

Quantitative Microbial Risk Assessment of Water Treatment Process for Reducing Chlorinous Odor

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Chapter 1

Introduction

1.1 Research Background

The primary goal of drinking water treatment is to protect public health by supplying water that is safe for the public to drink and use. Chlorination is widely used for the inactivation of pathogens causing waterborne diseases, and is the final treatment step before water is distributed through the pipeline network. Because of its residual effects, chlorine can preserve the water quality from bacterial regrowth along the distribution system. Present Japanese legislation requires that a minimum of 0.1 mg Cl₂/L free chlorine residual or 0.4 mg Cl₂/L combinative chlorine residual at tap to guarantee the microbial safety of drinking water (MHLW, 2007).

While chlorine is applied in conventional treatment processes to inactivate pathogens, it results in the formation of toxic halogenated organic compounds, including trihalomethanes (Rook, 1974), haloacetates and haloacetonitriles (Bull and Kopfler, 1991). Furthermore, chlorination impairs the taste and odor of the water. It often causes unpleasant odor called chlorinous odor, which is not the smell of chlorine itself but that of the reaction products of chlorine and organic/inorganic compounds in water. Free chlorine itself is perceptible even at concentrations below 0.05 p.p.m. (Bryan *et al.*, 1973). People naturally judge that odor-containing water is unsafe for consumption. Bad taste and odor can prompt complaints and loss of consumer confidence on drinking water quality. In a nation-wide survey in Japan, only 37.5% of the population drinks tap water directly, and 21.3% demands more advanced drinking water treatment even with higher cost (Cabinet Office, Government of Japan, 2008). Another questionnaire survey conducted by Itoh *et al.* (2007) showed that in total of 3186 investigators, only 22.6% of male and 11.9% of female consume tap directly. That is a outcome even for the tap water treated with ozone/granular activated carbon (GAC) treatment. Consumer complaints about drinking water quality are serious signals from the client in an increasingly market-orientated society. Hence, to enhance the reliability of people on drinking water quality, safe and odor-free water is needed. Several major water utilities in Japan have already launched an effort to reduce chlorinous odor in tap water (e.g., Kawatani and Ishimoto, 2009). Chlorinous odor is not a problem only in Japan. For example, in 1996, the American

Water Works Association conducted a survey on the drinking water industry and found that approximately 40% of water treatment plants had received customer complaints on the taste and odor of their water (Suffet *et al.*, 1996). Such complaints have resulted in water treatment plants in the US spending on average more than 4% of the total budgets on addressing the organoleptic problems. Similar situations also happened in France (Welte and Montiel, 1999) and in Western Australia (MaDonald *et al.*, 2009)

In order to better control chlorinous odor in tap water, one proposed solution is to develop a new water treatment process that can decrease chlorinous odor even after chlorination. For this purpose, the use of combination of ozone/vacuum ultraviolet (advanced oxidation process, AOP) and ion-exchange treatments to better control chlorinous odor in tap water has been proposed by Echigo *et al.* (2014). While not all the compounds responsible for chlorinous odor have been identified, trichloramine (Kajino *et al.*, 1999) and N-chloroaldimines (Froese, 1999; Freuse *et al.*, 2005) are known as major contributors to chlorinous odor. Trichloramine can be produced both inorganic (i.e., ammonium ion) and organic nitrogen (e.g., free amino acids). Also, other compounds responsible for chlorinous odor including N-chloroaldimines are formed from dissolved organic matter (DOM). In this new water treatment process, hydrophilic neutral fraction (a major DOM fraction) is converted to ionic species by AOP treatment, and then these ions and ammonium ion are effectively removed during ion-exchange processes.

Another promising approach is minimization of the residual chlorine level at tap water. Such a countermeasure would increase health risks and lead to a deterioration of drinking water quality by allowing bacterial regrowth with the distribution system. According to the Enforcement Regulations of the Waterworks Law in Japan (MHLW, 2007), a residual chlorine level of 0.1 mg Cl₂/L should be maintained at each tap, though many waterworks have been trying to keep a residual chlorine level of 0.3-0.4 mg Cl₂/L at each tap (JWWA, 2010). This residual chlorine level has worked effectively to inactivate bacteria in distribution systems and to provide a 'biologically stable' state. With lesser chlorination power, bacteria can regrow with a small amount of organics as substrate; therefore, stricter control of microbial safety of drinking water is needed at the same time with this approach.

The traditional way to control and manage the microbiological quality issue is by monitoring indicators and surrogates and by responding when a parameter value moves outside its target range. Parameters monitored include flow, turbidity, pH, disinfectant residuals and temperature. They are monitored at several points within the treatment

process if limits and targets are not achieved, remedial action must be taken. Although these measures of the process performance cannot be directly translated into pathogen removal, they still can prove to be a valuable source of information for undertaking assessment of risk. Water quality measurements are also carried out after the water has reached the consumers on follow up samples or in response to complaints.

Traditionally critical limits for pathogens have not been set from estimated risk. Rather they have been based on surrogate and microbial indicator measurement values which are seen as acceptable by experts and the public. In the case of the public a tasteless product lacking visible turbidity is usually acceptable. For water quality managers the lack of indicator bacteria in 100 ml water samples has been the key measure to decide if the water quality is acceptable (JDWQS, 2014).

This approach can be seen to have worked well as the incidence of water borne disease in developed countries is low. However, outbreaks of waterborne diseases have occurred over the past decades even though measuring and monitoring standards have been fulfilled (Hrudey and Hrudey, 2004).

A new risk based approach, the quantitative microbial risk assessment (QMRA), has been introduced by the World Health Organisation (WHO) as a new strategy for provision of water that is safe to drink. Analogous to the chemical risk targets, a target for risk of infection (not illness) below 10^{-4} per person per year was being advocated in QMRA. This method gives a detailed breakdown of the contribution of each step in the chain from source to tap to the overall risk reduction and some indication of data variability and uncertainty, rather than the focus on end-product monitoring. It provides the quantitative scientifically underpinned data about the importance of hazards based on health target. The water supplier can use this information to decide where optimisation or additional control would be most effective. Hence, QMRA is also a tool to guide the risk manager to efficient control. QMRA can be used on existing water supply systems to determine if these meet the health targets, but also on hypothetical systems to evaluate if design scenarios are potentially able to meet the health targets.

The major steps in the process of QMRA are (i) quantitative information of the relevant pathogenic micro-organisms in the source water and (ii) quantitative knowledge about the elimination (removal and inactivation) capacity of water treatment processes for pathogenic micro-organisms and the factors influencing elimination and (iii) calculation of the exposure and risk infection on the basis of these data, drinking water consumption

and the dose-response curves. Calculations can be made with a simple deterministic approach (point estimate) or by more complex stochastic calculations (often using Monte Carlo simulations). In this way QMRA enables calculation of very low risk of infection associated with exposure to pathogens in drinking water.

1.2 Research Needs and Objectives

Based on the background, upgrading the water system with using of the new water treatment process for reducing chlorinous odor and minimization of residual chlorine in the water supply under a stricter control of microbial safety of drinking water using QMRA method would be a realistic and effective strategy to improve customers' satisfaction with tap water.

The overall purpose of this study is to apply the QMRA method to provide a quantitative estimate of the level and variation of microbial risk in drinking water treated with this new water treatment process for reducing chlorinous odor. When undertaking a QMRA, the concentrations of pathogens in source water, elimination capacity of each process, consumption of unboiled drinking water and dose-response relationships need to be known.

Campylobacter jejuni (*C. jejuni*) is selected as a target pathogen since it is one of the major bacteria causing waterborne disease in Japan. *E.coli* is used as a surrogate for *C. jejuni* when assessing the elimination capacity of water treatment process. The six basic processes in the new water treatment process for reducing chlorinous odor water treatment are coagulation and sedimentation, rapid sand filtration (RSF), advanced oxidation process (AOP) with ozone/ultraviolet light, cation exchange, anion exchange, and chlorination. Different methods are developed and applied in this study to assess the elimination capacity of these six steps.

The most reliable calculations can be made if plant specific data are used. For the first steps in the treatment train as coagulation and sedimentation, direct measurement of indicator before and after treatment could provide a direct measurement of treatment efficacy. After one or more treatment processes, the concentration of indicator in treated water is usually too low to be determined with the routine microbiological methods. Dosing micro-organisms to full-scale drinking water treatment processes is generally not allowed and feasible. An alternative method is to conduct dosing experiments at pilot or

laboratory scale under controlled conditions, mimicking full-scale conditions. Such tests are more applicable to the local situation than general literature values. This method can be used for treatment steps of cation exchange, anion exchange, and chlorination in this study.

With respect to disinfection processes like AOP, there are significant differences in inactivation efficacy at different conditions such as configuration of the reactor, temperature, pH, water quality and operating conditions (feed-gas ozone concentration, liquid flow rate, and gas flow rate) and so on. Therefore, it is necessary to develop a mathematical model to simulate the performance of the water treatment and to use this model to predict the elimination capacity of water treatment process under full-scale hydraulic condition.

On the other hand, the water treatment plants usually have large amounts of historical monitoring data on the prevalence of faecal indicator bacteria in their source waters and the water further down the treatment, assessed with standard microbiological methods. These data yield valuable quantitative information of the first processes in water treatment on the elimination of these indicators. However, such routinely collected data usually include a large number of non-detects which are not suited to determine accurately elimination capacity of water treatment process. Thus, if we want to use those large amounts of routine monitoring data, there is a need to find some suitable methods to deal with them.

According to these research needs, the specific objectives of this study are to:

1. Develop and assess methods for handling non-detect environmental data.
2. Develop axial dispersion reactor model (ADR model) to address all the major components of advanced oxidation process: contactor hydraulics, ozone mass transfer, ozone demand and decay, and microbial inactivation.
3. Validate the ADR model and determine the inactivation rate constants by ozonation and UV using pilot-scale experimental data, including tracer testing results, ozone concentration profiles, and microbial inactivation tests results. Then use this model to predict the inactivation efficacy of AOP under well-defined full-scale hydraulic condition.
4. Assess the removal efficacy of cation exchange and anion exchange by laboratory column tests operated under conditions that can simulate full-scale conditions.
5. Assess the inactivation efficacy of chlorination by challenge tests on pilot plant scale under a condition of minimizing chlorine addition.

6. Develop measurement method for the target pathogen of *C. jejuni* and determine the ratio of *C. jejuni* to *E. coli* in the surface water.
7. Estimate of the yearly infection risk of *C. jejuni* in drinking water treatment with the new water treatment process for reducing chlorinous odor.
8. Identify the critical control point (CCP) with regard to stably produce safe drinking water during the water treatment process.
9. Perform uncertainty analyses of the assessment to identify the variable that has the greatest impact on the outcome and point out the components or variables that can contribute to improve the accuracy of the estimates. If necessary, identify items in the system whereby either more data is required to better characterize the risks.

1.3 The Structure of the Thesis

This thesis consists of six chapters. Overall contents are given by chapters as follows:

Chapter 1 gives the reader a short background to why this research is performed. The objectives are presented as well as the structures of the thesis. The expected contributions of this work are stated at final.

Chapter 2 provides the available information from previous studies and basic knowledge to this work. Topics cover development of QMRA, QMRA in drinking water guidelines and legislation, QMRA for risk management, QMRA framework, target pathogen and its indicator, the structure of water treatment process for reducing chlorinous odor, etc.

Chapter 3 A concentration interpolation method for handling non-detect values are developed and discussed by using routine monitoring data from a treatment plant located in the west of the Netherlands.

Chapter 4 An axial dispersion reactor (ADR) model that could be applied for full-scale modeling of AOP is developed and successfully validated with challenge tests under pilot-scale conditions. Then, this ADR model is further applied to predict the inactivation efficacy of AOP under well-defined full-scale condition.

Chapter 5 A full QMRA is performed in this chapter. First, the data needed to assess the elimination capacity of water treatment process were collected. Second, by combining with the information of elimination capacity of each step, the pathogen concentration in

the source water, consumption of unboiled drinking water and dose-response model, the yearly risk of *C. jejuni* infection was estimated. Third, sensitivity and uncertainty analyses were performed on the obtained results. As a result, the critical control point with regard to stably produce safe drinking water during the water treatment steps was identified and variables that can contribute to the improvement of the predictive accuracy of the estimates were highlighted.

Chapter 6 summarizes the major findings of this study.

1.4 Expected Contributions of this Research

Although the knowledge on QMRA has progressed over the last three decades, the drinking water industry is still just at the beginning of applying QMRA on a regulatory basis. This leads to new insights and adaptations of methods. This study describes how QMRA method can be used in a new system assessment and how the outcome of QMRA can be used as a basis for risk management in the water treatment industry.

With respect to the assessment of the elimination capacity of water treatment process, the most reliable calculations can be made if plant specific data are used. In fact, the water treatment plants generally have large amounts of routine monitoring data with non-detects. The concentration interpolation method developed in this study can overcome the limitations of using these data and improve the accuracy of estimates in QMRA. Thus greatest value could be obtained from these large amounts of routine monitoring data. When elimination capacity is not assessable with process indicator monitoring particularly for the last stages of water treatment, challenge tests with index pathogens or process indicators in a laboratory scale or pilot plant operated under full-scale conditions (dummy) is an alternative method as described in this study. The ADR model developed in this study can provide valuable insight into understanding the performance of AOP bubble-diffuser contactor under different conditions. Thus it can be used to predict the elimination capacity of AOP under any well-defined conditions for QMRA purpose or provide recommendations for AOP contactor design and optimization according to specified health targets. In addition, this study explores and analyses literature data on micro-organism removal in RSF treatment as a tool for assessment of the elimination capacity. The international literature on microbial inactivation and elimination collected from different studies during the past decades is a significant source of quantitative data and can provide a direct impression of the reduction efficacy of different processes

(LeChevallier and Au, 2004; Hijnen and Medema, 2007). If data is taken from a database like this, it is important to choose data from experiment that have the same or similar conditions as the case plant. In general, the methods or concepts developed and applied in this study provide a basic knowledge for the assessment of the elimination capacity and enable a broader implementation of QMRA.

The outcome demonstrated that the new water treatment process for reducing chlorinous odor is adequate to produce drinking water that meets the health based targets as well as the effectiveness of control chlorinous odor. The calculated infectious risk in this study is not an actual risk of drinking water produced at a specific treatment plant; however, it does provide a direct impression of treatment efficacy level and drinking water quality level in Japan. Locally generated data will always be of great value in setting national targets, such data and tests are more applicable to the local situation than general literature values. The findings of this study will be a basic knowledge to help the Japanese government carrying out the appropriate policies of applying QMRA in drinking water legislation for the forthcoming years.

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Chapter 2

Literature Review

2.1 Introduction

This chapter aims to present the basic knowledge and available information on QMRA, target pathogen, water treatment process for reducing chlorinous odor and advanced oxidation processes (AOP).

2.2 Quantitative Microbial Risk Assessment (QMRA)

This section provides some background information of QMRA. Topics cover development state of QMRA, the value of QMRA for risk management, QMRA in drinking water guidelines and legislation and QMRA framework.

2.2.1 Development state of QMRA

By the end of the nineteenth century, the presence of specific bacteria in drinking water was recognized as an indicator of unsafe water. The use of coliforms as indicator organisms to judge the microbial safety of drinking water was initiated (Greenwood and Yule, 1917). Verification of the absence of indicator organisms such as *Escherichia coli* (*E. coli*) in drinking water is still part of most legislation worldwide today (e.g., EUDWD, 1998; ADWG, 2011), and so is the current form of Japanese drinking water quality standards (JDWQS, 2014). In the 1970's the weakness of indicator concept became clear. Newly recognized waterborne pathogens, such as viruses and protozoa turned out to be more resistant to drinking water treatment processes such as chlorination than coliforms (Engelbrecht *et al.*, 1977&1979; Helmer and Finch, 1993; Payment and Franco, 1993). Hence, a disinfectant residual might only inactivate the indicator organisms, and the negative indicator tests observed in such situations may give rise to a misleading feeling of safety. The search for other, more resistant indicator organisms such as bacterial spores and bacteriophages was tried. However, their applicability turned out to be limited, as large outbreaks of waterborne diseases continued to occur over the past decades even when no indicator organisms were detected (Hrudey and Hrudey, 2004). Large drinking

water related outbreaks were generally picked up by epidemiology, but the prevalence of endemic illness caused by drinking water was so low in most developed countries that epidemiology was not sensitive enough to identify the source (Taubes, 1995). Apart from monitoring drinking water for the absence of indicator organisms, other ways to protect the drinking water consumer were sought. In the 1970's the National Academy of Sciences initiated chemical risk assessment for drinking water resulting in the 'Safe drinking water act' in 1974 (SDWA, 1974). Analogous to the chemical risk targets, a target for risk of infection (not illness) below 10^{-4} per person per year was being advocated in the USA.

Between 1983 and 1991, QMRA was used sporadically to assess microbial risks in drinking water (Haas, 1983; Gerba and Haas, 1988; Regli *et al.*, 1991; Rose *et al.*, 1991). These first assessments were focused on producing a reliable dose-response relationship for the very low pathogen doses expected in drinking water. These led to the 'single hit theory' stating that exposure to a single pathogenic organism could lead to infection and subsequently illness. The studies calculated the risk of infection from the monitored or estimated pathogen concentrations in drinking water. These studies recognized the limitations of drinking water monitoring for QMRA. Regli *et al.* (1991) concluded that: *'Inordinately large numbers of high volume samples (generally a total volume of >100,000 to 1,000,000 L) are required to ascertain whether a potable water is below the 10^{-4} risk level. Thus, finished-water monitoring is only practical to determine whether a very high level of risk exists, not whether a supply is reasonably safe.'*

To overcome the weaknesses of drinking water monitoring, computational methods were applied in QMRA. Regli *et al.* (1991) stated that: *'Determining pathogen concentration (or demonstrating its absence) in source waters and estimating the percentage-removal or inactivation by treatment allow for risk estimates of pathogen occurrence in finished water and the associated risk of infection.'* Initially rules of thumb and engineering guidelines were used to provide a point estimate of treatment efficacy. Rose *et al.* (1991) used QMRA to determine the required treatment efficacy to reach health-based targets, rather than actually assess the efficacy. As more research was performed, it became clear that treatment efficacy could vary substantially between treatment sites. LeChevallier *et al.* (1991) assessed treatment efficacy for *Cryptosporidium* and found substantial differences in treatment efficacy at very similar sites. These could not be explained by treatment characteristics such as filter to waste practice or choice of coagulant. Payment *et al.* (1993) studied removal and inactivation of viruses and indicator organisms. He used the mean of the observed concentrations before and after treatment steps to quantify

treatment efficacy, thus disregarding the effect of treatment variations. Other QMRA studies did not model treatment but started from a concentration in treated water, such as Haas *et al.* (1993) who based virus concentrations in drinking water reported by Payment (1985). Similarly Crabtree *et al.* (1997) did not estimate treatment efficacy for virus removal but assumed concentrations in drinking water of 1/1000 and 1/100 virus per litre. Gerba *et al.* (1996) assumed 4 log reduction of rotavirus by treatment based on SWTR credits.

Teunis *et al.* (1997) incorporated the variation in time and the uncertainty with regard to the efficacy at a specific site in a stochastic QMRA by the use of probability density functions (PDFs) to describe the concentrations of microorganisms and treatment efficacy. Microbial monitoring data before and after treatment were paired by date to provide a set of reduction values, and the PDF was fitted to these. Their conclusion was that (variation of) reduction by treatment dominated the uncertainty of this risk. Haas *et al.* (1999) provided an overview of methods for QMRA both in drinking water and other fields such as recreational waters and food. They found that identification of distributional form may be subject to error if a limited amount of data points are used. Consequently the risk analysis should not put too much weight on the tails of these distributions that would represent rare event of poor treatment. Haas *et al.* (1999) also discussed the use of monitoring data (virus removal by lime treatment) and process models (for virus decay in groundwater and chemical inactivation) to assess treatment efficacy. Teunis and Havelaar (1999) performed a full QMRA, including quantification of treatment efficacy using monitored reduction of Spores of Sulphite-reducing Clostridia (SSRC) as a surrogate for *Cryptosporidium* removal. Variability of filtration was modelled by a two-phase model: “good removal” and “poor removal”. Medema *et al.* (1999) applied similar methods. Variability of ozonation was modelled by running an inactivation model with monitored ozone concentrations. Payment *et al.* (2000) used log credits from the SWTR in risk assessment of *Giardia* since “*Attempting to actually enumerate indicator microorganisms or pathogens under actual plant conditions rarely provides useful data*”. Dewettinck *et al.* (2001) assessed the safety of drinking water production from municipal wastewater based on treatment efficacy reported in literature. Fewtrell *et al.* (2001) assessed the uncertainties in drinking water QMRA and found that treatment contributed the least uncertainty. However, this was based on a single experiment of *Cryptosporidium* removal by treatment. A 2001 USEPA study on *Cryptosporidium* removal (USEPA, 2001) found large ranges of removal (typically over 3 log) and generally less removal at full-scale than at laboratory or pilot scale. In an extensive literature review of treatment efficacy by LeChevallier and Au (2001), large variations in treatment efficacy between studies was

found. Masago *et al.* (2002) applied QMRA to assess the risk from *Cryptosporidium*, including the effect of rare events. Treatment was modelled bimodally with good removal (99.96%) or poor removal (70.6%).

In general it could be concluded that most QMRA studies used log credits to model treatment performance, which were not site specific. Site specific assessment of treatment efficacy for QMRA indicated that treatment efficacy at full-scale could be significantly higher or lower than the applied log credits (Teunis *et al.*, 1997&1999; Teunis and Havelaar, 1999; Medema *et al.*, 1999). Moreover, such an assessment could provide management strategies to be applied at the site to improve drinking water safety. Site specific assessment was complicated by the way pathogens were distributed in water, treatment variations and correlation between treatment steps.

2.2.2 The value of QMRA for risk management

QMRA gives a detailed breakdown of the contribution of each step in the chain from catchment-to-tap to the overall risk reduction, along with some indication of data variability and uncertainty. The water supplier can use this information to decide where optimisation or additional control would be most effective. By setting health-based targets based on the contribution of drinking water to the overall health risk of the human population, it becomes clear when safe is safe enough. Hence, QMRA is also a tool to guide the risk manager to efficient control. Risk management questions that can be quantified by QMRA are illustrated in **Figure 2-1**. Most of these questions especially relate to drinking water treatment, since it is there that the source water is transformed to safe drinking water.

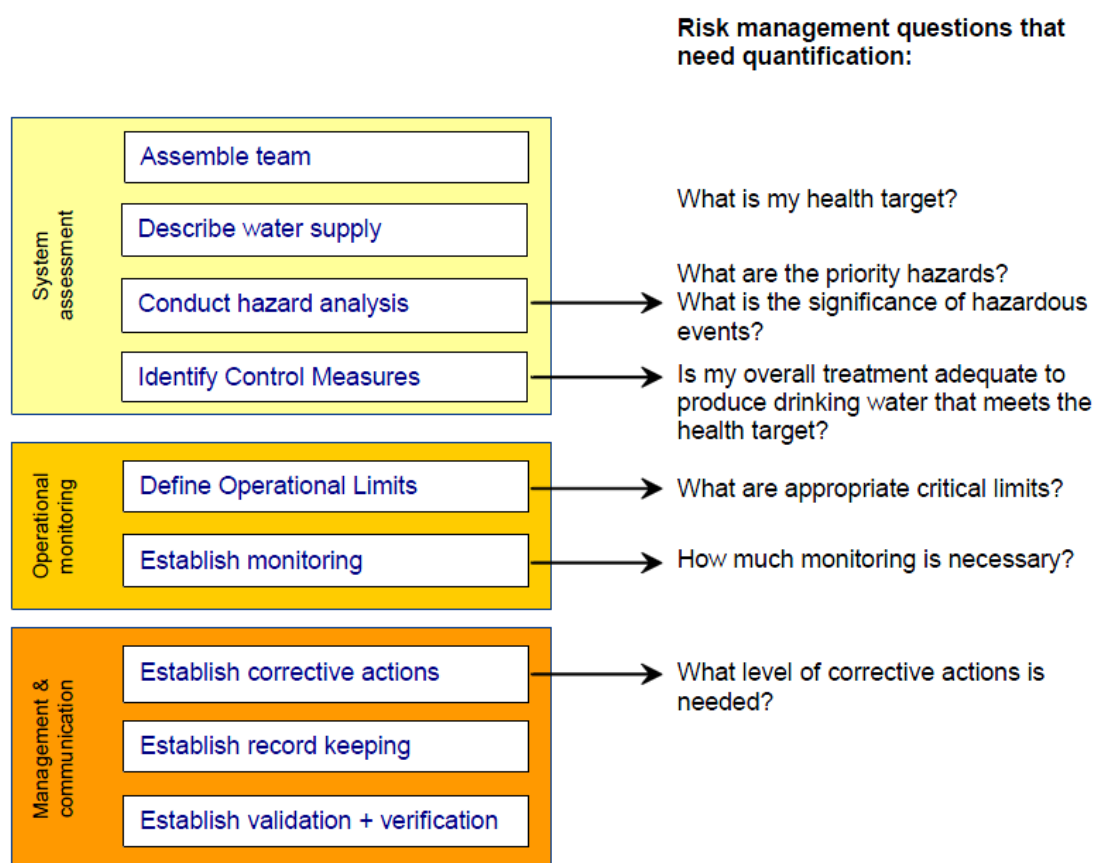


Figure 2-1 Risk management questions that can be quantified by QMRA

Complying with health targets

At the water utility level, a QMRA can be conducted to answer the question: "Do we meet the health target?" QMRA cannot only provide a quantitative estimate of the level and variation of risk. It also provides an indication of the uncertainty of the assessment, allowing for a balanced interpretation of the outcome. If the outcome of the assessment indicates that the drinking water could be unsafe under some conditions, QMRA can help to identify the most economic, sufficiently effective measure to bring the risk within the health-based targets. When drinking water is produced from surface water, drinking water treatment generally forms the means by which the water quality is controlled.

Setting critical limits

A treatment system can be designed to provide exactly the right level of treatment to meet the health-based targets. However, in practice the risk manager needs to account for variations and uncertainties in order to run a practical and stable process. Treatment systems are controlled by setpoints, operational limits and critical limits. During normal

operation at the setpoint, the treatment will run between operational limits. When the process deviates beyond the critical limits, corrective actions are required in order to meet health-based targets. Setting of appropriate operational and critical limits is complex since they depend on the (long term) treatment target, variability of the process, response time and the options for corrective actions. The applicable safety margin for treatment efficacy is limited due to other goals such as costs or prevention of disinfection by-products. QMRA can address these issues by quantifying the microbial risk outcome of different options both for individual and combined processes. Arriving at the optimal limits will need several iterations, using practical experience and ongoing scientific insights to further improve the operation of the treatment system. Critical limits will depend on circumstances such as water temperature or source water turbidity. For complicated systems a real-time computer model of the water supply system (for disinfection and other water quality parameters) may be helpful in maintaining optimal water quality and choosing the most appropriate corrective measures.

Designing monitoring programs

Monitoring of treatment systems serves two goals. On the one hand monitoring is applied to verify that the system nominally meets the health based targets. Microbial monitoring provides the most direct verification of system performance. However microbial monitoring requires resources and funds, and cannot be applied limitlessly. QMRA can be used to design the microbial monitoring plan so that results will provide a statistically valid verification of treatment performance at the required confidence level. Monitoring results can be used in QMRA to adapt the microbial monitoring program to match the site specific situation.

On the other hand monitoring to detect events requires a high measurement frequency, which is not feasible with microbial monitoring. Rather than quantifying efficacy, this type of monitoring should detect deviations that indicate that treatment is failing. Monitoring of surrogates (turbidity, particles), process conditions (flow, temperature, disinfectant residual) and equipment (dosing pump, valves) can provide an indication of failure and is generally easier and cheaper than microbial monitoring. Very short failure events can significantly impact the mean treatment efficacy. QMRA can be used to design frequency of (on-line) monitoring to verify that the health-based targets are not compromised by failure events.

Preparing corrective actions

When critical limits are exceeded, corrective actions are needed to restore system control

and prevent non-compliance with the health-based target. Different levels of corrective actions may be undertaken. These could be restricted to the control measure that is out of bounds, but could also include other control measures that may be enhanced or additional (emergency) control measures. QMRA can be used to select the most appropriate corrective actions under the given conditions, as it looks at the system as a whole, rather than at individual control measures. The level and duration of the required corrective action can also be determined through QMRA.

Treatment design: comparing alternatives

During the design of a water treatment plant, or when changes to a treatment plant are required, one needs to choose between different solutions. Each (combination of) solutions need to comply with the health-based targets. A QMRA can help identify the most economic alternative. Thus unnecessary investments can be avoided. Here QMRA can be used as a design tool. QMRA can also be used in the design stage to evaluate control strategies, determine required redundancy and prepare effective monitoring.

2.2.3 QMRA in drinking water guidelines and legislation

After the first attempts of QMRA in 1983, QMRA was applied in various ways to improve the microbial safety of drinking water. In 1996 the ILSI Risk Science Institute Pathogen Risk Assessment Working Group developed a conceptual framework to assess the risks of human disease associated with exposure to pathogenic microorganisms (ILSI, 1996) that was based on QMRA. This was later evaluated by Teunis and Havelaar (1999). Haas *et al.* (1999) wrote an extensive guide to risk assessment for pathogens in (drinking) water to which the reader is referred for details on the QMRA method.

In 1989 the USEPA used QMRA to develop technical requirements for drinking water treatment in the Surface Water Treatment Rule (USEPA, 1989) in order to roughly achieve a maximum risk of infection of 10^{-4} per person per year for *Giardia* and viruses. Later the SWTR was extended for *Cryptosporidium* in the IESWRT (USEPA, 1998), and was further elaborated in the LT1ESWTR (2002) and LT2ESWTR (2006). The rule awarded 'reduction credits' for treatment processes when these are sufficiently monitored. The combined processes needed to provide sufficient treatment for the level of source water contamination.

Other regulators did not set technical standards; instead they required a site specific QMRA for each drinking water system. In 2001 Dutch drinking water regulations included a maximum acceptable risk of infection of 10^{-4} per person per year, to be

verified with QMRA (Anonymous, 2001). The WHO Water Quality: Guidelines, Standards and Health (WHO, 2001) presented a harmonized framework for risk assessment and management. Apart from risk of infection, WHO (WHO, 2011) promoted a risk endpoint of 10^{-6} disability adjusted life years (DALYs) that includes the adverse health effects when an infected individual becomes ill. As this approach uses diseases burden, the estimated result can be compared to the risk caused by other chemical or microbial agents. The new proposed Canadian drinking water guidelines for viruses include QMRA to verify that sufficient treatment is applied to reach a health-based target of 10^{-6} DALYs (CDW, 2007). QMRA was also considered for legislation of bathing water (USEPA, 2007) and in Australia for water reuse (NWQM, 2006 & 2007).

A third development to improve drinking water safety focused on managing risks on an operational level. In 1994 the use of Hazard Analysis and Critical Control Point (HACCP), as applied for food safety, was tested for applicability in drinking water safety (Havelaar, 1994; Teunis *et al.*, 1994). Over the years this concept developed into Water Safety Plans (WSP) (Barry *et al.*, 1998; Deere and Davison, 1998; Davison *et al.*, 2006). In 2004 the IWA and WHO presented the Bonn charter (IWA/WHO, 2004) which set a high level framework for drinking water risk management. In addition WHO published the fourth edition of the Drinking Water Guidelines (WHO, 2011). Both promoted the use of Water Safety Plans (WSP) to manage drinking water safety in an integral manner. In 2002 the MicroRisk project was started (MicroRisk, 2002; Medema *et al.*, 2006) to bring together the WSP and QMRA methods.

The present study focuses on the estimate endpoint of QMRA to verify that the new proposed water treatment process for reducing chlorinous odor is adequate to produce drinking water that meets the health based target of 10^{-4} per person per year. The reader is referred to Asada (2013) for a complete estimate of the DALYs for a conventional treatment process including coagulation and sedimentation, rapid sand filtration (RSF) and chlorination based on the similar data of this study.

Although the QMRA in drinking water guidelines and legislation has progressed over the last three decades, the drinking water industry in Japan is still just at the beginning of take into account of applying QMRA on a regulatory basis. This study describes how QMRA method can be used in a new system assessment and how the outcome of QMRA can be used as a basis for risk management in the water treatment industry. The calculated infectious risk provides a direct impression of treatment efficacy level and drinking water quality level in Japan. Locally generated data will always be of great value in setting

national targets. The findings of this study will be a basic knowledge to help the Japanese government carrying out the appropriate policies of applying QMRA in drinking water legislation for the forthcoming years.

2.2.4 QMRA framework

QMRA is derived from the chemical risk assessment paradigm that encompasses four basic elements. A general framework for assessing microbial risk for drinking water is proposed in “Plan for QMRA for CTSs” a work within the Microrisk project. **Figure 2-2** describes a general QMRA framework.

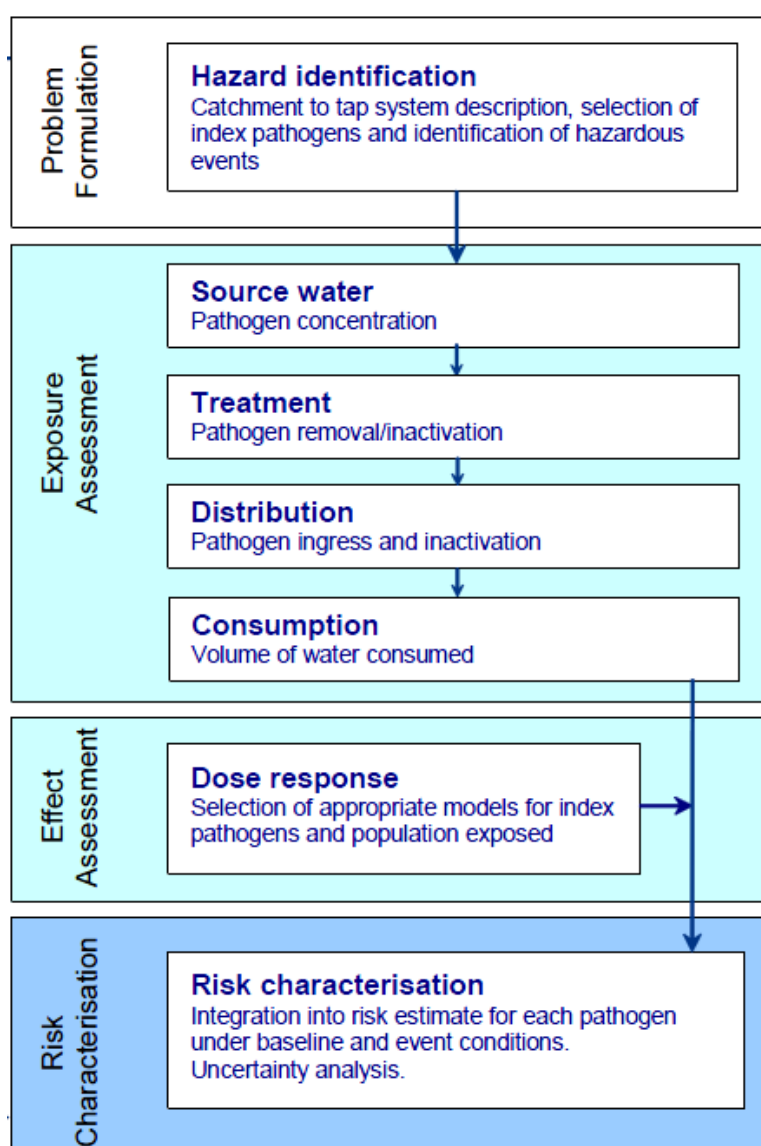


Figure 2-2 General QMRA framework (Medema and Ashbolt, 2006)

Element 1 Problem formulation and hazard identification

This is the initialising phase of QMRA to establish which specific questions need to be addressed. The scope and the boundaries of the QMRA process are determined in this phase. The basic questions to QMRA is: “Is my system able to meet the health targets?”. To conduct a QMRA, a good description of the system from catmint to top under evaluation is necessary and the hazards and hazardous events need to be identified. Hazard identification is the identification of the micro-organisms within the system boundaries that could cause human illness and the type of illnesses possible, the processes by which each micro-organism finally reaches the customner via drinking water and the type of illness possible (Haas *et al.*, 1999).

