419.6	416.1	417.85	2.47		
F4	F4 5cm	0.4	200.5	184.8	192.65	11.10			258.8	248.3	253.55	7.42		
F4	F4 10cm	0.8	105	107.2	106.1	1.56			118.4	120.8	119.6	1.70		
F4	F4 35cm	2.8	5	5	5	0.00			7.6	17.6	12.6	7.07		
F4	F4 effluent	5.6	5	5	5	0.00	98.24%	5.67%	12.3	15.2	13.75	2.05	96.71%	0.77%
After O3, O3/H2O2														
F3	F3 influent	0	309.3	307.8	308.55	1.06			429.1	429.7	429.4	0.42		
F3	F3 5cm	0.4	270.3	276.2	273.25	4.17			373.8	380	376.9	4.38		
F3	F3 10cm	0.8	203.8	197.3	200.55	4.60			271.7	264.2	267.95	5.30		
F3	F3 35cm	2.8	5	5	5	0.00			25.2	33.1	29.15	5.59		
F3	F3 effluent	5.6	5	5	5	0.00	98.38%	0.34%	10.2	12.5	11.35	1.63	97.36%	0.39%
F4	F4 influent	0	268.6	272.4	270.5	2.69			384.6	386.8	385.7	1.56		
F4	F4 5cm	0.4	225.4	244.5	234.95	13.51			306.9	322.6	314.75	11.10		
F4	F4 10cm	0.8	131.8	128.8	130.3	2.12			151.4	152.5	151.95	0.78		
F4	F4 35cm	2.8	5	5	5	0.00			24.6	22.1	23.35	1.77		
F4	F4 effluent	5.6	5	5	5	0.00	98.15%	0.50%	16.7	17.2	16.95	0.35	95.61%	0.41%

Experimental results from Feb 11, 1998 sample (Day 34)

	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
(18 h after O3/H2O2)														
F3	F3 influent	0	283.3	285.9	284.6	1.84			388.4	396	392.2	5.37		
F3	F3 effluent	5.6	5	5	5	0.00	98.24%	0.46%	7.5	10	8.75	1.77	97.77%	1.02%
F4	F4 influent	0	302.7	301.8	302.25	0.64			427.4	421.3	424.35	4.31		
F4	F4 effluent	5.6	98.9	5	50.95	64.98	83.14%	15.20%	14.7	11.7	13.2	2.12	96.89%	0.80%

Experimental results from Feb 12, 1998 sample (Day 35)

	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
(43 h after O3/H2O2)														
F3	F3 influent	0	291	291.9	291.45	0.64			420.7	426.6	423.65	4.17		
F3	F3 effluent	5.6	5	5	5	0.00	98.28%	0.15%	5.8	7.6	6.7	1.27	98.42%	0.73%
F4	F4 influent	0	303.8	303.9	303.85	0.07			430.4	433	431.7	1.84		
F4	F4 effluent	5.6	5	5	5	0.00	98.35%	0.02%	9.5	8.6	9.05	0.64	97.90%	0.32%

Experimental results from Feb 13, 1998 sample (Day 36)

	Sample	EBCT min	Acetate 1st repl (ug/L)	Acetate 2nd repl (ug/L)	Acetate average (ug/L)	Acetate sdev (ug/L)	Acetate %-removal	Acetate SDEV %-removal	Formate 1st repl (ug/L)	Formate 2nd repl (ug/L)	Formate average (ug/L)	Formate sdev (ug/L)	Formate %-removal	Formate SDEV %-removal
Before O3, O3/H2O2														
F3	F3 influent	0	240.1	226.1	233.1	9.90			384.2	387.1	385.65	2.05		
F3	F3 effluent	5.6	5	5	5	0.00	97.85%	3.00%	3.5	4.2	3.85	0.49	99.00%	0.39%
F4	F4 influent	0	234	223.6	228.8	7.35			388.3	388.2	388.25	0.07		
F4	F4 effluent	5.6	5	5	5	0.00	97.81%	2.27%	3.8	4.6	4.2	0.57	98.91%	0.10%
After O3, O3/H2O2														
F3	F3 influent	0	320.5	307.4	313.95	9.28			455.4	452.5	453.95	2.05		
F3	F3 effluent	5.6	5	5	5	0.00	98.41%	2.09%	9.7	10.7	10.2	0.71	97.75%	0.34%
F4	F4 influent	0	344	338.1	341.05	4.17			458.9	452.3	455.6	4.67		
F4	F4 effluent	5.6	98.1	5	50.55	64.42	85.18%	13.38%	28	20.1	23.05	4.17	94.94%	0.97%

