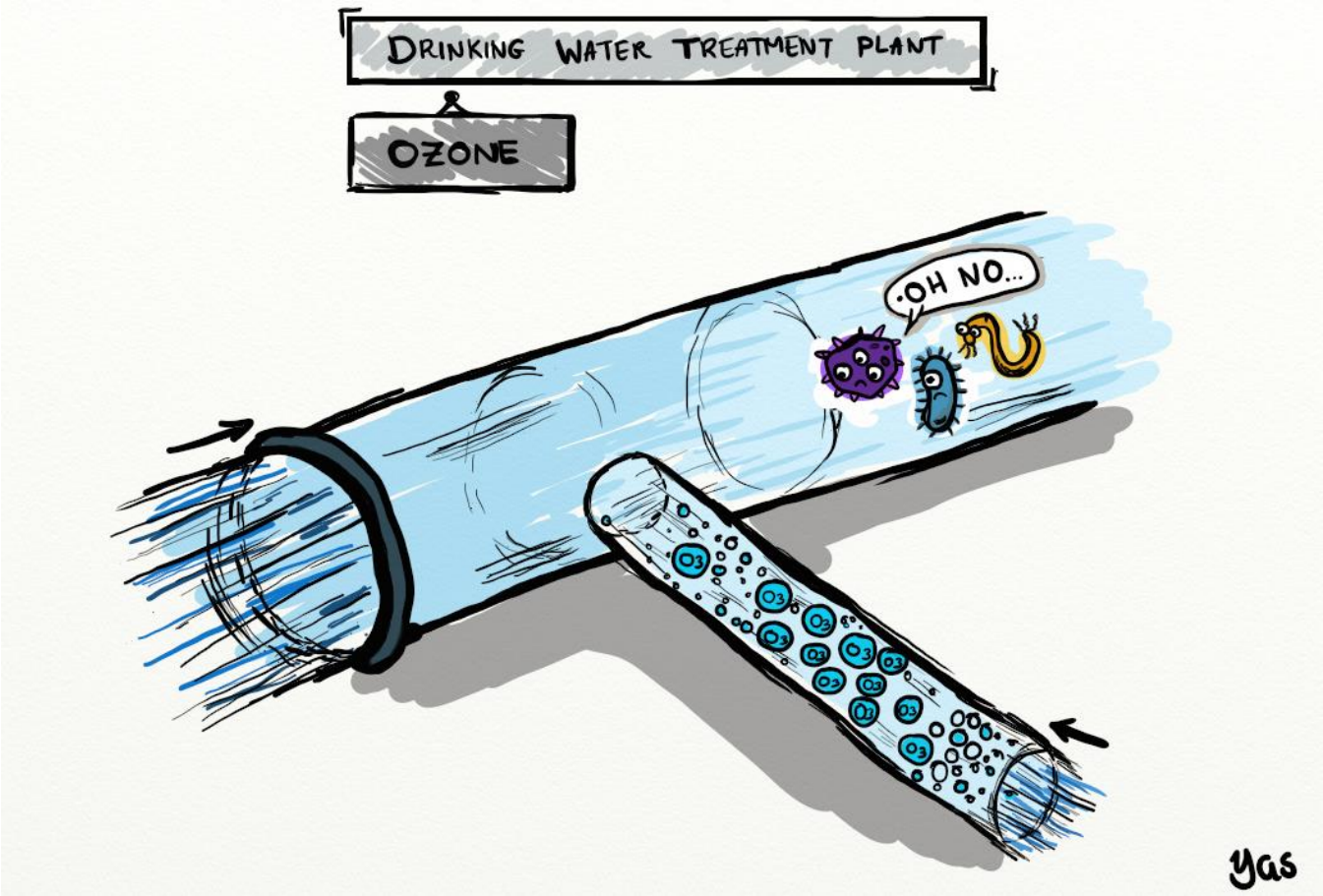
Efficiency and efficacy of ozonation for disinfection at the Weesperkarspel drinking water treatment plant

Evaluation of process modeling for ozone-efficient steering with verified inactivation data



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This research is conducted for, with and at:
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Summary

Steering the ozonation process for drinking water production at Weesperkarspel (Waternet, Amsterdam) is a challenge. The aim is to keep disinfection at the desired level: a constant disinfection is optimal, as using more ozone than necessary brings along costs and bromate formation. But verifying disinfection also remains a challenge: grab samples take time to analyze, may be inaccurate and do not enable direct response to changes in the influent water.

To tackle these problems, two steps were taken: quantitative disinfection research was conducted through literature study to gain better insight into disinfection kinetics of ozone in water. Using this knowledge, different steering mechanisms for the ozonation process were modeled to see which gives the best results.

Disinfection research has shown that there is a significant difference ($p > 0,005$) in inactivation between lab-grown bacteria and environmental bacteria, where inactivation constants can be 7 times larger for lab bacteria compared to environmental bacteria, which must be taken into account during disinfection experiments and research. The relation between CT (ozone concentration [mg/L] * contact time in the reactor [min]) and disinfection is usually assumed to be linear, but environmental data from this research shows this relation is more likely to be logarithmic.

Steering the ozonation process was carried out in four ways: steering for a constant ozone dosage, steering for a constant CT, steering for a constant disinfection and steering for a constant percentage decrease of UV_{254} absorbance of the water. Variation in bromate formation, ozone dosage and disinfection differs per steering mechanism: steering for a constant disinfection is the best way to meet disinfection goals while keeping ozone costs low. Five percent ozone could be saved on a yearly basis compared to steering for a constant ozone dosage.

Contents

1. Introduction

1.1 Disinfection by ozone

While most countries around the world use chlorine for disinfection, the 10 drinking water companies in the Netherlands rely on disinfection by UV or ozone. These techniques have the advantage of creating a pleasant taste and smell of the water, contrary to chlorine. Ozonation is used for disinfection and oxidation of organic matter in drinking water production (van der Helm et al., 2009). Ozone gas is injected into the water and functions to disinfect, oxidize micro-pollutants, to improve taste and color, and to break down organic matter into biodegradable, removable parts (van der Helm et al., 2009). In water, ozone gas (O_3) partly decomposes into ·OH radicals and oxygen (O_2). These ·OH radicals react with any organic matter at high speed. Ozone preferably reacts with double C bonds (C=C). A detailed overview of all chemical reactions can be found in work from Von Gunten (von Gunten, 2003a; Von Gunten, 2003b). An unwanted by-product of ozonation is bromate (BrO_3^-), which is possibly carcinogenic to humans and is typically not removed in the filters after ozonation (Ross et al., 2016).

Waternet is a water cycle company for the Amsterdam region, producing 90 million m^3 of drinking water per year. It has two drinking water production locations: Leiduin (producing 70% of drinking water) and Weesperkarspel (producing 30%). The Weesperkarspel drinking water plant is used as study location for this research project. The water used for drinking water production is taken from the Bethune polder as seepage water and is pre-treated by coagulation-sedimentation, self-purification in a surface water reservoir and rapid sand filtration. Treatment at the Weesperkarspel plant consists of ozonation, softening of the water through pellet reactors, biological activated carbon (BAC) filtration and slow sand filtration. The ozonation step serves as the main barrier for disinfection. In combination with carbon filtration, this way of treating drinking water is found to be very effective, as the ozone turns dissolved organic carbon (DOC) into biodegradable DOC which can be removed by the BAC and slow sand filtration (van der Aa et al., 2012).

Weesperkarspel has four ozone lanes with a capacity of 1400 m^3 water/h per lane. The installation was redesigned and rebuilt in 2013 and 2014, now using pure liquid oxygen to produce ozone gas. The ozone gas is added to the water via a side stream, which is again injected into the main stream. Static mixers are used at two points, see Figure 1. This results in homogenous spread of ozone gas through the water. The minimum ozone dosage (in the main stream) is 1 mg/L and the maximum dosage is 3 mg/L. The contact time is 13 ½ minutes at maximum flow capacity in its 5 contact chambers.

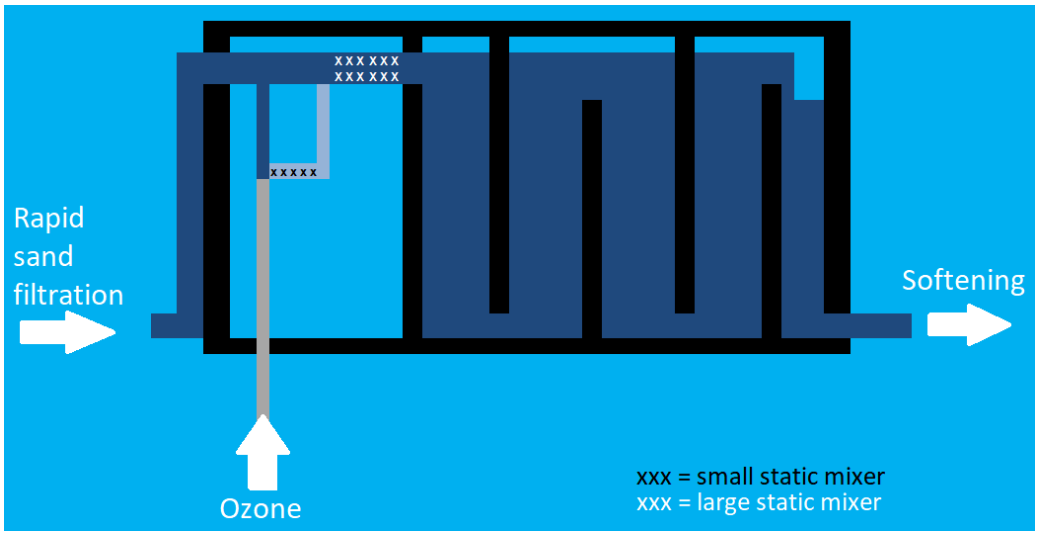

Figure 1: Schematic representation of the ozonation process at Weesperkarspel.

Currently, the ozone dosage at Weesperkarspel is kept at a constant rate, only varying when deemed necessary. This study will investigate whether it is more efficient to vary the ozone dosage based on other parameters or concepts. 'Efficiency' of the installation can be measured in terms of efficient ozone dosing (how much is used?), environmental impact (are bromate levels kept at a minimum?) and costs. Efficacy of the installation – the ability to produce the desired result – needs verification through quantitative disinfection research. As stated before, disinfection is the main purpose of ozonation at Weesperkarspel.

Infection risk through contaminants in water needs to be kept to a legal standard to prevent outbreaks (when over 1% of the population becomes ill (Smeets et al., 2008)). To assess microbial risk, Dutch drinking water regulations require a quantitative microbial risk assessment (QMRA) to verify that the risk of infection is below 1 in 10,000 persons per year, and that no indicator microorganism is detected in a 100 mL sample. Disinfection must therefore be in line with these requirements. Infection risks can be calculated from pathogen concentrations after removal, water consumption and dose-response relations.

For Weesperkarspel, the bacteria group *Campylobacter* is the microorganism of most interest. *Campylobacter* are S-shaped or curved bacteria, of which we currently know 17 species and 6 subspecies, causing *Campylobacteriosis*, of which symptoms include diarrhea, pain, fever, nausea and vomiting ("WHO | Campylobacter," 2017). The most often found strain of *Campylobacter* is *C. jejuni*. This microorganism is of concern because (re)contamination of the influent water before reaching the drinking water treatment plant of Weesperkarspel with *Campylobacter* through animals (for example birds) is common. However, due to the lack of data about *Campylobacter* inactivation with ozonation, *E. coli* will be used as reference organism in this study. Inactivation kinetics and results for the two are very similar and *E. coli* behaves a little more conservative, making it a valid indicator organism (Smeets et al., n.d.).

Most of the disinfection research conducted until now is based on inactivation tables as published by the U.S. EPA (United States Environmental Protection Agency) around 1989. These tables do not exist for *Campylobacter* or *E. coli*. KWR Watercycle Research, based in Nieuwegein, aims to develop a tool which

uses a database of all available literature on treatment efficacy for different microorganisms, to make it possible to filter on different parameters, species etc., to improve assessment of disinfection. Currently, this tool already exists for UV disinfection, and part of this research project will contribute to the development of a similar tool for ozonation.

1.2 Research aim and questions

Disinfection is validated by grab samples, but the issues of time and uncertainty play a role here. There are too little samples, of which often most are negative, giving much uncertainty about the efficacy of disinfection; getting these results is not a real-time operation but takes time. Using on-line measurements instead enables real-time steering of the operation, for example by using the two *i-scan* photospectrometers present before and after ozonation at Weesperkarspel. These measure the UV_{254} absorbance (UVA_{254}) of the water; research has shown that change in UVA is a good indicator of rapid ozone consumption (Rietveld, 2005). Ideally, uncertainty is decreased if various parameters can be linked correctly to inactivation of microorganisms. Inactivation values as currently used need to be revised, redefined, and their uncertainty and variability assessed, to better validate and optimize the ozonation model.

The aim of this research project is to increase the efficiency of steering the ozonation process at the Weesperkarspel drinking water treatment plant: through a better understanding of the effects of ozonation on microorganisms, using up to date scientific knowledge about microorganism inactivation; and by steering the ozonation process in an optimal way using on-line data. The goal of this is to ensure a constant effluent water quality, while influent water quality can vary. The research question is therefore twofold:

"How can we decrease uncertainty and improve the assessment of ozone disinfection in drinking water treatment?"

This will help answering the second research question:

"How can we steer the ozonation process at Weesperkarspel more efficiently?"

1.3 Approach

To simulate the ozonation process at Weesperkarspel, a mathematical continuous-states model is used in Matlab/Stimela. This model is adapted and calibrated for the current situation. It is then used to simulate 4 different scenarios using different steering mechanisms. These are described in the next chapter. Insight into disinfection kinetics is gathered through a quantitative literature study. Relevant data gathered is analyzed and used to improve the model disinfection calculations.

The end goal is to make the ozonation process as efficient as possible; therefore the different ways of steering need to be assessed based on practicality and certainty, as well as environmental impact and costs. The best option should be implemented in a functional ozonation model.

2. Methods

2.1 Model description

In 1909, both H. Chick and H. Watson proposed a disinfection law, describing the concentration of organisms based on the concentration of disinfectant (C) and contact time (T) (Masschelein, 2000). Their two laws combined form the Chick-Watson relationship for disinfection, yielding a certain CT-value for a requested inactivation. The CT-disinfection relationship is different for each type of microorganism. CT is defined as the product of concentration and contact time:

$$CT = concentration\ O_3\ * contact\ time \quad [1]$$

where concentration ozone = [mg-O_3/L] and contact time = [min].

Combining the laws of Chick and Watson gives the Chick-Watson law:

$$ln\frac{N}{N_0} = -k_{cw} * C * t \quad [2]$$

where N = concentration of organisms [CFU/volume], N_0 = initial concentration of organisms [CFU/volume], k_{cw} = specific lethality [L/(mg*min)] or inactivation rate constant, C = [mg-O_3/L] and t = time [min].

Note that Chick-Watson uses the natural logarithm, ln, to report disinfection. When reporting disinfection in general, it is common to use the 10 base log.

CT values depend on the contact time and therefore on the hydraulic characteristics of the reactor. Tracer tests are generally used to determine hydraulic retention time (HRT). Because short-circuiting can occur in some contact chambers, this is sometimes corrected for using CT10: T10 is the retention time in which 10 percent of the flow has passed through the contactor. To decrease short-circuiting, better plug flow conditions should be achieved.

Disinfection is validated by taking grab samples and measuring microorganism content. However, these measurements cannot give enough certainty about microorganism content as most measurements return negative values, meaning no microorganisms are detected in that sample. Because sample analysis time is long, results come too late to affect process control. Because of this difficulty to estimate how much ozone is needed through empirical measurements, an ozonation model for concentration and contact time was developed in Stimela/Matlab, using the CT concept.

The ozonation model was executed using Stimela, which is “an environment for standardized mathematical models of drinking water treatment processes in Matlab/Simulink” (GitHub, 2017). It calculates changes in water quality parameters in a series of continuous stirred tank reactors (CSTRs) and can be used for optimization of drinking water processes and research. Partial differential equations are numerically integrated and variations of water quality parameters in time and space can be followed (Rietveld et al., 2010). Matlab version 2012b was used on a Windows 10 x64 PC with 4GB RAM and i5-2520M CPU. The model works with several blocks: an input block where influent water quality and flow are defined; process blocks, where design and calibration parameters are defined; control blocks, which give varying parameter values to process blocks; and an output block, providing graphical output. A basic process model in Stimela contains 6 files: an initialization file, defining the number of parameters and

states; a parameter file, processing parameters from the process blocks; a system file, which contains equations and output parameters; a graphical output file; and two files for the graphical interface.

The original model of Van der Helm (2007) is used as a basis. Model relations (calculations) as well as parameter relations are based on his theory. The basis of his model, which will be adapted later, is the following equation:

$$\frac{\partial c_{O3}}{\partial t} = -u\frac{\partial c_{O3}}{\partial x} - k_{UVA}(UVA - UVA_{out})Y - k_{O3}c_{O3} \quad [3]$$

where t = time [s], u = water velocity (or $\frac{Q}{A}$) [m/s], x = length of reactor [m], k_{UVA}= UVA254 decay rate [L/(s*mg-O_3)], c_{O3} = ozone concentration [mg/L], UVA = UVA254 in water [1/m], UVA_{out} = stable UVA after ozonation [1/m], Y = yield factor for ozone consumed per UVA254 decrease [(mg-O_3/L)(1/m)] and k_{O3} = slow ozone decay rate [1/s].

The first term of Equation 3 describes transportation of ozone in water. The second term describes rapid ozone consumption as a function of UVA254. The third term describes slow ozone decay with first order kinetics.

The original relation for k_{O3} was tested for a larger variety of ozone dosages (including larger ones), though its temperature dependency is not clear from the experiments. This equation is kept as the values yielded seem reasonable (Equation 8). An Arrhenius equation is used to correct for temperature.

Adjustments made to the model structure are as follows:

- Bubble column characteristics were removed (ozone consumption term, short-circuiting);
- A temperature correction factor was introduced for fast ozone decay in k_{UVA} using Arrhenius. It has been shown that ozone decays faster and disinfection by ozone increases with increased temperature (Jamil et al., 2017) (Equation 6). The original relation for k_{UVA} by Van der Helm (2007) was unfit for the current situation, because it is based on significantly lower ozone dosages. Expanding the relation to ozone dosages relevant for Weesperkarspel would result in k_{UVA} values approaching zero;
- Rapid ozone consumption was multiplied by $O_{3,conc}$ to better simulate a chemical reaction equation (concentration A (ozone) times concentration B (UVA) times rate constant(s));
- Disinfection is now calculated by the model using new disinfection knowledge (Equations 13 and 14).

Data measured at Weesperkarspel can be used (both on-line and lab measurements). While it is always the case that data is limited, we must at any given time accept the data that are available (Jakeman et al., 2006).

In the end, the following assumptions were made:

- Y does not depend on ozone dosage, as it acts as a stoichiometric coefficient (van der Helm, 2007);

- $\%UVA$ reduction (or $UVA_{in} - UVA_{out}$) depends only on the ozone dosage and UVA_{in} (Equation 10), justified by the claims that it is a good indicator of rapid ozone consumption (Rietveld, 2005);
- k_{O3} and k_{UVA} decrease with increasing ozone dosage, following the assumption made by Van der Helm (2007). Assuming a constant contribution of the ozone decomposition cycle, this can be explained by the various types of sites within natural organic matter (NOM) that have different reactivity with ozone. For low ozone dosages only the fast-reacting sites consume ozone; at higher dosages, the rate of ozone consumption decreases as slow reacting sites are also oxidized (Gallard et al., 2003).

The following continuous states are calculated at every model step (adapted from (van der Helm, 2007)):

Ozone concentration:

$$\frac{\partial c_{O3}}{\partial t} = -u\frac{\partial c_{O3}}{\partial x} - k_{UVA}c_{O3}(UVA - UVA_{out})Y - k_{O3}c_{O3} \quad [4]$$

where u = water velocity (or $\frac{Q}{A}$) [m/s], t = time [s], x = length of reactor [m], k_{UVA}= UVA254 decay rate [L/(s*mg-O_3)], c_{O3} = ozone concentration [mg/L], UVA = UVA254 in water [1/m], UVA_{out} = stable UVA after ozonation [1/m], Y = yield factor for ozone consumed per UVA254 decrease [(mg-O_3/L)(1/m)] and k_{O3} = slow ozone decay rate [1/s].

k_{UVA} is calculated as follows:

$$k_{UVA,5} = 0{,}0841 - 0{,}022 * O_{3,dos}\left(\frac{DOC}{O_{3,dos}}\right)^2 \quad [5]$$

This is k_{UVA} for 5 degrees Celsius. This was fitted using the relation presented in Figure 2 and a DOC concentration of 5,9 [mg/L]. Next, calculate k_{UVA} for the actual temperature:

$$k_{UVA} = \frac{k_{UVA,5}}{e^{\frac{-70000}{8{,}314*(273+5)}}} * e^{\frac{-70000}{8{,}314*(273+Temp)}} \quad [6]$$

where $O_{3,dos}$ = ozone dosage [mg/L], DOC = dissolved organic content [mg/L], and Temp = water temperature [°C].

k_{O3} is calculated as follows:

$$k_{O3,10} = 0{,}0011 * \left(\frac{DOC}{O_{3,dos}}\right)^2 \quad [7]$$

This is k_{O3} for 10 degrees Celsius. Next, calculate k_{O3} for the actual temperature:

$$k_{O3} = \frac{k_{O3,10}}{e^{-\frac{70000}{8{,}314*273+10}}} * e^{-\frac{70000}{8{,}314*(273+Temp)}} \quad [8]$$

Note: Arrhenius constants as derived by Van der Helm (2007) were kept for the calculations above.

UV_{254} absorption:

$$\frac{\partial c_{UVA}}{\partial t} = -u\frac{\partial c_{UVA}}{\partial x} - k_{UVA}c_{O3}(UVA - UVA_{out}) \quad [9]$$

where u = water velocity (or $\frac{Q}{A}$) [m/s], t = time [s], x = length of reactor [m], k_{UVA}= UVA254 decay rate [L/(s*mg-O_3)], c_{O3} = ozone concentration [mg/L], UVA = UVA254 in water [1/m], UVA_{out} = stable UVA after ozonation [1/m].

UVA_{out} is calculated as follows:

$$UVA_{out} = UVA_{in} - 0{,}8185 * \sqrt{O_{3,dos}}\sqrt{UVA_{in}} \quad [10]$$

where UVA_{in} = initial UVA [m^{-1}] and $O_{3,dos}$ = ozone dosage [mg/L].

Bromate concentration:

$$\frac{\partial BrO3}{\partial t} = -u\frac{\partial c_{BrO3}}{\partial x} + k_{BrO3}c_{O3} \quad [11]$$

where u = water velocity (or $\frac{Q}{A}$) [m/s], t = time [s], x = length of reactor [m], k_{BrO3} = bromate formation constant [1/s] and c_{O3} = ozone concentration [mg/L].

k_{BrO3} is calculated as follows:

$$k_{BrO3} = 2{,}74 * 10^{-7} * pH^{5{,}82} * {c_{Br,in}}^{0{,}73} * 1{,}035^{(T-20)} \quad [12]$$

where $c_{Br,in}$ = influent bromide concentration [µg/L] and T = water temperature [°C].

