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## Monitoring and operation of ozonation -BAC filtration

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# Monitoring and Operation
## of
## Ozonation and BAC Filtration

Petra Ross

# MONITORING AND OPERATION OF OZONATION - BAC FILTRATION

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# MONITORING AND OPERATION OF OZONATION - BAC FILTRATION

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
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door

Petra Suzanne ROSS

civiel ingenieur
geboren te Woerden

# CONTENTS

# CHAPTER 1

**Introduction**

# THE ONGOING CHALLENGES DRINKING WATER COMPANIES FACE

Drinking water companies are required to produce safe drinking water that meets the quality standards defined in national and international guidelines. To be able to achieve this, continuous research is taking place and, if required, investments are done related to the construction of a new treatment plant or expansion of existing treatment plants. Some of the ongoing challenges the drinking water companies face the coming decades are summarized as follows (Frijns *et al.* 2013, Hope and Rouse 2013, van der Helm and Rietveld 2002):

- Higher customer demands, infrastructural safety and reliability requirements, but with lower revenues (Zehnder *et al.* 2003). Benchmarking and competition put tremendous pressure on capital improvement programs and operation expenditures. This requires companies to be more efficient and 'do more with less' (de Goede *et al.* 2016, Rautu *et al.* 2017).
- Loss of skills and experience due to retirement of personnel and the lack of young professionals interested in technological studies (Pederson and Yoder 2017). In 2011, the average age of an employee of a water utility or water board in the Netherlands, was above 46 (Rinnooy 2011).
- Emerging threats, organic micropollutants and endocrine disrupting compounds. In particular pharmaceuticals emerge in our surface water as a consequence of both an increasing industrial pressure on the environment and increased consumption of pharmaceuticals as a consequence of an aging population (Fatta-Kassinos *et al.* 2011, Fekadu *et al.* 2019). Ideally, pharmaceuticals are removed at the wastewater treatment plants to prevent from entering our source water and enable the supply of safe drinking water. At this stage, removal at wastewater treatment plants is still subject to research to determine most effective ways for adjustment or expansion. In absence of a full barrier at wastewater treatment plants, the drinking water treatment plants (WTPs) still need to implement/optimize their operation to produce drinking water that complies with the guidelines.

# OPTIMISATION STRATEGIES WTP

Above challenges ask for a continuous optimisation of the WTPs. According to van der Helm *et al.* (2008) the improvement of water quality should be the main objective for optimisation of WTPs and not the reduction in environmental impact and costs. Reason for this is the huge environmental impact and costs for the society as a whole when more bottled water would be used for drinking water as a result of insufficient (confidence in) quality of the tap water (van der Helm *et al.* 2008). By implementing water quality models, improvement of product quality, optimisation of chemical use and savings on energy costs could be achieved (van der Helm and Rietveld 2002). Bosklopper *et al.* (2004) suggested that optimisation of a WTP should focus on an integrated approach. By using a plant-wide model of the entire WTP as an instrument for operational support and for process control, the operation of a WTP can be further improved. Models are needed to determine how much adjustment is required (Yuan *et al.* 2019), allowing for maximal utilization of the installed infrastructure and postponement of new investments. Ayesa *et al.* (2001) indicated that the possibility of exploring different operational strategies using dynamic simulators originally developed for waste water treatment plants (WWTP) will be one of the most helpful tools to improve the plant operation. Until recently, the use of model-based control in the drinking water industry has mainly focussed on flow-control. This has resulted in a decrease in energy requirements (Bakker *et al.* 2003, van der Helm and Rietveld 2002) and lately has also proven to result in a better water quality due to a more stable operation (Bakker *et al.* 2013).

Van der Helm *et al.*(2009) described the model-based optimisation of operation of a WTP by direct control on water quality objectives through the offline implementation of embedded plant control, including control dynamics, in the model of a WTP. It was shown that this has a large potential for the model-based optimisation of operation of a WTP. To ensure a high standard of drinking water quality in fully automated WTPs, the design of the control system is essential. Therefore van Schagen *et al.* (2010) proposed a design methodology for a control system for WTPs. The design methodology consisted of 5 steps, (1) determine plant-wide objectives, (2) determine operational constraints, (3) identify important disturbances, (4) determine controlled variables and (5) determine control configuration. It was shown that the proposed design method was a useful tool to design an automatic control system of a WTP. It was also identified that there is a need for monitoring water quality parameters, preferably on-line, after each treatment step.

# WAYS TO GAIN REAL-TIME INFORMATION ON WATER QUALITY

To get information on the water quality a WTP is typically equipped with several on-line sensors. The type and number of sensors vary considerably between different WTPs, as indicated in Figure 1-1, which provides an overview of the installed sensors at three European WTPs treating surface water with a comparable treatment scheme. Due to confidentiality the WTPs are referred to as 1, 2 and 3.

All WTPs consist of a surface water intake followed by coagulation/flocculation (and sedimentation). Subsequently the water is filtered, ozonation is used followed by biological (activated carbon) filtration, post disinfection and clear water storage. The post disinfection step varies per WTP from dosing monochloramine or chlorine gas to slow sand filtration. WTP 1, only has one on-line measurement in place which consists of the ozone in water concentration. While WTP 2 and 3 are equipped with multiple on-line sensors after each treatment step. WTP 2 contains the most extensive on-line monitoring program. Most parameters measured on-line are general compliance parameters as described by the World Health Organization (WHO 2008). Figure 1-1 shows the variability in monitoring strategy that existed at the three WTPs.

Retrieving reliable and robust on-line information is important in order to control a WTP (van Schagen *et al.* 2010). This information can be retrieved from sensors that measure a specific parameter directly, but also from generic sensors that give indirect information. Roccaro *et al.* (2008), Rieger *et al.* (2004) and van den Broeke *et al.* (2008) showed the suitability of UV-Vis spectra measurements for the estimation of different parameters such as chlorine decay, nitrite and nitrate, ozone and assimilable organic carbon (AOC) concentrations. These estimations were derived from algorithms developed using principal component analysis followed by partial least squares regression, based on a change in UV/Vis absorbance during treatment which were linked to laboratory measurements. These types of generic sensors are so-called soft-sensors, sensors that require software to give the required information. The published results showed the potential of the use of generic sensors, however, the sensors always require local calibration first.
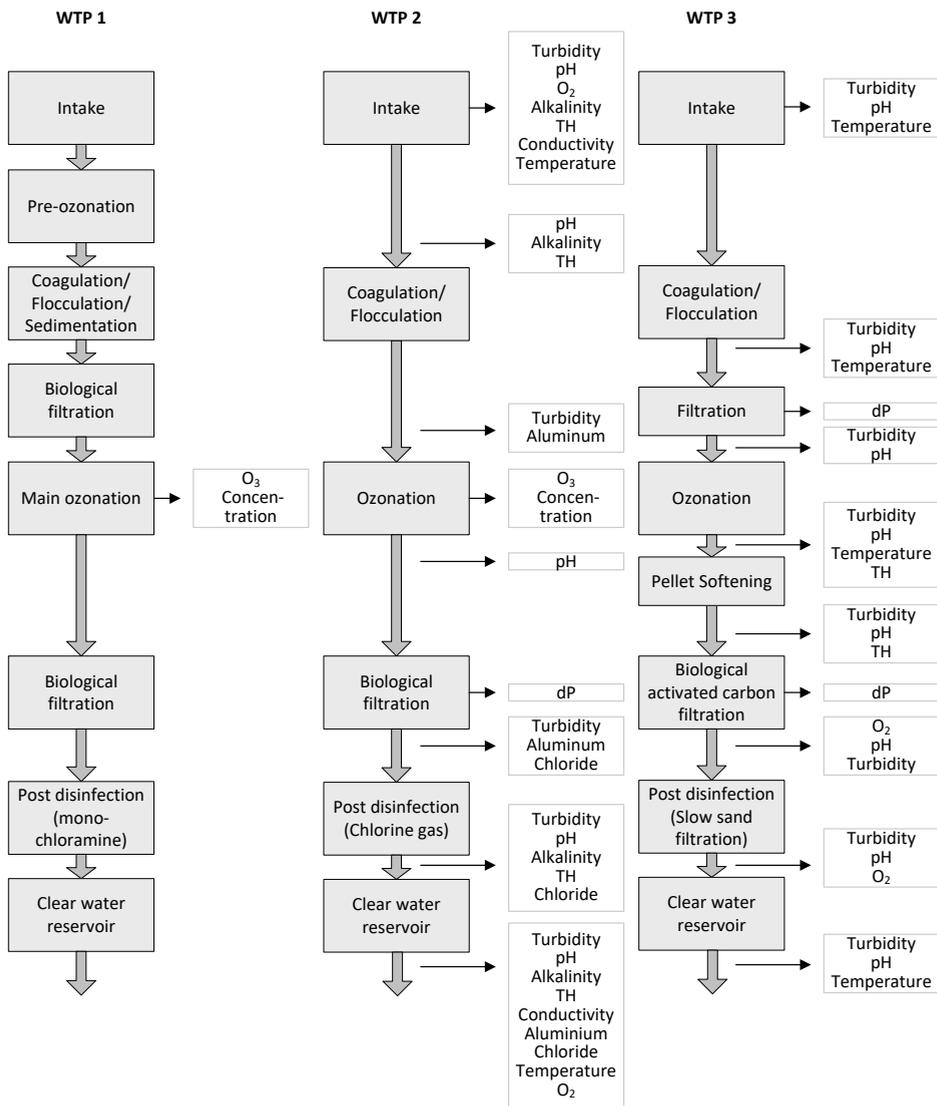
**Figure 1-1** Installed on-line measurements for three different WTPs.

It should be realized that the availability of sufficient trustworthy data are essential in developing a solid soft-sensor (Kadlec *et al.* 2009). A soft-sensor can be developed in different ways, based on black box, grey box or white box modelling. The black box approach is characterized by an empirical relation between the input and output. The relations are derived from historical, full-scale plant data. Thus, such a soft-sensor can only be used in the situation where it has been developed for, since a black box model is not valid when a process is operated outside the boundaries of calibration (Kano and Nakagawa 2008). Because the operation of a WTP is relatively constant, the calibration dataset is normally rather limited, hampering the application of black box modelling. Grey box models are a combination of black box models and white box models, such that it contains some more insight into the system through the white box model, while some parts of the model are still data driven (Zyngier *et al.* 2001). White box models mathematically describe the physical-chemical processes that take place in the treatment process. Developing these models is time consuming, however, once developed, the process knowledge of the treatment processes are captured, leading to more generically applicable models (van der Helm and Rietveld 2002). Several platforms, containing drinking water quality white box models have been available, such as OTTER (Head *et al.* 2002), Stimela (van der Helm and Rietveld 2002) and SimEau, the European Water Treatment Simulator, developed within the 6th framework TECHNEAU program funded by the European Union.

# OPTIMISED OPERATION
# BASED ON WATER QUALITY

Depending on the source water, one or multiple treatment steps are required to produce safe drinking water. Generally, the drinking water treatment plants are very robust and over-sized (Bosklopper *et al.* 2004) and, as a result, have not required stringent advanced control based on the incoming water quality. However, as a result of the challenges water companies are facing, this is changing. When the source water originates from surface water an extensive treatment system is required, since surface water can be characterized by seasonal variations influenced by temperature, algae blooms, rain-fall run off of pathogens, solids and pesticides, environmental spills upstream and, since recently, the increased threat by endocrine disrupting compounds. This continuous changing source water requires improved monitoring and operation of the WTP, anticipating on the disturbances in the process.

*The main objective of this thesis was to improve monitoring*
*and operation of ozonation and biological activated carbon (BAC) filtration*
*for the removal of pathogens and organic matter, for the optimisation*
*of drinking water production from surface water.*

Treatment processes such as coagulation/flocculation, filtration, ozonation and BAC filtration are susceptible to changes in the feed water quality. This research was carried out as part of the 6th Framework European integrated project TECHNEAU. Within TECHNEAU optimization of coagulation was taken on board by SINTEF (Eikebrokk *et al.* 2009). In this research the focus was on ozonation and BAC filtration. These processes have several operational control options and interaction between the two processes exists. The main objective for ozonation is disinfection and oxidation of organic matter, which results in an increase in the biodegradability of the natural organic matter (NOM) (van der Helm *et al.* 2009). The main objective for BAC filtration is the removal of organic micropollutants and biodegradation of NOM to ensure the production of biologically safe and stable drinking water (van der Aa *et al.* 2011). AOC measurements are frequently used to assess the biological stability of the water (Escobar *et al.* 2001). Since the original developed method by van der Kooij *et al.* (1982), several new methods for the determination of AOC have been published with the aim of being faster, more reliable and cheaper (Hammes and Egli 2005, Huck 1990, LeChevallier *et al.* 1993, Werner and Hambsch 1986). Understanding of the compatibility of the various AOC methods is required to be able to compare previously published results.

## Ozonation

The first ozone disinfection unit was installed in 1906 in Nice, France. Not until the 1970s disinfection with ozone gained importance (von Sonntag and von Gunten 2012), due to the fact that the limitations of chlorination became apparent. Von Gunten (2003a) provided an extensive overview on ozone decomposition in water and disinfection processes. Since then several models were developed to translate the processes taking place into a water quality model able to describe the processes of a full-scale WTP containing ozonation with the objective to optimise operation (Audenaert *et al.* 2010, Talvy *et al.* 2011, van der Helm *et al.* 2009). Important influent water quality parameters for the ozonation process are temperature, pH, DOC, UV absorbance at 254 nm ($UV_{254}$) and bromide concentration. Important effluent water quality parameters that were calculated are pathogen concentrations, $UV_{254}$ and ozone concentration, as well as the produced disinfection by-products such as AOC and bromate. Van der Helm *et al.* (2009) concluded that the ozone concentration measurement, measured with the indigo method as described by Bader and Hoigne (1982), was not accurate for concentrations below 0.1 mg-$O_3$/L. As a result, the 'measured' disinfection (Ct value) based on ozone measurements was too high. An indication that the modelled ozone concentrations and Ct value were more accurate than the measured ones was the fairly good prediction of the bromate concentration which has a linear relationship with Ct value (von Gunten 2003b). The Ct value is an important control parameter for ozonation when used for disinfection, an overestimation based on ozone measurements is therefore highly unwanted. Besides the Ct value and bromate concentration, the effluent $UV_{254}$ was fairly well predicted by the model as well. The model predictions for the effluent AOC concentrations were not accurate in the study of van der Helm *et al.* (2009) and require improvement.

## BAC filtration

Miller and Rice (1978) where one of the first to describe the BAC process for drinking water treatment. Laurent *et al.* (1999) investigated the applicability of the CHABROL model, which related the macroscopic functioning of biological filters used for eliminating dissolved organic matter in drinking water treatment to the kinetics of the basic microbiological processes involved (Billen *et al.* 1992). The model calculated the vertical distribution of fixed bacterial biomass and the effluent concentration in biodegradable organic matter from the characteristics of influent water for given values of contact time and temperature. Laurent *et al.* (1999) concluded that experimental results showed that modifications in the CHABROL model should be made to account for the acclimation to cold temperatures and to prevent under estimations of the biodegradable organic carbon (BDOC) removals. The results showed the applicability of using a model to predict the performance in dynamically operated filters, and which subsequently may be used for design and operation (Laurent *et al.* 1999). Van der Aa *et al.* (2006) developed a dynamic BAC model to simulate simultaneous adsorption and biodegradation of NOM, and adsorption of organic micro pollutants with the objective to understand the processes taking place. Important

measured parameters were DOC, UV$_{254}$, oxygen, phosphate, water temperature and adenosine tri-phosphate (ATP) on carbon. Van der Aa *et al.* (2006) concluded that the model predictions for biodegradation of substrates and biomass development were in the right order of magnitude, but the development of biomass in deeper filter layers needed more attention. Although researchers have tried to find correlations between biomass development and the observed biodegradation in the BAC filters under varying operating conditions, no clear correlations have been found (Dhawan *et al.* 2017, Velten *et al.* 2011). This underlines the complexity of the processes taking place in the BAC filters. To be able to understand the processes that take place in the BAC filters, measurements are required. Hammes *et al.* (2008) developed a method to rapidly determine the amount of viable bacterial cells (suspended bacteria) in the water by applying flow cytometry, in stead of using cultivation-based heterotrophic plate counts. The development of this method enabled to rapidly, and costs effectively, evaluate the requirements for optimised NOM removal by biodegradation. Velten *et al.* (2011) used ATP measurements and flow cytometry to follow the initial colonization and development of biomass in a pilot-scale granular activated carbon drinking water filter over time and vertical filter depth, in a long-term experiment subject to uncontrolled changes in feed water parameters. It was shown that the combination of ATP and total cell counts was successful in describing the system and could be a valuable tool for characterization of biological filters. The combination of these methods thus pose the opportunity to better identify how BAC filters react to different conditions and investigate the improvement of the biodegration in BAC filters. In addition, Besmer *et al.* (2016) published the first results of the use of on-line flow cytometry for direct determination of microbial dynamics. Besides modelling and monitoring of the behaviour of BAC filters related to NOM removal, recent studies have investigated the use of exitation-emmission matrices to predict the breakthrough of emerging contaminants (Anumol *et al.* 2015, Sgroi *et al.* 2018, Sgroi *et al.* 2017). Especially for waste water this has shown to be a promissing methodology.

# THIS THESIS

The observations discussed above show that quite some research has been carried out concerning water quality measurements, model development and subsequent optimisation of operation of ozonation and BAC filtration. However, some research gaps still exist to arrive at optimised monitoring and operation of ozonation – BAC filtration (see Figure 1-2).
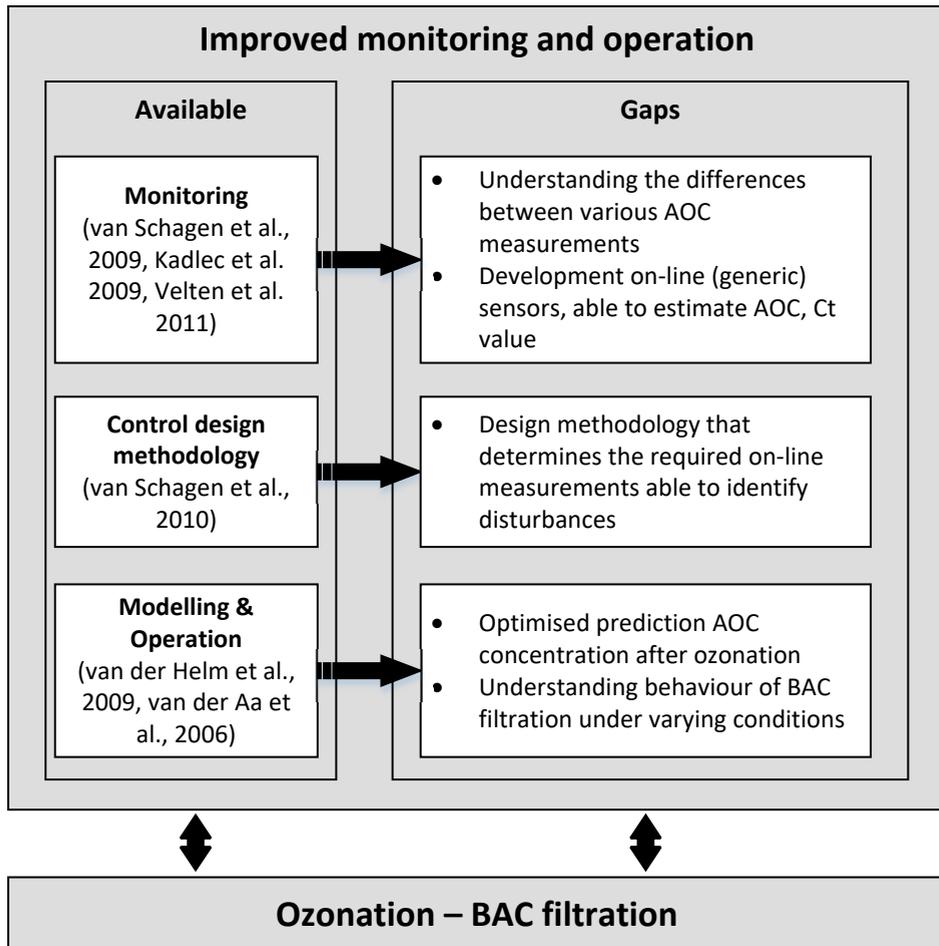


**Figure 1-2** Gap analysis on monitoring and operation of ozonation - BAC filtration.

Various methods have been developed for the determination of the AOC concentration. Understanding the differences between these methods enable interpretation and comparison of the results with previously published research. Another knowledge gap is a structural approach towards identifying the best monitoring strategy able to detect disturbances in the treatment process by measuring them cheaply, accurately and quickly. The modelling results for ozonation by van der Helm *et al.* (2009) showed that there is a requirements for an optimised prediction of AOC, preferably on-line. The use of newly available characterisation methods related to BAC filtration provide the opportunity to better understand biodegradation in BAC and the required operating strategy under varying conditions.

The described knowledge gaps form the basis of the main research questions, subsequently addressed per chapter as illustrated in Figure 1-3:

I.     What are the differences between the various AOC measurements (Chapter 2)?
II.    What measurements should be put in place to provide sufficient (real-time) information on water quality for optimised operation of ozone-BAC filtration (Chapter 3)?
III.   Is it possible to use on-line UV/Vis spectrometry for the on-line estimation of AOC, Ct value and bromate around ozonation (Chapter 4)?
IV.   How does BAC filtration respond to sudden changes in water quality and how does this affect the production of biological stable drinking water (Chapter 5)?
V.    Can the operation of backwashing of BAC filtration be optimised by using a simplified model to predict the head loss development (Chapter 6)?

In Chapter 2 a comparison between various methods to determine the AOC concentration, frequently used to assess the biological stability in water, was made. The methods discussed are all offline methods of which results are retrieved between 3 up to 30 days after sampling. In Chapter 3 a methodology is developed which enables identification of required real-time information that should be collected. Optimised operation requires on-line information on the water quality such as AOC. In Chapter 4 an algorithm was developed to estimate on-line the AOC formation during ozonation based on differential UV/Vis-spectrometry. Besides, an algorithm was developed for the on-line estimation of Ct value and bromate formation during ozonation. Chapter 5 addresses the question if operational adjustments are required to optimise the BAC filtration based on the immediate response to a change in feed water quality and long term effects of changes in treatment plant set-up. Different conditions were tested, resulting in advice for best operational practices, when focusing on biological stability. In Chapter 6 modelling of clogging BAC filters is discussed based on the different feed water qualities. To finish, the concluding remarks are given in Chapter 7, which highlight the results of this thesis and outlook for future research, as well as the full scale implementations currently applied at Waternet.
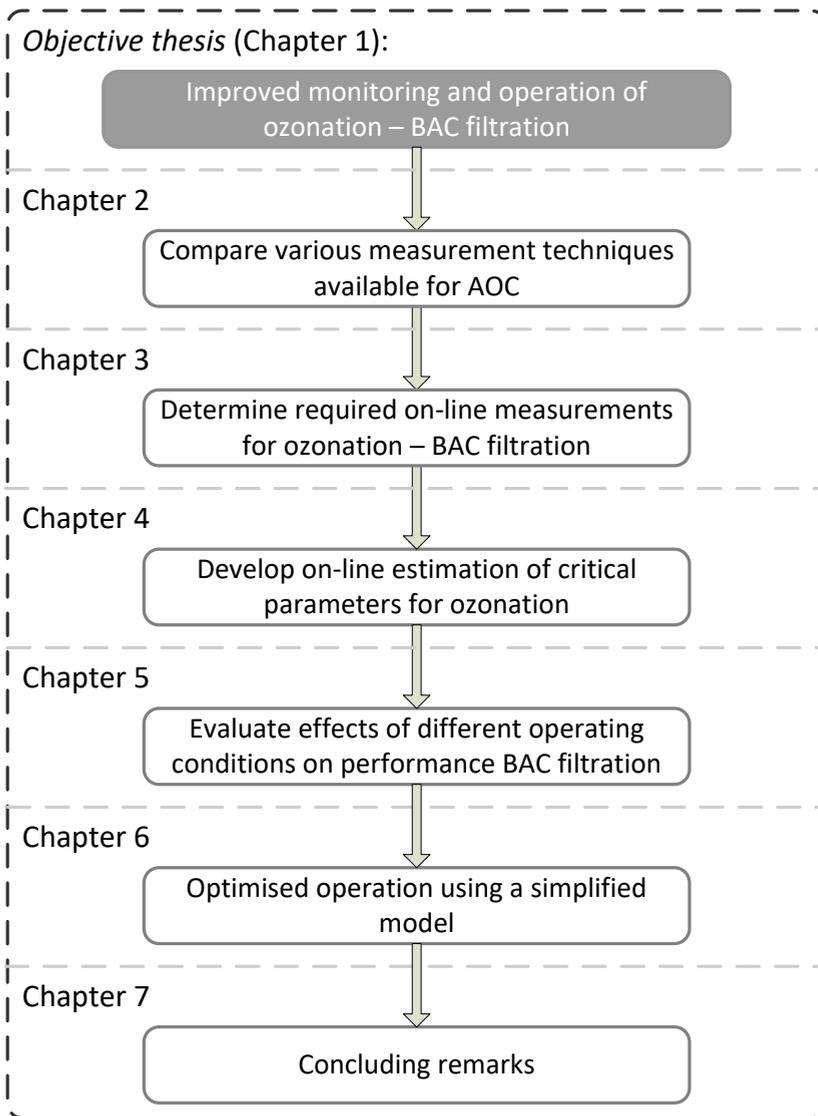
**Figure 1-3** Step-wise approach in developing optimised monitoring and operation strategy for ozonation and BAC filtration.

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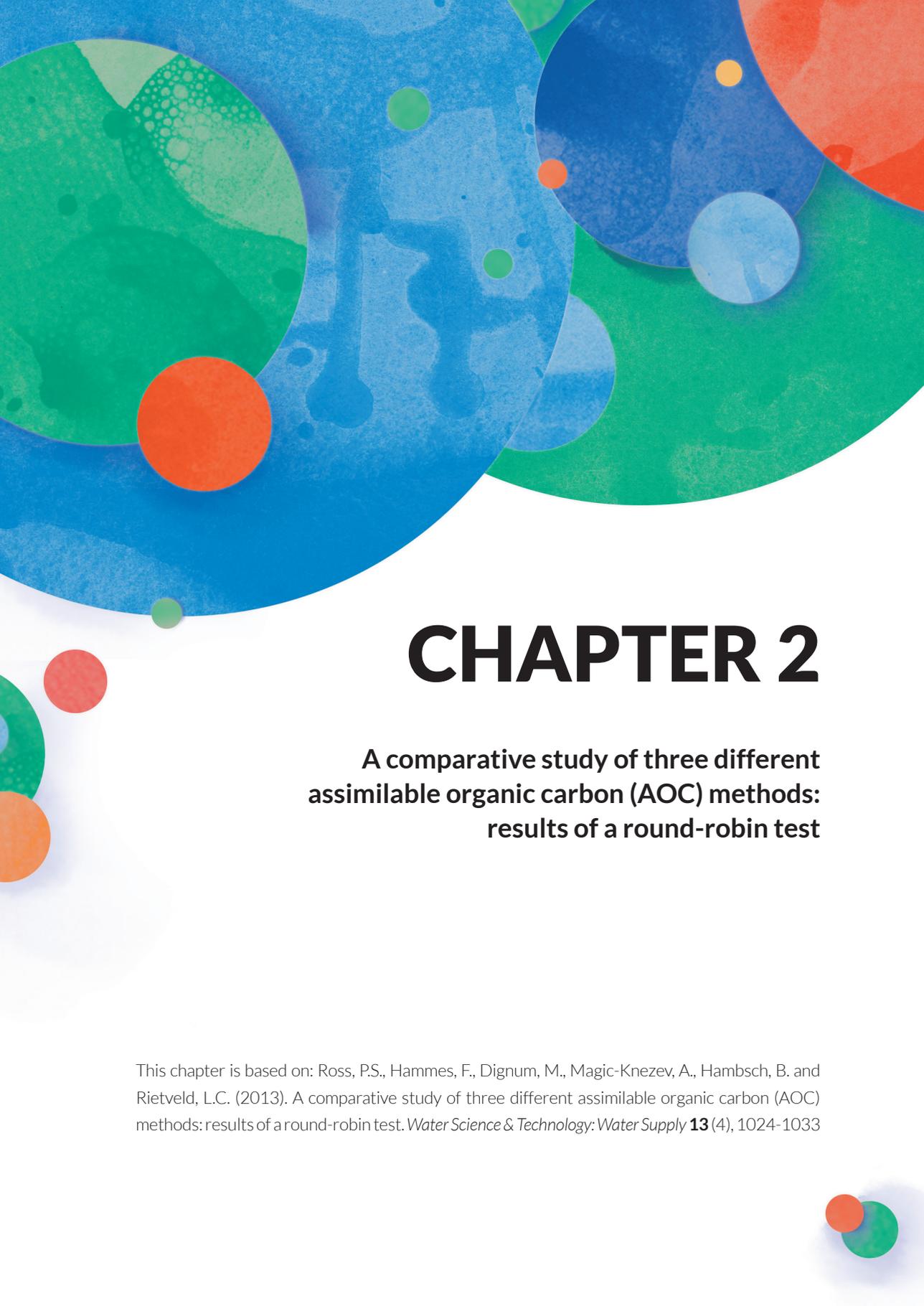
# CHAPTER 2

**A comparative study of three different assimilable organic carbon (AOC) methods: results of a round-robin test**

# ABSTRACT

Easily assimilable organic carbon (AOC) is frequently used for the assessment of biological stability of drinking water, which is an important consideration in the control of bacterial growth in distribution networks. The first AOC bioassay was developed in 1982 and is based on growth of two bacterial strains (Psuedomonas fluorescens P17 and Spirillum spp. NOX) in drinking water relative to their growth on acetate. Much research was subsequently conducted to modify, simplify and increase the speed of the assay which resulted in a number of alternative AOC assays. Application of these assays raises legitimate questions about the comparison of AOC data from different studies. In the present study, a round-robin test was performed to evaluate the correlation between three established AOC methods. A total of 14 water samples covering a wide range of AOC concentrations were analysed with the original "van der Kooij" method, the "Werner & Hambsch" method and "Eawag" method. Good correlations were found between AOC concentrations measured with the various methods. The data suggest an acceptable compatibility between different AOC methods, although deviations between the methods call for careful interpretation and reporting of AOC data.

# INTRODUCTION

Production of biologically stable drinking water is important to control bacterial growth and the deterioration of drinking water quality in distribution systems that are either not chlorinated or chlorinated at low doses. Microbial growth requires carbon (C), nitrogen (N) and phosphorus (P) in a typical ratio of 100:10:1 (C:N:P), and therefore it is assumed that in most waters organic carbon is the growth limiting nutrient for bacteria (Escobar *et al.* 2001, Liu *et al.* 2002) The readily available carbon for cell growth is also referred to as easily assimilable organic carbon (AOC). The first assay for AOC determination was developed by van der Kooij *et al.* (1982) and was based on the growth of *Pseudomonas fluorescens* strain P17 on endogenous substrate in a sample. In this assay, the AOC concentration, expressed as "acetate-carbon equivalents", is calculated from the maximum concentration of *P. fluorescens* strain P17 and the growth yield of this bacterium on sodium acetate as a sole carbon source. *P. fluorescens* strain P17 is capable of utilizing many of the easily biodegradable compounds: amino acids, carboxylic acids, hydrocarboxylic acids, alcohols and carbohydrates (excluding polysaccharides) (Stanier *et al.* 1966). However, some compounds, such as oxalic acid, which is produced during ozonation, cannot be degraded by P17, and therefore *Spirillum* spp. strain NOX was later added to the assay (van der Kooij and Hijnen 1984). Since the development of the first AOC bioassay, much research has been conducted to modify, simplify and increase the speed of the assay. A schematic overview of the important steps of an AOC assay and some of the proposed modifications to the "van der Kooij" method by different studies is given in Table 2-1.

The essential modifications concern sample pre-treatment, type of inoculum, growth measurement, incubation temperature and factors for the conversion of cell numbers into acetate-C equivalents as illustrated by Table 2-1. It is evident that the differences between assays are substantial and would not only alter the use (or practical aspects) of the assay, but also potentially the outcome of the assay.

In the present study a round-robin test with 14 water samples, taken from drinking water treatment plants, covering a wide range of AOC concentrations (4-130 µg/L acetate-C equivalents) was performed using three well-established AOC methods to elucidate the differences between results obtained with different assays. The assays applied were (1) the original "van der Kooij' assay (van der Kooij and Hijnen 1984, van der Kooij *et al.* 1982), (2) the "Werner & Hambsch" assay (Hambsch and Werner 1990, Werner and Hambsch 1986) and (3) the "Eawag" assay (Hammes *et al.* 2010a, Hammes and Egli 2005). By analysing the same samples with different methods, the study also investigated whether the various methods, provided comparable AOC concentrations.