Aldehydes

Experimental results from Feb 10, 1998 sample (Day 33)

Filter	Sample	EBCT min	Formald. 1st repl (ug/L)	Formald. 2nd repl (ug/L)	Formald. average (ug/L)	Formald. sdev (ug/L)	Formald. %-Removal	Formald. %-Removal SDEV	Glyoxal 1st repl Area glyoxalE	Glyoxal 1st repl Area glyoxalZ	Glyoxal 1st repl ug/L	Glyoxal 2nd repl Area glyoxalE	Glyoxal 2nd repl Area glyoxalZ	Glyoxal 2nd repl (ug/L)	Glyoxal average (ug/L)
Before O3/H2O2															
F1	Influent	0	84.2	85.2	84.7	0.71			78,880	128,232	9.74	238,498	414,429	27.55	18.65
F1	Effluent	5.6	14.8	15.2	15.0	0.29	82.3%	0.64%	32,156	50,539	4.87	44,356	77,188	6.42	5.64
F3	Influent	0	86.3	93.7	90.0	5.24			63,081	101,604	8.13	78,056	128,515	9.80	8.96
F3	Effluent	5.6	8.4	8.2	8.3	0.12	90.7%	4.12%	33,227	56,534	5.15	36,726	63,565	5.57	5.36
F4	Influent	0	77.8	88.3	83.1	7.42			39,253	55,728	5.36	115,287	190,076	13.73	9.54
F4	Effluent	5.6	3.2	3.2	3.2	0.08	96.1%	6.32%	21,916	41,038	4.08	20,191	37,338	3.87	3.98
After O3/H2O2															
F3	Influent	0	85.4	85.2	85.33	0.12			61,307	98,279	7.85	55,356	86,917	7.24	7.54
F3	Effluent	5.6	28.6	25.0	26.79	2.53	68.6%	2.10%	80,119	155,386	10.95	38,264	66,706	5.76	8.35
F4	Influent	0	88.2	95.4	91.79	5.13			57,494	87,411	7.34	109,992	175,649	12.94	10.14
F4	Effluent	5.6	9.2	6.2	7.76	2.12	91.6%	4.27%	44,023	66,341	6.77	18,717	30,663	3.54	5.16

Dissolved Oxygen

Dissolved Oxygen DO on Jan 26, 98, Day 18 after startup

	Sample	DO mg/L 1st	DO mg/L 2nd	Average mg/L	SDEV mg/L
F1	F1 influent	6.85	6.86		
F1	F1 effluent	6.55	6.50		
F1	delta	0.30	0.36	**0.33**	**0.04**
F4	F4 influent	7.42	7.55		
F4	F4 effluent	7.04	7.16		
F4	delta	0.38	0.39	**0.39**	**0.01**

F4 sampled 5 days after periodic addition of ozone

Dissolved Oxygen DO on Feb 9, 98, Day 32 after startup

	Sample	DO mg/L 1st	DO mg/L 2nd	Average mg/L	SDEV mg/L
F1	F1 influent	6.68	7.67		
F1	F1 effluent	6.00	7.06		
F1	delta	0.68	0.61	**0.65**	**0.049**
F3	F3 influent	7.95	7.9		
F3	F3 effluent	7.49	7.5		
F3	delta	0.46	0.4	**0.43**	**0.042**
F4	F4 influent	8.03	8.14		
F4	F4 effluent	7.49	7.66		
F4	delta	0.54	0.48	**0.51**	**0.042**

Dissolved Oxygen DO on Feb 27, 98, Day 50 after startup

	Sample	DO mg/L 1st	DO mg/L 2nd	Average mg/L	SDEV mg/L
F1	F1 influent	7.91	7.74		
F1	F1 effluent	7.57	7.51		
F1	delta	0.34	0.23	**0.29**	**0.08**
F4	F4 influent	7.75	7.80		
F4	F4 effluent	7.43	7.51		
F4	delta	0.32	0.29	**0.31**	**0.02**