E. coli concentration:

$$\frac{\partial N}{\partial t} = -u\frac{\partial c_{Ec}}{\partial x} - k_{cw}c_{O3} \quad [13]$$

where u = water velocity (or $\frac{Q}{A}$) [m/s], t = time [s], x = length of reactor [m], c_{Ec} = concentration *E. coli* [CFU/volume], k_{cw} = inactivation rate constant [L/(mg*s)] and c_{O3} = ozone concentration [mg/L].

k_{cw} is calculated using Arrhenius, of which A and E_a will be derived later in Equation 20 and Table 4. Deriving k_{cw} is possible as follows if removal and CT are known:

$$k_{cw} = \frac{ln\frac{N}{N_0}}{Ct} \quad [14]$$

CT "concentration":

$$\frac{\partial CT}{\partial t} = -u\frac{\partial c_{CT}}{\partial x} + c_{O3} \quad [15]$$

where u = water velocity (or $\frac{Q}{A}$) [m/s], t = time [s], x = length of reactor [m], c_{CT} = "concentration" CT [mg*s/L] and c_{O3} = concentration ozone [mg/L].

2.2 Model input

2.2.1 Default parameter values

Trial and error, based on Van der Helm (2007), resulted in the following approximate parameter ranges for k_{UVA}, Y and k_{O3}:

k_{UVA}: 0.01 – 0.5 [L/(s*mg-O_3)]
Y: 0.1 – 0.5 [(mg-O_3/L)/(1/m)]
k_{O3}: 0.005 – 0.01 [1/s]

The following influent water quality parameters can be adjusted manually but have the following default values:

Table 1: Default influent water quality parameters. These can be adjusted manually in the model's user interface. Some, such as pH, can be entered as time series; others, such as conductivity, are a static value.

Parameter	**Value**
DOC	5,9 [mg/L]
AOC	20 [µg/L]
Oxygen	10 [mg/L]
Conductivity	57 [mS/m]
pH	7,9 [-]
Bromide	100 [mg/L]
E. coli	15000 [cfu/volume]

Flow [m^3/h], temperature [°C] and UVA_{in} [m^{-1}] are always entered manually as time series. All other parameters, such as k_{UVA}, are calculated by the model.

2.2.2 Disinfection relation

The disinfection model of Chick-Watson (Equation 2) is the governing equation for calculating disinfection in our ozonation model. While other disinfection models exist, this one was chosen for its wide-spread use and simplicity.

When discussing pathogen inactivation in water, log inactivation is used. This corresponds to a percentage of inactivated microorganisms after treatment: for example, 2,0 log = 99% inactivation; 3,0 log = 99,9% etc. This should not be confused with the $ln\frac{N}{N_0}$ yielded by a Chick-Watson calculation (Equation 2). Log inactivation can be calculated by taking the log of the concentration out (N) divided by the concentration in (N_0) and is also referred to as decimal elimination capacity (DEC):

$$DEC = \log inactivation = log\frac{N}{N_0} \quad [16]$$

Influent water quality parameters (temperature, pH, DOC concentration, and UVA_{254}) play a role in influencing the ozone profile and thus log inactivation of microorganisms (van der Helm et al., 2009). Previous modeling has shown in theory that, by varying the ozone dosage based on a set microorganism inactivation value, predictable and steady inactivation can be reached as well as less bromate formation at the same disinfection capacity (van der Helm et al., 2009).

Several relations that are currently being used in the ozonation model need to be revised because inactivation data might be outdated. This includes relations between CT, temperature, microorganism inactivation (or DEC, decimal elimination capacity), DOC, ozone decay, and pH. In most literature found until now, *Giardia* is used as reference pathogen because for some time, this was a pathogen of concern which was considered persistent and needed research.

Much is still unknown about the inactivation kinetics of ozone. To implement inactivation in the model, quantitative inactivation data for *E. coli* is required. As stated before, *E. coli* functions as an indicator organism in this study as it behaves similarly to *Campylobacter*. Quantitative data is needed to derive inactivation relationships in the model. To get this data, a large amount of scientific papers is scanned and assessed through Scopus, Google Scholar, etc., and when deemed relevant and reliable and detailed enough, the reported data and its metadata is included in a database in Excel.

As described earlier, a database of inactivation measurements for UV disinfection already exists at KWR. A protocol to gather data also exists to ensure reliable source quality. A similar protocol document for collecting ozone disinfection data was composed (see Appendix A). Following the guidelines in this document, literature searches were conducted (using Scopus or similar search engines) and the results were assessed. From included literature, (meta)data was inserted into an Excel database.

The disinfection database contains information on the conducted literature searches, in- and excluded papers, linked publications, and all (meta)data given in the included publications. This collection of information can feed a future QMRA tool for ozone disinfection, as currently existing at KWR for UV disinfection (KWR, 2017). This database should give better insight into inactivation times and ozone dosages for *E. coli*. All gathered data in the database needs to be compared, and how it is used depends on the range, amount of measurements and other conditions.

Information from this database specifically relevant to this research was extracted and analyzed. IBM SPSS was used for exploring the data and performing linear regression analysis, to describe correlations and trends. Assumptions for linear regression are:

- Linearity, meaning each predictor has a linear relationship with DEC;
- Normality, meaning errors are normally distributed;
- Homoscedasticity, meaning the variance of errors is constant.

2.3 Model calibration and validation

Calibration of the model is carried out on measured ozone concentrations at the sample point at Weesperkarspel right before the first contact chamber (also see Figure 1, after the large static mixer). The database at Weesperkarspel was used to extract measured flow, UVA and ozone concentration data. Flow and temperature data were entered, and the model's calculations for k_{UVA} and Y were calibrated in various calibration runs at different flow patterns, UV absorbance and ozone dosages. The calculation of decrease in UVA was calibrated using Figure 2. Parameter values were initially based on findings of Van der Helm (2007), and adjusted by trial and error to find appropriate initial parameter values for calibration.

To automate calibration, a script was written which uses a nonlinear least-squares solver to try and fit the model to the data. However, parameter estimation for complex models usually involves non-convex

numerical optimization, with a risk that the global optimum is not found (Jakeman et al., 2006). The script was kept as simple as possible to avoid coding errors. It can be found in Appendix E.

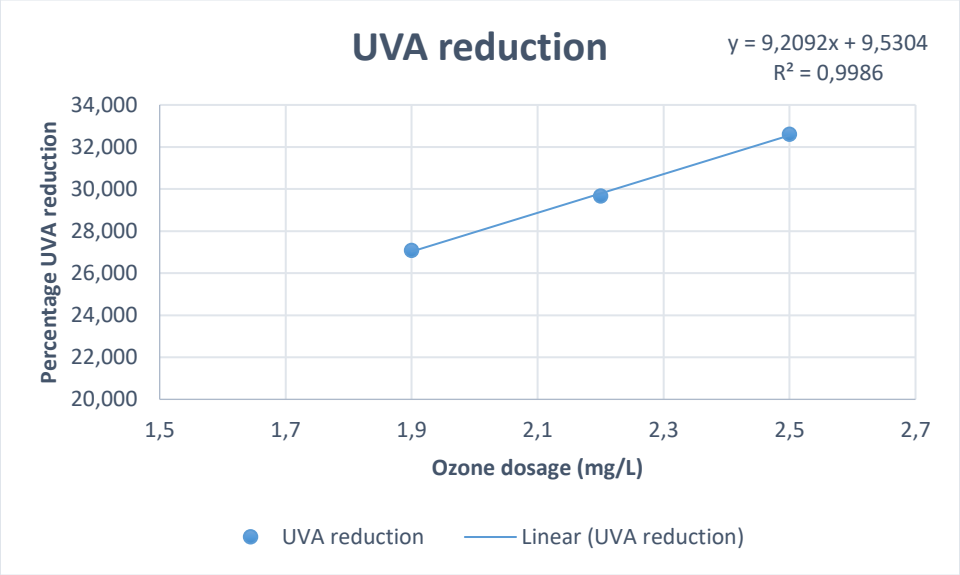

Figure 2: Percentage UV absorbance reduction ((UVAin-UVAout)/(UVAin/100)) versus ozone dosage, using 2018 Weesperkarspel measured data for temperatures ≈ 5°C measured in 2018.

In the current situation at Weesperkarspel, both UVA_{in} and UVA_{out} are measured by the i-scans. These should be inserted into the model by the user as known parameters. From the measurements presented in Figure 2, it can be seen that the percentage UVA reduction increases with increasing ozone dosage. There is no data to back up a relation with percentage UVA reduction and temperature.

2.4 Model scenarios

A selection of four steering mechanisms for the ozonation process was made. The results of the first mechanism are used as set points for the other runs.

2.4.1 General model input

There are many variables and parameters included in the model; the most important ones used are ozone dosage, ozone concentration throughout the reactor, UV absorption (UVA), CT, flow, pH and temperature. Most important calculated parameters are effluent UVA, effluent bromate, disinfection, ozone dosage and CT; they are summarized in Table 2.

Table 2: Overview of most important model inputs and outputs.

Input	Output
Bromide (µg/L)	Bromate (µg/L)
Conc. *E. coli* [CFU/volume]	Conc. *E. coli* [CFU/volume], log inactivation
Flow [m^3/h], temperature [°C], O_3 dose [mg/L],	CT [mg*min/L], ozone profile [mg/L per contact chamber]

pH	
UVAin [m^{-1}]	UVA profile [m^{-1} per contact chamber], UVAout [m^{-1}]

Throughout a year, parameters that fluctuate most clearly are flow and temperature. For the runs testing the 4 different steering mechanisms – which will be explained in the following section – a model run of 8 days was executed, simulating influent water behavior of a full year (fluctuating temperature and flow, shown in Figure 3 and 4 below, and fluctuating UVA_{in} from 16,6 in winter to 14,9 in summer). The first day was used to give the model initialization time; it was removed from the results. The results of the remaining 7 days are presented. This setup was used instead of simulating 365 days to save time running the model.

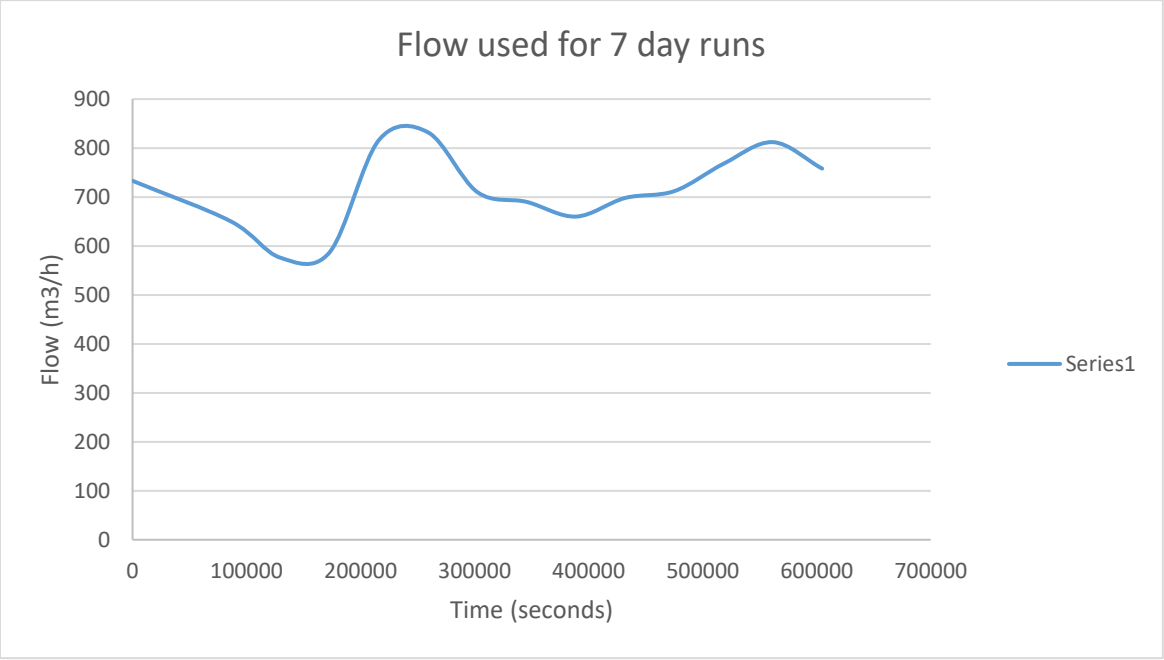

Figure 3: Fluctuating flow used for the different model runs, comparable with yearly flow fluctuations.

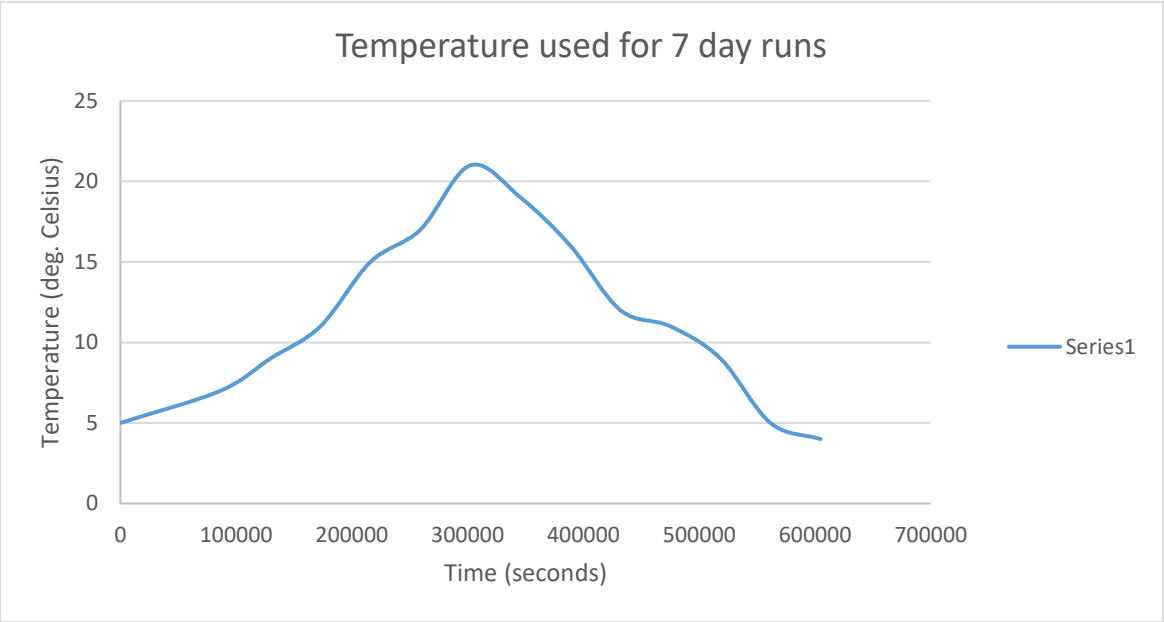

Figure 4: Fluctuating temperature used for different model runs, based on yearly temperature fluctuations.

2.4.2 Steering mechanisms

Water treatment based on constant ozone dosage

This is the current operational method at Weesperkarspel where a constant ozone dosage is applied. In the model, a feedback loop is operated by the control file. If the ozone set point is not met, for example when it is too low, ozone gas flow is increased to meet the set point.

Water treatment based on constant CT

It is also possible to steer for a constant CT value. If the desired CT is a known value (e.g. 2,2 mg-O_3*min/L), this can be steered for directly by entering this value in the control file. CT is regulated by increasing or decreasing the ozone dosage via the same feedback system until the desired CT value is reached. This way of operating can be useful if a certain CT value is linked to effluent water quality.

Water treatment based on constant disinfection

Research suggests that, in theory, steering for constant disinfection leads to a steady microorganism inactivation and less bromate formation (van der Helm et al., 2009).

Steering for a constant disinfection was first attempted by entering the desired log removal in the control file by dividing the current influent concentration of bacteria for example by 100 (this number depends on the desired log removal and influent concentration). Unfortunately, the model was too slow for this to work.

Steering for a constant disinfection is possible through reverse-engineering the calculation used in the model to calculate removal of *E. coli* (Equation 13). The desired amount of removed bacteria is known, as well as k, so the required CT is calculated and steered for with every time step. This is because disinfection in the model is calculated using Chick-Watson, as introduced previously.

Water treatment based on constant percentage decrease UVA_{254}

Steering for a constant percentage decrease of UV_{254} absorbance (UVA) is measurable and easy to apply in practice. At Weesperkarspel, two i-scan photospectrometers are placed before and after the ozonation process. These measure UVA, and thus percentage decrease of UVA can be monitored continuously. Steering for a constant percentage decrease is possible through adjusting the ozone dosage: if the decrease is too low, more ozone is dosed until the desired value is reached. This does require the i-scans to report reliable measurements.

Steering for a constant percentage decrease of UVA was first attempted by reading the in- and effluent UVA values into the control file, and calculating UVA_{out} as follows:

$$UVA_{out} = UVA_{in} * 0{,}7 \quad [17]$$

In this example, a constant decrease of 30% is steered for. Unfortunately, the model was too slow for this to work.

Steering for a constant percentage decrease of UVA is possible through reverse-engineering the model calculation for UVA_{out} (see Equation 10). In this equation, UVA_{out} depends on UVA_{in} and the ozone dosage; UVA_{in} and UVA_{out} are known, therefore the corresponding ozone dosage can be calculated and steered for at every time step.

2.5 Assessment

Inactivation data from the literature study and water quality measurements from Weesperkarspel were used to feed the updated models. This simulates a more realistic impression of the situation at Weesperkarspel. The model itself is assessed (how well it works, its drawbacks and shortcomings), and the results for each steering mechanism are assessed.

Factors on which to compare results were environmental impact (e.g. bromate formation), disinfection, economic impact (the amount of ozone used in a year) and model response time.

3. Results

3.1 Disinfection relation

Data gathered in previous experiments and samplings as well as literature data was used to create a database of water quality parameters, experimental conditions and DEC of different microorganisms. Because the efficacy of ozonation is influenced by many factors, as much metadata as possible is collected for each study. A complete overview of this can be found in Appendix B. From this database, the susceptibility of micro-organisms to ozone can be studied. To see which role certain factors play in influencing inactivation, a linear regression analysis was performed.

Linear regression analysis was run in IBM SPSS using the Forward method, meaning predictors are added one by one only if they are statistically significant ($p < 0{,}005$). The selected independent variables are CT [mg*s/L], origin of the bacteria (this was coded as a dummy variable), temperature [°C] and pH. From these, CT, origin and pH were selected by the Forward method. Adding all three increased the adjusted R square value, which gives an indication of the predictive power of this model, therefore all three are kept. This model, within the boundaries of the given dataset, can be described as:

$$DEC = -6{,}486 + 3{,}812 * CT + 1{,}038 * pH + 1{,}758 * origin_{E.coli} \quad [18]$$

where CT = concentration*contact time [(mg-O_3*min)/L] and $origin_{E.coli}$ = lab (1) or environmental (0).

Correlations between these coefficients are shown in Table 3:

Table 3: Coefficient correlations between independent variables CT, origin and pH. The dependent variable is DEC

Coefficient Correlations[a]

Model			CT	originDummy	pH
3	Correlations	CT	1,000	,436	,233
		originDummy	,436	1,000	-,248
		pH	,233	-,248	1,000
	Covariances	CT	,467	,171	,062
		originDummy	,171	,328	-,056
		pH	,062	-,056	,154

a. Dependent Variable: DEC

This shows 'internal' correlations between independent variables, showing how much one variable could explain another variable. If correlation is very high between two variables, the model could in theory be simplified by merging the two variables. The largest correlation is between CT and origin (0,436).

Results of the check for normality, homoscedasticity and linearity can be found in Appendix F. These checks indicate the linear regression results can be used and thus the analysis gives insight into which parameters predict *E. coli* inactivation and to what extent. CT and origin of the bacteria are found to be significant predictors. While this was expected for CT – simply because a larger concentration or contact time results in higher exposure to ozone – it is now also noted that the origin of an organism (lab or environmental) matters for disinfection results. Temperature was not included as a predictor in this model, but several studies have clearly shown that temperature does effect log inactivation of *E. coli*, therefore it will be taken into account. pH is also shown to be a significant predictor of log inactivation, a claim supported by literature (Jamil et al., 2017).

All collected data for *E. coli*, as can be found in Appendix B, is displayed in Figure 5, 6 and 7. These are used to explore the collected dataset more. What can be noticed from these figures is that ozone seems to inactivate lab *E. coli* much faster than environmental *E.* coli, while the environmental data reaches the same DEC values at higher CT, or not at all – with the exception of Gamage (2013), possibly due to different water used (waste water). Differences between studies may be due to different experimental conditions, and it depends on how the CT values are calculated. For example, different water types used were drinking water treatment plant influent, well water, phosphate buffer solution, tap water or ultrapure water.

