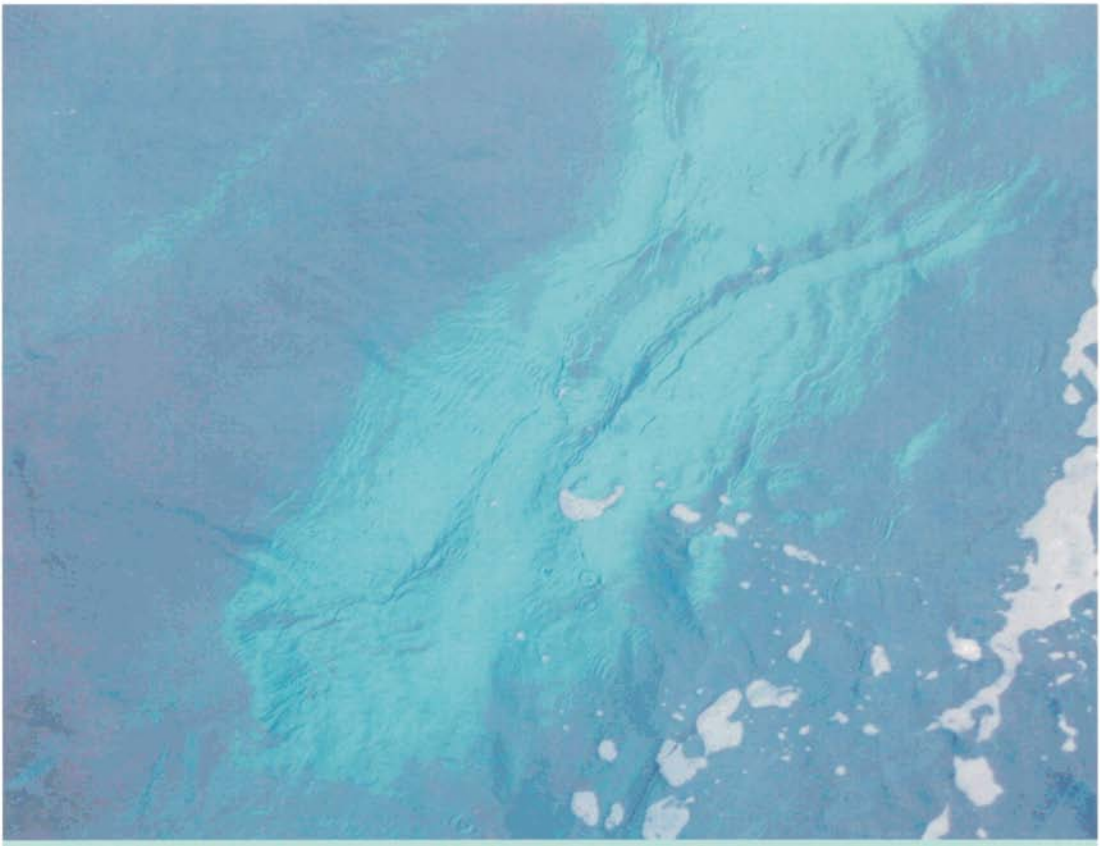
Kansanterveyslaitos
Folkhälsoinstitutet
National Public Health Institute

Publications of the National Public Health Institute A3 / 2004

Tiia Myllykangas

PREVENTION OF BROMINE-CONTAINING DISINFECTION BY-PRODUCTS DURING DRINKING WATER TREATMENT



National Public Health Institute
Department of Environmental Health

Kuopio, Finland
2004

Prevention of Bromine-Containing Disinfection By-Products During Drinking Water Treatment

Tiia Myllykangas

National Public Health Institute
Department of Environmental Health
Laboratory of Chemistry
P.O. Box 95, FIN-70701 Kuopio, Finland

and

University of Kuopio
Department of Environmental Sciences
P.O. Box 1627, FIN-70211 Kuopio, Finland

ACADEMIC DISSERTATION

To be presented with the permission of the faculty of Natural and Environmental Sciences of the University of Kuopio for public examination in Auditorium L2 in the Canthia Building, University of Kuopio, on Friday 20th February at 12 o'clock noon.

Publisher:

National Public Health Institute
Mannerheimintie 166
FIN-00300 Helsinki, Finland
Phone +358 9 47441
Telefax +358 9 47448408

Author's address:

National Public Health Institute
Department of Environmental Health
P.O. Box 95, FIN-70701 Kuopio, Finland
Phone +358 17 201181
Telefax +358 18 201265
E-mail: tiia.myllykangas@ktl.fi

Supervisors:

Professor Terttu Vartiainen, Ph.D.
National Public Health Institute
Kuopio, Finland

Assistant professor Arja Hirvonen, Ph.D.
University of Kuopio
Kuopio, Finland

Reviewers:

Professor Mika Sillanpää, Ph.D.
University of Kuopio
Kuopio, Finland

Professor Kalevi Pihlaja, Ph.D.
University of Turku
Turku, Finland

Opponent:

Professor Rein Munter, Ph.D.
Tallinn Technical University
Tallinn, Estonia

Myllykangas, Tiia. Prevention of Bromine-Containing Disinfection By-Products During Drinking Water Treatment. Publications of the National Public Health Institute A3/2004. 164 pages. ISBN 951-740-418-2, ISSN 0359-3584.

ABSTRACT

Bromide can be found from lakes, rivers, and groundwaters in concentrations from few micrograms to several thousand micrograms. In Finland up to 485 $\mu g\ L^{-1}$ of bromide has been found from raw waters. Bromide itself has not been found to cause negative health effects, but when bromide-containing waters are treated with strong oxidants or disinfectants, many harmful disinfection by-products (DBPs) are formed. Those DBPs have been found to be more harmful than their chlorinated analogues. Bromide can be removed from water in some extent with activated carbon filtration, electrochemically, with nanofiltration, or with ion exchange. However, those methods might not be feasible due to their high costs and specific requirements, resulting in a more intensive need to reduce the formation of brominated DBPs by choosing the disinfection method, which does not cause the formation of those compounds.

Chlorination is the most often used disinfection method due to chlorine's low cost, easy handling and storage, and good disinfection power, which continues in the distribution systems. However, chlorination produces a high amount of DBPs, which has put more emphasis on other disinfection methods, and also on improving the organic matter removal before disinfection. Ozone (possibly combined with hydrogen peroxide oxidation) is able to reduce the precursors of the DBPs before chlorination, thus, resulting in smaller amounts of DBPs than chlorination alone. Also mutagenicity of the water can be reduced by preozonation. Permanganate and UV treatment can be used to reduce the DBPs as well, and they have not been observed to cause any DBPs by themselves.

Most of the experiments in this study were made with laboratory-scale equipment, but one part was made using a pilot-scale water treatment plant, which is able to produce drinking water for 500 people's daily consumption. Ozonation (with and without hydrogen peroxide), permanganate oxidation, UV treatment, and chlorination were used alone or in various combinations to study their effects on the formation of bromine-containing DBPs, such as bromate, trihalomethanes, halogenated acetic acids, mutagenicity, and MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone). With the pilot-scale water treatment plant three coagulants (aluminum sulphate, ferric sulphate, and polyaluminum chloride) were tested, and the formation of DBPs were studied using UV, UV+Cl_2, and Cl_2 for disinfection.

Chlorine, ozone, hydrogen peroxide, and permanganate decomposed the organic matter, but no effect on the TOC value was observed. Trihalomethane formation and mutagenicity of the treated water was found to be enhanced when water contained bromide. However, the MX formation was found to be lower in bromide-containing waters than in bromide-free waters implicating the formation of brominated MX analogues. Bromate formation did not exceed the EU limit value of 10 $\mu g\ L^{-1}$ when a naturally high-bromide-containing water was ozonated with a relatively high (12 $mg\ L^{-1}$) ozone dose, suggesting that preozonation would be a good choice for that water to lower the trihalomethane formation. Ozone combined with hydrogen peroxide seemed to be a good preoxidation method to reduce the formation of DBPs, while UV treatment did not decrease the formation of DBPs.

Myllykangas, Tiia. Bromattujen desinfioinnin sivutuotteiden muodostumisen ehkäisy juomaveden valmistuksessa. Kansanterveyslaitoksen julkaisuja A3/2004. 164 sivua. ISBN 951-740-418-2, ISSN 0359-3584.

TIIVISTELMÄ (ABSTRACT IN FINNISH)

Luonnonvesissä bromidia esiintyy tyypillisesti 10 – 1000 µg L^{-1}, ja Suomessa raakavesistä on havaittu jopa 485 µg L^{-1} bromidia. Bromidi sinänsä ei ole terveydelle haitallinen, mutta se muodostaa vahvojen hapettimien ja desinfiointikemikaalien kanssa terveydelle haitallisia desinfioinnin sivutuotteita (DBP). Bromatut DBP:t on todettu haitallisemmiksi kuin niiden klooratut vastineet. Bromidia voidaan poistaa vedestä aktiivihiilisuodatuksella, elektrokemiallisesti, nanosuodatuksella sekä ioninvaihtohartseilla. Bromidin poisto raakavedestä ei välttämättä ole taloudellista tai teknisesti mahdollista, jonka vuoksi käytettävät hapetus- ja desinfiointimenetelmät täytyy optimoida, jotta saadaan vähennettyä bromattujen DBP:den muodostumista.

Klooraus on yleisimmin käytetty desinfiointimenetelmä maailmanlaajuisesti, johtuen kemikaalin suhteellisen alhaisesta hinnasta, helposta käsiteltävyydestä sekä hyvästä desinfiointitehosta. Klooraukseen aikana muodostuu kuitenkin suuria määriä halogenoituja ja ei-halogenoituja DBP:ta, joiden muodostumista pitää pyrkiä välttämään. Otsonointi (mahdollisesti yhdistettynä vetyperoksidihapetukseen) pystyy vähentämään kloorauksessa muodostuvia DBP:ta. Myös UV-käsittely ja permanganaattihapetus ovat mahdollisia esihapetusmenetelmiä, joiden avulla voidaan pyrkiä vähentämään DBP:den muodostumista juomaveden valmistuksessa. DBP:den muodostumiseen vaikuttaa myös hyvin paljon vedessä olevan orgaanisen aineksen määrä ja laatu, joka puolestaan on riippuvainen vedenkäsittelyn toimivuudesta. Etenkin saostuskemikaalin valinta sekä koagulaatio- ja flokkausprosessit vaikuttavat tähän hyvin merkittävästi.

Väitöskirjatyössä tutkittiin orgaanisen aineksen pilkkoutumista ja muuntumista, kun vettä käsiteltiin vahvoilla hapettimilla ja desinfiointiaineilla (otsoni, kloori, vetyperoksidi, permanganaatti), bromidin vaikutusta bromaatin, trihalometaanien ja mutageenisuuden muodostumiseen käsiteltäessä bromidipitoista vettä vahvoilla hapettimilla ja desinfiointikemikaaleilla, otsonoinnin vaikutusta bromaatin muodostumiseen kahdella eri bromipitoisella vedellä sekä eri esihapetusmenetelmien sopivuutta bromattujen desinfioinnin sivutuotteiden muodostumisen ehkäisemiseksi. Tutkimus tehtiin suurelta osin laboratoriomittakaavassa, mutta yhdessä osiossa käytettiin hyväksi pilotmittakaavaista vesilaitosta (pystyy tuottamaan vettä noin 500 henkilön tarpeisiin). Pilotmittakaavaisella vesilaitoksella tutkittiin orgaanisen aineksen poistumista kolmella eri saostuskemikaalilla ja DBP:den muodostumista käytettäessä UV:ta, UV+Cl_2:ta tai Cl_2:ta desinfiointina.

Kloori, otsoni, vetyperoksidi ja permanganaatti pilkkoivat humusta selvästi, mutta vaikutus ei näkynyt orgaanisen aineksen kokonaismäärässä (TOC). Trihalometaanipitoisuus ja mutageenisuus lisääntyivät, kun käsitellyssä vedessä oli bromidia, kun taas MX:n pitoisuus oli selvästi alhaisempi viitaten bromattujen MX-yhdisteiden muodostumiseen. Bromaatin muodostus jäi alle EU:n asettaman raja-arvon (10 µg L^{-1}), kun otsonoitiin vettä, jossa on luonnollisesti korkea bromidipitoisuus. Tämä viittaa siihen, että otsonointi olisi varteenotettava vaihtoehto tuota vettä käsiteltäessä, kun pyritään pienentämään DBP:den kokonaismäärää. Otsonointi-vetyperoksidi-yhdistelmä osoittautui tehokkaaksi esihapetusmenetelmäksi DBP:den vähentämiseksi, mutta UV-käsittely ei vähentänyt kloorauksessa syntyneiden DBP:den määrää.

ACKNOWLEDGEMENTS

This work was carried out in the Department of Environmental Health, National Public Health Institute, Kuopio, Finland, and in the Department of Environmental Sciences, University of Kuopio, Kuopio, Finland, during the years 1999-2003. I would like to thank the former Director of the Department of Environmental Health, Professor Jouko Tuomisto, M.D., and the Dean of the Department of Environmental Sciences, Professor Juhani Ruuskanen, for providing the facilities for this study. I would also like to thank Mr. Erkki Karttunen, Lic.Tech., from the Savonia Polytechnic for the possibility to work with their pilot-scale water treatment plant.

My deepest thanks are due to my main supervisor, Professor Terttu Vartiainen, Ph.D., for her enthusiastic and determined encouragement and guidance during my studies. She hired me as a student, and has helped me again and again when I've been striving towards the academic world. I also would like to thank my second supervisor, Assistant Professor Arja Hirvonen, Ph.D., for many fruitful conversations and ever so positive attitude during my darkest moments when I was almost ready to give in. My warmest thanks go to Mrs. Tarja Nissinen, Ph.D., who guided me into the world of bromide and brominated disinfection by-products.

I would like to thank the pre-examiners of my thesis, Professor Kalevi Pihjala, Ph.D., and Professor Mika Sillanpää, Ph.D., for the valuable comments and advice considering the content of the manuscript.

Professor Pertti Martikainen, Ph.D., and Senior Researcher Jorma Mäki-Paakkanen, Ph.D., are thanked for their contribution in the articles and help during this thesis. Mr. Markku Lehtola, Ph.D., and Docent Ilkka Miettinen, Ph.D., are thanked for their help and many interesting conversations during the studies. Mrs. Helena Partanen, M.Sc. (Civ. Eng.) and Mr. Pentti Keränen, M.Sc., from the Kuopio Water are thanked for co-operation and help.

Ewen MacDonald, D.Pharm., is thanked for revising the language in this thesis.

The staff of the Laboratory of Chemistry, especially Mrs. Teija Korhonen, Mrs. Mervi Ojala, Mrs. Eija Miettinen, and Mrs. Pirkko Ilkka, are thanked for their contribution of analyzing the "millions" of samples I brought to them. Mr. Panu Rantakokko, M.Sc., is thanked for ensuring that the methods of the analyses have been correct, and also for many interesting and enthusiastic conversations we've had. Special thanks are due to Ms. Miia Hämäläinen for helping me so many times in laboratory, and for being my friend. We did pour water from tub A to tub B many times, didn't we. ☺

I would also like to thank Mr. Matti Pessi for helping me with the technical equipment both in the laboratory and in the pilot-scale water treatment plant. Mr. Hannu Nykänen, Mr. Arto Moilanen, and Mr. Tero Kuhmonen are also thanked for their invaluable help during the study in the pilot-scale water treatment plant. Mr. Pekka Tiittanen is thanked for his help in the statistical analyses. Mr. Hannu Korva, Mr. Jani Toivonen, and Mrs. Mari Markkinen are thanked for computer assistance. All of these people made it possible to finish this thesis in good time.

This thesis was funded by the National Technology Agency of Finland (TEKES), the Academy of Finland, the Finnish Cultural Foundation, the Land and Water Technology Foundation, the Kuopio University Foundation, and the Finnish Konkordia Fund.

Without the help and encouragement from my family and friends this thesis would not have become true. Specially great and warm thanks are due to my mother for her ever lasting love and belief in me. And finally, I would like to thank Tomi, my becoming husband, for his support during the years of ups and downs of this study. Thank you for loving me. I ♥ U

Kuopio, February 2004

Tiia Myllykangas

Tiia Myllykangas

ABBREVIATIONS

AOC = assimilable organic carbon

AOP = advanced oxidation process

AOX = adsorbable organic halogens

AS = aluminum sulphate, $Al_2(SO_4)_3$, a coagulant

AW = artificially recharged groundwater

BAC = biologically active carbon

Ct = efficiency of the disinfectant calculated as the concentration of the disinfectant multiplied by the time the disinfectant is effective

DAF = dissolved air flotation

DBPs = disinfection by-products

DO_3 = concentration of the dissolved ozone in water

DOC = dissolved organic carbon

EU = the European Union

FS = ferric sulphate, $Fe_2(SO_4)_3$, a coagulant

GAC = granular activated carbon

HAAs = halogenated acetic acids

HP-SEC = high-pressure size exclusion chromatography

LW = lake water

MX = 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone

NOM = natural organic matter

PACl = polyaluminum chloride, a coagulant

PW = purified artificially recharged groundwater

r-SMSF = reduction of the sum of the molecular size fractions measured with HP-SEC

SMSF = sum of the molecular size fractions measured with HP-SEC

SOA = sum of the organic acids

SUVA = specific UV absorbance = $100*UV_{254}/TOC$

THMs = trihalomethanes

TTHMs = total trihalomethanes = the sum of the four THMs

TOC = total organic carbon

USEPA = United States Environmental Protection Agency

WHO = World Health Organization

LIST OF ORIGINAL PUBLICATIONS

The thesis consists of five original publications, which are referred to in the text by Roman numerals (I-V).

I. Myllykangas, T, Nissinen, TK, Rantakokko, P, Martikainen, PJ and Vartiainen, T. 2002. Molecular size fractions of treated aquatic humus. Water Research, 36(12): 3045-3053.

II. Myllykangas, T, Hirvonen, A, Nykänen, H, Rantakokko, P, Lehtola, M, Martikainen, PJ and Vartiainen, T. Organic matter removal and brominated disinfection by-products. Submitted to the Journal of Environmental Engineering (2003).

III. Myllykangas, T, Nissinen, T and Vartiainen, T. 2000. Bromate formation during ozonation of bromide containing drinking water – a pilot scale study. Ozone Science & Engineering, 22(5): 487-499.

IV. Myllykangas, T, Nissinen, TK, Hirvonen, A, Rantakokko, P and Vartiainen, T. The evaluation of ozonation and chlorination on disinfection by-product formation for a high-bromide water. Ozone Science & Engineering, accepted.

V. Myllykangas, T, Nissinen, TK, Mäki-Paakkanen, J, Hirvonen, A and Vartiainen, T. 2003. Bromide affecting drinking water mutagenicity. Chemosphere, 53(7): 745-756.

CONTENTS

CHAPTER 1: GENERAL INTRODUCTION

CHAPTER 2: MOLECULAR SIZE FRACTIONS OF TREATED AQUATIC HUMUS

CHAPTER 3: ORGANIC MATTER REMOVAL AND BROMINATED DISINFECTION BY-PRODUCTS

CHAPTER 4: BROMATE FORMATION DURING OZONATION OF BROMIDE CONTAINING DRINKING WATER

CHAPTER 5: THE EVALUATION OF OZONATION AND CHLORINATION ON DISINFECTION BY-PRODUCTS

CHAPTER 6: BROMIDE AFFECTING DRINKING WATER MUTAGENICITY

CHAPTER 7: GENERAL DISCUSSION

APPENDIX 1
APPENDIX 2
APPENDIX 3

CHAPTER 1: GENERAL INTRODUCTION

1. INTRODUCTION

Bromide can be found in lakes, rivers, and groundwaters. Its concentrations in natural waters have been found to range from a few micrograms to a few thousands of micrograms per liter[1], and in Finland up to 485 $\mu g\ L^{-1}$ of bromide has been found from raw water[2]. Both natural and anthropogenic sources of bromide are known.

Water treatment processes in water works can be divided into three categories[3]. The first category consists of physical treatment, which is based on the application of physical forces. The typical unit processes in this category are screening, mixing, gas transfer, sedimentation, flotation, and filtration. The second category utilizes chemicals and chemical reactions, e.g., precipitation, coagulation, and disinfection. The third category consists of biological treatments, which are not typically used in drinking water production but in the wastewater treatment, in which activated sludge process or slow sand filtration are often used. The purpose of all of these unit processes is to produce water that is both biologically and chemically safe for human consumption, and there are innumerable possible combinations to achieve that goal.

Conventional water treatment of waters containing high amounts of total organic carbon (TOC) involving variable combinations of the above mentioned unit processes is able to reduce the amount of the natural organic matter (NOM) by 70 to 80% in high-TOC waters[4]. During the conventional water treatment process, both the quality and quantity of the NOM are changed many times over. First, most of the high-molecular-weight NOM is removed during the coagulation-flocculation process followed by sedimentation or flotation, after which filtration improves further the water quality by removing the rest of the flocculated and even some of the dissolved compounds. Finally, the disinfecting chemical, such as ozone or chlorine, decomposes the dissolved NOM into smaller compounds, and these can cause problems in distribution system if they are not removed from the water. Permanganate oxidation is very effective in removing iron and manganese from water.

There are many ways to achieve disinfection: chlorine, ozone, UV, chloramines, chlorine dioxide, and combined disinfectants can all be used. Chlorine and ozone have been used for water disinfection for over a century, while the use of other agents has gained more attention recently due to the potential health hazards of chlorinated water. Large amounts of disinfection by-products (DBPs), such as trihalomethanes (THMs), halogenated acetic acids (HAAs), and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX) and its brominated analogues are formed during chlorination[5-7]. If bromide is present in the water, the formation of the DBPs is enhanced[5]. Ozonation, chloramines, and combined disinfection methods produce smaller amounts of the DBPs than chlorination[8-10], while UV treatment has not been found to produce any DBPs[11]. It has been estimated that the risks of microbial diseases from undisinfected water are 100 to 1000 times greater than the risks posed by the DBPs[12].

Due to the health-related effects, the limnits for many DBPs are regulated by the European Union (EU), the United States Environmental Protection Agency (USEPA), and the World Health Organization (WHO)[13-15]. Bromate is classified as a possible human carcinogen[16], and its limit value is set at 10 $\mu g\ L^{-1}$ by the EU and the USEPA based on a 10^{-5} risk level of 0.5 $\mu g\ L^{-1}$, while the WHO has set a limit value of 25 $\mu g\ L^{-1}$ based on a 10^{-5} risk level of 3 $\mu g\ L^{-1}$. Also the THMs have been classified as carcinogens or possible/probable carcinogens. The limit value for the THMs has been set at 100 $\mu g\ L^{-1}$ by the EU, and to 80 $\mu g\ L^{-1}$ by the USEPA as the total concentration of the four most common compounds (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform). The WHO provides a limit guideline for chloroform as 30 $\mu g\ L^{-1}$, which is based on a 10^{-5} additional risk if 2 liters of water per day are consumed. For HAAs, the USEPA has set a limit value of 60 $\mu g\ L^{-1}$ for the total concentration of five compounds (monochloro-, monobromo-, dichloro-, dibromo- and trichloro acetic acids).

2. LITERATURE REVIEW

2.1 BROMIDE

Bromide concentrations in the raw waters have been a cause of concern since the 1970's. Bromide itself has not been found to cause any direct health problems, but when bromide-containing waters are treated with strong oxidants, such as ozone and chlorine, many organic and inorganic DBPs, such as bromate, THMs, HAAs, and haloacetonitriles, are formed. Brominated DBPs are claimed to be even more harmful than their chlorinated analogues[7,17].

In Europe, the bromide concentrations in river waters have averaged around 70 µg L^{-1}, and in groundwaters 140 µg L^{-1} [18]. In the USA, on the other hand, the bromide concentrations in coastal rivers averaged around 210 µg L^{-1}, in river waters in general 101 µg L^{-1}, and in groundwaters 96 µg L^{-1} [19]. In Finnish surface waters, the highest bromide concentrations were 680 µg L^{-1} found in River Laihianjoki and 440 µg L^{-1} in River Sirppujoki[20]. Natural sources of bromide include geologic erosion and salt water intrusion[21,22], while anthropogenic sources include agricultural runoff (0.01 – 6.0 mg L^{-1} Br^-)[23], heavy auto traffic and boating[24], chemicals used for de-icing the roads[25], and leaks from oil wells[26].

Bromide is not removed efficiently during conventional water treatment processes[5], resulting in and increased bromide-to-TOC ratio and the formation of more brominated DBPs. However, bromide can be removed, e.g., by nanofilters[27], to some degree by granular activated carbon/biologically activated carbon (GAC/BAC) filtration[28], as well as electrochemically[29], or by ion exchange[30,31].

2.2 NATURAL ORGANIC MATTER

NOM must be removed during the water treatment process to avoid the formation of DBPs and other problems, such as microbial regrowth in the distribution systems. NOM consists of a wide variety of compounds, which are formed mostly from decaying plant material. The main functional groups of the NOM include carboxylic acids, and phenolic hydroxyl, carbonyl, and hydroxyl groups[32]. Especially in the boreal regions (Scandinavia, Russia, Canada, Northern USA), the amount of the TOC in natural waters can be as high as 50 mg L^{-1} due to the effect of bogs and swamps[32,33], while elsewhere the TOC in fresh waters varies from 1 to 10 mg L^{-1} [34], e.g. the average TOC in Finnish lakes has been estimated to be 12 mg L^{-1} [33]. In Norway, dissolved organic carbon (DOC) concentrations up to 160 mg/L have been observed[35]. Since surface waters contain high amounts of TOC, the use of groundwaters and the production of artificially recharged groundwaters are preferable[36]. The production of the artificially recharged groundwater has increased recently[36], and it has been shown to improve both the chemical and microbiological quality of the raw water and also to help in water processing in the water treatment plants[37-40].

NOM is often divided into two main groups, humic and fulvic acids, which together comprise the "humic compounds" of the organic matter. However, many other chemical groups, such as simple sugars, amino acids, fatty acids, and hydroxy acids are also considered as a part of NOM. Humic acids are generally considered to be larger than fulvic acids, but other distinctive characteristics have also been observed[32]. Separation processes of different humic compounds that have been tried in the past include precipitation, freeze concentration, liquid extraction, ultrafiltration, anion exchange, and XAD resin, of which the XAD resin has been found to be the best method[32,41]. The separation process using an XAD-8 resin is essentially as follows: 1) the water is filtered to remove suspended matter and is then acidified to pH 2 with HCl, 2) the NOM is concentrated using an XAD-8 resin, and the concentrated humic substances are eluted with NaOH and the water is acidified again, 3) the re-acidified sample is concentrated once more by passing it through a smaller XAD-8 resin column, and the low-molecular-weight organic acids are removed using gel filtration, 4) the DOC of the re-concentrate from gel filtration is adjusted to 500 mg L^{-1} DOC, and acidified to pH 1 with concentrated HCl, and after 24h the sample is centrifuged, and 5) at this point the humic acids are located in the precipitate and fulvic acids are in solution. A more detailed description of the separation method can be found in the article by Thurman and Malcolm[41]. The manufacturing of the XAD resin has now terminated, and it has been replaced by the DAX resin.

The possible size and structure of the organic matter have been studied using size exclusion chromatography, ultrafiltration, mass spectrometry and several other methods, but no unambiguous explanatory factors have been found so far, since both the quality and quantity of the organic matter seem to be highly dependent on local environment and conditions. Size exclusion chromatography has been found to be a good method for estimating the molecular weight distribution in waters[42-45]. It has been claimed that the molecular size of the NOM would be in the size range of 500 to 200,000 Da[46], but current understanding is that humic compounds can range from 500 to 10,000 Da in size[47,48]. It has been observed that most of the THMs, and possibly also the HAAs, are formed from organic matter size groups of <3000 Da[49-51]. Thus, by efficient coagulation and preoxidation which achieves a good removal of aromatic compounds and larger organic molecules, the formation of DBPs can be reduced.

The UV absorbance at the wavelength 254 nm (UV_{254}) can be used as a surrogate parameter for DBP formation[52]. When the specific UV absorbance (SUVA) is used ($100 \times UV_{254}/DOC$)[53], the aromatic content of the water can be estimated[54,55]. It has been proposed that from waters where the SUVA values are above 2 L mg^{-1} m^{-1}, then NOM is well removed by coagulation[53], which indicates that the SUVA values can be used when the treatment processes are planned and optimized for efficient NOM removal.

2.2.1 Organic matter removal

The NOM present in the surface waters places certain demands for water purification before disinfection to avoid the formation of the DBPs and to ensure the biological and chemical quality of the drinking water. The basic unit processes to remove organic compounds from the water are coagulation and flocculation, clarification, and filtration.

During the coagulation and flocculation processes, the dissolved organic compounds are brought together by chemical and mechanical treatment. First, the chemical (the coagulant), is added to the water with rapid mixing to result in the formation of microflocs. The most widely used coagulant worldwide is aluminum sulphate, alum[56]. Also ferric salts, such as ferric sulphate[57-59], have been used. Polyaluminum chloride has aroused a lot of interest as well[56,59,60]. In Finland the use of ferric sulphate has almost completely superseded the use of alum as the coagulant[61]. Second, the formed microflocs are brought together, flocculated, by mechanical mixing with blades or hydrodynamical mixing with walls situated in the basins.

After the coagulation and flocculation processes, the formed flocs are removed by sedimentation or flotation from the water. Sedimentation is based on gravitational separation of the flocs from water, while in flotation, small air bubbles lift the flocs to the surface of the water basin. Dissolved air flotation (DAF) is replacing the conventional sedimentation basins, since it has a smaller requirement for space and it achieves more efficient organic matter removal.

During the filtration step, the residual flocs and some of the dissolved organics still in the water are removed. Usually filters in drinking water production are one-layer rapid sand filters, but also double or multiple layer filters have been used. In addition to (quartz) sand, anthracite is often used in the multiple-layer filters, and different grain sizes can be used as the components of multiple layers.

2.3 DISINFECTION

The main goal of disinfection is to remove pathogenic microbes from the water so as to ensure the delivery of good quality water to the consumers without compromising hygienic standards. Pathogen-contaminated water is often perceived as a problem restricted to underdeveloped countries, but some severe outbreaks of waterborne diseases have occurred in the industrialized countries as well[62,63]. Even though disinfection has been praised as one of the major achievements of the 20th century, disinfection of drinking water cannot replace filtration in the fight against pathogens (see the review by Schoenen[64]), since some pathogens are not effectively removed by chlorination but they are retained onto the filters together with the particles to which they are attached. Thus, the sequential use of filtration and disinfection has been found to be a good combination to achieve safe drinking water.

The disinfection efficiency (d.e.) can be evaluated by using the equation i:

$$d.e. = c \cdot t \qquad \text{(i)}$$

in which c is the concentration of the disinfectant (mg/L), and t the time which the disinfectant concentration has been in the water (minutes). Disinfection has to be maintained at a minimum residual concentration for a given time, e.g., 0.4 mg L^{-1} × 12 min[65]. However, even though disinfection might be adequate for the most typical pathogens, the ct concept does not take into account the disinfection requirements of the more resistant microbes. The disinfection efficiency can be evaluated using the Chick-Watson equation (ii) [66,67]:

$$\log\left({}^{N}\!/_{N_0} \right) = -kc^n t \qquad \text{(ii)}$$

in which N_0 is the number of microorganism at time $t = 0$, N the number of vital organisms at time t, k the rate constant for the inactivation of a particular microorganism, c the concentration of a disinfectant, t the contact time, and n the fitting parameter for non-first-order behavior.

There are may disinfection options, and all of the agents work in a somewhat different way in destroying the bacteria, viruses and protozoa. If alternative disinfectants to chlorine are to be concerned, several criteria must be met: they must be 1) easily generated, 2) effective as biocides, 3) easily measurable as the residual, 4) less DBP forming than chlorine, and 5) cost-effective. Many disinfecting agents are also very effective in oxidizing organic and inorganic compounds present in the water. The most typical disinfection options and permanganate oxidation are discussed here. Tables 1-I and 1-II list the oxidation powers and relative effectiveness of various oxidizing compounds.

Table 1-I. Relative oxidation power of various oxidizing species[68].

Species	Oxidation potential (25°C), V[a]	Relative oxidation power[b]
Hydroxyl free radical	2.80	2.05
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Permanganate ion	1.49	1.10
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00
Hypobromous acid	1.33	0.98
Chlorine dioxide	1.275	0.94
Monochloramine	1.16	0.85
Hypoiodous acid	0.99	0.73

[a] Relative to the hydrogen electrode
[b] Based on chlorine as reference (= 1.00)

Table 1-II. Comparison of relative effectiveness of oxidants and disinfectants[68].

Oxidant	Disinfecting efficiency	Oxidizing efficiency	Halogenation capability
Chlorine	High	High	Low
Chlorine dioxide	High	High	Low
Monochloramine	Low	Low	Low
Ozone	High	High	Zero[c]
Potassium permanganate	Low	High	Zero
Hydrogen peroxide	Low	Moderate	Zero
Bromine	High	Low	High
Iodine	High	Very low	Low

[c] except when bromide is present

2.3.1 Chlorine

Chlorine is the most commonly used disinfection chemical, since it is relatively easy to transport and store due to its stability, and it is quite inexpensive[69]. Chlorination has been used for the first time in 1854 by John Snow, who attempted to disinfect the Broad Street Pump water supply in London after an outbreak of cholera[70]. Chlorination was first used in a practical way in 1886 during the typhoid fever epidemic in Pola, a harbor town on the Adriatic Sea[71]. Sims Woodhead, on the other hand, used “bleach solution” to disinfect the potable water distribution supply in Maidstone, Kent (England) following a typhoid outbreak in 1897 [72]. The first permanent system for water disinfection by chlorine was introduced in 1902 in Middelkerke, Belgium[71].

Chlorine can be added into the water as chlorine gas, sodium hypochlorite solution or in a solution prepared from dry calcium hypochlorite. All of the forms of chlorine are stable, enabling pre-manufacturing and storing of the chemicals[69,73]. The disinfection efficiency of chlorine is the greatest against bacteria and viruses[73], and chlorine (in the form of hypochlorous acid, hence, at a lower pH) penetrates easily through the negatively charged slime coating of microorganisms, destroying the pathogens[74]. However, protozoa, such as *Giardia* cysts and *Cryptosporidium* oocysts are highly resistant to chlorine[73]. Apart from disinfection, chlorine is very efficient in removing color, taste and odor, controlling the formation of algae, removing iron and manganese, destroying hydrogen sulfide, improving coagulation and maintaining clear filter media and water quality in the distribution systems[69,73].

The hydrolysis of the chlorine compounds used for water disinfection occurs via the following reactions (1 – 4)[75,76].

$$Cl_2(s) \rightleftharpoons Cl_2(aq) \qquad (1)$$

$$Cl_2(aq) + H_2O \rightleftharpoons HOCl + Cl^- + H^+ \qquad K_h = 4 \times 10^{-4} \qquad (2a)$$

$$NaOCl \rightleftharpoons Na^+ + OCl^- \qquad (2b)$$

$$Ca(OCl)_2 \rightleftharpoons Ca^{2+} + OCl^- \qquad (2c)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad K_a = 3 \times 10^{-8} \qquad (3)$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+ \qquad K_f = 1 \times 10^{-3} \qquad (4)$$

Table 1-III lists the fractions of reactive chlorine in different pH values. From the data it can be seen that hypochlorous acid is the most reactive species in typical water treatment conditions (circumneutral pH). The relative disinfection/oxidation efficiency of HOCl to OCl^- has been estimated to be 80:1 [77,78].

If bromide is present in the water to be chlorinated, it reacts with chlorine to form hypobromous acid (reactions 5 – 7)[75], resulting in the formation of a wide array of DBPs, since HOBr has been found to react much more rapidly than HOCl with the organic (and inorganic) compounds in the water[79-81], and HOBr has been found to be 25 times stronger than HOCl in its halogen substitution activity[81]. Table 1-IV summarizes the reactive bromine species at different pH values using two bromide concentrations.

Table 1-III. Fractions of total reactive chlorine and relative reactivities of chlorine species as a function of pH[76].

Chlorine Species	**Fraction of total reactive chlorine** **pH 2**	 **pH 4**	 **pH 6**	 **pH 8**	 **pH 10**	 **pH 12**
Cl_2	0.025	3×10^{-4}	2×10^{-6}	7×10^{-9}	1×10^{-12}	1×10^{-16}
HOCl	0.975	0.999	0.974	0.270	0.004	4×10^{-5}
OCl^-	3×10^{-6}	3×10^{-4}	0.026	0.730	0.996	0.999
H_2OCl^+	1×10^{-5}	1×10^{-7}	1×10^{-9}	3×10^{-12}	4×10^{-16}	4×10^{-20}
	Relative reactivity					
Cl_2	25	0.25	2×10^{-3}	7×10^{-6}	1×10^{-9}	1×10^{-13}
HOCl	0.975	0.999	0.974	0.270	0.004	4×10^{-5}
OCl^-	3×10^{-10}	3×10^{-8}	2.6×10^{-6}	7.3×10^{-5}	1×10^{-4}	1×10^{-4}
H_2OCl^+	1.0	1×10^{-2}	1×10^{-4}	3×10^{-7}	4×10^{-11}	4×10^{-15}
Total Net Reactivity	27.0	1.26	0.977	0.270	0.004	1×10^{-4}

$HOCl + Br^- + H^+ \rightleftharpoons Br_2 + H_2O + Cl^-$ (5)

$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$ $K_h = 5.8 \times 10^{-9}$ (6)

$HOBr \rightleftharpoons OBr^- + H^+$ $K_a = 2 \times 10^{-9}$ (7)

Table 1-IV. Fractions of total reactive bromine species in water at two bromide concentrations[75].

[Br] = 4 µg/L	**pH 5**	**pH 6**	**pH 7**	**pH 8**	**pH 9**	**pH 10**
Br_2	3×10^{-5}	3×10^{-6}	3×10^{-7}	3×10^{-8}	3×10^{-9}	3×10^{-10}
HOBr	1.00	1.00	0.98	0.83	0.33	5×10^{-2}
OBr^-	2×10^{-4}	2×10^{-3}	2×10^{-2}	0.17	0.67	0.95
$[Br^-]$ = 65 mg/L	**pH 5**	**pH 6**	**pH 7**	**pH 8**	**pH 9**	**pH 10**
Br_2	0.32	4.6×10^{-2}	5×10^{-4}	4×10^{-4}	2×10^{-5}	2×10^{-7}
HOBr	0.68	0.95	0.98	0.83	0.33	5×10^{-2}
OBr^-	1×10^{-4}	2×10^{-3}	2×10^{-2}	0.17	0.67	0.95

Chlorine forms many (halogenated) DBPs when reacting with the NOM in water. Thus, sufficient coagulation/flocculation and filtration steps should be taken place before chlorination. Reactions between chlorine and NOM in aqueous solutions are very complex, and pathways 8 and 9 show simplified reactions between both chlorine and bromine with organic matter producing organo-chlorine and organo-bromine compounds.

$HOCl + NOM \rightarrow TOCl$ (8a) and $HOBr + NOM \rightarrow TOBr$ (8b)

$OCl^- + NOM \rightarrow TOCl$ (9a) and $OBr^- + NOM \rightarrow TOBr$ (9b)

However, both HOCl and HOBr also react with NOM without producing any organo-halogen compounds (reactions 10 and 11).

$HOCl + NOM \rightarrow Cl^- + NOM_{ox}$ (10a) and $HOBr + NOM \rightarrow Br^- + NOM_{ox}$ (10b)

$OCl^- + NOM \rightarrow Cl^- + NOM_{ox}$ (11a) and $OBr^- + NOM \rightarrow Br^- + NOM_{ox}$ (11b)

2.3.2 Ozone

Ozone has been used for drinking water disinfection since 1893 when it was first applied in Oudshoorn (the Netherlands) with successive ozonation plants in France, Germany, USA, and Russia[82]. The large Bon Voyage water treatment plant in Nice, France, was established in 1906 and was able to produce 19,000 $m^3 d^{-1}$ drinking water. Thus, France is often looked as the "home" of ozonation for drinking water treatment[82]. By 1916, there were 49 ozonating water treatment plants worldwide and 26 of those were located in France[83]. Today there are more than 2000 facilities using ozone in drinking water production throughout the world[84].

Ozone is one of the most potent and effective germicides used in water treatment[68,85]. It is very effective against microorganisms[86,87], and the inactivation efficiency is not affected by pH or temperature (see the review by Kinman[88]). Ozone oxidizes the outer shell of microorganism, and may also oxidize the nuclear material[65]. Ozonation is effective in reducing taste, odor, and color[65,89-91]. It is also an efficient aid to the coagulation process[65,92-95]. Preozonation prior to chlorination is able to reduce the amount of DBP precursors of THMs, HAAs, haloacetonitriles, total and adsorbable organic halides, and mutagenicity[96-102].

Since ozone is a very unstable gas, it must be formed on-site with specific generators using oxygen or (synthetic) air as the production gas, more ozone is produced if oxygen is used[65]. Since ozone decomposes very rapidly in water[86,103-105], it should not be used for secondary disinfection.

The pH-dependent ozone decomposition (decreases 10-fold per pH unit) and hydroxyl radical formation in water are shown in reactions 12-17[106-108]. Ozone decomposition and its reactions in water have been discussed in detail in the book of Langlais et al.[65] and in recent reviews by von Gunten[10,87], thus only main reaction pathways are shown here.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k = 70\ M^{-1}\ s^{-1} \qquad (12)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2 \qquad k = 2.8 \times 10^6\ M^{-1}\ s^{-1} \qquad (13)$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \qquad k = 1.6 \times 10^9\ M^{-1}\ s^{-1} \qquad (14)$$

$$pH < 8\text{: } O_3^{\bullet -} + H^+ \rightleftharpoons HO_3^{\bullet} \qquad k_+ = 5.2 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (15a)$$

$$k_- = 3.3 \times 10^2\ s^{-1}$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \qquad k = 1.4 \times 10^5\ s^{-1} \qquad (15b)$$

$$pH > 8\text{: } O_3^{\bullet -} \rightleftharpoons O^{\bullet -} + O_2 \qquad k_+ = 2.1 \times 10^4\ M^{-1}\ s^{-1} \qquad (16a)$$

$$k_- = 3.3 \times 10^9\ s^{-1}$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad k = 10^8\ s^{-1} \qquad (16b)$$

$${}^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \qquad k = 1 \times 10^8\ M^{-1}\ s^{-1} - 2 \times 10^9\ M^{-1}\ s^{-1} \qquad (17)$$

There are some inhibitors, which can prevent the formation of the superoxide anion ($O_2^{\bullet -}$) and if these are present in water, the chain reaction for accelerated ozone decomposition is reduced, and, thus, there is stabilizing of the molecular ozone in water[106-109]. Such compounds include a fraction of NOM and carbonate/bicarbonate ions (reactions 18 and 19)[109-111].

$${}^{\bullet}OH + NOM \rightarrow NOM^{\bullet} + H_2O \qquad (18a)$$

$$NOM^{\bullet} + O_2 \rightarrow NOM{\bullet}O_2^{\bullet} \rightarrow \text{no } O_2^{\bullet -} \text{ formation} \qquad (18b)$$

$${}^{\bullet}OH + CO_3^{2-} \rightarrow CO_3^{\bullet -} + OH^- \qquad k = 3.9 \times 10^8\ M^{-1}\ s^{-1} \qquad (19a)$$

$${}^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet -} + H_2O \qquad k = 8.5 \times 10^6\ M^{-1}\ s^{-1} \qquad (19b)$$

Ozone reacts with NOM both via a molecular mechanism (reactions 20 and 21) and via a radical mechanism (reactions 22a and b) depending on the pH and whether other oxidants, such as hydrogen peroxide, are present leading to the production of several types of oxidized NOM, and enhanced ozone decomposition via radicals[87]. Ozonation does not produce halogenated DBPs, except in the presence of bromide ion[10,112], which results in bromate formation.

$$O_3 + NOM_1 \rightarrow NOM_{1ox} \qquad (20)$$

$$O_3 + NOM_2 \rightarrow NOM_2^{+\cdot} + O_3^{\cdot-} \qquad (21)$$

$$^{\cdot}OH + NOM_3 \rightarrow NOM_3^{\cdot} + H_2O \text{ or } NOM_3^{\cdot} + OH^- \qquad (22a)$$

$$NOM_3^{\cdot} + O_2 \rightarrow NOM - O_2^{\cdot} \rightarrow NOM_3^{+} + O_2^{\cdot-} \qquad (22b)$$

Ozonation results in the formation of small-molecular-weight organic compounds, such as aldehydes, ketones, and organic acids[10,113]. Those compounds are found to be more biodegradable than their precursors[114,115]. Also, a general reduction in the molecular weight fractions (from large to small) in humus has been observed to occur after ozonation[102,116].

2.3.3 Chloramines

Chloramines are formed on-site by the sequential addition of chlorine (hypochlorous acid) and ammonia or ammonium chloride[117], or a preformed monochloramine can be used. If chlorine is added first, it reacts with the organic matter in the water, resulting in a greater amount of DBPs than if the addition is made vice versa, i.e., the ammonium is added first and in excess, when the free chlorine is combined immediately with the ammonium group[5]. The most often used form is monochloramine[75]. Chlorine reacts in water with ammonia-N according to reactions 23 – 25. The reactions between organic N-compounds are considered to be analogous to the reactions of ammonia with chlorine (reaction 26)[118].

$$HOCl + NH_3 \rightleftharpoons NH_2Cl \text{ (monochloramine)} + H_2O \qquad (23)$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 \text{ (dichloramine)} + H_2O \qquad (24)$$

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 \text{ (trichloramine)} + H_2O \qquad (25)$$

$$HOCl + RNH_2 \rightleftharpoons RHNCl + H_2O \qquad (26)$$

Monochloramine has a much lower tendency to react with organic compounds present in water than chlorine[119]. This results in less taste and odor causing compounds[69], and also less DBP formation except for cyanogen chloride[97,120,121]. If chloramines are used for disinfection, a stable disinfection residual can be maintained over quite a long period of time[122,123].

Monochloramine is more effective than free chlorine in controlling biofilms, coliform bacteria, and *Cryptosporidium parvum* oocysts[121,123,124]. However, for disinfection purposes, free chlorine is 2.5 to 200 times more efficient than monochloramine, depending on the microorganism in question[72]. The organic chloramines have been found to have no disinfective effect on *Esherichia coli*[125].