**Table 2-1** Overview modifications made to the original AOC method by different researchers.

|  | van der Kooij *et al.* (1982) | Werner & Hambsch (1986) | Stanfield & Yago (1987) |
|---|---|---|---|
| **Sample preparation** | Pasteurization at 60 °C for 0.5 hours | Filter sterilization | Filter sterilization |
| **Inoculation** | 2 known strains; P17 and NOX | Inoculum retrieved from filter | Inoculum retrieved from filter |
| **Incubation** | 15 °C for 5-25 days | 20 °C for 3-5 days | 22 °C |
| **Growth measurement** | Plating | Turbidity at 12° forward scattering | ATP |
| **Conversion/ yield values** | $4.6 \times 10^6$ P17 $1.2 \times 10^7$ NOX | 2.3 ppm per 1 mg/L Acetate-C | N/A* |

*N/A indicates that the information is not available

**N/C indicates that no changes were made in the method compared with the 'van der Kooij' method

| | Kemmy *et al.* (1989) | Kaplan *et al.* (1993) | LeChevallier *et al.* (1993) | Haddix *et al.* (2004) | Hammes & Egli (2005) |
|---|---|---|---|---|---|
| | Filter sterilization | Pasteurization at 70 °C for 0.5 hours | Pasteurization at 70 °C for 0.5 hours | N/C** | Filter sterilization |
| | 4 species; *Pseudomonas Fluorescens Curtobacterium* sp. *Corynebacterium* sp. Unidentified coryneform | N/C | N/C | Bioluminescent derivatives of AOC test bacteria; P17 I5 NOX I3 | Natural inoculum |
| | 20 °C for 6 days | N/C | 22 °C for 2-4 days | N/C | 30 °C for 3-4 days |
| | N/C | N/C | ATP | ATP luminescence | Flowcytometry TCC |
| | N/A | N/A | N/A | N/A | $1 \times 10^7$ cells |

# MATERIAL AND METHODS

## Sampling locations

All samples were taken at two Waternet drinking water production locations, Leiduin (LDN) and Weesperkarspel (WPK). Waternet is the water cycle company of Amsterdam and surrounding areas, in the Netherlands. In total 14 samples were taken at different locations in the full-scale and pilot-scale treatment trains, summarized in Table 2-2. The treatment schemes of both locations are similar, however the raw water source and pre-treatment are different resulting in different water qualities. Location LDN receives water from the river Rhine, pre-treated by coagulation, sedimentation and rapid sand filtration. The water is further treated by dune infiltration and abstracted after a mean residence time of about 90 days. WPK raw water originates from seepage water from the Bethune polder, a peat-rich area that gives the water a relatively high natural organic matter concentration. The water is pre-treated by coagulation and sedimentation, followed by about 100 day's retention in a lake reservoir. Subsequently it is filtered over rapid sand filters (sample 2). Both treatments consist of ozonation ($O_3$), pellet softening (PS) (samples 9 and 10 for WPK and sample 6 for LDN), biological activated carbon filtration (BAC) (sample 5 for WPK and sample 3 for LDN) and slow sand filtration, with the difference that the post treatment at LDN is preceded by rapid sand filtration (sample 7). At the WPK production location, a pilot plant (WPK-PP) consisting of the same treatment steps as the full scale plant was also sampled. One of the experiments in this pilot plant involved increasing ozone dosage above standard operational values, providing highly oxidized samples (samples 12, 13 and 14). Additionally, at the pilot plant, a fluidized ion exchange (FIX) system (samples 1 and 8) was being tested to reduce the organic matter loading before ozonation (Grefte *et al.* 2011).

The samples covered a broad range of AOC concentrations present in drinking water treatment, with high and low NOM concentrations. In addition, the samples were also taken after different types of treatment, representing oxidised, non-oxidised, biodegraded, non-biodegraded samples and thus different organic carbon compositions.

## Sampling

The samples were taken according to the protocol of the relevant method. In short, samples for analyses according to the "van der Kooij" method were taken in 1L Erlenmeyer flasks with glass stoppers. Flasks were rinsed overnight in acid and subsequently heated at 550 °C for 6 hours. Flasks were filled to 600 mL, without pre-washing. Samples for the analyses according to the "Werner & Hambsch" method were taken in 1L Schott bottles with plastic caps. The bottles were soaked for 12 hours in detergent followed by 10 rinses with hot water and 3 rinses with de-ionised water. The bottles were pre-washed 2 times after which they were filled to 2 cm under the cap. The samples that were analysed according the "Eawag" method were taken

in 100 mL Schott bottles with Teflon-coated plastic caps. Bottles were rinsed in acid (HCl, 1 M, overnight) and subsequently heated at 500 °C for 4 hours. The caps were rinsed in a 10 % sodium persulfate solution at 60 °C for at least 1 hour. The bottles were filled to 2 cm under the cap without pre-washing.

**Table 2-2** Water quality aspects and AOC results measured with "van der Kooij (VdK), Werner & Hambsch (W&H) and Eawag" method of the samples taken at Weepserkarspel (WPK), Weesperkarspel pilot plant (WPK-PP) and Leiduin (LDN).

| Sample # | Location | $O_3$-dose [mg/L] | DOC [mg/L] | Temp [°C] | AOC VdK [µg-C/L] | AOC W&H [µg-C/L] | AOC Eawag [µg-C/L] |
|---|---|---|---|---|---|---|---|
| 1 | After FIX (WPK-PP) | 0.0 | 1.2 | 21 | 4 | 13 | 26 |
| 2 | Before $O_3$ (WPK) | 0.0 | 6.0 | 21 | 8 | 13 | 28 |
| 3 | After $O_3$-PS-BAC (LDN) | 0.7 | 1.0 | 17 | 9 | 10 | 10 |
| 4 | Before $O_3$ (WPK) | 0.0 | 6.3 | 20 | 10 | 16 | 16 |
| 5 | After $O_3$-PS-BAC (WPK) | 2.4 | 4.8 | 20 | 17 | 16 | 27 |
| 6 | After $O_3$ – PS (LDN) | 0.7 | 1.7 | 17 | 30 | 24 | 35 |
| 7 | Before $O_3$ (LDN) | 0.0 | 2.6 | 17 | 34 | 73 | 57 |
| 8 | After FIX - $O_3$ (WPK-PP) | 0.9 | 1.4 | 21 | 48 | 66 | 63 |
| 9 | After $O_3$-PS (WPK) | 2.3 | 2.1 | 21 | 51 | 70 | 77 |
| 10 | After $O_3$ – PS (WPK) | 2.4 | 5.2 | 20 | 59 | 92 | 78 |
| 11 | After $O_3$ (WPK) | 2.3 | 2.1 | 21 | 64 | 140 | **211** |
| 12 | After $O_3$ (WPK-PP) | 4.0 | 5.4 | 21 | 97 | 267 | 82 |
| 13 | After $O_3$ (WPK-PP) | 2.5 | 6.2 | 20 | 120 | 218 | 160 |
| 14 | After $O_3$ (WPK-PP) | 4.0 | 5.7 | 20 | 130 | 269 | 140 |

No addition of thiosulfate (or similar compounds) was necessary to quench ozone after the ozonation step, since the contact times in the ozonation chambers were sufficiently long that no residual ozone was present at the sampling points. All samples were taken from stainless steel taps with continuous water flow. Samples were transported below 4 °C to the laboratories and were analysed within 24 hours. All samples were taken in duplicate.

**AOC analysis: the "Van der Kooij" method**

Analysis was carried out as described by van der Kooij *et al.* (1982), van der Kooij and Hijnen (1984) and Standard Methods number 9217 (Eaton *et al.* 2005). In short, after pasteurization, samples (600 mL) were inoculated with an AOC-free suspension (ca. 500 cfu/mL) of pre-cultured cells of P17 and NOX. In contradiction to the protocol described in *Standard Methods*, no nutrient salts were added, since it generally assumed the water is not limited in nutrients other than carbon (personal communication with the laboratory). Inoculated samples were incubated at

15° C without shaking until the maximum number of colony forming units per millilitre (cfu/mL) was attained (analysis of cfu/mL was done once every 2 days over a period of 15 to 30 days). The AOC concentration was calculated from the maximum concentration of each of the two strains in a sample and the conversion factors (growth yield) of $4.6 \times 10^6$ cfu/μg-C for *P. fluorescence* strain P17 and $1.2 \times 10^7$ cfu/μg-C for *Spirillum* spp. NOX. AOC concentration was expressed as μg acetate-C equivalents/L. The detection limit was 1 μg acetate-C equivalents/L.

### AOC analysis: the "Werner & Hambsch" method

Analysis was carried out as described by Werner and Hambsch (1986) and Hambsch and Werner (1990). The method is based on correlation between turbidity and total bacterial cell number after growth of an undefined indigenous inoculum in a water sample. In short, samples were filtered (0.2 μm), placed into a cuvette, and a sterile carbon-free nutrient salt solution was added. To minimize the potential addition of organic carbon from the filters, those were rinsed prior to use with 1 L of ultra-pure water. Moreover, in every run of samples, a negative control (ultra-pure water) was analysed in parallel. The sample (250 mL) was inoculated to about 5 x $10^4$ cells/mL with a suspension of bacteria collected from the filter used for pre-treatment. The cuvette was incubated in a specially modified turbidimeter at approximately 22 °C. Turbidity was measured every 30 minutes for 2-4 days by applying 12-degrees forward scattering on a specifically designed instrument, until stationary phase was reached. Acetate-C-equivalents were calculated from the turbidity increase using the turbidity yield on acetate-C (1 mg/L Acetate-C: 2.3 ppm turbidity increase). The detection limit was 10 μg/L acetate-C-equivalents. Also, DOC-removal and total cell number increase were determined by analysing DOC and total cell number (epifluorescence microscopy after staining with acridine orange (Hobbie *et al.* 1977), of the samples in the cuvettes at the start and at the end of the experiments.

### AOC analysis: the "Eawag" method

Analysis was carried out according to the method described by Hammes and Egli (2005). In short, water samples were filtered (0.2 μm), after which the filtered sample (20 mL) was inoculated with an undefined indigenous bacterial community obtained from non-chlorinated drinking water. The filters were rinsed with 1L nano-pure water prior to use to minimize potential carbon contamination during filtration. The samples were incubated at 30°C until the bacteria reached stationary phase (2-4 days). Bacterial cells were counted by flow cytometry as described elsewhere (Hammes *et al.* 2008). The AOC concentration (expressed as μg C) was calculated based on the maximum cell concentrations (cells/mL) using a conversion value of $1 \times 10^7$ cells/(μg C) (Hammes *et al.* 2010a, Vital *et al.* 2007). The detection limit of the assay was about 10 μg/L.

**Statistical methods**

In this research a total of 14 ($n$= 14) sampling locations were selected across the treatment train in order to compare the performance of the three different methods for a wide range of AOC values. At each sampling location, triplicate samples were taken to check for variation of each method at the same AOC-value. As the triplicate samples taken at each sampling location were statistically interdependent of each other, the paired $t$-test should be applied to determine the statistical difference between the method results. The use of the paired t-test is only legitimate if the sample distribution of different methods was normal, which was affirmed by applying the Kolmogorov Smirnov test (Drezner *et al.* 2010), to the dataset containing the samples from all locations. The datasets were checked for outliers by applying the analysis of variance (ANOVA) test. If the $p$-value, determined by the tests, was larger than 0.05 it could be concluded that with a confidence interval of 95% the tested hypothesis was not significantly different. All statistical analyses were performed with the statistical toolbox available within Matlab® (Matlab 2009). Quality control was performed using blank controls.

# RESULTS

### AOC concentrations

In Table 2-2, AOC concentrations measured according to the three AOC assays are provided together with other water quality parameters of the samples. The samples are organized according to the lowest (4 µg-C/L) to highest (130 µg-C/L) AOC concentration determined with the conventional "van der Kooij" method. This range of values is considered typical for drinking water treatment and distribution systems (Escobar and Randall 2001).

Statistical analysis of the dataset indicated that AOC values determined by the "Eawag" method contained one outlier. This outlier (value = 211 µg-C/L, indicated in bold in Table 3-2) was ignored in the comparison made below.

A statistical comparison of the datasets obtained by the "van der Kooij" method and "Eawag" and "Werner & Hambsch" methods resulted in $p$-values of 0.01 and 0.04, respectively, indicating a significant difference between the van der Kooij method and the other two methods. Comparison between the datasets for the "Eawag" and "Werner & Hambsch" methods resulted in a $p$-value of 0.28, indicating that the results of the methods did not significantly differ.
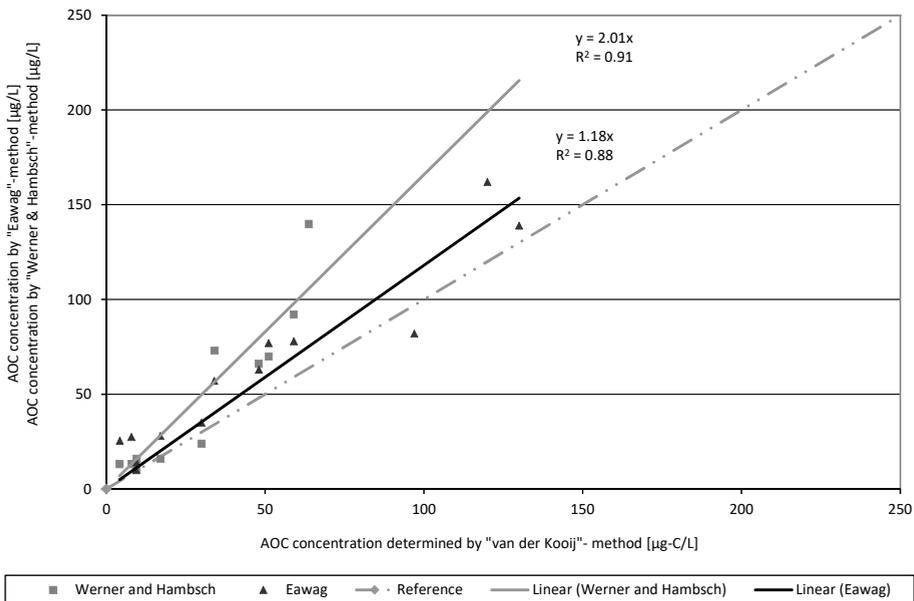


**Figure 2-1** AOC concentration measured with "Werner & Hambsch" and "Eawag"-methods compared to the "Van der Kooij"-method.

The AOC concentrations for the "Eawag" and "Werner & Hambsch" methods showed a good correlation with the "van der Kooij" method (Figure 2-1). However, both the "Werner & Hambsch" method and the "Eawag" method showed higher AOC results than the "van der Kooij" method (2.0 times and 1.2 times, respectively; Figure. 2-1).

In Figure 2-2 the increase in cell numbers during the "Werner & Hambsch" and "Eawag" assays versus the "van der Kooij" assay is given. As illustrated, the samples with the highest AOC concentrations measured by "Werner & Hambsch" were left out of this dataset. In this way only the effect of the use of a natural inoculum is illustrated, which is discussed in more detail below. The observed/found correlations were significant.
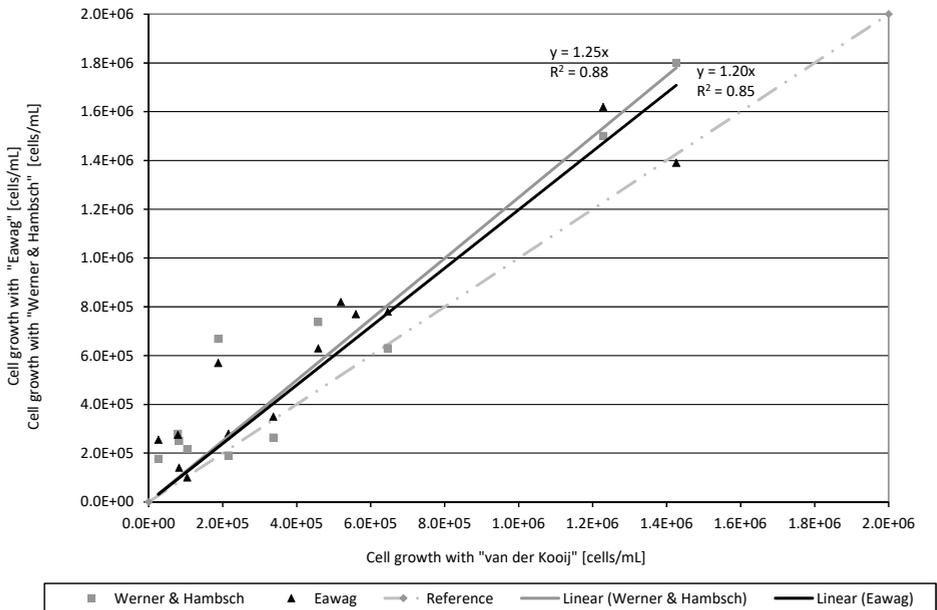


**Figure 2-2** Increase in cell counts during AOC assays.

The application of natural inoculum leads to an increase in cell numbers of approximately 20% (slopes of the linear regression lines are 1.20 and 1.25). In both assays, culture independent measurement of growth is applied and viable but not culturable cells will also contribute to the outcome. This is also reflected in the lower sensitivity of the two methods in the low range of AOC concentration beneath 10 µg/L.

# DISCUSSION

Because AOC assays are based on bacterial growth, variations in the methodology (e.g. inoculum, incubation temperature, measurement technique, conversion factors) can have a profound impact on the outcome. Below we discuss a number of critical steps in detail, being pre-treatment, incubation volume, inoculum and yield and conversion values.

**Pre-treatment**

Pre-treatment is applied to remove or collect indigenous bacteria. The use of pasteurization versus filtration is discussed. Possible disadvantage of pasteurization is that it can change the organic carbon quality of the sample (denaturation of proteins) as well as the inorganic quality (precipitation of minerals in the form of carbonates and phosphates). Disadvantage of filtration is possible contamination with organic carbon from the filters and materials used in filtration process. Therefore, in the "Werner & Hambsch" method, a negative control is analysed in parallel. Filtration is also not a sterilization step (Wang *et al.* 2007), and can therefore only be used in assays where a natural microbial community is used for the inoculum (some natural contamination would not matter). Depending on the method used for growth detection, either pasteurization or filtration should be used. Filtration is required in the methods of "Werner & Hambsch" and "Eawag", in order to remove particles/bacteria that can interfere with their detection methods. For the "van der Kooij" method pasteurization is needed since filtration is not sterilization. It was not possible to identify if any differences in the results of the round robin test were introduced because of the different pre-treatment methods. Higher cell yields in "Werner & Hambsch" and "Eawag" method than yield in "van der Kooij" method may be partly related to the pre-treatment, but other factors like difference in the type of inoculum and addition of inorganic nutrient salts seem to be more relevant.

**Incubation volume**

The different assays prescribe the use of differently sized and shaped bottles to incubate the water samples in. According to Krammer *et al.* (2008) the volume for batch growth should be at least 800 mL to decrease the possibility of the 'bottle effect', which could influence the bacterial growth. However, Hammes *et al.* (2010b) showed through several experiments that the size and shape of the bottle does not influence the bacterial growth such that it should be taken into account. Therefore, it was assumed that incubation in different bottles and volumes did not interfere with the retrieved results.

**Inoculum**

The inoculum (composition and quantity) can affect the outcome of the AOC assay profoundly. This is because different bacteria consume a different range of substrates (Vital *et al.* 2010), thus the range of targeted AOC compounds will be determined by the inoculum (Sack *et al.* 2011).

Moreover, as discussed below, different bacteria have profoundly different yields when consuming organic carbon, even for the same substrate. The type of inoculum used in the three assays varied from a known set of bacteria ("van der Kooij" method) to undefined indigenous bacteria ("Eawag" and "Werner & Hambsch" method). The advantage of the "van der Kooij" method is that it allows standardization of the assay. However, Huck (1990) and Servais *et al.* (1987) discussed already that the application of a known set of two species might not cover the full growth potential, since these species do not represent the whole spectrum a natural community covers. In this respect, recent research in the "van der Kooij group" suggested the additional use of *Flavobacterium johnsoniae* strain A3 that utilizes oligo- and polysaccharides (Sack *et al.* 2011). The "Werner & Hambsch" and "Eawag" methods used a natural inoculum, of which the first assay retrieved the indigenous bacteria from the filtered raw water sample taken at Weesperkarspel treatment plant, thus containing a natural occurring inoculum. The "Eawag" method used a natural microbial consortium consisting of a mixture of non-chlorinated tap water and bottled drinking water. While the use of indigenous drinking water communities has the advantage that it potentially broadens the substrate spectrum range, it has the disadvantage of being undefined, and thus more difficult to standardize. This could introduce a deviation in the values obtained, with the expectation that the results of AOC assays with a natural inoculum will be higher. Both the "Werner & Hambsch" and "Eawag" assays resulted in higher final cell numbers (25 and 20%, respectively; Figure 2-2), which confirms the idea that when a natural inoculum is applied, a broader range of substrates can be utilized, and consequently the AOC concentrations found would be higher.

### Incubation temperature

Effect of incubation temperature on yield could not be clearly derived from the obtained data. Although "Eawag" method applied highest incubation temperature, highest cell yields were observed in "Werner & Hambsch" method suggesting that incubation temperature, for this range, is not affecting maximal cell yield.

### Yield and conversion values

AOC assays convert measurements of cell numbers to equivalent carbon concentrations. This is an indirect approach, firstly since organic carbon itself is not measured, and secondly because the yield of different bacteria on different organic carbon substrates varies. As a result, some AOC assays convert growth relative to the growth on a pure AOC substrate such as acetate or oxalate. In the three assays compared in the present study, the conversion to (acetate-) C equivalents is retrieved by different yield values. The conversion values of "van der Kooij" method is $4.6 \times 10^6$ cfu/ μg acetate-C for P17 and $1.2 \times 10^7$ cfu/ μg acetate-C for NOX. Depending on the type of substrate the species P17 and NOX reach different levels of maximum growth. The conversion value of "Werner & Hambsch" was determined with the turbidity yield on acetate, 1 mg/L acetate-C equal to 2.3 ppm turbidity increase. The conversion value of "Eawag" method is constant with $1 \times 10^7$ cells/μg C. Hence, it is evident that conversion of cell concentrations (Figure 2-2) can potentially

lead to considerable differences in final AOC concentrations. It was shown that a natural inoculum resulted in higher increase in cell numbers. A difference in results between the AOC concentration determined by "van der Kooij' method and the "Eawag and Werner & Hambsch" method of 18 and 101% was found (Fig. 2-1). Based on the inoculum it was shown that a difference in cell yield of respectively 20 and 25% was introduced. When comparing the conversion values of the "van der Kooij" method with the "Eawag" method it is seen that for P17 the conversion values of Eawag are 117% higher, while for NOX these values are 17% lower than "van der Kooij" conversion values. The conversion of the cell numbers into equivalent carbon concentration resulted in a decrease in difference between the "van der Kooij" method and the "Eawag" method of 10%, indicating that NOX was dominantly present in the samples determined by the "van der Kooij" method. Since the conversion value of the "Werner & Hambsch" method is related to ppm instead of cell numbers it is difficult to quantify the effect of conversion value. However, the indicated difference between AOC concentrations determined by "van der Kooij" and "Werner & Hambsch" of 101% in relation to 25% (introduced by natural inoculum) does show that the applied conversion values might introduce a high difference. However, there is one other aspect that might play an important role in the difference between the cell numbers and AOC concentration, which is the addition of nutrient salts applied solely in the "Werner & Hambsch" method, discussed in detail below. When taking this effect into consideration and discarding the highest AOC concentrations it was found that the conversion values account for an increase from 25 to 66% (data not shown).

**AOC versus growth potential**

Multiple factors aside from the organic carbon content of a water sample determine the rate and extent of bacterial growth. The "Werner & Hambsch" method was the only assay in which a carbon free nutrient salt solution was added, which would ensure that AOC was indeed the limiting nutrient. If the water samples would be limited in a nutrient other than carbon this could result in higher results that represent the actual AOC concentration. The other two methods would represent the actual growth potential of the water if no additional source of nutrients would be introduced into the system. Several researchers have shown that humic rich surface water pre-treated with coagulation were limited in phosphate instead of carbon (Juhna and Rubulis 2004, Sathasivan *et al.* 1997), since during coagulation and sedimentation most of the phosphate was removed from the water. Without the addition of carbon free nutrient salt solution, it is not ensured anymore that the AOC is the limiting nutrient.

In Figure 2-1 the "Werner & Hambsch" method differs mostly in the higher ranges of AOC concentrations. The samples in these ranges originate from humic rich surface water that was pre-treated with coagulation-sedimentation, removing organic compounds as well as phosphate, and then ozonated, increasing the amount of readily available carbon. The phosphate levels in these waters were below detection limit, indicating a possible limitation in phosphate in the samples instead of organic carbon.

# CONCLUSIONS

A round-robin test was performed to evaluate correlation between three established AOC assays, "Werner & Hambsch", "Eawag" and "van der Kooij" method. An AOC assay consists of several steps, such as sample pre-treatment, incubation volume and temperature, inoculum, growth measurement, yield and conversion values, which may all contribute to variation in measured values. The use of indigenous bacteria instead of a set of two known strains resulted in an increase in cell growth of approximately 20%. In the application of culture independent measurement of growth, viable but non-culturable cells may contribute to the final outcome. The sensitivity of these assays is lower (detection limit is 10 μg/L) than for the "van der Kooij" method in which plating is used to determine growth (detection limit is 1 μg/L). The addition of a carbon free nutrient salt solution resulted in some samples in higher concentrations since samples seemed to be limited in nutrients other than organic carbon. The overall results of the round robin test suggest an acceptable compatibility between the different AOC methods, although deviations between the methods call for careful interpretation and reporting of AOC data.

# ACKNOWLEDGEMENTS

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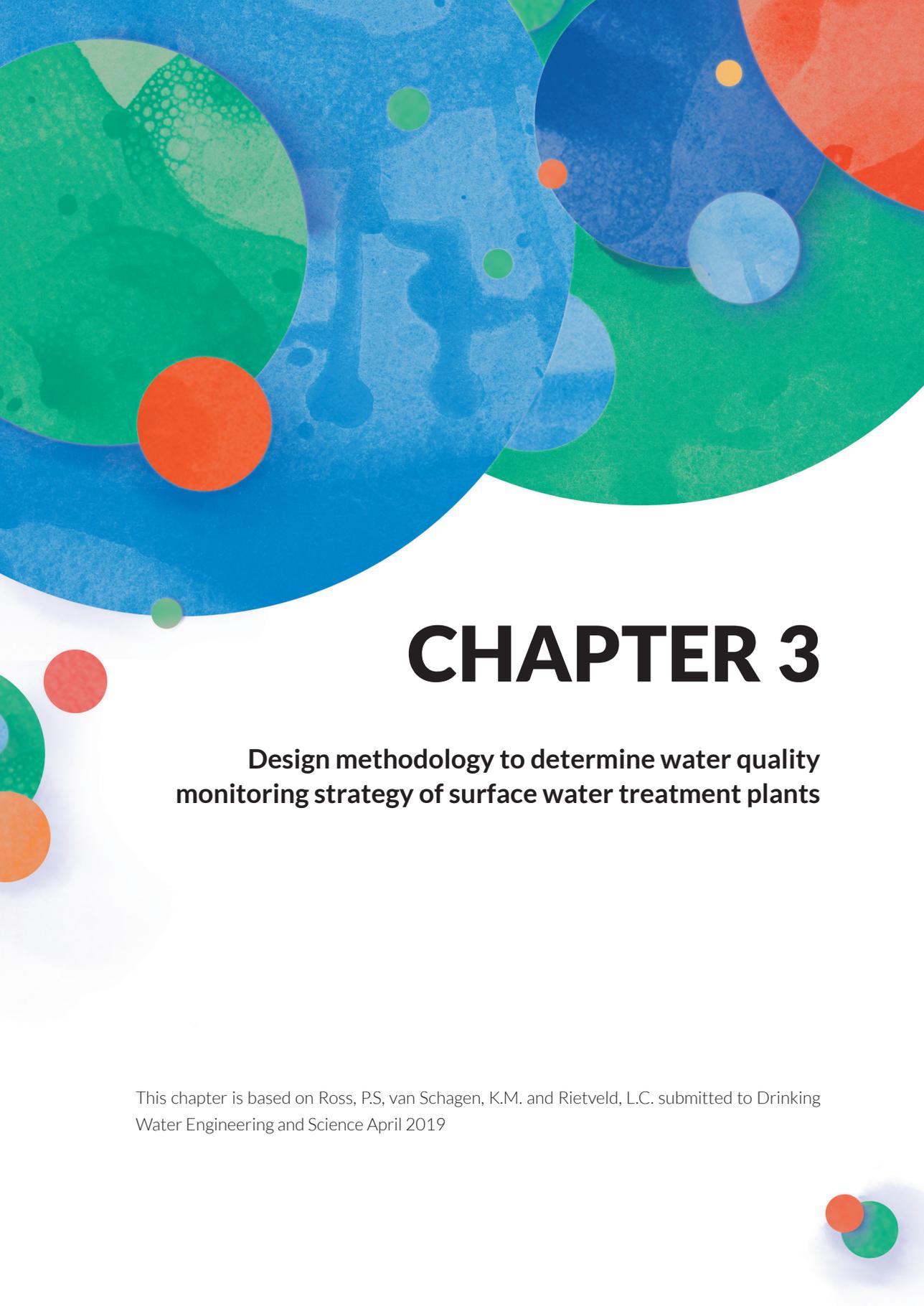
# CHAPTER 3

**Design methodology to determine water quality monitoring strategy of surface water treatment plants**

# ABSTRACT

Primary goal of a drinking water company is to produce safe drinking water fulfilling the quality standards defined by national and international guidelines. To ensure the produced drinking water meets the quality standards, sampling of the drinking water is carried out on a regular (almost daily) basis. It is the dilemma that the operator wishes to have a high probability of detecting a bias while minimizing his measuring effort. In this paper a seven step design methodology is described on how to come to an optimised water quality monitoring scheme. It was shown that the previous on-line monitoring program of a WTP could be optimised. Besides using soft-sensors as surrogate sensors for parameters currently not available on-line, they can also provide a cost effective alternative when used to determine multiple parameters required through one single instrument.

# INTRODUCTION

Primary goal of a drinking water company is to produce safe drinking water fulfilling the quality standards defined by national and international guidelines. To ensure the produced drinking water meets the quality standards, sampling of the drinking water is carried out on a regular (almost daily) basis.

Common practice is that (drinking) water treatment plants (WTPs) are designed in such a robust way that the effluent quality can be guaranteed without direct control on the incoming water quality (Bosklopper *et al.* 2004, Vanrolleghem and Lee 2003). A WTP consists of several individual treatment steps placed in series, with every treatment step being responsible for the removal (or addition) of certain compounds. All the interactions between the processes ask for an integrated plant-wide approach, optimising the effluent quality and operational costs (Bosklopper *et al.* 2004, Nopens *et al.* 2010).

Van der Helm *et al.* (2008b) investigated three possible objectives for plant-wide optimisation of operation of existing WTPs and concluded that the objective for integrated optimisation should be the improvement of water quality and not a reduction in environmental impact and costs. The effects of these latter two are negligible compared to the environmental impact and costs for the society as a whole when more bottled water is used for drinking water as a result of insufficient (confidence in) tap water quality.

Direct control of water quality becomes more and more important as a result of more stringent criteria and the deterioration of source water (van Schagen *et al.* 2010, Vanrolleghem and Lee 2003). Especially WTPs that use surface water as a source, experience increased pollution in the form of organic micropollutants and increased organic matter concentrations present in the surface water bodies (Bertelkamp *et al.* 2014, Verliefde *et al.* 2007). Besides, large fluctuations in water temperature and water quality can be noticed, which increases the need for improved monitoring and operation of the WTP.

Nowadays, many WTPs are monitored and controlled by SCADA (Supervisory Control and Data Acquisition) systems (Jansen *et al.* 1997). The functions of SCADA systems for WTPs include: (1) collection of on-line measurement data, (2) surveillance of the measuring chain including operations and (3) process control and other relevant operations (Gunatilaka and Dreher 2003). On-line measurements are the first indicators that give the operators information about the state the plant is in. Besides on-line measurements, laboratory measurements are taken at a regular interval to check that the produced drinking water meets the quality standards set by national and international guidelines. However, the time between sampling and results takes at least one day. This delay in results and interval between measurements makes it difficult to use

the laboratory measurements for real-time control of a treatment plant (van de Ven *et al.* 2010). In addition, it should not be underestimated that erroneous control and measurement devices can also cause disturbances (van Schagen *et al.* 2010).