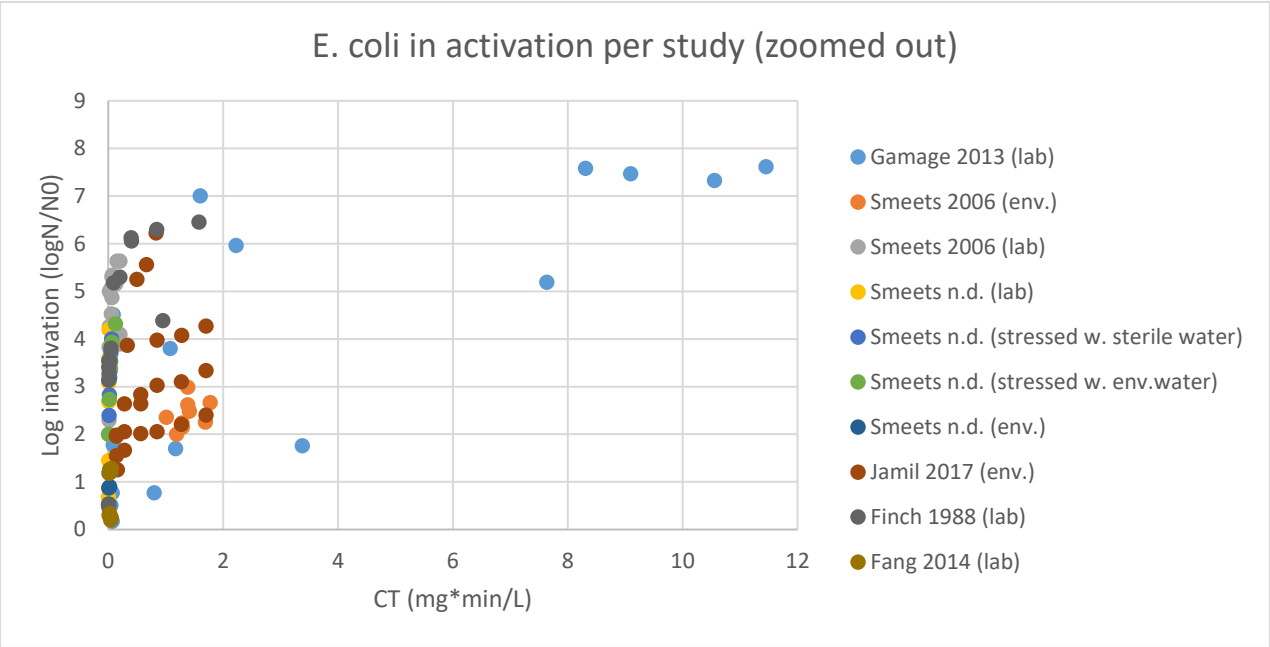

Figure 5: All E. coli inactivation data in a CT range of 0-14. (Fang et al., 2014; Finch et al., 1988; Gamage et al., 2013c; Jamil et al., 2017; Smeets et al., n.d., 2006)

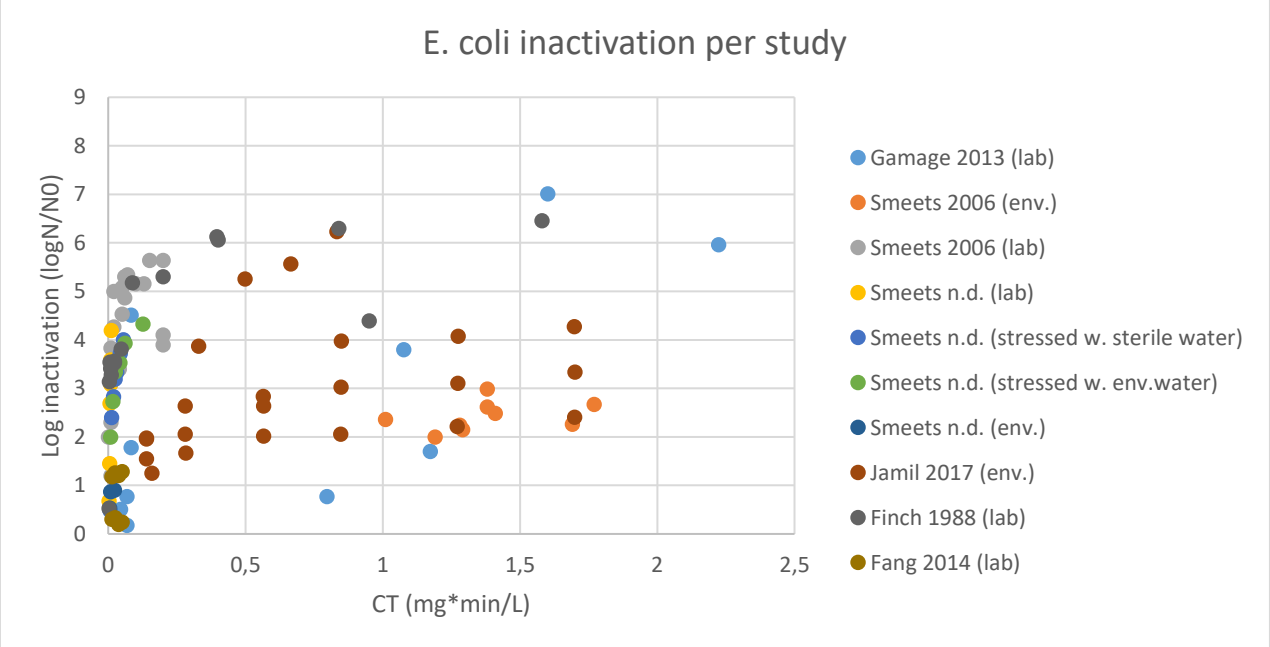

Figure 6: All E. coli inactivation data in a CT range of 0-3. (Fang et al., 2014; Finch et al., 1988; Gamage et al., 2013c; Jamil et al., 2017; Smeets et al., n.d., 2006)

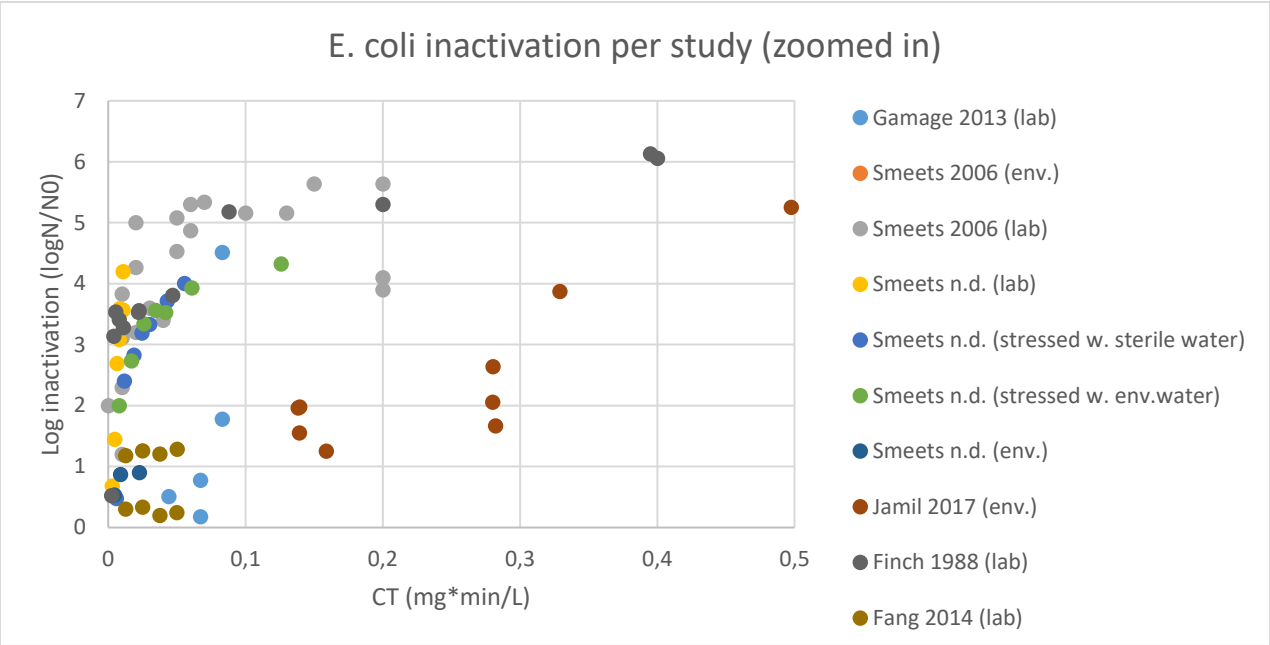

Figure 7: All E. coli inactivation data in a CT range of 0-0,5. (Fang et al., 2014; Finch et al., 1988; Gamage et al., 2013c; Jamil et al., 2017; Smeets et al., n.d., 2006)

To look into the difference between lab and environmental *E. coli* further, both are plotted in Figure 8:

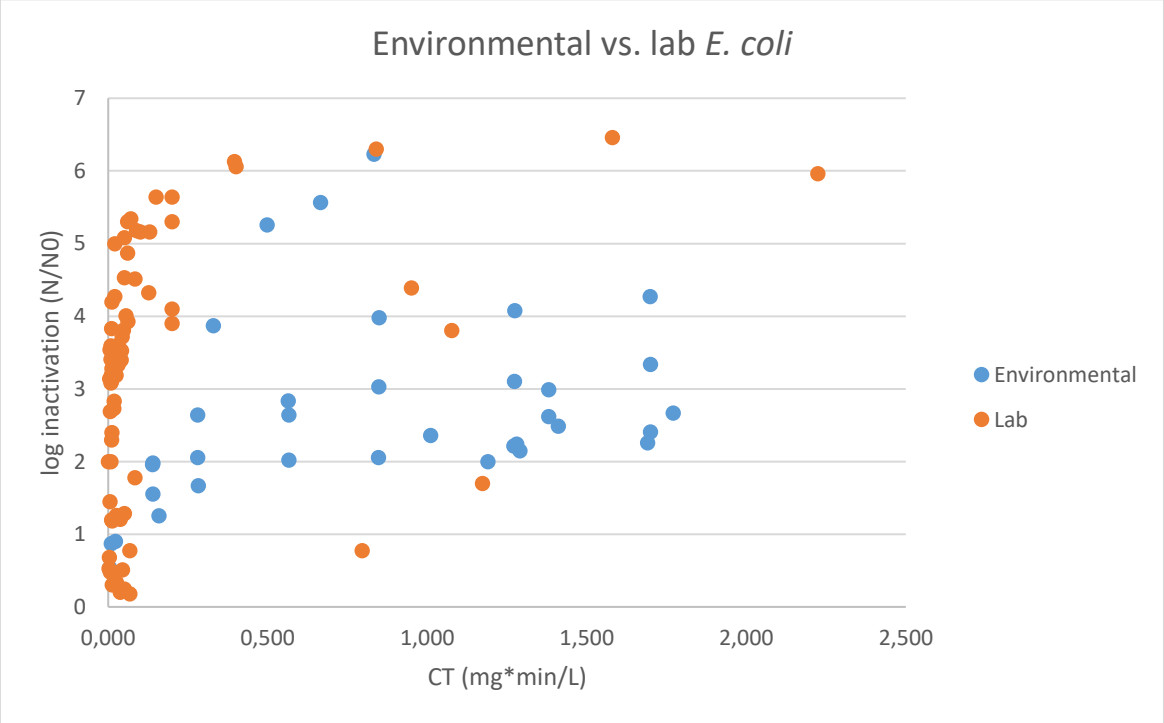

Figure 8: All E. coli inactivation data from the database, separated by origin of the bacteria (environmental or lab).

The inactivation rate of environmental *E. coli* is lower than of lab bacteria, and when looking at data more specifically, tailing can be observed. Two studies clearly illustrating this difference between lab and

environmental *E. coli* are those of Smeets (n.d.) and Jamil (2017), see Figure 9 and 10. These are just two examples of studies, but the trends in DEC and CT are clear. Much higher inactivation values are reached at much smaller CT values for lab bacteria compared to stressed or environmental bacteria. It seems that the more stress an *E. coli* has endured, the tougher it is and thus its survivability is larger than that of other, less stressed *E. coli*.

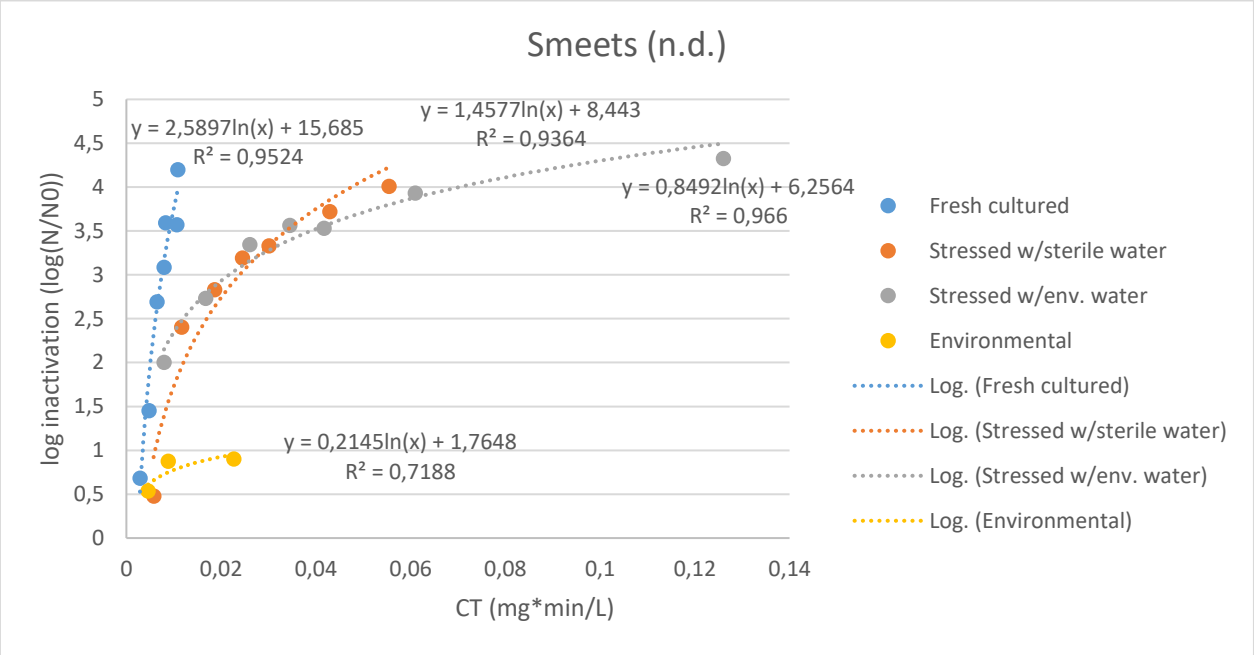

Figure 9: Inactivation kinetics for lab, stressed and environmental E. coli. Temperature = 7-11 deg. Celsius. Source: Smeets (n.d.)

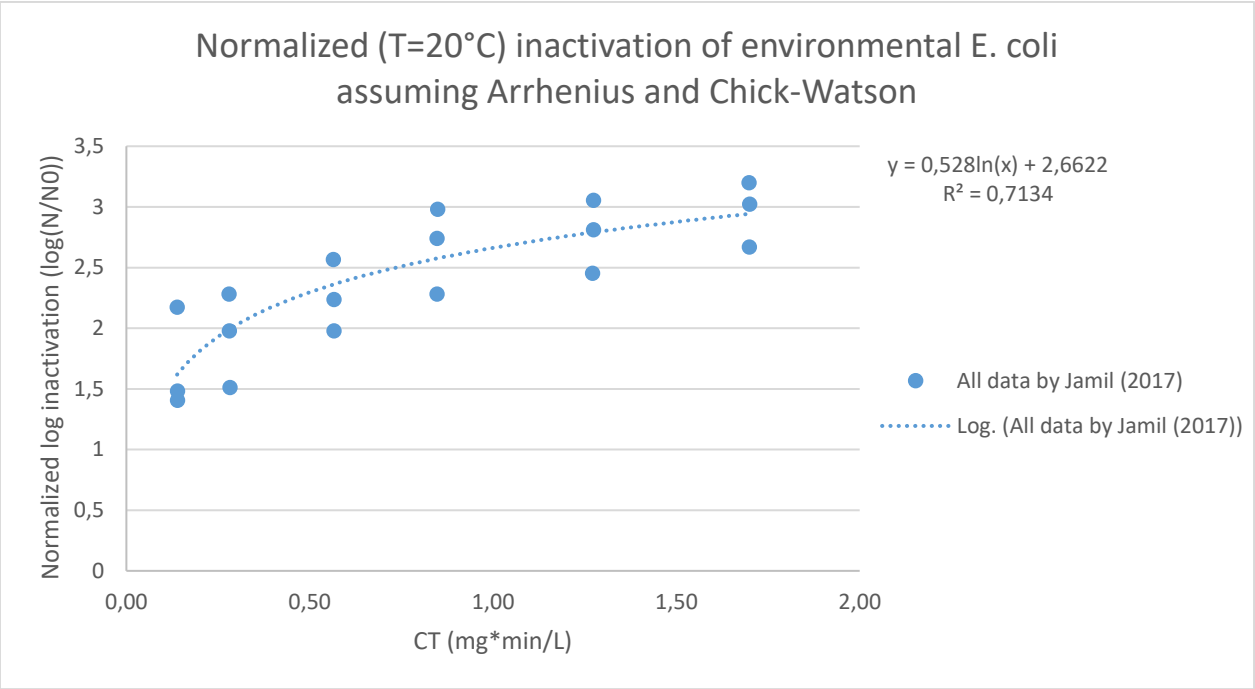

Figure 10: Log inactivation for environmental E. coli by Jamil (2017). The only variable in her experiments was temperature, all other parameters were kept constant; here, log inactivation is normalized to 20 degrees Celsius using Arrhenius for temperature correction to better see the tailing effect.

From the data presented by Smeets (n.d.), it seems that for environmental *E. coli*, the maximum log inactivation reached is around 2 when the relation is extrapolated. However, these measurements were conducted at very low CT values. The experiments by Jamil (2017) were conducted at CT values more comparable to those yielded at Weesperkarspel. Its inactivation values are also conservative compared to the rest of the data set. Because of this, it was decided this study was used to formulate the inactivation relations for the model. Environmental inactivation values from other studies lie within the same range (see Figure 11).

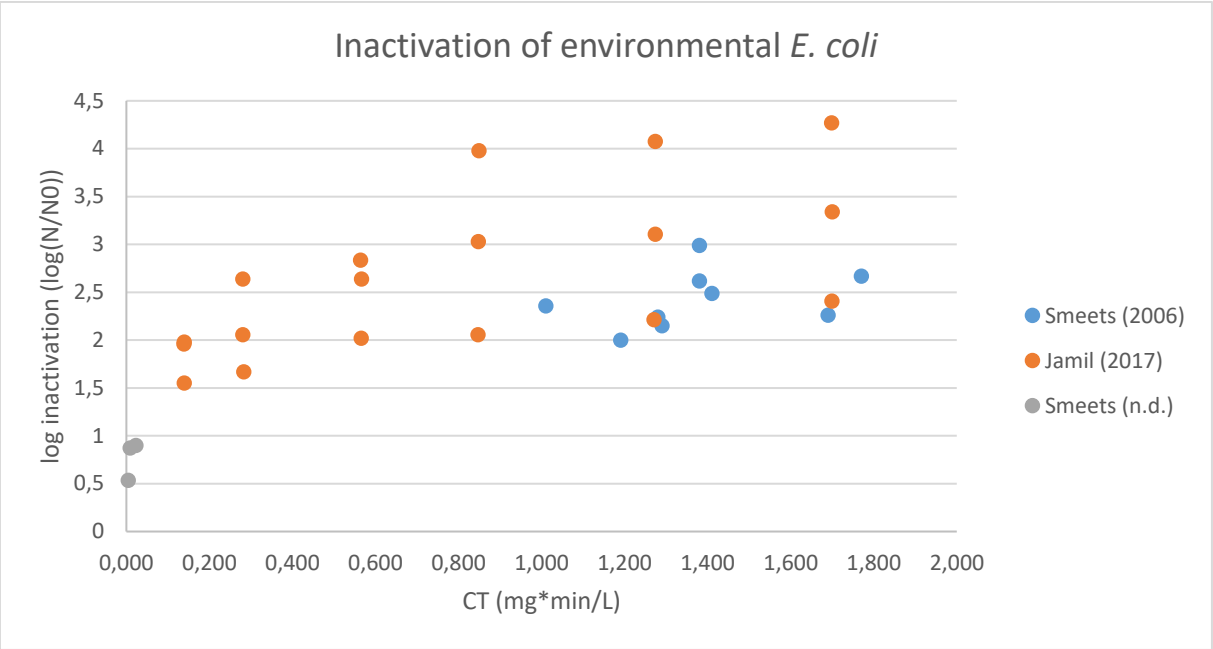

Figure 11: Inactivation data for E. coli for all studies in the dataset that included environmental E. coli's. Not normalized to a temperature.

This needs to be translated into a log inactivation calculation the model can make. Chick-Watson is used to describe inactivation. The inactivation rate constant k [L/(mg*min)] will be calculated at every model time step and depends on temperature following Arrhenius:

$$k = Ae^{-\frac{Ea}{RT}} \quad [19]$$

where A = frequency factor (unit depending on units of other constants), E_a = activation energy [J/mol], R = ideal gas constant = 8,314 [J/(mol*K)] and T = water temperature in Kelvin [°K].

The activation energy E_a and frequency factor A are derived from the data using an Arrhenius plot (see Figure 11). The resulting constants can be found in Table 4. These are used to calculate inactivation in the model using Chick-Watson.

Table 4: Arrhenius constants derived for the calculation of disinfection.

Arrhenius constant:	Value:
E	14466,5
A	3430,8
R	8,314
K	273,15

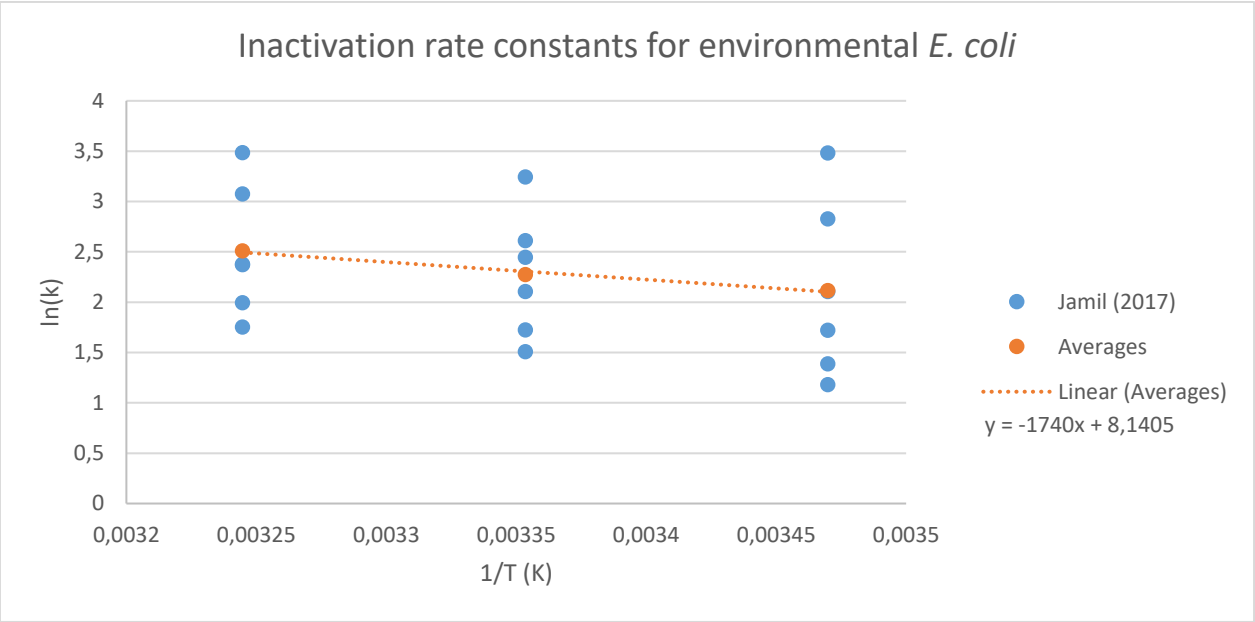

Figure 12: Arrhenius plot for data by Jamil (2017), showing 1/temperature (in Kelvin) versus log(k_e). Arrhenius constants E and A are derived from the trend line.

This results in the following model equation for calculating the Chick-Watson k:

$$k = -3430{,}8 * e^{-\frac{14466{,}5}{8{,}314*T}} \quad [20]$$

where T = temperature in Kelvin [°K], and k = inactivation rate constant [L/(mg*min)]. This calculation of k is used in Equation 13.

3.2 Model calibration and validation

After numerous calibration rounds, the following results were obtained (see Table 5):

Table 5: Calibration results for kUV and Y (calibrating on measured ozone in water concentration at the sample point). Temperature in degrees Celsius, flow in m^3/h, UVA in m^{-1}, and ozone in mg/L. In green are shown the differences between the average modeled ozone concentrations and the average measured ozone concentrations. kO_3 is calculated by the model using Equation 8.