Element 2 Exposure assessment

Exposure assessment is the quantitative assessment of the probability that drinking water consumers ingest pathogens through this drinking water. In QMRA of drinking water, this usually requires the assessment of the levels of pathogens in source water and the changes to these levels by treatment, storage and distribution, and finally the volume of water consumed.

Element 3 Effect assessment

The effect assessment is the determination of the health outcomes associated with any (level of) exposure to waterborne pathogens.

Element 4 Risk characterisation

As a last step in the QMRA a characterization of the risk is performed. Exposure that is entered into a dose-response relation results in an estimation of infection risk often expressed as the probability of infection per person per year or per day. This can be made as simple point estimation or be performed with Monte Carlo simulations so that distribution functions and uncertainty can be taken into account.

2.3 Target Pathogen

As described in 2.2.4, selection of target pathogen is the first step in QMRA. The QMRA of drinking water systems is usually focused on the ingestion of enteric pathogens and the potential for gastrointestinal illness. It will not be feasible to assess the risk of infection for all these individual organisms. Therefore it is suggested to assess the risk for a suite of index pathogens that are expected to cover the challenges posed by these existing and

new microbes (MicroRisk, 2006). Adequate control of these index pathogens implies that the health risk of other known pathogens is also adequately controlled by the system and that the system also offers protection against unknown pathogens.

Campylobacter bacteria are a major cause of waterborne diarrhoeal illness in humans and are the most common bacteria that cause gastroenteritis worldwide (Friedman *et al.*, 2000; Risebro *et al.*, 2006) - a large number of outbreaks of *Campylobacter* have been reported in Sweden for example, involving over 6000 individuals (Furtado *et al.*, 1998). They are also a frequent cause of waterborne enteric infections, and drinking water outbreaks of *Campylobacteriosis* have occurred in many developed countries (Hrudey and Hrudey, 2004; Miller and Mandrell, 2005).

The Dutch is the first country that has formally integrated the requirement to perform QMRA calculations to demonstrate the safety of water supply schemes. In Dutch drinking water legislation, assessment of the microbial safety of drinking water by QMRA for the so-called index pathogens *Enterovirus*, *Campylobacter*, *Cryptosporidium* and *Giardia* is required (Smeets *et al.*, 2009). According to a QMRA survey (Rutjes *et al.*, 2013) conducted from 2009 - 2012 for 12 Dutch production locations with surface water as a source, of the 46 infection risks that were assessed, 11 cannot meet the legal requirements of 10^{-4} . *Campylobacter* was the index pathogen with the highest non-compliance results, accounting for 45.5% of all cases. This result demonstrated that the required log reduction for *Campylobacter* is the largest among the four index pathogens.

In Japan, of the cases of waterborne infectious diseases transmitted through drinking water that were recently reported, 20.5% are due to *Campylobacter*, that is the second most important pathogenic bacteria after diarrheagenic *Escherichia coli* (*E.coli*) (Kaneko, 2006; Yamada and Akiba, 2007). The *Campylobacter* genus is currently composed of 22 species and eight subspecies (Debruyne *et al.*, 2009b). *Campylobacter jejuni* (*C. jejuni*), *Campylobacter coli* (*C. coli*) and *Campylobacter lari* (*C. lari*) species are among the most frequently isolated from humans. *C. jejuni* is the main cause of human infections accounting for > 63% of all cases (Kaneko, 2006; Yamada and Akiba, 2007).

It has been pointed out that close attention should be paid to *C. jejuni* as a potential cause of infection via drinking water, since surface water is the major source of drinking water in Japan. For these reasons, *C. jejuni* is selected as the target pathogen in this study.

Campylobacteriosis is the disease caused by the infection with *Campylobacter*. The onset

of disease symptoms usually occurs two to five days after infection with the bacteria, but can range from one to ten days. The most common clinical symptoms of *Campylobacter* infections include diarrhoea (frequently with blood in the faeces), abdominal pain, fever, headache, nausea, and/or vomiting. The symptoms typically last three to six days. Death from *Campylobacteriosis* is rare and is usually confined to very young or elderly patients, or to those already suffering from another serious disease such as AIDS. Complications such as bacteraemia (presence of bacteria in the blood), hepatitis, pancreatitis (infections of liver and pancreas, respectively), and miscarriage have all been reported with various degrees of frequency. Post-infection complications may include reactive arthritis (painful inflammation of the joints which can last for several months) and neurological disorders such as Guillain-Barré syndrome, a polio-like form of paralysis that can result in respiratory and severe neurological dysfunction or death in a small number of cases.

have been isolated from a variety of domestic and wild birds and animals, and are commonly found in nature, which makes waterborne transmission possible. Although drinking water may not be the primary vehicle for the transmission of these pathogens to human, they have been associated with several waterborne disease outbreaks throughout the world.

2.4 Overview of the Water Treatment Process for Reducing Chlorinous

Odor

“Knowing your system” is a prerequisite for undertaking QMRA. The target water treatment process in this study consists of six basic steps (as shown in **Figure 2-3**); coagulation and sedimentation, rapid sand filtration (RSF), advanced oxidation process (AOP) with ozone/ultraviolet light, cation exchange, anion exchange, and chlorination. AOP and ion-exchange treatments are the main stages for the reduction of chlorinous odor. Since it would be desirable to decrease the concentration of residual chlorine in the water supply in the future, in this study, the minimized residual chlorine level was set to approximately 0.1 mg/L.

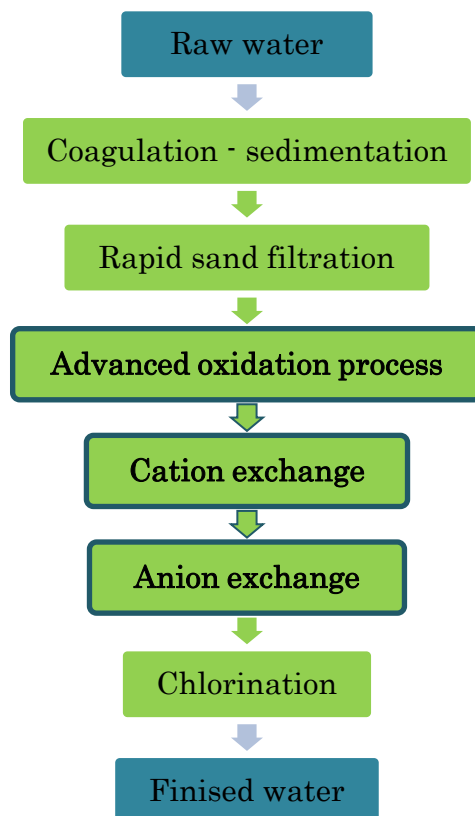


Figure 2-3 Water treatment process for reducing chlorinous odor

2.4.1 Reduction of chlorinous odor by the combination of AOP and ion-exchange treatments

In order to better control chlorinous odor in tap water, one proposed solution is the application of a strong oxidant to oxidize the precursors of chlorinous odor before chlorination. For this purpose, the use of combination of ozone/vacuum ultraviolet (advanced oxidation process, AOP) and ion-exchange treatments to better control chlorinous odor in tap water has been proposed by Echigo *et al.* (2014).

While not all the compounds responsible for chlorinous odor have been identified, trichloramine (Kajino *et al.*, 1999) and N-chloroaldehydes (Froese, 1999; Freuse *et al.*, 2005) are known as major contributors to chlorinous odor. Trichloramine can be produced both inorganic (i.e., ammonium ion) and organic nitrogen (e.g., free amino acids). Also, other compounds responsible for chlorinous odor including N-chloroaldehydes are formed from dissolved organic matter (DOM). Thus, the strict control of both ammonium ion and DOM is essential for the control of chlorinous odor. In this new water treatment process, hydrophilic neutral fraction (a major DOM fraction) is converted to ionic species by AOP

treatment, and these ions and ammonium ion are effectively removed during ion-exchange processes. The theoretical consideration is shown in **Figure 2-4**. Echigo *et al.* (2014) found that with combination of AOP at a high ozone dose and both cation and anion exchange, the chlorinous odor formation potential was reduced to approximately 30 TON from more than 100 TON. Also, DOC and ammonium ion were effectively removed with this process. The effectiveness of this process was also confirmed in continuous mode with plot-scale experiment.

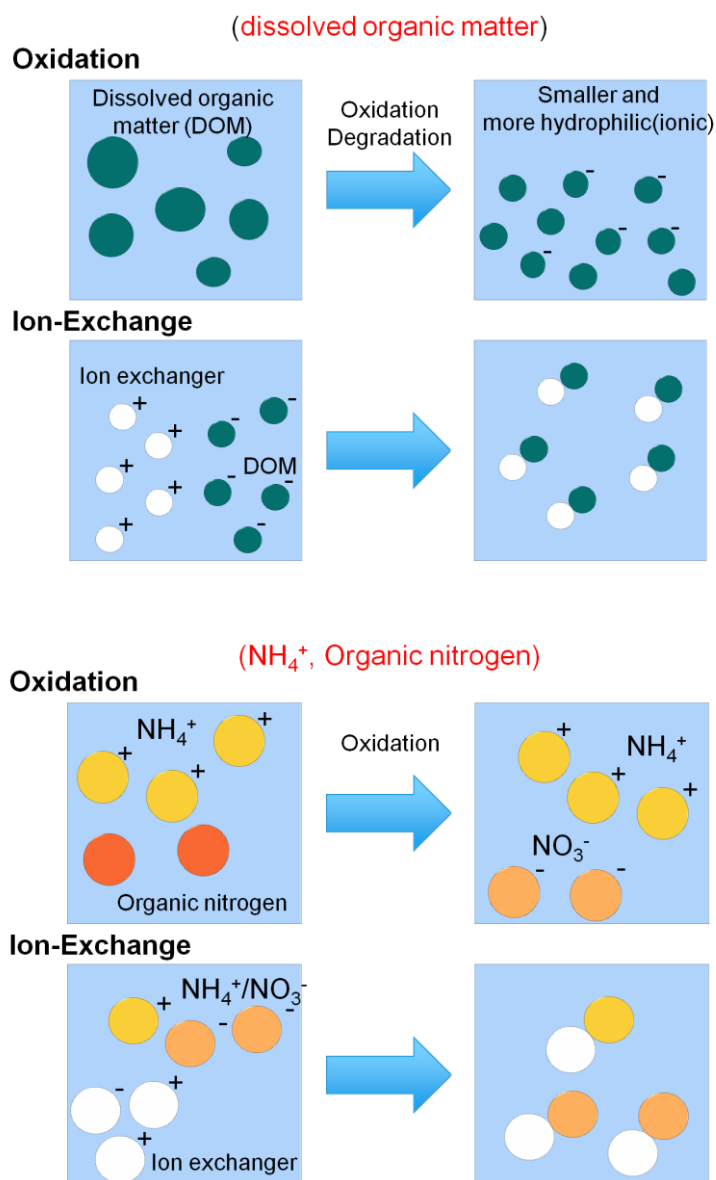


Figure 2-4 Reduction of the precursors of chlorinous odor

2.4.2 Treatment assessment approach

The goal of the treatment assessment is to describe micro-organism reduction performance for input into a QMRA. By combining this information with the micro-organism concentration in the source water, the number of micro-organism in the treated water can be estimated. When assessing the elimination capacity, all treatments that are known to affect micro-organisms are addressed, even if they were not originally aimed at reducing pathogens, such as RSF and ion exchange processes. The micro-organism concentration in the water leaving the treatment plant for distribution is represented as finished water. The distribution may function as a potential entrance for pathogens due to contamination through leaking pipes etc. However, the majority of the water reaching the consumers is expected to have the same pathogen concentration as the water leaving the treatment plant.

Elimination capacity data can be collected from various ways:

1. Routine water quality monitoring (e.g., micro-organisms in source water)
2. Direct measurement of indicator before and after treatment on full-scale plant (e.g., coagulation and sedimentation)
3. Quantitative analysis of literature data (e.g., RSF)
4. Mathematical model for disinfection process (e.g., AOP)
5. Laboratory column tests (e.g., cation exchange, anion exchange)
6. Challenge tests on pilot plant scale (e.g., chlorination)

2.4.3 Calculation of decimal elimination capacity

The elimination capacity of micro-organisms by the water treatment process is often expressed as $\log_{10}$ reduction. The reduction is a physical removal of organisms or inactivation thereof through a specific process, e.g., through disinfection. One $\log_{10}$ reduction is defined as 90% of the organism reduced or removed, two $\log_{10}$ reductions means a 99 % reduction, 3- $\log_{10}$ reduction equals 99.9% removal and 4- $\log_{10}$ reduction will remove 99.99% of the microorganisms (EPA, 2003 a). $\log_{10}$ reduction is explained in **Table 2-1**. In this study the word Log is used and refers to $\log_{10}$ if nothing else is pronounced.

Table 2-1 Explanation of log reduction

Log Reduction	% Reduction
1-Log	90
2-Log	99
3-Log	99.9
4-Log	99.99

Log reduction can be expressed as Decimal Elimination Capacity (DEC) with the following equation (Hijnen *et al.*, 2005).

$$\text{DEC} = \text{Log}_{10}\pi = \text{Log}_{10}C_{\text{in}} - \text{Log}_{10}C_{\text{out}} = \text{Log}_{10}\frac{C_{\text{in}}}{C_{\text{out}}} \quad (2-1)$$

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23. The microorganisms in drinking water are a highly diverse group that can be divided in four groups: bacteria, viruses, protozoa, and algae. The most common and widespread health risk associated with drinking water is infectious disease caused by pathogenic bacteria, viruses, and protozoa. Consumption of drinking water contaminated with human or animal excreta is the most significant route of exposure (Westrell, 2004)
24. The proposed new water treatment process requires ensuring that drinking water is microbiologically safe for drinking purposes while at the same time reducing chlorinous odor.
25. However, the full benefit of this new process is not achieved because of a lack of information from the viewpoint of microbial safety of drinking water. The overall purpose of this study is to apply the QMRA method to provide a quantitative estimate

of the level and variation of microbial risk in drinking water treated with this new water treatment process for reducing chlorinous odor. Besides knowledge about the presence of micro-organisms in the source water, QMRA requires quantitative knowledge about the capacity of water treatment processes.

26. This section gives an introduction of the main stages of the water treatment process and the basic knowledge with respect to the assessment of elimination capacity of water treatment process.
27. QMRA is a method to quantify microbial risk within a system and can be used to guide the risk manager to efficient control.
28. Since direct assessment of drinking water safety through drinking water pathogen monitoring is not feasible, quantifying treatment efficacy is a crucial step in QMRA.

Chapter 3

Concentration Interpolation Method for Data below Detection Limit in Quantitative Microbial Risk Assessment

3.1 Introduction

Quantitative Microbial Risk Assessment (QMRA) methods have been applied to quantify the microbial safety of drinking water since the 1980s (Hass *et al.*, 1999; Medema *et al.*, 2006); however, there have some limitations in monitoring microbial quality of drinking water by performing QMRA. For QMRA method, the most reliable calculations can be made if plant specific data are used. In fact, the water treatment plants usually have large amounts of historical monitoring data on the prevalence of faecal indicator bacteria in their source waters and the water further down the treatment, assessed with standard microbiological methods. These data yield valuable quantitative information of the first processes in water treatment on the elimination of these indicators. However, such routinely collected data usually include a large number of non-detects which are not suited to determine accurately elimination capacity of water treatment process. Although, concentrations of pathogenic microbes can easily be determined in the source water, after one or more treatment processes the concentrations decrease and a sample volume of 10 mL or 100 mL as tested in the routine microbiological methods is too small to measure the actual concentration. When there were no pathogenic microbes detected in these small volumes, the concentrations of pathogenic microbes below the detection limit were generally reported as ‘nondetect’ or values only known to be somewhere between zero and the reporting limit. Measurements are considered too imprecise to report as a single number, so the value is commonly reported as being less than an analytical threshold, for example “< 0.2”. Since the removal and inactivation efficacy of water treatment process was calculated from the concentration of pathogenic microbes in the influent (C_{in}) and effluent (C_{out}) in QMRA method, accurate information of removal and inactivation efficacy cannot be obtained when using these ‘non-detect’ data.

The worst practice when dealing with non-detects is to exclude or delete them. This produces a strong upward bias in all subsequent measures of location such as means and

medians. After exclusion, comparisons are being made between the mean of the top 20% of concentrations in one group versus the top 50% of another group, for example. This provides little insight into the original data. Excluding non-detects removes the primary signal that should be sent to hypothesis tests – the proportion of data in each group that lies above the reporting limit(s), the shift producing the difference between 20% and 50% detects.

The most common procedure within environmental chemistry to deal with non-detects continues to be substitution of some fraction of the detection limit. This method is better labeled as “fabrication”, as it reports and uses a single value for concentration data where a single value is unknown. Within the field of water research, one-half is the most commonly used fraction, so that 0.5 is used as if it had been measured whenever a <1 (detection limit of 1) occurs. Studies 20 years ago found substitution to be a poor method for computing descriptive statistics (Gilliom and Helsel, 1986). Subsequent justifications for using one-half the reporting limit when data follow a uniform distribution (Hornung and Reed, 1990) only considered estimation of the mean. Any substitution of a constant fraction of reporting limits will distort estimates of the standard deviation, and therefore all (parametric) hypothesis tests using that statistic. Also, justifications such as these have never considered errors due to changing reporting limits arising from changing interferences between samples or similar causes. Substituting values tied to those changing limits introduces a signal into the data that was not present in the media sampled. Substituted values using a fraction anywhere between 0 and 0.99 times the detection limit are equivalently arbitrary, equivalently precise, and equivalently wrong.

Statisticians use the term “censored data” for data sets where specific values for some observations are not quantified, but are known to exceed or to be less than a threshold value. Techniques for computing statistics for censored data have long been employed in medical and industrial studies, where the length of time is measured until an event occurs such as the recurrence of a disease or failure of a manufactured part. For some observations the event may not have occurred by the time the experiment ends. For these, the time is known only to be greater than the experiment’s length, a censored “greater-than” value. Methods for computing descriptive statistics, testing hypotheses, and performing correlation and regression are all commonly used in medical and industrial statistics, without substituting arbitrary values. These methods go by the names of “survival analysis” and “reliability analysis”. There is no reason why these same methods could not also be used in the environmental sciences, but to date, their use is rare.

Previous research indicated that microbiological counts obtained from a single well-mixed sample may be expected to follow a Poisson distribution. Even though pathogenic microbes may not have been detected in a particular sample volume, it is possible, due to sampling variability, that the mean concentration in the original sample is greater than zero. In order to overcome the limitation of experimental method and improve a broader implementation of QMRA, the goal of this chapter is to develop a statistical method that based on the theory of the MPN method and the Poisson distribution to deal with those non-detects in the application field of QMRA and to apply this method in a case study.

This chapter first described the case study, monitored data and the concentration interpolation method. Then the concentration interpolation method was applied to extrapolate the non-detects that were below the detection limit. Third, using the extrapolated data, the removal efficacy and inactivation efficacy of water treatment were determined. Finally, the overall removal efficacy of water treatment and the yearly risk of infection were calculated. The variations in removal efficacy and inactivation efficacy, and the impact on QMRA outcome by using or without using extrapolated data were elucidated by comparing and contrasting three different cases. In addition, the applicability and limitation of the proposed method for QMRA was described.

3.2 Methods

3.2.1 Case description (Itoh, 2010)

The Weesperkarspel treatment plant of Waternet (water cycle company for Amsterdam and the surrounding areas) located in the western Netherlands was used as a case study. With a production average of 115,000 m³/day, the plant supplies drinking water to the eastern part of Amsterdam and the suburbs. The source water for this plant is abstracted from a polder (the 5.4 km² Bethune Polder) that is a land reclaimed for agriculture and stock raising. The water is pumped out as surface water from the neighboring watercourses and is mainly seepage water flowing through a good permeable underground of the polder. When water demand is high, such as in the summer, water can also be abstracted from the nearby Amsterdam-Rhine Canal (ARK-water). The volume of ARK-water is 5% of the total annual produced volume. The Amsterdam-Rhine Canal water comes from the Rhine River, and is more polluted than the water from the Bethune Polder (Hijnen *et al.*, 2005).

Figure 3-1 shows the treatment process of the plant. The raw water is pre-treated by

coagulation, stored in the lake water reservoir, and then undergoes rapid sand filtration (RSF) at the Loenderveen plant. The average time in the reservoir (123 ha, $6.9 \times 10^6 \text{ m}^3$) is 89 days. After the RSF, the water is transported to the Weesperkarspel plant where it undergoes several treatment steps such as ozonation, softening, granular activated carbon (GAC) filtration and slow sand filtration (SSF). Among these treatment process, coagulation-storage, RSF, ozonation, and slow sand filtration are considered the main microbial barriers at the water treatment plant. Thus, removal and inactivation efficacy were estimated at these four steps.

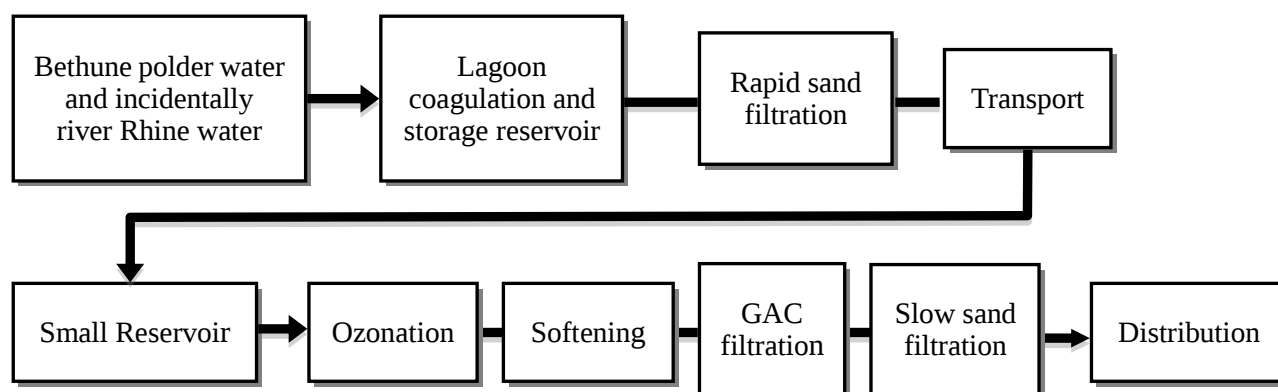


Figure 3-1 Treatment process of the plant

3.2.2 Pathogen and its indicator

Campylobacter was selected as a target pathogen in this study. Generally, it is not easy to measure the concentrations of pathogens in source water, treatment plant water or drinking water, and often there are not a large number of monitored concentrations. For pathogenic bacteria like *Campylobacter*, indicator bacteria like *E. coli* and enterococci have been proposed as process indicators to assess the elimination capacity of water treatment processes (Hijnen and Medema, 2010). For SSF, *E. coli* is a conservative surrogate for removal of *Campylobacter* as demonstrated by Hijnen *et al.* (2004) and Dullemont *et al.* (2006). For RSF, Hijnen *et al.* (1998) showed that *E. coli* is removed slightly better than environmental *Campylobacter*. It has been found that *E. coli* and *Campylobacter* can be similarly inactivated by ozonation (Smeets *et al.*, 2005).

Furthermore, *E. coli* is a microbe that is measured daily and thus many measurements are available for further analysis. Having more extensive data allowed us to obtain more

accurate estimation of the variation in the removal efficacy of water treatment. For these reasons, monitored *E. coli* was used as a surrogate for *Campylobacter* in this study. Then using the ratio of *Campylobacter* to *E. coli* (C/E ratio) measured in surface water, the *E. coli* concentration was translated into *Campylobacter* concentration. The data used to determine C/E ratio are concentrations of *E. coli* and *Campylobacter* in the Meuse river that were measured 22 times in one year in 1994 (Van Lieverloo *et al.*, 2006).

3.2.3 Monitored data

Data on *E. coli* in the raw water from the Bethune Polder were provided by Waternet. The analyses included *E. coli* concentrations that were measured 45 times from April, 2002 to December, 2004. The *E. coli* concentrations after coagulation-storage were measured 90 times from January, 2002 to August, 2005. The *E. coli* concentrations after RSF and after ozonation were measured 556 and 300 times, respectively, from January, 2003 to December, 2004. Four of the 300 measurements in ozonated water were performed with large volume samples ranging from 10 L to 100 L. The monitored *E. coli* data are shown in **Table 3-1**. *E. coli* was only detected in 44% and 5% of all samples after RSF and ozonation, respectively. Thus, concentration interpolation method was decided to use in these two steps. According to the detection method of *E. coli* concentration in this treatment plant, a detection limit was set to be 0.2 *E.coli*/100 mL.

Table 3-1 Summary of monitored *E. coli* data

	Number of samples	Number of positive	Positive detection rate (%)
Raw water	46	45	98%
After coagulation-storage	91	90	99%
After rapid sand filtration	556	243	44%
After ozonation	300	15	5%
After slow sand filtration	1393	1	0.07%

The final step in water treatment process before the water is supplied to the city is SSF. After this step, *E. coli* was detected only once (0.2 *E. coli*/100 mL) in a total of 1,393 times; all other samples were negative for *E. coli*. Pathogen concentrations in drinking water are generally below the detection limit. Therefore, the removal efficacy of SSF cannot be determined based only on the monitored data. In order to estimate the removal efficacy, we used the result of *E. coli* treatment in a pilot-scale plant, which had high enough densities of

the pathogen to obtain detection in the effluent (Dullemont *et al.*, 2006). A maximum value of 4.2 log₁₀, a mean elimination capacity (MEC) of 2.4 log₁₀, and a minimum value of 2.0 log₁₀ were obtained when determining the removal efficacy six times under conditions where the water temperature was below 13°C. A triangular distribution with these parameters was constructed.

3.2.4 QMRA procedure

E. coli concentrations in treated water C_{out} were calculated from the *E. coli* concentration in raw water C_{raw} and their reduction by the treatment processes in series using **equation 3-1**:

$$C_{out} = C_{raw} \times \pi_{coag} \times \pi_{rsf} \times \pi_{o3} \times \pi_{ssf} \quad (3-1)$$

where π_{coag} is the efficacy of coagulation-storage, π_{rsf} is the efficacy of rapid sand filtration, π_{o3} is the efficacy of ozonation and π_{ssf} is the efficacy of slow sand filtration. The treatment efficacy π was the fraction of organisms that passed a treatment step. The removal efficacy π was calculated from monitored concentrations of *E. coli* before and after a treatment process using **equation 3-2**:

$$\pi = \frac{C_{out}}{C_{in}} \quad (3-2)$$

where the concentration of *E. coli* after a treatment step is C_{out} and before a treatment step is C_{in} . As per the results of Itoh *et al.* (2010), who compared the date, rank and random methods using the same data as in this study, we selected the rank method because it proved to be the best validation method for treatment efficacy.

Daily exposure was calculated by multiplying the estimated *E.coli* concentration in the treated water with the amount of unboiled drinking water consumed per day. Then the *E. coli* dose was translated into the *Campylobacter* dose using the ratio of *Campylobacter* to *E. coli* (C/E ratio) in the surface water. The daily risk of infection from *Campylobacter* was calculated from the *Campylobacter* dose using a dose-response model for *Campylobacter*. The individual risk is represented by the average yearly risk of infection. Under the assumptions of a binomial process, the yearly risk of one or more infections is calculated using the following **equation 3-3**:

$$P_y = 1 - (1 - P_d)^{365} \quad (3-3)$$

The variables of C_{in} , π_{coag} , π_{rsf} , π_{O3} , π_{ssf} , C/E ratio and water consumption were represented by probability density functions (PDFs). Monte Carlo simulation was performed by drawing random values from each PDF of the *E.coli* concentration in the source water, four treatment steps, C/E ratio and water consumption to calculate the yearly infection risk P_y . This simulation assumes that there are no correlations between these variables. This procedure was repeated 100,000 times to achieve stable results.

3.2.5 Concentration interpolation method

Microbiological species consist of discrete entities or particles that cannot be assumed to be uniformly distributed throughout the water body. Rather, due to random variation in the location of microbial particles, microbiological counts obtained from a single well-mixed sample will rarely yield identical numbers (Eisenhart and Wilson, 1943; Greenwood and Yule, 1917). For instance, at low densities, the impact of sampling variability may be large. If the volume of water is considered well-mixed, the counts may be expected to follow a Poisson distribution:

$$P(N) = \frac{(\mu V)^N}{N!} e^{(-\mu V)} \quad (3-4)$$

where μ is the mean concentration of the water, V is the volume of the sample and N is the microbiological counts from the sample.

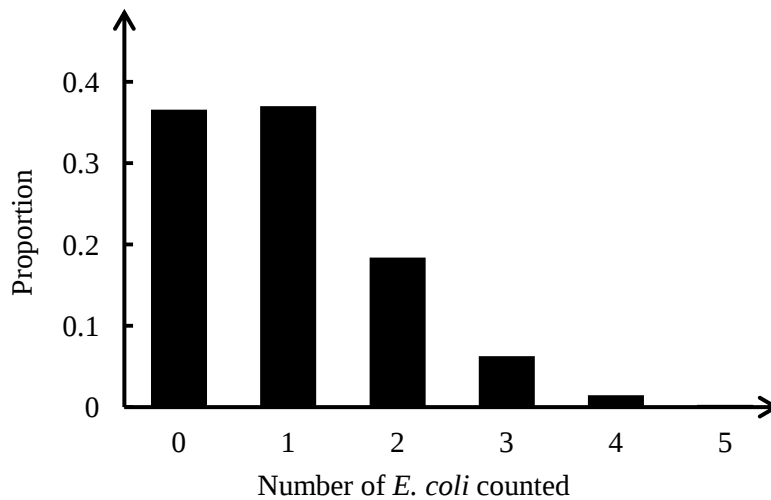


Figure3-2 The Poisson distribution with $\mu=1$

Because this distribution has only one parameter of μ , once the parameter of μ is determined, the Poisson count distribution can also be determined. An illustration of the Poisson count distribution with a mean μ of one is shown in **Figure3-2**. In a well-mixed water body, with a mean *E. coli* concentration of 1 *E. coli*/100 mL, replicate counts would be expected to vary from 0 to 4 98% of the time, with 2% of samples outside these limits. It is therefore possible that a collected sample may have 3 *E. coli*/100mL even though the mean concentration of the water body is 1 *E. coli*/100mL.

Similarly, for analytical techniques that rely on identifying the presence or absence of a target organism in the sample volume, sampling variability leads to uncertainty in interpreting analytical results. While the target organism may not have been identified in a particular sample volume, it is possible, due to sampling variability, that the mean concentration in the original sample was greater than zero. Suppose the number of *E. coli* counted in a 100 mL sample was 0, what was the actual mean concentration in the water body at that time?

When $N = 0$, $V = 100\text{mL}$

$$P(N = 0) = \frac{(100\mu)^0}{0!} e^{(-100\mu)} = e^{(-100\mu)} \quad (3-5)$$

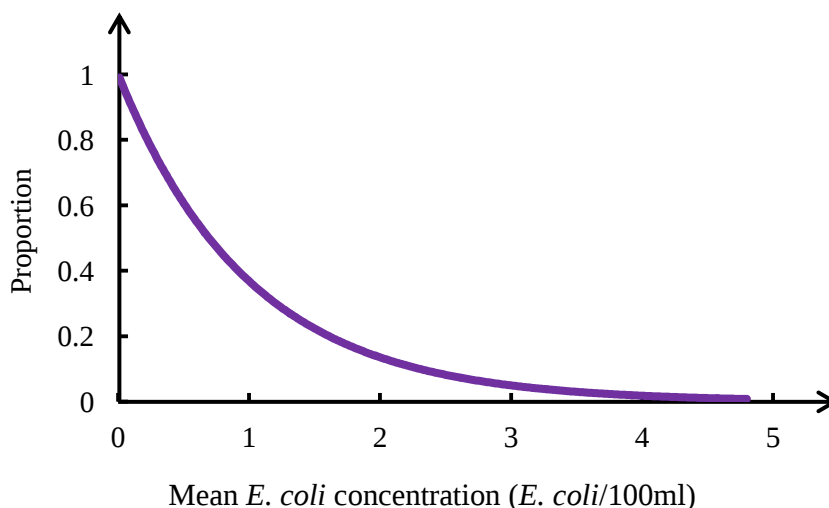


Figure3-3 The relationship between the mean *E. coli* concentration in the original sample and the probability that the number of *E. coli* counted in a 100 mL sample was 0.