Retrieving reliable and robust on-line information is therefore important in order to be able to control a WTP. This information can be retrieved from on-line sensors that measure a specific parameter directly, but also from generic sensors that give indirect information. Roccaro *et al.* (2008), Rieger *et al.* (2004) and van den Broeke *et al.* (2008) showed the ability of UV-Vis spectra measurements, measuring the absorbance of ultraviolet or visible light, to estimate different parameters such as chlorine decay, nitrite and nitrate, ozone and assimilable organic carbon (AOC) concentrations. These estimations were derived from algorithms developed, based on a change in UV-Vis absorbance during a treatment step and laboratory measurements, using principal component analysis followed by partial least squares regression. These types of generic sensors are so-called soft-sensors, sensors that require software to give the required information. Juntunen *et al.* (2013) developed a soft-sensor to predict the turbidity in treated water and to find the most significant variables affecting turbidity.

A soft-sensor can be developed in different ways, based on black box, grey box or white box modelling. The black box approach is characterized by an empirical relation between the input and output. The relations are derived from historical, full-scale plant, data. Thus, such a soft-sensor can only be applied in the situation where it has been developed for, since a black box model is not valid when a process is operated outside the boundaries of calibration (Kano and Nakagawa 2008). Since the operation of a WTP is relatively constant, the calibration dataset is normally rather limited, hampering the application of black box modelling. Grey box models are a combination of black box models and white box models, such that it contains some more insight into the system through the white box model, while still some parts of the model are data driven (Zyngier *et al.* 2001). White box models mathematically describe the physical-chemical processes that take place in the treatment process. Developing these models is time consuming, however, when developed, the process knowledge on the processes are captured, leading to more generically applicable models (van der Helm and Rietveld 2002).

Optimised control can only be reached if there is a high probability of detecting a bias in the operation of the WTP. At the same time, from an economical perspective, the data should be obtained with minimal measuring efforts and costs. Understanding the requirements with respect to on-line monitoring and data reliability is a first step towards direct control of the drinking water production based on the incoming water quality. Therefore, in this paper a design methodology is described on how to come to an optimised water quality monitoring scheme to support direct control. This will be explained by means of a case study for a WTP.

# MATERIALS AND METHODS

**Design methodology**

Van Schagen *et al.* (2010) developed a methodology for the design of a control system for drinking water treatment plants. This methodology was based on experiences with control design procedures for chemical plants and was modified to fit the main objectives of a drinking water treatment plant. In the basis, the same methodology was used for the design of an optimised water quality monitoring scheme. The methodology takes into consideration 1) the objectives, 2) operational constraints and 3) disturbances. These first three steps determine the required water quality parameters. The subsequent steps help to determine the conditions the water quality information should comply with:

1.   Determine treatment step objectives;
2.   Determine operational control options;
3.   Determine water quality parameters taking into consideration both process and control aspects;
4.   Identify process characteristics;
5.   Evaluate available (indirect) measurements;
6.   Determine individual monitoring strategy per treatment step.
7.   Determine integrated monitoring strategy of treatment plant.

*Treatment step objectives*

The treatment step objectives depend on the feed water quality and the type of treatment step considered. The overall objective of a drinking water treatment plant is the production of safe drinking water fulfilling the quality standards defined by national and international guidelines. The main objective of a treatment step for an existing plant should be the focus on water quality and less on the chemical or energy consumption (van der Helm *et al.* 2008b). Therefore, it should be evaluated which parameters, present in the feed water quality, can be influenced per treatment step. In order to do so process knowledge on the different treatment steps is indispensable (Poch *et al.* 2004). Van Schagen (2009) indicated that mathematical models are a powerful tool to evaluate the sensitivity to process objectives and disturbances and help find the appropriate controlled variables.

*Operational control options*

Depending on the design of the treatment step certain operational control options are available to make changes to the treatment process. Examples of operational control options are the change in chemical dosage, flow division and backwash and regeneration frequency. The primary focus was on the operational changes that can be performed within the existing plant lay-out.

### Required water quality parameters

Based on the treatment step objectives and existing operational control options, the water quality parameters that are influenced by the treatment step were determined. Ideally these water quality parameters should be monitored. Besides the water quality parameters that are influenced by a treatment step, there are water quality parameters that influence the efficiency of a treatment step. For example, the water temperature has an effect on the ozone decay rate. The decay rate increases with increasing temperatures (Elovitz *et al.* 2000). This may result in a higher required ozone dose in summer time, taking into consideration that the disinfection requirements are also different with different temperatures.

### Process characteristics

The required monitoring frequency and sensitivity of the selected water quality parameters may also vary depending on the process characteristics. The process characteristics describe the time interval during which changes occur and the order of magnitude in which changes occur. For instance, the contact time in an ozone reactor can vary from a couple of minutes to one hour, depending on the dimensions, while the time between two regeneration cycles of activated carbon typically is expressed in years. These different reaction times require different measurement frequencies. The order of magnitude relates to the required accuracy of the measurement. For example, ozone typically degrades quickly in water due to the reaction with organic compounds in the water. This determines that the required measurement sensitivity and accuracy should be high.

### Evaluate available measurements for the identified water quality parameters

Based on the evaluation of the required water quality parameters and existing process characteristics the available (on-line) measurements should be evaluated. A wide range of measurements exist for determining water quality parameters, from certified laboratory measurements to on-line measurements. Depending on the variability of the process, the turnaround time of laboratory measurements is not always fast enough. To come to an optimal water quality monitoring scheme also on-line water quality sensors should be considered. In this study the following evaluation criteria for the available on-line sensors were assessed:

- Easiness; is the sensor easy to use, is the measuring principle easy to understand;
- Sensitivity; is the measurement range sensitive enough;
- Maintenance; does the sensor require much maintenance;

Costs for laboratory measurements as well as the purchasing and maintenance costs for on-line sensors were indicated. Besides on-line sensors developed to measure one specific parameter, available surrogate sensors, used to estimate a water quality parameter value, and soft-sensors were assessed.

***Determine individual monitoring strategy per treatment step***

The individual monitoring strategy defines which water quality parameters per treatment step should be monitored, with a selected frequency and location. The evaluation, of available measurements for the identified water quality parameters forms the basis for the monitoring strategy, subsequently ranked by the most critical parameters in the treatment plant. Criticality is determined by two factors, 1) parameters of which the measured concentrations are close to the not to exceed limit and 2) parameters that can be potentially harmful to human health.

***Determine integrated monitoring strategy of treatment plant***

The integrated monitoring strategy defines which water quality parameters are monitored, taking into consideration the interaction between the different individual treatment processes. The evaluation, of available measurements for the identified water quality parameters forms the basis for the monitoring strategy, again ranked by the most critical parameters in the treatment plant. The monitoring strategy can be imbedded into the process control strategy to ensure optimised control based on the most critical parameters.

**Case study: Ozonation and biological activated carbon filtration at Waternet**

At the production location Weesperkarspel of Waternet, the water cycle company of Amsterdam and surroundings, ozonation, pellet softening, biological activated carbon (BAC) filtration and slow sand filtration are the main steps in the production of safe drinking water. The feed water is humics rich seepage water from the Bethune polder, which is pre-treated by coagulation, sedimentation, approximately 100 days retention in a lake reservoir followed by rapid sand filtration, before it is transported to the Weesperkarspel treatment plant. At Weepserkarspel, the production of drinking water is roughly divided into two parallel lanes, each consisting of several individual reactors/filters per treatment step. The control actions can be modified at individual level, however, for the purpose of this Chapter it has been chosen to focus on the mixed influent and effluent only and not on the individual reactor/filter level. The treatment processes ozonation and BAC filtration have been evaluated. These processes are frequently applied at surface WTPs and are susceptible to changes in the feed water quality. Besides, these processes have several control options and an interaction between the two processes exists.

Previously, the following on-line measurements were installed to monitor the ozonation and BAC filtration process (Figure 3-1). pH and turbidity were monitored at the influent of the ozonation step. The temperature was monitored in the influent of the BAC filtration. After BAC filtration dissolved oxygen (DO) and pH were measured, and the pressure drop was recorded over each of the individual BAC filters.
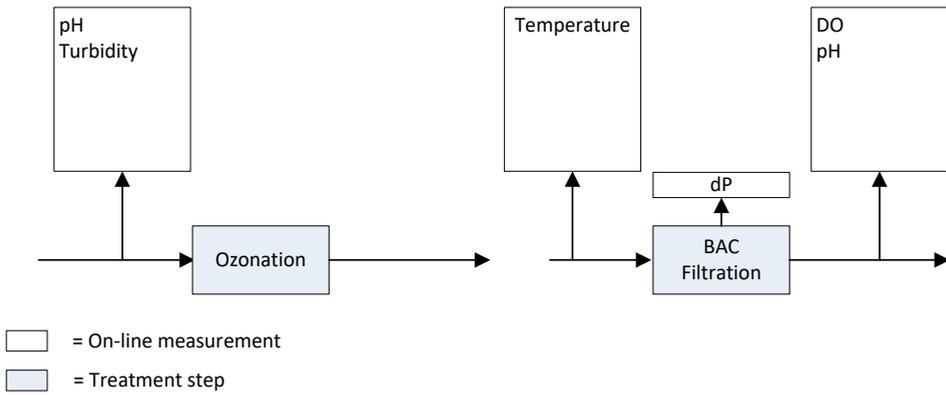
**Figure 3-1** Previous installed on-line measurements ozonation and BAC filtration at Weesperkarspel treatment plant.

# RESULTS

The results of the evaluation of each step, to come to an optimised water quality monitoring scheme, are described below, followed by a discussion on the outcomes of the assessment versus the previous and current monitoring strategy. Research carried out at the pilot plant of Weesperkarspel is used to obtain full understanding of the processes taking place and enabling the determination of the objectives and required water quality parameters.

**Treatment plant objectives**

In general the primary objective of ozonation is disinfection (von Gunten 2003b). Besides, ozonation is frequently used for the oxidation of organic micro pollutants, taste, odour and colour producing products and natural organic matter (NOM), transforming higher molecular weight compounds into lower molecular weight compounds. For the ozonation step at Weesperkarspel, the specific objectives are disinfection and oxidation of NOM (van der Helm 2007).

The general objective of activated carbon is the removal of organic micropollutants, removal of precursors of disinfection by-products and the removal of organic compounds causing colour, taste and odour issues (van der Aa *et al.* 2011). When activated carbon is preceded by a pre-oxidation step, the biological activity in the water and on the activated carbon is enhanced, resulting in BAC filtration. At the same time ozonation increases the polarity, resulting in a decrease in adsorption capacity (Sontheimer *et al.* 1988). As a result, NOM is removed through both biodegradation and adsorption. At Weesperkarspel the purpose of BAC filtration is the removal of organic matter, to prevent biological growth in the distribution system and to remove toxicity, taste and odour causing compounds (Graveland 1996). Besides, the BAC filters remove the carry-over from the preceding pellet softening step.

**Operational control options**

The production flow is controlled by the demand for drinking water. The buffering capacity in the treatment plant is the clean water storage reservoirs situated before the water is distributed to the customers (van Schagen *et al.* 2010). To ensure sufficient reliability, the treatment plant is set up in a redundant way with multiple lanes operated in parallel. It is possible to change the flow division over the different production lanes, however this is only done when one of the lanes has less treatment capacity or is out of production due to e.g. maintenance. Therefore, in this case, production flow was not considered as a control action.

The only remaining control action for ozonation is the ozone dosage. The ozone dosage is obtained by a combination of ozone in gas concentration and the gas flow. Both parameters can be adjusted to obtain the desired ozone dosage.

For BAC filtration the control actions within the existing treatment setup are the backwash frequency, currently operated at every couple of days till once a month interval per filter and backwash program, currently a combination of air and water is used. The activated carbon is regenerated every year to three years. Carbon dioxide is dosed before the BAC filters to correct for any high pH resulting from the caustic soda dosage in the pellet softeners. This control action is thus more related to the functioning of the pellet softeners and therefore not included in the overview provided in Figure 3-1. A high pH could negatively affect the biodegradation efficiency (Seredyńska-Sobecka *et al.* 2006) and promotes precipitation of calcium carbonate on the activated carbon grains. Oxygen and caustic soda can be dosed in the effluent of the BAC filters to correct low pH and oxygen concentrations as a result of the biological activity in the filters.

**Required water quality parameters**

As indicated previously, ozone is an unstable oxidant in water. Ozone decomposition in water consists of a fast initial phase (seconds range) and second phase (minutes range) during which ozone concentration decreases via first order kinetics and disinfection of the more resistant pathogenic microorganisms takes place (van der Helm *et al.* 2008a, von Gunten 2003a). A commonly used method to estimate the disinfection during ozonation is by calculating the exposure of pathogens to ozone, expressed as the Ct value, a product of the (residual) concentration of the disinfectant (C), in this case ozone and contact time (t) (WHO 2008).

Water quality parameters that influence the efficiency of the ozonation step are temperature, pH and, for Weesperkarspel relevant, scavengers such as NOM concentration and character (von Gunten 2003a). A measurement commonly used to indicate the NOM concentration is the dissolved organic carbon (DOC) concentration. The DOC concentration is determined by filtering the sample over a 0.45 µm filter and measuring the total organic carbon (TOC) concentration. In order to assess the character of NOM, the specific UV absorbance (SUVA) can be calculated by dividing the UV absorbance measured at a wavelength of 254 nm ($UV_{254}$) by the DOC concentration (Edzwald and Tobiason 1999, van der Helm *et al.* 2008b). These water quality parameters play a role in the ozone dosage required to achieve the desired disinfection and should therefore be monitored. For Weesperkarspel it was determined that disinfection of *Giardia*, *Cryptosporidium* and *Campylobacter* is sufficient to determine the microbiological safety of the water (van der Helm *et al.* 2008b). To be able to monitor the efficiency of the ozonation step, at least one of the following parameters should be measured:

- Pathogenic mirco-organisms such as *Cryptosporidium*, *Giardia* and *Campylobacter*.
- Ozone concentration at different contact times, to be able to determine the Ct value (van der Helm *et al.* 2009);

During ozonation disinfection by-products are formed. The oxidation of NOM promotes the presence of AOC concentration in water (van der Kooij *et al.* 1989). AOC promotes regrowth of bacteria in a distribution system, amongst others, and, therefore, should be sufficiently removed in the subsequent treatment steps. Water without residual chlorine is considered to be biologically stable if the AOC concentration is below 10 µg Acetate-C/L, whereas water with residual chlorine is defined as biologically stable for AOC concentrations below 50 µg Acetate-C/L (Escobar *et al.* 2001, van der Kooij 1992). Besides AOC, bromate is formed if bromide is present in the feed water. Bromate is possibly (IARC 1999) or probable (USEPA 2018) carcinogenic to humans.

During BAC filtration, biodegradation takes place by microorganisms, present on the external surface and in the macro-pores of the BAC filter grains, that biodegrade the NOM in the water (Servais *et al.* 1994). The activity of the microorganisms (biomass) determines the degradation rate of NOM (Lazarova and Manem 1995). The activity and concentration of the biomass depends on the concentration of nutrients (carbon, phosphate and nitrogen), the dissolved oxygen concentration, temperature, pH and residual disinfectant in the feed water (Simpson 2008). Uhl and Gimbel (2000) described that for the biological removal of ammonia, the deposit of bacterial cells from the influent was necessary to maintain a solid biofilm. However for Weesperkarspel it was shown that the feed in bacterial cells to the BAC filters was not necessary to obtain a sufficient biodegradation efficiency (Ross *et al.* 2019), hence no on-line measurement of ATP or flowcytometry was required. Besides biodegradation taking place, adsorption of NOM and toxic, colour, taste and odour compounds takes place. In addition, at Weesperkarspel, BAC filtration is simultaneously applied for the removal of suspended solids and carry-over. Due to clogging of the filter bed by suspended solids, carry-over and in some cases biomass, the filters need to be backwashed frequently. The pressure drop over the filters and turbidity in the effluent indicates the state the filter is in, and whether it needs to be backwashed. In case of Weesperkarspel the pressure drop is the determining parameter.

**Process characteristics**

Ozone is dosed to the water, after which reaction takes place in the seconds to minutes range. A change in ozone dose or change in feed water quality can have an immediate effect on the effluent quality. In the past, the dosing strategy was determined by the water temperature, with two different set points, below 12 °C and above 12 °C. Van der Helm *et al.* (2009) suggested that this negatively influenced the disinfection during ozonation. However, more detailed research by Wiersema (2018) could not confirm this. Since ozonation is one of the main processes that can achieve disinfection, high frequency monitoring is required enabling direct control of the ozonation step.

In contrast to ozonation, BAC filtration is not a dosing process, but a separation/degradation process by means of filtration, adsorption and biodegradation. The different processes all have their associated time intervals. The shortest time interval is the clogging of the filters, which, depending on the location in the treatment train, needs to be carried out every couple of days till once a month. Backwashing occurs based on pressure drop over the filter or after a maximum period of time. The pressure drop should be monitored on a regular basis.

As indicated in the required water quality parameters section, the activity of the biomass present on the carbon grains determines the biodegradation efficiency. Ross *et al.* (2019) showed that a change in feed water quality does not necessarily result in a change in effluent quality, hence there is no direct need for close monitoring of the filters. In case the feed water quality changes for a longer period of time, the biomass will adopt itself to the new situation, which can take up to 2-3 months (Servais *et al.* 1994).

Depending on the NOM loading, the activated carbon starts showing break-through of organic micro pollutants and pesticides after a run time of 6-9 months if no biodegradation takes place, while if biodegradation takes place this can last up to 2-5 years before the activated carbon needs to be regenerated (Simpson 2008). Although BAC filters have proven their ability to intercept sudden changes in water quality, the DO can be used as an indicator for the biological activity in the filter and identifying any disruptions taking place (van Schagen 2009).

**Evaluate available measurements for the identified water quality parameters**

A summary of the required water quality parameters, as determined in the paragraphs describing the water quality parameters, can be found in the first column of Table 3-1 (ozonation) and Table 3-2 (BAC filtration). In the second column it is indicated per parameter if an on-line measurement, able to measure at the limit of detection required, is available. Depending on the monitoring frequency required, as described in the process characteristics paragraphs, it was determined if a parameter should be available on-line. If the monitoring frequency should be daily or more, it was indicated with a yes in the third column. To gain a better understanding of the applicability of the on-line sensors, the ease of use, sensitivity and maintenance requirements were evaluated in columns four through six. The costs related to a measurement in lab and installation of an on-line sensor are listed in column seven.

Evaluation of availability on-line sensors and its characteristics was based on literature research, indicated by the references included per parameter. Besides on-line sensors that measure one specific parameter, available related surrogate parameters (column eight) and soft-sensors (column nine) were also captured. It should be noted that for some surrogate parameters and soft-sensors a start concentration is required first before the concentration of the requested parameter can be estimated.

**Determination of individual monitoring strategy per treatment step**

Figure 3-2 shows the individual monitoring strategy per treatment step determined by the water quality assessment captured in Table 3-1 for ozonation and Table 3-2 for BAC filtration. The results are described in detail below.
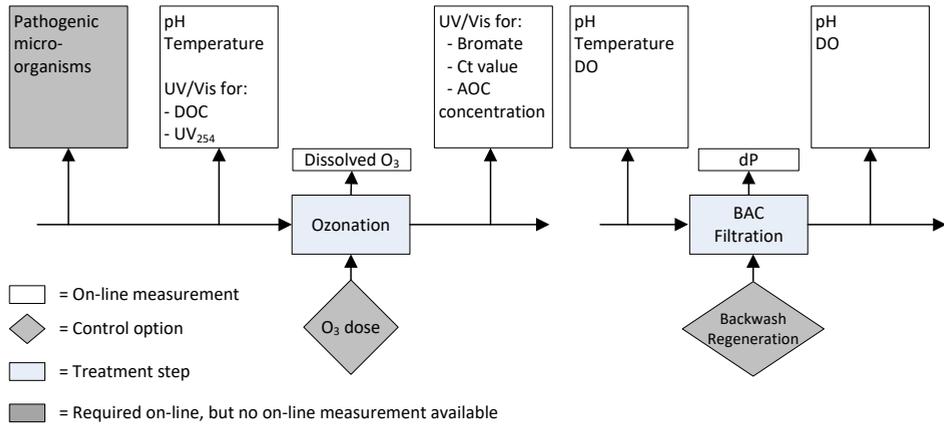


**Figure 3-2** Required on-line water quality information for optimised monitoring and control of ozonation and BAC filtration.

*pH, temperature, and DO*

Being compliance parameters published by the WHO, there are sufficient on-line sensors available to measure the pH, temperature, and DO. These sensors are relatively easy to use and sensitive enough. The pH sensor requires frequent maintenance. The costs of measurement, either on-line or in laboratory are low. The efficiency of ozone is, amongst others, determined by the pH and temperature and should therefore be monitored continuously. The DO and pH are a continuously controlled effluent parameter in BAC filtration. The pressure drop indicates if a filter needs to be backwashed. The DO and pH are an indicator for the biological activity in the filter and capable of identifying any disruptions taking place (van Schagen 2009).

**Table 3-1** Summary water quality parameters required to monitor ozonation and associated available on-line sensors.

| Parameter | On-line available | On-line required | Easy | Sensitive enough |
|---|---|---|---|---|
| pH | Yes (Banna *et al.* 2014) | Yes | Yes | Yes |
| Temperature | Yes (Banna *et al.* 2014) | Yes | Yes | Yes |
| DOC | Yes via TOC measurement (Hall *et al.* 2007) | Yes | Moderate | Yes |
| $UV_{254}$ | Yes (Hach 2018) | Yes | Yes | Yes |
| Pathogenic micro-organisms | No | Yes | n.a. | n.a. |
| AOC | No | Yes | n.a. | n.a. |
| Bromate | No (ThermoFisher 2018) | Yes | n.a. | n.a. |
| Bromide | No | No | n.a. | n.a. |
| Ozone concentration in water | Yes (Hach 2018) | Yes | Moderate | No |

n.a. = not applicable, n.r. = not required.

| Maintenance | Costs lab/ online | Surrogate parameters | Soft-sensor available |
|---|---|---|---|
| Moderate, needs regular calibration | lab/online: low | No | Yes through water quality (WQ) modeling after dosages of a base or acid based on measured influent pH (van Schagen *et al.* 2009) |
| Low | lab/online: low | No | No |
| High, 0.45 µm filters and reagents are required to be replaced | lab: moderate online: high | $UV_{254}$ or a $UV_{280}$, UV wavelength at 254 or 280 nm related to reactivity of the organic carbon with ozone (Westerhoff *et al.* 1999) | Yes, based on range of UV wavelengths (Langergraber *et al.* 2003) |
| Yes | lab: low online: moderate | UV/Vis measurement, measuring all wavelengths between 200 – 735 nm | n.r. |
| n.a. | lab: high online: n.a. | Ct value related to inactivation of Giardia after measuring influent concentration (USEPA 1989) | Yes, Ct value estimation by means of WQ modeling (van der Helm *et al.* 2009) or algorithm based UV/Vis-spectra measurements after measuring influent concentration (Ross *et al.* 2016) |
| n.a. | lab: high online: n.a. | Yes (Hammes and Egli 2005) | Yes, through WQ modeling by van der Helm *et al.* (2009) or algorithm based on UV/Vis-spectra measurements (Ross *et al.* 2016) |
| n.a. | lab: moderate online: n.a. | Yes, Ct value has linear relationship with bromate (van der Helm *et al.* 2008a) | Yes, through WQ modeling by van der Helm *et al.* (2009) or UV/Vis-spectra measurements (Ross *et al.* 2016) |
| n.a. | lab: moderate online: n.a. | n.r. | n.r. |
| Moderate, regular cleaning required | lab/online: moderate | Yes, UV absorbance from 185-350 nm  (Molina and Molina 1986) | Yes, developed based on UV measurement (van den Broeke *et al.* 2008) |

**Table 3-2** Summary water quality parameters required to monitor BAC filtration and associated available on-line sensors.

| Parameter | On-line available | On-line required | Easy | Sensitive enough |
|---|---|---|---|---|
| DO | Yes (Banna *et al.* 2014) | Yes | Yes | Yes |
| Phosphate | Yes (Hach 2018, Schlegel and Baumann 1996) | No | Yes | No |
| Nitrogen | No | No | n.a | n.a. |
| DOC | Yes via TOC measurement (Hall *et al.* 2007) | No | Moderate | Yes |
| AOC | No | No | n.a. | n.a. |
| Viable bacterial cells | Yes (Besmer *et al.* 2017) | No | Moderate | Yes |
| pH | Yes (Banna *et al.* 2014) | Yes | Yes | Yes |
| Temperature | Yes (Banna *et al.* 2014) | Yes | Yes | Yes |
| Pressure drop | Yes (van Schagen *et al.* 2008) | Yes | Yes | Yes |

n.a. = not applicable, n.r. = not required.

| Maintenance | Costs lab/ online | Surrogate parameters | Soft-sensor available |
|---|---|---|---|
| Low | lab/online: low | No | No |
| Moderate, reagents are required to be replaced | lab: moderate online: moderate | n.r. | n.r. |
| n.a | lab: moderate online: n.a. | n.r. | n.r. |
| High, 0.45 µm filters and reagents are required to be replaced | lab: moderate online: high | n.r. | n.r. |
| n.a. | lab: high online: n.a. | n.r. | n.r. |
| Moderate | lab: moderate online: high | n.r. | n.r. |
| Moderate, needs regular calibration | lab/online: low | No | Yes through water quality (WQ) modeling after dosages of a base or acid based on measured influent pH (van Schagen *et al.* 2009) |
| Low | lab/online: low | No | No |
| Low | lab: moderate online: low | n.r. | n.r. |

***DOC and UV$_{254}$***

The NOM concentration, measured through DOC, is a scavenger and does directly interfere with disinfection, requiring to be monitored in the influent of the ozone step. The used ozone dosages hardly affect the DOC concentration, limiting the need for monitoring downstream of the ozone step (van der Helm *et al.* 2008a). For TOC there is an on-line sensor available which measures sensitive enough. By inclusion of a 0.45 µm filtration step the DOC is determined. It does require frequent maintenance for replacing the 0.45 µm filters and reagents. The on-line sensors are still expensive whilst the lab measurements are cheap and around 20 euros per sample. Alternatively, an UV absorbance sensor measuring the UV absorbance at wavelength of 254 or 280 nm can be used as a generic sensor providing insights in the reactivity of ozone with the organic matter (Westerhoff *et al.* 1999). Besides direct measurement or a generic sensor, Langergraber *et al.* (2003) developed a soft-sensor allowing to estimate the DOC concentration based on measured UV/VIS wavelengths and by applying principal component analysis followed by partial least squares regression. These soft-sensors do require to be calibrated locally based on an obtained dataset from lab measurements. The UV/Vis sensor is, besides regular cleaning, easy to maintain, and less than half the price of a specific TOC sensor. Besides DOC, UV$_{254}$ also determines the efficiency of ozone and should therefore be monitored continuously. A specific on-line sensor is available which only measures UV$_{254}$, is easy to use, sensitive and low in maintenance and costs. An alternative generic sensor is the UV/Vis sensor which measures all wavelengths between 200-735 nm. This should only be used instead if the sensor is used to measure other parameters, such as DOC, as well.

***AOC, bromate and bromide***

AOC and bromate are disinfection by-products formed during ozonation. Depending on the influent concentrations of DOC and bromide and the amount of ozone dosed, the AOC and bromate concentration are determined. There is no on-line sensor available for measuring the AOC concentration in accordance with the approved standard methods (Eaton *et al.* 2005). AOC is one of the disinfection by-products that needs to be monitored. A change in organic matter composition and/or ozone dose will directly result in a change in AOC concentration, therefore requiring on-line monitoring in the effluent of the ozone step. AOC is subsequently biodegraded in BAC filtration step and enhances the microbiological activity in the filters. Ross *et al.* (2019) showed that a sudden change in AOC concentration does not result in a direct deterioration of the effluent quality of the BAC filters. Therefore, a continuous monitoring of the AOC concentration in the effluent of the BAC filter is not required. The lab measurements are high in costs, due to the labour intensity of the analysis. Hammes and Egli (2005) developed a quicker laboratory method to determine the AOC concentration using flow cytometry. Until now this method is only available as off-line method and therefore not suitable for on-line monitoring. The water quality model developed by van der Helm *et al.* (2009) is able to predict the formation of disinfection by-products such as AOC by using Matlab/Simulink®. Another soft-sensor is the software algorithm published by Ross *et al.* (2016) that uses different UV/Vis wavelengths to predict the AOC formation.

There are no on-line sensors available for measuring the bromate and bromide concentration. Bromate needs to be monitored for compliance since it is possibly carcinogenic and is not removed in existing downstream treatment steps. A change in bromide concentration or a change ozone dose can impact the bromate concentration directly. The bromide levels in the influent of the Weesperkarspel treatment plant have been very stable, requiring no need for continuous monitoring. Since the bromate levels can change with changing ozone dose, on-line monitoring of bromate in the effluent of the ozone step is proposed. The lab measurements are moderate in costs, due to the reagents required. Van der Helm et. al. (2008a) found a linear relationship between the bromate concentration and Ct value, allowing the Ct value to be a surrogate parameter once the initial bromate concentration is known. Cromphout *et al.* (2013), found a linear relationship between ozone dose, temperature and bromate formation. These models can be used to predict the bromate concentration based on the ozone dosed, temperature, pH and bromide concentration in the influent. Another available soft-sensor is the software algorithm published by Ross *et al.* (2016) using different UV/Vis wavelengths to determine the Ct value and bromate formation. It should be tested till what extent these algorithms can be locally calibrated for changing bromide concentrations.

**Pathogenic microorganisms and ozone concentration in water**

There are no on-line sensors available to specifically measure a certain pathogenic microorganism. The lab measurements are high in costs, due to labour intensity of the analysis. The pathogenic microorganism concentration in the influent together with above parameters do determine the required ozone dosage and therefore require continuous monitoring. The USEPA (1989) published Ct values for determining the log inactivation of pathogenic microorganisms for different water temperatures. This allows the Ct value to be used as a surrogate parameter if the influent concentration is known. The water quality model developed by van der Helm *et al.* (2009) is able to predict the Ct value based on above measured parameters and applied ozone dose. In addition, Ross *et al.* (2016) published a software algorithm that uses different UV/Vis wavelengths to determine the Ct value. Verification via lab analysis of pathogenic microorganisms on a weekly/monthly basis, depending on the variability of the source water quality, will help determine the log inactivation and associated Ct value to be achieved. Besides using soft-sensors to determine the Ct value based on a change in UV/Vis pattern, the ozone in water can be determined by on-line measurements. These measurements do require local calibration by means of lab measurements. It is an easy and sensitive measurements that does require regular maintenance to prevent biofouling. Cost of on-line and lab measurements are moderate due to the calibration fluid required. In order to be able to determine the Ct value based on the ozone in water concentrations, multiple sampling points are required in space.

*Viable bacterial cells*

Viable bacterial cells are present in the surface water. During ozonation typically disinfection of viable bacterial cells takes place, which subsequently can regrow in following treatment steps (Vital *et al.* 2012). The determination of viable bacterial cells has developed in the last couple of years from a laborious intensive measurement using microscopy, to rapid determination in the lab using flow cytometry to customizing the flow cytometry equipment for on-line applications (Besmer *et al.* 2017, Besmer *et al.* 2014). Ross *et al.* (2019) showed that the effect of viable bacterial cells in the influent of the BAC filters is limited in respect to the performance of the BAC filters, therefore discarding the need for on-line monitoring. The costs of both lab and on-line measurements are still high but expected to reduce in future as per the innovation taking place to enhance rapid detection.

*Pressure drop*

The pressure drop is typically measured to determine the clogging ratio in the filter bed. Pressure drop measurements are available on-line and have been fully developed. It is an easy measurement, which is sensitive and low in maintenance. The costs are low. For BAC filtration it is, besides turbidity, the main indicator if a filter is clogging and needs backwashing. On-line monitoring is therefore required and frequently applied.

**Determination of integrated monitoring strategy of treatment plant**

When evaluating the ozonation and BAC filtration step as an integrated system, it is not required to monitor the AOC in the effluent of the ozonation due to the robustness of the BAC filtration step (Ross *et al.* 2019). The DO concentration in the influent of the BAC filter will always be sufficient as a result of the preceding ozonation step, therefore there is no need to continuously monitor this concentration in the influent. For Weesperkarspel, the temperature of the water and pH will not change due to application of ozonation, hence there is no need to monitor this in the influent of the BAC filters.

In Figure 3-3 the current monitoring strategy of Weesperkaspel is shown. This strategy was adjusted per the outcomes of the different research described in this Chapter (Ross *et al.* 2016, van der Helm 2007, van Schagen 2009).