Run	**Temp. [°C]**	**Avg. Flow [m^3/h]**	**UVA_{in} [m^{-1}]**	**UVA_{out} [m^{-1}]**	**% red. UVA**	**$O_{3,dos}$ [mg/L]**	**k_{UVA}**	**Y**	**Modeled O_3 conc. [mg/L]**	**WPK measured O_3 [mg/L]**	**Difference in O_3 [mg/L]**
A	3,4	615	16,65	12,14	27,087	1,9	0,342	0,335	0,36	0,334	0,026
B	3,4	615	16,48	11,59	29,672	2,2	0,216	0,335	0,53	0,42	0,11
C	3,4	615	16,65	11,22	32,613	2,5	0,136	0,335	0,73	0,75	-0,02

The results for one day (86400 seconds) for run A and B are shown below. Run C did not have enough flow data to make a useful comparison graph.

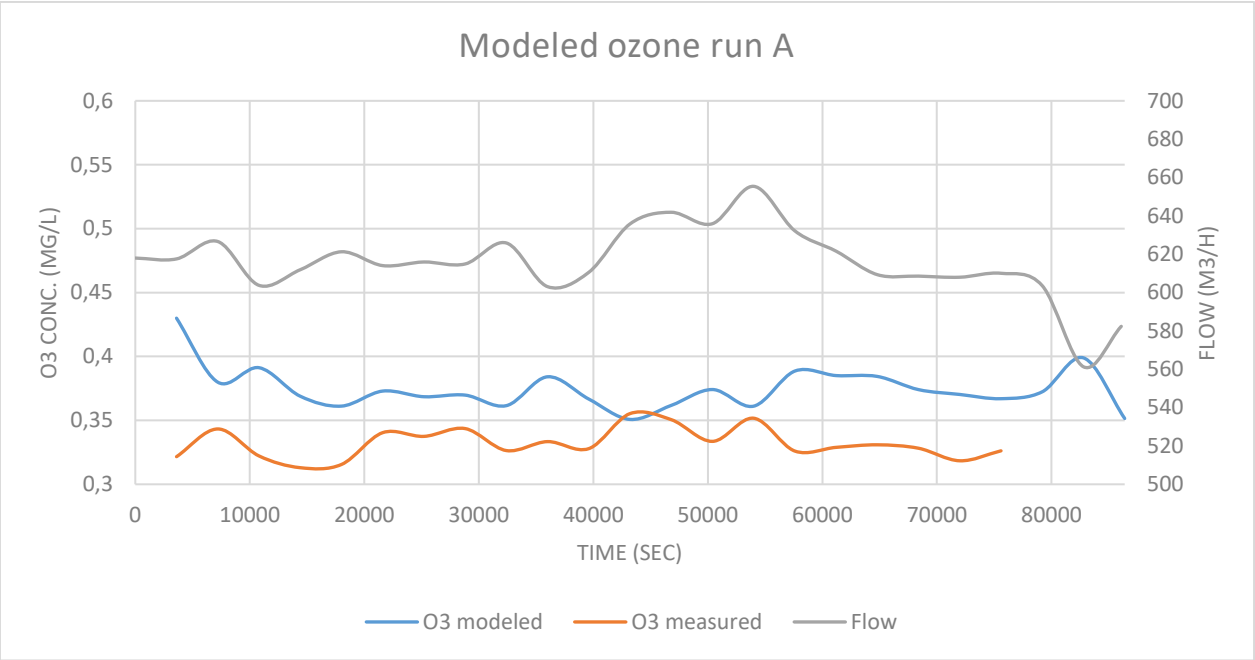

Figure 13: Model results versus measured ozone concentrations for one day with temperature = 3,4°C and ozone dosage = 1,9 mg/L. WPK flow and ozone data are from 14-2-2018.

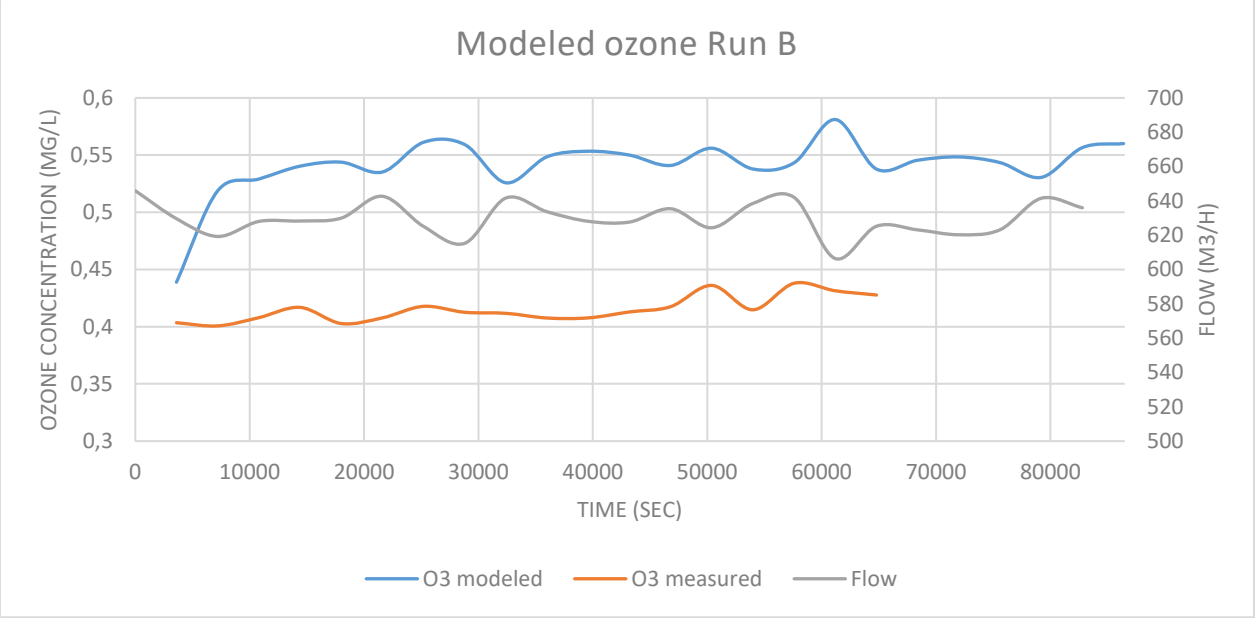

Figure 14: Model results versus measured ozone concentrations for one day with temperature = 3,4°C and ozone dosage = 2,2 mg/L. WPK flow and ozone data are from 14-2-2018.

It can be seen that for both runs, the modeled ozone concentrations seem to follow the flow, even though a lag in model results can be observed. Measured ozone concentrations (WPK) do not always seem to follow variations in flow: there is no explanation for the peaking in run A with the data available. One would expect that, at higher flow rates, the contact time at the sample point has been shorter, thus more ozone would be present than at lower flow rates. Ozone would be transported further into the

reactor. While using a different solver (ode45) sometimes solves the issue of model response lag, this is not always the case.

The following two figures, 15 and 16, attempt to illustrate this lag. The first, Figure 15, shows how ozone concentrations follow the flow when all model parameters except the flow are constant:

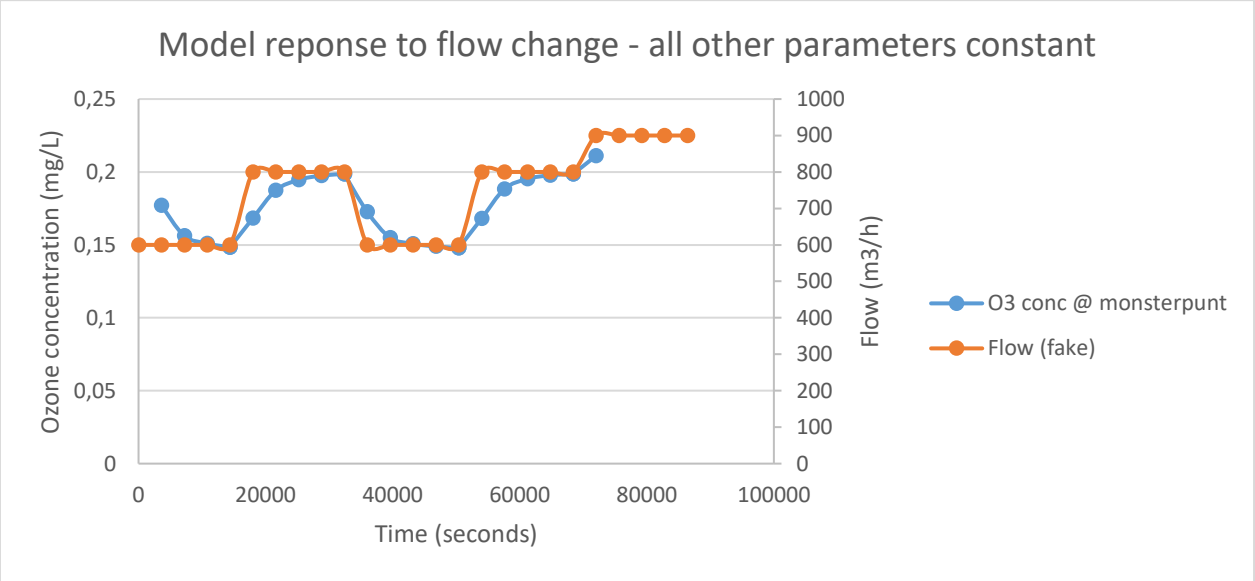

Figure 15: Ozone concentrations following the flow changes when all other parameters (including the calculation of kUVA, kO_3 and Y) are kept constant.

Figure 16 shows how changes in ozone concentration already become more delayed when one calculation at every time step is added to the model (namely the calculation of k_{UVA}):

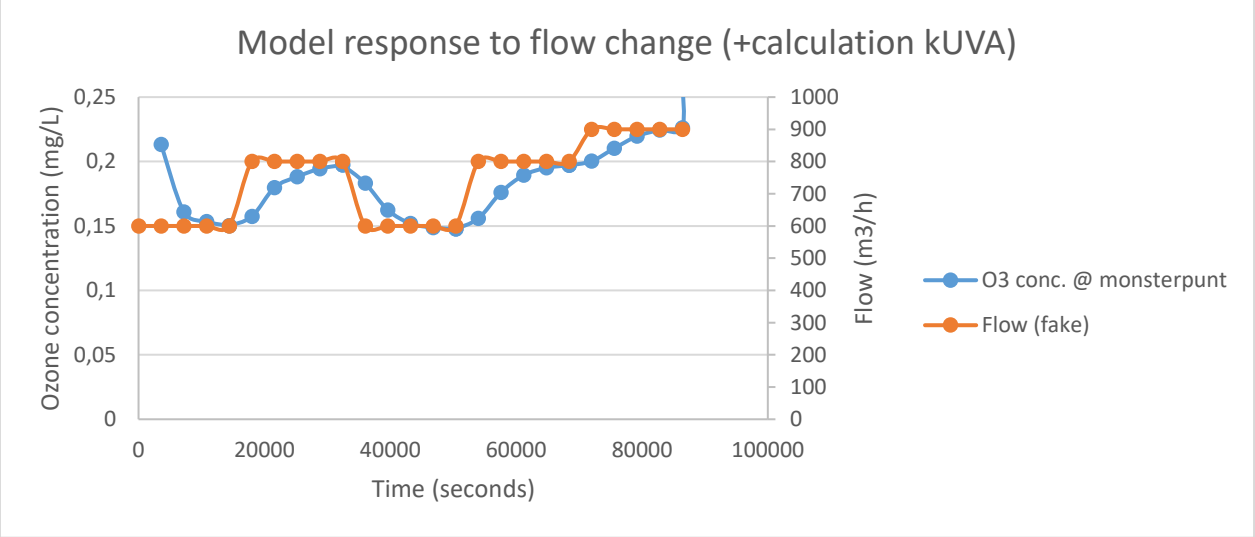

Figure 16: Ozone concentrations following the flow changes when one parameter (kUVA) is now calculated by the model at every time step. The more parameter calculations added, the more lag seems to occur at fluctuations in for example flow or temperature.

Various solvers were tested to see if they would give improvement of this lag in results, but no solution or pattern could be discovered, see Table 6. Using an initial state did speed up the model runtime moderately.

Table 6: Different solvers tested for this specific model. Model runtime refers to the amount of time taken before the Stimela model has finished a run. Result accuracy refers to how fast results seem to respond to changes in influent parameters.

Solver	**Solver reset method:**	**Model runtime**	**Result accuracy**
ode45	-	Minutes	Sometimes accurate Sometimes 7200 sec lag
ode15s	Robust	Hours	-
ode23tb	Robust	Minutes	7200 sec lag
ode23tb	Fast	Minutes	7200 sec lag

To validate the model, three runs at different temperatures and flow rates were performed. These can be found below in Figure 17, 18 and 19. Flow and temperature data was based on measured WPK data from 2017.

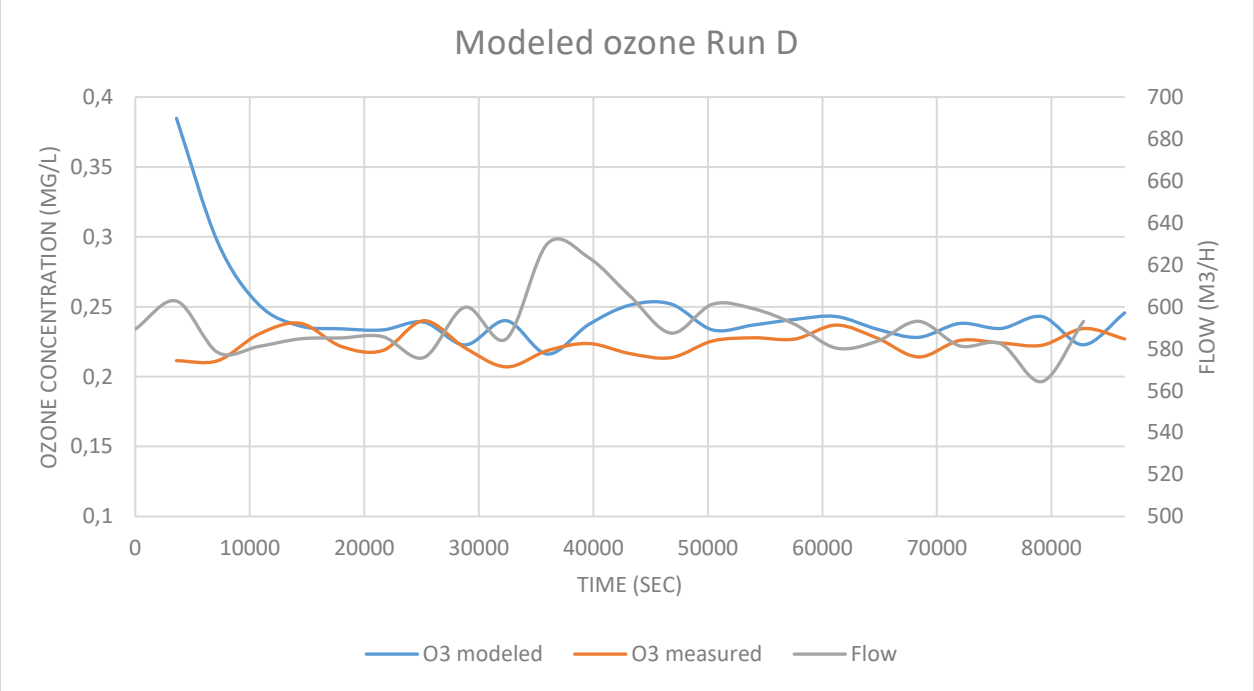

Figure 17: Model results versus measured ozone concentrations for one day with temperature = 9°C and ozone dosage = 1,9 mg/L. WPK flow and ozone data are from 2017.

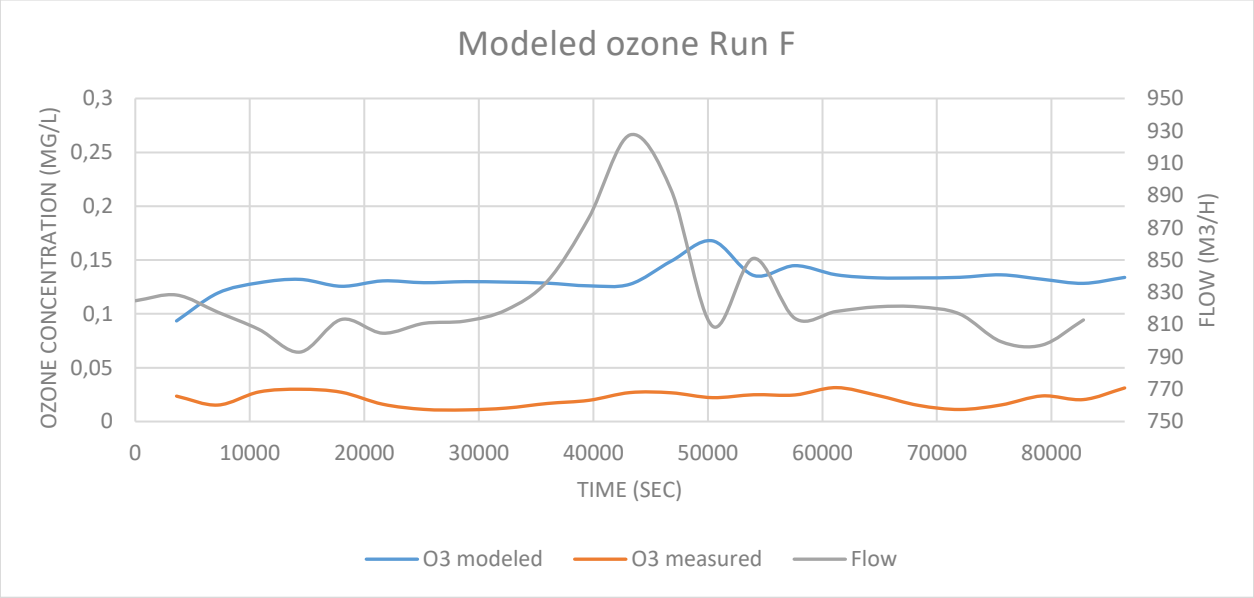

Figure 18: Model results versus measured ozone concentrations for one day with temperature = 15°C and ozone dosage = 1,9 mg/L. WPK flow and ozone data are from 2017. Do notice that the detection limit of ozone in water is around 0,05 mg/L.

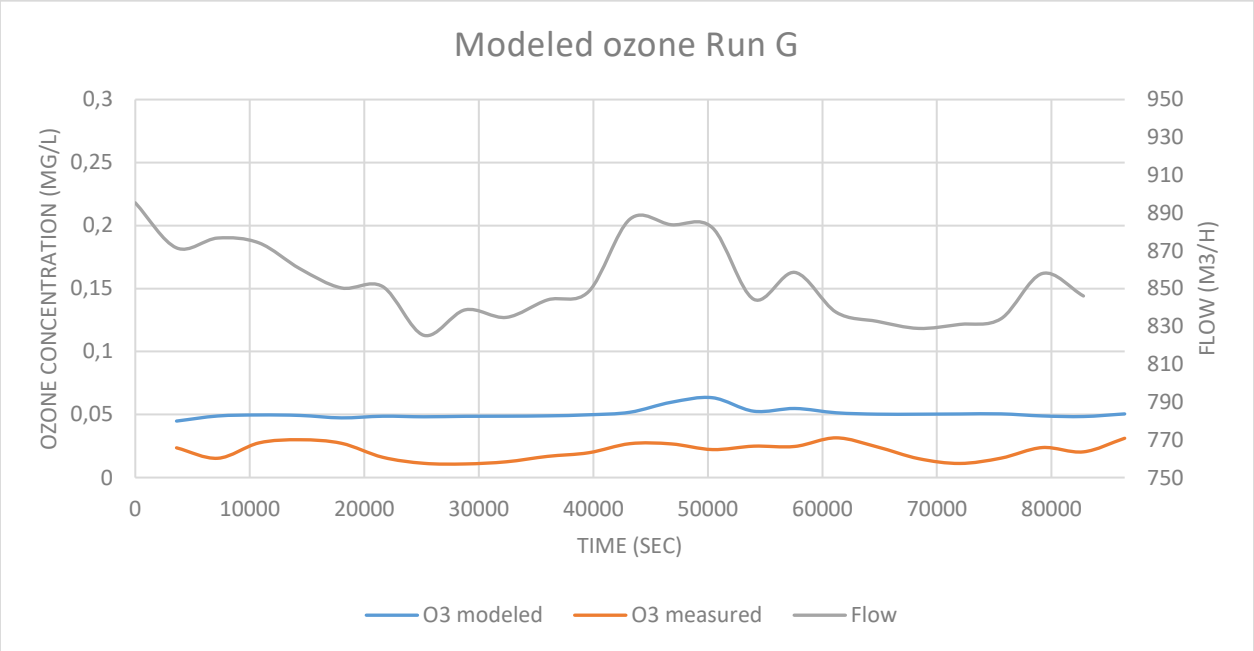

Figure 19: Model results versus measured ozone concentrations for one day with temperature = 20°C and ozone dosage = 1,9 mg/L. WPK flow and ozone data are from 2017.

It can be seen that all ozone concentrations lie in close range to the measured WPK ozone concentrations. Again, variations in flow are followed, sometimes with a clear lag (Figure 18) and sometimes with less lag (Figure 17).

Uncertainty in models stems from incomplete system understanding (which processes to include, which processes interact); from imprecise, finite and often sparse data and measurements; and from uncertainty in the baseline inputs and conditions for model runs, including predicted inputs (Jakeman et al., 2006).

It is very important that this model in its current state relies on the assumptions as listed earlier. If, for example, percentage reduction UVA depends on other factors besides ozone dosage, the model needs recalibration. However, so far, this has not been proven. Parameters can be recalibrated relatively easily without changing the model structure.

3.3 Model scenarios

For the complete functioning of the code for each steering mechanism, please refer to Appendix C. All steering mechanisms were employed using one control file (WSControl.m).

Constant ozone dosage

A constant dosage set point of 1,9 mg/L ozone was chosen here, as this value is mostly used in the current situation at Weesperkarspel. An overview of average ozone dosage, bromate formation and disinfection can be found in Table 7.

