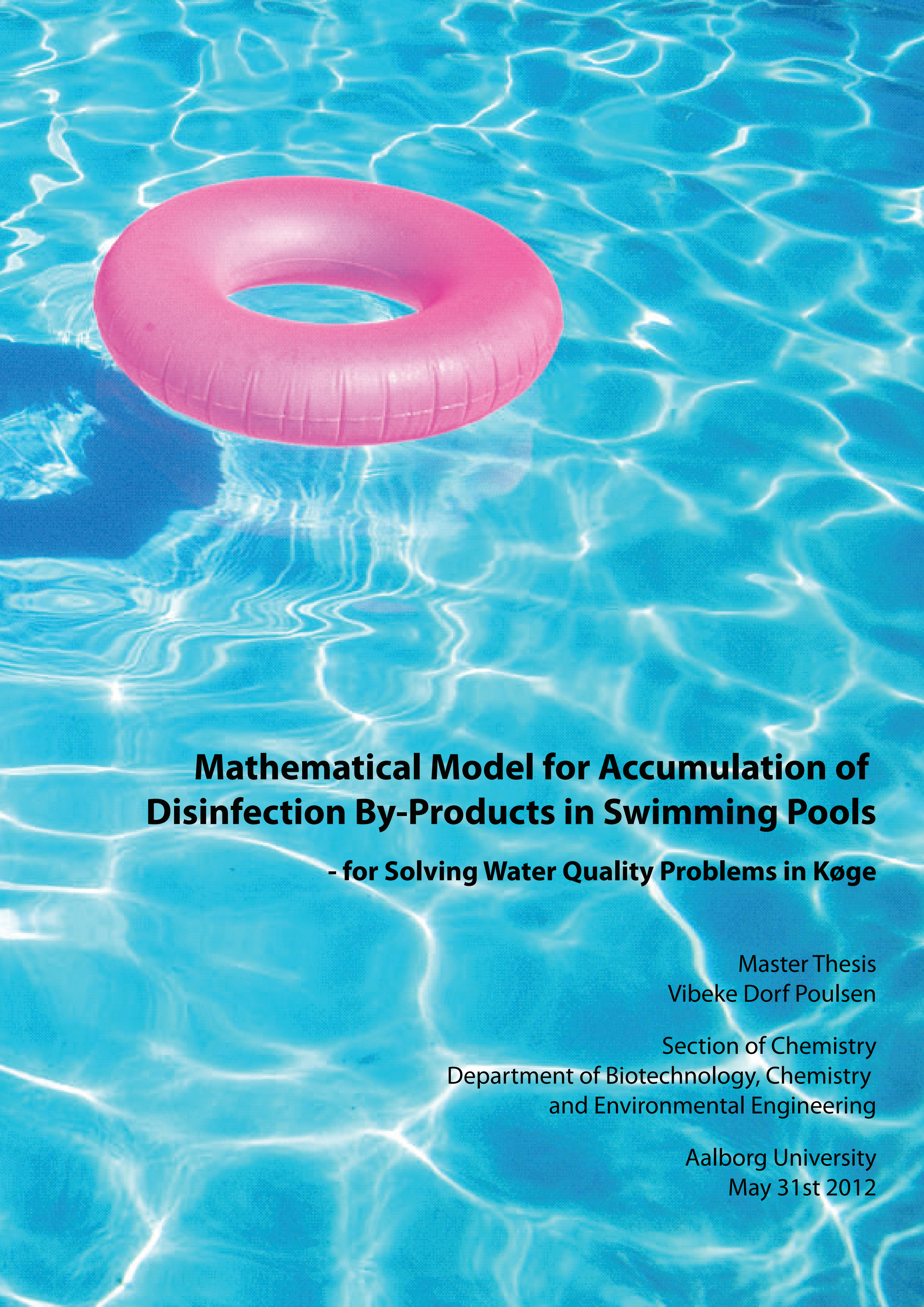

Mathematical Model for Accumulation of Disinfection By-Products in Swimming Pools

- for Solving Water Quality Problems in Køge

Master Thesis
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Synopsis:

In this thesis a mathematical model for accumulation of disinfection by-products is established. The model concerns combined chlorine, which has nitrogenous compounds as precursors. The model is based on knowledge gained by a literature review.

The validity of the model is tested using three sets of data. These tests show that the model is not in totally agreement with reality. However, the tendency of the curve for formation and removal of disinfection by-products is similar to those found in reality. For this reason the model is used for simulation of the effect of source water on the quality of pool water.

Three simulations are made. First the effect of ammonia from source water on the concentration of combined chlorine in pool water is studied. This simulation shows that source water does not affect the concentration of combined chlorine in pool water. The second simulation is focusing on calcium and carbonate species in the source water and shows that the source water alone is not enough to cause supersaturated pool water. Carbon dioxide is formed in the pool during breakdown of urea. The results of the final simulation show that this carbon dioxide does affect the saturation of pool water and for hard water may cause supersaturation.

Preface

This report the documentation of a long master thesis at Aalborg University as a part of the Master Programme in Chemical Engineering. It is written by a master student in the period September 2011 to May 2012 in cooperation with Skjølstrup & Grønborg.

I would like to address great thank to my supervisors Kristian Keiding and Morten Lykkegaard Christensen for inspiring supervision and constructive criticism during the project period. Great thank is also given to Ole Grønborg for supervision and discussions and also for, along with Jens Skjølstrup, letting me be a part of their company during the project period. Thanks is also given to Morten Møller Klausen and Gert Holm Kristensen from DHI for clarifying questions and finally to fellow students for helpful discussions during the project period.

The report is documented through calculations and argumentation and is divided into five parts. Part I contains an introduction, the thesis statement and some basic theory regarding pool water chemistry. Part II deals with the establishment of the mathematical model - considerations and assumptions during the set up - and validation. Part III contains simulations of pool water quality and part IV the conclusion and recommendations for future work. Finally part V contains appendices, which will be referred to throughout the report. Furthermore a CD with enclosures is attached. Here it will be possible to find Excel documents with the mathematical model and data of importance to the report along with some of the literature referred to in the report.

Throughout the report references in the form of the Harvard method will appear and these are all listed in the bibliography of the report. References from books, homepages or articles will appear with the last name of the author and the year of publication in the form of [Author, Year]. If the reference is placed before a full stop, only the respective sentence is referred to. If the reference is placed after a full stop, the whole paragraph is referred to. References to the CD with enclosures will occur with the file name in the form of [Enclosures-CD,File name].

Figures and tables in the report are numbered according to the respective chapter. In this way the first figure in chapter 3 has number 3.1, the second number 3.2 and so on. Explanatory text is found under the given figures and above the given tables. Figures and tables without references are created by the author.

Summary

This master thesis in Chemical Engineering at Aalborg University is based on water quality in swimming pools with focus on precipitation problems in Køge Swimming Pool. It is written in cooperation with Skjølstrup & Grønborg, a Danish engineering company specialised in water treatment processes.

Køge Swimming Pool experiences problems with turbid pool water, which is believed to be caused by precipitation of calcium carbonate. Previous studies and experiments have lead to the hypothesis that the precipitation is caused by the source water. Source water is added to the pool as compensation due to evaporation and back flushes of filters in the treatment plant. Thus, this thesis is focusing on the effect of source water on pool water quality and condition.

A literature review of basic swimming pool chemistry, water quality in pool and source water, disinfection, disinfection by-products and reactions occurring in pool water is made. In the light of this literature review, a mathematical model for accumulation of disinfection by-products is established. This model is used to simulate source water and pool water quality at selected locations in Denmark.

Two cases are simulated using the mathematical model. In both cases a model pool is used. This model pool fully lives up to the existing standards by Danish Standard [1996]. The temperature of the pool is set to 27 °C and the pH value to 7.00.

Case 1 examines the effect of the source water on pool water quality with respect to combined chlorine concentration. Four locations with different amount of ammonia in the source water are used for this simulation. The four locations are Tirstrup, Nørresundby, Køge and Bjerringbro. The simulations show that the concentration of combined chlorine accumulated in pool water does not differ as a function of source water content, due to a negligible addition compared to the one of bathers. Thus, with respect to combined chlorine the source water quality does not affect pool water quality and condition.

In case 2 simulations of the saturation of calcium carbonate in source water and its effect on pool conditions at four selected locations in Denmark are made. The four selected locations are Billund, Nørresundby, Køge and Femø. These locations are selected so four different hardness are simulated using the same model pool. These simulations show that the calcium and carbonate species content of source water does not cause supersaturation of pool water for the model pool used for simulation. Thus, no precipitation is expected to occur as a result of the source water quality.

A third case is examined using an equilibrium based programme, Visual Minteq. In case 3, the addition of carbon dioxide, from the breakdown of urea, and its effect on the calcium carbonate saturation is examined. The four locations from case 2 are also used for

these simulations. The results hereof show that supersaturation with respect to calcium carbonate occurs for the source water from Billund and Nørresundby only if the pH value is increased to 8. However, for source water from Køge and Femø supersaturation occurs at pH 7 even before carbon dioxide is formed. When carbon dioxide is formed in the water, the level of supersaturation increases.
The results of case 3 are not in accordance with those of case 2. Thus, the model is inaccurate and further development hereof is desired.

The simulations of case 1 lead to the conclusion that, with respect to combined chlorine, the source water does not affect the pool water quality. From case 2 and 3 the conclusion is that calcium carbonate from the source water may cause supersaturation upon entering pool condition. This is, however, only the case if the calcium and carbonate concentrations in source water are high. Furthermore the carbon dioxide formed in the pool leads to a higher level of (super)saturation.

Resumé

Dette afgangsprojekt ved Kemiingeniøruddannelsen på Aalborg Universitet omhandler vandkvalitet i svømmebade med udgangspunkt i kalkudfældningsproblemer i Køge Svømmeland. Projektet er udarbejdet i samarbejde med den danske ingeniørvirksomhed Skjølstrup & Grønborg som er specialiseret i vandbehandlingssystemer.

Køge Svømmeland oplever turbidt vand, som menes at opstå på grund af kalkudfældning. Tidligere undersøgelser har ledt til en hypotese om at disse kalkudfældninger skyldes spædevandets kvalitet og påvirkning af badevandet. Spædevandet påfyldes systemet for at udligne den vandmængde der forsvinder ved f.eks. fordampning og back-flush af filtre. På baggrund af denne problemstilling, omhandler dette afgangsprojekt spædevandets påvirkning af badevandets kvalitet og tilstand.

Indledende er der lavet et litteraturstudie af general svømmebadskemi, vandkvalitet i såvel badevand som spædevand, desinfektion, desinfektionsbiprodukter og reaktioner i badevandet. Ud fra litteraturstudiet er en matematisk model for akkumuleringen af desinfektionsbiprodukter i svømmebade opstillet. Denne model benyttes til simulering af spædevandets påvirkning.

Simuleringen laves for to cases. Til begge cases benyttes en modelpool. Denne modelpool lever fuldt ud op til nuværende standard jf. Danish Standard [1996]. Temperaturen for badevandet i poolen er fastsat til 27 °C og en pH-værdien på 7.00.

I Case 1 simuleres spædevandets påvirkning af koncentrationen af bundet klor i badevandet. Fire beliggenheder med forskellig koncentration af ammoniak benyttes i denne case. De fire udvalgte beliggenheder er Tirstrup, Nørresundby, Køge og Bjerringbro. Resultaterne viser, at badevandskvaliteten ikke påvirkes af spædevandet, i forhold til koncentrationen af bundet klor, som følge af en ubetydelig tilføjelse fra spædevandet sammenlignet med den fra badegæster.

I case 2 simuleres kalkmætningen af spæde- og badevandet fire udvalgte beliggenheder i Danmark. Disse beliggenheder er Billund, Nørresundby, Køge og Femø, hvoraf Femø har det hårdeste vand. Simuleringerne viser, at spædevandets kalcium og karbonat indhold ikke påvirker badevandet i en sådan grad, at en overmætning af kalciumkarbonat sker. Ud fra disse resultater er en kalkudfældning i vandet ikke forventeligt.

Case 3 er en undersøgelse af kuldioxids påvirkning af karbonatsystemet. Til denne case benyttes et ligevægtsprogram, Visual Minteq. Kuldioxid dannes i badevandet, når urea, som frigives af badegæster, nedbrydes. Dette kuldioxid påvirker karbonatsystemet og dermed mætningsgraden af kalk i badevandet. Undersøgelsen er lavet for de samme fire beliggenheder, som er anvendt i case 2. Resultaterne viser, at der ikke er tendens til overmætning af kalciumkarbonat i Billund og Nørresundby, så længe pH-værdien holdes

på 7. Der imod vil der både i Køge og på Femø være en overmætning af kalciumkarbonat allerede ved pH 7 og inden kuldioxid dannes i badevandet. Graden af denne overmætning stiger i takt med at kuldioxid dannes i vandet.
Resultaterne for case 2 og 3 ikke stemmer overens, hvorfor den matematiske model må være unøjagtig. På baggrund af dette ønskes videre udvikling af modellen.

Ud fra simuleringerne i case 1 er konklusionen, at badevandskvaliteten ikke påvirkes af spædevandets kvalitet og indhold. Dette gælder dog kun for bundet klor. Ud fra case 2 og 3 kan det konkluderes, at kalcium- og karbonatindholdet i spædevandet kan påvirke badevandet til overmætning af kalciumkarbonat. Dog vil dette kun være tilfældet for spædevande med højt indhold at kalcium og karbonat. Med hensyn til kuldioxiddannelsen i badevandet forårsager dette en højere grad af (over)mætning af kalciumkarbonat i badevandet.

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Part I

Introduction

"This part contains the introduction along with basic water chemistry theory. The first chapter is the introduction, which ends with the thesis statement and the delimitation hereof. Chapter 2 contains basis water chemistry in swimming pools. This chapter is build up around Langeliers saturation index, which will be used as a measuring method throughout the thesis. The last chapter in the part concerns disinfection processes when chlorine is used as a disinfectant"

Introduction 1

In a swimming pool, pollution is brought mainly by bathers who release sweat and urine in the water along with dirt, skin cells and lotion and make-up residuals among others. Besides these, waterborne microbial pathogens are spread through the water. Because of these waterborne pathogens swimming pools need disinfection in the pool water. If no disinfection is added to pool water the waterborne pathogens will spread from one bather to another before the infected water can reach the treatment plant as a regular pool has a turnover period of two to five hours depending on the depth [Miljøministeriet, 2010]. Chlorine is the most widely used disinfectant in swimming pools and other recreational waters [World Health Organization, 2006; Weaver et al., 2007; Weng et al., 2011; Li and Blatchley, 2007]. Besides disinfection of microbial pathogens chlorine reacts with pollutants in the pool producing disinfection by-products, DBP. These DBPs include trihalomethanes, THMs, and chloramines of which the latter is often referred to as combined chlorine. Hypochlorous acid and hypochlorite is often referred to as free chlorine [Stumm and Morgan, 1996]. Chloramines and THMs, are believed to be harmful to human health and even possibly carcinogen [Dahl, 2009; Lakind et al., 2010; Kanan and Karanfil, 2011].

Pool water contains a wide range of microbial organisms and chemical compounds, some of which are added for a purpose and others added by bathers or formed within the pool and are unwanted in recreational waters. The quality of the pool water depends on the amount of these organisms and compounds and will in this thesis be divided into three categories: Chemical water quality, biological water quality and human water quality.
The chemical water quality primarily concerns the carbonate system and chemicals that affect this. It is often measured by *Langeliers saturation index*. This is concerned of the calcium carbonate saturation and affected by the pH value, temperature and the amounts of dissolved solids in the water. This will be thoroughly explained later.
The biological water quality is the microbiological and bacterial state of the pool water. If this is not controlled, diseases are spread among bathers, for which reason most of these microorganisms are unwanted in pool water. However, they are added by bathers, thus disinfection is needed.
The last of the three water qualities, the human water quality is mostly concerning substances affecting human health. This category includes DBPs as they are believed to cause discomfort and at worst illness among bathers.

As it is important to keep a good quality of the pool water with respect to all three categories, standards for these are made. These standards differ from country to country but are similar. For Denmark the existing standard is DS477 along with executive orders from the Department of the Environment in Denmark [Danish Standard, 1996; Miljøministeriet, 2010]. The Danish standard is compared to the German DIN 19643 among others in appendix A as DIN 19643 currently is the strictest. These standards exist to ensure good and uniform water quality in swimming pools around Europe. Also USA and Australia have operational guidelines and codes for water quality in recreational waters [Colorado, 1998; Georgia, Undat.; Queensland Government, 2004]. These are also included in the comparison.

Even though a pool fulfils the requirements in Danish Standard [1996] and by Miljøministeriet [2010] the water quality can be unsatisfactory. An example of this is Køge swimming pool where the pool fully lives up to the standards for chemical water quality, but nonetheless records turbid water. The turbidity is believed to be caused by precipitation of calcium carbonate [Grønborg, 2012]. Several studies of the pool water quality have been made and the conclusions of these are that the source water may affect the pool water to precipitate calcium carbonate. From the former studies of pool water quality in Køge the following hypothesis has been made. [Grønborg, 2012]

- The source water affects the pool water to precipitate calcium carbonate.

The addition of matter from bathers and the reaction of this with free chlorine have been widely studied by several scientists such as Weaver et al. [2007], Kanan and Karanfil [2011] and Judd and Bullock [2003]. However, the matter added from the source water has not jet been a large subject to research. As the source water is believed to play a significant role in the water quality problems in Køge, a study of the source water composition and how this can affect the water quality in Køge is needed.

1.1 Thesis statement

With reference to in the pool water quality problem in Køge and the hypothesis that the source water affects pool water quality, it is in this thesis desired to contribute to the solving of the problem by means of a mathematical model. The purpose of this model is to predict the amount of by-products formed and to determine how this is affected by the combination of the source water. During the set up of this model it is necessary to

- Study and determine the chemistry and reactions of the pool water
- Study the composition of chemicals in the source water
- Determine how the chemical composition of the source water affects the reactions and quality of the pool water

Delimitation

Prior to the set up of the mathematical model, an input compound has to be chosen. This input compound is used during the set up of the model, but can afterwards be exchanged by another. Nitrogen is chosen as input compound for the mathematical model. When nitrogen containing compounds enter the pool they are oxidised by free chlorine to chloramines, or combined chlorine as they frequently are called. Nitrogenous compounds are added both by bathers and source water. When combined chlorine is formed in the pool water the human water quality is reduced. This leads to the following question.

- Does the nitrogenous compounds of source water affect the human quality of the pool water?

Besides the human water quality, the chemical water quality must be affected as well according to Grønborg [2012]. As the chemical water quality is correlated to the carbonate system and parameters affecting this, the calcium carbonate situation of the source water must be known. This is best known by the use of Langeliers saturation index, which will be described in the next chapter. When looking at the chemical water quality and thus the carbonate situation of the water, two questions appear.

- Is the source water under- or supersaturated with respect to calcium carbonate?
- Will the concentration of calcium and carbonate species in the source water cause precipitation under pool conditions?

One final question related to the saturation of the pool water with respect to calcium carbonate appears.

- Are other compounds, which can affect the saturation of calcium carbonate added to the pool water?

To answer these four questions, a mathematical model is to be made. However, before this Langeliers saturation index, which is the primary method of measurement of the chemical water quality, must be examined.

2 Chemical Water Quality in Swimming Pools

As stated in the introduction it is important to maintain a good quality of the pool water both from a bathers and a technicians point of view.
With respect to the chemical water quality it is important that the water is in balance with respect to calcium carbonate. Water is balanced if it is neither corrosive nor scale forming, i.e., has no tendency to dissolve or precipitate hardness salts. The water balance is calculated by Langeliers saturation index. If the saturation index is equal to zero, the pool water is in equilibrium with respect to calcium carbonate. In this way the water balance is another way to describe if the water is in equilibrium.

2.1 Saturation index

The saturation index is based on the difference between the actual and equilibrium pH value and is thus used to calculate how far the water is from equilibrium. If the water is in equilibrium it is totally balanced and no precipitation or dissolution of calcium carbonate will occur. A saturation index within -0.5 to 0.5 is accepted for pool water.

In 1936 Langelier presented the simple formula for calculating the saturation index. [Larson and Buswell, 1942; Wojtowicz, 1997b]

$$SI = pH_a - pH_e \tag{2.1}$$

Where:

SI	Saturation index [–]
pH_a	Actual pH value [–]
pH_e	Equilibrium pH value [–]

The pH value of the water is affected by the alkalinity and hence the carbonate system and calcium concentration. Thus the equilibrium for these reactions is included. The reactions in mention are

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \tag{2.2}$$

$$HCO^{-}_{3(aq)} \rightleftharpoons H^{+}_{(aq)} + CO^{2-}_{3(aq)} \tag{2.3}$$

Which can be combined to

$$CaCO_{3(s)} + H^{+}_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + HCO^{-}_{3(aq)} \tag{2.4}$$

The equilibrium constants for these three reactions are, respectively

$$K_S = \left[Ca^{2+}\right]\left[CO_3^{2-}\right] \tag{2.5}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{2.6}$$

$$K = \frac{[HCO_3^-][Ca^{2+}]}{[H^+]} \tag{2.7}$$

Where:

K_S	Equilibrium constant of calcium carbonate saturation [M^2]
K_2	Second equilibrium constant of the carbonate system [M]
K	Equilibrium constant for the combined reaction [M]

The pH value, calcium concentration and carbonate system are all included in the reaction in formula 2.4 [Stumm and Morgan, 1996; Snoeyink and Jenkins, 1980]. As the saturation index is the difference between actual composition and equilibrium, the reaction constants for the non-equilibrated and equilibrated reaction in formula 2.4 are listed in formula 2.8 and 2.9.

$$Q = \frac{\left[Ca^{2+}\right]_a\left[HCO_3^-\right]_a}{[H^+]_a} \tag{2.8}$$

$$K = \frac{\left[Ca^{2+}\right]_e\left[HCO_3^-\right]_e}{[H^+]_e} \tag{2.9}$$

Where:

K	Equilibrium constant [*various*]
Q	Reaction constant [*various*]
a	Concentration at actual composition
e	Concentration in equilibrium

Formula 2.10 is written based on the difference of actual composition and equilibrium by using formula 2.8 and 2.9.

$$log\frac{Q}{K} = log\frac{[Ca^{2+}]_a[HCO_3^-]_a[H^+]_e}{[Ca^{2+}]_e[HCO_3^-]_e[H^+]_a} \tag{2.10}$$

where Q represents the pH value at actual composition and K the pH value in equilibrium. Since

$$\frac{K_2}{K_S} = \frac{[H^+]_e}{[Ca^{2+}]_e\left[HCO_3^-\right]_e} \tag{2.11}$$

the formula can be written as

$$log\frac{Q}{K} = log\frac{\left[Ca^{2+}\right]_a\left[HCO_3^-\right]_a K_2}{[H^+]_a K_S} \tag{2.12}$$

which is the same as

$$log\frac{Q}{K} = log[Ca^{2+}]_a + log[HCO_3^-]_a + pH + log\frac{K_2}{K_s} \tag{2.13}$$

As $log\frac{Q}{K}$ is the difference between the actual composition and equilibrium it must be equal to the saturation index.
Thus

$$SI = log[Ca^{2+}]_a + log[HCO_3^-]_a + pH + log\frac{K_2}{K_s} \tag{2.14}$$

At pH $<$ 9 the total alkalinity in eq/L is interchangeably with the concentration of bicarbonate as the carbonate concentration is negligible. Thus

$$\left[HCO_3^-\right] \cong [Alk] \tag{2.15}$$

$$\Rightarrow SI = pH_a + \log\left[Ca^{2+}\right]_a + \log\left[Alk\right]_a + \log\frac{K_2}{K_S} \tag{2.16}$$

[Snoeyink and Jenkins, 1980].
By introducing factors for conversion of concentration from M to mg/L $CaCO_3$ for calcium and alkalinity and also correcting for ionic strength and temperature, formula 2.16 becomes

$$SI = pH + \log[Hard] + \log[Alk] + TC - 12.35 \tag{2.17}$$

Where:

$Hard$	Hardness [mg/L]
Alk	Alkalinity [mg/L]
TC	Temperature correction factor [–]

which is the saturation index equation published by Wojtowicz [1997b].[1] [Wojtowicz, 1997b,c; Snoeyink and Jenkins, 1980]. The calculations for the conversion factors from formula 2.16 to 2.17 are elaborated in appendix B.
Formula 2.17 can also be written as

$$SI = pH + CF + AF + TC - 12.35 \tag{2.18}$$

Where:

SI	Saturation index [–]
pH	pH value [–]
CF	Calcium hardness factor [–]
AF	Alkalinity factor [–]
TC	Temperature correction factor [–]

Which is the version known in the pool industry [PWTAG, 2009].

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[1] With the difference of -12.35 instead of -12.29. This difference origin from the use of different number of decimals during calculation. The formula written here will be used throughout this thesis.