When bromide is present in water containing both chlorine and ammonia, bromamines are formed via reactions 27 – 33 [126]. The formed bromamines react with the organics producing DBPs similar to chloramines, and they are found to be more efficient disinfectants than chloramines[126]. Kovacic et al.[127] have made a detailed study about the chemistry of N-bromamines and N-chloramines, from which the typical reactions and reaction products can be found. Bromamines can be used for prevention of bromate formation during ozonation due to the inhibiting effect of ammonia[128].

$$HOBr + NH_3 \rightleftharpoons NH_2Br + H_2O \qquad K_{eq} = 3.0 \times 10^{10} \qquad (27)$$

$$HOBr + NH_2Br \rightleftharpoons NHBr_2 + H_2O \qquad K_{eq} = 4.7 \times 10^{8} \qquad (28)$$

$$HOBr + NHBr_2 \rightleftharpoons NBr_3 + H_2O \qquad K_{eq} = 5.3 \times 10^{6} \qquad (29)$$

$$NH_2Br + NH_2Br \rightarrow NHBr_2 + NH_3 \qquad (30)$$

$$2NH_2Br + H^+ \rightarrow NHBr_2 + NH_4^+ \qquad (31)$$

$$NH_4^+ + NHBr_2 \rightarrow 2NH_2Br + H^+ \qquad (32)$$

$$NH_3 + NHBr_2 \rightarrow 2NH_2Br \qquad (33)$$

2.3.4 UV treatment

UV treatment was first used for drinking water disinfection in the early 1900s[11,129]. However, the use of UV treatment has increased only recently, today the world's largest UV facility is located in Helsinki, Finland[36]. UV treatment is often used for disinfection in small surface water treatment plants and groundwater plants[11,130].

Inactivation of bacteria and viruses is very efficient with relatively low UV fluences, but much higher fluences are required for protozoa, such as *Cryptosporidium* and *Giardia*[11,131,132]. When a microorganism absorbs UV light this evokes DNA breakage preventing the bacteria from multiplying. Its effect is proportional to the intensity (W/cm^2) multiplied by the time of exposure (seconds) and is dependent on many other factors such as the flow rate and the transmission efficiency of the water[11,129]. However, the so called photoreactivation is possible[11,129] if the water is exposed to natural light after UV treatment, thus nullifying or reducing the effect of disinfection. A typical UV fluence to achieve a 90% inactivation in bacteria and viruses is less than 10 mWs cm^{-2} = 10 mJ cm^{-2} [11], and an UV fluence of 25 to 35 mJ cm^{-2} has been proposed to be adequate for water disinfection[133].

UV light is generated with low or medium pressure UV lamps. The low pressure lamps emit a light with a peak intensity at wavelength 254 nm, which is close to the maximum germicidal wavelength of 260 nm, while the medium pressure lamps emit UV light with a broader spectrum[11,134]. In contrast to the other methods discussed here, UV is primarily a physical disinfectant, the other methods being mainly chemical. UV treatment is one of the "safest" disinfection methods, since it does not produce DBPs when conventional UV fluences are used[11,135,136]. Similar to ozone, UV treatment requires application of a secondary disinfectant for residual concentration in the distribution system.

2.3.5 Combined disinfectants

All of the above mentioned disinfectants can be used in combination with others, e.g., O_3/H_2O_2, UV/H_2O_2, and O_3/UV[9,137-140] have been used successfully for the removal of pesticides, pharmaceuticals etc. from polluted water, but they have been less used in drinking water production. Those processes are typical advanced oxidation processes (AOPs), which result in high concentrations of hydroxyl radicals[137], which are capable of oxidizing the compounds very unselectively in the water. Combined disinfectants can be used for primary and secondary disinfection, but also a synergistic effect for primary disinfection is possible. The formation of the DBPs is usually lower than that found after the use of individual disinfectants.

Hydrogen peroxide and ozone

Hydrogen peroxide combined with ozonation is an AOP, which is often used to remove pollutants, such as chlorinated ethylenes, pesticides, methyl *tert*-butyl ether, and pharmaceuticals from water[137,141-143]. It has also been used to increase the decomposition of NOM[144-146].

Similar to ozone alone, also hydrogen peroxide-ozonation is a very effective germicide used in water treatment[147,148]. The DBP formation during the process is similar to the use of ozone, and the use of O_3/H_2O_2 has been found to be more effective in removing DBP precursors than ozone alone[149]. However, if hydrogen peroxide-ozonation is applied with a constant ozone residual, an increase in the hydrogen peroxide concentration has been observed to increase bromate formation in bromide-containing waters, while hydrogen peroxide addition at a constant ozone dose has reduced the bromate yield[150].

Ozone reacts only marginally with H_2O_2, but if HO_2^- is present, then ozone decomposition becomes greatly accelerated (reactions 34 – 36)[106].

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^- \qquad pK\ H_2O_2: 11.6 \qquad (34)$$

$$O_3 + H_2O_2 \xrightarrow{\text{very slow}} \qquad kO_3, H_2O_2 < 10^{-2}\ M^{-1}\ s^{-1} \qquad (35)$$

$$O_3 + HO_2^- \xrightarrow{\text{fast}} \qquad kO_3, HO_2^- = 5.5 \times 10^6\ M^{-1}\ s^{-1} \qquad (36)$$

Hydrogen peroxide (hydroperoxyl ion) is able to reduce hypobromous acid back to bromide, resulting in the formation of lower amounts of brominated DBPs (reaction 37)[87].

$$HOBr + HO_2^- \rightarrow Br^- + H_2O + O_2 \qquad k = 7.6 \times 10^8\ M^{-1}\ s^{-1} \qquad (37)$$

2.3.6 Potassium permanganate

Potassium permanganate is not an efficient disinfectant[68,151]. However, it can be used to control taste and odor, and to remove color, iron, manganese, and endotoxins[72,91,152] from water instead of chlorine or other strong disinfecting chemicals. On the other hand, if potassium permanganate is used for pretreatment, the DBP formation during chlorination can be reduced[153-155], whereas it has not been found to form DBPs when used alone[72].

2.3.7 Disinfection by-products

Reactions between NOM and disinfecting or oxidating chemicals, in the presence or absence of bromide, result in the formation of many harmful and unwanted DBPs, which can be halogenated or non-halogenated. The chosen disinfection option has the most significant effect on DBP formation, since chlorination is observed to cause the most DBP formation, while other methods (including ozone, chloramines, UV) produce only some of those compounds. Many of the compounds and compound groups are regulated by legislation[13-15] due to their adverse health-effects on consumers.

In the chlorination process, THM formation is widely used as a surrogate for other DBPs. Ozonation produces many small-molecular-weight organic compounds, but the only halogenated species are those containing bromide. Chloramination has been found to form similar DBPs as chlorination though they occur at lower concentrations, while the formations of cyanogen chloride and bromide are enhanced. UV treatment and $KMnO_4$ oxidation have not been found to cause the formation of DBPs. Table 1-V lists the most commonly detected DBPs after disinfection.

Table 1-V. The most common disinfection by-products of different disinfection options in the presence of bromide. [5,10,112,113,116,156-167]

Disinfection option	Compound group	Compounds	Favoring conditions
Chlorination	Trihalomethanes (THMs)	Chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$), bromoform ($CHBr_3$), dichloroiodimethane ($CHCl_2I$), dibromoiodomethane ($CHBr_2I$)	High pH, high TOC, high chlorine dose
	Halogenated acetic acids (HAAs)	Monochloro acetic acid (MCAA), monobromo acetic acid (MBAA), dichloro acetic acid (DCAA), dibromo acetic acid (DBAA), bromochloro acetic acid (BCAA), bromodichloro acetic acid (BDCAA), chlorodibromo acetic acid (CDBAA), trichloro acetic acid (TCAA), tribromo acetic acid (TBAA)	Low pH, high TOC, high chlorine dose
	Hydroxy furanones	3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX), 3-bromo-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (BMX-1), 3-chloro-4-(dibromomethyl)-5-hydroxy-2(*5H*)-furanone (BMX-2), 3-bromo-4-(dibromomethyl)-5-hydroxy-2(*5H*)-furanone (BMX-3)	High TOC, improper organic matter removal
	Halogenated acetonitriles (HANs)	Bromo acetonitrile (BAN), chloro acetonitrile (CAN), bromochloro acetonitrile (BCAN), dibromo acetonitrile (DBAN), dichloro acetonitrile (DCAN), tribromo acetonitrile (TBAN), trichloro acetonitrile (TCAN), bromodichloro acetonitrile (BDCAN), chlorodibromo acetonitrile (DBCAN)	
	(Halogenated) organic compounds	(Halo)aldehydes ($C_1 - C_{14}$), (halo)ketones, chlorophenols, bromophenols, halonitromethanes, haloalcohols, haloacetates, halopyrroles, halobenzoic acids, trihalomethyl, haloaromatics, halomethanes, halonitromethanes, organic acids, esters, benzaldehydes, benzonitriles, amides, alkanes	
	(Halogenated) inorganic compounds	Hypochlorite ion, hypochlorous acid, chlorate, cyanogen chloride and bromide, chloro and bromopicrin, chloral hydrate, (mixed) halamines, haloamides, bromite	
Chloramines	THMs	$CHCl_3$, $CHCl_2Br$, $CHBr_3$, $CHBr_3$, $CHCl_2I$, $CHBr_2I$	
	HAAs	MCAA, DCAA, TCAA, BCAA, DBAA	
	HANs	DCAN, DBAN, TCAN	
	(Halogenated) organic compounds	(Halo)ketones, (halo)aldehydes ($C_1 - C_{14}$)	
	(Halogenated) inorganic compounds	Ammonia, chloropicrin, cyanogen chloride and bromide, (mixed) halamines	

Table 1-V. Continued.

Ozonation	Bromoorganic compounds	$CHBr_3$, bromoacetonitriles, brominated acetic acids, brominated acetones, bromobenzenes, bromohydrins, bromamines, (bromo)ketones, (bromo)aldehydes ($C_1 - C_{14}$), bromopicrin, bromoalkanes, bromohydrins	High bromide concentration, high TOC, high pH, high ozone dosage, temperature, alkalinity, amount of dissolved ozone
	Organic compounds	Aldoacids, ketoacids, dicarboxylic acids, aldehydes ($C_1 - C_{14}$), dialdehydes, carboxy aldehydes, carboxylic acids, aliphatic dibasic acids (C_4 to C_{10}), aliphatic monobasic acids (C_2 and higher), carboxyphenylglyoxilic acids, fatty acids ($C_9 - C_{14}$), organic peroxides, glyoxal, methyl glyoxal, biodegradable organic matter	
	(Brominated) inorganic compounds	Bromate (BrO_3^-), bromite, hypobromous acid, hypobromite, cyanogen bromide, bromopicrin, bromohydrin, nitrate, MnO_4^-, H_2O_2, hydrogen peroxide	
PEROXONE	Bromoorganic compounds	$CHBr_3$, MBAA, DBAA, DBAN	
	Organic compounds	Glyoxal, methyl glyoxal, aldehydes ($C_1 - C_{14}$), fatty acids ($C_9 - C_{14}$)	
	(Brominated) inorganic compounds	BrO_3^-, hydrogen peroxide	
Ozone-chlorine / Ozone-chloramine	THMs	$CHCl_3$, $CHCl_2Br$, $CHBr_3$, $CHBr_3$	
	HAAs	MCAA, MBAA, DCAA, TCAA, BCAA, DBAA, TBAA	
	HANs	DCAN, BCAN, DBAN, BDCAN, DBCAN, TBAN	
	(Halogenated) organic compounds	(halo)alkanes/alkenes, (halo)aldehydes, (halo)ketones, (halo) carboxylic acids, (halo)alcohols, (halo)nitromethanes, aldo and ketoacids, dicarbonyls	
	(Halogenated) inorganic compounds	Nitriles, halamides	

Bromate

It has been found that threshold levels of both bromide concentration and ozone dose in bromate formation are water-specific[8,169]. Bromate concentrations in European drinking waters have been found to range from below the detection limit to 20 μg L^{-1}, with most being below the EU limit value of 10 μg L^{-1} [170,171]. Bromate can be present also in hypochlorite solutions as an impurity[172,173], but no detectable concentrations (detection limit 10 μg L^{-1})[172] or only small amounts (0.05 – 7.7 μg L^{-1})[173] have been observed in finished drinking water. However, in the latter study[173], the observed bromate concentration (7.7 μg L^{-1}) is close to the health-based limit value set by the EU and the USEPA, thus the bromate concentrations in the hypochlorite solutions should be monitored frequently to avoid negative health effects for consumers. On the other hand, chlorination of sea water did result in significant amounts of bromate[174], but this result is not relevant for drinking water production, since sea water can not be used as the raw water without prior desalination. Also, monochloramine treatment of bromide-containing waters has been shown to result in bromate formation[175]. Many research groups have developed models to estimate the formation of bromate during water treatment processing[150,176-180].

Bromate formation during water treatment processes requires the presence of dissolved ozone in the water[181], which reacts with OBr^- via reactions 38 – 41[112,150,182-184].

$Br^- + O_3 \rightarrow OBr^- + O_2$ $k = 160\ M^{-1}\ s^{-1}$ (38)

$OBr^- + O_3 \rightarrow OOBr^- + O_2$ $k = 330\ M^{-1}\ s^{-1}$ (39a)

$OOBr^- \rightarrow Br^- + O_2$ (39b)

$OBr^- + O_3 \rightarrow BrO_2^- + O_2$ $k = 100\ M^{-1}\ s^{-1}$ (40)

$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$ $k = >10^5\ M^{-1}\ s^{-1}$ [115]

$k = 8.9 \times 10^4\ M^{-1}\ s^{-1}$ [187] (41)

When hydroxyl radicals are present in the water, bromate can also be formed due to the synergistic effects of molecular ozone and hydroxyl radicals (reactions 42 – 51), and hypobromous acid is formed (reaction 52)[174,183,185,186].

$Br^- + {}^{\bullet}OH \rightleftharpoons BrOH^-$ $k_+ = 1.06 \times 10^8\ M^{-1}\ s^{-1}$ (42)

$k_- = 3.3 \times 10^7\ s^{-1}$

$$\mathrm{BrOH^{-} + H^{+} \rightleftharpoons Br^{\cdot} + H_2O} \qquad k_{+} = 1.06 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}} \tag{43}$$

$$k_{-} = 1.36\ \mathrm{s^{-1}}$$

$$\mathrm{Br^{\cdot} + O_3 \rightarrow BrO^{\cdot} + O_2} \qquad k = 1.5 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}} \tag{44}$$

$$\mathrm{Br^{\cdot} + Br^{-} \rightarrow Br_2^{\cdot -}} \qquad k = 10^{10}\ \mathrm{M^{-1}\ s^{-1}} \tag{45}$$

$$\mathrm{Br_2^{\cdot -} + Br_2^{\cdot -} \rightarrow Br^{-} + Br_3^{\cdot -}} \qquad k = 2 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}} \tag{46}$$

$$\mathrm{Br_2^{-} + BrO \rightarrow BrO^{\cdot} + 2Br^{-}} \tag{47}$$

$$\mathrm{BrO^{\cdot} + H_2O \rightarrow BrO^{-} + BrO_2^{-} + 2H^{+}} \tag{48}$$

$$\mathrm{BrO^{\cdot} + BrO_2^{-} \rightarrow BrO_2 + BrO^{-}} \tag{49}$$

$$\mathrm{OH^{\cdot} + BrO_2^{-} \rightarrow BrO_2 + OH^{-}} \tag{50}$$

$$\mathrm{2BrO_2 + H_2O \rightarrow BrO_2^{-} + BrO_3^{-} + 2H^{+}} \tag{51}$$

$$\mathrm{Br_3^{\cdot -} + H_2O \rightarrow HOBr + 2Br^{-} + H^{+}} \tag{52}$$

Reduction strategies for bromate formation are listed in Table 1-VI.

Table 1-VI. Strategies for preventing bromate formation during ozonation.

Strategy	**References**
pH reduction	1,8,10,112
Ammonia addition	1,8,10
Ozonation at a higher DOC	171,187,188
Addition of OH radical scavengers*	181,183,189
Using a denitrifying bioreactor	190
Catalytic bromate destruction	191
Hydrodynamics and geometry	181,192,193

*such as ethanol, formate, acetate, oxalate or glucose

Once bromate is formed, it can be removed from water by activated carbon, high-energy electron beam radiation, UV irradiation, or by ferrous iron reduction[28,194-197].

Trihalomethanes

The formation of the THMs from chlorinated samples was first verified in 1974[156,198]. The chlorination of fulvic acid has been found to result in more THM formation than that of humic acid[199]. The THMs are the most often found DBPs in chlorinated waters, and they can be used as surrogate parameters in the estimation of total DBP yield in different waters after chlorination. Chloroform is the dominant species in bromide-free waters, but when bromide is present, more bromine-containing THMs are formed. Many research groups have developed models to estimate the formation of THMs during water treatment processes and for their measurement in distribution systems[52,176,200-209]. In a study of THMs levels present in tap water and blood, it was found that the THM concentrations were three orders of magnitude lower in the blood than in the tap water, and inhalation and dermal exposure to THMs during showering increased the THM concentration in the blood by approximately 4-fold[210]. THM concentrations in Finnish drinking waters have been observed to range from below the detection limit to 103 $\mu g\ L^{-1}$ (average 26 $\mu g\ L^{-1}$) when surface water was used as the raw water, and from below the detection limit to 13 $\mu g\ L^{-1}$ (average 6.3 $\mu g\ L^{-1}$) when artificially recharged groundwater was used[211]. In two out of 35 water works studied, the THM concentration exceeded 50 $\mu g\ L^{-1}$, and in one of those the value was 100 $\mu g\ L^{-1}$ [211], which is the limit value for the THMs in the EU. Table 1-VII lists the observed THM concentrations in several countries.

Bromide has been found to increase the formation of the THMs. For example, in lake water containg 2-mg L^{-1} Br^-, the brominated THMs (bromodichloromethane, chlorodibromomethane, bromoform) were found to account for up to 97% of the total THM concentration[212,213], with bromoform being the predominant compound (up to 52% of the THMs). Bromoform formation has been found to be greater than chloroform formation with bromide concentrations in a range 175 – 550 $\mu g\ L^{-1}$ [81,214,215]. Table 1-VIII lists the strategies used for reduction of the THM formation during water treatment. However, if water contains bromide and enhanced coagulation is used, the bromide-to-TOC ratio increases, enhancing the formation of brominated THMs[5,216].

Mutagenicity and MX formation

Chlorination of humic waters produces mutagenicity. The potential for mutagenicity has been shown to be similar after chlorination of humic and fulvic acids[6]. Several dozens of potential mutagens have been identified from drinking waters, including (halogenated) acetic and carboxylic acids, aromatic compounds, furanones, aliphatics, ketones, alcohols, ethers, methanes, alkanes and alkenes, nitriles, amides, and amines[6,217,218]. Bromide-containing waters have been found to be more mutagenic than bromide-free waters[17].

Table 1-VII. Average concentrations of trihalomethanes (THMs) in μg L^{-1} found in different countries.

Country / Area	Average THMs (μg L^{-1})	Reference
European Union	77.7 (sw) / 7.6 (gw)	219
Finland	26 (sw) / 13 (aw)	211
Ireland	32 (nk)	220
Czech Republic	8 (sw)	221
Greece	16 (sw)	222
Spain	45 (sw and gw)	223
Israel	150 (sw) / 85 (rw)	212
Canada / general	19 (nk) (winter)	224
	54 (nk) (summer)	
Canada / Quebec	62 (sw)	225
USA / general	40 (nk)	120
	60 (sw) / 19 (gw) / 33(mw)	226
USA / Massachussetts	39 (sw)	227
USA / North Carolina	40 (sw)	228
USA / Utah	31 (sw)	229
Australia	70* (sw)	230
Korea	13 (sw)	231
Vietnam	20 (gw)	232

sw = surface water; gw = groundwater; aw = artificially recharged groundwater; nk = the water source is not known; mw = mixed ground and surface water; *variation of 6 – 191 μg L^{-1} Br^- depending on study area

The Ames mutagenicity assay with *Salmonella typhimurium* strain TA100 without metabolic activation has proven to be a good way to estimate the direct acting mutagenicity of drinking water[217,240-243]. The Ames *Salmonella* assay has been proven to give good reproducibility in its the results, it has good sensitivity, is rapid and simple, requires only minimal resources (money and personnel), and there also is a large database available for comparison[244].

MX, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone, is the most potent known mutagen in drinking water, and was first found from chlorinated pulp liquors by Holmbom et al.[245]. Since then it has been found from the drinking waters throughout the world, corresponding up to ⅔ of the total mutagenicity[224,243]. The TA100 strain without metabolic activation has been found to be several times more sensitive for mutagenicity induced by the MX than other strains (TA92, TA97, TA98, TA102, TA1535, and TA1537) of *S. typhimurium*. A 70 – 90% reduction in TA100 mutagenicity resulting from the MX was observed in the presence of metabolic activation[247]. In the waters containing bromide, brominated MX compounds, which are known to be more mutagenic than MX, are formed[7,248]. MX and its three brominated analogues are presented in Figure 1-1.

Table 1-VIII. Strategies for reducing the trihalomethane formation during water treatment processes.

Strategy	Reference
Ammonia addition	233
pH reduction	200,214,234
Preozonation	215,235,236
GAC filtration	205
Coagulation	205,234,237-239
Dissolved air flotation	240
Ion exchange	205,238
Nanofiltration	216
Permanganate oxidation	154

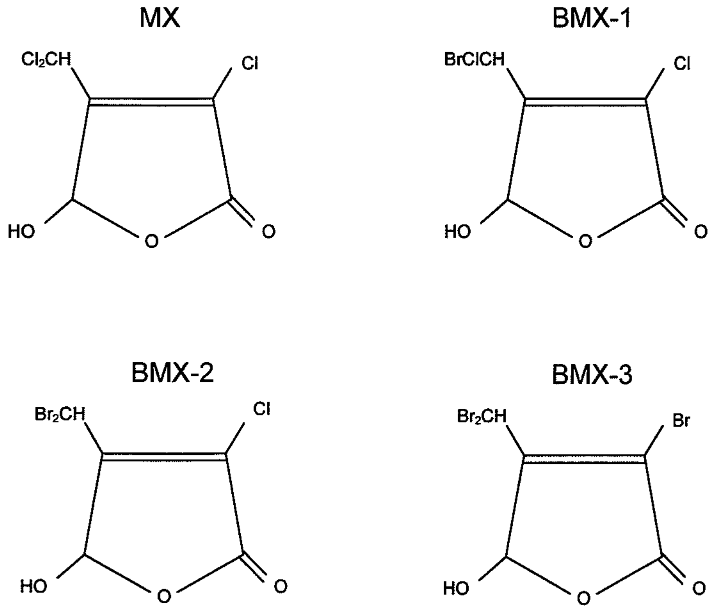


Figure 1-1. The four MX analogues. (MX = 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone; BMX-1 = 3-bromo-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone; BMX-2 = 3-chloro-4-(dibromomethyl)-5-hydroxy-2(*5H*)-furanone; BMX-3 = 3-bromo-4-(dibromomethyl)-5-hydroxy-2(*5H*)-furanone)

2.4 BROMIDE IN FINNISH DRINKING WATERS

The concentrations of bromide in Finnish drinking waters have been studied in the year 1998 [2]. Table 1-IX lists the results obtained during that study. The analyses of the samples were made by the same methods as those utilized in studies I – V. Bromate could not be analyzed in the Laboratory of Chemistry at that time, thus, no bromate results were available. The water works were chosen to obtain a representative sample of the largest surface water works in Finland including also the largest water works using artificially recharged groundwater and groundwater. One selection criteria was the assumption of high bromide concentration. Those water works represent 54% of the distributed drinking water in Finland. Of those water works, 15 use chlorine either in the form of hypochlorite solution or as chlorine gas (SW1 – SW3, SW6, SW11, SW12, SW15 – SW18, AW1, AW2, GW1 – GW3), one uses monochloramine (SW10), four use a combination of chlorine and monochloramine (SW7, SW8, SW14, SG1), one utilizes a combination of chlorine dioxide, hypochlorite and monochloramine (SW5), one water works disinfects with ozone and monochloramine (SW9), and two use UV treatment with monochloramine (SW4, SW13).

3. AIMS OF THE STUDY

The aims of this study were to evaluate

1. the effect of different oxidation or disinfection methods (ozone, chlorine, hydrogen peroxide and permanganate) on the decomposition of aquatic humus.
2. the effect of bromide on the formation of bromate, THMs, and mutagenicity.
3. the effect of ozonation on the formation of bromate in two bromide-containing waters.
4. alternative ways to prevent the formation of brominated DBPs.

Table 1-IX. The quality of raw water and purified water in 24 water works in Finland in the year 1998.[2] SW = surface water, SG = surface and groundwater (50%/50%), AW = artificially recharged groundwater, and GW = groundwater as the raw water. For treatment options, see the text.

Plant	Raw water			Drinking water										Average production m^3/d
	Br^- (µg/L)	TOC (mg/L)	HP-SEC (AU*s)	Br^- (µg/L)	TOC (mg/L)	Cl_2 dose (mg/L)	Res. Cl_2 (mg/L)	HP-SEC (AU*s)	Br-THMs (µg/L)	THMs (µg/L)	HAAs (µg/L)	Mutagenicity (net rev/L)	MX (ng/L)	
SW1	485	3.8	121 000	165	3.0	2.6	0.19	62 000	153	160	74	3 620	8	3 900
SW2	181	8.3	340 000	36	2.1	1.2	0.13	47 000	64	81	41	1 380	11	7 300
SW3	181	7.6	270 000	138	3.2	1.0	0.13	83 000	12	15	28	430	4	1 600
SW4	125	9.8	nm	126	3.1	0.6	0.32	nm	5	7	10	740	3	4 600
SW5	93	13	nm	40	2.6	0.9	0.34	nm	0.2	1	13	700	5	16 600
SW6	37	8.1	221 000	nd	2.6	1.0	0.13	43 000	15	32	27	710	15	14 000
SW7	41	7.7	401 000	nd	2.7	0.6	0.37	66 000	6	14	20	780	11	51 300
SW8	nd	7.6	507 000	nd	2.9	0.8	0.27	54 000	nd	1	10	450	8	22 000
SW9	nd	5.6	167 000	nd	3.3	0.6	0.37	35 000	nd	nd	17	750	12	100 200
SW10	nd	6.0	174 000	nd	1.8	0.3	0.23	17 000	nd	nd	4	440	5	96 800
SW11	nd	4.2	124 000	nd	2.5	1.1	0.11	65 000	2	16	22	480	10	34 600
SW12	nd	8.4	nm	nd	2.8	0.6	0.21	nm	0.6	3	10	660	5	15 300
SW13	nd	8.4	nm	nd	2.6	0.5	0.23	nm	0.5	5	10	980	14	12 100
SW14	nd	11.0	479 000	nd	2.2	0.9	0.52	41 000	6	9	23	1 180	12	6 700
SW15	nd	5.6	218 000	nd	2.8	1.0	0.16	78 000	1	13	28	530	10	2 400
SW16	nd	11.0	nm	nd	3.0	1.0	0.19	nm	2	29	56	2 730	51	5 400
SW17	nd	5.9	nm	nd	1.9	0.8	0.09	nm	1	35	20	1 070	34	3 800
SW18	nd	4.0	nm	nd	4.0	0.3	0.07	nm	0.1	8	7	120	6	2 100
SG1	nd	3.8 / 1.2	103 000 / 20 000	nd	1.6	0.4	0.17	25 000	0.6	0.6	3	360	11	7 000
AW1	nd	9.2	nm	nd	2.3	0.7	0.17	nm	4	24	17	570	13	23 500
AW2	nd	5.7	305 000	nd	2.4	0.5	0.12	76 000	2	15	13	320	12	33 700
GW1	26	1.8	nm	nd	3.3	0.4	0.31	nm	nd	2	9	300	3	6 400
GW2	25	2.2	66 000	nd	0.9	1.0	0.23	38 000	2	14	22	410	10	2 500
GW3	nd	2.3	56 000	nd	2.1	0.3	0.05	40 000	0.6	3	4	140	9	10 100

HP-SEC (AU*s) = integrated peak areas from the size exclusion chromatography (absorbance units multiplied by time in seconds); Br-THMs = the sum of the bromine-containing trihalomethanes (bromodichlorimethane, chlorodibromomethane, and bromoform); nd = not detected; nm = not measured; Res. Cl_2 = residual chlorine in the plant effluent

4. REFERENCES

1. von Gunten, U and Hoigné, J. 1992. Factors controlling the formation of bromate ion during ozonation of bromide-containing waters. Journal of Water Supply, Research and Technology - Aqua 41(5): 299-304.
2. Nissinen, T, Rantakokko, P, Myllykangas, T and Vartiainen, T. 1999. Bromide and brominated trihalomethanes in Finnish drinking waters. In: Proceedings, Fourth Finnish conference of environmental sciences, Tampere, May 21-22, 1999. Environmental science, technology and policy. Eds: Sari Kuusisto, Simo Isoaho and Jaakko Puhakka. Finnish Society for Environmental Sciences. Tampere, Finland.
3. Tchobanoglous,G and Schroeder, ED. 1987. Water quality. Characteristics, modeling, modification. Adison-Wesley Publishing Company, Reading, Massachusetts, USA. ISBN 0-201-05433-7.
4. Backlund, P, Kronberg. L, Pensar, G and Tikkanen, L. 1985. Mutagenic activity in humic water and alum flocculated humic water treated with alternative disinfectants. The Science of Total Environment, 47: 257-264.
5. Cooper, WJ, Zika, RG and Steinhauer, MS. 1985. Bromide-oxidant interactions and THM formation: a literature review. Journal American Water Works Association, 77(4): 116-121.
6. Horth, H. 1989. Identification of mutagens in drinking water. Aqua, 38: 80-100.
7. LaLonde, RT, Bu, L, Henwood, A, Fiumano, J and Zhang, L. 1997. Bromine-, chlorine-, and mixed halogen-substituted 4-methyl-2(5H)-furanones: synthesis and mutagenic effects of halogen and hydroxyl group replacements. Chemical Research in Toxicology, 10: 1428-1436.
8. Siddiqui, MS and Amy, GL. 1993. Factors affecting DBP formation during ozone-bromide reactions. Journal American Water Works Association, 85(1): 63-72.
9. Camel, V and Bermond, A. 1998. The use of ozone and associated oxidation processes in drinking water treatment. Water Research, 32(11): 3208-3222.
10. von Gunten, U. 2003. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Research, 37: 1469-1487.
11. Wolfe, RL. 1990. Ultraviolet disinfection of potable water. Environmental Science & Technology, 24(6): 768-773.
12. Regli, S, Berger, P, Macler, B and Haas, C. 1993. Proposed decision tree for management of risks in drinking water: consideration for health and socioeconomic factors. In: Safety of Water Disinfection: Balancing Chemical & Microbial Risks, First International Conference on the Safety of Water Disinfection. International Life Sciences Institute, Washington, DC, USA.
13. WHO. 1996. World Health Organization: Guidelines for drinking water quality. Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva, Switzerland.
14. EU. 1998. Official Journal of the European Community L330: Directive 98/83/EC.
15. USEPA. 1998. Stage 1 disinfectants and disinfection by-products rule. Unites States Environmental Protection Agency, EPA 815-F-98-010, December 1998.
16. IARC. 1990. Monographs on the evaluation of carcinogenic risks to humans, Vol 52, WHO (1990)

17. Nobukawa, T and Sanukida, S. 2001. Effect of bromide ions on genotoxicity of halogenated by-products from chlorination of humic acid in water. Water Research, 35(18): 4293-4298.

18. Legube, B. 1996. A survey of bromate ion in European drinking water. Ozone Science & Engineering, 18: 325-348.

19. Amy, G. Siddiqui, M, Ozekin, K and Westerhoff, P. 1993. Threshold levels for bromate formation in drinking water. Water Supply, 13(1): 157-162.

20. Mäkinen, I. 1978. Halogenidien pitoisuuksista vesistöissä. (The concentrations of the halogenides in water systems) National Board of Water, Report 138. Helsinki, Finland. *In Finnish.*

21. Carns, KE and Stinson, KB. 1978. Controlling organics: the East Bay Municipal Utility District experience. Journal American Water Works Association, 70(11): 637.

22. Lange, AL and Kawczynski, E. 1978. Controlling organics: the Contra Costa County Water District experience. Journal American Water Works Association, 70(12): 653.

23. Wegman, RC and Greve, PA. 1981. Methyl bromide ion and bromide ion in drainage water after leaching of glassware soils. Water, Air & Soil Pollution, 16:3.

24. Smith, VL, Cech, I, Brown, JH and Bogdan, GF. 1980. Temporal variations in trihalomethane content of drinking water. Environmental Science & Technology, 14(2): 190-196.

25. Luong, TV, Peters, CJ, Youg, RJ and Perry, R. 1980. Bromide and trihalomethanes in water supplies. Environmental Technology Letters, 1: 299-310.

26. Hudak, PF and Wachal, DJ. 2001. Effects of brine injection wells, dry holes, and plugged oil/gas wells on chloride, bromide, and barium concentrations in the Gulf Coas Aquifer, southeast Texas, USA. Environment International, 26: 497-503.

27. Laîné, J-M, Jacangelo, JG, Cummings, EW, Carns, KE and Mallevialle, J. 1993. Influence of bromide on low-pressure membrane filtration for controlling DBPs in surface waters. Journal American Water Works Association, 85(6): 87-99.

28. Asami, M, Aizawa, T, Morioka, T, Nishijima, W, Tabata, A and Magara, Y. 1999. Bromate removal during transition from new granular activated carbon (GAC) to biological activated carbon (BAC). Water Research, 33(12): 2797-2804.

29. Kimbrough, DE and Suffet, IH. 2002. Electrochemical removal of bromide and reduction of THM formation potential in drinking water. Water Research, 36: 4902-4906.

30. Singer, PC and Bilyk, K. 2002. Enhanced coagulation using a magnetic ion exchange resin. Water Research, 36(16): 4009-4022.

31. Vaaramaa, K and Lehto, J. 2003. Removal of metals and anions from drinking water by ion exchange. Desalination, 155: 157-170.

32. Thurman, E. 1985. Organic geochemistry of natural waters. Martinus Nijhoff / Dr. W. Junk Publishers, The Netherlands.

33. Kortelainen, P. 1993. Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics. Canadian Journal of Fisheries and Aquatic Sciences, 50: 1477-1483.

34. Martin, DF and Pierce, RH. 1971. A convenient method of analysis of humic acid in fresh water. Environmental Letters, 1: 49-52.

35. Abbt-Braun, G and Frimmel, FH. 1999. Basic characterization of Norwegian NOM samples: similarities and differences. Environmental International, 25(2/3): 161-180.

36. FEI (Finnish Environment Institute). 2003. (accessed 09-09-2003) http://www.vyh.fi/eng/environ/state/waterre/waterser/waterser.htm

37. Obst, U. 1984. Results of biochemical investigations of surface- and groundwater. Von Wasser, 63: 6-16.

38. Miettinen, IT, Vartiainen, T and Martikainen, PJ. 1996. Bacterial enzyme activities in ground water during bank filtration of lake water. Water Research, 30(10): 2495-2501.

39. Lindroos, A-J, Kitunen, V, Derome, J and Helmisaari, H-S. 2002. Changes in dissolved organic carbon during artificial recharge of groundwater in a forested esker in Southern Finland. Water Research, 36: 4951-4958.

40. Juhna, T, Klavins, M and Eglite, L. 2003. Sorption of humic substances on aquifer material at artificial recharge of groundwater. Chemosphere, 51: 861-868.

41. Thurman, EM and Malcolm, RL. 1981. Preparative isolation of aquatic humic substances. Environmental Science & Technology, 15(4): 463-466.

42. Becher, G, Carlberg, GE, Gjessing, ET, Hongslo, JK and Monarca, S. 1985. High-performance size exclusion chromatography of chlorinated natural humic water and mutagenicity studies using the microscale fluctuation assay. Environmental Science & Technology, 19(5): 422-426.

43. Vartiainen, T, Liimatainen, A and Kauranen, P. 1987. The use of TSK size exclusion columns in determination of the quality and quantity of humus in raw waters and drinking waters. Science of the Total Environment, 62: 75-84.

44. Chin, Y-P, Aiken, G and O·Loughlin, E. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental Science & Technology, 28(11): 1853-1858.

45. Kudryavtsev, AV, Perminova, IV and Petrosyan, VS. 2000. Size-exclusion chromatographic descriptors of humic substances. Analytica Chimica Acta, 407: 193-202.

46. Beckett, R, Jue, Z and Giddings, JC. 1987. Determination of molecular weight distributions of fulvic and humic acids using flow field-flow fractionation. Environmental Science & Technology, 21(3): 289-295.

47. Amy, GL, Sierka, RA, Bedessem, J, Price, D and Tan, L. 1992. Molecular size distribution of dissolved organic matter. Journal American Water Works Association, 84(6): 67-75.

48. Peuravuori, J and Pihlaja, K. 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Analytical Chimica Acta, 337: 133-149.

49. Rook, JJ. 1977. Chlorination reactions of fulvic acids in natural waters. Environmental Science & Technology, 11(5): 478-482.

50. Schnoor, JL, Nitzschke, JL, Lucas, RD and Veenstra, JN. 1979. Trihalomethane yields as a function of precursor molecular weight. Environmental Science & Technology, 13(9): 1134-1138.

51. Oliver, BG and Thurman, EM. 1983. Influence of aquatic humic substance properties on trihalomethane potential. Water chlorination – Environmental impact and health effects, Vol.4, Book 1: Chemistry and water treatment. Ann Arbor Science, Ann Arbor, Michigan, USA.

52. Edzwald, JK, Becker, WC and Wattier, KL. 1985. Surrogate parameters for monitoring organic matter and THM precursors. Journal American Water Works Association, 77(4): 122-132.

53. Edzwald, JK and van Benschoten, JE. 1990. Aluminum coagulation of natural organic matter. Proc. 4th International Guthenburg Symposium on Chemical Treatment. Madrid, Spain, October 1990.

54. Chin, Y-P, Aiken, GR and Danielsen, KM. 1997. Binding of pyrene to aquatic and commercial humic substances: the role of molecular weight and aromaticity. Environmental Science & Technology, 31(6): 1630-1635.

55. Weishaar, JL, Aiken, GR, Bergamaschi, BA, Fram, MS, Fujii, R and Mopper, K. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science & Technology, 37(20): 4702-4708.

56. Van Benschoten, JE and Edzwald, JK. 1990. Chemical aspects of coagulation using aluminum salts – I. Hydrolytic reactions of alum and polyaluminum chloride. Water Research, 23(12): 1519-1526.

57. Hanson, AT and Cleasby, JL. 1990. The effects of temperature on turbulent flocculation: fluid dynamics and chemistry. Journal American Water Works Association, 82(11): 56-73.

58. Crozes, G, White, P and Marshall, M. 1995. Enhanced coagulation: its effect on NOM removal and chemical costs. Journal American Water Works Association, 87(1): 78-89.

59. Duan, J and Gregory, J. 2003. Coagulation by hydrolysing metal salts. Advances in Colloid and Interface Science, 100-102: 475-502.

60. Matsui, Y, Yuasa, A, Furuya, Y and Kamei, T. 1998. Dynamic analysis of coagulation with alum and PACl. Journal American Water Works Association, 90(10): 96-106.

61. Aromaa, A. Kemira Kemwater Oy Ltd. 2003. Oral communication.

62. MacKenzie, WR, Hoxie, NJ, Proctor, ME, Gradus, MS, Blair, KA, Peterson, DE, Kazmierczak, JJ, Addiss, DG, Fox, KR, Rose, JB and Davia, JP. 1994. A massive outbreak in Milwaukee of cryptosporidium infection transmitted through the public water supply. New England Journal of Medicine, 331: 161-167.

63. Bowie, WR, King, AS, Werker, DH, Isaac-Renton, JL, Bell, A, Eng, SB and Marion, SA. 1997. Outbreak of toxoplasmosis associated with municipal drinking water. Lancet, 350: 173-177.

64. Schoenen, D. 2002. Role of disinfection in suppressing the spread of pathogens with drinking water: possibilities and limitations. Water Research, 36: 3874-3888.

65. Langlais, B, Reckhow, DA and Brink, DR. 1991. Ozone in water treatment – application and engineering. Lewis Publishers Inc., Michigan, USA.

66. Chick, H. 1908. An investigation of the laws of disinfection. Journal of Hygiene, 8: 92-158.

67. Watson, HE. 1908. A note on the variation of the rate of disinfection with change in the concentration of the disinfectant. Journal of Hygiene, 8: 536.

68. Rice, RG and Gomez-Taylor, M. 1986. Occurrence of by-products of strong oxidants reacting with drinking water contaminants - scope of the problem. Environmental Health Perspectives. 69: 31-44.

69. CCC (Chlorine Chemistry Council). 2003. Drinking water chlorination. A review of disinfection practices and issues. Internet access: http://c3.org (accessed 09-01-2003)

70. Snow, J. 1855. On the mode of communication of cholera. 2nd Ed., John Churchill, London, 1855

71. Baker, MN. 1981. The quest for pure water. The history of water purification; from the earliest records to the twentieth century. 2nd ed. American Water Works Association, Denver, CO, USA.

72. Borough of Maidstone. 1898. Epidemic of typhoid fever 1897: report of an inquiry and appendices. HMSO, London, UK.

73. USEPA. 1999. Alternative disinfectants and oxidants, guidance manual. EPA 815-R-99-014, April 1999.

74. Connell, GF. 1996. The chlorination/chloramination handbook. American Water Works Association, Denver, CO, USA.

75. Jolley, RL and Carpenter, JH. 1983. A review of the chemistry and environmental faith of reactive oxidant species in chlorinated water. In: Water chlorination, Environmental impact and health effects, vol. 4, Book 1: Chemistry and water treatment. Eds. RL Jolley, WA Brungs, JA Cotruvo, RB Cumming, JS Mattice and VA Jacobs. Ann Arbor Science, Ann Arbor, Michigan, USA.

76. Wachter, JK and Aldelman, JB. 1985. Nonpurgeable organohalide formation on chlorination of algal extracellular material In: Water chlorination, Chemistry, environmental impact and health effects, vol. 5. Eds. RL Jolley, RJ Bull, WP Davis, S Katz, MH Roberts, Jr. and VA Jacobs. Lewis Publishers, Inc., Chelsea, Michigan, USA.

77. Fair, GM, Morris, JC, Chang, SL, Weil, I and Burden, RP. 1948. The behavior of chlorine as a water disinfectant. Journal American Water Works Association, 40: 1051.

78. Chang, SL. 1971. Modern concept of disinfection. Journal of the Sanitation Engineering Division, 97: 689.

79. Cowman, GA and Singer, PC. 1996. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. Environmental Science & Technology, 30(1): 16-24.

80. Ichihashi, K, Teranishi, H and Ichimura, A. 1999. Brominated trihalomethane formation in halogenation of humic acid in the coexistence of hypochlorite and hypobromite ions, Water Research, 33 (2): 477-483.

81. Chang EE, Lin, YP and Chiang, PC. 2001. Effects of bromide on the formation of THMs and HAAs. Chemosphere, 43: 1029-1034.

82. Hill, AG and Rice, RG. 1982. Historical background, properties and applications. In: Handbook of ozone technology and applications, Eds. Rip G. Rice and Aharon Netzer. Ann Arbor Science Publishers, USA, 1982, pp. 1-37. ISBN 0-250-40324-2.

83. Vosmaer, A.1916. Ozone, its manufacture, properties and uses. D. Van Nostrand Co., New York, USA.

84. Scroggins, D and Deiters, S. 1992. Selection and design considerations of diffusers, piping systems, and basin configurations producing optimum performance for the ozone treatment of drinking water. Ozone Science & Engineering, 14: 487-500.

85. Morris, JC. 1975. Aspects on the quantitative assessment of germicidal efficiency. In: Disinfection: Water and wastewater. Ed. JD Johnson. Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, USA.

86. Glaze, WH. 1987. Drinking-water treatment with ozone. Environmental Science & Technology, 21(3): 224-230.

87. von Gunten, U. 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Research, 37: 1443-1467.

88. Kinman, RN. 1975. Water and wastewater disinfection with ozone: a critical review. Critical Reviews in Environmental Control, 5: 141-152.

89. Fløgstad, H and Ødegaard, HO. 1985. Treatment of humic waters by ozone. Ozone: Science & Engineering, 7(2): 121-136.

90. Hayes, KP and Burch, MD. 1989. Odorous compounds associated with algal blooms in South Australian waters. Water Research, 23(1): 115-121.

91. Glaze, WH, Schep, R, Chauncey, W, Ruth, EC, Zarnoch, JJ, Aieta, EM, Tate, CH and McGuire, MJ. 1990. Evaluating oxidants for the removal of model taste and odor compounds from a municipal water supply. Journal American Water Works Association, 82(5): 79-84.

92. Farvardin, MR and Collins, AG. 1989. Preozonation as an aid in the coagulation of humic substances - optimum preozonation dose. Water Research, 23(3): 307-316.

93. Chang, SD and Singer, PC. 1991. The impact of ozonation on particle stability and the removal of TOC and THM precursors. Journal American Water Works Association, 83(3): 71-79.

94. Paode, RD, Chandrakanth, MS, Amy, GL, Gramith, JT and Ferguson, DW. 1995. Ozone versus ozone/peroxide induced particle destabilization and aggregation: a pilot study. Ozone: Science & Engineering, 17: 25-51.

95. Paralkar, A and Edzwald, JK. 1996. Effect of ozone on EOM and coagulation. Journal American Water Works Association, 88(4): 143-154.

96. Reckhow, DA, Legube, B and Singer, PC. 1986. The ozonation of organic halide precursors: effect of bicarbonate. Water Research, 20(8): 987-998.

97. Jacangelo, JG, Patania, NL, Reagen, KM, Aieta, EM, Krasner, SW, and McGuire, MJ. 1989. Ozonation: assessing its role in the formation and control of disinfection by-products. Journal American Water Works Association, 81(8): 74-84.

98. Miltner, RJ, Shukairy, HM and Summers, RS. 1992. Disinfection by-product formation and control by ozonation and biotreatment. Journal American Water Works Association, 84(11): 53-62.

99. Price, ML, Bailey, RW, Enos, AK, Hook, M and Hermanowicz, SW. 1993. Evaluation of ozone/biological treatment for disinfection byproducts control and biologically stable water. Ozone Science and Engineering, 15: 95-130.

100. Backlund, P. 1994. Destruction of natural mutagen and trihalomethane precursors in water by ozonation, UV-irradiation, and photolytic ozonation. Environment International, 20(1): 113-120.

101. Tuhkanen, TA, Kainulainen, TK, Vartiainen, TK and Kalliokoski, PJ. 1994. The effect of preozonation, ozone/hydrogen peroxide treatment, and nanofiltration on the removal of organic matter from drinking water. Ozone Science & Engineering. 16: 367-383.

102. Kainulainen, T, Tuhkanen, T, Vartiainen, T, Heinonen-Tanski, H and Kalliokoski, P. 1994. The effect of different oxidation and filtration processes on the molecular size distribution of humic material. Water Science & Technology, 30(9): 169-174.

103. Hoigné, J and Bader, H. 1978. Ozonation of water: kinetics of oxidation of ammonia by ozone and hydroxyl radicals. Environmental Science & Technology, 12(1): 79-84.