F4 just after the periodic addition of ozone

Biomass (Phospholipid)

Biomass (phospholipid) results from March 2, 1998 (Day 53)

Filter	Sample	Depth cm	Abs 610nm 1st	media weight (g) 1st	nmole/g media 1st	nmole/cm3 fil. 1st	Abs 610nm 2nd	media weight (g) 2nd	nmole/g media 2nd	nmole/cm3 fil. 2nd	nmole/cm3 fil. Average	nmole/cm3 fil. SDEV
P1 (Control)	P1 4cm	4	0.642	0.203	89.79	71.83	0.793	0.212	107.24	85.79	78.81	9.87
P1 (Control)	P1 9cm	9	0.544	0.401	38.16	30.53	0.608	0.408	42.19	33.75	32.14	2.28
P1 (Control)	P1 19cm	19	0.334	0.554	16.31	13.04	0.318	0.576	14.85	11.88	12.46	0.82
F3 (H2O2/O3)	F3 4cm	4	1.379	0.317	126.90	101.52	1.31	0.286	143.49	114.79	108.16	9.38
F3 (H2O2/O3)	F3 9cm	9	0.846	0.433	55.16	44.93	0.764	0.366	59.75	47.80	46.36	2.03
F3 (H2O2/O3)	F3 19cm	19	0.514	0.61	23.62	18.89	0.446	0.46	28.91	21.52	20.21	1.85
F4 (O3)	F4 4cm	4	0.722	0.296	69.65	55.72	0.769	0.322	68.38	54.70	55.21	0.72
F4 (O3)	F4 9cm	9	0.757	0.354	61.19	48.95	0.647	0.257	68.83	55.06	52.01	4.32
F4 (O3)	F4 19cm	19	0.386	0.547	19.35	15.48	0.575	0.62	26.17	20.94	18.21	3.85

Average CV:

Biomass (Biomass Respiration Potential, BRP)

Results from Feb. 18, 1998 (Day 41)

Sample	Depth (cm)	Wet Weight (g)	Dry Weight (g)	Initial DO (mg/L)	Final DO (5h) (mg/L)	delta DO (mg/L)	delta DO mg/L/cm3 of filter	SDEV (mg/L)	CV (%)
Anth. (sterile) 1st		6.369	5.661	5.68	5.61	0.07	0.010		
Anth. (sterile) 2nd		7.409	6.585	5.51	5.47	0.04	0.005		
Anth. (sterile)						Average:	**0.007**	**0.004**	
F2 3cm 1st		1.354	1.203	5.8	5.04	0.76	0.505		
F2 3cm 2nd		1.496	1.330	5.6	4.87	0.73	0.439		
F2 3cm	3					Average:	**0.472**	**0.047**	9.88%
F2 8cm 1st		1.721	1.530	5.9	5.21	0.69	0.361		
F2 8cm 2nd		2.572	2.286	5.69	4.95	0.74	0.259		
F2 8cm	8					Average:	**0.310**	**0.072**	23.25%
F2 18cm 1st		2.608	2.318	5.58	4.81	0.77	0.266		
F2 18cm 2nd		3.653	3.247	5.76	5.18	0.58	0.143		
F2 18cm	18					Average:	**0.204**	**0.087**	42.51%
F2 33cm 1st		2.896	2.574	5.55	5.07	0.48	0.149		
F2 33cm 2nd		3.816	3.392	5.84	5.13	0.71	0.167		
F2 33cm	33					Average:	**0.158**	**0.013**	8.17%

avg CV : 21.0%

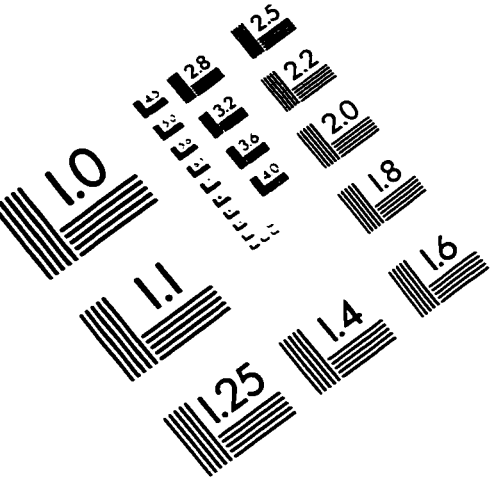
Results from March 4, 1998 (Day 54)