The **equation 3-5** is shown in **Figure3-3**. We can found that at low mean concentration, the probability that the number of *E. coli* counted in a 100 mL sample was 0 may be large. According to the detection method of *E. coli* concentration in the treatment plant, a detection limit was set to 0.2 *E. coli*/100 mL. Thus, the actual mean *E. coli* concentrations could be set below the detection limit of 0.2 *E. coli*/100 mL, when counted *E. coli* was 0.

$$\begin{aligned} \text{When } \mu &= 0.2 \text{ } E. coli/100\text{mL} \\ P(N = 0) &= e^{(-100 \times 0.2)} = 0.8187 \end{aligned} \quad (3-6)$$

The **equation 3-6** indicates when the average concentration of the water was below the detection limit of 0.2 *E. coli*/100 mL, the probability that the number of *E. coli* counted in a 100 mL sample was 0 would be expected to range from 0.8187 to 1. By repeatedly drawing numbers at random from the probability range (0.8187 to 1), the average concentrations (μ) below the detection limit were produced according to **equation 3-7**:

$$\begin{aligned} \mu &= -\frac{\ln P}{100} \\ (0.8187 < P < 1) \end{aligned} \quad (3-7)$$

3.3 Results and Discussion

3.3.1 *E. coli* concentrations after interpolation

In this study, zero data were considered to have a significant impact on the estimated removal efficacy of RSF and the estimated inactivation efficacy of ozonation. Therefore, we extrapolated data that were below the detection limit for 313 *E. coli* concentrations after RSF and 285 *E. coli* concentrations after ozonation via the proposed concentration interpolation method. Histograms of *E. coli* concentration before and after interpolation are shown in **Figure3-4** and **Figure3-5**.

3.3.2 Application of distribution type and estimation of yearly risk of infection

PDFs were selected to describe the distributions of *E. coli* concentrations in raw water, the removal and inactivation efficacy by coagulation-storage, RSF, ozonation and SSF, and C/E ratio. The 45 positive *E. coli* concentrations monitored in raw water were fitted by a gamma distribution. A logistic distribution was fitted to the removal efficacies of π_{coag} calculated from the monitoring data. Since no site-specific data was available for SSF, we

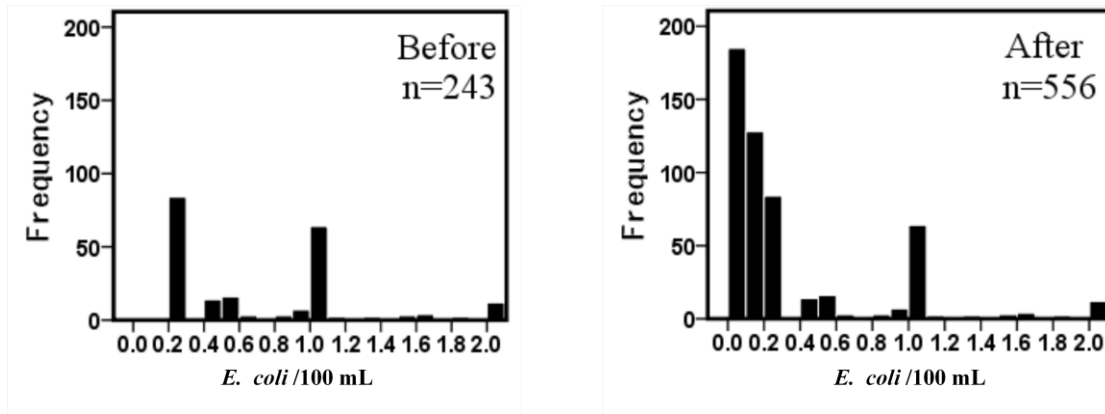


Figure3-4 Histogram of *E. coli* concentration after RSF

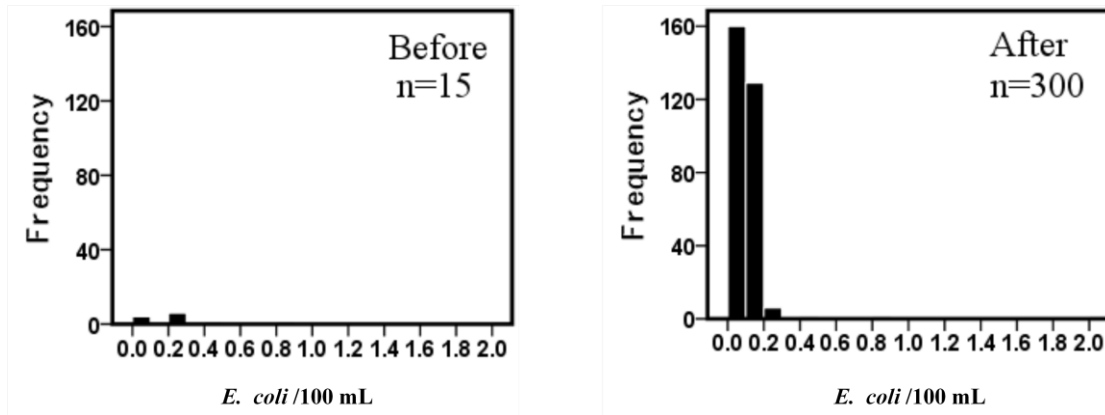


Figure3-5 Histogram of *E. coli* concentration after ozonation

used the result obtained from *E. coli* treatment in a pilot-scale plant. A triangular distribution with maximum value of 4.2 log₁₀, mean elimination capacity (MEC) of 2.4 log₁₀ and minimum value of 2.0 log₁₀ was fitted to the π_{ssf} data and used in the Monte Carlo simulation. A log-normal distribution was fitted to the C/E ratio.

To examine the impact of using *E. coli* concentrations extrapolated by the concentration interpolation method, the removal efficacy of RSF and the inactivation efficacy of ozonation were estimated in three cases using different types of data. The removal efficacy π was calculated from concentrations of *E. coli* before and after a treatment process using **equation 3-2**.

In case 1, when no *E. coli* was reported in the influent, then the removal efficacy could

not be estimated. When no *E. coli* was found in the effluent, the concentrations in the effluent below the detection limit were set to 0 *E. coli*/100 mL, assuming that no *E. coli* were present in the drinking water produced on that day. As a result, Weibull and normal distributions were fitted to the removal efficacies of π_{rsf} and π_{O_3} , respectively.

In case 2, the concentration interpolation method was applied to extrapolate the *E. coli* concentrations in the effluent that were below the detection limit. The results of the interpolation are as shown in **Figure3-4** and **Figure3-5**. Logistic distributions were fitted to the removal efficacies of π_{rsf} and π_{O_3} calculated from the *E. coli* concentrations after interpolation.

In case 3, the concentration interpolation method was applied to extrapolate both the concentrations in the influent and effluent that were below the detection limit. Weibull distribution was fitted to the removal efficacy of π_{O_3} . The selected PDFs and estimated parameters in cases 1, 2 and 3 are shown in **Tables 3-2, 3-3** and **3-4**, respectively.

The yearly risk of infection of *Campylobacter* was calculated with Monte Carlo simulation. The mean values of the yearly risk of infection were estimated to be 1.68×10^{-3} /person/year, 2.57×10^{-3} /person/year and 7.2×10^{-3} /person/year in cases 1, 2 and 3, respectively. The estimated risks in the three cases are shown in **Tables 3-5, 3-6** and **3-7**, respectively.

Table 3-2 Probability density functions (PDF) fitted to the target variables (**Case 1**).

Case 1		Number		PDF type	Mode	Estimated parameters
		C_{in}	C_{out}			
<i>E. coli</i> in the source water (<i>E. coli</i> /100 mL)				Gamma		$\mu = -2.50$; $\lambda = 383$; $\rho = 0.674$
Treatment efficacy (log reduction) of <i>E. coli</i>	Coagulation-storage	45	90	Logistic	1.48	$\mu = 1.48$; $\lambda = 0.15$
	RSF	90	556 ^{*1}	Weibull	1.27	$\mu = 1.74$; $\lambda = 0.59$; $\rho = 2.38$
	Ozonation	243	300 ^{*2}	Normal	1.91	$\mu = 1.91$; $\sigma = 0.88$
	SSF			Triangular	2.4	Min.= 2.00; MEC= 2.40; Max.= 4.20
C/E ratio				Lognormal		$\mu = 0.0415$; $\sigma = 0.104$

*1 313 negative *E. coli* concentrations after RSF were set to 0 *E. coli*/100 mL

*2 285 negative *E. coli* concentrations after ozonation were set to 0 *E. coli*/100 mL

Table 3-3 Probability density functions (PDF) fitted to the target variables (**Case 2**).

Case 2		Number		PDF type	Mode	Estimated parameters
		C_{in}	C_{out}			
<i>E. coli</i> in the source water (<i>E. coli</i> /100 mL)				Gamma		$\mu = -2.50$; $\lambda = 383$; $\rho = 0.674$
Treatment efficacy (log reduction) of <i>E. coli</i>	Coagulation-storage	45	90	Logistic	1.48	$\mu = 1.48$; $\lambda = 0.15$
	RSF	90	556 ^{*3}	Logistic	1.35	$\mu = 1.35$; $\lambda = 0.13$
	Ozonation	243	300 ^{*4}	Logistic	0.94	$\mu = 0.94$; $\lambda = 0.17$
	SSF			Triangular	2.4	Min.= 2.00; MEC= 2.40; Max.= 4.20
C/E ratio				Lognormal		$\mu = 0.0415$; $\sigma = 0.104$

*3 313 negative *E. coli* concentrations after RSF were extrapolated using concentration interpolation method

*4 285 negative *E. coli* concentrations after ozonation were extrapolated using concentration interpolation method

Table 3-4 Probability density functions (PDF) fitted to the target variables (**Case 3**).

Case 3		Number		PDF type	Mode	Estimated parameters
		C_{in}	C_{out}			
<i>E. coli</i> in the source water (<i>E. coli</i> /100 mL)				Gamma		$\mu = -2.50$; $\lambda = 383$; $\rho = 0.674$
Treatment efficacy (log reduction) of <i>E. coli</i>	Coagulation-storage	45	90	Logistic	1.48	$\mu = 1.48$; $\lambda = 0.15$
	RSF	90	556 ^{*3}	Logistic	1.35	$\mu = 1.35$; $\lambda = 0.13$
	Ozonation	556 ^{*3}	300 ^{*4}	Weibull	0.31	$\mu = 2.58$; $\lambda = 2.3$; $\rho = 8.22$
	SSF			Triangular	2.4	Min.= 2.00; MEC= 2.40; Max.= 4.20
C/E ratio				Lognormal		$\mu = 0.0415$; $\sigma = 0.104$

*3 313 negative *E. coli* concentrations after RSF were extrapolated using concentration interpolation method

*4 285 negative *E. coli* concentrations after ozonation were extrapolated using concentration interpolation method

Table 3-5 Statistics estimated in the QMRA (Case 1).

Case 1	Lower 95% CI boundary	Median	Mean	Upper 95% CI boundary
Overall log reduction	5.41	7.46	6.22	9.58
<i>E. coli</i> in the treated water (<i>E. coli</i> /100 mL)	1.07×10^{-8}	4.35×10^{-6}	1.64×10^{-4}	9.25×10^{-4}
<i>E. coli</i> dose (<i>E. coli</i> /day)	0	1.24×10^{-8}	2.99×10^{-4}	1.36×10^{-3}
<i>Campylobacter</i> dose(<i>Campylobacter</i> /day)	0	1.35×10^{-10}	9.52×10^{-6}	3.36×10^{-5}
Daily risk of infection (/person/day)	0	9.24×10^{-11}	6.51×10^{-6}	2.30×10^{-5}
Yearly risk of infection (/person/yr)	0	3.37×10^{-8}	1.68×10^{-3}	9.06×10^{-3}

Table 3-6 Statistics estimated in the QMRA (Case 2).

Case 2	Lower 95% CI boundary	Median	Mean	Upper 95% CI boundary
Overall log reduction	5.4	6.61	6.16	8
<i>E. coli</i> in the treated water (<i>E. coli</i> /100 mL)	10^{-7}	2.85×10^{-5}	1.77×10^{-4}	1.25×10^{-3}
<i>E. coli</i> dose (<i>E. coli</i> /day)	0	0	3.2×10^{-4}	2.48×10^{-3}
<i>Campylobacter</i> dose(<i>Campylobacter</i> /day)	0	0	10^{-5}	7×10^{-5}
Daily risk of infection (/person/day)	0	0	9×10^{-6}	5×10^{-5}
Yearly risk of infection (/person/yr)	0	0	2.57×10^{-3}	1.81×10^{-2}

Table 3-7 Statistics estimated in the QMRA (Case 3).

Case 3	Lower 95% CI boundary	Median	Mean	Upper 95% CI boundary
Overall log reduction	4.88	6.07	5.64	7.5
<i>E. coli</i> in the treated water (<i>E. coli</i> /100 mL)	5×10^{-7}	9.75×10^{-5}	5.89×10^{-4}	4.21×10^{-3}
<i>E. coli</i> dose (<i>E. coli</i> /day)	0	0	1.06×10^{-3}	8.49×10^{-3}
<i>Campylobacter</i> dose(<i>Campylobacter</i> /day)	0	0	4×10^{-5}	2.5×10^{-4}
Daily risk of infection (/person/day)	0	0	2.9×10^{-5}	1.71×10^{-4}
Yearly risk of infection (/person/ yr)	0	0	7.2×10^{-3}	6.07×10^{-2}

3.3.3 Removal efficacy of RSF

Figure3-6 shows the distributions of the removal efficacy of RSF in three cases. The removal efficacy of RSF was calculated from monitored concentrations of *E. coli* before

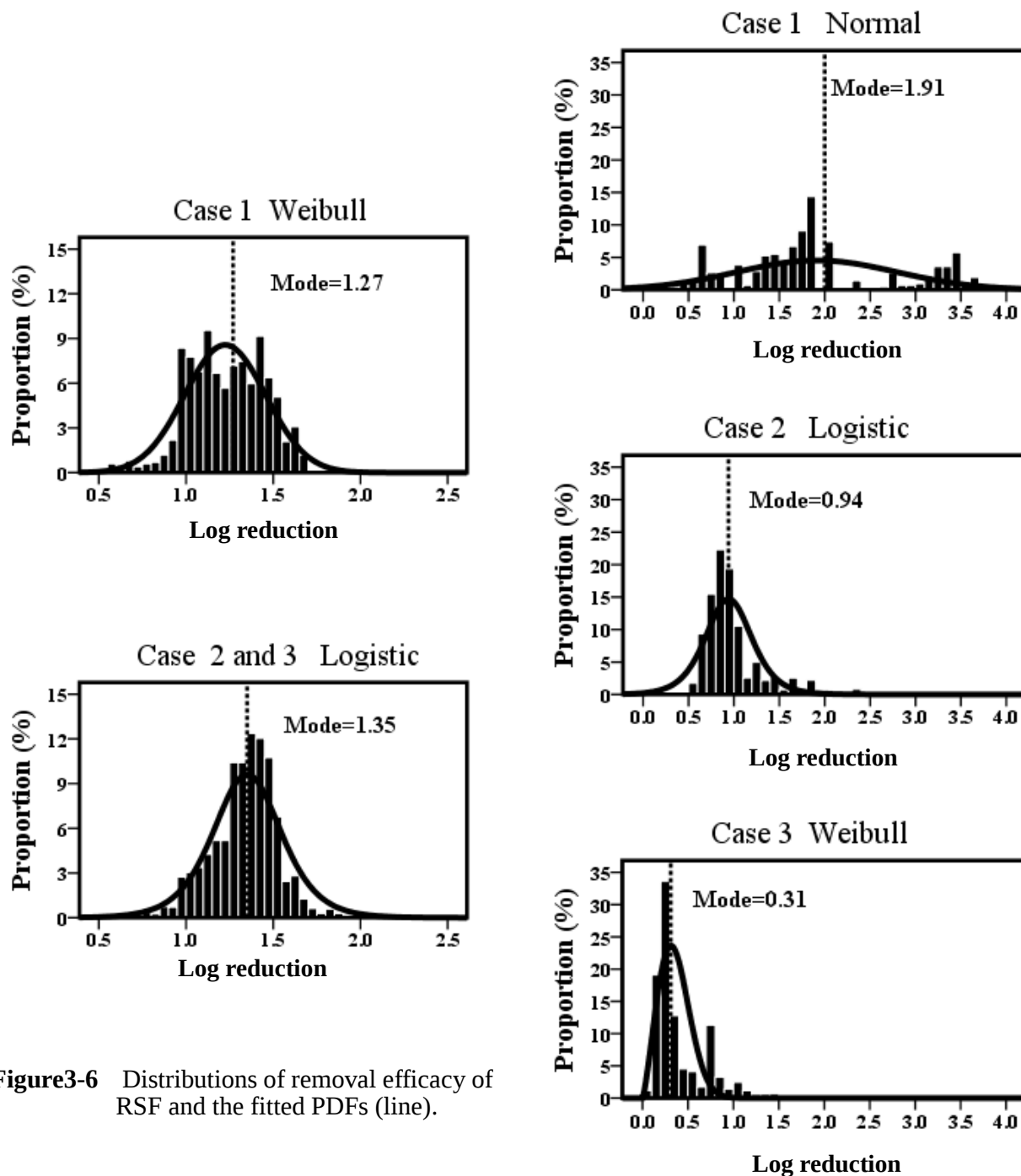


Figure3-6 Distributions of removal efficacy of RSF and the fitted PDFs (line).

Figure3-7 Distributions of inactivation efficacy of ozonation and the fitted PDFs (line).

and after RSF using **equation 3-2**. In case 1, since the 313 negative *E. coli* concentrations after RSF were set to 0 *E. coli*/100 mL, log reductions could not be estimated using these data. The mode of the log reduction of RSF was calculated to be 1.27 log₁₀ based on the other 243 positive data. In cases 2 and 3, the 313 negative *E. coli* concentrations after RSF were extrapolated by the concentration interpolation method with a range of 0 to 0.2 *E. coli*/100 mL and resulted in an increased log reduction. As a result, the mode of the log reduction of RSF was calculated to be 1.35 log₁₀ from the extrapolated concentrations in cases 2 and 3. For this reason, the removal efficacies of RSF in cases 2 and 3 were estimated to be greater than those in case 1.

3.3.4 Inactivation efficacy of ozonation

Figure3-7 shows the distributions of inactivation efficacy of ozonation in three cases. We found this to be opposite to the removal efficacy of RSF: the inactivation efficacy of ozonation in case 1 was estimated to be greater than the inactivation efficacies in cases 2 and 3.

As shown in **Figure3-7**, the pattern of log reduction in the inactivation efficacy of ozonation is different at the high end of the scale (2.4 – 4 log₁₀) between cases 1 and 2. In the calculation process, the section corresponding to 2.4 to 4 log₁₀ of the log reduction in case 1 resulted from 4 low *E. coli* concentrations that were measured in large volume samples of 10 L to 100 L. The rank method was applied in this study to determine the treatment efficacy. To enable pairing by rank, the samples of the influent and effluent concentrations were sorted in descending order by concentration before determining treatment efficacy. In case 1, 285 negative *E. coli* concentrations after ozonation were set to 0 *E. coli*/100 mL. As a result of sorting all 300 *E. coli* concentrations in descending order, the 4 low *E. coli* concentrations measured in large volume samples of 10 L to 100 L were paired with relatively large *E. coli* concentrations in the influent. As a result, relatively large log reductions were obtained and are shown in the log reduction range of 2.4 to 4 log₁₀ in case 1. In case 2, the 285 negative *E. coli* concentrations after ozonation were extrapolated via the concentration interpolation method with a range of 0 to 0.2 *E. coli*/100 mL. By sorting all 300 *E. coli* concentrations in descending order, the 4 low *E. coli* concentrations measured in large volume samples were located at the end of the sequence and paired with relatively low *E. coli* concentrations in the influent. Thus, in contrast to case 1, the log reduction range of 2.4 to 4 log₁₀ disappeared. It should be noted that low *E. coli* concentrations that were measured in large volume samples may confound estimations of treatment efficacy. Therefore, it is necessary to select an appropriate dataset and a

pairing method (Smeets *et al.*, 2008) before performing QMRA.

It was noted in **Figure3-7** that the inactivation efficacy of ozonation in case 3 was much lower than that in case 2. In case 3, the concentration interpolation method was applied to extrapolate both the concentrations in the influent and effluent that were below the detection limit. That is, the 313 negative *E. coli* concentrations after RSF and the 285 negative *E. coli* concentrations after ozonation were extrapolated with the same range of 0 to 0.2 *E. coli*/100 mL. The removal efficacy of ozonation was calculated from concentrations of *E. coli* before and after ozonation using equation 2. Since the values of C_{in} and C_{out} are close, large numbers of the log reduction were calculated to be approximately 0. As a result, a distribution with a mode of 0.31 $\log_{10}$ of the log reduction was obtained in case 3. This suggests that the mean yearly risk of infection of 7.2×10^{-3} /person/year estimated in case 3 is too high and not an appropriate estimate. This demonstrates that the concentration interpolation method is not applicable to simultaneously interpolate the data before and after treatment.

3.3.5 Applicability and limitation

The concentration interpolation method used in this study was based on a statistical principle, and we suggest this method is applicable when a large amount of data needs to be extrapolated. It is obvious that obtaining data using this method is easier than conducting an experiment. Furthermore, the concentration interpolation method can be more appropriate than either a graphical extrapolation method (Smeets *et al.*, 2007) or the arbitrary method of assigning non-detectable samples to “half of the detection limit”. It should be noted, however, that this method is not applicable to simultaneously interpolate data before and after treatment.

3.4 Summary

In this chapter, a statistical method, based on the theory of the MPN method and the Poisson distribution, was developed and applied to extrapolate *E. coli* concentrations that were measured below the detection limit. This concentration interpolation method can be used to improve the accuracy of estimates in QMRA. The first step of this chapter was to extrapolate the *E. coli* concentrations that were below the detection limit after RSF and ozonation using the Poisson distribution. The actual mean of *E. coli* concentrations were set below the detection limit of 0.2 *E. coli*/100 mL according to the actual detection limit. In order to determine the impact of using extrapolated data, the removal efficacy of RSF and

the inactivation efficacy of ozonation were estimated in three cases using different types of data. The overall removal efficacy of water treatment and the yearly risk of infection of *Campylobacter* were calculated using extrapolated data by the QMRA procedure. The mean values of the yearly risk of infection were estimated to be 1.68×10^{-3} /person/year, 2.57×10^{-3} /person/year and 7.2×10^{-3} /person/year in cases 1, 2 and 3, respectively.

It was concluded that this statistical method is applicable when a large amount of data needs to be extrapolated. Using the *E. coli* concentrations that were extrapolated by the concentration interpolation method, the removal efficacy of RSF increased from 1.27 log₁₀ (mode) to 1.35 log₁₀ (mode) in case 2. The results were obtained from one case study; thus, the applicability to other situations requires further investigation.

Finally, the limitation of the proposed method for QMRA was described. From the inactivation efficacy of ozonation analysis in cases 1 and 2, it is demonstrated that low *E. coli* concentrations measured in large volume samples may cause errors in the estimation of treatment efficacy. The importance of selecting an appropriate dataset and a pairing method before performing QMRA is stressed. Furthermore, the analysis of inactivation efficacy of ozonation in cases 2 and 3 indicates that the concentration interpolation method is not applicable to simultaneously interpolate the data before and after treatment.

The concentration interpolation method developed in this chapter will next be applied in **Chapter 5** for the QMRA calculation and uncertainty analysis.

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Chapter 4

Development, Validation, and Application of ADR Model for O₃/UV Advanced Oxidation Process

4.1 Introduction

Advanced oxidation process (AOP) with ozone and ultraviolet light radiation (O₃/UV) is considered as an effective process for oxidizing persistent organic pollutants (e.g., for taste and odor control). In the AOP condition, more hydroxyl radicals ($\bullet$ OH) are formed as a result of the decomposition of molecular ozone. OH radicals can oxidize persistent organic pollutants that cannot be oxidized by molecular ozone alone (Peyton *et al.*, 1988). While many studies verified the effectiveness of O₃/UV process for the oxidation of chemical pollutants, few reports are available on the microbial inactivation efficacy of this process. The overall purpose of this thesis is to apply the QMRA method to provide a quantitative estimate of the level and variation of microbial risk in drinking water treated with the newly proposed water treatment process for reducing chlorinous odor. For this purpose, the inactivation efficacy of O₃/UV needs to be determined.

Since there is no O₃/UV treatment used in existing water supply systems in Japan, a hypothetical full-scale O₃/UV contactor was supposed in this study based on an actual ozone bubble-diffuser contactor in the Kunijima water purification plant of Osaka City. Research has shown that the choice of ozone contactor configuration and operation conditions can affect the hydrodynamics and mass transfer, which in turn can impact the microbial inactivation efficiency. In addition, the performance of the contactor is also affected by water quality parameters, such as temperature, pH, natural organic matter (NOM) concentration, and alkalinity. Mathematical models present an attractive tool for simultaneous consideration of the effects of contactor configuration, operating conditions, and water quality parameters on the inactivation efficacy achieved in flow-through ozone bubble-diffuser contactors. The axial dispersion reactor (ADR) model is a common modeling approach for predicting of ozone bubble-diffuser contactors. It has been applied by Lev and Regli (1992a), Mariñas *et al.* (1993), Zhou *et al.* (1994), and Singer and Hull (2000) to predict hydrodynamics and ozone residual profiles in bubble diffuser contactors. Smith and Zhou (1994), Chen (1998), Kim *et al.* (2002b), and Tang *et al.* (2005) extended the ADR model by integrating microbial inactivation kinetics models for prediction of the

profiles of microorganisms in ozone bubble columns. Their modelling results were validated by pilot experimental data. As concluded by Chen (1998), the ADR model appears to be a good approach for representing the distribution of dissolved ozone concentration and the disinfection efficiency in bubble-diffuser ozone columns.

The main objective of this chapter is to expand the application of the ADR model for the prediction of inactivation efficacies achieved in full-scale O_3/UV contactor. Major tasks required includes: (1) Developing an ADR model to address all the major components of O_3/UV advanced oxidation process: contactor hydraulics, ozone mass transfer, ozone demand and decay, and microbial inactivation. (2) Validating the ADR model and determining the inactivation rate constants by ozonation and UV irradiation using pilot-scale experimental data, including tracer testing results, ozone concentration profiles, and microbial inactivation tests results. (3) Using the ADR model to predict the inactivation efficacy attained in full-scale O_3/UV contactor. The steps are shown in **Figure 4-1**.

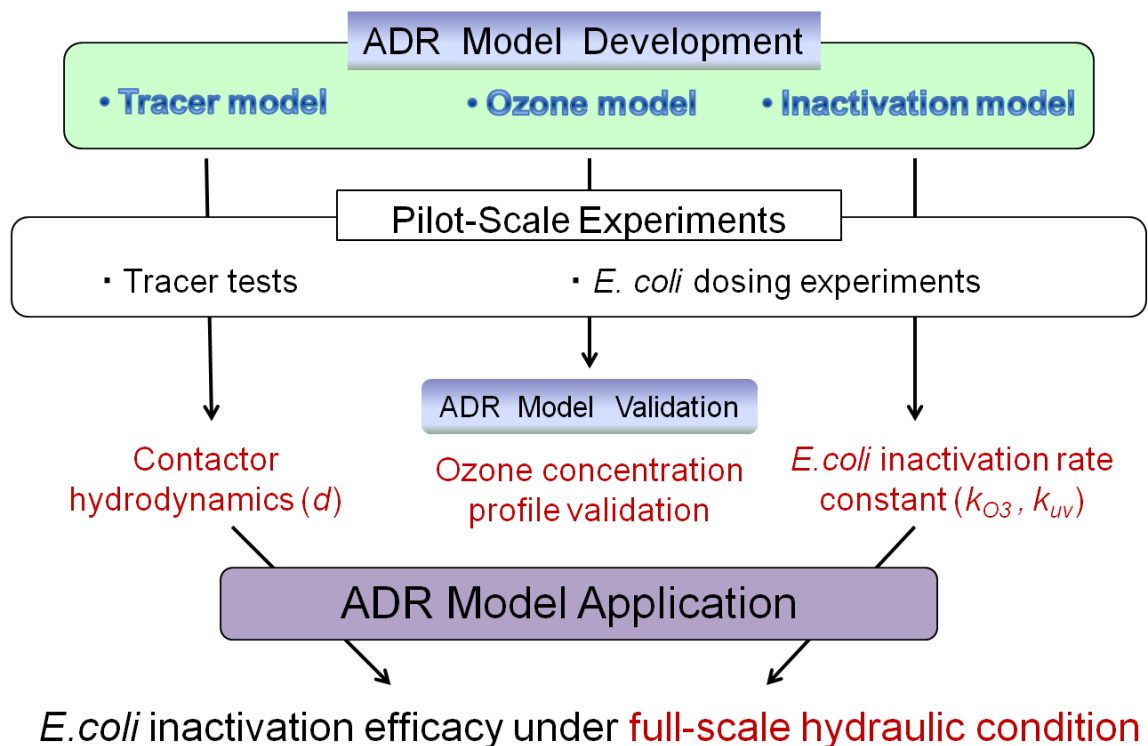


Figure 4-1 The steps in estimating inactivation efficacy of O_3/UV treatment under full-scale hydraulic condition.

4.2 Model Development

4.2.1 Configuration of the full-scale O₃/UV contactor

Full-scale ozone contactors with bubble-diffuser are typically comprised of several flows through chambers separated by baffles. These baffles are usually installed so that water flows in an over-under mode to reduce the overall back-mixing inside contactors (Blank *et al.*, 1993). **Figure 4-2** shows a typical ozone bubble-diffuser contactor. Chambers in which ozone is added through porous medium diffusers are usually called contactor chambers. Chambers in which no ozone is added to but ozone residual is present are called reaction chambers. Water and gas flows within a chamber are either counter-current or co-current.

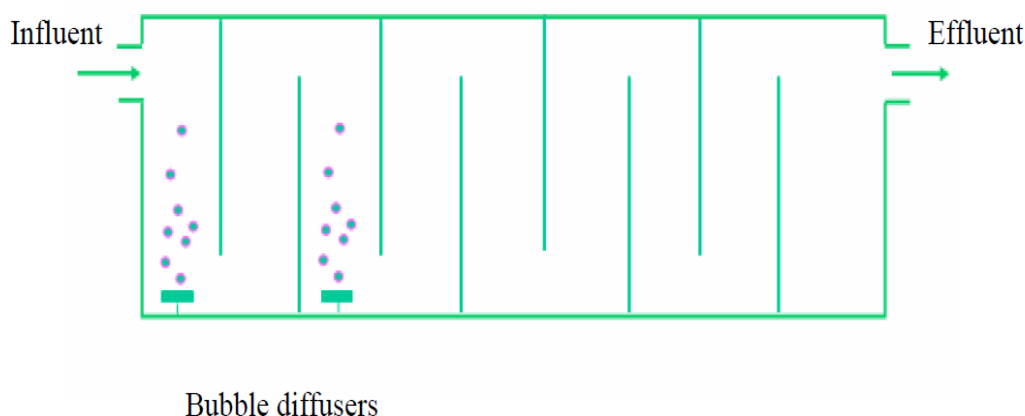


Figure 4-2 A typical full-scale ozone contactor with bubble-diffuser.

A simplified full-scale O₃/UV contactor was assumed in this study referring to a single contactor chamber of full-scale ozone contactor in the Kunijima water purification plant of Osaka City. The configuration of the hypothetical full-scale O₃/UV contactor is shown in **Figure 4-3**. The cylindrical reactor where ozone dissolved water flows was assumed to be 5.64 m in diameter and 5.9 m in length. A UV lamp of 5.9 m length was placed along the centre axis of the reactor. The dimension and operating conditions of the reactor are shown in **Table 4-1**. The reactor was designed to operate under continuous-flow and counter-current condition (water and gas flowing in the downward and upward directions, respectively).

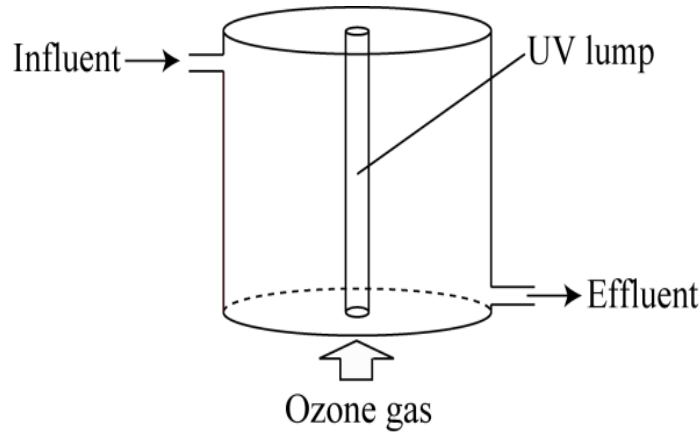


Figure 4-3 Configuration of the hypothetical full-scale O₃/UV contactor.

Table 4-1 The dimensions and operating conditions of the full-scale O₃/UV contactor.

Parameter (unit)	Value
Radius (m)	2.82
Depth of water column in contactor (m)	5.9
Water flow rate (m ³ /h)	3091.6
Mean hydraulic residence time (min)	2.86
Gas flow rate (m ³ /h)	463.74
Gas to liquid ratio	0.15
Ozone injection dose (mg/L)	0.25
Length of the lamp (m)	5.9
UV fluence (mJ/cm ²)	220

4.2.2 Governing equations

The model used in this research to simulate the inactivation efficacy by O₃/UV process in bubble-diffuser contactor is a modified form of the widely used axial dispersion model. To model the concentration profiles of ozone and viable microorganism in the O₃/UV contactor, it is necessary to quantify the rates of various physical transport and chemical oxidation and inactivation processes. The efficiency of the O₃/UV process is governed by several key components including contactor hydraulics, ozone mass transfer, ozone decomposition kinetics, and microbial inactivation kinetics. The ADR model is described in detail in this section.

4.2.2.1 Contactor hydraulics

Mixing conditions inside O₃/UV contactor is affected by ascending gas bubbles and water flow configuration, and can range from almost continuous-flow stirred tank reactor (CSTR) to plug flow reactor (PFR) conditions. The axial dispersion model has been widely applied to characterize the hydrodynamic behavior in bubble diffuser reactors. The mathematical expression for a liquid phase undergoing axial dispersion can be obtained by performing a mass balance for a conservative tracer corresponding to a contactor control volume of infinitesimal thickness:

$$\frac{\partial C}{\partial \theta} = d \frac{\partial^2 C}{\partial Z^2} - \frac{\partial C}{\partial Z} \quad (4-1)$$

where $d = E_L / (U_L \cdot L)$ = dispersion number; $Z = x/L$ = normalized distance; x = distance from the top of column; L = water column height; E_L = axial dispersion coefficient; $U_L = Q_L / A$ = superficial water velocity; A = contactor cross sectional area. The dispersion number d is a parameter which measures the extent of axial dispersion. When $d \rightarrow \infty$, the flow condition approaches complete mixing. As $d \rightarrow 0$, the flow condition tends to plug flow.