2.1.1 The thermodynamic basis of the saturation index

The saturation index has a thermodynamic basis and is related to the Gibbs free energy formula as follows.

The Gibbs free energy for any reaction is given by

$$\Delta G = 2.3RT \log \frac{Q}{K} \tag{2.19}$$

Where:

R	Gas constant [J/mol · K]
T	Temperature [K]
Q	Reaction constant at the actual composition [*various*]
K	Equilibrium constant [*various*]

In a thermodynamic context the solution of calcium carbonate is in equilibrium when Gibbs free energy is equal to zero. When the Gibbs free energy is positive, the calcium carbonate in solution can precipitate, i.e., the backwards reaction in formula 2.4 is possible. A negative Gibbs free energy represents the dissolution of calcium carbonate, i.e., the forward reaction in formula 2.4. The reaction constants Q and K are given earlier in formula 2.8 and 2.9, respectively. As $log\frac{Q}{K}$ is equal to the saturation index, formula 2.19 can be written as

$$\Delta G = 2.3RT \cdot SI \tag{2.20}$$

Thus it is possible to calculate Gibbs free energy of the system when the saturation index is known. As R and 2.3 are constants and T is treated as a constant, the saturation index in correlated to the Gibbs free energy.

2.2 Parameters affecting the water balance

2.2.1 Temperature

The temperature has an impact on the water quality as equilibrium constants are changing as a function of temperature. Thus, the temperature affects the saturation index equation as it contains parameters affected by equilibrium constants and precipitation.

2.2.2 pH value

It is essential to keep the pH value in the pool water within a certain range. According to Danish Standard [1996] the pH value should be within the range of 7.0 - 8.0. From a bathers point of view, the pH value has to be about neutral as the body is surrounded by a thin protective layer of fat, which is destroyed when exposed to high acidic or alkaline solutions [Yosipovitch et al., 1998]. From a chemist's point of view, the pH value has to be below 8 as disinfection by hypochlorous acid is most effective when hypochlorous acid is fully protonated. This occurs at pH values below 8 as pKa for hypochlorous acid is 7.54 [Snoeyink and Jenkins, 1980; Andersen et al., 2007]. The disinfection process is further explained in chapter 3. Further calcium carbonate precipitation is more likely to occur at high pH values, which will be examined later in this chapter.

A change in the pH value of the water affects, besides the disinfection process, different quality parameters and other properties of the water, including the water balance. When the pH value is changed, the saturation index is changed as wall. As it is seen from formula 2.18, an increase of the pH value yields, if all others are kept constant, an increase in the saturation index. However, a change in the pH value affects other parameters in the water as well, e.g., the precipitation of the hardness salts.

2.2.3 Hardness

The total hardness can be divided into two contributions: Temporary hardness and permanent hardness. The temporary hardness (calcium and magnesium with carbonate and bicarbonate) is the part of the total hardness that precipitates when boiling, whereas the permanent hardness (calcium and magnesium with sulphides and chlorides) is the part that does not precipitate when boiling. [PWTAG, 2009]

In swimming pools the hardness is measured as calcium hardness, which should not be too low. According to PWTAG [2009] a water with hardness lower than 40 mg/L as $CaCO_3$ is likely to be corrosive to the pool materials as it is undersaturated and thus corrosive to calcium carbonate containing solids, e.g., grout. [Snoeyink and Jenkins, 1980; PWTAG, 2009]. However, the solubility depends on the pH value of the water, for which reason this value can differ as a result of the pH value. [Snoeyink and Jenkins, 1980]
Figure 2.1a illustrates the solubility of calcium carbonate as a function of the pH value. It is seen that an increase in the pH value causes calcium carbonate solubility to a state of supersaturation and precipitation.

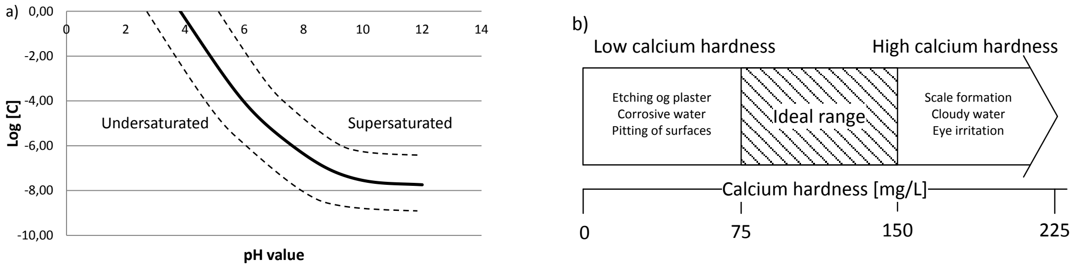

Figure 2.1. a) Calcium carbonate solubility as a function of the pH value. The area between the dotted lines illustrates a metastable zone. [Snoeyink and Jenkins, 1980; Stumm and Morgan, 1996]. b) The ideal level of hardness according to standards for pool water quality as described in appendix A.

When the hardness exceeds 75 mg/L $CaCO_3$, a protective scale is starting to form as the saturation is in a metastable zone. It is recommended that calcium hardness is being kept in the range 75-150 mg/L as illustrated in figure 2.1b and in appendix A. [PWTAG, 2009; Haan and Johanningsmeier, 1997]

The precipitation of calcium carbonate affects the saturation index as the concentration of aqueous calcium carbonate, which corresponds to the hardness, is lowered. A lower hardness leads to a lower saturation index cf. formula 2.18.

$$Ca^{2+}_{(aq)} + HCO^{-}_{3(aq)} \rightleftharpoons CaCO_{3(aq)} + H^{+}_{(aq)} \tag{2.21}$$

$$CaCO_{3(aq)} \rightleftharpoons CaCO_{3(s)} \tag{2.22}$$

The potential of calcium carbonate precipitation is increased when the pH value is raised above 8, as carbonate formation initiates at pH values just below 8. This is shown in figure 2.2.

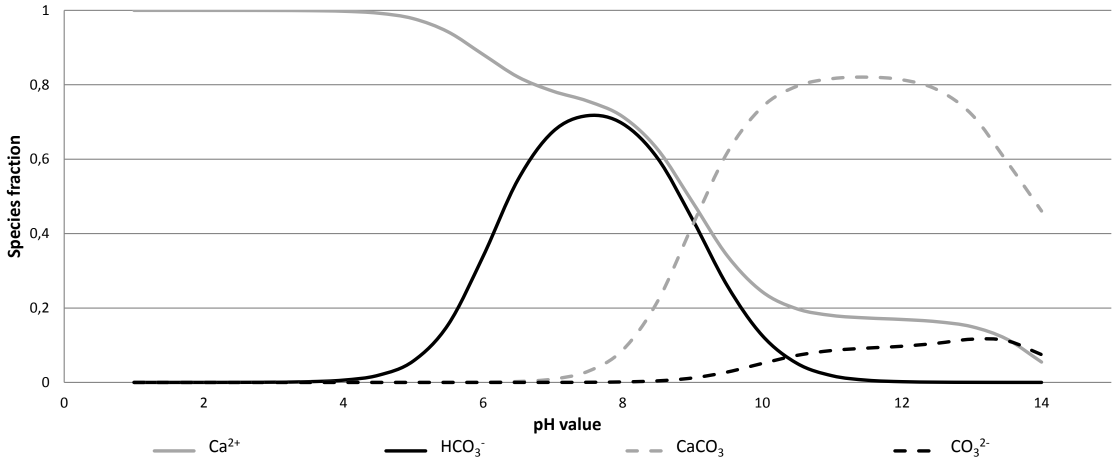

Figure 2.2. Calcium and carbonate species as a function of the pH value in water. Compounds other than the shown are also formed.

The figure illustrates the correlation between calcium ions, bicarbonate, carbonate and aqueous calcium carbonate. As it is seen the concentration of bicarbonate reaches its maximum level just before pH 8. At this point the concentration of aqueous calcium carbonate starts to increase due to carbonate formation which again results in a higher tendency to precipitate calcium carbonate. When the concentration of bicarbonate reaches zero as the pH value is raised, the concentration of calcium carbonate levels off to be constant. When the pH value is further increased, the concentration of aqueous calcium carbonate decreases. This decrease is caused by the favoured formation of calcium hydroxide when the pH value is raised above approx. 12.

Precipitation of calcium carbonate affects the carbonate system as the amount of dissolved carbonate and bicarbonate decreases upon precipitation.

The carbonate system

The carbonate system consists of the reaction of carbon dioxide with water.

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \tag{2.23}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)} \tag{2.24}$$

$$H_2CO_{3(aq)} \rightleftharpoons H^{+}_{(aq)} + HCO^{-}_{3(aq)} \tag{2.25}$$

$$HCO^{-}_{3(aq)} \rightleftharpoons H^{+}_{(aq)} + CO^{2-}_{3(aq)} \tag{2.26}$$

Aqueous carbon dioxide and carbonic acid concentrations are often treated as one under the term H_2CO_3*. The reaction of this specie is illustrated in formula 2.27. This is the combination of formula 2.24 and 2.25

$$H_2CO^*_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{2.27}$$

A swimming pool is considered as a closed system where no exchange of carbon dioxide with the atmosphere occurs, for which reason the reaction in formula 2.23 is not included. The pK_a and pK_b values for the carbonate system are listed in table 2.1.

Table 2.1. pKa and pKb values for the species of the carbonate system. [Andersen et al., 2007].

Species	pK_a value	pK_b values
$H_2CO^*_{3(aq)}$	6.37	
$HCO^-_{3(aq)}$	10.32	7.63
$CO^{2-}_{3(aq)}$		3.68

Changes in the pH value affect the carbonate system as the carbonate species are either protonated or deprotonated when the pH value is decreased or increased.

If the pH value drops below 8 the conversion of bicarbonate to carbonic acid is initiated and the equilibrium is thereby shifted to the left, creating a lack of bicarbonate and carbonate. This leads to corrosive water as calcium carbonate is undersaturated as illustrated in figure 2.1a. [Snoeyink and Jenkins, 1980; PWTAG, 2009]
With respect to the pH value the standards for pool water quality, as listed in appendix A, recommend pH 7.0 - 8.0, which is in accordance with the calcium carbonate equilibrium.

2.2.4 Alkalinity

The alkalinity is, along with the acidity, the buffering capacity of the water. Alkalinity is a measure of the capacity of a solution to neutralise strong acids to the equivalence point of primarily carbonate and bicarbonate. The alkalinity is hence caused by the carbonate, bicarbonate and hydroxyl ions in the water, for which reason a change in the carbonate system will affect the alkalinity. The alkalinity is divided into three parts: Total alkalinity, carbonate alkalinity and caustic alkalinity. The total alkalinity is defined as the stoichiometric amount of acid (H^+) required to reach the equivalence point of H_2CO_3*, i.e., the amount required to fully protonate all carbonate species as illustrated in figure 2.3. Formula 2.28 - 2.30 contains these reactions.

$$H^+_{(aq)} + OH^- \rightleftharpoons H_2O_{(l)} \tag{2.28}$$

$$H^+_{(aq)} + CO^{2-}_{3(aq)} \rightleftharpoons HCO^-_{3(aq)} \tag{2.29}$$

$$H^+_{(aq)} + HCO^-_{3(aq)} \rightleftharpoons H_2CO^*_{3(aq)} \tag{2.30}$$

The carbonate alkalinity is defined as the amount of acid required in order to complete the reactions in formula 2.28 - 2.29, i.e., titration till hydroxyl is fully protonated and all carbonate species are in the bicarbonate form.
The caustic alkalinity is defined as the amount of acid required for all hydroxyl to

be protonated. At this point all carbonate species are fully deprotonated. The three alkalinities are illustrated in figure 2.3. The caustic alkalinity cannot be determined directly by titration, but can be calculated when the total and carbonate alkalinities are known. The pH value at these alkalinity points are according to Snoeyink and Jenkins [1980] 4-5 (pH_{CO_2}), $\approx$ 8 ($pH_{HCO_3^-}$) and 9-11 ($pH_{CO_3^{2-}}$), respectively. In figure 2.3 the first alkalinity is marked at approx. pH 3 and the last just below pH 12. This difference is a consequence of figure 2.3 not being made for the standard solution with respect to concentration, which is the case for those by Snoeyink and Jenkins [1980]. The three points are also illustrated in figure 2.5 with the three circles denoted 1, 2 and 3, respectively. [Snoeyink and Jenkins, 1980]

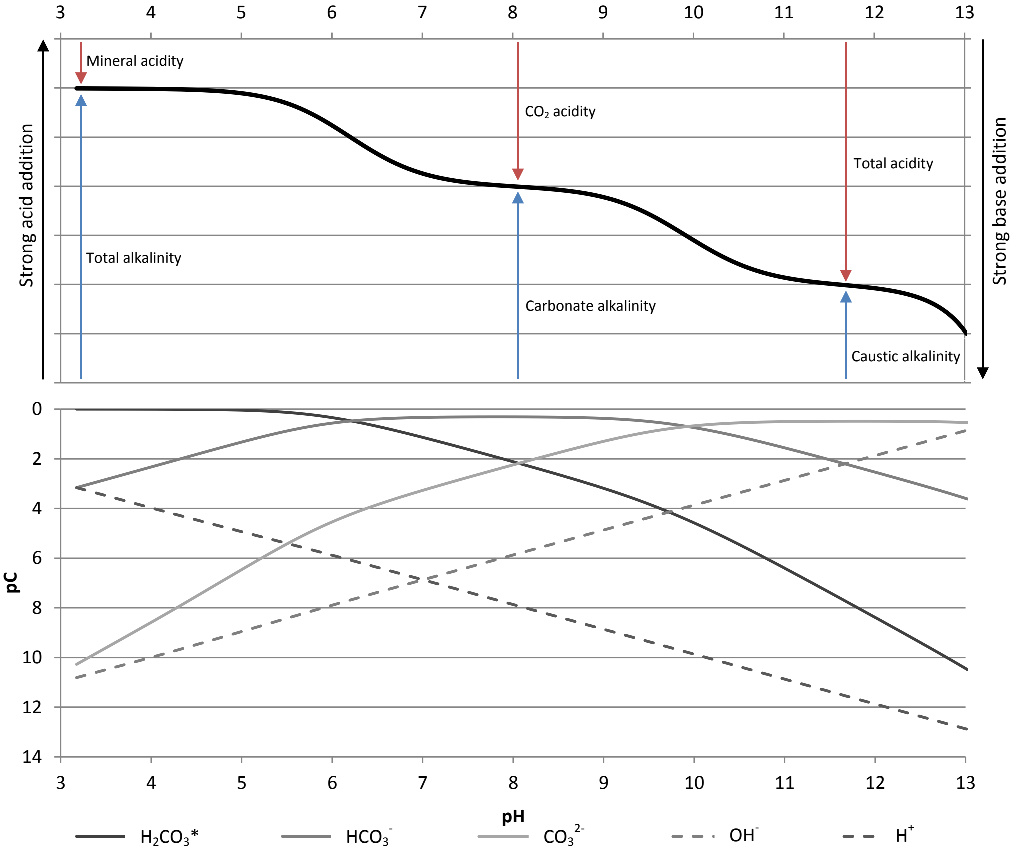

Figure 2.3. The correlation of the titration curve and pH-pC chart of the carbonate system at 25 °C . Modified from [Snoeyink and Jenkins, 1980].

Acidity is the opposite of alkalinity, i.e., the amount of base required to deprotonate the carbonate species and water. The three different acidities are also illustrated in figure 2.3. When the alkalinity is high, much acid is required for titration. Thus the solution contain hydroxyl and carbonate anions in excess and has thus a great buffering capacity. Thus, significant alkalinity or acidity prevents changes of the pH value, i.e. buffers the system. [Spellman, 1998; Snoeyink and Jenkins, 1980]

If the alkalinity in a pool is too low (below approx. 80 mg/L as $CaCO_3$), pH bounces can occur. On the contrary, if the alkalinity is too high (above 200 mg/L), it can be difficult to make necessary pH adjustments. This phenomenon is known as 'pH lock' because the buffering capacity gets so high that the pH is nearly locked. Figure 2.4 illustrates the recommended rages of alkalinity based on standards from appendix A. [PWTAG, 2009]

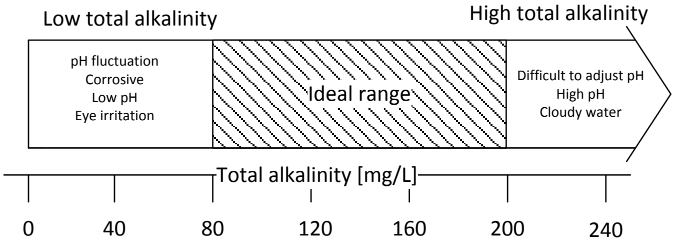

Figure 2.4. The recommended concentration range of alkalinity in swimming pools as examined in appendix A.

The aqueous carbon dioxide in the pool water is not in equilibrium with the carbon dioxide in the air, for which reason a higher alkalinity is present in pool water. As the system seeks to equilibrium, but has a higher alkalinity, the pH value is raised to a level that favours high alkalinities. However, due to the periodic pH adjustments in pool water, a supersaturated level of carbon dioxide exists [Wojtowicz, 1997a]. Because of this supersaturation, a loss of carbon dioxide can occur, even though the system is not in equilibrium with the atmospheric carbon dioxide. When the water loses carbon dioxide, the pH value increases, but the alkalinity is not affected. The loss of carbon dioxide follows the reactions listed in formula 2.23-2.26. The loss of aqueous carbon dioxide reduces the carbonic acid concentration and thus, increases the pH value. When the pH value is increased, bicarbonate is converted to carbonate at pH values above 8 as illustrated in figure 2.5. Contrary to the pH value, the alkalinity is not affected by the loss of aqueous carbon dioxide as the decrease of equivalents of bicarbonate is equal to the increase of equivalents carbonate. [Wojtowicz, 1995]

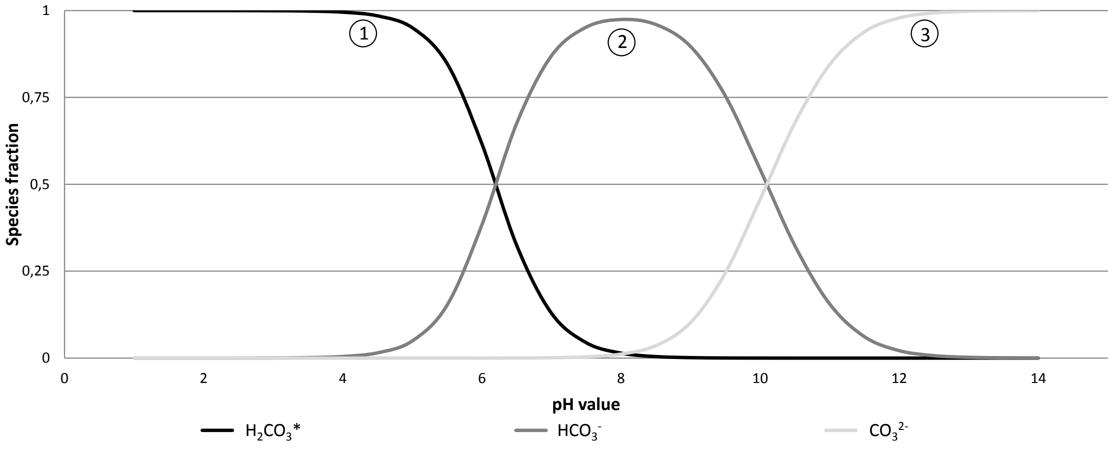

Figure 2.5. The species fraction of the carbonate species as a function of the pH value. The three numbered circles represent the total alkalinity, carbonate alkalinity and caustic alkalinity, respectively.

When the alkalinity is increased, i.e., the concentration of carbonate, bicarbonate and hydroxyl ions are increased, the saturation index is also increased.

If the alkalinity is too high it is difficult to change the pH value. This means that adding acid does not affect the pH value of the water. As more acid is added to change the pH value, the amount of dissolved solids is raised.

2.2.5 Total dissolves solids

The total dissolved solids (TDS) is a measure of the total amount of dissolves solids in the water. It can be calculated from a conductivity measurement of the water. The conductivity measurement is a measure of the ion activity expressed in terms of its capacity to conduct electrical current. TDS is directly related to the conductivity at low ionic strength. When the ion concentration, and thus, TDS is increased, the conductivity is increased as well. The ion concentration eventually reaches a point where cations and anions interact because of the density. This interaction decreases the ability of the ions to conduct electric current and the conductivity is no longer directly related to the amount of TDS. As the concentration of ions increases further, their impact on the conductivity is further decreased until it reaches a point where an increase in ion concentration no longer has an effect on the conductivity. [Snoeyink and Jenkins, 1980]
The ionic strength can be calculated from both the TDS and conductivity by the following formulae.

$$\mu = 2.5 \cdot 10^{-5} \cdot TDS \tag{2.31}$$

$$\mu = 1.6 \cdot 10^{-5} \cdot \kappa \tag{2.32}$$

Where:

μ	Ion strength [M]
TDS	Total dissolved solid [mg/L]
κ	Conductivity [μS/cm]

Combining these formulae, the relation between TDS and conductivity is found to be

$$TDS = 0.64 \cdot \kappa \tag{2.33}$$

[Snoeyink and Jenkins, 1980].
The amount of TDS increases when disinfectants, other chemicals and pollution from bathers are added to the pool water. The TDS should always be monitored by comparison between pool water and source water as the source water also contains some degree of dissolved solids. The TDS of the pool water should not be more than 1000 mg/L above source water concentration. [PWTAG, 2009; Queensland Government, 2004]

Chlorination 3

When chlorine is used for disinfection, the optimal pH value range is 7.5-9.3 with a maximum reaction rate at approx. pH 8.4 according to [Snoeyink and Jenkins, 1980]. When the pH value exceeds this range, the disinfection is no longer at its best as the pK$_a$ for hypochlorous acid and ammonia are 7.54 and 9.25, respectively [Andersen et al., 2007]. Three different forms of chlorine can be used as a disinfectant in pool water: Chlorine gas, sodium hypochlorite and calcium hypochlorite. When chlorine gas is added to the water it reacts with water to form hypochlorous and hydrochloric acid as described in formula 3.1.

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + HCl_{(aq)} \tag{3.1}$$

When sodium or calcium hypochlorite is added, it reacts with water, forming hypochlorous acid like the reactions in formula 3.2.

$$\begin{aligned} NaOCl_{(aq)} + 2H_2O_{(l)} &\rightarrow HOCl_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \\ Ca(OCl)_{2(aq)} + 2H_2O_{(l)} &\rightarrow 2HOCl_{(aq)} + Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \end{aligned} \tag{3.2}$$

When hypochlorous acid is formed in the water, it rapidly undergoes equilibrium with hypochlorite.

$$HOCl_{(aq)} + H_2O_{(l)} \rightleftharpoons OCl^-_{(aq)} + H_3O^+_{(aq)} \tag{3.3}$$

Because of this equilibrium, the pH value is an important parameter in the disinfection process. This will be further discussed in chapter 4.

When chlorine in the form of Cl_2, HOCl or OCl^- occurs in the pool water, it is referred to as *free chlorine*. Chlorine in the form of NH_2Cl, $NHCl_2$ and NCl_3 is referred to as *combined chlorine*. Together free chlorine and combined chlorine is referred to as *residual chlorine*. [Stumm and Morgan, 1996]

The progress of chlorination and breakpoint chlorination

When the level of combined chlorine approaches or exceeds the recommended, it can be reduced by the use of breakpoint chlorination. By using breakpoint chlorination, a high amount of chlorine is added to the pool. This chlorine reacts with DBPs, precursors and combined chlorine. As an example free chlorine in excess can react with ammonia as illustrated in formula 3.4.

$$3HOCl_{(aq)} + 2NH_{3(aq)} \rightarrow N_{2(g)} + 3HCl_{(aq)} + 3H_2O_{(l)} \tag{3.4}$$

If free chlorine is not in excess, combined chlorine are formed instead. Figure 3.1 illustrates the residual chlorine and nitrogen residual as a function of chlorine dose added to the pool in relation to the initial concentration of nitrogenous compound (here illustrated with ammonia). In figure 3.1a it is seen that the chlorine residual is raised proportional to the ratio of chlorine and ammonia until a ratio of 1 is reached. From this point it decreases till a ratio is 1.5 is reached. If the ratio is further raised, the combined chlorine is not affected. The dotted line represents the concentration of free chlorine, which increases when chlorine is added in ratios higher than 1.5.

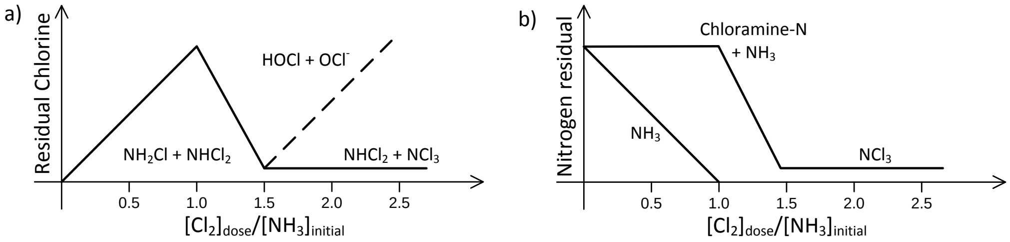

Figure 3.1. Chlorine and nitrogen residual as a function of chlorine to nitrogen ratio during chlorination [Snoeyink and Jenkins, 1980; Stumm and Morgan, 1996].