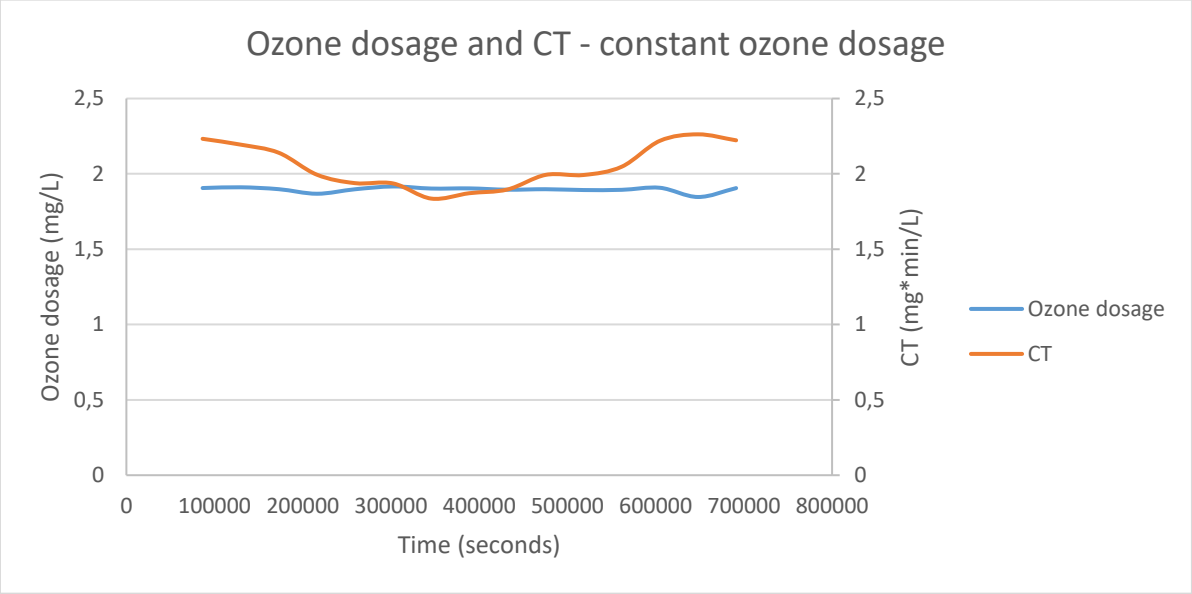

Figure 20: Ozone dosage and CT throughout the run.

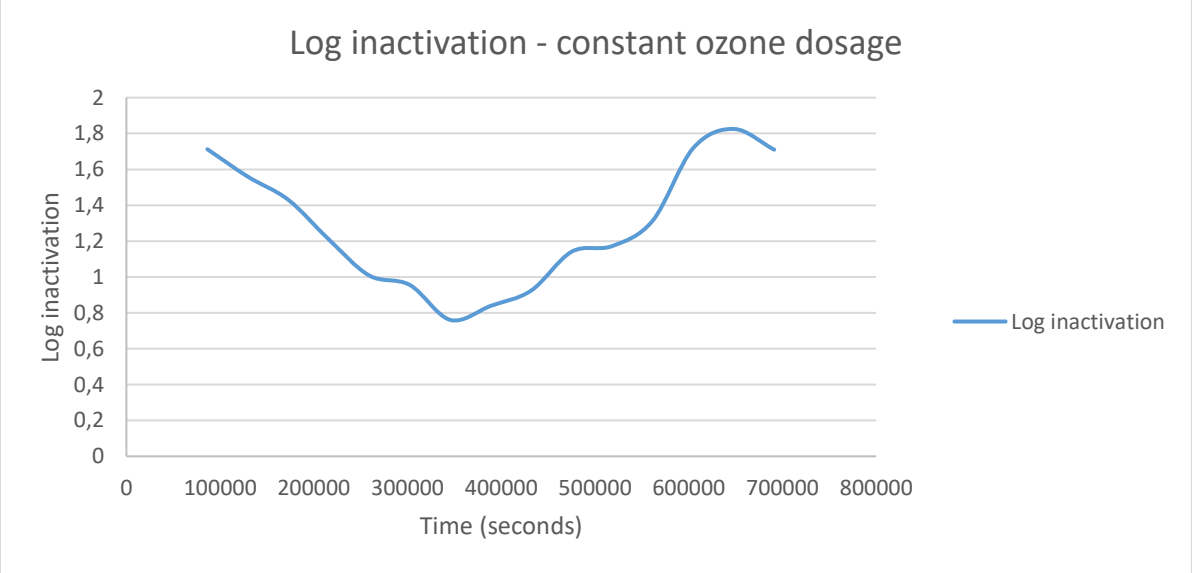

Figure 21: Disinfection over time (modeled), 7 days.

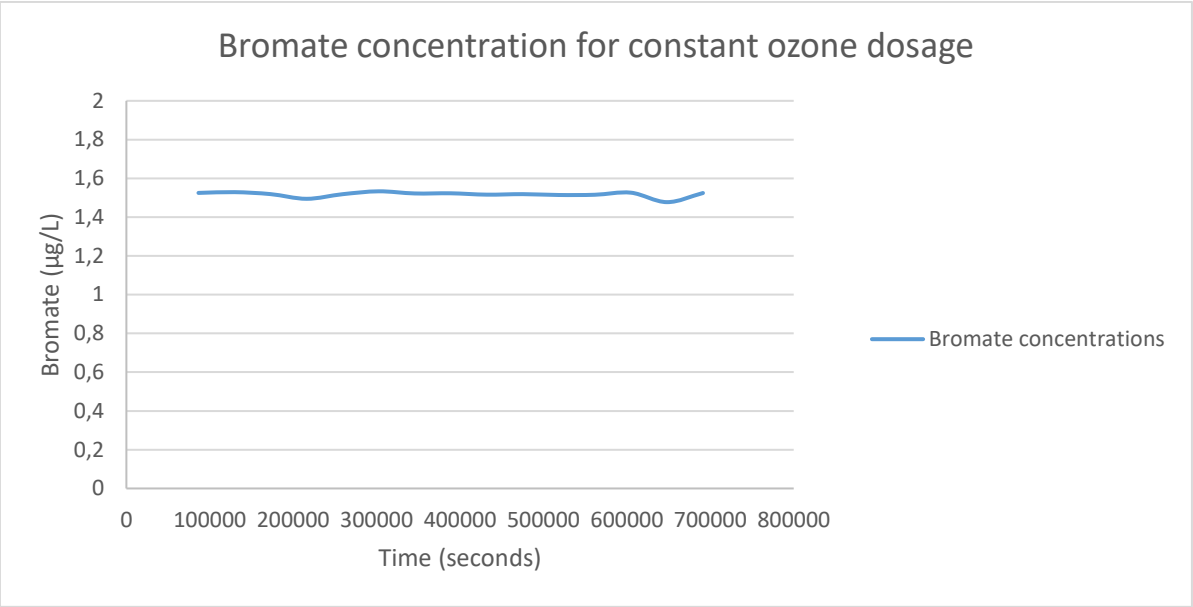

Figure 22: Bromate concentrations throughout the run for constant ozone dosage.

Figure 21, 21 and 22 show that CT and disinfection are lowest in summer. Since bromate formation depends on ozone dosage, it is logical it shows a similar straight line.

The results are summarized in Table 7:

Table 7: Results for steering for constant ozone dosage. Setpoint = 1,9 mg/L; the slight variation in ozone dosage values may be due to the model needing to adapt to other parameter changes every calculation step.

	Min.	*Average*	*Max.*
Ozone dosage [mg-O_3/L]	1,85	1,90	1,92
CT [(mg*s)/L]	1,84	2,05	2,26
Disinfection [logN/N_0]	0,76	1,16	1,83
Bromate [µg-BrO_3^-/L]	1,48	1,52	1,53
Percentage decrease UVA [1/m]	25,3%	28,4%	29,2%

The average CT of 2,05 [mg*min/L], disinfection of 1,16 log and percentage decrease UVA of 28,4% are used in the next runs as set points.

Constant CT

The average CT of 2,05 mg*min/L from the previous run was taken as a set point. This was now steered for using the control file.

The ozone dosage profile is now no longer a straight line throughout the run, but looks like this (Figure 23):

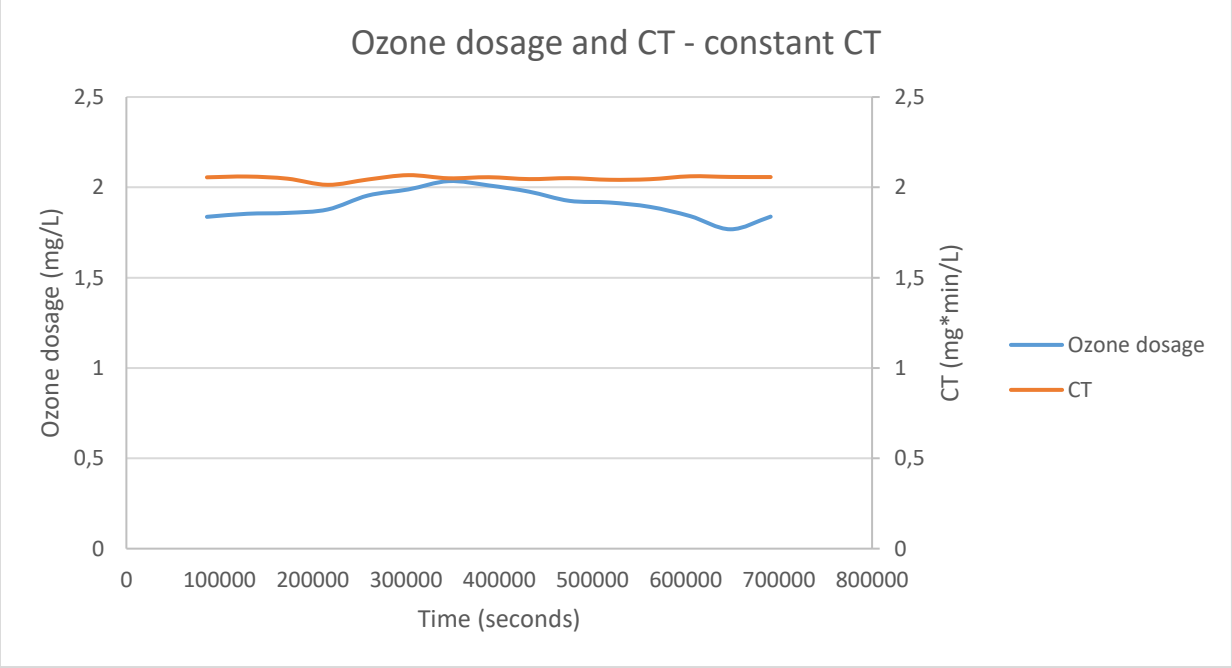

Figure 23: Ozone dosage profile and CT profile when steering for a constant CT.

As can be seen in Table 8, the average ozone dosage remained 1,9 mg-O_3/L. The disinfection increased from 1,16 to 1,23 log, but the disinfection throughout the run still varies, as can be seen below:

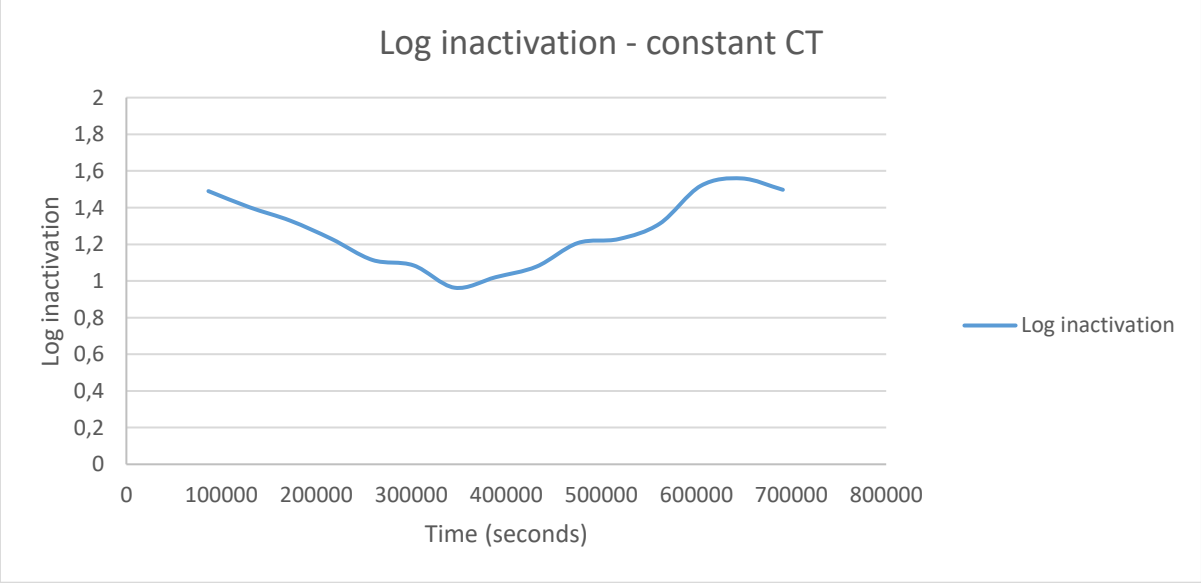

Figure 24: Log inactivation throughout the run when steering for the constant (average) CT of 2,05 obtained from the first run.

Bromate formation levels follow the ozone dosage again:

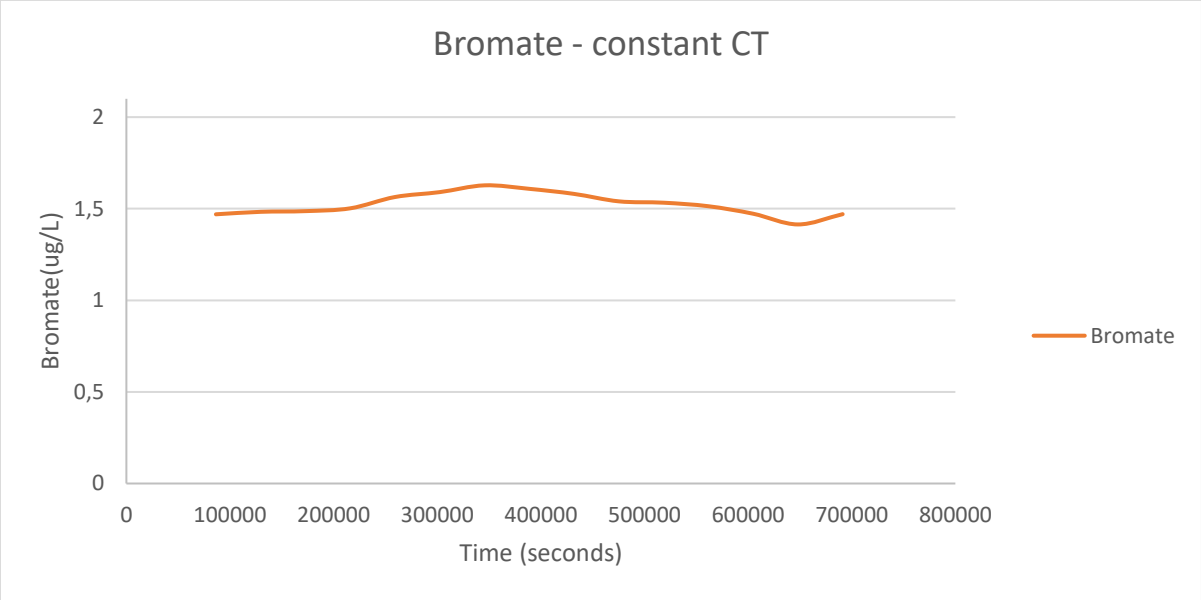

Figure 25: Bromate formation throughout the run.

The results are summarized in Table 8:

Table 8: Model results for steering for constant CT. UVA values were not saved during this run.

	Min.	*Average*	*Max.*
Ozone dosage [mg-O_3/L]	1,76	1,90	2,03
CT [(mg*min)/L]	2,01	2,05	2,10
Disinfection [logN/N_0]	0,96	1,23	1,56
Bromate [µg-BrO_3^-/L]	1,41	1,52	1,63
Percentage decrease UVA	-	-	-

Constant disinfection

To steer for a constant disinfection, CT needs to vary with temperature. This was derived from results of the previous run. A constant disinfection was rounded up to 1,2 log and was steered for. This yielded the following results:

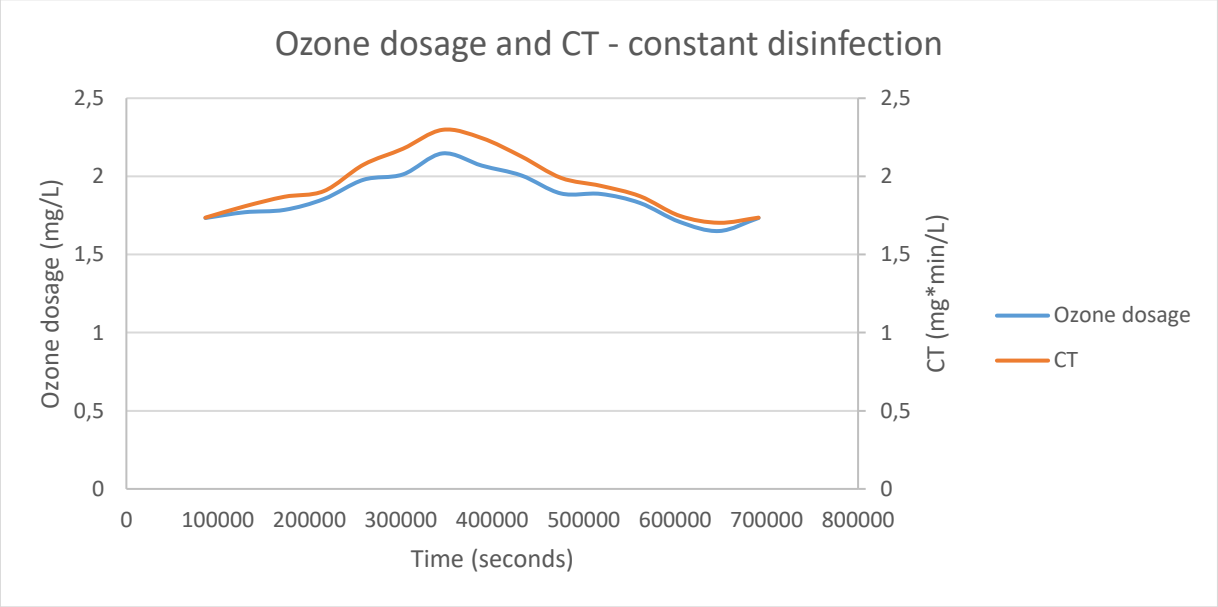

Figure 26: Ozone dosage and CT throughout the run when steering for a constant log inactivation of E. coli.

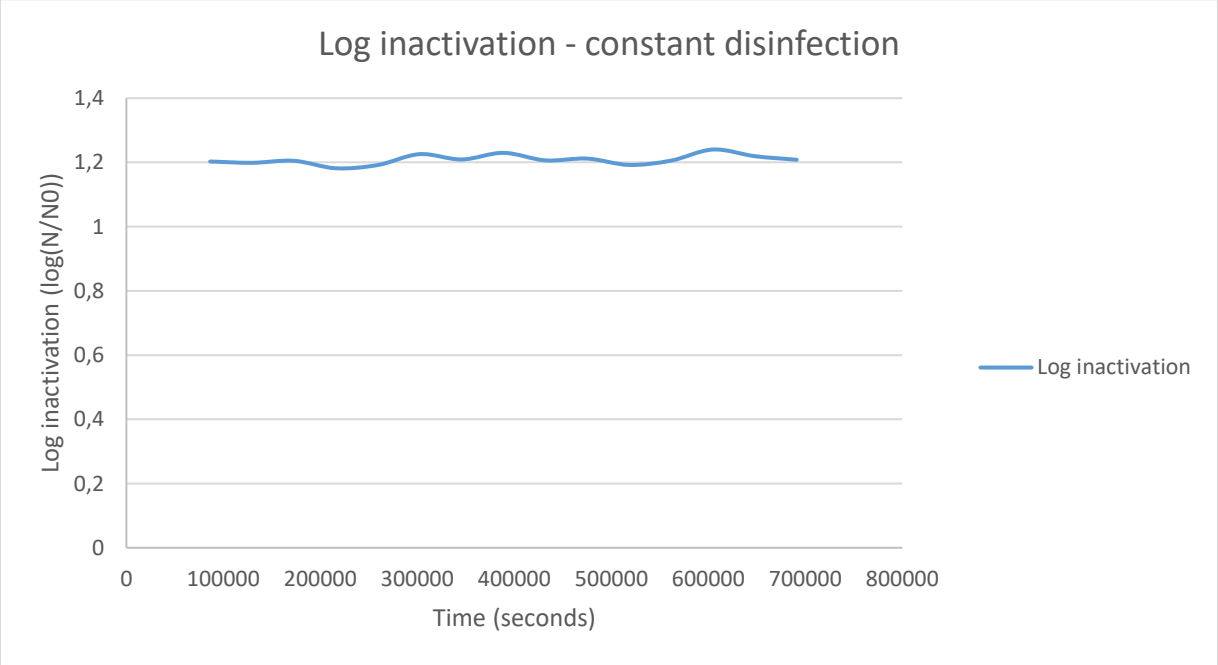

Figure 27: Log inactivation when steering for a constant one.

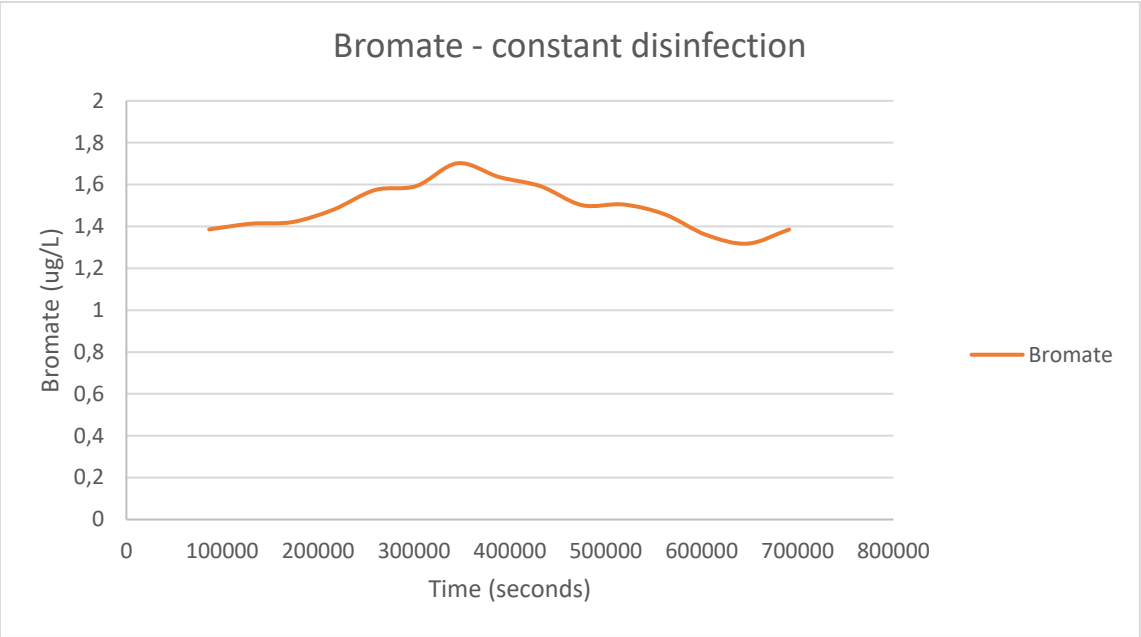

Figure 28: Bromate levels throughout the run when steering for a constant disinfection of E. coli. *Bromate levels need to stay below 5 ug/L as determined by law.*

In Figure 27, which shows log inactivation, there are slight variations due to imperfections of the CT temperature relation, but it is a lot more steady than for different steering mechanisms. The results are summarized in Table 9:

Table 9: Steering for constant disinfection through a modeled CT.