The axial dispersion model is based on the assumptions of infinite radial dispersion, uniform axial dispersion throughout the water column, negligible gas volume fraction, validity of Fick's Law to represent axial dispersivity, and closed vessel boundary conditions as defined by Levenspiel (1999). For a step-input tracer test, the boundary conditions at the inlet and outlet of the contactor, and the initial conditions are shown as **Eqs. 4-2, 4-3 and 4-4**, respectively.

$$C|_{z=0} = C_{in} + d \frac{\partial C}{\partial Z} \Big|_{z=0} \quad (4-2)$$

$$\frac{\partial C}{\partial Z} \Big|_{z=1} = 0 \quad (4-3)$$

$$C|_{\theta=0} = 0 \quad (4-4)$$

in which C_{in} is the influent tracer concentration. A finite-differences approach can be used to simulate a dimensionless step-input tracer test with **Eqs. 4-2~4-4**. Tracer concentrations obtained from this step-input equation can then be differentiated to obtain the equivalent dimensionless pulse-input concentrations.

The dispersion number for a closed vessel can be estimated from standard deviation (σ) and mean residence time ($\bar{t}$) obtained by means of performing tracer tests according to the following expression (Levenspiel, 1999):

$$2 \times d - 2 \times d^2 \times (1 - e^{-1/d}) = \frac{\sigma^2}{\bar{t}^2} \quad (4-5)$$

Experimental tracer curves can be predicted with **Eqs. 4-1 ~ 4-4** after estimating the dispersion number with **Eq. 4-5**. Deviation between experimental and predicted curves would give information on the non-ideal hydrodynamics of the system, such as heterogeneous mixing and short-circuiting.

4.2.2.2 Ozone mass transfer

Since ozone gas has limited solubility and it must first be dissolved into water to be effective against microorganisms, the transfer of ozone from gas phase to the liquid phase is of central importance in the study of ozonation systems applied for drinking water treatment.

According to the two-film theory developed by Lewis and Whitman (1924) as cited by Singer and Hull (2000), ozone mass transfer occurs across the gas and liquid films. For relatively insoluble gases such as ozone, the gas-phase resistance becomes negligible compared with the liquid-phase resistance. The rate of ozone mass transfer according to the two-film model is given by the following equation:

$$\frac{dC_L}{dt} = k_L a (C_L^* - C_L) \quad (4-6)$$

where C_L = liquid phase ozone concentration; C_L^* = saturation concentration of ozone in water; t = time; k_L = mass transfer coefficient; a = interfacial transfer area per unit volume; $k_L a$ = volumetric mass transfer coefficient; The saturation concentration of ozone in water C_L^* can be calculated according to Henry's law (Singer and Hull, 2000)

$$C_L^* = C_G / m \quad (4-7)$$

where C_G = gas phase ozone concentration; m = Henry's law constant; The effect of temperature on the ozone Henry's law constant can be approximated with the empirical

expression obtained by Mariñas *et al.* (1993) for the data reported by Perry and Chilton (1973):

$$\log m = \begin{cases} 3.25 - \frac{840}{T} & \text{for } 278\text{K} \leq T \leq 288\text{K} \\ 6.20 - \frac{1687}{T} & \text{for } 288\text{K} \leq T \leq 303\text{K} \end{cases} \quad (4-8)$$

The volumetric mass transfer coefficient $k_L a$ can be determined by multiplying the mass transfer coefficient k_L and interfacial transfer area obtained with the expressions:

$$k_L = \frac{Sh D_L}{d_B} \quad (4-9)$$

$$a = \frac{6 U_G}{(V_B - U_L) \times d_B} \quad (4-10)$$

in which Sh = Sherwood number (dimensionless). The Sherwood number can be represented by the empirical correlation developed by Hughmark (1967):

$$Sh = 2 + 0.0187 (R_G^{0.484} \cdot S_{CL}^{0.339} \left[\frac{d_B g^{\frac{1}{3}}}{D_L^{\frac{2}{3}}} \right]^{0.072})^{1.61} \quad (4-11)$$

with $R_G = (d_B V_B)/\nu_L$ = gas-phase Reynolds number (dimensionless); $S_{CL} = \nu_L/D_L$ = aqueous-phase Schmidt number (dimensionless); g = gravitational constant; D_L = molecular diffusivity of ozone in water; ν_L = kinematic viscosity of water; and d_B, V_B = average bubble diameter and rise velocity given by the expressions (Mariñas *et al.*, 1993):

$$d_B = d_{B,0} + 0.21 U_G \quad (4-12)$$

$$V_B = \begin{cases} 210 d_B \frac{1.004}{\mu_L} & \text{for } 0.05 \text{ cm} \leq d_B \leq 0.18 \text{ cm} \\ (20 + 33.8 e^{-4.88 d_B}) \frac{1.004}{\mu_L} & \text{for } 0.18 \text{ cm} \leq d_B \leq 0.40 \text{ cm} \end{cases} \quad (4-13)$$

with μ_L = absolute viscosity of water and $d_{B,0}$ = average bubble diameter extrapolated to $U_G = 0$. The specific units for the variables in **Eqs. 4-12** and **4-13** are cm for d_B and $d_{B,0}$, cm/s for V_B and U_G , and cP for μ_L . **Eq. 4-12** is valid only for $U_G < 0.6$ cm/s, and a bubble

column with inner diameter of approximately 0.15 m , and a spherical fine diffuser with a diameter of 2.54 cm.

4.2.2.3 Ozone decomposition kinetics

After dissolved in water, ozone decays through the main decomposition by UV irradiation, autodecomposition, and oxidation of impurities due to its extremely oxidative properties. Two primary pathways involving these reactions have been proposed: direct oxidation and oxidation by the radical intermediates of ozone-decomposition products.

For the autodecomposition and oxidation of impurities, the rate of decomposition depends on a multitude of system variables, including the water pH, temperature, the organic and inorganic constituents of the waters, and the presence of organic and inorganic initiators and inhibitors. It was observed that the rate of decomposition depends on the instantaneous ozone concentration, and the history of the ozonation process (Watt *et al.*, 1989). A modified rate expression was proposed, which is written as a pseudo-first-order expression with respect to the concentration of dissolved ozone but in which the rate constant is replaced by a variable called the specific ozone-utilization rate k_{dw} to account for the change in water character during the course of ozonation (Langlais *et al.*, 1991):

$$\frac{dC_L}{dt} = -k_{dw}C_L \quad (4-14)$$

in which t = time ; C_L = dissolved ozone concentration at time t ; $C_{L,0}$ = initial dissolved ozone concentration; k_{dw} = water quality dependent decomposition rate constant.

Although microorganisms also contribute to ozone demand and decay reactions, the amount of ozone they consume under full-scale condition is negligible due to the extremely low mass concentrations of microorganisms in water. For the case of challenge tests at pilot scale plant or laboratory, the effects of microorganisms in the inflow with high concentrations should be considered.

With regard to the ozone decomposition by UV irradiation, the rate of ozone decomposition kinetics can be also approximately expressed as first order (Nakanishi, 2013):

$$\frac{dC_L}{dt} = -2.3rI\epsilon C_L = -k_{dUV}C_L \quad (4-15)$$

in which t = time ; C_L = dissolved ozone concentration at time t ; $C_{L,0}$ = initial dissolved ozone concentration; $r = k_{dUV}$ = decomposition rate constant by UV irradiation.

4.2.2.4 Microbial inactivation kinetics

In O_3/UV treatment, two primary pathways involving microbial inactivation have been considered: inactivation efficacy by molecular ozone and inactivation efficacy by UV irradiation. Microbial inactivation by OH radicals is negligible because they usually react rapidly with many types of dissolved species and therefore scavenged before they encounter particles such as microorganisms (Labatiuk *et al.*, 1994). The unavailability of OH radicals that formed in AOP condition for microbial inactivation was also demonstrated experimentally by Yamasaki (2014). Therefore, the effects of OH radicals on microbial inactivation were not considered in this study, and the microbial inactivation process by molecular ozone and UV irradiation was modeled separately in the inactivation model.

The inactivation kinetics of microorganisms by molecular ozone and UV irradiation has often been expressed with an empirical rate expression with the form of that for a second-order elementary chemical reaction:

$$\frac{dN}{dt} = -k_{O_3} C_L N \quad (4-16)$$

$$\frac{dN}{dt} = -k_{UV} I N \quad (4-17)$$

Eqs. 4-16 and 4-17 can be integrated to obtain

$$\ln \left(\frac{N}{N_0} \right) = -k_{O_3} C_L T \quad (4-18)$$

$$\ln \left(\frac{N}{N_0} \right) = -k_{UV} I T \quad (4-19)$$

in which N and N_0 = number density of viable microorganisms at respective times t and 0 ; N/N_0 = survival ratio (dimensionless); C_L = dissolved ozone concentration; k_{O_3} = second-order inactivation rate constant by ozonation; k_{UV} = inactivation rate constant by UV; I = volume mean UV fluence rate. Since the UV fluence rate is changing with radius direction in an O_3/UV contactor, the UV fluence rate in this study was represented as

volume mean UV fluence rate. It can be calculated by the empirical correlation developed by Suidan (1986):

$$I = \frac{2I_0r_0}{(R^2-r_0^2)\alpha} [1 - \exp\{-\alpha(R - r_0)\}] \quad (4-20)$$

with R = inner radius of reactor; r_0 = outer radius of the quartz tube (In O_3 /UV reactor, the UV lamp is protected from the reaction solution by housing the lamp within a quartz tube); α = water absorption coefficient at 254nm using logarithms to the base e; I_0 = average flux of light energy, i.e., the total energy emitted per unit time per unit area averaged for the total surface of the quartz tube, given by the expression:

$$I_0 = \frac{P/L}{2\pi r_0} \quad (4-21)$$

in which P is represented as 30% of the total UV_{254} light output (W); L = the length of the UV lamp.

4.2.3 Axial dispersion reactor model

The application of the axial dispersion model concept for modeling two phase O_3 /UV contactors usually assume that the liquid phase is in uniform finite axial dispersion with infinite radial dispersion throughout the water column and the gas phase is in the plug flow. Both phases are flowing in the reactor under steady state conditions. Further assumptions include the following.

- The hydrodynamics of microorganism in the reactor could be represented as axial dispersion
- Microbial inactivation by OH radicals is negligible
- Ozone decay rate and decomposition rate by UV irradiation are pseudo first order in the liquid phase
- Henry's law applies
- Gas holdup, gas-phase dispersion and gas-phase ozone decomposition by UV irradiation are negligible
- The effect of pressure is negligible
- Mass transfer resistance for ozone absorption is confined to the liquid side and is not enhanced by the presence of ozone decay in the liquid phase

Mass balances can be performed in a control volume of infinitesimal thickness inside the O_3 /UV contactor operated in countercurrent mode (as shown in **Figure 4-4**) to obtain the ADR model expressions representing the steady-state liquid phase, gas-phase ozone concentrations and viable microorganism concentration (**Eqs. 4-22 ~ 4-24**). The derivation of mass balance expressions for dissolved ozone and viable microorganism is presented in **Table 4-2**. The first row in **Table 4-2** represents the overall mass balance equation in a conceptual format. The expressions in the second and fifth row of **Table 4-2** were derived from the first row with the assumptions of axial dispersion, two-film mass transfer, first-order ozone decomposition, and second-order microbial inactivation. The equations in the third and sixth row resulted from normalization of the equations in the second and fifth row. Independent tracer tests, ozone decomposition tests and literature information, microorganism dosing experiments are required to obtain the four parameters (d , k_D , k_{O_3} , and k_{UV}) in the normalized mass balance equation.

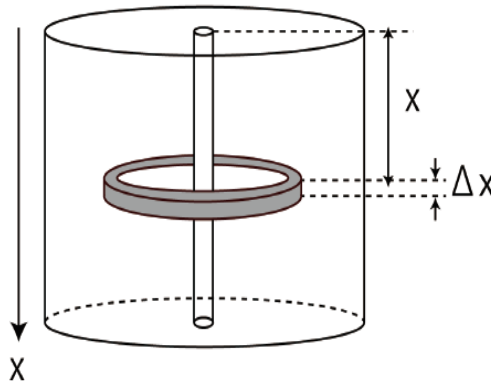


Figure 4-4 Schematic of an infinitesimal control volume for an O_3 /UV contactor.

Table 4-2 Development of mass balance expressions for dissolved ozone and viable microorganism in a control volume of O₃/UV contactor operated at countercurrent flow.

	(Mass Accumulation) =	(Mass In) - (Mass Out)	+ (Mass Transferred from Gas)	+ (Mass Reacted)
Dissolved Ozone	Mass Balance For Dissolved Ozone $\Delta(C_L \cdot A \cdot \Delta x) =$	$+A \cdot E_L \cdot \Delta\left(\frac{\Delta C_L}{\Delta x}\right) \cdot \Delta t - Q_L \cdot \Delta C_L \cdot \Delta t$	$+k_L a \cdot \left(\frac{C_G}{m} - C_L\right) \cdot A \cdot \Delta x \cdot \Delta t$	$-k_D \cdot C_L \cdot A \cdot \Delta x \cdot \Delta t$
	Normalize $\frac{\partial C_L}{\partial \theta} =$	$+d \cdot \frac{\partial^2 C_L}{\partial Z^2} - \frac{\partial C_L}{\partial Z}$	$+k_L a \cdot \frac{L}{U_L} \cdot \left(\frac{C_G}{m} - C_L\right)$	$-k_D \cdot \frac{L}{U_L} \cdot C_L$
	Corresponding Experimental Method	Tracer Test		Ozone Decomposition Test and Literature Information
Viable Microorganism	Mass Balance For Viable Microorganism $\Delta(N \cdot A \cdot \Delta x) =$	$+A \cdot E_L \cdot \Delta\left(\frac{\Delta N}{\Delta x}\right) \cdot \Delta t - Q_L \cdot \Delta N \cdot \Delta t$		$-k_{O_3} \cdot C_L \cdot N \cdot A \cdot \Delta x \cdot \Delta t$ $-k_{UV} \cdot I \cdot N \cdot A \cdot \Delta x \cdot \Delta t$
	Normalize $\frac{\partial N}{\partial \theta} =$	$+d \cdot \frac{\partial^2 N}{\partial Z^2} - \frac{\partial N}{\partial Z}$		$-k_{O_3} \cdot \frac{L}{U_L} \cdot C_L \cdot N$ $-k_{UV} \cdot \frac{L}{U_L} \cdot I \cdot N$
	Corresponding Experimental Method	Tracer Test		Dosing Experiments

The modified ADR model includes three major variables: liquid phase ozone concentration (C_L), gas phase ozone concentration (C_G), viable microorganism concentration (N). Under steady state operation, mass balance expressions for these variables are:

$$d \cdot \frac{d^2 C_L}{dZ^2} - \frac{dC_L}{dZ} + k_L a \cdot \frac{L}{U_L} \cdot \left(\frac{C_G}{m} - C_L \right) - k_D \cdot \frac{L}{U_L} \cdot C_L = 0 \quad (4-22)$$

$$\frac{d\left(\frac{C_G}{m}\right)}{dZ} - k_L a \cdot \frac{L}{m U_G} \cdot \left(\frac{C_G}{m} - C_L \right) = 0 \quad (4-23)$$

$$d \cdot \frac{\partial^2 N}{\partial Z^2} - \frac{\partial N}{\partial Z} - k_{O_3} \cdot \frac{L}{U_L} \cdot C_L N - k_{UV} \cdot \frac{L}{U_L} \cdot I N = 0 \quad (4-24)$$

where C_L = liquid phase ozone concentration; C_G = gas phase ozone concentration; N = concentration of viable microorganisms; $Z = x/L$ = normalized distance; x = distance from the top of column; d = dispersion number; L = depth of the reactor; U_L = liquid approach velocity; U_G = gas approach velocity; k_{O_3} = inactivation rate constant by ozonation; k_{uv} = inactivation rate constant by UV irradiation; I = fluence rate of UV₂₅₄ light; $k_L a$ = volumetric mass transfer coefficient; m = Henry's law constant; k_D = first order ozone decomposition rate constant. In this model, the water quality dependent decomposition rate constant (k_{dw}) and decomposition rate constant by UV irradiation (k_{dUV}) were represented as a overall first order ozone decomposition rate constant of k_D .

Table 4-3 Closed vessel boundary conditions
(Countercurrent condition)

$C_L _{z=0} = C_{L,0} + d \frac{dC_L}{dz} \Big _{z=0}$
$\frac{dC_L}{dz} \Big _{z=1} = 0$
$C_G _{z=1} = C_{G,0}$
$N _{z=0} = N_0 + d \frac{dN}{dz} \Big _{z=0}$
$\frac{dN}{dz} \Big _{z=1} = 0$

The boundary conditions required to integrate **Eqs. 4-22 ~ 4-24** can be approximated with those for an ideal closed vessel (Levenspiel, 1999) as shown in **Table 4-3**. In which $C_{L,0}$ = dissolved ozone concentration entering the reactor; and $C_{G,0}$ = gas phase ozone concentration entering the reactor. N_0 = concentration of viable microorganisms entering the reactor.

The solution of the ADR equations needs a numerical method as it is represented by a group of nonlinear differential equations with boundary conditions at two points. In this study, a computer program written in Mathematica using NDSolve function was adopted for solving these equations.

Predicting the performance of an O_3 /UV contactor under full-scale condition with a given set of operating conditions requires knowledge of reaction kinetics as a function of ozone decomposition kinetics (k_{dw} , k_{dUV}), microbial inactivation kinetics (k_{o3} , k_{UV}), and contactor hydrodynamics (d). Ozone water quality dependent decomposition rate constant k_{dw} and decomposition rate constant by UV irradiation k_{dUV} can be calculated from literature information and from **Eq. 4-16** using the parameter of UV lamp, respectively. Contactor hydrodynamics and microbial inactivation kinetics can be investigated by performing tracer tests and microorganism dosing experiments at pilot-scale plant.

4.3 Pilot-Scale Experiments

The main objective for conducting the pilot-scale experiments is to validate the ADR model and to obtain the necessary parameters for ADR model to further predict the inactivation efficacy of O_3 /UV process under a full-scale condition.

4.3.1 Material and methods

4.3.1.1 Pilot-scale O_3 /UV contactor

The schematic of the pilot-scale plant is shown in **Figure 4-5**. This pilot plant was comprised of two O_3 /UV contactors (i.e., the first and second columns) and one O_3 /UV reactor (i.e., the third column). The source water for this pilot plant was the water treated after rapid sand filtration (RSF) taken from the actual treatment facility. Ozone gas was injected into each contactor by bubble diffusers located at the bottom of the first two contactors and dissolved ozone further reacts in the third reactor. For the first and second contactors, VUV lamps with principle wavelengths of 254 and 185 nm and electric power

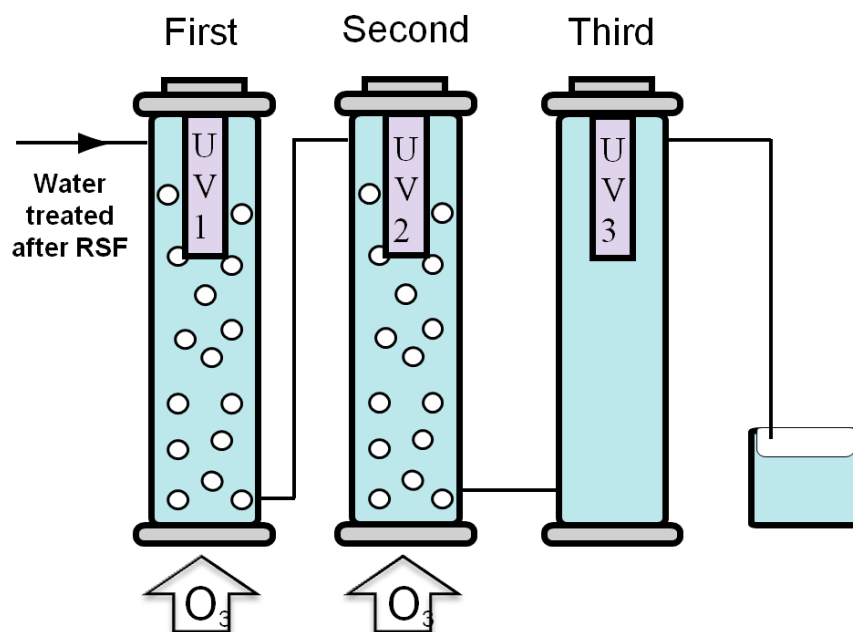


Figure 4-5 Schematic of the pilot-scale plant in the Kunijima water purification plant.

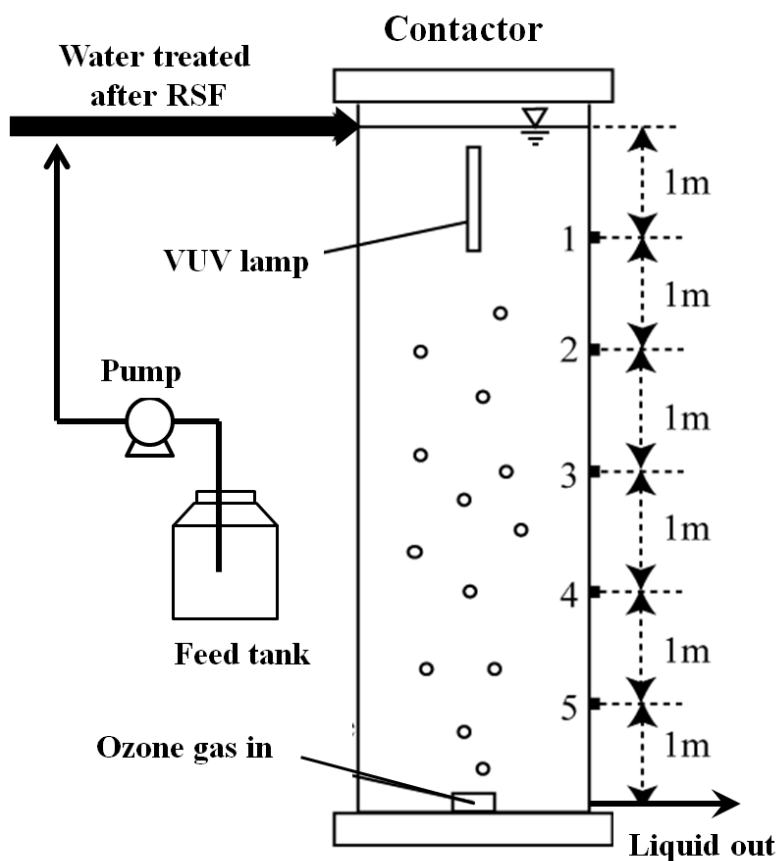


Figure 4-6 Schematic of the pilot-scale O_3 /UV bubble-diffuser contactor.

of 65W (QGL65-31, Iwasaki, Japan) were installed from the top of the column. For the third reactor, a conventional low-pressure mercury lamp (QGL65W-2, Iwasaki, Japan) was used.

The detail of the O₃/UV bubble-diffuser contactor is shown in **Figure 4-6**. It was used in this study to perform microorganism dosing experiments and corresponding tracer tests. The contactor was column-shaped with an inner diameter of 0.16 m and a height of 6.3 m. Samples could be withdrawn from five sampling ports equally spaced at 1m apart throughout the water column for the determination of dissolved ozone concentration, microorganism concentration and tracer concentration profiles inside the contactor. The water column height inside the contactor was set at 6 m for all experiments.

4.3.1.2 *E. coli* preparation

E. coli NBRC 3301 strain was selected as the test microorganism. It was first pre-cultured in a 20 mL LB broth at 37 °C for 18 hours. After pre-cultured, 1 mL of the sample was isolated and reinjected into a new 1L LB broth for a further 20~30 hours shake culture with the same temperature. In order to reach a target concentration of approximately 10⁹ CFU/mL, 20 L LB broth were prepared once. Cultured *E. coli* were then harvested by centrifugation and washed in 4L buffered solution for more than 3 times. *E. coli* spiking solution was prepared by suspending the final pellets in 5 L of test water.

4.3.1.3 Pilot-scale *E. coli* dosing experiments

A total of 14 runs of *E. coli* dosing experiments were performed at a flow rate of 1.2 m³/h and applied ozone dose with a range of 0.3 ~ 1mg/L (adjusted time by time in order to acquire viable *E. coli* in effluent water). For each test run, the liquid and gas flow rates were first controlled at the required levels, and then the designed input ozone dose was achieved by slow adjustment of the voltage knob of the ozone generator until the measured ozone concentration in the input-gas reached the target value. A dissolved ozone monitor was used for the continuous on-line monitoring of dissolved ozone concentration at the outlet of the contactor during experimental runs. However, this monitor was only used as an indicator for system stability. The reported ozone concentrations were always measured by the modified indigo method described subsequently. After changing operating conditions and obtaining steady readings on the dissolved ozone monitor, initial dissolved ozone concentrations throughout the water column were measured.

The stock *E. coli* spiking solution was then continuously injected into the influent water at

a flow rate of 20 mL/min just ahead of the contactor inlet (see **Figure 4-6**). The resulting seeded influent water was fed to the contactor operated in a counter-current mode (liquid flowing in the downward direction, and gas flowing in the upward direction) at a flow rate of 1.2 m³/h, corresponding to a hydraulic residence time of approximately 6 min. All experiments were performed at room temperature within a range of 7~30 °C throughout the year.

After 20 min (approximately three hydraulic detention times) for system to reach a steady state, samples were collected for viability assessment from the influent and effluent sampling ports of 1, 2, 4, 5. Due to the relatively low viable *E. coli* concentrations expected in effluent water, 200 ~ 1000 mL of samples were collected for viable *E. coli* concentration measurement. The dissolved ozone was quickly quenched by collecting the samples in sterile bottles containing 20 mL of 1% sterile sodiumthiosulphate. Three duplicated samples were taken at an approximately 7-minute interval to ensure the precision requirements. *E. coli* residual in the contactor effluent was inactivated by further reacting in the following O₃/UV reactor and mixing with a disinfectant solution of NaClO before discharging. *E. coli* were measured by direct filtration and direct inoculation of the filter, or by dilution and direct inoculation on XM-G agar medium, and then incubated at 37 °C for 18~24 hours. Measurements in triplicate showed good reproducibility with a standard deviation of 13%.

Samples were also collected for liquid phase ozone analyses. Since ozone in water is generally not very stable, all the analysis was performed immediately after sampling. Three duplicated samples were collected and detected for each sampling point. Liquid phase ozone concentrations were determined by the modified indigo method with 20 mL glass syringes, according to the following procedures: (1) a volume 10 mL indigo reagent was first extracted into the syringe (The indigo stock solution was prepared by following Method 4500 - O₃ in Standard Methods for the Examination of Water); (2) a volume 10 mL (5 mL at sampling port of 5) of liquid phase ozone sample was then extracted into the syringe directly from the sampling port (in order to minimize ozone losses by volatilization and self-decomposition); (3) the syringe was shaken vigorously immediately after sample extraction to provide sufficient reaction between ozone samples and indigo reagents; (4) reacted indigo solution was pre-filtration through a 0.45 µm pore size filter before injecting into the quartz cell of a spectrophotometer (MultiSpec - 1500, Shimadzu) to measure the absorbance at 600 nm, and the ozone concentration was calculated with **Eq. 4-25**. In some cases, volumes V_1 and V_2 were selected so that the decolorization of the indigo reagent was within the range of 50 to 80 % with respect to the initial color

intensity.

$$C_L = \frac{A-B}{2.1} \times \frac{V_1+V_2}{V_2} \quad (4-25)$$

where C_L = liquid phase ozone concentration (mg/L)

A = absorbance of MilliQ and indigo reagent mixture at 600nm

B = absorbance of sample and indigo reagent mixture at 600nm

V_1 = indigo reagent volume (mL)

V_2 = ozone sample volume (mL)

On the other hand, the *E. coli* concentration injected into the contactor and the influent water quality can affect the UV light transmission, which in turn can impact the inactivation efficacy of *E. coli* by UV lamp. Therefore, the water sample taken from sampling port of 1 was measured the absorbance at 254 nm using the same spectrophotometer (MultiSpec - 1500, Shimadzu) as that used for ozone concentration measurement. The water absorption coefficient at 254 nm was given by the expression:

$$\alpha = -\ln 10^{-A} \quad (4-26)$$

in which A = water absorbance at 254 nm; α = water absorption coefficient at 254nm using logarithms to the base e.

When conducting *E. coli* dosing experiments, all of the other operational parameters including ozone dose, gas/liquid flow rates, dissolved ozone concentration entering the contactor, gas phase ozone concentration entering the contactor, viable *E. coli* concentration entering the reactor and temperature were also recorded. The average bubble diameter inside of the contactor was measured by taking images with a camera. These parameters were used as the ADR model inputs. The dissolved ozone concentration profile data were used for validation of the ADR simulation results, and the viable *E. coli* concentration profile data were used to estimate the microbial inactivation kinetics (k_{o3} , k_{UV}).

4.3.1.4 Pilot-scale tracer tests

Mixing conditions inside O_3 /UV contactors are affected by ascending gas bubbles and water flow configuration, and can range from almost CSTR to PFR conditions. The extent

of dispersion can be determined from residence time distribution (RTD) data obtained by means of performing tracer tests.

There are two most commonly used methods of performing a tracer test for analyzing the overall hydrodynamic conditions inside a contactor: pulse-input and step-input tests. Both methods are related and provide the same information (Levenspiel, 1999). In the case of a step-input test, the tracer solution is added to the contactor influent at a constant rate starting at time zero and the tracer concentration at the contactor effluent is then monitored for several hydraulic detention times.

In this study, tracer tests were performed using the step-input method under identical operating conditions as those used for *E. coli* dosing experiments except that the ozone generator was run with the voltage turned off. KBr solution with concentration of 2g/L, used as the tracer compound, was continuously pumped into the influent water with a flow of 10mL/min so that the maximum concentration of tracer in the contactor would reach to be 1mg/L. Samples were collected at the effluent sampling ports of 1, 2, 5 for a period of time approximately 3~6 times the hydraulic residence time of the contactor.

The concentrations of bromide ions in samples were determined with an ion chromatograph (HPLC, Shimadzu). Bromide ion was analyzed with a Shim-pack-IC-SA2 column and a guard column (IC-SA2) with a carbonate buffer (mobile phase, 12 mmol/L NaHCO₃ and 0.6 mmol/L Na₂CO₃; detection, UV at 210 nm; and injection volume, 200 µL).

The RTD data collected from a tracer test is a collection of data pairs, each pair consisting of tracer concentration (C_i) and sampling time (t_i). In the case of a pulse-input test, the mean residence time ($\bar{t}$), and standard deviation (σ) of the RTD curve can be estimated from tracer test results with the expressions (Levenspiel, 1999):

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (4-27)$$

$$\sigma^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \quad (4-28)$$

The symbol Δ refers to an increment, and the subscript i denotes each data pair in the tracer data series. For the data obtained from step-input tests, one way is to convert these

data into pulse-input information by a finite increment approach and then to analyze the resulting data as indicated previously.

For the convenience of analysis and comparison between tracer tests, the tracer concentration and time can be normalized to obtain dimensionless values. The normalization performed are:

$$C_{\theta} = \frac{C \cdot Q_L \cdot \bar{t}}{m_t} \quad (4-29)$$

$$\theta = \frac{t}{\bar{t}} \quad (4-30)$$

where C = tracer concentration (mg/L)
 Q_L = liquid flow rate (L/min)
 t = residence time (min)
 $\bar{t}$ = mean residence time (min)
 m_t = Total mass of tracer added
 C_{θ} = dimensionless tracer concentration
 θ = dimensionless time

4.3.2 Results and discussion

4.3.2.1 Pilot-scale *E. coli* dosing experiments

A total of 14 *E. coli* dosing experiments were performed from October 2012 to November 2013 with different ozone dose. Four experiments were performed with the first O₃/UV contactor of the pilot plant, and the remaining experiments were performed in the second O₃/UV contactor (see **Figure 4-5**). The results were summarized in **Table 4-4** in terms of observed ozone concentrations in the effluent samples and calculated inactivation efficacy of *E. coli* at each sampling point. Also included in the table are test operating conditions (water and gas flow rates, feed-gas ozone concentration, dissolved ozone concentration and viable *E. coli* concentration in the influent water) and water quality parameters (temperature and water absorbance at 254nm). The inactivation efficacy of O₃/UV process expressed as Decimal Elimination Capacity (DEC) was calculated from the concentration of *E. coli* in the influent (C_{in}) and effluent (C_{out}) samples with the following equation.

$$\text{DEC} = \text{Log}_{10}\pi = \text{Log}_{10}C_{\text{in}} - \text{Log}_{10}C_{\text{out}} = \text{Log}_{10}\frac{C_{\text{in}}}{C_{\text{out}}} \quad (4-31)$$

The first four (i.e., No. 1 ~ 4) *E. coli* dosing experiments were performed at the first O₃/UV contactor. Since the water column of the O₃/UV contactor was fairly long (i.e., L= 6 m), and the ozone gas was flowed in the upward direction, the dissolved ozone concentrations (before decomposed by UV irradiation) at the top of first contactor were relatively low. In fact, it was much closer to be an independent UV disinfection condition at the top of first contactor.

Such a shortcoming was overcome by the use of the second O₃/UV contactor. The influent water that inflow from the first O₃/UV contactor contained a high dissolved ozone concentration (with a range of 0.2~0.7 mg/L), which achieved an AOP condition for the top of the second O₃/UV contactor. This high concentration of dissolved ozone in the influent water was decomposed by UV irradiation, as a result, a large amount of hydroxyl radicals (•OH) were formed. The experiment results performed at the second O₃/UV contactor were shown in **Table 4-4** with the run numbers of 5~14. Since the dissolved ozone concentration at the top of second contactor was much higher than the first one, the ozone doses were set at a low level in order to acquire viable *E. coli* in effluent samples.

Table 4-4 *E. coli* dosing test conditions and results of ozone and microbiological analysis.