Figure 3.1b illustrates the residual nitrogen as a function of chlorine-nitrogen ratio. As the concentration of nitrogenous compounds in the pool, here ammonia, is not zero at the beginning, the line does not start in origo as is the case for chlorine. When chlorine is added and thus, the ratio of chlorine and nitrogen is raised, the residual nitrogen in the ammonia form is decreased. However, the general residual nitrogen is not changed as combined chlorine is formed. When the chlorine-nitrogen ratio reaches 1 the residual nitrogen of ammonia reaches zero and the total residual nitrogen starts to decrease. When the ratio is raised to 1.5 the residual nitrogen reaches a minimum of which it stays, even when the ratio of chlorine-nitrogen is raised. The two graphs in figure 3.1 can be combined to a more general graph as illustrated in figure 3.2. [Snoeyink and Jenkins, 1980]

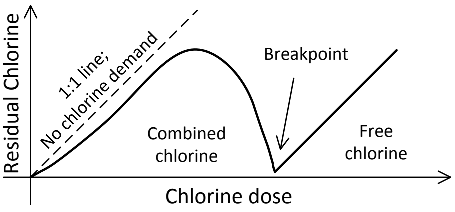

Figure 3.2. The progress of chlorination and breakpoint chlorination [Stumm and Morgan, 1996; Snoeyink and Jenkins, 1980].

Figure 3.2 illustrates the general progress of chlorination. When free chlorine is added to the pool, the amount of residual chlorine is increased till the ratio of 1 is reached. This decrease is caused by a depletion of combined chlorine precursors. The chlorine residual decreases till a point where free chlorine is added in excess, which typical is when the ratio of chlorine to nitrogen reaches 1.5 as illustrated in figure 3.1. The dotted line illustrates the chlorine residual if no precursors are in the pool. Breakpoint chlorination is chlorination to the point where the chlorine residual increases proportional to the chlorine dose. Thus, nitrogen residual is kept steady close to zero. [Stumm and Morgan, 1996; Snoeyink and Jenkins, 1980]

Part II

Mathematical Model

"This part contains the establishment, validation and discussion of the mathematical model. Chapter 4 concerns the establishment. In this chapter the considerations and assumptions made during the establishment are included. The next chapter includes the validation of the model. Here it is tested against three set of data. The last chapter in this part is the discussion of the model and the validity of it."

4 Mathematical Model for Accumulation in Swimming Pools

With basis in the literature review and problems in Køge a mathematical model is made in the form of a mass balance for combined chlorine in a pool. A sketch of the pool system with inlets, outlets and other that affects the mass of the combined chlorine in the water is illustrated in figure 4.1. The inlets are written in green and the outlets in red.

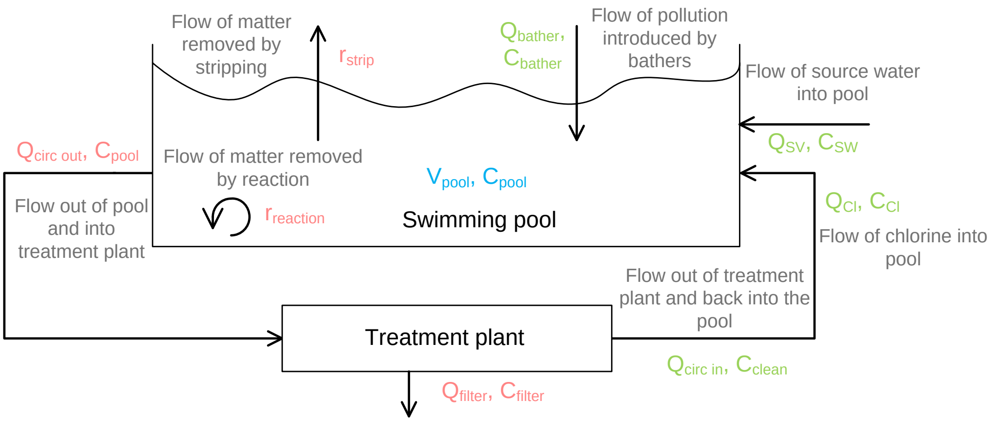

Figure 4.1. Sketch of a pool with in- and outlets, treatment plant and flow used for the mass balance.

The total flow of water in the pool system is a flow out of the pool and into the treatment plant, a flow out of the treatment plant and back into the pool along with a flow of source water and chlorine into the pool. The flow into the treatment plant is equal to the flow out of the pool and the flow out of the treatment plant is equal to the flow out of the pool minus the flow of water lost when filters are back flushed. A compensation is with a flow of source water into the pool. The chlorine is added to a part of the flow from the treatment plant into the pool. Besides the flow of water, a flow of pollution introduced by bathers is added to the system and a flow of matter removed from the pool by stripping. Finally some matter is removed and formed by reaction in the pool water.

4.1 The establishment of the mass balance

The mass balance is established from the general equation for mass balances.

$$Mass\ accumulated = mass\ added - mass\ removed - mass\ converted \tag{4.1}$$

[Fogler, 2006; Klausen, 2010]. By inserting the actual in- and outputs the accumulated mass is found by

$$\begin{aligned} V_{pool} \cdot \frac{dC}{dt} =& (C_{bather} \cdot Q_{bather} + C_{SW} \cdot Q_{SW} + C_{clean} \cdot Q_{circ} + C_{Cl} \cdot Q_{Cl}) \\ & - (C_{pool} \cdot Q_{circ} + C_{filter} \cdot Q_{filter} + r_{strip}) - r_{reak} \end{aligned} \tag{4.2}$$

Where:

V_{pool}	Pool volume [m^3]
dC	Change in concentration [mg/m^3]
dt	Time span [h]
C_{bather}	Concentration added by bathers [mg/pers $\cdot$ h]
Q_{bather}	Bather load [pers/h]
C_{SW}	Concentration added by source water [mg/m^3]
Q_{SW}	Flow of source water into the pool [m^3/h]
C_{clean}	Concentration in water from treatment plant [mg/h]
Q_{circ}	Circulation flow of the pool [m^3/h]
C_{Cl}	Concentration added by chlorine addition [mg/m^3]
Q_{Cl}	Flow of chlorine into the pool [m^3/h]
C_{pool}	Concentration in pool [mg/m^3]
C_{filter}	Concentration removed by filter [mg/m^3]
Q_{filter}	Flow of water lost by back flush of filter [m^3/h]
r_{strip}	Rate of matter removed by striping [mg/h]
r_{reak}	Rate of matter removed by reaction [mg/h]

[Klausen, 2010].

During the set-up of the mathematical model for accumulation in swimming pools, some considerations must be made with regard to the different in- and outputs.

4.1.1 Addition by bathers

As stated earlier, pollution is brought into the pool by both bathers and source water. This pollution reacts with the free chlorine in the pool and DBPs are formed. As an example of these DBPs are chloramines, which are formed when nitrogenous compounds are oxidised by free chlorine in the pool water. Chloramines will as stated in the introduction be used as a model compound for the set up of this model.

When matter is released into the pool by bathers, the term human body excretion (HBE) is used. Several studies of the composition of HBE and its reaction with free chlorine have been made and the two major contributors are found to be urine and sweat. World Health Organization [2006] states that the distribution of nitrogen in urine and sweat is as shown in table 4.1.

Table 4.1. The nitrogen distribution in urine and sweat [World Health Organization, 2006].

Compound	Urin % of total nitrogen	Sweat % of total nitrogen
Urea	68	84
Ammonia	18	5
Amino acids	5	2
Creatine	1	5
Others	8	4

The studies of these have lead to replica mixtures (body fluids analogs), which are to be used for experiments and laboratory scaled model pools. The composition of two of these body fluid analogs are listed in table 4.1.1. [Kanan and Karanfil, 2011]

Table 4.2. Composition of body fluid analog B and G by Kanan and Karanfil [2011].

Ingredients (B)	[mg/L]	Ingredients (G)	[mg/L]
Urea	23000	Urea	62.6
Creatinine	1250	Creatinine	4.3
Glutamic acid	300	Uric acid	1.5
Aspartic acid	850	Latic acid	3.3
Glycine	450	Albumin	9.7
Histidine	200	Glucuronic acid	1.2
Lysine	75	Ammonium chloride	7.0
		Sodium chloride	22.1
		Sodium sulfide	35.3
		Sodium bicarbonate	6.7
		Potassium phosphate	11.4
		Potassium sulfate	10.1

The volume of matter added by bathers is found in studies of bather pollution as by Judd and Bullock [2003], where it is found that the average pollution per bather is 50 mL of urine and 200 mL of sweat per hour. This is referred to as a guideline for matter brought into the pool by others. This will also be the reference for this model, even though others like World Health Organization [2006] states that an average bather releases 25-30 mL of urine and Cimetiere and De Laat [2009] states that an average bather releases 25-80 mL of urine and 200-1000 mL of sweat per hour, respectively. The volumes by Judd and Bullock [2003] are used in this work as these are often referred to by others.

The bather load varies depending on pool size, purpose and time of day, for which reason the bather load must be changeable. The maximum permitted bather load is defined by a certain surface area per bather. The areas are shown in the table 4.3.

Table 4.3. Bather area for different pool depts [Danish Standard, 1996].

Depth [m]	Water area per bather [m^2]
≥ 1.5	4.5
< 1.5	2.5
< 0.5	1.0

The contribution from bathers is entered into the model on [Enclosures-CD,Mathematical model] as a concentration, e.g., $C_{\text{bather}} = 50\,\text{mg/pers} \cdot \text{h}$ and a flow of bathers, which is equal to the bather load, e.g., $Q_{\text{bather}} = 30\,\text{pers}$.

4.1.2 Addition from source water

While the effect of HBE on pool conditions has been thoroughly studied, the effect of source water has not. The concentration and composition of matter added by the source water varies according to the location of the pool and the type of water used. In Denmark water from the drinking supply is used as source water. This water origins from groundwater of which the chemical composition varies as a result of different subsoil. Due to this fact a study of the content in the drinking water at different locations in Denmark is made. Figure 4.2 illustrates the selected locations.

Figure 4.2. The location of the selected waterworks for the study of composition of matter in source water that could affect the pool water quality.

The water analyses from the 12 waterworks are compared for content of nitrogenous compounds and compounds that affect the saturation index. Table 4.4 lists the average concentration of these in the drinking water from the 12 waterworks. An analysis of the composition of the matter from the specific waterworks is included in Appendix D.

Table 4.4. Average content of relevant compounds in drinking water from chosen waterworks in Denmark [Hansen, 2012].

Compound	Unit	Average content
Ammonium	[mg/L]	0.01
Nitrate	[mg/L]	3.45
Nitrite	[mg/L]	0.01
Calcium	[mg/L]	85.75
Bicarbonate	[mg/L]	260.75
Hardness	[°dH]	15.14
Conductivity	[mS/m]	58.62
pH	[–]	7.56
Temperature	[°C]	12.34

In case of an analysis with concentration below the detection limit, the limit is used for calculation of the average. This could lead to a small overestimate.

The contribution from source water is entered into the model as a concentration of nitrogenous compounds, which is converted into combined chlorine, e.g., $C_{SW} = 10$ mg/m^3 and the flow, which is equal to the water lost by back flush of filters per hour, e.g., $Q_{SW} = 0.3$ m^3/h.

4.1.3 Addition from chlorine solution

As chlorine is added to a small stream of the pool water, often in the liquid form sodium hypochlorite, it is not expected that the chlorine addition will introduce pollution to the pool water. However, the chlorine addition is incorporated into the model, as it makes it possible for later use of the model with other substances in focus.
It is not expected that the chlorine addition contributes to the chemical water quality with other than a raise in TDS, but a contribution to the human water quality by addition of DBPs are made. The chlorine addition is incorporated for later use.

4.1.4 Removal of matter by stripping

As ammonia and some of the chloramines are volatile, a remove of matter by stripping is possible. The effect of this is examined as it is a possible source to removal of matter from the pool water and thus has to be incorporated into the model.

Ammonia

To determine the effect of stripping of ammonia from the water on the chemical equilibrium and reactions in the water, the ratio of aqueous and gaseous ammonia is examined. This is done by converting the partial pressure of ammonia to a molar concentration of gaseous ammonia in an air volume equal to the pool volume. The concentration of aqueous and gaseous ammonia is plotted as a function of the pH value in figure 4.3. The conversion of the partial pressure to molar concentration makes it suitable for comparison and for determination of the stripping effect on the concentration of aqueous ammonia. In figure 4.3 the molar concentration of ammonia in water is read off the primary y-axis and in air off the secondary y-axis.

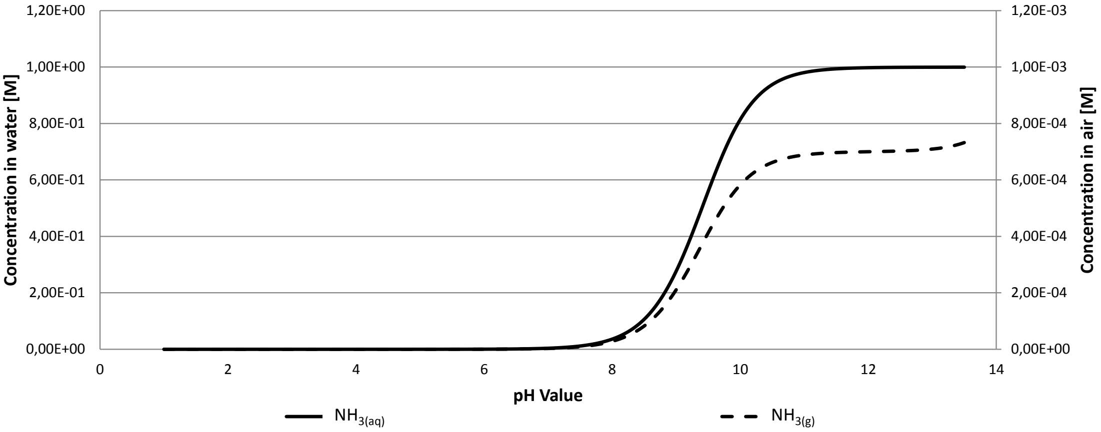

Figure 4.3. Concentration of ammonia in water and air in the pH range 1-13. The full line represents the aqueous ammonia and is read off the primary y-axis. The dashed line represents the gaseous ammonia, which is read off the secondary y-axis.

Figure 4.3 shows that the concentration of both aqueous and gaseous ammonia is increased when the pH value is increased. At pH 9 the aqueous concentration is increased to approx. 0.3 M, while the gaseous concentration is only increased to approx. 0.0003 M. By calculating the percentage of ammonia in water and air for each pH value it is evident that the aqueous form of ammonia is dominant. Table 4.5 lists the percentage distribution, which is the same for all pH values.

Table 4.5. Percentage of aqueous and gaseous ammonia with the assumption that the air volume is equal to the water volume. The percentage distribution is the same for every pH value in the range 1-13.

$NH_{3\,(aq)}$	$NH_{3\,(g)}$
99.9 %	0.1 %

Henry's constant for this equilibrium is 53.45 M/bar, which is in accordance with the data published on NIST.com by U.S. Secretary of Commerce [2011]. As the percentage of ammonia in the air is only 0.1 % of the total ammonia at any pH value the stripping of ammonia will be considered to be zero in the model. An Excel spreadsheet with the calculations can be found on [Enclosures-CD,Partial pressure of ammonia].

Chloramines

Chloramines are believed to be volatile and thus, can strip off to the air above the pool water. In a study of Henry's constant of chloramines in cooling towers by Holzwarth et al. [1984] it is found that trichloramine is the far most volatile. Henry's constants for all chloramines and ammonia are listed in table 4.6.

Table 4.6. Henry's constants for ammonia and chloramines found by Holzwarth et al. [1984].

	Henry's constant at 20°C	Henry's constant at 40°C
NH_3	0.71	—
NH_2Cl	0.45	1.28
$NHCl_2$	1.52	3.76
NCl_3	435.00	1067.00

Henry's constants were in the experiment by Holzwarth et al. [1984] measured as the mole fraction in the gaseous phase divided by the mole fraction in the aqueous phase. From table 4.6 it is seen that Henry's constants for mono- and dichloramine are at the same level as that of ammonia. As the stripping of ammonia is negligible so are the stripping of mono- and dichloramine.

However, trichloramine is a 1000 times more volatile and will thus evaporate to the air above the pool [Schmalz et al., 2011; Weaver et al., 2007]. According to Schmalz et al. [2011] Henry's constant of trichloramine is 11.6 bar/M at 25 °C . Compared to ammonia (0.019 bar/M), trichloramine is far more volatile and stripping of trichloramine must thus be accounted for in the model.

Schmalz et al. [2011] found fluxes for trichloramine transfer from water to air to be between $1.8 \cdot 10^{-3}$ g/m$^2 \cdot$ h and $12.6 \cdot 10^{-3}$ g/m$^2 \cdot$ h for pools with quiescent water surface and rough water surface, respectively. The conclusion of Schmalz et al. [2011] is that the flux for water to air transfer in pools is highly dependent on the water-air surface and thus, the bather load and ventilation system. This conclusion is second by Weng et al. [2011]. As the stripping of trichloramine is highly dependent of the bather load and ventilation system, it is not easily accounted for in the model but by use of data from a whirlpool in Lalandia collected by Klausen and Kristensen [2008], an estimate of the chloramine removed by stripping can be made.

4.1.5 Removal of matter by reaction

When matter enters the pool water some reactions will occur. Reactions of nitrogen containing compounds with free chlorine have been widely studied. An overview of the reactions based on the literature review is included in appendix D. As an example the reaction of ammonia with free chlorine is included here because it will be the compound used to set-up the mathematical model.

In water the added ammonia is in equilibrium with ammonium.

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{4.3}$$

The distribution of ammonia and ammonium as a function of the pH value is illustrated in figure 4.4 along with the hypochlorite and hypochlorous acid equilibrium distribution.

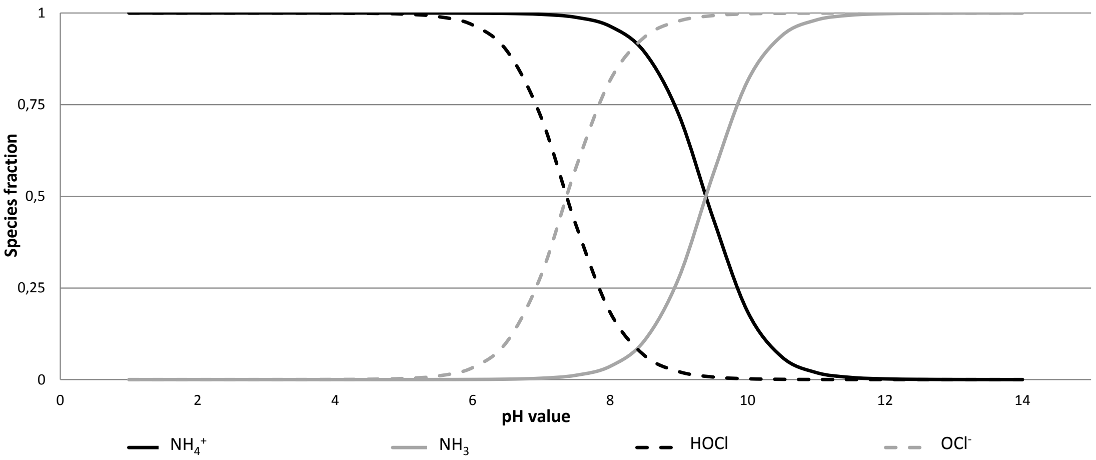

Figure 4.4. Ammonia - ammonium and hypochlorous acid - hypochlorite equilibrium distribution as a function of the pH value. The pKa value for ammonium and hypochlorous acid is 9.3 and 7.5, respectively.

The equilibrium for the hypochlorous acid and hypochlorite is

$$OCl^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons HOCl_{(aq)} + OH^-_{(aq)} \tag{4.4}$$

From these two equilibrium, four initial chlorination reactions are possible depending on the pH value.

$$NH_{3(aq)} + OCl^-_{(aq)} \rightarrow NH_2Cl_{(aq)} + OH^-_{(aq)} \tag{4.5}$$

$$NH_{3(aq)} + HOCl_{(aq)} \rightarrow NH_2Cl_{(aq)} + H_2O_{(l)} \tag{4.6}$$

$$NH^+_{4(aq)} + OCl^-_{(aq)} \rightarrow NH_2Cl_{(aq)} + H_2O_{(l)} \tag{4.7}$$

$$NH^+_{4(aq)} + HOCl_{(aq)} \rightarrow NH_2Cl_{(aq)} + H_3O^+_{(aq)} \tag{4.8}$$

Further reaction to di- and trichloramine is not as widely discussed in the literature, but is expected to follow the mechanism of the initial reaction. Studies of the initial reaction mechanism have been performed by several scientists including Deborde and von Gunten [2008], Schmalz et al. [2011] and Qiang and Adams [2004]. Qiang and Adams [2004] examined the reaction of ammonia and free chlorine using stopped-flow spectrophotometry and found the reaction in formula 4.6 to be the dominating of the four reactions. This is accepted and second by several scientists, e.g., Schmalz et al. [2011] and Deborde and von Gunten [2008]. It is found that under acidic conditions, where ammonium is the prevailing nitrogen species, the reaction of the initial disinfection step is slowed by a factor of 10^6, which supports the theory of Qiang and Adams [2004]. [Schmalz et al., 2011; Qiang and Adams, 2004]

With respect to chlorine it is found that when the pH value is lowered, the formation of combined chlorine is increased. This is in accordance with the pH dependent equilibrium of hypochlorite and hypochlorous acid. The formation of combined chlorine is considerably lower when the pH value is raised to 7.7, where hypochlorite is the main chlorine species. [Schmalz et al., 2011]

However, a decrease in the pH value below the pKa of ammonium, favour ammonium rather than ammonia and the initial step of the combined chlorine formation will be

slowed. On the contrary, the following two steps will be speeded as the hypochlorous acid is favoured. [Schmalz et al., 2011]
Thus, it is argued that the reaction in formula 4.6 is the dominating reaction of ammonia and free chlorine in pool water as stated by Qiang and Adams [2004]. The three others can thus be neglected.
The reaction between the elementary form of ammonia and hypochlorous acid is believed to be an electrophilic attack of the chlorine atom on the lone pair of the amine nitrogen.

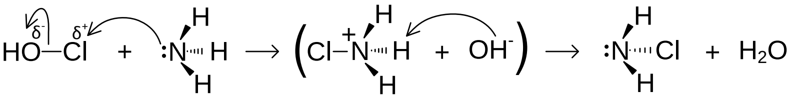

Figure 4.5. The electrophilic attack of the chlorine atom on the nitrogenous lone pair. As an intermediate $NH_3{-}Cl^+$ is formed.

This theory is confirmed by the fact that the chlorine reactivity decreases when the number of chlorine on the amine nitrogen increases, as mono-, di- and trichloramine is formed. This decrease in reactivity is caused by the high electronegativity of the chlorine atom. This pulls the free electrons towards the chlorine atom thus, creating a less nucleophilic molecule. [Deborde and von Gunten, 2008; Schmalz et al., 2011; McMurry and Simanek, 2007]
This theory is also in accordance with ammonia being more reactive than ammonium as the ammonium nitrogen no longer has a lone pair because it is preoccupied by the extra hydrogen atom.

The reaction of ammonia and hypochlorous acid is a redox reaction as the oxidation states of nitrogen and chlorine change during reaction. In formula 4.9 the initial step in the disinfection reaction is illustrated.

$$\overset{-III}{N}H_3 + HO\overset{+I}{Cl} \rightarrow \overset{-I}{N}H_2\overset{-I}{Cl} + H_2O \tag{4.9}$$

The oxidation states for nitrogen and chlorine are included and it is seen that the oxidation state of nitrogen increases with two simultaneously by the oxidation state for chlorine decreases by two. The product of reaction 4.9 undergoes further oxidation to form di- and later trichloramine.

$$\overset{-I}{N}H_2\overset{-I}{Cl} + HO\overset{+I}{Cl} \rightarrow \overset{+I}{N}H\overset{-I}{Cl}_2 + H_2O \tag{4.10}$$

Here the oxidation state of nitrogen increases by further two and the oxidation state of chlorine in hypochlorous acid decreases by two as before.
If excess hypochlorous acid is present like in the case of breakpoint chlorination, a third oxidation reaction of nitrogen can occur. That is the formation of trichloramine.

$$\overset{+I}{N}H\overset{-I}{Cl}_2 + HO\overset{+I}{Cl} \rightarrow \overset{+III}{N}\,\overset{-I}{Cl}_3 + H_2O \tag{4.11}$$

In this reaction the oxidation state of nitrogen is further increased by two to give plus three.