When comparing the sensors installed in Figure 3-3 with Figure 3-2, considering the sensors that can be skipped based on the integrated approach, only 4 differences are observed. In the influent of the ozone step only $UV_{254}$ is measured instead of $UV_{254}$ and DOC and the turbidity is measured. In the effluent of the ozone step the i::scan™ is installed measuring at a wavelength of 254 nm instead of the s::scan™ able to measure the full spectrum allowing for estimation of bromate and Ct value. However, the Ct value can also be calculated by the installed ozone measurements and the $UV_{254}$ can give a good indication of the achieved Ct as well (Westerhoff *et al.* 1999). No differences are observed for the BAC filtration step, when considering the integrated approach.
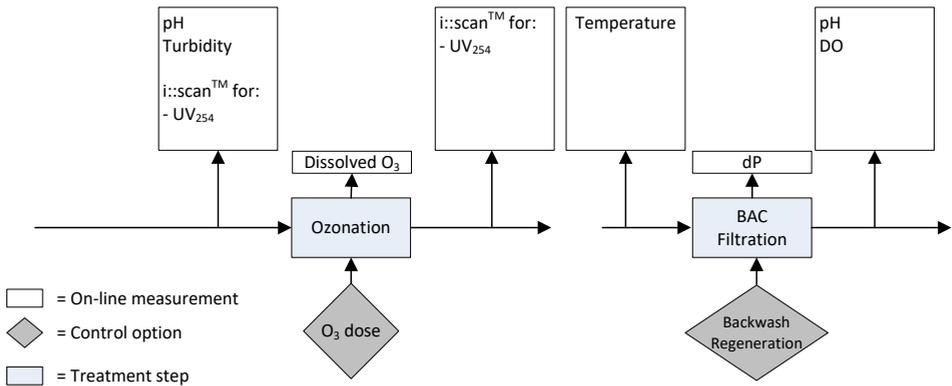
**Figure 3-3** Current on-line water quality monitoring of ozonation and BAC filtration at Weesperkarspel treatment plant.

# DISCUSSION

**Advances in on-line water quality monitoring**

Evaluation of available on-line sensors showed that the parameters typically measured to show compliance with the WHO standards are commonly available (Adu-Manu *et al.* 2017). Direct measurements of the more complex parameters such as AOC and bromate are not available on-line. When looking at required on-line information for integrated control of ozonation and BAC filtration, bromate is to be monitored continuously. In this case the use of soft-sensors, able to estimate the bromate and AOC formation, help to gain continuous on-line data. Besides using soft-sensors as surrogate sensors for parameters currently not available on-line, they can also provide a cost effective alternative when used to determine multiple parameters required through one single instrument. Examples in this case were the use of UV-Vis sensors for the determination of $UV_{254}$ concentration in the influent, the estimation of DOC in influent and effluent, formation of bromate and AOC during ozonation and estimation of Ct value in the effluent of the ozonation step.

**Reliability of the data**

On-line identification of disturbances is only possible if the identified water quality data are accurate and continuous (van Schagen *et al.* 2010). Furthermore the confidence the operators have in the data is crucial, especially when soft-sensors are applied instead of direct measurement (Ikonen *et al.* 2017). If possible, measurement via two different methods can be applied for a period of time, to gain confidence by the operators to rely on soft-sensors to provide with the correct information. In this case the Ct value can be obtained via ozone in water measurement multiplied by contact time or estimated via the change in UV-Vis measurement. It should be recognized that the use of on-line sensors does require knowledge of the use of the sensors and (frequent) maintenance to ensure the reliability of the data.

**Direct control based on water quality**

When comparing the previous on-line information (Figure 3-1) with the current on-line sensors placed at Weesperkarspel (Figure 3-3) it can be seen that in the current situation more on-line information is available. The current situation comes close to the required situation as depicted in Figure 3-2, when considering the integrated approach. Currently the installed sensors act as an early warning system to flag any deviations in water quality and operation. The next step would be the direct control based on water quality.

Fluctuations in incoming water quality and subsequent required change in ozone dose to achieve the objectives set forth of achieving sufficient disinfection while minimizing the disinfection by-product formation require direct continuous monitoring and direct control. Van der Helm *et al.* (2009) suggested that the control of ozonation step, and balancing between disinfection and disinfection by-product formation, can already be greatly enhanced when adjusting the ozone dose based on the measured water temperature. However, more detailed research by Wiersema (2018) could not confirm this. By adjusting the ozone dose on incoming NOM concentration, the balance between disinfection and by-product formation might be improved.

# CONCLUSIONS

The main objective was to develop a design methodology able to determine an optimised water quality monitoring strategy to support future direct control of the drinking water treatment plant based on incoming water quality. A seven step approach was defined, and each step was demonstrated for the treatment processes ozone and BAC filtration. It was shown how the previous on-line water quality monitoring program of the treatment plant Weesperkarspel was optimised and subsequently can be finetuned in future.

Evaluation of available on-line sensors showed that the parameters typically measured to show compliance with the WHO standards are commonly available. Direct measurements of the more complex parameters such as AOC and bromate are not available on-line. The use of soft-sensors, able to estimate the bromate and AOC formation, help to gain continuous on-line data. Besides using soft-sensors as surrogate sensors for parameters currently not available on-line, they can also provide a cost effective alternative when used to determine multiple parameters required through one single instrument. Examples in this case were the use of UV-Vis sensors for the determination of $UV_{254}$ concentration in the influent, the estimation of DOC in influent and effluent, formation of bromate and AOC during ozonation and estimation of Ct value in the effluent of the ozonation step. The on-line data obtained by the (soft-) sensors will help the operator to control the treatment plant based on its objectives and provide continuous information whether the processes are operating within the required operational window.

# ACKNOWLEDGEMENTS

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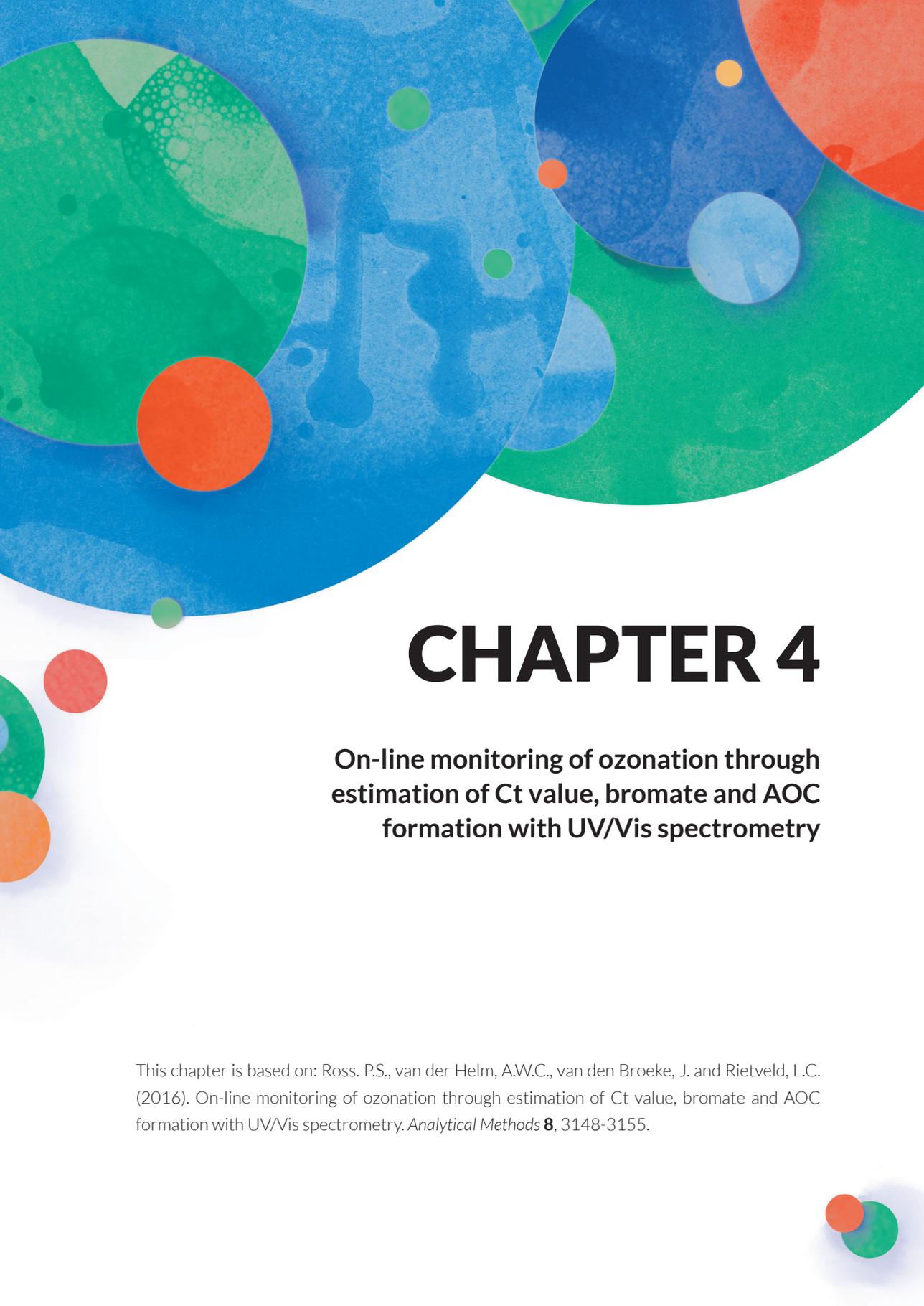
# CHAPTER 4

**On-line monitoring of ozonation through estimation of Ct value, bromate and AOC formation with UV/Vis spectrometry**

# ABSTRACT

The application of ozone in water treatment serves many purposes, such as disinfection and degradation of organic micropollutants. To optimise the applied ozone dosage by on-line control, real-time information on the actual Ct value, the bromate and assimilable organic carbon concentration (AOC) is necessary. With UV/Vis spectroscopy, algorithms have been developed for the on-line estimation of the Ct value and the formation of bromate and AOC during ozonation. It was shown that these algorithms allow for the calculation of the optimal ozone dosage and provide a reliable indication of the amount of bromate and AOC formed during ozonation.

# INTRODUCTION

The use of ozonation in water treatment serves several purposes, such as degradation of organic micropollutants, oxidation of taste, odour and colour producing compounds and the oxidation of organic matter. The primary use of ozonation in drinking water treatment plants, however, remains disinfection (von Gunten 2003a). Ozone has proven to be able to inactivate pathogenic microorganisms that have a high resistance to chlorination and chloramination such as protozoa. However, at the same time, undesired disinfection by-products are formed, in particular bromate, which is potentially carcinogenic to humans. Unlike other organic by-products formed during ozonation, bromate is not biodegradable in the biological filters typically used after ozonation (von Gunten 2003b).

Van der Helm *et al.* (2009) showed that direct control of ozonation based on water quality objectives (e.g. pathogen inactivation) resulted in a large reduction of uncertainty and variation of the process performance, also resulting in less by-product formation and in an improved drinking water quality. A commonly used method to estimate the disinfection of ozonation is by calculating the exposure of pathogens to ozone, which is expressed as the Ct value (WHO 2008). The Ct value is the product of the residual concentration of the disinfectant (C) and contact time (t). Depending on the type of pathogen (e.g., Giardia) to be inactivated, the necessary log removal and the water temperature, different Ct values are required (USEPA 1989). In order to be able to calculate the Ct value, the ozone concentration in water should be determined together with the hydraulic residence time. Several on-line sensors are available for the determination of ozone in water, for example amperometric ozone electrodes. In addition, the determination by means of UV/Vis spectrometry was also proven to be effective (van den Broeke *et al.* 2008). In a full-scale plant, however, the number of sampling points where the ozone concentration in water can be determined is usually limited, making it impractical to calculate Ct based on the dissolved ozone concentration. Therefore, several researchers have tried to identify indicator parameters able to estimate the disinfection, such as determination of the bromate concentration, which was proven to be linearly related to the Ct value (Jarvis *et al.* 2007, Legube *et al.* 2004, von Gunten *et al.* 2001). Although the linear relationship between the Ct value and bromate concentration has been shown to give a good indication of the Ct value, on-line measurement of bromate is currently not practical. An on-line measurement of Ct value to estimate the disinfection would make it possible to come to a direct control of the ozone dosage, minimizing the disinfection by-product formation.

Ozone is an unstable oxidant in water. In general when ozone is added to natural water, it decomposes in two phases: the initial phase and the second phase (von Gunten 2003a). The ozone decomposition in the initial phase is fast (duration in the seconds range, values of 20 – 60 seconds have been reported) and is mainly due to compounds that react very

rapidly with ozone such as natural organic matter (NOM) (Buffle *et al.* 2006, Westerhoff *et al.* 1999). During the second phase of ozone decomposition (minutes range), ozone decreases with first order kinetics and disinfection of more resistant microorganisms such as Cryptosporidium, Giardia and Bacillus spores takes place (van der Helm *et al.* 2008, von Gunten 2003a). The amount of NOM in the water interferes with the amount of ozone left for disinfection.

NOM in surface water bodies originates from run off, vegetative debris and humic substances. Furthermore, NOM can originate from in situ sources such as algae, in which case both extracellular and intracellular algal organic matter can contribute (Amy 2008). When NOM reacts with ozone, the high molecular weight compounds are broken down into smaller fractions, resulting in an increase in carbon available for uptake by bacteria. This can negatively influence the biological stability of the water, an important criterion in distribution systems where no residual disinfectant is used (van der Kooij *et al.* 1999). It is therefore a delicate balance between achieving sufficient disinfection while trying to minimize the by-product formation.

To be able to quantify the amount of NOM present in water, originally, the total organic carbon (TOC) concentration was measured (van Hall *et al.* 1963). When the sample is filtrated through a 0.45 μm filter, solids are removed and the dissolved organic carbon (DOC) concentration can be determined. The traditional TOC/DOC analysis consists in oxidation of the organic matter, either by high temperature combustion or oxidation with a chemical oxidizer (Foundation and PROAQUA 2002). Although automated versions of these methods have been developed for use under process conditions, these analysers are complicated instruments which require intensive maintenance. Because they lack the robustness required for application in process control (USEPA 2009) surrogate methods that are simple, rapid and allow monitoring of the operation and performance of a treatment plant in real-time have been studied (Dobbs *et al.* 1972, Edzwald *et al.* 1985). Many of these surrogate methods are based on the characteristic of NOM to absorb light across a broad range of wavelengths. The absorption spectra, however, are featureless, the absence of distinct peaks being due to the broad and overlapping absorption bands of a multitude of organic compounds that constitute NOM (Liu *et al.* 2010). This is reflected by the numerous correlations found between the NOM in water and the UV absorbance at different wavelengths, varying between 250 – 350 nm (Chin *et al.* 1994, Dobbs *et al.* 1972, Edzwald *et al.* 1985, Maes 1982). Of the many wavelengths that were identified as an on-line characterization of the organic content of the water, especially $UV_{254}$ has been widely adopted. However, collection and interpretation of absorbance data at only $UV_{254}$ fails to take advantage of the substantial information that might be embedded in other wavelengths of the UV/Vis spectral data (Korshin *et al.* 1997).

Besides the direct use of UV/Vis spectra, the decrease of UV absorbance during a treatment step (differential UV spectroscopy, ΔUV) was also applied to make sure the relations found, were independent of initial raw water quality parameters such as DOC concentration, pH and NOM properties (Gerrity *et al.* 2012, Roccaro and Vagliasindi 2009).

The oxidation of NOM promotes the presence of assimilable organic carbon concentration in water (van der Kooij *et al.* 1989). AOC is often used as an indicator parameter with respect to regrowth in (non-chlorinated) distribution systems (van der Kooij 1992). Water without residual chlorine is considered biologically stable if the AOC concentration is below 10 µg Acetate-C/L, whereas water with residual chlorine is defined biologically stable for AOC concentrations below 50 µg Acetate-C/L (Escobar *et al.* 2001, van der Kooij 1992).

Determination of the AOC concentration by the laboratory is a labour intensive procedure, and requires, depending on the method applied, at least 2 days up to 30 days (Hammes and Egli 2005, van der Kooij 1992, Werner and Hambsch 1986). A surrogate parameter would be needed if AOC is to be used for on-line assessment and control of biological stability during ozonation. Van der Kooij *et al.* (1989) found a linear relationship between the increase in AOC and the decrease in $UV_{254}$ absorbance of water after ozonation. Van den Broeke *et al.* (2008) described a correlation between the change in AOC concentration and the change in UV/Vis spectrum during ozonation, pellet softening and biological granular activated carbon (BAC) filtration. This algorithm was developed based on a highly inhomogeneous dataset, which described AOC formation during ozonation, AOC biodegradation during pellet softening as well as biodegradation and adsorption during BAC filtration. The algorithm showed a good correlation for the AOC formation during ozonation, however this only contained a limited amount of data points determined for only low water temperatures.

In this Chapter the development of algorithms for the on-line determination of the Ct value and the bromate and AOC formation using differential UV/Vis spectrometry is described. The dataset used to develop the algorithm contained a wide variety in applied ozone concentrations and seasonal changes. Real-time information on the actual Ct value helps to optimise the applied ozone dosage, ensuring sufficient disinfection, against minimal ozone dosages, limiting the formation of disinfection by-products. Real-time information about the amount of AOC that is formed during ozonation helps in optimising subsequent treatment steps that are affected by the AOC concentration, such as BAC filtration. The maximum bromate concentration is regulated by law since it is a possible carcinogen. Therefore, bromate formation might limit the allowable ozone dosage, since almost no bromate is removed in subsequent treatment steps.

# MATERIALS AND METHODS

**Origin of samples**

Water samples were collected from an ozonation pilot plant at the production location Weesperkarspel of Waternet, the water cycle company of Amsterdam and surrounding areas. Weesperkarspel raw water originates from seepage water from the Bethune polder, a peat-rich area that gives the water a high NOM concentration. This water is pre-treated by coagulation and sedimentation, followed by approximately 100 days retention in a reservoir. Subsequently, the water is filtered over rapid sand filters and transported to the Weesperkarspel treatment plant, which is composed of ozonation, pellet softening, BGAC filtration and slow sand filtration.

The pilot plant is a physical model of the full-scale plant located at Weesperkarspel. The flow through the pilot plant ranged from 4 to 15 m³/h. The ozone bubble columns were operated in counter-current mode and ozone was dosed in 2 subsequent bubble columns (diameter 0.388 m); the concentration was equally divided over both columns. The height of the columns was 4.2 and 3.6 m, respectively. After the bubble columns the water flowed through 4 contact chambers (diameter 1 m, and height 2.6 m) to ensure enough retention time was achieved and ensuring no residual ozone is present at the outlet of the contact chambers. The hydraulic retention times varied between 25 – 111 minutes (depending on the applied flow). The DOC concentration varied between 5.7 – 6.5 mg-C/L and the applied ozone dosages between 1.5 – 4.0 mg $O_3$/L. The applied ozone dosages per amount DOC varied from 0.23 to 0.68 (mg-$O_3$/L)/(mg-C/L), depending on the conducted experiment. The off-gas was very low compared to the applied ozone dose (about 0,4 %, except for the high ozone dosages of 4 mg/L an off-gas concentration of around 5.5% was measured). In the paper the results are related to Ct value and not to ozone dose, therefore the transferred dosage is less important in this case and the applied dosage is given. Four series of experiments (total of 30 different settings) were performed over a 4 year period, covering the seasonal variability in raw water NOM composition and temperature (between 2-22 °C). The water quality parameters of the water, the ozone dosages and the temperature are presented in Table 4-1.

The ozone dosage is determined by the ozone in gas flow, ozone in gas concentration and the water flow (eq. 4-1):

$$O_{3,dosage} = \frac{c_{g_{O_3}} \cdot Q_{g_{O_3}}}{Q_w}$$

where $O_{3,dosage}$ is the ozone dosage (mg-$O_3$/L), $c_{g,O3}$ is the ozone in gas concentration (g-$O_3$/Nm³), $Q_{g,O3}$ is the ozone in gas flow (Nm³/h) and $Qw$ is the water flow (m³/h). Nm³ is used as a measure for the gas volume under standard conditions (gas pressure of 101325 Pa and a gas temperature of 273.15 K).

## Analysis

Grab samples were collected from sampling points at the influent and effluent of the ozonation reactor. The grab samples were analysed by a laboratory for AOC (duplicate measurement) by applying the simultaneous incubation of strains P17 and NOX31, with a reporting limit of 1 µg-C/L and allowed standard deviation (SD) of 50%. DOC was measured according to the standard methods procedure, with a reporting limit of 0.1 mg-C/L, using a Shimadzu TOC5000a. $UV_{254}$, expressed as the absorbance per meter of cell length, and bromate was determined using standard procedures described in Standard Methods (Eaton *et al.* 2005). Ozone concentration in water was determined using the indigo method described by Bader and Hoigne (1982). On-line UV/Vis absorption measurements were performed using two spectrometers of the type spectro::lyser™, from s::can Messtechnik GmbH, which were equipped with a 35 mm measuring cell. These instruments measure absorbance of ultraviolet and visible light from 200 to 750 nm, with a resolution of 2.5 nm, resulting in a total of 221 wavelengths measured between 200 – 750 nm (Rieger *et al.* 2004). One spectrometer was located at the influent of the ozonation reactor and one spectrometer was located at the effluent of the contact chambers, with residence times long enough to ensure no residual ozone was left at this point. Before the start of the experiment both sensors were checked against any off-set, by simultaneous measurement of the same sample point. Any deviations were subsequently considered when calculating ΔUV. Interference with ozone bubbles was counteracted by positioning the sampling cells upwards, such that the excessive gas could escape through the top of the sampling cell. If there was still a lot of dissolved gas present, this was seen as turbidity and the spectral turbidity compensation was able to correct the spectrum for this scatter. The spectrometers were cleaned periodically once every 3 months as a precaution, however, no fouling was detected during cleaning.

## Ct value determination

When determining the *Ct* value for a full scale installation, normally a conservative approach is taken and typically the T10 is used for defining the contact time. The reason for this approach has to do with the fact that not a lot of sampling points are available to determine the concentration and full scale installation have a tendency to not behave ideally. The T10 value represents the time required for 10% of a tracer to travel through the reactor, so 90% is still left within the reactor (Hijnen *et al.* 2002, von Gunten 2003b). In this pilot plant an extensive number of sampling points are located between the outflow of the contact chamber and the dosage points showing a representative concentration gradient. In total 33 sampling points are available in the pilot plant, 5 for each column with a distance between the sampling points varying between 0.5 and 1 m. The residence time between the sampling points was determined based on tracer tests carried out for the different flow settings described above.

**Table 4-1** Water quality parameters influent, applied ozone dosages, temperature and formed AOC, Bromate concentration and Ct value (n.d. = not determined).

| Experiment | ozone dosages mg-O$_3$/L | DOC mg-C/L | UV$_{254}$ Abs/m | Temp °C | Ct value mg-O$_3$/ L*min | AOC µg-C/L | Bromate µg/L |
|---|---|---|---|---|---|---|---|
| 1 | 2.4 | 5.9 | 14.6 | 2.3 | n.d. | 200 | n.d. |
| 2 | 2.4 | 6.5 | 14.6 | 3.2 | n.d. | 179 | n.d. |
| 3 | 2.4 | 6 | 15.0 | 3.3 | n.d. | 178 | n.d. |
| 4 | 2.4 | 5.8 | 14.8 | 4.2 | n.d. | 169 | n.d. |
| 5 | 2.4 | 5.8 | 14.8 | 4.7 | n.d. | 126 | n.d. |
| 6 | 2.4 | 6 | 14.7 | 6.4 | n.d. | 35 | n.d. |
| 7 | 4.0 | 6.4 | 15.1 | 7.1 | 9.58 | 203 | 5.59 |
| 8 | 2.4 | 5.7 | 14.4 | 7.8 | n.d. | 65 | n.d. |
| 9 | 2.5 | 5.9 | 15.4 | 8.1 | 1.64 | 91 | 1.33 |
| 10 | 2.0 | 6.4 | 15.3 | 8.1 | 0.98 | n.d. | 0.65 |
| 11 | 2.5 | 6.3 | 14.7 | 8.7 | 1.9 | n.d. | 1.15 |
| 12 | 2.0 | 5.9 | 14.8 | 9.1 | 0.72 | n.d. | 0.49 |
| 13 | 1.5 | 6.6 | 15.0 | 9.6 | 0.17 | n.d. | 0.31 |
| 14 | 2.5 | 6.5 | 14.9 | 9.6 | 2.31 | n.d. | 1.35 |
| 15 | 0.0 | 6.3 | 14.9 | 9.9 | n.d. | 0 | n.d. |
| 16 | 3.0 | 6.5 | 15.1 | 9.9 | 3.87 | 45 | 2.54 |
| 17 | 1.5 | 6.5 | 14.6 | 11.6 | 0.21 | 66 | 0.11 |
| 18 | 3.5 | 6.0 | 14.8 | 11.7 | 5.51 | n.d. | 3.88 |
| 19 | 2.5 | 5.9 | 14.4 | 11.7 | 1.41 | n.d. | 1.05 |
| 20 | 3.5 | 6.1 | 14.7 | 12.4 | 5.35 | 85 | 4.6 |
| 21 | 3.5 | 5.9 | 14.6 | 13.1 | 5.51 | 85 | 3.92 |
| 22 | 1.5 | 6.2 | 13.1 | 19.1 | 0.57 | 56 | 0.48 |
| 23 | 2.5 | 6.1 | 13.4 | 19.2 | 2.43 | 65 | 2.63 |
| 24 | 4.0 | 5.9 | 13.1 | 19.2 | 8.29 | 76 | 9.53 |
| 25 | 1.5 | 6.4 | 13.3 | 19.8 | 0.59 | 55 | 0.61 |
| 26 | 4.0 | 6.4 | 13.0 | 20.0 | 8.35 | 120 | 9.08 |
| 27 | 2.5 | 6.4 | 13.0 | 20.0 | 2.45 | 110 | 2.38 |
| 28 | 4.0 | 5.9 | 14.5 | 21.0 | n.d. | 154 | n.d. |
| 29 | 2.5 | 6.2 | 14.2 | 21.7 | n.d. | 89 | n.d. |
| 30 | 4.0 | 6.2 | 14.3 | 22.2 | n.d. | 102 | n.d. |

The *Ct* value was calculated based on the concentration of dissolved ozone and the contact time, according to equation 4-2 (van der Helm *et al.* 2007) (eq. 4-2):

$$Ct = \sum_{i=o}^{n_{sp}} c_{O_3,i}(t_i/60 - t_{i-1}/60)$$

where *Ct* is the ozone exposure ((mg-$O^3$/L)*min), $n_{sp}$ is the number of sampling points (-), $c_{O3}$ is the ozone concentration in water (mg-$O_3$/L) and t is the time (s).

**Calibration procedure spectral algorithms**

Based on the principles for determining concentration-spectra relationships described by Otto (1999) and Langergraber *et al.* (2003) developed a multivariate calibration procedure using partial least squares (PLS) regression models evaluating the entire spectra. Langergraber *et al.* (2003) used normalized spectra and reference measurements. Instead of using normalized raw spectra, Karlsson *et al.* (1995) and Thomas and Cerda (2007) suggested using the derivative spectra, either second or first derivative, respectively. The derivative spectrum gives information about the slope of the spectrum and shows the shoulders and inflection points, therefore enhancing the visibility of the fine structure. The derivative gives the relative changes between absorbance values obtained at adjacent wavelengths and it can help in removing the undesired contribution of turbid media (Thomas and Cerda 2007). When trying to link the change in concentration during a treatment step, differential spectra can be used as described by van den Broeke *et al.* (2008). In this study Stepwise regression in Matlab® (Matlab 2009) was used to determine the wavelengths that have a statistically significant contribution in the regression. This is a systematic method for adding and removing terms from a multi-linear model. The approach is similar to partial least squares (PLS) regression (Matlab 2009). Subsequently multiple linear regression (MLR) analysis was carried out to determine the combination of model terms that best expresses the response (target parameter, e.g., change in AOC concentration and Ct value) (Cao *et al.* 2014). Since this study focused on the change in concentration during ozonation, the differential spectra were used. The changes in UV absorbance were obtained by subtraction of the effluent spectra from the concurrent influent spectra. The spectra were compensated for turbidity by using the ana::pro Version 5.9c software from s::can Messtechnik GmbH. Because of the precision of the instruments, only spectra with a differential value of more than 0.2 Abs/m were considered (van den Broeke *et al.* 2008). For this type of water, the 35 mm probe was out of range between 200-230 nm. These wavelengths were not taken into consideration when developing the algorithms. For each algorithm it was evaluated whether differential spectra, normalized differential spectra or the first derivative of the differential spectra gave the best results. Subsequently the algorithm giving the best results is given as the proposed model in the results section.

The change in AOC concentration was calculated from the AOC concentrations obtained from the laboratory analyses. Since the AOC concentration was determined in duplicate, the mean values were used during the development of the algorithm. The combined SD varied between 4 and 25%, indicated by means of the error bars in Figure 4-5. The Ct values were determined based on equation 4-2 using a total of 33 ozone in water concentrations and corresponding residence times. The bromate concentration was determined by laboratory analyses.

# RESULTS AND DISCUSSION

### Ozone concentration, Ct value and bromate formation

At the ozonation pilot plant a total of 33 sampling points were available for sampling and determination of the dissolved ozone concentration. In Figure 4-1, the dissolved ozone concentration across the plant is displayed for 3 settings from Table 4-1 (a low ozone in water dosage 1.5 mg-$O_3$/l (experiment 12), average dosage 2.5 mg-$O_3$/l (experiment 9) and the highest dosage of 4.0 mg-$O_3$/l (experiment 22) for a DOC concentration of 5.9 mg-C/l)

In Figure 4-1, the ozone dosage points can be distinguished by the increase in the dissolved ozone concentration. Since the flow through the contact columns was different for some of the experiments the contact time also differed, therefore the peaks for the 3 runs are displayed at different times. The calculated Ct values, together with the bromate and AOC concentrations measured during the experiments are listed in Table 4-1. In this Table the experimental conditions are summarized as well.
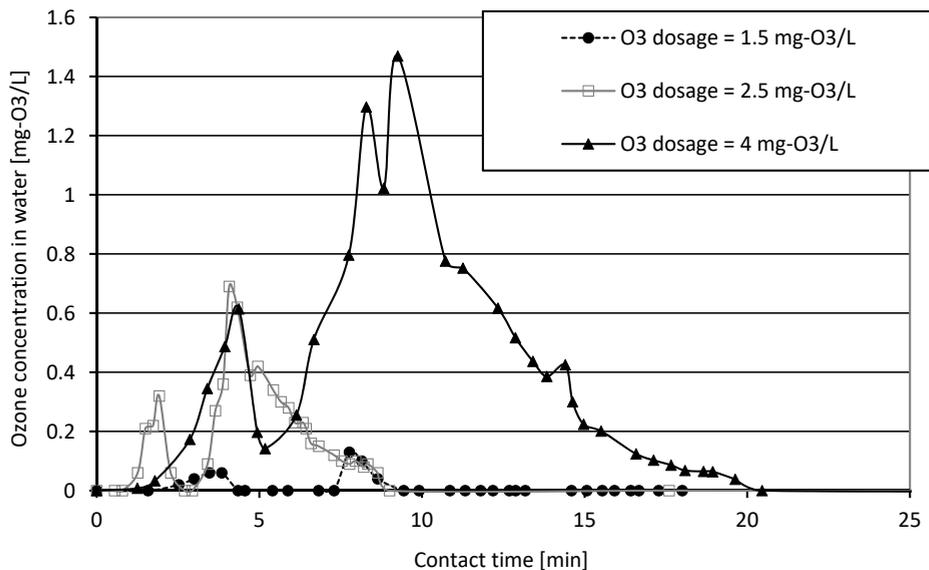


**Figure 4-1** Dissolved ozone concentration measured at 33 sampling points for three different dosages.

Since the formation of bromate is an undesired by-product of ozonation, in Figure 4-2 the bromate concentrations measured at the outflow of the contact chambers for the different experiments listed in Table 4-1 is plotted against the total *Ct* values.