No.	Date	Ozone dose (mg/L)	Q _L (m ³ /h)	Q _G (L/min)	T (°C)	N ₀ (CFU/mL)	α	C _{G,0} (Z=1) (mg/L)	C _{L,0} (Z=0) (mg/L)	SP 1		SP 2		SP 4		SP 5	
										C _L (mg/L)	DEC	C _L (mg/L)	DEC	C _L (mg/L)	DEC	C _L (mg/L)	DEC
1	2012/10/3	1	1.2	0.8	24	1.67×10 ⁶	0.358	24.68	0	0	-	0.001	2.54	0.033	5.17	0.543	5.10
										0.019	2.95	0.025	3.65	0.030	5.70	0.451	5.62
										0	3.28	0	4.03	0.019	6.44	0.423	6.08
2	2012/12/11	1	1.2	1.06	8.4	1.1×10 ⁶	0.286	18.84	0	0.031	2.46	0.005	3.28	0.062	5.56	0.623	7.34
										0.022	2.90	0.020	4.37	0.147	5.49	0.876	5.71
										0.010	3.87	0.033	4.19	0.259	4.64	0.592	4.68
3	2012/12/21	1	1.2	0.99	8.6	6.5×10 ⁵	0.229	20	0	0	5.41	0.048	6.81	0.148	-	0.786	-
										0.007	6.27	0.059	6.64	0.111	-	0.673	6.41
										0	6.00	0.04	5.30	0.133	7.11	0.573	6.58
4	2013/1/10	1	1.2	1	7.2	3.23×10 ⁵	0.188	20	0	0.010	4.12	0.020	2.79	0.129	4.58	0.726	4.58
										0.024	4.23	0.016	3.08	0.385	4.91	0.833	5.38
										0.050	4.28	0.030	3.67	0.288	5.11	0.729	5.42
5	2013/7/10	0.5	1.2	0.615	29.3	8.5×10 ⁵	0.240	16	0.35	0.0329	-	0.011	-	0.044	7.59	0.222	7.14
										0.011	5.69	0.0424	3.98	0.076	-	0.194	7.59
										0.0557	6.01	0.0367	7.33	0.067	7.89	0.188	8.18
6	2013/7/10	0.5	1.2	0.615	29.9	8.5×10 ⁵	0.240	16	0.3	0.030	-	0.009	-	0.095	-	0.267	8.18
										0.049	6.25	0.040	7.33	0.107	7.81	0.224	8.18
										0.020	7.33	0	7.03	0.037	8.29	0.211	7.89
7	2013/7/31	0.35	1.2	0.33	29.1	2.17×10 ⁶	0.170	20.31	0.7	0.0352	-	0.0543	6.85	0.0119	8.26	0.3171	8.73
										0.0181	6.78	0.021	7.45	0	8.49	0	-
										0.0219	7.14	0.019	-	0.1281	8.73	0.4357	7.32
8	2013/7/31	0.35	1.2	0.33	29.8	2.17×10 ⁶	0.170	20.31	0.61	0.0119	-	0.0281	7.92	0.0419	8.49	0	-
										0.0186	-	0.0310	7.26	0.0429	8.34	0.11	8.49
										0.0252	7.32	0.0424	7.92	0.0419	8.49	0.1314	8.86
9	2013/10/31	0.3	1.2	0.265	18	1.64×10 ⁶	0.323	22	0.21	0	7.96	0	7.51	0.0571	7.06	0.09	8.21
										0.0419	8.07	0	7.73	0.0419	7.71	0.1457	7.15
										0.0476	7.77	0.039	7.91	0.0314	8.41	0.14	8.11
10	2013/10/31	0.3	1.2	0.265	18.1	1.64×10 ⁶	0.323	22	0.23	0.0405	7.60	0.03	8.03	0.0510	7.66	0.0629	7.18
										0.0271	8.21	0.0329	-	0.0424	7.96	0.15	7.53
										0.0224	7.16	0.0357	8.21	0.0433	8.51	0.1414	7.75
11	2013/11/19	0.3	1.2	0.48	13.8	1.93×10 ⁶	0.377	12.1	0.33	0.0519	6.95	0.0595	8.41	0.0614	8.64	0.209	6.85
										0.091	8.41	0.0462	7.98	0.0605	8.34	0.1019	8.34
										0.0595	8.24	0.0681	7.73	0.0681	7.89	0.0647	8.59
12	2013/11/19	0.3	1.2	0.48	13.7	1.93×10 ⁶	0.377	12.1	0.23	0.0795	7.68	0.031	8.11	0.0538	6.77	0.1629	8.11
										0.0576	7.63	0.0405	8.41	0	7.40	0.3371	7.93
										0.0376	7.63	0.029	8.59	0.0671	7.91	0.0357	7.04
13	2013/11/26	0.3	1.2	0.55	12.4	9.23×10 ⁶	0.301	11.3	0.25	0.0405	9.09	0.0424	8.72	0.0814	9.27	0.1157	9.17
										0	9.39	0.0195	9.39	0.0271	9.57	0.1871	8.55
										0.03	9.87	0.0414	8.66	0.0662	8.79	0.0257	9.02
14	2013/11/26	0.3	1.2	0.525	12.7	9.23×10 ⁶	0.301	11.3	0.3	0.0557	-	0.0329	9.17	0.051	9.44	0.1486	9.02
										0.0424	8.74	0.0224	9.02	0.0443	9.07	0.0957	8.97
										0	9.32	0.0386	9.87	0.0538	9.44	0.2171	9.07

SP: Sampling port; Q_L = water flow rate; Q_G = gas flow rate; T = temperature; N₀ = concentration of viable microorganisms entering the reactor; α = water absorption coefficient at 254nm using logarithms to the base e; C_{L,0} = dissolved ozone concentration entering the reactor; C_{G,0} = gas phase ozone concentration entering the reactor; C_L = dissolved ozone concentration at the different locations of the contactor; DEC : Decimal Elimination Capacity

4.3.2.2 Pilot-scale contactor hydrodynamics

Four tracer tests were performed at the target water flow rate of 1.2 m³/h. The experimental data were first analyzed to obtain the mean residence time ($\bar{t}$) and standard deviation (σ) of the RTD curve with the Eqs. 4-28 and 4-29, through the effluent sampling ports of 1, 2 and 5. Then the dispersion number were estimated from $\bar{t}$ and σ according to the Eq. 4-6. The results are shown in Table 4-5.

Table 4-5 Results of tracer tests

No.	Date	Sampling Port 1			Sampling Port 2			Sampling Port 5		
		$\bar{t}$ (min)	σ^2	d	$\bar{t}$ (min)	σ^2	d	$\bar{t}$ (min)	σ^2	d
1	2011/10/12	1.36	0.59	0.200	2.19	0.92	0.107	5.62	1.60	0.026
2	2011/10/12	1.32	0.20	0.062	2.12	0.69	0.083	5.94	2.67	0.039
3	2011/11/8	1.81	0.01	0.001	2.95	1.12	0.069	5.88	2.13	0.032
4	2011/11/8	1.75	1.32	0.308	2.21	0.33	0.035	5.52	3.41	0.060
Mean		1.56		0.143	2.37		0.074	5.74		0.039

The dispersion number estimated at the sampling point 1 was little greater than the value estimated at sampling point 5. This discrepancy could be explained by the occurrence of local high mixing. The high mixing could have been the result of the injection of water stream and corresponding water surface instability at the top of contactor. Different dispersion numbers could be used to represent the different levels of contactor hydrodynamics taking place at the different locations of the contactor. However, because the ADR model developed in this study has an assumption that the liquid phase was in uniform axial dispersion throughout the water column, and it is difficult in estimating by using more than one dispersion number, the mean dispersion number of 0.039 that estimated at sample port 5 could be represented the contactor hydrodynamics. The assumption of negligible contactor hydrodynamics discrepancy, perhaps the most arguable, was considered acceptable because the water column (6 m) of the O₃/UV contactor was much longer than that high mixing part at the top of contactor. Uniformly, the mean residence time of 5.74 min at sampling port 5 was adopted, corresponding to a mean residence time of 6.888 min for the entire water column height (6m) in the O₃/UV contactor, and an actual water flow rate of 1.05 m³/h, a value within 87.57% of the target flow rate of 1.2 m³/h.

As depicted in 4.2.2, using the estimated dispersion number ($d=0.039$) with tracer model

(Eqs. 4-1 ~ 4-4), theoretical tracer concentration throughout the contactor at various times could be obtained by solving the tri-diagonal matrix resulting from applying finite differences by the Thomas algorithm (Chapra and Canale, 1988). Experimental tracer result measured at sample port 5 and the corresponding predicting with tracer model is presented in **Figure 4-7**. Generally good agreement was found between tracer model prediction and experimental tracer results. In comparison with tracer model prediction, the experimental tracer curve had a longer tail. This discrepancy might caused by unavoidable dead- water zones in the contactor.

The tracer concentrations obtained from these efforts can then be converted from step-input to the equivalent pulse-input information. The concentration and time values were then normalized according to Eqs. 4-30 ~ 4-31 to obtain dimensionless parameters. The normalized result is shown in **Figure 4-8** in terms of dimensionless concentration and time.

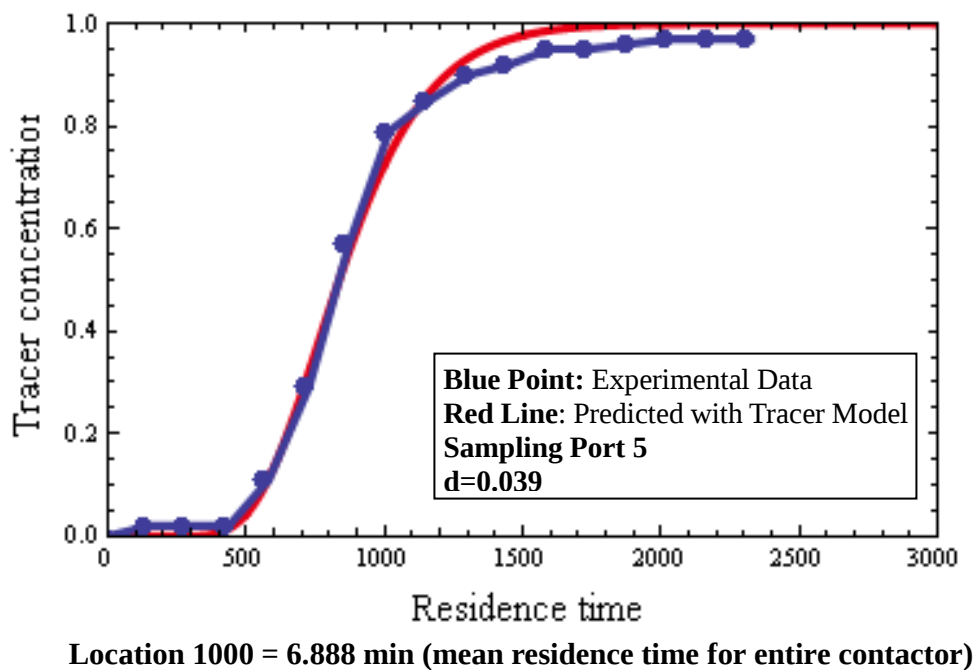


Figure 4-7 Comparison of tracer test curves (step-input type) determined experimentally and predicted with tracer model.

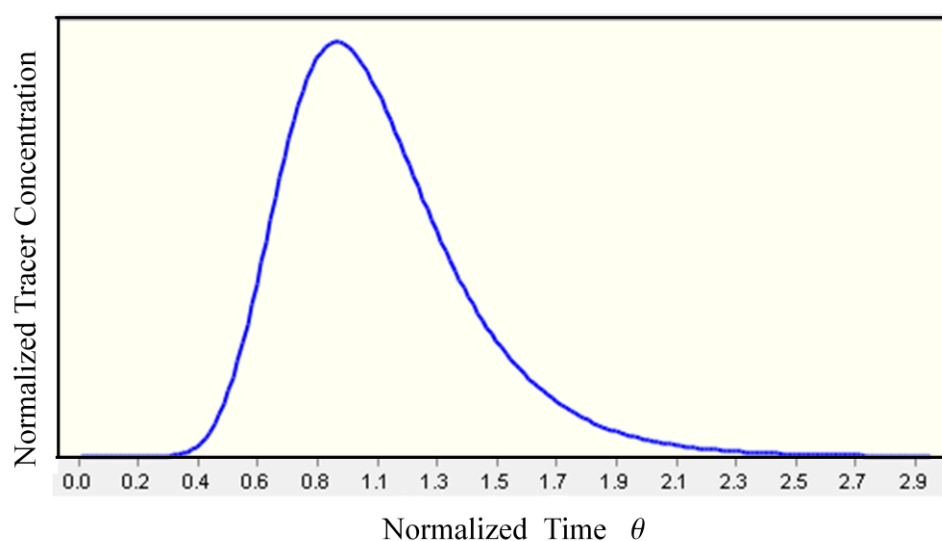


Figure 4-8 Normalized result (pulse-input type) from tracer model prediction.

4.4 Model Validation

The concentration profiles of ozone throughout the water column of the pilot-scale O₃/UV contactor were predicted with the ADR model by using the obtained dispersion number and corresponding operating conditions in **Table 4-4**. The decomposition rate constant by UV irradiation (k_{dUV}) used in model prediction was calculated to be 0.0841 s⁻¹ from **Eq. 4-15** using the UV fluence rate, the dimensions of UV lamp and pilot-scale O₃/UV contactor.. The average bubble diameter inside of the contactor was measured by taking images with a camera and then calculated with **Eq. 4-12**.

Ozone water quality dependent decomposition rate constant (k_{dw}) used in this study was a calculation based on literature information. For full-scale condition, the effects of *E. coli* concentration in water to ozone demand and decay reactions was identified to be negligible. In the case of *E. coli* dosing experiments, the ozone demand by high concentration of injected *E. coli* were considered. Total organic carbon (TOC) was select as a parameter to represent the water quality and *E. coli* concentration level in water. An assumption in this study was that the ozone water quality dependent decomposition rate constant is proportional to the TOC content. Hunt *et al.* (1999) indicated that the average organic carbon content of each *E. coli* cell was approximately 2.56×10^{-10} mg C/CFU. Therefore, the total organic carbon content of *E. coli* in water could be estimated from *E. coli* concentration (N_0) with the following expression:

$$\text{TOC}_{\text{E.coli}} = 2.56 \times 10^{-10} \times N_0 \quad (4-32)$$

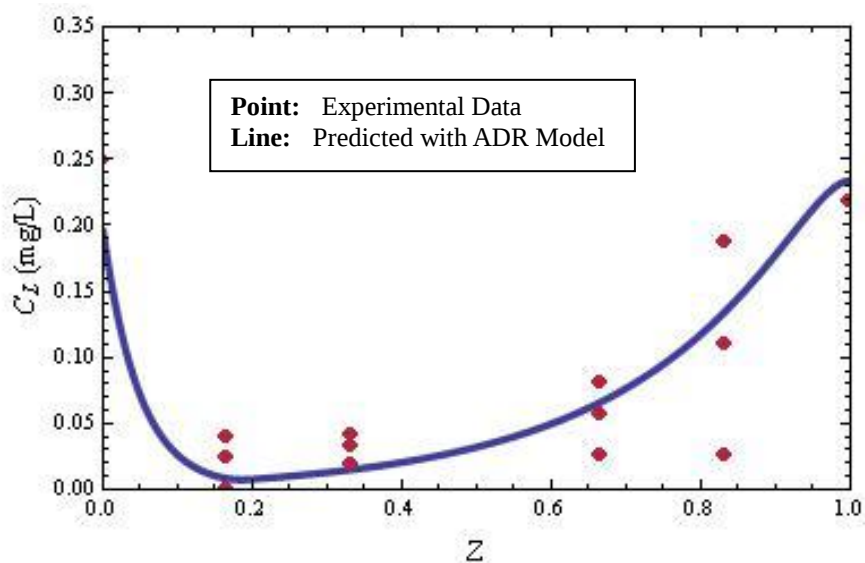
The water quality of the pilot plant used in this study had been analyzed by Hisamoto (2012). The TOC content of influent water (i.e., water treated after RSF) of O₃/UV contactor was estimated to be 0.94 mg C/L. An investigation (Kyoto, 2005) on Lake Biwabi was adopted as a reference, in which an ozone decomposition rate constant of 0.0055 s⁻¹ was determined with batch-scale tests, corresponding to the water TOC content of 4.2 mg C/L. Thus, the ozone water quality dependent decomposition rate constant (k_{dw}) used in this study can be estimated with the following expression:

$$k_{\text{dw}} = \frac{(2.56 \times 10^{-10} \times N_0 + 0.94)}{4.2} \times 0.0055 \quad (4-33)$$

The simplified assumption of the ozone decomposition rate constant is proportional to the TOC content, perhaps arguable, was considered acceptable because the estimated k_{dw} in this study with a range of 0.001~0.002 s⁻¹ appeared to be consistent with the values developed by others studies (Kim *et al.*, 2002b; Smeets *et al.*, 2006). Actually in the ADR model, the water quality dependent decomposition rate constant (k_{dw}) was combined with the ozone decomposition rate constant by UV irradiation (k_{dUV}) to be one parameter that represents as the overall first order ozone decomposition rate constant (k_{D}). In comparison with decomposition rate constant by UV irradiation ($k_{\text{dUV}} = 0.08414 \text{ s}^{-1}$), the water quality dependent decomposition rate constant (k_{dw}) is a much smaller value with a range of 0.001~0.002 s⁻¹. It can be concluded that the variability of k_{dw} in overall first order ozone decomposition rate constant is almost negligible.

An example of experimental data and the results of the simulation with ADR model is shown in **Figure 4-9**. A complete set of experimental tests and model predicting are presented in **Appendix C**. As depicted in **Figure 4-9**, experimental data of dissolved ozone concentrations observed in the lower sampling ports showed larger variances. Uneven distribution of ozone gas bubbles in the radial direction and the occurrence of large eddies formed at the bottom of the contactor might have played a role in the variability observed. In general, there was a good agreement between experimental data and predictions. Some of the discrepancies observed might have resulted from a combination of analytical and experimental errors, variability in the water quality, and deviations from ADR model assumptions, such as occurrence of high mixing near the diffuser and at the top of contactor rather than uniform axial dispersion throughout the water column.

(a) Dissolved ozone concentration (2013.11.26)



(b) Gas-phase ozone concentration (2013.11.26)

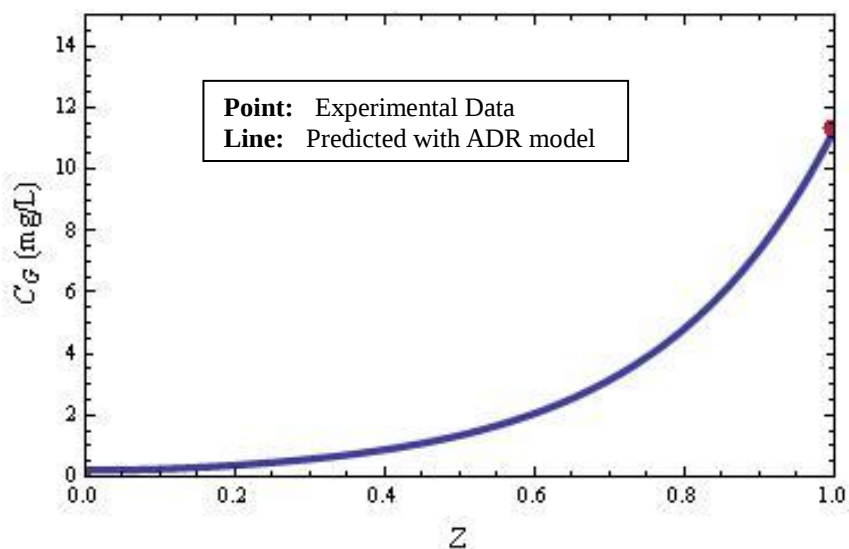


Figure 4-9 Comparison of ozone concentration profiles measured experimentally and predicted with ADR throughout water column height of the pilot-scale O_3 /UV contactor: (a) dissolved ozone concentration; (b) gas-phase ozone concentration. (Applied water flow rate = $1.05 \text{ m}^3/\text{h}$, gas flow rate = 0.55 L/min , ozone dose = 0.3 mg/L , feed-gas ozone concentration = 11.3 mg/L , dissolved ozone concentration in influent water = 0.25 mg/L , mean residence time = 6.888 min , dispersion number = 0.039 , temperature = $12.4 \text{ }^\circ\text{C}$)

The results presented in this section and in section 4.3.2.2 indicate that the ADR model developed in this study is a promising tool to represent the hydrodynamics and the distribution of ozone concentration in O₃/UV contactor. Thus, the model will next be applied to simulate the performance of O₃/UV contactor under full-scale condition.

4.5 Determination of the Inactivation Rate Constants

4.5.1 Determined with ADR model

The *E. coli* concentration and inactivation efficacy throughout the water column of the pilot-scale O₃/UV contactor can be also simulated with the ADR model by using operating conditions of *E. coli* dosing experiments. There are two inactivation rate constants in the ADR model, inactivation rate constant by molecular ozone and inactivation rate constant by UV irradiation. The *E. coli* dosing experimental results corresponding to sampling port 1 were fitted with the ADR model by least-squares using these two inactivation rate constants as the fitting parameters. The obtained values are shown in **Table 4-6**. Because the UV lamp installed at the top of the pilot-scale O₃/UV contactor only has a length of 1 m, it is considered that the reaction inside of the contactor consist of two parts: advanced oxidation reaction at the top 1 m of the contactor, and ozonation at the remaining section. In order to obtain the inactivation rate constants under O₃/UV condition, only the experimental data observed at sampling port 1 was used. An additional reason for this option was that the *E. coli* inactivation results observed at the lower sampling ports (i.e., sampling ports of 2, 4, 5) showed that after treated by O₃/UV, *E. coli* turned out to be more resistant to ozonation. Using those experimental results may result in an underestimate of *E. coli* inactivation rate constant.

4.5.2 Determined with Chick - Watson model

An alternative simplified method for assessing microorganism inactivation was also employed in this study. The inactivation kinetic for chemical disinfectants is most commonly described by the first-order disinfection model of Chick-Watson (1908) and the same model can be applied for UV disinfection. The inactivation of microorganisms is usually described by the log inactivation of *N*. Based on the first-order model the relationship between log inactivation and the ozone dose and UV fluence is described by:

$$\ln \left(\frac{N}{N_0} \right) = -k_{O_3} C_L T - k_{UV} I T \quad (4-34)$$

For the convenience of analysis, the residence time (T) at the different locations of the contactor was normalized to obtain dimensionless values. **Eq. 4-34** can be transformed to obtain:

$$\ln\left(\frac{N}{N_0}\right) = -k_{O_3} \cdot \theta \cdot C_L \bar{T} - k_{UV} \cdot \theta \cdot I \bar{T} \quad (4-35)$$

in which N and N_0 = concentration of viable *E. coli* at respective times T and 0; C_L = dissolved ozone concentration at the different locations of the contactor; k_{O_3} = inactivation rate constant by molecular ozone; I = volume mean UV fluence rate (only for the top 1 m of the contactor) ; k_{UV} = inactivation rate constant by UV irradiation; T = residence time at the different locations of the contactor; $\bar{T}$ = mean residence time at the different locations of the contactor; $\theta = T/\bar{T}$ = dimensionless time.

According to **Eq.4-35**, inactivation rate constant of k_{O_3} and k_{UV} can be estimated by regression analysis if the $\ln(N/N_0)$, θ , along with the corresponding $C_L \bar{T}$ and $I \bar{T}$ values are known. The $\ln(N/N_0)$ was estimated based on pilot-scale *E. coli* dosing experimental results. The mean residence time ($\bar{T}$) at sampling port of 1, 2, 4, 5 were estimated to be 68.88 s, 137.76 s, 275.52 s, 344.4 s, respectively, according to the tracer test result. The volume mean UV fluence rate (I) was estimated according to **Eqs.4-20 ~ 4-21** using the parameter of UV lamp and water absorption coefficient measured in *E. coli* dosing experiments (as shown in **Table 4-4**). The dissolved ozone concentration (C_L) used for the determination of $C_L \bar{T}$ is defined as average concentration which can estimate from ADR model (**Eqs. 4-22 ~ 4-23**) combined with the following expression:

$$C_L = \int_{Z=0}^{Z=i} C_L(Z) dZ \quad (4-36)$$

in which $i = 1/6, 2/6, 4/6, 5/6$, corresponding to the mean residence time of $\bar{T}=68.88$ s, 137.76 s, 275.52 s, 344.4 s, respectively.

The parametric distribution of θ is as shown in **Figure 4-8**. A Monte Carlo simulation was performed by drawing random values from this parametric distribution to calculate the $\ln(N/N_0)$ with **Eq. 4-35**. The two inactivation rate constants, inactivation rate constant by molecular ozone and inactivation rate constant by UV irradiation, were determined by least squares regression analysis of the *E. coli* dosing experimental results with the Chick - Watson model predictions. The resulting values are presented in **Table 4-6** together with

the ADR model results.

Table 4-6 *E. coli* inactivation rate constants

No.	Date	Determined with		Determined with	
		ADR model		Chick - Watson model	
		k_{03} (L•mg ⁻¹ s ⁻¹)	k_{UV} (cm ² •mJ ⁻¹)	k_{03} (L•mg ⁻¹ s ⁻¹)	k_{UV} (cm ² •mJ ⁻¹)
1	2012/10/3	0.13	0.1	0.076	0.042
2	2012/12/11	0.17	0.08	0.093	0.038
3	2012/12/21	0.1	0.23	0.057	0.056
4	2013/1/10	0.1	0.12	0.104	0.023
5	2013/7/10	0.15	0.24	0.218	0.036
6	2013/7/10	0.25	0.29	0.181	0.045
7	2013/7/31	0.2	0.27	0.267	0.033
8	2013/7/31	0.22	0.3	0.286	0.036
9	2013/10/31	0.1	0.5	0.243	0.062
10	2013/10/31	0.2	0.45	0.201	0.064
11	2013/11/19	0.15	0.49	0.225	0.068
12	2013/11/19	0.18	0.52	0.214	0.069
13	2013/11/26	0.1	0.65	0.328	0.066
14	2013/11/26	0.17	0.62	0.344	0.066

4.5.3 *E. coli* inactivation in literature

The results of *E. coli* inactivation rate constants obtained in this study can be compared with inactivation data reported in the literatures. The inactivation of *E. coli* by ozone has been studied by several researchers (Finch *et al.*, 1988; Zhou and Smith, 1994; Hunt and Mariñas, 1997; Hijnen *et al.*, 2001; Yamasaki, 2014). All have used different types of reactors (Continuous Stirred Tank Reactor CSTR, Plug Flow Reactor PFR, Batch Reactor) and different types of water. When compared with the data reported in these literatures, the inactivation rate constants by ozone obtained in this study were found to be extremely small values. For instance, the inactivation rate constant by ozone estimated by Yamasaki (2014) for the same strain of *E. coli* with using a lab-scale continuous-flow reactor was 51 L•mg⁻¹s⁻¹. Hijnen *et al.* (2001) compared the observed inactivation kinetics in full-scale ozone systems with inactivation kinetics determined under laboratory conditions. They concluded that ozonation in practice appears to be much less effective

than could be expected from the lab-obtained inactivation kinetics. Suboptimal hydraulics of full-scale ozone systems are known to reduce the efficacy of ozonation in practice (Ducoste *et al.*, 2001). This is also applicable in this study to explain the difference between lab-obtained results and those obtained under polite-scale condition. In general, the discrepancies of inactivation rate constant by ozone obtained in this study and other literatures might have resulted, at least in part, from a combination of using different *E. coli* strains and culture conditions, different reactor design and experimental conditions, suboptimal hydraulics of polite-scale contactor, and some deviations from ADR model assumptions and simulations.

On the other hand, the inactivation rate constants by UV determined with ADR model showed a generally agreement with other literatures (Hijnen *et al.*, 2006; Yamasaki, 2014). It was observed from **Table 4-6** that the inactivation rate constants by UV determined with ADR model were approximately ten times higher than those determined with Chick - Watson model. This discrepancy may result from the different analytic method for these two models. Therefore, it was decided that the *E. coli* inactivation rate constants determined in this study were model dependent and could not be extrapolated to other models.

4.6 Model Application for Full-Scale Condition

In this section, the ADR model developed was applied to predict the inactivation efficacy of *E. coli* attained in full-scale O₃/UV contactor. Since there is no O₃/UV treatment used on existing water supply systems in Japan, the full-scale O₃/UV contactor used in this study was a simplified assumption based on a single contactor chamber of an actual full-scale ozone contactor in the Kunijima water purification plant of Osaka City. The configuration and dimensions are shown in **Figure 4-3** and **Table 4-1**.

4.6.1 Base case ($d = 0.297$, ADR model)

Predicting the performance of the full-scale O₃/UV contactor requires determinations of ozone decomposition kinetics (k_{dw} , k_{dUV}), microbial inactivation kinetics (k_{o3} , k_{UV}), and contactor hydrodynamics (d). The influent water of this full-scale O₃/UV contactor was the same as the influent water of pilot plant; therefore, the ozone water quality dependent decomposition rate constant (k_{dw}) can be calculated using the same method as described in **4.4**. The only difference is that for full-scale condition, the affects of *E. coli* concentration in influent water to ozone demand and decay reactions is negligible. The

decomposition rate constant by UV irradiation (k_{dUV}) can be calculated with the **Eq. 4-15** using UV fluence rate, the dimensions of the UV lamp and full-scale O_3 /UV contactor. The calculated results of k_{dw} and k_{dUV} are presented in **Table 4-7**, together with the overall first-order ozone decomposition rate constant (k_D).

With respect to the *E. coli* inactivation rate constants (k_{o3} , k_{UV}), the values obtained from pilot-scale *E. coli* dosing experiments were considered to be also suitable for full-scale condition. As shown in **Table 4-6**, a total of 14 pairs of inactivation rate constants were obtained for each method. The predictions of the inactivation efficacy of *E. coli* under full-scale conditions were made by varying these inactivation rate constants pairs while other parameters were held constant.

With respect to dispersion number (d), since dosing tracer to full-scale drinking water treatment process is not allowed and feasible, the dispersion number used for full-scale O_3 /UV contactor in this study was an estimation based on the value determined in the pilot-scale contactor ($d = 0.039$) and the value calculated from a reference (Tang *et al.*, 2005) where the full-scale ozone contactor has a similar shape and size to the one in the Kunijima Water Purification Plant of Osaka City. Tang *et al.* (2005) performed a series of tracer tests in a full-scale ozone contactor at the ACWD treatment plant and estimated a dispersion number of $d_A = 1.45$ corresponding to a water approach velocity ($U_{L,A}$) of 196.73 m/h. Tang *et al.* (2005) also indicated that the dispersion number for the same contactor under various operating conditions could be obtained from $d_A = 1.45$ after correcting for the difference in water approach velocity with the following expression:

$$\frac{d_B}{d_A} = \frac{U_{L,A}}{U_{L,B}} \quad (4-37)$$

The water approach velocity selected for the full-scale condition in this study was 123.66 m/h; therefore, the dispersion numbers was calculated to be 2.258 according to the **Eq. 4-37**. Then, taking 0.039 of the dispersion number determined in the pilot-scale ozone-bubble diffuser contactor as the smallest, and the calculated value of 2.258 as the largest, we used 0.297 (the geometric average of the two values) as the base case's dispersion number for the full-scale O_3 /UV contactor.

The estimated parameters and selected operating conditions for base case model simulation are summarized in **Table 4-7**. Then, by using the obtained dispersion number, the 14 *E. coli* inactivation rate constants pairs that fitted with ADR model in **Table 4-6**,

and other parameters and operating conditions in **Table 4-7**, the profiles of dissolved ozone concentration, gas-phase ozone concentration, and decimal elimination capacity of *E. coli* throughout the full-scale O₃/UV contactor were predicted with the ADR model. The resulting dissolved ozone and gas-phase concentration profiles are presented in **Figure 4-10 (a)** and **(b)**, respectively, and an example of decimal elimination capacity of *E. coli* profile is presented in **Figure 4-10 (c)**. As depicted in **Figure 4-10**, three ozone doses of 0.25, 0.5 and 1 mg/L were used for model simulations. However, since the injected ozone was immediately decomposed by UV irradiation under AOP condition, the dissolved ozone concentration throughout the O₃/UV contactor was quite low and there was not great difference among these three ozone doses. Because of the low dissolved ozone concentration, the variation of ozone dose was almost negligible. Therefore it shows that the decimal elimination capacity of *E. coli* throughout the O₃/UV contactor was almost the same for these three different ozone doses as shown in **Figure 4-10 (c)**. It can be indicated that, inside of the full-scale O₃/UV contactor, *E. coli* inactivation by UV irradiation resulted in a much higher level compared to that obtained by dissolved ozone, which means that the large variation in *E. coli* inactivation rate constant by UV irradiation as shown in **Table 4-6** can greatly affect the prediction of overall inactivation efficacy of O₃/UV. This was also verified by sensitivity analysis in **Chapter 5**. For the convenience of analysis and comparison with other conditions, the ozone injection dose of 0.25 mg/L was selected as the **base case** for the full-scale model simulations.

With the ozone injection dose of 0.25 mg/L, the inactivation efficacies of *E. coli* predicted with ADR model under full-scale O₃/UV condition are summarized in **Table 4-8**, together with the corresponding *E. coli* inactivation rates constants that fitted with ADR model in **4.5**. A maximum value of 8.59 log₁₀, mean elimination capacity (MEC) of 3.43 log₁₀ and minimum value of 2.49 log₁₀ were obtained for the inactivation efficacy of *E. coli*. A triangular distribution with these parameters was constructed as shown in **Figure 4-11**.