The reaction rate constant, k_r, of these reactions has also been studied and several have been published. Jafvert and Valentine [1992] and Deborde and von Gunten [2008] collected some of these in an overview.

Table 4.7. Reaction rate constants for reactions of ammonia and hypochlorous acid. [Jafvert and Valentine, 1992; Qiang and Adams, 2004; Deborde and von Gunten, 2008].

Reaction	k_r (25°C) $[M^{-1}h^{-1}]$	Reference
$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$	$1.5 \cdot 10^{10}$	[Jafvert and Valentine, 1992]
	$1.11 \cdot 10^{10}$	[Qiang and Adams, 2004]
	$1.51 \cdot 10^{10}$	[Deborde and von Gunten, 2008]
	$1.04 \cdot 10^{10}$	[Deborde and von Gunten, 2008]
$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	$1.0 \cdot 10^{6}$	[Jafvert and Valentine, 1992]
	$5.4 \cdot 10^{5}$	[Deborde and von Gunten, 2008]
	$1.26 \cdot 10^{6}$	[Deborde and von Gunten, 2008]
$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$	—	
$NHCl_2$ + 2 HOCl + H2O $\rightarrow$ $NO_3^- + 5H^+ + 4Cl^-$	$8.3 \cdot 10^{5}$	[Jafvert and Valentine, 1992]

The reaction rate constants listed in table 4.7 for the formation of monochloramines are $1.29 \cdot 10^{10} \pm 0.25$ $M^{-1}h^{-1}$. With regard to dichloramine, the rate constant is $0.93 \cdot 10^{6} \pm 0.36$ $M^{-1}h^{-1}$. The standard deviation implies a small disagreement for the reaction rate constants for the formation of the first two chloramines. This could easily be caused by different conditions during the experiments. For trichloramine no specific reaction rate has been determined or suggested by neither Jafvert and Valentine [1992] or Deborde and von Gunten [2008]. The reaction rate constant for the ammonia reaction is a factor four higher than that of monochloramine, which is in accordance with the theory of an electrophilic attack of the hypochlorous acid on the nucelophilic ammonia. This supports the theory of a less reactive oxidation when chlorine is attached to the nitrogen.

The unit of the reaction rate constants tells that the formation of mono- and dichloramines are of second order, i.e., depend both on the ammonia/monochloramine concentration and the concentration of hypochlorous acid. The reaction rate for these reactions are thus found by

$$-r = k_r \cdot [N][HOCl] \tag{4.12}$$

Where:

$-r$	Reaction rate [M/h] or [mg/h]
k_r	Reaction rate constant $[M^{-1}h^{-1}]$ or $[m^3/mg \cdot h]$
$[N]$	Concentration of the nitrogen containing compound [M] or $[mg/m^3]$
$[HOCl]$	Concentration of hypochlorous acid [M] or $[mg/m^3]$

As the model is set up with concentrations given in mg/m^3, the reaction rate constant is recalculated from M to mg/m^3. The reaction rate constant is typed into the Excel

spreadsheet with the molar concentration unit and recalculated to the mass concentration unit. The reaction rate is calculated as a function of the current ammonia/monochloramine and hypochlorous acid concentrations.
The reaction rate is calculated by the model using formula 4.12 and the average reaction rate constant from table 4.7.

4.1.6 Removal of matter by treatment and flow of treated water back into the pool

The water cleaned in the treatment plant is transported back into the pool. As the treatment plant does not remove all contamination and foreign matter, this water will contain some degree of matter.
The removal of matter in the treatment plant involves different methods including sand filter and UV radiation. These methods are briefly elaborated in appendix C.
As the model is set up using nitrogenous compounds, which form combined chlorine, the treatment method in focus is UV radiation.
The removal of matter in the treatment plant is determined by the use of data from Klausen and Kristensen [2008] where the efficiency for a UV lamp is found.

Table 4.8. Combined chlorine decay rate constant found by Klausen and Kristensen [2008]. The UV lamp was on for two nights and off for one night. The decay rate constant when the UV lamp was off describes the natural decay of combined chlorine, which includes reaction and stripping.

	On, night 1	On, night 2	Off
Combined chlorine decay rate constant [g/m^{3}h]	0.0303	0.0267	0.0197
Decay rate constant without natural decay [g/m^{3}h]	0.0106	0.0070	

When the UV lamp was off, a decay of 0.0197 g/m^{3}h was found. This decay is a result of stripping and further reaction, e.g., to nitrate. When the natural decay is subtracted from the UV decay rate constant, it is seen that removal by the natural decay is greater than the contribution of the UV lamp.
The decay rate constants for the UV lamp listed in table 4.8 are recalculated to a percentage, due to the fact that removal of a constant mass will lead to a high cleaning efficiency at a low bather load and a low cleaning efficiency at a high bather load. The percentage is calculated under the assumption that the combined chlorine level is 0.7 mg/L in the pool water. This may lead to an error, which will be discussed in chapter 6.

After considering the parameters of the model represented by formula 4.2, data can be entered and the concentration of accumulated matter in the pool calculated. The final formula for the concentration of combined chlorine accumulated in the pool is

$$\begin{aligned}&V_{pool} \cdot \frac{dC_{pool,n}}{dt} = \\ &C_{pool,n-1} + ((C_{bather} \cdot Q_{bather} + C_{SW} \cdot Q_{SW} + C_{Cl} \cdot Q_{Cl} + C_{clean} \cdot Q_{clean}) \\ &- (C_{pool,n-1} \cdot Q_{pool} + r_{strip} + r_{reaction}))\end{aligned} \tag{4.13}$$

An Excel spreadsheet with the mathematical model can be found on [Enclosures-CD,Mathematical model].

Validation of the Mathematical Model

5

The mathematical model is tested with data collected from two public swimming pools and an aqua park in Denmark to determine if the model correlates with reality. The validation is based on data collected by Klausen and Kristensen [2008], Pedersen [2012] and Andersen [2012].

5.1 Whirlpool - Lalandia

For this test data from Klausen and Kristensen [2008] is used. These data are from an outdoor whirlpool in the Danish aqua park Lalandia. The important system parameters for the test are

Volume	35	m^3
Circulation flow	90	m^3/h
Turnover period	0.1	h
UV rate constant	7	$mg/m^3 \cdot h$
Cleaning efficiency	0.13	%
Natural decay rate constant	19.7	$mg/m^3 \cdot h$
Natural decay efficiency	0.28	%
Bather load	30	pers.
Bather standardised formation rate	100	$mg/pers \cdot h$ as Cl_2

The efficiency percentages are calculated from the rate constants of UV and natural decay and the assumption that the combined chlorine concentration in the pool is 0.7 mg/L as Cl_2. The UV and natural decay rate constants are adopted from Klausen and Kristensen [2008] along with the bather standardised formation rate of $100\,mg/pers \cdot h$ as Cl_2 as it was found to be the formation and removal rates for these data. The bather standardised formation rate is calculated from the formation and removal rates. When using this along with the removal rate constants, the results from the model must be identical with the results by Klausen and Kristensen [2008] if the model is in accordance with reality.

Besides the data listed above, the reaction rate constants from Schmalz et al. [2011] (listed in table 5.1) are used to produce the graph in figure 5.1. This graph should have a proper distribution of mono-, di- and trichloramine.

Table 5.1. Reaction rate constants for the chloramine formation from $NH_3/NH_2Cl/NHCl_2/NCl_3$ with free chlorine [Schmalz et al., 2011].

	NH_3 $[M^{-1}h^{-1}]$	NH_2Cl $[M^{-1}h^{-1}]$	$NHCl_2$ $[M^{-1}h^{-1}]$	NCl_3 $[h^{-1}]$
Reaction rate constant	$1 \cdot 10^{10}$	$1 \cdot 10^{6}$	$5 \cdot 10^{4}$	$2.7 \cdot 10^{-2}$

Figure 5.1 illustrates the concentration of trichloramine as the concentration of both mono- and dichloramine is zero. The concentration of trichloramine reaches a maximum level of 0.4 mg/L as Cl_2 and a minimum of approx. 0.1 mg/L as Cl_2, which is much lower than the results of Klausen and Kristensen [2008].

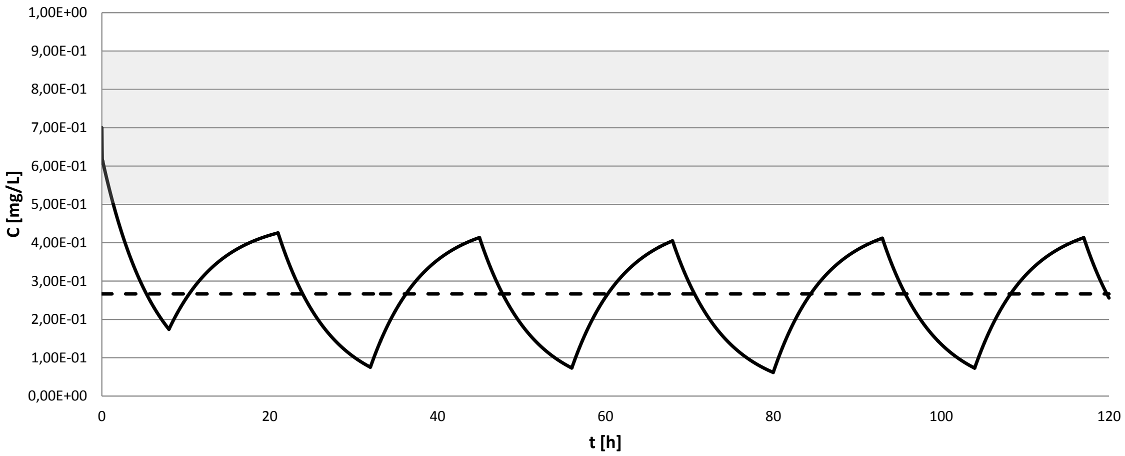

Figure 5.1. Concentration of trichloramine in the whirlpool in Lalandia found by the model. The combined chlorine is all in the trichloramine form. The grey area illustrates the expected level of combined chlorine and the dashed line the mean value of the results.

The tendency of the curve is matching the data by Klausen and Kristensen [2008], but the level is too low as the expected level is 0.6 to 0.9 mg/L as Cl_2. Furthermore the combined chlorine is all in the form of trichloramine. This does not agree with reality where the distribution of chloramines according to Schmalz et al. [2011] is approx. 80 % as monochloramine and 20 % as di- and trichloramine together. This percentage distribution is incorporated into to model instead of the reaction rate constants to see if this yields more realistic results. Figure 5.2 illustrates graphs for both mono- and dichloramine concentration with a distribution of 80 % of monochloramnie and 10 % of each di- and trichloramine. As the distribution of di- and trichloramine is equal, the concentrations of Cl_2 bound as di- and trichloramine are identical. Di- and trichloramine are set to be equal even though this possibly gives a higher trichloramine concentration than in a real pool. However, examining the actual distribution is beyond the scope of this thesis.

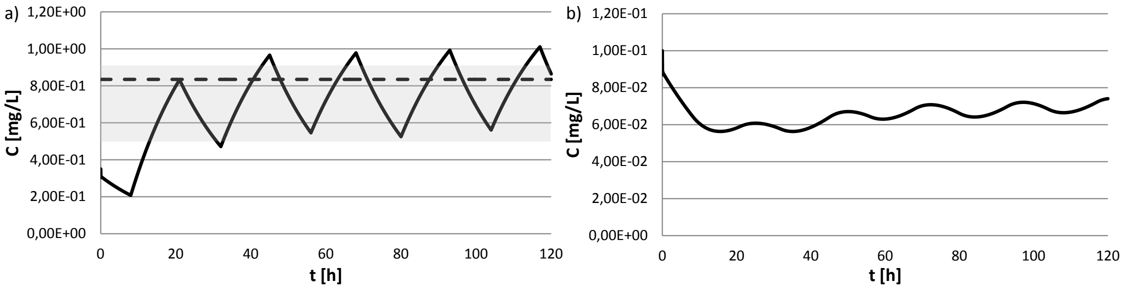

Figure 5.2. Graph of combined chlorine concentration given in mg/L as Cl_2. a) illustrates monochloramine and b) illustrates both di- and trichloramine concentration as the distribution of these is identical. The grey area illustrates the expected level and the dashed line the mean value of the resluts.

The concentration of monochloramine levels off at a maximum concentration of approx. 1.0 mg/L as Cl_2 at quasi steady state, which corresponds to the expected value of approx. 0.9 mg/L as Cl_2. Di- and trichloramine concentrations are both approx. 0.08 mg/L as Cl_2, which gives a total combined chlorine (covering both mono-, di- and trichloramine) concentration of approx. 1.16 mg/L as Cl_2. This is a bit higher than the measured 0.9 mg/L as Cl_2. It implies that the model is not in total agreement with reality. The slope for the increase in concentration is found to be 0.0351 mg/L · h, which is a bit lower than the expected 0.0593 mg/L · h from Klausen and Kristensen [2008].

For all the former graphs, a bather standardised formation rate of 100 mg/pers · h as Cl_2 is used as an input concentration. From the literature it is found that an average bather releases 50 mL urine and 200 mL sweat per hour [Kanan and Karanfil, 2011; Judd and Bullock, 2003]. If the composition of urine and sweat is as stated in section 4.1.1, each bather will release 690 mg of nitrogenous containing compounds, which will form combined chlorine when oxidised by hypochlorous acid. When the input concentration is set to 690 mg/pers · h as N the combined chlorine concentration develops as shown in figure 5.3.

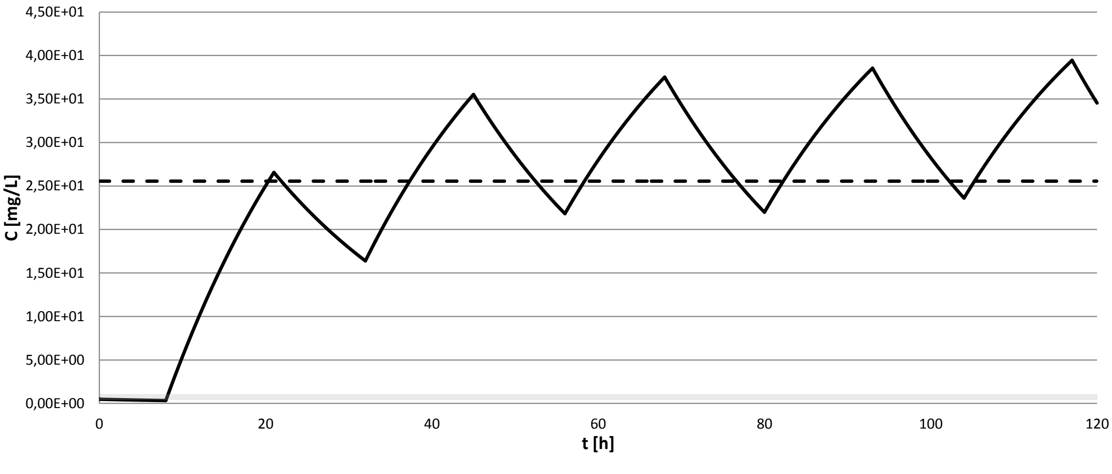

Figure 5.3. Combined chlorine formation when nitrogenous compound added by bathers is set to 690 mg/pers · h. Notice the concentration scale is times 10^1. The grey area illustrates the expected level of combined chlorine and the dashed line the mean value of the results.

When the input concentration by bathers is set to 690 mg/pers · h as N, the combined chlorine concentration in the pool reaches a maximum of above 40 mg/L as Cl_2. This is a very high concentration of combined chlorine as the maximum permitted concentration allowed by the Danish Standard [1996] is 1.0 mg/L and the German DIN 19436-1 is even stricter at only 0.2 mg/L. This deviation is discussed in chapter 6.

5.2 50 meter regular pool - Nørresundby

The model is also tested for regular pools. Data from a 50 meter regular pool in Nørresundby is used along with the 25 meter regular pool in Køge, which has problems with scale forming water as stated in the introduction. The swimming pool in Nørresundby is tested with three rates of natural decay and two bather loads. The parameters for the pool system in Nørresundby are

Volume	1600	m^3
Circulation flow	470	m^3/h
Turnover period	3.4	h
UV rate constant	10.3	$mg/m^3 \cdot h$
Cleaning efficiency	5.01	%
Natural decay rate constant	19.7/9.9/1.5	$mg/m^3 \cdot h$
Natural decay efficiency	9.58/4.81/0.73	%
Bather load	200/100	pers.
Bather standardised formation rate	500	mg/pers · h as Cl_2

When the volume, circulation rate and turnover period for the swimming pool in Nørrssundby are entered along with the UV rate constant and the natural decay rate constant for the whirlpool, the accumulation of combined chlorine are as shown in figure 5.4a. The curve starts at 0.7 mg/L as Cl_2, which is the initial concentration entered into the model, and decreases rapidly to zero. When bathers enter the pool, the combined chlorine concentration raises to approx. 0.05 mg/L as Cl_2. This quasi steady state level is extremely low for a 50 meters regular pool and is caused by the high natural decay rate entered into the model. As described earlier the stripping of primarily trichloramine is highly dependent of the water-air surface and the ventilation systems. Schmalz et al. [2011] found the water to air flux to be $12.6 \cdot 10^{-3}$ $g/m^2 \cdot h$ for pools with a rough water surface (whirlpool) and $7.0 \cdot 10^{-3}$ $g/m^2 \cdot h$ for a pools with a rippled water surface (normal used pool). If the ratio between these is transferred to the rate constant of the natural decay, it decreases from 19.7 $mg/^3 \cdot h$ to 9.9 $mg/m^3 \cdot h$. When this is entered into the model the accumulation for a pool with a rough water surface reaches 0.12 mg/L as Cl_2 as seen in figure 5.4b.

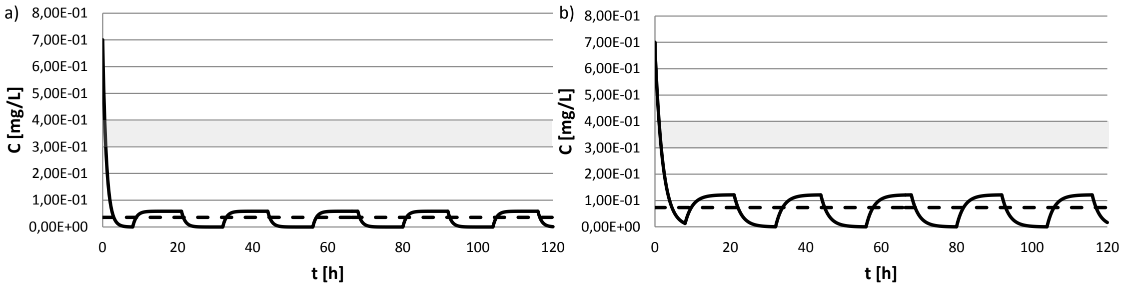

Figure 5.4. Concentration of accumulated combined chlorine of Nørresundby swimming pool with a natural decay of a whirlpool and a rippled surface pool, respectively. The expected level is illustrated with the grey area. The dashed line illustrates the mean value of the graph.

This is, however, nearly half as high as the expected 0.3 - 0.4 mg/L as Cl_2. When the pool accommodates no bathers, the accumulated concentration of combined chlorine drops to zero. This is not realistic as no pools have combined chlorine concentrations that reaches zero at night. For this reason the ratio between the flux for a pool with a rough water surface and a pool with a quiescent surface is used. The graph of this is shown in figure 5.5a. This gives a natural decay rate of $1.5\,\mathrm{mg/m^3 \cdot h}$ which gives a decay efficiency of 0.73 %. This efficiency is more similar to that found for the whirlpool in Lalandia. When this is entered into the model, the accumulated concentration reaches a quasi steady state level just above $0.5\,\mathrm{mg/L}$ as Cl_2. This is similar to the expected value of 0.3-0.4 mg/L as Cl_2 and the tendency of the curve is as expected.

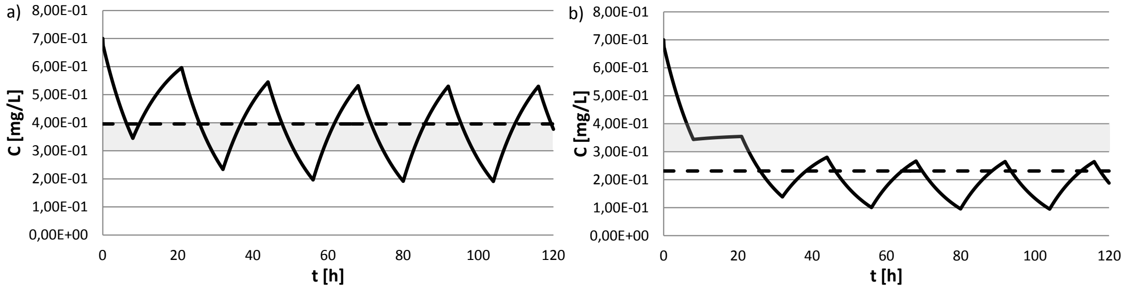

Figure 5.5. Combined chlorine concentration of a pool with a smooth water-air surface and a bather load of 200 and 100, respectively. The mean value is illustrated with the dashed line and the expected concentration of combined chlorine with the grey area.

The concentration increases when bathers enter the pool and decreases linearly when the bather load is zero as seen in figure 5.5a. The slope of the formation of combined chlorine is for the pool with a quiescent surface found to be $0.0279\,\mathrm{g/m^3 \cdot h}$ which is lower than expected, but similar to that found for the whirlpool in the previous section.
The graph in figure 5.5b illustrates, the accumulated concentration for half as many (100) bathers. It is seen that the concentration nearly reaches $0.3\,\mathrm{mg/L}$ which is approx. half as much as with 200 bathers.

Prior to the test of the stripping effect on chloramines concentration in Nørresundby pool, a test of the bather standardised formation rate was carried out. When the bather standardised formation rate for the whirlpool in Lalandia is used, the concentration of accumulated combined chlorine is very low as seen in figure 5.6a.

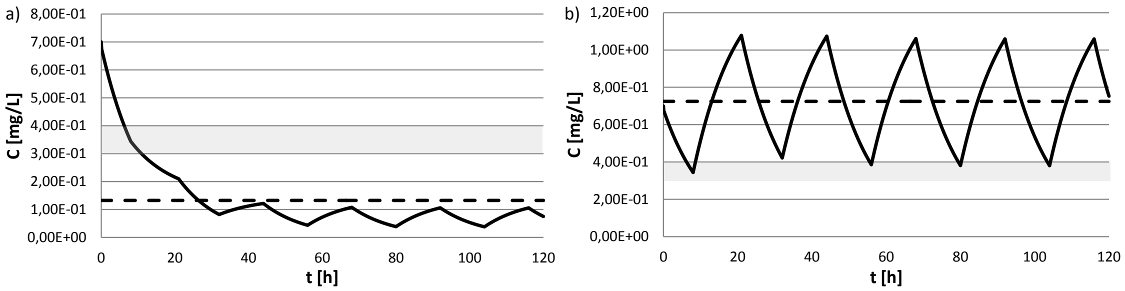

Figure 5.6. Combined chlorine in the regular pool with an input of 100 and 1000 mg/pers · h as Cl_2, respectively. The expected level is illustrated with the grey area. The dashed line illustrates the mean value of the results.

The natural decay rate used for these tests is equal to a pool with a quiescent surface. Thus, these graphs are comparable to figure 5.5a. The graph in figure 5.6b is when the bather standardised formation rate is set to 1000 mg/pers · h as Cl_2, which gives much higher concentrations of accumulated combined chlorine in the pool. As a bather standardised formation rate of 500 mg/pers · h as Cl_2 gives concentrations similar to those of the data from Pedersen [2012], this is used for testing of stripping rate and further tests as well.

5.3 25 meter regular pool - Køge

The parameters for the 25 meter regular pool in Køge (tested for a bather load of both 80 and 40) are

Volume	643	m^3
Circulation flow	291	m^3/h
Turnover period	2.21	h
UV rate constant	10.3	$mg/m^3 \cdot h$
Cleaning efficiency	3.25	%
Natural decay rate constant	1.5	$mg/m^3 \cdot h$
Natural decay efficiency	0.47	%
Bather load	80/40	pers.
Bather standardised formation rate	500	mg/pers · h as Cl_2

The UV rate constant is equal to that of Nørresundby swimming pool. However, as a result of different pool sizes, the UV cleaning efficiency is lower, 3.25 % against 5.01 % for Nørresundby. The bather load is scaled so the bather per volume ratio is the same. Figure 5.7a shows the concentration of combined chlorine for a bather load of 80 bathers, which reaches 0.7 mg/L as Cl_2 at day and drops to approx. 0.35 mg/L as Cl_2 at night.