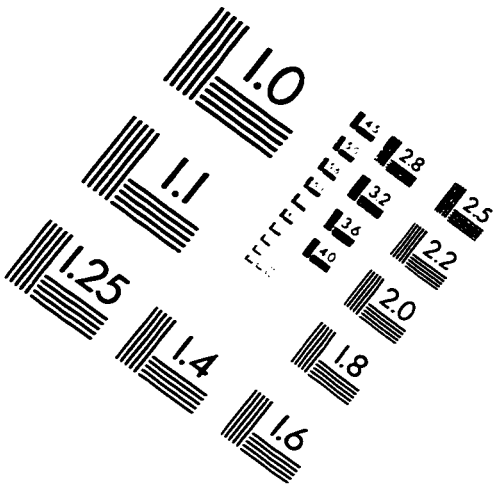
Sample	Depth (cm)	Wet Weight (g)	Dry Weight (g)	Initial DO (mg/L)	Final DO (5h) (mg/L)	delta DO (mg/L)	delta DO mg/L/cm3 of filter	SDEV (mg/L)	CV (%)
F1 4cm 1st		1.871	1.661	9.42	8.82	0.6	0.289		
F1 4cm 2nd		3.655	3.246	5.57	4.89	0.68	0.168		
F1	4					Average:	**0.228**	**0.086**	37.6%
F1 9cm 1st		3.286	2.918	9.42	8.51	0.91	0.249		
F1 9cm 2nd		2.778	2.467	5.6	5.01	0.59	0.191		
F1	9					Average:	**0.220**	**0.041**	18.7%
F1 19cm 1st		3.725	3.308	9.42	8.67	0.75	0.181		
F1 19cm 2nd		3.257	2.892	5.61	5.15	0.46	0.127		
F1	19					Average:	**0.154**	**0.038**	24.8%
F3 4cm 1st		3.609	3.205	9.42	7.8	1.62	0.404		
F3 4cm 2nd		2.908	2.582	5.62	4.15	1.47	0.455		
F3	4					Average:	**0.430**	**0.036**	8.4%
F3 9cm 1st		4.019	3.569	9.42	7.97	1.45	0.325		
F3 9cm 2nd		3.866	3.433	5.68	4.38	1.3	0.303		
F3	9					Average:	**0.314**	**0.016**	5.0%
F3 19cm 1st		4.002	3.554	9.42	8.42	1	0.225		
F3 19cm 2nd		2.647	2.351	5.74	5.13	0.61	0.208		
F3	19					Average:	**0.216**	**0.012**	5.7%
F4 4cm 1st		3.278	2.911	9.42	8.56	0.86	0.236		
F4 4cm 2nd		2.469	2.192	5.67	5.05	0.62	0.226		
F4	4					Average:	**0.231**	**0.007**	3.1%
F4 9cm 1st		2.978	2.644	9.42	8.56	0.86	0.260		
F4 9cm 2nd		3.091	2.745	5.68	4.94	0.74	0.216		
F4	9					Average:	**0.238**	**0.031**	13.2%
F4 19cm 1st		3.369	2.992	9.42	8.65	0.77	0.206		
F4 19cm 2nd		3.052	2.710	5.78	5.15	0.63	0.186		
F4	19					Average:	**0.196**	**0.014**	7.2%
								Average C	**13.7%**

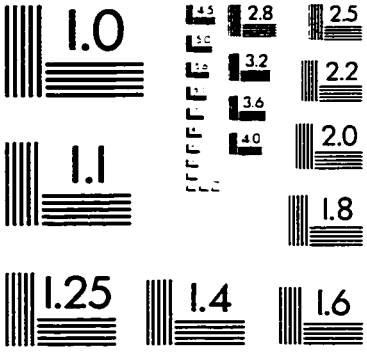
Results from March 12 1998 (Day 63)