104. Gurol, MD and Singer, PC. 1982. Kinetics of ozone decomposition: a dynamic approach. Environmental Science & Technology, 16(7): 377-383.

105. Staehelin, J and Hoigné, J. 1985. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. Environmental Science & Technology, 19(12): 1206-1213.

106. Staehelin, J and Hoigné, J. 1982. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. Environmental Science & Technology, 16(10): 676-681.

107. Sehested, K, Holcman, J, Bjergbakke, E and Hart, EJ. 1984. Formation of ozone in the reaction of O_3^- and the decay of the ozonide ion radical at pH 10-13. Journal of Physical Chemistry, 88: 269-273.

108. Elliot, AJ and Maccracken, DR. 1989. Effect of temperature on $O^{\bullet-}$ reactions and equilibria: a pulse radiolysis study. Radiation Physics and Chemistry, 33: 69-74.

109. Hoigné, J, Bader, H, Haag, WR and Staehelin, J. 1985. Rate constants of reactions of ozone with organic and inorganic compounds in water - III inorganic compounds and radicals. Water Research, 19(8): 993-1004.

110. Tomiyasu, H, Fukutomi, H and Gordon, G. 1985. Kinetics and mechanisms of ozone decomposition in basic aqueous solution. Inorganic Chemistry, 24: 2962-2966.

111. Buxton, GV, Greenstock, CL, Helman, WP and Ross, WP. 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. Journal of Physical and Chemical Reference Data, 17: 513-886

112. Haag, WR and Hoigné, J. 1983. Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environmental Science & Technology, 17(7): 261-267.

113. Richardson, SD, Thruston Jr., AD, Caughran, TV, Chen, PH, Collette, TW, Floyd, TL, Schenk, KM, Lykins Jr, BW, Sun, G-R and Majetich, G. 1999. Identification of new ozone disinfection byproducts formed in drinking water. Environmental Science & Technology, 33(19): 3368-3377.

114. Van der Kooij, D, Hijnen, WAM and Visser, A. 1982. Determinating the concentration of easily assimilable organic carbon. Journal American Water Works Association, 74: 540-545.

115. Van der Kooij, D and Hijnen, WAM. 1984. Substrate utilization by an oxalate consuming Spirillum species in relation to its growth in ozonated water. Applied Environmental Microbiology, 47: 551-559.

116. Edwards, M and Benjamin, MM. 1992. Transformation of NOM by ozone and its effect on iron and aluminum solubility. Journal American Water Works Association, 84(6): 56-66.

117. White, GC. 1999. Handbook of chlorination and alternative disinfectants. 4th edition. Wiley, New York, USA.

118. Armesto, XL, Canle, M and Santaballa, JA. 1992. α-Amino acids chlorination in aqueous media. Tetrahedron, 49(1): 275-284.

119. Jensen, JN, St. Aubin, JJ, Christman, RF and Johnson, JD. 1985. Characterization of the reaction between monochloramine and isolated aquatic fulvic acid. In: Water chlorination, Chemistry, environmental impact and health effects, vol. 5. Eds. RL Jolley, RJ Bull, WP Davis, S Katz, MH Roberts Jr. and VA Jacobs. Lewis Publishers Inc., Chelsea, Michigan, USA.

120. Krasner, SW, McGuire, MJ, Jacangelo, JG, Patania, NL, Reagan, KM and Aieta, EM. 1989. The occurrence of disinfection by-products in US drinking water. Journal American Water Works Association, 81(8): 41-53.

121. Carlson, M and Hardy, D. 1998. Controlling DBPs with monochloroamine. Journal American Water Works Association, 90(2): 95-106.

122. Bryant, EA, Fulton, GP and Budd, GC. 1992. Disinfection alternatives for safe drinking water. New York: Van Nostrand Reinhold.

123. Norton, CD and LeChevallier, MW. 1997. Chloramination: its effect on distribution system water quality. Journal American Water Works Association, 89(7): 66-77.

124. Rennecker, JL, Kim, J-H, Corona-Vasquez, B and Mariñas, BJ. 2001. Role of disinfectant concentration and pH in the inactivation kinetics of *Cryptosporidium parvum* oocysts with ozone and monochloramine. Environmental Science & Technology, 35(13): 2752-2757.

125. Donnermair; MM and Blatchley III, ER. 2003. Disinfection efficacy of organic chloramines. Water Research, 37: 1557-1570.

126. Isaac, RA, Wajon, JE and Morris, JC. 1985. Subbreakpoint modeling of the HOBr-NH_3-Org-N reactions. In: Water chlorination, Chemistry, environmental impact and health effects, vol. 5. Eds. RL Jolley, RJ Bull, WP Davis, S Katz, MH Roberts Jr. and VA Jacobs. Lewis Publisherd Inc., Chelsea, Michigan, USA.

127. Kovacic, P, Lowery, MK and Field, KW. 1970. Chemistry of N-bromamines and N-chloramines. Chemical Reviews, 70(6): 639-665.

128. Hoffman, R and Andrews, RC. 2001. Ammoniacal bromamines: a review of their influence on bromate formation during ozonation. Water Research, 35(3): 599-604.

129. Angehrn, M. 1984. Ultraviolet disinfection of water. Aqua. No 2, pp. 109-115.

130. Parrotta, MJ and Bekdash, F. 1998. UV disinfection of small groundwater supplies. Journal American Water Works Association, 90(2): 71-81.

131. Rice, EW and Hoff, JC. 1981. Inactivation of *Giardia lamblia* cysts by ultraviolet irradiation. Applied Environmental Microbiology, 42(3): 546-547.

132. Sommer, R, Pribil, W, Appelt, S, Gehringer, P, Eschweiler, H, Leth, H, Cabaj, A and Haider, T. 2001. Inactivation of bacteriophages in water by means of non-ionizing (UV-253.7 nm) and ionizing (gamma) radiation: a comparative approach. Water Research, 35(13): 3109-3116.

133. Qualls, RG, Oddoff, SF, Chang, JCH, Dorfman, MH, Dumais, CM, Lobe, DC and Johnson, JD. 1985. Factors controlling sensitivity in ultraviolet disinfection of secondary effluents. Journal of the Water Pollution Control Federation 57(10), 1006-1011.

134. Bolton, JR. 2000. Calculation of ultraviolet fluence rate distributions in an annular reactor: significance of refraction and reflection. Water Research, 34(13): 3315-3324.

135. Jolley, RL, Cumming, RB, Lee, NE, Lewis, LR, Thompson, JE and Mashni, CI. 1983. Nonvolatile organics in disinfected wastwater effluents: chemical characterization. In: Water chlorination, Chemistry, environmental impact and health effects, vol. 4, Book1. Eds. RL Jolley, WA Brungs, JA Cotruvo, RB Cumming, JS Mattice and VA Jacobs. Ann Arbor Science, Ann Arbor, Michigan, USA.

136. Kool, HJ, van Kreijl, CF and Hrubec, J. 1985. Mutagenic and carcinogenic properties of drinking water. In: Water chlorination, Chemistry, environmental impact and health effects, vol. 5. Eds. RL Jolley, RJ Bull, WP Davis, S Katz, MH Roberts Jr. and VA Jacobs. Lewis Publishers Inc., Chelsea, Michigan, USA.

137. Glaze, WH, Kang, J-W and Chapin, DH. 1987. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Science & Engineering, 9: 335-352.

138. Munter, R, Preis, S, Kallas, J, Trapido, M and Veressinina, Y. 2001. Advanced oxidation processes (AOPs): water treatment technology for the twenty-first century. Kemia-Kemi, 28(5): 354-362.

139. Guzzella, L, Feretti, D and Monarca, S. 2002. Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply. Water Research, 36(17): 4307-4318.

140. Hernandez, R, Zappi, M, Colucci, J and Jones, R. 2002. Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water. Journal of Hazardous Materials, 2789: 1-18.

141. Beltrán, F, Acedo, B and Rivas, J. 1999. Use of ozone and hydrogen peroxide to remove alachlor from surface water. Bulletin of Environmental Contamination and Toxicology, 63: 9-14.

142. Acero, JL, Haderlein, SH, Schmidt, T, Suter, MJF and von Gunten, U. 2001. MTBE oxidation by conventional ozonation and the combination ozone/hydrogen peroxide: efficiency of the process and bromate formation. Environmental Science & Technology, 35: 4252-4259.

143. Huber, MM, Canonica, S, Park, G-Y and von Gunten, U. 2003. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environmental Science & Technology, 37(5): 1016-1024.

144. Volk, C, Renner, C, Roche, P, Paillard, H and Joret, JC. 1993. Effects of ozone-hydrogen peroxide combination on the formation of biodegradable dissolved organic carbon. Ozone Science & Engineering, 15: 405-418.

145. Carr, SA and Baird, RB. 2000. Mineralization as a mechanism for TOC removal: study of ozone/ozone-peroxide oxidation using FT-IR. Water Research, 34(16): 4036-4048.

146. Speitel Jr., GE, Symons, JM, Mialaret, JM and Wanielista, MME. 2000. AOP/biofilm processes for DOX precursors. Journal American Water Works Association, 92(10): 59-73.

147. McGuire, MJ and Davis, MK. 1988. Treating water with peroxone: a revolution in the making. Water Engineering and Management, 135: 42-49.

148. Wolfe, RL, Stewart, MH, Scott, KN and McGuire, MJ. 1989. Inactivation of *Giardia muris* and indicator organisms seeded in surface water supplies by PEROXONE and ozone. Environmental Science & Technology, 23(6): 744-745.

149. Duguet, JP, Brodard, E, Dussert, B and Mallevialle, J. 1985. Improvement in the effectiveness of ozonation of drinking water through the use of hydrogen peroxide. Ozone Science & Engineering, 7: 241-258.

150. von Gunten, U, Bruchet, A and Constentin, E. 1996. Bromate formation in advanced oxidation processes. Journal American Water Works Association, 88(6): 53-65.

151. Yahya, MT, Landeen, LK and Gerba, CP. 1990. Inactivation of *Legionella pneumophila* by potassium permanganate. Environmental Technology, 11: 657-662.

152. Knocke, WR, Van Benschoten, JE, Kearney, MJ, Soborski, AW and Reckhow, DA. 1991. Kinetics of manganese and iron oxidation by potassium permanganate and chlorine dioxide. Journal American Water Works Association, 83(6): 80-87.

153. Singer, PC, Borchardt, JH, and Colthurst, JM. 1980. The effects of permanganate pretreatment on trihalomethane formation in drinking water. Journal American Water Works Association, 72(10): 573-578.

154. Colthurst, JM and Singer, PC. 1982. Removing trihalomethane precursors by permanganate and manganese dioxide adsorption. Journal American Water Works Association, 74(2): 78-83.

155. Vartiainen, T, Liimatainen, A, Keränen, P, Ala-Peijari, T and Kalliokoski, P. 1987. Effect of permanganate oxidation and chlorination of the mutagenic activity and other quality parameters of artificially recharged ground water processed from humus-rich surface water. Chemosphere, 16(7): 1489-1499.

156. Rook, JJ. 1974. Formation of haloforms during chlorination of natural waters. Water Treatment and Examination, 23: 234-243.

157. Sweetman, JA and Simmons, MS. 1980. The production of bromophenols resulting from the chlorination of waters containing bromide ion and phenol. Water Research, 14: 287-290.

158. Glaze, WH. 1986. Reaction products of ozone: a review. Environmental Health Perspectives, 69: 151-157.

159. Glaze, WH, Koga, M, and Cancilla, D. 1989. Ozonation by-products. 2. Improvement of an aqueous-phase derivatization method for the detection of formaldehyde and other carbonyl compounds formed by the ozonation of drinking water. Environmental Science & Technology, 23(7): 838-847.

160. Reckhow, DA, Singer, PC and Malcolm, RL. 1990. Chlorination of humic materials: byproduct formation and chemical interpretations. Environmental Science & technology, 24(11): 1655-1664.

161. Cavanagh, JE, Winberg, HS, Gold, A, Sangalah, R, Marbury, D, and Glaze, WH. 1992. Ozonation byproducts: identification of bromohydrins from the ozonation of natural waters with enhanced bromide levels. Environmental Science & Technology, 26(8): 1658-1662.

162. Trussell, RR. 1993. Treatment for the control of disinfectant residuals and disinfection by-products. In: Safety of water disinfection: Balancing chemical & microbial risks. Ed. Gunther F. Graun. ILSI Press, Washington, D.C., USA.

163. Peters, RJB, de Leer, EWB and Versteegh, JFM. 1994. Identification of halogenated compounds produced by chlorination of humic acid in the presence of bromide. Journal of Chromatography A, 686: 253-261.

164. Heller-Grossman, L, Idin, A, Limoni-Relis, B and Rebhun, M. 1999. Formation of cyanogen bromide and other volatile DBPs in the disinfection of bromide-rich lake water. Environmental Science & Technology, 33(6): 932-937.

165. Richardson, SD, Thruston Jr., AD, Caughran, TV, Chen, PH, Collette, TW, Floyd, TL, Schenk, KM, Lykins Jr, BW, Sun, G-R and Majetich, G. 1999. Identification of new drinking water disinfection by-products formed in the presence of bromide. Environmental Science & Technology, 33(19): 3378-3383.

166. Zhang, X, Echigo, S, Minear, RA and Plewa, MJ. 2000. Characterization and comparison of disinfection by-products of four major disinfectants. In: Natural organic matter and disinfection by-products: characterization and control in drinking water. Eds. S.E. Barrett, S.W. Krasner and G.L. Amy. American chemical Society, Washington, D.C., USA.

167. Richardson, SD. 2003. Water analysis: emerging contaminants and current issues. Analytical Chemistry, 75(12): 2831-2857.

168. Richardson, SD, Thruston Jr., AD, Rav-acha, C, Groisman, L, Popilevsky, I, Juraev, O, Glezer, V, McKague, AB, Plewa, MJ and Wagner, ED. 2003. Tribromopyrrole, brominated acids, and other disinfection by-products produced by disinfection of drinking water rich in bromide. Environmental Science & Technology, 37(17): 3782-3793.

169. Ozekin, K and Amy, GL. 1997. Threshold levels for bromate formation in drinking water. Ozone: Science & Engineering, 19: 232-337.

170. Lefebvre, E, Racaud, P, Parpaillon, Th and Deguin, A. 1995. Results of bromide and bromate monitoring at several water treatment plants. Ozone Science & Engineering, 17: 311-327.

171. Legube, B, Koudjonou, BK, Croué, JP and Merlet, N. 1995. Influence of the presence of natural organic matter on bromate formation by ozonation. Water Supply. 13: 51-59.

172. Bolyard, M, Snyder Fair, P and Hautman, DP. 1992. Occurrence of chlorate in hypochlorite solutions used for drinking water disinfection. Environmental Science & Technology, 26(8): 1663-1665.

173. Weinberg, HA, Delcomyn, CA and Unnam, V. 2003. Bromate in chlorinated waters: occurrence and implications for future regulation. Environmental Science & Technology, 37(14): 3104-3110.

174. Richardson, LB, Burton, DT, Helz, GR and Rhoderick, JC. 1981. Residual oxidant decay and bromate formation in chlorinated and ozonated sea-water. Water Research, 15: 1067-1074.

175. Bousher, A, Bimblecombe, P and Midgley, D. 1990. Bromate production in chlorinated waters: reaction of monochloramine and hypobromite, Water Research, 24(10): 1285-1294

176. Siddiqui, M, Amy, G, Ozekin, K, Zhai, W and Westerhoff, P. 1994. Alternative strategies for removing bromate. Journal American Water Works Association, 86(10): 81-96.

177. Song, R, Minear, R, Westerhoff, P and Amy, G. 1996. Modeling and risk analysis of bromate formation from ozonation of bromide-containing waters. Water Science and Technology, 34(7-8): 79-85.

178. Song, R, Donohoe, C, Minear, R, Westerhoff, P, Ozekin, K and Amy, G. 1996. Empirical modeling of bromate formation during ozonation of bromide-containing waters. Water Research, 30(5): 1161-1168.

179. Uhl, W and Gimbel, R. 1998. Modeling the formation of bromate during ozone-disinfection of drinking-water in different type reactors. Conference preprint: Specialized Conference on Drinking Water Distribution With or Without Disinfectant Residual; Mülheim an der Ruhr, Germany.

180. Westerhoff, P, Amy, GL, Song, R and Minear, RA. 1996. Simplifying bromate formation kinetic analysis with a linear bromate yield concept. In: Water Disinfection and Natural Organic Matter, Chapter 18, eds. Roger A. Minear and Gary L. Amy, American Chemical Society, Washington, D.C., USA.

181. Siddiqui, MS, Amy, GL and Rice, RG. 1995. Bromate ion formation: a critical review. Journal American Water Works Association, 87(10): 58-70.

182. Taube, H. 1942. Reactions of solutions containing O_3, H_2O_2, H^+ and Br^-. The specific rate of the reaction O_3+Br^-. Journal of the American Chemical Society, 64: 2468-2474.

183. von Gunten, U and Hoigné, J. 1994. Bromate formation during ozonation of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. Environmental Science & Technology, 28: 1234-1242.

184. Nicoson, JS, Wang, L, Becker, RH, Huff Hartz, KE, Muller, CE and Margerum, DW. 2002. Kinetics and mechanisms of the ozone/bromide and ozone/chlorite reactions. Inorganic Chemistry, 41: 2975-2980.

185. Klaening, UK and Wolff, T. 1985. Laser flash photolysis of HClO, ClO^-, HBrO, and BrO^-, in aqueous solution. Reaction of Cl^- and Br^- atoms. Berichte der Bunsen-Gesellschaft - Physical Chemistry Chemical Physics, 89: 243-245.

186. von Gunten, U and Oliveras, Y. 1998. Advanced oxidation of bromide-containing waters: bromate formation mechanisms. Environmental Science & Technology, 32: 63-70.

187. Najm, IN and Krasner, SW. 1995. Effects of bromide and NOM on by-product formation. Journal American Water Works Association, 87(1): 106-115.

188. Song, R, Minear, R, Westerhoff, P and Amy, G. 1996. Bromate formation and control during water ozonation. Environmental Technology, 17: 861-868.

189. Song, R, Westerhoff, P, Minear, R and Amy, G. 1997. Bromate minimization during ozonation. Journal American Water Works Association, 89(6): 69-78.

190. Hijnen, WAM, Jong, R and van der Kooij, D. 1999. Bromate removal in a denitrifying bioreactor used in water treatment. Water Research, 33(4): 1049-1053.

191. Mills, A, Belghazi, A and Rodman, D. 1996. Bromate removal from drinking water by semiconductor photocatalysis. Water Research, 30(9): 1973-1978.

192. Krasner, SW, Glaze, WH, Weinberg, HS, Daniel, PA and Najm, IN. 1993. Formation and control of bromate during ozonation of waters containing bromide. Journal American Water Works Association, 85(1): 73-81.

193. Roustan, M, Dugiet, J-P, Lainé, J-M, Do-Quang, Z and Mallevialle, J. 1996. Bromate ion formation: impact of ozone contactor hydraulics and operating conditions. Ozone Science & Engineering, 18: 87-97.

194. Siddiqui, M, Amy, G, Ozekin, K and Westerhoff, P. 1994. Empirically and theoretically-based models for predicting brominated ozonated by-products. Ozone & Science Engineering, 16: 157-178.

195. Bao, ML, Griffini, O, Santianni, D, Barbieri, K, Burrini, D and Pantani, F. 1999. Removal of bromate ions from water using granular activated carbon. Water Research, 33: 2959-2970.

196. Kirisits, MJ, Snoeyink, VL and Kruithof, JC. 2000. The reduction of bromate by granular activated carbon. Water Research, 34(17): 4250-4260.

197. Gordon, G, Gauq, RD, Emmert, GL, Walters, BD and Bubnis, B. 2002. Chemical reduction methods for bromate ion removal. Journal American Water Works Association, 94(2): 91-98.

198. Bellar, TA, Lichtenberg, JJ and Kroner, RC. 1974. The occurrence of organohalides in chlorinated drinking water. Journal American Water Works Association, 66(12): 703-706.

199. Pomes, ML, Larive, CK, Thurman, EM, Green, WR, Orem, WH, Rostad, CE, Coplen, TB, Cutak, BJ and Dixon, AM. 2000. Sources and haloacetic acid/trihalomethane formation potentials of aquatic humic substances in the Wakarusa River and Clinton Lake near Lawrence, Kansas. Environmental Science & Technology, 34(20): 4278-4286.

200. Peters, CJ, Young, RJ and Perry, R. 1980. Factors influencing the formation of haloforms in the chlorination of humic materials. Environmental Science & Technology, 14(11): 1391-1395.

201. Amy, GL, Collins, MR, Kuo, CJ and King, PH. 1987. Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. Journal American Water Works Association, 79(1): 43-49.

202. Morrow, CM and Minear, RA. 1987. Use of regression models to link raw water characteristics to trihalomethane concentrations in drinking water. Water Research, 21(1): 41-48.

203. Garcia-Villanova, RJ, Garcia, C, Gomez, JA, Garcia, MP and Ardanuy, R. 1997. Formation, evolution and modeling of trihalomethanes in the drinking water of a town: I. At the municipal treatment utilities. Water Research, 31(6): 1299-1308.

204. Golfinopoulos, SK, Xilourgidis, NK, Kostopoulou, MN and Lekkas, TD. 1998. Use of a multiple regression model for predicting trihalomethane formation. Water Research, 32(9): 2821-2829.

205. Ivancev-Tumbas, I, Dalmacija, B, Tamas, Z and Karlovic, E. 1999. The effect of different drinking water treatment processes on the rate of chloroform formation in the reactions of natural organic matter with hypochlorite. Water Research, 33(18): 3715-3722.

206. Nokes, CJ, Fenton, E and Randall, CJ. 1999. Modelling the formation of brominated trihalomethanes in chlorinated drinking waters. Water Research, 33(7): 3557-3568.

207. Elshorbagy, WE, Abu-Qdais, H and Elsheamy, MK. 2000. Simulation of THM species in water distribution systems. Water Research, 34(13): 3431-3439.

208. Gang, DD, Segar Jr., RL, Clevenger, TE and Banerji, SK. 2002. Using chlorine demand to predict THM and HAA9 formation. Journal American Water Works Association, 94(10): 76-86.

209. Golfinopoulos, SK and Arhonditsis, GB. 2002. Multiple regression models: a methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics. Chemosphere, 47: 1007-1018.

210. Miles, AM, Singer, PC, Ashley, DL, Lynberg, MC, Mendola, P, Langlois, PH and Nuckols, JR. 2002. Comparison of trihalomethanes in tap water and blood. Environmental Science & Technology, 36(8): 1692-1698.

211. Nissinen, TK, Miettinen, IP, Martikainen, PJ and Vartiainen, T. 2002. Disinfection by-products in Finnish drinking waters. Chemosphere, 48(1): 9-20.

212. Rebhun, M, Manka, J, and Zilberman, A. 1988. Trihalomethane formation in high-bromide Lake Galilee water. Journal American Water Works Association 80(6): 84-89.

213. Heller-Grossman, L, Manka, J, Limoni-Relis, B, and Rebhun, M. 1993. Formation and distribution of haloacetic acids, THM and TOX in chlorination of bromide-rich lake water. Water Research, 27(8): 1323-1331.

214. Luong, TV, Peters, CJ and Perry, R. 1982. Influence of bromide and ammonia upon the formation of trihalomethanes under water-treatment conditions. Environmental Science & Technology, 16: 473-479.

215. Amy, GL, Tan, L and Davis, MK. 1991. The effects of ozonation and activated carbon adsorption on trihalomethane speciation. Water Reasearch, 25(2): 191-202.

216. Chellam, S. 2000. Effects of nanofiltration on trihalomethane and haloacetic acid precursor removal and speciation in waters containing low concentrations of bromide ion. Environmental Science & Technology, 34(9): 1813-1820.

217. Meier, JR, Ringhand, HP, Coleman, WE, Schenk, KM, Munch, JW, Streicher, RP, Kaylor, WH and Kopfler, FC. 1986. Mutagenic by-products from chlorination of humic acid. Environmental Health Perspectives, 69: 101-107.

218. Kargalioglu, Y, McMillan, BJ, Minear, RA and Plewa, MJ. 2002. Analysis of the cytotoxicity and mutagenicity of drinking water disinfection by-products in *Salmonella typhimurium*. Teratogenesis, Carcinogenesis, and Mutagenesis, 22: 113-128.

219. Palacios, M, F.-Pampillón, J, and Rodriguez, ME. 2000. Organohalogenated compounds levels in chlorinated drinking waters and current compliance with quality standards throughout the European Union. Water Research, 34(3): 1002-1016.

220. Stack, MA, Fitzgerald, G, O•Connell, S and James, KJ. 2000. Measurement of trihalomethanes in potable and recreational waters using solid phase micro extraction with gas chromatography-mass spectrometry. Chemosphere, 41: 1821-1826.

221. El-Shafy, MA and Grünwald, A. 2000. THM formation in water supply in South Bohemia, Czech Republic, Water Research, 34(13): 3453-3459.

222. Golfinopoulos, SK. 2000. The occurrence of trihalomethanes in the drinking water in Greece. Chemosphere, 41: 1761-1767.

223. Villanueva, CM, Kogevinas, M and Grimalt, JO. 2003. Haloacetic acids and trihalomethanes in finished drinking waters from heterogeneous sources. Water Research, 37: 953-958.

224. Williams, DT, LeBel, GL, and Benoit, FM. 1997. Disinfection by-products in Canadian drinking water. Chemosphere, 34(2): 299-316.

225. Sérodes, J-B, Rodriguez, MJ, Li, H and Bouchard, C. 2003. Occurrence of THMs and HAAs in experimental chlorinated waters of the Quebec City area (Canada). Chemosphere, 51: 253-263.

226. Arora, H, LeChevallier, MW and Dixon, KL. 1997. DBP occurrence survey. Journal American Water Works Association, 89(6): 60-68.

227. Wright, JM, Schwartz, J, Vartiainen, T, Mäki-Paakkanen, J, Altshui, L, and Dockery, DW. 2002. Mutagenic compounds in Massachusetts• drinking water. Environmental Health Perspectives, 110(2): 157-164.

228. Singer, PC, Obolensky, A, and Greiner, A. 1995. DBPs in chlorinated North Carolina drinking waters. Journal American Water Works Association, 87(10): 83-92.

229. Nieminski, EC, Chaudhuri, S, and Lamoreaux, T. 1993. The occurrence of DBPs in Utah drinking waters. Journal American Water Works Association, 85(8): 98-105.

230. Simpson, KL and Hayes, KP. 1998. Drinking water disinfection by-products: and Australian perspective. Water Research, 32(5): 1522-1528.

231. Yoon, J, Choi, Y, Cho, S and Lee, D. 2003. Low trihalomethane formation in Korean drinking water. The Science of the Total Environment, 302: 157-166.

232. Duong, HA, Berg, M, Hoang, MH, Pham, HV, Gallard, H, Giger, W and von Gunten, U. 2003. Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam. Water Research, 37: 3242-3252.

233. Amy, GL, Chadik, PA and King, PH. 1984. Chlorine utilization during trihalomethane formation in the presence of ammonia and bromide. Environmental Science & Technology, 18: 781-786.

234. Liang, L and Singer, PC. 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. Environmental Science & Technology, 37(13): 2920-2928.

235. Glaze, WH, Peyton, GR, Lin, S, Huang, RY and Burleson, JL. 1982. Destruction of pollutants with ozone in combination with ultraviolet radiation. 2. Natural trihalomethane precursors. Environmental Science & Technology, 16(8): 454-458.

236. Galapate, RP, Baes, AU and Okada, M. 2001. Transformation of dissolved organic matter during ozonation: effects on trihalomethane formation potential. Water Research, 35(9): 2201-2206.

237. El-Rehaili, AM and Weber Jr, WJ. 1987. Correlation of humic substance trihalomethane formation potential and adsorption behavior to molecular weight distribution in raw and chemically treated waters. Water Research, 21(5): 573-582.

238. Bolto, B, Dixon, D, Eldridge, R, King, S. 2002. Removal of THM precursors by coagulation or ion exhange. Water Research, 36: 5066-5073.

239. Page, DW, van Leeuwen, JA, Spark, KM, Drikas, M, Withers, N and Mulcahy, DE. 2002. Effect of alum treatment on the trihalomethane formation and bacterial regrowth potential of natural and synthetic waters. Water Research, 36: 4884-4892.

240. Gehr, R, Swartz, C and Offringa, G. 1993. Removal of trihalomethane precursors from eutrophic water by dissolved air flotation. Water Research, 27(1): 41-49.

241. Maron, DM and Ames, BN 1983. Revised methods for the Salmonella mutagenicity test. Mutation Research, 113: 173-215.

242. Noot, DK, Anderson, WB, Daignault, SA, Williams, DT and Huck, PM. 1989. Evaluating treatment processes with the Ames mutagenicity assay. Journal American Water Works Association, 81(9): 87-102.

243. DeMarini, DM, Abu-Shakra, A, Felton, CF, Patterson, KS and Shelton, ML. 1995. Mutation spectra in Salmonella of chlorinated, chloraminated, or ozonated drinking water extracts: comparison to MX. Environmental and Molecular Mutagenesis, 26(4): 270-285.

244. Bartsch, H and Malaveille, C. 1987. The Ames test. ISI: Atlas of Science: Pharmacology. Institute for Scientific Information, Philadelphia, USA.

245. Holmbom, B.R., Voss, R.H., Mortimer, R.D. and Wong, A. 1981. Isolation and identification of an Ames-mutagenic compound present in kraft chlorination effluents. Tappi, 64(3): 172-174.

246. Smeds, A, Vartiainen, T, Mäki-Paakkanen, J and Kronberg, L. 1997. Concentrations of Ames mutagenic chlorohydrofuranones and related compounds in drinking waters. Environmental Science & Technology, 31(4): 1033-1039.

247. Meier, JR, Knohl, RB, Coleman, WE, Ringhand, HP, Munch, JW, Kaylor, WH, Streicher, RP and Kopfler, FC. 1987. Studies on the potent bacterial mutagen, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone: aqueous stability, XAD recovery and analytical determination in drinking water and in chlorinated humic acid solutions. Mutation Research, 189: 363-373.

248. Lloveras, M, Ramos, I, Molins, E and Messeguer, A. 2000. Improved synthesis of three brominated analogues of the potent mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX). Tetrahedron, 56: 3391-3397.

CHAPTER 2: MOLECULAR SIZE FRACTIONS OF TREATED AQUATIC HUMUS

T. Myllykangas*[1], T.K. Nissinen[1], P. Rantakokko[1], P.J. Martikainen[2] and T. Vartiainen[1,2]

[1]National Public Health Institute, Division of Environmental Health, P.O. Box 95, FIN-70701 Kuopio, Finland
[2]University of Kuopio, Department of Environmental Sciences, P.O. Box 1627, FIN-70211 Kuopio, Finland
*The corresponding author. [Email: Tiia.Myllykangas@ktl.fi, tel. +358 17 201 181, fax. +358 17 201 265]

Published in Water Research, 36(12), 3045-3053 (2002).
Reproduced here with kind permission from Elsevier.

1. ABSTRACT

The effects of ozone, chlorine, hydrogen peroxide, and permanganate on the aquatic humic matter with different molecular size fractions and the organic acid formation in drinking water treatment were studied. Aquatic humus in lake water (LW), artificially recharged groundwater (AW), and purified artificially recharged groundwater (PW) were fractionated by high-pressure size-exclusion chromatography (HP-SEC) with UV-254 nm detection before and after oxidation, a technique which resulted generally in seven peaks. The sum of the molecular size fractions (SMSF) of the LW was reduced by 47% during the bankfiltration process, and the SMSF of the AW was reduced by 55% during the process in the water treatment plant. The oxidation of the AW resulted in reductions in the range of 18 to 35% of the SMSF; the respective range of the PW was 15 to 69%. However, the content of the total organic carbon (TOC) reduced only slightly, and a high correlation between the TOC and the SMSF (0.911) was observed in the whole material. The greatest decreases appeared in the highest-molecular-weight fractions while the low-molecular-weight fractions remained nearly unchanged. The total content of the six organic small-molecular-weight acids (SOA) (formate, acetate, propionate, pyruvate, oxalate, and citrate) varied between 0.1-5.1% and 0.1-9.7% of the reduced TOC in the AW and the PW, respectively. The formation of the SOA, especially of oxalate, was the greatest after hydrogen peroxide combined with ozonation (as much as 1100 μg/L), while chlorination resulted in the SOA of less than 50 μg/L.

Key words: Ozonation, chlorination, aquatic humus, molecular size distribution, organic acids, drinking water

2. INTRODUCTION

Humic substances in water reacts with oxidative chemicals and results in undesired by-products (for example during the disinfection process). The oxidized material then represent nutrients for microbes in water distribution systems. These are the main reasons for the removal of the humic substances from drinking water. Humic substances are ubiquitous in all surface waters, especially in boreal regions. The production of artificially recharged groundwater is an effective technique to remove humus from the surface water. Depending on the technique used, the water still contains humus and, hence, needs further purification. Some of the humus is removed in the waterworks by flocculation and sedimentation after precipitation, but the rest should be removed by other methods, such as oxidation, before releasing the water to the distribution system. Changes in aquatic humus have been shown to cause changes in reactivity[1], the formation potential of disinfection by-products[2-4], and microbially available carbon[5].

The total amount of aquatic humus (total organic carbon, TOC) is analyzed by burning the organic matter in the water sample to CO_2, which is then analyzed by an infrared analyzer. If one wishes details on the structure of the extremely complex humus matter there are many techniques, for example ultra filtration[6,7], membrane filtration[8], biofiltration[9], acidity measurement[10], measurement of the degree of aromaticity[11,12], and different chromatographic[6,12,13] and mass-spectrometric techniques[14] which can be employed. The acidic character and strong UV-absorbance of humus can be used for quantification. One highly visual method to analyze changes in the quality and quantity of the aquatic humus is to measure the molecular size distribution by high-pressure size-exclusion chromatography (HP-SEC) and UV-detection[12,13,15]. However, HP-SEC is not effective for the analyses of small-molecular-weight (acidic) compounds, which are possible degradation products of humus[16]. If also small organic carboxylic acids are measured in addition to the HP-SEC fractions, it is possible to achieve a reasonably detailed knowledge of the changes in the quality of humus.

We studied the effect of chlorine, ozone, hydrogen peroxide, and permanganate on the molecular size distribution of the aquatic humus and the formation of organic acids in artificially recharged groundwater and in further purified water.

3. MATERIALS AND METHODS

3.1 WATER USED IN THE EXPERIMENTS

The water used in the experiments was artificially recharged groundwater (AW) made from Lake Kallavesi by bank filtration[17]. The AW was further processed by coagulation (with $Al_2(SO_4)_3$), flotation, and sand filtration in the Kuopio waterworks to produce purified water (PW).

3.2 EXPERIMENTAL PROCEDURES

The treatment train of our study is described in Fig. 2-1. The water was treated either during the fall 1998 or the summer 1999. Both the AW and the PW were treated using four different chemical oxidative agents partly alone or in combination (chlorine, ozone, ozone followed by chlorine, hydrogen peroxide with ozone and chlorine, and permanganate plus chlorine). The PW was ozonated also at three different pH values, four different alkalinities and two different temperatures. Chemicals and doses for different tests were selected to simulate current practice at full-scale treatment plants.

Chlorination. The pH of the water (15 L) was adjusted to 8.5 with 1M $Ca(OH)_2$ solution before the chlorination. The desired NaOCl-dose was Cl_2:TOC = 1:3, except for the second ozone-chlorine experiment (Table 2-II). The residual chlorine concentration was measured after one hour, and the samples were taken after 96 hours of reaction time at 4 °C.

Ozonation. The ozonation was carried out with a pilot-plant consisting of an ozone generator, a column (18 L), a water pump, analyzers for dissolved and gaseous ozone, and computer programs for recording the data[18].

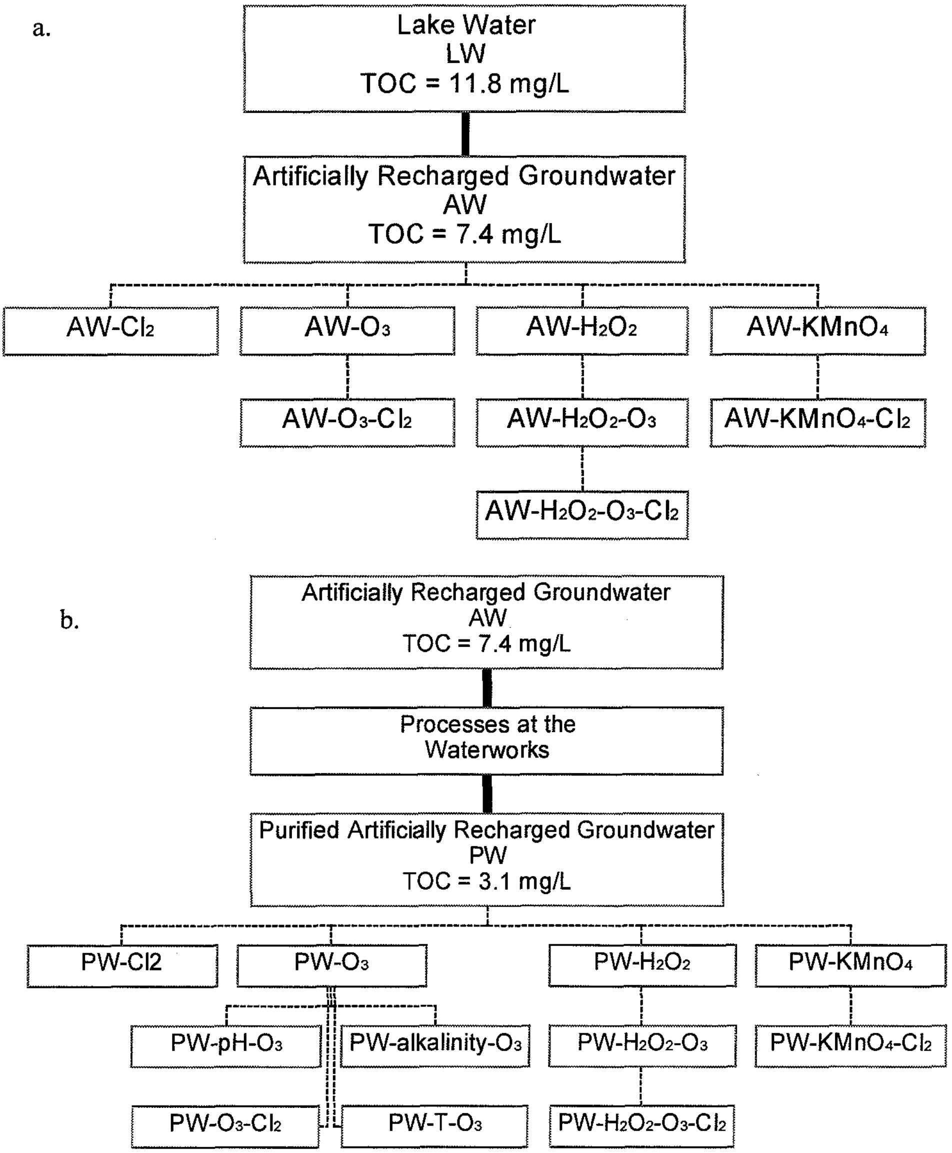


Figure 2-1. The treatment train of the water used in the experiments. The treatment of (a) the artificially recharged groundwater (AW) and (b) the purified artificially recharged groundwater (PW). Both figures: Cl_2 = chlorination; O_3 = ozonation; H_2O_2 = hydrogen peroxide addition; $KMnO_4$ = oxidation; T = higher temperature; pH = higher pH; and alkalinity = higher alkalinity.

Hydrogen peroxide. The appropriate amount of hydrogen peroxide was added to the water before ozonation. The ratio was calculated as mg H_2O_2/mg O_3. The concentration of the H_2O_2 was measured by a titration method[19].

Potassium permanganate was added to the water three hours before chlorination. The $KMnO_4$/Mn ratios used were 2, 3, and 4.

Alkalinity was adjusted with either 1 M $CaCO_3$ or 1 M $NaHCO_3$ solution, and it was measured according to the Finnish Standard SFS 3005 [20].

TOC was measured according to the Finnish Standard SFS-EN 1484 [21].

HP-SEC method. Molecular size distribution of organic matter was measured by the method of Vartiainen and co-workers[13]: HP-SEC using a TSK G3000SW column (7.5 mm × 30 cm; pre-column TSK SW, 7.5 mm × 7 cm) with UV-detection at 254 nm with sodium acetate buffer (pH 7) as the eluent. The sum of the molecular size fractions (SMSF) was calculated as the sum of the peak areas (expressed as absorption units × seconds, AU×s). The calibration of the HP-SEC system has been presented earlier[12,13].

Organic acids. The organic acids measured were formate, acetate, propionate, pyruvate, oxalate and citrate. The sum of organic acids (SOA) was calculated. The measurements were conducted with series 4000 I ion chromatography (IC) instrument (Dionex, Sunnywale, CA, USA) with the Ionpac AG11-HC Guard Column (4×50 mm), and Ionpac AS11-HC Analytical Column (4×250 mm). Anion Trap Column (ATC-1) was used for eluent clean up. An On-Guard H^+ cartridge was installed on-line between the autosampler and the sample loop (392 μL). The self-regenerating suppressor was ASRS-ULTRA (4-mm). As a preservative, 0.2% (v/v) $CHCl_3$ was added to the samples before analyzing. The IC run program consisted of equilibration (1 mM NaOH for 9 min), injection, isocratic analysis (1 mM NaOH for 8 min), and three gradient phases (from 1 to 15 mM NaOH during the following 10 min, from 15 to 30 mM NaOH during the next 10 min, and from 30 to 60 mM NaOH during the last 10 min). The eluent flow rate was 1.5 ml/min. The sample was loaded to the sample loop with a flow of 1 mL/min during the equilibration period. The limits of quantitation for the organic acids studied were (calculated as 10 times the standard deviation of 6 replicates of a low concentration standard): formate 5.9 μg/L, acetate 8.7 μg/L, propionate 4.0 μg/L, pyruvate 6.4 μg/L, oxalate 3.7 μg/L, and citrate 7.8 μg/L.

4. RESULTS

Table 2-I lists the characteristic values of the lake water (LW), artificially recharged groundwater (AW), and purified artificially recharged groundwater (PW) before the oxidation. Up to seven molecular-size fractions were observed from the HP-SEC grams; the largest fractions eluted first and the smallest last (Fig. 2-2). The long-time average values of the TOC concentrations from the waterworks of Kuopio are (average ± standard deviation): LW 11.8 ± 1.4 mg/L, AW 7.4 ± 1.5 mg/L, and PW 3.1 ± 0.5 mg/L. The bank filtration process from the LW to the AW decreased the sum of the molecular size fractions (SMSF) by 47%, and the process at the waterworks from the AW to the PW resulted in a reduction of the SMSF (r-SMSF) of 55%. The sum of the organic acids (SOA), as the total concentration of the compounds, was 40 μg/L in the AW, and 20 μg/L in the PW. Our chemical experiments reduced the TOC levels of the AW and the PW slightly (Table 2-II). The oxidation methods decreased mostly the high-molecular-weight fractions measured by HP-SEC and increased the concentrations of oxalate, acetate, and formate (Fig. 2-3; Table 2-II).

4.1 CHLORINATION

Chlorination alone reduced the SMSF of the AW and the PW by approximately one third, while the SOA increased from 20 and 40 μg/L to 91 and 166 μg/L of the PW and the AW, respectively (Table 2-II). The r-SMSF of the AW was greater than that of the PW.

4.2 OZONATION

Ozonation had a great effect on the humus fractions though it virtually had no effect on the TOC content (Table 2-II). However, ozonation of the AW did not enhance the r-SMSF as compared to chlorination, while the r-SMSF of the PW increased. The SOA increased significantly during ozonation as compared to chlorination alone (Fig. 2-3, Table 2-II). As the ozone dosage increased (from $[O_3]$ = 2.6 mg/L to 3.3. 4.8, 6.3, and 12.3 mg/L), the SOA of the PW increased from 373 to 512 μg/L.

Table 2-I. The peak areas and their reductions obtained from size exclusion analysis. SMSF = sum of the molecular size fractions (expressed as AU×s; see caption to Fig. 2-2). Reductions [red-%] are expressed as percents as compared the AW to the LW, and the PW to the AW.

	Lake water	Artificially recharged groundwater [red-%]	Purified water [red-%]
Peak1	57 800	15 000 [74]	1 100 [93]
Peak2	54 200	23 700 [56]	2 400 [90]
Peak3	79 700	41 100 [48]	10 600 [74]
Peak4	81 400	47 700 [41]	26 400 [45]
Peak5	56 000	35 300 [37]	27 200 [23]
Peak6	26 900	22 000 [18]	16 000 [27]
Peak7	6 700	7 000 [+4]	2 800 [60]
SMSF	363 000	192 000 [47]	86 500 [55]

4.3 CHLORINATION AFTER OZONATION

Chlorination after ozonation did not cause any further reduction of the SMSF of the AW as compared to chlorination or ozonation alone, but the r-SMSF of the PW increased by 10%. When the ozone and chlorine dosages of the PW doubled, the r-SMSF increased by 15%. The results suggest that as much as one fourth (22%) of the r-SMSF could be accounted for by the small-molecular-weight acids (953 μg/L) (Table 2-II).

4.4 OZONATION PH, ALKALINITY AND TEMPERATURE

An increase in the ozonation pH increased the r-SMSF, while the SOA remained at the same level as the unadjusted pH. An increase in the alkalinity before ozonation did not affect the r-SMSF, but the SOA decreased slightly. An increase in the ozonation temperature increased the r-SMSF significantly. The increase of the SOA was not as significant (Table 2-II). Ozonation at a lower dose (3.3 mg/L) at the elevated temperature increased both the r-SMSF and the SOA as compared to ozonation at the ambient temperature even at the highest applied (12.3 mg/L) ozone dose.