	Min.	*Average*	*Max.*
Ozone dosage [mg-O_3/L]	1,65	1,82	2,15
CT [(mg*s)/L]	1,70	1,95	2,29
Disinfection [logN/N_0]	1,18	1,20	1,24
Bromate [µg-BrO_3^-/L]	1,32	1,48	1,70
Percentage decrease UVA	25,9%	28,3%	31,6%

Constant percentage reduction UVA_{254}

The average percentage decrease in UVA from the first run (constant ozone dosage of 1,9 mg/L) was used to steer for. This was 28,4% as reported in Table 7. This yielded the following results (Table 10):

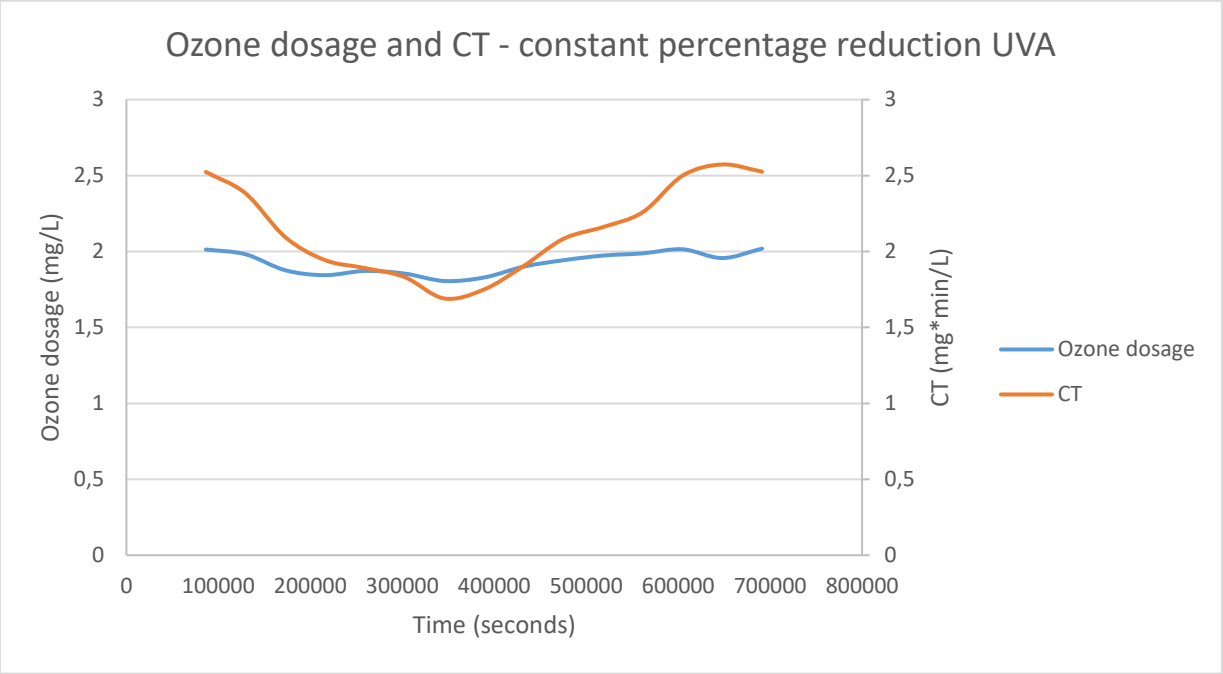

Figure 29: Ozone dosage and CT profile when steering for a constant percentage UVA reduction (28,4%).

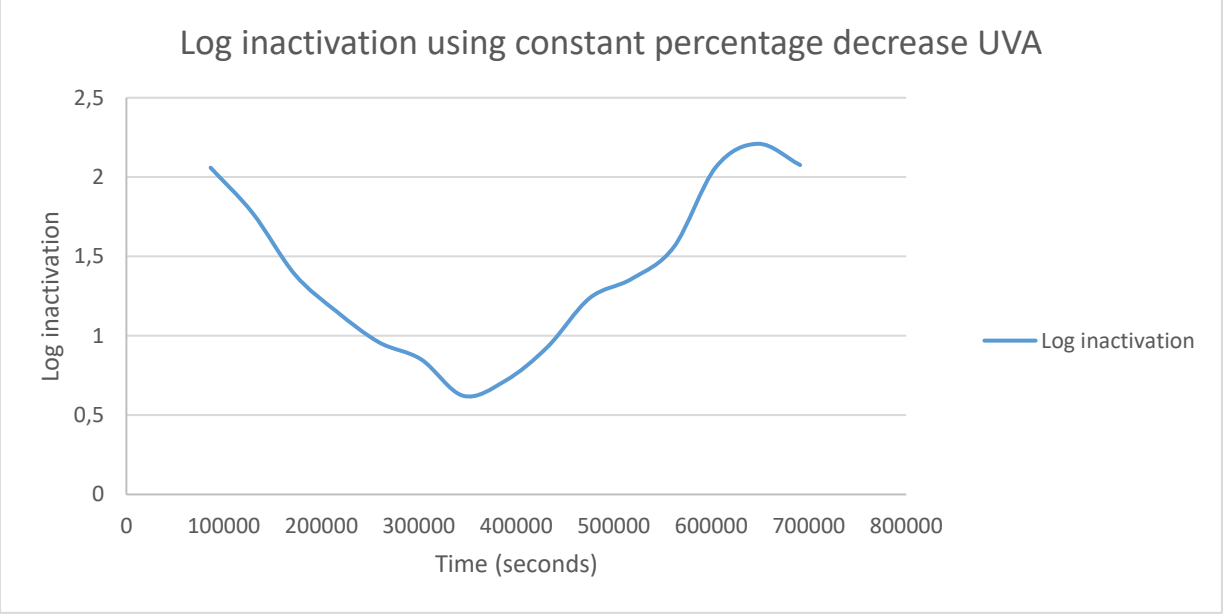

Figure 30: Modeled disinfection (run = 7 days) while steering for constant percentage decrease UVA

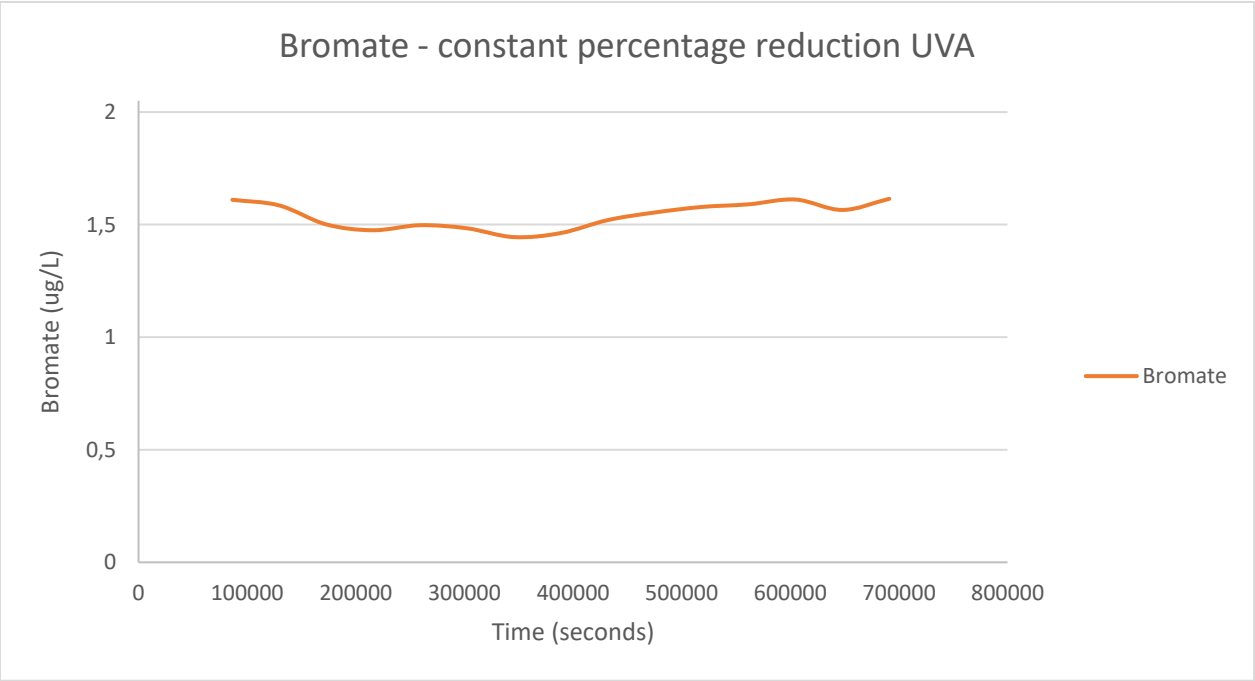

Figure 31: Bromate levels during the run when steering for a constant percentage reduction of UVA.

Figure 29, 30 and 31 show the ozone dosage and thus bromate formation are steady in this run. Log inactivation shows roughly the same pattern as for the constant ozone dosage run, but with slightly more variation in minimum and maximum values. The results are summarized in Table 10:

Table 10: Model results for steering for constant percentage reduction UVA (28,4%), the average from the first run.

	Min.	*Average*	*Max.*
Ozone dosage [mg-O_3/L]	1,81	1,92	2,02
CT [(mg*s)/L]	1,69	2,14	2,57
Disinfection [logN/N_0]	0,62	1,14	2,20
Bromate [µg-BrO_3^-/L]	1,44	1,54	1,62
Percentage decrease UVA	28,01%	28,4%	28,6%

3.4 Assessment

A comparison of the results is shown in Table 11 below:

Table 11: A brief comparison of the different steering mechanisms, tested for a model run of 7 days with fluctuating influent water temperature and flow. pH, DOC and other parameters were kept constant to reduce calculation time.

Steering mechanism	Average bromate (ug BrO_3^-/L)	Average ozone usage (mg O_3/L)	Average disinfection (logN/N0)
Constant ozone dosage (1,9 mg/L)	1,52	1,90	1,16
Constant CT (2,05 mg*min/L)	1,52	1,90	1,23
Constant disinfection (1,2 log)	1,48	1,82	1,20
Constant percentage ΔUVA = 28,4%	1,54	1,92	1,14

Bromate formation does not vary a lot; all bromate levels are well below the standard of 5 µg/L set by law.

Log inactivation is known to increase at higher temperatures, but at the same time, ozone decays faster at higher temperatures. According to these results, the ozone decay increase is much larger than the log inactivation increase, resulting in a net inactivation decrease at higher temperatures.

Model runtime for most steering mechanisms was comparable; steering for constant disinfection seemed to take longer, perhaps because more calculations per time step were necessary.

As stated before, steering for percentage reduction UVA looks very similar to steering for a constant ozone dosage (except for the dosing profile). While the ozone dosage profile fluctuates, the average is still 1,9 mg/L.

4. Discussion

4.1 Disinfection

What clearly stood out, is the difference in inactivation behavior between lab bacteria and environmental bacteria. The data set used for this paper is definitely not complete, many more articles should be added, but it already shows the clear difference in inactivation between lab and environmental *E. coli*.

First, inactivation of environmental bacteria seems to require a larger CT and may not reach values as high as lab bacteria. This seriously needs to be taken into account, as many experiments found in literature are based on cultured organisms; these conclusions may not be in line with what happens in the real world. More research on the difference between lab and environmental bacteria is required: possibly not only for ozonation, but in a wider water disinfection context, too. What has not been looked at in this paper but should be attempted in any further research is entering water type as an independent variable when running statistical analysis, to see if this has any relation to this discussion.

Second, it was always assumed that the relation between CT and log inactivation is linear, but multiple studies with environmental bacteria suggest that there is some cutoff point at which disinfection no longer (significantly) increases, and that the relation is better described logarithmically. When modelling or calculating disinfection, it is more accurate to assume a logarithmic relation. In the Stimela model, disinfection of *E. coli* was previously not calculated. By adding this calculation based on environmental bacteria data found in literature, the model can now predict inactivation. Chick-Watson is used to calculate disinfection. This is a linear model (y=ax). Taking into account the findings with regards to tailing of disinfection data and a possible maximum disinfection, it is possible that this model overestimates disinfection at high CT values, and underestimates disinfection at very low CT values. A point of future improvement would be to calculate disinfection using a different (logarithmic) model.

When calculating disinfection efficacy, for example in QMRA, this difference should at least be taken into account. More inactivation experiments with environmental bacteria would give more insight into this mechanism. The disinfection relation entered in the model is assumed to be representative for Weesperkarspel. One of the results of this research is that there is very little knowledge about these specific inactivation kinetics. Tailing of disinfection data is probably caused by some organisms being more resistant to oxidation, because they were previously stressed by their environment which made them harder to inactivate, or because they entered the viable-but-not-cultivatable (VBNC) state, or because they are Gram-negative. How to correct for this and adapt process control in practice, remains a challenge.

E. coli is said to be a good indicator for *Campylobacter*. Caution must be taken when verifying this: are these claims based on lab bacteria? Would this relation also hold for environmental *E. coli* and *Campylobacter*? It could be that lab tests are not as representative as was previously thought. Furthermore, it is desirable to translate *E. coli* disinfection knowledge to other pathogens. Other bacteria of interest besides *E. coli* and *Campylobacter* are for example *EHEC*, *salmonella* and *bacillus*; it could be estimated that when bacteria are similar, for example Gram-negative, they are more likely to behave similarly. Of course, it would be safest to conduct ozonation disinfection experiments with environmental *Campylobacter*, but this may not be worth the time and effort if it can be proven that *E. coli* is indeed a good indicator, also in an environmental setting.

4.2 Model

One of the limitations of the current Stimela model is that it seems to have a 7200 second lag in results in responding to changes, which sometimes appears. This may be due to numerical dispersion, but this is unsure. For the research conducted for this paper, it has no large effect; it is noted but has no influence on the results. When this model would be used for real-time steering, however, it can be problematic that this lag appears sporadically. If it was consistent, it could just be taken into account. Stimela works great for process modelling because it works with blocks, but large portions of the code are outdated by now and need updating. For the ozone model specifically, it might be worth looking into rewriting it in Python for a more popular coding language and possibly runtime improvement, as well as open/free access (the user would not need to buy Matlab). Matlab requires very specific programming experience. In addition to that, working with such an ozonation model does not only require the programming knowledge but also knowledge about the process and microbiology.

A better quantitative validation of the model is needed before it can be trusted enough to be implemented in practice. As of now, no UVA data for a year was available to use in validation, only ozone concentrations at the sample point. This validation should be executed when data is available.

4.3 Steering

Disinfection is the primary goal of ozonation at Weesperkarspel. Steering for a constant disinfection gives the least amount of uncertainty about disinfection. It seems to require slightly lower ozone dosages and produces slightly less bromate compared to other steering mechanisms. Therefore, this is the recommended steering method out of the four tested. On a yearly basis, roughly 5% ozone could be saved. On a basis of €0,10 per kg ozone and €0,05 per kWh, ozone production costs around €100.000,- per year – implementing this steering mechanism would save €5.000,- (estimated).

For the other steering mechanisms, disinfection varies roughly 1 log unit for constant ozone dosage, constant CT and constant percentage decrease UVA. Most variation is observed when steering for percentage decrease UVA, and least variation is observed when steering for a constant CT. Bromate and ozone dosage levels are very similar for constant ozone dosage and constant CT. Steering for a constant CT would therefore in theory be the second choice.

Bromate levels are most steady at a constant ozone dosage; if bromate levels are of concern, it is recommended to keep steering for a constant ozone dosage to avoid unexpected bromate peaks. However, this is not the priority of Waternet.

For the *i-scans* to be used and trusted in the future, it needs to be made sure that they report accurate values. As of now, they are known to drift away from time to time as a result of biofilm accumulating around the effluent scanners. If periodically flushing this scanner works and is automated and calibration is still performed at some time interval, these scanners enable fast real-time steering of the process.

It may be possible to directly correlate percentage decrease in UV_{254} absorbance and log inactivation. This was attempted before by (Gerrity et al., 2012) by plotting $\%\Delta UVA_{254}$ versus log inactivation of E. coli. This assumes linearity and no interference of other water parameters. There is not enough reliable inactivation data available from Weesperkarspel to build this correlation, and of all the data gathered in the disinfection database, none had included UVA data. Measurements taken by Gerrity *et al.* can be used as an example, taking into account that they used nine different tertiary wastewater effluents. The found correlation is as follows (R^2=0,47):

$$-\log\left(\frac{N}{N_0}\right) = 0{,}13 * \left(\left(1 - \frac{UVA}{UVA_0}\right) * 100\%\right) - 1{,}2 \qquad [21]$$

The slope and intercept of this correlation would be different for Weesperkarspel due to the different nature of the influent water. Therefore, this is not used in the current model.

Steering for constant percentage UVA gives slightly less disinfection for similar bromate and ozone dosage values. It is however a very easily applicable tactic in practice. This steering mechanism would be more useful if percentage decrease values can be linked to disinfection, as shown by Gerrity et al. (2013), or if there could be steered for a constant disinfection by linking it to some percentage decrease UVA:

$DEC \rightarrow CT \rightarrow O_{3,dos} \rightarrow \%\Delta UVA$ where some percentage decrease UVA is related to some ozone dosage, and this ozone dosage to some CT, and this CT to some log inactivation. The percentage

decrease UVA would be steered for using the *i-scans*. Steering on UVA has the most potential in terms of real-time steering: UVA is measured continuously and can be responded to immediately.

Alternatively, it was suggested by several authors that relative change in UV_{254} absorption can be used to predict microbial inactivation by relating it to the ratio O_3:TOC or O_3:DOC instead of log inactivation directly (Gamage et al., 2013a; Gerrity et al., 2012). The O_3:DOC ratio is used as an accurate dosing strategy in wastewater ozonation, as it estimates the oxidation of trace organic compounds, and was found to strongly correlate with ΔUVA_{254} (Gamage et al., 2013b). However, for this mechanism to be valid, a moderate to strong correlation between O_3:DOC and *E. coli* inactivation must be found for drinking water. This was not covered within this research.

5. Conclusions

It became clear from this study that environmental bacteria require a larger CT (so either ozone concentration, contact time, or both) to reach the same inactivation as lab bacteria, and may not even reach log inactivation values as high as lab bacteria do. This is an important conclusion that should be taken into account by any water company calculating their disinfection capacity. Also, the relation between disinfection and CT may not be linear but rather shows tailing. This is a claim that needs to be researched more.

This research can function as a first step towards better verifying disinfection capacity in drinking water treatment. The disinfection database built will be expanded and published as a web tool, facilitating open access to disinfection data. Focus was more on disinfection in practice rather than statistical QMRA practices. It is also the answer to the first research question, “How can we decrease uncertainty and improve the assessment of ozone disinfection in drinking water treatment?”

The current Stimela ozonation model still needs improvement and validation before its results will be trusted enough to be implemented in practice. More expert knowledge is required for its implementation. It was adapted for the current situation at Weesperkarspel and calibrated. The most important addition is the calculation of *E. coli* disinfection based on environmental data.

It has been shown that steering for a constant disinfection is a more efficient way of steering the ozonation process: it saves on ozone, produces less bromate, and most importantly disinfection is more trustworthy. In the future, linking constant disinfection to a percentage decrease in UVA would create an even more optimal hybrid model. UVA is an on-line parameter which can be steered on in real time. This results in process operation being fast in responding to water quality changes while securing a steady disinfection. This is also the answer to the second research question, “How can we steer the ozonation process at Weesperkarspel more efficiently?”.

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I am very thankful for the following people dedicating time to this thesis during their busy lives: René, Patrick, Marcel; Alex (for digging deep into his memory), Vera (for the Statistics 101), Eric (for general wisdom), Joost (for sharing the burden of being an intern and observing *meerkoeten*) and Isabella (for telling me what is in the thesis manual).

Works cited

Fang, J., Liu, H., Shang, C., Zeng, M., Ni, M., & Liu, W. (2014). E. coli and bacteriophage MS2 disinfection by UV, ozone and the combined UV and ozone processes. *Frontiers of Environmental Science & Engineering*, *8*(4), 547–552. https://doi.org/10.1007/s11783-013-0620-2

Finch, G. R., Smith, D. W., & Stiles, M. E. (1988). Dose—response of Escherichia coli in ozone demand-free phosphate buffer. *Water Research*, *22*(12), 1563–1570. https://doi.org/10.1016/0043-1354(88)90169-8

Gallard, H., Von Gunten, U., & Kaiser, H. P. (2003). Prediction of the disinfection and oxidation efficiency of full-scale ozone reactors. *Journal of Water Supply: Research and Technology - AQUA*, *52*(4), 277–290.

Gamage, S., Gerrity, D., Pisarenko, A. N., Wert, E. C., & Snyder, S. A. (2013a). Evaluation of Process Control Alternatives for the Inactivation of Escherichia coli, MS2 Bacteriophage, and Bacillus subtilis Spores during Wastewater Ozonation. *Ozone: Science and Engineering*, *35*(6), 501–513. https://doi.org/10.1080/01919512.2013.833852

Gerrity, D., Gamage, S., Jones, D., Korshin, G. V., Lee, Y., Pisarenko, A., … Snyder, S. A. (2012). Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation. *Water Research*, *46*(19), 6257–6272. https://doi.org/10.1016/j.watres.2012.08.037

GitHub. (2017). GitHub | Stimela. Retrieved November 30, 2017, from https://github.com/Stimela/Stimela

Jakeman, A. J., Letcher, R. A., & Norton, J. P. (2006). Ten iterative steps in development and evaluation of environmental models. *Environmental Modelling and Software*, *21*(5), 602–614. https://doi.org/10.1016/j.envsoft.2006.01.004

Jamil, A., Farooq, S., & Hashmi, I. (2017). Ozone Disinfection Efficiency for Indicator Microorganisms at Different pH Values and Temperatures. *Ozone: Science and Engineering*, *39*(6), 407–416. https://doi.org/10.1080/01919512.2017.1322489

KWR. (2017). QMRA. Retrieved December 15, 2017, from http://beta.tools.watershare.eu/qmra/$/

Masschelein, W. J. (2000). Considerations on the Chick-Watson Law Applied to the Ozonation of Drinking Water. *Ozone: Science & Engineering*, *22*(3), 227–239. https://doi.org/10.1080/01919510008547206

Rietveld, L. C. (2005). Improving operation of drinking water treatment through modelling :: TU Delft Institutional Repository, 141. Retrieved from http://repository.tudelft.nl/view/ir/uuid:4f4e110a-a1ea-4d51-b645-3c9c58c67c92/

Rietveld, L. C., van der Helm, A. W. C., van Schagen, K. M., & Van Der Aa, L. T. J. (2010). Good modelling practice in drinking water treatment, applied to Weesperkarspel plant of Waternet. *Environmental Modelling and Software*, *25*(5), 661–669. https://doi.org/10.1016/j.envsoft.2009.05.015

Ross, P. S., van der Helm, A. W. C., van den Broeke, J., & Rietveld, L. C. (2016). On-line monitoring of ozonation through estimation of Ct value and AOC formation with UV/Vis spectrometry. *Russell The Journal Of The Bertrand Russell Archives*, 1–11.

Smeets, P. W. M. H., Dullemont, Y. J., Medema, G. J., & van Dijk, J. C. (n.d.). *E. coli as surrogate for*

Campylobacter inactivation at bench-scale and full-scale and high ozone resistance of environmental E. coli and Campylobacter.