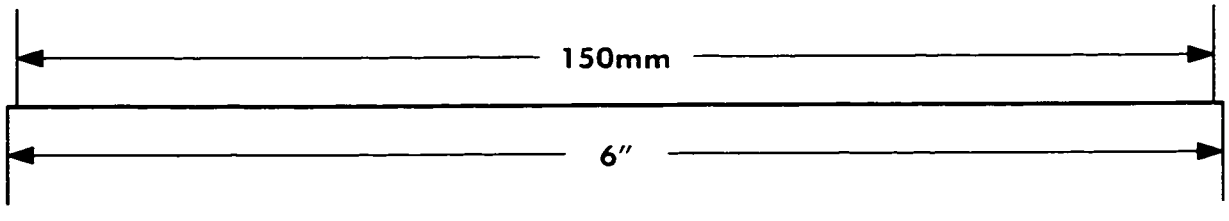
Sample	Depth (cm)	Wet Weight (g)	Dry Weight (g)	Initial DO (mg/L)	Final DO (5h) (mg/L)	delta DO (mg/L)	delta DO_{sa} mg/L/cm3 of filter	SDEV (mg/L)	CV %
F2 Top 1st		1.561	1.387	8.27	4.9	3.37	1.943		
F2 Top 2nd		1.733	1.540	8.32	4.7	3.62	1.880		
F2 Top	**0**					Average:	**1.912**	**0.045**	2.33%
F2 5cm 1st		3.25	2.889	8.25	5.48	2.77	0.767		
F2 5cm 2nd		3.732	3.317	8.3	4.44	3.86	0.931		
F2 5cm	**5**					Average:	**0.849**	**0.116**	13.64%
F2 15cm 1st		4.278	3.802	8.29	7.09	1.2	0.252		
F2 15cm 2nd		5.361	4.765	8.32	7.08	1.24	0.208		
F2 15cm	**15**					Average:	**0.230**	**0.031**	13.60%
F2 30cm 1st		4.075	3.622	8.32	7.74	0.58	0.128		
F2 30cm 2nd		4.897	4.352	8.33	7.65	0.68	0.125		
F2 30cm	**30**					Average:	**0.127**	**0.002**	1.75%
F2 45cm 1st		5.072	4.508	8.31	8.11	0.2	0.067		
F2 45cm 2nd		7.86	6.986	8.34	8.01	0.33	0.071		
F2 45cm	**45**					Average:	**0.069**	**0.003**	4.43%
F2 60cm 1st		6.712	5.966	8.25	8.06	0.19	0.048		
F2 60cm 2nd		8.051	7.156	8.34	8.05	0.29	0.061		
F2 60cm	**60**					Average:	**0.054**	**0.009**	16.96%
								avg CV:	**8.8%**

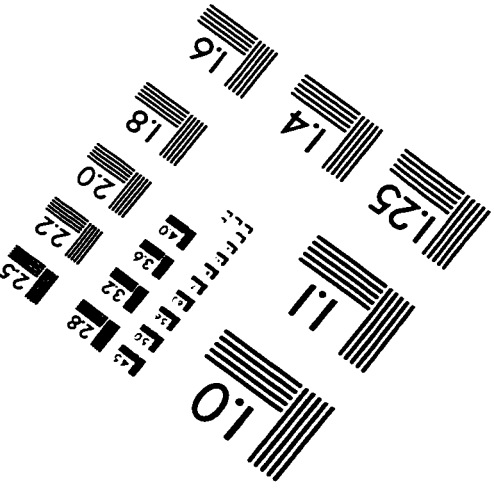
IMAGE EVALUATION
TEST TARGET (QA-3)

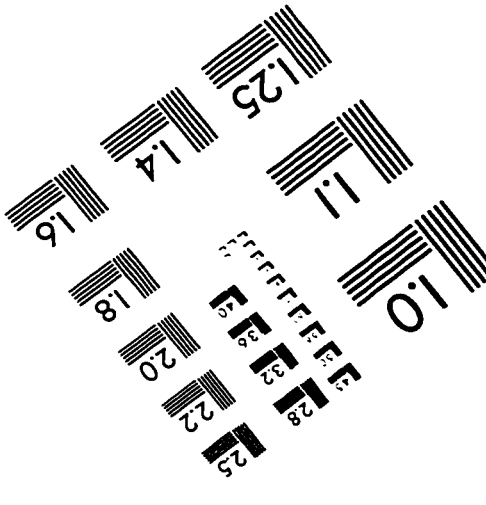












APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989