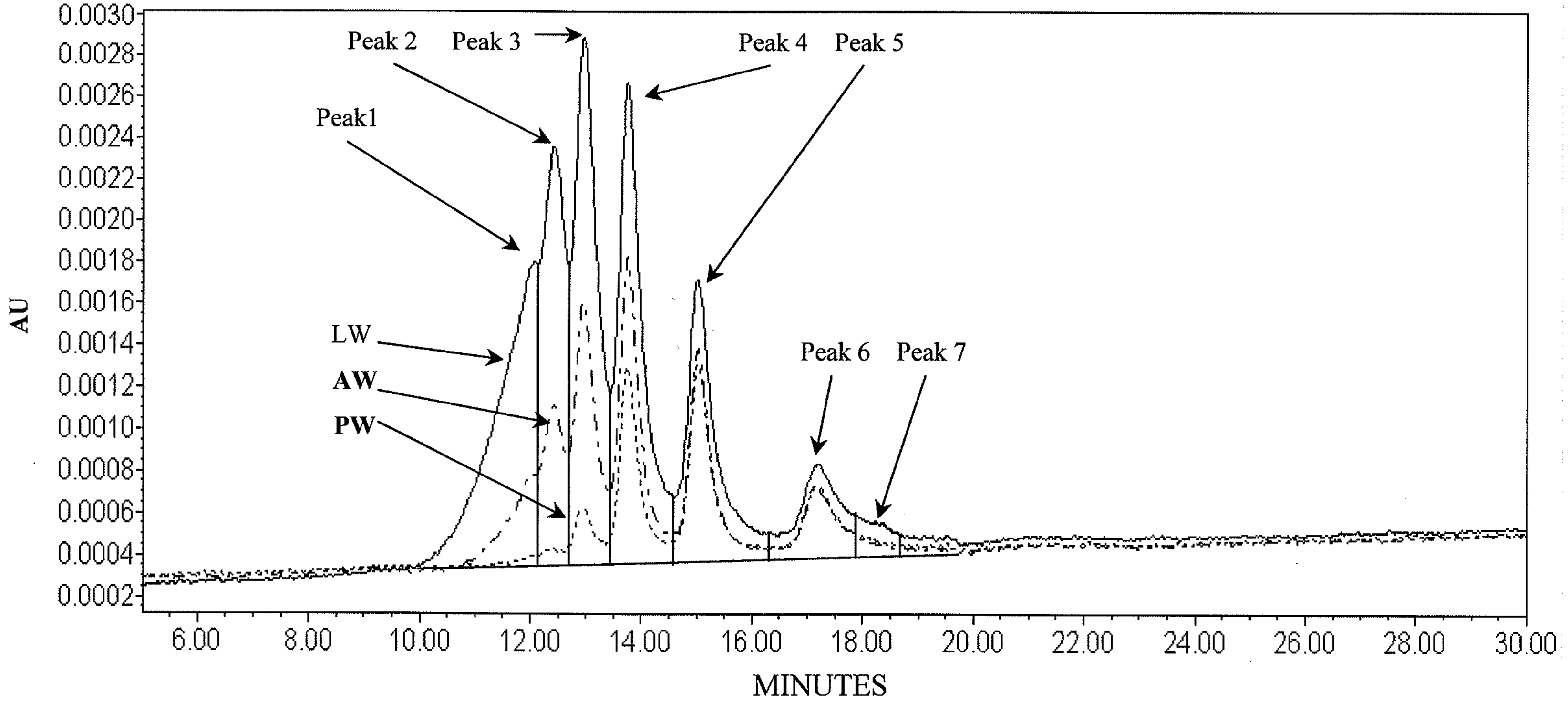


Figure 2-2. A typical chromatogram of the aquatic humus fractions in HP-SEC of the lake water (LW) (solid line), the artificially recharged groundwater (AW) (dash-dot line), and the purified water (PW) (dotted line). AU (absorption units), the UV absorbance response from the detector. The vertical lines represent the peak-area limits used for calculation of the results. The peak areas are limited to the base line.

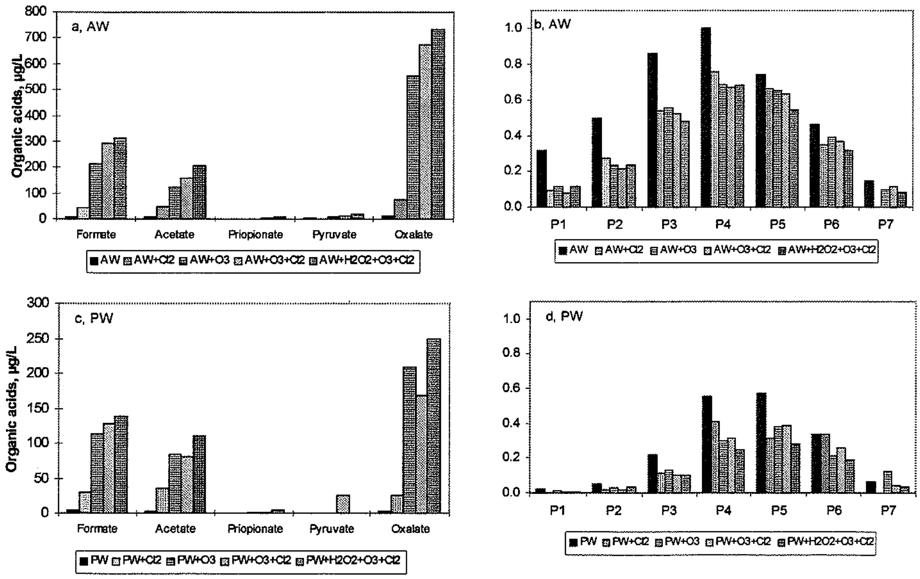


Figure 2-3. The effect of chlorination, ozonation, ozone-chlorination and hydrogen peroxide-ozone-chlorination on the organic acid formation and the molecular size distribution of the artificially recharged groundwater (AW) (a, b), and the purified artificially recharged groundwater (PW) (c, d). P1 = peak No.1, P2 = peak No.2, P3 = peak No.3, P4 = peak No. 4, P5 = peak No.5, P6 = peak No. 6, P7 = peak No.7. The heights of all peaks of the HP-SEC have been normalized to the highest peak measured (untreated AW, P4).

4.5 HYDROGEN PEROXIDE AND OZONATION

When hydrogen peroxide was combined with ozonation, the r-SMSF of the AW did not increase as compared to ozonation only. However, with the PW, the increase of the r-SMSF was significant, while the increase in the SOA was not (Table 2-II). When chlorine was added, there was no change in either the r-SMSF or the SOA, when compared to the treatments without chlorination (data not shown).

Table 2-II. The H_2O_2, $KMnO_4$, O_3, and Cl_2 doses of the treated waters. The TOC values in the beginning of the treatments (TOC_{INI}), and the percentage reduction of the TOC during treatments (TOC_{red}). The percentage removal of the sum of the molecular size fractions (r-SMSF). The percentages of the sum of the organic acids (SOA) and the unspecified compounds (USC) of the TOC. Average TOC values from long-time follow-up studies from the waterworks of Kuopio of the waters are: lake water 11.8 mg/L, artificially recharged groundwater 7.4 mg/L, and purified water 3.1 mg/L.

	Chemical(s) used (mg/L)							
				Artificially recharged groundwater (AW)				
	O_3	Cl_2	H_2O_2 or $KMnO_4$	TOC_{INI} (mg/L)	TOC_{red} (%)	r-SMSF (%)	SOA (% of the TOC_{red})	USC (% of the TOC)
Cl_2		2.0		4.3	2	34	1.3	33
O_3	4.7			6.1	6	29	3.9	25
O_3+Cl_2	4.7	2.0		5.9	6	29	5.1	24
H_2O_2+O_3			1.5	5.6	6	33	4.6	28
$KMnO_4$+Cl_2		2.0	0.22	6.5	4***	18	0.1	18
$KMnO_4$+Cl_2		2.0	0.34	6.8	2***	21	0.3	21
$KMnO_4$+Cl_2		2.0	0.44	6.5	4***	20	0.3	20

TOC_{INI} = the initial TOC concentration; TOC_{red} = reduction of the TOC from the initial value upon oxidation; ** = average used in the experiments as the initial TOC value; *** = TOC increased during oxidation; 1) alkalinity = 0.8 mmol/L; 2) alkalinity = 1.4 mmol/L; 3) alkalinity = 1.8 mmol/L; 4) pH = 7.2; 5) pH = 9.0; 6) temperature = 20 °C

Table 2-II. Continued.

	Purified water (PW)							
	O_3	Cl_2	H_2O_2 or $KMnO_4$	TOC_{INI} (mg/L)	TOC_{red} (%)	r-SMSF (%)	SOA (% of the TOC_{red})	USC (% of the TOC)
Cl_2		1.0		2.6	4	27	0.9	26
O_3	2.6			3.8	0	36	3.2	33
O_3	3.3			3.0**	3	31	4.2	27
O_3	4.8			3.8	0	41	8.8	32
O_3	6.3			3.0**	7	52	5.7	46
O_3	$6.3^{1)}$			3.0**	3	58	3.1	55
O_3	$6.3^{2)}$			3.0**	17	59	3.3	56
O_3	$6.3^{3)}$			3.0**	6	57	4.7	52
O_3	$6.3^{4)}$			3.0**	7	58	4.3	54
O_3	$6.3^{5)}$			3.0**	7	69	5.6	63
O_3	$3.3^{6)}$			3.0**	4	42	4.6	37
O_3	$6.3^{6)}$			3.0**	0	62	5.7	56
O_3	12.3			3.0**	3	59	4.4	55
O_3+Cl_2	2.6	1.0		3.1	18	39	4.5	35
O_3+Cl_2	4.8	2.0		3.2	11	45	9.7	35
$H_2O_2+O_3$			1.3	3.0**	3***	63	5.7	57
$H_2O_2+O_3$			2.5	3.0**	9***	61	5.9	55
$H_2O_2+O_3$			3.8	3.0**	13***	66	6.0	60
$KMnO_4+Cl_2$		1.0	0.04	3.3	0	15	0.1	15
$KMnO_4+Cl_2$		1.0	0.06	3.5	2***	19	0.2	19
$KMnO_4+Cl_2$		1.0	0.08	3.6	0	20	0.2	20

TOC_{INI} = the initial TOC concentration; TOC_{red} = reduction of the TOC from the initial value upon oxidation; ** = average used in the experiments as the initial TOC value; *** = TOC increased during oxidation; 1) alkalinity = 0.8 mmol/L; 2) alkalinity = 1.4 mmol/L; 3) alkalinity = 1.8 mmol/L; 4) pH = 7.2; 5) pH = 9.0; 6) temperature = 20 °C.

4.6 CHLORINATION COMBINED WITH PERMANGANATE OXIDATION

The initial manganese concentrations were 0.11 mg/L in the AW and 0.02 mg/L in the PW. The oxidation experiments of the AW or the PW with $KMnO_4$ alone (data not shown) and in combination with chlorine did not affect markedly the reduction of the SMSF nor influence the formation of the SOA (Table 2-II).

4.7 CORRELATIONS BETWEEN TOC AND SMSF AND SOA

The Pearson's correlation between the TOC and the SMSF was 0.911 (significant) and between the TOC and the organic acids was 0.314 (non-significant) in the whole material. The Pearson's correlation revealed also a relationship between the r-SMSF and the SOA (0.678).

5. DISCUSSION

A detailed understanding of humus, which is the main organic component present in raw water, is important, because safe drinking water production is essential for all communities. The analysis of humus is a complicated task due to its macromolecular structure. Exclusion chromatography in conjunction with the UV detection at 254 nm was used in this study to measure the molecular size fractions of the aquatic humus.

5.1 CHROMATOGRAPHIC COLUMNS MEASURING AQUATIC HUMUS

Only a few chromatographic columns have been used to ascertain the molecular size composition of humus. As far as we know, the column (TSK G3000SW) used in our study is the only column able to separate efficiently different molecular-size fractions from aquatic humus. Amy with co-workers[8] have stated that the molecular-weight distribution of the aquatic fulvic and humic acids ranged from 500 to 10000 Daltons, which is in agreement with the results of Peuravuori and Pihlaja[7]. However, column calibration, as well as the adsorption interactions and the electrostatic repulsion effects between the humic compounds and the HP-SEC gel can affect the accuracy of the method. It is not known whether humus contains separate molecular fractions, but it certainly contains different molecular sizes, and the TSK column used in this study clearly separates seven fractions present in the aquatic humus. Cabaniss and co-workers[22] have proposed that aquatic fulvic acids can be modeled as a log-normal distribution, and with a Waters Protein-Pac 125 modified silica column, the shape of the model was similar to the measured peak. However, the measured peak contained only four slightly separated peaks. A similar TSK column to ours has been used for more than 15 years, and it has been shown to highlight the changes of natural aquatic humus in a highly visual manner[12,13,23].

None of the oxidation methods used in this study removed totally the organic matter (oxidized to carbon dioxide and water), giving no superior oxidative chemical among these. However, the quality of the organic matter changed significantly during the oxidation processes, which is observed as r-SMSF and the formation of the organic acids. Since the UV absorption measures the intensity of the chromophores, such as double bonds, of the solutes in question, the observed reductions may be due to decomposition of the original humic bulk material to lower molecular-size fractions (observed as organic acid formation), resulting in less UV-absorptive chromophores. Strong correlations between the molar absorptivity, total aromaticity, and the average molecular weights at 280 nm have been observed in previous studies[12,24]. However, lack of aromaticity is the source of major uncertainty on the quantitative analysis of small humic structures at UV 254 nm[25], the most commonly ulitized wavelength in the methods used to monitor water quality changes.

5.2 CORRELATION BETWEEN TOC AND SMSF AND SOA

The total amount of the aquatic humus is most often measured by the TOC content. In natural waters, the SMSF (measured at UV-254) and TOC correlated well in our earlier studies (r = 0.954, ref. 13), which was seen also in this study (r = 0.911) even if the waters were treated with strong oxidation agents. However, the correlation between the TOC and the SOA was only 0.314. In our study the high-molecular-weight fractions, peaks number one to four, dominated, as described by others when surface waters have been tested[12,13,15,23,26]. The r-SMSF did show similarity to the removal of TOC from the AW to the PW (55 and 58%, respectively). Small-molecular-weight organic acids were formed accounting for 22% of the r-SMSF. The difference between the r-SMSF and the increase of the organic acid content might partly be due to compounds which have lower molecular-weights than can be detected with the HP-SEC, about 1400 Daltons, but larger than those of the organic acids analyzed, where the highest molecular weight was 194 Daltons.

5.3 EFFECT OF CHLORINATION ON AQUATIC HUMUS

The method used in this study is able to measure oxidation effects on aquatic humus but not chlorinated by-products. Chlorination of the AW resulted in a reduction of the humus fractions. The UV-254-absorbable organic matter was reduced by approximately 34%, and there was a significant shift to smaller fractions. Chlorination of the PW did not result in a great r-SMSF, but a similar change in molecular size was observed. Our results are in accordance with the results of Becher et al.[15]. In our experiments, chlorination also resulted in clear increases in the concentrations of the SOA.

5.4 EFFECT OF OZONATION ON AQUATIC HUMUS

Ozonation of the AW resulted in the greatest reductions in the four largest molecular size fractions. However, ozonation of the AW did not result in as significant a shift to smaller fractions as ozonation of the PW. The greater the ozone dosage, the greater the effect in this respect. An increase in the ozonation temperature increased humus degradation. Ozonation resulted in much higher concentrations of the organic acids as chlorination did. Similar results have been observed by others[10,27]. Ozonation has been shown to cause a major increase in the content of assimilable organic carbon (AOC) in humus-rich waters[28]. AOC might consist of SOA-like compounds. Ozonation can thus increase the potential for microbial growth in water distribution networks.

An increase in the ozonation alkalinity increased the r-SMSF at a similar rate as the increase in pH or hydrogen peroxide addition. Alkalinity, and especially bicarbonate ion, traps hydroxyl radicals, resulting in a 10-fold increase in the half-life of ozone at pH 7 [29]. Reckhow with his co-workers[30] showed that small amounts of bicarbonate improved the organohalide precursor destruction due to a shift of reaction mechanism towards the direct oxidation pathway.

5.5 EFFECT OF HYDROGEN PEROXIDE ON AQUATIC HUMUS

The r-SMSF due to the hydrogen peroxide-ozonation was significant in spite of the fact that the TOC did not decrease. The hydrogen peroxide-ozonation resulted in more than 60% removal of the SMSF from the PW, but only half of that from the AW. Hydrogen peroxide-ozonation and ozonation at a high pH (>8.5), which were used in these experiments, are examples of advanced oxidation processes, in which a great many hydroxyl radicals are formed[31]. OH radicals react much faster, to a greater extent and more non-selectively with the organic matter in the water than molecular ozone. The addition of hydrogen peroxide increased the formation of the organic acids to the greatest extent in the PW. Ozonation at the highest pH reduced the largest molecular-size fraction by almost 80%.

5.6 EFFECT OF PERMANGANATE ON AQUATIC HUMUS

Permanganate is used for the oxidation of iron (Fe^{2+}) and manganese (Mn^{2+}) from drinking water[32]. Stoichiometrically 1.92 mg $KMnO_4$ is needed to oxidize 1 mg Mn at a pH ≥5.5 [33]. This knowledge was used in choosing the $KMnO_4$/Mn-ratios (2, 3, and 4) for the experiments, resulting in excess concentrations of permanganate, and, thus, allowing it also to react with organic matter. The addition of the $KMnO_4$ before chlorine did resulted in a reduction of only 20% of the SMSF of the AW and the PW. Chlorination after the $KMnO_4$ oxidation reduced the humus fractions only marginally, which indicated that the $KMnO_4$ acted as a preoxidant, which, on the other hand, prevented the molecular decomposition reactions between chlorine and the aquatic humus. Permanganate oxidation did not increase the concentrations of the organic acids during our experiments, as compared to the untreated water.

6. CONCLUSIONS

- Changes in humus caused by different oxidants as well as by natural processes can be monitored from virgin water samples by this straightforward and rapid HP-SEC method. The changes are visually easy to discern.
- The processes resembling advanced oxidation processes reduced the SMSF by as much as two thirds without any visible decrease in the TOC. Also the concentrations of the SOA were greatest among with these processes.
- As much as one fourth (22%) of the r-SMSF could be identified in the SOA, but in many cases as much as 60% of the r-SMSF remained unknown.

7. ACKNOWLEDGEMENTS

This study was funded by the Academy of Finland and the Technology Development Centre of Finland (project no. 34538). Special thanks to Mrs. Teija Korhonen, Mrs. Mervi Ojala and Ms Miia Hämäläinen from the Laboratory of Chemistry for technical assistance.

8. REFERENCES

1. Schnoor, JL, Nitzschke, JL, Lucas, RD and Veenstra, JN. 1979. Trihalomethane yields as a function of precursor molecular weight. Environmental Science & Technology, 13: 1134-1138.
2. Rook, JJ. 1974. Formation of haloforms during chlorination of natural waters. Journal of Water Treatment and Examination, 23: 234-243.
3. Bellar, TA, Lichtenberg, JJ and Kroner, RC. 1976. The occurrence of organohalides in chlorinated drinking water. Journal American Water Works Association, 66: 703-706.
4. Vartiainen, T, Liimatainen, A, Kauranen, P and Hiisvirta, L. 1988. Relations between drinking water mutagenicity and water quality parameters. Chemosphere, 17: 189-202.
5. Miettinen, IT, Vartiainen, T and Martikainen, PJ. 1996. Bacterial enzyme activities in ground water during bank filtration of lake water. Water Research, 30: 2495-2501.
6. Amy, GL, Collins, MR, Kuo, CJ and King, PH. 1987. Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. Journal American Water Works Association, 79(1): 43-49.
7. Peuravuori, J and Pihlaja, K. 1997. Isolation and characterization of natural organic matter from lake water: comparison of isolation with solid adsorption and tangential membrane filtration. Environment International, 23: 441-451.
8. Amy, GL, Sierka, RA, Bedessem, J, Price, D and Tan, L. 1992. Molecular size distribution of dissolved organic matter. Journal American Water Works Association, 84(6): 67-75.
9. Collins, MR and Vaughan, CW. 1996. Characterization of NOM removal by biofiltration: impact of coagulation, ozonation, and sand media coating. In: Disinfection by-products in water treatment - the chemistry of their formation and control. (Ed. by Roger A. Minear & Gary L. Amy, CRC Press, Inc., pp. 449-476, 1996).
10. Edwards, M and Benjamin, MM. 1992. Transformation of NOM by ozone and its effect on iron and aluminum solubility. Journal American Water Works Association, 84(6): 56-66.
11. Krasner, SW, Croué, J-P, Buffle, J and Perdue, EM. 1996. Three approaches for characterizing NOM. Journal American Water Works Association, 88(6): 66-79.
12. Peuravuori, J and Pihlaja, K. 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Analytica Chimica Acta, 337: 133-149.
13. Vartiainen, T, Liimatainen, A and Kauranen, P. 1987. The use of size exclusion columns in determination of the quality and quantity of humus in artificially recharged ground waters and drinking waters. Science of the Total Environment, 62: 75-84.
14. Peuravuori, J, Paaso, N and Pihlaja, K. 1999. Characterization of lake-aquatic humic matter isolated with two different sorbing solid techniques: pyrolysis electron impact mass spectrometry. Analytica Chimica Acta, 391: 331-344.
15. Becher, G, Carlberg, GE, Gjessing, ET, Hongslo, JK and Monarca, S. 1985. High-performance size exclusion chromatography of chlorinated natural humic water and mutagenicity studies using the microscale fluctuation assay. Environmental Science & Technology, 19(5): 422-426.

16. Richardson, SD, Thruston, AD, Jr., Caughran, TV, Chen, PH, Collette, TW, Floyd, TL, Schenck, KM, Lykins, BW, Jr., Sun, G-R and Majetich, G. 1999. Identification of new ozone disinfection byproducts formed in drinking water. Environmental Science & Technology, 33: 3368-3377.

17. Miettinen, IT, Martikainen, PJ and Vartiainen, TK. 1994. Humus transformation at the bank filtration water plant. Water Science & Technology, 30(10): 179-187.

18. Myllykangas, T, Nissinen, T and Vartiainen, T. 2000. Bromate formation during ozonation of bromide containing drinking water – a pilot scale study. Ozone Science & Engineering, 22(5): 487-499.

19. AOAC. 1980. Official methods of analysis of the association of official analytical chemists. (Ed. by W. Hoewitz, 1980), p. 545.

20. Finnish Standards Association SFS. SFS 3005. 1981. Determination of alkalinity and acidity in water. Potentiometric titration. Finnish Standards Association SFS, Helsinki, Finland, 1981.

21. Finnish Standards Association SFS. SFS-EN 1484. 1997. Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). Finnish Standards Association SFS, Helsinki, Finland, 1997.

22. Cabaniss, SE, Zhou, Q, Maurice, PA, Chin, Y-P and Aiken, G. 2000. A log-normal distribution model for the molecular weight of aquatic fulvic acids. Environmental Science & Technology, 34: 1103-1109.

23. Kainulainen, T, Tuhkanen, T, Vartiainen, T, Heinonen-Tanski, H and Kalliokoski, P. 1994. The effect of different oxidation and filtration processes on the molecular size distribution of humic material. Water Science & Technology, 30: 169-174.

24. Chin, Y-P, Aiken, G and O'Loughlin, E. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental Science & Technology, 28(11): 1853-1858.

25. Korshin, GV, Li, C-H and Benjamin, MM. 1996. Use of UV spectroscopy to study chlorination of natural organic matter. In: Water disinfection and natural organic matter: Characterization and control. Eds. R.A. Minear and G.L. Amy, ACS Symposium Series 649, USA. ISBN 0-8412-3464-7.

26. Nissinen, TK, Miettinen, IT, Martikainen, PJ and Vartiainen, T. 2001. Molecular size distribution of natural organic matted in raw and drinking waters. Chemosphere, 45: 865-873.

27. Garcia-Araya, JF, Croué, JP, Beltrán, FJ and Legube, B. 1995. Origin and conditions of ketoacid formation during ozonation of natural matter in water. Ozone: Science & Engineering, 17: 647-656.

28. Miettinen, I, Vartiainen, T, Nissinen, T, Tuhkanen, T and Martikainen, PJ. 1998. Microbial growth in drinking waters treated with ozone, ozone/hydrogen peroxide or chlorine. Ozone Science & Engineering, 20: 303-315.

29. Hoigné, J and Bader, H. 1978. Ozone hydroxyl radical-induced oxidations of organic and organometallic trace impurities in water. In: Organometals and organometalloids: Occurrence and fate in the environment. Eds. R.R. Brinkman & J.M. Bellama, ACS Symposium Series 82, Washington D.C.: American Chemical Society, 1978, pp. 292-313.

30. Reckhow, DA, Legube, B and Singer, PC. 1986. The ozonation of organic halide precursors: effect of bicarbonate. Water Research, 20: 987.

31. Glaze, WH, Kang, J-W and Chapin, DG. 1987. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Science & Engineering, 9: 335-352.

32. Ficek, KJ. 1978. Potassium permanganate for iron and manganese removal. In: Water treatment plant design for the practicing engineer. (Ed. By R.J. Sanks, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan)

33. Pouvreau, P. 1984. Elimination spécifique du fer et du manganése. Journal Francais d'hydrologie 2, 169.

CHAPTER 3: ORGANIC MATTER REMOVAL AND BROMINATED DISINFECTION BY-PRODUCTS

Tiia Myllykangas[1], Arja Hirvonen[2], Hannu Nykänen[3], Panu Rantakokko[4], Markku Lehtola[5], Pertti Martikainen[6], and Terttu Vartiainen[7]

1 MSc (eng.), National Public Health Institute, Department of Environmental Health, P.O.Box 95, FIN-70701 Kuopio, Finland
2 PhD, Assistant Professor, University of Kuopio, Department of Environmental Sciences, P.O.Box 1627, FIN-70211 Kuopio, Finland
3 MSc, University of Kuopio, Department of Environmental Sciences, P.O.Box 1627, FIN-70211 Kuopio, Finland
4 MSc, National Public Health Institute, Department of Environmental Health, P.O.Box 95, FIN-70701 Kuopio, Finland
5 PhD, National Public Health Institute, Department of Environmental Health, P.O.Box 95, FIN-70701 Kuopio, Finland
6 Professor, University of Kuopio, Department of Environmental Sciences, P.O.Box 1627, FIN-70211 Kuopio, Finland
7 Professor, National Public Health Institute, Department of Environmental Health, P.O.Box 95, FIN-70701 Kuopio, Finland, and University of Kuopio, Department of Environmental Sciences, P.O.Box 1627, FIN-70211 Kuopio, Finland

Submitted for publication in the Journal of Environmental Engineering (2003).

1. ABSTRACT

Organic matter removal and the formation of disinfection by-products (DBPs) were studied using three coagulants, aluminum sulfate (AS), ferric sulfate (FS), and polyaluminum chloride (PACl), followed by chlorination and/or UV treatment in a pilot-scale water treatment plant. The experiments were made with and without spiked bromide. The use of all coagulants resulted in similar removals of organic matter, and bromide had no effect on it. The lowest required coagulant concentration for efficient organic matter removal was observed with the use of AS, while the FS required the highest concentration. No big differences in the formation of trihalomethanes (THMs) were observed between the experiments without bromide, but in the presence of bromide the

THMs increased clearly, and the highest concentrations were found after the FS coagulation. Chlorination and UV treatment plus chlorination produced similar amounts of the THMs, and the mutagenicity of the finished water was found to be even higher when the latter method was used.

Key Words: Coagulation, organic carbon, bromide, disinfection, disinfection by-products

2. INTRODUCTION

Surface waters in boreal regions contain up to 50 mg/L of total organic carbon (TOC)[1]. In the conventional water treatment coagulation and flocculation, clarification, and filtration are used to remove TOC. The remaining proportion of the organic carbon causes problems in many ways: the formation of the disinfection by-products (DBPs) causes health problems to the consumers, while microbial regrowth in the distribution systems causes both technical and health-related problems.

Bromide concentration in the natural waters varies from 10 to 1000 μg/L[2], and in Finland up to 500 μg/L Br^- [3] has been found in raw water sources. If bromide is present in the raw water, it is difficult to remove during the conventional water treatment processes[4], resulting in higher bromide-to-TOC ratios and formation of more brominated DBPs[5]. Bromide-containing DBPs are suspected to be more harmful and much stronger carcinogens and mutagens than their chlorine-containing analogues[7,8].

Humic substances in natural waters have a negative charge, so called zeta potential, which has to be destabilized to be able to remove those compounds in the coagulation-flocculation process. For optimum coagulation, the pH of the water, TOC content, alkalinity, hardness, and temperature range have to be optimized for every coagulant and water in question. Of the coagulants used for water production, aluminum sulfate (alum, AS) has been under the most intensive research due to its commonness in the field[9-13]. AS in water solutions forms only monomeric compounds, while more than 90% of the polyaluminum chloride (PACl) has been found to consist of polymeric species[9]. For these two aluminum-containing chemicals, the PACl is prehydrolyzed resulting in more stable aluminum compounds in the water up to a pH of 9, while the AS is more demanding on the pH value, since it hydrolyzes only in the water[9]. Both AS and ferric sulfate (FS) have been found to hydrolyze according to the same principles[14]. However, FS has been found to act more efficiently producing stronger flocs with less time than AS or PACl, and both the pH and temperature affect the FS coagulation less[14-19]. Also, PACl has been found to dominate AS as the coagulant for similar reasons[9,14,20].

According to Jacangelo et al.[21], the coagulation of organic matter in the water advances in three mechanisms of colloid destabilization, precipitation, and coprecipitation. The colloid destabilization progresses through electrical double-layer compression, charge neutralization, enmeshment, or bridging, while the coprecipitation needs surfaces to which adsorption and occlusion are possible. There are two main routes to result in coagulation and the formation of microflocs: 1) destabilizing the negative charge of the humic substances by adding metallic salts (usually Al or Fe salts), and 2) sweep coagulation (flocculation). The microflocs are enlargened in the proceeding process of flocculation, e.g. by mechanical mixing, after which the flocs are removed either by flotation or sedimentation.

Duan and Gregory[14] studied the effect of coagulant dose on the coagulation efficiency concluding that there exist four zones which affect the efficiency of the process: 1) too low coagulant dose to destabilize the negatively charged particles, 2) dose is sufficient for charge neutralization and coagulation, 3) higher dose causes both charge neutralization and restabilization resulting in poorer quality of the treated water, and 4) even higher dose resulting in sweep coagulation by hydroxide precipitate ($Al(OH)_3$ (s) or $Fe(OH)_3$ (s)). In other words, the coagulant dose should be optimized either to zone 2 or zone 4 to result in efficient coagulation. In the process of sweep flocculation, the floc formation and size are greater than in charge neutralization yielding better organic matter removal[14]. Coagulation by charge neutralization needs more accurate pH values than sweep flocculation[14], and also the effect of rapid mixing is more pronounced[20,22].

The purpose of this study was to compare the influence of three coagulating chemicals, AS, FS, and PACl, on the removal of the organic matter. The formation of the DBPs in the treatment of a humus-rich lake water was tested with chlorine and/or UV disinfection with and without spiked bromide. Also, the coagulation process was optimized for a pilot-scale water treatment plant using FS to improve the organic matter removal.

3. MATERIALS AND METHODS

3.1 PILOT-PLANT

The pilot-plant is shown in Figure 3-1, and it is constructed and planned for drinking water production. It consists of rapid and slow mixing, dissolved air flotation (DAF), anthracite-quartz sand rapid filter, UV-lamp (ProMinent 45W) and disinfection basin, in which also pH, hardness and alkalinity of the purified water are adjusted. The pH adjustments can be made with lime ($Ca(OH)_2$) and lye (NaOH), and CO_2 is used for adjustments of hardness and alkalinity in the finished water. The pilot-plant is logic controlled, but manual operation is also possible.

Rapid mixing consists of two small basins (à 20 – 40 L; R1 and R2 in Fig. 3-1), which both have their own mixer. In addition to the volume, the speed of mixing and the point of chemical additions can be adjusted. In the rapid mixing basins, the coagulating and pH adjustment chemicals are added to the water to result in microflocs. Slow mixing is taken place in three successive basins (à 300 – 500 L; S1 – S3 in Fig. 3-1). The modifications available are as with rapid mixing basins, and also the shape of the blades can be changed. During slow mixing, microflocs are brought together by mechanical mixing for flocculation. The efficiency and adequacy of mixing is controlled using so-called Gt-value (unitless), which is calculated by multiplying the velocity gradient (G, s^{-1}) with time (in seconds). The velocity gradient is calculated as

$$G = \sqrt{\frac{C_o A v^3}{2V\upsilon}} \qquad (1)$$

in which C_0 = roughness coefficient of the blade (for a smooth, straight blade ≈ 1.8), A = area of the blades (m^2), v = the blades' proportional velocity to the water's (m/s; usually ¾ of the blades' absolute velocity), V = the volume of the flocculation basin (m^3), υ = the kinematic viscosity of the water (m^2/s). The G-value should be about 100 s^{-1} (the Gt-value about 10^5) in the beginning of flocculation, and in the end about 10 s^{-1} (the Gt value

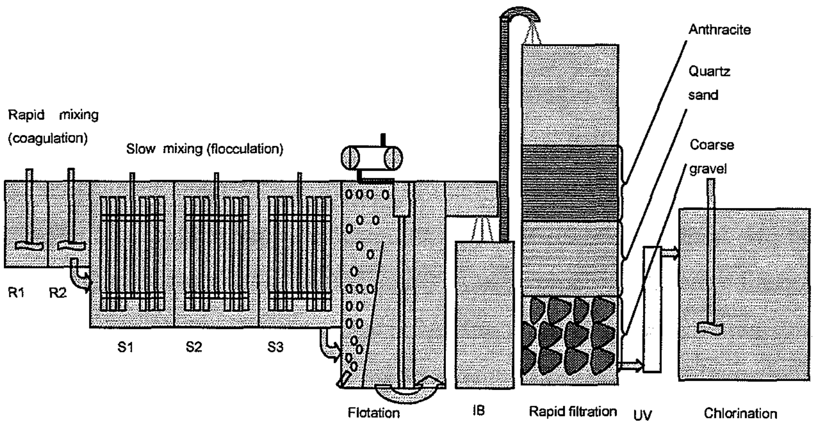


Figure 3-1. The pilot-scale water treatment plant used to carry out the experiments. The treatment plant consists of rapid mixing (coagulation), slow mixing (flocculation), flotation as the clarifying step, rapid filtration with a double layer filter (anthracite and quartz sand), UV treatment (optional), and postdisinfection with hypochlorite.

DAF (basin volume of 290 – 500 L) works as the clarification step. The inlet wall of the basin is adjustable (the angle can vary between 20° and 40° from the vertical wall). In the DAF unit, the coagulated and flocculated organic matter is removed from the water by small-diameter air bubbles, which are then removed from the water surface by lifting the water table and using an extra water shower. However, in Fig. 3-1 there is presented a skimmer, which removes the formed floc from the water surface. It was installed after all optimizing tests, since the water shower caused some flocs to be broken, and some organic matter was released down flow the water treatment plant. After the DAF there is an intermediate basin (IB in Fig. 3-1), in which the pH can be adjusted before filtration if needed.

For filtration, a dual media filter was used. The layers of both anthracite and quartz sand are approximately 60 cm in depth, and the surface load used was about 6 m/h. UV with and without following chlorination step were used for disinfection. UV fluence was about 250 mJ/cm^2, and chlorine dose about 1 mg/L. UV fluence was the calculated value of the intensity measured from the UV lamp and water flow without extra modifications. UV fluence of 30-40 mJ/cm^2 has been found to be enough for disinfection purposes[23]. The chlorine dose was chosen according to the disinfection practice of the water works of Kuopio, which uses artificially recharged groundwater from Lake Kallavesi as the raw water, and have found the concentration to be high enough to ensure disinfection. The raw water in the water works of Kuopio is purified by alum coagulation, clarification and sand filtration before disinfection. Chlorination was conducted at the basin in which the pH of the finished water was adjusted, and the pH values can be seen from Table 3-I.

Table 3-I. Coagulant doses and pH values, and the Gt-values for each group of the experiments.

Coagulant	Dose (mg/L) / M^{3+} (mg/L)	pH	Gt_1	Gt_2	Gt_3	Time-lag in slow mixing	Blade area in slow mixing (m^2)	Filtration pH
AS	63 / 5.7	5.8	31500	16700	6900	44 min	0.066	am
FS[1]	118 / 13.8	4.4	31500	16700	6900	44 min	0.066	>9
FS[2]	94 - 115 / 11 - 13.5	4.7 - 4.8	89600	45900	13000	60 min	0.212	~5
PACl	80 / 7.1	5.9	31500	16700	6900	44 min	0.066	am

AS = aluminum sulphate, FS = ferric sulphate, PACl = polyaluminum chloride, FS[1] = the experiments made under similar conditions as the AS and PACl experiments, FS[2] = the modified values after all the optimization experiments, M^{3+} = the concentration of the active metal (Al^{3+} or Fe^{3+}), Gt_1 = the velocity gradient multiplied by time in basin No. 1, Gt_2 = the velocity gradient multiplied by time in basin No. 2, Gt_3 = the velocity gradient multiplied by time in basin No. 3, am = ambient pH

3.2 WATER

Raw water was taken from the Lake Kallavesi, which is a typical humus-rich lake (TOC 10 – 12 mg/L) in the Eastern Finland. The water was pumped from two depths (5 m and 15 m), and it was filtrated with a drum filter and a rapid sand filter both to prevent twigs and other larger impurities from entering the water treatment process and to make sure that the water is of as uniform quality as possible. The raw water does not naturally contain bromide allowing us to conduct experiments with and without spiked bromide to compare the DBP formation. The bromide was spiked as NaBr-solution to the raw water, and the bromide concentration (400 – 500 µg/L) was chosen to simulate the highest observed bromide concentration in Finnish raw waters[3]. Only in the PACl experiments with UV disinfection only the bromide concentration was lower (200 µg/L) due to difficulties with the sodium bromide solution dispenser.

3.2.1 Comparing the coagulants

In these studies, the coagulants used were aluminum sulphate ($Al_2(SO_4)_3$, AS), ferric sulphate ($Fe_2(SO_4)_3$, FA), and polyaluminum chloride (PACl), i.e. three groups of experiments were conducted. The doses of the coagulants were AS 63 mg/L (corresponding to 5.7 mg/L as Al^{3+}), FS 118 mg/L (13.8 mg/L Fe^{3+}), and PACl 80 mg/L (7.1 mg/L as Al^{3+}). The AS experiments were made in April, the FS experiments in August, and the PACl experiments in November. Mixing velocities and times (the Gt-times) for coagulation and flocculation, the water flow ($Q = 1.8\ m^3/h$), and the angle of the inlet wall for flotation (28° from the vertical wall) were the same in every group of experiments. The best coagulant doses and appropriate pH values were tested and chosen for every group of experiments. Further information can be found from Table 3-I.

3.2.2 Further optimization

The system was further optimized using FS without spiked bromide after the above mentioned experiments. FS was chosen, since it is increasingly more often used in water treatment, and because of the claimed health problems, such as Alzheimer's disease and Parkinson's disease, associated with the use of aluminum compounds[24-26]. The effects of the rapid mixing, the coagulation pH, the dose of the FS, the coagulation temperature, the water flow (lag-time in the flocculation basins), and the change of the blades in the slow mixing on the organic matter removal were studied. Also, the effect of the filtration pH (adjusted with NaOH) for removing the iron residual was studied. Most of the tests were made with the water treatment plant and the samples were taken from S3 (see Fig. 3-1) and analyzed after 1-2 hour sedimentation at the room temperature. However, the effects of the enlargened Gt-values and increased temperature on the coagulation efficiency were tested in small separate basins (à 30 L). The water treatment plant was then modified according to the optimized parameters.

The effect of the water temperature (6.2°C vs. 18.1°C) was tested as follows: the chemicals were dosaged directly into the small basins (two parallel for each temperature), the water-chemical mixture was mixed rapidly with a drilling machine and a special blade, and the slow mixing was made with a specific mixer. The slow mixer had larger blade area in relation to the water basin's area than the water treatment plant resulting in larger Gt-values. The lower temperature of the water was maintained by leading cold water outside the basin, while the higher temperature was achieved by warming the water outside the basin. After mixing, the water was clarified by sedimentation for 2 hours before sampling.

3.3 WATER QUALITY MEASUREMENTS

Several parameters were analyzed routinely to ensure the proper water quality. The results obtained were compared to the values of the EC directive on the quality of water intended for human consumption[27].

Both *temperature* and *pH* were measured *in situ* during the experiments, either with pilot-plants' meters or with a calibrated WTW pH320-meter. The latter one was used as a reference for system's pH-meters' results. *Conductivity* was measured with inoLab cond Level 2 meter. *$KMnO_4$-number* (mg/L) was measured according to SFS 3036 [28], and *alkalinity* according to SFS 3005 [29]. *UV_{254}-absorbance* was measured with Shimadzu UV-mini 1240 spectrophotometer. The *specific UV absorbance (SUVA)* was calculated as $100*UV_{254}/TOC$[30]. *Color* (mg/L PtCo), *hardness* (mmol/L), *Al*, and *Fe* were measured with a spectrophotometer HACH DR/2010 according to methods 8025, 8030, 8012, and 8008 [31], respectively.

TOC was measured according to the Finnish Standard SFS-EN 1484 [32]. Molecular size distribution of the organic matter (*HP-SEC method*) was measured using the method of Vartiainen and co-workers[33], which is described in more detail in Myllykangas et al.[34]. *Organic acids* (formate, acetate, propionate, pyruvate, oxalate and citrate) were measured with an ion chromatogram system[34]. *Trihalomethanes* (THMs) were analyzed according to the standard CEN/prEN 30301 [35], and the sum of the four THMs (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform) was calculated. *Bromide* analysis was made with 270-HT High Throughput Capillary Electrophoresis System (Applied Biosystems, San Jose, CA, USA) according to the method developed by Rantakokko et al.[36]. *Inorganic anions* (chloride, nitrite, sulfate, nitrate, fluoride, and phosphate) were analyzed with the same device as bromide[6]. *Mutagenicity* of the water was tested using the Ames *Salmonella* assay on extracts obtained by an adsorption method[37], and the more detailed description can be found in Myllykangas et al.[6].

Adsorbable organic halogens (AOX) determination was made according to standard SFS-EN 1485 [38] with slight modifications. Method measures the amount of organically bound chlorine, bromine, and iodine, but not fluorine. Residual oxidants were first quenched by adding sodium sulfite solution. Samples were acidified with nitric acid to a pH of less than 2 and shaken with activated carbon for 1h. Suspension was filtrated and washed with nitrate washing solution to remove inorganic, unbound halogens, from the activated carbon filter cake. Moist filter and filter cake was moved to a ceramic burning vessel and combusted in pure oxygen at 1000 °C. Hydrogen halides formed from organically bound halogen compounds during combustion were quantified with microcoulometric titration.

Halogenated acetic acids (HAAs; monochloro-, monobromo-, dichloro-, trichloro-, bromochloro-, dibromo-, bromodichloro-, chlorodibromo-, and tribromo acetic acids) were determined with a method slightly modified from EPA Method 552.2 [39]. Internal standard 2-bromopropionic acid was added to water samples, which were acidified with sulfuric acid, sodium sulfate was added, and HAAs were extracted with MtBE containing syringe standard 1,2,3-tricloropropane. MtBE phase was separated and HAAs were methylated by adding acidic methanol (10 % sulfuric acid), and keeping at +50 °C for 2 hours. MtBE phase was separated from acidic methanol and analyzed using gas chromatograph (Hewlett Packard 6890) coupled with high-resolution mass spectrometer (Autospec Ultima, Waters). Column used was DB-5MS (Hewlett Packard: 30 m, i.d. 0.25 mm, film 0.25 μm). Limit of quantitation was 0.3 μg/L, except for chlorodibromoacetic acid (1.5 μg/L) and tribromoacetic acid (4.5 μg/L).

4. RESULTS

4.1 ORGANIC MATTER

Approximately ⅓ of the raw water's permanganate value was observed after the water purification process independably on the coagulant used. The highest absolute values, i.e. the lowest reductions, were obtained after AS coagulation, but the chemicals were found to work quite similarly in the removal of permanganate values (Table 3-II). When the reduction of permanganate values was standardized in respect of mg of active metal (i.e. Al^{3+} or Fe^{3+}), the AS produced the highest reductions (6.1 mg per mg of Al^{3+}), while the FS was clearly the least effective (2.2 mg per mg of Fe^{3+}). The TOC values were reduced about 60% during coagulation experiments (Table 3), while the most effective reduction was observed after AS coagulation (1.2 mg C per mg of Al^{3+}), and the worst after FS coagulation (0.4 mg C per mg of Fe^{3+}). The organic matter removal (measured as permanganate value and TOC) was not affected by disinfection options or the presence of bromide.

The lowest total reduction in the HPSEC fractions of the water was observed after the AS coagulation experiments, while the most effective coagulant was the FS. If the reductions were standardized for the active metal concentrations, the best results were again observed after the AS coagulation (53500 AU*s per mg of Al^{3+}), and the worst after the FS coagulation (24600 AU*s per mg of Fe^{3+}). On the other hand, especially chlorine due to its high oxidation potential on the organic matter caused additional decomposition of humus into smaller compounds, while bromide had no effect on it. The concentrations of the organic acids measured after the AS and FS experiments were lower when bromide was present in the treated water, while after the PACl treatment the opposite was true. During the UV treatment, the lowest concentrations of the organic acids were observed, while chlorine and UV plus chlorine treatments produced similar concentrations (Table 3-II).

Generally, the reduction in the UV_{254}-absorbance was more than 80% in every experiment, and the lowest absolute values were observed after coagulation with PACl. The differences in color values (in mg/L PtCo) reflect the amount of organic matter as well. The lowest color values were observed after the PACl coagulation, while the highest ones were observed after the AS coagulation. However, the relative reduction was again the lowest after the FS coagulation (2.9 mg per mg Fe^{3+}), while the highest value was observed after the AS coagulation (9.0 mg per mg Al^{3+}). The disinfection method used or the presence of bromide did not affect in either of the parameters (Table 3-II).

The SUVA values indicated that the PACl coagulation resulted in the greatest reduction in the aromatic content of the organic matter, while both the AS and PACl resulted about three times larger reduction in SUVA per mg Al^{3+} than the FS did per mg Fe^{3+}. Also, differences between the disinfection methods were clearly seen, and the UV treatment only caused the lowest SUVA reductions regardless of the coagulation chemical used (Table 3-II) due to lower oxidation potential than chlorine on the organic compounds in the water.

Table 3-II. Permanganate value (Perm. value), UV_{254}-absorbance (UV_{254}-abs.), SUVA values, total organic carbon (TOC), the sums of the peak areas obtained from the HPSEC, the organic acids (org. acids, formate, acetate, propionate, pyruvate, oxalate, and citrate), the anions (chloride, nitrite, sulfate, citrate, fluoride, and phosphate) and the Al or Fe residue (Al or Fe res.) of the treated waters. Raw water values are averaged from the data (6 or 7 samples per analysis). AS = aluminium sulphate; FS = ferric sulphate; PACl = polyaluminium chloride. Chlorine dose was 1 mg/L and UV fluence 250 mJ/cm^2. SUVA = specific UV absorbance, calculated as $100 \cdot UV_{254}/TOC$. The experiments with and without bromide are arranged by the disinfection method, i.e. chlorination with and without bromide are next to each other etc.