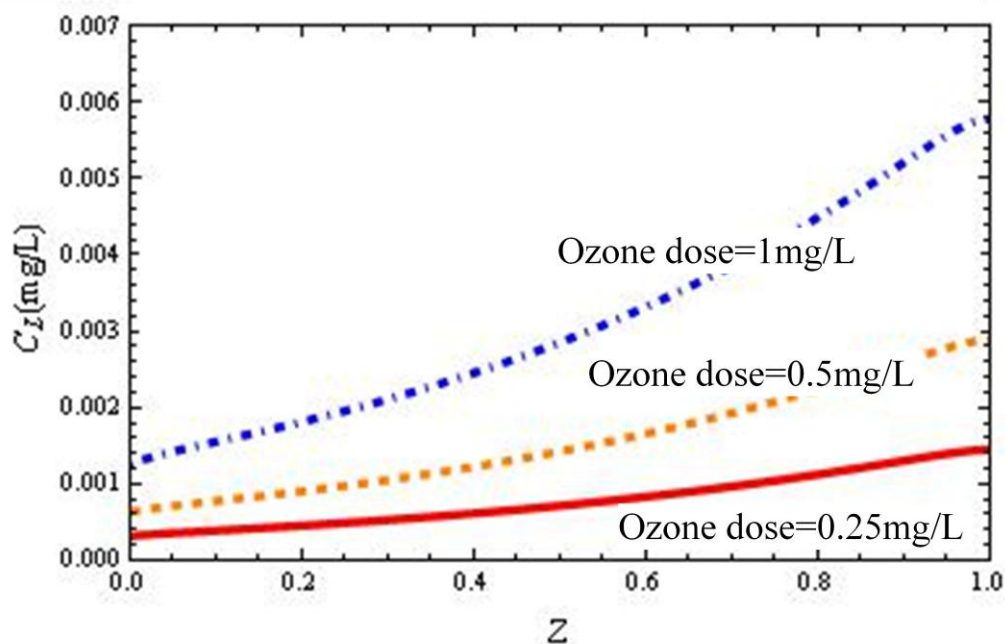
Table 4-7 Parameters and operating conditions for full-scale model simulations.**(Base case: ozone injection dose=0.25 mg/L, $d=0.297$, ADR model)**

Mark	Parameter	Value	Unit
d	dispersion number	0.297	dimensionless
	ozone injection dose	0.25	mg/L
k_{dw}	ozone water quality dependent decomposition rate constant	0.001	1/s
k_{dUV}	ozone decomposition rate constant by UV irradiation	1.444	1/s
k_D	overall first-order ozone decomposition rate constant	1.445	1/s
H	depth of water column in contactor	5.9	m
L	length of the lamp	5.9	m
R	contactor radius	2.82	m
$\bar{t}$	mean hydraulic residence time	2.863	min
Q_L	water flow rate	3091.6	m ³ /h
U_L	water approach velocity	123.66	m/h
Q_G	gas flow rate	463.74	m ³ /h
U_G	gas approach velocity	18.55	m/h
	gas to liquid ratio	0.15	
J	UV fluence	220	mJ/cm ²
I	UV fluence rate	1.29	mW/cm ²
$C_{G,0}(Z=1)$	influent gas phase ozone concentration	1.67	mg/L
N_0	initial <i>E. coli</i> concentration	200	CFU/mL
T	temperature	20	°C
m	Henry's law constant	2.788	dimensionless
$k_L a$	volumetric mass transfer coefficient	0.004	1/s
$d_{B,0}$	average bubble diameter with $U_G = 0$	0.5	cm
d_B	average bubble diameter	0.608	cm
V_B	bubble rise velocity	21.72	cm/s
μ_L	absolute viscosity of liquid phase	1.005	cP
Sh	Sherwood number	472.71	dimensionless
R_G	gas phase Reynolds number	1315.51	dimensionless
Sc_L	liquid phase Schmidt number	587.79	dimensionless
ν_L	kinematic viscosity of liquid phase	0.01004	cm ² /s
g	gravitational constant	9.8	m/s ²
D_L	molecular diffusivity of ozone in water	1.708×10^{-9}	m ² /s

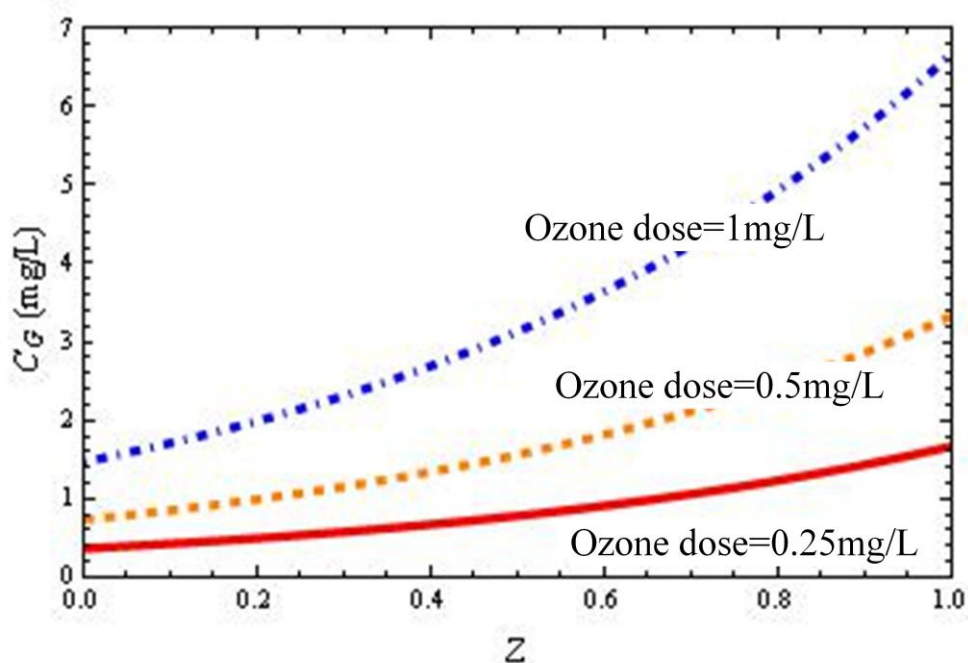
Table 4-8 Inactivation efficacy of *E. coli* predicted with ADR model under full-scale O₃/UV condition.

No.	<i>E. coli</i> inactivation rate constants		Base case (<i>d</i> =0.297)	Case 1 (<i>d</i> =0.039)	Case 2 (<i>d</i> =2.258)
	<i>k</i> _{O₃} (L•mg ⁻¹ s ⁻¹)	<i>k</i> _{UV} (cm ² •mJ ⁻¹)	Log ₁₀ reduction	Log ₁₀ reduction	Log ₁₀ reduction
1	0.13	0.1	2.87	6.03	1.00
2	0.17	0.08	2.49	5.08	0.86
3	0.1	0.23	4.76	10.88	1.69
4	0.1	0.12	3.22	6.91	1.12
5	0.15	0.24	4.88	11.13	1.73
6	0.25	0.29	5.45	11.26	1.94
7	0.2	0.27	5.23	11.28	1.86
8	0.22	0.3	5.56	11.24	1.98
9	0.1	0.5	7.43	13.66	2.66
10	0.2	0.45	7	13.33	2.50
11	0.15	0.49	7.34	13.40	2.63
12	0.18	0.52	7.59	13.13	2.72
13	0.1	0.65	8.59	15.33	3.08
14	0.17	0.62	8.37	15.27	3.00
		Min.	2.49	5.08	0.86
		MEC	3.43	6.17	1.54
		Max.	8.59	15.33	3.08

(a) Dissolved ozone concentration



(b) Gas-phase ozone concentration



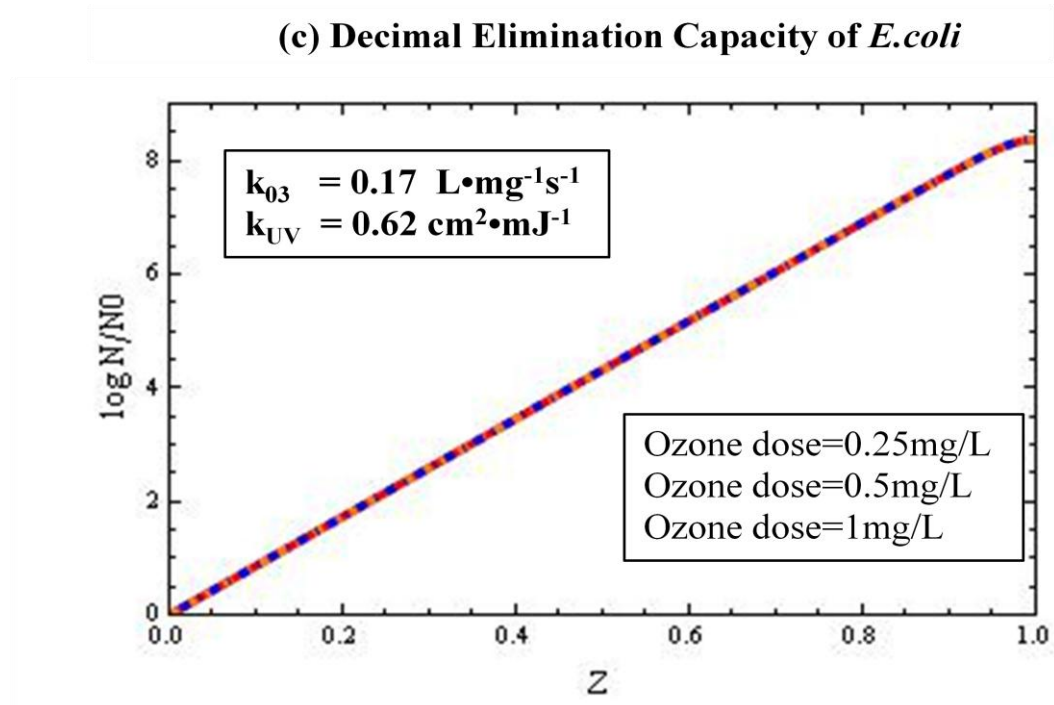


Figure 4-10 ADR model simulation of full-scale O_3/UV contactor performance at various ozone injection doses: (a) dissolved ozone concentration; (b) gas-phase ozone concentration; (c) decimal elimination capacity of *E. coli* (Applied inactivation rate constant by molecular ozone $k_{03} = 0.1 \text{ L}\cdot\text{mg}^{-1}\text{s}^{-1}$, inactivation rate constant by UV irradiation $k_{UV} = 0.62 \text{ cm}^2\cdot\text{mJ}^{-1}$).

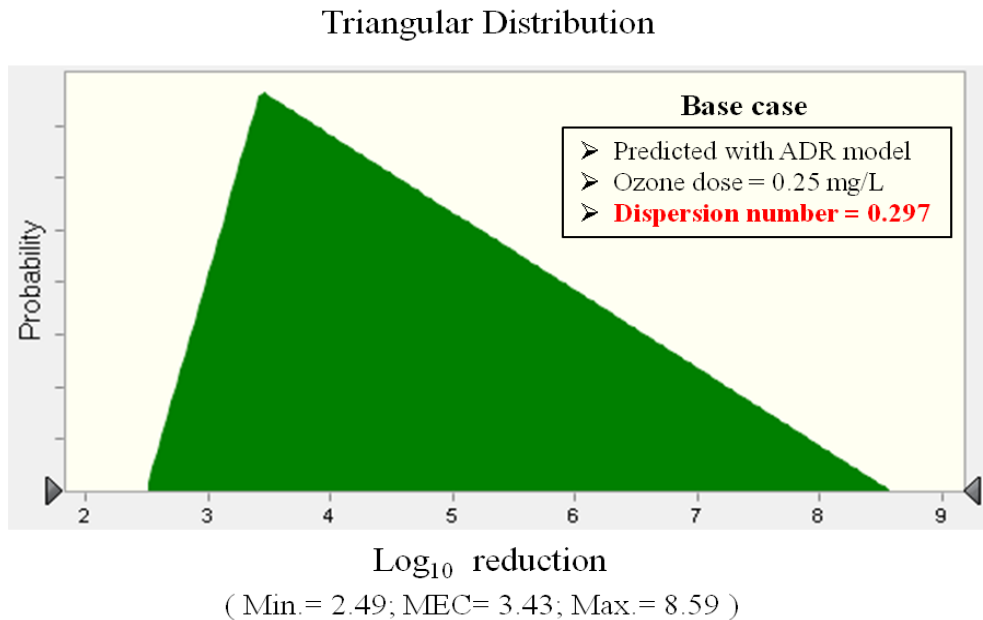


Figure 4-11 Triangular distribution of inactivation efficacy of *E. coli* predicted with ADR model under full-scale O_3/UV condition (Base case with $d = 0.297$).

4.6.2 Case 1 and Case 2 ($d_1 = 0.039$, $d_2 = 2.258$, ADR model)

It is natural that the estimated value of the dispersion number used for the full-scale O_3 /UV contactor has large uncertainty. Therefore, the impact of the dispersion number on the prediction of inactivation efficacy of *E. coli* was analyzed. With taking 0.039 of the dispersion number determined in the pilot-scale ozone-bubble diffuser contactor as the smallest (hereinafter referred to as **case 1**), and the calculated value of 2.258 from Tang *et al.* (2005) as the largest (hereinafter referred to as **case 2**), model simulations similar to the base case were performed to assess the inactivation efficacy of *E. coli* of these two cases. The results are listed in the **Table 4-8**, and the corresponding triangular distributions of the predicted inactivation efficacy of *E. coli* for these two cases are shown in **Figure 4-12** and **Figure 4-13**, respectively. As depicted in **Table 4-8**, when the dispersion number was set at 2.258, the mean value of *E. coli* inactivation efficacy was estimated to be a very low at $1.54 \log_{10}$. On the other hand, when the dispersion number was set at 0.039, the mean value increased to $6.17 \log_{10}$. It is clear that dispersion number significantly affects the prediction of *E. coli* inactivation efficacy. A further uncertainty analysis regarding to the influence of dispersion number on the yearly risk of infection for the QMRA purpose was conducted in **Chapter 5**. Taking into consideration the significant influence of dispersion number on the model outcomes, experimental measurement or an accurate model estimation of the dispersion number in the actual full-scale contactor is highly required to improve the accuracy of model prediction.

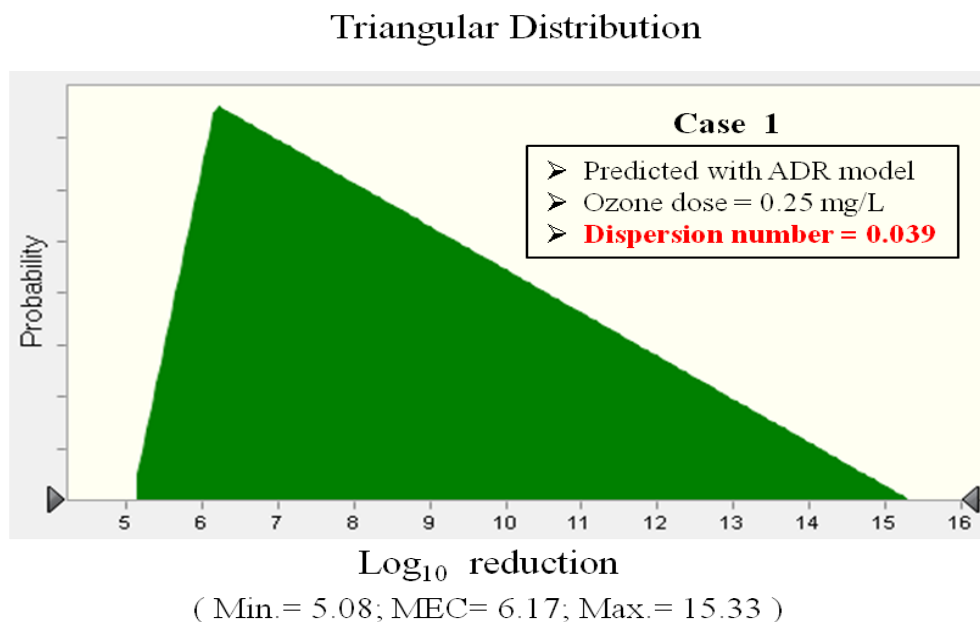


Figure 4-12 Triangular distribution of inactivation efficacy of *E. coli* predicted with ADR model under full-scale O_3 /UV condition (Case 1 with $d = 0.039$).

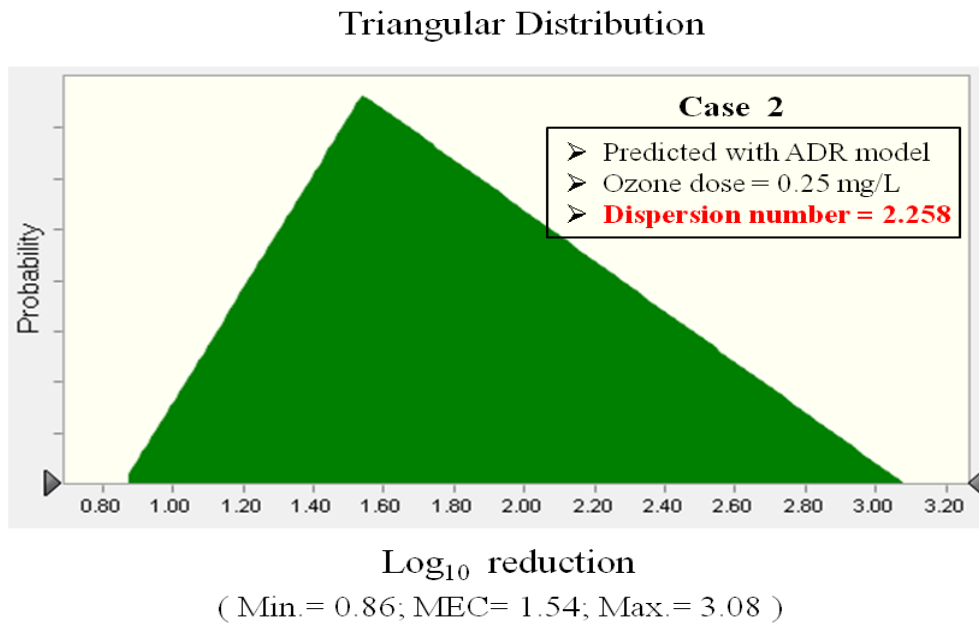


Figure 4-13 Triangular distribution of inactivation efficacy of *E. coli* predicted with ADR model under full-scale O₃/UV condition (Case 2 with $d = 2.258$).

4.6.3 Case 3 ($d = 0.297$, Chick - Watson model)

For **case 3**, Chick - Watson model and the 14 pairs of *E. coli* inactivation rate constants that fitted with Chick - Watson model in **Table 4-6** were used to predict the inactivation efficacy of *E. coli* attained in full-scale O₃/UV contactor. Among the data and parameters required, $C_L \bar{T}$ and $I \bar{T}$ were estimated to 0.134 mg•s/L and 221.56 mW•s /cm², respectively, according to the operating conditions. The parametric distribution of θ was obtained by analyzing the full-scale dispersion number of 0.297 with tracer model (**Eqs. 4-1 ~ 4-4**) by the finite differences by the Thomas algorithm (Chapra and Canale, 1988). The parametric distribution of θ is shown in **Figure 4-14**.

Then, a Monte Carlo simulation was performed by drawing random values of θ from this parametric distribution to calculate the $\ln (N/N_0)$ with **Eq. 4-35**. By this way, the result from Chick - Watson model could be used to characterize the hydrodynamic behavior in O₃/UV contactor. Since there were 14 pairs of inactivation rate constants ((k_{O_3}, k_{UV})), a total of 14 dataset and corresponding parametric distributions of $\ln (N/N_0)$ were obtained. For the convenience of comparison with other cases, the $\ln (N/N_0)$ were transformed into $\log_{10} (N/N_0)$. An example of parametric distribution of inactivation

efficacy of *E. coli* is shown in **Figure 4-15**. A complete set of Chick - Watson model predictions are summarized in **Table 4-9**. In comparison with ADR model, the result from Chick - Watson model was expressed as a parametric distribution which characterized the hydrodynamic behavior in O₃/UV contactor rather than a single value. As depicted in **Figure 4-15**, the inactivation efficacy of *E. coli* varied greatly from 1.57 (2.5%) to 17.17 (97.5%) log₁₀.

Table 4-9 Inactivation efficacy of *E. coli* predicted with Chick – Watson model under full-scale O₃/UV condition (**Case 3, $d=0.297$**).

No.	<i>E. coli</i> inactivation rate constants		Log ₁₀ reduction				
	k_{O_3} (L•mg ⁻¹ s ⁻¹)	k_{UV} (cm ² •mJ ⁻¹)	2.5%	10%	Mean	Median	97.5%
1	0.076	0.042	0.99	1.48	1.96	3.38	10.90
2	0.093	0.038	0.90	1.34	1.84	3.06	9.87
3	0.057	0.056	1.33	1.97	2.36	4.50	14.53
4	0.104	0.023	0.55	0.81	1.31	1.85	5.98
5	0.218	0.036	0.85	1.27	1.77	2.90	9.37
6	0.181	0.045	1.07	1.58	2.05	3.62	11.70
7	0.267	0.033	0.78	1.16	1.67	2.66	8.60
8	0.286	0.036	0.86	1.27	1.77	2.91	9.38
9	0.243	0.062	1.47	2.18	2.52	4.99	16.12
10	0.201	0.064	1.52	2.25	2.57	5.15	16.63
11	0.225	0.068	1.61	2.39	2.67	5.47	17.67
12	0.214	0.069	1.63	2.43	2.70	5.55	17.93
13	0.328	0.066	1.57	2.32	2.62	5.32	17.17
14	0.344	0.066	1.57	2.32	2.63	5.32	17.17
		Min.	0.55	0.81	1.31	1.85	5.98
		MEC	1.22	1.53	2.05	2.72	6.86
		Max.	1.63	2.43	2.70	5.55	17.93

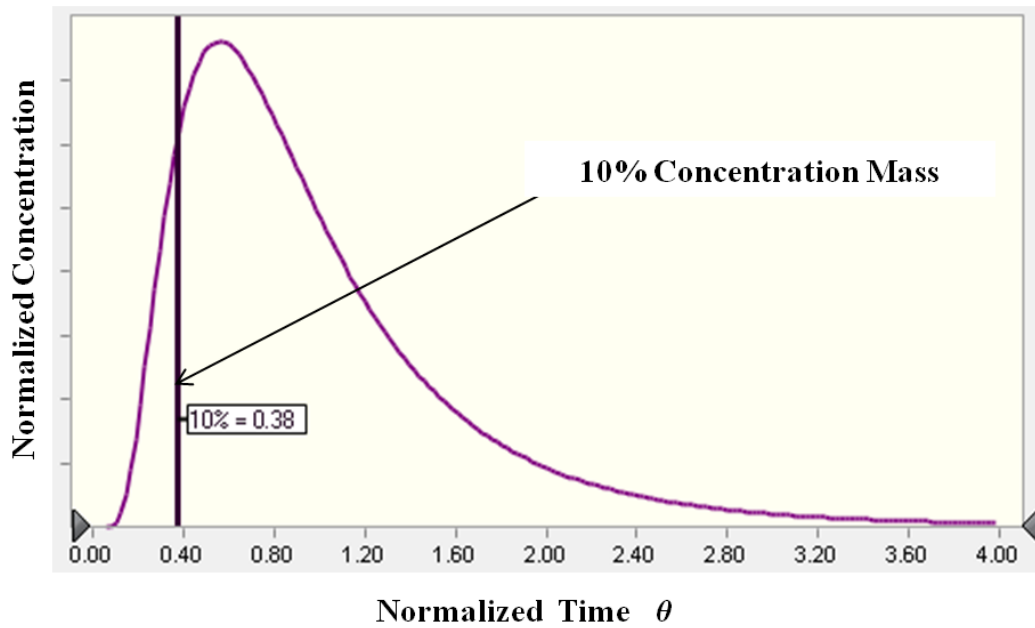


Figure 4-14 Parametric distribution of θ ($d=0.297$) in full-scale contactor

Lognormal Distribution

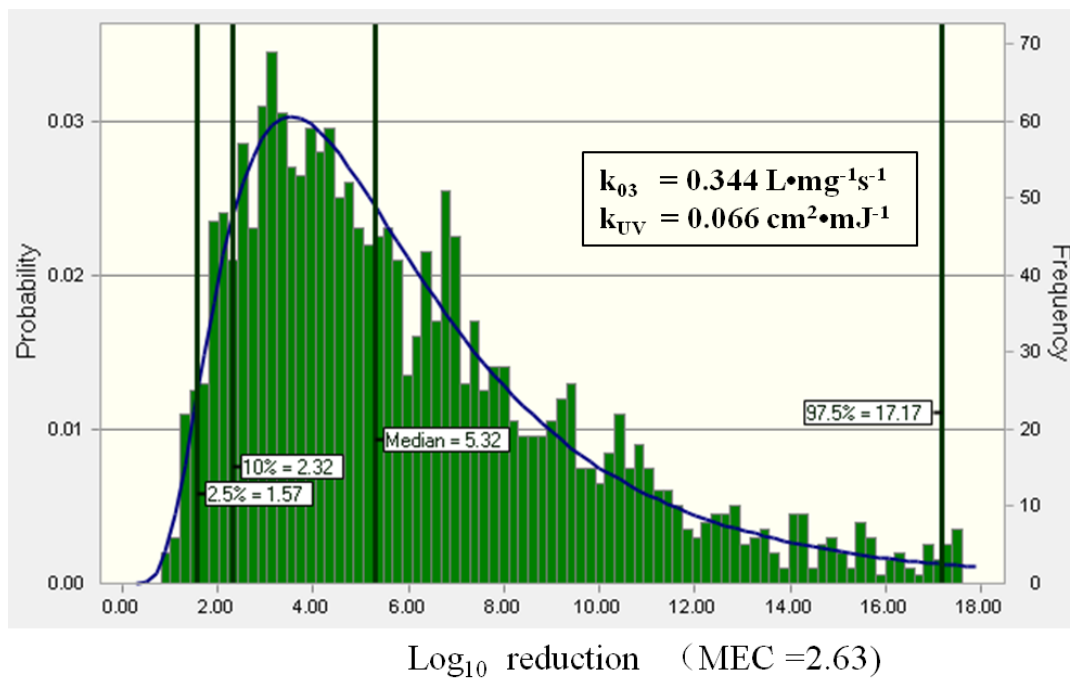


Figure 4-15 An example of parametric distribution of inactivation efficacy of *E. coli* predicted with Chick - Watson model under full-scale O_3/UV condition. (Applied inactivation rate constant by molecular ozone $k_{03} = 0.344 \text{ L} \cdot \text{mg}^{-1} \cdot \text{s}^{-1}$, inactivation rate constant by UV irradiation $k_{UV} = 0.066 \text{ cm}^2 \cdot \text{mJ}^{-1}$).

For QMRA calculation purpose, it is appropriate to select a representative value for each parametric distribution. The T_{10} method is commonly used in the research field of disinfection. T_{10} is the residence time of the earliest ten percent of microorganisms to travel from the contactor inlet to outlet (as shown in **Figure 4-14**). It ensures a minimum exposure for ninety percent of the water and microorganisms entering the disinfection contactor to disinfectants. Therefore, corresponding to the T_{10} value, the 10% $\log_{10}$ reduction of each parametric distribution was selected for the QMRA calculation. This option provided a safety margin to compensate for losses in disinfection efficiency resulting from hydrodynamic non-idealities inside contactors. As a result, a total of 14 values were obtained from those 14 parametric distributions as shown in **Table 4-9**. Then, using these values, a triangular distribution with a maximum value of 2.43 $\log_{10}$, MEC of 1.53 $\log_{10}$ and minimum value of 0.81 $\log_{10}$ was constructed as shown in **Figure 4-16**. An uncertainty analysis for case 3 was conducted in **Chapter 5**.

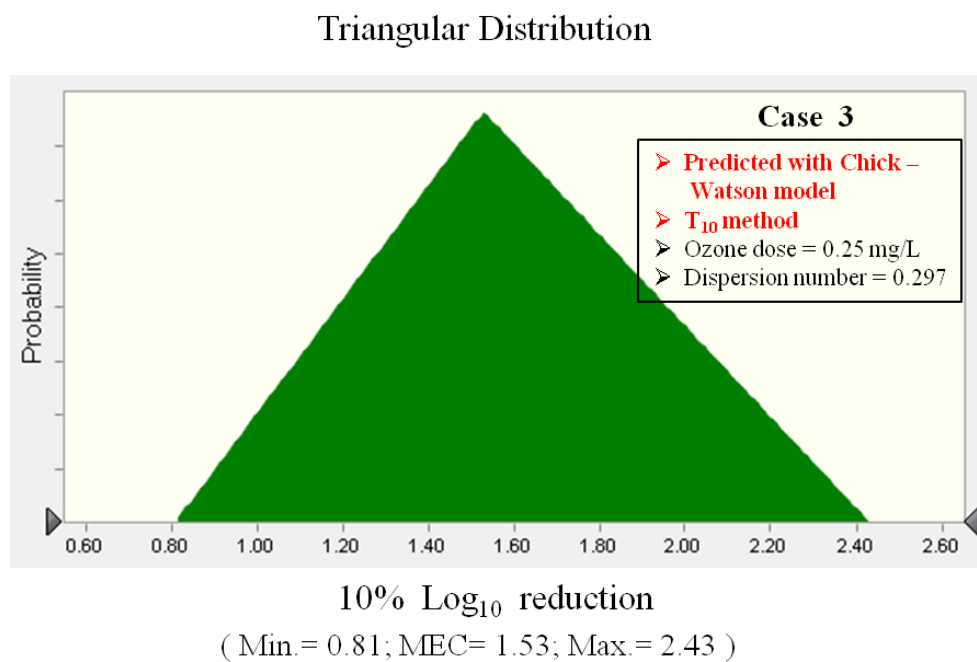


Figure 4-16 Triangular distribution of inactivation efficacy of *E. coli* predicted with Chick – Watson model under full-scale O_3 /UV condition (Case 3 with $d = 0.297$).

4.7 Summary

In order to predict the inactivation efficacy of O₃/UV process under full-scale condition, an ADR model was developed in this chapter. All the main components of O₃/UV process, including contactor hydraulics, ozone mass transfer between two phases, ozone decomposition kinetics, and microbial inactivation kinetics, were integrated within the ADR model through the use of species transport equations with appropriate source terms.

Predicting the performance of the full-scale O₃/UV contactor requires determinations of microbial inactivation kinetics (k_{o3} , k_{UV}) and contactor hydrodynamics (d). Therefore, a series of tract tracer tests and *E. coli* dosing tests were performed in a pilot-scale O₃/UV contactor to obtain these parameters and to validate the ADR model simultaneously. The simulated dissolved ozone concentration profiles throughout the pilot-scale O₃/UV contactor agreed well with the experimental data. This further validated the ADR model for predicting the performance of full-scale O₃/UV contactor.

The full-scale O₃/UV contactor used in this study was a simplified assumption based on an actual full-scale ozone contactor in the Kunijima Water Purification Plant of Osaka City. With using the *E. coli* inactivation rate constants that obtained from the pilot-scale *E. coli* dosing experiments, the inactivation efficacy of O₃/UV process under full-scale condition were predicted with ADR model. A total of 3 cases of ADR model simulation were performed with using different dispersion numbers. In addition, a Chick - Watson model for estimating *E. coli* inactivation was also employed in this study. The results of these 4 cases will next be applied in **Chapter 5** for the QMRA calculation and uncertainty analysis.

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Chapter 5

Quantitative Microbial Risk Assessment of Drinking Water Treated with Water Treatment Process for Reducing Chlorinous Odor

5.1 Introduction

In order to guarantee the microbial safety of drinking water in Japan, drinking water is currently maintained with a sufficient concentration of residual chlorine by law. However, chlorination raises problems, e.g. chlorination by-products and chlorinous odor, in addition to benefits. The increase in customer's complaints about chlorinous odor in drinking water has led water utilities and researchers to seek new processes to improve the water quality. The use of combination of ozone/vacuum ultraviolet (advanced oxidation process, AOP) and ion-exchange treatments to better control chlorinous odor in tap water has been proposed by Echigo *et al.* (2014). In this process, hydrophilic neutral fraction (a major DOM fraction) is converted to ionic species by AOP treatment, and then these ions and ammonium ion are effectively removed during ion-exchange processes. However, the full benefit of this new process is not achieved because of a lack of information from the viewpoint of microbial safety of drinking water. On the other hand, it is desirable to decrease the concentration of residual chlorine in the water supply in the future, such a countermeasure would increase health risks and lead to a deterioration in drinking water quality. Advanced management technique for microbial risk is required.

Quantitative microbial risk assessment (QMRA) is increasingly being applied to quantify the microbial safety of drinking water since the 1980s (Haas *et al.*, 1999; Medema *et al.*, 2006). Risk of infection is calculated from the exposure to pathogens (the chance of ingesting one or more pathogens) and the dose-response relation (the chance of infection from the number of pathogens ingested). QMRA can estimate how safe the water is, how much the safety varies and how certain the estimate of safety is. This can be used in the system assessment to determine whether treatment is meeting health-based targets with the required level of certainty. The water supplier can also use this information to decide where optimisation or additional control would be most effective. Thus QMRA can contribute to efficient and effective management of microbial drinking water safety.

The aim of this chapter is to apply the QMRA method to provide a quantitative estimate of the level and variation of microbial risk in drinking water treated with the new water treatment process for reducing chlorinous odor. First, the data needed to assess the elimination capacity of water treatment process were collected. Second, techniques that were developed by this thesis and previous QMRA studies were applied, and by combining with the data of elimination capacity of six water treatment processes, the pathogen concentration in the source water, consumption of unboiled drinking water and dose-response model, the yearly risk of *C. jejuni* infection was estimated. Third, sensitivity analysis was performed on the obtained results. Thus, one of the aims of this study is to identify the critical control points with regard to stably produce safe drinking water during the water treatment steps. Fourth, uncertainty analyses of the assessment were performed. As a result, the most important variables to affect the yearly risk of infection were identified, and components or variables that can contribute to improve the accuracy of the estimates were highlighted.

5.2 Methods

5.2.1 Case description

Figure 5-1 shows the model water treatment process for reducing chlorinous odor. It consists of six steps; coagulation and sedimentation, rapid sand filtration (RSF), advanced oxidation process (AOP) with ozone/ultraviolet light, cation exchange, anion exchange, and chlorination. The removal and inactivation efficacy was estimated for these six steps. Since it would be desirable to decrease the concentration of residual chlorine in the water supply in the future, the inactivation efficacy of chlorination was estimated for a case where the minimized residual chlorine level was set to approximately 0.1 mg/L. The water source for this treatment process is the Yodo River where located in Osaka city in Japan.

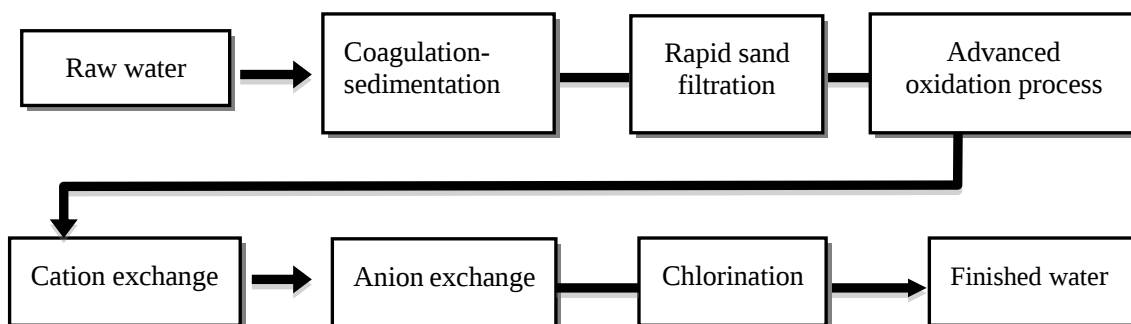


Figure 5-1 Water treatment process for reducing chlorinous odor

5.2.2 Target pathogen and its indicator

Campylobacter jejuni (*C. jejuni*) was selected as a target pathogen since it is one of the major bacteria causing waterborne disease in Japan (Yamada *et al.*, 2007). Pathogen concentrations in drinking water are generally below detection limits. Stochastic methods have therefore been proposed to calculate pathogen concentrations in the treated water using monitored pathogen concentrations in the raw water and the estimated treatment efficacy. In a stochastic assessment, the treatment efficacy is represented by a variable value. A large dataset of pathogen concentrations monitored before and after water treatment would be ideal for assessing treatment efficacy. However, it is not easy to measure the concentrations of pathogens, and often there are not a large number of monitored concentrations. For pathogenic bacteria such as *C. jejuni*, indicator bacteria like *E. coli* and enterococci have been proposed as process indicators to assess the elimination capacity of water treatment processes (Hijnen and Medema, 2010). In this study, *E. coli* was selected as a surrogate for *C. jejuni*. *E. coli* are present in the source water in higher concentrations than *C. jejuni*, and they can often be detected further down the treatment train. This, and the fact that they are more frequently measured for legislative purposes makes the indicator data valuable for treatment assessment.