Smeets, P. W. M. H., Dullemont, Y. J., Van Gelder, P. H. A. J. M., Dijk, J. C. Van, Medema, G. J., & Smeets, A. P. W. M. H. (2008). Improved methods for modelling drinking water treatment in quantitative microbial risk assessment; a case study of Campylobacter reduction by filtration and ozonation. *Journal of Water and Health*, *06*(3), 301–314. https://doi.org/10.2166/wh.2008.066

Smeets, P. W. M. H., van der Helm, A. W. C., Dullemont, Y. J., Rietveld, L. C., van Dijk, J. C., & Medema, G. J. (2006). Inactivation of Escherichia coli by ozone under bench-scale plug flow and full-scale hydraulic conditions. *Water Research*, *40*(17), 3239–3248. https://doi.org/10.1016/j.watres.2006.06.025

van der Aa, L. T. J., Kolpa, R. J., Rietveld, L. C., & van Dijk, J. C. (2012). Improved removal of pesticides in biological granular activated carbon filters by pre-oxidation of natural organic matter. *Journal of Water Supply: Research and Technology—AQUA*, *61*(3), 153. https://doi.org/10.2166/aqua.2012.031

van der Helm, A. W. C. (2007). *Integrated modeling of ozonation for optimization of drinking water treatment*.

van der Helm, A. W. C., Van Der Aa, L. T. J., Van Schlagen, K. M., & Rietveld, L. C. (2009). Modeling of full-scale drinking water treatment plants with embedded plant control. *Water Science and Technology: Water Supply*, *9*(3), 253–261. https://doi.org/10.2166/ws.2009.355

von Gunten, U. (2003a). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Research*, *37*(7), 1469–1487. https://doi.org/10.1016/S0043-1354(02)00458-X

Von Gunten, U. (2003b). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*, *37*, 1469–1487. Retrieved from https://ac-els-cdn-com.proxy.library.uu.nl/S0043135402004578/1-s2.0-S0043135402004578-main.pdf?_tid=87aecf16-0a77-11e8-bf7c-00000aacb360&acdnat=1517837093_55303f2bdf3c9e0800b5229787777996

WHO | Campylobacter. (2017). Retrieved November 30, 2017, from http://www.who.int/mediacentre/factsheets/fs255/en/

Appendix A: Reference document O_3 disinfection database

Collection, assessment and structuring of data.

Data collection

Search terms are defined. Literature research is done online by using e.g. Science Direct, Scopus, PubMed and Google Scholar. Search results are saved in Endnote format and exported to Excel and other uses. Abstract and title are screened; duplicates are removed and irrelevant studies are excluded. Of potentially relevant studies, the full text is obtained. If impossible, this study is excluded. The full text is screened; study might be excluded because it is not on topic, outside scope, of insufficient detail, inadequately designed, unoriginal, etc. Next, data in the study is assessed and the study might be excluded for the same reasons as listed above. The remaining relevant studies with relevant data are checked for rectifications, updates and reviews; if issues arise, these are discussed within the team. The study is then either excluded or included in the database.

To identify original data and avoid duplicates, start with the most recent source; create a tree of sources used to find original sources (this might go a few levels deep). The linked list of studies helps keep track of which studies use which other studies, to avoid over representing a certain data table that is used by many different studies.

Defining search terms should be based on process specific criteria, such as inactivation mechanism, techniques used, process conditions and process models described. Search terms should be direct, e.g. describing both 'pathogen' and the specific microorganism required; use alternative names of processes; search reference lists of relevant publications for alternative search terms; exclude unwanted results such as outdated publications.

Literature is found through online databases (e.g. through PubMed) and by using references from existing literature studies. At a later stage, grey literature can be considered as well. This includes reports of water companies, institutes, EU, BTO; books, the internet, studies in a foreign language (not Dutch or English).

Data is often represented in figures. To extract data from figures, the WebPlotDigitizer tool should be calibrated and used for more accuracy (Rohatgi, 2011).

Data assessment

Screening the title and abstract

Process is applied to water; process is comparable to Dutch drinking water practices; organisms are relevant for drinking water sector; process is standalone and not combined with another process.

All boxes checked? → potentially relevant studies

Screening the full text

Reassessment of the above; data is of enough detail; experimental conditions are described in enough detail; experiments are adequate to research aspect of interest; research is original and not copied from prior research; study is of high enough quality compared to other studies.

All boxes checked? → relevant studies

Assessing data in study

Methods need to be explained clearly and accurately, and inaccuracies need to be checked or documented; experimental conditions need to be explained in full detail when this is relevant for effect on disinfection (e.g. temperature); clear description of how results are obtained.

All boxes checked? → relevant studies with data

Check rectifications, updates, reviews

If these exist, include in linked list.

All boxes checked? → extract data and metadata; convert data to right units; discuss with team

Insert into database

Split data atomically to make it searchable and unambiguous; remove repetitive groups; make sure all information on a row is related; make sure rows contain unique combinations; when quantity increases, review quality.

Structuring of data

Everything is recorded in the Ozone_QMRA_Database_2018.xlsx Excel file. Information from the beginning until the end of the search process is recorded in the following tabs in the file.

Searches

Search queries are recorded here, including the date, search terms, searched fields, total number of papers, total number of new papers, and amount of papers in-/excluded based on title and abstract.

Paper evaluations

This is a list of all papers initially included. All available information such as author, title, date, journal, issue etc. is recorded. Again, papers are in- or excluded; reason for this is recorded (e.g. off-topic of insufficient details).

Data

This tab contains the extracted data from included publications. It contains the desired values (e.g. log reduction) as well as all relevant metadata (such as water type, organism type, temperature, pH) and author and publication information.

Figures from data

This tab contains any figures that were made by the user using data from the Data tab.

Figure extractions

This tab contains figures containing data from publications, such as graphs and tables. Always include publication reference with the figure.

Linked data

This is a list of parent and child publications to create a linked list.

READ ME

This explains abbreviations used and how to go about certain operations.

Inclusion / exclusion requirements ozone publications

Adjust search terms to obtain relevant results. Search terms could include: inactivation, pathogens, microorganisms, ozonation, ozone, water, drinking water, disinfection, Campylobacter, DWTP, drinking water treatment

Title and abstract screening

Exclude if:

- Research not relevant for topic
- Combining with other treatment
- Pre-treatment effect not measured or taken into account
- Water type or quality is too different from target water (pre-treated influent water at DWTP)
- Research is not about microorganisms in water (e.g. in food)

Full text screening

Exclude if:

- Research not relevant for topic
- Data is not reported
- Data is not of enough detail
- Experimental conditions are not or insufficiently described
- Research is reproduced from prior research
- Quality seems too low compared to other research
- The following information is not included: type of installation (on-site, test, lab, modelled), type of contactor (bubble columns, static mixer, deep well), ozone dosage (amount + how), type of reactor (plug flow (PFR), continuous stirred tank reactors (CSTR), batch reactor);
- optional: ozone in gas concentration, amount of contact chambers, flow, temperature, bromate concentration, AOC, DOC

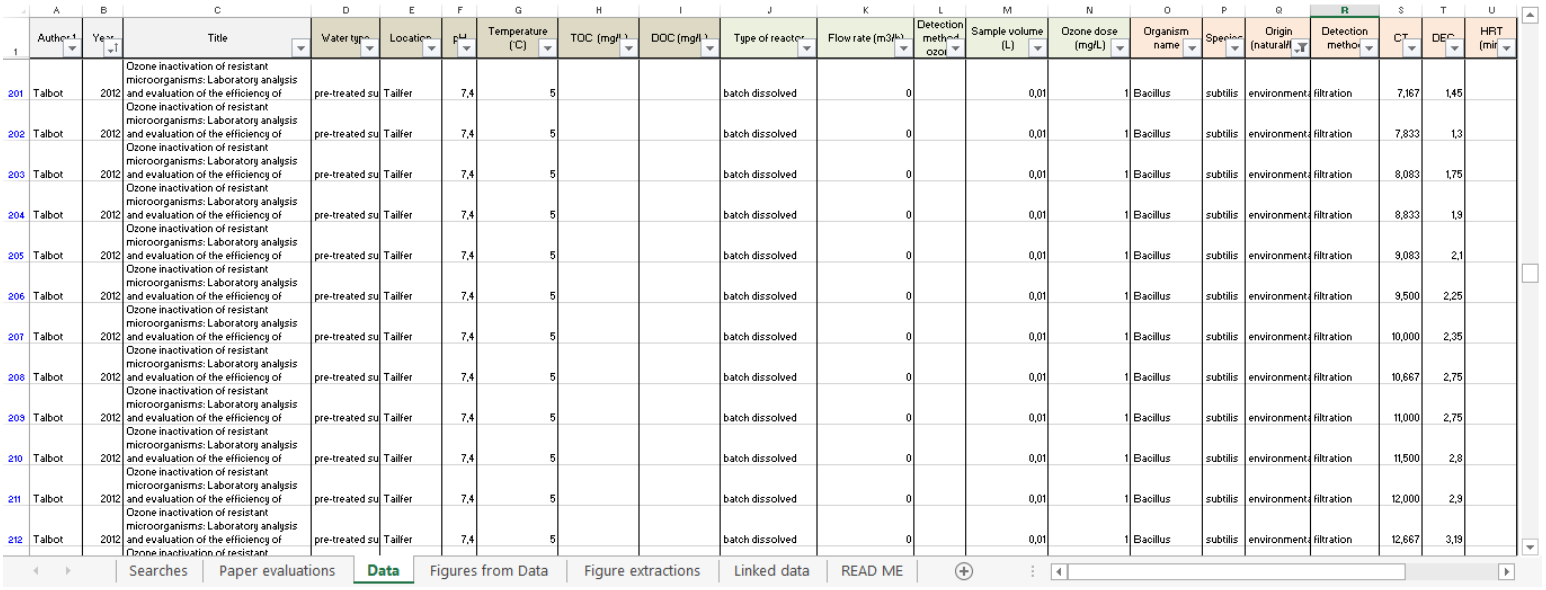
Data quality screening

Exclude if:

- Reassess full text screening points
- Measurement data not or insufficiently reported
- Data unreadable (e.g. small graphs with no axis titles)
- Origin of data unclear (e.g. no time stamp, sample point or units given)

Appendix B: Ozone disinfection database

The file is too large to be neatly converted into an appendix. Structuring of the Excel file is done as outlined in Appendix A: Structuring of data. Below, a screenshot can be found.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
1	Author	Year	Title	Water type	Location	pH	Temperature (°C)	TOC (mg/L)	DOC (mg/L)	Type of reactor	Flow rate (m3/h)	Detection method ozo	Sample volume (L)	Ozone dose (mg/L)	Organism name	Species	Origin (natural/l	Detection metho	CT	DEC	HRT (mi
201	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	7,167	1,45	
202	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	7,833	1,3	
203	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	8,083	1,75	
204	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	8,833	1,9	
205	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	9,083	2,1	
206	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	9,500	2,25	
207	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	10,000	2,35	
208	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	10,667	2,75	
209	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	11,000	2,75	
210	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	11,500	2,8	
211	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	12,000	2,9	
212	Talbot	2012	Ozone inactivation of resistant microorganisms: Laboratory analysis and evaluation of the efficiency of	pre-treated su	Tailfer	7,4	5			batch dissolved	0		0,01	1	Bacillus	subtilis	environmenta	filtration	12,667	3,19	

Searches | Paper evaluations | **Data** | Figures from Data | Figure extractions | Linked data | READ ME

Figure 32: Screenshot of the Excel disinfection database. In the bottom, the different tabs can be seen; this screenshot shows a snippet of the Data tab.

The Excel file can be provided by the author or KWR upon request (author: yjwiersema@gmail.com or KWR: Patrick.smeets@kwrwater.nl).

Appendix C: Matlab model: control file

A .zip file of the complete Stimela model including all necessary files can be provided by the author upon request (yjwiersema@gmail.com). This is the overriding control file used, `WSControl`.

```
function WSControl

global CurrentInput

% construct controller
persistent O3Dos_Controller
% initialize controller

% Controller for ozone gas flow with setpoints
if isempty(O3Dos_Controller)
  % PID (P, I, D, y0, ymin, ymax)
  % initialize at current value
  % evalin(A,B) executes B in workspace A. B can be a character vector or
string scalar with any valid Matlab code.
  O3Dos_Controller = PID(2, 1200, 0,  evalin('base','W630DD01FIT011'), 0, 20);
% 20 was 11.8
end

% CurrentTime
CurrentTime = evalin('base','WSStimelaTime');

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Reading Tags from Model
Raw_water_Flow               = evalin('base','Raw_Water_Flow');        %
Debiet ruw water [m3/h]
OZ_R1_O3DOS                  = evalin('base','OZ_R1_O3DOS');           % Bruto
ozondosering ozonstraat 1 [mg/l]
OZ_R1_CT                     = evalin('base','OZ_R1_CT');              % CT10
voor alleen de contact kolommen [(mg/l)*min]
OZ_MI_Temp                   = evalin('base','OZ_MI_Temp');            %
Temperatuur influent ozon [oC]
OZ_MI_UVA254                 = evalin('base','OZ_MI_UVA254');          %
UVA254 influent [1/m]
OZ_R1_UV254                  = evalin('base','OZ_R1_UV254');           %
UVA254 effluent [1/m]
OZ_R1_ECout                  = evalin('base','OZ_R1_ECout');              % E
coli effluent [CFU/100l]

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% % % % Calculations % % % %
% Comment out the ones you DON'T need!

%% Setpoint for CT10 for Giardia inactivation
% SP_CT10=1.4671*exp((-0.0723*OZ_MI_Temp)); % Log Giardia inactivation 1.5
USEPA Table
% SP_CT10=1.9159*exp((-0.0713*OZ_MI_Temp)); % Log Giardia inactivation 2 USEPA
Table

%%%%%
%% Setpoint for CT E.coli
```

```
% % Arrhenius constants (Yasmine 2018):
% ArrhE = 14466.5; % activation energy
% ArrhA = 3430.8; % frequency factor
% ArrhR = 8.314; % gas constant
% ArrhT = 273.15; % 0 degrees Kelvin
%
% SP_K=ArrhA*exp(-(ArrhE/(ArrhR*(ArrhT+OZ_MI_Temp)))); % Arrhenius k
% SP_DEC=5; % choose your log inactivation setpoint
% SP_CT=(SP_DEC*2.3)/SP_K;

% Alternative (USED):
% SP_CT=1.8+0.036*OZ_MI_Temp;
% SP_EC = 1500;
% O3Dos_Controller =
PIDupdate(O3Dos_Controller,CurrentTime,SP_EC,OZ_R1_ECout);
% O3Dos_Controller = PIDupdate(O3Dos_Controller,CurrentTime,SP_CT,OZ_R1_CT);

%%%%%
%% Setpoint constant percentage reduction in UV absorbance
% Okay, so UVA0 depends on UVAini and O3Dos:
% ceUVA254=iniUVA254-0.8185*ceO3Dos^0.5*iniUVA254^0.5
% We know what we want UVA0 to be (namely UVAini reduced by some percentage)
% So we can fill that in the formula above to find the corresponding O3Dos.
% This way, the O3Dos will change if UVAini changes. #reverseengineering
%
% SP_Reduc_UVA=33; % 28.46 for 2,5 log inactivation
% SP_UVA0 = (OZ_MI_UVA254*((100-SP_Reduc_UVA)/100));
% SP_OZ_R1_O3DOS = ((SP_UVA0-OZ_MI_UVA254)/(0.8185*OZ_MI_UVA254^0.5))^2;
%
% O3Dos_Controller =
PIDupdate(O3Dos_Controller,CurrentTime,SP_OZ_R1_O3DOS,OZ_R1_O3DOS);
%
% %%%%%
%% 16-1-2018 Setpoint for constant ozone dosage
SP_OZ_R1_O3DOS=1.9;
O3Dos_Controller =
PIDupdate(O3Dos_Controller,CurrentTime,SP_OZ_R1_O3DOS,OZ_R1_O3DOS);
%
% %%%
%% Setpoint luchtflow Ozon doseer installatie voor straat 1 obv de PID
controller "O3Dos_Controller" [Nm3/h]
W630DD01FIT011    = PIDoutput(O3Dos_Controller);

% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% writing resulting data to control input
% Ozonization
assignin('base','W630DD01FIT011',                    W630DD01FIT011);
```