Treatment (T(°C)/final pH)	Perm. value (mg/L)	UV_{254}-abs. (1/cm)	SUVA (L/(mg×m))	TOC (mg/L)	HPSEC (AU×s)	Org. acids (µg/L)	Anions (mg/L)	Al or Fe res. (µg/L)
AS-coagulation								
Raw water (2.5/7.4)	48.6	0.401	3.55	11.3	436600	63	11	--
Cl_2 (4.3/8.1)	14.0	0.078	1.70	4.6	128000	140	41	130
Cl_2 + 400µg/L Br^- (5.0/8.6)	12.9	0.076	1.66	4.6	133400	63	34	140
UV + Cl_2 (5.1/7.9)	15.1	0.071	1.58	4.5	119300	150	37	250
UV + Cl_2 + 400µg/L Br^- (5.2/8.0)	13.8	0.078	1.70	4.6	134100	100	37	40
UV (4.5/8.2)	13.7	0.088	1.92	4.6	150100	89	36	130
UV + 400µg/L Br^- (5.1/8.3)	13.7	0.080	1.82	4.4	124000	64	36	110
FS-coagulation								
Raw water (14.0/6.8)	42.5	0.352	3.59	9.8	430900	48	11	--
Cl_2 (15.6/8.9)	13.9	0.061	1.64	3.7	100800	110	38	60
Cl_2 + 270µg/L Br^- (15.5/7.5)	11.6	0.062	1.63	3.8	86100	39	30	70
Cl_2 + 500µg/L Br^- (15.8/7.6)	9.6	0.064	1.73	3.7	62600	54	32	100
UV + Cl_2 (15.3/8.5)	11.1	0.062	1.77	3.5	89200	86	39	90
UV + Cl_2 + 500µg/L Br^- (15.6/7.8)	12.0	0.061	1.64	3.7	65700	49	37	90
UV (15.4/9.4)	12.2	0.071	1.93	3.7	118500	34	32	70
UV + 500µg/L Br^- (15.7/7.7)	13.0	0.070	1.85	3.8	112700	47	35	70
PACl-coagulation								
Raw water (7.2/7.1)	41.9	0.343	3.61	9.5	400500	62	8.7	--
Cl_2 (10.6/7.7)	11.3	0.056	1.44	3.9	109900	62	21	110
Cl_2 + 500µg/L Br^- (8.7/8.0)	10.2	0.060	1.58	3.8	69500	110	19	20
UV + Cl_2 (10.0/8.1)	10.6	0.058	1.53	3.8	114800	67	21	200
UV + Cl_2 + 500µg/L Br^- (8.2/7.9)	12.1	0.062	1.50	4.1	74300	97	21	150
UV (8.8/8.0)	11.4	0.067	1.76	3.8	83300	29	21	160
UV + 200µg/L Br^- (7.8/7.9)	11.6	0.071	1.73	4.1	90800	39	19	150

4.2 INORGANIC COMPOUNDS

The initial spiked bromide ion concentrations ranged from 200 to 500 µg/L. The coagulation process did not cause reduction in bromide concentration, and only after chlorination (independently on the coagulating agent) a noticeable bromide ion reduction was observed (about 70% of the initial value). The concentration of the inorganic anions (except for bromide) in the raw water was approximately 10 mg/L, and it increased up to 3.5 fold during the experiments due to chemical treatment (Table 3-II). The lowest concentrations of the inorganic anions were observed when PACl was used as the coagulant, and no difference between the disinfectants was observed (Table 3-II).

4.3 DBPs

THMs were formed only when chlorination (with or without UV) was used (Table 3-III). The THMs of bromide-free waters were 26 – 37 μg/L, and in the PACl experiments the concentrations were the lowest. In the presence of bromide, up to 70 μg/L of THMs were observed (the FS experiments), and the concentration was generally higher than in bromide-free waters.

HAAs concentration was found to be lower in the bromide-containing waters than in bromide-free waters in the AS and FS experiments (Table 3-III). However, when the PACl was used as the coagulant, the bromide-containing waters had higher HAAs concentrations than bromide-free waters. No HAAs formation was observed after UV treatment.

The highest concentrations of the AOX of non-bromide-containing waters were observed when the AS was used as the coagulant (Table 3-III). After UV treatment only some (if any) AOX formation was observed. When the AS was the coagulating agent, the AOX concentrations were the greatest, but no differences were observed between the FS and PACl experiments.

4.4 OTHER PARAMETERS

The mutagenicities were somewhat lower when PACl was the coagulant as compared to the FS experiments independently on the presence of bromide (Table 3-III). However, the mutagenicities after the AS experiments were not measured.

The Al and Fe residue in the treated water must not exceed 200 μg/L (EC, 1998). On these experiments the concentrations remained below that limit value in all but one experiment (residue Al concentration 250 μg/L), and in one experiment the concentration Al was 200 μg/L. It seemed to be easier to limit and control the residual Fe concentrations than the residual Al concentrations during the experiments (Table 3-II).

Color (in mg PtCo/L) varied in the AS experiments from 3 – 5, in the FS experiments from 2 – 10, and in the PACl experiments 2 – 3. The conductivity of the finished water was in the range of 150 – 190 μS/cm, the alkalinity 0.6 – 1.2 mmol/L, and the hardness 0.4 – 0.6 mmol $CaCO_3$ /L after the experiments, while the initial values were 58 – 63 μS/cm, 0.3 mmol/L, and 0.2 – 0.3 mmol $CaCO_3$ /L, respectively.

Table 3-III. The trihalomethanes (TTHMs; chloroform, bromodichloromethane, chlorodibromomethane, and bromoform); bromide concentration after disinfection; mutagenicity; concentration of the adsorbable organic halogens (AOX); and the sum of the halogenated acetic acids (THAAs; monochloro-, monobromo-, dichloro-, trichloro-, bromochloro-, dibromo-, bromodichloro-, chlorodibromo-, and tribromo acetic acids). AS = aluminium sulphate; FS = ferric sulphate; PACl = polyaluminium chloride. Chlorine dose was 1 mg/L and UV fluence 250 mJ/cm^2. The experiments are arranged by the disinfection method, i.e. chlorination with and without bromide are next to each other etc.

Treatment	TTHMs (μg/L)	Br^- (μg/L)	Mutagenicity (net rev/L)	AOX (μg/L)	THAAs (μg/L)
AS-coagulation					
Cl_2	32		--	180	27
Cl_2 + 400μg/L Br^-	41	280	--	120	22
UV + Cl_2	31		--	190	29
UV + Cl_2 + 400μg/L Br^-	8.7	360	--	90	11
UV	BDL		--	30	BDL
UV + 400μg/L Br^-	BDL	400	--	40	BDL
FS-coagulation					
Cl_2	33		1270	140	24
Cl_2 + 270μg/L Br^-	49	170	1750	100	14
Cl_2 + 500μg/L Br^-	59	340	2150	95	15
UV + Cl_2	37		1810	140	26
UV + Cl_2 + 500μg/L Br^-	70	350	2600	100	22
UV	BDL		<100	10	BDL
UV + 500μg/L Br^-	BDL	500	<100	20	BDL
PACl-coagulation					
Cl_2	26		1360	140	16
Cl_2 + 500μg/L Br^-	57	330	1980	110	28
UV + Cl_2	27		1240	135	12
UV + Cl_2 + 500μg/L Br^-	54	500	2150	115	25
UV	BDL		<100	<10	BDL
UV + 200μg/L Br^-	BDL	200	<100	<10	BDL

BDL = below the detection limit

4.5 CORRELATIONS BETWEEN PARAMETERS

The highest Pearson correlation coefficients (R) for the whole data, water with bromide and water without bromide are presented in Table 3-IV. Very high correlations were observed for the whole data (includes raw water data and the data from the experiments) for all the parameters measuring the amount of the organic matter. For the DBPs, the UV and HPSEC were found to correlate well with the THMs and mutagenicity when the whole data was compared, but differences in the bromide-free and bromide-containing waters were significant. However, the DBPs correlated well with each other, and no big differences due to the presence of bromide were observed.

4.6 FURTHER OPTIMIZATION

The pH of the water at the time the coagulant was added to the water had more effect on the coagulation process than the velocity of the rapid mixing. According to this experiment, and another one comparing a wider range of coagulation pH, the optimum pH for FS coagulation was found to be greater than 4.6 and less than 4.9 at this temperature (about 3 °C), which was higher than the one observed and used in the earlier experiments at a temperature about 15 °C (Table 3-I). On the other hand, the best residual Fe concentrations (measured after S3 in Fig. 3-1) were found when the FS feed was approximately 11 mg/L as Fe^{3+}, which was lower than in the earlier experiments (Table 3-I). The chemical (NaOH or $Ca(OH)_2$) used for pH adjustment of coagulation step did not affect the coagulation efficiency.

The coagulation temperature did not affect the results. However, the results showed that the Gt-values have a great effect on the water quality. Inspired by these results, the effectiveness of rapid mixing was tested when water was siphoned off of the R2 basin of the water treatment plant into the smaller basin, and similar Gt-values were used as in the temperature experiments. The following results were obtained: color 6 mg/L PtCo, $Fe_{residual}$ 0.24 mg/L, and UV_{254}-absorbance 0.067, when the number of tests was 2. Due to the good outcomes, the blades of the slow mixing of the water treatment plant were changed (Fig. 3-3).

In the studies of comparing the coagulants, the pH of the filtrated water was increased to 9 and higher to improve the removal of residual Fe from the water when FS was the coagulating chemical. However, the pH value was now tested with a wider pH range (from

5.0 to 9.1), and the best results were found at a pH of 5.0, which is the ambient pH of the water after the DAF.

Table 3-IV. Part 1: Pearson correlation coefficients (R) of the parameters describing the amount and quality of organic carbon. Part 2: Pearson correlation coefficients (R) of the parameters describing the amount of disinfection by-products.

Part 1

	$KMnO_4$ – color	$KMnO_4$ – UV_{abs}	$KMnO_4$ – TOC	$KMnO_4$ – HPSEC	Color - UV_{abs}	Color – TOC	UV_{abs} – TOC	UV_{abs} – HPSEC	TOC – HPSEC
Whole data(a)	0.989*	0.993	0.993	0.973	0.992*	0.993*	0.996	0.980	0.977
With Br$^-$ (b)	0.617*	0.753	0.712	0.845	0.797*	0.771*	0.837	0.923	0.838
Without Br$^-$(b)	0.519	0.591	0.725	0.505	0.825	0.685	0.758	0.730	0.775

Part 2

	UV_{abs} – TTHMs	UV_{abs} – mutag.	HPSEC – mutag.	TTHMs – AOX	TTHMs – THAAs	TTHMs – mutag.	AOX – THAAs	AOX – mutag.	THAAs – mutag.
With Br$^-$ (b)	-0.789	-0.124☆	-0.708☆	0.803	0.870	0.945☆	0.918	-0.061☆	0.243☆
Without Br$^-$(b)	-0.479	-0.619☆	-0.851☆	0.933	0.951	0.723☆	0.935	0.911☆	0.673☆

(a) includes raw water results; (b) includes no raw water results; $KMnO_4$ = permanganate value in mg/L; color = color in mg PtCo/L; UV_{abs} = UV absorbance measured at 253.7 nm; TOC = TOC in mg/L; HPSEC = the sum of the peak areas obtained from the HPSEC analysis; * color values of the FS experiments with bromide are excluded; ☆ only mutagenicities >100 net rev/L are included.

Table 3-I, line FS^2, lists the changed parameter values for the FS coagulation and the water treatment plant after all the experiments and improvements were made.

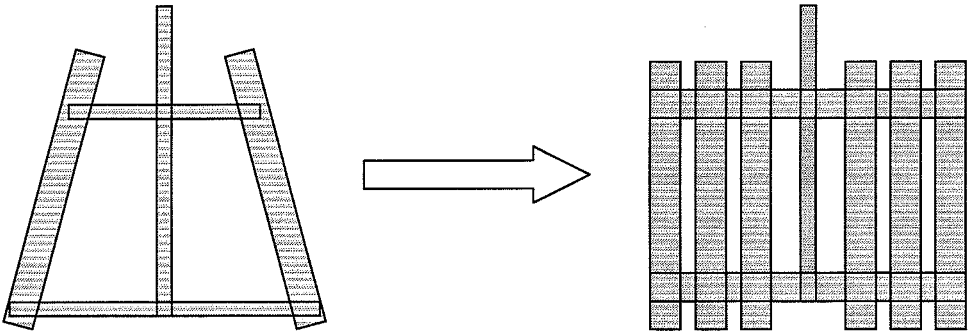


Figure 3-2. The change of the slow mixing blades after the coagulation experiments using ferric sulphate. The blade area was 0.066 m^2 before the change, and 0.212 m^2 after.

5. DISCUSSION

In this study, the organic matter removal was found to be best in the AS coagulation and worst in the FS coagulation, if the removal was standardized to the active metal concentration, i.e. mg Al^{3+} /L or mg Fe^{3+} /L. On the other hand, if the standardization was made to the molar concentration of the active metal, the organic matter removals per mM of Al^{3+} or Fe^{3+} in the AS and FS experiments approached each other, and the UV_{254}-absorbance removal was even higher when the FS was used. The PACl seemed to work worst in the latter dissection. It seems according to these results that the AS works best for this type of water (low alkalinity, hardness, and pH) under fixed conditions. However, the organic matter removal was improved in a great deal when the FS was used, and the process was optimized further, including a detailed study about the slow mixing (change of blade geometry and water flow/lag-time in the basins). And, since aluminum has its possible health effects[24-26], the use of the FS would be an intriguing and a functional alternative for organic matter removal in water treatment process.

In our experiments, the coagulation can be assumed to be in the region of sweep flocculation, since Kan et al.[22] found that aluminum concentration above 5 mg/L Al^{3+} is sufficient for the process, and both in AS and PACl experiments a higher aluminum concentration was used. Further, at the pH range of 5.5 – 8.0 (5.8 or 5.9 for AS and PACl coagulation in these experiments) the coagulation is occurring dominantly by adsorbing to the aluminum hydroxide surfaces[40], which is typical for sweep flocculation. Also, because AS and FS hydrolyzation proceeds along the same lines, the FS treatment can be also assumed to have occurred by sweep flocculation rather than charge neutralization during these experiments.

During coagulation, mainly the humic fraction of humus (size >2000 Da, ref. 1) are removed. Even though the THM precursors have been found to be the fulvic fraction of humus, 800 – 2000 Da[41-44], efficient coagulation has shown good results in reducing THM formation in chlorination[43,45-47]. However, in these experiments, the highest concentrations of the THMs were formed in the FS experiments, where the high-molecular-weight organic compounds as seen in the reduction in the HPSEC fractions were removed most effectively, which is opposite to that knowledge. In the experiments the reduction in the TOC (approximately 60%) was found to be lower than the reduction in the UV_{254}-absorbance (81%), which has been found by other researchers as well[12,14,17].

The water temperature and pH have great effect on the success of the coagulation process, and in low temperatures especially the effectiveness of the AS has been found to decrease more than of the PACl or FS[13-15,20]. Some of the differences found in the experiments using different coagulants might be due to the change of seasons: the AS experiments were made in the spring, the FS experiments in the summer, and the PACl experiments in the late fall. When water temperature decreases, the viscosity increases resulting in lower settling rates of the flocs. The G-values and the hydrolyzation and precipitation reactions of the metals (Al^{3+} and Fe^{3+}) decreased, and the ion product of the water changes resulting in lower amounts of OH^- ions, which are important in the hydrolyzing reactions[20]. The effect of temperature was observed in the experiments made in this study as well, since the optimum pH for FS coagulation was found to be higher when the temperature decreased from 15 to 3 °C. It is suggested in the literature that the negative effects of the lower temperature can be avoided (or minimized) by increasing the water pH by 0.4 to 0.8 units, depending on the coagulant[14], and in this study the necessary increase for the FS was 0.3-0.4 units, while the coagulant dose remained almost the same.

Since the bromide concentration was not observed to reduce during the coagulation/-flocculation process, the lowered concentration in the end was solely a result from the disinfection chemical (chlorine) used. Bromide concentration decreased, i.e. the bromide was utilized to form DBPs, during the chlorination experiments approximately 30%.

The formation of the DBPs remained below the EU limit values in our experiments[27]. However, the maximum trihalomethane concentration was quite high, 70 µg/L. As has been previously observed[4,6], trihalomethane concentrations were higher in the bromide-containing waters after corresponding treatments.

In the European Union, there is no limit value for HAAs, but the USEPA regulates it with a limit value for total HAAs concentration of 60 µg/L for five compounds[48]. However, the results of our experiments show that <30 µg/L as the sum of the nine HAAs compounds analyzed was formed in any case. Interesting finding is that the HAAs concentrations of bromide-containing waters were lower in the AS and FS experiments than the corresponding values of bromide-free waters. Only during the PAC experiments, the HAAs concentrations of bromide-containing waters were higher than bromide-free waters. As with the HAAs, also the AOX results were interesting, since bromide-containing samples had lower AOX concentrations than their bromide-free counterpart. We have observed similar results many times in our previous studies as well. One possible cause might be if bromide is consuming the oxidant (chlorine in this case) resulting in some other (inorganic) compounds, such as the HOBr, than the ones that can be found from the results of the analysis made, and/or that the oxidizing power of the disinfectant is consumed by bromide resulting in lower amounts of other DBPs in the process. Zhang et al.[49] offered an explanation on this phenomenon by stating that bromide causes a small reduction in oxidizing power of the oxidant declining the concentrations of the DBPs, which is parallel to our findings.

6. CONCLUSIONS

- The coagulation process was found to work well when the AS, FS, or PACl were used as the coagulant. However, during the FS experiments, the residual metal concentration was found to be controlled more easily than in the other experiments.
- Organic matter removal per amount of the coagulant (mg/mg or mg/mmol) was found to be the best when the AS was the coagulant.
- By changing the slow mixing blades to larger ones, the organic matter removal was improved clearly when the FS was used. This result could be assumed to be similar with the use of AS or PACl as well. However, the use of the FS would be preferable due to the negative effects of aluminum compounds to health.
- Bromide increased the total concentration of the THMs and mutagenicity observed. However, the presence of bromide decreased the formation of AOX, HAAs, and organic acids. The three coagulants did not differ much on that account without bromide, but with bromide the FS coagulation seemed to be the less effective.

7. ACKNOWLEDGEMENTS

The authors would like to thank TEKES (Technology Development Centre of Finland) for funding, Kemira Chemicals Oyj Ltd. Kemwater for the coagulating chemicals used in the study, and Mr. Matti Pessi, Mr. Tero Kuhmonen and Mr. Arto Moilanen for technical assistance. Also, the staff of the Laboratory of Chemistry in the National Public Health Institute is thanked for analyzing the samples.

8. REFERENCES

1. Thurman, E. 1985. Organic geochemistry of natural waters. Martinus Nijhoff / Dr. W. Junk Publishers, The Netherlands, 1985.
2. von Gunten, U and Hoigné, J. 1992. Factors controlling the formation of bromate ion during ozonation of bromide-containing waters. J. Water SRT – Aqua, 41(5): 299-304.
3. Nissinen, T, Rantakokko, P, Myllykangas, T and Vartiainen, T. 1999. Bromide and brominated trihalomethanes in Finnish drinking waters. Proceedings, Fourth Finnish conference of environmental sciences, Tampere, May 21-22, 1999. Environmental science, technology and policy. Kuusisto, S., Isoaho, S., Puhakka, J. (Eds.). Finnish Society for Environmental Sciences. Tampere 1999.
4. Cooper, WJ, Zika, RG, and Steinhauer, MS. 1985. Bromide-oxidant interactions and THM formation: a literature review. Journal American Water Works Association, 77: 116-121.
5. Myllykangas, T, Nissinen, T and Vartiainen, T. 2000. Bromate formation during ozonation of bromide containing drinking water – a pilot plant study. Ozone Science & Engineering, 22(5): 487-499.
6. Myllykangas, T, Nissinen, TK, Mäki-Paakkanen, J, Hirvonen, A and Vartiainen, T. 2003. Bromide affecting drinking water mutagenicity. Chemosphere, 53(7): 745-756.
7. LaLonde, RT, Bu, L, Henwood, A, Fiumano, J and Zhang, L. 1997. Bromine-, chlorine- and mixed halogen-substituted 4-methyl-2(5H)-furanones: synthesis and mutagenic effects of halogen and hydroxyl group replacements. Chemical Research in Toxicology, 10: 1427-1436.
8. Nobukawa, T and Sanukida, S. 2001. Effect of bromide ions on genotoxicity of halogenated by-products from chlorination of humic acid in water. Water Research, 35(18): 4293-4298.
9. Van Benschoten, JE and Edzwald, JK. 1990. Chemical aspects of coagulation using aluminum salts – I. Hydrolytic reactions of alum and polyaluminum chloride. Water Research, 23(12): 1519-1526.
10. Van Benschoten, JE and Edzwald, JK. 1990. Chemical aspects of coagulation using aluminum salts – II. Coagulation of fulvic acid using alum and polyaluminum chloride. Water Research, 23(12): 1527-1535.
11. Gregor, JE, Nokes, CJ and Fenton, E. 1997. Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation. Water Research, 31(12): 2949-2958.

12. Vrijenhoek, EM, Childress, AE, Elimelech, M, Tanaka, TS and Beuhler, MD. 1998. Removing particles and THM precursors by enhanced coagulation. Journal American Water Works Association, 90(4): 139-150.

13. Exall, KN and Vanloon, GW. 2000. Using coagulants to remove organic matter. Journal American Water Works Association, 92(11): 93-102.

14. Duan, J and Gregory, J. 2003. Coagulation by hydrolysing metal salts. Advances in Colloid Interfacial, 100-102: 475-502.

15. Hanson, AT and Cleasby, JL. 1990. The effects of temperature on turbulent flocculation: fluid dynamics and chemistry. Journal American Water Works Association, 82(11): 56-73.

16. Crozes, G, White, P and Marshall, M. 1995. Enhanced coagulation: its effect on NOM removal and chemical costs. Journal American Water Works Association, 87(1): 78-89.

17. Bell-Ajy, K, Abbaszadegan, M, Ibrahim, E, Verges, D and LeChevallier, M. 2000. Conventional and optimized coagulation for NOM removal. Journal American Water Works Association, 92(10): 44-58.

18. Volk, C, Bell, K, Ibrahim, E, Verges, D, Amy, G and Lechevallier, M. 2000. Impact of enhanced and optimized coagulation on removal of organic matterand its biodegradable fraction in drinking water. Water Research, 34(12): 3247-3257.

19. Nierop, KGJ, Jansen, B and Verstaten, JM. 2002. Dissolved organic matter, aluminium and iron interactions: precipitation induced by metal/carbon ratio, pH and competition. Science of the Total Environment, 300: 201-211.

20. Matsui, Y, Yuasa, A, Furuya, Y and Kamei, T. 1998. Dynamic analysis of coagulation with alum and PACl. Journal American Water Works Association, 90(10): 96-106.

21. Jacangelo, JG, SeMarco, J, Owen, DM and Randtke, SJ. 1995. Selected processes for removing NOM: an overview. Journal American Water Works Association, 88(1): 64-77.

22. Kan, C, Huang, C and Pan, JR. 2002. Time requirement for rapid-mixing in coagulation. Colloid and Surfaces A, 203: 1-9.

23. Qualls, RG, Oddoff, SF, Chang, JCH, Dorfman, MH, Dumais, CM, Lobe, DC and Johnson, JD. 1985. Factors controlling sensitivity in ultraviolet disinfection of secondary effluents. Journal of the Water Pollution Control Federation, 57(10): 1006-1011.

24. Crapper, DR, Krishnan, SS and Quikat, S. 1976. Aluminum, neurifibrillary degeneration and Alzheimer's disease. Brain, 99: 67-80.

25. Nayak, P and Chatterjee, AK. 1999. Biochemical view of aluminum-induced neurohazards. Journal of Environmental Biology, 20: 77-84.

26. Ravi, SM, Prabhu, BM, Raju, TR and Bindu, PN. 2000. Long-term affects of aluminum exposure on acetylcholinesterase activity and biogenic amine neurotransmitters in rat brain. Indian Journal of Physiological Pharmacology, 44: 473-478.

27. European Council (EC). 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal L 330, 05/12/1998 p. 0032-0054.

28. SFS 3036. 1981. Determination of chemical oxygen demand (COD Mn or $KMnO_4$ number) in water. Oxidation with permanganate. Finnish Standards Association SFS, Helsinki, Finland, 1981.

29. SFS 3005. 1981. Determination of alkalinity and acidity in water. Potentiometric titration. Finnish Standards Association SFS, Helsinki, Finland, 1981.

30. Edzwald, JK and van Benschoten, JE. 1990. Aluminum coagulation of natural organic matter. Proc. 4th International Guthenburg Symposium on Chemical Treatment. Madrid, Spain, October 1990.

31. HACH. 2002. Water Analysis Handbook. (Oct. 20, 2003) <www.hach.com/wateranalysishandbook/english/eng%5Fa.htm>

32. SFS-EN 1484. 1997. Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). Finnish Standards Association SFS, Helsinki, Finland, 1997.

33. Vartiainen, T, Liimatainen, A and Kauranen, P. 1987. The use of TSK size exclusion columns in determination of the quality and quantity of humus in raw waters and drinking waters. Science of the Total Environment, 62: 75-84.

34. Myllykangas, T, Nissinen, TK, Rantakokko, P, Martikainen, PJ and Vartiainen, T. 2002. Molecular size fractions of treated aquatic humus. Water Research, 36(12): 3045-3053.

35. ISO/DIS 10301:1994. 1994. Water quality – determination of highly volatile halogenated hydrocarbons – gas-chromatographic methods. International Organization for Standardization (ISO).

36. Rantakokko, P, Nissinen, T and Vartiainen, T. 1999. Determination of bromide ion in raw and drinking waters by capillary zone electrophoresis. Journal of Chromatography A, 839(1-2): 217-225.

37. Vartiainen, T and Liimatainen, A. 1986. High levels of mutagenic activity in chlorinated drinking water in Finland. Mutation Research, 169: 29-34.

38. SFS-EN 1485. 1997. Water quality – determination of adsorbable organically bound halogens (AOX). Finnish Standards Association SFS, Helsinki, Finland, 1997.

39. EPA Method 552.2. 1995. Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatisation and gas chromatography with electron capture detection. EPA-600-R-95-131, U.S. Environmental Protection Agency, August 1995.

40. Gregory, D and Carlson, K. 2003. Relationship of pH and floc formation kinetics to granular media filtration performance. Environmental Science & Technology, 37(7): 1398-1403.

41. Schnoor, JL, Nitzschke, JL, Lucas, RD and Veenstra, JN. 1979. Trihalomethane yields as a function of precursor molecular weight. Environmental Science & Technology, 13(9): 1134-1138.

42. Oliver, BG and Thurman, EM. 1983. Influence of aquatic humic substance properties on trihalomethane potential. Water chlorination – Environmental impact and health effects, Vol.4, Book 1: Chemistry and water treatment. Ann Arbor Science, Ann Arbor, Michigan.

43. Chang EE, Lin, YP and Chiang, PC. 2001. Effects of bromide on the formation of THMs and HAAs. Chemosphere, 43: 1029-1034.

44. Imai, A, Matsushige, K and Nagai, T. 2003. Trihalomethane formation potential of dissolved organic matter in a shallow eutrophic lake. Water Research, 37: 4284-4294.

45. Bolto, B, Dixon, D, Eldridge, R and King, S. 2002. Removal of THM precursors by coagulation or ion exhange. Water Research, 36: 5066-5073.

46. Page, DW, van Leeuwen, JA, Spark, KM, Drikas, M, Withers, N and Mulcahy, DE. 2002. Effect of alum treatment on the trihalomethane formation and bacterial regrowth potential of natural and synthetic waters. Water Research, 36: 4884-4892.

47. Liang, L and Singer, PC. 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. Environmental Science & Technology, 37(13): 2920-2928.

48. EPA Stage1. 1998. Stage 1 disinfectants and disinfection byproducts rule. EPA 815-F-98-010, United States Environmental Protection Agency, December 1998.

49. Zhang, X, Echigo, S, Minear, RA and Plewa, MJ. 2000. Characterization and comparison of disinfection by-products of four major disinfectants. Natural organic matter and disinfection by-products: characterization and control in drinking water (eds., S.E. Barrett, S.W. Krasner and G.L. Amy), pp. 299-314. Washington, D.C.: American chemical Society.

CHAPTER 4: BROMATE FORMATION DURING OZONATION OF BROMIDE CONTAINING DRINKING WATER – A PILOT SCALE STUDY

Tiia Myllykangas[1], Tarja Nissinen[1] and Terttu Vartiainen[1,2]

[1]National Public Health Institute, Division of Environmental Health, Laboratory of Chemistry, P.O. Box 95, FIN-70701 Kuopio, Finland
[2]University of Kuopio, Department of Environmental Sciences, P.O. Box 1627, FIN-70211 Kuopio, Finland

Published in Ozone Science & Technology, 22(5), 487-499 (2000).
Reproduced here with kind permission from the CRC Press.

1. ABSTRACT

The effect of bromide ion concentration, pH, temperature, alkalinity, and hydrogen peroxide content on bromate formation was studied. Increase in pH was found to increase the bromate formation the most. Also increase in the ozonation temperature, bromide ion concentration and hydrogen peroxide content increased the observed bromate concentration. Only increased alkalinity decreased the bromate formation during the ozonation experiments. Bromate formation exceeded the EU limit value for bromate ion, 10 μg/L, when the initial bromide ion concentration was around 100 μg/L, except for the alkalinity of 1.4 mmol/l, when the bromate formation was 9.4 μg/L.

Key Words: Ozone; Bromate Ion; Bromide Ion Concentration; Ozonation; Pilot Scale Study; Drinking Water Treatment

2. INTRODUCTION

Brominated by-products are of concern in the areas where raw water contains high concentrations of bromide ion. Bromide can originate from saltwater intrusion, natural fractionation, anthropogenic bromide emissions (such as potassium and coal mining), water disinfection with chlorine (bromide as a trace impurity), agricultural applications (methyl bromide is a widely used additive in fumigating crops and soil), or heavy traffic (ethylene bromide is a common additive to leaded gasoline)[1-5].

Even if bromide ion in drinking water supplies has not been observed to cause direct public health problems[5], it is a precursor of the formation of bromate ion and other brominated oxidation-DBPs, which are known to be harmful to people's health. Both ozone and bromide ion threshold levels for the formation of by-products are compound-specific as well as source-specific[6,7].

According to Siddiqui & Amy[6], only a fraction of the Br^- reacts with ozone. However, bromide is considered to increase the rate of oxidation reactions8,9. The reaction of ozone with Br^- is expected to be at least 100 times faster than that with Cl^- [10].

Ozonation transform bromide efficiently into hypobromous acid and hypobromite[3]. The reaction of O_3 with protonated HOBr is negligible. Hypobromite ion can be oxidized further to bromate by ozone and brominated organic compounds can be formed in reactions between hypobromous acid and organic carbon[11]. Bromate ion formation occurs only in the presence of dissolved ozone (DO_3)[5].

Bromate ion has been found to be carcinogenic in rats and hamsters[12,13], and it is classified as a potential carcinogen for humans. The European Union (the EU) limit value for bromate formation is 10 µg/L[14].

The purpose of this study was to examine the effect of pH, ozone dosage, bromide ion concentration, temperature, hydrogen peroxide and alkalinity on the formation of bromate in humus-rich drinking water.

3. MATERIALS AND METHODS

The pilot-plant situated in the Environmental Research Hall of the University of Kuopio. The pilot-plant consisted of an ozone generator (Pacific Technology mdl OI), a column (in which the water circulates and is in touch with ozone), a water pump (Sigma 07220 PVT membrane pump, ProMinent Finland Oy), an analyzer for ozone from the gas flow (Dasibi 1180-HC), an analyzer for the dissolved ozone (Orbisphere 3600) and computer programs for recording the data (Ozone © Tirkkonen & Löfström, Moca3600 © Orbisphere Laboratories) (Fig. 4-1). All the parts in touch with ozone were made from PTFE (Teflon), acrylic, or nylon.

The amount of water used per one batch-test ozonation was 18 liters. The column and the pipelines were disinfected and cleaned with Virkon (Antec Int. Ltd, Suffolk, England) cleansing agent after or before different group of tests. The water from the water works of Kuopio was coagulated and sand filtrated prior to ozonation in the research hall. The water to be ozonated was spiked with sodium bromide solution to achieve the required bromide ion concentration, because the water itself contained no bromide ions.

The ozone generator formed ozone from pressurized air by corona discharge. The ozone concentration in the gas flow was measured and adjusted by leading the gas flow through a by-pass pipeline to the Dasibi analyzer instead of the column using a corresponding counter pressure to adjust the mass flow right. The gas mixture containing ozone was bubbled through KI-solution (20 g/L KI, 7.3 g/L $Na_2HPO_4 \cdot H_2O$, and 3.5 g/L KH_2PO_4) to remove the residual ozone prior to releasing the gas to the atmosphere. The adjusted gas flow (both in ozone concentration and flow rate) was then switched to go through the water column, in which the water was recirculated by the pump. The gas flow was bubbled through the water column till the desired O_3/TOC (total organic carbon) ratio was achieved. Chemicals and dosages for different tests were selected to simulate current practice at full-scale treatment plants. The Ct-value (Concentration × time) was calculated as the residual ozone concentration (as DO_3, in mg/L) times the time of ozonation (in minutes).

All the samples analyzed, except for the THM samples, were stored in a freezer (at a temperature lower than -18 °C) after sampling, prior to analyzing. All reagents used were of analytical grade.

Bromide analysis was made with 270-HT High Throughput Capillary Electrophoresis System (Applied Biosystems, San Jose, CA, USA) according to the method developed by Rantakokko et al.[15]. The detection limit was 15 μg/L, and the error was ±10%. Three initial bromide ion concentrations (50, 100 and 500 μg/L) were used.

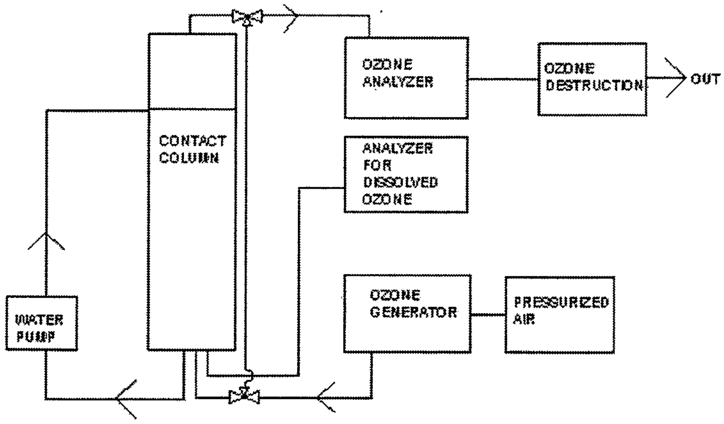


Figure 4-1. The ozonation equipment in the Environmental Research Hall (University of Kuopio).

Bromate samples were filtered through a 0.45-μm MilliPore syringe-filter prior to freezing. The samples were analyzed by ion chromatography with inductively coupled plasma mass spectrometric detection (IC-ICP/MS)[16] in the Research Center of Lahti, Finland. The detection limit was 0.2 μg/L.

TOC was measured by an accredited method (laboratory T77) with Shimadzu Total Organic Carbon analyzer, model 5000-TOC (Kyoto, Japan). The samples were acidified by adding concentrated H_3PO_3 acid to achieve a pH value ≤ 2 prior to analyzing.

Both temperature and pH were measured *in situ.* Temperature was measured on-line with Orbisphere 3600 analyzer for dissolved ozone. pH measurement was made with calibrated WTW pH320-meter. The effect of the initial temperature on the bromate formation was studied at two initial temperatures. The effect of the initial pH on the bromate formation was studied at three initial pHs.

The alkalinity was adjusted by adding 1 M $CaCO_3$ solution into the water. Higher alkalinities were tested to reach the conditions, which agree with the actual conditions in water distribution systems. Alkalinity was measured according to the Finnish Standard SFS3005. It is based on the potentiometric titration of the sample with HCl (of a known concentration) to pH value 4.5. Increased alkalinity was tested in three ozonation experiments. Alkalinity was not readjusted during the ozonation experiments, but it was measured prior to and after the ozonation experiment.

The concentration of H_2O_2 used was approximately 0.1 *N*, which was checked by titration of the solution with 0.1 *N* $Na_2S_2O_3$ after the addition of 4 *N* H_2SO_4, 1 *N* KI, 1 *N* $(NH_4)_2Mo_7O_{24}$, and starch solution[17]. The appropriate amount of hydrogen peroxide was added to the water prior to ozonation. The ratio was calculated as mg H_2O_2/mg O_3. Hydrogen peroxide was spiked to the waters of three ozonation experiments.

4. RESULTS

The initial conditions of the water are listed in Table 4-I. The bromide ion concentration was spiked to the water prior to ozonation.

Table 4-II shows the results obtained from the ozonation experiments. Less than 35 mole-% of the Br^- consumed during ozonation was converted to bromate ion, except for the initial pH 9.0, when 65 mole-% of the Br^- consumed was converted to bromate.

Table 4-I. The initial conditions of the ozonated water.

Experiment	**A**	**B**	**C**	**D**	**E**	F	G	**H**	**I**
[Br], µg/L	0	50	50	50	100	500	500	500	500
H_2O_2/O_3 mg/mg	0	0	0.3	0	0	0	0	0	0
Alkalinity, mmol/l	0.3	0.3	NA	1.8	0.3	0.3	0.3	0.3	NA
$[O_3]$ in Gas (ppm)	0	2000	3900	3900	1900	0	1600	2200	1900
Initial T (°C)	12	13	13	12	13	12	12	13	14
Experiment	**J**	**K**	**L**	**M**	**N**	**O**	**P**	**Q**	
[Br], µg/L	500	500	500	500	500	500	500	500	
H_2O_2/O_3 mg/mg	0	0	0	0.3	0.6	0.9	0	0	
Alkalinity, mmol/l	NA	0.3	0.3	NA	NA	NA	0.8	1.4	
$[O_3]$ in Gas (ppm)	1800	1800	3900	3600	3900	3800	3600	4000	
Initial T (°C)	14	20	13	13	13	13	12	11	

NA = Not Adjusted

No bromate formation was observed from the blank sample (unozonated, no bromide ion addition), nor when measured from unozonated water with spiked bromide ion.

Increasing the initial Br^- concentration from 50 to 100 µg/L, the bromate formation increased by the factor of 10 from 1.2 µg/L to 12 µg/L. However, increasing the bromide concentration from 100 to 500 µg/L had no further impact on bromate formation under these ozonation conditions. Figure 2 shows the results obtained.

Table 4-II. Bromate ion concentrations of ozonated waters. The O_3/TOC ratio was 2.1, alkalinity 0.3 mmol/l and the initial temperature between 12 and 14 °C unless otherwise noted.

Experiment	**Note**	**Ct value (mg/L ×min)**	**pH**		**TOC (mg/L)**		**Bromide Ion (µg/L)**		**Bromate formation (µg/L)**
			Initial	**Final**	**Initial**	**Final**	**Initial**	**Final**	
A	Blank	0	6.2	6.2	3.0	3.0	0	0	0
B	$[Br^-]_{ini}$ = 50 µg/L	2.6	6.2	6.7	3.0	2.8	50	52	1.2
C	H_2O_2/O_3 = 0.4 mg/mg	1.1	6.2	6.4	3.0	2.6	50	38	1.5
D	Alkalinity = 1.8 mmol/l	4.7	6.5	6.8	3.0	2.3	50	48	3.4
E	$[Br^-]_{ini}$ = 100µg/L	3.3	6.3	7.1	3.0	2.6	100	77	12
F	Br^- spiked, non-ozonated	0	6.2	6.2	3.0	3.0	500	500	0
G	Br^- spiked, ozonated	1.8	6.2	6.7	3.0	3.1	500	405	11
H	Br^- spiked, ozonated	3.3	6.1	6.6	3.0	2.9	500	437	13
I	Different pH	2.2	7.2	7.3	3.0	2.8	500	427	30
J	Different pH	2.3	9.0	8.2	3.0	2.8	500	403	100
K	t = 20 °C	2.4	NA	NA	3.0	3.0	500	330	88
L	O_3/TOC = 4.1	5.6	NA	NA	3.0	3.1	500	377	28
M	H_2O_2/O_3 = 0.2 mg/mg	1.6	6.2	6.4	3.0	2.4	500	394	24
N	H_2O_2/O_3 = 0.4 mg/mg	1.0	6.3	6.4	3.0	2.4	500	418	23
O	H_2O_2/O_3 = 0.6 mg/mg	0.8	6.2	6.3	3.0	2.4	500	401	15
P	Alkalinity = 0.8 mmol/l	4.7	6.5	6.7	3.0	2.5	500	446	11
Q	Alkalinity = 1.4 mmol/l	5.0	6.5	6.8	3.0	2.7	500	460	9.4

NA = Not Adjusted

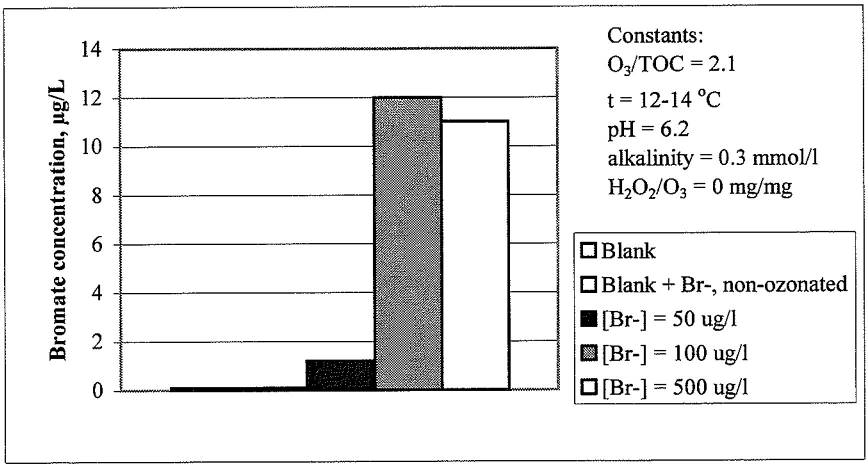


Figure 4-2. The effect of the initial Br^- concentration on the bromate formation during the ozonation experiments.

The bromate formation increased when the O_3/TOC ratio increased from 0 to 1.05, 2.1 and 4.1 (1.4, 13 and 28 µg/L, respectively). The corresponding Ct values were 0.8, 1.7, and 5.6 mg/L×min. The results are shown in Figures 4-3 and 4-4. No bromate formation was observed in the blank sample or in the unozonated sample containing bromide.

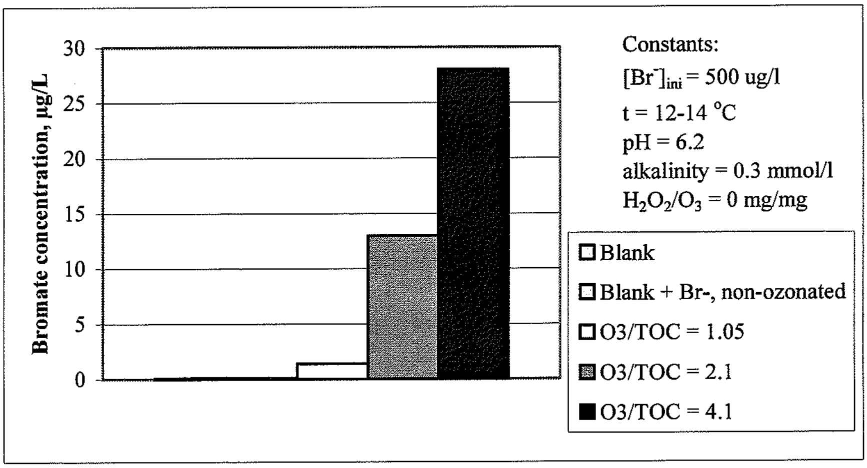


Figure 4-3. The effect of the O_3/TOC ratio on the bromate formation during the ozonation experiments.

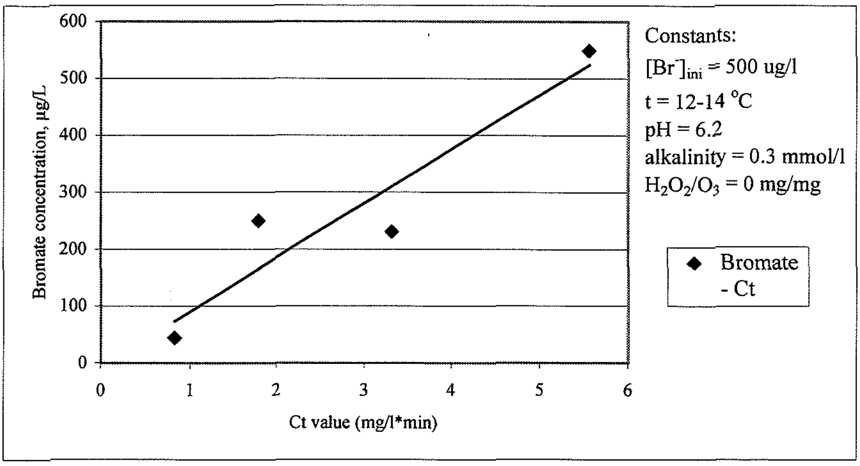


Figure 4-4. The effect of the Ct value on the bromate formation during the ozonation experiments.

When the initial temperature increased from 12 to 20 °C, the bromate formation increased from 11 to 88 µg/L. The results can be seen from Figure 4-5.

Increasing the pH increased the bromate formation (Figure 4-6). At the lower pH of 6.2, and at O_3/TOC ratio of 4.1 the formation of bromate was equal to the one of the ozonation at pH 7.2. When pH increased to 9.0, the formation of bromate increased drastically to 100 µg/L, which was the highest observed bromate formation during these ozonation experiments.

When the alkalinity of the water increased from 0.3 to 0.8 and 1.4 mmol/l, the bromate formation decreased from 13 to 11 and 9.4 µg/L, respectively. When the initial Br^- concentration was low (50 µg/L), the bromate formation was 3.4 µg/L at a high alkalinity (1.8 mmol/l). The effects of the alkalinity on the bromate formation have been shown in Figure 4-7. Alkalinity was found to remain at the initial level during the ozonation experiments.

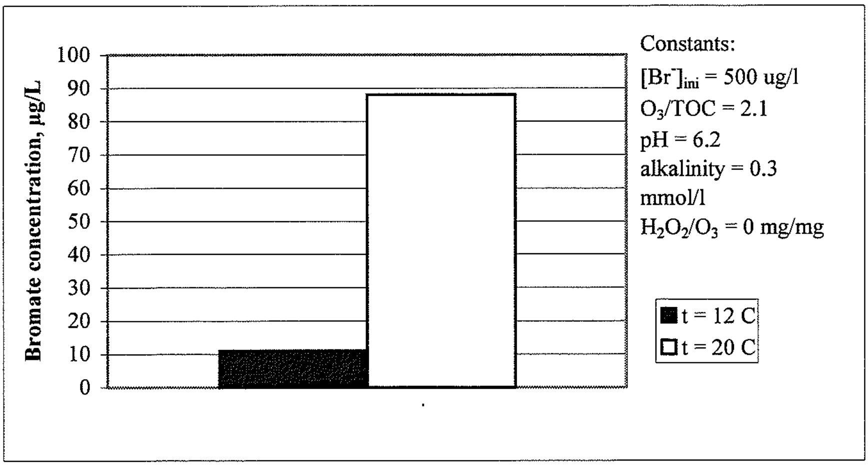


Figure 4-5. The effect of the initial temperature on the bromate formation during the ozonation experiments.