It can be observed that the bromate formed during ozonation is linearly related with Ct. Besides the bromate formation in summer (temperature between 19 – 22 °C) is higher than in winter (at lower temperatures between 3 -13 °C), which is in accordance with previous studies (Galey *et al.* 2004, van der Helm 2007). The observed differences in bromate concentration stems from the changing water matrix and seasonal effects (e.g., temperature), since the bromide concentration in the raw water did not fluctuate. Based on the Ct values required for the inactivation of Giardia for different temperatures published by the USEPA (1989), roughly half of the Ct value is required in summer to achieve same log-removals as in winter. Although the bromate formation in summer is higher than in winter (slope is almost 2 times as steep), the negative effect on bromate formation is counteracted since only half of the Ct value is required in summer to achieve similar log-removals.
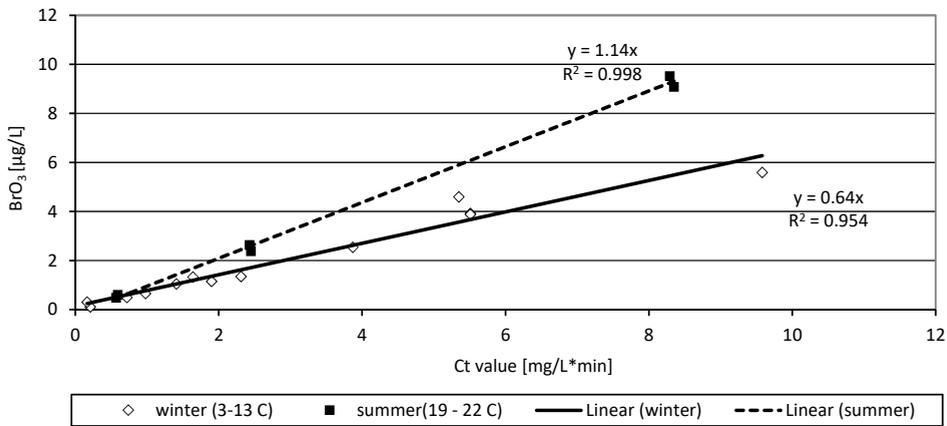


**Figure 4-2** Bromate concentration versus the Ct value distinguished between summer and winter.

**Algorithm for on-line estimation of Ct value achieved during ozonation**

A total of 19 *Ct* values and differential absorbance spectra were available to develop an algorithm for the on-line estimation of *Ct* value during ozonation. The strongest relationship was found with the first derivative of the differential spectrum and *Ct* values. The change in slope at a wavelength of 265 nm ($\Delta UV_{265}$) was found to be the only wavelength demonstrating a statistically significant relation with the Ct values ($R^2 = 0.88$) (eq. 4-3 and Figure 4-3):

$$Ct_{est} = -2.42 \text{-} 193.1 \cdot \Delta UV'_{265}$$

with *ΔUV'* representing the first derivative of the differential spectrum. No additional wavelengths were required to correct for the influence of other substances present in the water. The dataset displayed in Figure 4-3 contains 5 *Ct* values determined in summer and 11 *Ct* values

determined in winter. As can be seen the Ct results cover a wide range of values, both in summer and winter, highlighting the strength of the dataset used for the development of the algorithm. Ozone preferentially oxidizes electron rich moieties such as aromatic carbon-carbon double bonds and aromatic alcohols (Hoigne and Bader 1983).

Westerhoff *et al.* (1999) indicated that a good correlation was found between reactivity of ozone and the $UV_{254}$ and $UV_{280}$ nm. Double bonds and aromatic alcohols can be typically measured between 254 and 280 nm (Chin *et al.* 1994, Edzwald *et al.* 1985). The found differential wavelength indicates that a change in slope occurs at $UV_{265}$ nm which lies within the range of wavelengths that are known to have a strong correlation with aromatic bonds being susceptible to ozone and therefore is likely to react.
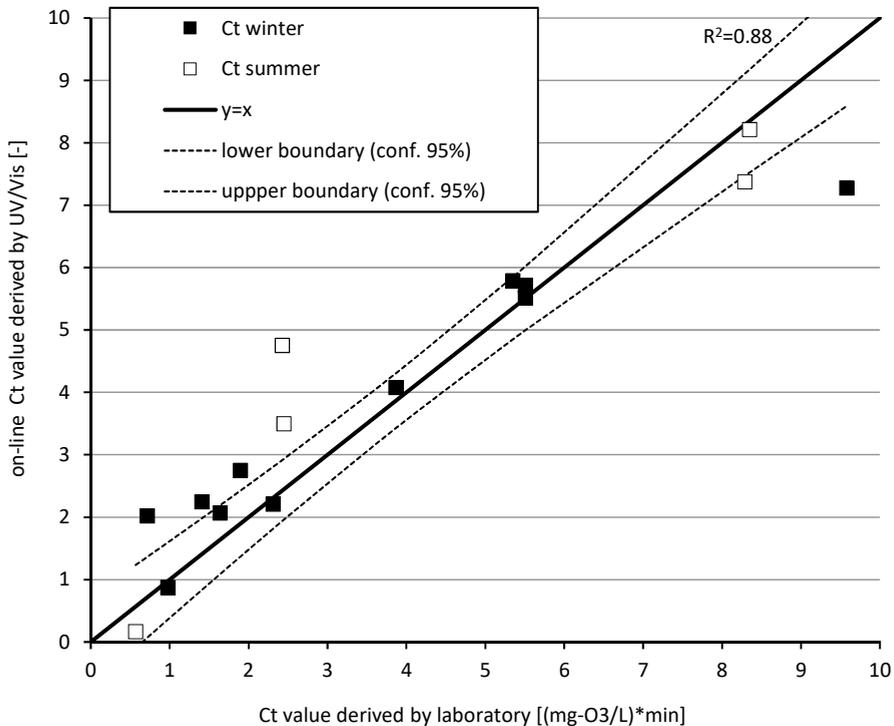


**Figure 4-3** Correlation between the Ct value during ozonation determined from the dissolved ozone concentration measured by the laboratory (X-axis) and from the change in UV absorbance (Y-axis).

Although a good correlation is found, the algorithm sometimes overestimates the *Ct* value. If immediate control would be applied based on these overestimated values, the ozone dosage would be lowered, resulting in a lower *Ct* value and thus lower disinfection than is required. This could affect the log-removal and thus the disinfection achieved by the system. Therefore, it is important to realize that based on this algorithm it is possible to get a good impression of the *Ct* value achieved during ozonation, but that for operational purposes it is important to check the predicted *Ct* value on a regular basis. Verification can be done by measuring the bromate formation and relating this to the *Ct* value using the linear relation observed, and by taking large volume samples which should be tested on the presence of indicator organisms.

**Algorithm for on-line estimation of bromate formation during ozonation**
A total of 19 bromate concentrations and differential absorbance spectra were available to develop an algorithm for the on-line estimation of bromate formation during ozonation. The strongest correlation was found between the normalized differential spectra (differential spectrum divided by the influent spectra) and the bromate concentrations. In total 2 wavelengths turned out to show a significant relationship with bromate concentration ($R^2 = 0.92$) (equation 4-4 and Figure 4-4):

$$BrO_{3,est} = 13.21 + 273.96 \Delta UV_{250,norm} - 236.15 \Delta UV_{270,norm}$$

Peldszus *et al.* (2004) reported that potassium bromate absorbs light well at low wavelengths, with the highest absorbance at 190 nm gradually decreasing to zero at 270 nm. The wavelengths found were at 250 and 270 nm. The first wavelength lies within the absorbance range to what Peldszus *et al.* (2004) reported. The other wavelength lies at the boundary and is likely to correct for other compounds present in the water. The found relationship can help to directly control the bromate formation. The concentration ranges the algorithm was calibrated for varied between 0 – 10 μg $BrO_3$/L, temperatures ranged between 3 – 22 °C and *Ct* values 0.2 and 10 mg/L.min. The average bromide levels were 92 μg/L with a standard deviation of 3 μg/L. These ranges represent a wide spectrum applicable for drinking water applications.

**Algorithm for on-line estimation AOC formation during ozonation**
Besides the on-line estimation of the disinfection, the formation of AOC is also important, since the AOC concentration affects the biological stability of the water produced. In literature it was shown that during ozonation a correlation exists between the change in $UV_{254}$ and the AOC formation (van der Kooij *et al.* 1989). Figure 4-5 illustrates the change in $UV_{254}$ against the amount of AOC formed as observed during this study.
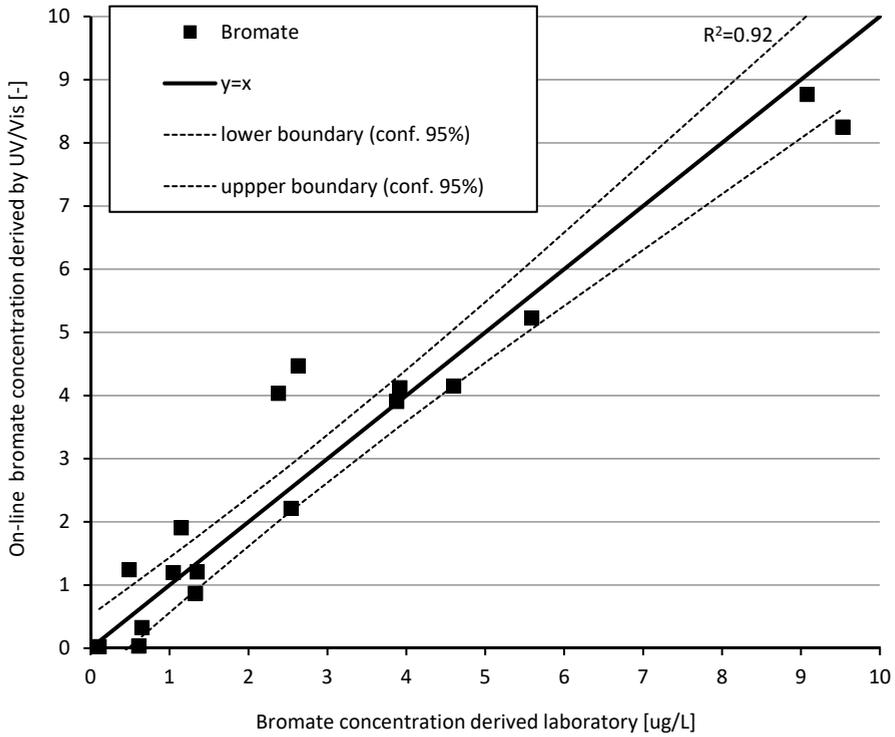
**Figure 4-4** Correlation between the bromate formation measured by the laboratory (X-axis) and from the change in UV absorbance (Y-axis).
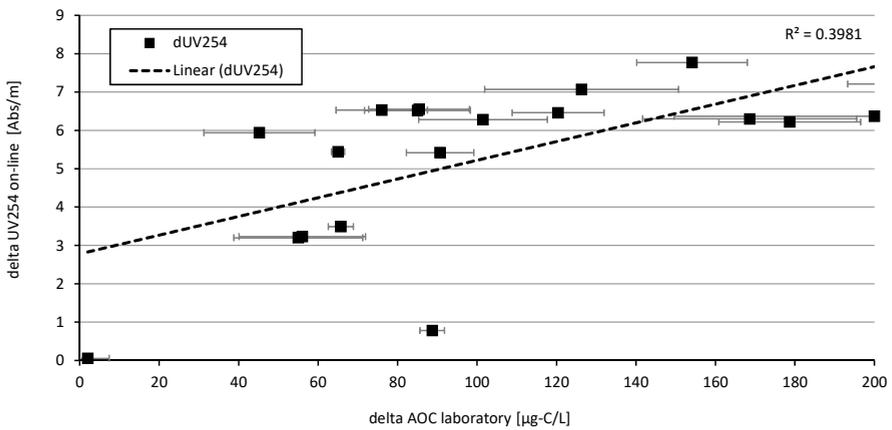


**Figure 4-5** Correlation between AOC formation during ozonation and the change in $UV_{254}$.

In contrast to the strong linear correlations found by van der Kooij *et al.* (1989), during this research the correlation between the AOC formation and ΔUV254 was not very strong. Another method could be the application of a two slope approach as applied by Chys *et al.* (2017). In this research it was investigated whether it was possible to find a stronger correlation based on the use of multiple wavelengths. A total of 19 data points were available to calibrate the algorithm on. The strongest calibration was found by using the derivatives of the differential spectrum. The calibration resulted in an algorithm developed based on a total of 4 wavelengths and a $R^2$=0.74 (Figure 4-6 and equation 4-5):

$$\Delta AOC_{est} = 37.5677 + 7467.54 \cdot \Delta UV'_{320} - 17533.3 \cdot \Delta UV'_{347.5} + 7558.3 \cdot \Delta UV'_{427.5} + 16028.2 \cdot \Delta UV'_{435}$$

It can be observed that the found correlation using multiple wavelengths shows a much better correlation with the amount of AOC formed during ozonation than only using the single wavelength at 254 nm. The algorithm was developed based on a wide variation in AOC concentrations formed as a result of different applied ozone dosages, varying temperatures and raw water compositions as can be seen based on the $UV_{254}$ values (Table 4-1). The wavelengths used for the algorithm range between 320 – 435 nm. The first two wavelengths $UV_{320}$ and $UV_{347.5}$ are located within the area defined as the area organic matter is typically detected (Rieger *et al.* 2004). The other two wavelengths are in the area colour and turbidity are normally detected. These wavelengths might well be related to other processes going on but did turn out to be statistically significant contributing to the amount of AOC formed. This algorithm makes it possible to estimate on-line the amount of AOC formed during ozonation.

The AOC concentrations were measured in duplicate, indicated by the error bars. For some sample quite a wide spread in AOC concentration was measured between the duplicate samples. For the algorithm development the average values were taken. The variations in laboratory results affect the strength of the found correlation.
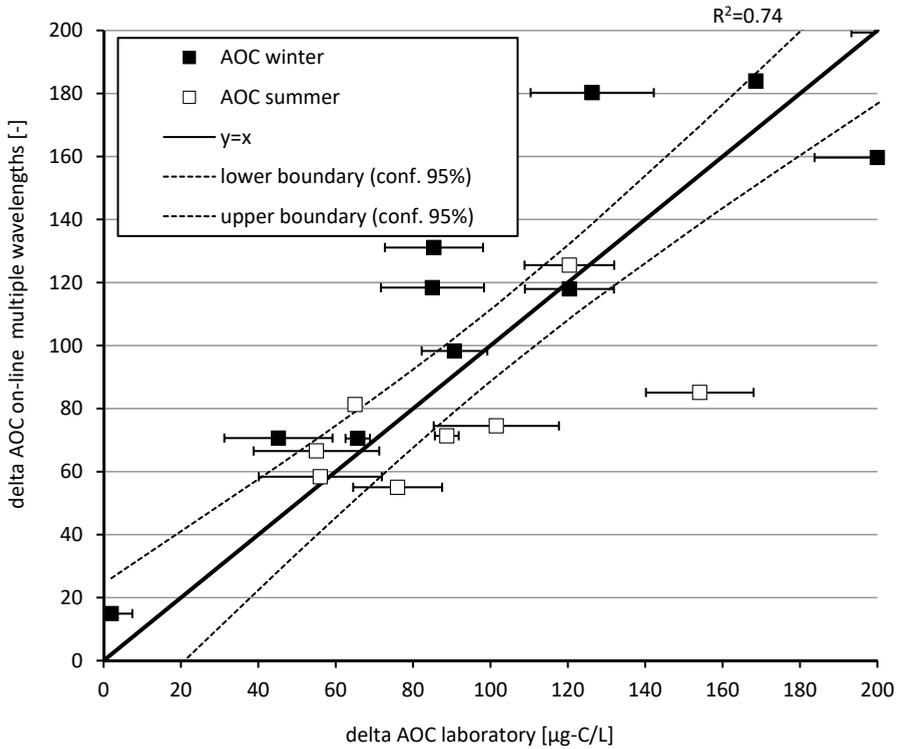
**Figure 4-6** Correlation between AOC formations during ozonation measured by the laboratory and predicted AOC formations based on change in UV/Vis absorbance using equation 4-5.

# CONCLUSIONS

The objective of this study was the development of algorithms that make on-line monitoring of the ozonation process in water treatment possible through a real-time estimation of AOC formation and $Ct$ value based on UV/Vis spectra collected in process. The results show that it was possible to use differential UV/Vis spectroscopy to produce surrogate parameters for the on-line estimation of AOC formation and the Ct value achieved during ozonation. Based on these results it will be possible to optimise the ozone dosage at the Weesperkarspel plant and give a direct indication of the amount of AOC formed during ozonation by only using UV/Vis spectrometers. This information enables operators to better control the subsequent treatment steps such as BAC filtration. On-line monitoring of the $Ct$ values during ozonation gives the operators certainty on the performance of an important disinfection step. Besides, monitoring of the $Ct$ value helps in optimising the ozone dose, leading to less overdosing of ozone, and subsequently less harmful by-products formed. Direct control of the harmful by-products, such as bromate, might results in limiting the applicable ozone dosage to ensure the bromate formation does not exceed the allowed threshold values. Nevertheless, the conventional ways of controlling the ozone dose through the measurement of bromate and determination of indicator organisms in large volume samples should be continued to crosscheck the sensitivity of the developed algorithms.

The algorithms were developed for a certain type of water relatively high in NOM content with DOC values fluctuating between 5.9 – 6.5 mg-C/L and undergoing seasonal changes, such as algal blooms and temperature fluctuations. When wanting to apply this algorithm to different water types it must be tested if the coefficients match the local situation or if a new calibration needs to be developed. Nevertheless, this study shows that it is possible to develop an algorithm for the on-line estimation of $Ct$ value, bromate and AOC formation based on UV/Vis spectra.

# ACKNOWLEDGEMENTS

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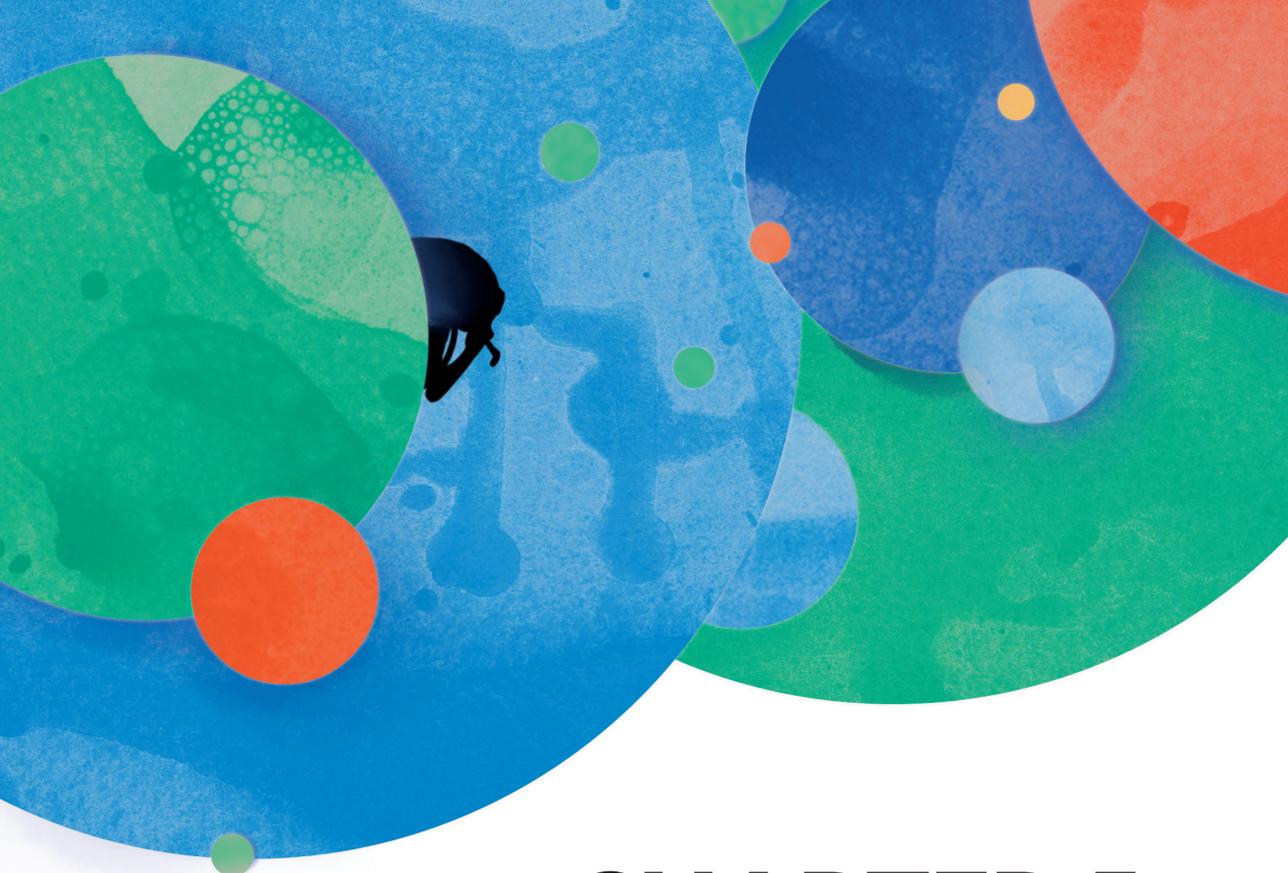
# CHAPTER 5

**Effects of water quality changes on performance of biological activated carbon (BAC) filtration**

# ABSTRACT

Biological activated carbon (BAC) filtration is an important treatment step in the production of drinking water especially if drinking water is produced from surface water. The performance and processes within a BAC filter have been of interest for researchers since the 1980's, mainly because of its ability to remove natural organic matter known as disinfection precursors. A malfunction of one of the pre-treatment steps might affect the feed water quality into the BAC filters. The main objective of this study was to determine the immediate response of the BAC filters to a rapid change in feed water quality. It was shown that with the studied setup it was possible to compare the effect of different pre-treatment steps and subsequent different water qualities on the performance of the BAC filters on the long term adaptation. However, especially the immediate response was not studied in detail before. All filters were able to mitigate a sudden change in feed water quality, either through improved adsorption or increased activity of the biomass on the filter. As a result of this resilience against sudden changes, it is therefore concluded that there is no direct need for very stringent on-line monitoring and continuous adjustments of the feed water quality of the BAC filters. The addition of phosphate resulted in the lowest dissolved organic carbon (DOC) concentration in the effluent of the BAC filters. In this study the influence of intact cells in the feed water on the performance of the BAC filters was shown to be limited.

# INTRODUCTION

Granular activated carbon (GAC) filters in drinking water treatment are used for the removal of organic compounds such as organic micropollutants, organic matter causing colour, taste and odour and precursors for disinfection by-products (van der Hoek *et al.* 1999). Removal of these organic compounds takes place by means of adsorption. The presence of natural organic matter (NOM) in the water can have a negative impact on the organic micro-pollutant removal due to pore blocking and competition (van der Aa *et al.* 2006a, Weber 2004). When GAC filters are preceded by an oxidation step, the large organic molecules are converted into low molecular weight molecules enhancing the biological activity in the water and on the GAC grains. This turns the GAC filters into biological activated carbon (BAC) filters (Graveland 1996, Nishijima *et al.* 1992), where simultaneous removal of NOM by adsorption and biodegradation takes place. This has a positive effect on the required regeneration frequency, due to less pore blocking by NOM, and typically makes BAC filtration more (cost) effective than GAC filtration (Graveland 1996). The drawback of converting NOM into biodegradable NOM is the negative effect this has on the biological stability of the drinking water (Escobar *et al.* 2001). A balance exists between the amount of biodegradable NOM that is produced during oxidation and the amount that can be biodegraded in the BAC filters (van der Aa *et al.* 2011).

Biodegradation of NOM takes place via microorganisms (biomass) that grow on the external surface and in the macro-pores of the BAC filter grains (Servais *et al.* 1994). The biomass activity determines the degradation rate of NOM (Lazarova and Manem 1995). Persson *et al.* (2006) described that the activity and concentration of biomass depends on the concentration of nutrients, intact cell concentration in the feed water and predation. In 2006, van der Aa *et al.* set up a computer model to describe the simultaneous adsorption and biodegradation of NOM in BAC filters. From this model it was concluded that, in addition to substrate concentration and predation, maintenance, attachment/detachment and transport of bacteria could not be neglected when determining the biomass development. This is in line with what Uhl and Gimbel (2000) found, indicating the need for deposition of bacterial cells from the influent to maintain a solid biofilm. On the other hand Simpson (2008) described that efficient substrate removal took place even when the number of bacterial cells in the influent was low. Recently, Liao *et al.* (2016) found that nutrients play a more important role than bacterial cells in the development of biomass density. However, when the nutrient conditions are similar, the biomass in the influent becomes the determining factor.

Due to the complexity of the measurements to determine bacterial cells and biomass activity, there has been a lack of available datasets representing the biomass development over a long period of time and over the height of the filter bed (Velten *et al.* 2011). In 2005, Hammes and Egli published a method for the determination of intact cell concentrations in water with flow

cytometry. It was shown that this technique was a rapid, easy and sensitive method to determine concentrations of intact cells in water (Hammes *et al.* 2008). By combining flow cytometry data with adenosine tri-phosphate (ATP) measurements it was possible to describe the initial colonization and development of biomass (Velten *et al.* 2011). Furthermore, it was investigated if a correlation existed between biomass growth and the assimilable organic carbon (AOC) concentration. AOC represents the readily available carbon for cell growth. No correlation was found between the AOC concentration and biomass growth.

Microorganisms require carbon (C), nitrogen (N) and phosphorus (P) as main nutrients. Van der Kooij *et al.* (1982) established that the typical ratio of C:N:P is 100:10:1. Therefore it is often assumed that biodegradable organic matter is the growth limiting nutrient for NOM reducing bacteria. However, in some cases it was found that microbial growth in drinking water was limited by phosphorus (Juhna and Rubulis 2004, Lehtola *et al.* 2002, Sathasivan *et al.* 1997, van der Aa *et al.* 2002) or nitrogen (Liao *et al.* 2016) instead of carbon. Dhawan *et al.* (2017) investigated the influence of nutrient supplementation on DOC removal by BAC filters by testing different types of ratios. Increased nutrient concentrations beyond the typical ratio of 100:10:1, resulted in increased removal of DOC. In addition to DOC removal, the effect of increased nutrient concentrations on biomass development was determined by means of phospholipid and ATP analysis. In this case no correlation could be found between the DOC removal and the biomass measurements applied.

Although researchers have tried to find correlations between biomass development and the observed biodegradation in the BAC filters under varying operating conditions, no clear correlations have been found (Dhawan *et al.* 2017, Velten *et al.* 2011). This underlines the complexity of the processes taking place in the BAC filters. BAC filters are frequently used in the production of drinking water for the removal of organic micro pollutants and organic matter, especially when produced from (humic rich) surface water. Differences in feed water quality are the result of pre-treatment steps (coagulation/flocculation, ozonation and phosphate addition), commonly applied in the production of drinking water. These long term effects of changes in feed water quality were investigated and compared to previously published research. However, to the best of our knowledge, the immediate responses of BAC filters, which have been in operation for multiple years, to rapid changes in feed water quality have not been studied previously. A malfunction of one of the pre-treatment steps might affect the feed water quality into the BAC filters, therefore being representative for possible events taking place in common drinking water treatment trains. Investigating the immediate responses of BAC filters to changes in water quality is an important step towards understanding the ability of BAC filters to produce a stable drinking water quality under varying conditions and was the main objective of the presented study.

# MATERIALS AND METHODS

**Pilot plant set-up and operation**

The experiments were carried out at the pilot plant of Waternet, the water-cycle company of Amsterdam and surrounding areas, location Weesperkarspel (the Netherlands). The pilot plant was fed with humic rich surface water (average DOC concentration of 9.2 mg-C/L), pre-treated by coagulation/sedimentation, followed by 100 days retention in a reservoir and subsequently filtered over rapid sand filters. The pilot plant includes all treatment processes of the full-scale plant, consisting of ozonation, pellet softening, BAC filtration and slow sand filtration as final disinfection step.

Four BAC filters with a surface area of 0.43 m$^2$, bed height of 3.2 m, filtration velocity of 4 m/h and an empty bed contact time (EBCT) of 48 minutes, were operated at the pilot plant. Before the experiment started, the pilot plant was operating at the same setpoints as the full-scale plant. The filters were fed with pre-ozonated (0.42 mg-O$_3$/L)/(mg-DOC/L) and softened water, resulting in a feed water quality with an average DOC concentration of about 5.5 mg-C/L and an AOC concentration of about 60 µg-C/L. The activated carbon (type: Norit GAC 830P) was taken from the full scale plant and had been in service for 5 years in the pilot plant to minimize the effect of adsorption during the experiments. Adsorption processes were neglected to represent the worst case scenario from an operating point of view. The BAC filters are supposed to be less robust if only biodegradation processes are considered, than if both biodegradation and adsorption takes place.

At the start of the experiment (day 1), the feed water quality to BAC 1, 2 and 3 was changed (see Figure 5-1), while the feed water quality of BAC 4 remained unchanged. BAC 4 served as a reference filter containing a moderate concentration of bacterial cells due to bacterial growth in the softening step, and high biodegradable NOM concentration, measured as AOC. BAC 1 was fed with pre-treated water only (coagulation/sedimentation followed by rapid sand filtration). This resulted in high intact cell concentrations and a low AOC concentration. BAC 2 received ozonated water directly, resulting in the highest AOC concentration and low concentration of intact cells. BAC 3 was fed with water similar to the original situation (moderate concentration of intact cells and AOC) with added phosphate in the form of phosphoric acid (approximately 50 µg-P/L) to promote bacterial growth in the BAC filter. Phosphate was added to be able to investigate the effect of coagulation/sedimentation on biological activity in the filter bed.

**Sampling and water quality analysis**

Water samples were taken from the influent and effluent of the four filters. The natural organic matter, dissolved in water, was determined by measuring the DOC concentration. The DOC, pH and phosphate concentration were analysed according to the Standard Methods (Eaton *et al.* 2005). The readily available carbon for cell growth was determined by measuring the AOC concentration. AOC was measured in duplicate, applying the simultaneous incubation of the strains P17 and NOX as described by van der Kooij and Hijnen (1984).



DOC = 6.1 mg-C/L
AOC = 20 µg-C/L

Ozonation
(0.4 mg-O$_3$/L)/(mg-DOC/L)

Pellet Softening

Phosphate dosing

Original situation

High intact cell concentration:
*4.2 (± 2.2) x10$^4$ cells/mL*
Low AOC concentration:
*22 (±25) µg-C/L*
Low phosphate concentration:
*0.002 mg-P/L*

Low intact cell concentration:
*1.1 (± 0.5) x10$^4$ cells/mL*
High AOC concentration:
*85 (±37) µg-C/L*
Low phosphate concentration:
*0.002 mg-P/L*

Intact cell concentration:
*2.2 (± 1.2) x10$^4$ cells/mL*
High AOC concentration:
*77 (±24) µg-C/L*
Increased phosphate concentration:
*0.05 mg-P/L*

Intact cell concentration:
*1.9 (± 1.2) x10$^4$ cells/mL*
High AOC concentration:
*66 (±14) µg-C/L*
Low phosphate concentration:
*0.002 mg-P/L*

Intact cells
Total and free
ATP
DOC
AOC
pH
Phosphate

BAC 1    BAC 2    BAC 3    BAC 4

ATP on carbon

Intact cells
Total and free
ATP
DOC
AOC
pH
Phosphate

**Figure 5-1** Schematic overview of pilot plant BAC filters.

Vital *et al.* (2012) showed that flow cytometry for measuring cell concentrations and ATP analysis were able to describe major bacteriological changes in the Weesperkaspel full scale treatment plant. In this study similar methods were used, with intact cell concentration being determined by fluorescent staining and flow cytometry as described by Hammes *et al.* (2008). The total ATP was determined using the BacTiter-GloTM reagent (Promega Corporation, Madison, WI, USA) and a luminometer (Glomax, Turner Biosystems, Sunnyvale, CA, USA) as described by Hammes *et al.* (2010). The data were collected as relative light units and converted to ATP by means of a calibration curve made with a known ATP standard (Promega). Free ATP was determined by filtering the sample through a 0.1 μm sterile syringe filter (Millex®-GP, Millipore, Billerica, MA, USA), followed by analysis described above. The cell-bound ATP was calculated by subtracting the free ATP from the total ATP. The intact cell concentration and cell bound ATP enabled the calculation of the ATP-per-cell concentration, as expressed in equation 5-2.

Activated carbon samples were taken from 0.1 m and 1.6 m below the top of the filter bed, corresponding with an EBCT of 1 and 22 minutes, respectively. The biomass activity of the carbon samples was determined by ATP on carbon according to the method described by Magic-Knezev and van der Kooij (2004).

**Calculations and statistics**

To compare the microbiological activity between the four BAC filters, the overall ATP concentration in the filters was determined as described by Velten *et al.* (2011). Each filter was partitioned into two parts. The line of demarcation was in the middle of the two sampling points. In line with Velten *et al.* (2011) it was assumed that the measured ATP on carbon at the sampling points represented the average ATP concentration on carbon for the segment. This resulted in the following equation for the determination of ATP in filters (eq. 5-1):

$$ATP_{segment1} = A \cdot h_{layer1} \cdot \overline{ATP_{on\_carbon\_EBCT\_1min}} \cdot \rho_{NoritGAC830P}$$

$$ATP_{segment2} = A \cdot h_{layer2} \cdot \overline{ATP_{on\_carbon\_EBCT\_22min}} \cdot \rho_{NoritGAC830P}$$

$$ATP_{overall} = ATP_{segment1} + ATP_{segment2}$$

where $A$ represents the surface area in m$^2$, $h_{layer1}$ represents the height of layer 1 in m, $ATP_{on\_carbon\_EBCT\_1min}$ represents the ATP concentration on carbon at an EBCT of 1 min in (g ATP/g carbon) and $\rho_{NoritGAC830P}$ represents the density of Norit GAC830P carbon in g/m$^3$.