Appendix D: Matlab model

A .zip file of the complete Stimela model including all necessary files can be provided by the author upon request (yjwiersema@gmail.com). The most important one of the 6 Stimela files is shown below, namely the system file, `ozoncc_s`.

```
function [sys,x0,str,ts] = ozoncc_s(t,x,u,flag,B,x0,U,P)
%% Model
% General purpose calculations
if any(abs(flag)==[1 2 3])

  %%%% MODEL-SPECIFIC => %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
  % optional: convert input vector to user names
  % eg. Temp = u(U.Temperature);
  % in the code it is also possible to use u(U.Temparature) directly.

  Areact       = P.Areact;       % oppervlakte ozon reactor [m2]
  dh           = P.dh;           % hoogte per volledig gemengd vat (NumCel)
[m]
  MeeTe        = P.MeeTee;       % 1=meestroom en 0=tegenstroom
  db0          = P.db0;          % initiele beldiameter [m]
  kUV_Sel      = P.kUV_Sel;      % 1=kUV is given manual and 0=kUV is
determined by the model
  kUV          = P.kUV;          % UVA254 decay rate [1/s]
  Y            = P.Y;            % Yield factor for ozone use per UVA decrease
[(mg/l)/(1/m)]
  KafbO3_Sel   = P.KafbO3_Sel;   % 1=kO3 is given manual and 0=kO3 is
determined by the model
  KafbO3       = P.KafbO3;       % langzame afbraakconstante O3
  ceUVA254_Sel = P.ceUVA254_Sel; % 1=UVAo is given manual and 0=UVAo is
determined by the model
  ceUVA254     = P.ceUV254;      % effluent waarde UVA254
  F_BrO3init   = P.F_BrO3init;   % FBrO3,ini constant for initial bromate
formation (F*ozone dosage)
  kCt_BrO3_Sel = P.kCt_BrO3_Sel; % 1=kBrO3 is given manual and 0=kBrO3 is
determined by the model
  kCt_BrO3     = P.kCt_BrO3;     % kBrO3 bromate formation rate constant
  F_AOC_Sel    = P.F_AOC_Sel;    % 1=FACO is given manual and 0=FAOC is
determined by the model
  F_AOC        = P.F_AOC;        % FAOC constant for AOC formation (F*ozone
dosage) [(ug-C/l)/(mg-O3/l)]
  kEc_Sel      = P.kEc_Sel;      % 1=kEc is given manual and 0=kEc is
determined by the model
  kEc          = P.kEc;          % k inactivation rate for E.coli
  Ct_lagEc     = P.Ct_lagEc;     % Ctlag for E.coli
  NumCel_All   = P.NumCel';      % Reeks van volledig gemengde vaten [-]
  NumCel       = sum(NumCel_All);% Totaal aantal volledig gemengde vaten [-]
  Tl      = u(U.Temperature);    % watertemperatuur            [Celsius]
  Ql      = u(U.Flow);           % waterdebiet                 [m3/h]
  coO3    = u(U.Ozone);          % influent concentratie O3    [mg/l]
  coDOC   = u(U.DOC);            % influent concentratie DOC   [mg/l]
  coUVA254= u(U.UV254);          % influent UV waarde          [1/m]
  iniUVA254= u(U.Initiele_UVA254);% initiele UVA254 waarde      [1/m]
  coBrO3  = u(U.Bromate);          % influent Bromate waarde     [ug/l]
  coO3Dos = u(U.Ozone_dosed);    % hoeveelheid gedoseerde ozon
  coO3Dos_kUV = u(U.Ozone_dos_kUV); % hoeveelheid gedoseerde ozon voor kUV
```

```
  coEc     = u(U.Ecoli);          % influent pathogen concentration
  copH     = u(U.pH);             % influent pH                    [pH]
  coBrmin  = u(U.Bromide);        % influent bromide concentratie [ug/l]
  coAOC    = u(U.AOC);            % influent AOC concentratie    [ug/l]

  Qg       = u(U.Number+1);       % luchtdebiet                  [m3/h]
  cgoO3    = u(U.Number+4);       % ozone concentration in gas   [g/Nm3]

  coCt     = 0;                   % The initial Ct
  %%%% <= MODEL-SPECIFIC  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


  %%%% MODEL-SPECIFIC => %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
  % optional: calculated values used for al flags
  % eg. TempArea = u(U.Temperature)/P.Area;

  %Afronden van de luchttemperatuur op gehele getallen
  Tg      = Tl;                   % Lucht temperatuur in graden Celsius
  Tg      = round(Tg);            % De luchttemperatuur wordt afgerond op
hele graden
  nu      = (497e-6)/(42.5+Tl)^1.5;  % kinematische viscositeit m2/s voor 0oC
tot 35oC
  rho     = 1000;                 % Dichtheid van water kg/m3
  SurfTen= -1.47e-4*Tl+7.56e-2;   % Surface tension voor 0oC tot 30oC

  %Bepalen van benodigde grootheden met betrekking tot de debieten en
verblijftijden
  Ql        = Ql/3600;            % Omzetten van het debiet van m3/h -> m3/s
  Qg        = Qg/3600;            % Omzetten van het debiet van m3/h -> m3/s
  vl        = [];
  for countvl = 1:size(NumCel_All,1);
      vlnew   = (Ql*ones(NumCel_All(countvl,1),1))/Areact(countvl,1);
      vl      = cat(1,vl,vlnew);
  end
  vl = vl*ones(1,NumCel+1);

  vb0     =
0.0135*((20000*SurfTen)/(rho*db0))^0.5;%=0.0135*(70*2/(100*db0))^0.5; %
Belstijgsnelheid
  %vb0     = 0.27;                % Belstijgsnelheid in stilstaand water in m/s
  hreact = flipud(cumsum(flipud(dh))-flipud(dh)/2); % gedefinieerd voor
meestroom

  %De relatieve molecuulmassa's [g/mol]
  MrO2     = 31.9988;
  MrO3     = 31.9988*3/2;
  MrN2     = 28.0134;

  %Constanten voor de berekening van de gasconcentraties in de lucht
  Po      = 101325;               % Po = standaarddruk zeeniveau [Pa]
  pw      = [  611   657   706   758   814   873   935  1002  1073  1148 ...  %
pw = waterdampspanning 0-50 Celsius [Pa]
             1228  1313  1403  1498  1599  1706  1819  1938  2064  2198 ...
             2339  2488  2645  2810  2985  3169  3363  3567  3782  4008 ...
             4246  4495  4758  5034  5323  5627  5945  6280  6630  6997 ...
```

```
             7381  7784  8205  8646  9108  9590 10094 10620 11171 11745 ...
            12344];
  Tn     = 273.15; % standaard temperatuur K
  alfa   = (Po+hreact(:,1)*10000-pw(Tg+1))/Po*Tn/(Tn+Tg);
      % Bepaal ozondosis
  O3Dos       = (Qg*cgoO3)/Ql; % ((ozon-in-gas * gas flow) / water flow)
ozondosering
  ceO3Dos     = coO3Dos+O3Dos; %
  O3Dos_kUV   = (Qg*cgoO3)/Ql;
  if ceO3Dos~=0 % If ozone is dosed:
      if Qg~=0
          coO3Dos_kUV=0;
      end
      ceO3Dos_kUV = coO3Dos_kUV+O3Dos_kUV;
      % Bereken kUV
      if kUV_Sel==0
%           kUV=1.155-0.4*ceO3Dos_kUV; % Gebruik deze als Arrhenius niet
werkt!
          kUV_5=(0.0841-0.022*ceO3Dos)*(coDOC/ceO3Dos)^2; % voor 5 graden
Celsius
          kUV=(kUV_5/(exp(-70000/(8.314*(Tn+5)))))*exp(-
70000/(8.314*(Tn+Tl))); % Arrh.

      end
      % Bereken kO3
      if KafbO3_Sel==0
          KafbO3_10=0.0011*(coDOC/ceO3Dos)^2; % decay rate coefficient at 10
deg. C. (Van der Helm 2007)
          KafbO3=(KafbO3_10/(exp(-70000/(8.314*(Tn+10)))))*exp(-
70000/(8.314*(Tn+Tl)));
      end
      % Bereken UVAout
      if ceUVA254_Sel==0
              ceUVA254=iniUVA254-0.8185*ceO3Dos^0.5*iniUVA254^0.5; % constante
recalibrated (Yasmine 2018)
      end
      % Bereken kBrO3
      if Qg==0 % Dit geldt voor het geval van de DOPFR
          BrO3init = F_BrO3init*coO3;
      else     % Voor contact chambers vul je bij de parameters 0 in voor de
F_BrO3init
          BrO3init = F_BrO3init*ceO3Dos;
      end
      coBrO3   = coBrO3+BrO3init;

      if kCt_BrO3_Sel==0
          kCt_BrO3=2.74e-7*copH^5.82*coBrmin^0.73*1.035^(Tl-20); % (ug-
BrO3/mg-O3)*1/min
          kCt_BrO3=kCt_BrO3*1/60;                                % (ug-
BrO3/mg-O3)*1/s
      end
      % Bereken AOC
      if F_AOC_Sel==0
          F_AOC=3.55e15*exp(-80500/(8.314*(Tn+Tl)));
      end
      if ceO3Dos~=0 % Qg~=0 % if ozone is dosed:
          ceAOC=F_AOC*ceO3Dos*coDOC+coAOC;
```

```
      else
          ceAOC=coAOC;
      end
      % Bereken E. coli verwijdering
      % Arrhenius constants (Yasmine 2018):
      ArrhE = 14466.5; % activation energy
      ArrhA = 3430.8; % frequency factor
      ArrhR = 8.314; % gas constant

      if kEc_Sel==0 % k is on a log 10 base!
          kEc=ArrhA*exp(-(ArrhE/(ArrhR*(Tn+Tl))));
          kEc=kEc*(1/60); % convert from min. to seconds
      end
%       kEc_lag    = kEc*ones(NumCel,1);
  else % No ozone is dosed:
      ceO3Dos_kUV = 0;
      kUV         = 0;
      KafbO3      = 0;
      ceUVA254    = coUVA254;
      coBrO3      = coBrO3;
      kCt_BrO3    = 0;
      F_AOC       = 0;
      ceAOC       = coAOC;
      kEc         = 0;
      kEc_lag     = kEc*ones(NumCel,1);
  end

  MatQ1 = Matrix1(1,NumCel);

%%%% <= MODEL-SPECIFIC  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

end; % of any(abs(flag)==[1 2 3])

if flag == 1, % Continuous states derivative calculation

  % default derivative =0;
  sys = zeros(B.CStates,1);

  %%%% MODEL-SPECIFIC => %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
  % fill sys with the derivatives of the CONTINUOUS STATES:
  % eg. sys(1) = (u(U.Temperature)-x(1))/P.Volume;

  if MeeTe==1   % MEESTROOM - altijd het geval voor statische menger
%   Get rid of negative values
  x(x<0)=0;
% The new, actual, final model calculations for model states:
  sys(1:NumCel)=(vl./dh).*MatQ1*[coO3;x(1:NumCel)]-
(kUV.*(x(1:NumCel)).*(x(2*NumCel+1:3*NumCel)-ceUVA254).*Y)-KafbO3*x(1:NumCel);
  sys(NumCel+1:2*NumCel)=((vb0+vl)./dh).*MatQ1*[cgoO3;x(NumCel+1:2*NumCel)];
  sys(2*NumCel+1:3*NumCel)=(vl./dh).*MatQ1*[coUVA254;x(2*NumCel+1:3*NumCel)]-
kUV.*(x(1:NumCel)).*(x(2*NumCel+1:3*NumCel)-ceUVA254); % kUV*O3conc*deltaUVA
sys(3*NumCel+1:4*NumCel)=(vl./dh).*MatQ1*[coBrO3;x(3*NumCel+1:4*NumCel)]+kCt_B
rO3*x(1:NumCel);
  sys(4*NumCel+1:5*NumCel)=(vl./dh).*MatQ1*[coEc;x(4*NumCel+1:5*NumCel)]-
kEc.*x(1:NumCel).*x(4*NumCel+1:5*NumCel); % Chick-Watson
```

```
sys(5*NumCel+1:6*NumCel)=(vl./dh).*MatQ1*[coCt;x(5*NumCel+1:6*NumCel)]+x(1:Num
Cel);
  end

  %%%% <= MODEL-SPECIFIC %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

elseif flag ==2, %discrete state determination

  % default next sample same states (length is B.DStates)
  sys = x(B.CStates+1:B.CStates+B.DStates);

  %%%% MODEL-SPECIFIC => %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
  % fill sys with the state value on the next samplemoment (determined by
  % B.SampleTime)
  % eg. sys(1) = (x(1)+u(U.Temperature))/P.Volume;

  %%%% <= MODEL-SPECIFIC %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

elseif flag ==3, % output data determination

  % default equal to the input with zeros for extra measurements
  sys = [u(1:U.Number); zeros(B.Measurements,1)];

  %%%% MODEL-SPECIFIC => %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
  % Send calculated values to appropriate output
  % eg. sys(U.Flow) = x(1);
   x(x<0) = 0;
   coEc=x(5*NumCel);

   sys(U.Ozone)=coO3;
   sys(U.UV254)=ceUVA254;
   sys(U.Bromate) =coBrO3;
   sys(U.Ecoli)=coEc; % coEc;
   sys(U.AOC)=ceAOC;
   sys(U.Ozone_dosed)=ceO3Dos;
   sys(U.Ozone_dos_kUV)=ceO3Dos_kUV;

  % Determine extra measurements
  % eg. sys(U.Number+1) = x(1)/P.Opp;
%    Get rid of negative values; ozone concentrations cannot be negative;
   x(x<0) = 0;
   sys(U.Number+1:U.Number+(NumCel+1))=[coO3;x(1:NumCel)];

sys(U.Number+1+(NumCel+1):U.Number+2*(NumCel+1))=[cgoO3;x(NumCel+1:2*NumCel)];

sys(U.Number+1+2*(NumCel+1):U.Number+3*(NumCel+1))=[coUVA254;x(2*NumCel+1:3*Nu
mCel)];

sys(U.Number+1+3*(NumCel+1):U.Number+4*(NumCel+1))=[coBrO3;x(3*NumCel+1:4*NumC
el)];

sys(U.Number+1+4*(NumCel+1):U.Number+5*(NumCel+1))=[coEc;x(4*NumCel+1:5*NumCel
)];
```

```
sys(U.Number+1+5*(NumCel+1):U.Number+6*(NumCel+1))=1/60*[coCt;x(5*NumCel+1:6*N
umCel)];


  %%%% <= MODEL-SPECIFIC %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

elseif flag == 0
  % initialize Model
  % [cs,ds,out,in,,direct]
  sys = [B.CStates,B.DStates,U.Number+B.Measurements,U.Number+B.Setpoints, 0,
B.Direct,1];
  ts = [B.SampleTime,0];
  str = 'ozoncc'; % ozonox
  x0=x0;
else
    % If flag is anything else, no need to return anything
    % since this is a continuous system
    sys = [];
end
```

Appendix E: Calibration script

This script requires three files. These are included in the .zip file of the Stimela model, available on request (yjwiersema@gmail.com).

```
% 1. initcalWPK

% Calibration initialization
% ozone model WPK
% march 2018

function initcalWPK
clear
tic % start stopwatch
% Load initial state xFinal
% load('BeginOzon27maart.mat');
% Files used
FileNameAll={...
       ['OZON_A'] % 5 deg. 1.9
%        ['OZON_B'] % 5 deg. 2.2
%        ['OZON_C'] % 5 deg. 2.5
%        ['OZON_D'] % 10 deg. 1.9
%        ['OZON_E'] % 10 deg. 2.15
%        ['OZON_F'] % 15 deg. 1.9
%        ['OZON_G'] % 20 deg. 1.9
%        ['OZON_H'] % 20 deg. 2.15
           };

% Initialize model and blocks

ModelUsed = ['WPK_GDS_Yasmine'];
Block_INI = ['WPK_GDS_Yasmine/Water quality' 10 'parameters'];
Block_PAR = ['WPK_GDS_Yasmine/Ozone contact column1'];

% Open and close parameter files

open(ModelUsed);
for i=1:size(FileNameAll,1);
    FileName=FileNameAll{i,1};
    st_ParameterInput('init',Block_INI, ['./StimelaData/' FileName
'_INI.mat'],'invruw');
    st_ParameterInput('exit',Block_INI, ['./StimelaData/' FileName
'_INI.mat'],'invruw');
    st_ParameterInput('init',Block_PAR, ['./StimelaData/' FileName
'_PAR.mat'],'ozoncc');
    st_ParameterInput('exit',Block_PAR, ['./StimelaData/' FileName
'_PAR.mat'],'ozoncc');

    startcalWPK([ FileName ]);
end
```

```
% 2. startcalWPK

% Start calibration
% ozone model WPK
% march 2018

function [cal] = startcalWPK(FileName)

% Indicate which parameters need to be calibrated and on which parameters is
calibrated

% CalPar is the parameter with all the parameters that can be calibrated
CalPar={'kUV' 'Y' 'KafbO3'};

% Calno give the parameters that are chosen to calibrate
Calno = [1 2]; % [1]=kUV, [2]=Y, [3]=KafbO3 %Calno = [1 2 3]

% CalTarget are the parameters on which is calibrated
CalTarget={'Ozone'}; % ; 'UV'

% For the CalInit the estimated value must be entered
CalInit = [0.31 0.35]; % was [0.2 0.2 0.005]

% The CalMin and CalMax give the range for the parameter
CalMin = [0.09 0.3 0.002];
CalMax = [0.5 0.5 0.03];

% The CalMagPar changes the size of the steps taken for the calibration
% routine a high CalMagPar (1e7) gives large steps and a low CalMagPar
% (1) gives small steps
CalMagPar = [1 1 1];
CalMagPar1 = [1]; % max(CalMagPar); 1e7

% In CalOpt the options for the calibration must be entered. (vraag Alex
waarom)
% The first is the maximum number of calibrations that will be done,
% the second is the tolerance for the x,
% the third is the tolerance for the function F(x)
CalOpt  = [10000 1e-1/CalMagPar1 1e-7];

% Calibration calculation %%% used to be 'LargeScale', 'off', at start
options = optimset('Display','iter',...
      'MaxFunEvals',CalOpt(1,1),'TolX',CalOpt(1,2),'TolFun',CalOpt(1,3));
Cal       = lsqnonlin(@calWPK, CalInit(Calno)./CalMagPar(Calno),
CalMin(Calno)./CalMagPar(Calno), CalMax(Calno)./CalMagPar(Calno), options,
FileName, CalMagPar(Calno),CalPar(Calno),Calno,CalTarget);
CalF      =
calWPK(Cal,FileName,CalMagPar(Calno),CalPar(Calno),Calno,CalTarget);
Fkwadraat = sum(CalF.^2);
CalResult = [Cal.*CalMagPar(Calno) Fkwadraat];

% Put all data in a structure and save it
Calibration.Name      = FileName;
Calibration.Par       = CalPar(Calno);
Calibration.Init      = CalInit(Calno);
```

```
Calibration.CalMagPar = CalMagPar(Calno);
Calibration.Min       = CalMin(Calno);
Calibration.Max       = CalMax(Calno);
Calibration.Option    = CalOpt;
Calibration.Res       = CalResult;
Calibration.F         = CalF;

CurrentDate = datestr(datenum(clock),30);
save(['CalResults_' FileName '_' CurrentDate(1,3:8) '.mat'],'Calibration')
datestr(now)
toc % end stopwatch



% 3. calWPK

%% Calibration function
% ozone model WPK
% march 2018

function F = calWPK(Cal,FileName,CalMagPar,CalPar,Calno,CalTarget)
% % Replacing the parameter value with a new one to run the calibration with
FileName
load(['./StimelaData/' FileName '_PAR.mat'],'P');

if sum(Calno==1)>0
    calkUV = Cal(strcmp(CalPar,'kUV'))*CalMagPar(strcmp(CalPar,'kUV'));
    P.kUV    = num2str(calkUV,12);
end

if sum(Calno==2)>0
    calY   = Cal(strcmp(CalPar,'Y'))*CalMagPar(strcmp(CalPar,'Y'));
    P.Y      = num2str(calY,12);
end

if sum(Calno==3)>0
    calKafbO3 =
Cal(strcmp(CalPar,'KafbO3'))*CalMagPar(strcmp(CalPar,'KafbO3'));
    P.KafbO3 = num2str(calKafbO3,12);
end

save(['./StimelaData/' FileName '_PAR.mat'],'P');

sim('WPK_GDS_Yasmine')

%% Load variables
load(['./StimelaData/' FileName '_PAR.mat'],'P'); %OZ_R1_CC_Dimensions.mat
P         = st_getPdata(['./StimelaData/' FileName '_PAR.mat'], 'ozoncc');
Number    = P.NumberCC;     % number of CC [m]
Vol       = P.VolCC;        % volume per CC [m3]
NumCel    = P.NumCel;       % number of CSTRs [-]
Areact    = P.VolCC.^(2/3); % area per CC [m2]
NumCelTot = sum(P.NumCel);
NumCelCum = cumsum(P.NumCel);
```

```
%% Evaluate %%

% Needed: an array of ozone concentration values @ CC1

datapoints = 100; % 10, this can (should) be more

eval(['load ./StimelaData/Ozoncheck.sti -mat']) % reason for using .sti?
Lengte = size(OzoncheckCC1,2); % length of the array, probably like 1200
% Pick values from the entire range with a for-loop
SimOzone = zeros(1,datapoints);
for counting = 1:datapoints
    SimOzone(1,counting) = OzoncheckCC1(((int16(Lengte./datapoints)-
1)*counting));
end

% SimOzone=SimOzone(2:2:end,:);

% Optional: Only using second half of array of values:
% This is to skip the initialization part values
% SimOzone = SimOzone((ceil(length(SimOzone)/2)+1):end);

% Same is needed for UVA254, this is measured at OZ_R1_UVA254_Meas (I think).
% eval(['load ./StimelaData/UVcheck.sti -mat'])
% SimUV254 = zeros(1,datapoints);
% for counting2 = 1:datapoints
%     SimUV254(1,counting2) = UVcheck(((int16(Lengte./datapoints)-
1)*counting2));
% end
% SimUV254 = SimUV254(2:2:end,:);

% Optional: Only using second half of array of values:
% SimUV254 = SimUV254((ceil(length(SimUV254)/2)+1):end);

% Should SimTimeWPK be related to length of reactor?
SimTimeWPK = zeros(1,datapoints);
for counting3 = 1:datapoints
    SimTimeWPK(1,counting3) = OzoncheckCC1(1,((int16(Lengte/datapoints)-
1)*counting3));
end
% SimTimeWPK = SimTimeWPK(2:2:end,:); % (50:end)
% If it needs to be related to the reactor, relate to number of
% CSTRs? datapoints should then be NumCel (= currently 10)
%%

% Load measured ozone .txt file
% (first column time (sec), second column ozone concentrations (mg/L))
% Files need . as decimal separator and not a comma
MeasuredO3 = load('OZON_C_O3.txt'); % ([ FileName '_O3.txt']);
TimeMeasO3 = MeasuredO3(:,1); % hele reeks
MeasO3     = MeasuredO3(:,2); % hele reeks
% TimeMeasO3 = MeasuredO3(size(MeasuredO3,1),1); % laatste v/d reeks
% MeasO3 = MeasuredO3(size(MeasuredO3,1),2); % laatste v/d reeks

% Load measured UVA txt file (same structure as ozone)
% MeasuredUV254 = load([ FileName '_ConstanteUV.txt']); % was UV.2.txt
```

```
% TimeMeasUV254 = MeasuredUV254(2:end,1);  % Gebruik de hele UV reeks
% MeasUV254     = MeasuredUV254(2:end,2);  % Gebruik de hele UV reeks
% TimeMeasUV254 = MeasuredUV254(size(MeasuredUV254,1),1);  % Gebruik alleen de
laatste waarde van de UV
% MeasUV254     = MeasuredUV254(size(MeasuredUV254,1),2);  % Gebruik alleen de
laatste waarde van de UV

% 1-D data interpolation
SimOzoneInterp =
interp1(SimTimeWPK,SimOzone,TimeMeasO3,'linear','extrap');%,'spline');
% SimUV254Interp =
interp1(SimTimeWPK,SimUV254,TimeMeasUV254,'linear','extrap');%,'spline');


%Methode 1
%Eenvoudige methode niet gewogen, dimensieverschillen tussen parameters kunnen
zorgen voor een onevenredige
%nadruk op een parameter.
% FO3            = SimOzoneInterp-MeasO3;
% FUV254         = SimUV254Interp-MeasUV254;

%Methode 2
%Methode van Kim waarbij de afwijking procentueel is en iedere parameter even
zwaar
%gewogen wordt. Dit werkt niet indien je waarde naar nul gaat.
% FO3 = ((SimOzoneInterp-MeasO3)./MeasO3)*sqrt(1/length(MeasO3));
% FUV254 = ((SimUV254Interp-MeasUV254)./MeasUV254)*sqrt(1/length(MeasUV254));

%Methode 3
%Methode waarbij de afwijking wordt betrokken op het verschil van het
%minimum en het maximum zodat ook een waarde verkregen wordt indien een
%parameter naar nul gaat.
dO3 = max(MeasO3)-min(MeasO3);
FO3 = ((SimOzoneInterp-MeasO3)/dO3)*sqrt(1/length(MeasO3));
% dUV254 = max(MeasUV254)-min(MeasUV254);
% FUV254 = ((SimUV254Interp-MeasUV254)/dUV254)*sqrt(1/length(MeasUV254));

% F=[FO3 ; FUV254];
F=[FO3];

sum(F.^2)
```

Appendix F: Linear regression analysis

To inspect how well the assumptions are met, the residuals plot was inspected.

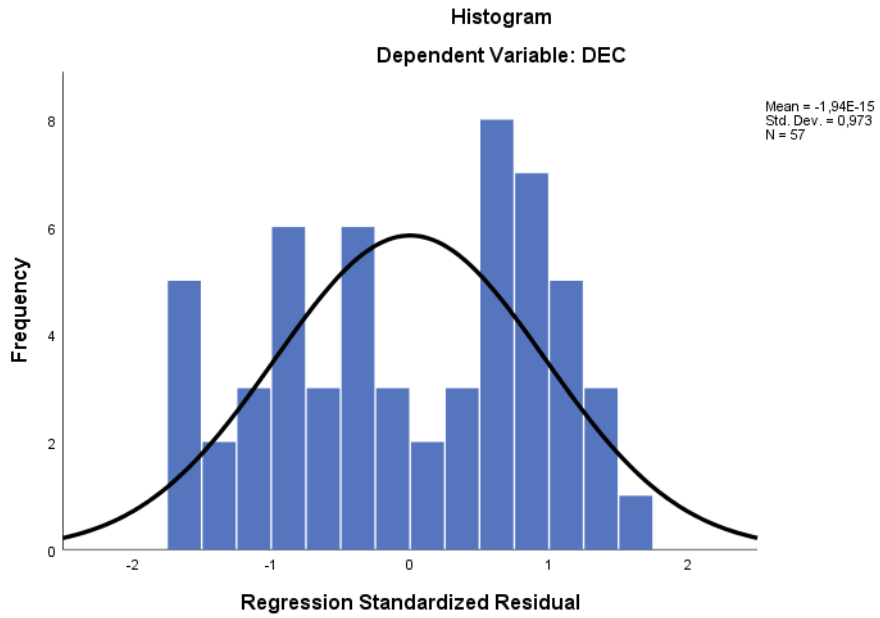


Figure 33: Residuals histogram; this should be roughly normally distributed. Residuals are the difference between the observed value and the predicted value.

To check homoscedasticity and linearity, standardized residuals were plotted against predicted values.

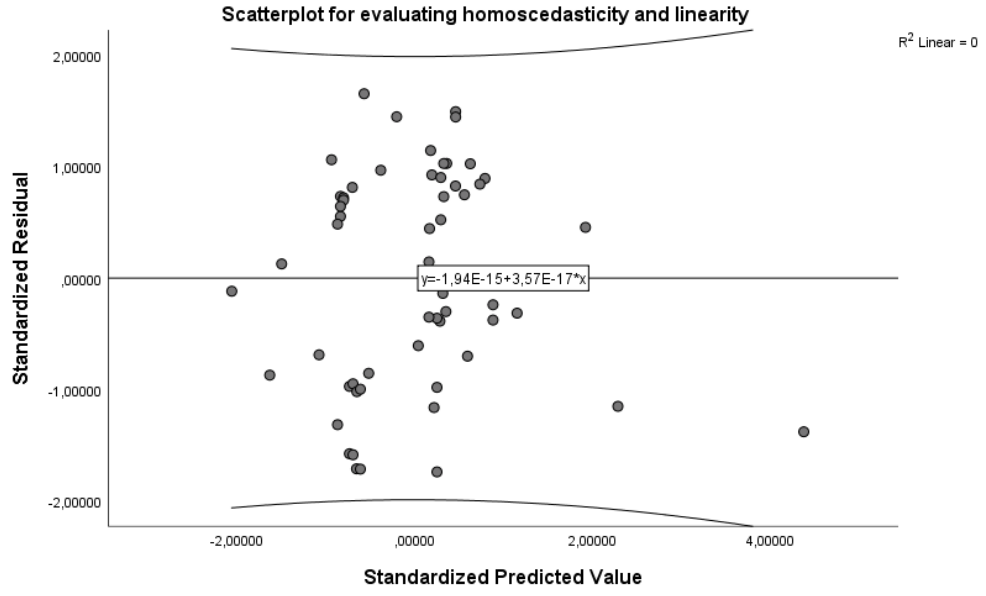


Figure 34: Scatterplot of standardized residuals versus predicted values for log inactivation.

The values seem to be dispersed roughly equally, except a few outliers. There is at least no clear sign of heteroscedasticity.