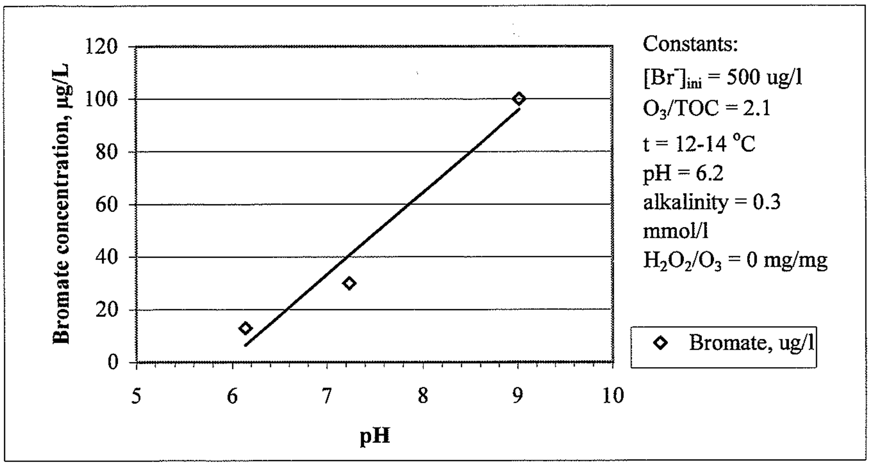


Figure 4-6. The effect of the initial pH on the bromate formation during the ozonation experiments.

When the H_2O_2/O_3 ratio (in mg/mg) increased from 0 to 0.2 or 0.4, the bromate yield increased from 11 to 24 or 23 µg/L, respectively. When the H_2O_2/O_3 ratio was 0.6, the bromate yield was 15 µg/L. Figure 4-8 shows the relationship between hydrogen peroxide content and the bromate formation.

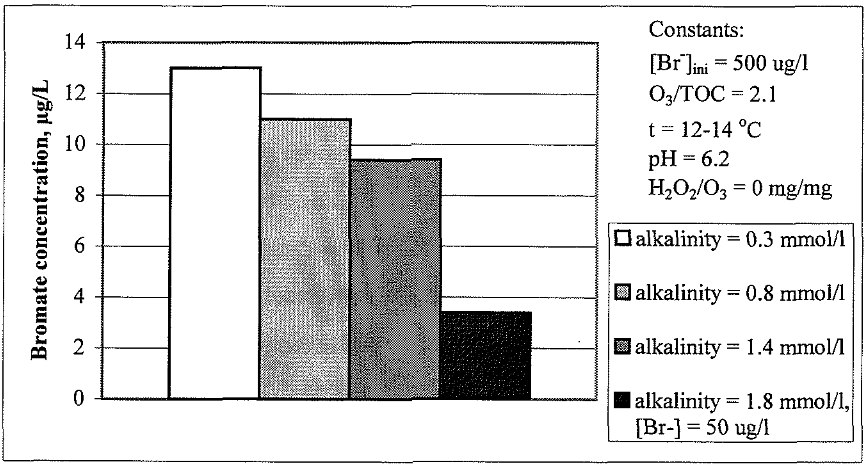


Figure 4-7. The effect of the alkalinity on the bromate formation during the ozonation experiments.

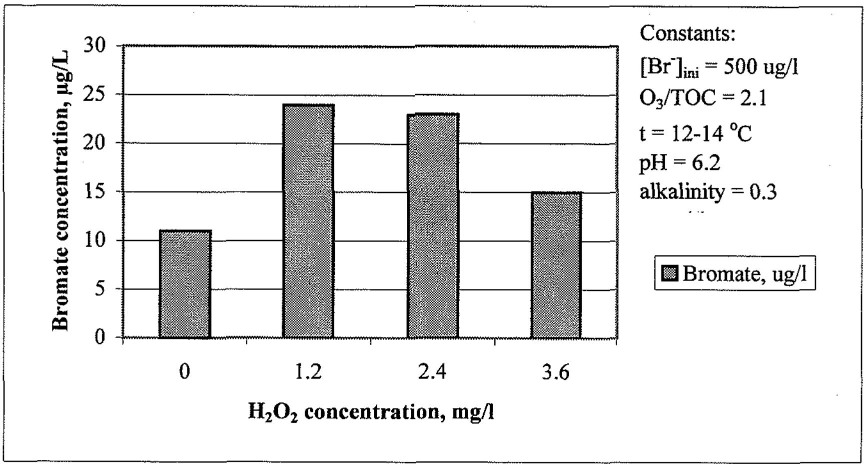


Figure 4-8. The effect of the H_2O_2 concentration on the bromate formation during the ozonation experiments.

5. DISCUSSION

The bromate formation did not increase as the initial bromide ion concentration increased from 100 to 500 µg/L. This result is in contrast with the results of Glaze et al.[18], who found that at higher bromide levels the bromate formation was greater with DOC and ozone dose remaining the same. The threshold concentration of bromide ion for bromate formation has been observed by several authors[6], and it has been found to depend on the water source[7]. However, Croué et al.[19] as well as Legube[20] observed no threshold bromide ion concentration on bromate formation. The observations by Croué et al.[19] and Legube[20] are in accordance with our results, because at as a low bromide ion level as 50 µg/L, bromate was formed. The observed threshold concentrations of bromide ion were probably due to inaccuracies in the quantitation limits of the processes used.

Because bromate is formed only in the presence of dissolved ozone, the change in ozone residual affects the formed bromate concentration. Our results are in accordance with the results of Krasner et al.[21], Siddiqui and Amy[6], and Ozekin and Amy[7], increasing with increasing ozone residual. Glaze et al.[18] and Krasner et al.[21] have observed that at a low O_3-to-TOC-ratio (≤ 1:1) there was probably not enough ozone to complete the reactions to form BrO_3^-, which was possibly the case in our experiments as well. The Ct values at the O_3/TOC ratios of 1.05, 2.1, and 4.1 were found to be 0.8, 1.7, and 5.6 mg/L×min, respectively. E.g. the studies of Shukairy et al.[11] yielded similar results as was found in our studies: the bromate formation increased with increasing Ct.

pH adjustment has been observed to be a way to control bromate formation. Croué et al.[19] found that the production of bromate ion was less important at pH 6.4 than at pH 8.4. In our study the bromate formation was greater at elevated pH levels than at the ambient pH, which is in accordance with previous results. The effect of pH is due to HOBr formation at a lower (<7) pH[5]. HOBr does not react with ozone to form bromate. The presence of OBr^- (at a higher pH) does enhance bromate formation, because it has been found to be the requisite intermediate in bromate formation[22,23]. At a higher pH (>8), the decomposition of ozone is accelerated, which yields to greater bromate formation during ozonation[5].

An increase in ozonation temperature has been observed to affect more on bromate formation than a corresponding increase in incubation temperature[6]. In our study, the increase in the ozonation temperature from 12 °C to 20 °C increased the bromate formation 8 fold, from 11 to 88 µg/L.

Alkalinity has been observed to both increase[24] and decrease[18] the bromate formation. Our results are in accordance with the observation of Glaze et al.[18] that the bromate formation was at the greatest at the lowest alkalinity, decreasing with increasing alkalinity. When the initial bromide ion concentration was 50 µg/L, the increased alkalinity increased the bromate formation, which is in accordance with the results of Amy et al.[24].

In our study the H_2O_2/O_3 ratio of 0.4 is in the optimal range (0.35-0.45 mg H_2O_2/mg O_3) in the oxidation of organic matter[25], and the two other ratios (H_2O_2/O_3 = 0.2 and 0.6) were used for research purposes. In the study of Croué et al.[19], the addition of hydrogen peroxide increased the formation of bromate ion, which is in accordance with our results. In general, the studies made with hydrogen peroxide addition have yielded mixed results. Some studies have shown that hydrogen peroxide increases the bromate formation[6], while the others have observed a decrease in the bromate formation[26]. The presence of hydrogen peroxide causes the reduction of HOBr/OBr^- to Br^- [5,22], and, thus, reduces the bromate formation.

In summary, the bromate formation was found to increase during the ozonation experiments at higher initial temperature and pH values as well as with increase in residual ozone and hydrogen peroxide concentration. Increasing alkalinity decreased the bromate formation. Bromate formation exceeded the EU limit value of 10 µg/L for bromate when the initial bromide ion concentration was 100 or 500 µg/L, except for the high alkalinity (1.4 mmol/l).

6. CONCLUSIONS

1. Bromide ion concentration as low as 50 µg/L was sufficient to promote the formation of bromate during these ozonation experiments with coagulated and sand filtrated water. When ozonated at the initial bromide ion concentration of 50 µg/L, the bromate formation did not exceed the EU limit value for bromate, 10 µg/L, being 1.2 µg/L.
2. The EU limit value for bromate exceeded with water containing bromide ion 100 or 500 µg/L at ozone concentrations used in this study. Only at an alkalinity as high as 1.4 mmol/l, even if the bromide ion concentration was 500 µg/L, the limit value was not exceeded.
3. According to these results, less than 35 mole-% (except for pH 9.0 being 65 mole-%) of the bromide ion consumed during ozonation was converted to bromate ion, which indicates that other brominated organic compounds are formed as well.

7. ACKNOWLEDGEMENTS

This study was funded by the Academy of Finland (project no. 34538), the Technology Development Centre of Finland, and the University of Kuopio. The facilities for this study were provided by the National Public Health Institute of Finland.

8. REFERENCES

1. Cooper, WJ, Zika, RG and Steinhauer, MS. 1985. Bromide-oxidant interactions and THM formation: a literature review. Journal American Water Works Association, 77(4): 116-121.
2. von Gunten, U and Hoigné, J. 1992. Factors controlling the formation of bromate ion during ozonation of bromide-containing waters. Journal of Water Supply, Research and Technology - Aqua 41(5): 299-304.
3. von Gunten, U and Hoigné, J. 1996. Ozonation of bromide-containing waters: bromate formation through ozone and hydroxyl radicals. In: disinfection by-products in water treatment - the chemistry of their formation and control. Edited by Roger A. Minear & Gary L. Amy, CRC Press, Inc., p. 187-206.
4. Krasner, SW, Sclimenti, MJ and Means, EG. 1994. Quality degradation: implications for DBP formation. Journal American Water Works Association, 86(6): 33-47.
5. Siddiqui, MS, Amy, GL and Rice, RG. 1995. Bromate ion formation: a critical review. Journal American Water Works Association, 87(10): 58-70.
6. Siddiqui, MS and Amy, GL. 1993. Factors affecting DBP formation during ozone-bromide reactions. Journal American Water Works Association, 85(1): 63-72.
7. Ozekin, K and Amy, GL. 1997. Threshold levels for bromate formation in drinking water. Ozone: Science & Engineering, 19: 232-337.
8. Luong, TV, Peters, CJ and Perry, R. 1982. Influence of bromide and ammonia upon the formation of trihalomethanes under water-treatment conditions. Environmental Science & Technology, 16: 473-479.
9. Rice, RG and Gomez-Taylor, M. 1986. Occurrence of by-products of strong oxidants reacting with drinking water contaminants - scope of the problem. Environmental Health Perspectives. 69: 31-44.
10. Hoigné, J, Bader, H, Haag, WR and Staehelin, J. 1985. Rate constants of reactions of ozone with organic and inorganic compounds in water - III inorganic compounds and radicals. Water Research, 19(8): 993-1004.
11. Shukairy, HM, Miltner, RJ and Summers, RS. 1994. Bromide's effect on DBP formation, speciation, and control: part 1, ozonation. Journal American Water Works Association, 86(6): 72-87.
12. International Agency for Research on Cancer. 1986. Some naturally occurring and synthetic food components, furocoumarins and ultraviolet radiation. Lyon, 1986: 207-220 (IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, Volume 40).
13. Joint FAO/WHO Expert Committee on Food Additives (JECFA). 1989. Toxicological evaluation of certain food additives and contaminants. Cambridge, Cambridge University Press, 1989 (WHO Food Additives Series, No. 24).

14. EU. 1998. Official Journal of the European Community L330: Directive 98/83/EC.

15. Rantakokko, P, Nissinen, T and Vartiainen, T. 1999. Determination of bromide ion in raw and drinking waters by capillary zone electrophoresis. Journal of Chromatography A, 839(1-2): 217-225.

16. Pantsar-Kallio, M and Manninen, PKG. 1998. Speciation of halogenides and oxyhalogens by ion chromatography-inductively coupled plasma mass spectrometry. Analytica Chimica Acta, 360(1998): 161-166.

17. AOAC. 1980. Official methods of analysis of the association of official analytical chemists. Edited by W. Hoewitz, p. 545.

18. Glaze, WH, Weinberg, HS and Cavanagh, JE. 1993a. Evaluating the formation of brominated DBPs during ozonation. Journal American Water Works Association, 85(1): 96-103.

19. Croué, JP, Koudjonou, BK and Legube, B. 1996. Parameters affecting the formation of bromate ion during ozonation. Ozone Science & Engineering, 18: 1-18.

20. Legube, B. 1996. A survey of bromate ion in European drinking water. Ozone Science & Engineering, 18: 325-348.

21. Krasner, SW, Glaze, WH, Weinberg, HS, Daniel, PA and Najm, IN. 1993a. Formation and control of bromate during ozonation of waters containing bromide. Journal American Water Works Association, 85(1): 73-81.

22. von Gunten, U and Oliveras, Y. 1997. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural systems. Water Research, 31(4): 900-906.

23. Richardson, LB, Burton, DT, Helz, GR and Rhoderick, JC. 1981. Residual oxidant decay and bromate formation in chlorinated and ozonated sea-water. Water Research, 15: 1067-1074.

24. Amy, G. Siddiqui, M, Ozekin, K and Westerhoff, P. 1993. Threshold levels for bromate formation in drinking water. Water Supply, 13(1): 157-162.

25. Paillard, H. 1990. Elimination of atrazine by a combined O_3-H_2O_2 treatment on the Seine river, in Proc. 6th European Symposium on Organic Micropollutants in the Aquatic Environment, (Lisbon, May 22-24, 1990).

26. Daniel, PA, Zafer, MA and Meyerhofer, PF. 1993. Bromate control: water quality, engineering, and operational considerations. IWSA Workshop, Paris, 1993.

CHAPTER 5: THE EVALUATION OF OZONATION AND CHLORINATION ON DISINFECTION BY-PRODUCT FORMATION FOR A HIGH-BROMIDE WATER

T. Myllykangas*[1,2], T.K. Nissinen[1], A. Hirvonen[2], P. Rantakokko[1] and T. Vartiainen[1,2]

[1]National Public Health Institute, Division of Environmental Health, P.O. Box 95, FIN-70701 Kuopio, Finland
[2]University of Kuopio, Department of Environmental Sciences, P.O. Box 1627, FIN-70211 Kuopio, Finland
*The corresponding author. [Email: Tiia.Myllykangas@ktl.fi, tel. +358 17 201 181, fax. +358 17 201 265]

Accepted for publication in Ozone Science & Engineering (2003).
Reproduced here with kind permission from the CRC Press.

1. ABSTRACT

High-bromide raw water was ozonated or chlorinated with and without hydrogen peroxide to study the effect of the disinfectants on the disinfection by-product (DBP) formation. Less bromate was formed when ozonation was made at the ambient pH of 5.8 as compared to ozonation at pH 7, showing the effectiveness of pH reduction in controlling the bromate formation. When chlorine dose was 1 mg/L instead of 2.3 mg/L, the trihalomethane formation was 50 μg/L instead of >100 μg/L, and the proportional distribution of the trihalomethanes was similar. The use of ozone for this water could provide good results in respect of the DBP formation.

Keywords Ozone; chlorine; bromide; bromate; disinfection; disinfection by-products

2. INTRODUCTION

Bromide can be found in natural waters from a few micrograms to several thousands of micrograms per liter[1], and in Finland the westcoastal surface waters contain up to 485 μg/L bromide[2]. Bromide has not been observed to cause direct health effects if it is present in the drinking water. On the other hand, hypobromous acid reacts with the (organic) constituents of the water much faster than hypochlorous acid resulting in high amounts of disinfection by-products (DBPs). Those compounds cause direct and indirect health problems for the consumers, and many compounds are regulated by legislation both in the EU[3] and in the USA[4], and they are found to be more harmful than their chlorinated analogues[5,6].

Ozonation of bromide-containing waters has been found to result in the formation of bromate[6-8]. Even if many bromoorganic compounds, such as bromoform, bromopicrin, dibromoacetonitrile, bromoacetone, bromoacetic acid, bromoalkanes, and bromohydrins, are also formed during ozonation, their concentrations are usually very low, and the main concern should be addressed towards bromate formation[9,10].

The amount of humus, measured as total organic carbon (TOC), and the quality of it, are important factors in the formation of the DBPs. Because of the high amount of organic matter typically found in the waters in boreal regions (up to 40 mg/L as TOC; ref. 11), postdisinfection with chlorine or other chlorine-containing oxidants is mandatory to avoid or restrict the microbial regrowth in the distribution system. In the reactions between chlorine and organic matter, high amounts of trihalomethanes (THMs), halogenated acetic acids (HAAs), 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX), and other halogenated DBPs are typically found[12-16]. Many of the compounds are found to be carcinogenic or mutagenic[17], and other effects are observed as well. Ozonation with or without hydrogen peroxide can be used as a preoxidation method before chlorination resulting in lower chlorine demand and lower amounts of DBPs in the finished water due to the high oxidation potentials of the two oxidants[18,19]. However, the obtainable results are highly case-specific, and the on-site experiments are necessary to make sure that the treatment is adequate for that water to ensure the quality of drinking water.

The aim of this study was to compare ozonation and chlorination to reduce the formation of DBPs of a high-bromide containing surface water used for drinking water production.

3. MATERIALS AND METHODS

3.1 WATER USED IN THE EXPERIMENTS

The water used in the experiments was taken from the water works in Uusikaupunki, Finland (lat. 60°48', long. 21°25'), in which a high-bromide-containing surface water is used as the raw water. The water treatment process in the water works consists of coagulation and flocculation (coagulant ferric sulphate, 75 mg/L, with a polymer, 0.05 mg/L), flotation, sand filtration, and disinfection (hypochlorite, feed approximately 2.3 mg/L as Cl_2). In Table 5-I are presented results obtained after the treatment process in the water works during the year before the experiments. The clarified, non-chlorinated water was used in our experiments. The water was transported in plastic containers by bus, and the time from shipping to receiving the containers was approximately one day. The experiments were made next day from the receiving of the containers. Ozonation experiments were made in the winter (February-March), while chlorination experiments were made in the fall (November-December) of the same year.

Table 5-I. Characteristics of the raw water used in this experiment and drinking water of the city Uusikaupunki, Finland (average [range; number of samples]).

	Raw water	Drinking water
TOC (mg/L)	5.8 [3.8-6.8; 7]	3.3 [3.0-3.5; 7]
Br^- (µg/L)	340 [200-520; 7]	110 [70-165; 7]
Inorganic anions (mg/L)	80 [70-85; 3]	140 [135-150; 3]
Cl_2 dose (mg/L)		2.3
TTHMs (µg/L)		124 [102-160; 8]
Mutagenicity (net rev/L)		3750 [3360-4530; 6]

TOC = total organic carbon; inorganic anions = the sum of the six inorganic anions (chloride, nitrite, sulfate, nitrate, fluoride and phosphate); TTHMs = the sum of the four trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane, bromoform).

3.2 EXPERIMENTAL METHODS

3.2.1 Ozonation

The ozonation experiments were carried out with a system consisting of an ozone generator, a column, a water pump, analyzers for dissolved and gaseous ozone, and computer programs for recording the data[20]. The O_3/TOC mass ratio used in the experiments was approximately 4, except in the experiment C it was 5.3, which allowed us to examine the effect of very high ozone concentration on this particular water with high bromide concentration. The ozone doses (in mg/L) are presented in Table 5-II. Since the surface water temperature in Finland varies typically from 2 to 20°C during the course of the year, and the water temperature influences on the water's characteristics and reaction kinetics, ozonation was made at two temperatures (10°C and 17°C). Raw water alkalinity in Finland is usually low, <0.3 mM. Two alkalinities of 0.3 mM and 0.5 mM were tested to study the effect of small alkalinity increase on the formation of bromate. The higher pH of 7 (vs. the ambient pH of 5.8) was chosen, since ozone decomposition is accelerated at increased pH values resulting in higher reaction rates with many organic and inorganic compounds present in water[21]. The pH of the water was adjusted with $Ca(OH)_2$. The disinfection exposure of the ozonation experiments (CT) was calculated by multiplying the average residual ozone concentration (mg/L, from the beginning to the end of ozonation) with time (minutes), since the ozonation was conducted only till the desired ozone dosage was achieved and no extra reaction time was used before sampling. By doing so, it is possible to estimate the effectiveness of ozonation as disinfection method, because the CT is the time-dependent concentration of the disinfectant integrated for the time of its action[9]. During the ozonation experiments, the initial bromide concentration of the water varied from 340 to 490 μg/L

3.2.2 Chlorination

In the water works of Uusikaupunki, chlorination was made at pH 8.5-8.7 at the time of the experiments, and a pH of 8.5 was chosen for laboratory study. The desired NaOCl-dose was Cl_2:TOC = 1:3, corresponding to 1 mg/L of Cl_2 when the TOC was approximately 3 mg/L, and the temperature for chlorination was 4°C. The residual chlorine concentration was measured after one hour, and the samples for the other analyses were taken after 96 hours of reaction time. Chlorine dose was lowered from 2.3 mg/L used in the water works of Uusikaupunki to 1 mg/L to study its effect on the THM formation, since the THM concentrations in the water works were found to be very high (Table 5-I) and reductions in them are necessary both for the legislation and the health effects. The chlorine dose was chosen to be 1 mg/L, since in Finland a chlorine dose of 0.3-1.0 mg/L is often used for disinfection resulting only in low (0-0.2 mg/L) residual in the distribution systems[22]. No chlorine residual was observed at this point except in the hydrogen peroxide-chlorination experiment. During the chlorination experiments the range was 250 - 340 μg/L Br^-. In the experiments where the TOC concentration was lowered (from 3 mg/L to 2 mg/L or 1.5 mg/L) by diluting the water with distilled water to study the effect of the bromide-to-TOC mass ratio on the disinfection by-product formation, bromide ion concentration was kept constant (at about 250 µg/L) by adding an appropriate amount of NaBr solution to the waters before the chlorine treatment.

3.2.3 Hydrogen peroxide oxidation

Hydrogen peroxide was added to the water just before ozonation or chlorination. In the ozonation experiments, two doses were used, H_2O_2/O_3 mass ratios of 0.05 and 0.3 (molar ratios of 0.1 and 0.4), while in the chlorination experiments, a mass ratio H_2O_2/Cl_2 of 1.0 (molar ratio of 0.5) was used. The concentration of the H_2O_2 solution was measured by a titration method[23].

3.2.4 Analytical methods

Bromide analysis was made with 270-HT High Throughput Capillary Electrophoresis System (Applied Biosystems, San Jose, CA, USA) according to the method developed by Rantakokko et al.[24]. The detection limit was 15 µg/L, and the measurement uncertainty of the analysis was ±15 %.

Inorganic anions (chloride, nitrite, sulfate, nitrate, fluoride and phosphate) were analyzed with the same device as bromide. Main features of the chemistry of this application for the analysis of common inorganic anions can be found on the web page of Waters Corporation[25].

Bromate analysis. Dionex 4000I series ion chromatograph (Dionex Sunnywale, CA, USA) with conductivity detector was used. Guard- and separation columns were AG11-HC and AS11-HC (4-mm). ASRS-ULTRA supressor in recycle mode (current 300 mA) was used. Eluent A was MQ-water and eluent B was 50 mM NaOH. Gradient program of the run: from 0.0 to 13.5 min 84% A and 16% B; linear increase to 100 % B; from 14.0 to 24.0 min 100% B. Flow rate was 1.5 mL/min and sample (1000 µL loop) was injected at 9 min after column equilibration. On-Guard Ag^+- and H^+-cartridges were installed on line between autosampler and sample loop to precipitate chloride present in the samples. Limit of detection was 1.3 µg/L.

TOC was measured using Shimadzu TOC-5000/5050 equipment by acidifying the sample (to pH 3) with concentrated hydrochloric acid resulting in the releasing of carbonates as carbon dioxide, and measuring the remaining carbonic compounds[26].

THMs were analyzed according to the standard CEN/prEN 30301 [27], which is a gas chromatographic method with an electron capture detection. Free chlorine was quenched from the samples with sodium thiosulphate. The sum of the four THMs (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform), the TTHMs, was calculated.

Alkalinity was adjusted with either 1M $CaCO_3$ or 1M $NaHCO_3$ solution, and it was measured according to the Finnish Standard SFS 3005 [28], which is based on potentiometric titration of the sample with HCl (of a known concentration) to pH value 4.5.

Both *temperature* and *pH* were measured *in situ* during the ozonation experiments. Temperature was measured on-line with Orbisphere 3600 analyzer for dissolved ozone, and the pH measurement was made with a calibrated WTW pH320-meter.

High performance size exclusion chromatography (HP-SEC) method. Molecular size distribution of organic matter was measured by the method of Vartiainen and coworkers[29] using HP-SEC with a TSK G3000SW column (7.5 mm * 30 cm; pre-column TSK SW, 7.5 mm * 7 cm) with UV-detection at 254 nm with sodium acetate buffer (pH 7) as the eluent. The calibration of the HP-SEC system has been presented earlier[29].

Organic acids. The organic acids measured were formate, acetate, propionate, pyruvate, oxalate and citrate. Dionex 4000I series ion chromatograph (Dionex Sunnywale, CA, USA) with the Ionpac AG11-HC Guard Column and Ionpac AS11-HC Analytical Column was used. The more detailed description of the analysis is described in Myllykangas et al.[30].

Mutagenicity of the water was tested using the Ames *Salmonella* assay on extracts obtained by an adsorption method[31], and the more detailed description can be found in Myllykangas et al.[32].

4. RESULTS

4.1 BROMATE FORMATION

The bromate formation ranged from 2.8 to 9.1 µg/L when ozonation was conducted at a pH of 5.8 and at an alkalinity of 0.3 mM using two different ozone dosages (O_3/TOC mass ratios ~4 and 5.3) or temperatures (Table 5-II). The increase in the pH from 5.8 to 7 increased the bromate formation at the ambient alkalinity of 0.3 mM (from 2.8 to 23 µg/L, experiments A and D), while the increase in the alkalinity from 0.3 to 0.5 mM caused a clear increase in the bromate formation as well (from 9.1 to 35 µg/L, experiments C and E). The highest bromate formation (118 µg/L) was observed after H_2O_2/O_3 treatment (H_2O_2/O_3 molar ratio of 0.07) at a pH of 7, alkalinity of 0.5 mM, and temperature of 10°C. At this alkalinity (0.5 mM) only the H_2O_2/O_3 molar ratio of 0.07 was tested. Bromate formation throughout the experiments varied from 0.22 to 8.1 µg per mg of O_3. The bromate concentration and dissolved ozone concentration (DO_3) or the bromate concentration and CT did not correlate well ($r = -0.463$ and $r = -0.444$, respectively, $N = 8$; Tables 5-II and 5-III). However, at the ambient pH, the correlation between the bromate concentration and the DO_3 was good ($r = 0.984$, $N=3$).

Table 5-II. The concentrations of the oxidants, total organic carbon (TOC), bromide ion, organic acids (OA), and bromate (BrO_3^-). The TOC did not change during oxidation of the ozonation experiments. The initial OA concentration was approximately 91 ± 47 µg/L.

Exp.	O_3 / H_2O_2 (mg/L)	T (°C) / pH	Alk. (mM)	TOC_{INI} (mg/L)	Br^-_{INI} (µg/L)	Br^-_{FINAL} (µg/L)	OA (µg/L)	BrO_3^- (µg/L)
A	12.6 / 0	10 / 5.8	0.3	3.4	460	270	560	2.8
B	14.4 / 0	17 / 5.8	0.3	3.4	490	240	620	5.9
C	18.0 / 0	10 / 5.8	0.3	3.4	480	210	650	9.1
D	12.5 / 0	10 / 7.0	0.3	3.4	420	300	620	23
E	17.0 / 0	10 / 7.0	0.5	3.9	390	380	1050	35
F	14.8 / 0.8	10 / 7.0	0.3	3.4	410	400	1370	71
G	13.0 / 3.8	10 / 7.0	0.3	3.5	340	330	1100	32
H	14.6 / 0.8	10 / 7.0	0.5	3.4	460	340	1100	118

Exp. = experiment; Alk. (mM) = alkalinity in mmol/L; OA = the sum of the organic acids (formate, acetate, propionate, pyruvate, oxalate and citrate); $_{INI}$ = the initial concentration; $_{FINAL}$ = the concentration after the experiment

4.2 TRIHALOMETHANES

Approximately 50 µg/L of TTHMs were observed after chlorination (Table IV). When the bromide concentration and the Cl_2:TOC mass ratio were kept constant and TOC concetration was lowered down to 50% of the original, the total THM concentration decreased by 40%, and more brominated THMs were formed (Fig. 5-1). TTHMs were formed 52-76 µg per mg of Cl_2 used. However, when hydrogen peroxide was used as the preoxidant, the TTHM concentration was found to be higher. When hydrogen peroxide (at a dose of 1 mg/L) was used without chlorination, 7.9 μg/L of TTHMs were observed, all of which were bromide-containing THMs and half of which was bromoform. The bromide-containing THMs corresponded up to 94% to 97% of the THM formation during the chlorination experiments, except in the experiment N, where only 12% of the THM formation consisted of the bromide-containing THMs.

Table 5-III. The CT-values (residual ozone concentration multiplied by the time it has affected the water; mg-min/L) and maximum concentrations of dissolved ozone (Max. DO_3, μg/L) observed in the ozonation experiments. CT-values are calculated using the average dissolved ozone concentration from the beginning to the end of ozonation, since the samples were taken when the ozone feed was cut off and no extra reaction time was used.

Experiment	O_3 (mg/L)	CT (mg-min/L)	Max. DO_3 (μg/L)
A	12.6	25	1600
B	14.4	64	2000
C	18.0	106	2800
D	12.5	19	1500
E	17.0	11	870
F	14.8	7.4	880
G	13.0	0	0
H	14.6	9.5	1000

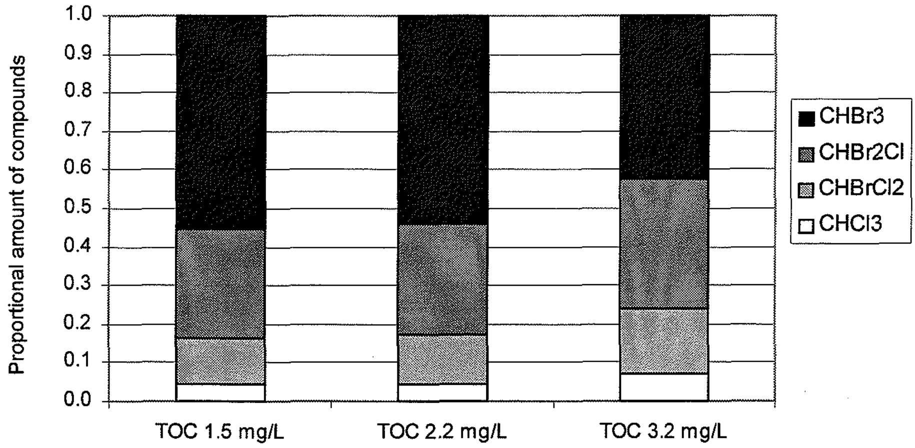


Figure 5-1. The proportional formation of bromoform, chlorodibromomethane, bromodichloromethane, and chloroform. The Br/TOC mass ratios (μg Br^- to μg TOC) 0.17, 0.11, and 0.08 and the Cl_2/Br mass ratios (μg Cl_2 to μg Br^-) were 2, 2.7, and 3.8, respectively. See Table 5-IV for more details.

4.3 INORGANIC ANIONS

The concentrations of the inorganic anions (chloride, nitrite, sulfate, nitrate, fluoride, and phosphate) ranged in the experiments between 155 and 173 mg/L, and the oxidation chemicals did not change their concentrations.

4.4 ORGANIC CARBON

Even though the TOC did not change during any oxidation or disinfection experiment, the amount of humus fractions analyzed by the HPSEC method decreased clearly. Especially the higher molecular weight portions decreased during the treatments (Figs. 5-2a and 5-2b).

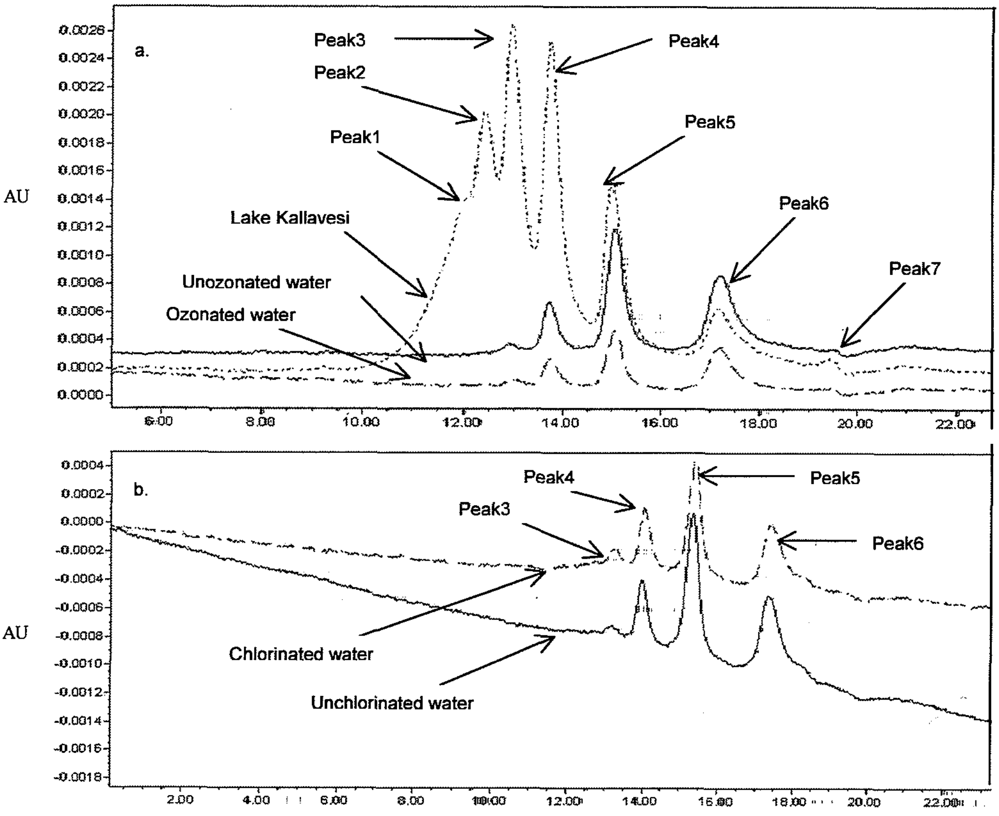


Figure 2. a. The effect of ozonation on the humus size fractions. For comparison, the seven humus peaks of Lake Kallavesi (a humus-rich lake with a TOC of 10-12 mg/L in the Eastern Finland) are presented. AU = absorbance units. b. The effect of chlorination on the humus size fractions. AU = absorbance unit.

Ozonation resulted in several times higher organic acid concentrations than chlorination (total concentration of about 600 µg/L vs. less than 200 µg/L). When ozonation was combined with hydrogen peroxide (H_2O_2 doses 0.8 mg/L and 3.8 mg/L) and/or at a higher alkalinity (0.5 mM vs. 0.3 mM), the formation of organic acids was even higher, being more than 1000 µg/L. After ozonation experiments, the formation of the organic acids was 37 to 86 µg per mg of O_3. The values after chlorination experiments ranged from 0 to 78 µg per mg of Cl_2. The above mentioned organic acid formations were calculated as the difference between organic acid concentration before and after oxidation.

4.5 MUTAGENICITY

The mutagenicity of the water leaving the water works was found to be 3750 net rev/L (Table 5-I; N = 6). Mutagenicity was tested after the experiments I, M, and N (Table 5-IV). The highest mutagenicity (2800 net rev/L) was found after chlorination, while hydrogen peroxide combined with chlorination reduced the mutagenicity to 1700 net rev/L even though the bromide concentration was higher in the water. Hydrogen peroxide only resulted in a mutagenicity of 350 net rev/L.

Table 5-IV. The concentrations of the oxidants, total organic carbon (TOC), bromide ion, organic acids (OA), trihalomethanes (THMs) and mutagenicity (Mut.) of the chlorination experiments. The TOC did not change during oxidation. Alkalinity was 0.3 mmol/L. The initial OA concentration was approximately 86 ± 8 µg/L.

Exp.	Cl_2 (mg/L)	H_2O_2 (mg/L)	TOC_{INI} (mg/L)	Br^-_{INI} (µg/L)	Br^-_{FINAL} (µg/L)	OA (µg/L)	THMs (µg/L)		Mut. (net rev/L)
							Br-THMs	all	
I	1.0	0	3.1	250	190	170	51	53	2800
J	0.95	0	3.2	250	240	140	46	49	nm
K	0.67	0	2.2	250	230	90	37	39	nm
L	0.50	0	1.5	250	230	100	28	29	nm
M	0	1.0	3.2	340	nm	70	7.9	7.9	350
N	1.0	1.0	3.2	340	nm	140	9.5	77	1700

Exp. = experiment; OA = the sum of the organic acids (formate, acetate, propionate, pyruvate, oxalate and citrate); $_{INI}$ = the initial concentration; $_{FINAL}$ = the concentration after the experiment; THMs = the sum of the four trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane, bromoform); Br-THMs = the sum of the bromine-containing THMs; nm = not measured

5. DISCUSSION

5.1 BROMATE FORMATION

Bromide is oxidized to bromate in several consecutive reactions, in which either the molecular ozone (O_3) or $OH^\bullet$ are acting as the oxidizing agent (o.a.)[33]: $Br^- \rightarrow OBr^-$ (O_3 as the o.a.); $HOBr/OBr^- \rightarrow BrO^\bullet$ ($OH^\bullet/CO_3^{\bullet -}$ as the o.a.) followed by: 2 $BrO^\bullet \rightarrow OBr^- +$ BrO_2^- (natural conversion), or $OBr^- \rightarrow BrO_2^-$ (O_3 as the o.a.); and $BrO_2^- \rightarrow BrO_3^-$ (O_3 as the o.a.). It is noteworthy, that molecular ozone can oxidize only the deprotonated form of HOBr (i.e., OBr^-) to result in bromate formation. Also, the $OH^\bullet$ can initiate the bromate formation resulting in $Br^\bullet$ and further $BrO^\bullet$ by molecular ozone[33].

Once bromate is formed, it is very difficult to remove from water[8], pinpointing the importance of preventing methods. In a recent review by von Gunten[9], the author lists two most important methods for bromate minimization during ozonation process, namely ammonia addition and pH depression, which have given promising results in several studies. The lower the pH, the higher the HOBr proportion in the $HOBr/OBr^-$ equilibrium, which reduces the reactions between ozone and OBr^- resulting in less bromate formation on the presumption that ozone dose is normalized[8,9]. At pH 7, two percents of the total reactive bromine is present as OBr^- and the rest (98%) is HOBr, while the corresponding values at pH 6 are 0.2% and 99.8%[34]. Thus, more than a ten-fold increase in the OBr^- concentration is gained when ozonation pH is increased from 5.8 to 7 (as in this study), increasing the bromate formation as well (2.8 µg/L vs. 23 µg/L, respectively) despite of the high O_3/TOC mass ratio of 4, since ozone reacts with bromine only as the OBr^-. The water pH in the Finnish raw waters is most often below 6 [22], which reduces the reactions between bromide and ozone and, thus, reduce the bromate formation during ozonation.

Ozonation is often combined with hydrogen peroxide, if some hard-to-remove-by-ozone micropollutants, such as pesticides, are present in the water. Hydrogen peroxide-ozonation is a typical advanced oxidation process (AOP) during which the OH radical formation is increased. In the AOPs, the formation of bromate as a result of the synergism of ozone and OH radicals is emphasized[9]. In this study, the bromate formation increased from 23 µg/L to 71 µg/L when H_2O_2 was introduced into the treatment system (at H_2O_2/O_3 molar ratio of 0.1), while further increasing the H_2O_2 dose (to H_2O_2/O_3 molar ratio of 0.4), the bromate formation reduced back to 32 µg/L, when the ozonation pH was 7 and the ozone dose was similar in each case. Croué et al.[37] gained similar results, and they proposed that the optimum H_2O_2/O_3 molar ratio for maximum bromate formation would be 0.2-0.3, and above or below that ratio the bromate formation would be lower, which was observed in this study as well. When the H_2O_2/O_3 molar ration is increased to the optimum value, the bromate formation increases with each addition of hydrogen peroxide[35]. This phenomenon has been found to yield from the reactions between H_2O_2 and O_3: at low H_2O_2 doses the bromate formation was high due to the accelerated OH radical production (i.e., the synergistic effect of molecular ozone and OH radicals was prevalent), while at high H_2O_2 doses the bromate formation decreased due to the increasing speed (becoming too fast) of ozone transformation to OH radicals, and preventing the reactions between molecular ozone and Br^- or OBr^- [33]. This effect was also seen in the F and G experiments. In the experiment G, the ozone reduction was very efficient, no residual ozone concentration was observed, and also the OH radicals were consumed effectively.

The carbonate radical ($CO_3^{\bullet -}$) can increase the reaction rates of the intermediates in the bromate formation (from OBr^- to BrO_2^-) resulting in more bromate[36]. On the other hand, carbonate ion (CO_3^{2-}) does not react with ozone but consumes OH radicals[21], stabilizing the molecular ozone in the water, and increasing the reactions between ozone and OBr^- and, thus, bromate formation. Our results showed increase in bromate formation when the alkalinity was increased from 0.3 mM to 0.5 mM, which might indicate the participation of carbonate radical on the bromate formation reactions.

5.2 TRIHALOMETHANES

Since the chlorine dose in these experiments was less than half of the value used in the Uusikaupunki's water works (1 mg/L vs. 2.3 mg/L), the THM formation was also less than half (50 µg/L vs. >100 µg/L) after chlorination, which was expected from the previous results. In our study, as in the study of Rebhun et al.[37], brominated THMs contributed more than 90% of the TTHMs, and bromoform was the dominant one (Fig. 5-1). In the experiments using hydrogen peroxide oxidation before chlorination, the THM concentrations were the highest observed in this study. However, the EU limit value for THM formation of 100 µg/L was not exceeded in the experiments. Even though the bromide concentration was higher (340 vs. 250 µg/L) in the hydrogen peroxide-chlorine experiment than the one during chlorination only, the proportional formation of bromide-containing THMs was much lower when hydrogen peroxide was used before chlorination as compared to chlorination only. For a medium-bromide water, Batterman et al.[38] found that at H_2O_2/Cl_2 molar ratio of 21 (TOC 1.7 mg/L, bromide concentration 120 µg/L, temperature 25°C and pH 7) the THM levels were reduced drastically, by 72 ± 9%. The differences in the results of Batterman et al.[38] and of this study are probably because of the quite different H_2O_2/Cl_2 molar ratios (21 and 0.5, respectively), indicating the high oxidation power of hydrogen peroxide towards the precursors of the THMs. However, in the study of Batterman et al.[38], the hydrogen peroxide was used to quench the chlorine after chlorination to prevent the formation of the DBPs, while in this study, hydrogen peroxide was used as the preoxidant to study its effect on the DBP formation during chlorination.

5.3 BROMIDE ION REDUCTION

In this study, virtually all utilized bromide was found as bromate formation (calculated as moles of bromide found in bromate per moles of utilized bromide) when ozonation was made at a pH of 7 and an alkalinity of 0.5 mM or with hydrogen peroxide addition. When ozonation was made at the ambient pH (5.8) and alkalinity (0.3 mM), the highest amounts of utilized bromide were observed (up to 56% of the initial concentration, Table II), and the bromate formation corresponded only a few percents of utilized bromide suggesting the formation of other bromide-containing DBPs. The rest of the "not-seen" bromide can be in the water as HOBr or organic DBPs, such as bromoform, bromoacetic acid, bromoalkanes[9]. Also, bromide and hypobromous acid can react to form bromine (Br_2)[39]. Hypobromous acid, on the other hand, has been found to react quite slowly with the organic matter in water[33], which makes is quite stable in that environment once it has gained the steady-state concentration. When ozonation was made with the presence of bromide in the water, up to 70% of the bromide was measured as the formation of total organic bromine[40,41]. Glaze et al.[40] found bromoform formations of 42 µg/L and 76 µg/L when they ozonated a water with spiked bromide (100 µM) at the pHs of 5 and 7, respectively. However, when the spiked bromide concentration was close to the one used in this study (5.4 µM vs. 6.3 µM), the bromoform formations were 0.9 µg/L and below the detection limit (0.2 µg/L) at the pHs of 5 and 7, respectively[40], suggesting that in our experiments as well only small amounts of bromoform could have been found. According to the review article by von Gunten[9], the formation of bromoorganics has been found to be very low, and the most intensive research should be made upon the prevention of bromate formation.

Even though bromide ion concentration often decreases during the treatment processes, the total bromine (including both inorganic and organic bromine compounds) concentration does, in fact, remain at the same level, since the water treatment processes do not remove those compounds effectively. The formation of bromoform ($CHBr_3$, corresponding up to all bromide ions reduced during the experiments of this study) is a clear indicator that brominated DBPs are formed in high quantities, when bromide-containing waters are treated with strong oxidants such as chlorine, ozone and hydrogen peroxide. Bromide can be removed, e.g., with nanofilters[42], at some degree with GAC/BAC filtration[43], or electrolytically[44]. However, many of the bromide-removing techniques cost too much for water works due to high energy consumption, and the optimizing of the disinfection processes seems to be more usable method.

6. CONCLUSIONS

According to the results of this study, even if the ozone dose was high, ozonation at the ambient conditions (pH 5.8, alkalinity 0.3 mM) seems to work efficiently in respect of bromate formation, since the observed bromate concentrations remained below the EU limit value of 10 μg/L. Also, when chlorination was conducted at a chlorine dose of 1 mg/L (as compared to 2.3 mg/L used currently in the water works, and the formation of TTHMs thereby), the THM formation could be lowered below the EU limit value of 100 μg/L the TTHMs.

7. ACKNOWLEDGEMENTS

This study was funded by the Academy of Finland and the Technology Development Centre of Finland (project no. 34538). Special thanks to Ms. Miia Hämäläinen, Mrs. Teija Korhonen and Mrs. Mervi Ojala from the Laboratory of Chemistry of the National Public Health Institute, and Mr. Matti Pessi from the University of Kuopio for technical assistance.