The ATP-per-cell was determined by equation 5-2 (Siebel *et al.* 2008):

$$ATP-per-cell = \frac{Cell-bound\_ATP \times 10^{-9}}{Intact\_cells \times 10^{3}}$$

where *Cell-bound ATP* is expressed in ng/L, the *Intact cells* is expressed in cells/mL. The *ATP-per-cell* is expressed in g ATP/cell.

The Mann-Whitney U test (ranksum), a nonparametric test fit in Matlab (Matlab 2009) to test skewed datasets (not normally distributed), was used to evaluate statistically if the influent and effluent water qualities of the BAC filters were significantly different. The statistical difference is expressed by the *p*-value, where values smaller than 0.05 indicate a significant difference with a confidence interval of 95%. For average values the standard deviation was displayed as well as the number of samples (*n*) based on which the average was determined.

**Immediate response and long term adaptation**
The sampling frequency at the beginning of the experiment was high and taken at day 1, 5, 8 and 13 after switching to the different pre-treatment steps. To determine the effects of the change in pre-treatment on the long term adaptation of the biomass and the biodegradation efficiency, the filters were sampled once every four weeks for a period of 436 days.

# RESULTS

**Differences in influent quality**

Comparison of the influent qualities of BAC 1 and BAC 4 showed the effect of additional treatment steps versus direct treatment of pre-treated surface water (Figure 5-1). The pre-treated surface water contained low AOC concentrations since most biodegradable organic matter had been consumed during the long residence times in pre-treatment. Without disinfection by ozonation the intact cell concentration in BAC 1 was high. The feed waters of BAC 1 and 4 were statistically different for both intact cells and AOC (p-values of 0.005 and 0.003, respectively). Comparison of BAC 2 and 4 showed the effect of a limited concentration of intact cells (*p*-value of 0.02) in the feed water due to the addition of ozone, and subsequent disinfection of bacterial cells. By applying ozone, part of the organic matter was converted into biodegradable organic matter, expressed by the increased AOC concentrations in the influent of BAC 2 (van der Helm *et al.* 2008). Biological growth, occurring in the pellet softening step, reduced the AOC concentration and increased the concentration of intact cells in the influent of BAC 3 and 4 (Hammes *et al.* 2011). No significant statistical difference was observed between the AOC concentrations in the feed of BAC 2, 3 and 4, although BAC 3 and 4 were preceded by the pellet softening step. The addition of phosphate to the feed water of BAC 3 provided insight in possible limitation in phosphate (*p*-value of 0.0002), when comparing BAC 3 with BAC 4.

**Biomass development**

The active biomass on the granular activated carbon grains was measured at the start of the experiment at two different bed heights, equivalent with an EBCT of 1 and 22 minutes. Based on these measurements the total amount of ATP on the activated carbon in the filters was determined using equation 5-1. At the start of the experiment the total ATP was statistically similar for all four filters (Table 5-1), with *p*-values of 1.0, 0.1 and 0.3 when comparing the individual filters with BAC 4. The increase in active biomass calculated for BAC 1 and BAC 4 (reference filter) was limited compared to the increase in ATP measured for BAC 2 and 3.

**Table 5-1** Total amount of ATP on activated carbon at the start of experiment (average of three measurements) and end of experiment (average measurement based on last three sampling days).

|  | BAC 1 [g ATP] | BAC 2 [g ATP] | BAC 3 [g ATP] | BAC 4 [g ATP] |
|---|---|---|---|---|
| Start of experiment | 0.24 | 0.33 | 0.24 | 0.24 |
| End of steady state situation | 0.28 | 0.60 | 0.72 | 0.33 |
| Change in ATP concentration | 0.03 | 0.27 | 0.48 | 0.09 |

The highest concentrations of active biomass were found in the top of the filter and decreased with increasing depth (Table 5-2). Similar to what was found by Urfer and Huck (2001). The measured active biomass concentrations were in the same order of magnitude as found by van der Aa *et al.* (2006a) and Velten *et al.* (2011).

**Table 5-2** ATP on carbon concentrations in steady state situation based on the average (and standard deviation) of the last three sampling days for different EBCTs.

|  | BAC 1 | BAC 2 | BAC 3 | BAC 4 |
|---|---|---|---|---|
|  | g ATP/g carbon | g ATP/g carbon | g ATP/g carbon | g ATP/g carbon |
| EBCT 1 min | $1.12 (\pm0.60) \times 10^{-6}$ | $2.93 (\pm1.87) \times 10^{-6}$ | $3.38 (\pm1.35) \times 10^{-6}$ | $1.21 (\pm0.68) \times 10^{-6}$ |
| EBCT 22 min | $0.20 (\pm0.03) \times 10^{-6}$ | $0.26 (\pm0.11) \times 10^{-6}$ | $0.35 (\pm0.09) \times 10^{-6}$ | $0.29 (\pm0.04) \times 10^{-6}$ |

**Intact cell concentration, cell-bound ATP and bacterial changes**

A comparison was made between changes in intact cells, over the individual filters, immediately after start of the experiment (first three days) and after reaching steady state (average of 8 samples taken during the period of one year), see Table 5-3. In BAC 1 the removal percentage of intact cells varied from 30% immediately after start to an average 23% removal after reaching steady state. Similarly, BAC 4 also showed a small variation with 47% removal of intact cells the first three days after start experiment while based on the yearly average 42% removal was observed. The intact cell concentration in the effluent of BAC 2 showed an increase of 442% compared to the influent of BAC 2 in the first three days after the start of the experiment, indicating a considerable growth or detachment of bacteria. An increase in intact cells was still observed in BAC 2 during the steady state situation, but only with a percentage of 35%, still indicating growth or detachment of bacteria (Lautenschlager *et al.* 2014). BAC 3 also responded with a direct increase in intact cells of 28% when changing the feed water quality whilst in the steady state situation a decrease of 26% was observed over the filter.

**Table 5-3** Difference in intact cells measured in influent and effluent expressed in change over the filter by subtracting the effluent concentration minus the influent concentration divided by the influent concentration and multiplied with 100 to obtain the percentage.

|  | Immediate response [effluent – influent] expressed in % | Steady state [effluent – influent] expressed in % |
|---|---|---|
| BAC 1 | -30 | -23 |
| BAC 2 | +442 | +35 |
| BAC 3 | +28 | -26 |
| BAC 4 | -47 | -42 |

In the steady state situation, the concentration of intact cells in the feed water of BAC 1 was the highest, due to the absence of a disinfection step, with on average $3.5 \times 10^4$ ($\pm 1.7 \times 10^4$, n=8) cells/mL, being about two times higher than in the feed of BAC 4 (Figure 5-2). The cell-bound ATP concentration in the feed of BAC 1 was 50% higher, thus resulting in lower ATP-per-cell concentrations. The intact cell concentration in the effluent of BAC 1 decreased on average with 23% compared to the influent, while the cell-bound ATP concentration decreased with 28%.

The intact cell concentration in the feed water of BAC 2 was the lowest with on average $9.7 \times 10^3$ ($\pm 4.7 \times 10^3$, $n$=8) cells/mL, 43% less than in the feed of BAC 4, as a result of the applied ozone step. However, the cell-bound ATP concentration was similar to that of the feed of BAC 4. This deviation in pattern between intact cell and cell-bound ATP concentration during ozonation has also been observed by Vital $et\ al.$ (2012).

The increased intact cell concentration in the influent of BAC 3 and 4 was the result of biological growth taking place in the pellet softening step, as also observed by Hammes $et\ al.$ (2011) and Vital $et\ al.$ (2012). The concentration of intact cells in the influent of BAC 3 and 4 was similar with $1.7 \times 10^4$ ($\pm 0.8 \times 10^4$, $n$=8) cells/mL. Both filters showed a decrease in intact cells after filtration with 26% for BAC 3 and 42% of BAC 4. The large variation in cell-bound ATP measurements also resulted in the ATP-per-cell concentration to fluctuate a lot, making it difficult to compare the results (data not shown).

**Phosphate uptake**

The phosphoric acid dosage upstream of BAC 3 resulted in significant higher phosphate concentrations in the influent. At the start of the experiment almost all phosphate dosed was taken up completely, measured by the difference between influent and effluent concentration. After 5 days the uptake started to decrease gradually until a steady state uptake of about 0.005 ($\pm 0.001$, $n$= 5) mg-P/L was reached (Figure 5-3).

The ortho-phosphate concentration in the influent of BAC 3 showed some variation with higher concentrations in the beginning of the experiment. Measurements showed that the concentrations in the influent of BAC 1, 2 and 4 were stable, and variations in BAC 3 was therefore the result of variations in dosing, due to variances in the operation of the dosing pump. Since the uptake was significantly lower than the measured influent concentrations it can be concluded that the fluctuations in the dosing did not interfere with the intended setup of the experiment.
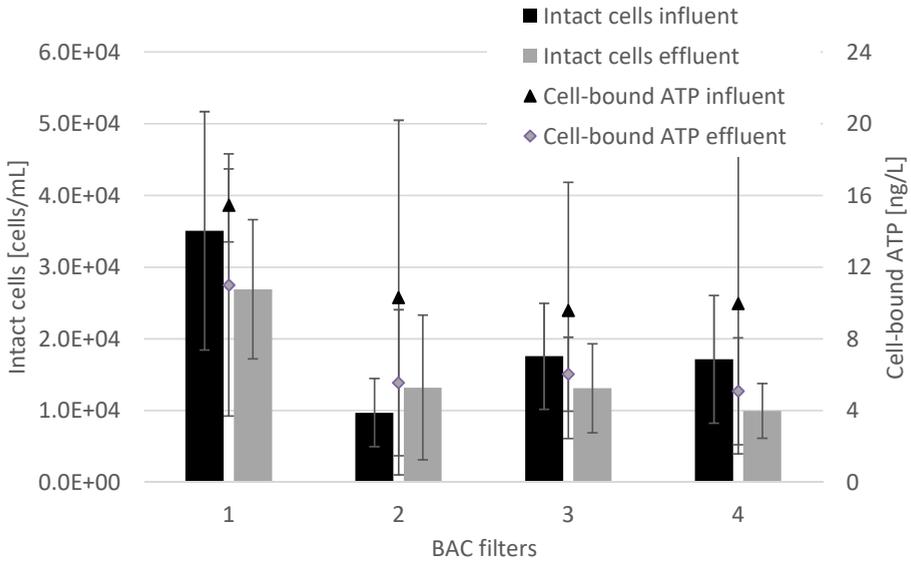
**Figure 5-2** Steady state (average of 8 measurements, covering a one year timeframe) intact cell concentration (left axis) and cell-bound ATP (right axis) measured in both influent as effluent of the four BAC filters.
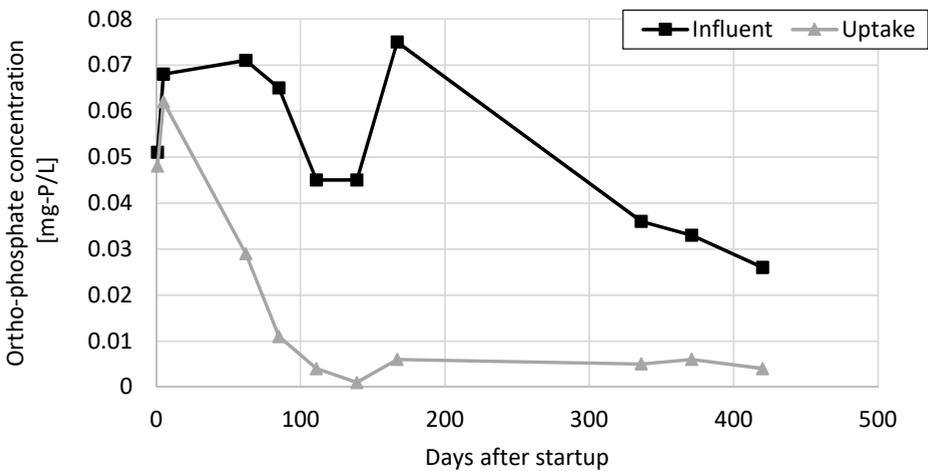


**Figure 5-3** Measured ortho-phosphate concentration in influent of BAC3 and calculated uptake of ortho-phosphate based on the difference between influent and effluent.

## Removal efficiency DOC

The non-ozonated water (BAC 1 feed) had the highest DOC concentration (6.0 ± 0.1 mg/L, n=8) and, consequently, also had a yellowish colour (Figure 5-4a). The colour was subsequently removed by treatment with ozone which slightly reduced (not significantly) the DOC concentration and significantly increased the readily biodegradable NOM concentration (expressed as AOC).
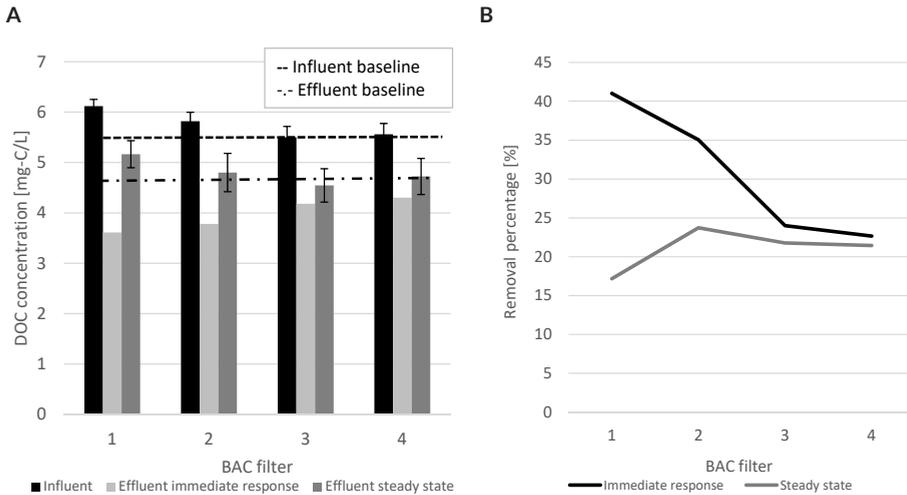


**Figure 5-4** a) DOC concentration measured in influent and effluent for both the immediate response and steady state situation (left) and b) removal percentage DOC per filter for immediate response and steady state situation. The indicated baseline refers to the original situation (BAC 4) and is included for easy comparison.

Direct feed of ozonated water (BAC 2) resulted, immediately after the start of the experiment, in a lower DOC effluent concentration with 4.2 (± 0.03, *n=2*) mg/L and higher removal percentage of 35% versus 24% and 23% for BAC 3 and 4, respectively. After reaching steady state, the removal percentages in BAC 2 were still the highest with 24%, followed by BAC 3 with 22% and BAC 4 with 21% (Figure 5-4b). The lowest DOC concentrations was reached by BAC 3 with 4.5 (± 0.2, *n=8*) mg-C/L (not significant with *p*-value of 0.1679) followed by BAC 4 with 4.7 (± 0.2, *n=8*) and BAC 2 with 4.8 (± 0.2, *n=8*) mg-C/L (not significant with *p*-value of 0.0891).

**Bacterial growth potential produced water**

The measured AOC concentration in the effluent was used as an indicator of the bacterial growth potential of the water. No additional source of nutrients were introduced when measuring the growth of the two bacterial strains *Pseudomonas fluorescens* P17 and *Spirillum spp.* NOX. Therefore it was assumed that the measured AOC concentration represented the actual growth potential of the water instead of just carbon limitation (Ross *et al.* 2013). Thus, the lower the AOC concentration the lower the bacterial growth potential. The effluent from BAC 1 had, in steady state, the lowest AOC concentration. The application of a disinfection step for the treatment of surface water before BAC filtration, has shown to be beneficial with respect to regrowth potential and control of disinfection by-products, such as chlorinated hydrocarbons (Graveland 1996). Because of this, BAC 1 was not discussed in further detail when evaluating the growth potential.

The influent AOC concentration of BAC 2 showed the highest variability in the measurement, caused by seasonal variation of the influent quality and subsequent influence of ozone on production of biodegradable organic matter (Figure 5-5a). The influent AOC concentration of BAC 3 and 4 showed less seasonal influences as a result of the pellet softening step between the ozone and BAC filters, levelling out the differences. The AOC concentration in the feed water of BAC 2 was the highest followed by BAC 3 and 4. The difference observed between the AOC concentration in BAC 3 and 4 is explained by the addition of phosphate and the AOC measurement representing the growth potential instead of just the carbon growth potential, indicating phosphate limitation of the water (Ross *et al.* 2013).

When comparing the AOC concentration of the produced water from BAC 2, 3 and 4, BAC 2 resulted in the lowest AOC concentration for both the immediate response (17 µg-C/L) as well as the steady state situation (36 ± 6 µg-C/L, n=4). With the highest AOC concentration, on average 74 (± 24, n=4) µg-C/L, in the influent of BAC 2, this also resulted in the highest removal percentage of 51% (Figure 5-5b). Statistical analysis showed that the removal percentages were not significantly different. The immediate response of BAC 3 resulted in a higher AOC concentration in the effluent than BAC 4, while the steady state consolidated with removal percentages similar to the reference situation (BAC 4). Even though the AOC concentrations and removal percentages were not statistically different, it was shown that sufficient nutrients positively influence the performance of the BAC filters and bacterial growth potential of the water.
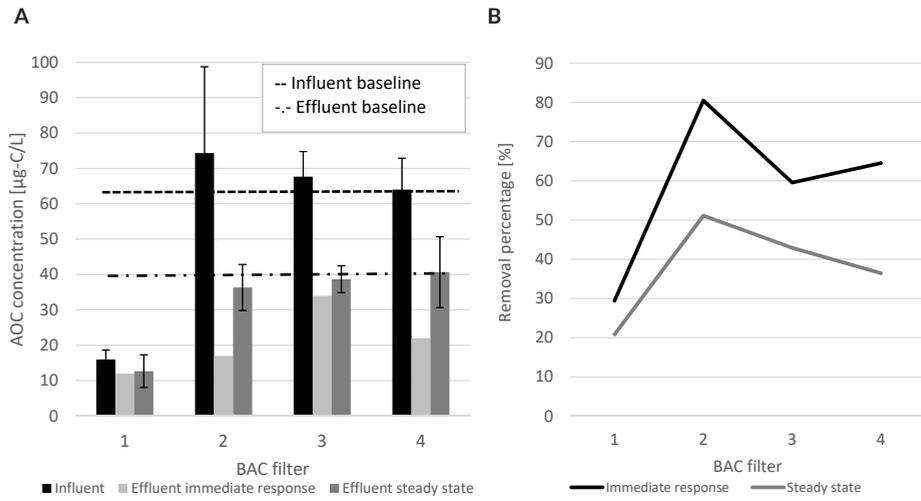
**Figure 5-5** a) AOC concentration measured in influent and effluent for both the immediate response and steady state situation (left) and b) removal percentage AOC per filter for immediate response and steady state situation. The indicated baseline refers to the original situation (BAC 4) and is included for easy comparison.

# DISCUSSION

## Long term effects of changes in treatment plant set-up

The ATP on carbon, intact cell concentration, cell-bound ATP and ATP-per-cell concentration provided insight in the behaviour of the filters and development of biomass. All filters showed an increase in active biomass concentration until the steady state situation was reached after 111 days. This was in line with the periods between 2 to 8 months that have been reported for the biomass to fully adapt to the new feed water quality (Servais *et al.* 1994, van der Aa *et al.* 2006a). The highest concentrations of active biomass were found in the top of the filter and decreased with increasing depth, similar to what was found by Urfer and Huck (2001). The measured active biomass concentrations were in the same order of magnitude as found by van der Aa *et al.* (2006a), Velten *et al.* (2011).

The ATP-per-cell concentration is correlated with size and physiological activity of the cells (Hammes *et al.* 2010). Lower ATP-per-cell concentrations indicate the presence of smaller or less active cells in the feed of BAC 1 compared to the feed of BAC 4. The decrease in intact cells and cell-bound ATP coincided with the limited growth of biomass found in BAC 1, measured through the ATP on carbon concentrations (Tables 5-1 and 5-2). Although the intact cell concentration in the feed water of BAC 2 was lower, during steady state, the intact cell concentration in the effluent of BAC 2 was 32% higher than in the effluent of BAC 4 (Figure 5-4). The increase in intact cell concentration showed a considerable growth of bacteria in BAC 2. This was also reflected by the ATP on carbon concentrations increasing in time in BAC 2 (Table 5-1). The increase in ATP on carbon concentration in BAC 3 reflected biological growth, even though the intact cell concentration decreased. For BAC 4 no direct increase in ATP was expected since the filter had been operating under similar conditions for 5 years. The observed increase might be the result of the sampling period and subsequent seasonal fluctuations. Reactor biomass and ATP on carbon measurements reported by Velten *et al.* (2011) also showed fluctuations occurring in the filter bed after reaching steady state situation.

The highest DOC concentration of all filters was measured in the effluent of BAC 1, which still contained a yellowish colour. The water quality of the effluent of BAC 1 showed the importance of a disinfection pre-treatment step before BAC. The addition of phosphate to the influent of BAC 3 resulted on average, in an increased DOC removal. The intact cell concentration in the feed water of both filters was similar, indicating that a higher nutrient concentration resulted in a better performance of the filter, also found by Dhawan *et al.* (2017). Juhna and Rubulis (2004) found similar results for possible phosphate limitation due to pre-treatment with coagulation/flocculation. It would be interesting to investigate if the addition of phosphate to BAC 2 would also have enhanced the DOC removal. In general, the removal percentages found for DOC were similar to the percentages found by Velten *et al.* (2011), even though the influent concentrations in this study were almost 5 times higher.

The effect of intact cell concentration was determined by comparing BAC 2 with BAC 4. The feed water of BAC 2 contained 43% less intact cells, whilst the AOC concentration, representing the bacterial growth potential of the water, was only 9% higher than BAC 4. Contrary to what Liao *et al.* (2016) found, the intact cell concentration in the influent had no determining factor in the performance of the BAC filters.

**Phosphate dosing requirements**

The phosphate uptake showed a gradual decrease until a steady state was reached (Figure 5-3). The high uptake in the beginning suggested the adsorption of phosphate onto the activated carbon, as seen by several researchers (Kumar *et al.* 2010, Nishijima *et al.* 1997). On the other hand, Momba and Cloete (1996) described that the uptake of phosphate in a wastewater treatment plant and subsequent removal changes depending on growth state the biomass was in. High phosphate uptake was found during the lag and logarithmic growth phase and low phosphate uptake was found during the stationary phase. Due to the absence of precipitating chemicals and filter operating conditions it was not expected that precipitation of the dissolved phosphate took place. Being able to understand the processes taking place might help to understand and develop an optimised dosing scheme.

**Immediate response to change in feed water quality**

BAC 2 and 3 showed a different behaviour in intact cells directly after the start of the experiment and once steady state was reached. Both filters showed an increase in intact cells in the effluent, whilst this either reduced (BAC 2) or changed to a decrease in intact cells for the steady state situation. In BAC 3 the nutrient balance in the feed water changed by the addition of phosphate. In BAC 2 the significant increase was likely caused by an increase in nutrient concentration (readily available carbon) since the filter was directly fed with ozonated water without any intermediate biological treatment step, in this case pellet softening. The increased biodegradability of the organic matter in the water resulted in an immediate response by the biomass, converting more DOC for both filters. Interestingly the DOC concentration in the effluent of BAC 1 also improved compared to BAC 4. Even though the DOC concentration was the highest in BAC 1 feed water, the immediate response, after start-up of the experiment, showed an increased removal of DOC resulting in the lowest effluent concentration (Figure 5-4a). The application of ozone, prior to start experiment, had resulted in higher concentration of DOC with polar groups within the organic molecules, having reduced the adsorption capacity of DOC (Sontheimer *et al.* 1988, van der Aa *et al.* 2006b). Thus, even though the BAC filters were in operation for five years, switching the feed water quality from ozonated to non-ozonated water probably resulted in increased (non-polar) DOC adsorption.

The reaction of the biomass and improved adsorption resulted in an improved effluent quality immediately after the water quality of the feed water changed.

# CONCLUSIONS

The main objective of this study was to determine the immediate response of the BAC filters to a rapid change in feed water quality. First, it was shown that with the studied setup it was possible to compare the effects of different pre-treatment steps and subsequent different water qualities on the performance of the BAC filters on the long term adaptation. However, especially the immediate response of the BAC filters on water quality changes was not studied in detail before. It was observed that all filters were able to mitigate a sudden change in feed water quality, either through improved adsorption or increased activity of the biomass on the filter media. As a result of this resilience against sudden changes, it could therefore be concluded that there is no direct need for very stringent on-line monitoring and continuous adjustments of the feed water quality of the BAC filters.

The long term adaptation of the BAC filters confirmed the need for sufficient nutrients (readily available carbon and phosphate) in the feed water for optimal performance. The influence of intact cells was shown to be limited. Interestingly the storage of phosphate in the BAC filters as a result of adsorption or uptake by the biomass does not necessitate continuous dosing of phosphoric acid. It is recommended to further investigate the optimised dosing scheme.

# ACKNOWLEDGEMENTS

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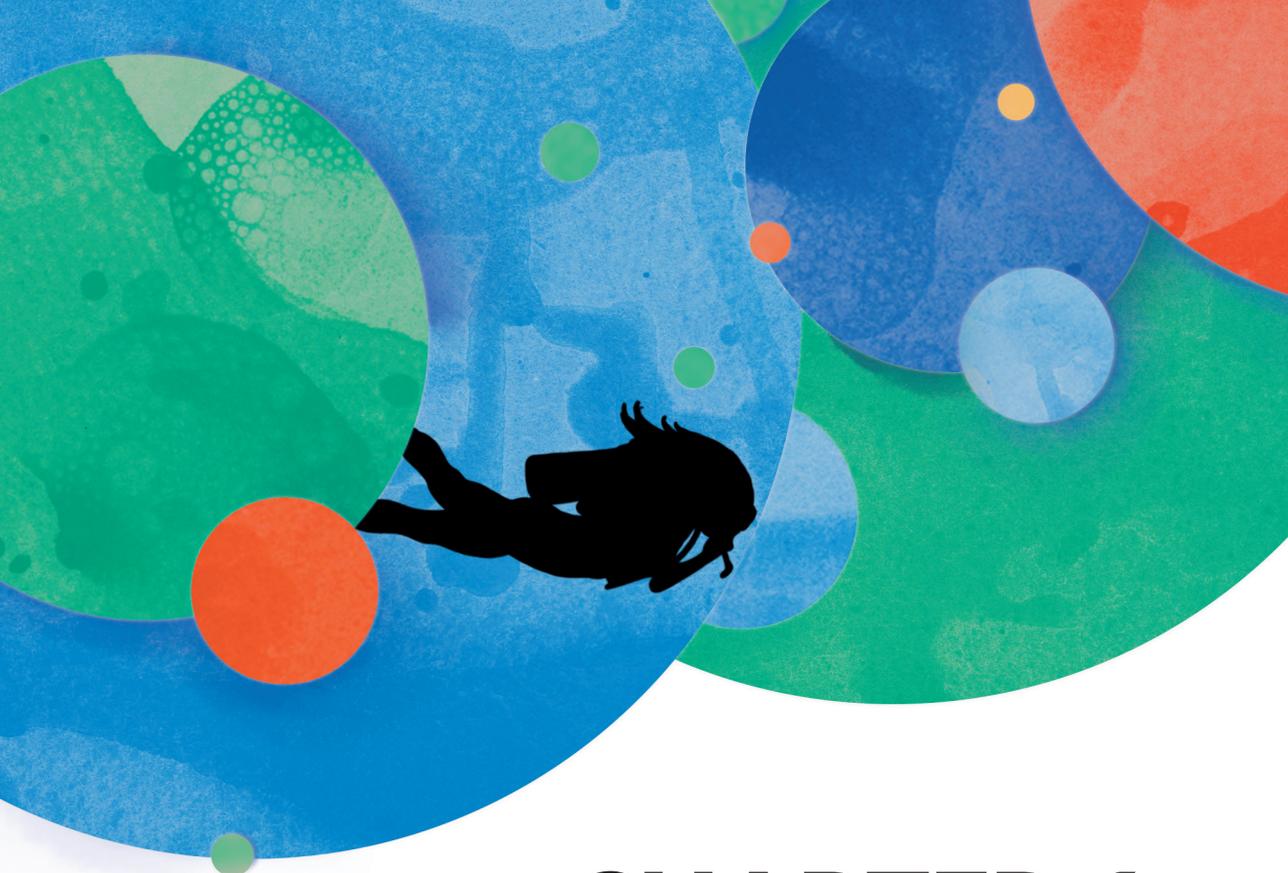
# CHAPTER 6

**Prediction of Clogging of Biological Activated Carbon Filters during variations in operation of drinking water treatment plant**

# ABSTRACT

In the biological activated carbon (BAC) filters for drinking water treatment clogging takes place. The objective of this research was to determine which of the mechanisms, physical, chemical or biological processes, were responsible for rapid clogging of the BAC filters of water treatment plant Weesperkarspel of Waternet, the Netherlands. A simplified model, based on retention and mass balances, to predict the filter run times was developed. Results showed that clogging in the BAC filters was a combination of chemical and biological mechanisms. The simplified model was able to accurately predict the head loss development. The model subsequently allowed for optimising the process control of the full scale BAC filters in terms of predicting the pressure drop and subsequently optimising the backwash sequence, saving water.

# INTRODUCTION

Surface water is frequently used as a source to produce drinking water. Common treatment steps to treat surface waters into drinking water include water intake/screening, coagulation, flocculation, sedimentation, rapid sand filtration and disinfection processes (Sakoda *et al.* 1996, Simpson 2008). However, surface water contains natural organic matter (NOM), which influences the performance of treatment processes as well as the drinking water quality. For example, during disinfection with chlorination a part of the NOM reacts with chlorine and chlorinated by-products are formed. In alternative disinfection methods, without residual disinfectants, nutrients need to be removed to low concentrations to produce biologically stable water prior to distribution (Graveland 1996, Prieto *et al.* 2013, van der Hoek *et al.* 1999). Biological activated carbon (BAC) filtration can be used for the removal of NOM as well as the removal of organic micropollutants, odour, colour and taste causing matter. The advantage of BAC filtration over granular activated carbon filtration (GAC) is that simultaneous removal of NOM takes place by adsorption and biodegradation (Kim *et al.* 1997). This has a positive effect on the required regeneration frequency, due to less pore blocking by NOM, and typically makes BAC filtration more (cost) effective than GAC filtration (Graveland 1996, Simpson 2008).

During BAC filtration the water quality improves by particles and flocs being captured in the pores of the filter bed, by adsorption of dissolved organic compounds taking place in the (micro- and meso-) pores of the carbon grains, and by biodegradation of NOM via biomass present on the external surface and in the macro-pores of the BAC filter grains (Servais *et al.* 1994). Simpson (2008) stated that the microbial biodegradation of organic substrates on the GAC media serves to decrease the backwash frequency of BAC filters compared to GAC filters. However, several researchers have also reported that the presence of biofilms resulted in a more rapid clogging of filters (Jeong *et al.* 2018, Xia *et al.* 2014). Especially the presence of extracellular polymer substances (EPS) (Mauclaire *et al.* 2004, Zhou *et al.* 2016), facilitating the adherence to surfaces and, therefore, the development of biofilms. Increased EPS production is typically seen when the conditions for biomass are not optimal. Kirisits *et al.* (2013), e.g., found that limitation of the nutrients nitrogen and phosphorus resulted in an increased EPS production resulting in increased head loss in biofilters.

BAC filters have two main control options being backwashing and regeneration. Backwashing typically takes place every couple of days till once a month, while regeneration occurs every year to three years. Backwashing occurs when either the effluent quality deteriorates, typically measured as turbidity, or the pressure drop over the filters is too high. Clogging mechanisms could be physical, chemical and/or biological. However, only limited research has been performed to differentiate between the different clogging mechanisms in (sand) filtration for drinking water treatment (Grace *et al.* 2016). Matsui and Tambo (1995) described the removal efficiency

and head loss increase mathematically for deep-bed filtration. They measured the filtration coefficients in clean filters. Erdim *et al.* (2015) investigated the pressure drop-water flow rate correlation for packed beds of spheres. A review of 38 different correlations, found from literature, was provided for different friction coefficients in relation to the Reynolds number, none of which were tested to include the effect of suspended solids removal or biodegradation of compounds in the filters.