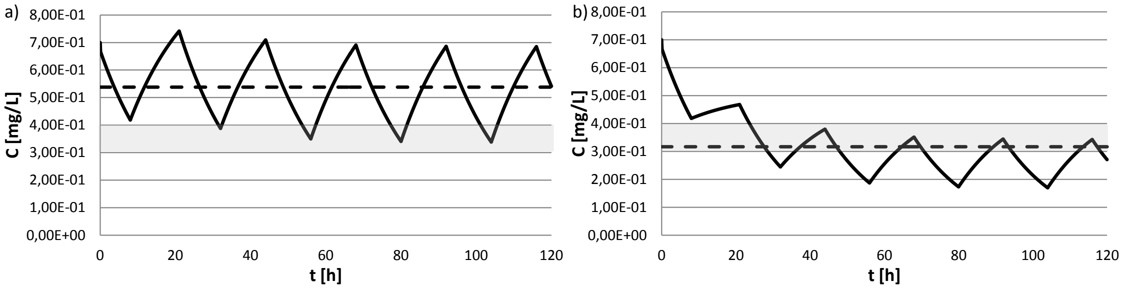

Figure 5.7. Combined chlorine in Køge swimming pool for a bather load of 80 and 40 persons, respectively. The dashed line represents the mean value of the results. The expected level of combined chlorine is illustrated with the grey area.

In figure 5.7b a graph of half the bather load is presented. The concentration of combined chlorine reaches a maximum concentration at quasi steady state of approx. 0.35 mg/L as Cl_2 at day and 0.2 mg/L as Cl_2 at night. This is partly in accordance with the data by Andersen [2012].

5.3.1 Variable bather load

A test of the pool in Køge is made with variable bather load during a week, to see the how the model accounts for this. The estimated bather load is listed in table 5.2

Table 5.2. The dynamic bather load for a week with higher bather load in the weekend.

Time	Weekday	Weekend
7.00-8.00	10	10
8.00-9.00	30	30
9.00-10.00	20	20
10.00-11.00	40	60
11.00-12.00	20	70
12.00-13.00	20	70
13.00-14.00	20	50
14.00-15.00	40	70
15.00-16.00	60	100
16.00-17.00	100	110
17.00-18.00	110	100
18.00-19.00	40	40
19.00-20.00	50	50
20.00-21.00	80	80
21.00-22.00	20	20

Figure 5.8 shows the concentration of the accumulated combined chlorine in the pool during a week with variable bather load as listed above.

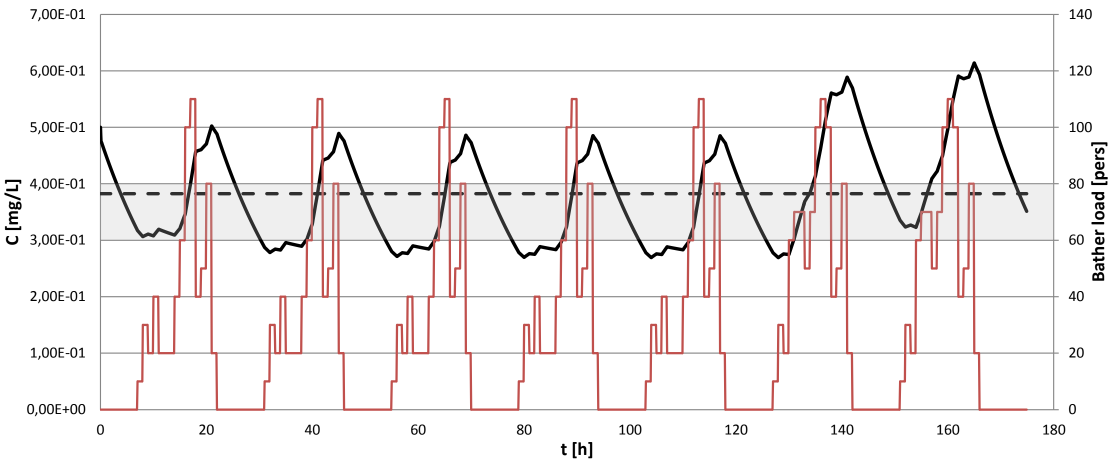

Figure 5.8. Concentration of accumulated combined chlorine for Køge swimming pool over a week with the dynamic bather load from table 5.2. The bather load is illustrated with the red line and is read off the secondary y-axis. The dashed line shows the mean value of the combined chlorine concentration and the grey area illustrates the expected level of combined chlorine.

It is seen from the graph that the amount of accumulated combined chlorine correlates with the bather load, which also is seen in figure 5.7. For figure 5.8 the bather load is illustrated with the red curve. When the bather load is increased or decreased during the open hours, the concentration of accumulated combined chlorine follows this increase or decrease. When the pool is closed and the bather load is zero for nine hours, the concentration decreases linearly.

It is seen that both the night and day concentrations for Monday are higher than for the rest of the working days. This is a result of a higher bather load during the weekend, i.e., it takes the pool an extra day to reach quasi steady state once again due to the extra combined chlorine formed during the weekend. After Tuesday the quasi steady state is found, where the maximum day concentration and the minimum night concentration is equal for Tuesday to Friday. In the weekend the accumulated combined chlorine reaches higher concentration as a result of the increased bather load. The level of combined chlorine is in general as expected, which is illustrated with the gray area in figure 5.8.

Discussion of the Mathematical Model and its Validity

6

The mathematical model is set up based on a formula published by Klausen [2010]. The model includes contributions from bathers, source water, chlorine and matter transported back from the treatment plant and also removal from stripping, reaction and the treatment plant. For all inputs and outlets some considerations and assumptions have been made.

With respect to contribution by bathers, the nitrogen percentage distribution from the World Health Organization [2006]. This is used rather than the mass distribution from the body fluid analogs, due to the composition and distribution varying a lot, as illustrated in table 4.1.1 on page 23. The amount of urine and sweat is in literature found to be 25-80 mL and 200-1000 mL per bather per hour, respectively. The amount of urine in the model is set to 50 mL per bather and for sweat 200 mL as these are often referred to. For this reason the results of the model will be comparable to work done by others [Kanan and Karanfil, 2011; Judd and Bullock, 2003].

Source water composition in Denmark is studied by means of water analyses from 12 scattered locations in Denmark. As this is only a small part of all waterworks in Denmark, the average composition may not be accurate. However, as the average composition is not to be used for any validation or simulation of the model, it is not significant to this work. For validation and simulations, specific locations and thus waterworks are used, which eliminates the error.

Chlorine is added to a small side-steam of the pool water separated in the treatment plant. It is in the model expected to be added as sodium hypochlorite and thus, the amount of nitrogen added by chlorine addition equals zero. As the model is set up with focus on an easy change of input compounds, the chlorine addition is entered as one might wish to use it for later work.

When ammonia enters the pool, an equilibrium of aqueous and gaseous ammonia appears. As this has an effect on nitrogen concentration in the pool water, the amount removed by stripping is determined. For an easy comparison, the partial pressure is converted to a molar concentration in an air volume equal to the pool volume. This gives a distribution with 99.9 % as aqueous ammonia. Thus it is reasonable to neglect the stripping of ammonia. With respect to chloramines, trichloramine is highly volatile and will evaporate from pool water, which will be discussed later in this chapter.

As the matter added by bathers and source water is oxidised by free chlorine in the pool water, some matter is removed and others are formed. The reaction is found to be an electrophilic attack of the chlorine atom of hypochlorous acid on the lone pair of the amine nitrogen. This is in accordance with the theory of an electrophilic attack [McMurry and Simanek, 2007] and the products of the reaction, which is enclosed in appendix D.

The removal of matter in the treatment plant is based on the results of Klausen and

Kristensen [2008], where the removal was found to 0.3 g/h. This removal is recalculated to a percentage, as the amount removed is a function of the concentration in the pool. The recalculation is based on an average concentration in the pool of 0.7 mg/L, which is not the case for all pools. This leads to an inaccuracy in the model. In cases where the concentration is higher than 0.7 mg/L, the model removes less than would be the case in the pool. If the pool concentration is less than 0.7 mg/L the model removes more than would be the case in the pool. This will lead to a small deviation in accuracy.

The reliability of the pool has been tested. In the first test the reaction rate constants for the oxidation by hypochlorous acid were incorporated into the model. This does not give a realistic concentration of the accumulated combined chlorine. Further ammonia entered into the model is completely turned into trichloramine, which is not in accordance with reality [Schmalz et al., 2011]. Qiang and Adams [2004] questioned the reliability of the published reaction rate constants and studied these and their pH and temperature dependence. They found that reaction rates are highly dependent on both pH, temperature and chlorine to nitrogen ratio. This is also suggested by Donnermair and Blatchley [2003]. The rate constants found by Qiang and Adams [2004] are in the same level as those found by Jafvert and Valentine [1992] and Deborde and von Gunten [2008], but some difference exists. This difference must be caused by different conditions with respect to pH value, temperature and ratio of chlorine and nitrogen. Thus these reaction rates cannot be directly entered into the model, as the conditions may differ.
As the model does not give the correct results, e.g. all ammonia is transformed to trichloramine, using the reaction rate constants, there must be an inaccuracy. The reaction rate constant for the oxidation of ammonia to monochloramine is $1 \cdot 10^{10}$ $M^{-1}h^{-1}$. This means that ammonia is removed with $4.93 \cdot 10^{23}$ mg/h when 30 bathers (each releasing 20 mg/h as N) use the pool and the concentration of free chlorine is 1.1 mg/L. This gives a formation rate of monochloramine of $2.89 \cdot 10^{22}$ mg/L as Cl_2. The reaction rate for the oxidation of monochloramine to dichloramine, i.e., the removing rate of monochloramine, is $2.44 \cdot 10^{19}$ mg/L as Cl_2. This indicates that an excess of monochloramine is formed in the pool. The same is the case for di- and trichloramine, which have removal rates of $1.22 \cdot 10^{18}$ mg/L as Cl_2 and $1.29 \cdot 10^{3}$ mg/L as Cl_2, respectively. From this it is seen that the model is not in accordance with reality.

The reaction rates are exchanged by a percentage distribution of the three chloramines. Schmalz et al. [2011] states that the distribution of chloramines is 80 % as monochloramine and 20 % as di- and trichloramine together. As no distribution of di- and trichloramine is known, the model defines half of each. This yields an error as it is most likely that the amount of dichloramine is much higher than trichloramine. This is implied by the reaction rate constants discussed above. However, as the concentration is measured in mg/L as Cl_2, the combined chlorine concentration is the same, independent of the ratio of mono-, di- and trichloramine. The combined chlorine could be calculated with the difference of mono-, di- and trichloramine, but as the distribution is wanted for the model, the percentages are used instead.
If the percentage distribution of chloramines is calculated from the formation and removal rates listed above, the distribution is as listed in table 6.1.

Table 6.1. Percentage distribution of chloramines. *The percentage represents the amount not reacted, e.g., only 0.1 % of NH_2Cl reacts to $NHCl_2$ and of this 5 % reacts to give NCl_3. **Only $4.5 \cdot 10^{-5}$ % is removed. ***20 % of chloramine as $NHCl_2$ and NCl_3 together.

	NH_2Cl	$NHCl_2$	NCl_3
Reaction rate*	99.9 %	95 %	100 %**
[Schmalz et al., 2011]	80 %	— 20 %*** —	

The distribution calculated from the reaction rates does not agree with that stated by Schmalz et al. [2011]. This indicates that either the reaction rate constants or the percentage distribution is wrong.

When the percentage distribution by Schmalz et al. [2011] is entered instead of the reaction rate constants, the distribution is similar to reality and the tendency of the graph is much similar to that expected from Klausen and Kristensen [2008]. The higher concentration of total combined chlorine of 1.16 mg/L shows that the model is still not totally accurate. This could be due to the model converting 100 % of the entered ammonia to monochloramine and 20 % of the formed monochloramine to dichloramine. 50 % of the formed dichloramine is converted to trichloramine. This is likely to cause the inaccuracy. However, the concentration of combined chlorine and the tendency of the graph is much similar to the data found by Klausen and Kristensen [2008]. Despite the minor inaccuracies the model is used for further work. Firstly the bather added pollution is examined.

Articles state that an average bather releases 50 mL of urine and 200 mL of sweat. When using the composition of urine and sweat as stated in section 4.1.1 on page 22, the added nitrogen is 690 mg per bather per hour. The graph of this, figure 5.3, shows a concentration of accumulated combined chlorine at 40 mg/L as Cl_2 which is 40 times higher than expected. This indicates that not all nitrogen of the nitrogenous compounds that enters the pool water will form combined chlorine. This could possibly explain why the concentrations of the model are too high. Klausen and Kristensen [2008] found the bather standardised formation rate as the slope of the formation curve. This is also found for the data from the model for comparison.

Table 6.2. Combined chlorine rates of formation and removal. The standardised formation rate includes the amount of combined chlorine removed by UV radiation and natural decay, while the formation rate displays the amount formed after removing has occurred.

	Formation [$g/m^3 \cdot h$]	Removal [$g/m^3 \cdot h$]	Bather standardised formation rate [$g/pers \cdot h$]
Figure 5.1	0.0261	0.0296	0.065
Figure 5.2 part 1	0.0351	0.0394	0.087
Figure 5.3	1.21	1.35	2.99
[Klausen and Kristensen, 2008]	0.0289	0.0303	0.1
	0.0593	0.0267	0.09

The formation and removal rates for combined chlorine are found by the slopes of the graph for the accumulation of combined chlorine in the pool. These are listed in table 6.2 along with a bather standardised formation rate, which accounts for the total formed amount of combined chlorine, i.e., both the formed and the removed combined chlorine are taken into account. The formation rates for the graphs in figure 5.1 and 5.2 are in the same level as those found by Klausen and Kristensen [2008]. For figure 5.3, the one with the bather added concentration of 690 mg/pers · h as N, the formation rate is higher. The formation and removal rates are in accordance with the data for the whirlpool in Lalandia, but are closer to the data collected with 23 bathers in the pool than that collected with 30 bathers in the pool. This indicates that the model is not totally accurate as it is set up with 30 bathers, but the tendency of the result is similar to the data from Lalandia. The bather standardised formation rate of the first graph, the one with the reaction rate constants, is approx. half as high as the expected 0.1 g/pers · h. For figure 5.2a the bather standardised formation rate is very close to that found by Klausen and Kristensen [2008]. For the graph in figure 5.3 the bather standardised formation rate is 30 times as high. This difference in bather standardised formation rate is a result of a higher input mass than the formed mass of combined chlorine. In the previous test the input mass was set to be equal to the formed mass, which gave a correct accumulation of combined chlorine. As the input of the theoretically mass of nitrogen from urine and sweat gives higher concentrations of combined chlorine, not all of the added nitrogen form combined chlorine.
The reactions of ammonia, urea and creatinine with hypochlorous acid are listed in appendix D. Other products of the oxidation are nitrate and gaseous nitrogen for both urea, ammonia and creatinine [Jafvert and Valentine, 1992; Blatchley and Cheng, 2010; Wojtowicz, 2001]. Nitrate formation occurs if free chlorine is in excess, typically under breakpoint chlorination. Nitrogen gas is formed when two moles of dichloramine reacts with one mole of water and hence, is not dependent on the free chlorine concentration as was the case of nitrate. Urea is oxidised to 1,1,3,3-tetrachlorourea and then split into one mole of carbon dioxide, one mole hydrochloric acid, one mole NCl and one mole of trichloramine, which reacts as those formed of ammonia [Blatchley and Cheng, 2010; Wojtowicz, 2001]. Creatinine can be split into urea, which reacts as mentioned before and also N-Chlorosetcosine, which is oxidised to the organic chloramine CH_3NCl_2 [Li and Blatchley, 2007].
Another option could be that some of the matter does not react at all. This would be the case if the free chlorine concentration is too low. However, as chlorine is added continuously and automatically, this is not the most believable reason. Further it will leave the pool unsatisfactory disinfected. For this reason it is not believed to be the reason.

When the volume and circulation rate of a regular pool is entered into the model, the first result is a very low concentration of accumulated combined chlorine. This is partly a result of a low input and partly a high natural decay rate. The formation rate adopted from the whirlpool will be higher in a regular pool, as the amount of children is lower for a whirlpool than for a regular pool and it is believed that children release more urine than adults. Thus a test of the formation rate is made with inputs of 20, 100 and 200 mg/pers · h as N. In table 6.3 the formation rate and removal rates for the three inputs are listed.

Table 6.3. Formation and removal rates for inputs of 20, 100 and 200 mg/pers · h as N.

	Formation [g/m^3 · h]	Removal [g/m^3 · h]
20 mg/pers · h	0.0056	0.0056
100 mg/pers · h	0.0279	0.0287
200 mg/pers · h	0.0558	0.0558

It is seen that both the input of 100 and 200 mg/pers · h as N gives formation rates similar to those found by Klausen and Kristensen [2008]. As the concentration of accumulated combined chlorine for the input of 100 mg/pers · h as N is closer to that measured in Nørresundby, this input is used for further tests and simulations. This input has no experimental background, for which reason it is possible that this causes the model to make inaccurate concentrations. However, as the level of accumulation is similar to that measured in the pool it is used throughout this work.

The difference in bather standardised formation rate for the whirlpool and the regular pool is believed to be due to different regulations of water area per bather in whirlpools and regular pools. This will be discussed later.

The low concentration of accumulation is also partly caused by a high natural decay rate, which is valid for a whirlpool because of a rough water surface, but not for a regular pool, where the water surface is much smoother. For these tests the stripping fluxes of trichloramine found by Schmalz et al. [2011] are used.

Table 6.4. The flux of stripping of trichloramine found by Schmalz et al. [2011].

Whirlpool Rough water surface [g/m^2 · h]	Normal used pool Ripped water surface [g/m^2 · h]	Unused pool Quiescent water surface [g/m^2 · h]
$12.6 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$

By applying the ratio of the stripping fluxes from Schmalz et al. [2011] to the natural decay, the graphs in figure 5.4 and 5.5a are found. As the flux for stripping of trichloramine is measured in g/m^2 · h and the natural decay rate in g/m^3 · h as it also includes further reactions, these are not directly comparable. In the test it is assumed that the stripping of trichloramine is so high for a whirlpool that the further reaction can be neglected. If the natural decay is recalculated to g/m^2 · h these can be directly compared. This would yield the stripping flux of trichloramine for the whirlpool in Lalandia if the reactions are negligible. With the assumption that the whirlpool have a surface area of 10 m^2, the stripping flux becomes 69 g/m^2 · h, which is far higher than that found by Schmalz et al. [2011]. This proves that the reactions are not negligible, which yields an error in the test of the model. The matter removed by reaction does not depend on the water-air surface, so this will be constant independent of water-air surface. When using the assumption that reactions are a negligible contribution to the decay, the amount of matter removed is made smaller. This leads to smaller concentration of accumulated combined chlorine in the model than is the case in reality.

In figure 5.4a the very low concentration is as mentioned caused by the high natural decay rate. In figure 5.4b, where the flux of a pool with a rippled water surface is used, the concentration of accumulated combined chlorine is only half of the expected [Pedersen, 2012]. Furthermore the graph reaches zero when no bathers use the pool, which is not in accordance with reality. The graph for the pool with the rippled water surface is not in accordance with reality, so the flux for a quiescent surface is examined. Figure 5.5a shows that the tendency of this is similar to reality. However, the level of combined chlorine is a bit higher than expected. The modelled concentration is only approx. 0.1 mg/L higher than the measured. The difference is not significant, so the model will be further used in this thesis. The natural decay rate has a large influence on the concentration of combined chlorine and even though the model is not accurate, the influence of the natural decay rate is seen in the test.

Finally the bather load is tested. First by reducing it by half to see the effect of bather load on the accumulated concentration. From figure 5.5 and 5.7 it is seen that the accumulated concentration of the model depends on the bather load. The matter brought by bathers is reduced when the bather load is reduced, for which reason a lower combined chlorine concentration will occur.
For Køge a dynamic bather load for one week is entered into the model. From this it is seen that the accumulation of combined chlorine is affected by a higher bather load in the weekend and that it takes the pool one day extra to reach the quasi steady state in the weekdays again. Furthermore the concentration is affected by a change in bather load during the day and decreases linearly when no bathers use the pool. Thus, the model correlates with the expected pattern as a function of dynamic bather load.

Even though the model does not give 100 % correct concentrations, the tendency of the curves is similar to reality. The model is affected by the natural decay as expected. Furthermore the model follows the bather load as expected for a pool. The model is not 100 % accurate but despite of its shortcomings, it is used as a tool and guidance for further work in this thesis. Recommendations for future work and improvements of the model is outlined in chapter 10.

Part III

Simulations using the Mathematical Model

"This part contains simulations using the mathematical model and the discussion hereof. Chapter 7 includes the simulations and chapter 8 the discussion. The simulations are divided into three cases which together answer the questions presented in the thesis statement."

7 Simulation using the Mathematical Model

It is, as stated in the introduction, believed that the turbid pool water in Køge is caused by precipitation of calcium carbonate and that the source water to some extent causes this precipitation. The source water has been examined for compounds that could affect the water quality and carbonate system. Further a mathematical model has been made as a tool to examine the effect of source water on pool conditions.

This chapter includes three cases of the source water effect n pool water quality. For all three cases a model pool is used for simulation. A sketch (not in scale) of this model pool is shown in figure 7.1.

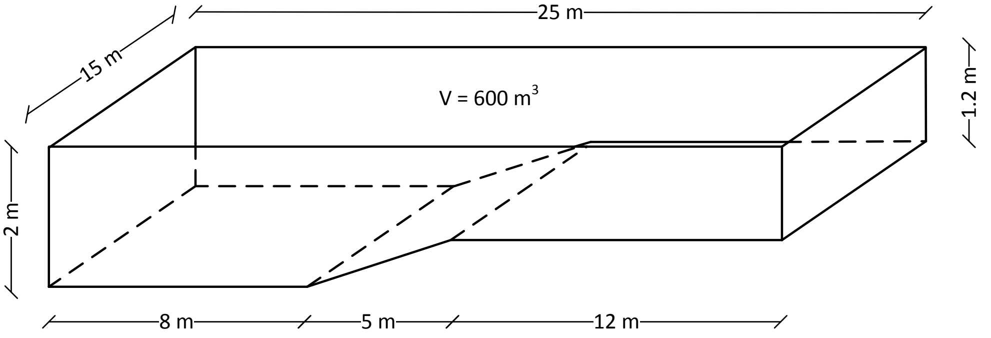

Figure 7.1. A sketch (not in scale) of the model pool used for simulation.

The pool is 25 m long and 15 m wide. The depth of the pool varies from 1.2 m to 2.0 m with a 5 m long slanted bottom. The shallow end is 12m long and the deep end 8 m. The total water volume of this pool is 600 m^3. The important system parameters are

Circulation flow	191.4	m^3/h
Turnover period	3.13	h
Circulation flow of source water	0.3	m^3/h
UV rate constant	10.3	$mg/m^3 \cdot h$
Cleaning efficiency	4.61	%
Natural decay rate constant	1.5	$mg/m^3 \cdot h$
Natural decay efficiency	0.67	%
Bather load	80	pers.
Bather standardised formation rate	500	$mg/pers \cdot h$ as Cl_2
pH value	7.0	
Temperature	27.0	°C

7.1 Case 1 - The effect of nitrogenous compounds on human water quality

The source water is blamed to cause scale forming and turbid pool water. Thus, the model is used to simulate the pool in figure 7.1 with different source waters found in Denmark. The model is concerning combined chlorine, which have nitrogenous compounds as precursors. In section 4.1.2 the nitrogenous compounds of source water are examined and the only compound that forms combined chlorine is ammonia. The ammonia content of the four locations used for this case is listed in table 7.1.

Table 7.1. Ammonia concentration and rate of addition for source water at four locations in Denmark. The rate is based on a source water flow of 0.3 m^3/h [Hansen, 2012].

	Tirstrup	Nørresundby	Køge	Bjerringbro
NH_3 [mg/m^3]	31	22	17	8
Rate [mg/h]	9.3	6.6	5.1	2.4

The ammonia content is entered into the model using the model pool. The model calculated the concentration of combined chlorine accumulated in the pool. The progress of the concentrations for the four locations are shown in figure 7.2.

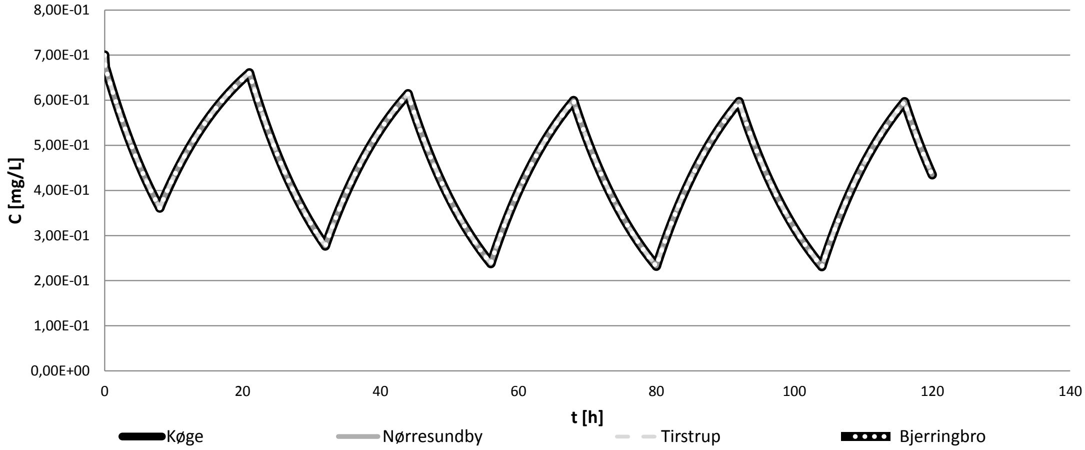

Figure 7.2. Combined chlorine concentration for the model pool at four locations with different ammonia content in the source water.