An additional reason for this option was that the *E. coli* and *C. jejuni* can be similarly removed and inactivated by the water treatment process. Since the sizes of *E. coli* and *C. jejuni* are almost the same, it is reasonable to assume the same removal efficacy of coagulation-sedimentation for these bacteria. For RSF process, Hijnen *et al.* (1998) showed that *E. coli* is removed slightly better than environmental *Campylobacter*. With respect to AOP (O₃/UV) process, it has been found that *E. coli* and *C. jejuni* can be similarly inactivated by ozonation, and *E. coli* can survive in UV disinfection better than *C. jejuni* (Smeets *et al.*, 2005; Butler *et al.*, 1987). Therefore, it is safe enough to use *E. coli* as a surrogate for *C. jejuni* when assessing the inactivation efficacy of AOP. For ion-exchange treatments, bacteria were considered to be removed by ion-exchange and the adsorption to the resin. Since *E. coli* and *C. jejuni* are similar in cell sizes and cell quantity of electric charges, it is reasonable to assume the same removal efficacy of ion-exchange for these two species of bacteria. Furthermore, according to Vidar *et al.* (1996), it has been found that *E. coli* and *C. jejuni* can be similarly inactivated by chlorination.

5.2.3 QMRA procedure

The QMRA procedure is as shown in **Figure 5-2**. *E. coli* concentration in treated water was calculated from the *E. coli* concentration in source water and their reduction through water treatment process. An essential step in risk assessment is determining the reduction of *E. coli*

by drinking water treatment. Reduction was estimated from different methods such as; Measures of *E.coli* concentrations in influent and effluent water, process removal credits from literature, challenge tests on laboratory or pilot plant scale, and modelling of disinfection process. Daily exposure (*E.coli* dose) was calculated by multiplying the estimated *E. coli* concentration in treated water with the consumption of unboiled drinking water per day. The *E. coli* dose was then translated into the *C. jejuni* dose using the ratio of *C. jejuni* to *E. coli* (C/E ratio) measured in a surface water (Katsura River). The daily risk of infection (P_d) with *C. jejuni* was calculated from the *C. jejuni* dose using the dose-response model. The individual health risk was expressed by the average yearly risk of infection (P_y). Under the assumptions of a binomial process, the yearly risk of one or more infections was calculated by $P_y = 1 - (1 - P_d)^{365}$.

Among the data and parameters required, the *E. coli* concentration in the source water and the removal efficacy of coagulation-sedimentation were determined by a survey at an actual treatment plant. The inactivation efficacy of AOP was predicted from an axial dispersion reactor model (ADR model) under a well-defined full-scale condition. The *E. coli* inactivation kinetics and AOP contactor hydraulics parameter were obtained from pilot-scale experiments. The removal and inactivation efficacy by ion-exchange and chlorination were estimated by conducting *E.coli* dosing experiments at laboratory column and pilot plant, respectively, under controlled conditions, mimicking full-scale conditions. The ratios of *C. jejuni* to *E. coli* in the Katsura River were obtained by field surveys. Literature values were used for other data and parameters.

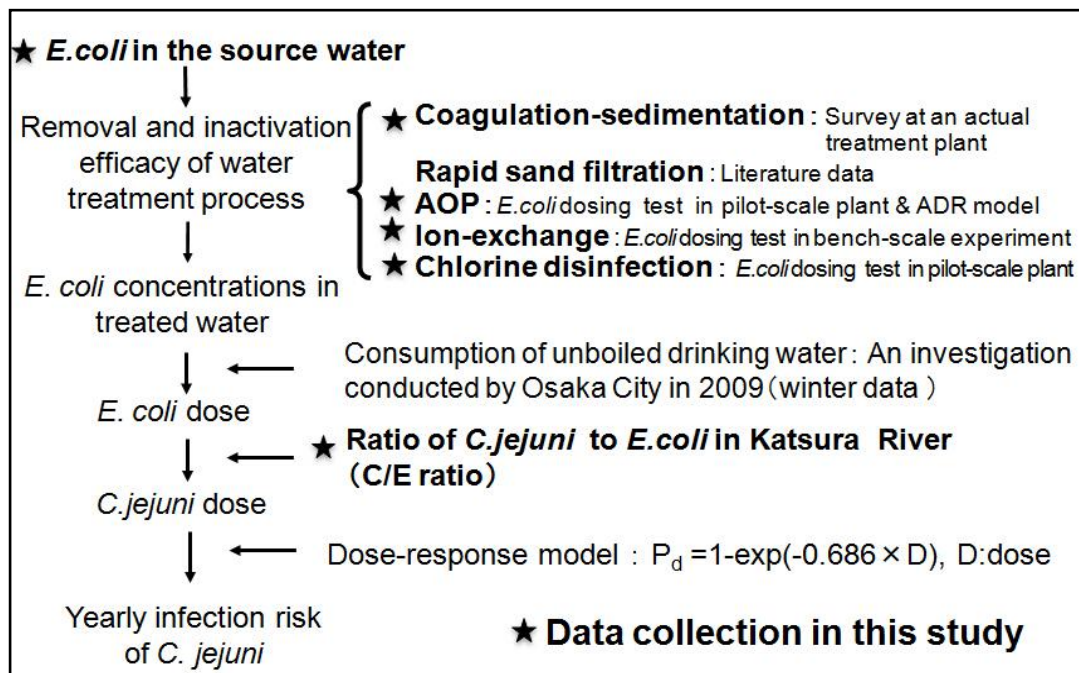


Figure 5-2 QMRA procedure

5.2.4 Removal and inactivation efficacy of the water treatment process

5.2.4.1 Coagulation-sedimentation

Over a period from November 2009 to January 2014, the concentrations of *E. coli* in the source water and in water treated by coagulation-sedimentation of the actual treatment plant were measured at the same time for 35 times. The *E. coli* concentration was determined by the most probable number (MPN) method using O-Nitrophenyl- β -D- Galactoside and 4-Methylumbelliferyl- β -D-Glucuronide cultures with Isopropyl- β -D- Thiogalacto-pyranoside. The removal and inactivation efficacy of coagulation- sedimentation was calculated from the concentration of *E. coli* in the influent (C_{in}) and effluent (C_{out}) with the following equation.

$$\text{Log}_{10}\pi = \text{Log}_{10}C_{in} - \text{Log}_{10}C_{out} = \text{Log}_{10} \frac{C_{in}}{C_{out}} \quad (5-1)$$

Generally, there are three pairing methods (Smeets *et al.*, 2008), e.g. rank method, date method and random method, to determine the removal and inactivation efficacy of the water treatment process. Pairing by date has been widely used to determine the reduction efficacy. In this method, influent and effluent samples taken on the same day are compared and the reduction efficacy is calculated for each pair. This assumes that samples before and after treatment are correlated in time. On the other hand, pairing by rank assumes that there is a complete correlation between the influent and effluent concentrations (lowest influent concentrations correlate to lowest effluent concentrations, etc.). To enable pairing by rank, the samples of the influent and effluent concentrations are sorted by concentration in descending order before determining the treatment efficacy. The other pairing method is the random method, which assumes no correlation by date or rank. In this method, the influent and effluent sample concentrations are paired randomly. Smeets *et al.* (2008) demonstrated that the date and random methods resulted in similar removal, while the rank method proved to be the best method to validate the treatment efficacy in a water treatment process in the Netherlands. However, the applicability of the rank method to different situations is not known. Therefore, the rank, date, and random methods were compared in this study.

The confidence interval for the monitored *E. coli* concentrations was determined by adapting a standard nonparametric bootstrapping procedure. Thus, bootstrap samples of *E. coli* concentrations were produced for the monitored water before and after coagulation-sedimentation. The observed treatment efficacy was calculated from the bootstrap samples paired by rank, date, and random. By comparing the predicted concentrations to the monitored effluent concentrations, the accuracy of the rank, date, and random methods was compared.

5.2.4.2 Rapid sand filtration

The removal efficacy of RSF could be supposed to be lower than those of other treatment processes based on literature information. For example, 12 experimental studies have shown that mean elimination capacity (MEC) of bacteria such as *E. coli*, coliforms and fecal streptococci is just 0.6 log₁₀, with a range of 0.1 log₁₀ to 1.5 log₁₀ (Medema *et al.*, 2006). Therefore, in this study, the removal efficacy of RSF was tentatively set according to a literature value. The 12 experimental studies above include the results obtained by experiments conducted in laboratories with cultured bacteria with or without a preceding coagulation. With a preceding coagulation process, the removal efficacy by RSF normally increases. Based on Hijnen and Medema (2010), a maximum of 1.5 log₁₀, MEC of 0.9 log₁₀ and minimum of 0.4 log₁₀ were adopted in this study. A triangular distribution with these parameters was constructed as a probability density function that describes the removal efficacy of RSF.

5.2.4.3 Advanced oxidation process (refer to Chapter 4)

In order to estimate the inactivation efficacy of AOP, an axial dispersion reactor model (ADR model) were developed in Chapter 4. All the main components of advanced oxidation process, including contactor hydraulics, ozone mass transfer between two phases, ozone decomposition kinetics, and microbial inactivation kinetics, were integrated within the ADR model. The modeling results were validated by pilot experimental data, including tracer testing results, ozone concentration profiles, and microbial inactivation tests results. The inactivation rate constants of *E.coli* were obtained by fitting the pilot-scale *E.coli* dosing experimental results with the ADR model by least-square method. The full-scale O₃/UV contactor used was a simplified assumption based on an actual full-scale ozone contactor in the Kunijima water purification plant of Osaka City. With an ozone injection dose of 0.25 mg/L and a dispersion number of 0.297 as a base case, the inactivation efficacy of AOP under a well-defined full-scale hydraulic condition were predicted with ADR model. As a result, a maximum value of 8.59 log₁₀, mean elimination capacity (MEC) of 3.43 log₁₀ and minimum value of 2.49 log₁₀ were obtained. A triangular distribution with these parameters was constructed.

Since dosing tracer to full-scale drinking water treatment process is not allowed and feasible, the dispersion number used for full-scale O₃/UV contactor in this study was an estimation based on the value determined in the pilot-scale contactor ($d=0.039$) and the value calculated from a reference ($d=2.258$, Tang *et al.*, 2005) where the full-scale ozone contactor has a similar shape and size to the one in the Kunijima water purification plant of Osaka City. Thus, the impact of the dispersion number on the yearly risk of infection was analyzed in

uncertainty analysis with the results of Case 1 and Case 2 that estimated in **Chapter 4**. In addition, a Case 3 of using Chick - Watson model to assess *E. coli* inactivation was also performed in **Chapter 4**. This result was also analyzed in uncertainty analysis.

5.2.4.4 Ion-exchange

The removal efficacies of ion-exchange treatments were estimated by laboratory column experiments as shown in **Figure 5-3**. The dimensions and operating conditions for ion exchange is shown in **Table 5-1**. For cation exchange, a Na^+ forms of cation exchange resin named as DIAION UBK16 (Mitsubishi Chemical) was employed. For anion exchange, a Cl^- forms of anion exchange resin named as DIAION PA308 (Mitsubishi Chemical) was used. Each ion-exchanger was packed in two glass columns ($\phi 40 \times 500$ mm, Kiriya Glass) in series with a total length of 1m, which is the same as full-scale contactor. Before the spiking experiment the ion-exchanger was washed with Milli-Q water, regenerated with 3 L of 20% NaCl solution, and washed again with 5 L of Milli-Q water for several times. Cultured *E. coli* was suspended in 5L of RSF water (with a target concentration of approximately 10^3 CFU/mL) and then fed to the glass columns packed with ion-exchanger at a flow rate of 105.5 mL/min (mimicking the linear velocity of ion-exchange treatment under full-scale condition) by a Master Flex pump (Model 7518-00) continuously. After achieving a steady state (approximately 20 minutes after starting the *E. coli* injection), the effluent water was collected for 3 times in total at a five-minute interval. The concentration of viable *E. coli* in effluent water was determined with XM-G agar medium. The *E. coli* dosing test was repeated for each of 15 times for cation exchange and anion exchange in order to get a reliable data set to construct a triangular distribution.

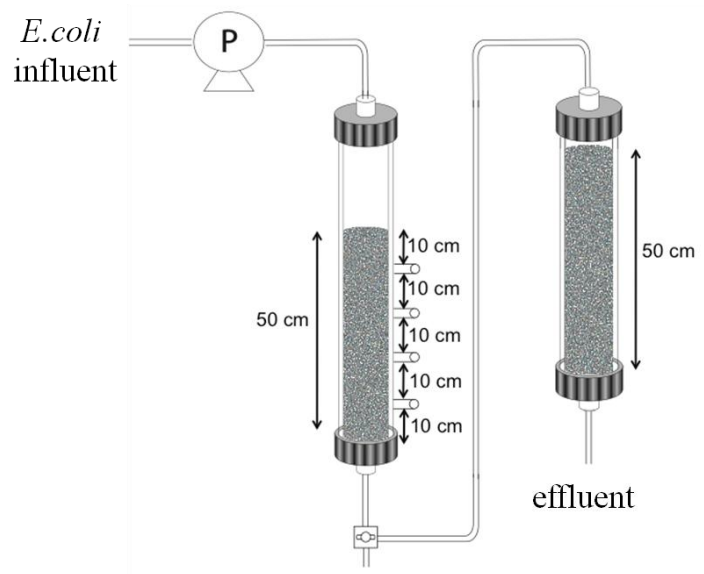
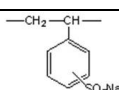
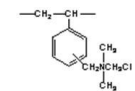


Figure 5-3 Schematic of the laboratory column for ion-exchange

Table 5-1 The dimensions and operating conditions for ion exchange

Item	Value	Remarks
Cation exchange	DIAION UBK16	 Na ⁺ forms
Anion exchange	DIAION PA 308	 Cl ⁻ forms
The total filling depth of resins	1m (φ40 x 500 mm x 2 units)	The same as full-scale contactor
Regenerant	20% NaCl solution	
Influent water	RSF treated water	Dosed with <i>E.coli</i>
<i>E. coli</i> concentration in influent	10 ³ ~10 ⁴ CFU/mL	
Water flow rate	105.5 mL/min	
Linear velocity	5.04 m/h	The same as full-scale condition
Contact time	4.74 min	
<i>E.coli</i> measurement method	XM-G agar medium	

5.2.4.5 Chlorination

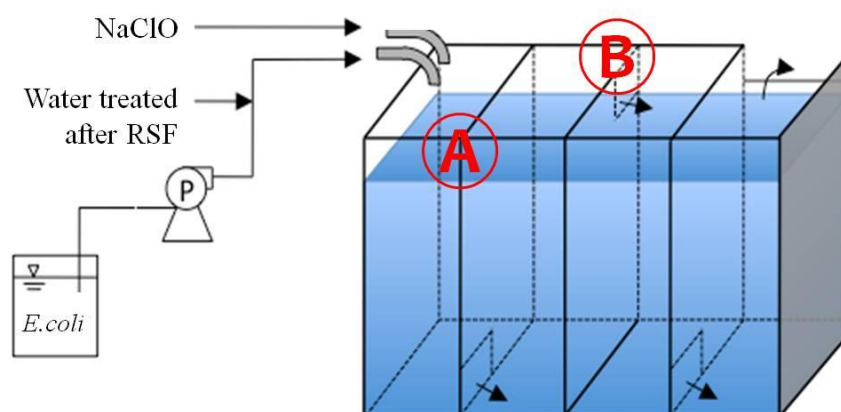
Water treated by chlorination is the drinking water supplied to the city. *E. coli* concentrations in drinking water are generally below the limit of detection. Therefore, the inactivation efficacy of *E.coli* was determined by conducting *E.coli* dosing tests in a pilot-scale chlorination reactor which located in the Kunijima water purification plant of Osaka City

Experimental set up

The pilot-scale chlorination reactor as shown in **Figure 5-4** had four contact chambers with a total volume of 0.53 m³. The average hydraulic residence time at a flow of 0.035 m³/min was 15 min. The source water for this pilot plant was the water treated after RSF taken from an actual treatment facility. The *E.coli* spiking solution was fed to the influent water with a flow of 100mL/min. The NaClO solution was injected to the chlorination reactor from another inflow pipe with a target minimized residual chlorine level in a range of 0.05 and 0.15 mg/L free chlorine concentration. The dimensions and operating conditions for chlorination is shown in **Table 5-2**.

There were two sampling point in this chlorination reactor. One (point A) located at the outlet of first contact chamber, and the other one (point B) located at the outlet of second contact chamber. Free chlorine concentration was measured at both point A and B. Then, by combining with the hydraulic residence times of the first and second contact chambers, the

CT value could be calculated. Viable *E. coli* concentration was only measured in point B. The inactivation efficacy of chlorination was calculated from the concentration of *E. coli* in the influent and effluent (Sample in point B).



Sampling point A+B: measurement of free chlorine concentration

Sampling point B: measurement of viable *E. coli* concentration

Figure 5-4 The schematic of pilot-scale chlorination reactor

Table 5-2 The dimensions and operating conditions for chlorination

Item	Value
Total volume of chlorination reactor	0.53 m ³
Hydraulic residence time	15 min
Influent water	RSF treated water
Influent water flow rate	0.035 m ³ /min
Concentration of <i>E. coli</i> spiking solution	10 ⁷ ~10 ⁹ CFU/mL
<i>E. coli</i> spiking flow rate	100mL/min
Target residual chlorine concentration	0.05 ~0.15 mg/L
<i>E. coli</i> measurement method	XM-G agar medium

Microbial methods

E. coli NBRC 3301 strain was selected as the test microorganism. It was first pre-cultured in a 20 mL LB broth at 37 °C for 18 hours. After pre-cultured, 1 mL of the sample was isolated and reinjected into a new 1L LB broth for a further 20~30 hours shake culture with the same temperature. In order to reach a target concentration of approximately 10⁹ CFU/mL, 20 L LB

broth were prepared once. Cultured *E. coli* were then harvested by centrifugation and washed in 4L buffered solution for more than 3 times. *E.coli* spiking solution was prepared by suspending the final pellets in 5L of test water.

Microbiological samples were taken in 250 ml sterile bottles containing 20 ml 0.1% sterile sodiumthiosulphate to immediately quench any remaining chlorine. Samples were analyzed by direct filtration and direct inoculation of the filter, or by dilution and direct inoculation on XM-G agar medium. Analysis in triplicate showed good reproducibility with a standard deviation of 13%.

Chlorine analysis

Free chlorine concentration in water for the pilot tests was analysed using DPD Colorimetric method in the presence of iodide ion where the extinction of colour was determined with an UV/VIS-spectro-photometer at 515 nm (UV mini-1240, SHIMADZU).

Experimental procedures

Before the spiking experiment, initial free chlorine concentration in chlorination reactor was adjusted in order to achieve the target residual chlorine level after the *E.coli* injection. Then, the *E.coli* spiking solution (with a high concentration of approximately $10^7 \sim 10^9$ CFU/mL) was continuously injected into the influent water with a flow of 100mL/min. After achieving a steady state (10 minutes after starting the *E. coli* injection), the free chlorine concentration samples and microbiological sample were collected at the same time for a total of 5 times at a three-minute interval. **Figure 5-5** and **Figure 5-6** show the photos of the experimental site.

In addition, the impact of temperature change on the variability of inactivation efficacy was considered. The spiking experiments were conducted in winter (January, 2011) and autumn (September and October, 2013) 4 and 5 times, respectively, for each season.



Figure 5-5 *E.coli* spiking solution and pump
(Cultured *E. coli* was suspended in 5L of test water)

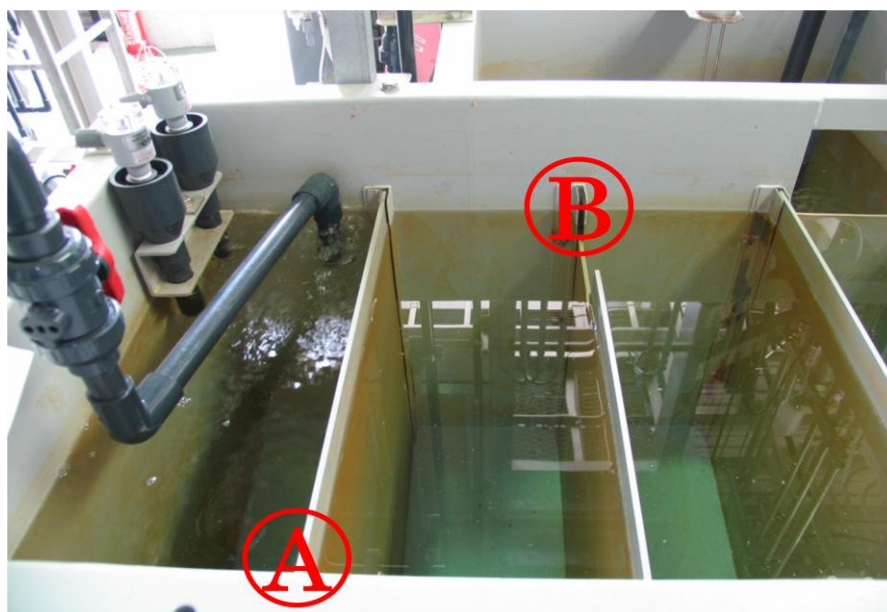


Figure 5-6 Pilot-scale chlorination reactor

5.2.5 Measurements of *C. jejuni* and *E. coli* in river water

The occurrence of *C. jejuni* in the actual source water (the Yodo River) is not clear to date. In order to estimate the C/E ratio, a survey was conducted in the Katsura River (Note: at the point of the Miyamae Bridge, where the river water was mixed with a large volume of effluent from a wastewater treatment plant) where a higher frequency of *C. jejuni* would likely be detected. *E.*

coli and *C. jejuni* concentrations were measured in the same water taken from the Katsura River. The *E. coli* concentration was determined by the most probable number (MPN) method in the same manner as described in 5.2.4.1.

With respect to the measurements of *C. jejuni*, a large-volume river water samples range 30~90 L were collected in sterile plastic containers. The samples were then filtered with 10, 1, and 0.1 L through a 0.2 μm pore size, 47 mm diameter membrane filter. *C. jejuni* on the membrane filter were cultured in Bolton broth at 37 $^{\circ}\text{C}$ for 24 hours, and then the temperature was changed to 42 $^{\circ}\text{C}$ for a further 24 hours of culture. After the enrichment culture, 10% of the cultured sample was pelleted by centrifugation. DNA was extracted and identified using a polymerase chain reaction (PCR) method that detects a *C. jejuni*-specific DNA sequence. Then, the *C. jejuni* concentration was determined by means of the MPN method based on the PCR results.

5.2.6 Consumption of unboiled drinking water

Water consumption data obtained by Osaka City Waterworks Bureau in 2009 (Komatsu *et al.*, 2013) were used in this study. To account for the variability in water consumption with the population, an exponential distribution with a mean value of 327 mL/day was applied for performing the QMRA.

5.2.7 Dose-response model

A dose-response relationship of *C. jejuni* presented by Tenuis *et al.* (2005) is a Beta-Poisson model where $\alpha = 0.024$ and $\beta = 0.011$. When the Beta-Poisson model was applied, however, it was noted that the Beta-Poisson model can exceed the maximum risk curve at low doses (Medema *et al.*, 2006). Therefore, an exponential model ($P_d = 1 - \exp(-0.686 \times D)$, D: dose) proposed by Itoh (2010) was applied in this study.

5.2.8 Risk calculation

The parametric distributions of *E. coli* concentrations in source water, the removal and inactivation efficacy of each process, the consumption of unboiled drinking water, and the C/E ratios in surface water were expressed by probability density functions (PDFs). A Monte Carlo simulation was performed by drawing random values from each PDF to calculate the yearly infection risk (P_y). Correlations between the variables were not assumed in the simulation. Stable results were achieved with acceptable calculations of 100,000 times. Crystal Ball 7® (Oracle Corporation) was used to select the parametric PDFs fitted to

variables and to perform the Monte Carlo simulation.

5.2.9 Sensitivity analysis

Because the model contained a series of steps, sensitivity analysis was performed to identify which components or variables within the model were most important to the outcome. The sensitivity of the overall removal efficacy by six treatment steps, *E. coli* concentrations in treated water, *E.coli* dose, and the yearly risk of infection were analyzed. For a sensitivity analysis, Spearman's rank correlation coefficients are computed between the assumed variables and predicted variables. Contribution to variance is calculated by squaring the rank correlation coefficients and normalizing them to 100%. Contribution to variance shows sensitivities as values that range from 0 to 100% and indicate relative importance by showing the percentage of the variance of the predicted variable contributed by each model variable.

5.2.10 Uncertainty analysis

It is natural that the estimated values of target variables and the yearly risk of infection have large uncertainty. Therefore, the influence of any hypothesis or assumption that can greatly affect the outcome was tested by uncertainty analysis. Uncertainty analysis was performed to examine the impact of the hydraulic condition of the AOP contactor, the impact of using Chick - Watson model to assess *E. coli* inactivation in AOP, the impact of using concentration interpolation method for non-detect data in water treated by coagulation-sedimentation, the impact of the C/E ratio in river water, and the uncertainty of using or without using chlorination process.

5.3 Results and Discussion

5.3.1 Removal and inactivation efficacy of the water treatment process

5.3.1.1 Coagulation-sedimentation

(1) Concentration interpolation for undetected data

Concentrations of *E. coli* in source water and in water treated by coagulation- sedimentation were measured at the same time for 35 times. *E. coli* was detected only 19 times in water treated with coagulation-sedimentation. Therefore, a statistical method based on the theory of the MPN method and the Poisson distribution developed in **Chapter 3** was used here to extrapolate these undetected data. Since this data set has two detection limits (at 0.036 *E.coli*/100mL and 1.8 *E.coli*/100ml), we extrapolated 10 undetected data that were below the

detection limit of 0.036 *E.coli*/100mL and 6 undetected data that were below the detection limit of 1.8 *E.coli*/100mL respectively. **Figure 5-7** shows the histograms of *E.coli* concentrations in water treated with coagulation-sedimentation before and after interpolation. Before interpolation, the mean of 19 positive data in water treated after coagulation-sedimentation is 2.68. This is an obvious over estimate. After interpolation, the 16 negative data were extrapolated with a range of 0 to 0.036 or 0 to 0.18 *E.coli*/100ml and resulted in a decreased mean concentration. Since it is assumed that the concentration interpolation method has uncertainty, the impact of the concentration interpolation method on the yearly risk of infection was analyzed in uncertainty analysis.

Figure 5-8 shows the concentrations of *E. coli* in the source water and water treated by coagulation-sedimentation (after interpolation) as CCDF. In this study, the distribution of the concentrations was presented by a CCDF (Complementary Cumulative Distribution Function) on a double log scale, which is well-suited for magnifying data from rare events (Smeets *et al.*, 2008). This form of presenting data is generally applied in other fields of risk assessment.

(2) Comparison of the data pairing methods

The *E. coli* concentrations in the water treated by coagulation-sedimentation that were predicted by the date, rank and random methods were compared to the monitored *E. coli* concentrations. **Figure 5-9 (a) and 5-9 (b)** show examples of the predicted and monitored *E. coli* concentrations after coagulation-sedimentation. It was found that the pairing method by date resulted in an overestimation of effluent concentrations, indicating that the date method tends to assess the removal efficacy at a lower value. This reduced value is because the date method often yielded a low removal efficacy and could even predict “negative removal”. “Negative removal” would imply that microbes were occasionally “produced” by the treatment, which is unlikely. However, the rank method did not allow for negative removal. The rank method provided an appropriate estimate of the removal efficacy for Monte Carlo simulation since the monitored concentrations in **Figures 5-9 (a)** were consistent with the predicted concentrations. The random and the date method resulted in a similar estimate of the removal efficacy (data are not shown). Consequently, the rank method was used in the following analyses.

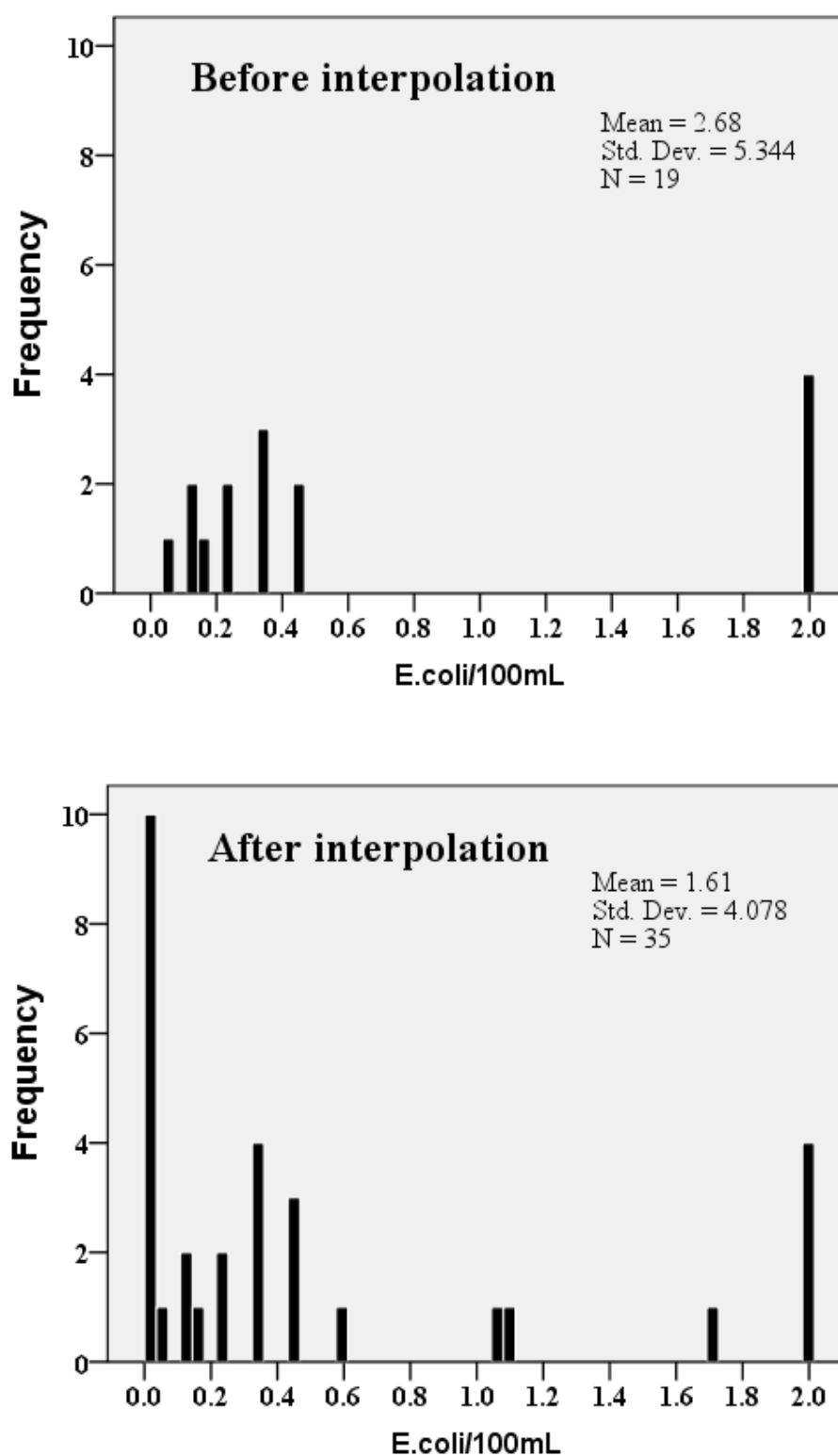


Figure 5-7 *E.coli* concentrations in water treated with coagulation-sedimentation before and after interpolation (only show the data values ≤ 2 *E.coli*/100mL).

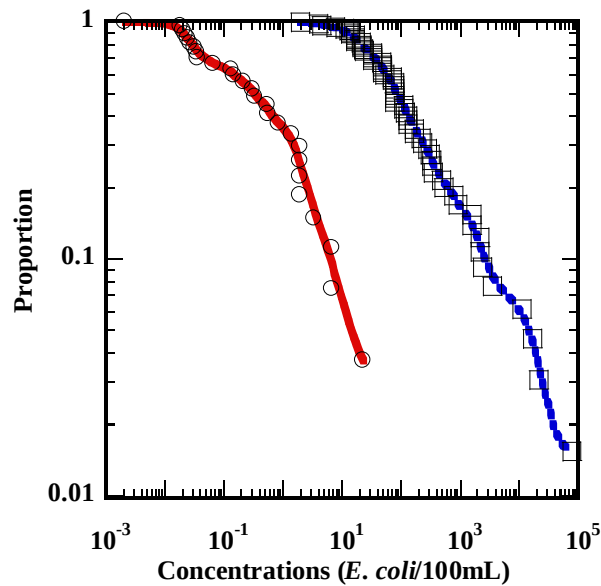


Figure 5-8 The concentrations of *E. coli* in the source water ($\square$) and water treated by coagulation sedimentation ($\circ$).