A treatment plant typically contains several filters in parallel treating a portion of the water which is divided as equally as possible amongst the filters. In order to ensure sufficient production of drinking water and optimal use of the backwash water treatment installation, one filter at a time is backwashed instead of multiple filters at once. Depending on the filter run time, the filter is scheduled to be backwashed. Typically, the filters do not show the same clogging behaviour, due to differences in flows, load or grain sizes. To avoid several filters requiring to be backwashed at the same time, the filters are backwashed at a conservative pressure drop level (Ross 2006). Being able to predict the head loss development in BAC filters will enable to optimise the backwash sequence of the filters and subsequently will enhance the control options around BAC filtration.

Therefore, the objective of this study was to determine which of the mechanisms, physical, chemical or biological processes, were responsible for rapid clogging of the BAC filters. A simplified model, based on retention and mass balances, to predict the filter run times was developed. The insights from the model were then used to optimise the backwash sequence, which could result in a reduction of the amount of backwash water needed.

# MATERIALS AND METHODS

**Pilot plant set-up and operation**

The experiments were carried out at the pilot plant of Waternet, the water-cycle company of Amsterdam and surrounding areas, location Weesperkarspel, the Netherlands. The pilot plant was fed with humic rich surface water (average dissolved organic carbon (DOC) concentration of 9.2 mg-C/L), pre-treated by coagulation/sedimentation, followed by 100 days retention in a reservoir and subsequently filtered over rapid sand filters. The pilot plant includes all treatment processes of the full-scale plant, consisting of ozonation, pellet softening, BAC filtration and slow sand filtration.

Four BAC filters with a surface area of 0.43 m², bed height of 3.2 m, a supernatant water level of 2.5 m, filtration velocity of 4 m/h and an empty bed contact time of 48 min, were operated. The influent turbidity values were below 0.8 NTU, due to the extensive pre-treatment. The activated carbon (type: Norit GAC 830P) was taken from the full scale plant and had been in service for 1.5 years to ensure the carbon grains in the filters were sufficiently ripened.

In total three different experiments were carried out each with a maximum filter run time of three weeks. To be able to differentiate between the clogging (physical, chemical and biological) mechanisms, all filters received a different pre-treatment (see Figure 6-1). BAC 1 received water from the pilot plant which was pre-treated with ozone ($O_3$) and pellet softening (PS) followed by an additional acid dosing to ensure the saturation index (SI) was negative, ruling out possible calcium carbonate precipitation/crystallization coming from the PS. BAC 2 received pilot plant water which was pre-treated by $O_3$ and PS without acid dosing and thus a high SI. To study the effect of enhanced precipitation/crystallisation of calcium carbonate flocs on clogging, the PS in the pilot plant was operated such that the SI>0.3, to ensure the effluent was supersaturated with calcium carbonate. BAC filter 3 was preceded by pilot plant $O_3$ only, to investigate the effect of enhanced biological growth. BAC 4 served as a reference filter for the full scale plant and BAC 1, receiving full scale effluent water from the PS, which was preceded by $O_3$, and an acid dosing.

The water quality parameters and process settings per experiment are summarized in Table 6-1. Experiment 1 was used to determine the effect of suspended solids. Experiment 2 and 3 were used to determine the effect of biofilm growth and calcium carbonate ($CaCO_3$) deposits. The readily available carbon for cell/biofilm growth was determined by measuring the assimilable organic carbon (AOC) concentration. In Table 6-1 the amount of AOC degraded by the BAC filters per bed volume is indicated, as well as the $CaCO_3$ deposition per bed volume. These concentrations have been determined by the difference in influent and effluent concentration.
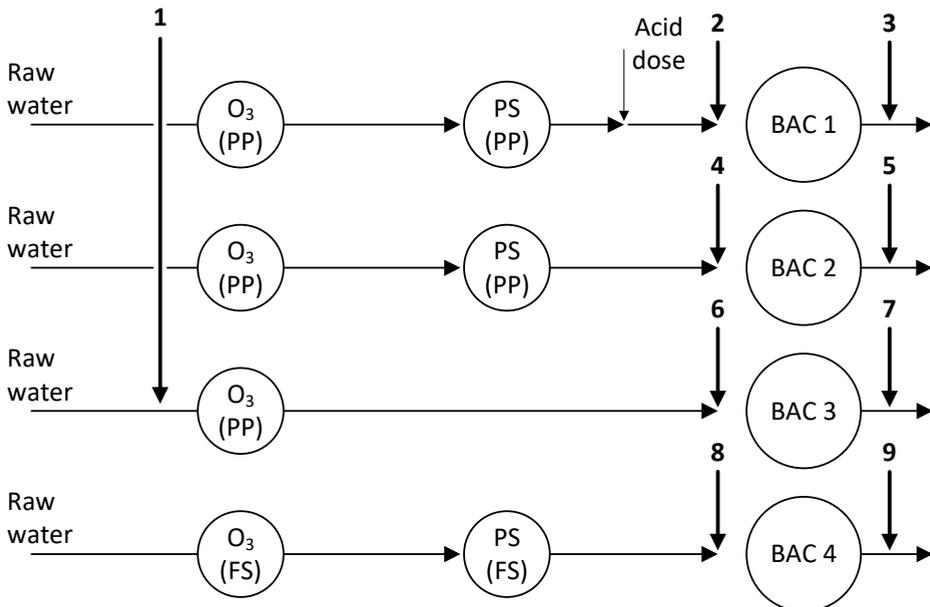
**Figure 6-1** Experimental set up, including sampling points indicated by the numbers (PP= pilot plant, FS= full scale water).

**Sampling, on-line measurements and water quality analysis**

During the experiments the pressure drop was measured on-line by pressure gauges of the type WIKA Tronic Line with a range of 0-0.4 bar, applied at a height of 20 and 120 centimetres below the top of the filter bed. A 4-20 milliAmpere signal was transferred to a Volt-signal by means of relays. The Volt-signal was continuously logged by a NI-USB6008 module in the VI Logger software of National Instruments. The output of the measurements was further evaluated using Matlab® and Excel®. In addition to the on-line pressure measurements, grab samples were taken once a week at the sampling points 1-9, indicated in Figure 6-1, and analysed for the following parameters: DOC; turbidity; $Ca^{2+}$; $HCO_3^-$; pH; temperature; EC and suspended solids were determined, using standard procedures as described in Standard Methods (Eaton *et al.* 2005). AOC was measured in duplicate, applying the simultaneous incubation of strains P17 and NOX (van der Kooij *et al.* 1982). AOC was measured at the start of each experiment. The biomass activity of the carbon samples was determined by ATP on carbon according to the method described by Magic-Knezev and van der Kooij (2004).

**Table 6-1** Process settings and water quality parameters per experiment BAC filters (RW= raw water, n.d. = not determined). The average water quality (and standard deviation) is based on three samples per experiment.

| | **BAC 1** RW+$O_3$+PS+acid dose | **BAC 2** RW+$O_3$+PS | **BAC 3** RW+$O_3$ | **BAC 4** RW+$O_3$+PS (reference FS) |
|---|---|---|---|---|
| **Experiment 1 (only used to determine the effect of suspended solids)** | | | | |
| $O_3$ dose (mg/L) | 0 | 0 | 0 | 2.4 |
| $SI_{inf}$ (-) | -0.22 (±0.04) | 0.32 (±0.03) | 0.09 (±0.01) | -0.09 (±0.10) |
| $\Delta C_{AOC}$ (mg-C/L) | 0 | 0 | 0 | 0.05 |
| $\Delta C_{caCO3}$ (mg/L) | n.d. | 6.6 (±0.8) | n.d. | n.d. |
| Turbidity$_{inf}$ (NTE) | 0.24 (± 0.10) | 0.41 (±0.11)) | 0.17 (±0.08) | 0.24 (±0.06) |
| $DOC_{inf}$ | n.d. | n.d. | 5.8 (±0.6) | n.d. |
| $ATP_{start}$ (ng/g) | 340 | 330 | 290 | 260 |
| $ATP_{end}$ (ng/g) | 160 | 250 | 27 | 220 |
| Temperature$_{inf}$ (°C) | 11.0 (± 1.0) | 11.2 (± 1.1) | 11.1 (± 1.1) | 11.3 (± 1.0) |
| **Experiment 2** | | | | |
| $O_3$ dose (mg/L) | 1.9 | 1.9 | 1.9 | 1.9 |
| $SI_{inf}$ (-) | -0.03 (±0.07) | 0.64 (±0.10) | 0.29 (±0.13) | 0.15 (±0.24) |
| $\Delta C_{AOC}$ (mg-C/L) | 0.04 | 0.04 | 0.078 | 0.04 |
| $\Delta C_{caCO3}$ (mg/L) | n.d. | 8.2 (±0.8) | n.d. | n.d. |
| Turbidity$_{inf}$ (NTE) | 0.16 (±0.07) | 0.44 (±0.05) | 0.15 (±0.05) | 0.29 (±0.08) |
| $DOC_{inf}$ | n.d. | n.d. | 6.0 (±0.3) | n.d. |
| $ATP_{start}$ (ng/g) | 160 | 250 | 27 | 220 |
| $ATP_{end}$ (ng/g) | 1400 | 1100 | 1100 | 1600 |
| Temperature$_{inf}$ (°C) | 15.5 (±1.7) | 15.5 (±1.7) | 15.4 (±1.7) | 15.4 (±1.7) |
| **Experiment 3** | | | | |
| $O_3$ dose (mg/L) | 1.8 | 1.8 | 1.8 | 2.4 |
| $SI_{inf}$ (-) | -0.05 (±0.06) | 0.69 (±0.07) | 0.25 (±0.05) | 0.01 (±0.09) |
| $\Delta C_{AOC}$ (mg-C/L) | 0.03 | 0.03 | 0.074 | 0.05 |
| $\Delta C_{caCO3}$ (mg/L) | n.d. | 12.0 (±1.1) | n.d. | n.d. |
| Turbidity$_{inf}$ (NTE) | 0.29 (±0.10) | 0.75 (±0.33) | 0.16 (±0.11) | 0.28 (±0.10) |
| $DOC_{inf}$ | n.d. | n.d. | 5.8 (±0.6) | n.d. |
| $ATP_{start}$ (ng/g) | 1400 | 1100 | 1100 | 1600 |
| $ATP_{end}$ (ng/g) | 210 | 290 | 560 | 490 |
| Temperature$_{inf}$ (°C) | 15.4 (±0.3) | 15.5 (±0.3) | 15.4 (±0.4) | 15.4 (±0.4) |

The saturation index (SI), which is a measure for the driving force in the crystallisation process, and the theoretical calcium carbonate crystallization potential (TCCP), which is the amount of calcium in (mmol/L) that crystallises to obtain water in chemical equilibrium (SI=0), describe the super-saturation of calcium carbonate in water (van Schagen *et al.* 2008). The change in TCCP during a filter run was used to determine the amount of $CaCO_3$ that was removed by the BAC filters. The TCCP was calculated using the model developed by van Schagen *et al.* (2008).

**Modelling**

During filtration suspended solids, present in the feed water, are transported towards the filter material resulting in a change in concentration (*c in g/m³*) of the suspended solids and colloids in the water (eq. 6-1):

$$c \rightarrow c + \frac{\partial c}{\partial t} dt$$

At the same time the suspended solids deposit (*σ in g/m³*) in the pores of the filter bed (eq. 6-2):

$$\sigma \rightarrow \sigma + \frac{\partial \sigma}{\partial t} dt$$

It was chosen to apply a simple model (semi-empirical) based on mass balances (equation of continuity) and equation of motion as described by Huisman (1984).

The rate of deposition of the particles (equation of motion) was described as a first order relation to the concentration of the particles in the bulk stream (eq. 6-3):

$$\frac{\partial c}{\partial y} = -\lambda c$$

where λ is the filtration coefficient, an indication of the filter efficiency.

A mass balance can be completed for determining 1) the effluent quality and 2) suspended solids remaining in the filter bed based on the processes described in Figure 6-2.

**IN = OUT + STORAGE + DEPOSITION**
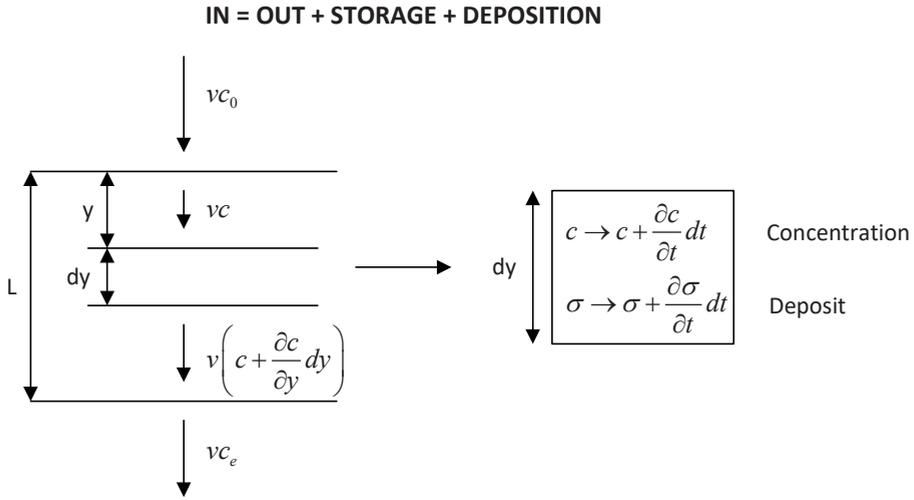


**Figure 6-2** Change in water quality and deposition of particles in filter bed (Huisman 1984).

Subsequently, the mass balance of suspended solids in the water can be described by (eq. 6-4):

$$\frac{\partial c}{\partial t} = -\frac{v}{p} \cdot \frac{\partial c}{\partial y} - \frac{v}{p} \cdot \lambda \cdot c$$

While the accumulation of the particles in the pores can be described by (eq. 6-5):

$$\frac{\partial \sigma}{\partial t} = -v \cdot \frac{\partial c}{\partial y}$$

where $p$ is the filter bed porosity, excluding the porosity of the grains [%] and $v$ the surface velocity [$m/s$].

The filtration coefficient depends on its initial value ($\lambda_0$) and the deposit of particles during the filtration process. The filtration coefficient must thus be written as a function of the specific, volumetric deposit $\sigma_v$ ($m^3/m^3$). To convert the specific mass deposit into the specific volume deposited, the specific bulk factor was used (Ojha and Graham 1993) (eq. 6-6):

$$\sigma_v = \frac{\sigma}{\rho}$$

where ρ is the actual density of the deposited solid in the floc. This means that if the porosity of the floc is 98%, the actual density of the deposited solid will be $(1-0.98)*(p_d)$, with $p_d$ the density of the deposited solid in kg/m$^3$.

Many relations between λ and $\sigma_v$ exists to fit the experimental results. Here the simple relation determined by Maroudas and Eisenklam (1965) was used, where the $k_1$ was replaced by $1/n_{max}$, resulting in a termination of the filtration process when the deposits have filled the pores until a maximum fraction $n_{max}$ of the initial porosity (eq. 6-7):

$$\lambda = \lambda_0 \left( 1 - k_1 \frac{\sigma_v}{p_0} \right)$$

where $p_0$ is the initial porosity.

Although the origin of the deposits varied, either from suspended solids (SS), CaCO$_3$ or as a result of AOC degradation, the clogging mechanisms were expressed as physical clogging. For CaCO$_3$, it was assumed that the CaCO$_3$ flocs were already formed after PS, and subsequently being captured by physical straining in the BAC filters. For AOC it was assumed that the removal of AOC directly resulted into biofilm growth, taking up pore space, and which can thus also be expressed as physical clogging. In reality more complex processes take place including attachment, detachment, transportation of bacteria, death and predation than taking into account in this model (Camprovin *et al.* 2017, van der Aa *et al.* 2006), but it was assumed that for control purposes, the simplified model would give sufficiently accurate results.

The change in concentration and deposit of particles for the three clogging origins could subsequently be written as the deposition of SS, CaCO$_3$ flocs and blocking of the pores through biofilm growth (eq. 6-8, with *i* representing SS, CaCO$_3$ and AOC):

$$\frac{\partial c_i}{\partial t} = -\frac{v}{p} \cdot \frac{\partial c_i}{\partial y} - \frac{v}{p} \cdot \lambda_{0_i} \cdot k_2 \cdot c_i$$

$$\frac{\partial \sigma_i}{\partial t} = -v \cdot \frac{\partial c_i}{\partial y}$$

where $k_2$ (eq.6-9):

$$k_2 = 1 - \frac{1}{p_0 \cdot n_{max}} \cdot \left( \frac{\sigma_{SS}}{(1 - p_{d,SS})\rho_{SS}} + \frac{\sigma_{CaCO_3}}{(1 - p_{d,CaCO_3})\rho_{CaCO_3}} + \frac{\sigma_{AOC}}{(1 - p_{d,aoc})\rho_{AOC}} \right)$$

The initial porosity was derived from the initial head loss as the columns were fed with a constant water velocity. The initial filtration coefficients ($\lambda_{0,SS}$, $\lambda_{0,CaCO3}$, $\lambda_{0,AOC}$) and the actual densities of the deposits ($\rho_{SS}$, $\rho_{CaCO3}$, $\rho_{AOC}$) were determined with the results of the experiments and are described in the results section.

As a result of the filtration processes, the head loss increases due to the volume occupied by the deposits and biomass. The head loss development is then determined by the clean bed resistance and the specific deposit (Huisman 1984) (eq. 6-10):

$$H = H_0 \cdot \left( \frac{p_0}{p_0 - \sigma_v} \right)^2$$

where $H$, the head loss in m, $H_0$ the initial head loss, which is dependent on the initial porosity, grain size, velocity and temperature. For laminar flows with Reynolds number below 5, the Carman-Kozeny equation can be applied (eq. 6-11):

$$I_0 = \frac{H_0}{L} = 180 \cdot \frac{\upsilon}{g} \cdot \frac{(1 - p_0)^2}{p_0^3} \cdot \frac{v}{d_0^2}$$

where $I_0$, the initial resistance gradient, $L$ filter bed height [m], $\vartheta$ the kinematic viscosity [m²/s] and $d_0$ the grain size [m].

The changes in concentrations ($\partial c_{SS}$, $\partial c_{CaCO3}$, $\partial c_{AOC}$) were measured over the filter runs.

The model was developed within the Stimela environment using Matlab/Simulink® as platform (van der Helm and Rietveld 2002).

**Calibration and validation strategy**

BAC 3 was used to calibrate the initial filtration coefficient and actual density of biomass deposits. Based on these values, BAC 2 was used to calibrate the initial filtration coefficient and actual density for deposit of $CaCO_3$ flocs. In BAC 2 clogging was a combination of biofilm growth and $CaCO_3$ flocs deposits. Experiment 3 was used for calibration. Because the clogging as a result of suspended solids was negligible (see Results and Discussion) the initial filtration coefficient and actual density of suspended solids were not estimated.

The results were validated based on the head loss development in BAC 1 and 4 during experiment 3 and the head loss development in all filters during experiment 2.

# RESULTS AND DISCUSSION

**Head loss development**

The head loss development over the height of the filter bed after 3 weeks for experiments 1, 2 and 3 are shown in Figure 6-3. In experiment 1, no ozone was dosed to BAC 1, 2 and 3. The head loss development in Figure 6-3a shows that hardly any clogging occurred in BAC 1, 2 and 3 during the filter run of 3 weeks. Clogging did occur in BAC 4, which was preceded by full scale $O_3$ dosing and PS. The SI of the influent of BAC 4 was negative, limiting the possibility of calcium carbonate to precipitate. For verification the TCPP concentration was calculated being -0.0003 mmol/L. As a result, only clogging due to suspended solids and biomass remained as possible contributors. Since no clogging occurred in BAC 1, 2 and 3, clogging as a result of suspended solids was assumed to be negligible for the remainder of this study.

For all three experiments the clogging only occurred in the top layer of the filter bed. Results from the ATP on carbon measurements also showed that the biological activity was the highest in the top layer of the filter bed (data not shown). This is similar to what was found by Urfer and Huck (2001). Since the clogging only occurred in the top layer, only this top 20 cm was further considered in the model.

The clean filter bed resistance measured at 20 cm below the top was equal to 0.076 m, resulting in an initial resistance gradient ($I_0$) of 0.38. With the clean filter bed resistance the initial porosity was calibrated resulting in $p_0$=38%. This is in line what is typically found for sand filter beds with similar grain sizes (Rietveld 2005), although Clements (2004) found porosity values of around 50% for GAC filters.

From the influent and effluent measurements the changes in concentration for the different fractions were determined, see Table 6-1. The $CaCO_3$ concentration was derived from the change in TPCC concentration.

**Calibration biological clogging**

The main clogging mechanism in BAC 1, 3 and 4 was biological, since the SI in the influent of these filters was below 0.3 and the calculated TPCC was low too (data not shown). The ATP on carbon measurements were the highest at the beginning of experiment 3 with values of 1.4, 1.1, 1.1 and 1.6 x $10^{-6}$ g ATP/g carbon for BAC 1-4, respectively. These values were similar to the values reported by van der Aa *et al.* (2006) and Velten *et al.* (2011). The highest pressure drop occurred in BAC 3, also receiving the highest AOC concentration of all filters. It was chosen to use this filter and experiment 3 for calibration of the initial filtration coefficient ($\lambda_{0,AOC}$) and actual density of the deposits/biofilm ($\rho_{AOC}$).
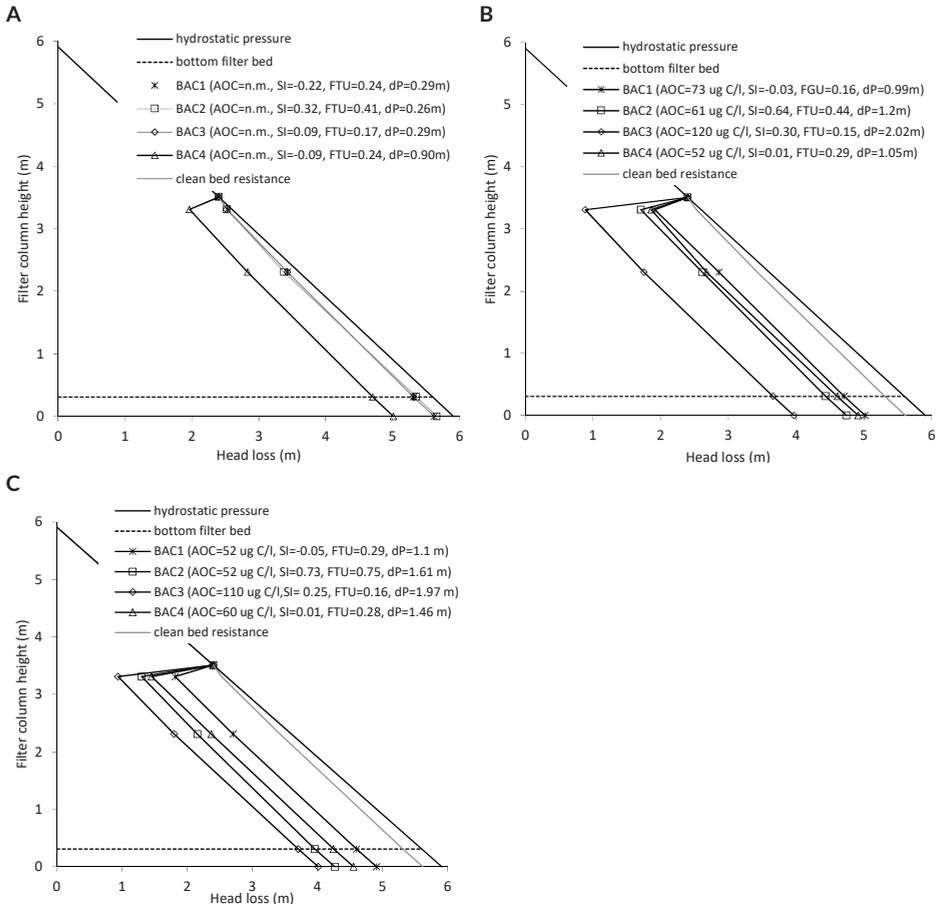
**Figure 6-3** (a, b and c) Head loss development at the end of the run time of experiment 1(top-left), 2 (top-right) and 3 (bottom).

An indication of the actual density of the deposit could be calculated by combining equations 6-5 and 6-10 with equation 6-7, since the initial porosity in the filter bed was determined based on the clean filter bed resistance. This density was used as starting point for the calibration. The calibration results and values found for $\lambda_{0,AOC}$ (300 1/m) , actual density $\rho_{AOC}$ (1.46 kg/m$^3$) and porosity $p_{AOC}$ (98.5%) are indicated in Figure 6-4.

The theoretical density of the biomass was determined by assuming that all consumed AOC was transferred into biomass. By determining the volume of biomass formed per gram of consumed AOC, the measured decrease in AOC could be translated into a biological specific deposit. The theoretical density of biomass derived in Box 6-1 resulted in 99.21 kg/m$^3$. The highest density reported in literature for EPS was 130 kg/m$^3$ (Christensen and Characklis 1990).
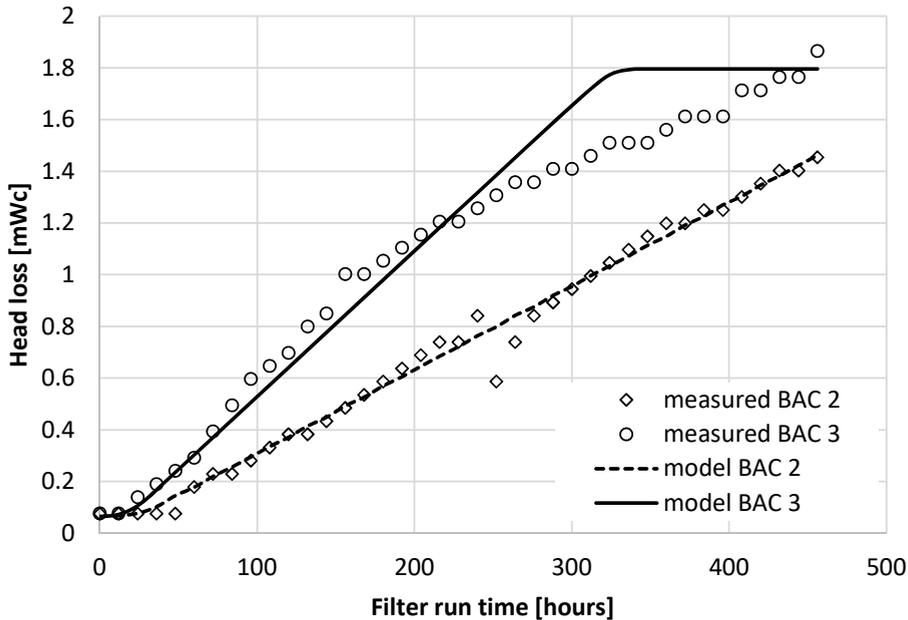
**Figure 6-4** Calibration of biological and chemical clogging for BAC filters 2 and 3 based on measurements experiment 3.

The calibration results thus showed that the volume of bacteria was very small (1.5% based on the theoretical density as calculated in Box 6-1 versus the density found by the model, based on fitting the head loss from the model with the measured head loss) compared to the volume of the whole biofilm. However, this is in line with the values reported by Mauclaire *et al.* (2004), with the volume of bacteria covering 0.1-1.2% compared to the volumes of EPS. EPS biopolymers are highly hydrated and form a matrix, which keeps the biofilm cells together and retains water (Flemming *et al.* 2016), explaining the low densities for AOC/biofilm found from the model.

**Box 6-1** Calculation of density of biomass.

1 gram AOC = $0.8.10^6$ ng ATP on carbon (Yield$_{BDOC}$, Magic-Knezev, 2006)

$2.5.10^{-8}$ ng ATP on carbon =1 cell (Van der Aa et al., 2006)

1 cell = $0.315.10^{-18}$ $m^3$ biomass (Van der Aa et al., 2006)

$2.5.10^{-8}$ ng ATP on carbon = $0.315.10^{-18}$ $m^3$ biomass

1 ng ATP on carbon = $(0.315.10^{-18}/2.5.10^{-8})$ = $1.26.10^{-11}$ $m^3$ biomass

1 gram AOC = $(0.8.10^6 \cdot 1.26.10^{-11})$ = $1.008.10^{-5}$ $m^3$ biomass

$r_{AOC}$ = $1/1.008.10^{-5}$ gr/$m^3$ = 99.21 kg/$m^3$

**Calibration chemical clogging**

The clogging mechanism in BAC 2 was a combination of biological clogging and chemical clogging as a result of the supersaturated influent water coming from the PS. The head loss development of BAC 2 during experiment 3 was used to determine the initial filtration coefficient ($\lambda_{0,CaCO3}$) and actual density ($\rho_{CaCO3}$). Similar to the biological clogging, the starting point for the actual density was calculated by combining equations 6-5, 6-7 and 6-10, resulting in an initial calculated actual density of calcium carbonate flocs of 1300 kg/m$^3$. The calibration results are given in Figure 6-4. The found actual density of the CaCO$_3$ flocs show that the flocs consisted for about 52% of water, taking into consideration that the density of pure CaCO$_3$ is 2711 kg/m$^3$.

**Validation model**

The validation results for experiment 3 (BAC 1 and 4) and experiment 2 (all filters) are shown in Figure 6-5.
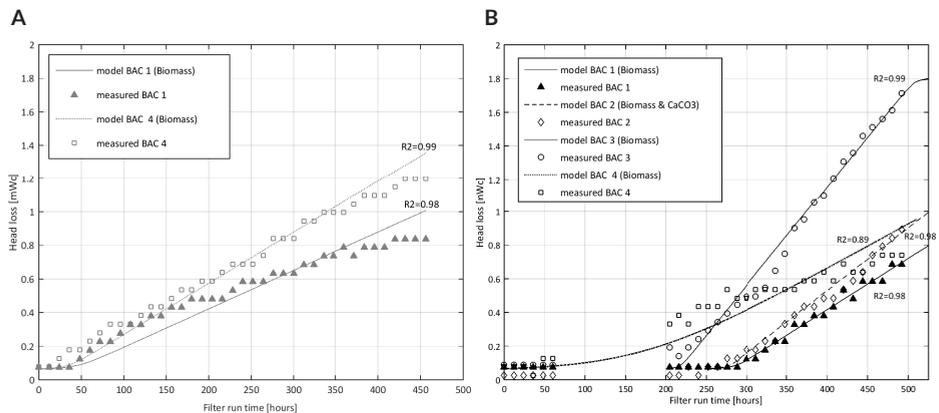


**Figure 6-5** a) and b) Validation model to predict biological and chemical clogging in BAC filters for experiment 3 (left) and experiment 2 (right).

The pressure drop during experiment 2 for BAC 1-3 showed an initial ripening period of the filters due to the absence of ozonation during the first experiment, see Figure 6-5b. To account for this ripening period, the model calculations of experiment 2 were shifted in time.

The validation runs showed the model was able to predict the clogging based on the biological (AOC removal) and chemical (calcium carbonate flocs) concentrations captured in the filters. Typically, the increase in head loss showed a linear relation. This is commonly seen when fouling takes place in the top of the filter (formation of cake layer), most likely due to rapid clogging of the top layer gradually increasing in depth.

**Quantification of different clogging mechanisms**

From the model calculations the influence of the different mechanisms on the clogging of the filter beds could be determined by comparing the results of BAC 1-3, using the slope of the curves to quantify the effect of different feed concentrations.

The highest pressure drop during experiment 2 and 3 was recorded for BAC 3 confirming that clogging due to biofilm formation was the dominant mechanism in this case. Although the applied ozone dosage was the same for all three filters, the AOC concentration in the influent of BAC 3 was respectively 49% (experiment 2) and 59% (experiment 3) higher than the AOC concentration in the influent of the other filters, due to the biological activity in the PS process as described by Hammes *et al.* (2011). Comparison between BAC 1 and 3 from experiment 2 and 3 showed that the increase in AOC concentration resulted in a similar increase in head loss with 43% and 53%, respectively.

Comparison between BAC filter 1 and 2 showed the influence of the calcium carbonate flocs on the pressure drop in combination with clogging due to the presence of a biofilm. The concentration of calcium carbonate flocs compared to the concentration of AOC was more than 100 times higher. However, the calculated specific deposit due to AOC was 10 times higher than for $CaCO_3$, due to the very low density of the biofilm, confirming that already concentrations of 0.03 mg/L nutrients can result in clogging. In experiment 3 the concentration of calcium carbonate removed in BAC 2 was 50% higher than in experiment 2. To be able to obtain an indication of the increase of pressure drop related to the calcium carbonate floc removal, the slope difference between BAC 1 and 2 for experiment 2 was compared to the slope difference for experiment 3. The slope increase between BAC 1 and 2 was 120% while the removed concentration of calcium carbonate was only 50% higher. Even though it was only one experiment, the results suggest interaction between the calcium and biofilm. Li *et al.* (2011) investigated and confirmed the effect of calcium adsorption on membranes and subsequent bridging with colloidal NOM via binding of functional groups leading to increased fouling.