As it is seen from the graph the difference in ammonia content in source water in Denmark does not affect the combined chlorine concentration of the model pool. The flow of source water is 0.3 m^3/h which gives rates of source water ammonia between 2.4 and 9.3 mg/h. Compared to the bather introduced nitrogen of 8000 mg/h this is negligible. From figure 7.2 an effect of the source water on pool water conditions cannot be seen.

7.2 Case 2 - The effect of calcium and carbonate on chemical water quality

Turbid pool water is most likely to be caused by precipitation of calcium carbonate which has a large influence on the pool water quality and balance. The precipitation occurs when the concentration of calcium carbonate gets too high for the given pH value and/or temperature. Calcium and carbonate species are added to the pool by the source water. Figure 7.3 is a sketch of the calcium and carbonate species entering the pool.

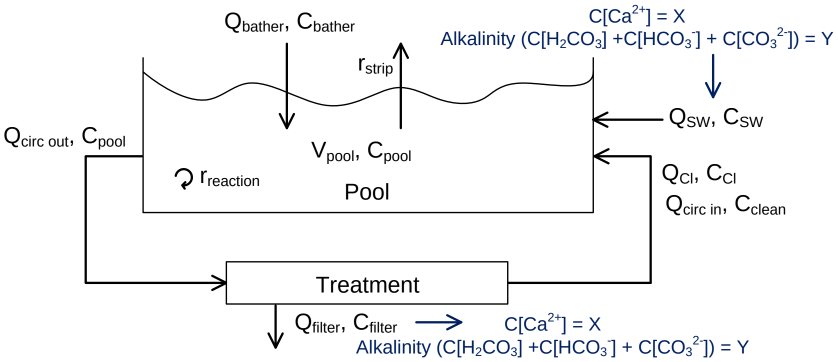

Figure 7.3. Calcium and carbonate species mass balance of a swimming pool. The addition by bathers is assumed to be zero. Stripping of carbonate species are zero as the pool acts as a closed system.

Calcium and carbonate species only enter the pool water by source water addition, so the amount of calcium and carbonate species removed from the pool by back flush of filters etc. is equal to the amount entering the pool by source water.

Precipitation of calcium carbonate can be caused by changes in pH value and/or temperature of the water. The source water added to the pool has a lower temperature than the pool water and might have another pH value as well. This makes it obvious to examine if the changes in temperature and pH value are enough to cause precipitation of calcium carbonate.

Graphs of the solubility of calcium carbonate as a function of both pH value and temperature are shown in figure 7.4.

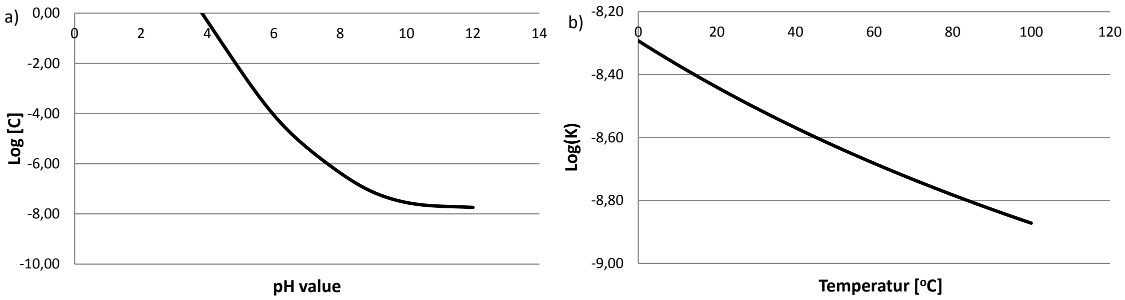

Figure 7.4. a) Calcium carbonate solubility as a function of the pH value. b) Calcium carbonate solubility as a function of temperature.

When the solubility of calcium carbonate is plotted as a function of the pH value, it is seen that the solubility decreases as the pH value increases. Thus, the pH value of the source water must be lower than that of the pool water if precipitation should be caused by changes in the pH value. When the temperature is increased, the solubility of calcium carbonate is decreased, which means that that an increase in temperature from source to pool water could possibly cause precipitation.

As both the pH value and temperature are changed when the source water enters the pool, the saturation index from chapter 2 is used to determine the condition of the source water before and after entering the pool.
The model pool from figure 7.1 is used to simulate the difference in saturation index of the source water in Denmark. Four locations with calcium and bicarbonate concentrations as listed in table 7.2 are used for the simulation.

Table 7.2. Calcium and bicarbonate concentrations and hardness of source water at four locations in Denmark along with the temperature and pH value [Hansen, 2012].

	Billund	Nørresundby	Køge	Femø
Ca^{2+} [mg/L]	35	88	80	132
HCO_3^- [mg/L]	132	201	458	449
Hardness [°dH]	7.2	14.9	20.9	26.3
Temperature [°C]	16	9.3	11.8	12.9
pH value	7.1	7.8	7.2	7.4

The saturation index is used to find the state of the source waters listed in table 7.2. Figure 7.5 and 7.6 are plots of the temperature and pH dependence of the saturation index for four locations in Denmark. The saturation index is plotted as a function of the pH value in a regular co-ordinate system with lines dictating the temperature.

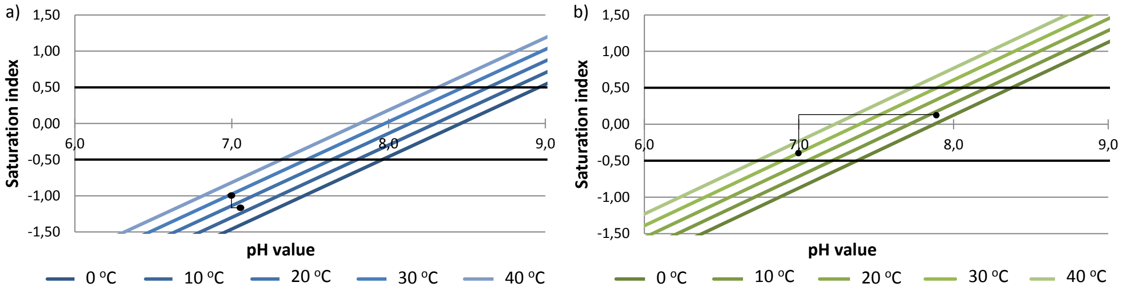

Figure 7.5. Saturation index of source water as a function of the pH value and temperature. The pH value is plotted along the x-axis and the temperature is included as the lines in the graphs, each representing a 10 °C interval. The blue graph is for Billund and the green is for Nørresundby source water.

For swimming pools it is recommended that the saturation index is between 0.5 and -0.5. These two boundaries are marked with black lines. Both graphs in figure 7.5 illustrates that an increase in the pH value, and no change in temperature, increases the saturation index proportionally to the change in pH value. Thus, causes precipitation if the pH value

increases enough. This is in accordance with figure 7.4a. An increase in temperature at a constant pH value gives according to figure 7.5 a higher saturation index, which at some point will cause supersaturation and precipitation - also in accordance with figure 7.4b.
In Billund the source water has a temperature of 16 °C and a pH value of 7.1. This gives a saturation index of -1.10. This is less than recommended for pool water as it tends to dissolve calcium carbonate from grout and other pool material containing solid calcium carbonate. When the temperature is increased to pool level and the pH value is decreased to 7.0, the saturation index becomes -1.02. This is still lower than recommended. However, no precipitation will occur as a result of the pH and temperature changes.
In Nørresundby the temperature of the source water is 9.3 °C and the pH value 7.8. The saturation index of this source water is 0.01. When entering the pool it decreases to -0.44. Both the source water and pool water saturation index is within the recommended range. However, it is changed from an almost totally balanced water, to having a slight tendency to dissolve calcium carbonate. This decrease in saturation index is caused by the decrease in pH value from 7.8 to 7.0.

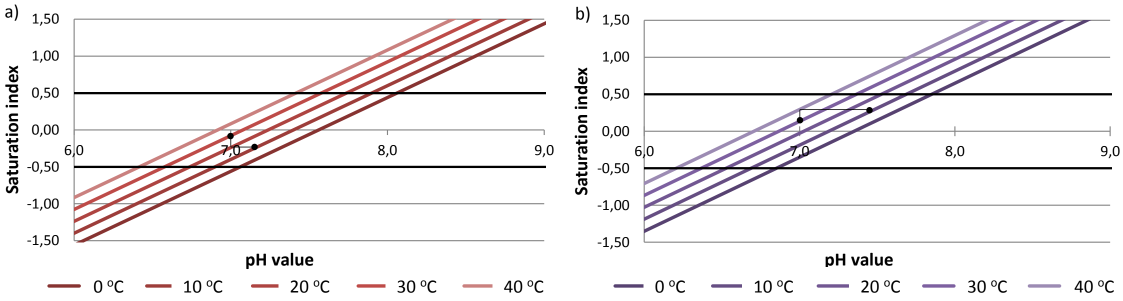

Figure 7.6. Saturation index of Køge and Femø waters, respectively. a) illustrates the source water in Køge as a function of the pH value with the temperature accounted for by the line. b) is for source water on Femø.

Figure 7.6 is the saturation index of the last two source waters. 7.6a is for Køge source water, which has a temperature of 11.8 °C and a pH value of 7.2. The saturation index for this source water is -0.17. When the pH value and temperature is changed to pool conditions the saturation index becomes -0.12, which is a small increase. However, the water still has a slight tendency to dissolve calcium carbonate.
The last source water for the simulation is from Femø and is the one with the highest hardness of the four locations. The source water has a saturation index of 0.26 before entering the pool. After entering the saturation index is decreased to 0.09. The source water from Femø is the only of the four test locations that seems to have a small tendency to precipitate calcium carbonate. This is in accordance with Femø having the highest hardness.
The saturation indices of the four waters before and after entering the pool are summed up in table 7.3.

Table 7.3. Saturation index for the four source water locations before and after entering pool conditions.

	Billund	Nørresundby	Køge	Femø
SI, Source water	-1.10	0.08	-0.17	0.26
SI, Pool water	-1.02	-0.44	-0.12	0.09

The sum up shows that it is not likely that precipitation occurs if the pool is placed in Billund, as the saturation index is much lower than both zero and the recommended minimum of -0.5. For the three other locations the saturation index is closer to zero and all within the recommended interval, both before and after entering the pool. The saturation index of the water from Femø is higher than zero, which indicates a slight supersaturation of calcium carbonate.

7.3 Case 3 - The effect of carbon dioxide on chemical water quality

Both water from Nørresundby and Køge have saturation indices close to zero and Femø has a saturation index that is higher than zero. Thus it is possible that precipitation can be caused by carbon dioxide formed in the water when urea is broken down as illustrated in figure 7.7. For this reason the amount of carbon dioxide formed in the water is found and added to the carbonate system.

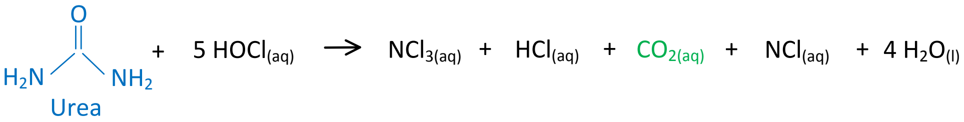

Figure 7.7. Reaction of urea and free chlorine. The full reaction in steps are in appendix D [Blatchley and Cheng, 2010].

Figure 7.8 illustrates the mass balance of calcium and carbonate species in the pool when carbon dioxide from urea is taking into account. It is assumed that the matter removed by back flush of filters is equal to the matter added by source water. Thus the carbon dioxide added by bather accumulates in the pool. When 100 mg/pers·h an N is added to the pool, one fifth of this originates from urine of which 68 % of N is from urea. This gives 13.6 mg. The other four fifths originate from sweat where 84.0 % of N is from urea. This gives 67.2 mg. Together 80.8 mg N of the 100 mg added is from urea, i.e., 80.8 % of nitrogen added is from urea. The pool used for simulation has 80 bathers for all 13 opening hours a day. This gives 104 g of nitrogen pollution per day. The urea part of this is 84.0 g as N. As urea forms one mole of carbon dioxide per mole combined chlorine formed the yield of carbon dioxide formed per day is 264.0 g. The calculation is based on the percentages listed in table 4.1 on page 23 and the reaction in figure 7.7.

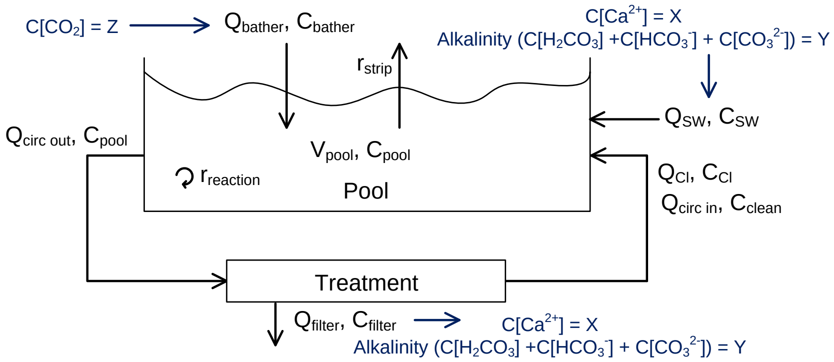

Figure 7.8. Mass balance of calcium and carbonate species in the pool. Carbon dioxide is added by bathers as urea is broken down upon reaction.

The simulations of the effect of carbon dioxide on the saturation index of pool water are done using Visual Minteq, an equilibrium based programme. The concentration of carbonate species is raised with the concentration of carbon dioxide formed in the water for each day. The data from the four locations are listed in table 7.4, 7.5, 7.6 and 7.7, respectively.

Table 7.4. Concentration of supersaturated calcium carbonate in the pool water in Billund at the pH values 7, 8 and 9 for five days with 80 bathers.

pH value	Day 0 [M]	Day 1 [M]	Day 2 [M]	Day 3 [M]	Day 4 [M]	Day 5 [M]
7	0	0	0	0	0	0
8	$3.734 \cdot 10^{-4}$	$3.758 \cdot 10^{-4}$	$3.780 \cdot 10^{-4}$	$3.801 \cdot 10^{-4}$	$3.822 \cdot 10^{-4}$	$3.843 \cdot 10^{-4}$
9	$8.071 \cdot 10^{-4}$	$8.075 \cdot 10^{-4}$	$8.079 \cdot 10^{-4}$	$8.083 \cdot 10^{-4}$	$8.087 \cdot 10^{-4}$	$8.091 \cdot 10^{-4}$

Table 7.4 shows that supersaturation of calcium carbonate only occurs if the pH value is raised to 8. If the pH value is raised to 8, supersaturation of 3.734 $\cdot 10^{-4}$ M will occur at day 0. After five days the supersaturated concentration has increased to 3.843 $\cdot 10^{-4}$ M. The formation of 264.0 g of carbon dioxide per day leads to an increase in supersaturated calcium carbonate of 1.1 $\cdot 10^{-5}$ M. Supersaturation occurs only if the pH value is raised to 8. Thus, there is no reason to believe that supersaturation of calcium carbonate will occur in the model pool with pH at 7.0. This is in accordance with the saturation index for Billund listed in table 7.3.

Table 7.5. Concentration of supersaturated calcium carbonate in the pool water in Nørresundby at the pH values 7, 8 and 9 for five days with 80 bathers.

pH value	Day 0 [M]	Day 1 [M]	Day 2 [M]	Day 3 [M]	Day 4 [M]	Day 5 [M]
7	0	0	0	0	0	0
8	$1.654 \cdot 10^{-3}$	$1.656 \cdot 10^{-3}$	$1.659 \cdot 10^{-3}$	$1.661 \cdot 10^{-3}$	$1.663 \cdot 10^{-3}$	$1.666 \cdot 10^{-3}$
9	$2.123 \cdot 10^{-3}$	$2.124 \cdot 10^{-3}$	$2.124 \cdot 10^{-3}$	$2.125 \cdot 10^{-3}$	$2.125 \cdot 10^{-3}$	$2.126 \cdot 10^{-3}$

As for Billund the water in Nørresundby must have a pH value of 8 before supersaturation occurs according to table 7.5. The saturation index from table 7.3 for this pool water is close to the lower limit of -0.5, which indicates a corrosive water which is in accordance with the data in table 7.5. The saturation index for Nørresundby is higher than for Billund, which is in accordance with the hardness of Nørresundby water being higher than for Billund water.

Table 7.6. Concentration of supersaturated calcium carbonate in the pool water in Køge at the pH values 6, 7 and 8 for five days with 80 bathers.

pH value	Day 0 [M]	Day 1 [M]	Day 2 [M]	Day 3 [M]	Day 4 [M]	Day 5 [M]
6	0	0	0	0	0	0
7	$2.083 \cdot 10^{-4}$	$2.103 \cdot 10^{-4}$	$2.122 \cdot 10^{-4}$	$2.141 \cdot 10^{-4}$	$2.160 \cdot 10^{-4}$	$2.179 \cdot 10^{-4}$
8	$1.822 \cdot 10^{-3}$	$1.823 \cdot 10^{-3}$	$1.823 \cdot 10^{-3}$	$1.823 \cdot 10^{-3}$	$1.823 \cdot 10^{-3}$	$1.824 \cdot 10^{-3}$

The source water in Køge has a higher hardness and saturation index than Billund and Nørresundby. When the formed carbon dioxide is added to this water, supersaturation occurs at pH 7. Because of the high hardness of the water, supersaturation may already occur at initial conditions. This is not in agreement with the saturation index of -0.12. The amount of supersaturated calcium carbonate starts at approx. 0.108 mM and ends at 0.179 mM. Thus, the carbon dioxide added from urea has an effect on the amount of supersaturated calcium carbonate.

Table 7.7. Concentration of supersaturated calcium carbonate in the pool water in Femø at the pH values 6, 7 and 8 for five days with 80 bathers.

pH value	Day 0 [M]	Day 1 [M]	Day 2 [M]	Day 3 [M]	Day 4 [M]	Day 5 [M]
6	0	0	0	0	0	0
7	$1.177 \cdot 10^{-3}$	$1.180 \cdot 10^{-3}$	$1.182 \cdot 10^{-3}$	$1.185 \cdot 10^{-3}$	$1.187 \cdot 10^{-3}$	$1.190 \cdot 10^{-3}$
8	$3.065 \cdot 10^{-3}$	$3.066 \cdot 10^{-3}$	$3.066 \cdot 10^{-3}$	$3.067 \cdot 10^{-3}$	$3.067 \cdot 10^{-3}$	$3.068 \cdot 10^{-3}$

When the hardness is further increased and water from Femø is used as source water in the model pool, supersaturation occurs also at initial conditions. The concentration of supersaturated calcium carbonate is approx. ten times higher than in the simulation with Køge water. At day 0 the concentration of supersaturated calcium carbonate is 1.18 mM and five days later the concentration is increased to 1.19 mM. This saturation index may lead to precipitation of calcium carbonate.

Discussion 8

8.1 Mathematical model - Set up and validation

A mathematical model for accumulation of DBPs is set up and tested in part II of this thesis. The model is based on a general mass balance equation and accounts for bather load and pollution, source water pollution, reactions in pool water, stripping of matter to the pool air and removal of matter in the treatment plant. The model is tested using data from Klausen and Kristensen [2008], Pedersen [2012] and Andersen [2012], which results in slightly higher concentrations of accumulated combined chlorine than expected. Even though the concentrations are higher than expected, the tendency of the curves are much similar to the data and follows the bather load as expected. Hence, the mathematical model is used for further work in this thesis. Further discussion of this is in chapter 6.

8.2 Simulation using the model

The simulations are made for a model pool of 600 m^3. The circulation flow is based on the existing standards for swimming pools according to Miljøministeriet [2010]. For a depth $\leq$ 1.5 m, a turnover period of 2 h is required whereas for depths $>$ 1.5 m, a 5 h turnover period is accepted. These requirements are along with a circulated water flow of 20 m^3/pers $\cdot$ h fulfilled. The bather load used is the maximum permitted bather load calculated based on a water area per bather of 4.5 m^2 for water deeper than 1.5 m and 2.5 m^2 for water shallower than 1.5 m as stated in Danish Standard [1996]. The model pool has a temperature of 27 °C and a pH value of 7.0. Both in accordance with the existing standard [Danish Standard, 1996; Miljøministeriet, 2010]. Thus, the model pool used for the simulations fully meets the existing standards for swimming pools in Denmark.

The cleaning efficiency of the pool is adopted from the validation of the model and is based on results from Klausen and Kristensen [2008]. Further the pool operation parameters are similar to those of Køge swimming pool, which makes it possible to compare the results of the simulation to the problem in Køge.

The volume used in the simulations, is the pool volume and not the total system volume, which leads to an error as the total system volume (including tanks, pipes and so on) is larger than the pool volume alone. This leads to higher concentrations of matter in the pool than would be the case if the total volume was used.

8.2.1 Case 1 - The effect of nitrogenous compounds on human water quality

When four source waters with different nitrogen content are used for simulation of the combined chlorine concentration in the model pool, the accumulated concentration does not appear to change, as seen in figure 7.2 on page 50. The flow of source water into the pool is approx. 0.3 m^3/h, which give rates of nitrogen from source water of 2.4 - 9.3 mg/h. Compared to the bather induced nitrogen of 8000 mg/h, this is negligible. Thus, from the simulation of a pool placed at four different locations in Denmark, the combined chlorine concentration is not changing due to a very small contribution from the source water. Hence, the nitrogenous compounds of the source water do not affect the human water quality in swimming pools in Denmark.

The model is set up to calculate the combined chlorine concentration, so it can be seen from the result that with respect to nitrogenous compounds and combined chlorine formation, the source water does not have a direct effect on the pool conditions. However, as the model only deals with nitrogenous compounds and combined chlorine, it cannot be seen if other compounds such as organic matter in the source water affects the human water quality by producing THMs upon reaction with free chlorine.

8.2.2 Case 2 - The effect of calcium and carbonate on chemical water quality

Precipitation of calcium carbonate can be caused by a change in pH value and/or temperature as stated in chapter 7. For which reason an examination of the calcium and carbonate conditions of the source water are made. As the saturation index takes both the pH value and temperature into account, this is used to determine the chemical water quality of source water and pool water. The saturation index of the source water is for Billund and Køge less than zero both before and after entering the pool. Thus, no precipitation is expected for the model pool when placed in Billund or Køge.

Nørresundby has a slightly supersaturated water before entering the pool where it due to the pH decrease is undersaturated. Thus, no precipitation is expected.

Femø water is decreased from a saturation index of 0.26 to slightly above zero, which is acceptable for pools and no precipitation is expected as the nucleation necessary prior to precipitation is energy-consuming and the saturation is only slightly supersaturated. Trussell [1972] made an experiment of the precipitation of calcium carbonate and found that the solubility can be exceeded by 40 to 50 times before evidence of precipitation was observed [Snoeyink and Jenkins, 1980].

The saturation of the source water thus depends on the calcium carbonate solubility and can be both under- and supersaturated. Thus, the saturation index of the pool water depends on the source water quality.

Only Billund water is not within the recommended range of -0.5 to 0.5. Thus, if the model pool is placed in Billund, the water will have a tendency to dissolve calcium carbonate from pool materials. This is unwanted for a pool as the grouts slowly will dissolve in the pool water leading to higher needs of maintenance and renovation. For the three other locations, Nørresundby, Køge and Femø the saturation index is within the recommended range and the pool water will be categorised as balanced with respect to calcium carbonate. Thus, no precipitation or dissolution problems caused by the source water are expected to occur.

8.2.3 Case 3 - The effect of carbon dioxide on chemical water quality

The reactions of nitrogenous compounds and free chlorine are studied for by-products that may affect the calcium carbonate equilibrium of the pool water. As calcium carbonate solubility decreases when the pH value increases, the formation of hydroxyl or other bases will lead to supersaturation. In the study of the reactions, no base formation is found. However, only the reactions for combined chlorine formation are studied, so it is possible that other reactions lead to the formation of base. As the pH value of the pool water is continuous regulated, the formation of base will be neutralised by the addition of acid. For this reason, base formation caused by source water content is not believed to cause supersaturation or precipitation of calcium carbonate in pool water.