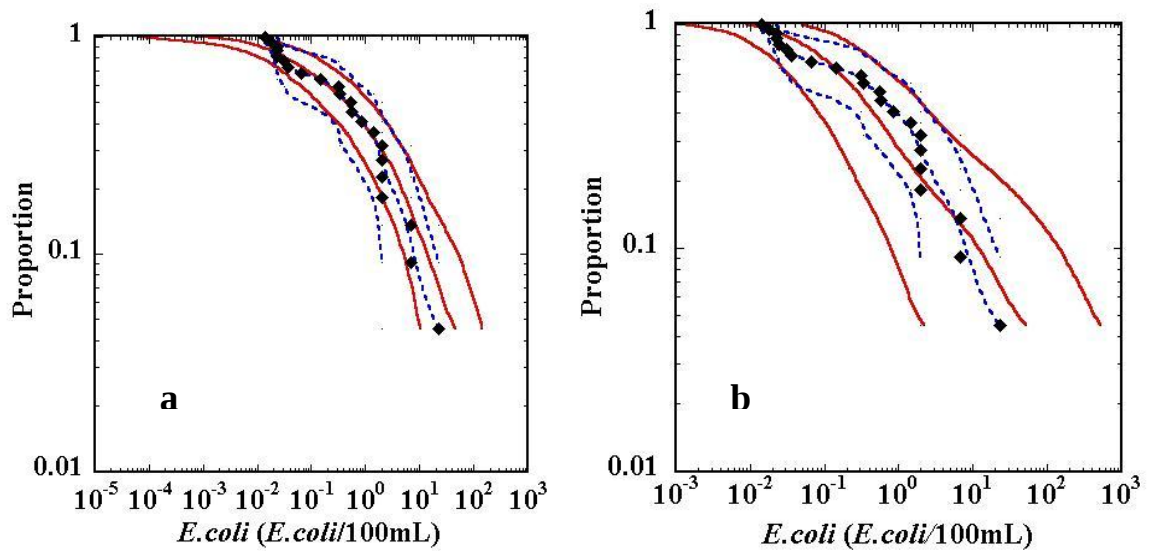


Figure 5-9 *E. coli* concentration after coagulation-sedimentation calculated with the non-parametric model validated by the rank (a) and date (b) methods. Calculated concentrations by the rank and date methods (dashed) are compared to monitored concentrations (line and markers). Median concentration (thick) and 95% CI (fine) are shown.

(3) Removal efficacy of coagulation-sedimentation

To examine the impact of using concentration interpolation method, the removal efficacies of coagulation-sedimentation without (**case A**) and with concentration interpolation (**case B**) were calculated and compared in this section. The results are shown in **Figure 5-10**. PDFs were selected to describe the distributions. It was found that the removal efficacy of coagulation-sedimentation in case B was estimated to be greater than the removal efficacy of coagulation-sedimentation in case A.

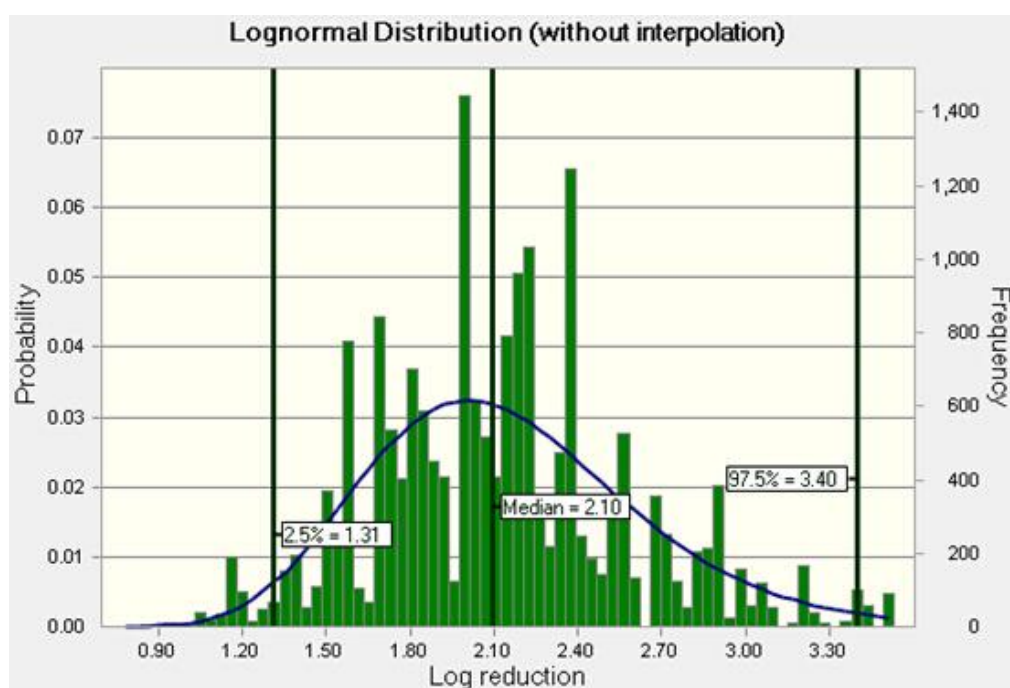
According to **equation 5-1**, the removal and inactivation efficacy of coagulation-sedimentation was calculated from the concentration of *E. coli* in the influent and effluent. In case A, the 16 negative *E. coli* concentrations reported as 0 in the effluent could not be used to estimate the log reduction. Thus the median of the log reduction was calculated to be 2.10 log₁₀ based on the 19 positive data (top 54%) in the effluent.

In case B, the 16 negative *E. coli* concentrations after coagulation-sedimentation were extrapolated by the concentration interpolation method with a range of 0 to 0.036 and 0 to 0.2 *E. coli*/100 mL. This resulted in a decreased of mean concentration of effluent. As a result, the median of the log reduction was calculated to be 2.56 log₁₀.

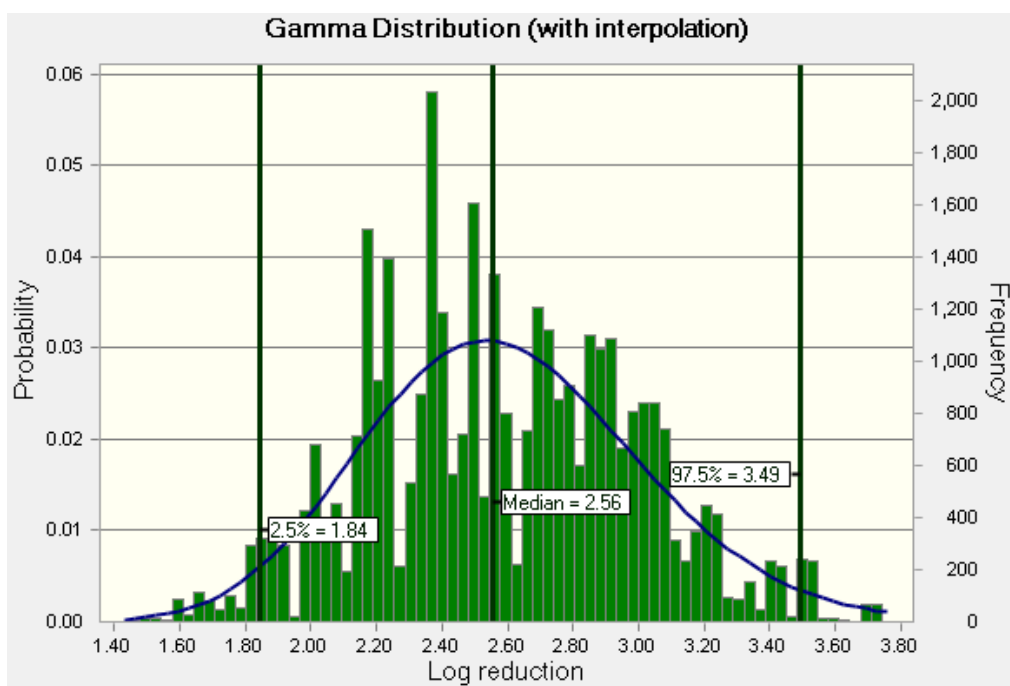
5.3.1.2 Ion-exchange

The removal efficacies of cation and anion exchange treatments are summarized in **Figure 5-11**. From this figure, anion exchange was found to be effective, whereas cation exchange was almost non-effective to the elimination of *E.coli*.

The reason of the large difference of the removal efficacies between the cation and anion exchange is considered to be caused by the fact that *E.coli* has negatively charged groups owing to various phospholipids and proteins contained on the surface of it. It is considered that the negative groups were partially anion exchanged for Cl⁻ ions of DIAION PA308 and the *E.coli* cells were strongly held on the surface of the resin.



Case A



Case B

Figure 5-10 Distribution of removal efficacy of coagulation-sedimentation without (case A) and with (case B) concentration interpolation and the fitted PDFs (line).

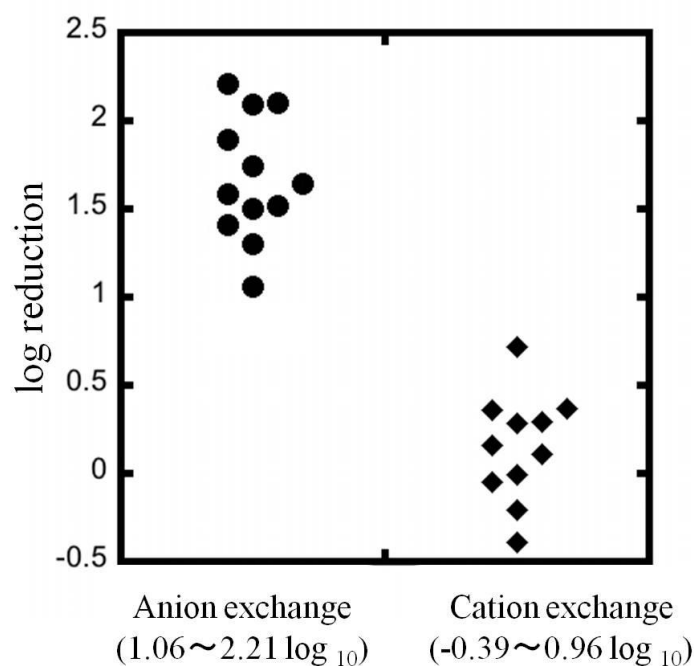


Figure 5-11 The removal efficacies of cation and anion exchange

5.3.1.3 Chlorination

With free residual chlorine level ranging from 0.05 to 0.15 mg/L, the inactivation efficacies of chlorination in the pilot-scale plant are summarized in **Table 5-3**. The log reduction of chlorination ranged between 3.44 and 5.83 $\log_{10}$.

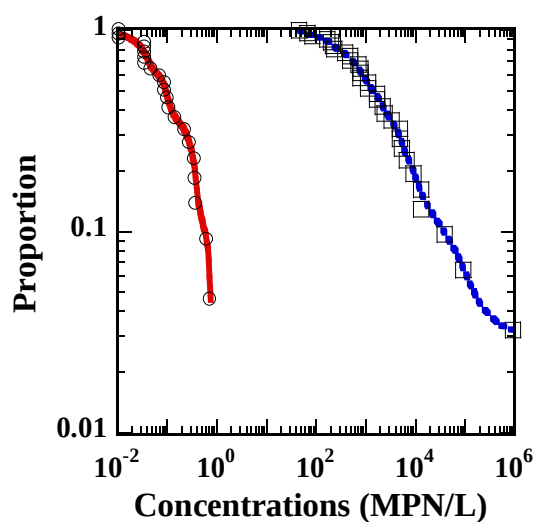
In this study, injected free residual chlorine was minimized in order to detect survived *E. coli* after the chlorination. Therefore, log reductions by actual chlorination are expected to be much larger than those shown in **Table 5-3**. On the other hand, it is assumed that the chlorination at an actual treatment plant and the calculation of Ct value through a distribution system with long pipes are much more complex than pilot-scale experiment. The uncertainty of inactivation efficacy of chlorination was analyzed. Thus, the yearly risk of infection without chlorination process was calculated as a case in uncertainty analysis.

5.3.2 Measurements of *C. jejuni* and *E. coli* in river water

E. coli and *C. jejuni* concentrations were measured in the Katsura River at the point of the Miyamae Bridge a total of 29 times from December 2011 to January 2014. As *C. jejuni* was detected 24 times in the water, a total of 24 C/E ratios were obtained. **Figure 5-12** shows the CCDF of the measured *E. coli* and *C. jejuni* concentrations in the Katsura River (without undetected data).

Table 5-3 Results of pilot-scale experiment of chlorination

Date		Residual chlorine (mg/L) (at point B)	CT (mg min/L)	<i>E.coli</i> in (CFU/mL)	<i>E.coli</i> out (CFU/mL)	Log reduction
2011/1/11	Run1	0.14	1.23	8.25×10^6	12.47	5.82
2011/1/11	Run2	0.14	1.06	8.25×10^6	12.26	5.83
2011/1/21	Run1	0.09	0.78	1.45×10^6	64	4.36
2011/1/21	Run2	0.07	0.68	1.45×10^6	71.9	4.30
2013/9/2		0.09	0.57	7.4×10^6	325.6	4.36
2013/10/3	Run1	0.22	1.51	3.09×10^6	36.81	4.92
2013/10/3	Run2	0.18	1.26	3.09×10^6	26.47	5.07
2013/10/10	Run1	0.12	0.95	1.63×10^5	50.4	3.51
2013/10/10	Run2	0.15	1.07	1.63×10^5	59.68	3.44

**Figure 5-12** *E. coli* concentrations ($\square$) and *C. jejuni* concentrations ($\circ$) in the Katsura River (N=24)

5.3.3 Risk calculation

5.3.3.1 Application of distribution type

PDFs were selected to describe the distributions of the *E. coli* concentrations in the source

water; the removal and inactivation efficacy by coagulation-sedimentation, RSF, AOP, cation exchange, anion exchange, and chlorination; the C/E ratio; and the consumption of unboiled drinking water. In general, extreme events can dominate the average health risk. Therefore, the PDF should fit the extremes (tail) of the observed variations. From the point of emphasizing the fit to rare events, the results of the Anderson-Darling test were more emphasized than the results of the chi-square test and the Kolmogorov-Smirnov test when selecting a distribution type. The selected PDFs and estimated parameters are summarized in **Table 5-4**.

Table 5-4 Probability density functions (PDFs) fitted to the target variables.

		PDF type	Estimated parameters
<i>E.coli</i> in the source water (<i>E.coli</i> /100 mL)		Lognormal	$\mu=1526$; $\sigma=26650$
Treatment efficacy (log reduction) of <i>E.coli</i>	Coagulation-sedimentation	Gamma	$\alpha=-0.37$; $\beta=0.06$; $c=49.67$
	RSF	Triangular	Min.=0.4; MEC= 0.9; Max.= 1.5
	AOP	Triangular	Min.= 2.49; MEC= 3.43; Max.= 8.59
	Cation exchange	Triangular	Min.= -0.39; MEC= 0.13; Max.= 0.96
	Anion exchange	Triangular	Min.= 1.06; MEC= 1.62; Max.= 2.21
	Chlorination	Triangular	Min.= 3.44; MEC= 4.03; Max.=5.83
C/E ratio		Lognormal	$\mu=4.81 \times 10^{-3}$; $\sigma=0.394$
Water consumption		Exponential	$\lambda=3.06 \times 10^{-3}$

MEC: Mean Elimination Capacity

It shows that the six treatment steps have removal/inactivation efficacy in the following order: Chlorination (MEC=4.03 $\log_{10}$) > AOP (MEC=3.43 $\log_{10}$) > Coagulation- sedimentation ($\mu=2.59 \log_{10}$) > Anion exchange (MEC=1.62 $\log_{10}$) > RSF (MEC=0.9 $\log_{10}$) > Cation exchange (MEC=0.13 $\log_{10}$). Although the chlorination and ozone doses were minimized in this study, the removal efficacy by cation exchange was the lowest.

The data used to determine the C/E ratio were the *E. coli* and *C. jejuni* concentrations in the Katsura River that were measured 24 times from December 2011 to January 2014. In general, there is a large variation in pathogen to *E. coli* ratios. Therefore, PDFs were applied to the distribution of these ratios. As a result, the Lognormal distribution was best fitted as shown in **Table 5-4**. The variation of C/E ratio given by the Lognormal distribution includes all factors such as faecal contamination by livestock and waterfowl, possible contamination caused by combined sewer overflows, agricultural activity, rainfall, snow melting, water temperature, and so on. However, this is not the C/E ratio in the actual source water (Yodo River water). Since it is assumed that the C/E ratio has large uncertainty, the impact of the C/E ratio on the

yearly risk of infection was analyzed.

5.3.3.2 Overall removal efficacy and yearly risk of infection

The mean and median of the overall log reduction were estimated to be 12.95 log₁₀ and 14.50 log₁₀, respectively, by the Monte Carlo simulation as shown in **Figure 5-13** and **Table 5-5**. It is noteworthy that the overall log reduction was estimated to be 14.50 log₁₀ (median) instead of setting the overall removal to 100%, although almost all of the *E. coli* concentrations measured after chlorination were 0.

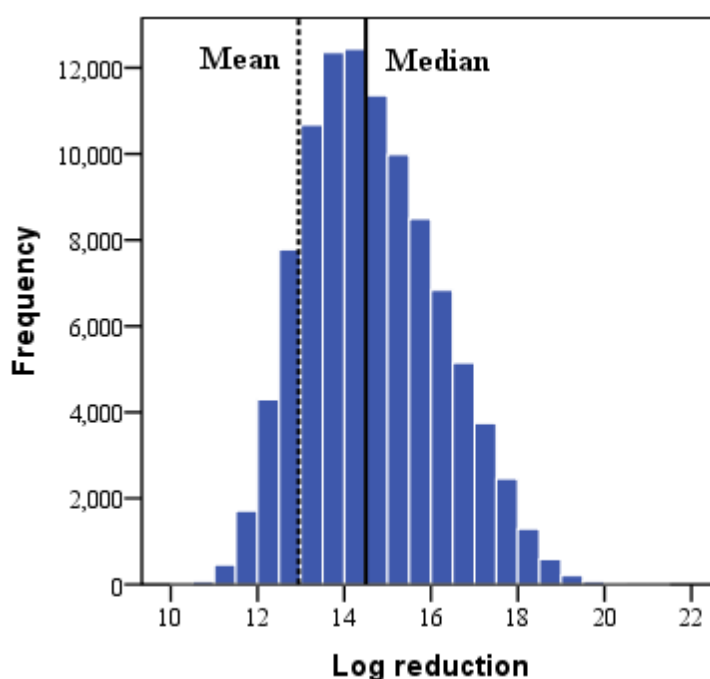


Figure 5-13 Monte Carlo frequency distribution of overall log reduction.

Table 5-5 Statistics estimated in the QMRA.

	Lower 95% CI boundary	Median	Mean	Upper 95% CI boundary
Overall log reduction	12.04	14.50	12.95	17.90
<i>E.coli</i> in the treated water (<i>E.coli</i> /100 mL)	4.23×10^{-17}	2.7×10^{-13}	1.33×10^{-10}	4.86×10^{-10}
<i>E. coli</i> dose (<i>E.coli</i> /day)	5.07×10^{-17}	4.88×10^{-13}	4.23×10^{-10}	1.28×10^{-9}
<i>C. jejuni</i> dose (<i>C. jejuni</i> /day)	1.29×10^{-21}	3.51×10^{-17}	1.29×10^{-12}	5.41×10^{-13}
Daily risk of infection (infection /person/day)	0	0	8.88×10^{-13}	3.71×10^{-13}
Yearly risk of infection (infection/person/yr)	0	0	3.24×10^{-10}	1.35×10^{-10}

Since this calculated overall reduction is applied to the *E. coli* concentrations in the source water, the *E. coli* concentrations in the treated water were not estimated to be 0 as shown in **Table 5-5**. As a result, the mean was calculated to be 1.33×10^{-10} *E. coli*/100 mL, and the median was 2.7×10^{-13} *E. coli*/100 mL. The *E. coli* dose is calculated by multiplying the *E. coli* concentration in the drinking water by water consumption. The mean and median were estimated to be 4.23×10^{-10} and 4.88×10^{-13} *E. coli*/day, respectively.

After translating the *E. coli* dose into the *C. jejuni* dose using the C/E ratio, the *C. jejuni* dose-response relationship was applied. As a result, the daily risk of *C. jejuni* infection was estimated to be a mean of 8.88×10^{-13} infection/person/day and a median of 0 infection/person/day. As a result of calculating the yearly risk of infection from the daily risk of infection, a mean of 3.24×10^{-10} infection/person/yr and a median of 0 infection/person/yr were obtained. This estimate is called the base case (shown in **Table 5-6**). The mean, median, and 97.5 percentile of the yearly risk of infections are far below 10^{-4} infection/person/yr that is the acceptable yearly risk of infection proposed by the World Health Organization and the United States Environmental Protection Agency (EPA) (US EPA, 1989). This result demonstrates that the new water treatment process for reducing chlorinous odor produces safe drinking water in terms of eliminating *C. jejuni*.

In other words, based on the information of the *E. coli* concentrations in the source water, the C/E ratio in river water, and the consumption of unboiled drinking water shown in **Table 5-4**, an overall removal and inactivation efficacy with a mean value of 7.8 log₁₀ is sufficient to achieve the mean yearly risk of infection of 10^{-4} infection/person/yr.

5.3.4 Sensitivity analysis and effects of water consumption

The sensitivity of the overall removal efficacy by six treatment steps, *E. coli* concentrations in treated water, *E. coli* dose, and the yearly risk of infection were analyzed. **Figure 5-14** shows the result of the sensitivity analysis for the yearly risk of infection. It exhibits that the AOP has the largest impact on the yearly risk of infection, which means that the rank correlation coefficient between the removal efficacy by AOP and the yearly risk of infection was the largest. This is because the *E. coli* removal efficacy by AOP varies greatly from 2.49 to 8.59 log₁₀. Therefore, the stable performance of AOP inactivation is the most important to stably produce safe drinking water by the water treatment process for reducing chlorinous odor.

In addition, it was found that the statistical methods used to analyze the water consumption data have large impacts on the results of the sensitivity analysis, although they do not have

large effects on the probability of infection. It should be noted that statistical methods used to analyze water consumption data may complicate the results of sensitivity analysis if the water consumption data are not analyzed by an appropriate statistical method. To avoid this problem, it is preferable to apply a continuous model like the Exponential model rather than a discrete model like the Poisson model.

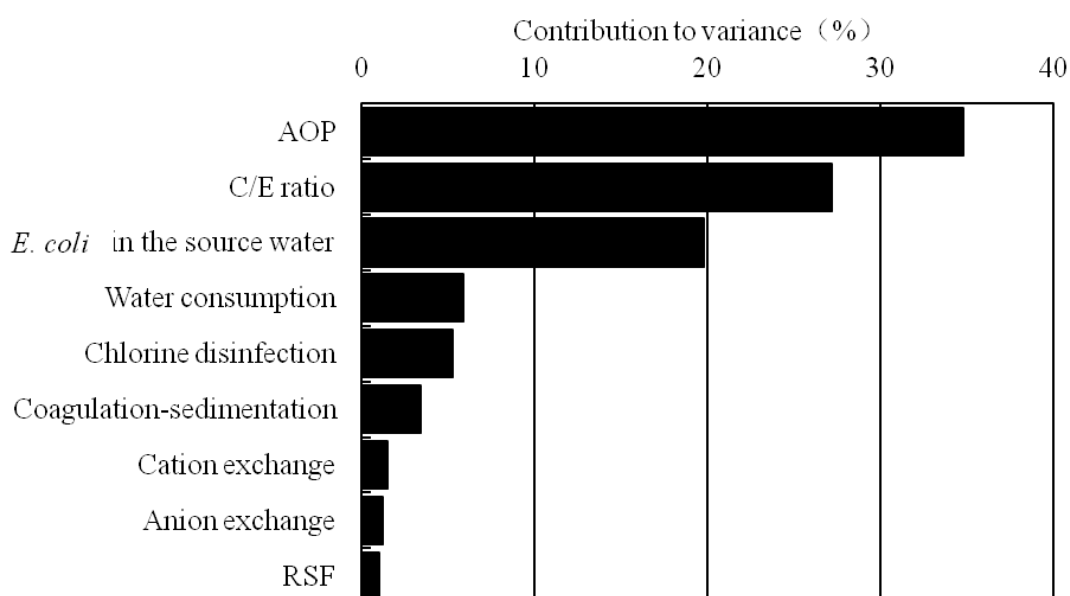


Figure 5-14 Sensitivity analysis of yearly risk of infection.

5.3.5 Uncertainty analysis

After selecting the target variables that might greatly affect the estimates of the yearly risk of infection, uncertainty analysis was conducted. The results of the analysis are shown in **Table 5-6**.

5.3.5.1 Impact of dispersion number

In order to estimate the inactivation efficacy of AOP under full-scale hydraulic conditions, The dispersion number of 0.297 used for the full-scale O₃/UV contactor was an estimation based on the value determined in the pilot-scale contactor ($d = 0.039$) and the value calculated from a reference ($d = 2.258$, Tang *et al.*, 2005) where the full-scale ozone contactor has a similar shape and size to the one in the Kunijima water purification plant of Osaka City. It is clear that the dispersion number used for the full-scale O₃/UV contactor has large uncertainty on the prediction of inactivation efficacy of *E.coli*. Therefore, the dispersion number of 0.297

was used for the base case, the smallest value of 0.039 (**case 1**) that determined in the pilot-scale ozone-bubble diffuser contactor and the largest value of 2.258 (**case 2**) that calculated from Tang *et al.* (2005) were examined in the uncertainty analysis.

The result of calculating yearly risk of infection is shown in **Table 5-6**. In the case of setting 0.039, the mean value was estimated to be a very low value of 4.11×10^{-13} infection/person/yr. On the other hand, in the case of setting 2.258, the mean value increased to 5.17×10^{-8} infection/person/yr. It is clear that dispersion number affects estimated yearly risk of infection significantly. Taking into consideration the significantly influence of dispersion number on the QMRA outcomes, it can be pointed out that experimental measurement or an accurate model estimation of the dispersion number in the actual full-scale contactor is highly required to improve the accuracy of the risk calculation model.

5.3.5.2 Impact of Chick - Watson model

For **case 3**, Chick - Watson model and the 14 pairs of *E.coli* inactivation rate constants that fitted with Chick - Watson model were used to predict the inactivation efficacy of *E.coli* attained in full-scale O₃/UV contactor in **Chapter 4**. The result from Chick - Watson model was expressed as a parametric distribution which characterized the hydrodynamic behavior in O₃/UV contactor rather than a single value. For QMRA calculation purpose, it was decided to select the 10% log₁₀ reduction of each parametric distribution, which corresponding to the T₁₀ value, to provide a safety margin to compensate for losses in disinfection efficiency resulting from hydrodynamic non-idealities inside O₃/UV contactors. The result is as shown in **Table 5-6**. The mean values increased to 7.62×10^{-8} infection/person/yr.

On the other hand, the *E. coli* inactivation rate constants of ozonation and UV obtained in **Chapter 4** were extremely small values when compared to the rate constants reported in literature (Finch *et al.*, 1988; Zhou and Smith, 1994; Hunt and Mariñas, 1997; Hijnen *et al.*, 2001; Yamasaki, 2014). The small inactivation rate constants may lead to an under-estimation of the inactivation efficacy of AOP and a large yearly risk of infection.

5.3.5.3 Impact of concentration interpolation method

Without concentration interpolation in coagulation-sedimentation process, the yearly risk of infection was calculated to be a mean of 9.86×10^{-10} infection/person/yr. It was found that the yearly risk of infection in case 5 was estimated to be slightly greater than that in base case.

The removal and inactivation efficacy of coagulation- sedimentation was calculated from the concentration of *E. coli* in the influent and effluent with rank method in this study. To enable

pairing by rank, the samples of the influent and effluent concentrations were sorted in descending order by concentration before determining treatment efficacy. In case 5, the 16 negative *E. coli* concentrations after coagulation- sedimentation were set to 0 *E. coli*/100 mL. As a result of sorting all 35 *E. coli* concentrations in descending order, the 19 positive data were paired with relatively large *E. coli* concentrations in the influent. As a result, the median of the log reduction was calculated to be 2.10 log₁₀ based on the 19 positive data (top 54%). In base case, the values calculated by those 19 positive data were the same as case 5. On the other hand, the 16 negative *E. coli* concentrations after coagulation-sedimentation were extrapolated by the concentration interpolation method with a range of 0 to 0.036 and 0 to 0.2 *E. coli*/100 mL. These extrapolated small data were then paired with relatively small *E. coli* concentrations in the influent and resulted in a little larger values of log reduction than that obtained with the 19 positive data. Then by averaging all of these 35 log reduction, the median log reduction of the base case was increased to be 2.56 log₁₀, which in turns resulted in a decreased yearly risk of infection in base case.

5.3.5.4 Without chlorination process

Without using chlorination process, the yearly risk of infection was calculated to be a mean of 4.50×10^{-6} infection/person/yr, which means that even without using chlorination, this water treatment process is still qualified for produce safe drinking water in terms of eliminating *C.jejuni*.

5.3.5.5 Impact of C/E ratio

An uncertainty analysis for the C/E ratio could not be performed due to limited information. The C/E ratios used were values obtained in river water (the Katsura River) that was mixed with a large volume of effluent from a wastewater treatment plant, and are not the values of the actual source water (the Yodo River) for the water treatment plant. Taking into consideration the difference in the viability of *C. jejuni* and *E. coli* when found in surface water, and the variability of *C. jejuni* and *E. coli* concentrations with respect to season and location, data collection of C/E ratio in the actual source water throughout the year is highly required to improve the accuracy of the QMRA. In addition, it is preferable to directly monitor the *C. jejuni* concentration, when possible.

Table 5-6 Uncertainty analysis of yearly risk of infection.

	Yearly risk of infection (infection/person/yr)		
	Lower 95% CI boundary	Mean	Upper 95% CI boundary
Base case	0	3.24×10^{-10}	1.35×10^{-10}
Case 1: dispersion number = 0.039	0	4.11×10^{-13}	1.22×10^{-13}
Case 2: dispersion number = 2.258	0	5.17×10^{-8}	3.53×10^{-8}
Case 3: Chick - Watson model	0	7.62×10^{-8}	5.40×10^{-8}
Case 4: without concentration interpolation in coagulation-sedimentation process	0	9.86×10^{-10}	4.04×10^{-10}
Case5: without chlorination process	0	4.50×10^{-6}	2.92×10^{-6}

5.4 Summary

A QMRA was conducted to estimate the infectious risk of *C. jejuni* for a new water treatment process for reducing chlorinous odor.

With respect to the assessment of the removal and inactivation efficacy of water treatment process, field surveys, laboratory column test, challenge test on pilot plant, mathematical model and literature data were used. Non-detect data were extrapolated by a method developed in Chapter 3 before assessing the removal and inactivation efficacy.

The mean yearly risk of infection was estimated to be 3.24×10^{-10} infection/person/yr – far below the acceptable yearly risk of infection of 10^{-4} infection/ person/yr. It was demonstrated that the water treatment process supposed in this study produces safe drinking water in terms of eliminating *C. jejuni*.

Among the six treatment steps, chlorination contributes most to the decrease of the yearly risk of infection, while cation contributes least. On the other hand, from the sensitivity analysis, AOP was identified as the most important process affecting the variance of the yearly risk of infection. Stable performance in inactivation *E. coli* by AOP is the most important factor in the reliable production of safe drinking water.

The uncertainty analysis demonstrated that an estimation of dispersion number for the full-scale ozone contactor is needed to improve the accuracy of QMRA. In addition, data

collection to determine the C/E ratio in the source water is highly required. It is preferable to directly monitor the *C. jejuni* concentration, when possible.

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Chapter 6

Conclusions

This study applied the QMRA method to provide a quantitative estimate of the level and variation of microbial risk in drinking water treated with this new water treatment process for reducing chlorinous odor.

In chapter 3, a statistical method, based on the theory of the MPN method and the Poisson distribution, was developed and applied to extrapolate *E. coli* concentrations that were measured below the detection limit. This concentration interpolation method can be used to improve the accuracy of estimates in QMRA. It was concluded that this statistical method is applicable when a large amount of data needs to be extrapolated. The results were obtained from one case study; thus, the applicability to other situations requires further investigation. The importance of selecting an appropriate dataset and a pairing method before performing QMRA is stressed. Furthermore, the analysis of inactivation efficacy of ozonation in cases 2 and 3 indicates that the concentration interpolation method is not applicable to simultaneously interpolate the data before and after treatment.

In chapter 4, in order to predict the inactivation efficacy of O₃/UV process under full-scale condition, an ADR model was developed in this chapter. All the main components of O₃/UV process, including contactor hydraulics, ozone mass transfer between two phases, ozone decomposition kinetics, and microbial inactivation kinetics, were integrated within the ADR model through the use of species transport equations with appropriate source terms. A series of tract tracer tests and *E.coli* dosing tests were performed in a pilot-scale O₃/UV contactor to obtain these parameters and to validate the ADR model simultaneously. The simulated dissolved ozone concentration profiles throughout the pilot-scale O₃/UV contactor agreed well with the experimental data. This further validated the ADR model for predicting the performance of full-scale O₃/UV contactor. The full-scale O₃/UV contactor used in this study was a simplified assumption based on an actual full-scale ozone contactor in the Kunijima water purification plant of Osaka City. With using the *E. coli* inactivation rate constants that obtained from the pilot-scale *E. coli* dosing experiments, the inactivation efficacy of O₃/UV process under full-scale condition were predicted with ADR model. A total of 3 cases of ADR model simulation were performed with using different dispersion numbers. In addition, a Chick - Watson model for assessing *E. coli* inactivation was also employed in this study.

In chapter 5, a QMRA was conducted to estimate the infectious risk of *C. jejuni* for the new water treatment process for reducing chlorinous odor. With respect to the assessment of the removal and inactivation efficacy of water treatment process, field surveys, laboratory column test, challenge test on pilot plant, mathematical model and literature data were used. Non-detect data were extrapolated by a method developed in Chapter 3 before assessing the removal and inactivation efficacy. The mean yearly risk of infection was estimated to be 3.24×10^{-10} infection/person/yr – far below the acceptable yearly risk of infection of 10^{-4} infection/ person/yr. It was demonstrated that the water treatment process supposed in this study produces safe drinking water in terms of eliminating *C. jejuni*.

Among the six treatment steps, chlorination contributes most to the decrease of the yearly risk of infection, while cation contributes least. On the other hand, from the sensitivity analysis, AOP was identified as the most important process affecting the variance of the yearly risk of infection. Stable performance in inactivation *E. coli* by AOP is the most important factor in the reliable production of safe drinking water. The uncertainty analysis demonstrated that an estimation of dispersion number for the full-scale ozone contactor is needed to improve the accuracy of QMRA. In addition, data collection to determine the C/E ratio in the source water is highly required. It is preferable to directly monitor the *C. jejuni* concentration, when possible.

The outcome demonstrated that the new water treatment process for reducing chlorinous odor is adequate to produce drinking water that meets the health based targets as well as the effectiveness of control chlorinous odor. The calculated infectious risk in this study is not an actual risk of drinking water produced at a specific treatment plant; however, it does provide a direct impression of treatment efficacy level and drinking water quality level in Japan. Given the current level of uncertainty in quantitative risk assessments of drinking water supplies, the outcome should be regarded as an indication of the level of safety, rather than an absolute assessment of health risk. The outcome can be used to guide the risk management direction to pathogen control and to select the most appropriate control measures. Locally generated data will always be of great value in setting national targets, such data and tests are more applicable to the local situation than general literature values. The findings of this study will be a basic knowledge to help the Japanese government carrying out the appropriate policies of applying QMRA in drinking water legislation for the forthcoming years.