8. REFERENCES

1. von Gunten, U and Hoigné, J. 1992. Factors controlling the formation of bromate ion during ozonation of bromide-containing waters. Journal of Water Supply, Research and Technology - Aqua 41(5): 299-304.

2. Nissinen, T, Rantakokko. P, Myllykangas, T and Vartiainen, T. 1999. Bromide and brominated trihalomethanes in Finnish drinking waters. In: Proceedings, Fourth Finnish conference of environmental sciences, Tampere, May 21-22, 1999. Environmental science, technology and policy. (Eds: Sari Kuusisto, Simo Isoaho and Jaakko Puhakka. Finnish Society for Environmental Sciences. Tampere 1999).

3. EU. 1998. Official Journal of the European Community L330: Directive 98/83/EC.

4. USEPA. 1998. Stage 1 disinfectants and disinfection by-products rule. Unites States Environmental Protection Agency, EPA 815-F-98-010.

5. LaLonde, RT, Bu, L, Henwood, A, Fiumano, J and Zhang, L. 1997. Bromine-, chlorine-, and mixed halogen-substituted 4-methyl-2(5H)-furanones: synthesis and mutagenic effects of halogen and hydroxyl group replacements. Chemical Research in Toxicology, 10: 1428-1436.

6. Nobukawa, T and Sanukida, S. 2001. Effect of bromide ions on genotoxicity of halogenated by-products from chlorination of humic acid in water. Water Res. 35(18): 4293-4298.

7. Haag, WR and Hoigné, J. 1983. Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environmental Science & Technology, 17(7): 261-267.

8. Siddiqui, MS, Amy, GL and Rice, RG. 1995. Bromate ion formation: a critical review. Journal American Water Works Association, 87(10): 58-70.

9. von Gunten, U. 2003. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Research, 37: 1469-1487.

10. Zhang, X, Echigo, S, Minear, RA and Plewa, MJ. 2000. Characterization and comparison of disinfection by-products of four major disinfectants. In: Natural organic matter and disinfection by-products: characterization and control in drinking water (eds., S.E. Barrett, S.W. Krasner and G.L. Amy, pp. 299-314. Washington, D.C.: American Chemical Society, 2000).

11. Backlund, P, Kronberg, L, Pensar, G and Tikkanen, L. 1985. Mutagenic activity in humic water and alum flocculated humic water treated with alternative disinfectants. Science of the Total Environment, 47:257-264.

12. Arora, H, LeChevallier, MW and Dixon, KL. 1997. DBP occurrence survey. Journal American Water Works Association, 89(6): 60-68.

13. Boorman, GA, Dellarco, V, Dunnick, JK, Chapin, RE, Hunter, S, Hauchman, F, Gardner, H, Cox, M and Sills, RC. 1999. Drinking water disinfection by-products: review and approach to toxicity evaluation. Environmental Health Perspectives, 107 (Supplement 1): 207-217.

14. Nikolaou, AD, Kostopoulou, MK and Lekkas, TD. 1999. Organic by-products of drinking water chlorination. Global Nest: the International Journal, 1(3): 143-156.

15. Chang, EE, Chiang, PC, Ko, YW and Lan, WH. 2001. Characteristics of organic precursors and their relationship with disinfection by-products. Chemosphere, 44: 1231-1236.

16. von Gunten, U, Driedger,A, Gallard, H and Salhi, E. 2001. By-products formation during drinking water disinfection: a tool to assess disinfection efficiency? Water Research, 35(8): 2095-2099.

17. Integrated Risk Information System, IRIS. U.S. Environmental Protection Agency. http://www.epa.gov/iris/ (accessed 09-09-2003)

18. Glaze, WH. 1987. Drinking-water treatment with ozone. Environmental Science & Technology, 21(3): 224-230.

19. Glaze, WH, Kang, JW and Chapin, DH. 1987. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Science & Engineering, 9: 335-352.

20. Myllykangas, T, Nissinen, T and Vartiainen, T. 2000. Bromate formation during ozonation of bromide containing drinking water – a pilot plant study. Ozone Science & Engineering, 22(5): 487-499.

21. Hoigné, J, Bader, H, Haag, WR and Staehelin, J. 1985. Rate constants of reactions of ozone with organic and inorganic compounds in water - III inorganic compounds and radicals. Water Research, 19(8): 993-1004.

22. Finnish Environment Institute. (accessed 09-09-2003)

http://www.vyh.fi/eng/environ/state/waterre/waterser/waterser.htm

23. AOAC. 1980. Official methods of analysis of the Association of Official Analytical Chemists, 13 edition. (Ed. W. Horwitz, Washington, Association of Official Analytical Chemists, 1980), p. 545.

24. Rantakokko, P, Nissinen, T and Vartiainen, T. 1999. Determination of bromide ion in raw and drinking waters by capillary zone electrophoresis. Journal of Chromatography A 839(1-2): 217-225.

25. Waters Corporation. 4140 Determination of Inorganic Anions Using Capillary Ion Electrophoresis. (accessed 09-09-2003) http://www.waters.com/WatersDivision/ContentD.asp?ref=JDRS-5LV8A2

26. Finnish Standards Association SFS. SFS-EN 1484. 1997. Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). Finnish Standards Association SFS, Helsinki, Finland.

27. ISO/DIS 10301. 1994. Water quality – determination of highly volatile halogenated hydrocarbons – gas-chromatographic methods. International Organization for Standardization (ISO).

28. Finnish Standards Association SFS. SFS 3005. 1981. Determination of alkalinity and acidity in water. Potentiometric titration. Finnish Standards Association SFS, Helsinki, Finland.

29. Vartiainen, T, Liimatainen, A and Kauranen, P. 1987. The use of size exclusion columns in determination of the quality and quantity of humus in artificially recharged ground waters and drinking waters. Science of the Total Environment, 62: 75-84.

30. Myllykangas, T, Nissinen, TK, Rantakokko, P, Martikainen, PJ and Vartiainen, T. 2002. Molecular size fractions of treated aquatic humus. Water Research, 36(12): 3045-3053.

31. Vartiainen, T and Liimatainen, A. 1986. High levels of mutagenic activity in chlorinated drinking water in Finland. Mutation Research, 169: 29-34.

32. Myllykangas, T, Nissinen, TK, Mäki-Paakkanen, J, Hirvonen, A and Vartiainen, T. 2003. Bromide

affecting drinking water mutagenicity. Chemosphere, 53(7): 745-756.

33. von Gunten, U and Hoigné, J. 1994. Bromate formation during ozonation of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. Environmental Science & Technology, 28: 1234-1242.

34. Jolley, RL and Carpenter, JH. 1983. A review of the chemistry and environmental faith of reactive oxidant species in chlorinated water. In: Water chlorination, Environmental impact and health effects, vol. 4, Book 1: Chemistry and water treatment. (Eds. R.L. Jolley, W.A. Brungs, J.A. Cotruvo, R.B. Cumming, J.S. Mattice and V.A. Jacobs. Ann Arbor Science, Ann Arbor, Michigan, USA, 1983.)

35. Croué, JP, Koudjonou, BK and Legube, B. 1996. Parameters affecting the formation of bromate ion during ozonation. Ozone Science & Engineering, 18: 1-18.

36. von Gunten, U, Bruchet, A and Constentin, E. 1996. Bromate formation in advanced oxidation processes. Journal American Water Works Association, 88(6): 53-65.

37. Rebhun, M, Manka, J and Zilberman, A. 1988. Trihalomethane formation in high-bromide Lake Galilee water. Journal American Water Works Association, 80(6): 84-89.

38. Batterman, S, Zhang, L and Wang, S. 2000. Quenching of chlorination disinfection by-product formation in drinking water by hydrogen peroxide. Water Research, 34(5): 1652-1658.

39. Engel, P, Oplatka, A and Perlmutter-Hayman, B. 1954. The decomposition of hypobromite and bromite solutions. Journal American Chemical Society, 76: 2010-2015.

40. Glaze, WH, Weinberg, HS and Cavanagh, JE. 1993. Evaluating the formation of brominated DBPs during ozonation. Journal American Water Works Association, 85(1): 96-103.

41. Song, R, Westerhoff, P, Minear, R and Amy, G. 1997. Bromate minimization during ozonation. Journal American Water Works Association, 89(6): 69-78.

42. Laîné, JM, Jacangelo, JG, Cummings, EW, Carns, KE and Mallevialle, J. 1993. Influence of bromide on low-pressure membrane filtration for controlling DBPs in surface waters. Journal American Water Works Association, 85(6): 87-99.

43. Asami, M, Aizawa, T, Morioka, T, Nishijima, W, Tabata, A and Magara, Y. 1999. Bromate removal during transition from new granular activated carbon (GAC) to biological activated carbon (BAC). Water Research, 33(12): 2797-2804.

44. Kimbrough, DE and Suffet, IH. 2002. Electrochemical removal of bromide and reduction of THM formation potential in drinking water. Water Research, 36: 4902-4906.

CHAPTER 6: BROMIDE AFFECTING DRINKING WATER MUTAGENICITY

T. Myllykangas*[1,2], T.K. Nissinen[1], J. Mäki-Paakkanen[1], A. Hirvonen[2] and T. Vartiainen[1,2]

[1]National Public Health Institute, Division of Environmental Health, P.O. Box 95, FIN-70701 Kuopio, Finland
[2]University of Kuopio, Department of Environmental Sciences, P.O. Box 1627, FIN-70211 Kuopio, Finland
*The corresponding author. [Email: Tiia.Myllykangas@ktl.fi, tel. +358 17 201 181, fax. +358 17 201 265]

Published in Chemosphere, 53(7), 745-756 (2003).
Reproduced here with kind permission from Elsevier.

1. ABSTRACT

The effect of bromide on the mutagenicity of artificially recharged groundwater and purified artificially recharged groundwater after chlorine, ozone, hydrogen peroxide, permanganate, and UV treatments alone and in various combinations was studied. The highest mutagenicity was observed after chlorination, while hydrogen peroxide-ozone-chlorine treatment produced the lowest value for both waters. Chlorinated waters, which were spiked with bromide, had up to 3.7 times more mutagenic activity than waters without bromide after every preoxidation method. 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX) was found to correspond as much as 76% of the overall mutagenicity in the waters not spiked with bromide. MX formation was found to be lower when the treated water contained bromide, implicating the formation of brominated MX analogues. Trihalomethane formation increased when the treated water contained bromide.

Keywords: bromide, preoxidation, disinfection, mutagenicity, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX), trihalomethanes

2. INTRODUCTION

Mutagenic activity of chlorinated water has been studied extensively since the beginning of the 1980s[1-3]. Chlorine is a very powerful disinfection chemical with a strong oxidizing potential. Chlorination of organic matter in water results in disinfection by-products (DBPs), such as trihalomethanes (THMs). On the other hand, less attention has been paid to the mutagenicity of the corresponding waters treated with alternative disinfectants, such as ozone and UV, even if some of those have a higher oxidation potential than chlorine.

Bromide has been found to form harmful DBPs with the disinfectants used for water disinfection[4,5]. Brominated by-products are suspected to be more harmful to health, and also much stronger carcinogens and mutagens than their chloride-containing analogues[5,6]. High bromide concentration is typical in surface and groundwaters in the coastal areas. Otherwise, bromide concentrations are low, only some micrograms per liter. Bromide concentrations in drinking water samples from the coastal Finland were as high as 485 μg/L[7].

The highly mutagenic compound, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX), first identified in chlorinated pulp liquors[8], has been found also from chlorinated drinking waters in the United States[9], Finland[10,11], the United Kingdom[12], Japan[13], Netherlands[14], Spain[15], Poland[16], the Peoples Republic of China[17], and Australia[18]. MX has been found to represent up to 63 to 67% of the total mutagenicity of the drinking waters[11,19]. MX contains three chlorine atoms, but chlorine can be replaced by bromine corresponding to the speciation of THMs when treating bromide-containing waters[4,11]. The mutagenicity of MX and its brominated analogues is greatly affected by the site of the halogen substitutions and other substitutions[6].

Surface waters especially in boreal regions (Scandinavia, Canada, Northern USA, Russia) contain a considerable amount of organic matter, up to 40 mg/L total organic carbon (TOC)[20]. TOC contains precursors for mutagenic and other possibly harmful compounds formed during disinfection. Since drinking waters are in many cases produced from surface waters, such as rivers and lakes, the amount of the TOC has a strong influence on the products formed during the purification steps. One technique to remove humus from the surface water is to produce artificially recharged groundwater, the production of which has gradually increased in boreal regions[21]. Even if the TOC is removed by 70 to 80% during conventional water treatment, bromide is not removed effectively enough[4]. In fact, when the removal of organic matter from raw water is improved, the bromide-to-organic matter ratio increases, which further enhances the reactions between bromide and oxidants resulting in more brominated organic compounds.

Chlorination is the most typical disinfection method in the waterworks. Chlorine reacts with the organic matter in water resulting in many chlorinated by-products[22]. Ozone and advanced oxidation processes, e.g. hydrogen peroxide combined with ozonation[23], chloramine[24], and UV[25], have proven to be effective disinfection agents as alternatives to chlorination. Those methods can be used to decrease the amount of DBPs formed during the production of drinking water due to oxidation of organic matter in water. Potassium permanganate is used mainly for oxidation of metals (manganese and iron) from drinking water[26].

The aim of these experiments was to study the effect of bromide on the mutagenic activity and the THM and MX concentrations of humus-containing artificially recharged groundwater (AW) and purified AW (PW) after several preoxidation methods and UV treatment with postchlorination.

3. MATERIALS AND METHODS

3.1 TREATED WATERS AND THE TREATMENT TRAIN

The AW from Lake Kallavesi, and in the Kuopio waterworks by coagulation with $Al_2(SO_4)_3$, flotation, and sand filtration purified PW were used in our experiments. Since the water does not contain natural bromide, it was added as sodium bromide (Merck, extra pure) solution to the initial concentration of 500 µg Br^-/L to the water. The treatment train is described in Fig. 1 in Myllykangas et al.[27], and the chemical dosages used in the experiments are presented in the Table 6-I. Both waters were treated with chlorine, ozone-chlorine, hydrogen peroxide-ozone-chlorine, and permanganate-chlorine combinations. The PW was also treated with hydrogen peroxide-chlorine, and UV-chlorine combinations. The dosages of chemicals for the experiments were selected to simulate current practice at full-scale treatment plants.

Table 6-I. Bromide concentrations; ozone, hydrogen peroxide, permanganate, and ammonium chloride doses; UV fluence; total organic carbon (TOC) content; mutagenicity; MX and THM concentrations in the artificially recharged groundwater (AW) and purified water (PW). AW: chlorine dose = 2 mg/L; PW: chlorine dose = 1 mg/L except for two cases indicated with an asterix (*) where the chlorine dose was 2 mg/L.

Note	$[Br^-]$, µg/L spiked/residual	$[O_3]$, mg/L	Others	[TOC], mg/L	Mutagenicity, net rev/L	[MX], ng/L	MX's contribution[a] to mutagenicity in %	THM, µg/L	
								total	brominated
AW + Cl_2	0			4.3	3800	101	68	45	1.4
AW + Cl_2	500/280			4.3	4800	63	34	89	73
PW + Cl_2	0			3.9	2200	65	76	21	1.3
PW + Cl_2	500/370			3.7	3000	23	20	52	47
AW + O_3 + Cl_2	0	4.86		6.1	3500	75	55	34	2.7
AW + O_3 + Cl_2	500/330	4.80		5.7	3500	40	29	73	57
PW + O_3 + Cl_2	0	2.60		3.3	1700	20	30	10	0.4
PW + O_3 + Cl_2	500/330	2.60		2.8	2300	6	6	58	58
PW + O_3 + Cl_2 (*)	0	4.80		3.0	2100	35	43	28	2.6
PW + O_3 + Cl_2 (*)	1000/420	4.70		3.3	7800	21	7	171	171
AW + H_2O_2 + O_3 + Cl_2	0	4.76	1.5	5.8	2300	53	59	22	0.4
AW + H_2O_2 + O_3 + Cl_2	500/430	4.75	1.5	5.4	2700	44	42	30	15
PW + H_2O_2 + Cl_2	0		1.0	3.2	510	nd (3)	- (16)	7.9	0.1
PW + H_2O_2 + Cl_2	500/500		1.0	3.3	940	18	49	11	3.5

THM total = trihalomethanes, the sum of the concentrations of chloroform, chlorodibromomethane, bromodichloromethane and bromoform; THM brominated = THM total – chloroform; net rev/L = net revertants per litre from the Ames test; MX = 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, nd = not detected, na=not analyzed

Table 6-I. Continued.

Note	$[Br^-]$, µg/L spiked/residual	$[O_3]$, mg/L	Others	[TOC], mg/L	Mutagenicity, net rev/L	[MX], ng/L	MX's contribution[a] to mutagenicity in %	THM, µg/L	
								total	brominated
PW + H_2O_2 + O_3 + Cl_2	0	2.60	0.8	2.9	520	8	40	3.5	0.1
PW + H_2O_2 + O_3 + Cl_2	500/500	2.60	0.8	3.0	760	7	23	5.0	2.4
AW + $KMnO_4$ + Cl_2	0		0.34	6.9	3200	79	64	35	0.8
AW + $KMnO_4$ + Cl_2	500/290		0.34	6.6	3300	49	38	53	31
PW + $KMnO_4$ + Cl_2	0		0.06	3.3	1500	37	64	21	1.1
PW + $KMnO_4$ + Cl_2	500/410		0.06	3.6	1800	12	17	33	27
PW + UV + Cl_2	0		48	2.5	1800	30	43	32	1.4
PW + UV + Cl_2	500/290		48	2.6	2500	na	na	55	42

THM total = trihalomethanes, the sum of the concentrations of chloroform, chlorodibromomethane, bromodichloromethane and bromoform; THM brominated = THM total – chloroform; net rev/L = net revertants per litre from the Ames test; MX = 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, nd = not detected, na=not analyzed

3.2 OXIDATION METHODS

The pH of the water (15 L) was adjusted to 8.5 with 1 M $Ca(OH)_2$ solution before chlorination. The NaOCl-solution at a ratio of Cl_2:TOC = 1:3 was applied, and the water was mixed for 5 minutes after the solution was added. Permanganate (MnO_4^-) was added as $KMnO_4$-solution to the waters three hours before chlorination. The chosen $KMnO_4$/Mn mass ratios for the experiments were 2, 3, and 4, with the initial manganese concentrations of 0.11 mg/L in the AW and 0.02 mg/L in the PW. Ozonation and hydrogen peroxide-ozone experiments were carried out in a semi-batch reactor, which is explained in detail in Myllykangas et al.[28].

3.3 UV EXPERIMENTS

UV-experiments were conducted using a 20-cm-wide (total area facing the lamps was 800 cm^2), roofless water channel and 10 adjacent UV-lamps (Philips TUV 15 W G15T8 low-pressure mercury lamps). The water flowed through the channel as a thin water layer (approximately 2-3 mm thick) with a 1-L/min flow. The UV intensity was measured by Macam Spectroradiometer (Model SR 9910, Macam Photometrics ltd., Livingstone, UK) at the wavelength range of 240 to 260 nm. The intensity average was 5.7 mW/cm^2 at 30 cm distance (three measuring points: ¼, ½, ¾ of the length at the center of the lamp row), and the flow-through time was 8.5 s achieving the fluence of 48 mJ/cm^2.

3.4 MUTAGENICITY AND MX

Mutagenicity of the water was tested using the Ames *Salmonella* assay on extracts obtained by an adsorption method[2]. The water was acidified to pH <2 with concentrated HCl before the adsorption of the inorganic compounds onto the XAD-7 resin. The adsorbed compounds were eluted from the resin with ethyl acetate, which was evaporated in a rotavapor to almost complete dryness and exchanged to dimethyl sulfoxide[3]. Mutagenicity was assayed using the Ames test with *Salmonella typhimurium* TA 100 test strain without enzymatic activation[29]. The value of mutagenicity was obtained from a regression analysis with values $R^2 > 0.960$ and ANOVA significance F from 1.5E-8 to 7.0E-16, when the number of measured points was 10-14. The quantitation limit of 100 net revertants per litre can be used, since it is the amount of spontaneous mutations in control (blank) sample. MX was derivatized after XAD-7 extraction with ethyl acetate by sulfuric acid isopropanol. Formed derivative was extracted with hexane and analyzed gas chromatographically (Hewlett-Packard 6890) with high-resolution mass spectrometry (VG 70-250SE). Distinction column J&W Scientific DB-DIOXIN (60 m, ID 0.25 mm, film 0.15 µm) was used. The detection limit for MX was 5 ng/L. Fragment ions ($M-OC_3H_7$) were 198.9120 and 200.9091 with theoretical ratio 100/96 when analyzed with the high resolution GC-MS. Mutagenicity of MX was assumed to be 5600 net rev/nmol[10] when calculating the contribution of MX of the overall mutagenicities.

3.5 OTHER ANALYTICAL METHODS

THMs were analyzed according to the standard CEN/prEN 30301 [30], and the sum of the four THMs (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform) was calculated. TOC was measured according to the Finnish Standard SFS-EN 1484 [31].

3.6 STATISTICAL ANALYSIS

Pearson correlation coefficients (R) between the different parameters were calculated using SPSS 9.0 for Windows.

3.7 MUTAGENICITY MODEL

The equation developed by Vartiainen et al.[24] describes the quantitative relationship between the mutagenicity of water extracts and organic carbon, chlorine dose and the concentration of ammonia: **Mutagenicity in TA100** $= A\ (1 - e^{-kc})$. In the equation A and k are constants ($A = 4000$ and $k = 0.054$ for TOC values) and c is a parameter dependent on organic carbon (TOC, $KMnO_4$-number, or color), chlorine dose and ammonia $[(1-NH_3)^2]$ concentrations. Mutagenicity is the sum of mutagenicities produced by prechlorination and postchlorination[24]. For our data set, new values for the constants A and k were determined using the multiplications of the oxidant's doses and the TOC as the c-value to compare whether the equation would suit for our results. The estimation was done with the NLIN procedure using the Marquardt, Gauss-Newton and Newton iterative least squares methods[32].

4. RESULTS

4.1 MUTAGENICITY AND MX FORMATION

4.1.1 Effect of chlorination alone

Bromide increased the mutagenicity of tested waters during chlorination as compared to waters without bromide (Table 6-I, Fig. 6-1). The mutagenicities of chlorine treated AW and PW with bromide were 1.3 to 1.4 times the mutagenicities of chlorinated waters without bromide. With bromide, the contribution of MX of the overall mutagenicities were 34 and 20% for AW and PW, respectively, while without bromide, the respective values were 68 and 76% (Table 6-I).

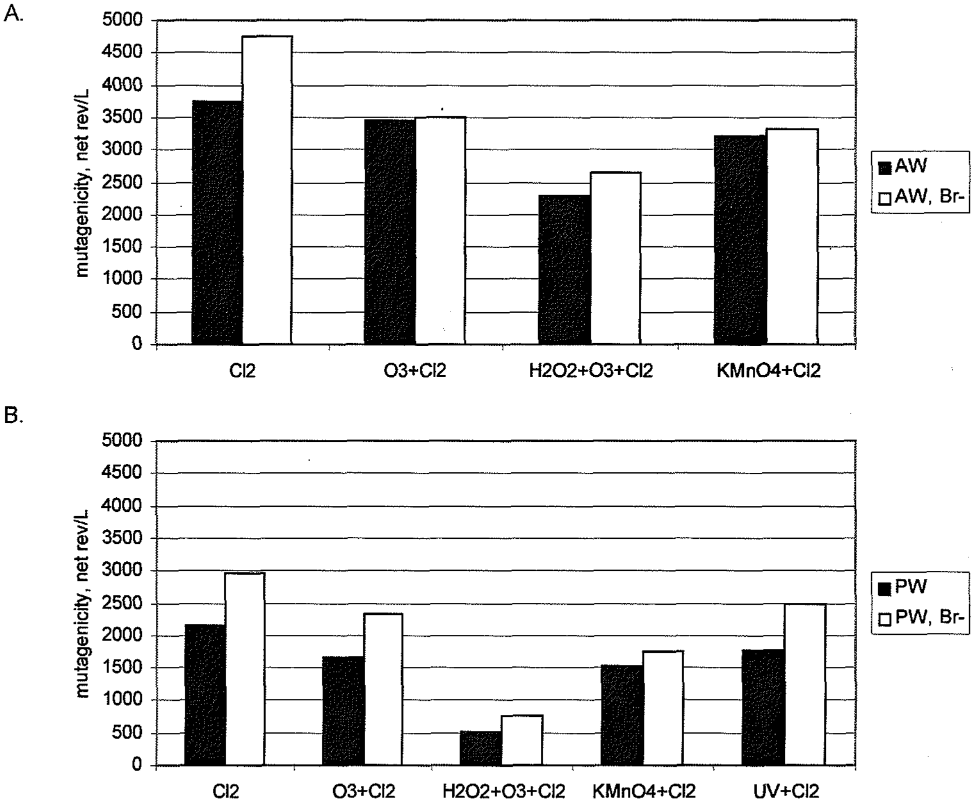


Figure 6-1. The observed mutagenicities of A. the treated artificially recharged groundwater (AW); and B. the treated purified artificially recharged groundwater (PW) with and without spiked bromide.

4.1.2 Effect of ozonation combined with chlorination

Bromide did not change the mutagenicity of the AW that was treated with ozone and chlorine (Table 6-I, Fig. 6-1). However, the mutagenicity of the bromide containing PW was 1.4 times the one of the similarly treated water without bromide. Ozonation before chlorination of bromide containing AW and PW resulted in approximately 0.75 times the mutagenicities found after chlorination. However, without bromide, ozonation before chlorination hardly did alter the mutagenicity of the AW, while the mutagenicity of the PW was 0.75 times the one formed during chlorination. MX contributed 29 and 6% of the overall mutagenicities of bromide-containing AW and PW after ozone-chlorine -treatments, while the respective values of bromide-free waters were 55 and 30% (Table 6-I).

When the PW was treated using doubled ozone and chlorine doses at doubled initial bromide concentration, the mutagenicity was 2.6 times higher than after mere chlorine treatment without bromide (Table 6-I). On the other hand, doubled ozone and chlorine doses used for the PW without bromide resulted in approximately similar mutagenicity than chlorination alone. Ozone treatment alone increased only the mutagenicity of the AW slightly, while no effect on the mutagenicity of the PW was found. The increased ozone and chlorine doses increased the contribution of MX of the overall mutagenicity from 6 to 7% with, and from 30 to 43% without bromide (Table 6-I).

4.1.3 Effect of hydrogen peroxide, ozone and chlorine

Hydrogen peroxide combined with ozone and chlorine treatments of the bromide-containing AW and PW induced mutagenicities (Table 6-I, Fig. 6-1) which were 0.5 and 0.25 times the ones after chlorination only, respectively. Similar treatments of bromide-free waters caused mutagenicities of 0.7 and 0.25 times the ones found after chlorination. 42 and 23% of the overall mutagenicities could be found as MX formation after the treatments of bromide-containing AW and PW, respectively. The contributions in waters without bromide were 59 and 40% for the AW and PW, respectively. On the other hand, hydrogen peroxide-chlorine treatment of the PW resulted in 0.3 and 0.25 times the mutagenicity found after chlorination with and without bromide, respectively, while the contribution of MX of the overall mutagenicity was 49% with and 16% without bromide (Table 6-I).

4.1.4 Effect of permanganate and chlorine

Bromide increased only slightly the mutagenicities of the AW and PW after permanganate and chlorine treatment (Table 6-I, Fig. 6-1). The mutagenicities of the AW and PW after permanganate and chlorine treatments were 0.6 to 0.9 times the ones found after chlorine treatment alone. The results are shown only after the treatments at a $KMnO_4$/Mn –ratio of 3. The MX contributed 38 and 17% of the overall mutagenicities of AW and PW with bromide, while the value without bromide was 64% for both waters (Table 6-I).

4.1.5 Effect of UV and chlorine

Bromide increased the mutagenicity 1.4-fold of the PW after UV and chlorine treatment as compared to non-bromide water. 43% of the mutagenicity of the treated PW without bromide could be found as MX, and no result is available for bromide-containing water (Table 6-I, Fig. 6-1).

Figure 6-2 shows the colony numbers with regression of three experimental pairs (with and without bromide) of this study.

4.2 TRIHALOMETHANE FORMATION

When the treated water contained bromide, the THM formation increased clearly as compared to the waters without bromide (Table 6-I). The bromide-induced increase varied from 1.3 to 6.2-fold, being the greatest in ozone-chlorine treated PW with doubled bromide concentration (1000 µg/L). It was clearly seen that when the treated water contained bromide, the concentrations of more brominated THMs increased, while the chloroform concentrations remained at the same level or even decreased (results not shown).

4.3 TOC AFFECTING MUTAGENICITY

The effect of the TOC content on the mutagenicity was obvious when comparing AW and PW. Regardless of the presence of bromide, a low TOC (3 mg/L) resulted in 0.2 to 0.8 times the mutagenicity of the experiments, in which the TOC was higher (6 mg/L). The increasing effect of the TOC was dependent on the oxidation method used: the greatest effect was found after hydrogen peroxide-ozone-chlorine treatment, and the smallest after permanganate-chlorine treatment.

4.4 CORRELATION COEFFICIENTS

The Pearson correlation coefficients (R) for bromide-containing and bromide-free waters are listed in Table 6-II, and Fig. 6-3 shows the distributions of the values. The highest correlations regardless of the presence of bromide between mutagenicity and MX (0.950), between mutagenicity and TOC (0.998), as well as between mutagenicity and

THM formation (0.994) occurred when hydrogen peroxide-ozone-chlorine treatment was used.

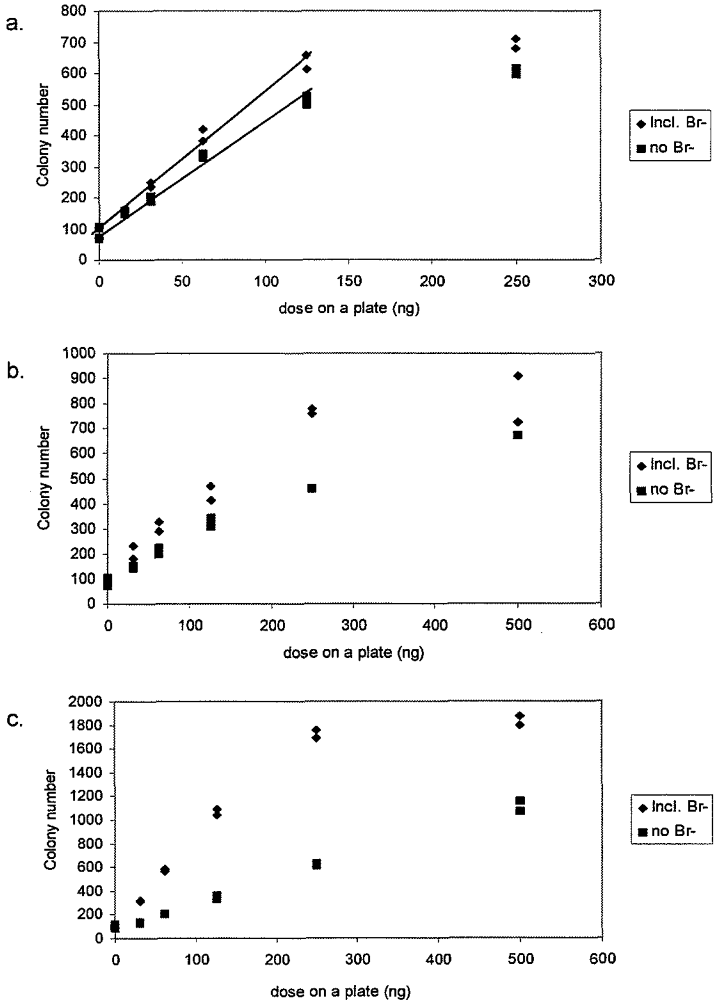


Figure 6-2. Colony numbers and regression obtained from the Ames assay with and without spiked bromide of a. chlorinated artificially recharged groundwater (AW+Cl_2); b. chlorinated purified artificially recharged groundwater (PW+Cl_2); and c. purified artificially recharged groundwater ozonated and chlorinated with double doses (PW+O_3+Cl_2(*)). Additional information can be found from the Table 6-I.

4.5 COMPARISON TO THE MODEL

The constants *A* and *k* were iterated with the SAS-software. Table 6-III lists the results obtained from the iteration of the constants *A* and *k* of the model presented by Vartiainen et al.[24].

Table 6-II. The Pearson correlation coefficients (r) for the waters with and without bromide. The results after ozonation and UV as well as those not detected or analyzed are omitted from the results.

	N	Mutagenicity - TOC	Mutagenicity - MX	Mutagenicity - THM
AW, no Br^-	4	0.547 (*)	0.926	0.940
AW, Br^-	4	0.535 (*)	0.719	0.889
PW, no Br^-	7	0.256	0.846	0.786
PW, Br^-	7	0.118	0.543	0.991
All, no Br^-	11	0.791 (*)	0.952	0.895
All, Br^-	11	0.210 (*)	0.377	0.970
Whole material	22	0.367 (*)	0.405	0.930

(*) AW+Cl_2 treatment omitted, N = number of experiments

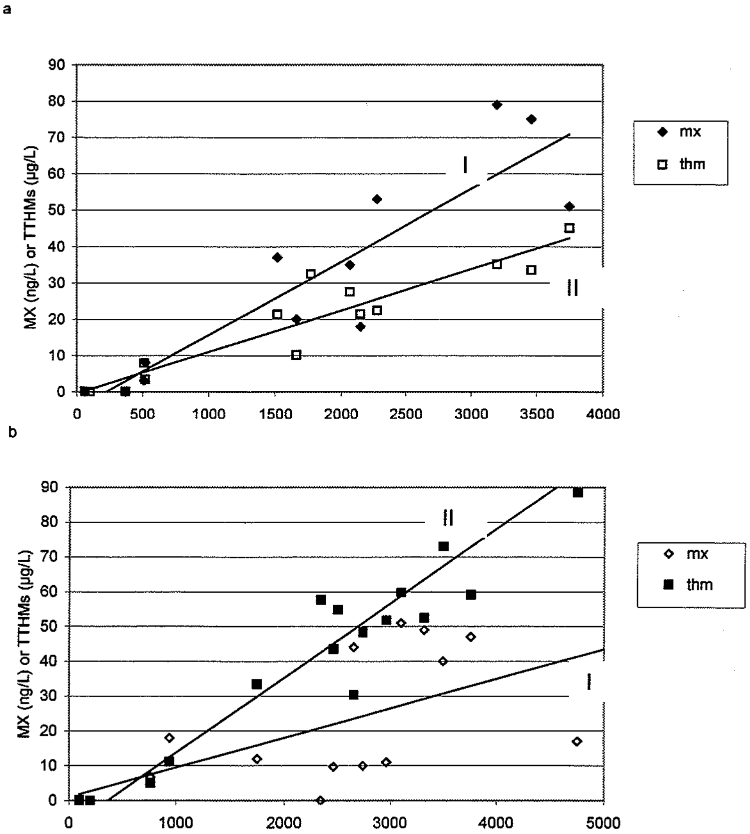


Figure 3. The correlations (correlation coefficients, R) between mutagenicity and MX formation (I) and THM-concentration (II) for the whole material. a: values obtained from the experiments without spiked bromide. $R_{a,I} = 0.899$, $R_{a,II} = 0.939$. b: values obtained from the experiments with spiked bromide. $R_{b,I} = 0.596$, $R_{b,II} = 0.976$.

Table 6-III. The parameters *A* and *k* according to the model by Vartiainen et al., 1988 estimated with the NLIN procedure using the Marquardt, Gauss-Newton and Newton iterative least squares methods (SAS/STAT ®, 1989). All the methods provided same parameter values. Presumed values were *A* = 4000 and *k* = 0.054.

	$[Cl_2]$*[TOC]	$[O_3]$*$[Cl_2]$*[TOC]	[others]*$[Cl_2]$*[TOC]	[all]*$[Cl_2]$*[TOC]
A	3176	3590	2705	2437
k	0.238	0.073	0.470	0.142

Others = H_2O_2 and $KMnO_4$; all = all oxidative agents (except chlorine) used.

5. DISCUSSION

The effect of bromide on the mutagenic activity and MX concentrations of post-chlorinated natural water is clearly seen from the results. The waters with spiked bromide were more mutagenic and also had more THM formation than the corresponding waters without bromide. MX formations of the bromide-spiked waters were lower than the ones of the waters without bromide. Without chlorination, i.e. during ozonation and UV treatment alone, no mutagenic activity, MX formation, or THM formation was observed. On the other hand, both ozonation and UV treatment did reduce the mutagenicity of post-chlorinated water as compared to only chlorinated water. Mutagenicity of drinking water has been shown to depend on the disinfectant and its dosage, disinfection pH and the quality of the organic matter in the water[3,33,34].

Very few publications are available concerning the effects of bromide on drinking water mutagenicity. Nobukawa and Sanukida[5] recently published some interesting results about chlorination of isolated humic acid in the presence of bromide ions. They found that bromide ions increased the mutagenicity up to 3.3 times of the value of non bromine-spiked water. Our results show that the presence of bromide ions increases also the mutagenicity of disinfected natural waters. The effect could be seen not only after chlorination but also after treatment with several preoxidants used widely for the production of drinking water.

5.1 MUTAGENICITY AFTER OZONE-CHLORINE TREATMENT

Ozone is one of the most powerful oxidants used in drinking water production, and it is often used as an alternative for chlorination to avoid the formation of DBPs. However, as with every preoxidant tested, ozonation before chlorination decreased both the mutagenicity and the formation of MX with and without bromide as compared to chlorination only. The decrease in mutagenicity is in accordance with the results of Matsuda et al.[35]. Anyhow, in our experiments, the mutagenicity was higher all but one time when the water contained bromide, when compared the results with bromide-free waters. Only after ozone-chlorine treatment of the AW, the mutagenicities were the same regardless of the presence of bromide. Ozone is known to reduce the reactivity of humus, but, on the other hand, it also increases the formation of hypobromous acid (HOBr)[36], which can then react further with organic matter and chlorinated compounds resulting in higher mutagenicity and lower MX concentrations in the presence of bromide.

5.2 MUTAGENICITY AFTER HYDROGEN PEROXIDE-OZONE-CHLORINE TREATMENT

The lowest mutagenicity during our experiments was observed from waters oxidized by hydrogen peroxide before ozonation and chlorination at the H_2O_2/O_3 mass ratio of 0.3. Hydrogen peroxide-ozone treatment before chlorination has been observed to remove mutagenicity totally for similar AW to the one used in these experiments at the optimal H_2O_2/O_3 mass ratio of 0.7 (mg/mg)[37]. Hydrogen peroxide combined with ozonation represents an advanced oxidation process[23], which results in greater amount of hydroxyl radicals, which are non-selective oxidants in water[38]. The reaction between hydroxyl radicals and bromide is exceedingly faster than between ozone and bromide[39], and the reduction of hypobromous acid back to bromide is also very likely. On the other hand, the reactions between hydroxyl radicals and organic matter decrease the amount of reactive sites very rapidly reducing the formation of DBPs and mutagenicity.

5.3 MUTAGENICITY AFTER PERMANGANATE-CHLORINE TREATMENT

Bromide increased the mutagenicity of permanganate-chlorine –treated water only slightly (1.05 to 1.2) as compared to the treatments of bromide-free waters. However, permanganate-chlorine –treatment reduced mutagenicities of both waters as compared to chlorination only, with and without bromide. Stoichiometrically 1.92 mg $KMnO_4$ is needed to oxidize 1 mg Mn at a pH ≥5.5 [40]. Thus, in all of our experiments there was more MnO_4^- than is needed for manganese oxidation, which resulted in the oxidation of organic matter as well. Permanganate oxidation reduced some of the mutagenicity in our experiments, which is parallel with the results of Vartiainen et al.[3]. They found that permanganate oxidation before chlorination removed almost completely the mutagenicity of the AW. They suggested it to be due to excess permanganate oxidizing the by-product precursors of, for example, the THMs. Furthermore, according to their results, that causes a decrease in the chlorine consumption and a reduction in the mutagenicity of chlorinated AW[3].

5.4 MUTAGENICITY AFTER UV TREATMENT

The UV fluence capable to destroy the microbes in the water has been proposed to be 25 to 35 mJ/cm^2 [41]. According to that knowledge, the UV fluence (48 mJ/cm^2) applied in our experiments was applicable to disinfect the treated water. In our experiments, UV before chlorination decreased the mutagenicity of the PW. Spiked bromide concentration decreased more during UV and chlorine treatment than during ozone-chlorine – treatment (210 vs. 170 µg/L reductions, respectively). Still, both of the reduction values are in accordance with our unpublished results that one half, or even more, of the bromide found in raw water is consumed during the water treatment processes. UV disinfection has been found both to decrease and increase drinking water mutagenicity[25].

5.5 MUTAGENICITY AND MX

The relation between mutagenicity and MX formation has been observed to be very constant after water treatment processes[10,11,19]. However, when the treated water contained bromide in our experiments, it was observed that the mutagenicity/MX –ratio changed noticeably.

Our results from the MX analyses are in accordance with observations by others[10,11,34,42] that the formation of MX is the single most potent increasing factor of drinking water mutagenicity, corresponding up to 76% of the overall mutagenicity. The contribution of MX to the overall mutagenicity of bromide containing waters varied between 29 and 42% of the AW and between 6 and 49% of the PW, while the respective values of bromide-free waters were from 55 to 68% of the AW and from 16 to 76% of the PW. When MX formation (ng/L) was calculated per mg/L of TOC, the MX formation was similar (approximately 11 mg MX / mg TOC) after any treatment of the AW without bromide in spite of the changes in mutagenicity, while the effect on the PW was not as clear. Hydrogen peroxide seemed to lower the MX formation the most in both waters when no bromide was present.

It was observed that since the mutagenicity increases and the MX formation decreases with the presence of bromide, other compounds than MX are causing the mutagenicity. This observation in turn foreshadows the formation of brominated MX analogues, which are found to form similarly to the brominated THMs, during the oxidation experiments. However, the formation of brominated MX analogues in drinking waters is yet to be confirmed, and the work for those results is in progress. Moreover, brominated MX-compounds are not solely responsible for the extra mutagenicity, but also other bromide-containing compounds have their share in the pool of mutagenicity-inducers.

If the mutagenicity of brominated MX analogues is assumed to be 7400 net revertants per nanomole (ref. 6; the highest observed mutagenicity of the dibromochloro-MX, BMX2, in their experiments), the increases in mutagenicities implicate that 5 – 70 ng/L of those compounds were formed during the experiments assuming that the contribution of the MX compounds to the total mutagenicity remained the same in corresponding experiments with and without bromide. Ramos with co-workers[43] observed mutagenicities of 5775, 8772 and 13078 rev per nanomole for BMX1, BMX2, and BMX3, respectively. The concentration of the brominated MX analogues can be assumed to be even higher (>110 ng/L) in the experiment, in which the PW was ozonated and chlorinated at double dosages with 1000 μg/L bromide in the water.

5.6 TRIHALOMETHANES

THM formation during our experiments complied with the results obtained earlier: more bromide-containing compounds were formed when the treated water contained bromide[4]. The formation of chloroform decreased, or even stopped completely, when the treated water contained bromide, and bromoform was found to form at even higher concentrations than chloroform would in the respective water without bromide. The THM formation was dependent on the disinfectant(s) used, which is also in accordance with other researchers' results[44].

5.7 CORRELATION COEFFICIENTS (R)

A good linear correlation between mutagenic activity and MX concentration without bromide (0.899) was observed. However, when bromide spiked waters were treated, the correlation between mutagenicity and MX formation was considerably lower (0.596). Also, for the whole material, inspite of the presence of bromide a quite good correlation coefficient between mutagenicity and MX formation was obtained (0.649 vs. 0.894 [ref. 10] and 0.86 [ref. 19]). Mutagenicity and THM concentration correlated well both with and without bromide (0.976 and 0.939, respectively), being somewhat greater in the presence of bromide. In a similar manner, the correlation between mutagenicity and THM concentration for the whole material was high (0.942 vs. 0.37 [ref. 19] and 0.93 [ref. 45]). On the other hand, when mutagenicity was compared to TOC concentration, the correlation was relatively weak for the whole material, non-bromide and bromide-containing waters (0.379, 0.377 and 0.355, respectively, vs. 0.478 [ref. 24] and 0.89 [ref. 46]). This indicates that the TOC content is not the only decisive factor in the formation of mutagenicity, and, e.g., the presence of bromide ions in the water has effective contribution.

5.8 COMPARISON TO THE MUTAGENICITY MODEL

The model by Vartiainen et al.[24] can be used to predict the mutagenicity formation during disinfection processes. The parameters A and k estimated using the data from our results appeared to be quite close to the values presented earlier ($A = 4000$, $k = 0.054$), and all three NLIN procedures used showed similar results. However, the k-values were 4.4-fold higher for no pre-oxidation experiments, and 8.7-fold higher for other pre-oxidation methods used (see Table 6-III) as compared to the old model. The present results are also parallel with the ones of Nissinen and co-workers[45], who used the results from several water treatment plants and compared those with the results from this model. Thus, our results showed that this model can be used also for predicting mutagenicity during disinfection experiments made in laboratory-scale.

6. CONCLUSIONS

1. Bromide increased the mutagenicity of the water with all preoxidation agents used.
2. MX contribution of the overall mutagenicity varied between 6 and 49% in bromide-containing waters, while it varied between 16 and 76% without bromide. This result implicates the possible formation of brominated MX analogues. The contribution of other brominated disinfection by-products to the total mutagenicity should be studied more thoroughly.
3. Bromide containing waters had higher THM concentrations than waters without bromide.

7. ACKNOWLEDGEMENTS

This study was funded by the Academy of Finland and the Technology Development Centre of Finland (project no. 34538). Special thanks to Ms. Miia Hämäläinen, Mrs. Teija Korhonen and Mrs. Mervi Ojala from the Laboratory of Chemistry, and Mr. Matti Pessi from the University of Kuopio for technical assistance. Also thanks to Mr. Pekka Tiittanen for helping out with the statistical analyses.