During the study of the reactions of nitrogenous compounds with free chlorine it was, however, found that urea, which is added to the pool by bathers, is broken down to carbon dioxide. This carbon dioxide will interfere with the carbonate system and may cause precipitation. Thus, other compounds that may affect the calcium carbonate saturation is added to the pool.

The amount of urea added to the pool is calculated based on a input of 100 mg/pers · h as N and that 80.8 % of this origins from urea. The calculation is based on the combination of sweat and urine from World Health Organization [2006]. The result of this is 264.0 g carbon dioxide produced per day if the bather load is constantly 80 during the 13 open hours. This will not be the case for a real pool, but is the maximum permitted bather load for any time, which will give the absolute highest possible addition of carbon dioxide - a worst-case-scenario.

For Billund, where the source water has the lowest content of both calcium and carbonate the amount of supersaturated calcium carbonate is zero at pool conditions determined for the model pool. If the pH value is kept at 7, the supersaturation of calcium carbonate is still zero even after five days at maximum bather load. However, if the pH value is raised to 8, which is the highest permitted pH value according to Miljøministeriet [2010], supersaturation will occur at day 0. Hence, as long as the pH value is in the lower part of the recommended range, no supersaturation occurs and thus, no precipitated calcium carbonate is formed.
In Nørresundby where the hardness is 14.9 °dH, no supersaturation occurs at day 0. After five days at maximum bather load, the supersaturation is still zero at pH 7. Like in Billund, supersaturation will occur if the pH value is raised to 8. The concentration of supersaturated calcium carbonate is higher for Nørresundby than for Billund, which was expected, because the water in Nørresundby is harder than in Billund.
In Køge where the water is harder than in Nørresundby, supersaturation of calcium carbonate already occurs at day 0 and pH 7 even though the concentration is low. This is, however, not in accordance with the results in case 2. This divergence is discussed later. At day 0 the supersaturated concentration of calcium carbonate is $2.083 \cdot 10^{-4}$ M and is during the five days raised to $2.179 \cdot 10^{-4}$ M. These results indicate that supersaturation occurs even before the carbon dioxide from urea is added to the water. When bathers release urea in the water and carbon dioxide is formed, the amount of supersaturated

calcium carbonate is raised. This could be the reason that Køge swimming pool experiences turbid water. As stated earlier, Trussell [1972] found that the equilibrium constant for saturation of calcium carbonate can be exceeded by 40 to 50 times before evidence of precipitation is observed, as the nuclei formation is an energy-consuming process. However, if energy is added to the system in form of, e.g., heat formed in the treatment plant, precipitation of calcium carbonate from the supersaturated water from Køge can occur at day 0.
If the pool instead is placed on Femø, the concentration of supersaturated calcium carbonate will be higher. At day 0 it is 1.177 $\cdot 10^{-3}$ M, which after five days is raised to 1.190 $\cdot 10^{-3}$ M. As in the case with water from Køge the supersaturated water will be stable until nuclei are formed or added to the water, but as soon as nuclei are present in the water, precipitation occurs.

These data are based on the assumption that the carbon dioxide formed from the breakdown of urea is accumulated in the pool. This is in accordance with the semi-batch nature of a pool, as described by Kanan and Karanfil [2011]. However, the assumption that all carbon dioxide entering the pool over five days is accumulated in the pool will lead to an overestimated concentration of carbon dioxide. This will be diluted even though the nature of the pool is semi-batch. Thus the result is a worst-case-scenario. From the results of adding carbon dioxide, a small supersaturation of the water in Køge is found. In one day at maximum bather load during the opening hours, the maximum possible addition of carbon dioxide leads to an increase in supersaturated calcium carbonate of 1.48 $\cdot 10^{-6}$ M, which is quite small. As this is based on a worst-case-scenario, the actual addition of carbon dioxide will probably be smaller. This leads to an even smaller raise in the concentration of supersaturated calcium carbonate. However, if the pH value is increased to or near 8, the supersaturation of the water is even higher. The higher the supersaturation, the higher the risk of precipitation of calcium carbonate. Precipitation occurs when nuclei have been formed or added to the water and these grow into crystals [Snoeyink and Jenkins, 1980]. Nucleation can be formed in the water if energy is added. A nucleus is an organised structure with a defined surface that has to be formed in a random unorganised solution of ions, so this process requires energy. Because this process is energy consuming, the solution has to be supersatureted before nucleation can occur. [Snoeyink and Jenkins, 1980]
As bathers bring seeds such as skin cells and hair into the pool, these can act as a foreign surface in the water on which heterogeneous nucleation can be initiated. The energy can also be added to the system somewhere in the treatment plant, given that several of the treatment processes may produce heat upon cleaning the water.

The results of case 2 and 3 do not agree. The result of case 2 (saturation index of -0.12) leads to no supersaturation or precipitation of calcium carbonate. Contrary to this, the result of case 3 states the pool water for Køge is slightly supersaturated at day 0. These two results should be in accordance. The result of case 2 is based on the saturation index, which was derived in chapter 2. The formula is

$$SI = pH + CF + AF + TC - 12.35 \tag{8.1}$$

This differs from that published by Wojtowicz [1997b].

$$SI = pH + CF + AF + TC - 12.29 \tag{8.2}$$

The differences in these formulae are explained by the use of a different number of decimals during the derivation. Another publication of this formula is

$$SI = pH + CF + AF + TC - 12.1 \tag{8.3}$$

This is found in PWTAG [2009], an English standard for pool treatment and quality. If the latter formula is used to calculate the saturation index for Køge water in the model pool it gives 0.22, which classify the water as supersaturated and indicates that precipitation can occur. Thus, a disagreement of the saturation index formulae exists. A comparison of the one derived in this thesis and that by Wojtowicz [1997b] indicates that the disagreement lies within the temperature correction.
The results of case 3 are found by use of an equilibrium based programme and taking the disagreement of the saturation index formula into account, it is reasonable to believe that the result of case 3 is more correct than that of case 2. Furthermore the supersaturation of source water from Køge is in accordance with the problems experienced in Køge swimming pool.

8.2.4 General discussion

The inaccuracies of the model are all caused by assumptions during the set up and test of the model. These assumptions lead to an overestimated concentration of combined chlorine. For which reason the results of the model are not totally accurate as earlier mentioned. The inaccuracy results in higher concentrations than would be the case in the given pool. However, when having these in mind during the use the model, it is still usable for simulations, although further development is preferred. Those are discussed in chapter 10.

The reaction of free chlorine with nitrogenous compounds depends on the ratio of chlorine and nitrogen as explained in chapter 3. This is not included into the model. Due to this the model cannot be used for simulation of breakpoint chlorination and may give errors with respect to the reactions in the water. This was also seen from the results of the test with reaction rate constants. If the model is to be used as a tool to predict pool conditions in the pool industry, this should be included. By this the reaction rate constants should be usable as well.

The German standard DIN 19643 has besides standards for pool water conditions also a standard for source water conditions, because the water entering the pool must not have a poorer quality than the pool water [DIN, 1997-2004; Kristensen et al., 2007]. The result of case 3 showed that the calcium and bicarbonate concentrations of the source water in Køge and Femø alone are enough to cause supersaturation of calcium carbonate in the pool water. Thus source water quality could be a good point of research for the Danish standard. If standards for source water quality and possibly pre-treatment of source water are made, problems like in Køge could be prevented.

Part IV

Study Closure

"This part contains chapter 9 - the conclusion of both the mathematical model and the simulations using it. And also chapter 10 - recommendations for future work. In this chapter improvements of the model are outlined along with ideas for further studies and experiments of the precipitation problems in Køge Swimming Pool."

Conclusion 9

The scope of this thesis is to set up a mathematical model, which can be utilised to simulate water quality in swimming pools as a function of source water quality and composition.

9.1 Mathematical model

The mathematical model is set up using the simple formula for a general mass balance. During the set up some considerations and assumptions are made. These were discussed in chapter 6. A validation of the model is made and the results of this show that the model yields the correct tendency for accumulation of combined chlorine. However, concentrations of combined chlorine found by the model are higher than the data it is tested against. Even though the model overestimates the concentration of combined chlorine it can be used for simulation of the source water effect on pool water quality at different locations in Denmark.

9.2 Simulation

The mathematical model is used for simulation of a model pool located different places in Denmark. The model pool used for simulations, lives fully up to the existing standards for swimming pools in Denmark with respect to size, turnover period, bather load and concentrations of chemicals.

9.2.1 Case 1 - The effect of nitrogenous compounds on human water quality

The simulations with four different amount of ammonia in the source water give the same concentration of combined chlorine in the model pool. As the flow of source water is small, the rate of nitrogen from source water into the pool is negligible compared to the flow of nitrogen from bathers. Thus, the nitrogen content in source water has no effect on the human water quality of the pool. However, the model is only used for combined chlorine precursors, so the effect of, e.g., organic matter from the source water on pool conditions cannot be concluded on.

9.2.2 Case 2 - The effect of calcium and carbonate on chemical water quality

Simulations of source water of four different hardness are made. Of the four locations, Femø has the hardest source water. The saturation index of the model pool placed on Femø does, however, not indicate a tendency to precipitate calcium carbonate as the water is only slightly supersaturated (SI = 0.09). Thus, it is found that precipitation problems are not caused by hard water alone.

9.2.3 Case 3 - The effect of carbon dioxide on chemical water quality

Urea is broken down in pool water under release of carbon dioxide, which affects the saturation index of the water in the model pool.
The mass of carbon dioxide is found to be 264.0 g per day, when the pool is open 13 hours and is fully stressed during all opening hours. When simulations are made over a five day period, no precipitation is expected in Billund and Nørresundby. However, for water from both Køge and Femø supersaturation is the case even for day 0. As the pool water is supersaturated, precipitation of calcium carbonate can be partly caused by the carbon dioxide formed in the pool during breakdown of urea. The water is only slightly supersaturated, so the precipitation process must be initiated by, e.g., seeds or heat.

The results of case 2 and 3 are not in accordance. This is caused by a disagreement of the saturation index formula. The result of case 3 is believed to be more reliable than those of case 2.

Recommendations for Future Work

10

As the model, which is set up in this thesis, is not accurate and further studies of the problem in Køge are necessary, this chapter includes recommendations for future work.

10.1 Mathematical model

With respect to the model several improvements can be made. Firstly with respect to the cleaning, which is based on a single experiment in a whirlpool in Lalandia. A large part of the decay of combined chlorine is caused by reaction and stripping, so further experiments are desirable. These experiments should be carried out in different types of pools as the stripping in a whirlpool is higher than in a regular pool. From this study the difference in stripping for different pool types should be found.
In the large perspective a study of both the bather activity and ventilation systems' effect on the stripping is desirable. Some scientists are working on this, e.g., Schmalz et al. [2011].

For the reactions of precursors and free chlorine improvements, are also desired. By incorporating the reaction rate constants, the model should be able to give a correct distribution of mono-, di- and trichloramine. This was not the case for the model in this thesis while using the reaction rate constants from the literature. To be able to use reaction rate constants in the model, an experiment of the reaction rates and their pH and temperature dependency must be made. This is believed to be the reason for inaccurate results when using reaction rate constants from the literature.
Furthermore the chlorine to nitrogen ratio affects the reactions and is not included in the model. This has a large influence of the DBPs, for which reason it is desired to be taken into account in the model. This also enables the simulation of breakpoint chlorination and the chlorine consumption.
The last point with respect to the reactions is the input concentration of precursors. In the model is set up for this thesis, it is assumed that all matter entering the pool reacts to combined chlorine. However, this is not the case in reality. This is linked to the chlorine to nitrogen ratio. If this is included along with correct reaction rate constants, the amount of precursors reacting will be in accordance with reality. An experiment of the formation rate of combined chlorine like that by Klausen and Kristensen [2008] would give some perspective to the reaction rate constants.

Stripping of primarily trichloramine is important to pool water and pool air conditions. Thus, it is desired to simulate the trichloramine concentration of both pool water and air. Firstly, the air concentration depends on the pool concentration, so a simulation of this is desired. This is possible if the correct reaction rates are incorporated into the model.

Secondly, the stripping of trichloramine is affected by the bather load and ventilation systems. This dependence is jet to be studied closer.

Finally the pH dependence of the pool water quality is desired to include in the model. As shown from the results of case 3, the pH value has a large influence of the saturation of calcium carbonate. If this pH dependence is included in the model, it is possible to predict supersaturation and precipitation problems. Furthermore it is possible to predict and reduce these problems, e.g., by decreasing the pH value if possible according to the standards or by introducing pre-treatment of the source water.

The saturation index formula is incorporated into the model but is only affected by the pH value, temperature and calcium and bicarbonate concentrations. The amount of TDS increases when chlorine and acid is added to the pool along with the formation of DBPs, which affects the saturation index. This is, however, not accounted for in the model. For this reason it is desired to incorporate this in order to achieve more accurate results of the saturation.
With respect to the saturation index formula some disagreement occurs, so a thorough study of the formula is desired to conclude on the correct form.

10.2 Pool water quality in Køge

With respect to the precipitation problem in Køge, a measure of the calcium concentration and alkalinity in the pool as a function of the bather load is desired. This could confirm or disprove the hypothesis that precipitation is partly caused by carbon dioxide formed in the pool water.
As the precipitation process is energy-consuming, some energy must be added to the pool system for calcium carbonate to precipitate. A study of heat formed in the treatment plant could be performed as this is a likely source of energy. Another way of initiating precipitation is by adding seeds. As, e.g., skin cells and hair is added to the pool by bathers, it is desirable to examine if these are possible seeds for initiating precipitation.
Finally, standards for source water quality could be made. For this to be possible, further experiments of source water effect on pool conditions must be made. These experiments must include DBP formation and calcium carbonate saturation.

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Nomenclature

Symbols:

A	Variable	[–]
AF	Alkalinity factor	[–]
Alk	Alkalinity	[mg/L]
C	Concentration	[mg/(pers · h)] or [mg/m^3]
d	Density	[–]
dC	Change in concentration	[mg/m^3]
dt	Time span	[h]
ΔH	Enthalpy	[kJ/mol]
$Hard$	Hardness	[mg/L]
HF	Hardness factor	[–]
k_r	Reaction rate constant	[M/h] or [mg/h]
K	Equilibrium constant	[–], [M^{-1}], [M] or [M^2]
pH	pH value	[–]
Q	Flow/Bather load	[m^3/h] or [pers/h]
Q	Reaction constant	[–], [M^{-1}], [M] or [M^2]
r	Rate	[mg/h]
R	Gas constant	[J/mol · K]
ΔS	Entropy	[kJ/mol · K]
SI	Saturation index	[–]
t	Time	[h]
t	Temperature	[°C]
T	Temperature	[K]
TC	Temperature correction factor	[–]
TDS	Total dissolved soldis	[mg/L]
V	Volume	[M^3]
z	Ion charge	[–]
γ	Activity coefficient	[–]
ϵ	Dielectric constant	[K^{-1}]
κ	Conductivity	[μS/cm]
μ	Ion strength	[M]

Indices:

2	Second reaction of the carbonate system
a	Actual composition
$bather$	From bathers
$circ$	Circulation
Cl	Chlorine addition
$clean$	Cleaned water
e	Equilibrium
$filter$	Lost to filters/treatment
$pool$	Pool
$reak$	Reaction
ref	Reference
S	Saturation
$strip$	Stripping
SW	Source water

Abbreviations:

DBP	Disinfection by-products
HBE	Human body excretion
TDS	Total dissolved solid
THM	Trihalomethanes

Part V

Appendices

"This part contains appendices which are referred to in the thesis. These appendices include Standards for water quality and operation parameters in swimming pools, Saturation index - derivation, Water treatment in swimming pools and Water analysis and reactions in pool water."

A Standards for Water Quality and Operation Parameters in Swimming Pools

It is necessary to ensure a good quality of the water in the pool. To be sure that the water quality is kept at an acceptable level, some guidelines and standards exist. These are not the same in all countries, for which reason this appendix will include a comparison of the requirements for some countries in Europe, USA and Australia.

A.1 Water quality in Europe, USA and Australia

Initially, the chemical water quality standards are compared for the three continents Europe, USA and Australia. This comparison is based on minimum and maximum values for selected countries/states.

A.1.1 Standards for saturation index parameters

The first step to maintain a swimming pool with an acceptable chemical water quality is to keep the chemical quality parameters affecting the saturation index at the recommended level. If these are not kept at the recommended level, the saturation index of the water will not be acceptable. In relation to this, standards for pH value, hardness, alkalinity and TDS are made. The recommendations from Europe, USA and Australia for these parameters are listed in table A.1.

Table A.1. Water quality parameter requirements for Europe, USA and Australia. The data is the minimum and maximum permitted values within the continent. Data is from [Colorado, 1998; Georgia, Undat.; Queensland Government, 2004; PWTAG, 2009; DIN, 1997-2004].

	pH	Hardness [mg/L] $CaCO_3$	Alkalinity [mg/L] $CaCO_3$	TDS [ppm]
Europe	6.5 - 8.3	75 - 150	80 - 200	$<$ 1000 above source water
USA	7.2 - 7.8	150 - 600	60 - 180	—
Australia	7.2 - 7.8	—	80 - 200	$<$ 1000 above source water

The temperature depends on the pool type, so a standard for this does not exist. In Danish Standard [1996] a guidance for temperatures of different pools is made. The guidance states a temperature between 24 - 28 °C for a regular pool and higher temperatures for pools of recreational purposes. [Danish Standard, 1996]
The recommendations for the pH value are all at neutral pH values. This is in accordance with the chemical background as described in chapter 2. The recommended level for calcium hardness is much higher for USA than for Europe. The alkalinity recommendations are all in the same interval and are in accordance with the theory described in chapter 2. With respect to TDS the recommendation is less than 1000 ppm above the source water value. If TDS is higher than 1000 ppm above source water, it is a sign that the pool should be diluted, as pollution, DBPs and chemicals are accumulated inside the pool.
With respect to the turbidity, the recommendation is *"a clear view to the bottom"* for both Europe and USA. The main reason for this is bather safety, as they should be able to see clearly regardless their position in the pool. [Colorado, 1998; Georgia, Undat.; Queensland Government, 2004; PWTAG, 2009; DIN, 1997-2004]

All things considered, the three continents are generally in agreement with respect to the parameters directly affecting the chemical water quality. With respect to factors that affect the microbiological and human water quality more disagreement occurs.

A.1.2 Microbiological and human water quality

On the following pages two tables with the maximum permitted values for microbiological matter and matter affecting the human health and safety are listed for selected countries in Europe and states in USA and Australia.

For the microbiological maximum values listed in table A.2, Denmark stands out in three categories. The total bacterial count, where Denmark is among the countries with the lowest permitted value, $\leq$ 10 cfu/100mL, only surpassed by Georgia, USA. Faecal coliform bacteria and *Pseudomonas aeruginosa*, where Denmark has the highest permitted value of $<$ 10 cfu/100mL compared to the other countries, which have less than 1 or not to be detectable. With respect to the microbiological content, the Danish requirements in general are strict, but have less strict requirements for some specific microorganisms.

For the chemical parameters listed in table A.2, Denmark also stands out in three categories. For the amount of free chlorine, Denmark has the highest permitted values for both indoor and outdoor pools in Europe. Compared to USA, Denmark has a bit lower maximum value. A high concentration of free chlorine is from a disinfection point of view good because pollution is oxidised. With respect to the bather comfort it is not good, because the amount of DBPs are high and the risk of bather discomfort and illness is increased. For the combined chlorine, the requirement for Danish pool water is among the highest, but other countries have requirements as high as Denmark. With regard to the THM content, the Danish requirements are far higher than the German values, which leads to a poorer human water quality because THMs are believed to be harmful for humans and possibly carcinogen [Lakind et al., 2010; Kanan and Karanfil, 2011].

Table A.2. Microbiological and chemical maximum permitted values for swimming pools in European countries, USA and Australia. [Kristensen et al., 2007; Georgia, Undat.; Colorado, 1998; Queensland Government, 2004].

Country	Total bacterial count [cfu/mL]	*E. Coli* [cfu/100 mL]	Coliform bacteria [cfu/100 mL]	Faecal coliform bacteria [cfu/100 mL]	*Pseudomonas aeruginosa* [cfu/100 mL]	*Legionella pneumophila* [cfu/mL]	*Staphylococcus aureus* [cfu/100 mL]
Europe							
Germany	≤ 100	n.d	n.d	—	n.d	n.d	—
Denmark	≤ 10	—	—	$\leq 10^2$	< 10	—	—
Great Britain	≤ 10	n.d	n.d	—	n.d	—	—
Italy	≤ 200	—	≤ 1	n.d	—	—	≤ 10
Spain, Gal.	≤ 200	—	≤ 10	n.d	n.d	—	n.d
USA							
Georgia	None	—	—	—	—	—	—
Florida	—	—	—	—	—	—	—
Colorado	< 200	< 235	—	< 1	—	—	—
Australia							
Queensland	< 100	n.d	—	n.d	n.d	—	—

Country	Free Chlorine [mg/L]	Combined Chlorine [mg/L]	Total Chlorine [mg/L]	Trihalomethane [μg/L]
Europe				
Germany	0.3 - 0.6	≤ 0.2	—	≤ 20
Denmark	I: 1.0 - 3.0 O: 1.0 - 5.0	0.5 - 1.0	—	I: 25 - 50 O: 50 - 100
Great Britain	1.0 - 3.0	≤ 1.0	—	—
Italy	≤ 1.0	—	—	—
Spain, Gal.	1.4	≤ 0.5	—	—
USA				
Georgia	1.5 - 5.0	≤ 0.2	—	—
Florida	1 - 10	—	5	—
Colorado	0.25 - 5.0	≤ 1.0	—	—
Australia				
Queensland	min. 1.5	—	Free Cl+1	—

Where:

Gal.	Galicien
n.d	Not detectable
[1]	In busy periods < 1000
[2]	Thermo tolerant coliforme bacteria instead of coliforme bacteria
[3]	Only examined in warm water or at aerosol formation

The pH value is recommended to be within the overall interval 6.5 - 8.3. For some countries, the interval is in the lower part of the recommended interval and others in the higher part. However, all lies within this range both in Europe, USA and Australia.

A.2 Comparison of the German DIN 19643 and the Danish standard DS477

The strictest standard is the German norm, DIN 19643. Kristensen et al. [2007] compared the German DIN 19643 and the Danish requirements for water quality. This comparison is seen in table A.3. The column named 'Treated water' is from DIN 19643 and referrers to the treated water before addition of chlorine. This is included, as water added to the pool must not have a poorer quality than the water within the pool.

The comparison is made for both microbiological and chemical parameters. For the microbiological parameters in DIN 19643, the concentration of *Pseudomonas aeruginosa*, *E. Coli* and *Legionella Pneumophila* must not be detectable. The Danish requirements from Kristensen et al. [2007] have a maximum of <10 cfu/100mL for all but *Legionella Pneumophila.* A maximum value for total bacterial count exists for both DIN 19643 and the Danish requirements. The maximum value for the total bacterial count is higher for DIN 19643 than for the Danish requirements.

DIN 19643 has stricter requirements for the content of free chlorine and a much stricter requirement for combined chlorine and THM concentrations, which both contribute to bather discomfort. Besides the requirements for the quality of the pool water, DIN 19643 also has requirements for control of the treatment plant, which may affect the quality of the pool. [Kristensen et al., 2007; DIN, 1997-2004]

Table A.3. Comparison of the German DIN norm 19643 and the Danish requirements for water quality in swimming pools. Modified from [Kristensen et al., 2007; DIN, 1997-2004].

	Unit	Treated water		Pool water D		Pool water DK	
		min	max	min	max	min	max
Pseudomonas aeruginosa 36±1 °C	[cfu/100mL]		n.d		n.d		< 10
E. Coli	[cfu/100mL]		n.d		n.d		< 10
Legionella Pneumophila	[cfu/mL]				n.d[2]		
	[cfu/100mL]		n.d[1]				
Total bacterial count, 20±2 °C	[cfu/mL]		20		100		
Total bacterial count, 36±1 °C	[cfu/mL]		20		100		< 10
Turbidity	[FNU]		0.2		0.5		0.3
Clarity				Clear view to the bottom		Water must be clear	
pH value (freshwater)		6.5	7.6	6.5	7.6	7.0	8.0
Free chlorine[4] $_{\text{Regular pools}}$	[mg/L]	0.3	As required	0.3[5]	0.6[5]	0.5	3.0
Free chlorine $_{\text{Whirlpool,DK} > 25\text{ m}}$	[mg/L]	0.7		0.7[5]	1.0[5]	1.0	5.0
Combined chlorine[6]	[mg/L]		0.2		0.2	0.5	1.0
Trihalomethane	[mg/L]				0.020[7]		
Trihalomethane[6] $_{\text{DK} \leq 25}$	[mg/L]						0.050
Trihalimethane $_{\text{DK others}}$	[mg/L]						0.100

Where:

n.d	Not detectable
1	In the filtrate at pool temperature ≤ 23 °C
2	In pool water for whirlpools and other aerosol forming water circuits at pool temperature ≤ 23 °C
3	If the oxidation value in the filtrate is lower than for the source water, this value is used as a reference
4	As long as no stricter requirements in the following norms exist
5	The concentrations are only valid when no lower concentrations are given in the following norms
6	Not valid for cold water pools $\leq 2\,\mathrm{m}^3$
7	Higher values are possible in outdoor pools with higher chlorination

A.3 Danish standards for pool operation parameters

The Danish standards for turnover rate, circulation flow and bather load are listed in table A.4.