**Optimisation of backwash sequence full scale filters**

Based on the obtained insights in the clogging mechanisms and the found linear pressure drop increase, an evaluation of the full scale pressure data was carried out. These data also showed a similar linear increase after an initial threshold pressure was achieved. This made it possible to predict the filter run times using a simplified linear model. The slopes were different for each filter, due to differences in flows and load per filter. Furthermore, the slope per filter varied in time as the result of changes in water temperature and water quality in time as well as flow. In theory the filters only need to be backwashed when a head loss of 2 mWc is reached or if the filter run time is two weeks. Because the head loss can increase suddenly by changes in flow or water quality, the filters are backwashed much earlier before the backwash criteria are

met. By predicting the head loss increase with a simplified model, less safety margin is required when backwashing the filters. In Figure 6-6 the calculated number of backwashes per year is given for a sample set of 7 BAC filters compared to the number of backwashes currently applied in practice. These BAC filters cover one side of the filters located in lane 'Zuid' of the Weesperkarspel treatment plant. In total 26 BAC filters are present at the full scale treatment plant.
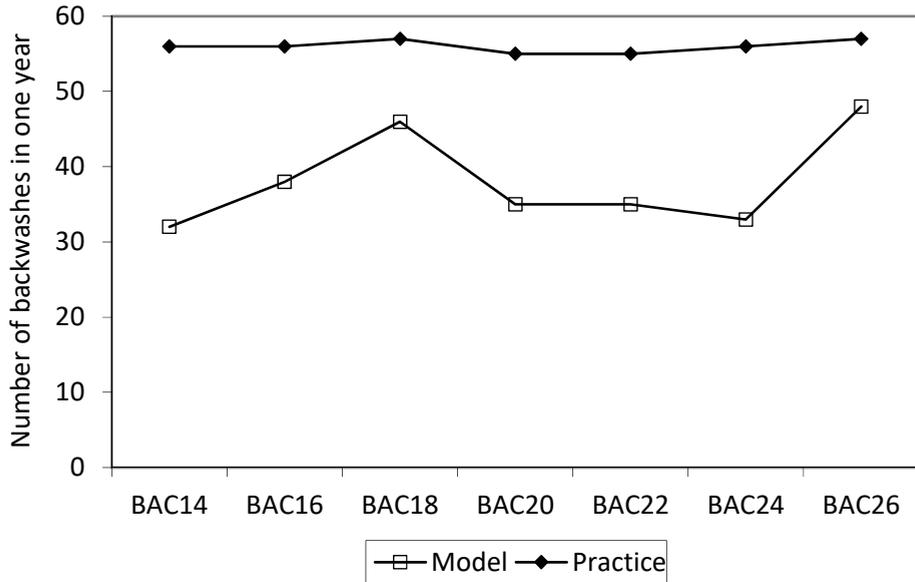


**Figure 6-6** Number of calculated backwash times required versus the number of backwashes currently applied.

For the 7 BAC filters a total of 125 backwash sequences out of 392 backwashes in one year could have been saved (32% reduction), indicating the opportunities left for optimising the control of the BAC filters. The water quality will not change as long as backwashing takes place in a timely manner. The operational costs will go down, since there is less drinking water used for backwashing, requiring less drinking water to be produced, requiring less energy for pumping and treatment of backwash water.

# CONCLUSIONS

The objective of this research was to determine which of the mechanisms, physical, chemical or biological processes, were responsible for rapid clogging of the BAC filters. A simplified model, based on retention and mass balances, to predict the filter run times was developed. Results showed that clogging in the BAC filters was a combination of chemical and biological mechanisms. Already small concentrations of AOC resulted in the development of a biofilm. This biofilm caused the formation of a cake layer and accounted for the majority of the pressure build up in the BAC filters. The density of the biofilm was found to be much lower than the theoretical density calculated based on the conversion of AOC into bacterial mass. This confirmed that the biofilm was highly hydrated. An almost linear relationship was found between the amount of AOC removed and the increase in pressure drop in time. In combination with calcium carbonate flocs a steeper increase was found, suggesting interaction between calcium and biofilm.

The simplified model was able to accurately predict the head loss development. The model subsequently allowed for optimising the process control of the full scale BAC filters in terms of predicting the pressure drop and subsequently optimising the backwash sequence, saving water.

# ACKNOWLEDGEMENTS

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# CHAPTER 7

**Conclusions and Outlook**

# CONCLUSIONS

The main objective of this thesis was to improve monitoring and operation of ozonation and biological activated carbon (BAC) filtration for the removal of pathogens and organic matter, for the optimisation of drinking water production from surface water. The combination of pilot plant research, testing of various assimilable organic carbon (AOC) measurements, frequently used to assess the biological stability of drinking water, and the installation of, and processing of information from, UV-Vis spectra measurements throughout the pilot plant have resulted in the following main conclusions:

> *The monitoring strategy of ozonation-BAC filtration could be improved through implementation of the established design methodology in combination with the developed algorithms allowing for on-line estimation of AOC, bromate and Ct value around ozonation, based on the measured change in UV-Vis spectrum. The operation of BAC filters could be improved through a better understanding of the direct response of the BAC filters to a change in feed water quality and the use of simplified models to optimise the operational strategy around backwashing of BAC filters.*

Knowledge on what is being measured is important when using the outcomes of the measurement for operational control or evaluation of process performance. Although for many parameters a standard methodology has been captured in the global standard methods (Eaton *et al.* 2005) or local legislation, continuous research takes place in developing new methods which aim to be faster, more reliable and cheaper. Assimilable organic carbon (AOC) is an important and frequently used parameter when ozonation and BAC filtration are concerned. In Chapter 2, a round-robin test was performed to evaluate the correlation between three established AOC methods: 'Werner & Hambsch', 'Eawag' and 'van der Kooij' (Hammes and Egli 2005, van der Kooij *et al.* 1982, Werner and Hambsch 1986). It was shown that an AOC assays consists of several steps, such as sample pre-treatment, incubation volume and temperature, inoculum, growth measurement, yield and conversion values, which may all contribute to variations in the reported values. The use of indigenous bacteria as inoculum instead of a set of two known strains resulted in an increase in cell growth of approximately 20%. This confirmed the idea that when a natural inoculum is applied, a broader range of substrates can be utilized and consequently the AOC concentrations found would be higher. AOC assays convert measurements of cell numbers to equivalent carbon concentrations. This is an indirect approach, firstly since organic carbon itself is not measured, and secondly because the yield of different bacteria on different organic carbon substrate varies. It was found that the applied conversion values from cell numbers to equivalent carbon concentrations

account for an increase from 25 to 66%. There was one other aspect that could play an important role in interpretation of the results, which was the addition of a carbon free nutrient salt solution. It resulted in higher concentrations in some samples of up to 101% compared to the 'van der Kooij' method, since the studied samples seemed to be limited in nutrients other than organic carbon. Especially this result showed the importance of understanding the possible limitations if it was assumed all waters tested were limited in carbon, while test results showed this was not the case. This latter requires careful interpretation of obtained results.

One of the knowledge gaps identified in Chapter 1 was the lack of a design methodology able to determine the required (on-line) measurements enabling operational control. In order to achieve this, it is inherent that the water quality data provide the correct information, through being reliable, measured at the right location and with the required frequency. In this thesis a seven step design methodology was developed (Chapter 3) enabling the determination of the required water quality monitoring strategy around ozonation and BAC filtration. The previous on-line monitoring program around ozonation – BAC filtration at Weesperkarspel contained six on-line sensors of which one was identified not to be required, leaving with five sensors being correctly placed. In addition, another three on-line sensors should have been installed to allow for optimal operational control. In the current situation it was chosen to install i::scan™ before and after ozonation to allow for monitoring the UV absorbance at 254 nm.

Evaluation of available on-line water quality sensors showed that the parameters typically measured to show compliance with the WHO standards (WHO 2008) were commonly available. Direct measurement of the more complex parameters such as AOC and bromate were not available on-line. In Chapter 4, different algorithms based on using differential UV/Vis-spectra measurements were developed, making on-line monitoring of the ozonation process possible through a real-time estimation of AOC and bromate formation (being two of the main disinfection by-products from ozonation), as well as determination of the Ct value. For estimation of the Ct value the change in slope at a wavelength of 265 nm was found to be the only wavelength demonstrating a statistically significant relation with the Ct values. A correlation ($R^2$) of 0.88 was found, although the algorithm sometimes overestimated the Ct value. Therefore, it was recommended to check the predicted Ct value on a regular basis if used for operational purposes. When the algorithm for bromate formation during ozonation was developed it was found that the strongest correlation was obtained between the normalized differential spectra (differential spectrum divided by the influent spectra) and the bromate concentrations. In total two wavelengths, 250 and 270 nm, turned out to show a significant relationship with an $R^2$ of 0.92. For the AOC formation a total of 4 wavelengths, 320, 347.5, 427.5 and 435 nm, were found to give the best correlation with an $R^2$ of 0.74. Using multiple wavelengths significantly improved the estimation compared to only using the frequently applied single wavelength of 254 nm, which in this case resulted in an $R^2$ of 0.398.

The use of the above mentioned soft-sensors, able to estimate the bromate and AOC concentration, help to gain continuous on-line data. Besides using soft-sensors as surrogate sensors for parameters currently not available on-line, they can also provide a cost effective alternative when used to estimate multiple parameters through one single instrument. Examples in this case were the use of UV-Vis sensors for the determination of DOC and UV absorbance at a wavelength of 254 nm ($UV_{254}$) concentration in the influent in combination with the formation of bromate and AOC and the determination of the Ct value in the effluent of the ozonation step.

Changes in water quality might require a change in operational control of a treatment process. It is important to understand how a treatment process reacts to such change in water quality. Changes in water quality can occur due to changes in the source water quality, such as seasonal fluctuations in temperature, algal blooms or pollution plumes, or due to the malfunction of a preceding treatment step. Especially BAC filters are assumed to be susceptible to sudden changes upstream of the filters. The immediate response of the BAC filters to a rapid change in feed water quality was investigated to be able to determine the monitoring and subsequent control requirements of the filters. It was observed that all filters were able to mitigate a sudden change in feed water quality. The non-ozonated water contained the highest DOC concentration, with an increase of 11% compared to the reference filter, while immediately after the change in feed water quality, the DOC concentration in the effluent was 5% lower than the reference filter, most likely due to improved adsorption. Direct feed of ozonated water resulted in an increase in DOC concentration in the feed water of 7% while the DOC concentration in the effluent was 7% lower compared to the reference situation, due to increased activity of the biomass on the filter media. Similarly, the addition of phosphate to the feed water resulted in an increased DOC removal of 3% while no changes in feed water concentration was observed. For AOC similar responses were observed. As a result of this resilience against sudden changes, it could therefore be concluded that there was no direct need for very stringent on-line monitoring and continuous adjustments of the water quality of the BAC filters. Only the pressure drop and the pH and oxygen concentration in the effluent should be measured as discussed in Chapter 3. By also investigating the long term effects of changes in the feed water quality it was possible to link these findings with previously published research. The long term adaptation of the BAC filters confirmed the need for sufficient nutrients (readily available carbon and phosphate) in the feed water for optimal performance. The influence of intact cells was shown to be limited. Interestingly the storage of phosphate in the BAC filters as a result of adsorption or uptake by the biomass does not necessitate continuous dosing of phosphoric acid. It was recommended to further investigate the optimised dosing scheme of phosphate.

One parameter in the BAC filters that requires enhanced control and understanding is the clogging of the filters, especially when the water temperature starts to increase in spring and summer time. In Chapter 6 it was investigated which of the mechanisms, physical, chemical or

biological, were responsible for the rapid clogging of the BAC filters. To gain this understanding a simplified model to predict the filter run times, based on retention and mass balances, was developed. It was shown that even small concentrations of AOC of 0.03 mg-C/L resulted in the development of a biofilm causing the formation of a cake layer which accounted for the majority of the pressure build up in the BAC filters. The model provided valuable insight into the density of the biofilm associated with the found clogging patterns. The density of the biofilm was found to be only 1.5% of the theoretical density calculated based on the theoretical conversion of AOC into bacterial mass. This confirmed that the biofilm was highly hydrated. An almost linear relationship was found between the amount of AOC removed and the increase in head loss in time. For calcium carbonate flocs a steeper increase of 120% compared to an increase in calcium carbonate of only 50% was found, suggesting interaction between the calcium and biofilm. Through the development of the model more insight was gained into the development of the head loss in the filters, once again confirming the importance of models in increasing, applying and capturing knowledge (van der Helm 2007).

A treatment plant typically contains several parallel filters treating a portion of the water which is divided as equally as possible amongst the filters. In order to ensure sufficient production of drinking water, one filter at a time is backwashed instead of multiple filters at once. Depending on the filter run time, the filter is scheduled to be backwashed according to a sequence set by the operator. Typically, the filters do not show the same clogging behaviour, due to differences in flows, load or grain sizes. To avoid several filters requiring to be backwashed at the same time, the filters are backwashed at a conservative head loss level (Ross 2006). Real-time prediction of the head loss development in BAC filters could optimise the backwash sequence of the filters. Based on the obtained insights in the clogging mechanisms and the found linear head loss increase (Chapter 6), an evaluation of the full scale pressure data was carried out. These data also showed a similar linear increase after an initial threshold pressure was achieved. This made it possible to predict the filter run times using a simple linear model. The slopes were different for each filter, due to differences in flows and load per filter. Furthermore, the slope per filter varied in time as the result of changes in water temperature and water quality in time as well as flow. For the 7 BAC filters a total of 125 backwash sequences out of 392 backwashes in one year could have been saved (32% reduction), indicating the opportunities left for optimising the control of the BAC filters.

# OUTLOOK

At Waternet, location Weesperkarspel, some of the findings from this and previous studies (van der Helm 2007, van Schagen 2009, Worm 2012) have been taken and tested at full scale. The on-line monitoring options identified in this study for ozonation triggered Waternet to purchase i::scans™ from s::can Messtechnik GmbH capable of measuring turbidity, $UV_{254}$ and derived parameters requiring local calibration such as dissolved organic carbon (DOC). Contrary to our experience with the spectro::lyser™, the i::scans™ suffered from frequent fouling, expressed by the observed drift in the measurement data. To overcome this, frequent cleaning was performed at first. Based on the gained experience through working with the sensors, a more sustainable solution was put in place by installing an autosampler which switches between influent and effluent, allowing to calculate the differential measurement, resulting in less maintenance efforts required since. It does however underline the challenges related to full-scale on-line monitoring. During the installation and test phase continuous attention is required to be able to identify any deviations or maintenance requirements at an early stage.

With the installation of the i::scans the next step for Waternet was to determine the optimised control strategy of the ozonation. Wiersema (2018) performed a literature study to gain better insight into the disinfection kinetics of ozone in water. This understanding was subsequently used to evaluate the different control options for ozonation. A significant difference in inactivation between lab-grown bacteria and environmental bacteria was found, challenging the ability of using linear relation between the Ct value and disinfection. The research showed the need for constant monitoring of the disinfection of environmental bacteria through lab measurements and gain understanding on the local situation before direct control of ozonation can be implemented. Evaluation of the control options did however show opportunities to gain 5% ozone reduction on a yearly basis if control based on constant disinfection was to be implemented.

Experiences in the full-scale treatment plant of Waternet do underline the gap that still needs to be overcome to switch to full scale implementation of direct control based on water quality. The first step being the effort required to get acquainted with the on-line measurements. The next step would be the actual change in control strategy without potentially compromising the drinking water quality produced. To make these changes a solid change program needs to be developed, through validation of the presented results and subsequently gain confidence in the benefits these changes might bring. "It takes years to build up a reputation, but it takes only seconds to destroy it." Therefore, it is recommended to focus on the opportunities with less direct impact on water quality, and as a first step install the identified required on-line sensors to enable continuous monitoring of the drinking water treatment plant.

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# APPENDICES

# SUMMARY

The primary goal of a drinking water company is to produce safe drinking water that meets the quality standards defined in national and international guidelines. Depending on the source water, one or multiple treatment steps are required to produce safe drinking water. Generally, the drinking water treatment plants (WTP) are very robust and over-sized and, as a result, have not required stringent advanced control based on the incoming water quality. However, water companies are facing increased challenges due to changes in feed water qualities and increased (micro-) pollution loads. When the source water originates from surface water an extensive treatment system is required, since surface water can be characterized by seasonal variations influenced by temperature, algae blooms, rain-fall run-off containing pathogens, solids and pesticides, environmental spills upstream and, since recently, the increased threat by endocrine disrupting compounds. This continuous changing source water requires improved monitoring and operation of the WTP, anticipating on the disturbances in the process.

*THESIS OBJECTIVE:*

*Improved monitoring and operation of ozonation and biological activated carbon (BAC) filtration for the removal of pathogens and organic matter, for the optimisation of drinking water production from surface water.*

Ozonation and BAC filtration processes are susceptible to changes in the feed water quality. Besides, these processes have several control options and interaction between the two processes exists. The main objective for ozonation is disinfection and oxidation of organic matter, which results in an increase in the biodegradability of the natural organic matter (NOM). The main objective for BAC filtration is the removal of organic micropollutants and biodegradation of NOM to ensure the production of biologically safe and stable drinking water. In this thesis, pilot plant research was carried out at Waternet, water cycle company for Amsterdam and surrounding areas, location Weesperkarspel, the Netherlands.

Easily assimilable organic carbon (AOC) is frequently used for the assessment of biological stability of drinking water, which is an important consideration in the control of bacterial growth in distribution networks. The first AOC bioassay was developed in 1982 and is based on growth of two bacterial strains (Psuedomonas fluorescens P17 and Spirillum spp. NOX) in drinking water relative to their growth on acetate. Since the original developed method, several new methods for the determination of AOC have been published with the aim of being faster, more reliable and cheaper. Application of these assays raises legitimate questions about the comparison of AOC data from different studies. In this thesis, a round-robin test was performed

to evaluate the correlation between three established AOC methods. A total of 14 water samples covering a wide range of AOC concentrations were analysed with the original "van der Kooij" method, the "Werner & Hambsch" method and "Eawag" method. Good correlations were found between AOC concentrations measured with the various methods. The data suggest an acceptable compatibility between different AOC methods, although deviations between the methods call for careful interpretation and reporting of AOC data. The results from the round robin test emphasized the need to understand which measurement method was used to obtain the reported concentration, since the method gives insight in the actual meaning of the results.

Sampling of the drinking water is carried out on a regular (almost daily) basis, to ensure the produced drinking water meets the quality standards. There is a trade-off between having a high probability of detecting a deviation while minimizing the measuring effort. In order to determine which measurements should be put in place, in this thesis, a seven step design methodology was developed. This enabled the determination of the required water quality monitoring strategy around ozonation and BAC filtration. It was shown how the previous on-line monitoring program of the treatment plant Weesperkarspel was optimised. Evaluation of on-line water quality sensors showed that the parameters typically measured to show compliance with the WHO standards were commonly available. Direct measurement of the more complex parameters such as AOC and bromate were not available on-line. It was shown that real-time information on the actual Ct value, the bromate and AOC concentration was necessary for continuous optimisation of the applied ozone dosage. To address this gap, algorithms were developed for the on-line estimation of the Ct value and the formation of bromate and AOC during ozonation, based on the measured change in UV-Vis spectrum before and after ozonation. It was shown that these algorithms allow for the calculation of the optimal ozone dosage and provide a reliable indication of the amount of bromate and AOC formed during ozonation. Besides using these soft-sensors as surrogate sensors for parameters currently not available on-line, they also provide a cost effective alternative when used to determine multiple parameters through one single instrument.

BAC filters are frequently used in the production of drinking water for the removal of organic micro- pollutants and organic matter, especially when produced from (humic rich) surface water. Differences in filter feed water quality are the result of differences in pre-treatment steps (coagulation/flocculation, ozonation and phosphate addition) commonly applied in the production of drinking water. Understanding of how BAC filters react to a change in feed water quality helps to identify where the focus in operating the BAC filters should be on. In this thesis, the immediate response of the BAC filters to a rapid change in feed water quality was investigated as well as the long term effects. The immediate response showed that all filters were able to mitigate a sudden change in feed water quality, either through improved adsorption or increased activity of the biomass on the filter. As a result of this resilience against sudden changes, it

was therefore concluded that there is no direct need for very stringent on-line monitoring and continuous adjustments of the feed water quality of the BAC filters. Only the pressure drop and the pH and oxygen concentration in the effluent should be measured. The long term effects of changes in feed water quality were compared to previously published research and confirmed the need for sufficient nutrients (readily available carbon and phosphate) in the feed water for optimal performance. The addition of phosphate resulted in the lowest dissolved organic carbon (DOC) concentration in the effluent of the BAC filters. In this study the influence of intact cells in the feed water on the performance of the BAC filters was shown to be limited.

One parameter in the BAC filters that requires enhanced control and understanding is the clogging of the filters, especially when the water temperature starts to increase in spring and summer time. In the BAC filters clogging takes place as a result of the physical, chemical and biological processes occurring in the filters. A simplified model, based on retention and mass balances, to predict the filter run times was developed. Results showed that clogging in the BAC filters was a combination of chemical and biological mechanisms. Already small concentrations of AOC resulted in the development of a biofilm. This biofilm caused the formation of a cake layer and accounted for the majority of the pressure build up in the BAC filters. The simplified model was able to accurately predict the head loss development. The model subsequently allowed for optimising the process control of the full scale BAC filters in terms of predicting the pressure drop and subsequently optimising the backwash sequence, saving 32% backwash water.

In this thesis it was shown that the current monitoring strategy of ozonation-BAC filtration could be improved through implementation of the established design methodology in combination with the developed algorithms allowing for on-line estimation of AOC, bromate and Ct value around ozonation, based on the measured change in UV-Vis spectrum. The operation of BAC filters could be improved through a better understanding of the direct response of the BAC filters to a change in feed water quality and the use of simplified models to optimise the operational strategy around backwashing of BAC filters.

At Waternet, location Weesperkarspel, some of the findings from this and previous studies have been taken and tested at full scale. As a result, on-line monitoring of ozonation was extended with UV/Vis sensors before and after ozonation and with ozone in water sensors in the influent of the first ozonation contact chambers.

# SAMENVATTING

Het primaire doel van een drinkwaterbedrijf is het produceren van veilig drinkwater dat voldoet aan de kwaliteitsnormen die zijn vastgelegd in nationale en internationale richtlijnen. Afhankelijk van het bronwater zijn één of meerdere zuiveringsstappen vereist om veilig drinkwater te produceren. Over het algemeen zijn de drinkwaterzuiveringsinstallaties (WTP) zeer robuust en over gedimensioneerd, met als gevolg dat er geen geavanceerde regeling nodig is die direct stuurt op basis van de inkomende waterkwaliteit. Waterbedrijven worden echter geconfronteerd met toenemende uitdagingen als gevolg van veranderingen in de inkomende waterkwaliteit en toename in (micro-) verontreinigingen. Wanneer gebruik wordt gemaakt van oppervlaktewater voor de productie van drinkwater, is een uitgebreide zuivering noodzakelijk. Oppervlaktewater wordt gekarakteriseerd door seizoen variaties zoals wisselende temperatuur, algenbloei, regenwaterafvoer dat ziekteverwekkers, vaste stoffen en pesticiden kan bevatten, stroomopwaartse milieuverontreiniging en sinds kort een verhoogde bedreiging van hormoon verstorende stoffen. Deze continu veranderende oppervlaktewaterkwaliteit vereist verbeterde monitoring en besturing van de WTP, zodat het mogelijk is te anticiperen op verstoringen.

### PROBLEEMBESCHRIJVING:
### Verbeterde monitoring en besturing van ozon – biologisch actief koolfiltratie (BAC) voor de verwijdering van pathogenen en organisch materiaal voor de optimalisatie van drinkwaterproductie van oppervlaktewater.

Veranderingen in de kwaliteit van het voedingswater kunnen invloed hebben op ozon en BAC-filtratie. Daarnaast zijn er verschillende besturingsmogelijkheden en is er een hoge mate van interactie tussen de twee zuiveringsstappen. Het belangrijkste doel van ozon is desinfectie en oxidatie van organisch materiaal, wat resulteert in een toename van de biologische afbreekbaarheid van natuurlijk organische materiaal (NOM). Het belangrijkste doel van BAC-filtratie is de verwijdering van organische microverontreinigingen en de biologische afbraak van NOM om zo een biologisch stabiele drinkwaterkwaliteit te garanderen. Voor dit proefschrift is proefonderzoek uitgevoerd bij Waternet, het watercyclusbedrijf voor Amsterdam en omgeving, locatie Weesperkarspel, Nederland.

Makkelijk assimileerbaar organische koolstof (AOC) wordt vaak gebruikt om de biologische stabiliteit van drinkwater vast te stellen. Het is een belangrijke indicator voor de beheersbaarheid van bacteriegroei in distributienetwerken. De eerste AOC-bio assay werd ontwikkeld in 1982 en is gebaseerd op de groei van twee bacteriestammen (*Psuedomonas fluorescens* P17 en *Spirillum* spp. NOX) in drinkwater in verhouding tot hun groei op acetaat. Sinds de oorspronkelijk ontwikkelde

methode zijn verschillende nieuwe meetmethoden voor de bepaling van AOC gepubliceerd welke als doel hadden sneller, betrouwbaarder en goedkoper te zijn. Toepassingen van deze verschillende meetmethoden roept legitieme vragen op over de vergelijking van AOC-gegevens uit verschillende onderzoeken. In dit proefschrift is een ringonderzoek uitgevoerd om de correlatie tussen drie gevestigde AOC-methoden te evalueren. Een totaal van 14 watermonsters met een breed scala aan AOC-concentraties werd geanalyseerd door de originele "van der Kooij" -methode, de "Werner & Hambsch" -methode en de "Eawag" -methode. Er zijn goede correlaties gevonden tussen de, met verschillende meetmethoden bepaalde, AOC-concentraties. De gegevens suggereren een aanvaardbare compatibiliteit tussen verschillende AOC-methoden, hoewel afwijkingen tussen de meetmethoden om een zorgvuldige interpretatie en rapportage van AOC-gegevens vragen. De resultaten van het ringonderzoek benadrukken de noodzaak om begrip te hebben van de toegepaste meetmethode behorende bij de gerapporteerde concentratie, aangezien de meetmethode inzicht geeft in de werkelijke betekenis van de resultaten.

Bemonstering van het drinkwater gebeurt op een regelmatige (bijna dagelijkse) basis om ervoor te zorgen dat het geproduceerde drinkwater voldoet aan de gestelde kwaliteitsnormen. Er is een spanningsveld tussen de kans op het detecteren van een afwijking en het minimaliseren van de meetinspanning. Om te bepalen welke metingen moeten worden toegepast is in dit proefschrift een, uit zeven stappen bestaande, ontwerpmethode ontwikkeld. Deze methode maakt het mogelijk te bepalen wat de minimale monitoringstrategie voor de waterkwaliteit rondom ozonisatie en BAC-filtratie moet zijn. Er is aangetoond hoe het voorgaande online monitoringsprogramma van de zuiveringsinstallatie Weesperkarspel geoptimaliseerd is. Evaluatie van bestaande online waterkwaliteitssensoren liet zien dat met name de parameters gelinkt aan de WHO-normen beschikbaar waren. Online metingen van de meer complexe parameters zoals AOC en bromaat waren niet online beschikbaar, terwijl deze wel noodzakelijk zijn voor de continue optimalisatie van de ozondosering, naast online informatie over de Ct-waarde. Om dit gat te dichten, zijn verschillende algoritmen ontwikkeld voor de online schatting van de Ct-waarde en de vorming van bromaat en AOC tijdens ozon, op basis van de gemeten verandering in UV/VIS-spectrum voor en na ozon. Deze algoritmen maken het mogelijk om de optimale ozondosering te bepalen en een betrouwbare indicatie te geven van de hoeveelheid bromaat en AOC die gevormd is. Naast het gebruik van deze soft sensoren als surrogaatsensoren voor parameters die momenteel niet online beschikbaar zijn, bieden ze ook een kosteneffectief alternatief wanneer ze worden gebruikt om meerdere parameters te bepalen via één enkel instrument.

BAC-filters worden vaak gebruikt bij de productie van drinkwater voor de verwijdering van organische microverontreinigingen en organische stof, vooral als (humusrijk) oppervlaktewater gebruikt wordt als bron. Variatie in inkomende waterkwaliteit is het resultaat van verschillende voorbehandelingsstappen (coagulatie/ flocculatie, ozonisatie en fosfaattoevoeging) die worden toegepast bij de productie van drinkwater. Inzicht in hoe de BAC-filters reageren op een verandering

in de inkomende waterkwaliteit, helpt de juiste focus op de besturing van de BAC-filters te leggen. In dit proefschrift is de directe response van de BAC-filters op een verandering in inkomende waterkwaliteit onderzocht, evenals de langetermijneffecten. De directe response toonde aan dat alle filters in staat waren om een plotselinge verandering in de inkomende waterkwaliteit op te vangen, hetzij door verbeterde adsorptie of een verhoogde activiteit van de biomassa in het filter. Met als conclusie dat er geen directe noodzaak is om de inkomende waterkwaliteit van de BAC-filters continue te monitoring en bij te sturen. De langetermijneffecten van de verandering in de inkomende waterkwaliteit zijn vergeleken met eerder gepubliceerd onderzoek, welke bevestigen dat voldoende voedingsstoffen (gemakkelijk afbreekbaar koolstof en fosfaat) van belang zijn voor optimale prestaties. De toevoeging van fosfaat resulteerde in de laagste concentratie opgeloste organische koolstof (DOC) in het effluent van de BAC-filters. In deze studie was de invloed van intacte cellen in het inkomende water op de prestaties van de BAC-filters beperkt.

Waar wel aandacht aan besteed moet worden is de verstopping van de BAC-filters, vooral wanneer de watertemperatuur begint te stijgen in de lente en de zomer. In de BAC-filters vindt verstopping plaats als gevolg van de fysische, chemische en biologische processen die in de filters optreden. Er is een vereenvoudigd model ontwikkeld, om de looptijden van de filters te voorspellen, gebaseerd op retentie en massabalansen. De resultaten toonden aan dat verstopping in de BAC-filters een combinatie was van chemische en biologische mechanismen. Lage concentraties AOC resulteerden al in de ontwikkeling van een biofilm. Deze biofilm veroorzaakte de vorming van een koeklaag welke het grootste deel van de drukopbouw in de BAC-filters veroorzaakte. Het vereenvoudigde model was in staat om de ontwikkeling van drukopbouw nauwkeurig te voorspellen. Het model maakte het mogelijk om de procesregeling van de BAC-filters te optimaliseren door de drukopbouw te voorspellen en daarmee de terugspoelfrequentie te optimaliseren. Hiermee was het mogelijk 32% terugspoelwater te besparen.

In dit proefschrift is aangetoond dat de huidige monitoringstrategie van ozon-BAC-filtratie verbeterd kan worden door implementatie van de beschreven ontwerpmethodologie in combinatie met de ontwikkelde algoritmen die een online schatting, gebaseerd op de gemeten verandering in UV/VIS-spectrum, van AOC, bromaat en Ct-waarde rond ozon mogelijk maken. De werking van BAC-filters kan worden verbeterd door een beter begrip van de directe response van de BAC-filters op een verandering in de inkomende waterkwaliteit en het gebruik van vereenvoudigde modellen om de operationele strategie rond het terugspoelen van BAC-filters te optimaliseren.

Bij Waternet, locatie Weesperkarspel, zijn enkele bevindingen uit dit en eerdere onderzoeken getest in de hoofdzuivering. Met als resultaat dat de online monitoring van ozon is uitgebreid met UV/Vis-sensoren voor en na ozon en met ozon in water metingen in het influent van de eerste ozon contactkelder.

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# BIOGRAPHY

Petra Suzanne Ross was born in Woerden, the Netherlands on August 2nd, 1979. In 1998 she graduated from secondary school Stella Maris College in Meerssen and started her study Technical Mathematics in Delft. After the first year she decided to switch to Civil Engineering at Delft University of Technology. For her MSc thesis she performed pilot plant research at Waternet, the water cycle company for Amsterdam and surrounding. After graduating in 2007 she started her PhD research within the 6th European Framework program TECHNEAU and under the guidance of Prof. Luuk Rietveld. The research entitled 'Monitoring and Operation of Ozonation-BAC filtration' was presented at many (international) IWA conferences. Her articles have been published in international refereed journals. She was one of the founders of the 1st IWA Young Water Professionals BeNeLux conference in Eindhoven in 2009. From 2011 to February 2018 she worked as a consultant water for Arcadis. In February 2018 she made the switch to MSD, to become a project manager in the Global Engineering Solutions department responsible for the delivery of capital projects.