8. REFERENCES

1. Kool, HJ, van Kreijl, CF, de Greef, E and van Kranen, HJ. 1982. Presence, introduction and removal of mutagenic activity during the preparation of drinking waters in the Netherlands. Environmental Health Perspectives, 46: 207-214.
2. Vartiainen, T and Liimatainen, A. 1986. High levels of mutagenic activity in chlorinated drinking water in Finland. Mutation Ressearch, 169: 29-34.
3. Vartiainen, T, Liimatainen, A and Kauranen, P. 1987. Comparison of solvent extractions and resin adsorption for isolation of mutagenic compounds from chlorinated drinking water with high humus content. Water Research, 21(7): 773-779.
4. Cooper, WJ, Zika, RG and Steinhauer, MS. 1985. Bromide-oxidant interactions and THM formation: a literature review. Journal American Water Works Association, 77(4): 116-121.
5. Nobukawa, T and Sanukida, S. 2001. Effect of bromide ions on genotoxicity of halogenated byproducts from chlorination of humic acid in water. Water Research, 35(18): 4293-4298.
6. LaLonde, RT, Bu, L, Henwood, A, Fiumano, J and Zhang, L. 1997. Bromine-, chlorine- and mixed halogen-substituted 4-methyl-2(5H)-furanones: synthesis and mutagenic effects of halogen and hydroxyl group replacements. Chemical Research in Toxicology, 10(12): 1427-1436.
7. Nissinen, T, Rantakokko, P, Myllykangas, T and Vartiainen, T. 1999. Bromide and brominated THMs in Finnish drinking waters. In: Proceedings, Fourth Finnish conference of environmental sciences, Tampere, May 21-22, 1999. Environmental science, technology and policy. Eds: Sari Kuusisto, Simo Isoaho and Jaakko Puhakka. Finnish society for environmental sciences. Tampere 1999. ISBN 952-15-0196-0.
8. Holmbom, BR, Voss, RH, Mortimer, RD and Wong, A. 1981. Isolation and identification of an Ames-mutagenic compound present in kraft chlorination effluents. Tappi, 64(3): 172-174.
9. Meier, JR, Knohl, RB, Coleman, WE, Ringhang, HP, Munch, JW, Kaylor, WH, Streicher, RP and Kopfler, FC. 1987. Studies on the potent bacterial mutagen, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone: Aqueous stability, XAD recovery and analytical determination in drinking water and in chlorinated humic acid solutions. Mutation Research, 189: 363-373.
10. Kronberg, L and Vartiainen, T. 1988. Ames mutagenicity and concentration of the strong mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone and of its geometric isomer E-2-chloro-3-(dichloromethyl)-4-oxo-butenoic acid in chlorine-treated tap waters. Mutation Research, 206: 177-182.

11. Smeds, A, Vartiainen, T, Mäki-Paakkanen, J and Kronberg, L. 1997. Concentrations of Ames mutagenic chlorohydroxyfuranones and related compounds in drinking waters. Environmental Science & Technology, 31(4): 1033-1039.

12. Horth, H, Fielding, M, Gibson, T, James, HA and Ross, H. 1989. Identification of mutagens in drinking water. Water Research Centre Technical Report. PRD 2038-M.

13. Suzuki, N and Nakanishi, J. 1990. The determination of strong mutagen, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone in drinking water in Japan. Chemosphere, 21(3): 387-392.

14. Peters, RJB, Erkelens, C, de Leer, EWB and de Galan, L. 1991. The analysis of halogenated acetic acids in Dutch drinking water. Water Research, 25(4): 473-477.

15. Romero, J, Ventura, F, Caixach, J, Rivera, J, and Guerrero, R. 1997. Identification and quantification of the mutagenic compound 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) in chlorine-treated water. Bulletin of the Environmental Contamination Toxicology, 59: 715-722.

16. Nawrocki, J, Andrzejewski, P, Kronberg, L and Jelén, H. 1997. New derivatization method for determination of 3-chloro-4(dichloromethyl)-5-hydroxy-2(5H)-furanone in water. Journal of Chromatography A, 790: 242-247.

17. Zhou, SW, Xu, FD, Li, SM, Song, RX, Qi, S, Zhang, Y and Bao, YP. 1997. Major origin of mutagenicity of chlorinated drinking water in China: humic acid or pollutants. Science of the Total Environment, 196(3): 191-196.

18. Simpson, KL and Hayes, KP. 1998. Drinking water disinfection by-products: an Australian pespective. Water Research, 32(5): 1522-1528.

19. Wright, JM, Schwartz, J, Vartiainen, T, Mäki-Paakkanen, J, Altshul, L, Harrington, JJ and Dockery, DW. 2002. 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) and mutagenic activity in Massachussetts drinking water. Environmental Health Perspectives, 110(2): 157-164.

20. Backlund, P, Kronberg, L, Pensar, G and Tikkanen, L. 1985. Mutagenic activity in humic water and alum flocculated humic water treated with alternative disinfectants. Science of the Total Environment, 47: 257-264.

21. National Board of Waters and the Environment. 1994. Water supply and sewer systems 1993. Publications of the Water and the Environment Administrations – series A192, Helsinki, 1994.

22. Rook, JJ. 1974. Formation of haloforms during chlorination of natural waters. Water Treatment and Examination, 23: 234-243.

23. Glaze, WH, Kang, J-W and Chapin, DH. 1987. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Science & Engineering, 9: 335-352.

24. Vartiainen, T, Liimatainen, A, Kauranen, P and Hiisvirta, L. 1988. Relations between drinking water mutagenicity and water quality parameters. Chemosphere, 17(1): 189-202.

25. Wolfe, RL. 1990. Ultraviolet disinfection of potable water – Current technology and research needs. Environmental Science & Technology, 24(6): 768-773.

26. Knocke, WR, van Benschoten, JE, Kearney, MJ, Soborski, AW and Reckhow, DA. 1991. Kinetics of manganese and iron oxidation by potassium permanganate and chlorine dioxide. Journal American

Water Works Association, 83(6): 80-87.

27. Myllykangas, T, Nissinen, T, Rantakokko, P, Martikainen, PJ and Vartiainen, T. 2002. Molecular size fractions of treated aquatic humus. Water Research, 36(12): 3045-3053.
28. Myllykangas, T, Nissinen, T and Vartiainen, T. 2000. Bromate formation during ozonation of bromide containing drinking water – a pilot scale study. Ozone Science & Engineering, 22 (5): 487-499.
29. Maron, DM and Ames, BN 1983. Revised methods for the Salmonella mutagenicity test. Mutation Research, 113: 173-215.
30. International Organization for Standardization (ISO). 1994. Water quality – determination of highly volatile halogenated hydrocarbons – gas-chromatographic methods. ISO/DIS 10301.
31. Finnish Standards Association SFS, SFS-EN 1484. 1997. Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). Finnish Standards Association SFS, Helsinki, Finland, 1997.
32. SAS Institute Inc. 1999. SAS OnlineDoc®, Version 8. Cary, NC: SAS Institute Inc.
33. Backlund, P, Wondergem, E, Voogd, K and de Jong, A. 1989. Influence of chlorination pH and chlorine dose on the formation of mutagenic activity and the strong bacterial mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) in water. Chemosphere, 18(9/10): 1903-1911.
34. DeMarini, DM, Abu-Shakra, A, Felton, CF, Patterson, KS and Shelton, ML. 1995. Mutation spectra in salmonella of chlorinated, chloraminated or ozonated drinking water extracts: comparison to MX. Environmental Molecular Mutagenicity, 26(4): 270-285.
35. Matsuda, H, Hibino, M, Sato, T, Ose, Y, Nagase, H and Kito, H. 1993. Mutagenicity of ozonated and chlorinated humic substances. Journal of Environmental Science and Health A, 28(4): 821-837.
36. Haag, WR and Hoigné, J. 1983. Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environmental Science & Technology, 17(7): 261-267.
37. Tuhkanen, TA, Kainulainen, TK, Vartiainen, TK and Kalliokoski, PJ. 1994. The effect of preozonation, ozone/hydrogen peroxide treatment, and nanofiltration on the removal of organic matter from drinking water. Ozone Science & Engineering, 16: 367-383.
38. Staehelin, J and Hoigné, J. 1982. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. Environmental Science & Technology, 16(10): 676-681.
39. von Gunten, U and Hoigné, J. 1994. Bromate formation during ozonation of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. Environmental Science & Technology, 28(7): 1234-1242.
40. Pouvreau, P. 1984. Elimination spécifique du fer et du manganése. Journal Francais d'hydrologie 2: 169.
41. Qualls, RG, Oddoff, SF, Chang, JCH, Dorfman, MH, Dumais, CM, Lobe, DC and Johnson, JD. 1985. Factors controlling sensitivity in ultraviolet disinfection of secondary effluents. Journal of the Water Pollution Control Federation, 57(10): 1006-1011.

42. Noot, DK, Anderson, WB, Daignault, SA, Williams, DT and Huck, PM. 1989. Evaluating treatment processes with the Ames mutagenicity assay. Journal American Water Works Association, 81(9): 87-102.

43. Ramos, I, Lloveras, M, Solans, X, Huici, A and Messeguer, A. 2000. Brominated analogs of 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone: preparation of 3-chloro-4-(bromochlorome-thyl)-5-hydroxy-2(5H)-furanone and mutagenicity studies. Environmental Toxicology and Chemistry, 19(11): 2631-2636.

44. Oxenford, JL. 1996. Disinfection by-products: current practices and future directions. In: Disinfection by-products in water treatment - the chemistry of their formation and control. Edited by Roger A. Minear & Gary L. Amy, CRC Press, Inc., p. 3-16.

45. Nissinen, TK, Miettinen, IT, Martikainen, PJ and Vartiainen, T. 2002. Disinfection by-products in Finnish drinking waters. Chemosphere, 48(1): 9-20.

46. Miettinen, I, Martikainen, P and Vartiainen, T. 1991. Mutagenicity formation potential of artificially recharged ground water from humus-rich surface water. Finnish Humus News, 3(3): 227-232.

CHAPTER 7: GENERAL DISCUSSION

1. BROMIDE IN NATURAL WATERS AND IN FINLAND

Bromine-containing DBPs are problematic due to their potential to damage the health of water consumers. Bromide itself has not been observed to cause health problems, but bromine-containing DBPs are known to be more mutagenic and more harmful than their chlorinated counterparts.

Chlorination is the most often used disinfection method in drinking water production, and it has been found to produce high amounts of DBPs, such as THMs, HAAs, and MX, compounds which are known to be hazardous. Chloramination produces smaller amounts of similar DBPs than chlorination, but it is a weaker disinfectant than chlorine. Preoxidation with ozone has been found to reduce the formation of those compounds, and ozone combined with chlorination produces smaller amounts of chlorinated DBPs. Ozone alone produces smaller amounts of halogenated DBPs than chlorination, but in the presence of bromide, bromate and bromoform are formed. Ozonation oxidizes the organic matter very efficiently resulting in the formation of a high amount of small-molecular-weight organics, such as aldehydes, ketones, and many organic acids, which represent potential food sources for microbes living in the distribution systems leading to biofilm growth in the pipes. Ozone with hydrogen peroxide is often used to treat waters with persistant contaminants, such as pesticides, producing similar DBPs as are obtained with ozone alone. Permanganate and UV treatments alone have not been found to produce any DBPs.

Appendices 1 – 3 show the results obtained from the experiments of this study including also some extra information, which has not been included in articles I – V. Those results are compared with the ones obtained from 24 Finnish water works (Table 1-IX). From Table 1-IX one can observe that those water works which had bromide present in their raw water in concentrations varying from 25 to 362 μg L^{-1}. Only one water works had a bromide concentration exceeding 350 μg L^{-1} (SW1), while three of them had 100 – 200 μg L^{-1} bromide (SW2, SW3, and SW4), and five had less than 100 μg L^{-1} bromide (SW5, SW6, SW7, GW1, and GW2) in their water. Thus, 15 of the studied water works did not have any detectable bromide (above 20 μg L^{-1}) in their raw water.

2. EFFECT OF BROMIDE ON THE DISINFECTION BY-PRODUCTS

2.1 BROMATE FORMATION

Bromate formation was observed at a spiked bromide concentration of 50 μg L^{-1}. When bromide concentration increased from 50 – 100 μg L^{-1}, the bromate formation increased more than nine times (III). This result is in parallel with earlier observations that bromate formation increases with increasing bromide concentration[1-4]. However, no further enhanced bromate formation was observed at a bromide concentration of 500 μg L^{-1} under similar conditions (III).

It has been observed that the threshold levels for bromate formation of both bromide and ozone concentrations are water specific[5,6]. In a study of a humus-rich water with spiked bromide at a level of 500 μg L^{-1} (III), the bromate formation was more than four times higher than in a study of a water source with a naturally high bromide concentration of 460 μg L^{-1} (IV) in spite of a doubled ozone dose in the latter study (6.3 vs. 12.6 mg L^{-1}). Thus, the threshold levels of bromide and ozone for bromate formation were clearly different between these two waters.

On the other hand, in both studies III and IV, the bromate formation increased with increasing ozone dose, hydrogen peroxide concentration, and pH, which are in agreement with previous studies showing similar effects of those parameters on bromate formation[2-4]. The effect of hydrogen peroxide was similar to previous results, which have shown that hydrogen peroxide increases bromate formation until the optimum H_2O_2/O_3 molar ratio of 0.2 – 0.3 has been reached[3], and at higher concentrations of hydrogen peroxide, the formation is again reduced[7]. With increasing alkalinity, the change in the bromate formation was observed only in study IV. An increase in alkalinity has been observed either to increase or to decrease bromate formation in earlier studies[1,2,8]. An increase in the ozonation temperature increased the bromate formation in the study III more than in the study IV, but the results in both experiments were rather similar to previously published observations[5].

The effect of different water matrices on bromate formation were clearly seen when the results from studies III and IV were compared. Whereas the water in study III was taken from an inland humus-rich lake water with no effect of sea-water resulting in relatively low concentrations of the inorganic anions, the water in study IV was taken from the coast and was greatly influenced by sea-water and the old sea-bed with several times higher concentrations of inorganic anions (Table 7-II). Even though the concentrations of the inorganic anions did not change in the course of ozonation, the matrix effect should not be neglected.

Table 7-II. The average concentrations (± standard deviation, mg L^{-1}) of the inorganic anions of the non-oxidized water samples from study III with a humus-rich, bromide-free lake water, and the corresponding values from study IV with a high-bromide surface water.

	Cl^-	NO_2^-	SO_4^{2-}	NO_3^-	F^-	PO_4^{3-}
III (N = 14)	1.9 ± 0.2	0	23 ± 2	0.3 ± 0.1	0.03 ± 0.02	0
IV (N = 12)	43 ± 4	0	109 ± 4	7.3 ± 1.1	0.8 ± 0.1	0

N = number of samples

Several hypotheses were examined to study the effects of the different parameters on the bromate formation, and correlation coefficients were calculated. The initial bromide concentration, ozone dose, ozonation temperature and pH, or the oxidation of the organic matter were not found to explain the bromate formation in studies III and IV, when the comparisons were made with separate or combined data (Appendix 1). However, the organic acid concentration in the treated water did correlate well with bromate formation in the data from study IV. No bromate formation was observed in the data from the Finnish water works, thus, no correlation between experimental and full-scale results could be made.

Bromate was not analyzed from the data from the 24 Finnish water works. However, if bromide-containing waters were treated with ozone, the potential for bromate formation would have had to be taken into account, which was seen in the study III (Chapter 4) showing that at an ozone dose of approximately 6 mg L^{-1}, over 10 µg L^{-1} bromate was formed under ambient pH (6.2) when the treated water was typical Finnish inland water with a high organic content in the raw water. On the other hand, when the water had a different quality of the humus as in the water taken from the coastal area (study IV, Chapter V), bromate formation remained significantly lower (less than 3 µg L^{-1}) than in the study III even if the ozone dose was 12 mg L^{-1} at a pH 5.8. Thus, the ozonation option should be evaluated with laboratory or pilot-scale experiments every time individually to avoid any possible bromate formation.

2.2 THMs

The presence of bromide in chlorinated waters has been found to increase the formation of THMs by increasing the bromine-incorporation into the compounds[9] (II, V; Appendices 2 and 3). An increase in the Br-to-TOC ratio did not change the proportional Br-THM formation (94 – 97%), but the proportional bromoform formation increased from 42 to 56% (IV; Appendix 2). When the bromide concentration was sufficiently high, bromoform was the main THM observed, and the formation of chloroform decreased[9-11] (II, IV, V). Bromoform formation was found to increase continuously when the bromide concentration increased from 0 up to 2400 μg L^{-1} [10,11]. In study IV, bromoform formation exceeded chloroform formation when the bromide concentration was 250 μg L^{-1}, which is close to a previous result showing the same effect at a bromide concentration of 300 μg L^{-1} [11], and similar to the observations of Amy et al.[12] and Luong et al.[13] of 185 μg L^{-1} and 175 – 550 μg L^{-1}, respectively.

From 60 to 100% of the THMs in the bromide-containing chlorinated with or without preozonated or pretreated by UV or $KMnO_4$ waters were brominated (II, IV, V), while preoxidation by hydrogen peroxide decreased the proportion of the brominated THMs (IV, V). The highest contributions of the brominated THMs were found after chlorination alone or combined with ozonation or UV treatment (II, V). These results are in accordance with previous ones highlighting the major effect of bromide on the DBP concentrations[9,11-14].

The bromide concentration, and its changes during chlorination, correlated well with the THM formation (Table 1-IX and Appendices 2 and 3). The chlorine dose affected the THM formation most clearly in the data from the water works, while in the laboratory experiments it explained moderately well the THM formation. The removal of the organic matter measured as the HPSEC fractions, explained well the THM formation in study II (Appendix 3), while its effect on the THM formation in other studies was less important. The THM formation explained the formation of HAAs and mutagenicity well in all of the studies. However, its capability to explain the MX formation was not as good. The concentration of the anions (not shown) did not correlate at all with the THM formation in any study.

In Finnish waters, the SW1 (Table 1-IX) had the highest observed bromide concentration, and the bromine-containing THMs (bromodichloromethane, chlorodibromomethane, and bromoform) corresponded to up to 96% of the sum of the THMs in that water. Bromoform and dibromochloromethane were found in the largest concentrations. Similar observations were made in this study as well after chlorination alone (PW2, AS2, FS3, and PACl2 in Appendices 2 and 3) even though the chlorine doses were not the same, i.e. in the water works SW1 the chlorine dose was 2.6 mg L^{-1}, and in the experiments PW2, AS2, FS3, and PACl2 they were about 1 mg L^{-1}. In all of these cases, the initial bromide concentration of the treated water was 400 – 500 μg L^{-1}. On the other hand, in the next three water works (SW2 – SW4) having 100 – 200 μg L^{-1} bromide in their raw waters, the bromine-containing THMs corresponded to approximately 80% of the sum of the THMs. The concentrations of bromodichloromethane and chlorodibromomethane were highest. In the experiment FS2 (Appendix 3), the initial bromide concentration was 270 μg L^{-1}, and the proportional concentrations of the bromine-containing THMs were similar to the values of SW2 – SW4. In water works treating water containing less than 100 μg L^{-1} bromide, the corresponding value was found to be less than 50%, while in the groundwater works treating bromide-containing raw water only very small concentrations of the bromine-containing THMs were found.

2.3 MUTAGENICITY OF BROMIDE-CONTAINING WATERS

Chlorination produced the highest mutagenicities with and without bromide (II, IV, V). Preoxidation either by hydrogen peroxide with or without ozonation or permanganate decreased clearly the mutagenicity (IV, V), while UV treatment before chlorination decreased much less (V) or even increased the mutagenicity (II). Bromide increased the mutagenicity in 94% (15/16) of the cases (II, V), thus observation being similar to published findings[15].

The highest contribution of MX on the mutagenicity of bromide-free waters was observed after chlorination, while hydrogen peroxide with or without ozonation as the preoxidation method produced the lowest proportional MX formation (V). MX contributed 68 and 76% of the mutagenicity of chlorinated, bromide-free waters, while in bromide-containing waters, the contributions were only 34 and 20%, which points to the formation of brominated MX analogues (V). Previously it has been found that MX accounts for up to 67% of drinking water mutagenicity[16,17].

Mutagenicity was most most dependent on the consumed bromide concentration in study II (Appendix 3), while in other studies the effect was not so clear. However, in the data taken from the Finnish water works, the initial bromide concentration correlated well with mutagenicity as compared to the other results (Table 1-IX and Appendices 2 and 3). Neither the initial bromide concentration nor the anion concentration (not shown) affected the MX formation substantially in any of the studies. The chlorine dose influenced clearly the mutagenicity and MX formation in the laboratory studies, but the effect was only marginal in the data from the Finnish water works. As with the THMs, also mutagenicity and the reduction in the HPSEC fractions during chlorination correlated well in the data from study II, but in other studies this effect was not seen.

The average mutagenicity in the Finnish drinking waters (Table 1-IX) was 990 net rev L^{-1} for surface water works, 450 net rev L^{-1} for artificially recharged groundwater works, and 280 net rev L^{-1} for groundwater works when the average is used. On the other hand, when the average-production-weighted average was used, the corresponding values were found to be 710 net rev $(m^3/d)^{-1}$, 420 net rev $(m^3/d)^{-1}$, and 230 net rev $(m^3/d)^{-1}$. The mutagenicity results obtained from studies II, IV, and V for the PW, Uusikaupunki's water, or water treated in the pilot-scale water treatment plant were found to be 1.3 to 3.0 times of the average mutagenicity calculated from the water works data (Table 1-IX). Only when hydrogen peroxide was used either alone or in combination with ozone, were the mutagenicities obtained from study V found to be lower than the average from Table 1-IX. Even though the TOC range of the surface water works data was narrowed to the one close to the values used in the experiments II, IV, and V (2.5 – 4.0 mg L^{-1}), the average of 1040 net rev L^{-1} was still clearly lower than the values observed in the laboratory and pilot-scale experiments. The difference of the mutagenicity values cannot be explained solely by the chlorine dose, since in most of the surface water works, the Cl_2/(TOC in the finished water) in % varied from 20 to 40%, while the corresponding values obtained from the experiments of this study were 25 – 40%. Thus, other processes in the water works have a great influence on the quality of the finished water, since they change the quality and quantity of the constituents in the water resulting in the variation in the observed mutagenicities even though the chlorine dose and TOC were close to each other.

2.4 OTHER EFFECTS

The bromide concentration was not found to correlate with the organic matter removal during the experiments. However, the initial bromide concentration and the reduction in the bromide concentration during the oxidation seemed to correlate with the reduction in the HPSEC fractions both in study II (Appendix 3) and in study IV (Appendix 2), while in the data from the water works, no such correlation was observed (Table 1-IX).

Changes in the organic acid concentrations and the HPSEC fractions correlated well with the formation of the THMs, HAAs, and mutagenicity (Table 1-IX and Appendices 2 and 3). Otherwise, the DBP formation was not affected substantially by the amount of the initial TOC, and the bromate formation was not affected at all by the quality changes in the organic matter.

3. METHODS TO PREVENT THE FORMATION OF BROMINE-CONTAINING DISINFECTION BY-PRODUCTS

Efficient organic matter removal before disinfection has been found to be one of the most important methods to prevent the formation of (brominated) DBPs during disinfection. In this study also the organic matter removal was mainly done before oxidation or disinfection, since the TOC did not change appreciably during the experiments (I, III, IV, V). However, since bromide is not removed effectively during the coagulation process, the Br-to-TOC ratio increased, which enhanced the proportional formation of brominated DBPs such as bromoform[9], even though the total THM formation decreased (IV, V). Also, bromate formation during ozonation can be assumed to increase when the organic content of the water decreases due to enhanced reactions between ozone and bromide (OBr^-).

One way to estimate the DBP formation potential is to measure the UV absorbance at 254 nm (UV_{254}), and to calculate to SUVA value ($100 \times UV_{254}/DOC$ or $100 \times UV_{254}/TOC$). The UV_{254} and TOC, and the UV_{254} and THM formation have been found to correlate well, enabling its use as a surrogate parameter for DBP formation[18-21] (II). However, the TOC and THM formation have not been found to correlate well[22] (II, IV, V). On the other hand, if SUVA values are calculated and used, the aromatic content of the organic matter can be estimated, and the efficiency of certain unit processes can be evaluated already in the planning stage of a water treatment plant[23,24]. It has been stated that coagulation would be an efficient process for organic matter removal from waters with SUVA values above 2 mg L^{-1} m^{-1} [23]. In study II, where the raw had a SUVA value of approximately 3.6 mg L^{-1} m^{-1}, the organic matter was removed very efficiently by more than 60%, resulting in SUVA values 1.5 – 1.9 mg L^{-1} m^{-1}, hence, the aromatic content of the treated water decreased by about 50%. Also, the coagulation removed all of the "excess-SUVA" (1.7 to 2.1 mg L^{-1} m^{-1}), evidence that the process worked well.

Ozonation at a lower pH, as compared to an increased pH, was a very efficient method to reduce bromate formation (III, IV), which has been found earlier as well[2,4]. At a lower pH bromide is mainly in the form of HOBr, which reduces the reactions between ozone and bromide, and, hence, decreases the bromate formation. Since bromate formation requires dissolved ozone in the water[2], the ozone dose and its optimal use are very important factors in minimizing bromate formation. However, even though the ozone dose was as high as 18 mg L^{-1} in study IV, bromate formation remained below the EU limit value of 10 µg L^{-1} for bromate when ozonation was carried out at the ambient pH (5.8) and alkalinity (0.3 mM). On the other hand, in study III, bromate formation exceeded the limit value in spite of the much lower ozone dose (6.3 mg L^{-1}) at a pH of 6.2 and alkalinity of 0.3 mM. These two results show clearly that pilot-testing with a specific water and conditions should be carried out before their introduction to full-scale water treatment processing.

Hydrogen peroxide can be used to decrease the amount of bromine-containing DBPs, since it causes the reduction of hypobromite back to bromide[7]. However, in this study, bromate formation increased when hydrogen peroxide oxidation was combined with ozonation (III, IV), and in study V, the THM formation decreased clearly when hydrogen peroxide was combined with ozonation and chlorination. On the other hand, in study III, the bromate formation was approximately the same as without hydrogen peroxide at the highest H_2O_2/O_3 molar ratio of 0.8. The use of hydrogen peroxide with ozonation reduced the amount of dissolved ozone as was found in the studies III and IV, but increased the amount of hydroxyl radicals, which react very rapidly and unselectively in the water.

Since chlorination produces the highest amount of DBPs when many alternatives are compared, the effect of preoxidation was tested in studies I, II, IV, and V. The effect of ozonation with or without hydrogen peroxide was tested in studies III and IV without chlorination. Activated carbon filtration was not used in any of the studies before the ozonation step so it was possible to study the potential for DBP formation when chlorine was the post-disinfectant. Ozonation proved to be an efficient method to reduce both the levels of THMs and the mutagenicity (V). On the other hand, hydrogen peroxide potentiated even better reduction in mutagenicity (IV, V), but its effect on the THMs was mixed (IV, V).

Ozonation is often followed by activated carbon filtration, which results in biologically activated carbon treatment, in the water works. However, this combination was not tested in this study even though it has been observed to be an effective method to prevent the formation of (brominated) disinfection by-products[25,26].

4. PRACTICAL IMPLICATIONS

Since chlorination produced the highest amount of DBPs during water treatment, organic matter removal before disinfection must be given priority in preventing the formation of these compounds. Enhanced coagulation/flocculation followed by effective filtration has achieved good results both in the organic matter removal and in the reduction in the DBP formation. Also, a multiple-barrier approach for water disinfection consisting of preoxidation by ozone with or without hydrogen peroxide or permanganate and postchlorination both reduced the formation of the DBPs and enhanced the water quality together with better preparedness for prevention of microbiological contamination.

High bromide concentrations in raw waters from certain geographical areas placed even more demands on the water purification process, since the DBP formation increased in the presence of bromide. Bromide removal by nanofiltration, activated carbon, electrochemical reactions, or ion exchange[27-31] may not be economically feasible, and other ways to reduce the formation of brominated DBPs are needed. Ozonation without activated carbon filtration showed potential for DBP reduction in this study (I, V), while in full-scale water works it is often followed by activated carbon filtration to enhance the removal of the DBP precursors and small-molecular-weight organics[26]. However, the formation of bromate has to be taken seriously[2,4] (III, IV).

5. CONCLUSIONS

Bromate formation was found to vary in different ozonated waters, even though the bromide concentration, TOC, pH, and alkalinity of the waters were the same. The low-molecular-weight organic compounds in the water produced less bromate than the high-molecular-weight organic compounds. The molecular-weight fractions were measured using high pressure size exclusion chromatography. The concentrations of the inorganic anions in raw water did not affect the bromate formation.

The formation of total THMs increased when the water contained bromide as compared to the corresponding waters without bromide.

Mutagenicity was found to be higher in bromide-containing waters compared to bromide-free waters. However, the MX formation was found to be lower in bromide-containing waters pointing to the formation of brominated MX analogues and mutagenic compounds other than MX.

Ozonation combined with hydrogen peroxide seemed to be a promising choice as the preoxidation method to reduce the formation of DBPs. In contrast, UV treatment before chlorination did not reduce the DBPs below the levels observed after chlorination in these humus-rich waters.

Bromide had no effect on the decomposition of the organic matter. Chlorine and ozone were found to result in the formation of small-molecular-weight compounds from the organic matter. Chlorine decreased both the molecular size fraction of the aquatic humus and the amount of double bonds in the compounds more efficiently than ozone. Ozonation produced more organic acids per mg of oxidant than chlorination, except for the treatment with ozone-hydrogen peroxide-chlorine, in which the production of the organic acids was more than 3 times higher than observed with any of the other ozonation options. Even though the quality of the organic matter changed clearly, the TOC value remained virtually unchanged.

6. REFERENCES

1. Glaze, WH, Weinberg, HS and Cavanagh, JE. 1993. Evaluating the formation of brominated DBPs during ozonation. Journal American Water Works Association, 85(1): 96-103.

2. Siddiqui, MS, Amy, GL and Rice, RG. 1995. Bromate ion formation: a critical review. Journal American Water Works Association, 87(10): 58-70
3. Croué, JP, Koudjonou, BK and Legube, B. 1996. Parameters affecting the formation of bromate ion during ozonation. Ozone Science & Engineering, 18: 1-18.
4. von Gunten, U. 2003. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Research, 37: 1469-1487.
5. Siddiqui, MS and Amy, GL. 1993. Factors affecting DBP formation during ozone-bromide reactions. Journal American Water Works Association, 85(1): 63-72.
6. Ozekin, K and Amy, GL. 1997. Threshold levels for bromate formation in drinking water. Ozone: Science & Engineering, 19: 232-337.
7. von Gunten, U and Hoigné, J. 1994. Bromate formation during ozonation of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. Environmental Science & Technology, 28: 1234-1242.
8. Amy, G. Siddiqui, M, Ozekin, K and Westerhoff, P. 1993. Threshold levels for bromate formation in drinking water. Water Supply, 13(1): 157-162.
9. Cooper, WJ, Zika, RG and Steinhauer, MS. 1985. Bromide-oxidant interactions and THM formation: a literature review. Journal American Water Works Association, 77(4): 116-121.
10. Ichihashi, K, Teranishi, H and Ichimura, A. 1999. Brominated trihalomethane formation in halogenation of humic acid in the coexistence of hypochlorite and hypobromite ions, Water Research, 33 (2): 477-483.
11. Chang EE, Lin, YP and Chiang, PC. 2001. Effects of bromide on the formation of THMs and HAAs. Chemosphere, 43: 1029-1034.
12. Amy, GL, Tan, L and Davis, MK. 1991. The effects of ozonation and activated carbon adsorption on trihalomethane speciation. Water Reasearch, 25(2): 191-202.
13. Luong, TV, Peters, CJ and Perry, R. 1982. Influence of bromide and ammonia upon the formation of trihalomethanes under water-treatment conditions. Environmental Science & Technology, 16: 473-479.
14. Rebhun, M, Manka, J, and Zilberman, A. 1988. Trihalomethane formation in high-bromide Lake Galilee water. Journal American Water Works Association 80(6): 84-89.
15. Nobukawa, T and Sanukida, S. 2001. Effect of bromide ions on genotoxicity of halogenated by-products from chlorination of humic acid in water. Water Research, 35(18): 4293-4298.
16. Smeds, A, Vartiainen, T, Mäki-Paakkanen, J and Kronberg, L. 1997. Concentrations of Ames mutagenic chlorohydrofuranones and related compounds in drinking waters. Environmental Science & Technology, 31(4): 1033-1039.
17. Wright, JM, Schwartz, J, Vartiainen, T, Mäki-Paakkanen, J, Altshui, L, and Dockery, DW. 2002. Mutagenic compounds in Massachusetts' drinking water. Environmental Health Perspectives, 110(2): 157-164.
18. Edzwald, JK, Becker, WC and Wattier, KL. 1985. Surrogate parameters for monitoring organic matter and THM precursors. Journal American Water Works Association, 77(4): 122-132.

19. Najm, IN, Patania, NL, Jacangelo, JG and Krasner, SW. 1994. Evaluating surrogates for disinfection by-products. Journal American Water Works Association, 86(6): 98-106.

20. Kitis, M, Karanfil, T, Wigton, A and Kilduff, JE. 2002. Probing reactivity of dissolved organic matter from disinfection by-products formation using XAD-8 resin adsorption and ultrafiltration fractionation. Water Research, 36: 3834-3848.

21. Korshin, GV, Wu, WW, Benjamin, MM and Hemingway, O. 2002. Correlations between differential absorbance and the formation of individual DBPs. Water Research, 36(13): 3273-3282.

22. Arora, H, LeChevallier, MW and Dixon, KL. 1997. DBP occurrence survey. Journal American Water Works Association, 89(6): 60-68.

23. Edzwald, JK and van Benschoten, JE. 1990. Aluminum coagulation of natural organic matter. Proc. 4th International Guthenburg Symposium on Chemical Treatment. Madrid, Spain, October 1990.

24. Chin, Y-P, Aiken, GR and Danielsen, KM. 1997. Binding of pyrene to aquatic and commercial humic substances: the role of molecular weight and aromaticity. Environmental Science & Technology, 31(6): 1630-1635.

25. Nissinen, T. 2002. The effect of ozonation on the chemical quality of drinking water. Academic dissertation. Publications of the National Public Health Institute, A7/2002. ISBN 951-740-270-8.

26. Vahala, R. 2002. Two-step granula activated carbon filtration in drinking water treatment. Academic dissertation. Helsinki University of Technology, Laboratory of Water and Wastewater Engineering, TKK-VHT-33. ISBN 951-22-6163-4.

27. Laîné, J-M, Jacangelo, JG, Cummings, EW, Carns, KE and Mallevialle, J. 1993. Influence of bromide on low-pressure membrane filtration for controlling DBPs in surface waters. Journal American Water Works Association, 85(6): 87-99.

28. Asami, M, Aizawa, T, Morioka, T, Nishijima, W, Tabata, A and Magara, Y. 1999. Bromate removal during transition from new granular activated carbon (GAC) to biological activated carbon (BAC). Water Research, 33(12): 2797-2804.

29. Kimbrough, DE and Suffet, IH. 2002. Electrochemical removal of bromide and reduction of THM formation potential in drinking water. Water Research, 36: 4902-4906.

30. Singer, PC and Bilyk, K. 2002. Enhanced coagulation using a magnetic ion exchange resin. Water Research, 36(16): 4009-4022.

31. Vaaramaa, K and Lehto, J. 2003. Removal of metals and anions from drinking water by ion exchange. Desalination, 155: 157-170.

APPENDIX 1

Appendix 1. The quality of the raw water and ozonated water in the laboratory experiments of the studies III and IV. K = experiments of the study III; U = experiments of the study IV. Alkalinities of the waters were 0.3 mM except in the following experiments (alkalinity in brackets): K3 (1.8 mM), K15 (0.8 mM), K16 (1.4 mM), U5 (0.5 mM), and U8 (0.5 mM).

Water (temperature °C / pH)	Raw water					Treated water									Pre-oxidant
	Br^- (µg/L)	TOC (mg/L)	HP-SEC (AU*s)	OA (µg/L)	Anions (mg/L)	O_3 dose (mg/L)	Ct (mg/L ×min)	DO_3 (µg/L)	Br^- (µg/L)	TOC (mg/L)	HP-SEC (AU*s)	OA (µg/L)	Anions (mg/L)	BrO_3^- (µg/L)	
K1 (12 / 6.2)	50	3.0	92 000	10	23	6.3	2.6	820	50	2.8	38 000	510	25	1.2	none
K2 (12 / 6.2)	50	3.0	92 000	10	23	6.3	1.1	355	40	2.6	37 000	620	27	1.5	H_2O_2
K3 (12 / 6.5)	50	3.0	92 000	10	23	6.3	4.7	1 470	50	2.3	36 000	460	18	3.4	none
K4 (12 / 6.3)	100	3.0	92 000	10	23	6.3	3.3	1 020	80	2.6	25 000	680	26	12	none
K6 (12 / 6.2)	500	3.0	92 000	10	23	6.3	1.8	565	410	3.1	43 000	410	23	11	none
K7 (12 / 6.1)	500	3.0	92 000	10	23	6.3	3.3	1 040	440	2.9	44 000	360	25	13	none
K8 (12 / 7.2)	500	3.0	92 000	10	23	6.3	2.2	690	430	2.8	34 000	420	26	30	none
K9 (12 / 9.0)	500	3.0	92 000	10	23	6.3	2.3	710	400	2.8	25 000	550	25	100	none
K10 (20/6.2)	500	3.0	92 000	10	23	6.3	2.4	760	330	3.0	35 000	550	24	88	none
K11 (12/6.2)	500	3.0	92 000	10	23	12.3	5.6	1 750	380	3.1	35 000	430	26	28	none
K12 (12/6.2)	500	3.0	92 000	10	23	6.3	1.6	490	390	2.4	26 000	440	25	24	H_2O_2
K13 (12/6.3)	500	3.0	92 000	10	23	6.3	1.0	320	420	2.4	33 000	560	25	23	H_2O_2
K14 (12/6.5)	500	3.0	92 000	10	23	6.3	0.8	245	400	2.4	29 000	570	25	15	H_2O_2
K15 (12/6.5)	500	3.0	92 000	10	23	6.3	4.7	1 485	450	2.5	35 000	310	25	11	none
K16 (12/6.5)	500	3.0	92 000	10	23	6.3	5.0	1 580	460	2.7	34 000	330	27	9.4	none
U1 (10 / 5.8)	460	3.4	69 000	50	170	12.6	25	1 620	270	3.8	31 000	560	170	2.8	none
U2 (17 / 5.8)	490	3.4	68 000	60	170	17	64	2 000	240	3.0	27 000	620	150	5.9	none
U3 (10 / 5.8)	480	3.4	56 000	70	160	18	106	2 760	210	3.3	30 000	650	150	9.1	none
U4 (10 / 7.0)	420	3.4	61 000	70	170	12.5	19	1 535	300	3.3	40 000	620	160	23	none
U5 (10 / 7.0)	390	3.9	68 000	480	160	17	11	870	380	4.1	46 000	1 050	160	35	none
U6 (10 / 7.0)	410	3.4	63 000	100	160	14.8	7.4	880	400	3.3	36 000	1 370	160	71	H_2O_2
U7 (10 / 7.0)	340	3.5	46 000	190	160	13.0	0	0	330	3.0	35 000	1 100	110	32	H_2O_2
U8 (10 / 7.0)	460	3.4	68 000	80	160	14.6	9.5	1 010	340	3.3	27 000	1 100	150	118	H_2O_2

HPSEC (AU*s) = integrated peak areas from the size exclusion chromatography (absorbance units multiplied by time in seconds); OA = the sum of organic acids (formate, acetate, propionate, pyruvate, oxalate, and citrate); nd = not detected; nm = not measured; Res. Cl_2 = residual chlorine in the water at the time of sampling

Appendix 2. The quality of the raw water and chlorinated water in the laboratory experiments of the studies I, IV, and V. AW = artificially recharged groundwater, PW = purified water (treated by alum coagulation, sedimentation, and sand filtration). U = purified water (study IV).

Water	Raw water				Chlorinated water									
	Br^- (µg/L)	**TOC (mg/L)**	**HP-SEC (AU*s)**	**OA (µg/L)**	**Br^- (µg/L)**	**TOC (mg/L)**	**Cl_2 dose (mg/L)**	**Res. Cl_2 (mg/L)**	**HP-SEC (AU*s)**	**OA (µg/L)**	**THMs (µg/L)**	**Mutagenicity (net rev/L)**	**MX (ng/L)**	**Pre- oxi-dant**
AW1	0	4.2	192 000	nm	0	4.3	2.0	0.87	128 000	170	45	3 750	100	none
AW2	500	4.2	186 000	nm	280	4.3	2.0	0.54	122 000	200	89	4 750	63	none
AW3	0	6.5	192 000	20	0	6.2	0	0	113 000	920	nd	370	nd	O_3
AW4	500	6.2	196 000	40	500	6.0	0	0	122 000	820	nd	200	nd	O_3
AW5	0	6.4	210 000	20	0	6.1	2.0	0.73	124 000	1 140	34	3 460	75	O_3
AW6	500	6.1	203 000	100	330	5.7	2.0	0.28	146 000	760	73	3 500	40	O_3
AW7	0	6.2	187 000	120	0	5.8	2.0	0.24	117 000	1 270	22	2 280	53	$O_3+H_2O_2$
AW8	500	6.6	181 000	140	430	5.4	2.1	0.26	119 000	950	30	2 650	44	$O_3+H_2O_2$
AW9	0	6.4	189 000	60	0	6.9	2.0	0.64	156 000	190	35	3 200	79	$KMnO_4$
AW10	500	7.2	178 000	30	410	6.6	2.0	0.52	157 000	180	53	3 320	49	$KMnO_4$
PW1	0	2.5	87 000	nm	0	2.6	1.0	0.51	57 000	90	21	2 150	65	none
PW2	500	2.5	81 000	nm	370	2.6	1.0	0.29	65 000	50	52	2 960	23	none
PW3	0	3.8	109 000	20	0	3.8	0	0	53 000	400	nd	nd	nd	O_3
PW4	500	3.7	90 000	10	500	3.7	0	0	59 000	370	nd	nd	nd	O_3
PW5	0	2.6	81 000	nm	0	3.3	1.0	0.43	53 000	410	10	1 660	20	O_3
PW6	500	2.8	84 000	nm	330	2.8	1.0	0.53	49 000	410	58	2 340	nd	O_3
PW7	0	3.2	93 000	30	0	3.2	1.0	0.16	82 000	70	8	510	3	H_2O_2
PW8	500	3.3	82 000	20	500	3.3	1.0	0.24	92 000	70	11	940	18	H_2O_2
PW9	0	3.0	74 000	60	0	2.9	1.0	0.20	43 000	500	3	520	8	$O_3+H_2O_2$
PW10	500	3.3	78 000	90	500	3.0	1.0	0.22	51 000	430	5	760	7	$O_3+H_2O_2$
PW11	0	3.3	nm	10	0	3.3	1.0	0.54	65 000	70	21	1 520	37	$KMnO_4$
PW12	500	3.7	84 000	90	290	3.6	1.0	0.39	71 000	90	33	1 750	12	$KMnO_4$
PW13	0	2.6	80 000	20	0	2.7	0	0	82 000	60	nd	nd	nd	UV
PW14	500	2.7	89 000	50	470	2.6	0	0	90 000	50	nd	nd	nd	UV
PW15	0	2.6	80 000	20	0	2.5	1.0	0.50	59 000	150	32	1 770	30	UV
PW16	500	2.7	89 000	50	290	2.6	1.0	0.20	88 000	140	55	2 500	nm	UV
U9	250	3.1	83 000	85	190	3.3	1.0	0.34	72 000	170	53	2 800	nm	none
U10	250	3.2	nm	nm	240	3.2	0.95	0.38	72 000	140	49	nm	nm	none
U11	250	2.2	nm	nm	230	2.2	0.67	0.28	44 000	90	39	nm	nm	none
U12	250	1.5	nm	nm	230	1.5	0.50	0.26	31 000	100	29	nm	nm	none

HPSEC (AU*s) = integrated peak areas from the size exclusion chromatography (absorbance units multiplied by time in seconds); OA = the sum of organic acids (formate, acetate, propionate, pyruvate, oxalate, and citrate); nd = not detected; nm = not measured; Res. Cl_2 = residual chlorine in the water at the time of sampling

Appendix 3. The quality of raw water and treated water in the study II. Treatment consisted of coagulation/flocculation, flotation, sand filtration, and disinfection. AS = aluminum sulphate, FS = ferric sulphate, PACl = polyaluminum chloride.

Water	Raw water				Treated water									
	Br⁻ (µg/L)	**TOC (mg/L)**	**HP-SEC (AU*s)**	**OA (µg/L)**	**Br⁻ (µg/L)**	**TOC (mg/L)**	**Cl_2 dose (mg/L)**	**Res. Cl_2 (mg/L)**	**HP-SEC (AU*s)**	**OA (µg/L)**	**THMs (µg/L)**	**HAAs (µg/L)**	**Mutagenicity (net rev/L)**	**Pre-oxidant**
AS1	0	11.2	452 000	80	0	4.6	1.0	nm	128 000	140	32	27	nm	none
AS2	400	11.5	446 000	80	280	4.6	1.0	0.05	133 000	60	41	22	nm	none
AS3	0	11.6	461 000	70	0	4.5	1.0	0.22	119 000	150	31	29	nm	UV
AS4	400	11.3	445 000	60	360	4.6	1.0	0.06	134 000	100	9	11	nm	UV
AS5	0	10.8	402 000	40	0	4.6	0	0	150 000	90	nd	nd	nm	UV
AS6	400	11.2	414 000	50	400	4.4	0	0	124 000	60	nd	nd	nm	UV
FS1	0	10.0	430 000	50	0	3.7	1.0	0.10	101 000	110	33	24	1 270	none
FS2	270	9.8	500 000	60	170	3.8	1.0	0.07	86 000	40	49	14	1 750	none
FS3	500	10.0	423 000	50	340	3.7	1.0	0.03	67 000	50	59	15	2 150	none
FS4	0	9.8	405 000	50	0	3.5	1.0	0.20	89 000	90	37	26	1 810	UV
FS5	500	9.6	397 000	50	350	3.7	1.0	0.04	66 000	50	70	22	2 600	UV
FS6	0	10.0	433 000	40	0	3.7	0	0	119 000	30	nd	nd	nd	UV
FS7	500	9.5	431 000	40	500	3.8	0	0	113 000	50	nd	nd	nd	UV
PACl1	0	9.6	419 000	50	0	3.9	1.0	0.12	110 000	60	26	16	1 360	none
PACl2	500	9.6	431 000	60	330	3.8	1.0	0.15	70 000	110	57	28	1 980	none
PACl3	0	9.3	359 000	40	0	3.8	1.0	0.09	115 000	100	27	12	1 240	UV
PACl4	500	9.6	505 000	50	330	4.1	1.0	0.11	74 000	100	54	25	2 150	UV
PACl5	0	9.5	352 000	50	0	3.8	0	0	83 000	30	nd	nd	nd	UV
PACl6	200	9.6	338 000	120	200	4.1	0	0	91 000	40	nd	nd	nd	UV

HPSEC (AU*s) – integrated peak areas from the size exclusion chromatography (absorbance units multiplied by time in seconds); OA = the sum of organic acids (formate, acetate, propionate, pyruvate, oxalate, and citrate); nd = not detected; nm = not measured; Res. Cl_2 – residual chlorine in the plant effluent