Table A.4. Turnover rate and maximum bather load for different types of pools [Miljøministeriet, 2010; Danish Standard, 1996]. *From [DIN, 1997-2004].

Pool type	Depth [m]	Turnover rate [h]	Water area per bather [m^2]
Diving and swimming	≥ 1.5	5	4.5
Education	< 1.5	2	2.5
Padding	< 0.5	0.5	1.0
Whirlpool*	< 1.0	0.1	1 seat

These standards are used as a reference for the model pool used for simulations.

Saturation Index - Derivation B

The saturation index is derived to the form used in swimming pools in three steps.

B.1 Conversion of concentration units

First by conversion of the concentration of Ca^{2+} in M to mg/L $\mathrm{CaCO_3}$.

$$\begin{aligned} Xeq/L \cdot 50g/eq &= 50Xg/L \\ 50Xg/L \cdot 1000mg/g &= 5 \cdot 10^4 Xmg/g \\ X &= 5 \cdot 10^{-4} \\ log\frac{1}{5 \cdot 10^4} &= -4.7 \end{aligned} \tag{B.1}$$

Where mole is replaced by equivalents and the molar mass of $\mathrm{CaCO_3}$ is equal to 100 mol/L. As one Ca^{2+} has a valens of two equivalents, the mass per equivalent is 50 g/eq. Thus, the hardness contribution is found by

$$CF = log[Ca^{2+}] - 4.7$$

Where:

$[\mathrm{Ca}^{2+}]$	Calcium concentration [M]

With respect to the alkalinity, the unit conversion of M to mg/L $\mathrm{CaCO_3}$ is as follows.

$$\begin{aligned} Xeq/L \cdot 100g/eq &= 100Xg/L \\ 100Xg/L \cdot 1000mg/g &= 10^5 Xmg/g \\ \Rightarrow X &= 10^{-5} \\ log\frac{1}{10^5} &= -5.0 \end{aligned} \tag{B.2}$$

The alkalinity is then found by

$$AF = log[\mathrm{HCO_3^-}] - 5.0 \tag{B.3}$$

Where:

$[\mathrm{HCO_3^-}]$	Bicarbonate concentration [M]

B.2 Temperature dependence

The second step is calculation of the temperature dependence of $log\frac{K_2}{K_S}$. For this the Van't Hoff equation is used.

$$ln\left(\frac{K}{K_{ref}}\right) = \frac{-\Delta H^o}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_{ref}}\right) \tag{B.4}$$

$$K = K_{ref}\cdot e^{\frac{-\Delta H^o}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \tag{B.5}$$

$$ln\left(K_{ref}\right) = \frac{-\Delta H^o}{R}\cdot\frac{1}{T_{ref}}+\frac{\Delta S^o}{R} \tag{B.6}$$

$$K_{ref} = e^{\frac{-\Delta H^o}{R}\cdot\frac{1}{T_{ref}}+\frac{\Delta S^o}{R}} \tag{B.7}$$

By inserting K_{ref} into formula B.5, K gives

$$K = e^{\frac{-\Delta H^o}{R}\cdot\frac{1}{T_{ref}}+\frac{\Delta S^o}{R}}\cdot e^{\frac{-\Delta H^o}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \tag{B.8}$$

This formula can be used to calculate the temperature dependence of $log\left(\frac{K_2}{K_S}\right)$. K is calculated for both K_2 and K_S using formula B.8 and the data displayed in table B.1.

Table B.1. Data used for calculation K.

		K_2	K_S
ΔH^o	[kJ/mol]	16.77	-11.28
ΔS^o	[kJ/mol · K]	-0.141	-0.199
R	[kJ/mol · K]	0.00831	0.00831
T_{ref}	[K]	298.15	298.15

The equilibrium constants for K_2 and K_S are used to calculate the $log\frac{K_2}{K_S}$ at different temperatures. A plot of $log\frac{K_2}{K_S}$ is shown in figure B.1.

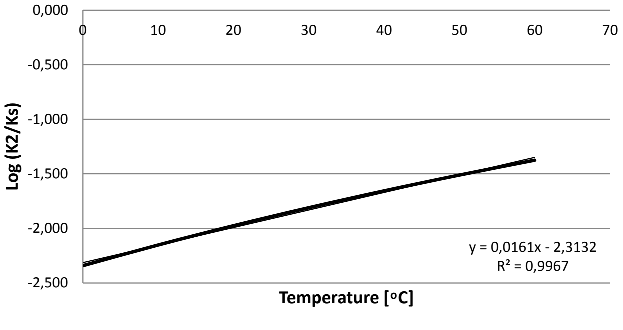

Figure B.1. Temperature dependence of $log\frac{K_2}{K_S}$.

A linear regression is made for the curve for $log\frac{K_2}{K_S}$. The formula for this line is

$$y = 0.016x - 2.31 \tag{B.9}$$

From this regression it is seen that a correction of -2.31 for $log\frac{K_2}{K_S}$ at 0 °C must be made and further that the temperature is to be corrected by -0.016. This yields the formula for temperature dependence

$$TC = 0.016 \cdot t \tag{B.10}$$

Where:

t	Temperature [°C]

B.3 Ionic strength correction

Finally an ion strength correction of TDS is made. The correlation of ion strength and TDS is

$$\mu = 2.5 \cdot 10^{-5} \cdot TDS \tag{B.11}$$

$$\mu = 2.5 \cdot 10^{-5} \cdot 1000 = 0.025 \tag{B.12}$$

Where:

μ	Ion strength [M]
TDS	Total dissolved solids [mg/L]

The correction factor is calculated by the Davies approximation [Stumm and Morgan, 1996]

$$log\gamma = A \cdot z^2 \cdot \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \tag{B.13}$$

Where:

γ	Activity coefficient [–]
A	Variable [–]
z	Ion charge [–]

The variable is found by

$$A = 1.82 \cdot 10^6 \cdot d^{0.5} \cdot (\epsilon T^{-1.5}) \tag{B.14}$$

Where:

d	Density [–]
ϵ	Dielectric constant [K^{-1}]
T	Temperature [K]

Where the dielectric constant can be found by

$$\epsilon = \frac{60854}{T + 116} - 68.937 \tag{B.15}$$

d is assumed to be 1.

$log\gamma$ is calculated for both Ca^{2+} and HCO_3^- at 25 °C .

$$log\gamma_{Ca2+} = 0.51 \cdot 2^2 \cdot \left(\frac{\sqrt{0.025}}{1+\sqrt{0.025}} - 0.3 \cdot 0.025 \right) = -0.27 \tag{B.16}$$

$$log\gamma_{HCO-} = 0.51 \cdot 1^2 \cdot \left(\frac{\sqrt{0.025}}{1+\sqrt{0.025}} - 0.3 \cdot 0.025 \right) = -0.07 \tag{B.17}$$

$$log\gamma_{Total} = log\gamma_{Ca2+} + log\gamma_{HCO-} = -0.34 \tag{B.18}$$

All calculations can be found on [Enclosures-CD,Saturation index].

Inserting the corrections into the saturation index equation yields

$$SI = pH_a + \log\left[Ca^{2+}\right]_a + \log\left[Alk\right]_a + \log\frac{K_2}{K_S} \tag{B.19}$$

$$SI = pH_a + \log\left[Hard\right]_a - 5.0 + \log\left[Alk\right]_a - 4.7 + TC - 2.31 - 0.34 \tag{B.20}$$

$$SI = pH + \log\left[Hard\right] + \log\left[Alk\right] + TC - 12.35 \tag{B.21}$$

which is somewhat equivalent to the saturation index equation published in [Wojtowicz, 1997b].

$$SI = pH + \log\left[Hard\right] + \log\left[Alk\right] + TC - 12.29 \tag{B.22}$$

The derivation is based on the work done by Wojtowicz [1997b,c].

The difference in correction factors is a result of difference in numbers of decimals used for derivation. Formula B.21 is used throughout this thesis.

Water Treatment in Swimming Pools C

The treatment process is divided into two parts; mechanical treatment and chemical treatment. The mechanical treatment concerns filtration, often by the use of sand filters, but also covers disinfection. The chemical treatment covers, besides addition of disinfection chemicals, addition of chemicals to adjust the water balance.

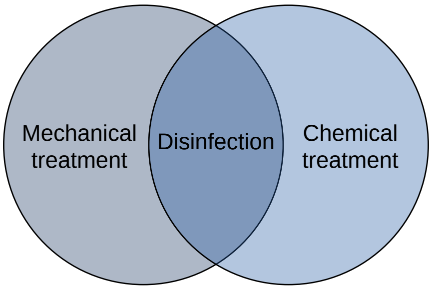

Figure C.1. Overlap of the chemical and filtration treatment (disinfection) [PWTAG, 2009].

As illustrated in figure C.1 the two treatment types overlap. This overlap is the disinfection. It is an important part of the mechanical treatment, which would not be sufficient if no disinfectant were added. The disinfection is indeed also a chemical process, which is explained later in this chapter. [PWTAG, 2009]

C.1 Mechanical treatment

Different methods of mechanical filtration treatment exist, including the most common method for swimming pool treatment; sand filters. Other mechanical filtration methods can be used as well. Mostly in addition to sand filters. A few of these methods along with the sand filter are outlined in the following.

C.1.1 Sand filter

Sand filtration consists of a sand bed in a large tank. It is often used for filtration, as it is an efficient and cost effective way to reduce turbidity of the pool water.

The sand bed consists of sand packed with a certain density. The denser the packing of the sand grains, the lower the porosity of the filter. A low porosity results in smaller particles being trapped in the filter and thus, removed from the water. As small particles are trapped in the pores, the pore size decreases and it is thus possible for smaller particles to get trapped. This is called mechanical straining.

The efficiency of the filter depends on the size of the particles, which have to be separated from the water. Small particles are displaying Brownian motions, which eventually will make them bump into the collector particles. Large particles will have a greater downwards velocity than the water. For this reason they will not follow the water flow around the collector particles, but bump into them.

As the water passes through the sand bed, some particulate matter will have a greater downward velocity than the water and is possible to deposit on top of the sand grains. This sedimentation will decrease the pore size of the sand filter. As the pore size is reduced the velocity of the water is increased and particulate matter will be carried to a deeper part of the sand bed where it will deposit. Other particles within the water are adsorbed to the sand grains because of the van der Walls force between the molecules. This adsorption of particulate matter only influences the particles on extreme short range (0.0001 - 1.0 μm), but is the most purifying mechanism of the sand filter. [Keiding, 2009; PWTAG, 2009]

C.1.2 Membrane filtration

As an addition or alternative to sand filters, membranes can be used for filtration of the pool water. Different types of membrane filtration exist, but those used for water treatment in swimming pools are pressure-driven. The type of membrane used is an ultra filtration membrane, which can separate particles in the range of 0.05 μm - 1 nm. This range includes macromolecules and colloids. [Mulder, 1997]

C.1.3 Coagulation and flocculation

Coagulation or flocculation is a process in which chemicals are added to the water to react with dissolved, colloidal and suspended matter to bring it out of solution, coagulate. After coagulation the coagulated solids flocculate and can be completely separated from the water. This method is often used in addition to sand filters.

The coagulants used for coagulating colloids and other dispersed matter have an optimal pH value. If the pH of the pool water increases this point the coagulants gets less effective. [PWTAG, 2009]

C.2 Chemical treatment

Chemical treatment consist primarily of disinfection, but also of addition of other chemicals to ensure a good quality of the water.

C.2.1 Disinfection

A disinfectant must be added to the water to keep it 'clean' until it is brought to the plant room for mechanical cleaning. This is necessary due to large turnover periods. The most commonly used disinfectant is chlorine, which can be added both in the gas (Cl_2), solid ($Ca(OCl)_2$) and liquid state ($NaOCl$). The mechanism of chlorine disinfection is described in chapter 3. [PWTAG, 2009]

C.2.2 Ozone

Ozone is a plant room disinfection method which can be used as a contribution to the chlorine disinfectant in the pool water. The ozone kills microorganisms and decomposes organic and inorganic by-products. Ozone is generated in the plant room. It is very reactive because of its rapid reversion to oxygen and thus, quickly oxidises the pollutants and disinfection by-products in the water. [PWTAG, 2009]

C.2.3 Ultra violet radiation

Another plant room disinfection method, is the use of Ultra-Violet (UV) radiation, which also is used in addition to the chlorine treatment. UV radiation is a method to complete chlorination and breakdown of combined chlorine and other organic pollutants by photo-oxidation. UV radiation should make it possible to run the treatment system with lower chlorine residual. [PWTAG, 2009]

Water Analysis and Reactions in Pool Water D

D.1 Source water analysis

The source water is analysed for nitrogenous compounds and chemical species that affect the saturation index. 12 allocated waterworks are selected for this comparison. All source water analyses are made by Hansen [2012].

Table D.1. Source water content of five of the 12 selected waterworks [Hansen, 2012].

Compound	Unit	Bjerringbro Viborg	Femø Lolland	Gørløse Hillerød	Lellinge Køge	Lindved Odense
Ammonium	[mg/L]	0.008	< 0.006	0.006	0.017	0.013
Nitrate	[mg/L]	< 0.5	4.8	3.85	2.4	3.9
Nitrite	[mg/L]	<0.005	0.007	< 0.0016	< 0.005	< 0.005
NVOC	[mg/L]	0.9	2.8	2.8	1.8	3.6
Calcuim	[mg/L]	67	132	91	80	120
Bicarbonate	[mg/L]	165	449	345	458	293
Hardness	[^{o}dH]	9.8	26.3	17.1	20.9	18.9
Conductivity	[mS/m]	39	120	66	78	69
pH	[–]	7.8	7.4	7.6	7.2	7.6
Temperature	[°C]	12.8	12.9		11.8	11.8

Table D.2. Source water content of four of the 12 selected waterworks [Hansen, 2012].

Compound	Unit	Nørresundby Aalborg	Rødekro Aabenraa	Tirstrup Syddjurs	Vestervig Thisted
Ammonium	[mg/L]	0.022	0.014	0.031	0.02
Nitrate	[mg/L]	14	3.2	4.2	0.73
Nitrite	[mg/L]	< 0.005	< 0.005	0.11	< 0.005
NVOC	[mg/L]	0.98	1.2	0.98	1.4
Calcuim	[mg/L]	88	83	89	85
Bicarbonate	[mg/L]	201	218	190	220
Hardness	[^{o}dH]	14.9	12.5	13.7	13.9
Conductivity	[mS/m]	53.3	44	54	
pH	[–]	7.8	7.4	7.6	7.7
Temperature	[°C]	9.3	9.7	8.9	

Table D.3. Source water content of three of the 12 selected waterworks and the average content of the 12 analyses [Hansen, 2012].

Compound	Unit	Vorbasse Billund	Østerlars Bornholm	Videbæk Ringkøbing-Skjern	Average
Ammonium	[mg/L]	0.006	< 0.006	< 0.006	0.01
Nitrate	[mg/L]	< 0.5	2.9	< 0.4	3.33
Nitrite	[mg/L]	<0.005	< 0.005	< 0.003	0.01
NVOC	[mg/L]	0.82	1.1	0.6	1.58
Calcuim	[mg/L]	35	120	39	85.75
Bicarbonate	[mg/L]	132	312	146	260.75
Hardness	[^{o}dH]	7.2	19.8	6.7	15.14
Conductivity	[mS/m]	28	66	27.5	58.62
pH	[–]	7.1	7.6	8.13	6.93
Temperature	[°C]	16	12.5	14.7	12.34

D.2 Reactions in pool water

An overview of the matter entering the pool from both bathers and source water is included in figure D.1. This overview is based on the study of bather and source water contribution in chapter 4.

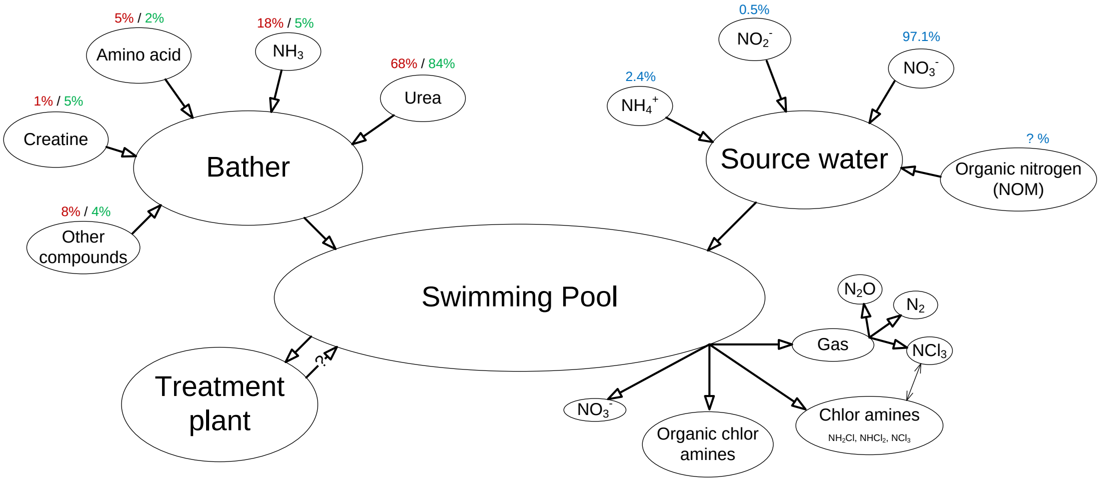

Figure D.1. Nitrogenous compounds added to the pool water by bathers and source water and the major DBPs formed by reaction with free chlorine. The percentages of the added nitrogen in the given compound are compared to the total amount of nitrogen added by bathers or source water, respectively. For the products, the percentage are for nitrogen of all nitrogen-DBPs formed. The green percentages is for urine, red for sweat and blue for source water content.

The reactions between free chlorine and the nitrogenous containing compounds from figure D.1 are listed in figure D.2 to D.4.

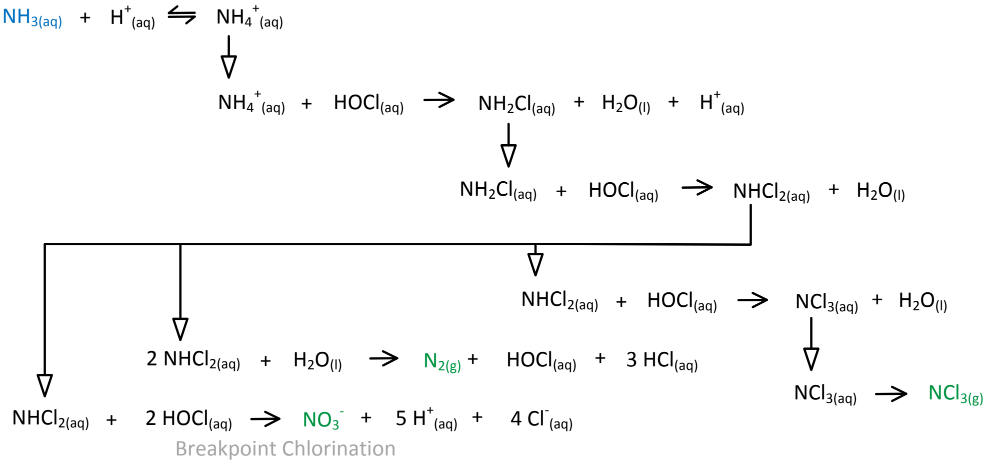

Figure D.2. Reactions of hypochlorous acid and ammonia in pool water. The initial nitrogenous compound is marked with blue and the nitrogenous end-products are marked with green.

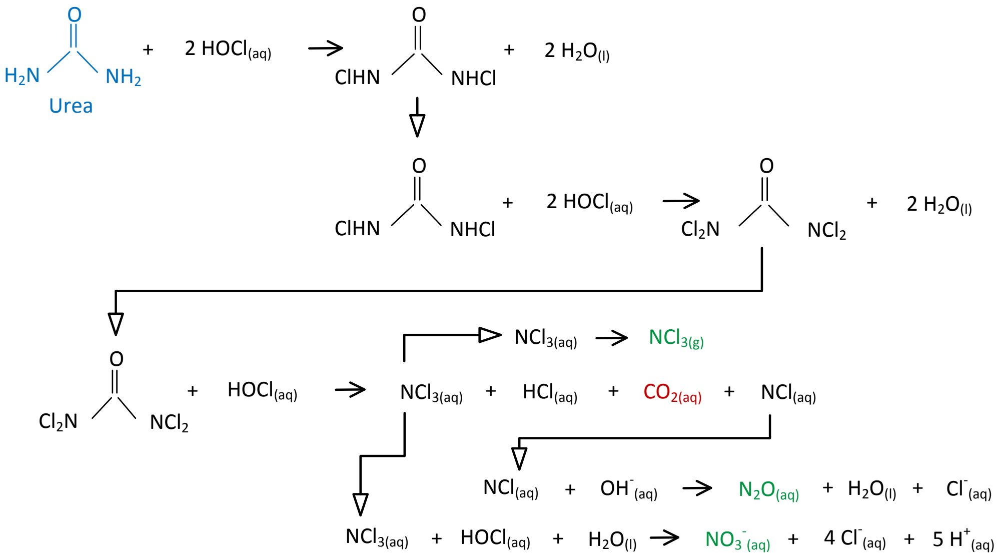

Figure D.3. Reactions of hypochlorous acid and urea in pool water. The initial nitrogenous compound is marked with blue, the nitrogenous end-products are marked with green and carbon dioxide with red.

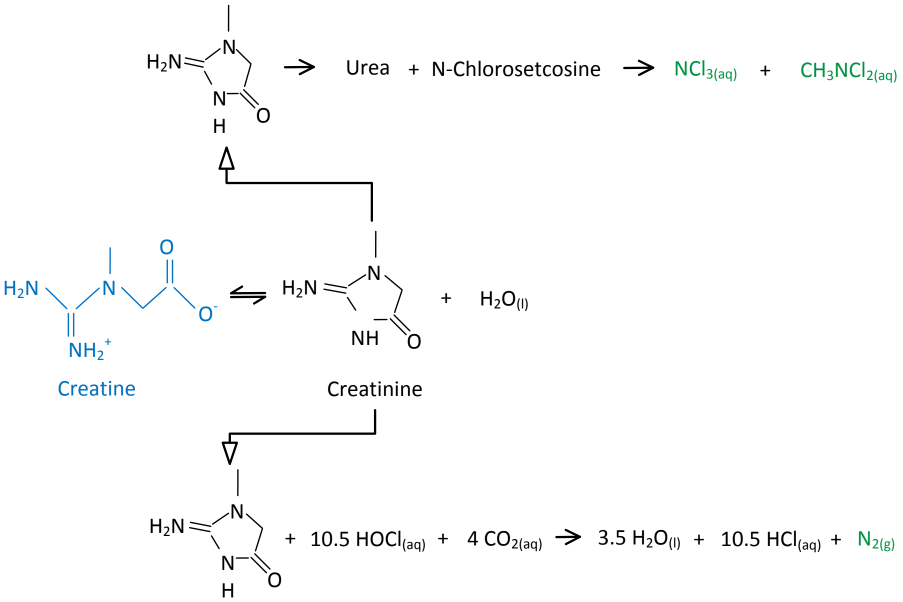

Figure D.4. Reactions of hypochlorous acid and creatinine in pool water. The initial nitrogenous compound is marked with blue and the nitrogenous end-products with green.

D.3 Urine and sweat calculations

The calculation of the mass of nitrogen in the urine and sweat released by bathers is listed in the following.

Table D.4. Mass of urea, ammonia and creatinine in urine and sweat, respectively. Based on data from Putnam [1971] and Robinson and Robinson [1954].

	Urine	Sweat	Total
Urea [mg]	1165	142.5	1307.5
Ammonia [mg]	36.5	22.5	59
Creatinine [mg]	107.5	1	108.5

In 250 mL of urine and sweat the molar distribution of urea, ammonia and creatinine is

Table D.5. The mass, molar amount and concentration of nitrogen in a 300 mL mixture of urine and sweat where 50 mL is urine and 250 mL is sweat.

	Mass [mL]	Molar amount of N [mol]	Concentration [mM]
Urea	4258.33	2	145.3
Ammonia	196.67	1	11.5
Creatinine	361.57	3	7.5
Total N			145.3

$$145.3\,\text{mM} \cdot 14\,\text{g/mol} = 2300\,\text{mg/L} \tag{D.1}$$

$$\frac{2300\,\text{mg/L}}{0.3\,\text{L}} = 690\,\text{mg} \tag{D.2}$$

Thus, each bather releases 690 mg N, which can form combined chlorine per hour.